

**Structural Determination of Copolymers from the Cross-catalyzed
Reactions of Phenol-formaldehyde and Polymeric Methylenediphenyl
Diisocyanate**

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ABSTRACT

This work reports the elucidation of the structure of a copolymer generated by the cross-catalyzed reactions of PF and pMDI prepolymers. The electronic behavior of phenolic monomers as perturbed by alkali metal hydroxides in an aqueous environment was studied with ^1H and ^{13}C NMR. Changes in electronic structure and thus reactivity were related to solvated ionic radius, solvent dielectric constant, and their effect on ion generated electric field strength. NMR chemical shifts were used to predict order of reactivity for phenolic model compounds with phenyl isocyanate with good success. As predicted, 2-HMP hydroxymethyl groups were more reactive than 4-HMP in forming urethane bonds under neutral conditions and 2-HMP hydroxymethyl groups were more reactive than 4-HMP in forming urethane bonds under alkaline conditions.

The structure of the reaction products of phenol, benzyl alcohol, 2-HMP, and 4-HMP with phenyl isocyanate were studied using ^1H and ^{13}C NMR under neutral organic and aqueous alkaline conditions. Reactions in THF- d_8 under neutral conditions, without catalyst, were relatively slow, resulting in residual monomer and the precipitation of 1,3-diphenyl urea from the carbamic acid reaction. The reactions of phenol, 2-HMP, and 4-HMP in the presence of TEA catalyst favored the formation of phenyl urethanes (PU). Reactions with benzyl alcohol, 2-HMP, and 4-HMP in the presence of DBTL catalyst favored the formation of benzyl urethanes (BU). Reactions of 2-HMP and 4-HMP led to formation of benzylphenyldiurethane (BPDU). DBTL catalysts favored formation of BDPU strictly by a benzyl urethane pathway, while TEA favored its formation mostly via phenyl urethane, although some BU was also present. Under aqueous alkaline conditions, 2-HMP was more reactive than 4-HMP, exhibiting an enhanced reactivity that was attributed to intramolecular hydrogen bonding and a resulting resonance stabilization of the phenolic aromatic ring.

ATR-FTIR spectroscopic studies generated real time structural information for model compound reactions of the cross-catalyzed system, differentiating among reaction peaks

generated by the carbamic acid reaction, PU and BU formation. ATR-FTIR also permitted monitoring of propylene carbonate hydrolysis and accelerated alkaline PF resole condensation. ATR-FTIR data also showed that the overall reaction stoichiometry between the PF and pMDI components drove copolymer formation. Benzyl urethane formation predominated under balanced stoichiometric conditions in the presence of ammonium hydroxide, while phenyl urethane formation was favored in its absence. Accelerated phenolic methylene bridge formation became more important when the PF component was in excess in the presence of sufficient accelerator. A high percentage of free isocyanate was present in solid copolymer formed at ambient temperature. The combination of ammonium hydroxide and tin (II) chloride synergistically enhanced the reactivity of the materials, reducing the residual isocyanate.

From ^{13}C CP/MAS NMR of the copolymer, the presence of ammonium hydroxide and tin (II) chloride and the higher PF concentration resulted in substantial urethane formation. Ammonium hydroxide favored formation of benzyl urethane from the 2-hydroxymethyl groups, while phenyl urethane formed in its absence. The low alkalinity PF resole with ammonium hydroxide favored benzyl urethane formation. Comparison of these results with the ^{13}C NMR model compound reactions with phenyl isocyanate under alkaline conditions confirmed high and low alkalinity should favor phenyl and benzyl urethane formation respectively. These cross catalyzed systems are tunable by formulation for type of co-polymer linkages, reactivity, and cost.

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Chapter 1: Introduction

1.1. Background

Phenol-formaldehyde (PF) resins have been the world's oldest fully synthetic polymer in industrial usage ever since Leo Baekeland first patented a process in 1909.¹ In practice they have proven to be cost effective, exhibiting excellent properties such as moisture durability, thermal resistance, and low smoke toxicity. Currently, PF resins are used to adhesively bond a wide variety of veneered wood composites such as plywood and laminated veneer lumber, structural lumber composites such as oriented strand lumber, parallel strand lumber, and scrim based lumber, as well as particle based panels like oriented strand board, particleboard, medium density fiberboard, and high density fiberboard. PF resins are also used in a wide variety of impregnated papers including high pressure laminate, medium density overlays, high density overlays, and paint based overlays.

In spite of this broad usage, PF resins suffer from relatively slow cure speed compared to the conventional alternatives of urea-formaldehyde (UF), melamine-formaldehyde (MF), resorcinol-formaldehyde (RF), and polymeric methylene diphenyl diisocyanate (pMDI). This deficiency was recognized very early. Already in 1918, none less than Thomas Alva Edison was granted US patent 1,283,706 for a para-phenylene diamine substance "comprising ingredients which react upon application of heat to form a hardened phenolic condensation product".² The process was "...to provide an improved substance and process of such a character that the speed of the chemical reaction which causes the formation of the final hardened product is greatly increased" for use in phonographic records.

In spite of the efforts over the ensuing years to accelerate PF resins, their cure in lignocellulosic composite manufacture still requires substantial energy and time. A practical and economical technique solving this problem would provide a significant breakthrough in PF application technology. Both industry and society at large would enjoy substantial benefits if adhesive cure can be accelerated at ambient temperatures. The lower press temperatures, and shorter press

cycles would result in major energy savings. In addition, these reductions would simultaneously decrease emissions of volatile organic compounds (VOC) and hazardous air pollutants (HAP) during pressing. Of course, the shorter press cycles would improve the productivity of expensive capital equipment. Also, adhesive costs savings might be realized by substituting the less expensive phenol-based adhesives for more expensive resorcinol-based adhesives. Finally, improved product properties from modified composite density profiles could become technically feasible due to greater adhesive tolerance of moisture content variation and rapid bond formation at low temperatures. This solution would not be limited to the manufacture of lignocellulosic composites, but also suit other applications such as impregnated papers, coatings, insulation binders, foams, and abrasives.

Others have recognized the desirability of low temperature curing adhesive systems for wood composites. According to The Forest Products Industry Technology Roadmap, there are two top R&D priorities for wood composites³: the first is energy-efficient technologies such as moisture-activated or non-heat activated adhesives or reduced materials drying time, and the second is reduced manufacturing VOC and HAP emissions through reduced dryer and press emissions.³ Technology is available to address these issues. In this light, Griffith has advocated development of rapid, low-temperature electron beam-curable resin systems for wood adhesives. The reported estimates of such technologies could result in potential energy savings to the wood composites industry of 65 Trillion BTU's/year at full market penetration. A reduction of curing temperatures from 450 °F to 250 °F, possible with the example of beam-curing systems also offers the potential of reducing unit capital costs and doubling throughput. The lower curing temperatures would also decrease process emissions by reducing VOCs and HAPs. Griffith's report also states that "the global objective for this project is to produce new adhesives for wood composites that can be cured at low temperatures, with little drying of raw materials, and virtually instantaneously. This offers tremendous energy savings over more commonly used methods to cure wood adhesives."⁴ Unfortunately, radiation cure adhesives will likely be more expensive than any of the adhesive systems currently used in industrial production of wood composites. Hence, Griffith's example provides a well analyzed case of the

impact of low energy, high moisture curing systems, but other technologies, perhaps using current industrial adhesive systems, are required and may be easier to implement.

To address the need of low energy adhesive curing systems, recent work by Haupt indicated that rapid cure of PF resins is possible by use of a two component system comprising a first component of a PF prepolymer resin and a polyurethane catalyst, and a second component of an pMDI prepolymer resin and a PF accelerator.⁵ In the examples, ammonium hydroxide or stannous chloride are used as the polyurethane catalyst while propylene carbonate (PC) is used as the PF accelerator. A combination of these materials has exhibited gel times in as little as 30 seconds at 22 °C, shown in Table 1.⁵ One potential difficulty with such fast reactions is controlling the physical mixing of the two components so that the reaction can be initiated on demand to avoid polymerization prior to adhesive bond formation, also known as pre-cure. It provides a unique two-part crosslinking system, however, that utilizes currently accepted industrial adhesives to form a network co-polymer.

Table 1.1. Reactivity of a cross-catalyzed two part system of a PF resole with NH₄OH polyurethane catalyst and pMDI with propylene carbonate as a PF accelerator⁵

pMDI:PC wt. ratio	wt. % MDI	Gel time in seconds at 22 °C for pMDI/PC volume with 1.0 mL PF			
		0.2 mL	0.4 mL	0.6 mL	0.6 mL (no NH ₄ OH)
3:1	75	182	52	32	50
9:1	90	1998	133	66	93
19:1	95	9030	563	163	196
1:0	100	> 147600	5078	900	> 28800

Importantly, the exact structure of this rapid-curing polymer is unknown, whether it can be considered a copolymer or an interpenetrating network. Thus, the determination of the polymer structure generated by this two part system is the focus of this research project. The central hypothesis regarding structure is that the material can be formed as a co-polymer generated by two mechanisms; (1) catalytic step growth polymerization by reaction of the PF

and pMDI components to form phenolic and benzylic urethanes, and (2) accelerated methylene bridge formation among the oligomers of the PF component.

1.2. Technical issues/hypotheses to be addressed

Attempting a research program to test this central hypothesis faced numerous technical issues. The main challenge arises from distinguishing the multiple reactions that can occur simultaneously since the system involved four different raw materials. For instance, the PF pre-polymer further comprised three components: PF oligomers with an alkali hydroxide base in aqueous solution. The pMDI pre-polymer and PF accelerator form an organic phase that will exhibit limited phase compatibility with the aqueous PF pre-polymer and polyurethane catalyst making the two combined components a heterogeneous system. Limited information is available on the structures of the reaction products of phenol-formaldehyde pre-polymers and MDI pre-polymers. A wide variety of polyurethane catalysts and PF accelerators that impact polymer structure may be used. Furthermore, the PF and MDI pre-polymers may be varied in their pH, molecular weight distribution, functionality, and water content.

The scope of this project is focused on identifying the copolymer structure through spectroscopic methods; research findings on topics related to microencapsulation have been placed in the Appendices. Microencapsulation is envisioned as a means to deliver the reactive materials in a manner that could be triggered by heat and/or pressure in an industrial setting. Microencapsulation technical issues include formulation to usable viscosities for the devices and setting up equipment for application and evaluation of the devices and their product microcapsules for mechanical and on demand adhesive properties. Suitable microencapsulation methods could include ultrasonic, electrospray, or microfluidic devices and would require selection of appropriate device and process configurations to achieve the desired results. In addition, careful safety procedures and equipment would be necessary to avoid potential hazards working with isocyanates, phenol, formaldehyde, strong bases, and organic solvents.

1.3. Approach

A summary of the approach taken to resolve co-polymer structure of the ambient cured system is listed:

- (1) Elucidate the structure of accelerated and catalyzed PF-pMDI model compound reaction products
- (2) Relate the reaction stoichiometry of accelerated and catalyzed PF-pMDI model compounds to polymer structure
- (3) Use results from the model compound studies to build understanding of the structure of accelerated and catalyzed PF-pMDI blends.

The two main analytical methods applied to structural determination were nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR). The NMR techniques included ^1H , and ^{13}C for samples in solution and cross polarized magic angle spinning (CP MAS) NMR for samples in the solid state. The FTIR techniques included attenuated total reflectance (ATR) FTIR for samples in liquids and transmission FTIR for samples in the solid state. The ATR-FTIR technique permitted following reactions *in situ* and the generation of time dependent dynamic spectra. Rheological methods were also applied to testing the base oligomers for material that is presented in the Appendices.

Model compound reactions were used for structural determination. The basic strategy was to establish baseline spectra for the model compounds as references and then to react them in with other model compounds, catalysts, accelerators, and solvents for comparison of the changes with the baseline references. For solid state studies, ATR-FTIR was used to track the polymerization reaction progress of cross-catalyzed reactions to gels, while ^{13}C CP/MAS NMR and transmission FTIR were used to generated spectra of the reacted polymer. Thus, the experimental methods provided a means of covering the changes that occurred from starting materials through the reactions to the solid polymer. By isolating the different possible reactions and side reactions with model compounds, reference spectra were generated that proved valuable in interpreting the dynamic spectra of the more complex reactions.

1.4. Project description and summary

The goal of this research was to determine the structure of a novel low-temperature curing adhesive. The adhesive was formed by the combination of two common thermosetting adhesives, phenol formaldehyde (PF) and poly(methylene diphenyl diisocyanate) (pMDI), by addition of a polyurethane catalyst and a PF accelerator to the aqueous PF and organic pMDI phases, respectively. The central hypothesis was that the reaction of these materials would result in a copolymer formed from phenol urethanes, benzyl urethanes, and phenolic methylene bridges. Thus, the focus was determination of polymer structure and relating this structure to specific formulation parameters. Work with model compounds was used to understand the effects of alkali metal hydroxide content, solvent, catalysts, hydroxymethyl position, and accelerators on reaction pathways to assist in polymer structure determination. Parameters that were studied included modification of the PF oligomer chemistry with NH_4OH and SnCl_2 as polyurethane catalysts and varied blending ratios of PF to pMDI to better understand the role of stoichiometry in forming the polymer.

The significance of this research is the development of knowledge of the effects of formulation parameters on the polymer structure will provide control over the reactivity and performance of the adhesive. As a result the novel adhesive will permit manufacture of wood composites at lower temperatures and/or shorter pressing times resulting in substantial energy savings and greatly improved productivity.

1.5. References

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Chapter 2: Literature Review

2.0. Overview

Four major areas related to acceleration of phenol-formaldehyde (PF) resin cure have been reviewed to provide a foundation for this project. In section 2.1, PF chemistry and its cure acceleration are reviewed, focusing on the chemistry of resoles. Section 2.2 summarizes findings on polymeric methylene diphenyl diisocyanate (pMDI) chemistry, reactions, and their catalysis. Germane to the dissertation topic, recent work with blends of PF and pMDI is surveyed in Section 2.3, especially in view of application to lignocellulosic materials. Current knowledge of microencapsulation technology and methods is appraised in Section 2.4.

2.1. Phenol-formaldehyde chemistry

2.1.1. Overview

Phenol-formaldehyde became the first fully synthetic commercial polymer in 1907. Although Adolf von Baeyer had already observed by 1872 that the combination of pyrogalllic acid, a phenolic material, and bitter almond oil, an aldehyde, reacted to form a reddish-brown mass, the material was too difficult to characterize and expensive to synthesize.¹ Beginning from the 1890's, numerous attempts to commercialize phenol-formaldehyde reaction products failed.¹ Commercialization required Baekeland's development of a specialized reactor in 1907, eventually patented in 1909.² The introduction of the resulting material, dubbed Bakelite, commenced the era of synthetic polymers.

PF resins comprise two major types: novolaks and resoles. Novolaks have a formaldehyde to phenol (F:P) molar ratio less than 1.0, while the resoles have an F:P molar ratio greater than 1.0. Novolaks are usually acid catalyzed at a pH less than 4. They require a source of methylene, usually hexamethylenetetramine (HMTA) or hexa for short, for crosslinking. Resoles are usually base catalyzed at a pH above 7. They have a sufficient excess of hydroxymethyl groups present to self-crosslink during cure, forming methylene bridges and a thermoset, network, polymer.³

Since alkaline PF resoles are so important for bonding wood, their chemistry has garnered much interest, with particular emphasis on the addition and condensation reactions of hydroxymethylphenols. One objective of this research has been to apply these insights into PF chemistry to enhance resin cure speed. Although PF resins have been in use for over a hundred years, understanding of PF chemistry is still incomplete and even now some aspects remain controversial. Research since 1995 has shed new light on PF addition, condensation, and acceleration reactions with a view to improve PF reactivity.⁴

2.1.2. Resole chemistry

Knop and Pilato detail three stages of alkaline resole polymerization: addition, condensation, and cure.³ First, addition of formaldehyde to phenol in an alkaline environment forms hydroxymethylphenol monomers. Then, the hydroxymethylphenols self-condense to hydroxymethyl diphenylmethane isomers and other structurally related oligomers, resulting in a prepolymer resin. Finally, these prepolymer resins cure via cross-linking to form a polymer network.³

2.1.2.1. Formaldehyde addition reactions

Phenoxide anion and methylene glycol are the reactive species in the previously mentioned base-catalyzed addition reaction of formaldehyde to phenol. The phenoxide anion forms by basic deprotonation of the phenolic hydroxyl group. Due to resonance stabilization, higher electron density is present at the ortho and para carbons on the aromatic ring, drawing electrophilic substitution to those positions (Figure 2.1). In aqueous solution, formaldehyde is present mostly as oligomers of methylene glycol, with equilibria chemistry determining the methylene glycol concentration.³

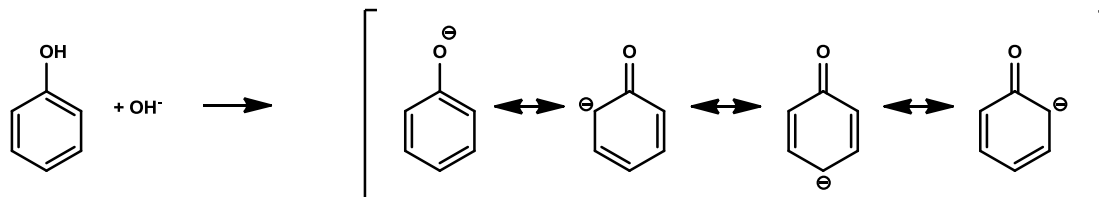


Figure 2.1. Phenol resonance structures under basic conditions

Formaldehyde adds to phenol in up to three successive reactions under alkaline conditions. The first reaction produces 2-hydroxymethylphenol (2-HMP) or 4-hydroxymethylphenol (4-HMP). The second leads to 2,6-dihydroxymethylphenol (2,6-DHMP) or 2,4-dihydroxymethylphenol (2,4-DHMP). The third reaction results in 2,4,6-trihydroxymethylphenol (2,4,6-THMP or THMP) (Figure 2.2).

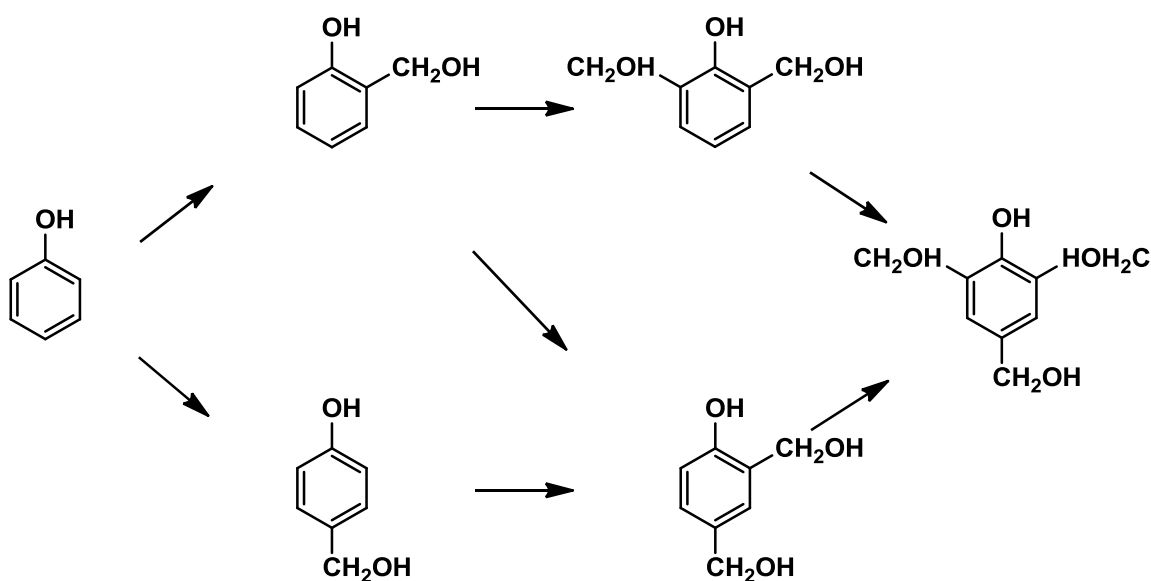


Figure 2.2. Hydroxymethylphenols formed by addition of formaldehyde to phenol

Researchers have studied the addition reaction kinetics (Table 2.1), finding that the addition of one hydroxymethyl group activates the phenol ring towards further addition reactions at the remaining unreacted sites.⁵ Freeman and Lewis's paper chromatography experiments generated plots of hydroxymethylphenol concentrations against elapsed reaction time at 30 °C for estimating the kinetic rate constants.⁶ Others used gel permeation chromatography (GPC) to construct similar plots and found close agreement with theoretical predictions based on a kinetic model.⁷ The kinetics of the formaldehyde addition reaction is second order with respect to phenoxide and methylene glycol concentrations, following the expression below.³

$$\text{Reaction rate} = k[\text{C}_6\text{H}_5\text{-O}^-][\text{HO-CH}_2\text{-OH}]$$

Higuchi et al. developed a computational model for the addition reaction with a hydroxide to phenol molar ratio (OH:P) of less than 1.0. The model was based on the kinetic parameters determined by the earlier researchers. From those results, they were able to show that the

literature rate constants would result in different compositions of mono-, di-, and tri-substituted hydroxymethylphenols.

Table 2.1. Relative rate of hydroxymethylation⁸

Reaction	Rate Constants Relative to the P + F → 2-HMP Reaction = 1.0				
	Freeman & Lewis 1954 (30 °C) ⁶	Minami & Ando 1956 (40 °C) ⁹	Zsavitsas & Beaulieu 1968 (30 °C) ¹⁰	Eapen & Yeddanapalli 1968 (30 °C) ¹¹	Higuchi, Nohno, Morita, & Tohmura 1998 (20, 30, & 40 °C) ⁸
Phenol + F ^a → 2-HMP ^b	1.00	1.00	1.00	1.00	1.00
Phenol + F → 4-HMP	1.18	2.08	1.09	1.46	1.46
2-HMP + F → 2,6-DHMP ^c	1.66	1.08	1.98	1.70	1.87
2-HMP + F → 2,4-DHMP	1.39	2.58	1.80	3.80	3.35
4-HMP + F → 2,4-DHMP	0.71	0.83	0.79	1.02	0.91
2,6-DHMP + F → THMP ^d	7.94	3.25	3.33	4.54	4.73
2,4-DHMP + F → THMP	1.73	1.25	1.67	1.76	1.75
^a Formaldehyde	^b Hydroxymethylphenol		^c Dihydroxymethylphenol		^d Trihydroxymethylphenol

To verify their model predictions, Higuchi and co-workers determined concentrations of the reaction products of phenol and formaldehyde in water with sodium hydroxide. They set the molar ratio for F:P at 3.0 over a range of OH:P molar ratios from 0.3 to 1.0 with temperatures of 20, 30, and 40 °C . The hydroxymethylphenol reaction products were analyzed by HPLC using UV absorption to measure concentration over time. They corrected for differences among the extinction coefficients of phenol and the other five hydroxymethylphenol monomers based upon actual compounds. The data of Higuchi et al. is compared to that provided by Grenier-Loustalot et al. in Table 2.2.

Table 2.2. UV absorption intensities of six phenolic compounds

Phenolic compound	Relative‡ UV absorption intensity ¹²	Molar absorption coefficients† at 273 nm ¹³
Phenol	1.000	1700
2-HMP ^b	1.709	1700
4-HMP	1.316	1500
2,6-DHMP ^c	1.955	1900
2,4-DHMP	1.564	1500
THMP ^d	1.992	1900
4,4'-DHDPMe ^e	---	3000

‡ relative to phenol

† in L/mol

^b Hydroxymethylphenol ^c Dihydroxymethylphenol ^d Trihydroxymethylphenol ^e dihydroxydiphenylmethane

Higuchi and co-workers calculated activation energies differed substantially from previous work reported by Eapen & Yeddapanalli (Table 2.3).¹¹

Table 2.3. Activation energies of hydroxymethylation reactions¹²

Reaction	Activation energy in kJ/mol	
	Eapen & Yeddapanalli (30 °C) ¹¹	Higuchi, Nohno, Morita, & Tohmura (20, 30, & 40 °C) ¹²
Phenol + F ^a → 2-HMP ^b	68.6	83.2
Phenol + F → 4-HMP	65.3	78.7
2-HMP + F → 2,6-DHMP ^c	67.8	79.0
2-HMP + F → 2,4-DHMP	60.7	92.3
4-HMP + F → 2,4-DHMP	77.4	88.0
2,6-DHMP + F → THMP ^d	58.2	81.0
2,4-DHMP + F → THMP	60.2	98.7

^a Formaldehyde

^b Hydroxymethylphenol

^c Dihydroxymethylphenol

^d Trihydroxymethylphenol

Computer simulations based upon their data indicated that higher temperatures and lower OH:P result in higher concentrations of unreacted free phenol and THMP. They attributed these results to differences in monomer acidity (Table 2.4) influencing their activation energies. Higher F:P molar ratios favored formation of THMP, while lower ratios favored 2-HMP and 4-HMP. They confirmed the higher reactivity of the 4-position over the 2-position, as found by others.¹²

Table 2.4. Acid dissociation constants for hydroxymethylphenols¹⁴

Phenolic compound	Experimental pK _a	Thermodynamic pK _a
Phenol	9.85	9.94
2-HMP	9.83	9.92
4-HMP	9.74	9.83
2,6-DHMP	9.68	9.77
2,4-DHMP	9.57	9.66
THMP	9.47	9.56

Poljansek et al. performed a comprehensive study of addition kinetics based on the Higuchi model⁸ using in-situ FTIR spectroscopy, covering a broad range of OH:P molar ratios from 0.1 to 1.0, F:P ratios from 2.0 to 3.0, and temperatures from 30 to 60 °C. The concentration of the 4 substituted positions was greater than the 2 substituted positions. The relative order of

reactivity towards further formaldehyde addition was 2-HMP greater than 4-HMP; the rates for 2,4-DHMP and 2,6-DHMP were greater than 4-HMP. At OH:P ratios above 0.5, the rate of formaldehyde and phenol consumption was about the same, but was retarded at the 0.1 molar ratio. Additionally, formation of THMP was accelerated at high F:P molar ratios.¹⁵

Knop noted the phenoxide anion reaction product of phenol and an alkali hydroxide is resonance stabilized by the aromatic ring with preference for the 2- and 4-positions. Knop provides dipole moment data for phenols (Table 2.5). The marked difference in dipole moment between phenol and phenoxide explains why polar protic solvents like water are necessary to dissolve alkaline PF resins.³

Table 2.5. Dipole moment of phenols and some common solvents

Compound	Dipole moment (Debye)
Phenol ³	1.52
Phenoxide ³	7.89
2-Hydroxymethylphenol ³	1.55
4-Hydroxymethylphenol ³	1.92
Water ¹⁶	1.85
Methanol ¹⁶	1.70
Ethanol ¹⁶	1.69
Urea ¹⁶	4.56

Knop relates reactivity to the positional electron density of the anions for phenol and the HMPs through CNDO/2 & CNDO/S (Complete Neglect of Differential Overlap) calculations and not to their neutral molecules. Phenoxide has higher electron density at the 4-position versus the 2-position. The effect of 2-hydroxymethyl substitution is to increase electron density at the 6-position and decrease it at the 4-position. The 4 substitution decreases electron density at both the 2-and 6-positions.³

In a series of studies, Grenier-Loustalot et al. found pH dependence due to OH⁻ concentration for the addition and condensation reaction rates. At elevated pH, the relative reactivity of phenolics towards formaldehyde is: substituted dimers > substituted monomers> phenol.¹³

The cation type affected condensation addition reactions. They concluded that hydrated ionic radius and valence charge of the hydroxide counter-cation affected rate constants for the

formaldehyde addition reaction. Rates were proportional to the hydrated cation size and valence, with the addition rate of the 2^+ valence cations being higher than the 1^+ cations. The kinetic rate constants followed the order $k_{\text{Li}^+} > k_{\text{Na}^+} > k_{\text{K}^+}$ for the monovalent catalysts KOH, NaOH and LiOH. The divalent catalysts $\text{Ba}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ followed the order $k_{\text{Mg}^{2+}} > k_{\text{Ca}^{2+}} > k_{\text{Ba}^{2+}}$. NaOH and KOH displayed only minor compositional differences among their addition monomers, while LiOH monomers changed significantly due to additional substitution and condensation reactions. Divalent Ba^{2+} altered the substitution pattern, directing towards formation of 2,6-DHMP and 2,4,6-THMP rather than 2,4-DHMP. The 2,6 directing mechanisms were thought to be favored by chelate formation.¹⁷

2.1.2.2. Condensation reactions

The hydroxymethylphenol addition reaction products condense to form oligomeric prepolymers. Running these two reactions in two stages is safer with addition at or below 60 °C and condensation between 60 and 100 °C. Addition at lower temperatures reduces risk of an uncontrollable exothermic polymerization and is followed by condensation at higher temperatures once some of the heat of reaction is dissipated.³ Continuous formalin addition (instead of charging the reactor) also mitigates the exothermic risk, by allowing the heat generated by the addition reactions to be exchanged over time.⁴ Sprung and Gladstone performed early studies on the chemistry and kinetics of 2-HMP condensation reactions, finding that the product of uncatalyzed 2-HMP reaction was a dibenzylether (Figure 2.3).¹⁹

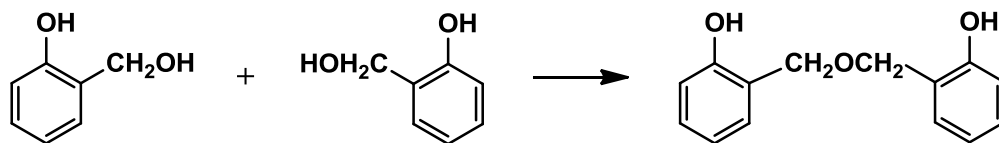


Figure 2.3. Uncatalyzed condensation of 2-HMP to dibenzylether

Grenier-Loustalot et al. found that the cation type also affected condensation reactions. Methylene bridge formation was slow with NaOH and KOH, taking more than 48 hours while requiring 24 hours with LiOH, $\text{Mg}(\text{OH})_2$, and $\text{Ba}(\text{OH})_2$. For all alkali metal catalysts, 4,4' methylene bridges comprised the greatest proportion of oligomers, followed by 2,4', while 2,2'

linkages were not detected.¹⁷ The condensation reactions only favored 2-4' methylene bridge formation when para concentrations were diminishing.¹⁸

Others, such as Yeddanapalli and Francis investigated the self-condensation kinetics of 2-HMP and 4-HMP and their reaction with phenol under alkaline conditions. Paper chromatographic techniques revealed that the reactions yield dihydroxydiphenylmethanes (DPM) and water. Compared to phenol and hydroxymethylphenols (HMP), the self-condensation of two HMPs was much faster than the condensation of phenol and an HMP. Self-condensation of HMPs yields formaldehyde in addition to water. The reactivity order is 4-4' > 2-4' > 2-2'. They found that formaldehyde is added more slowly to DPM than to phenol and proposed that PF dimers form more readily by HMP self-condensation than by addition of formaldehyde to DPM (Figure 2.4).²⁰ Based on ¹³C NMR and GPC results for a single PF resin that was sampled multiple times during condensation, Kim et al. studied the formation of an oligomeric PF resole. They concluded that the process proceeded initially by formation of 4-4' methylene bridges, followed by 2-4' methylene bridges, with the eventual formation of 6-4' linkages leading to a branched structure. The 2-2' bridges form only after most 4-carbons are unavailable, with end nuclei comprising many 2,6'-HMP groups.²⁴

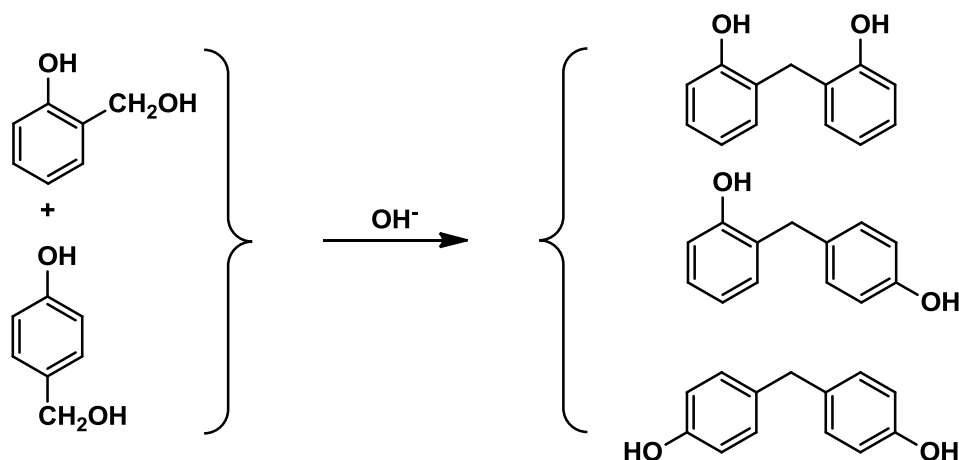


Figure 2.4. Self-condensation of 2-HMP and 4-HMP to dihydroxydiphenylmethanes²⁰

Quinone methides (QM) (Figure 2.5) are thought to be important intermediates in PF condensation reactions, since they are powerful electrophiles.²¹ Merijan and Gardner said their

role in the formation of diarylmethanes was that a DPM could be formed not only by the reaction of a QM and phenol, but also by reaction of two HMPs via a QM intermediate.²²



Figure 2.5. Structure of reactive intermediates 2-QM and 4-QM³

Wan and Hennig found that not only do QMs form under thermal conditions but also due to photolysis. The researchers found that an aqueous alkaline solution would enhance their thermal formation, since the presence of a deprotonated phenolic hydroxyl significantly enhances QM formation. In 1987 they discovered, however, that 2-HMP can also form a QM under photolysis by 254 nm UV light at sub-ambient temperatures. They applied photolysis to 2-HMP in basic solution and formed PF oligomers via photochemical reaction below 25 °C.²³

Haupt and Waagø studied the effect of PF resole formulation parameters on condensation rate and molecular weight distributions. Relative reaction rates were estimated by plotting GPC determined molecular weights during the course of condensation. They concluded that condensation rate was dependent on pH, with a maximum condensation rate around pH 10. They inferred that the condensation reaction must occur between an anionic and non-ionic or neutral monomers.²⁵ As Sprengling and Lewis have shown with pK_a data (Table 2.4), the monomers, all of which have pK_a in the 9 to 10 range, become more acidic as more methylol groups are added to the phenolic nuclei.¹⁴ As further support for this hypothesis, they also demonstrated that PF resoles condensed at pH less than 9 or pH greater than 11 developed higher polydispersity indices at a given M_n during the course of condensation. The broader molecular weight distributions were attributed to unreacted components present in the composition. The reaction pH influenced the concentration of ionic and neutral species, since condensation required an anionic and a neutral monomer; the result was excess unreacted neutral monomers at low pH and anionic monomers at high pH.²⁵

Higuchi et al. thoroughly investigated PF condensation chemistry, studying condensation kinetics and reaction mechanisms using the model compounds 2-HMP and 4-HMP.^{27,28} Morita et al. performed similar work for 2,4-DHMP²⁹ and 2,4,6-THMP.^{29,30,31} The studies looked at PF model compounds condensing under aqueous alkaline conditions, demonstrating that 2-HMP self-condensation was truly first order. Reaction rate depended on the NaOH:2-HMP molar ratio, increasing to a maximum at NaOH: 2-HMP = 0.1 and then decreasing thereafter. They attributed the results to quinone methide formation.²⁷ They also examined the base-catalyzed self-condensation of 4-HMP, finding a fractional reaction order of 1.3 due to concurrent unimolecular and bimolecular reaction mechanisms. The rate controlling unimolecular reaction was attributed to the formation of quinone methide intermediates. They regarded the bimolecular reaction as the reaction of three possible HMP combinations in neutral (ϕ -OH) and anionic (ϕ -O⁻) forms: $[\phi\text{-OH}]\cdot[\phi\text{-OH}]$, $[\phi\text{-OH}]\cdot[\phi\text{-O}^-]$, and $[\phi\text{-O}^-]\cdot[\phi\text{-O}^-]$. They established that the unimolecular reaction had a maximum reaction rate for the NaOH:4-HMP molar ratio of 0.1, while the bimolecular reaction had a maximum reaction rate for the NaOH:4-HMP molar ratio of 0.5.²⁷ The simultaneous occurrence of two different reaction mechanisms helps explain why Haupt and Waagø saw a maximum condensation rate near an NaOH:P molar ratio of 0.25, near pH 9.5, instead of 0.50 as their proposed reaction would have predicted.²⁵ They also concluded that 2-HMP self-condensed slower than 4-HMP, due to intramolecular hydrogen bonding of the 2-HMP hydroxymethyl to the phenolic hydroxyl.²⁷

Kamo et al. researched the self-condensation of 2,4-DHMP and 2,4,6-THMP. The 2,4-DHMP self-condensation had a fractional order of 1.1. Remarkably, the reaction order for self-condensation of 2,4,6-THMP was 2.0 when its concentration was greater than 1.5 mol/L, suggesting that only the bimolecular mechanism was operative. But when the concentration was less than 1.5 mol/L, the reaction order varied from 1.2 to 1.6 over the NaOH:P molar ratio range, indicating that the unimolecular and bimolecular mechanism were active. The unimolecular mechanism was attributed to QM formation. The concentration of 1.5 mol/L likely represented a critical overlap concentration. They concluded that the reaction kinetic rates, mechanisms, and order depended on the exact species and reactant concentration present.²⁹

For greater insight into these concentration effects, Kamo et al. further experimented on the self-condensation of 2,4-DHMP and 2,4,6-THMP. The condensation rate of THMP exhibited complex dependence on concentration and NaOH:P molar ratio. For concentrations above 1.0 mol/L the maximum rate was at an NaOH:P molar ratio of 0.5, but for concentrations below 1.0 mol/L, the maximum was at about an NaOH:P of 0.2. Again, the THMP self-condensation mechanism varied with concentration, with the unimolecular reaction operative at low concentrations and the bimolecular reaction at high concentrations. This explanation may be understood as a dilute solution effect. At concentrations less than 1.0 mol/L, solvent molecules separated reactants from one another, favoring the unimolecular mechanism. At concentrations greater than 1.5 mol/L, the reacting molecules overlapped or were in close proximity, leading to the predominance of the bimolecular mechanism. The intermediate concentrations were transitional from dilute solution to intermolecular entanglement. Thus, while the unimolecular QM mechanism prevailed at lower concentrations; bimolecular reactions between dissociated and undissociated HMPs became more important at higher concentrations. These higher concentrations are more representative of commercial PF resoles.³⁰

To further elucidate the concentration effect of THMP molecular interactions on condensation reactions, Kamo et al. quantified the effect of THMP concentration and reaction temperature on intermolecular hydrogen bonding with ¹³C-NMR spin-lattice relaxation time (T_1). Their assumption was that T_1 depends on the resumption of molecular aggregation after magnetic field perturbation. Calculating molecular orbitals of the HMP monomers for theoretical confirmation of their experimental results, they found that T_1 time decreased linearly with increasing concentration, displaying an inflection point at a critical concentration near 1.2 mol/L. They concluded that while THMP is present as an individual molecule in solution at lower concentrations, it is present as an associated aggregate above that critical concentration. They determined that while the association of all hydroxymethyl groups increased with concentration, the 4-HMP group did so more than the 2-HMP group. Thus, 4-HMP has a greater barrier to rotation in solution due to association. The molecular orbital calculations defined the most stable configurations for individual molecules and for two- or three-molecule

complexes. For unassociated molecules, the 4-HMP group rotated freely, while the 2-HMP group was either free or hydrogen bonded to the phenolic hydroxyl, thus requiring a higher overall rotational energy. But as the molecules associated due to higher concentration, the 4-HMP groups formed intermolecular hydrogen bonds and all groups had higher rotational energies. These ^{13}C -NMR T_1 results were consistent with their molecular orbital calculations.³¹

Monni et al. applied Raman spectroscopy to in-line measurement during PF resole synthesis for real-time data acquisition. They identified useful peaks from the Raman spectra of model compounds for the real-time in situ study of PF synthesis. Reactions were monitored at four different temperatures (80, 90, 100, and 110 °C). For resole synthesis, they correlated Raman results with liquid ^{13}C NMR, solid state CP/MAS ^{13}C NMR, and DSC. Based on the model compound studies, they were able to identify peaks useful for following the decrease in free phenol and formaldehyde concentrations as well as the hydroxymethylation and the methylene bridge forming condensation reactions. Peaks at 1046 and 1300-1296 cm^{-1} were useful for tracking changes in hydroxymethyl groups and methylene bridges respectively. The peaks at 1469-1438 cm^{-1} were most useful for the determining the ratios of methylene bridges to hydroxymethyl groups. These ratios from Raman correlated with the corresponding data from CP/MAS ^{13}C NMR with a R^2 value of 0.96. The DSC results also showed reasonable correlation with the Raman results.³²

Christjanson et al. studied condensation of 2-HMP and 4-HMP in the melt at 120 °C for 2 hours under neutral conditions and subsequently with NaOH present. Under neutral conditions, 2,2'-, 4,4'-, and 2,4'-dibenzylethers formed from the respective monomers. Under alkaline conditions, few or no dibenzylethers formed, but 2-4', and 4-4' methylene linkages formed, with the latter being the most prevalent. They concluded that in the melt, the dibenzylethers cleave by reaction with free 2-or 4-sites on another phenol ring rather than by release of formaldehyde. Their ^{13}C NMR identified 2- and 4-benzonquinones as present in the spectra but they were interpreted as minor oxymethylene intermediates (Figure 2.6). In an alkaline environment, resole structure and mechanism depended far more on the phenoxide anion,

while benzoquinones are insignificant. Hemiformals (Figure 2.7), though present, did not appear to have a major role in the reactions either.³³



Figure 2.6. 2- and 4-benzoquinone



Figure 2.7. Phenol hemiformals and 2-hydroxymethylhemiformals³³

2.1.3. Relation of characteristic resole properties to formulation variables

Haupt and Sellers characterized a range of PF resole resins in 3 x 2 experimental design prepared at a constant condensation temperature. F:P molar ratios were 1.70, 2.00, and 2.30 and NaOH:P molar ratios were 0.40 and 0.60. Multiple samples covering a broad viscosity range of about 20 to 1000 mPa·s were drawn from each resin synthesis on the basis of elapsed synthesis time. The bulk properties of pH, gel time, viscosity, alkalinity, nonvolatiles, density, surface tension, contact angle were characterized as a function of the fundamental property of molecular weight, which was determined by GPC. The bulk property data were plotted against either M_n or M_w and a linear regression best fit was found for the data set from each resin synthesis. Slopes and constants from the data sets were used for statistical analysis of the experimental design. The results showed that viscosity and gel time depended on M_w and the NaOH:P molar ratio. The condensation rate measured as M_n versus elapsed cook time varied with F:P ratio, with higher reaction rates for higher F:P ratios and NaOH:P of 0.40. Drops in alkalinity observed for some of the syntheses were attributed to the Cannizzaro reaction that occurred only at high alkalinity and the higher F:P ratios under conditions where excess free

formaldehyde would be present. The Cannizzaro reaction reduced alkalinity due to generation of formic acid that neutralized NaOH thus increasing viscosity and gel time. A PF synthesis procedure with a second phenol charge created a bimodal molecular weight distribution comprising a low molecular weight fraction and an advanced high molecular weight fraction. The result was a faster gelling resin than the reference resin across the same molecular weight range.³⁴

Pizzi and Stephanou found that the gel time of high pH resoles (above pH 9) did not decrease as they expected, but rather increased. To explain this behavior, they proposed a ring formation mechanism for the 2-HM position via hydrogen-bonding that would lead to reaction retardation.³⁵ They also submitted that formation and accumulation of quinone methides would hinder the condensation reaction, contrary to most other theory and research on the role of quinone methides.^{23, 35} Other researchers, however, have demonstrated the pH dependent role of ionic and neutral species in condensation reactions Higuchi et al. and the importance of quinone methides to condensation.^{21, 23, 25, 31, 36}

Because resulting formation of PF composition is influenced by the phenol and formaldehyde ratios, this aspect has been the focus of many studies over the years. Grenier-Loustalot et al. investigated the relationship of PF resole prepolymer structure to formulation of by using CP-MAS NMR, ¹³C solution NMR, and FTIR. High cross-link density in cured PF resoles depended upon a high F:P molar ratio to form sufficient methylene bridges and an oligomeric composition with high hydroxymethyl content. Knowledge of the prepolymer NMR shifts and features was important for accurate interpretation of the broadened shifts found in the CP-MAS NMR data.²⁶

Banerjee et al. studied high temperature PF gel formation near 140°C. The F:P molar ratio was 3.5 and the pH range was 9.6 to 12.0. The gel formation is found to be strongly dependent on the pH at this elevated temperature, with the fastest gelation at pH 10.4. Banerjee results at 140 °C were similar to an optimal pH of about 9.9 found by Haupt & Waagø for an F:P molar ratio of 2.0 condensed at 85 °C.³⁶

2.1.4. Resole cure chemistry

Kim et al. characterized the structure of a cured PF resole made at an F:P molar ratio of 2.10 with CP/MAS ^{13}C NMR. The molar ratio of methylene groups to phenolic rings was between 1.35 and 1.46, indicating a well cured polymer structure. The remaining formaldehyde was found in other oxidized derivatives, with very low levels of formaldehyde emissions during cure.³⁷

Zhang et al. investigated the cure rate of MgO catalyzed PF resoles with DSC over the pH range 3 to 9, finding that pH, formulated molar ratios, and catalyst content all affected cure rate; the fastest cure was below pH 7.5. Higher catalyst to phenol molar ratios resulted in reduced cure rate.³⁸

Lee et al. probed the curing behavior of PF resoles with three different molar ratios (F:P = 1.3, 1.9, and 2.5) using atomic force microscopy (AFM). The method was also useful for measuring contact angle, surface free energy, acid-base character, and provided a means for calculation of adhesion force. They found that a hydrophobic effect was a significant factor in the adhesion force. The 2.5 F:P resin was more hydrophobic and had a lower adhesion force than the more hydrophilic F:P 1.9 and 1.3 resins. In apparent contrast, Haupt [Thesis 1992] found that for given molecular weight, an F:P 2.3 resin had higher work of adhesion than an F:P 1.7 resin.³⁹

2.1.5. PF resole acceleration

PF cure acceleration has been an issue since the early days of its commercial application. In 1918, the United States Patent Office granted (one) Thomas A. Edison US Patent 1,283,706 for an additive that accelerated phenolic condensation hardening.⁴⁰

2.1.5.1 Research literature

Research activity in PF polymerization accelerators has continued since the Edison patent, as slow reactivity remains an unsolved challenge of commercial importance. Although considerable progress towards understanding the fundamental chemistry of PF acceleration has

been made, some controversy persists and work is still needed to resolve and harmonize the investigator's disparate findings.

Park and Riedl analyzed the effects of propylene carbonate (PC), sodium carbonate (Na_2CO_3), and potassium carbonate (K_2CO_3) on cure acceleration of PF resins with DSC and ^{13}C -NMR. From DSC, they observed that the relative acceleration rate was $\text{PC} > \text{Na}_2\text{CO}_3 > \text{K}_2\text{CO}_3$, though they concluded that PC would be difficult to handle during wood composite manufacture because the resin pot life would be too short. Na_2CO_3 and K_2CO_3 increased conversion with concentration, but PC did so only up to 4% then became slower as concentration increased. This observation was interpreted as the effect of a reduced diffusion rate on reactivity. The PC displayed autocatalytic kinetics above 110 °C, while the Na_2CO_3 & K_2CO_3 showed both n^{th} order and autocatalytic rate kinetics.⁴¹ From ^{13}C -NMR, PC resulted in increased reactivity and possibly functionality of the PF resin due to reaction with decomposed ester. K_2CO_3 and Na_2CO_3 led to the appearance of 2-2' linkages, in contradiction to what other researchers found for conventional PF cure reactions. Solid state ^{13}C -NMR identified 2-2' linkages with PC, but since those peaks were obscured for the Na_2CO_3 and K_2CO_3 samples, caution was urged with regard to the peak assignment. All the carbonates gave a more flexible, less rigid resin than the PF control, with the PC being more flexible than Na_2CO_3 or K_2CO_3 .⁴² Although the results demonstrated the cure acceleration of organic and inorganic carbonates, and hinted at the possibility of 2-2' linkage formation, questions remain as to the actual reactions, mechanisms, and structures. In addition, the lack of on demand reactivity control with resulting pot life problems and pre-cure risk is a potential drawback of accelerated PF systems for wood adhesives.

Several studies summarized below have concentrated on elucidating the acceleration mechanism. Miller & Detlefsen proposed a two-step ester acceleration mechanism: transesterification of the ester acyl group to a phenolic hydroxymethyl (methylol) group, forming a benzyl ester, followed by decomposition of the benzyl-ester to a quinone methide and carboxylate. They pointed out that a carboxylate is a better leaving group than a hydroxyl group.⁴³ Conner et al. investigated accelerated curing reactions of the PF model compounds 2-

HMP and 4-HMP using ethyl formate, propylene carbonate, gamma butyrolactone, and triacetin. The relative rate of accelerator disappearance followed the order ethyl formate > propylene carbonate > gamma butyrolactone > triacetin. The accelerators were consumed in the reaction either by alteration or incorporation. The data suggested that the accelerator was not incorporated into the cured structure. The structures formed were consistent with a quinone methide mechanism or a bimolecular nucleophilic substitution (S_N2) mechanism. The relative self-condensation rate of 4-HMP was faster than 2-HMP without accelerator. Both 2-HMP and 4-HMP condensed faster with accelerator, with 2-HMP being the faster of the two. Since accelerator was consumed and reaction could be resumed by adding more accelerator, the accelerators were not considered to be true catalysts.⁴⁴

Kamo et al. also studied the cure acceleration mechanisms of propylene carbonate with hydroxymethylphenols by comparing the effects of PC on HMP condensation reactions with PC hydrolysate, sodium bicarbonate and ethyl formate. They found that PC decomposes to bicarbonate (HCO_3^-) and propylene glycol (Figure 2.8), accelerating the formation of 2,4'-DPM like ethyl formate, while PC hydrolysate accelerated formation of 4-4'-DPM from THMP like NaHCO_3 . Apparently, PC increased the reactivity of the 2-HMP hydroxymethyl group, while PC hydrolysate and NaHCO_3 increased the reactivity of the 4-HMP hydroxymethyl group. Thus for THMP, PC would have first accelerated the 2-HMP condensation and then the 4-HMP reaction as hydrolysate. Although they regarded transesterification as the mechanism (see Figure 2.9), they observed no transesterification intermediates.⁴⁵

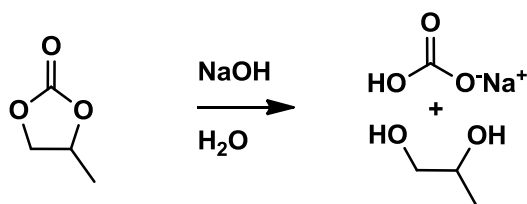


Figure 2.8. Alkaline hydrolysis of propylene carbonate by sodium hydroxide⁴⁵

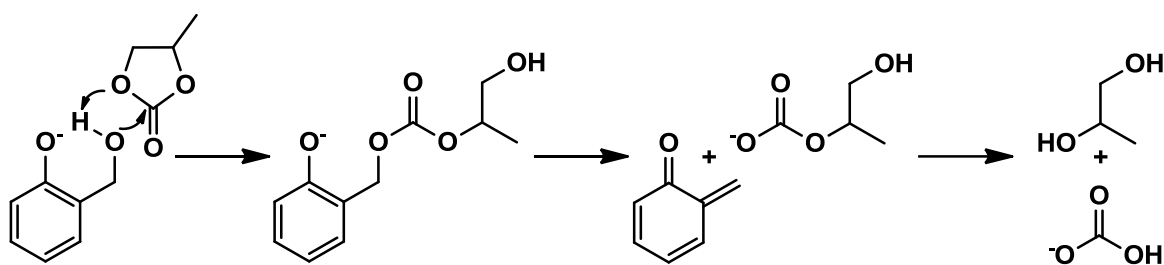


Figure 2.9. Transesterification reaction of 2-HMP by propylene carbonate⁴⁵

As a follow-up study, Kamo et al. compared the catalytic effects of sodium bicarbonate (NaHCO_3) on 2-HMP, 4-HMP, and THMP condensation reactions by measuring concentration with HPLC and structural details with ^{13}C NMR. They also performed molecular orbital calculations for the reactants. They concluded that the 4-HMP and bicarbonate (HCO_3^-) facilitated a resonance effect on the dissociation of the HMP phenolic hydroxyl group. Computational models showed that HCO_3^- forms hydrogen bonds with two 4-HMP hydroxymethyls or with one 4-HMP hydroxymethyl and a phenolic hydroxyl group. A proposed mechanism is electron delocalization with an electron forming an active species such as a 4-carbocation or 4-QM (see Figure 2.5) upon interaction of the 4-HMP hydroxymethyl and the bicarbonate. Bicarbonate did not contribute to the structure of the product. The ^{13}C -NMR chemical shifts indicated a change in the electronic environment on all carbons of the phenolic ring due to the presence of the bicarbonate, with the 4-position gaining higher electron density.⁴⁶

Most of the acceleration studies focused on relative reaction rates and likely mechanisms. An area that was virtually unexplored, except by Kamo et al. is the fate of the accelerator after reaction, as those products might have indicated what reactions took place. In addition, the studies were not comprehensive, in that while some covered PC and inorganic carbonates, others covered PC and inorganic bicarbonates, and others covered organic carbonates and esters. Most, though not all, researchers were in general agreement as to the possibility of two mechanisms occurring, one for esters and organic carbonates at the 2-HMP position and one for inorganic bicarbonates and carbonates at the 4-HMP position. Further, comprehensive work may be needed to harmonize the available findings and clarify PF cure acceleration reaction mechanisms.

2.1.5.2 Patents

Since PF acceleration has been an important commercial issue, the patent literature is replete with abundant examples of rapid cure phenolics.

Resorcinol-formaldehyde (RF) and phenol-resorcinol-formaldehyde (PRF) resins bond wood at ambient temperatures. PF resins modified with resorcinol-based additives take advantage of resorcinol's high reactivity. US 6,608,162, discloses a stable, fast-curing, spray-dried PF composition containing a resorcinol curing accelerator that functions as a cross-linking agent reacting with the methylol groups of PF resin under heat and pressure experienced during wood composite manufacture.⁴⁷ PF resins have also been modified with potassium hydroxide (KOH) to improve reactivity.⁴⁸

Esters, organic carbonates, and lactones are effective PF resin accelerators.⁴⁹ Orth et al. disclosed in 1957 the application of lactones to accelerate hardening of PF resins in German Patent DE 1065605, and with esters of monocarboxylic acids requiring an alkalinity of at least 7.5% in DE 1171606 in 1958 by Orth alone.⁵⁰ US 4,831,067 revealed a method for manufacture of shaped frictional elements for brake linings, pads, and clutch facings from an alkaline PF resin with a liquid ester curing catalyst. The pH must be above 10 and M_w must be above 300 in order for gelation to occur at ambient temperature.⁵¹ US 4,961,795 disclosed a process for bonding lignocellulosic material under sufficient heat and pressure. The method comprises combining an alkaline phenol-formaldehyde resin binder with an ester, organic carbonate, or lactone accelerator and an aliphatic alcohol moderator.⁵² The reactivity of phenolic resole coatings in impregnated paper films was increased by using an ester such as lactones, organic carbonates, carboxylic acid esters, their derivatives and/or mixtures.⁵³ The carbamate reaction product of ammonia and a cyclic carbonate provided a delayed curing reaction when used as a curing agent for phenol-aldehyde resins (US 4,977,231).⁵⁴

Some more recent patents combine features of resorcinol and ester accelerators. A two-part adhesive was useful for production of lignocellulosic panels. The first part comprises a PF resole resin containing a methylene donor such as oxazolidine or methylol urea. The second part comprises a stable RF resin and an optional ester functional compound that can accelerate

the cure of the PF resin part, while the methylene donor accelerates cure of the RF resin part.⁵⁵ Another patent described accelerating the cure of a phenol-aldehyde resin with concurrent use of a cyclic carbonate and an amine. The cure rate can be further accelerated by the addition of a resorcinol source.⁵⁶

2.2. Methylene diphenyl diisocyanate (MDI) chemistry

2.2.1. Overview

Otto Bayer of I.G. Farben in Germany ushered in the polyurethane polymer age following his discovery of macromolecules based upon a diisocyanate and a diamine. His discovery was patented in 1937 and eventually reported in 1947.⁵⁷ The patent application "A process for the production of polyurethanes and polyureas" relates to products suitable for spinning fibers made of hexane-1,6-diisocyanate (HDI) and hexa-1,6-diamine (HDA).⁵⁸

2.2.2. MDI and pMDI synthesis

MDI and polymeric MDI or pMDI are prepared by phosgenation of oligomeric polyamines, which in turn are produced by the acid catalyzed condensation reaction of formaldehyde with aniline. MDI and pMDI are produced together and separated into pMDI and pure MDI, a solid that melts at 41 °C.⁵⁹ The name pMDI is somewhat of a misnomer as it is actually oligomeric MDI with 2, 3, 4, or 5 aromatic rings per molecule.

Modern industrial isocyanate production is usually accomplished by phosgenation, though other processes are possible. MDI and pMDI production requires a sequence of reactions, first generating polyamines followed by their phosgenation to form polyisocyanates. Phosgenation involves reaction of an amine with phosgene (COCl_2), a highly toxic gas, to form an N-substituted carbamoyl chloride intermediate in a very exothermic reaction. This intermediate then undergoes elimination of hydrochloric acid at high temperature, yielding an isocyanate. An excess of phosgene will inhibit formation of ureas and isocyanurates. Polyamine synthesis entails reacting formaldehyde with aniline and a hydrochloric acid catalyst.⁶⁰

2.2.2.1. Polyamine generation

Formaldehyde and hydrochloric acid are added continuously to excess aniline at ambient temperature to initiate polyamine synthesis. The amount of hydrochloric acid present is less than stoichiometric. The temperature is ramped to 100 °C over 120 to 240 minutes. The exothermic condensation reaction requires cooling.⁵⁹

Aniline-formaldehyde condensation begins when they react in the presence of the hydrochloric acid to form N-substituted carbonium ions that then react with aniline at the ortho and para positions, yielding oligomeric benzylamines (Figure 2.10). These benzylamines are subject to further reaction with the carbonium ions, thus leading to oligomerization. Reaction at the para position is faster than at the ortho position, resulting in higher concentrations of para aniline benzylamine (PABA) than ortho aniline benzylamine (OABA). PABA as an intermediate will form 2,4'- and 4,4'-methylenediphenylamine (MDA), while OABA leads to 2,2'- and 2,4'-MDA. Thus, 4,4'-MDI is the major reaction product and very little 2,2'-MDI is produced.⁵⁹

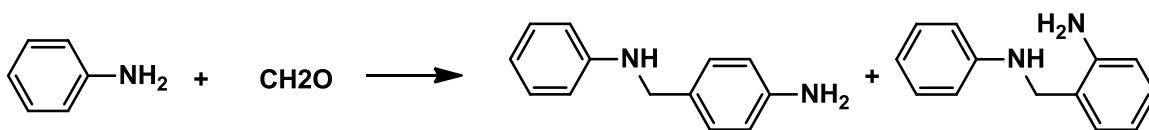


Figure 2.10. Reaction of aniline and formaldehyde to form PABA (left) and OABA (right)⁵⁹

When the benzylamines dissociate after the condensation, they form another carbonium ion that proceeds irreversibly to form MDA or the oligomeric amines via a carbon-carbon bond (Figure 2.11). Since the unreacted para sites are most reactive towards the carbonium ion, 2,2'-MDA and then 2,4'-MDA are most likely to form triamines and hence triisocyanates.⁵⁹

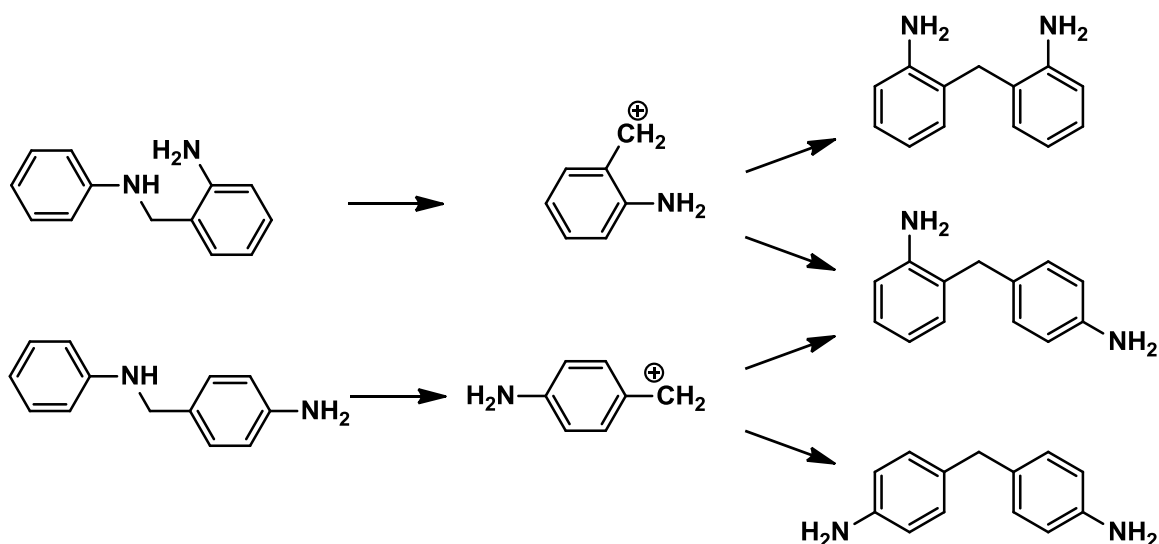


Figure 2.11. Reaction pathway of aminobenzylanilines to methylenediphenylamines

Product composition is a function of aniline concentration, hydrochloric acid concentration, and temperature. Excess aniline leads to more diamines, while high hydrochloric acid results in more 4,4'-MDA (Table 2.6). High temperature results in more 2,2'-MDA and 2,4'-MDA. Water and unreacted aniline are eliminated from the polyamine reaction mix prior to phosgenation. If the aniline were not completely removed, hazardous phenyl isocyanate would be produced during phosgenation.⁵⁹

Ratios of the aniline isomers can be controlled by reacting polymeric MDA (PMDA) in the presence of catalytic aniline hydrochloride as shown in table 2.6. These ratios may also be influenced by adjustment of the aniline to formaldehyde ratio as shown in table 2.7. Obviously, the ability to direct the MDA isomeric composition will directly effect pMDI composition after phosgenation.⁵⁹

Table 2.6. Isomeric composition of PMDA reactions at 190 °C⁵⁹

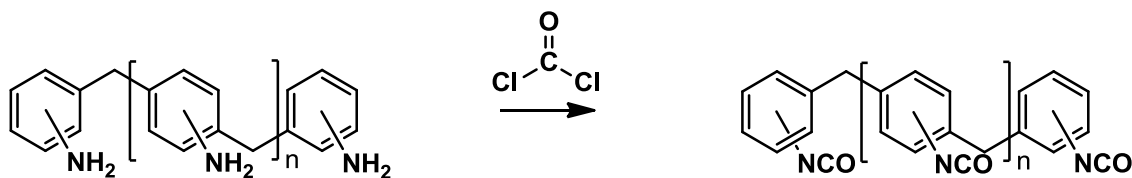
Inputs		MDA Isomers		
Time (h)	MDA yield %	2,2'	2,4'	4,4'
0	68	---	0.5	99.5
1	70	1	39	60
2	71	2	49	49

Table 2.7. Effect of aniline to formaldehyde (A:F) molar ratio on MDA yield and isomeric composition⁵⁹

A:F	MDA yield %	2,4'	4,4'
2.85	79	4.7	95.3
2.50	75	3	97
2.00	68	2	98

2.2.2.2. Polyamine phosgenation

Hentschel first synthesized isocyanate in 1884 using a phosgenation process that is still in use today. The reaction is usually run continuously on the aromatic diamines, in chlorobenzene as a solvent, with excess phosgene, and under pressure in highly corrosion resistant reaction vessels (Figure 2.12). The temperature is ramped from ambient to 180 °C. The hydrochloric acid and phosgene by-products are vented and separated. The phosgene is reused and some of the hydrochloric acid is used for aniline/formaldehyde condensation while the rest is sold or oxidized to chlorine and used to make more phosgene. Although other processes have been attempted to replace the phosgenation process, it is still used today as none are as economical. Iron impurities due to corrosion can affect the reactivity of the finished pMDI.⁵⁹

Figure 2.12. Phosgenation of polyamines to polyisocyanates⁵⁹

2.2.2.3. MDI distillation

The isocyanates produced from aromatic polyamines result in a mixture of pMDI and pure MDI. Pure MDI comprises a blend of mostly the 2,4' and 4,4' isomers; very little 2,2' isomer will be present due to the nature of MDA formation as shown in table 2.6. The mixture may then be refined by distillation to isolate useful fractions, the exact proportions of isomers and oligomers will depend on the quantity of pure MDI removed. Pure 4,4'-MDI is removed from the reaction composition by continuous thin film or climbing film distillation along with minor quantities of the 2,2', and 2,4' isomers. The remainder is about 50% MDI and 50% oligomeric, with functionality greater than or equal to three. The other isomers boil at temperatures lower than 4,4'-MDI and therefore are removed early from the distillation and then back-added to the pMDI remainder. Mixtures of the three isomers have substantial melting point reductions that allow for liquid handling at ambient temperatures.⁵⁹

Among the MDI monomers, the 4,4' isomer is about three times as reactive as the 2,4' isomer. The 4,4' isomer is usually solid at ambient temperature, with a melting point of 38-41 °C, while a 4,4'/2,4' isomer blend is usually liquid with a melting point of 18 °C. Storage is an important issue for the solid 4,4' isomer as it is prone to dimerization, even in the crystalline form. Blends of the 2,4' and 4,4' isomers therefore provide a reasonable trade-off between reactivity, handling, and ease of storage (Table 2.8).^{61,62}

Table 2.8. Melting points of mdi isomers and eutectic blends⁵⁹

MDI isomer or MDI isomer blend	Melting point in °C
2,2'-MDI	46
2,4'-MDI	35
4,4' -MDI	41
Binary eutectic: 60:40/2,4':4,4'	14
Ternary eutectic: 22.7:42:35.5/2,2':2,4':4,4'	< 0

2.2.3. Isocyanate reactions

Isocyanates undergo a wide variety of reactions, many of which could occur in the PF-MDI system under consideration, affecting the resulting reaction products that would be present. Thus, a good understanding of these reactions is important for interpreting experimental data.

The reactivity of active hydrogen occurs because of protonated nucleophilic addition reactions that occur across the carbon-nitrogen double bond of the isocyanate group. The classical definition of active hydrogen is a hydrogen atom that sodium can replace. Electron withdrawing substituents on aromatic rings accelerate such reactions more than on aliphatic substrates, while electron donating substituents have the opposite effect. In the reaction, the active proton adds to the nitrogen, while the rest of the radical attaches to the central carbonyl carbon of the isocyanate group.⁶⁰ The isocyanate carbon has positive charge character as seen in the resonance structure (Figure 2.13); negative charge can be further delocalized on an aromatic ring, thus explaining the higher reactivity of aromatic isocyanates.⁶³

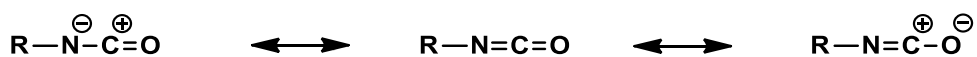


Figure 2.13. Isocyanate resonance structures

2.2.3.1. Urethane reaction

The reaction of isocyanates with alcohols and phenols forms urethane groups (Figure 2.14). The order of reactivity for aliphatic alcohols is $1^\circ > 2^\circ \gg 3^\circ$.^{60, 63} The reactivity of a phenolic hydroxyl is slower due to the greater acidity of phenol than the aliphatic alcohols; this reaction will only go forward with catalyst. In addition this reaction is less stable and is reversible at temperatures greater than 100 °C. Phenols are used to make blocked isocyanates with thermal release.⁶⁰ The more nucleophilic (i.e. electron rich) the reactive hydroxyl group is, the higher its reactivity. But at higher temperature the reactants can be restored, implying that urethane formation is a reversible equilibrium reaction. This reversibility is the basis of blocking technologies based on phenols, oximes, lactams, CH acidic compounds, and bisulfite.⁶³ Table 2.9 shows relative reactivity towards phenyl isocyanate of various reactive functional groups.

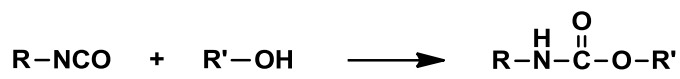


Figure 2.14. Urethane formation reaction

Table 2.9. Reactivity of phenyl isocyanate in toluene⁶³

Reactive compound	Rate constant [†]		Activation energy (Kcal/Mol)
	25 °C	80 °C	
Aromatic amine	10-20	---	8-9
Primary -OH	2-4	30	10
Secondary -OH	1	15	---
Tertiary -OH	0.01	---	11
Water	0.4	6	---
Phenol	0.005	---	---
Urea	0.01	2	---

[†] k x 10⁴ 1/mol· sec. @ 99% stoichiometry

2.2.3.2. Urea

Isocyanate reacts with primary and secondary amines to yield ureas and substituted ureas (Figure 2.15). Primary aliphatic amines can be quite reactive, sometimes reacting at a second hydrogen to give a biuret. Aromatic amines are less reactive and biuret formation is less likely due to inductive and steric considerations.⁶⁰



Figure 2.15. Urea formation reaction

2.2.3.3. Water

Reactions of isocyanates with water are important for pMDI wood binders, as they react with the moisture present in the substrate to form polyureas. These reactions with water are also important to blended PF-MDI systems since the PF component is usually in aqueous solution. Water reacts with an isocyanate to form carbamic acid, followed by its decomposition to an amine with evolution of carbon dioxide (Figure 2.16).⁶⁴ The amine then reacts further to form biuret. The net effect of the gas generation, chain extension, and branching imply that a small

amount of water can have a major effect on the polymer structure.⁶⁰ An important question to consider for PF-MDI blends is whether the reactions of isocyanate with water are faster or slower than those with alcohols and phenols. If Szycher's data table (Table 2.9) is accurate, then the reaction of MDI or pMDI isocyanate groups with PF methylol (hydroxybenzyl) groups should be faster than their reaction with water which is in turn faster than their reaction with the phenolic hydroxyl group. The reaction of the aryl amine, once it is formed, however, will be even faster.

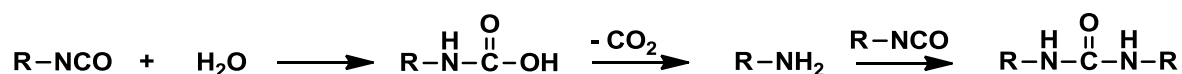


Figure 2.16. Carbamic acid reaction with subsequent urea formation

2.2.3.4. Isocyanate-polymer

Reactions of polyisocyanates with polyols, polyamines, or polycarboxylic acids form step growth polymers. Polyols form carbamates (polyurethanes) that will reverse upon heating, while polyamines form polyureas. With polyamines, the polymerization reaction rate is strongly dependent on the basicity of the amine. The carboxylic acids react with aryl isocyanates at high temperatures, forming anhydrides. These anhydrides then decompose with carbon dioxide emission into amines that then further react to amides in the presence of excess anhydride, giving a useful synthetic route to high value polyamides and polyimides. Base catalysis is preferred to avoid formation of substituted ureas.⁶⁰

2.2.4. Polyols and chain extenders

Polyols possess at least two reactive hydroxyl groups attached to the molecule, while polyamines possess at least two reactive amine groups. Reaction of a polyisocyanate with a hydroxy-polyol will form polyurethane, while reaction with a polyamine will form polyurea. The four main classes of polyols in conventional polyurethane chemistry are polyether polyols, amine-terminated polyethers, polyester polyols, and polycarbonates.⁶⁰

Chain extenders, a polyol subset, are differentiated among polyols chiefly by their low molecular weights; they comprise at least two active hydrogen end groups, again usually either hydroxyl or amine groups. If the isocyanate reactive compound has exactly two reactive end groups, it is a chain extender and will form a thermoplastic polymer, but only if it is reacted with a diisocyanate; if it has three or more reactive end groups, it is a cross-linker and will form a thermoset polymer. Low molecular weight diols, such as 1,4-butane diol, and diamines, for instance ethylene diamine, are typical chain extenders, while a triol like glycerol or a triamine such as diethylene triamine are examples of cross-linkers. The chain extender forms the hard segment of a polyurethane or polyurea elastomer together with a diisocyanate, and imparts important mechanical properties to the material. The relationship of these polymer constituents to polymer characteristics are given in Table 2.10.⁶⁰

Table 2.10. Relationship of polymer constituents to polymer characteristics⁶⁰

Molecular weight	Functionality	Polyol	Polyamine
40 to 300 g/mol	$f = 2$	Thermoplastic polyurethane, hard segment chain extender	Thermoplastic polyurea, hard segment chain extender
	$f > 2$	Thermoset polyurethane cross-linker	Thermoset polyurea cross-linker
> 300 g/mol	$f = 2$	Thermoplastic polyurethane, soft segment	Thermoplastic polyurea, soft segment
	$f > 2$	Thermoset polyurethane	Thermoset polyurea

2.2.5 Isocyanate catalysis

Useful isocyanate catalysts for polyurethane formation stabilize the resonance structure of the functional group, and may be either nucleophilic or electrophilic. This stabilization maintains the group in a higher energy state than without the catalyst. Also, stereochemical orientation must favor the structure of the transitional state. Weak acid salts and tertiary amine bases are nucleophilic while organometallic catalysts are electrophilic. Acids such as mineral and acid halides prolong reaction while bases, especially tertiary amines accelerate nucleophilic

reactions. Metals such as Sn, Zn, or Fe salts also promote reaction rate. Amine-tin catalyst combinations are known to provide synergistic catalysis (Table 2.11), while delayed action catalysts may be formulated from polyamines and carboxylic acids like formic acid.⁶³

Table 2.11. Relative reactivity and synergies of polyurethane catalysts⁶⁵

Catalyst	Concentration %	Relative reactivity
Uncatalyzed	---	1
DBTL	0.1	210
DABCO	0.2	260
DBTL + DABCO	0.1 + 0.2	1000
SnOct	0.1	540
TMBDA	0.5	160
SnOct + TMBDA	0.1 + 0.5	1410
SnOct	0.3	3500
DABCO	0.3	330
SnOct + DABCO	0.3 + 0.3	4250
TMBDA = Tetramethylbutanediamine	DABCO = 1,4-Diaza(2,2,2)bicyclooctane	SnOct = Tinocatoate

The isocyanate resonance structure illustrates how the relative electronegativity of carbon, nitrogen, and oxygen affects its electron distribution (Figure 2.13). During reaction, electrophilic reactive hydroxyls will coordinate to and bond with the nucleophilic isocyanate nitrogen atom. With the proton now linked to the nitrogen, the rest of the reactive hydroxyl compound becomes nucleophilic and attacks the electron deficient carbon atom. Catalysts accentuate this basic electronic mechanism through a coordinated complex between the catalyst, isocyanate and reactive hydroxyl groups.⁶⁰

Tertiary amine catalysts coordinate reaction through their nitrogen free electron pair. Their catalytic strength is a function of availability for complexation and is affected by steric hindrance and substituent electronic effect. Increasing reaction rates correspond to increased base strength. One proposed mechanism is formation of an activated complex with the catalyst between the hydroxyl and isocyanate groups. The nucleophilic amine free electrons can easily draw reacting hydrogen away from its oxygen or nitrogen, facilitating its reaction

with the isocyanate nitrogen. Another mechanism is complexation of amine nitrogen free electron pair to the partial positively charged carbon, thereby enhancing reaction of the reactive hydrogen at the nitrogen with increased electron density.⁶⁰

Organometallic catalysts, more specifically tin based salts like dibutyltin dilaurate (DBTL) or tin octoate, strongly mediate the isocyanate-hydroxyl reaction. These catalysts can form three-way complexes with either the isocyanate group or the hydroxyl group.⁶⁰ Reegen and Frisch studied the formation of isocyanate-catalyst and alcohol-catalyst complexes and found evidence for ternary complexes intermediates for DBTL catalyzed urethane reactions.⁶⁶ Wong and Frisch developed an HPLC technique to study the effects of different catalysts on competing isocyanate reactions of phenyl isocyanate and n-butanol in acetonitrile at 50°C. Catalysts included dibutyltin dilaurate and several tertiary amines. They measured NCO disappearance and reaction product formation. They determined catalytic specificity, relating it to catalyst structure.⁶⁷

Gaunt & Baker provided early evidence for the formation of a hydrogen bonded complex vital to the urethane formation reaction. A complex comprising a free base, an alcohol, and an isocyanate in a transition state was identified via IR spectroscopy. The value of the reaction rate constant decreased according to the series ROH = methanol > ethanol ~ phenol > isopropyl alcohol > t-butyl alcohol.⁶⁸

Amine catalyzed reaction of alcohols and aromatic isocyanates are considered to proceed by one of two mechanisms. The first is complex formation by an isocyanate and a base, subsequently reacting with an alcohol to a urethane. The second possible mechanism involves the alcohol and amine catalyst complexing prior to reaction with the isocyanate. The first mechanism is thought to predominate due to less steric effects than the alternative mechanism as weakly basic, unhindered amines have been shown to have higher activity than more basic hindered amines. Also, tertiary amines facilitate isocyanate trimerization, clear evidence that an amine-isocyanate complex forms.⁶⁹

Flynn and Nenortas studied reaction kinetics of phenyl isocyanate with 2-ethylhexanol, methanol, and deuterium methoxide under amine catalysis. They discovered that

heptamethylbisguanide had greater catalytic activity than other amines due to its basicity. They proposed that the base strength of the amine in the amine-isocyanate complex increases the participation of the complex in reactions. Deuterium isotope studies indicated that proton abstraction by the amine is unlikely.⁶⁹

Farkas and Strohm studied the reaction kinetics of phenyl isocyanate with phenol using triethylamine or triethylene diamine as catalysts, with measurement of the basicity of the catalysts and their hydroxyl association constants. They found that solvent affected basicity, with high association constants for a triethylene diamine-phenol complex, and that the reaction of phenol with phenyl isocyanate did not depend on phenol concentration. They concluded that amine-catalysis proceeded by formation of an amine-phenol complex, followed by a subsequent rate controlling reaction with phenyl isocyanate.⁷⁰

Bechara described how catalyst combinations of amines and tin carboxylates exhibited synergistic catalysis of isocyanates and alcohols mediated by formation of organotin-amine complexes. These complexes assisted transformation of tin carboxylates to very active tin alkoxides, quickly adding the isocyanate group to the tin-oxygen linkage and forming a tin carbamate adduct. A second alcohol reacts with the adduct to form a urethane product and the tin alkoxide.⁷¹

2.2.6. Polyurethane thermal stability

Since the reactions of polyol hydroxyl groups with isocyanates are relatively slow, organometallic catalysts, such as DBTL, are useful for achieving faster reactions. An inherent drawback of such catalysts is that they may lead to thermal degradation of urethane polymers.⁶⁰ The urethane functional group in polyurethanes can depolymerize reversibly to its original components. Allophanates and biurets will depolymerize at high temperature, but most urethane and urea bonds require much higher temperatures to cleave, while isocyanurates are the least temperature susceptible. Table 2.12 details the dissociation temperatures for various polyurethane linkages.⁶⁰

Table 2.12. Thermal dissociation temperatures of polyurethane linkages⁶⁰

Functional linkage	Dissociation onset temperature in °C
Aliphatic Allophanate	85-105
Aromatic Allophanate	100-120
Aliphatic Biuret	100-110
Aromatic Biuret	115-125
Aliphatic Urea	140-180
Aromatic Urea	160-200
Aliphatic Urethane	160-180
Aromatic Urethane	180-200
Disubstituted Urea	235-250

Szycher provides three types of thermal urethane dissociation reactions: 1) reversible formation of the polyol and isocyanate, 2) formation of a primary amine, an olefin, and carbon dioxide, and 3) formation of a secondary amine and carbon dioxide. Clearly, the reactions that form carbon dioxide would be irreversible.⁶⁰

2.3. PF resole-pMDI chemistry and adhesive binders

PF and pMDI resins are useful for binders and coatings, finding broad application in wood composites and paper impregnation. These resins provide good storage life, ease of application, and impart durability to the composite product. In spite of many benefits, their disadvantages have proven difficult to overcome, especially those of the relatively slow PF reactivity and expensive cost of MDI. To overcome these drawbacks some researchers have modified the basic PF or pMDI resins, while others have combined them by direct blending to draw upon the best attributes of each resin. The ability to cure PF resin quickly at ambient or moderate temperatures would be desirable for the wood composites industry.

2.3.1. Overview of ambient and low temperature wood adhesive cure research

Recent research and development efforts have focused on ambient or low temperature cure technologies for wood composites, indicating that such technology is valuable. Griffith advocated rapid, low-temperature, electron beam-curable adhesives systems for wood composites, estimating that such systems offer potential energy savings to the wood composites industry of 65 trillion BTU/year. Electron beam-curing systems could reduce cure

temperatures from 450 °F to 250 °F (232 °C to 121 °C), but also offer the potential of reducing unit capital costs and doubling throughput. Reducing pressing temperatures would also decrease volatile organic compounds (VOC), thereby cutting process emissions also. Such technology would challenge the current wood composite manufacturing paradigm by minimizing wood drying. Some obstacles, however, are the high cost of the polymer resins needed and the electron beam equipment capital expense.⁷²

Frazier and Heinemann have worked on a novel adhesive for the cold-press fabrication of laminated veneer lumber. The objective is to cold-press laminated veneer lumber made from high moisture content wood with moisture-curable polyurethane adhesives. If successful, such adhesives would reduce energy consumption by eliminating hot pressing and reducing wood drying with the additional benefit of curtailed VOC production. The adhesives would comprise either 100% organic isocyanate-reactive polyurethanes or reactive latexes crosslinked with polyisocyanates.⁷³

2.3.1.1 Research literature

The Frazier research group at Virginia Tech characterized PF-pMDI hybrid adhesive systems. Their work with PF-pMDI hybrids wood adhesive binders was assumed that combining the two resins could maximize their advantages while minimizing their shortcomings. An important observation was that the aqueous PF and neat pMDI phase separate, forming a two-phase emulsion. This emulsion behavior is thought to be an impediment to industrial usage of PF-pMDI hybrid adhesives.⁷⁴ In further follow-up studies of PF-pMDI systems, they found that pMDI droplets formed a separate organic phase in the aqueous PF continuous phase. The pMDI droplets were fixed in place as a separate morphological domain in the cured resin. They also established with DSC that pMDI accelerated the cure of the PF continuous phase, but did not detect the effect with dielectric analysis of a wood composite bondline during pressing.⁷⁵

2.3.1.2. Patent literature

Rosthauser disclosed a process for binding wood with an adhesive composition comprising a polyisocyanate and a solid PF resole. Wood composites are made by pressing at 177 °C for 4.5

minutes.⁷⁶ Another Rosthauser patent, US 6294117, details a comparable method, but uses solid novolak instead of solid resoles. Wood composites are made by pressing at 177 °C for 4.5 minutes. Both patents claim to cure the adhesive and bond the composite within 2 to 10 minutes at temperatures between 120 and 225 °C.⁷⁷ US patent 6297313 details a sprayable adhesive system for bonding wood at low cost, with fast cure and good performance. The adhesive composition includes an aldehyde resin and a polymeric isocyanate. The adhesive mix can also incorporate a carbonate material like propylene carbonate, though no examples are mentioned of its use or of its effect on viscous stability, pot life, and cure speed. The viscosity of the mixed adhesive composition should not be more than 500 mPa·s and should have a pot life of at least two hours. The DSC onset temperature of the preferred system is about 115 to 125 °C. The adhesive composition can be mixed prior to application or it can also be mixed in-line with a static mixer. In the example, wood wafers are pressed for 120 seconds at 216 °C.⁷⁸

US 3,872,034 discloses a PF resole rigid foam composition which is non-friable, non-corrosive, exhibits no “punking”, and needs only room temperature curing. The foam is obtained from a mixture of a PF resole, an organotin catalyst, an organic polyisocyanate and a blowing agent. The foam is obtained by foaming and curing, at a temperature below 32 °C, a reaction mixture consisting of a PF resole, an alkylene glycol, a halo-organic phosphate, stannous chloride or a non-acidic organotin catalyst, a surfactant, a difunctional diisocyanate, and a halogenated alkane. In an example, the foam achieves tack free time formed in 1 minute 50 seconds at ambient.⁷⁹

2.3.1.3 Model compound studies

Papa and Critchfield investigated reactions of the PF model compounds 2-HMP and 4-HMP with phenyl isocyanate in the context of production of hybrid PF-PU foams. Reactions were run in chloroform at temperatures ranging from 25 to 85 °C. The reactions were uncatalyzed, or with triethyl amine (TEA) or DBTL catalysts. Reaction with TEA favored urethane formation at the phenolic hydroxyl, while DBTL favored formation of urethanes at the hydroxymethyl groups. Uncatalyzed reactions favored the formation of phenyl anilines. Reactions at the hydroxymethyl group with DBTL were found to be fastest, while the uncatalyzed reactions were

slowest. Table 2.13 shows the reaction products identified for the various model compound and catalyst combinations.⁸⁰

Table 2.13. Reactions of PF monomers and phenyl isocyanate in CHCl_3 ⁸⁰

Catalyst (Temp)	PF Monomer (Yield)	
	2-HMP	4-HMP
None (75°C)	N-(2-hydroxybenzyl)aniline (36% on P) 1,3-diphenylurea (82% on PI) + CO_2	p-carbamylbenzyl N-phenylcarbamate (26%) + Tar + CO_2
TEA	Phenol carbamate 2-benzyl alcohol (70%)	Phenol carbamate 4-benzyl alcohol (86%)
DBTL	N,N-bis(2-hydroxybenzyl)aniline (52%) o-hydroxybenzyl N-phenylcarbamate (3.7%) N-(2-hydroxybenzyl)aniline (4.2%)	p-carbamylbenzyl N-phenylcarbamate (55%)

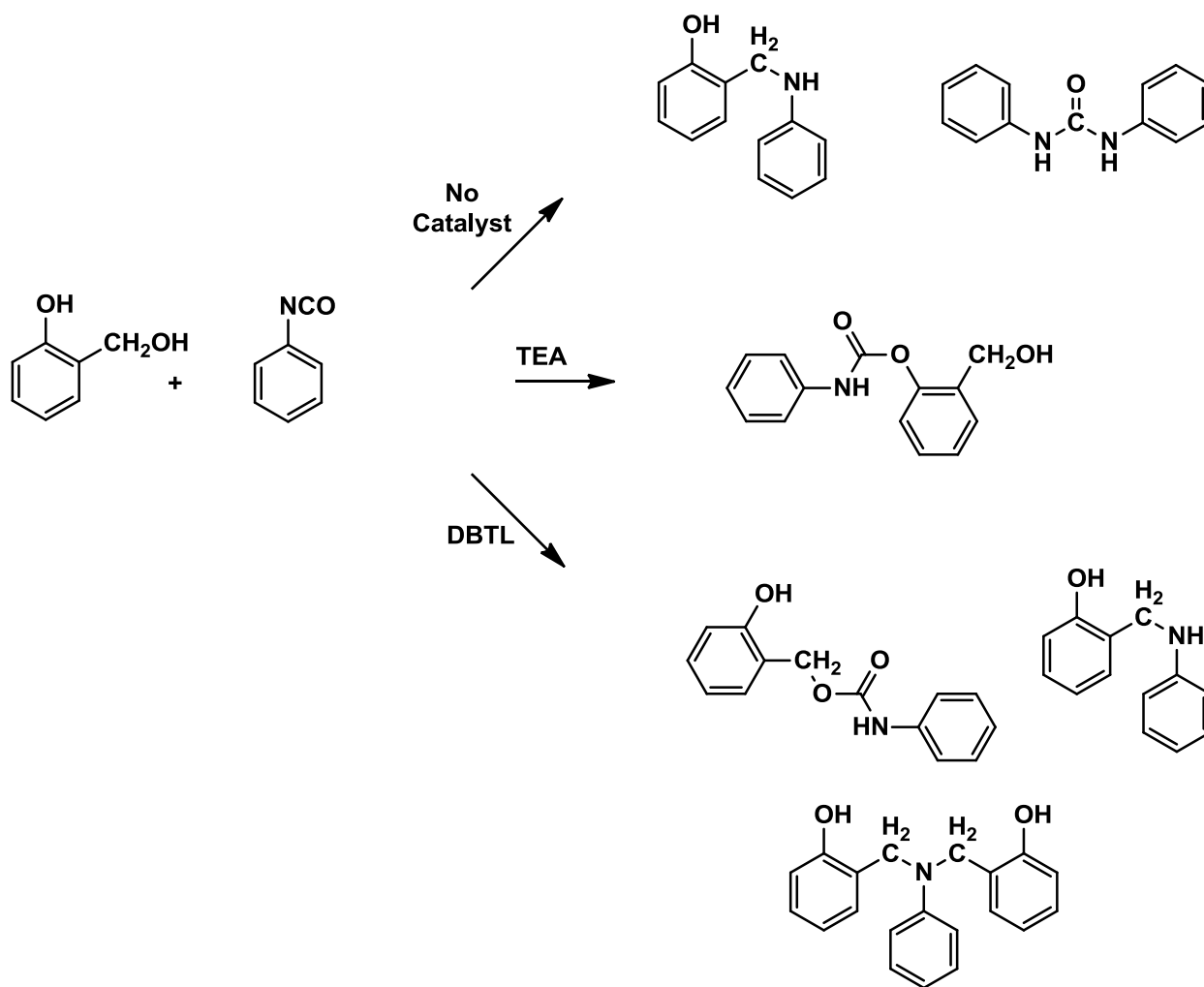


Figure 2.17. Reaction products of 2-HMP and phenyl isocyanate⁸⁰

Papa and Critchfield also found that 4-HMP reacted more slowly than 2-HMP with TEA or DBTL. Without catalyst, the 4-HMP required more time (4.5 hours vs. 2 hours) at a higher temperature (85 °C vs. 75 °C) to yield less product (26% vs. 36% and 82%). They concluded that while TEA accelerated the isocyanate reaction of the more acidic phenolic hydroxyl, DBTL catalyzed the reaction with the 2-HM group (i.e. not the phenolic hydroxyl) of 2-HMP, while DBTL enhanced reaction on 4-HMP at both the phenolic hydroxyl and the 4-HM group.⁸⁰ Figure 2.17 and 2.18 show the reaction products for 2-HMP and 4-HMP with the respective catalysts.

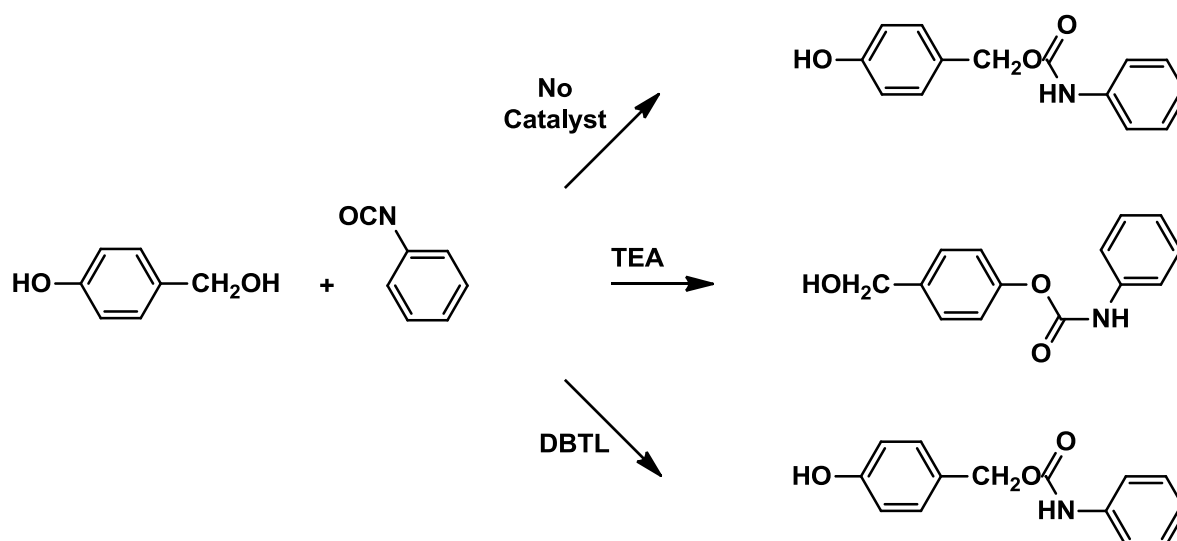


Figure 2.18. Reaction products of 4-HMP and phenyl isocyanate⁸⁰

Zhuang and Steiner studied the thermal reactions of 4,4'-MDI with phenol, benzyl alcohols, and hydroxybenzyl alcohols as model compounds with a view to facilitating wood adhesive moisture stability through the use of blocked isocyanates. Reactions were run in toluene or in the melt at temperatures ranging from 45 to 115 °C using tributyl amine as a catalyst. Adducts and polymers formed using 2-HMP, 4-HMP, p-methoxy phenol, p-methoxy benzyl alcohol, benzyl alcohol, and p-fluoro phenol. They also ran reactions in THF at 25 °C to provide kinetic data. The reactions were analyzed with DSC, ¹H NMR, IR, and MS. The order of reactivity found was p-fluoro phenol < phenol < p-methoxy benzyl alcohol and 4-HMP > 2-HMP > benzyl alcohol > phenol. Differences in reactivity were attributed to the effect of substituents on aromatic ring electron density and the hydrogen bonding effects of 2-HMP. Benzyl alcohol effects were

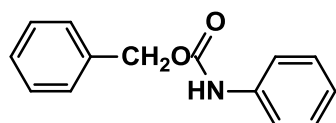
attributed to higher electron density on the benzylic hydroxyl group and reduced steric hindrance in attacking the NCO group. MDI adducts of benzyl alcohol had lower IR wavenumber (1703 cm^{-1}) than the MDI-phenol adduct ($1716\text{-}1723\text{ cm}^{-1}$), a potentially important point for differentiation among possible reaction products. NMR integrals showed more benzylic linkages than phenolic linkages, implying that the hydroxymethyl group is more reactive than the phenolic hydroxyl group.⁸¹

Table 2.14. Reaction rate constants for 4-hydroxybenzyl alcohol and 4,4'-MDI at various temperatures using TEA and DBTL catalysts⁸²

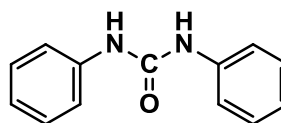
Temperature (°C)	Rate constants K ($1/(\text{mol} \times \text{s})$)		
	No catalyst	Triethylamine	DBTL
35	1.2×10^{-1}	3.0×10^{-1}	
40		4.1×10^{-1}	
45		5.3×10^{-1}	
55		8.3×10^{-1}	4.9×10^{-1}
60	3.6×10^{-1}	11.3×10^{-1}	6.9×10^{-1}

Batubenga et al. researched MDI-PF copolymer by catalytic co-polymerization. They reacted 4,4'-MDI and 4-HMP in THF using TEA, morpholine, or DBTL as catalysts to form urethane reaction products. The kinetic data generated showed that TEA was faster than DBTL (Table 2.14).⁸²

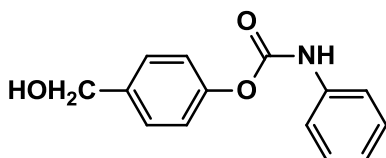
Haider et al. studied the reaction of phenyl isocyanate with phenol, benzyl alcohol, and 4-HMP in alkaline-aqueous and 1,4-dioxane environments at temperatures of 25 and 100 °C. Base catalysis was used in the aqueous environment. They found that the reaction products (Figure 2.19) were phenol carbamate, benzyl carbamate, and diphenyl urea (DPU). In dioxane at 100 °C, the formation of DPU was favored, but at ambient in dioxane some urethane formed as well as DPU. Surprisingly, under basic aqueous conditions at 100 °C, the formation of phenyl and benzyl urethane was enhanced, with the formation of benzyl urethane being preferred over DPU (Table 2.15). They attributed the high urethane yields to greater stability of the urethane and the higher reactivity of the hydroxymethyl group in this environment.⁸³



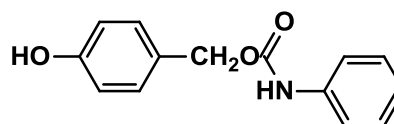
benzyl carbamate



diphenyl urea



4-(hydroxymethyl)phenyl
N-phenyl carbamate



4-(hydroxy)benzyl
N-phenyl carbamate

Figure 2.19. Reaction products of Haider et al. model compound study⁸³

Baker and Gaunt have shown that base has a strong catalytic effect on the reaction of isocyanate with the phenolic hydroxyl.⁶⁸ The 4-HMP probably self-condensed in a competitive reaction at high temperature. In addition, commercial PF and MDI resins were cured together at 125 °C and analyzed with IR spectroscopy. The IR results suggested that they had indeed formed a polyurethane-PF copolymer in addition to polyureas. Their work was the only one in an aqueous system, but it lacked information about the alkaline- aqueous system at ambient temperature. These results show that water present reacting with the isocyanate will still lead to formation of the diphenyl urea due to the carbamic acid reaction.⁸³

Table 2.15. Reactions of PF model compounds and phenyl isocyanate in water and 1,4-dioxane⁸³

Solvent	Temp.	PF monomer (% yield)		
		Phenol	Benzyl alcohol	4-HMP
Dioxane	25 °C	66% DP Urethane 34% DP Urea	8% BP Urethane 92% DP Urea	48% DP Urea 52% 4-HMP NPC
	100 °C	0% DP Urethane 100% DP Urea	5% BP Urethane 95% DP Urea	99% DP Urea 0% 4-HMP NPC
Water/ NaOH	100 °C	28% DP Urethane 72% DP Urea	62 % BP Urethane 38% DP Urea	0% 4-HMP NPC 8% 4-HB NPC 53% DP Urea

Key to table abbreviations: DP = Diphenyl; BP = Benzyl phenyl; 4-HMP NPC = 4-(hydroxymethyl)phenyl N-phenyl carbamate; 4-HB NPC = 4-(hydroxy)benzyl N-phenyl carbamate

Friebe and Siesler reacted phenol with phenyl isocyanate to produce DPU and continuously monitored the reaction with in situ FTIR. Chloroform was the solvent and anhydrous AlCl_3 was the Lewis acid catalyst. They used temperatures between 26 and 58 °C to determine kinetic reaction rates. The reaction was quenched by the addition of water, producing aniline. The urethane amide bond showed up at 1440 cm^{-1} and isocyanate at 2260 cm^{-1} ; the latter peak was used for quantitative evaluation, since it represented consumption of the phenyl isocyanate. Absorption bands at 1730 cm^{-1} and 1700 cm^{-1} corresponded to free and hydrogen bonded carbonyl groups. The amide II bands at 1530 cm^{-1} and 1440 cm^{-1} characterized evolution of the reaction product. Results were correlated with concentration data determined by HPLC. Molar absorption constants were determined for phenol and phenyl isocyanate. From the HPLC data, concentration profiles of the raw materials were plotted over time for each temperature and used to calculate rate constants. An Arrhenius plot of the rate constants yielded an activation energy of 36 kJ/mol.⁸⁴

2.3.2. Miscibility of PF and MDI blends

The works of Zheng and Reidlinger have shown that blending PF resin and pMDI results in emulsification. Their relative volume fraction determines which blend component functions as the continuous phase and which as the dispersed phase. Zheng and Frazier found that dispersing pMDI within a PF continuous phase-toughened the resulting polymer.^{74, 85} Reidlinger and Frazier showed that the blends created micro-dispersions when cured rather than a homogeneous system.^{75, 86} Their findings lead to the question: could the performance properties of PF-pMDI blends be improved by increasing their miscibility and therefore compatibility?

2.3.2.1. Surface properties

The surface properties of PF and pMDI will influence their compatibility. Previous research by Haupt on PF surface properties indicates that surface tension development is related to hydrogen bonding and degree of polymerization. As the degree of polymerization increases and the F:P molar ratio increases, the number of hydroxymethyl groups per molecule also increases. The result is more intermolecular hydrogen bonding and higher surface tension.

These hydroxyl groups and their specific interactions will ultimately affect the miscibility of a PF resole with pMDI.^{34, 87}

Other factors to take into consideration regarding miscibility are the effect of water, the polar and ionic character of phenoxide salts in the PF prepolymer, and the respective dispersive, polar, and hydrogen bonding characteristics of the pMDI prepolymer. Water is very polar and highly hydrogen bonding, resulting in specific interactions. An ionic polyphenolic salt will have a very different dipole moment and electron density distribution than a neutral polyphenol or a prepolymer like PMDI with polar isocyanate groups and non-polar aromatic rings linked by methylene bridges (See table 2.5).³

2.3.2.2. Solubility parameters

Hansen has been a strong proponent of solubility parameters for understanding polymer surface interactions, relating this interfacial contact to dispersive, polar, and hydrogen bonding properties. Hansen also gives a useful equation relating solubility parameters (δ) to the difference between a solvent and a polymer in order to predict solubility or swelling of the polymer (p) in the solvent (s):

$$RA^2 = 4(\delta_{Dp} - \delta_{Ds})^2 + (\delta_{Pp} - \delta_{Ps})^2 + (\delta_{Hp} - \delta_{Hs})^2$$

where D is dispersive, P is polar, and H is hydrogen bonding. The value of R_0 is the difference in solubility parameter that can be tolerated for the dissolution or swelling of the polymer or solute. It is proportional to the decrease in quality of interaction, i.e. it will be small when it is soluble, while limited swelling will display a relatively larger spherical radius.⁸⁸

In addition, Hansen's review of the ultrastructure of wood from a solubility parameter view point is useful in assessing the interaction of wood with various adhesives, including pMDI and PF. Hansen concluded that wood ultrastructure is partly related to its major constituents: cellulose, hemicellulose, and lignin. The ability of these materials to orient in the wood ultrastructure relates to their surface properties as influenced by the chemical functional groups present. The polar hydroxyl groups of cellulose would orient towards the hydroxyl

regions of hemicellulose and lignin, while avoiding interaction with the less polar aromatic regions of lignin and the hemicellulose acetyl groups.⁸⁹

Limited research literature is available regarding solubility parameters of PF resoles for wood adhesives. Very little information exists on the surface interactions of blended PF-MDI systems. Schmidt studied swelling parameters for polymer-solvent interaction with PF systems (Table 2.16) and calculated solubility parameters for several PF polymer repeat units using a group contribution method (Table 2.17). These calculated results were compared to swelling parameters for a partly cured PF resin and subjected to a range of organic solvents of known solubility parameters. The selection of solvents made correlation of swelling results to solvent structural features more difficult. Another way of providing data more easily related to chemical structure would be to blend two solvents at the higher and lower end of the range in several ratios, assuming the miscibility of the selected solvent pair.⁹⁰

Table 2.16. PF solvent swelling mass increase due as a function of solubility parameters⁹⁰

Solvent	δ (MPa ^{1/2})	PF mass increase (%)
A-Methyl styrene	16.0	0%
Dicyclohexyl	17.4	0%
2-Ethyl hexanol	19.4	0%
1,2-dichloroethane	20.1	1%
Dimethyl oxalate	22.7	0%
2-Methyl pyrrolidone	23.1	28%
Dimethyl sulfoxide	24.6	63%
Ethylene glycol	29.7	26%
Ethylene carbonate	30.1	1%

Table 2.17. Solubility parameters by group contribution method for PF repeat units⁹⁰

Repeat unit	Solubility parameter (MPa ^{1/2})
2,4,6-CH ₂ -	28.0
2,4-CH ₂ - ; 6-CH ₂ -OH	30.9
2,-CH ₂ - ; 4,6-CH ₂ -OH	33.2
2,6-CH ₂ -	28.3
2-CH ₂ - ; 6-CH ₂ -OH	31.6

Group contribution calculations to estimate solubility parameters would provide a stronger theoretical basis for predicting surface interactions and optimizing the co-miscibility of PF and

MDI. The calculations would require theoretical calculations of PF hydroxyl content as a function of molar ratio and molecular weight coupled with detailed information of all structural elements present.

Work in the field of enology on polyphenols has used group contribution theory to provide a theoretical treatment for surface interactions. The study evaluated the effect of solvent polarity on polyphenol recovery from red-grape seeds in ethanol-water. Experimental results were compared with solubility parameters calculated by group contribution method to validate using Hansen solubility parameters in solvent selection. This work illustrated a working method for calculating group contributions to surface energetics that can be broken down into the three components: dispersive, polar, and hydrogen bonding.⁹¹ One question that remains with this approach is whether it is adequate to estimate the surface properties of phenoxides as they would exist in an aqueous alkaline solution. In principle, at least, group contribution theory can be applied to both PF and MDI oligomers and calculations can be made for the wide variety of molecular species typically found in PF resins and in MDI. As such, more in-depth calculations of hydroxyl content as a function of molar ratio and molecular weight coupled with group contribution calculations would provide a stronger theoretical basis for estimating and predicting surface interactions of PF and pMDI.

Understanding the effects of solvents such as water or propylene carbonate on the solubility parameters of PF and pMDI respectively may provide important insight into miscibility. Barton describes a method of calculating an approximate solubility parameter for multi-solvent mixes. The theory assumes that the molar volume of all the components is comparable. The solubility parameter of the blend ($\langle\delta\rangle$) is related to the volume fraction (φ_i) and the solubility parameter of the component (δ_i) by the equation:

$$\langle\delta\rangle = \sum_i \varphi_i \delta_i$$

The calculation is not entirely accurate, considering whether the assumption of comparable molar volumes is always the case, but nonetheless useful from a practical point of view.⁹²

2.3.2.3. Phase diagrams

Solubility parameters are a useful practical tool for industrial chemists, especially for polymers in solution, but are subject to an uncertainty in their estimation that limits their suitability for predicting the miscibility of polymer blends. Another approach, phase diagrams, provides a more rigorous means of understanding polymer miscibility behavior. Phase diagrams characterize the miscibility of polymer blends, their monomers, and solvents. Phase diagrams graph the boundary conditions of phase co-existence and spinodal curves for plots of temperature against component volume fraction.⁹³

Phase diagrams relate the free energy of mixing of two components as influenced by volume fractions, degree of polymerization, and interfacial interactions. Nonspecific interactions are described by the General Flory-Huggins Relationship for the free energy of mixing of a monomer, polymer, or solvent.

$$\frac{\Delta G^M}{RT} = \frac{\varphi_A}{N_A} \ln \varphi_A + \frac{\varphi_B}{N_B} \ln \varphi_B + \varphi_A \varphi_B \chi$$

ΔG^M is the free energy of mixing, φ_A and φ_B are the volume fractions, and N_A and N_B are the degree of polymerization of components A and B respectively, and χ is the Flory-Huggins interaction parameter.⁹³ Since the Flory-Huggins parameter is not valid for specific interactions such as the hydrogen bonding encountered with PF polymers and water, Coleman et al. add a term, ΔG_H , to account for those favorable intermolecular interactions:

$$\frac{\Delta G^M}{RT} = \frac{\varphi_A}{N_A} \ln \varphi_A + \frac{\varphi_B}{N_B} \ln \varphi_B + \varphi_A \varphi_B \chi + \frac{\Delta G_H}{RT}$$

This term cannot be evaluated directly, but may be evaluated by means of IR spectroscopy.⁹⁴ In addition, by deriving the χ parameter value combined with knowledge of the degrees of polymerization of the components, one may then calculate the free energy of mixing for the system as a function of temperature and plot the phase diagram.⁹⁵ Coleman et al. demonstrate that polymer blending can be quantified by balancing unfavorable physical interactions in terms

of non-hydrogen bonded solubility parameters and favorable, specific interactions. The critical value for chi defining the limit of miscibility is calculated by the equation

$$\chi_{critical} = \frac{1}{2} \left[\frac{1}{N_A^{1/2}} + \frac{1}{N_B^{1/2}} \right]^2$$

Solubility parameters close in value and higher strength intermolecular interactions increase the likelihood of miscibility. The chi parameter is equated with the Hildebrand solubility parameter of the two components by:

$$\chi = \frac{V_t}{RT} [\delta_A - \delta_B]^2$$

where δ_A and δ_B are the solubility parameters of components A and B respectively, and V_t is an assumed molar reference volume. Their method is suitable for predicting miscibility trends for many polymer blends. This application of solubility parameters, however, may be limited by the uncertainty in its determination, causing the error in estimation to be larger than the actual difference of the ideal theoretical value. Fortunately, while this caveat holds true for high molecular weight polymers, blends of PF and pMDI comprise oligomeric materials, leaving open the possibility that the Coleman-Painter treatment based on Hansen solubility parameters is valid.⁹⁵

Many of the phase diagrams that can be constructed base upon such analysis are characterized by an upper critical solution temperature (UCST) or a lower critical solution temperature (LCST) behavior, depending on the nature of the interacting materials.

Table 2.18. Critical values of χ and $\Delta\delta$ ⁹⁵

Intermolecular interactions	Critical interaction parameter $\chi_{critical}$	Solubility parameter difference at $\chi_{critical}$ $\Delta\delta$ (cal/cm ³) ^{1/2}
Dispersive forces	< 0.002	< 0.1
Dipole-dipole	0.002 - 0.02	0.1 - 0.5
Weak hydrogen bonds	0.02 - 0.2	0.5 - 0.1
Moderate hydrogen bonds	0.2 - 1.0	1.0 - 2.5
Strong hydrogen bonds	1.0 - 1.5	2.5 - 3.0

Table 2.18 relates intermolecular interactions to the chi critical and solubility parameter differential.⁹⁵

Scarce literature is available regarding the miscibility of polyols and pMDI, especially PF and pMDI. Mikhailov et al. provided partial phase diagrams for the diisocyanate and butane diol components of a polyurethane block copolymer using a micro-interference detection technique in the temperature range of 20 to 130°C. The component structures significantly affected their mass transfer rate and thermodynamic compatibility and thus had a marked effect on the resulting copolymer structure.⁹⁶

2.3.2.4. Phase behavior of materials with specific interactions

Specific interactions of polymer constituents lead to non-Flory-Huggins behavior, resulting in different phase diagrams from the typical LCST and UCST diagrams. According to Coleman et al., LCST and closed loop behavior may be influenced by either mixture of polar materials, usually hydrogen bonding types, where the effects of entropy changes due to the specific interactions of association or free volume differences are critical.⁹⁴

The behavior of the closed loop system may be understood as a two region phase diagram with a higher UCST and a lower LCST. Such systems are again characterized by specific interactions with their resulting effects on entropy and enthalpy of the system. At low temperatures, the contribution of free energy of mixing generated by the formation of specifically interacting groups is greater than the loss of free energy due to the decreased entropy from reduced temperature and specific orientation, resulting in a one-phase system. As temperature increases, specific interactions decrease and dispersive forces become predominant, leading to repulsive interactions; two phases form within the loop to minimize energy. As temperature increases above the UCST, the entropic contributions again dominate over the repulsive interactions of the two polymers and the materials form one phase.⁹⁷ Increasing molecular weight of the closed loop system decreases entropy thus increasing the size of the immiscibility loop.⁹⁸ This effect of increasing molecular weight can be understood as less free energy being present in the system because of the effect of decreased entropy due to the decreased conformational entropy associated with longer polymer chain lengths. Lower molecular

weights should be chosen for smaller immiscibility loops, while higher molecular weights should be selected for larger loops. The implication for the miscibility of PF and pMDI oligomers is that lower molecular weights will be more miscible.

Behavior of an hour-glass-shaped phase diagram may be described as the merging of a combination of two phase diagrams, the first with a higher LCST above a second diagram with a lower UCST. A single phase region present in the middle at low molecular weights merges as molecular weight increases to form a two phase region in the middle. The origin of the LCST/UCST behavior may be attributed to the effect of temperature on the χ parameter with respect to energetic interactions (enthalpy) and free volume.⁹⁴ The effect of increasing molecular weight is due to the decrease in entropy due to molecular weight and its effect on the Flory-Huggins parameter. As χ decreases due to increasing molecular weight, the UCST and LCST will approach until they merge and form the hour glass shape. Thus the values selected for N_A and N_B should be high enough to achieve this merged phase region.

2.4. Microencapsulation technology

2.4.1 Overview

One application of a rapid-curing PF-pMDI co-polymer is for bonding lignocellulosic particles, where performance requires delivering the components to the substrate unreacted. These components should also react on demand, in-situ, upon application of heat or pressure to form an adhesive bond. The high reactivity of the mixed oligomers, along with their tendency to phase separate, however, could limit the application, as proper mixing is necessary for intermolecular contact and co-reaction. Then again, since the components begin to react immediately upon contact, premature reaction could occur prior to wetting of the substrate and polymerization. Complete co-reaction would be especially important for low temperature curing, since unmixed PF and pMDI would not cure without thermal energy.

Microencapsulation of the reactive PF and pMDI components is one solution for latent delivery of reaction on demand. It is the process of encasing small liquid droplets or solid particles within another layer of material. Microcapsules usually range in size from a few microns to a

few millimeters in diameter. Although there are many different means to produce microcapsules, in practice method selection depends on the nature of the encapsulated material, or the core, and the encasing material, known as the wall or shell. One potential advantage of this process for PF-pMDI co-polymers is that the microcapsule architecture would keep the components close, but separate until mixing is needed. The active materials may then be released by mechanical rupture.

As a hypothesis, a PF-pMDI co-polymer for adhesively bonding lignocellulosic particles may be formed by mixing the contents of a microcapsule comprising a liquid PF oligomer with a PU catalyst in one part and a pMDI oligomer with a PF accelerator in the other part. A further aspect of this hypothesis is that a co-polymer membrane will form after contact of the two components due to interdiffusion and interfacial polymerization. The co-polymer membrane would limit further interdiffusion and co-reaction, prohibiting additional diffusive mixing of the components, thus preventing premature reaction of the remaining oligomers. In another aspect of the hypothesis, the co-polymeric membrane imparts mechanical strength to the microcapsule, permitting application of the components to lignocellulosic particles in droplet form. The microcapsule would have a liquid shell and a liquid core separated by a solid co-polymeric membrane. The relatively thin co-polymer membrane would rupture under applied pressure, releasing the core liquid, inducing flow, contact with the shell liquid, and interdiffusion, thus initiating further co-polymerization. One question regarding such microcapsules is whether the materials would mix completely upon rupture.

Factors influencing component mixing would include miscibility, diffusion, droplet volume, and flow inducing forces. The thermodynamics of mixing controls miscibility, i.e. the formation of a homogeneous mixture, and is influenced by volume fraction, temperature, degree of polymerization, and specific interactions among the component functional groups. The diffusion coefficient, D , of a spherical particle in a liquid is expressed by the Stokes-Einstein relation

$$D = \frac{kT}{6\pi\eta R}$$

where k is the Boltzmann constant, T is the temperature, η is the viscosity, and R is the particle radius. Viscosity and the particle radius are influenced in turn by the molecular weight of the molecule(s) involved. The application device and its processing parameters, as well as the liquid properties, would affect the droplet size. The adherend surfaces and applied pressure would create flow.⁹³

2.4.2. Microencapsulation methods

Microencapsulation methods vary due to the diverse materials used. Thus, no one method is suitable for all materials. Therefore, process development is usually necessary for most new applications. Jabbari categorized microencapsulation techniques as chemical methods or physical methods.⁹⁹ Gouin reviewed typical industrial microencapsulation techniques for food ingredients including spray drying, spray cooling/chilling, spinning disk and centrifugal coextrusion, extrusion, fluidized bed, coacervation, alginate beads, and liposomes.¹⁰⁰ Yow and Routh evaluated the merits of different techniques for forming liquid core-polymer shell microcapsules. Those methods were: formation of colloidosomes or copolymer vesicles, phase separation, interfacial polymerization, layer-by-layer deposition, and surface polymerization.¹⁰¹

Jabbari and Khakpour evaluated the morphology and release behavior of polyurethane microspheres made from 4,4'-MDI, polyethylene glycol 400, and 1,4-butanediol. The particles were made in a homogenized aqueous dispersion by suspension condensation polymerization. The microspheres were characterized with FTIR in attenuated total reflectance (ATR) mode to verify depletion of the isocyanate peak at 2272 cm^{-1} . Carbon dioxide generated by the carbamic acid reaction of water and 4,4'-MDI increased the microsphere porosity. A higher ratio of polyethylene glycol 400 to 1,4-butanediol in the polymer influenced the shell properties, providing more flexibility, less phase separation, and a smoother particle surface.⁹⁹

2.4.3. Laboratory microencapsulation methods

Among the many microencapsulation techniques, suitable methods for the proposed adhesive system would include coaxial ultrasonic atomization, microfluidic droplet formation, and vibrational cleavage of a fluid jet.

2.4.3.1. Microfluidic methods

Microfluidic methods can create droplets within droplets and microcapsules. Shah et al. used co-flow glass capillary microfluidic devices to generate multiple emulsions.¹⁰² Utada et al. and Chu et al. have shown that triple and other higher order emulsions were formed through configurations of co-flow and flow focusing arrangements using flow cascades.^{103,104} Various monodisperse triple emulsions were configured with controlled size variation and droplet number within each phase.¹⁰² Nisisako et al. generated monodisperse double emulsions using an upstream junction design, synthesizing water-oil-water and oil-water-oil emulsions depending on the placement of hydrophobic junctions. Control of droplet dimension and their number enclosed was achieved by altering flow conditions. Droplet sizes ranged from 40 to 200 μm .¹⁰⁵

2.4.3.2. Electrospray methods

Jaworek reviewed electrospray micro- and nano-encapsulation methods. Electrospray processes use electrical potentials to overcome surface tension forces in liquid atomization. The process achieves smaller droplet size than other methods of microencapsulation, even to the nanometer scale. The droplets formed possess a charge during spraying, but not afterwards. Liquid flow rate and applied nozzle voltage control droplet size and charge.¹⁰⁶ Electrospray devices can operate in ambient environments and the flow rate and voltage are easy to control. The technique permits electrostatic micro- and nano-encapsulation for production of sub-micron capsules from a broad variety of core and shell materials, just as other larger scale microencapsulation techniques. Passing materials as a fluid jet through an electrical field often improves the encapsulation process. Useful electrospray-microencapsulation processes include collision of oppositely charged droplets drawn together by coulombic attraction and evaporation of electrosprayed colloidal suspensions followed by solvent evaporation for shell formation. Other processes are gelatinization of electrosprayed colloidal suspension accomplished by spraying into vessel with a gelatinizing or polymerizing media to form the shell, or electro-co-extrusion by concurrent spraying of two dissimilar liquids from two coaxial feeds.¹⁰⁷

2.4.4. Coaxial ultrasonic atomization

2.4.4.1. Ultrasonic atomization and microencapsulation methods

Ultrasonic atomization offers numerous applications advantages: soft, low-velocity spray, micro-flow capability, spray-shaping, and freedom from clogging. Gelling polyurethanes can solidify in the nozzles of conventional spray application equipment, but residues tend not to collect on the surfaces of vibrating ultrasonic nozzles. Their flow rate control is excellent due to low atomization pressure and they are well suited for highly accurate gear or syringe pumps. Droplet size is determined by density, surface tension, and nozzle operational frequency.¹⁰⁸

Several parameters need to be controlled for ultrasonic microencapsulation. Liquids must be less than 50 mPa·s for good atomization and at maximum flow rate should be less than 1.0 mL/min. Long chain polymers in solution may interfere with proper atomization due to their potential for spanning the bulk solvent in the nozzle. Although the titanium housing used in ultrasonic nozzles offers good acoustical properties, high strength, and chemical resistance, it should not be exposed to corrosive acids such as HF or H₂SO₄ (p 62-3).¹⁰⁸

2.4.4.2. Ultrasonic atomization research

Zhang used ultrasonic atomization for application of pMDI resin to wood, achieving average droplet sizes of 90 µm. He reported more uniform droplet size distribution than would be possible with spinning disk atomizers often used for wood composite manufacture and fewer of the hazardous, small-size droplets. The maximum flow rate was 0.7 mL/min. The nozzle self-heated due to the vibration with a measured temperature range of 32 to 38 °C. As a result the pMDI had an apparent viscosity around 80 to 150 mPa·s, a decrease from 233 mPa·s at 25 °C.¹⁰⁹

2.4.4.3. Ultrasonic methods

Yeo and Park made reservoir-type microcapsules with a coaxial ultrasonic atomizer from two separate liquids, one comprising a polymer solution and the other an aqueous solution. They studied the microencapsulation mechanism by atomizing in various modes. Their results

indicated that the reservoir-type microcapsules were formed by colliding airborne microdroplets.¹¹⁰

2.4.4.4. Vibrational jet atomization

Superimposing vibration on a laminar liquid jet will atomize the fluid stream into monodisperse droplets. Droplet dimensions may be controlled by variation of vibrational frequency, jet velocity, and nozzle diameter; parameter settings are verified with a strobe light leading to a reproducible process. The droplet stream is electrically charged in flight by sending it through an electrostatic field; otherwise the droplets within the stream might collide and coalesce into larger droplets. This process can produce monodisperse spherical microcapsules with diameters between 0.1 and 3.0 mm at flow rates up to 200 L/hour.¹¹¹

2.4.5. Microcapsule testing and mechanical properties of microcapsules

Tian-Zhong studied the mechanical properties of UF microcapsules using a micromanipulation technique. The U:F molar ratio was 1.9, the average microcapsule diameter was $82 \pm 2 \mu\text{m}$, and wall thickness was approximately 0.5 to 0.8 μm . The finding was that UF capsules were mostly elastic at small compressive deformation, but plastic under large deformation. A transition from elastic to plastic deformation occurred at 14% compression. All the capsules would disrupt under compression and burst force was a linear function of capsule diameter.¹¹²

Sun and Zhang investigated the mechanical strength of microcapsules made from melamine-formaldehyde (MF), urea-formaldehyde (UF), and gelatin-gum Arabic with micromanipulation. They studied the deformation response to compressive force. While the MF and UF microcapsules burst under compression, the gelatin microcapsules did not, although they required less force than the MF or UF capsules to deform. Wall material properties were not well correlated with wall material composition.¹¹³

Zhang introduced a novel micromanipulation technique for quantifying the relationship between the force applied and the resulting deformation with its bursting yield. Zhang developed the method for testing the mechanical strength of MF microcapsules that are

typically used in carbonless paper. He demonstrated a useful method for testing single capsules that yields quantitative results for statistical comparison of various wall materials. The method entails mounting the microcapsules on a glass slide and placing it in a microscope equipped with a 10 μm diameter probe attached to a force transducer. Upon compression, the applied force is measured as a function of deformation time and displacement until bursting. Microcapsule diameter was estimated from this data.¹¹⁴

Brown et al. made UF walled microcapsules with a dicyclopentadiene core via an in-situ polymerization method of an oil-in-water emulsion for self-healing epoxy applications. They studied surface morphology and wall dimensions by optical and electron microscopy. They found that the inner membrane was smooth textured and 160-220 nm thick. The outer surface was porous and rough, comprising aggregated UF nanoparticles. Factors influencing the surface morphology were the pH of the oil-in-water emulsion and the core-water interfacial surface area.¹¹⁵

Ni et al. prepared a series of polyurethane microencapsulated ammonium polyphosphates (PU/MCAPP) by in situ polymerization from toluene-2,4-diisocyanate, polyethylene glycol, and pentaerythritol. PEG of M_w 400, 1000, 2000, and 4000 g/mol were tested. The chemical structure of the microcapsules was characterized by FTIR and XPS. They used scanning electron microscopy (SEM) and a water solubility test to optimize and select the PEG M_w for the microcapsule design. The PEG 400 led to a crimped appearance, while the PEG 4000 was too viscous, resulting in poor linkages between the chain extender and the soft segments. Using PEG 1000 gave the optimal surface smoothness and linkages. The combustion and thermal degradation behaviors of PU blended APP or MCAPP were examined by TGA, UL-94 fire test, and micro-combustion calorimetry. The results showed that the PU/MCAPP had better thermal stability and flame retardancy, due to the stable char forming materials by the APP and PU shell. Moreover, the water resistance of the flame retarded PU composite was greatly improved.¹¹⁶

2.5. References

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Chapter 3: Electronic Behavior of Phenolic Monomers in Solution and Implications for Self-Condensation and Polyurethane Polymerization

3.0. Overview

Alkali metal counter-cations alter the electron density of phenolates in solution by electrostatic interactions correlated to hydrated ionic radius and solvent dielectric properties. This change in electron density affects their reactivity towards formaldehyde, hydroxymethylphenols, and isocyanates during polymerization. The electronic perturbation of phenolic model compounds in the presence of alkali metal hydroxides was investigated with ^{13}C and ^1H NMR in polar solvents relative to non-ionic controls, altering the chemical shifts of the model compounds, thus indicating changes in electron density. These shifts were attributed to Coulombic electrostatic interactions of the counter-cation with the phenolate anion that correlated to hydrated ionic radius and solvent dielectric constants. The predicted relative reaction rates for formaldehyde addition based on electron density ranking from ^{13}C NMR of the phenolic models corresponded to literature reactivity in good agreement. Predictions for condensation reactions of 2- and 4-hydroxymethylphenol from chemical shifts were consistent with published results. The results permitted predictions for reactions of phenolic and isocyanate compounds for the formation of thermosetting polymeric materials.

3.1. Introduction

Phenolic and phenolic derivatives make up an important class of monomers for polymeric materials used in engineering and structural applications. Phenolic-based polymers are known for their stiffness and durability. Furthermore, nature uses these monomers via the radical coupled polymerization of phenylpropane units in the example of lignification; both stiffness and durability are key performance properties for terrestrial plants. In addition to radical coupling, a number of other synthetic polymerization chemistries have been developed over the years related to condensation pathways. The number of reactive sites on the aromatic groups arising from the resonance structures of these monomers, combined with the ability of

some of the compounds to form quinone methide (QM) intermediates, create a complicated chemical structure. As a result, there remains uncertainty around the curing mechanism for these polymers, such as phenol-formaldehyde (PF), in the presence of different catalysts.

PF adhesives have been used extensively for manufacture of moisture-durable building products and wood composites such as plywood, oriented strand board, and other engineered composites. One drawback of PF technology is that it requires relatively high temperatures and long press times to cure. One approach to enhance reactivity (polymerization/cure speed) has been to add different alkali metal hydroxides to the resin as a catalyst. Faster PF resin polymerization permits pressing at lower temperatures with shorter press cycles. Benefits of enhanced reactivity include energy savings, increased productivity, and lower emissions of temperature sensitive volatile organic compounds. Because of the continued industrial relevance of these monomers, additional study is required into the electronic behavior of phenolic monomers to understand how different metal catalysts enhance reactivity. Daisy recognized that PF resin cure was accelerated by using potassium hydroxide instead of sodium hydroxide as a catalyst.¹ Grenier-Loustalot et al. found that the use of different alkali metal hydroxides affected the kinetic rate constants for addition of formaldehyde to phenol.² Higuchi et al. showed that alkali metal hydroxides affect the composition of hydroxymethylphenols upon addition of formaldehyde to phenol as well as their kinetic rate constants for addition.^{3,4} These experiments suggest a strong effect of the alkali catalyst on the composition and cure of the PF adhesive without explaining the underlying mechanism for the changes in cure.

Other compounds like esters, lactones, and organic carbonates also accelerate PF resin cure and these mechanisms are better understood compared to the change of alkali hydroxides. Conner et al. studied the mechanism of how these compounds accelerate the condensation of PF model compounds, concluding that transesterification of the phenolic hydroxymethyl functional group was the initial reaction. A subsequent reaction likely proceeded by displacement by either a bimolecular nucleophilic substitution (S_N2 mechanism) of a negatively charged ortho or para carbon or by conversion to a QM that then reacted with the negatively

charged anion (QM mechanism).⁵ Kamo et al. also concluded that the transesterification/QM mechanism was critical for acceleration. They showed how sodium bicarbonate and sodium hydroxide altered the ^{13}C nuclear magnetic resonance (NMR) chemical shifts of various carbon atoms of PF model compounds in studies of organic carbonate-facilitated PF acceleration.⁶ The work suggests that NMR chemical shift information can be used to help elucidate the mechanism behind the reactivity of PF.

Other additives or solvents are also known to impact the reactivity of PF adhesives and PF-urethane co-polymers. Haupt has demonstrated that the PF reactivity can be enhanced by accelerated copolymerization and self-condensation with polymeric methylenediphenyl diisocyanate (pMDI), a PF accelerator, and a polyurethane catalyst.⁷ Han et al. found that a polar solvent environment affects the kinetic rates constants for co-reaction of 2-hydroxymethylphenol (2-HMP) and phenyl isocyanate to form urethanes, altering the reactivity and selectivity of the phenolic hydroxyl versus the hydroxymethyl group. Reactivity of phenolic hydroxyl group increased while reactivity of the hydroxymethyl group decreased with increasing solvent polarity.⁸

The altered reactivities of the chemistries described above may be understandable as changes in the electron density of various functional groups making them more or less nucleophilic or electrophilic. Electron density is reflected by NMR chemical shift, with low electron density deshielding the nucleus, resulting in greater chemical shift values.⁹ Thus, changes in chemical shift may be studied as a proxy for electron density to better understand the impact of counter ions, accelerators, and solvents on phenolic reactivity.⁹ The objective of this study is to better understand how PF oligomers participate in addition, self-condensation, acceleration, and copolymerization reactions by perturbing the electronic structure of PF model compounds with alkali metal hydroxides and/or solvent selection. The chemical shifts are determined by ^{13}C and ^1H NMR to elucidate the effect of alkali metal counter ions and solvent selection on the relative electron density of PF model compounds and the resulting effect on reactivity reported in the literature.

3.2. Experimental

3.2.1. Materials:

Phenolic model compounds were phenol, 2-hydroxymethyl alcohol (2-HMP), and 4-hydroxymethyl alcohol (4-HMP), purchased from Sigma-Aldrich. Alkali metal hydroxides were of lithium (Fisher 100% anhydrous), sodium (Sigma-Aldrich 98%), potassium (Acros 85%), rubidium (Sigma-Aldrich 50% solution in H₂O), and cesium (Sigma-Aldrich 50% solution in H₂O). The NMR solvents were D₂O (Sigma-Aldrich), CD₃OD (Sigma-Aldrich and Cambridge Isotope Labs), DMSO-d₆ (Cambridge Isotope Labs), and THF-d₈ (Cambridge Isotope Labs). The materials were used as received.

3.2.2. Preparation of NMR sample solutions:

All NMR samples were dissolved in approximately 0.80 mL of solvent in a glass vial then transferred to a 5-mm glass NMR tube. The samples were prepared to provide at least 25 mg of model compound for strong NMR signals

3.2.3. Phenol treated with alkali metal hydroxides and dissolved in D₂O or CD₃OD

Phenol (501.1 mg) was dissolved in 10.0071 g D₂O for a 4.768 weight % solution; 499.2 mg phenol was dissolved in 1967.9 mg CD₃OD for a 20.234 weight % solution. The phenol solutions were combined with the alkali metal hydroxides of lithium, sodium, potassium, rubidium, and cesium in separate glass sample vials. The target molar ratio of alkali metal hydroxide to phenol was equal to or greater than 1.0. Sample weights were measured to 0.1 mg accuracy to calculate the formulated molar ratios. Two replicates were made for each sample-solvent combination.

3.2.4. Phenol, 2-HMP, and 4-HMP treated with alkali metal hydroxides and dissolved in D₂O/CD₃OD

PF model compounds phenol, 2-HMP, and 4-HMP were combined with the alkali metal hydroxides of lithium, sodium, potassium, rubidium, and cesium in separate glass sample vials. The target molar ratio of alkali metal hydroxide to phenol model compound was equal to or greater than 1.0. Moisture was removed from the 2-HMP and 4-HMP samples by placing the vials in a vacuum oven at ambient temperature overnight. Since phenol sublimates under vacuum, the alkali metal phenolate salts were not vacuum dried, leaving a small amount of residual H₂O in the rubidium and cesium treated NMR samples. The NMR sample solvent was a mixture 9.9482 g CD₃OD (0.2758 mol) and 20.0504 g D₂O (1.0010 mol) for a molar ratio of CD₃OD to D₂O of 0.2755.

3.2.5. Phenol in dissolved in DMSO-d₆ and THF-d₈

Additional samples of phenol were dissolved in DMSO-d₆ and THF-d₈ for NMR analysis. Samples of phenol in DMSO should be handled carefully in a hood with proper personal protective equipment for the skin due to the penetrating characteristic of DMSO and phenol's toxicity.

3.2.6. ¹H and ¹³C NMR

NMR spectra were acquired using a Varian Inova 400 model at 400 MHz proton frequency. Both ¹H and ¹³C spectra were taken for all materials studied. Chemical shift data were analyzed with MestReNova software. All spectra except for those deuterium oxide ¹³C spectra were adjusted to the solvent peak reference chemical shift; the ¹³C spectra for model compounds in deuterium oxide were used as is without adjustment.

3.3. Results

3.3.1. Phenol treated with alkali metal hydroxides and dissolved in D₂O or CD₃OD

3.3.1.1. Effect of alkali metal counter cations

The phenolic model compounds and their corresponding numbering schemes are shown in Figure 3.1. For the different carbon atoms of the alkali metal phenolate salts in D₂O or CD₃OD solution, strong deshielding occurred at C-1 as indicated by the increase in chemical shift, with moderate shielding at C-2 and C-6 in comparison to unperturbed phenol.

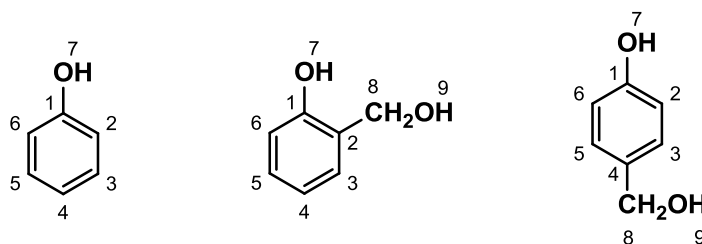


Figure 3.1. NMR numbering scheme for phenol, 2-HMP, and 4-HMP

Weak shielding was observed at C-3 and C-5, while moderate shielding was observed at C-4 for all the phenolates from the phenol reference (Figure 3.2). The overall pattern of chemical shifts followed principles well known from resonance structures for aromatic rings with electronegative substituents (Figure 3.3).¹⁰ From the shift position it is noted the 2, 4, and 6 positions had high electron density; the 1 position had low electron density, while the 3 and 5 positions had intermediate density. The effect of alkali metal cation elements was more complex: at C-1 the series from Li to Cs exhibited strongly increased deshielding from Li to K, while deshielding leveled out from K to Cs. There was increased deshielding from Li to Cs at C-2 and C-6. For C-3 and C-5, a minimum occurred at potassium, although the chemical shifts were more tightly grouped than for the other positions. Finally, C-4 increased shielding from Li to Cs (Figure 3.2).

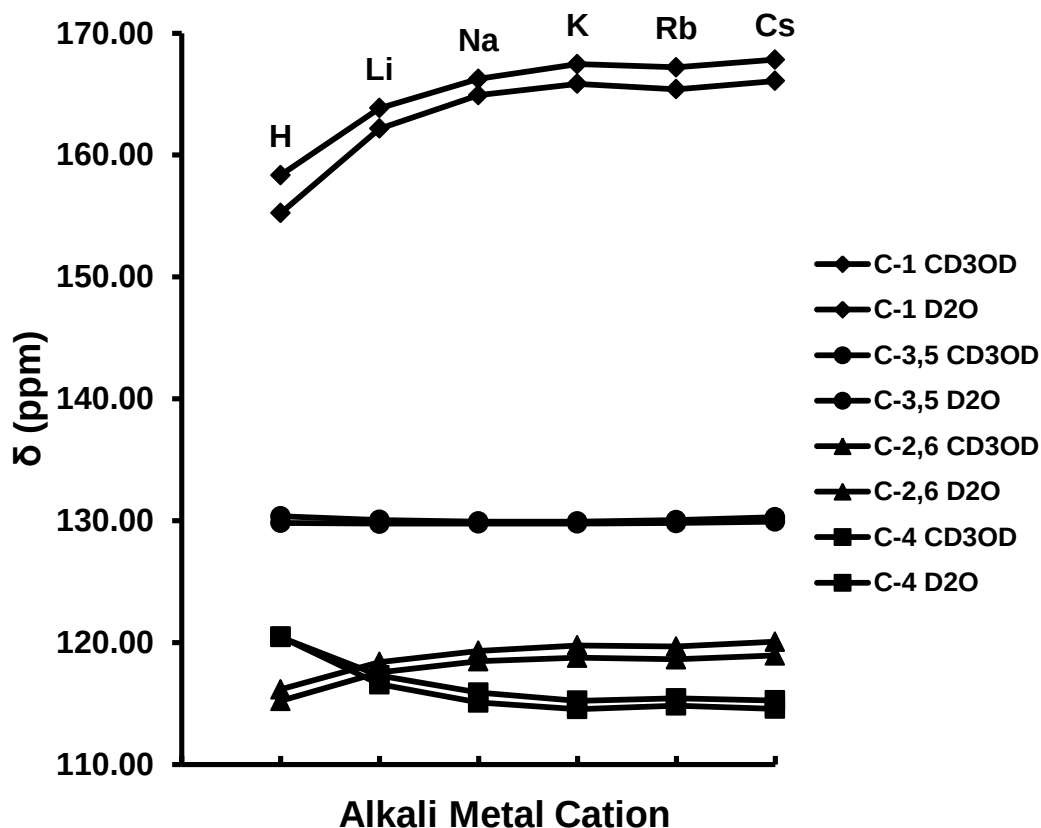


Figure 3.2. ^{13}C Chemical shifts of alkali metal phenolates in CD_3OD and D_2O

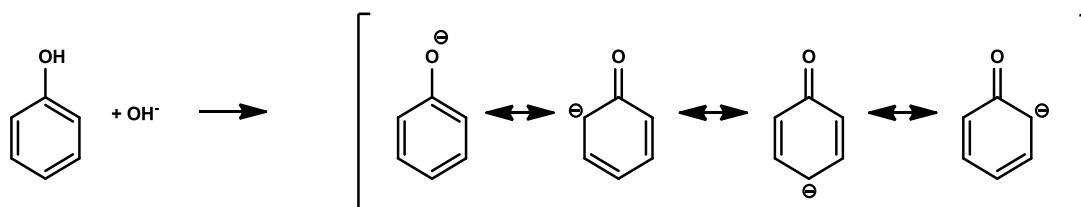


Figure 3.3. Deprotonation of phenol by hydroxide and phenol resonance structures

Table 3.1 shows the differences for the average chemical shifts between the alkali metal phenolates in D_2O and CD_3OD solvent. Overall the CD_3OD had a greater deshielding effect than the D_2O , being on average 0.93 ppm greater. Among the ring positions, the differences from largest to least were C-1 (1.63) > C-2,6 (0.98) > C-4 (0.70) > C-3,5 (0.24). Among the cations, the differences were in ppm: H, 1.15; Li, 0.89; Na, 0.79; K, 0.87; Rb, 0.92; Cs, 0.98. The minimum

difference occurred with Na and the maximum difference with Cs. The effect of solvents is attributed to dielectric effects, which will be considered further in the discussion on electrostatic effects.

Table 3.1. Δ of $\delta^{13}\text{C}$ from phenol in ppm ($\text{CD}_3\text{OD} - \text{D}_2\text{O}$)

Cation	C-1	C-2,6	C-3,5	C-4	Average
H	3.12	0.95	0.55	-0.02	1.15
Li^+	1.67	0.85	0.31	0.73	0.89
Na^+	1.34	0.85	0.16	0.81	0.79
K^+	1.62	1.01	0.16	0.68	0.87
Rb^+	1.79	1.05	0.23	0.59	0.92
Cs^+	1.75	1.13	0.35	0.68	0.98
Average	1.63	0.98	0.24	0.70	0.93

Kremer and Schleyer applied computational methods to provide theoretical values for the ^{13}C and ^1H NMR chemical shifts of the alkali metal phenolates.¹¹ Their predicted ^{13}C values are compared to the measurements performed in the current study (Figure 3.4).

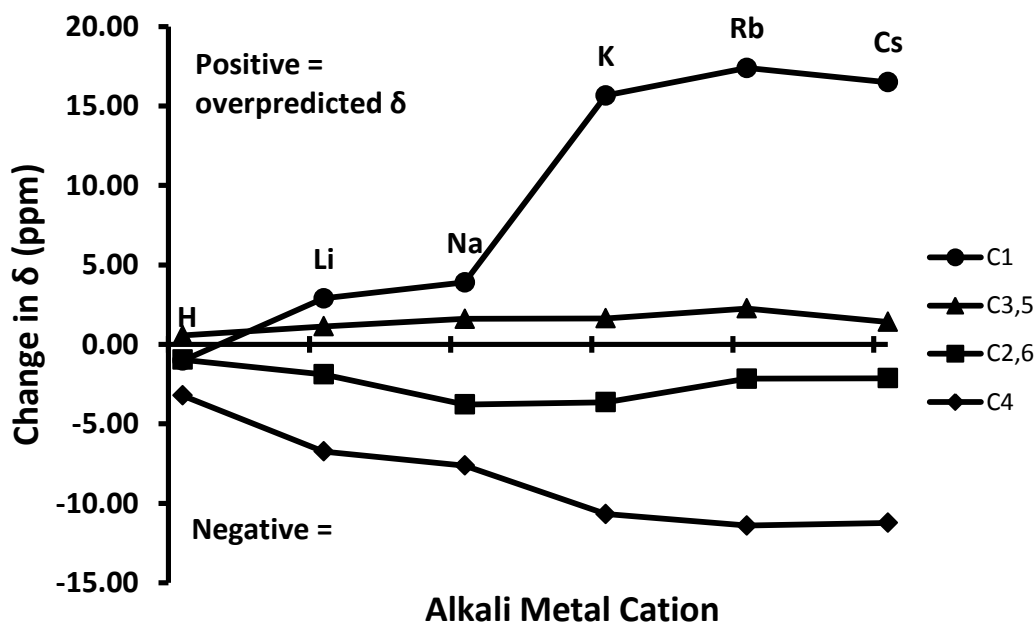


Figure 3.4. Phenol ^{13}C NMR deviation from theoretical: $\Delta = \delta_{\text{predicted}}^9 - \delta_{\text{measured}}$

The major difference is that the magnitude of the theoretical chemical shift is too high for the C-1 carbon and too low for the C-4 carbon. One possible explanation of this discrepancy between theory and practice is that their theoretical model did not take into account the distance between the solvated cation and anion. Their model may assume a very short distance between the anion-cation pair. Kremer and Schleyer gave one set of calculations showing natural charges as a function of lithium cation-phenolate anion distance,⁹ illustrating the effect of the distance between the anion-cation pair on their effective charge (Table 3.2). Hence, a lower value can be interpreted as more of the electron density remains on the phenolate oxygen because the effective field strength of the cation is stronger due to the shorter distance between the ions.

Table 3.2. Natural charges in lithium phenolate as a function of the Li-O distance⁹

d (Li-O) (Å)	O	M
1.617	-1.137	0.978
2.0	-1.093	0.982
3.0	-1.015	0.991
4.0	-0.968	0.997
5.0	-0.942	0.999
6.0	-0.926	0.999
7.0	-0.916	1.000
8.0	-0.909	1.000
∞	-0.904	1.000

3.3.1.2. Phenol, 2-HMP, and 4-HMP treated with alkali metal hydroxides and dissolved in D₂O/CD₃OD

The solvent mix of D₂O and CD₃OD was used to assure dissolution of all the model compound-alkali metal combinations. The three alkali metal phenolates exhibited the same general trends of shielding and deshielding in reference to neutral phenol as for D₂O and CD₃OD alone, although some specific variations occurred. Table 3.3 provides an overview of results for the effects of alkali metal hydroxides on the chemical shifts of phenol, 2-HMP, and 4-HMP.

Table 3.3. General effects of perturbing phenolic model compounds with alkali metal hydroxides in D₂O/CD₃OD for H/Li→Cs

Position	phenol		2-HMP		4-HMP	
	e ⁻ effect	δ for H/Li→Cs	e ⁻ effect	δ for H/Li→Cs	e ⁻ effect	δ for H/Li→Cs
C-1	deshielded	156.7/162.5-167	deshielded	156.7/162.5-167	deshielded	156.5/164-167
C-2,6	deshielded	116/118-120	2 deshielded 6 shielded	2-127.7/130.1- 129.6;6-116/115	deshielded	116/119-120
C-3,5	low change	131	shielded	3-129.2/5-130.0	low change	130.5
C-4	shielded	121.3/118-115	shielded	121/120	deshielded	133.3/129-127
-CH ₂ -	---	---	deshielded	60.6/62.3	deshielded	64.6/65.2
-CH ₂ -	---	---	deshielded	4.63/4.90	deshielded	4.51/4.90
-CH ₂ -OH	---	---	shielded	4.85/4.63	shielded	4.87/4.43

Figures 3.5 and 3.6 show the effects for 2-HMP and Figure 3.7 for 4-HMP. The effect at C-1 is strong deshielding for all compounds when exposed to an alkali metal hydroxide. The effect of the alkali metal counter-cation at C-2 and C-6 is deshielding, except for 2-HMP, where the hydroxymethyl substituted C-2 is deshielded and C-6 is shielded. The effect at C-3 and C-5 is minimal change for phenol and 4-HMP, while 2-HMP indicated shielding of these two positions. The effect at C-4 is shielding for phenol and 2-HMP, while 4-HMP was deshielded due to the electronegative oxygen of the hydroxymethyl group attached to the C-4 carbon. The effect on the hydroxymethyl methylene group was deshielding for ¹³C and ¹H NMR, while the hydroxymethyl hydroxyl proton was shielded for both 2 and 4-HMP. The phenolic hydroxyl proton (H-7) was not detected in ¹H NMR due to solvent exchange of this acidic proton. Compared to the respective phenol C-2 and C-4 positions, the equivalent ring positions on 2-HMP and 4-HMP were deshielded in the range of 8 to 12 ppm due to the oxygen containing substituent. Overall, the chemical shifts of the phenolic model compounds were affected by the introduction of the alkali metal hydroxides.

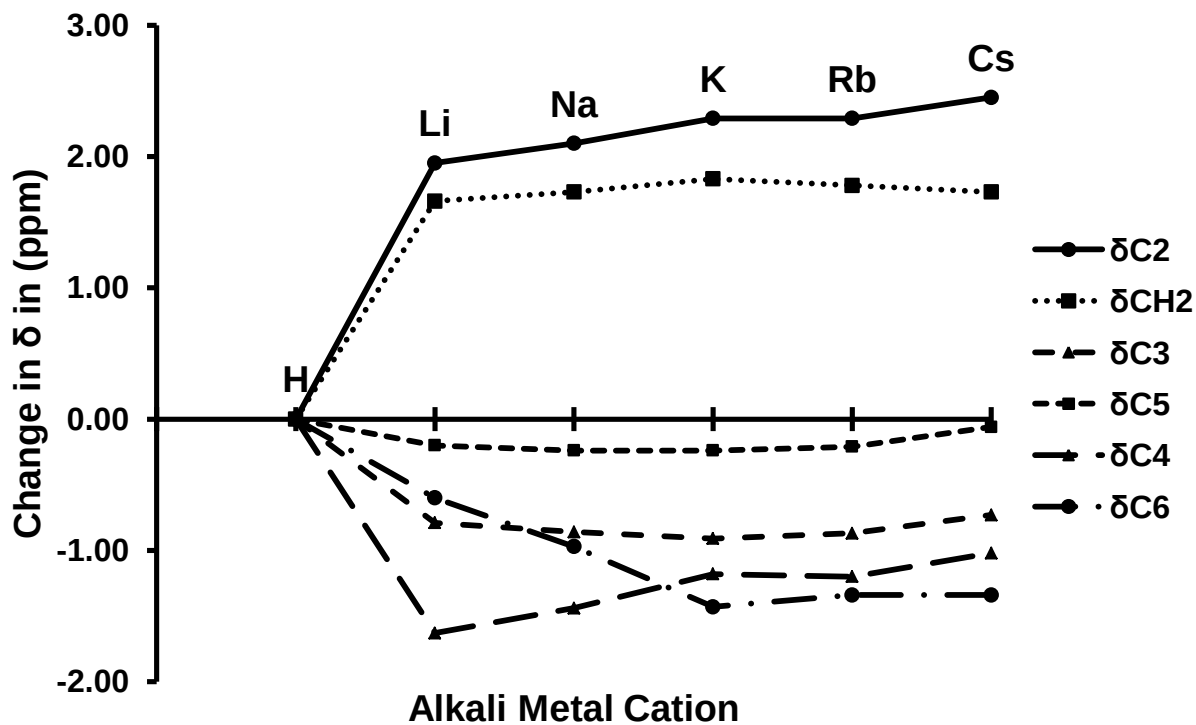


Figure 3.5. Change in ^{13}C NMR chemical shifts of 2-HMP alkali metal phenolates

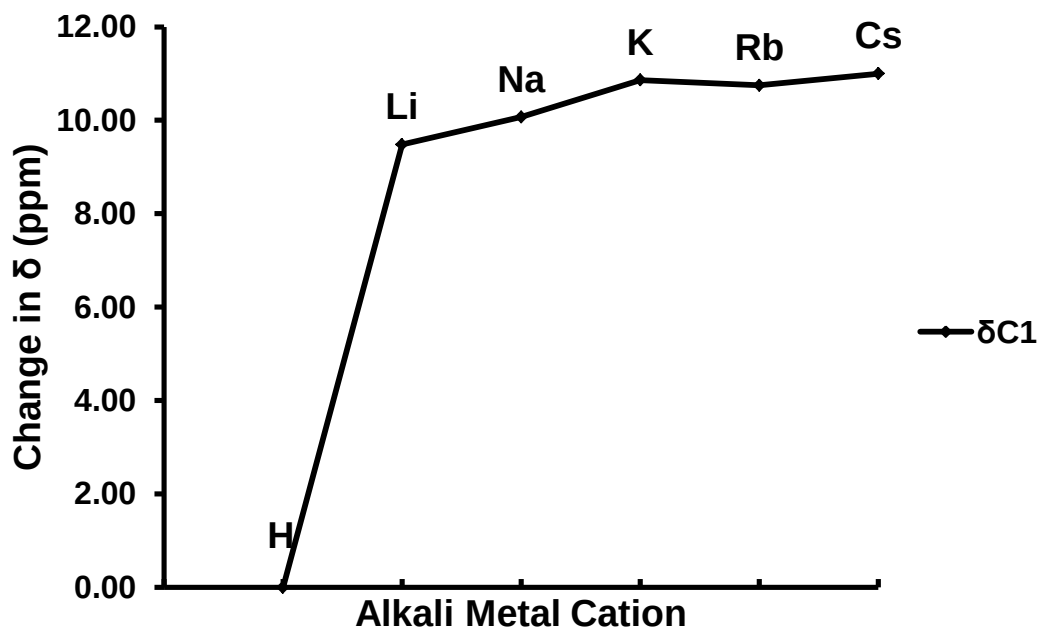


Figure 3.6. Change in ^{13}C NMR chemical shifts of alkali metal phenolates of 2-HMP at C-1

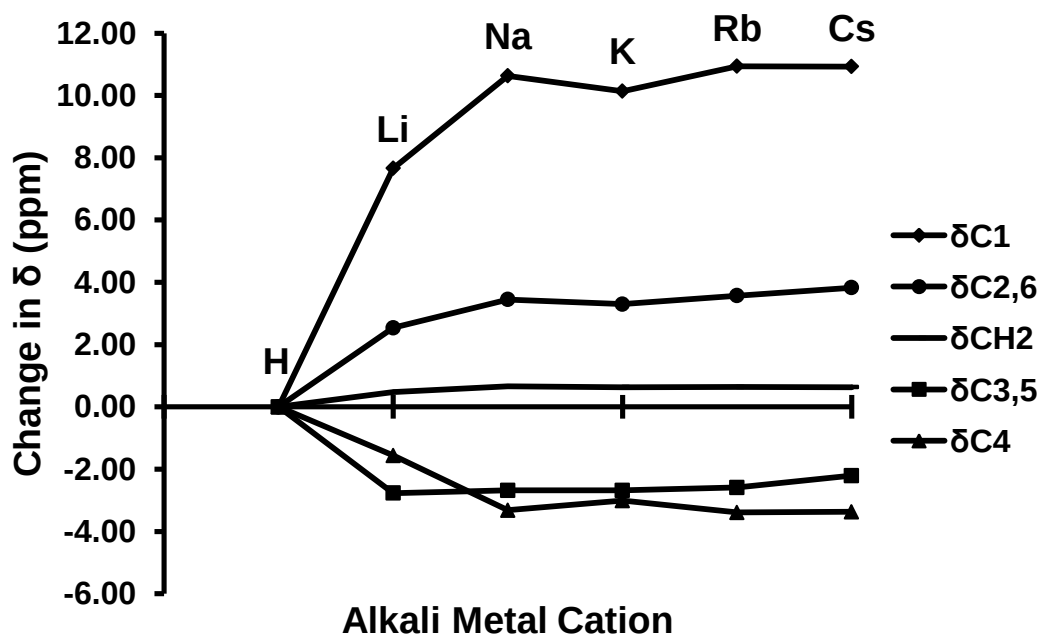


Figure 3.7. Changes in ^{13}C NMR chemical shifts of alkali metal phenolates from 4-HMP

3.3.2. Electrostatic interactions

The Coulombic interaction of the alkali metal cation and phenolate anion may be interpreted as the electrostatic interaction of two point charges in a solvent medium. A derivation of Coulomb's law provides a model for the strength of an electrostatic field (E) in a dielectric solvent.¹²

$$E = \left(\frac{1}{4\pi\epsilon_0} \right) \left(\frac{q}{\epsilon_r r^2} \right)$$

Where	ϵ_0	=	permittivity in a vacuum
	q	=	single point charge (e.g. a proton)
	ϵ_r	=	dielectric constant of the medium
	r	=	the distance of separation from the charge

The important variables for consideration here are the separation distance between the point charges (anion-cation pair) and the dielectric constant of the medium. In an ionic solution, hydration or solvation creates a region of solvent molecules associated with the ions in equilibrium. These solvent molecules are constantly exchanging with the bulk, unassociated solvent.¹³

Lee and Rasaiah found that water molecules in the first solvation shell of Li^+ associated with the ion as a loosely bound entity for an average of 190 picoseconds (ps), while they bound to Na^+ for 35 ps, and about 8- 11 ps for K^+ , Rb^+ , and Cs^+ , before exchange with the bulk solvent ensued.¹³ This finding provides a rationale for the higher average number of water molecules hydrating lithium than cesium. And since the hydrated (or solvated) ionic radius defines the effective radius of the ionic solvation sphere,¹² it will influence the strength of the electrostatic field as related to its localized dielectric constant. The solvation spheres of the phenoxide anion and alkali metal cation will determine the distance “r” between their charges, and thus the electrical field strength.

Hydrated ionic radius is influenced by the type of cation. Lithium, for example, is more hydrated in its primary hydration layer than rubidium or cesium with their larger ionic radii.¹³⁻¹⁵ A lithium cation has only 2 valence electrons, while a cesium cation has 54 valence electrons. These electrons influence the electrical field strength generated by the positive cation as indicated by properties like electronegativity and ionization potential. The solvent can also screen the electrical charge of the cations, a property represented by its dielectric constant. The effects of ionic radius and hydrated ionic radius on ionic volume and the hydration shell volume are represented in Figure 3.8. At the atomic and molecular level the dielectric effect is subject to local fluctuations since the dielectric constant is a bulk property.¹⁵ Table 3.4 provides literature values for important properties of alkali metal cations in solution.

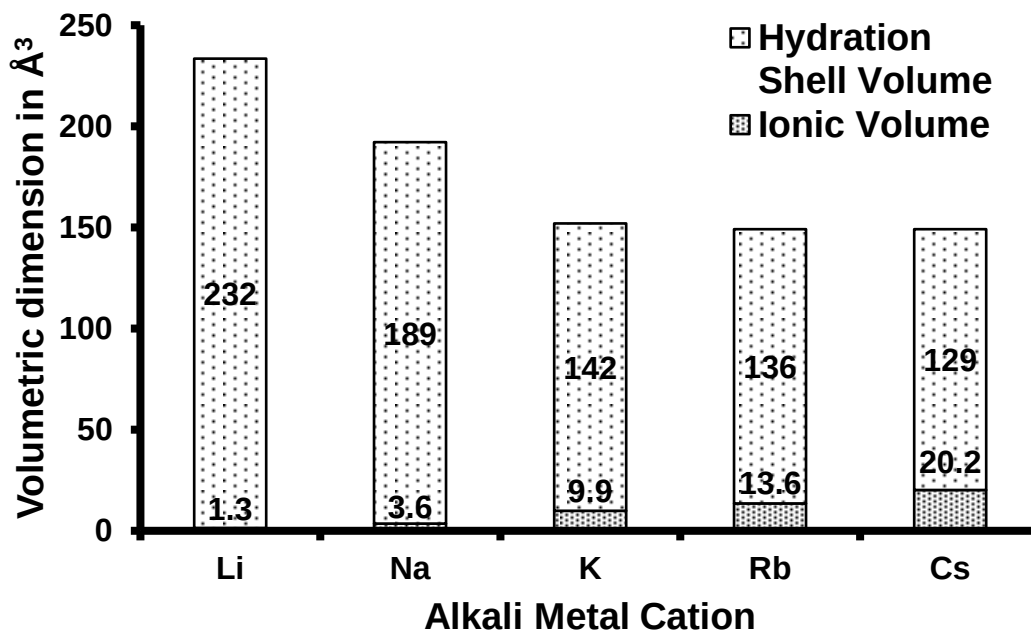


Figure 3.8. Ionic volume and hydrated shell volume for alkali metal hydroxides in water

Table 3.4. Physical properties of alkali metal cations

Cation	Number of Coordinated H ₂ O molecules ¹³	Diffusion Coefficient ¹³	Decay Time ¹³ (ps)	Crystalline Ionic Radius ¹⁴ (Å)	Hydrated Ionic Radius ¹⁴ (Å)
Li ⁺	6.0	0.66	184	0.60	3.82
Na ⁺	6.6	0.78	37.6	0.95	3.58
K ⁺	8.0	0.84	14.9	1.33	3.31
Rb ⁺	8.9	1.06	8.4	1.48	3.29
Cs ⁺	10.0	0.83	11.1	1.69	3.29

A model has been developed for approximating the Coulombic attraction of the alkali metal cations in solution and relating those values to the ¹³C chemical shifts of phenol (δ_{OH}) as perturbed by the alkali metal hydroxides (δ_{OM}). In the model, the strength of the point charge is adjusted for the screening effects of the core electrons by using the Pauling electronegativity value (χ).¹² The screening effects of the dielectric medium and the charge separation distance created by the hydration radius are modeled by the volume of the hydration shell (V_{HS}). The

hydration shell is the hydrated ionic volume (V_{HI}) calculated from the hydrated ionic radius (r_{HI}) minus the ionic volume (V_I) calculated from the crystalline ionic radius (r_I). The combination of Pauling electronegativity in the numerator and the hydration shell volume in the denominator gives an approximation of the Coulombic electric field strength, with the equation:

$$E \approx \frac{\chi}{V_{HS}} = \frac{\chi}{(V_{HI} - V_I)}$$

The relative chemical shifts are calculated from the equation:

$$\Delta = \delta_{\phi OM} - \delta_{\phi OH}$$

The plot of Δ versus χ/V_{HS} is shown in Figure 3.9 for phenol where χ/V_{HS} is normalized to the value for lithium with that being 1.00. As indicated by the R^2 values, the correlations are good for electronically sensitive positions at C-1, C-2,6, and C-4, while the little correlation is found at the electronically insensitive position for C-3,5.

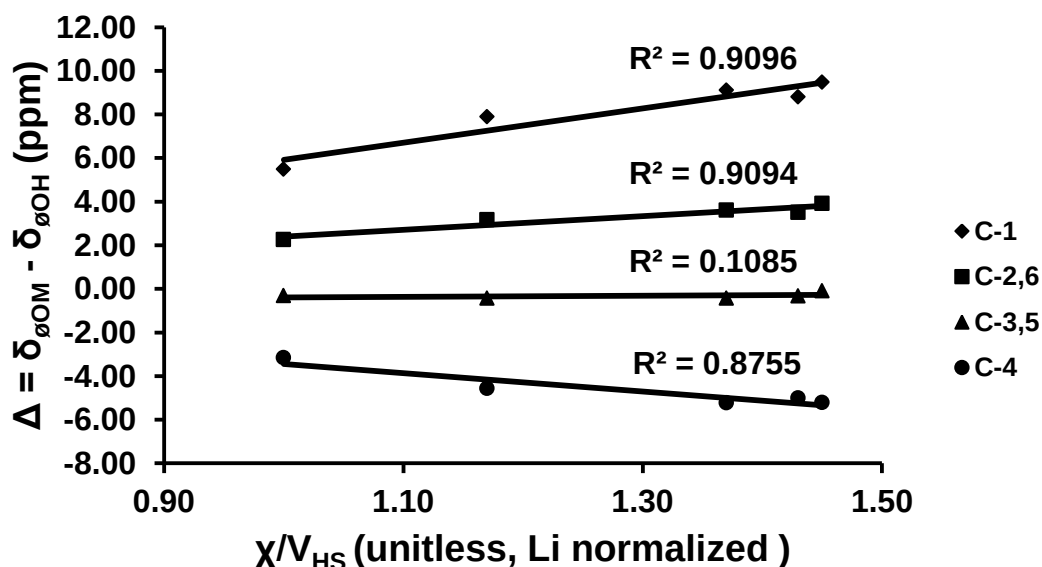


Figure 3.9. Correlation of change in chemical shifts of phenol versus the Coulombic electrical field strength modeled from Pauling electronegativity (χ) and hydrated shell volume (V_{HS})

3.3.3. Phenol in dissolved in D₂O, DMSO-d₆, CD₃OD, and THF-d₈

Figure 3.10 shows the ¹³C chemical shifts of phenol in D₂O, DMSO-d₆, CD₃OD, and THF-d₈ along with each solvent's respective dielectric constant (Table 3.5). The C-1 carbon has the highest correlation of decreasing chemical shift with increasing dielectric constant, while the R² correlation coefficients are progressively lower for the other ring positions in the order C-1 > C-2,6 > C-3,5 > C-4. In other words the C1 carbon is most strongly affected by the solvent and possibly the C-2,6 carbons to a lesser extent due to their proximity to C-1. D₂O and CD₃OD undergoing hydrogen bonding with the phenol would likely alter the electron density of the hydroxyl oxygen; these results suggest that solvent interactions added to the electron density, resulting in increased shielding at the adjacent C-1 and a lower observed δ . The DMSO-d₆ may have some hydrogen bonding interaction at the sulfoxide oxygen, while THF-d₈ has relatively little interaction. The low correlation coefficients for C-3,5 and C-4 indicate the solvent interaction has little to no effect at these positions more distant from C-1.

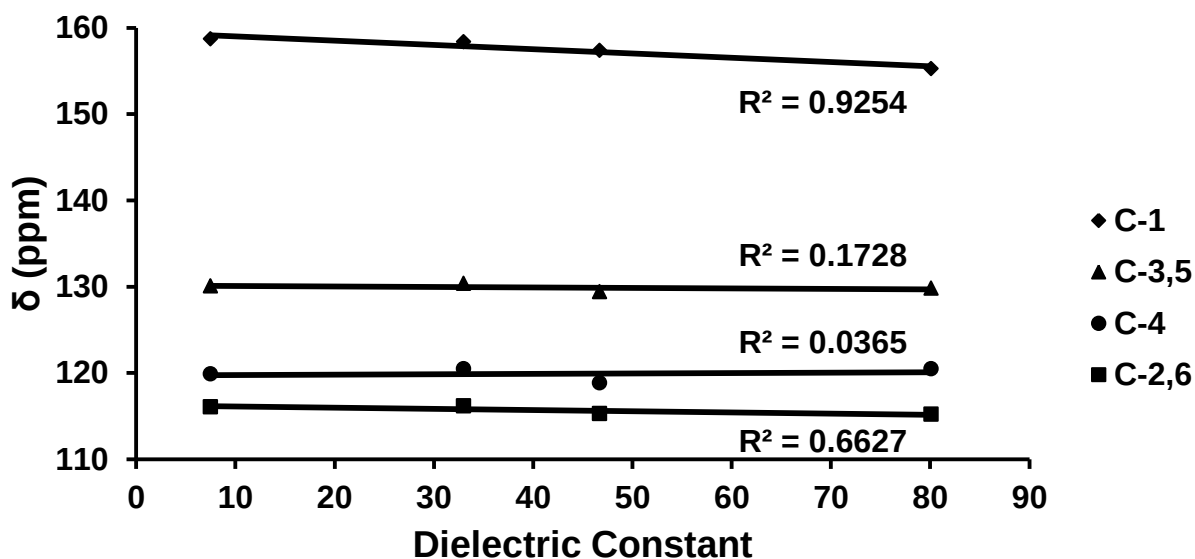


Figure 3.10. ¹³C NMR of phenol in THF-d₈, DMSO-d₆, CD₃OD, and D₂O

Table 3.5. Chemical shifts of phenol in select solvents in ppm

Solvent	Dielectric Constant ³⁰	Phenol Ring Carbon Position			
		C-1	C-2,6	C-3,5	C-4
D ₂ O	78.5	155.24	115.21	129.82	120.48
DMSO-d ₆	46.7	157.36	115.26	129.40	118.83
CD ₃ OD	32.7	158.36	116.16	130.37	120.46
THF-d ₈	7.6	158.70	116.07	130.07	119.86

3.4. Discussion

3.4.1. Implications for reactivity

The electron density of the unsubstituted ring carbons in the 2, 4, and 6 positions should indicate the directing effect on formaldehyde addition reactions. The electron density of the hydroxymethyl carbon and hydrogen atoms, along with the substituted ring carbon in the 2,4, and 6 positions should influence reactivity in phenolic self-condensation, accelerated self-condensation, and urethane formation with isocyanate functionalized compounds. Table 3.6 presents the relative chemical shifts reflecting the electron density of these particular structural groups.

Table 3.6. Chemical shift (ppm) for hydroxymethyl functional groups and the attached ring carbon

In D ₂ O/CD ₃ OD	2-HMP		4-HMP	
	Neutral Phenol	Anionic Phenolate	Neutral Phenol	Anionic Phenolate
-OH	4.85	4.40	4.87	4.44
-CH ₂ -	4.65	4.65	4.51	4.94
-CH ₂ -	60.59	62.34	64.60	65.21
-CH ₂ -	127.67	129.89	130.24	127.31

3.4.2. Addition reactions: electrophilic aromatic substitution

For electrophilic aromatic substitution, higher electron density on unsubstituted ring carbons in the 2, 4, and 6 positions would be expected to be more reactive, thus lower chemical shift values should indicate the more reactive sites and reactivity can be ranked accordingly. The NMR chemical shift data of these experiments was ranked for phenol, 2-HMP, and 4-HMP at the unsubstituted ring carbons in the 2, 4, and 6 positions and was compared to the literature kinetic rate constants for formaldehyde addition reactions. Based on the data used in Figure 3.2, found in Table 3.7, under alkaline conditions the C-4 position of phenol will be more reactive than the C-2 position. The relative reactivity for the alkali metal hydroxide cations, however, will vary by species: the rate constants for the positions at C-2 and C-4 in the presence of lithium should be close to each other, while the kinetic rates for C-4 position should be greater than C-2 in the presence of sodium and potassium ions. The addition reaction rate constants for C-2 and C-4 under rubidium and cesium catalysis should be similar to those for potassium. From this data, the directing effects for a specific catalyst may be predicted. The preferential direction of formaldehyde addition to phenol for the alkali metal hydroxides should be in the order $\text{Li} > \text{Na} > \text{Rb} > \text{K} > \text{Cs}$ for the C-2 position and $\text{Cs} > \text{K} > \text{Rb} > \text{Na} > \text{Li}$ at C-4.

Table 3.7. ^{13}C NMR chemical shifts for unreacted ring sites of alkali metal phenolates

Counter Ion	Phenol		2-HMP		4-HMP	Statistics	
	$\delta_{\text{C-4}}$	$\delta_{\text{C-2,6}}$	$\delta_{\text{C-4}}$	$\delta_{\text{C-6}}$	$\delta_{\text{C-2,6}}$	Avg.	Rank
Li	117.34	118.59	119.60	115.65	118.64	117.96	2
Na	115.33	119.78	119.79	115.28	119.55	117.95	1
K	117.08	118.74	120.05	114.82	119.40	118.02	3
Rb	117.60	118.06	120.03	114.91	119.67	118.05	4
Cs	118.13	118.13	120.21	114.91	119.93	118.26	5
Avg.	117.10	118.66	119.94	115.11	119.44	(Highest e^- density = 1	
Rank	2	3	5	1	4	Lowest e^- density = 5)	

For 2-HMP, the addition rate to C-6 position should be faster than to C-4 position due to the higher overall electron density on C-6, although this prediction directly contradicts published literature rate constants (see Table 3.8).^{4,26-29} In principle, the ranking of direction of formaldehyde addition to 2-HMP for the alkali metal hydroxides should be Cs > K > Rb > Na > Li for the C-6 position and Li > Na > Rb > K > Cs for the C-4 position. The ranking of the direction of formaldehyde addition to 4-HMP for the alkali metal hydroxides should be equal, since C-2 and C-6 are chemically equivalent.

Table 3.8. Relative rate of hydroxymethylation³

Literature Rate Constants Relative to the Phenol + Formaldehyde $\rightarrow$ 2-HMP Reaction = 1.0							
Reaction	δ Rank	1	2	3	4	5	(Avg)
Phenol + F ^a $\rightarrow$ 2-HMP ^b	(3)	1.00	1.00	1.00	1.00	1.00	(1.00)
Phenol + F $\rightarrow$ 4-HMP	(2)	1.18	2.08	1.09	1.46	1.46	(1.45)
2-HMP + F $\rightarrow$ 2,6-DHMP ^c	(1)	1.66	1.08	1.98	1.70	1.87	(1.65)
2-HMP + F $\rightarrow$ 2,4-DHMP	(5)	1.39	2.58	1.80	3.80	3.35	(2.58)
4-HMP + F $\rightarrow$ 2,4-DHMP	(4)	0.71	0.83	0.79	1.02	0.91	(0.85)
2,6-DHMP + F $\rightarrow$ THMP ^d		7.94	3.25	3.33	4.54	4.73	(4.76)
2,4-DHMP + F $\rightarrow$ THMP		1.73	1.25	1.67	1.76	1.75	(1.63)
^a Formaldehyde	^b Hydroxymethylphenol	^c Dihydroxymethylphenol		^d Trihydroxymethylphenol			
1 = Freeman & Lewis 1954 (30 °C) ²⁶							
2 = Minami & Ando 1956 (40 °C) ²⁷							
3 = Zsavitsas & Beaulieu 1968 (30 °C) ²⁸							
4 = Eapen & Yeddanapalli 1968 (30 °C) ²⁹							
5 = Higuchi, Nohno, Morita, & Tohmura 1998 (20, 30, & 40 °C) ⁴							

Most of the change in chemical shift relative to phenol is generated by the addition of an alkali metal hydroxide, but the specific cation also affects the chemical shift to a lesser extent.

Grenier-Loustalot has previously demonstrated that the alkali metal cation affects the addition reaction rate.² The reactivity of the alkali metal phenolates towards formaldehyde depends on the availability of high electron density at the 2, 4, and 6 ring positions for electrophilic substitution. This electron density is approximated by the chemical shift of the respective ring carbon atoms. The relative shielding for each of these positions for phenol, 2-HMP, and 4-HMP have been ranked by the average ion of the alkali metal hydroxide series to give an expected

relative reaction rank. The comparison rankings are generated from the relative rate constants averaged from the five separate measurements for the alkali metal hydroxides, since the literature rate constants showed substantial divergence among themselves.^{4,26-29} While the ranking from the chemical shifts (Table 3.7) correctly predicts the average relative reaction rate of 4 of 5 reactions based on the literature (Table 3.8), the prediction for formaldehyde addition to the 4 position of 2-HMP, however, is substantially off. Freeman and Lewis attributed the faster addition of formaldehyde to 2-HMP, 2,4-DHMP, and 2,6-DHMP to resonance enhancements generated by intramolecular hydrogen bonding. These hydrogen bonds would chelate with the quinoidal anionic oxygen, giving it a higher electronegativity. A double bond present within the chelate ring would stabilize it, enhancing the resonance contribution.²⁶ This data shows that the composition of PF hydroxymethyl phenols may be directed by catalyst selection towards specific ring carbon sites during formaldehyde addition and the chemical shift data can be used as a first approximation in most cases. Some caution, however, is necessary; the data should be corroborated with information generated by other methods.

3.4.3. Implications in condensation reactions: neutral conditions

Under neutral conditions, HMPs are known to form dibenzyl ether bridges from two hydroxymethyl groups.^{18,19} A probable mechanism for this reaction is shown in Figure 3.11. This reaction depends on the electron density distribution between the methylene carbon and hydroxyl oxygen favoring the oxygen atom. The relatively electron rich oxygen will attack the lower electron density methylene carbon, forming the ether bridge with elimination of water. The more deshielded methylene carbon of 4-HMP would indicate that this reaction may have a somewhat lower activation energy than the same reaction for 2-HMP. This reaction for the 2-HMP is known to be a relatively slow, requiring a high activation energy input.¹⁹

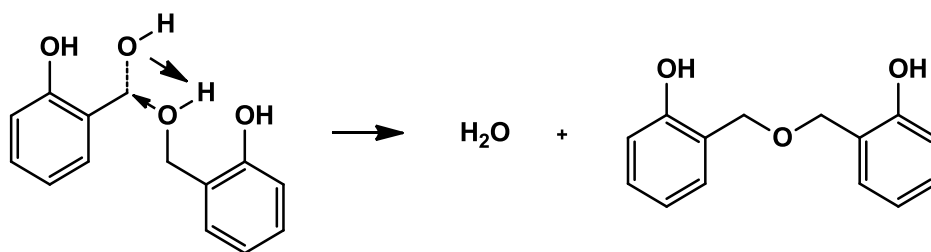


Figure 3.11. Benzylic ether formation mechanism

3.4.4. Implications in condensation reactions: anionic (alkaline) conditions

The self-condensation reactivity of the alkali metal salts of 2- and 4-HMP is directed to the electron density at the 2 and 4 hydroxymethyl substituted ring positions. The condensation kinetic rates will be dependent on the electron density at the reaction sites and the particular mechanism involved, which is thought to be mediated by a quinone methide mechanism.²⁰⁻²²

The resonance structures of quinone methides that can form from 2- and 4-HMP are shown in Figure 3.12 of which the carbocation is a powerful electrophile. The reaction is considered to occur between a neutral monomer and an anionic monomer.^{23,24}

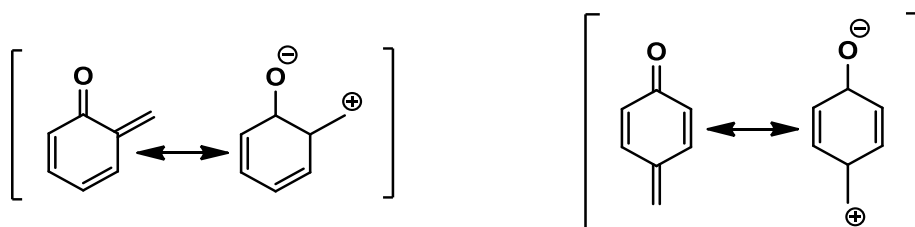


Figure 3.12. Carbocation resonance structures for 2 and 4 quinone methides

One possible mechanism involves attack of the electron rich, hydroxymethyl substituted ring carbon by a quinone methide carbocation with subsequent emission of a formaldehyde molecule as illustrated in Figure 3.13. For the phenolate salts of 2- and 4-HMP, the ¹³C chemical shifts for the substituted ring carbons are found in the range of 129.62 to 130.12 ppm for 2-

HMP and 126.85 to 128.68 ppm for 4-HMP. The higher electron density of the 4-HMP ring carbon agrees with the established self-condensation reactivity order of 4-4' > 4-2' > 2-2'.^{2,24,25}

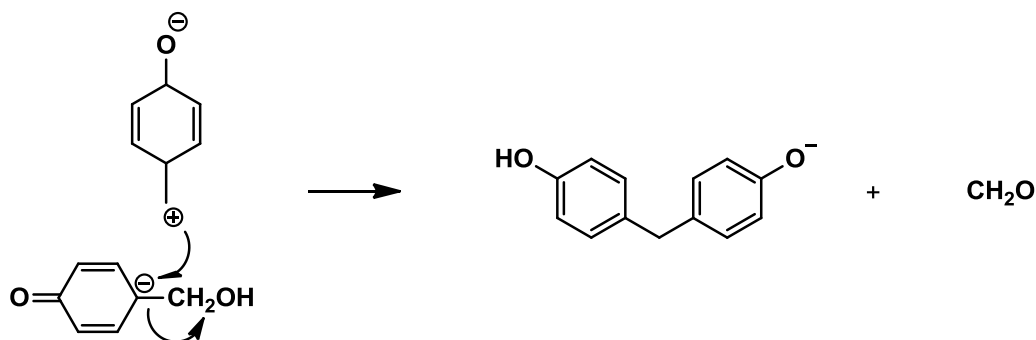


Figure 3.13. Mechanism of 4-HMP self-condensation by electrophilic attack of a quinone methide carbocation resonance structure on an anionic resonance structure of 4-HMP

When considering the faster PF reactivity of potassium observed by Daisy¹, the ¹³C chemical shift at C-2 of 2-HMP was 129.77 and 129.96 ppm, while at C-4 of 4-HMP it was 126.92 and 127.23 ppm for sodium and potassium respectively. In both cases the electron density at the ring carbon is higher for sodium than potassium, inconsistent with the expected results for the QM carbocation mechanism attacking the substituted ring carbon with the highest electron density. This discrepancy suggests that the basis for enhanced reactivity may not be found with the anionic HMP species, but possibly that potassium may foster a faster rate of QM formation than sodium.

3.4.5. Predictions for urethane formation reactions in polar aprotic solvents under neutral conditions

Furthermore, when considering the reactivity of phenolic model compounds with functional groups such as isocyanates in urethane formation, the role of the reactive hydroxyl hydrogen and oxygen will influence their interaction with an isocyanate nitrogen and carbon respectively. Deprotonation or solvent exchange prevents chemical shift determination of phenolic hydroxyls

in alkaline or protic solvents, respectively. Thus, the polar aprotic solvents DMSO-d₆ or THF-d₈ were used to avoid solvent exchange and deprotonation.

Under neutral conditions in DMSO-d₆ and THF-d₈, ¹H NMR showed that the chemical shifts of the 2- and 4-HMP hydroxymethyl hydroxyl protons were between 4.13 and 4.94 ppm, and the phenolic hydroxyl protons were between 8.21 and 9.34 ppm (Table 3.9) indicating deshielding of these more acidic protons. As a solvent, THF-d₈ shielded the phenolic hydroxyl and benzylic hydroxyl protons relative to DMSO-d₆; the inverse case occurred for THF-d₈ relative to DMSO-d₆ with deshielding of the protons located on the C-1, methylene, and substituted ring carbons. This behavior may be explained by hydrogen bonding of the hydroxyl groups to the DMSO-d₆ sulfinyl group, leading to a net electron density contribution to the carbon backbone, but electron withdrawal effect at the bonded protons.

Table 3.9. Chemical shift (ppm) for hydroxyl functional groups and related carbons

NMR Structure	Model Compound					
	Phenol		2-HMP		4-HMP	
	DMSO-d ₆	THF-d ₈	DMSO-d ₆	THF-d ₈	DMSO-d ₆	THF-d ₈
C-O <u>H</u>	9.34	8.27	9.29	8.46	9.23	8.21
<u>C</u> -OH	157.36	158.70	154.16	156.46	156.21	157.75
CH ₂ -O <u>H</u>	---	---	4.94	4.58	4.96	4.13
-C <u>H</u> ₂ -	---	---	4.49	4.68	4.36	4.44
- <u>C</u> H ₂ -	---	---	58.28	61.97	62.84	64.86
<u>C</u> -CH ₂ -	---	---	128.55	128.65	132.78	134.19

3.4.6. Predictions for urethane formation reactions in polar protic solvents under neutral and alkaline conditions

Under neutral conditions in D₂O/CD₃OD, ¹H NMR showed that the chemical shifts of the 2- and 4-HMP hydroxymethyl hydroxyl protons were 4.85 and 4.87 ppm respectively, and 4.40 and 4.94 ppm respectively under alkaline conditions (Table 3.6). The electron rich isocyanate nitrogen should prefer the more electron deficient or deshielded protons of the 4-HMP. Another factor to consider in urethane formation reactions, however, is that the hydroxyl

oxygen must form a bond with the isocyanate carbon, which may be more important than the electron density of the reacting hydrogen. The reactivity of this system will likely be influenced by the electron density of the hydroxyl oxygen, as the isocyanate carbon will be electrophilic as shown by the resonance structures in Figure 3.14.

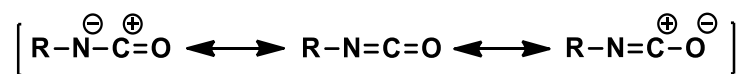


Figure 3.14. Isocyanate resonance structures

Here again, ^{13}C NMR is helpful in pointing out reactivity potential, as the chemical shifts of the 2- and 4-HMP methylene groups were 60.59 and 64.60 ppm respectively under neutral conditions, and 62.34 and 65.21 ppm respectively under alkaline conditions (Table 3.6). With the lower values indicating higher electron density on the methylene carbon, the adjacent hydroxyl oxygen would also have higher electron density making it more electrophilic towards the isocyanate carbon. Thus the prediction would be that the hydroxymethyl of the neutral 2-HMP would be more reactive than the 4-HMP towards isocyanates, while the hydroxymethyl groups in alkaline solution should be less reactive than the neutral ones. Future work will attempt to confirm this hypothesis.

3.5. Conclusions

This research has identified the fundamental importance of the electrostatic interactions on the electronic structure of the substituted or unsubstituted phenolic aromatic rings and related this to the reactivity of compounds previously published in the literature. Subtle effects relate to how the solvated ionic radius and solvent dielectric constant affect the strength of the electric field generated by the ions. Reactivity in turn is dependent on the electronic structure of the various reactants, thus is affected by changes in the alkali metal hydroxide and solvent.

- Alkali metal cations act as an electron withdrawing force on the phenolic monomer's electronic structure, with the strength of their effect mostly dependent on proximity the

phenoxide anion and resonance effects. The effect of the cation is related to the dielectric screening of their inner shell electrons and the local dielectric effects of the solvation shell. The greatest effect is deshielding at the C-1 carbon, while the C-3 & C-5 carbons are mostly unaffected by the perturbation.

- Solvents shift the electron density, probably due to hydrogen bonding interactions with the hydroxyl groups. Methanol was found to be more deshielding than water, lowering electron density at reactive sites. For neutral compounds, DMSO was more shielding of the carbon backbone than THF, but more deshielding of the hydroxyl protons.
- The hydroxymethyl substituted carbon at C-2 or C-4 is deshielded, while the unsubstituted C-2, C-4, and C-6 positions when shielded are thus made more reactive towards formaldehyde addition. The correct order of reactivity was predicted for formaldehyde addition for 4 of 5 reactions.
- Hydroxymethyl substitution on the C-2 or C-4 position has the overall effect of deshielding the C-2 ring carbon, while the C-4 position is more shielded than their respective ring carbons in the neutral state. The chemical shift of the substituted C-2 position is more deshielded in the anionic form than C-4. The implication is that an HMP would be more susceptible to electrophilic substitution by a quinone methide carbocation at the C-4 position than the C-2 position in the anionic form, consistent with the order of reactivity published in the literature.
- The data predicted that 2-HMP hydroxymethyl groups would be more reactive than 4-HMP in forming urethane bonds under neutral conditions. 2-HMP hydroxymethyl groups would be more reactive than 4-HMP in forming urethane bonds under alkaline conditions. Neutral reactivity was predicted to be faster than alkaline reactivity for 2- and 4- HMP.

Future work will look for further evidence of the predicted reactivity. Overall, NMR chemical shift data is most useful for interpreting reactivity when combined and corroborated with information on reaction kinetics, mechanism, and physical properties.

3.6. References

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Chapter 4: ^1H and ^{13}C NMR of the Reactions of PF and pMDI Model Compounds

4.0. Overview

With ^1H and ^{13}C NMR, this study investigated the reactions of phenyl isocyanate with the phenolic model compounds phenol, benzyl alcohol, 2-HMP, and 4-HMP under neutral conditions in organic solvent and in an alkaline environment. The effects of amine and tin-based catalysts on the molecular structure of the products were also studied. NMR chemical shifts that were predicted for the models and their reaction products were used to aid in peak assignments for the complex spectra. Reactions of 2-HMP, and 4-HMP with phenyl isocyanate resulted in formation of benzyl urethanes (BU), phenyl urethanes (PU), and benzyl phenyl diurethanes (BDPU) compounds. Under neutral conditions in organic solvent, reactions catalyzed by the amine catalyst favored the formation of phenyl urethanes, while reactions catalyzed by the tin-based catalyst favored the formation of benzyl urethanes.

The same reactions were investigated in DMSO-d_6 ranging from neutral to alkaline conditions. The reaction environment was adjusted by the presence of NaOD, with ND_4OD and SnCl_2 as catalysts. Overall the reactions consumed more 2-HMP than 4-HMP. For 2-HMP, alkaline conditions favored PU formation over BU formation, while for neutral conditions favored BU formation over PU formation. The latter case was especially evident when no catalyst was present. However, for 4-HMP under neutral conditions when no catalyst was present, no BU and only modest amounts of PU formed as products. Small amounts of BDPU formed with 2-HMP, but essentially none formed with 4-HMP. Overall, the anionic phenolate group was most reactive towards the isocyanate, suggesting that it was reacting as a strong nucleophile.

4.1. Introduction

One drawback of PF technology is that it requires relatively high temperatures and long press times to cure in the manufacture of wood composites. Haupt has demonstrated that the PF reactivity can be enhanced at ambient temperatures by accelerated copolymerization and self-

condensation with polymeric methylenediphenyl diisocyanate (pMDI), a PF accelerator, and a polyurethane (PU) catalyst.¹ The structure of this copolymer, however, is uncertain.

Others have undertaken research to determine the structure of reaction products of PF and pMDI model compounds. Multiple studies have investigated the reactions of PF and pMDI model compounds in organic solvents. Some of this research has focused on the role of catalysts in kinetics and the structure of reaction products,²⁻⁵ while others have examined the effect of the solvents themselves on reaction kinetics.⁶⁻⁸ Papa and Critchfield studied the reactions of 2-HMP and 4-HMP with phenyl isocyanate in chloroform using ¹H NMR and infrared spectroscopy. The reactions were reacted at temperatures between 56 and 94 °C and were run either uncatalyzed or in the presence of dibutyltin dilaurate (DBTL) or triethylamine (TEA) catalysts.² They did not run reactions at ambient temperature and structural determinations were somewhat limited by the use of ¹H NMR without any ¹³C data. They found that TEA directed towards phenyl urethane formation and DBTL directed towards benzyl urethane formation, while uncatalyzed reactions produced 1,3-diphenyl urea.

In a set of experiments that most resemble the aqueous, alkaline environment of blended PF and pMDI wood adhesives, Haider et al. investigated the reactions of phenol, benzyl alcohol, and 4-HMP with phenyl isocyanate in 1,4-dioxane at temperatures of 25 and 100 °C and in an aqueous solution of sodium hydroxide at 100 °C. The reaction products were characterized by NMR, IR and HPLC.⁵ They did not, however, investigate the reactions of 2-HMP or any reactions in the presence of catalysts.

What needs to be expanded upon from these previous studies is an investigation of the effects of polyurethane catalysts on these model compound reactions in the aqueous-alkaline environment with ¹H and ¹³C NMR. The objective of this study was to fill in this knowledge gap by employing NH₄OH and SnCl₂ as catalysts. NMR spectroscopy was used to generate data for structural determination of the reaction products of the model compounds in first in organic solvent, then in the aqueous-alkaline environment.

4.2. Experimental

4.2.1. ^1H and ^{13}C NMR

NMR spectra were acquired using a Varian Inova model at 400 MHz proton frequency. Both ^1H and ^{13}C spectra were taken for all materials studied. Chemical shift data were analyzed with MestReNova software. All spectra except for those deuterium oxide ^{13}C spectra were adjusted to the solvent peak reference chemical shift; the ^{13}C spectra for model compounds in deuterium oxide were used as is without adjustment.

4.2.2 .Reactions of PF model compounds with phenyl isocyanate in THF- d_8

4.2.2.1. Model compounds

Samples of the model compounds phenol (Sigma-Aldrich >99%), benzyl alcohol (Sigma-Aldrich >99.8%), 2-hydroxymethyl phenol (Sigma-Aldrich 99%), 4-hydroxymethyl phenol (Sigma-Aldrich 99%), and phenyl isocyanate (Fluka > 99.0%) were weighed out in 0.0650 to 0.0750 g quantity and placed in separate glass sample vials. All model compounds were used as received. To each vial 0.650 mL of THF- d_8 was added (Cambridge Isotope Labs) to dissolve the sample. Each dissolved sample was placed in a labeled 5-mm NMR tube for NMR analysis.

The catalysts used in this study were dibutyltin dilaurate (Sigma-Aldrich 95%), triethylamine (Sigma-Aldrich $\geq 99\%$), NaOD in D_2O (Sigma-Aldrich, 40 wt. %, 99.5 atom %), SnCl_2 (anhydrous, Sigma-Aldrich 98%), and ND_4OD (25% wt./wt. solution in D_2O , Sigma-Aldrich 99+ atom%).

4.2.2.2. Uncatalyzed reactions of model compounds

Phenyl isocyanate 119.8 mg was reacted with phenol 93.5 mg in 0.500 mL of THF- d_8 . Phenyl isocyanate 121.5 mg was reacted with benzyl alcohol 107.8 mg in 0.500 mL of THF- d_8 . Phenyl isocyanate 121.4 mg was reacted with 2-hydroxymethyl phenol 123.1 mg in 0.500 mL of THF- d_8 . Phenyl isocyanate 120.1 mg was reacted with 4-hydroxymethyl phenol 120.5 mg in 0.500 mL of THF- d_8 . The samples were allowed to react for at least 24 hours prior to running NMR analysis. Since the reaction products precipitated from the solvent, the solvent was air

evaporated at ambient temperature and the residual solid material was dissolved in 0.700 mL DMSO-d₆ (Cambridge Isotope Labs). Each dissolved sample was placed in a labeled 5-mm NMR tube for NMR analysis. The NMR sample masses of the respective phenyl isocyanate reaction products were 37.9 mg for phenol, 32.0 mg for benzyl alcohol, 59.3 mg for 2-hydroxymethyl phenol, and 37.6 mg for 4-hydroxymethyl phenol.

4.2.2.3. Catalyzed reactions of model compounds

Phenyl isocyanate 120.8 mg was reacted with phenol 95.5 mg and 3.8 mg DBTL catalyst in 1 g of THF-d₈. Phenyl isocyanate 125.0 mg was reacted with benzyl alcohol 107.9 mg and 4.0 mg DBTL catalyst in 1 g of THF-d₈. Phenyl isocyanate 138.2 mg was reacted with 2-hydroxymethyl phenol 124.1 mg and 4.0 mg DBTL catalyst in 1 g of THF-d₈. Phenyl isocyanate 155.0 mg was reacted with 4-hydroxymethyl phenol 124.4 mg and 4.4 mg DBTL catalyst in 1 g of THF-d₈. The samples were allowed to react at ambient (24 °C) for at least 24 hours prior to running NMR analysis.

Phenyl isocyanate 119.7 mg was reacted with phenol 96.8 mg and 7.6 mg TEA catalyst in 1 g of THF-d₈. Phenyl isocyanate 117.1 mg was reacted with benzyl alcohol 108.6 mg and 3.3 mg TEA catalyst in 1 g of THF-d₈. Phenyl isocyanate 121.4 mg was reacted with 2-hydroxymethyl phenol 124.0 mg and 4.7 mg TEA catalyst in 1 g of THF-d₈. Phenyl isocyanate 124.5 mg was reacted with 4-hydroxymethyl phenol 124.5 mg and 3.6 mg TEA catalyst in 1 g of THF-d₈. The samples were allowed to react at ambient (22 °C) for at least 24 hours prior to running NMR analysis.

4.2.3. Reactions of PF model compounds with phenyl isocyanate under alkaline conditions

4.2.3.1. NMR of phenolic model compounds in DMSO-d₆

Samples of the model compounds phenol (Sigma-Aldrich ≥99%), 2-hydroxymethyl phenol (Sigma-Aldrich 99%), 4-hydroxymethyl phenol (Sigma-Aldrich 99%), and 1,3-diphenylurea (Sigma-Aldrich 98%) were weighed out in 0.0330 to 0.0430 g quantity into separate glass vials. All model compounds were used as received. To each vial, 0.700 mL of DMSO-d₆ (Cambridge Isotope Labs) was added to dissolve the sample. Each dissolved sample was placed in a labeled 5-mm NMR tube for NMR analysis.

4.2.3.2. NMR of phenolic model compounds in the presence of SnCl₂ and ND₄OD in CD₃OD

Samples of the model compounds phenol (Sigma-Aldrich >99%), 2-hydroxymethyl phenol (Sigma-Aldrich 99%), and 4-hydroxymethyl phenol (Sigma-Aldrich 99%) were weighed out in 0.0344 to 0.0581 g quantity in separate glass sample vials. Catalysts were added to perturb the electronic environment of the model compounds. Those catalysts were NaOD in D₂O (Sigma-Aldrich, 40 wt. %, 99.5 atom %), SnCl₂ (anhydrous, Sigma-Aldrich 98%), and ND₄OD (25% wt./wt. solution in D₂O, Sigma-Aldrich 99+ atom%). All model compounds were used as received. Each vial had NaOD or ND₄OD added to it to provide a molar ratio of the hydroxide source to phenolic model compound of 1.0. Each model compound had one vial with NaOD and one vial with ND₄OD. After preparation of the model compounds and catalysts, 1 g of CD₃OD (Cambridge Isotope Labs) was added to each vial to dissolve the sample. Each dissolved sample was placed in a labeled 5-mm NMR tube for analysis and the ¹H and ¹³C NMR spectra were acquired for each of these samples.

After acquisition was completed, the samples were decanted back into their original sample preparation vials for the SnCl₂ sample perturbation experiments, and 0.10 mL of a pre-dissolved solution of SnCl₂ in D₂O (1.67 wt. %) was added to it. Each sample was further diluted with approximately 0.15 mL CD₃OD and 0.30 mL D₂O filtered through a 0.20 µm nylon 13 mm Alltech syringe filter and placed in a labeled 5-mm NMR tube for analysis.

4.2.3.3. Reactions of PF model compounds with phenyl isocyanate under neutral and alkaline conditions in DMSO-d₆

Samples of the model compounds 2-hydroxymethyl phenol (Sigma-Aldrich 99%) and 4-hydroxymethyl phenol (Sigma-Aldrich 99%) were weighed out in 0.2821 to 0.3683 g quantity in separate glass sample vials. Eleven solutions were prepared for further blending to prepare individual samples. Solution 1 was 0.1241 g of 2-HMP dissolved in 1.2492 g DMSO-d₆ (Cambridge Isotope Labs). Solution 2 was 0.1241 g of 2-HMP and 0.0505 g NaOD in D₂O (Sigma-Aldrich, 40 wt. %, 99.5 atom %) dissolved in 1.2482 g DMSO-d₆. Solution 3 was 0.1241 g of 2-HMP and 0.0999 g NaOD in D₂O dissolved in 1.2442 g DMSO-d₆. Solution 4 was 0.1241 g of 4-

HMP dissolved in 1.2289 g DMSO-d₆. Solution 5 was 0.1241 g of 4-HMP and 0.0510 g NaOD in D₂O dissolved in 1.2533 g DMSO-d₆. Solution 6 was 0.1241 g of 4-HMP and 0.1064 g NaOD in D₂O dissolved in 1.2533 g DMSO-d₆. Solution 7 was 0.0974 g ND₄OD (25% wt./wt. solution in D₂O, Sigma-Aldrich 99+ atom%) in 2.4728 g DMSO-d₆. Solution 8 was 0.0959 g ND₄OD (25% wt./wt. solution in D₂O, Sigma-Aldrich 99+ atom%) and 0.0040 g SnCl₂ (anhydrous, Sigma-Aldrich 98%) in 2.4469 g DMSO-d₆. Solution 9 was 0.0041 g SnCl₂ in 2.4438 g DMSO-d₆. Solution 10 was 0.7138 g phenyl isocyanate (Fluka > 99.0%) in 4.8905 g DMSO-d₆. Solution 11 was 0.0050 g SnCl₂ in 4.8905 g DMSO-d₆.

Solutions 1, 2, and 3 were used for samples with molar ratios of NaOD to 2-HMP of 0.0, 0.5, and 1.0 respectively. Solutions 4, 5, and 6 were used to prepare samples with molar ratios of NaOD to 4-HMP of 0.0, 0.5, and 1.0 respectively. Within each level of NaOD to 2- or 4-HMP molar ratio, four separate sample treatments were made with combinations of ND₄OD and SnCl₂. One set of treatments was the control group, without ND₄OD or SnCl₂. A second set of treatments was with ND₄OD using solution 7. A third set of treatments was with ND₄OD and SnCl₂ using solution 8. A fourth set of treatments was with SnCl₂ using solution 9. The solution amounts were added such that the molar ratio of ND₄OD to 2- or 4-HMP was 0.20 and the amount of SnCl₂ added was about 2% of the weight of the 2- or 4-HMP.

To each of the sample vials, a sufficient amount of phenyl isocyanate was added via solution 10 to provide a molar ratio of phenyl isocyanate to 2- or 4-HMP of 1.0. For those samples with less added liquid from catalyst treatments, sufficient DMSO-d₆ was added to increase the total sample volume to between 0.70 and 0.75 mL for optimal NMR sample tube volume. Each dissolved sample was placed in a labeled 5-mm NMR tube for analysis and the ¹H and ¹³C NMR spectra were acquired for each of these samples.

4.3. Results and discussion

4.3.1. Predicted ^{13}C chemical shifts of reactions products of phenolic model compounds with phenyl isocyanate

Figures 4.1 and 4.2 depict the reactions of 2-HMP and 4-HMP with phenyl isocyanate leading to the formation of phenyl urethanes (PU) at the phenolic hydroxyl, benzyl urethanes (BU) at the benzylic hydroxyl, or benzyl phenyl diurethanes (BPDU) at both phenolic and benzylic hydroxyls. ChemDraw Ultra software was used for NMR spectral estimation of chemical shifts for these structures, to aid in identification of specific peaks encountered. The predicted ^{13}C shifts are shown in Tables 4.1, 4.2, and 4.3. Figures 4.3 and 4.4 depict the peaks typically found in a ^{13}C or ^1H spectrum for phenol, 2-HMP, and 4-HMP.

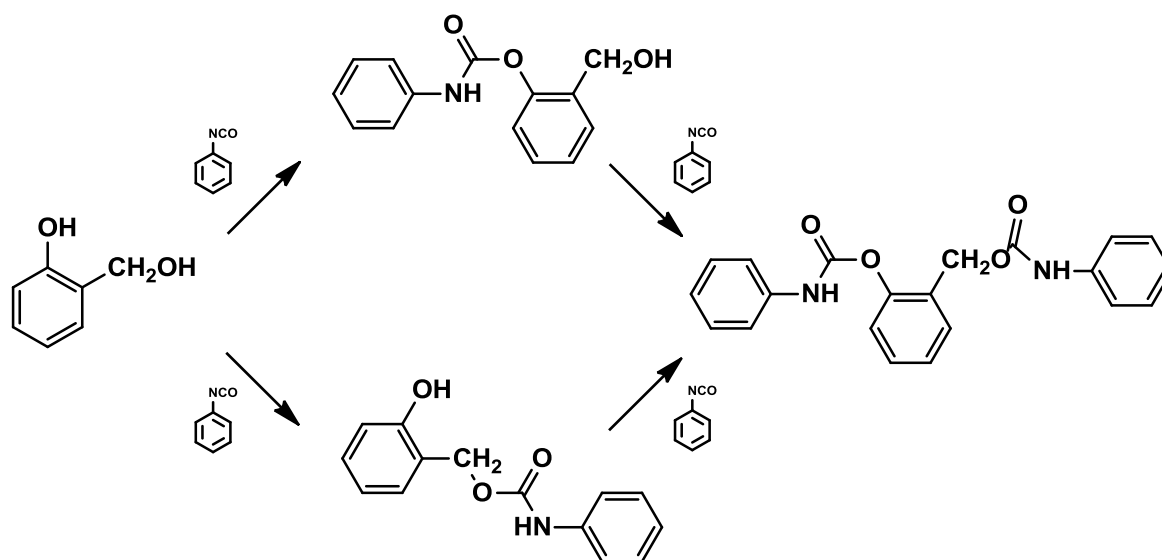


Figure 4.1. Reactions of 2-HMP and phenyl isocyanate

These predicted results were useful for identifying the approximate chemical shift in the complex NMR spectra of the reaction products which contained the spectra for multiple compounds. They were helpful in identifying key “reporter” positions that would provide information on residual reactants and the formation of benzyl or phenyl urethanes. By simulating neutral and ionic phenolic model compounds and their reaction products with phenyl isocyanate, the identification of compounds in alkaline environment was also possible.

The most important positions that were indicative of reactions were the C-1 position, the CH₂ position, and the urethane carbonyl carbon. The changes in the substituted C-2 and C-4 positions were also helpful in confirming interpretations at the other positions.

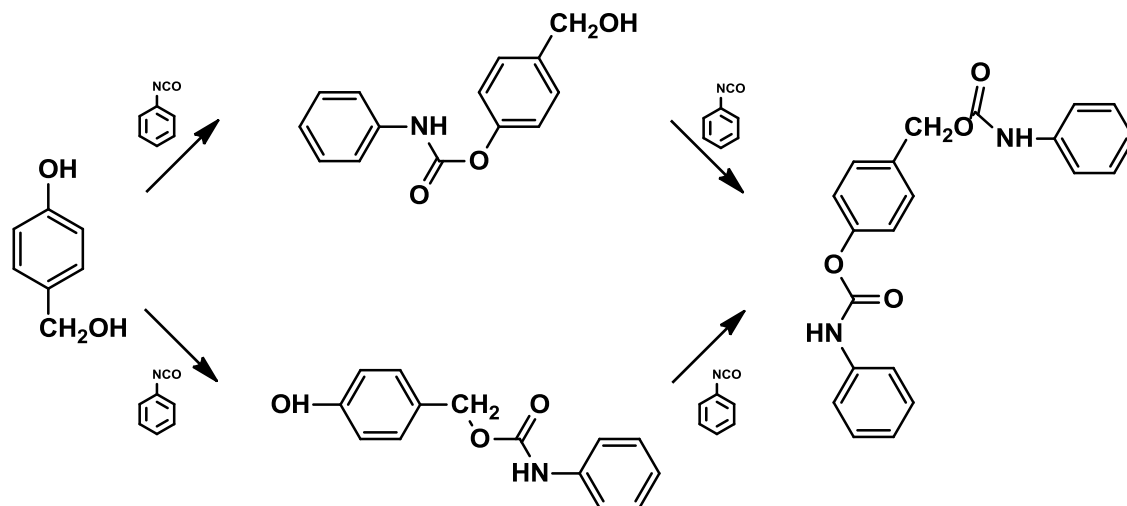


Figure 4.2. Reactions of 4-HMP and phenyl isocyanate

4.3.1.1. Predicted chemical shifts for the phenolic residue

The important aspect of the predicted chemical shifts is to identify the presence or lack of certain peaks as a result of reactions. One must keep in mind that when an alkaline phenolate is present, no PU form is allowed, thus there are no predicted values for phenyl urethanes in the alkaline environment. The numbering system used here for the phenolic residue starts with C-1 as the hydroxyl substituted carbon, followed by C-2 in the ortho position, C-3 in the meta position, C-4 in the para position, C-5 in the second meta position, and C-6 in the second ortho position. The carbon from the hydroxymethyl group is denoted as CH₂.

At the C-1 carbon, the alkaline environment results in deshielding, as the electron density concentrates on the more stable anionic oxygen with a range of increase from 6 to 10 ppm. Upon PU formation the predicted C-1 δ drops from 158.5 to 151.3 ppm indicating that the urethane adds electron density to C-1. The ranking of predicted shifts for reactions of 2-HMP was ϕ -OH = BU > PU = BPDU (156.2 ppm > 148.4 ppm), from increasing electron density at the C-1 position due to the formation of phenyl urethane. The ranking of predicted shifts for

reactions of 4-HMP was ϕ -OH = BU > PU = BPDU (157.4 ppm > 150.2 ppm) due to increasing electron density at the C-1 position due to the formation of phenyl urethane. The phenyl urethane isomer of 2-HMP had a lower δ (148.4 ppm) than 4-HMP (150.2 ppm) probably due to its closer proximity to the electron rich phenolic oxygen.

The C-3 and C-5 carbons had predicted δ between 127.1 and 130.6 ppm. They were slightly affected by alkaline conditions, with neutral condition being lower for phenol by about 0.5 ppm, higher for 2-HMP by 2 to 3 ppm, and higher for 4-HMP by 2.6 ppm. The effect of the urethane reaction product formation was very minor on these two carbon positions, less than about 1 ppm total.

The C-2 carbon δ was predicted to be lower by about 3 to 5 ppm when in the neutral form than the anionic alkaline form. The effect with 2-HMP is strong, as phenol and the BU form deshielded by 6.7 ppm at this carbon (128.8 to 135.5 ppm). In the neutral form, the PU and BPDU products also deshielded 5.7 ppm relative to the shifts predicted for phenol and BU, at 134.5 ppm versus 128.8 ppm respectively. The predicted ranking of the δ values for the urethane products of 2-HMP under neutral conditions was PU = BPDU > ϕ -OH = BU (134.5 ppm > 128.8 ppm). The predicted ranking of the δ values for the urethane products of 2-HMP under neutral conditions was PU = BPDU > ϕ -OH = BU (121.8 ppm > 116.1 ppm). The effect of PU and BPDU formation of 4-HMP was to deshield relative to phenol and BU by 5.7 ppm, with an increase from 116.1 to 121.8 ppm.

At the C-4 carbon, the δ for phenol under alkaline conditions was lower than for neutral conditions (115.1 ppm versus 121.3 ppm respectively), but substantially higher for 2-HMP and (128.9 ppm versus 124.3 ppm respectively) and 4-HMP (141.2 ppm versus 133.8 ppm respectively for phenol and 136.1 ppm versus 128.7 ppm respectively for BU). The ranking of the reaction products of 4-HMP under neutral conditions was PU > ϕ -OH > BPDU > BU (138.0 ppm > 133.8 ppm > 132.9 ppm > 128.7 ppm). The benzyl urethanes appear to effectively add electron density, while the phenyl urethanes effectively withdraw electron density from the C-4 ring position.

The C-6 carbon chemical shift was lower for neutral conditions at 116.1 ppm, but higher for alkaline conditions at 119.5 ppm. Among the reaction products the unreacted phenol and BU forms were predicted at 116.1 ppm, while the PU and BPDU were at 121.8, indicating that the effect of phenyl urethane substitution should be deshielding at C-6.

The hydroxymethyl CH₂ group was very important as it was the only aliphatic group involved in the predicted compound and could provide a clear indication of its associated structure for identification purposes. Under alkaline conditions the δ was predicted to be much higher (i.e. deshielded) for 2-HMP than 4-HMP, likely due to proximity to C-1 carbon and phenolic oxygen. The CH₂ carbon of 4-HMP showed no predicted change between neutral and alkaline conditions. The reaction product ranking of chemical shifts was PU > ϕ -OH > BPDU > BU (60.1 ppm > 59.9 ppm > 59.6 ppm > 59.4 ppm) for 2-HMP under neutral conditions. The reaction product ranking of chemical shifts was BU = BPDU > PU = ϕ -OH (66.8 ppm > 64.7 ppm) for 4-HMP under neutral conditions. The reaction product ranking of chemical shifts was BU > ϕ -OH (66.8 ppm (4-HMP) > 65.6 ppm (2-HMP) > 64.7 ppm (2-HMP and 4-HMP)) for both 2-HMP and 4-HMP under alkaline conditions. Alkalinity affected the CH₂ δ of 2-HMP the most raising it substantially from about 59-60 ppm to 65-66 ppm, indicating that the methylene group was substantially deshielded when its associated phenolic hydroxyl group was in the anionic form.

Table 4.1. Predicted ^{13}C chemical shifts of the phenolic residue for model compound reactions with phenyl isocyanate (ppm)

Experimental Probe		Reactant/Product				
Carbon	pH	Model	ϕ -OH	PU	BU	BPDU
C-1	Neutral	Phenol	158.5	151.3	---	---
		2-HMP	156.2	148.4	156.2	148.4
		4-HMP	157.4	150.2	157.4	150.2
	Alkaline	Phenol	168.1	---	---	---
		2-HMP	162.8	---	162.8	---
		4-HMP	166.2	---	166.2	---
C-2	Neutral	Phenol	115.9	121.6	---	---
		2-HMP	128.8	134.5	128.8	134.5
		4-HMP	116.1	121.8	116.1	121.8
	Alkaline	Phenol	120.5	---	---	---
		2-HMP	135.5	---	135.5	---
		4-HMP	119.5	---	119.5	---
C-3	Neutral	Phenol	130.1	129.1	---	---
		2-HMP	130.1	129.1	130.1	129.1
		4-HMP	129.7	128.7	129.7	128.7
	Alkaline	Phenol	130.6	---	---	---
		2-HMP	127.1	---	127.1	---
		4-HMP	127.1	---	127.1	---
C-4	Neutral	Phenol	121.3	125.5	---	---
		2-HMP	124.3	128.5	124.3	128.5
		4-HMP	133.8	138.0	128.7	132.9
	Alkaline	Phenol	115.1	---	---	---
		2-HMP	128.9	---	128.9	---
		4-HMP	141.2	---	136.1	---
C-5	Neutral	Phenol	130.1	129.1	---	---
		2-HMP	129.0	128.0	129.0	128
		4-HMP	129.7	128.7	129.7	128.7
	Alkaline	Phenol	130.6	---	---	---
		2-HMP	124.4	---	124.4	---
		4-HMP	127.1	---	127.1	---
C-6	Neutral	Phenol	115.9	121.6	---	---
		2-HMP	116.1	121.8	116.1	121.8
		4-HMP	116.1	121.8	116.1	121.8
	Alkaline	Phenol	120.5	---	---	---
		2-HMP	119.5	---	119.5	---
		4-HMP	119.5	---	119.5	---
CH_2	Neutral	Phenol	---	---	---	---
		2-HMP	59.9	60.1	59.4	59.6
		4-HMP	64.7	64.7	66.8	66.8
	Alkaline	Phenol	---	---	---	---
		2-HMP	64.7	---	65.6	---
		4-HMP	64.7	---	66.8	---

4.3.1.2. Predicted chemical shifts for the phenyl isocyanate residue

Table 4.2 presents the predicted chemical shifts for the reaction products of phenyl isocyanate with the phenolic model compounds under neutral and alkaline conditions. The aromatic ring numbering starts with the isocyanate substituted carbon as C-1, followed by the ortho, meta, and para positions as C-2, C-3, C-4 respectively. The last meta and ortho positions are C-5 and C-6 respectively. Neither the chemical environment, nor the model compound structure affected the predicted values, but only the ring position affected the chemical shift. The C-1 position is found at a higher δ of 138.9 ppm and may serve as a marker in a spectral region that does not have many other signals present.

Table 4.2. Predicted ^{13}C chemical shifts of the phenyl isocyanate residue for reactions with phenolic model compounds (ppm)

Experiment		Ring Carbon			
pH	Model	C-1	C-2,6	C-3,5	C-4
Neutral	Phenol	138.9	121.6	128.9	128.0
	2-HMP	138.9	121.6	128.9	128.0
	4-HMP	138.9	121.6	128.9	128.0
Alkaline	Phenol	138.9	121.6	128.9	128.0
	2-HMP	138.9	121.6	128.9	128.0
	4-HMP	138.9	121.6	128.9	128.0

4.3.1.3. Predicted chemical shifts for the urethane carbonyl carbon

Table 4.3 presents the predicted chemical shifts for the urethane carbonyl carbon of the reaction products of phenyl isocyanate with the phenolic model compounds under neutral and alkaline conditions. The most difference is between the benzyl and phenyl urethanes with predicted shifts of 153.8 ppm and 150.0 ppm respectively. The presence of the adjacent methylene group versus an adjacent oxygen results in lower electron density on the urethane carbonyl carbon, with resulting deshielding and a higher δ value.

Table 4.3. Predicted ^{13}C chemical shifts of the urethane carbonyl carbon for reactions of phenyl isocyanate with phenolic model compounds (ppm)

Experiment		Product	
pH	Model	BU	PU
Neutral	Phenol	---	150.0
	2-HMP	153.8	150.0
	4-HMP	153.8	150.0
Alkaline	Phenol	---	150.0
	2-HMP	153.8	150.0
	4-HMP	153.8	150.0

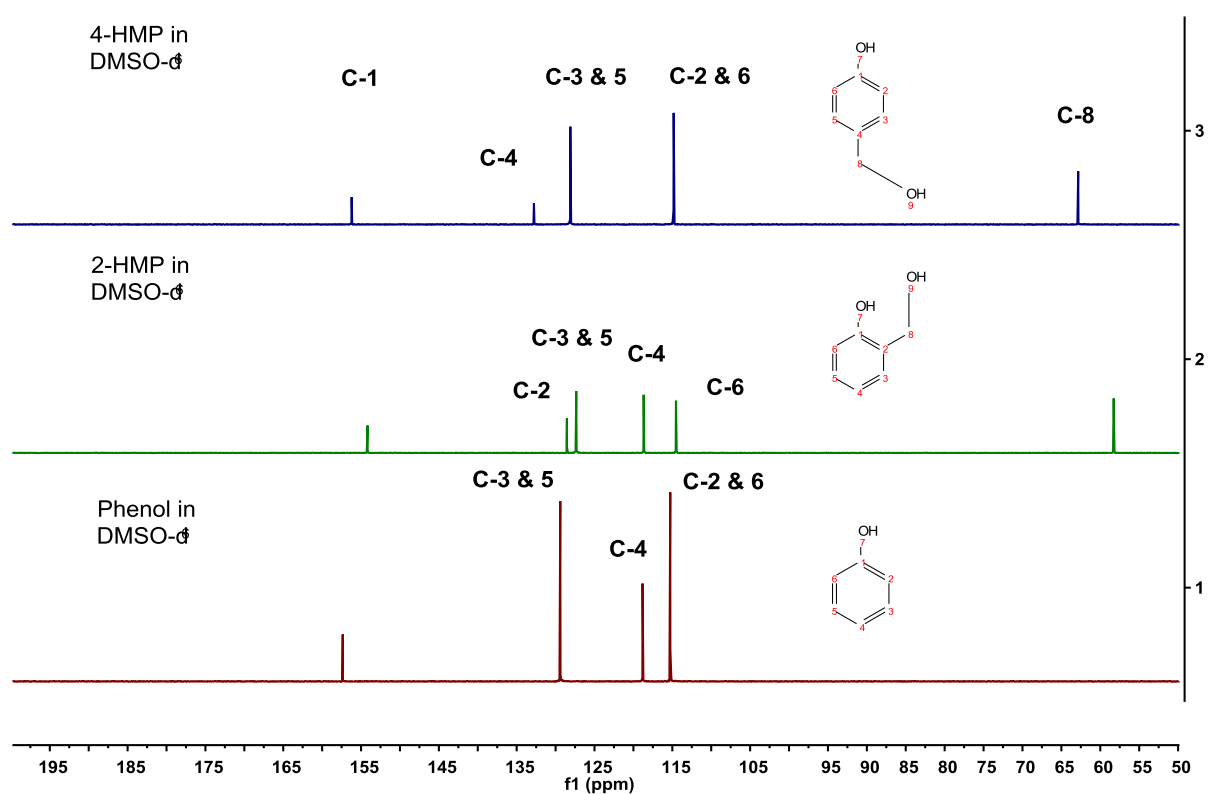


Figure 4.3. ^{13}C NMR chemical shifts for phenol, 2-HMP, and 4-HMP in DMSO-d_6

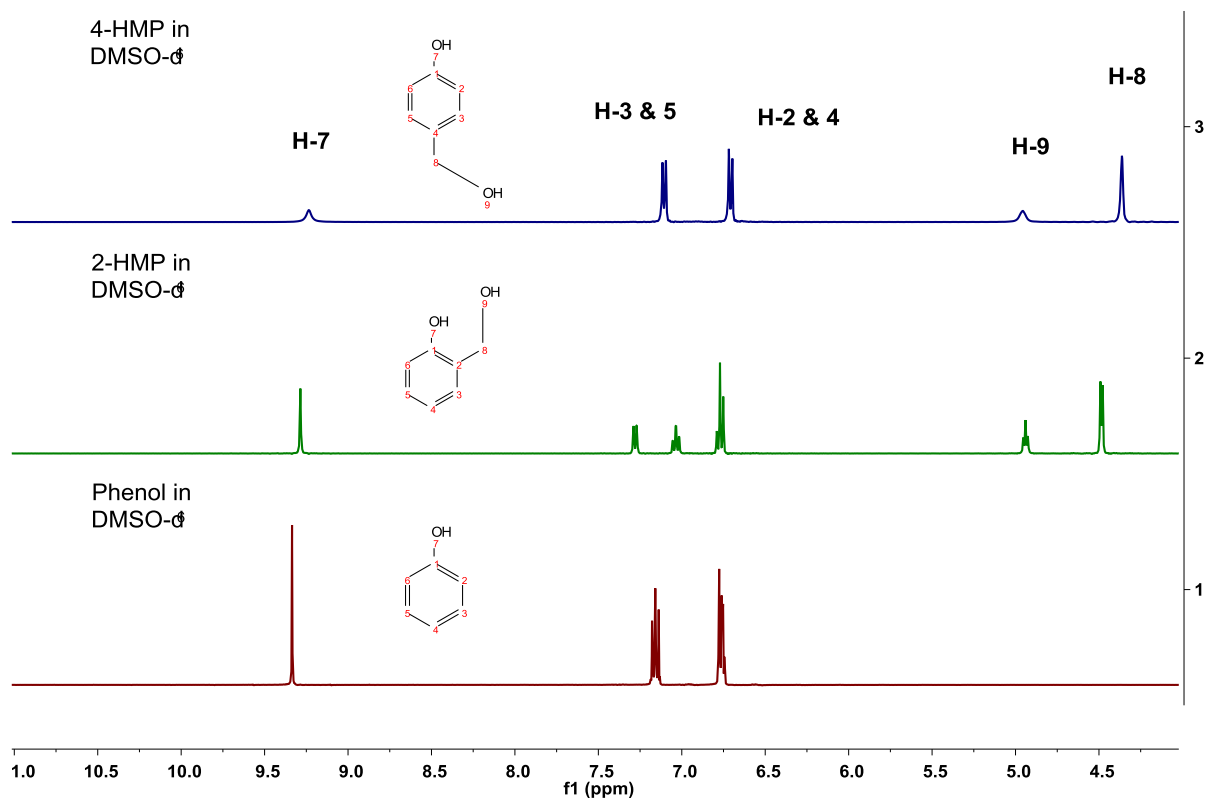


Figure 4.4. ^1H NMR chemical shifts for phenol, 2-HMP, and 4-HMP in DMSO-d_6

4.3.2. Reactions of model compounds in organic solvents

4.3.2.1. Model compound spectra in THF-d_8 and DMSO-d_6

The spectra of the base model compounds provided a reference set for the presence of unreacted material. Mapping the chemical shifts of these peaks aided in identification of specific structures of the reaction product peaks. Comparison of spectra based on phenol and benzyl alcohol also helped in identifying specific effects with 2-HMP and 4-HMP since these two models possessed both phenolic and benzylic hydroxyl groups. The ^{13}C NMR spectra of for phenyl isocyanate revealed unexpected peaks that were identified as 1,3-diphenyl urea (1,3-DPU), due to contact of the phenyl isocyanate with water and the carbamic acid reaction. The water reacted with the phenyl isocyanate to form carbamic acid, emitting carbon dioxide to form aniline, then reacting with another phenyl isocyanate to form the 1,3-DPU. Identification

of this 1,3-DPU proved important for interpretation of spectra based on reactions of phenyl isocyanate with HMP's in an aqueous, alkaline environment.

4.3.2.2. Reactions of model compounds without catalyst in THF-d₈

Reactions of the model compounds with phenyl isocyanate in THF-d₈ without catalyst resulted in the formation of insoluble precipitates. Therefore, the THF-d₈ was allowed to evaporate and the samples were dissolved in DMSO-d₆ for NMR. NMR identified the precipitate as 1,3-DPU by comparison with the spectra of its model compound in DMSO-d₆. The 2-HMP formed 83.5% PU, with about 4 to 6% of residual 2-HMP, BU, and BPDU. The 4-HMP was much less reactive, as would have been expected from the data shown in Table 3.6, forming 20.4% PU, with about 72.8% of residual 4-HMP, 6.7% of BU, and no BPDU. In both cases, PU products were more preferred than BU products. Figures 4.5 and 4.6 represent mechanisms for the formation of PU and BU respectively from phenyl isocyanate and 2-HMP. Tables 4.4 and 4.5 present the composition of the reaction products of phenyl isocyanate and 2-HMP or 4-HMP respectively without catalyst, based upon the relative ¹H integration values for the CH₂ group of the various reaction products.

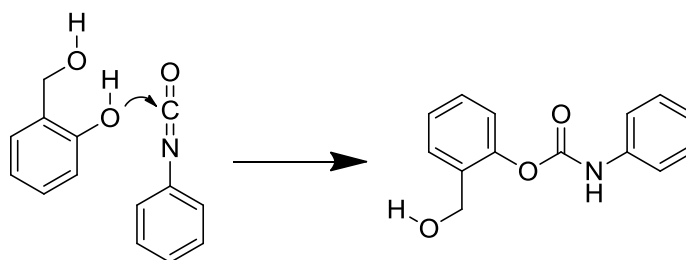


Figure 4.5. Reaction mechanism for formation of a phenyl urethane under neutral conditions

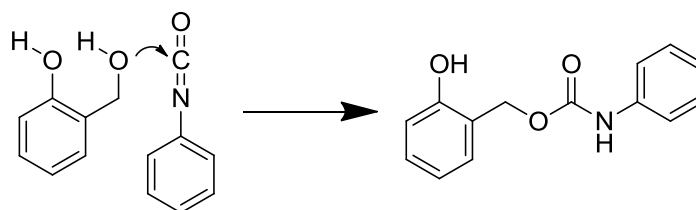


Figure 4.6. Reaction mechanism for formation of a benzyl urethane under neutral conditions

Table 4.4. Reactions of 2-HMP and phenyl isocyanate in THF-d₈ (no catalyst)

Compound	¹³ C (ppm)	¹ H (ppm)	¹ H integral	% comp.
2-HMP	64.86	4.51	0.12	5.5%
BU	67.09	5.12	0.14	6.4%
PU	64.44	4.55	1.82	83.5%
BPDU	66.49	5.19	0.10	4.6%

Table 4.5. Reactions of 4-HMP and phenyl isocyanate in THF-d₈ (no catalyst)

Compound	¹³ C (ppm)	¹ H (ppm)	¹ H integral	% comp.
4-HMP	64.91	4.36	10.9	72.8%
BU	67.09	5.01	1.01	6.7%
PU	64.44	4.51	3.06	20.4%
BPDU	66.48	NA	0.00	0.0%

4.3.2.3. Reactions of model compounds with phenyl isocyanate and TEA catalyst in THF-d₈

The reactants were noticeably warm to the touch when reacted with TEA, indicating a relatively fast, exothermic reaction. The 2-HMP formed 14.7% BU, with about 18.7% of residual 2-HMP, 48.7% PU, and 18.0% BPDU. The 4-HMP formed 3.0% BU, with about 13.0% of residual 4-HMP, 73.5% PU, and 10.4% BPDU. The TEA catalyst showed somewhat preferential direction towards the phenolic hydroxyl group, resulting in higher PU content although a BU pathway was evident. Between the 4-HMP and 2-HMP, the 4-HMP indicated a stronger preference for the PU pathway with its lower content on BU and BPDU. This may be a result of the catalytic mechanism of TEA coordinating with the phenolic hydroxyl group to form an amine-phenol

complex, as suggested by Farkas and Strohm.¹⁰ Another mechanism may be that TEA functions as a base, facilitating deprotonation of the phenolic hydroxyl to the strongly nucleophilic phenoxide anion that will readily attack the isocyanate carbon, forming phenyl urethane. Tables 4.6 and 4.7 present the composition of the reaction products of phenyl isocyanate and 2-HMP or 4-HMP respectively with TEA catalyst, based upon the relative ¹H integration values for the CH₂ group of the various reaction products, suggesting the importance of the catalyst for completing reactions of 4-HMP.

Table 4.6. Reactions of 2-HMP and phenyl isocyanate in THF-d₈ (TEA)

Compound	¹³ C (ppm)	¹ H (ppm)	¹ H integral	% comp.
2-HMP	62.05	4.74	15.9	18.7%
BU	63.87	5.24	12.47	14.7%
PU	59.92	4.69	41.38	48.7%
BPDU	62.91	5.27	15.28	18.0%

Table 4.7. Reactions of 4-HMP and phenyl isocyanate in THF-d₈ (TEA)

Compound	¹³ C (ppm)	¹ H (ppm)	¹ H integral	% comp.
4-HMP	64.91	4.49	4.83	13.0%
BU	67.09	5.06	1.11	3.0%
PU	64.44	4.6	27.25	73.5%
BPDU	66.48	5.16	3.86	10.4%

4.3.2.4. Reactions of model compounds with phenyl isocyanate and DBTL catalyst in THF-d₈

The reactants were noticeably warm, almost hot, to the touch when reacted with DBTL, indicating a relatively fast, exothermic reaction. The 2-HMP formed 83.1% BU, with about 0.8% of residual 2-HMP, no PU, and 16.1% BPDU. The 4-HMP formed 67.5% BU, with about 2.1% of

residual 4-HMP, no PU, and 30.4% BPDU. The DBTL catalyst clearly showed preferential direction towards the benzylic hydroxyl group, leaving no PU and minor residuals of HMP. This may be a result of the catalytic mechanism of DBTL coordinating and forming a ternary complex with the primary benzylic hydroxyl group and the phenyl isocyanate, as described by Reegen and Frisch.⁹ Tables 4.8 and 4.9 present the composition of the reaction products of phenyl isocyanate and 2-HMP or 4-HMP respectively with DBTL catalyst, based upon the relative ¹H integration values for the CH₂ group of the various reaction products.

Table 4.8. Reactions of 2-HMP and phenyl isocyanate in THF-d₈ (DBTL)

Compound	¹³ C (ppm)	¹ H (ppm)	¹ H integral	% comp.
2-HMP	61.97	4.68	0.01	0.8%
BU	63.87	5.27	1.03	83.1%
PU	59.92	4.69	0.00	0.0%
BPDU	63.00	5.29	0.20	16.1%

Table 4.9. Reactions of 4-HMP and phenyl isocyanate in THF-d₈ (DBTL)

Compound	¹³ C (ppm)	¹ H (ppm)	¹ H integral	% comp.
4-HMP	64.86	4.51	0.07	2.1%
BU	67.09	5.06	2.22	67.5%
PU	64.44	4.60	0.00	0.0%
BPDU	66.49	5.16	1.00	30.4%

The earlier research of Papa and Critchfield also found directing effects of the catalysts. They found that uncatalyzed reaction of 2-HMP with phenyl isocyanate yielded phenyl aniline and 1,3-diphenyl urea, while the reaction of 4-HMP with phenyl isocyanate resulted in BPDU. In the presence of TEA, however, both 2-HMP and 4-HMP yielded phenyl urethanes. When catalyzed by DBTL, 2- HMP gave an aniline reaction product, while 4- HMP produced BPDU.² One benefit

of the present research is that it has clearly demonstrated that the reaction products are either due to the three urethane formation reactions or due the formation of DPU. Table 4.10 provides an overview of the composition of the uncatalyzed and catalyzed reactions of 2-HMP and 4-HMP with phenyl isocyanate by ^1H NMR in THF-d_8 based upon the relative ^1H integration values for the CH_2 group of the various reaction products.

Table 4.10. Composition of catalyzed reactions of 2-HMP and 4-HMP with phenyl isocyanate by ^1H NMR in THF-d_8

Compound	2-HMP			4-HMP		
Catalyst	None	TEA	DBTL	None	TEA	DBTL
HMP	5.5%	18.7%	0.8%	72.8%	13.0%	2.1%
BU	6.4%	14.7%	83.1%	6.7%	3.0%	67.5%
PU	83.5%	48.7%	0.0%	20.4%	73.5%	0.0%
BPDU	4.6%	18.0%	16.1%	0.0%	10.4%	30.4%

4.3.3. Reactions of model compounds under alkaline conditions

4.3.3.1. NMR of phenolic model compounds in the presence of SnCl_2 and ND_4OD in CD_3OD

Table 4.11. ^{13}C NMR δ (ppm) for perturbation of phenol with SnCl_2 and ND_4OD in CD_3OD

SnCl_2	ND_4OD	C-1	C-3,5	C-2,6	C-4	Avg.
-	-	167.71	129.90	119.88	115.05	133.14
+	-	167.25	130.15	119.76	115.20	133.09
-	+	158.47	130.45	116.33	120.45	131.43
+	+	157.91	130.54	116.33	120.71	131.37
Avg.		162.84	130.26	118.08	117.85	

Understanding the effects of SnCl_2 and ND_4OD on the changes in chemical shifts ($\Delta = \delta_{(+)} - \delta_{(-)}$) would be important for interpretation of their effects in a reactive system with phenyl isocyanate. These changes were modeled by studying their effects on the ^{13}C chemical shifts of

phenol, 2-HMP, and 4-HMP in CD₃OD as a common solvent. ¹³C chemical shifts (δ) for perturbation with SnCl₂ and ND₄OD in CD₃OD of phenol, 2-HMP, and 4-HMP are presented in tables 4.11, 4.12, and 4.13 respectively.

Table 4.12. ¹³C NMR δ (ppm) for perturbation of 2-HMP
with SnCl₂ and ND₄OD in CD₃OD

SnCl ₂	ND ₄ OD	C-1	C-2	C-3	C-4	C-5	C-6	CH ₂	Avg.
-	-	166.79	130.16	129.02	120.31	129.41	114.69	64.05	122.06
+	-	166.18	130.03	129.05	120.16	129.57	114.76	63.13	121.84
-	+	156.14	128.53	129.31	120.32	129.42	116.07	61.11	120.13
+	+	155.96	128.24	129.51	120.60	129.64	116.23	60.89	120.15
Avg.		161.27	129.24	129.22	120.35	129.51	115.44	62.30	

Table 4.13. ¹³C NMR δ (ppm) for perturbation of 4-HMP
with SnCl₂ and ND₄OD in CD₃OD

SnCl ₂	ND ₄ OD	C-1	C-3,5	C-2,6	C-4	CH ₂	Avg.
-	-	167.81	130.07	119.28	127.36	65.91	122.09
+	-	167.52	130.25	119.64	127.10	65.63	122.03
-	+	158.09	129.86	116.21	133.29	65.08	120.51
+	+	157.36	130.01	116.25	133.23	64.80	120.33
Avg.		162.70	130.05	117.85	130.25	65.36	

For the perturbation of the phenolic model compounds by SnCl₂ and ND₄OD in CD₃OD, the average effect of each additive was to increase electron density. The factor effects for δ's of all positions were -0.05 to -0.12 ppm and -1.64 to -1.81 ppm for the addition of SnCl₂ and ND₄OD respectively. The C-1 carbon, due to its proximity to the anionic oxygen, was the strongest reporter of these trends. In the presence of SnCl₂, the average Δ values for C-1 were -0.51, -0.40, and -0.51 ppm respectively for phenol, 2-HMP, and 4-HMP. In the presence of ND₄OD, the

average Δ values for C-1 were -9.29, -10.42, and -9.96 ppm respectively for phenol, 2-HMP, and 4-HMP, indicating that the ammonium hydroxide had a much stronger additive effect to the electron density of the aromatic ring. For the CH_2 group, the SnCl_2 treatment resulted in average Δ of -0.57 and -0.28 ppm for 2-HMP and 4-HMP, while the ND_4OD treatment gave average Δ of -2.59 and -0.83 ppm for 2-HMP and 4-HMP, pointing towards a stronger effect for the 2-HMP. Interestingly, the change in electron density for the substituted 2 and 4 rings positions varied dramatically based on treatment with ND_4OD but not SnCl_2 . The SnCl_2 treatment resulted in average Δ values of -0.21 and -0.16 ppm for 2-HMP and 4-HMP, while the ND_4OD treatment gave average Δ values of -1.71 and 6.03 ppm for 2-HMP and 4-HMP. The significance of these results for the study of reactions products of phenyl isocyanate with phenolic model compounds is that the catalysts change the chemical shifts in the aqueous, alkaline environment in a way that will make spectral comparison and structural identification more difficult. The data results for changes of ^{13}C chemical shifts (Δ) due to perturbation with SnCl_2 and ND_4OD in CD_3OD of phenol, 2-HMP, and 4-HMP at the ring carbon positions are presented in tables 4.14, 4.15, and 4.16 respectively. Table 4.17 shows the effect of the presence of the SnCl_2 and ND_4OD catalysts on the average values of the ^{13}C NMR chemical shifts (δ , ppm) for all the carbons of phenol, 2-HMP, and 4-HMP.

Table 4.14. Changes in ^{13}C chemical shifts (Δ) for perturbation of phenol by SnCl_2 and ND_4OD in CD_3OD

Catalyst &		$\Delta = \delta_{(+)} - \delta_{(-)}$ (ppm)			
Level		C-1	C-3,5	C-2,6	C-4
SnCl_2	-	-0.46	0.25	-0.12	0.15
	+	-0.56	0.09	0.00	0.26
ND_4OD	-	-9.24	0.55	-3.55	5.40
	+	-9.34	0.39	-3.43	5.51

Table 4.15. Changes in ^{13}C chemical shifts (Δ) for perturbation of 2-HMP by SnCl_2 and ND_4OD in CD_3OD

Catalyst &		$\Delta = \delta_{(+)} - \delta_{(-)}$ (ppm)						
Level		C-1	C-2	C-3	C-4	C-5	C-6	CH_2
SnCl_2	-	-0.61	-0.13	0.03	-0.15	0.16	0.07	-0.92
	+	-0.18	-0.29	0.20	0.28	0.22	0.16	-0.22
ND_4OD	-	-10.65	-1.63	0.29	0.01	0.01	1.38	-2.94
	+	-10.22	-1.79	0.46	0.44	0.07	1.47	-2.24

Table 4.16. Changes in ^{13}C chemical shifts (Δ) for perturbation of 4-HMP by SnCl_2 and ND_4OD in CD_3OD

Catalyst &		$\Delta = \delta_{(+)} - \delta_{(-)}$ (ppm)				
Level		C-1	C-3,5	C-2,6	C-4	CH_2
SnCl_2	-	-0.29	0.18	0.36	-0.26	-0.28
	+	-0.73	0.15	0.04	-0.06	-0.28
ND_4OD	-	-9.72	-0.21	-3.07	5.93	-0.83
	+	-10.16	-0.24	-3.39	6.13	-0.83

Table 4.17. Average ^{13}C NMR δ all carbon for catalysts (ppm)

Catalyst	Level	Phenol	2-HMP	4-HMP
SnCl_2	-	132.28	121.10	121.30
	+	132.23	121.00	121.18
ND_4OD	-	133.11	121.95	122.06
	+	131.40	120.14	120.42

4.3.3.2. Reactions of phenolic model compounds with phenyl isocyanate under neutral or alkaline conditions with SnCl_2 and ND_4OD catalyst in DMSO-d_6

The 2-HMP was more reactive with phenyl isocyanate than 4-HMP as it had less residual HMP present under comparable treatments. Whenever moisture was present in the form of D_2O , the formation of 1,3-DPU was evident, indicating that the carbamic acid reaction effectively competed with the urethane formation reactions. Phenyl urethane formed under all conditions: neutral or alkaline, uncatalyzed or catalyzed, for 2-HMP or 4-HMP, while benzyl urethane formed almost exclusively for 2-HMP only. 2-HMP formed 1 to 5% BDPU, while 4-HMP formed 0 to less than 1% BDPU. These initial indications did not show any substantial reaction preference by the SnCl_2 and ND_4OD catalysts, indicating the substitution pattern and alkalinity had the greatest effect on reaction product composition. The lack of directing effect by the catalysts was in contradistinction to the directing effects of DBTL and TEA earlier observed in neutral, organic systems.

For 2-HMP, the 1.0 level of NaOD:P favored PU formation over BU, while conversely the 0.0 level of NaOD:P favored, BU formation over PU, especially without catalyst. For 4-HMP, no BU formed, while modest levels of PU formed (5 to 10%). The picture that emerges is of an unreactive 4-hydroxymethyl group when compared to the 2-hydroxymethyl group in the aqueous environment, reacting mostly at the phenolic hydroxyl group, similar to the organic system. Since little to no BU or BDPU formed with 4-HMP, while both formed readily with 2-HMP, some mechanism must be present to enhance the reactivity of the 2-hydroxymethyl group. One plausible mechanism could involve the 2-hydroxymethyl group forming a resonance stabilizing hydrogen bond with the phenolic oxygen under either condition (Figure 4.6), leading to a higher electron density on the 2-hydroxymethyl oxygen and carbon, enhancing its attractiveness to the electrophilic isocyanate carbon. Likewise, the phenolic oxygen 2-HMP should be more electron rich than the 4-HMP as indicated by the predicted and experimental ^{13}C NMR chemical shifts for their respective C-1 carbons. Whether neutral or anionic, the higher electron density of the 2-HMP phenolic oxygen should make it a stronger nucleophile than that of the 4-HMP, favoring its comparative reactivity towards phenyl isocyanate (see Figure 4.7). The high levels of BU formed under neutral conditions are readily

related to the higher electron density also found on the methylene carbon of 2-HMP as shown by the predicted and measured ^{13}C NMR chemical shifts for neutral versus alkaline conditions. The higher electron density of the 2-HMP hydroxymethyl carbon and oxygen should reduce the activation energy of its reaction with phenyl isocyanate as compared to the alkaline condition and the 4-HMP. The clear significance of these reactions is that hydroxymethyl substitution position and alkalinity will determine the reaction product composition. Table 4.18 shows the ^1H NMR results for the composition of uncatalyzed or SnCl_2 and ND_4OD catalyzed reactions of 2-HMP and 4-HMP with phenyl isocyanate in DMSO-d_6 under neutral or alkaline conditions, with considerable differences to Table 4.10.

Table 4.18. Composition of catalyzed reactions of 2-HMP and 4-HMP by ^1H NMR with phenyl isocyanate in DMSO-d_6

Compound	2-HMP					4-HMP		
NaOD:P	0.0	0.0	1.0	1.0	0.0	0.0	1.0	1.0
ND_4OD	-	+	-	+	-	+	-	+
SnCl_2	-	+	-	+	-	+	-	+
HMP	52.1%	69.0%	64.7%	56.0%	94.8%	91.6%	89.9%	93.7%
BU	42.4%	26.0%	12.6%	13.4%	0.0%	1.3%	0.0%	0.0%
PU	3.7%	3.8%	20.1%	26.0%	5.2%	7.1%	9.6%	6.3%
BPDU	1.8%	1.2%	2.6%	4.6%	0.0%	0.0%	0.6%	0.0%

Haider et al. observed that refluxing phenyl isocyanate with phenol, benzyl alcohol, or 4-HMP in dioxane at 100 °C without catalyst produced DPU in 95 to 100% yield. Only the reaction with benzyl alcohol produced 5% BU. Clearly their materials must have absorbed atmospheric moisture leading to the carbamic acid reaction and formation of DPU. At 25 °C, uncatalyzed reactions of phenol, benzyl alcohol, and 4-HMP with phenyl isocyanate yielded 66% PU, 5% BU, and 52% PU respectively. In each case the remainder was DPU. In the presence of sodium hydroxide at 100 °C, the reaction of phenyl isocyanate with phenol gave 72% PU while benzyl alcohol gave 62% BU, with the remainder DPU in both cases. Under the same conditions, 4-HMP yielded only 8% BU, no PU, and 53% DPU.⁵ The latter results indicated that the 4-HMP

had a directing effect towards BU, which was not seen in the present research. Here, the reaction of 4-HMP with phenyl isocyanate in an uncatalyzed alkaline environment at ambient temperature resulted in 89.9% 4-HMP, 9.6% PU and 0.6% BPDU as indicated by the ^1H and ^{13}C NMR results in Table 4.18. Temperature may have played an important role in these reactions, as the results of Haider et al. at 100 °C differed from these findings at 23 to 25 °C.

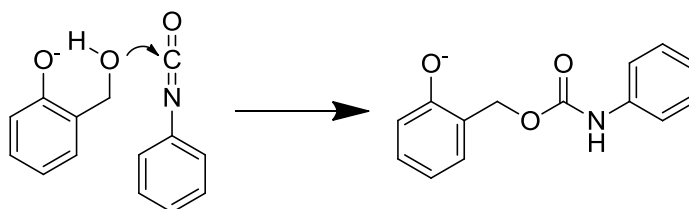


Figure 4.7. Reaction mechanism for formation of a benzyl urethane under alkaline conditions

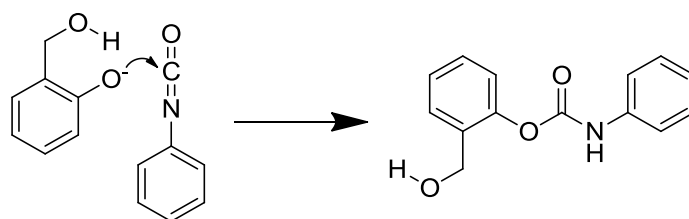


Figure 4.8. Reaction mechanism for formation of a phenyl urethane under alkaline conditions

4.4. Conclusions

- The ^{13}C NMR peaks have been identified for residual reactants of phenolic model compounds with phenyl isocyanate.
- Reactions of phenyl isocyanate with the phenolic model compounds phenol, benzyl alcohol, 2-HMP, and 4-HMP in THF- d_8 under neutral conditions without catalyst were relatively slow. The result was residual monomer and the precipitation of 1,3-diphenyl urea due to the carbamic acid reaction of phenyl isocyanate with water, likely of atmospheric origin. The reactions needed to be conducted in DMSO- d_6 to keep the 1,3-

DPU dissolved. The DMSO- d_6 had a net shielding effect on the chemical shifts of the respective carbon peaks when compared to THF- d_8 .

- The reaction of phenyl isocyanate with the phenolic model compounds phenol, 2-HMP, and 4-HMP favors the formation of phenyl urethanes with TEA catalyst, likely due to the formation of nucleophilic phenoxide anion.
- The reaction of phenyl isocyanate with the phenolic model compounds benzyl alcohol, 2-HMP, and 4-HMP favors the formation of benzyl urethanes with DBTL catalyst.
- All the catalyzed reactions occurred much faster than those in the uncatalyzed system as noted by the generation of heat and the lack of 1,3-DPU as an impurity, indicating that the phenyl isocyanate was consumed.
- Reactions of 2-HMP, and 4-HMP with phenyl isocyanate resulted in formation of benzyl urethanes (BU), phenyl urethanes (PU), and benzyl phenyl diurethanes (BDPU) compounds. DBTL catalysts favored formation of BDPU strictly by the benzyl pathway, while TEA favored formation of BDPU mostly by the PU pathway, although some BU was present.

Several differences occurred under (aqueous) alkaline conditions.

- 2-HMP had less residual monomer than 4-HMP, implying that 2-HMP was more reactive.
- For 2-HMP, alkaline conditions favored PU formation over BU formation. Neutral conditions favored BU formation over PU formation, especially when no catalyst was present.
- For 4-HMP, however, under neutral conditions when no catalyst was present, no BU and only modest amounts of PU formed. Small amounts of BDPU formed with 2-HMP, but essentially none formed with 4-HMP.

Intramolecular hydrogen bonding of the 2-HMP is proposed to contribute to resonance stabilization, enhancing its reactivity and thus urethane formation. Higher reactivity of the 2-hydroxymethyl group towards isocyanates would be beneficial in reactions of PF resins with pMDI, as alkaline PF resins contain high proportions of 2- and 6-hydroxymethyl functional groups. Benzyl urethane formation of PF resins in wood composites would also be beneficial,

as the hydroxymethyl groups would be conserved during polymerization instead of being lost as formaldehyde due to condensation.

4.5. References

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Chapter 5: FTIR of the Urethane Forming Reactions of PF and pMDI Model Compounds

5.0. Overview

The objective of this investigation was to understand the FTIR spectra of polyurethane and polyurea structures that could form during the cross-catalyzed polymerization reactions of PF and pMDI by employing ATR-FTIR techniques. Acquisition of spectra for model compounds provided reference baselines for studies of their real time reactions. The carbamic acid side reaction of pMDI and water was researched to identify specific peaks associated with it. Real time reactions of phenol or benzyl alcohol with pMDI in the presence of DBTL or TEA catalysts were investigated to provide spectral data regarding phenyl and benzyl urethane structures. Reaction products of phenyl isocyanate and phenolic model compounds in THF-d₆ were studied to confirm these product structures and correlate them with the reaction product composition results for the NMR studies of Chapter 4. The results will provide a basis for interpreting the complex product structures for the cross-catalyzed reactions of PF and pMDI.

5.1. Introduction

Vibrational spectroscopy is useful for identifying the functional groups in polymer structures. The covalently bonded atoms in every molecule may be described by characteristic vibration modes. These vibrations occur at frequencies that may be modeled as simple harmonic oscillators and thus may be predicted from known atomic weights and bond strength force constants. Since multiple vibration modes, such as bending, stretching, and wagging are possible for the same functional groups, multiple absorption peaks occur, and functional group identity confirmation is possible from other spectral regions. Infrared and Raman spectroscopy are the important vibrational spectroscopy methods. Infrared methods quantify the absorption of infrared radiation, while Raman techniques measure the inelastic scattering of monochromatic light.¹

Phenol-formaldehyde and polyurethane condensation reactions have been studied by Vibrational spectroscopy. In-line FTIR spectroscopy has been used to follow the formation of hydroxymethyl phenols, PF prepolymers, and phenol-urea-formaldehyde resins,²⁻⁴ and has also

been applied to predict PF characteristics.⁵ Raman spectroscopy has also been used for in-line study the course of PF polymerization⁶ and for correlation with solid state ¹³C NMR of novolac resins.⁷ Raman spectroscopy was used to investigate polyurethane condensation kinetics.⁸

The reactions of PF and pMDI model compounds have seen some study by vibrational spectroscopy. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) with a fiber-optic cable was used to observe the in-situ urethane formation reaction of phenyl isocyanate and phenol in chloroform in the presence of AlCl₃ catalyst.⁹ IR spectroscopy was used to confirm the co-reaction of PF and pMDI to form a co-polymer as part of a model compound study.¹⁰ The structures of the reaction products of phenyl isocyanate and phenolic model compounds were confirmed by ¹H NMR and IR spectroscopy.¹¹ Reactions of 4-HMP and 4,4'-MDI dissolved in THF in the presence of DBTL, TEA, or morpholine catalyst were monitored with IR spectroscopy,¹² and the reaction products of 4,4'-MDI with substituted phenols in THF were identified by IR spectroscopy.¹³

The cross-catalyzed PF-pMDI system has several other side-reactions associated with it such as alkaline hydrolysis of the PF accelerator and the carbamic acid reaction in addition to PF methylene bridge and urethane formation. Although some of these reactions have been studied by other techniques such as NMR, HPLC, and even FTIR,¹⁰⁻¹⁶ as a whole they have not been investigated under dynamic conditions using ATR-FTIR. Thus, the objective of this study was to build a comprehensive overview of the dynamic reactions of the cross-catalyzed PF-pMDI system using ATR-FTIR. This goal was accomplished by employing ATR-FTIR for structural determination of the reaction products of the model compounds, PF, and pMDI oligomers under dynamic conditions. The ATR method permitted the study of two important side reactions: the carbamic acid reaction and alkylene carbonate hydrolysis; and three step polymerization reactions: PF methylene bridge formation as well as urethane formation at phenolic and benzylic hydroxyl groups. The experimental strategy was to first acquire spectra of the model compounds of the system components, then to understand their reactions and

identify important peaks associated with reactions before applying these insights to the cross-catalyzed systems.

5.2. Experimental

5.2.1. Materials

5.2.1.1. Model compounds

Samples of the model compounds phenol (>99%), benzyl alcohol (>99.8%), 2-hydroxymethyl phenol (99%), 4-hydroxymethyl phenol (99%), phenyl isocyanate (Fluka, > 99.0%), 4,4'-Methylenebis(phenyl isocyanate) (4,4'-MDI, 98%), and 1,3-diphenyl urea (>99%) were purchased from Sigma-Aldrich. The model compounds were used as received.

5.2.1.2. pMDI

Rubinate 1245, a low viscosity pMDI, was supplied by Huntsman Polyurethanes. Rubinate 1245 had a specified isocyanate functionality of 2.22, an isocyanate content of 32.8%, and an equivalent weight of 128 g/mol. Its specified specific gravity was 1.23 at 25 °C, and its nominal viscosity was 25 mPa·s at 25 °C.¹⁷ The pMDI was used as received and stored under a dry nitrogen blanket.

5.2.1.3. Catalysts

The catalysts used in this study were dibutyltin dilaurate (95%) and triethylamine ($\geq 99\%$). All catalysts were from Sigma-Aldrich and were used as received.

5.2.1.4. Solvents

The solvents used in these experiments were deionized (DI) water was used, chloroform (CHCl_3), and tetrahydrofuran (THF).

5.2.2. ATR-FTIR technique

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was performed using a Nicolet 8700 spectrometer equipped with a Pike Technologies Gladiator ATR accessory.

The ATR had a diamond crystal with dimensions of 2.2 x 3.0 mm. Absorbance was measured between 4000 and 500 cm^{-1} , using 32 scans at 4 cm^{-1} resolution unless otherwise specified, and ATR correction.

For neat liquids such as benzyl alcohol, or samples in aqueous solution, a droplet of the liquid was placed on the surface of the ATR diamond crystal and covered with either an inverted watch glass or a covered solvated sample holder to prevent evaporation and contamination. Samples in organic solvents such as CHCl_3 or THF were placed in intimate contact with the ATR crystal by an evaporative deposition technique. A droplet of the solution was dispensed onto the ATR crystal from a glass pipette or a 1.0 mL microliter syringe. The solvent was permitted to evaporate until a film of the sample formed on the ATR crystal and FTIR data acquisition was begun.

5.2.3. ATR-FTIR experiments

The ATR-FTIR experiments were run qualitatively to provide information on the types of structures produced due to reaction. The inability to precisely quantify the amount of material deposited and the possibly incomplete nature of micro-mixing on the ATR diamond crystal made quantitative experimentation extremely difficult to perform.

5.2.3.1. Carbamic acid side-reaction

The carbamic acid side-reaction was induced by mixing a droplet of the pMDI with a droplet of DI water on the ATR crystal under an inverted watch glass. Successive spectra were taken over time at ambient temperature (22 to 25 $^{\circ}\text{C}$) after a background spectrum was acquired.

5.2.3.2. Acquisition of the model compound baseline spectra

Baseline spectra for the model compounds phenol, benzyl alcohol, 2-HMP, 4-HMP, 4,4'-MDI, and 1,3-DPU were acquired with by ATR-FTIR with the Nicolet 8700 spectrometer. Background spectra were also acquired for the catalysts DBTL and TEA and for the solvents DI water, CHCl_3 , THF, and DMSO. Phenol, benzyl alcohol, 2-HMP, 4-HMP were prepared by evaporative deposition from THF. The benzyl alcohol, pMDI, solvents, and catalysts were applied as neat

liquids. The 4,4'-MDI was prepared by evaporative deposition from CHCl_3 . The 1,3-DPU was dissolved in CHCl_3 and prepared for data acquisition by evaporative deposition.

5.2.3.3. Real time reactions of PF model compounds with pMDI

The model compounds phenol and benzyl alcohol were reacted with the pMDI in THF using DBTL or TEA as the catalyst. The model compounds and catalysts were pre-dissolved in THF prior to mixing as μL -droplets on the ATR diamond crystal. Successive spectra were taken over time at ambient temperature (22 to 25 °C) after a background spectrum was acquired.

5.2.3.4. Reactions products of PF model compounds with phenyl isocyanate in THF- d_6

Droplets of the reaction product solutions of section 4.2.2.3., "Catalyzed reactions of model compounds", were deposited on the surface of the ATR diamond crystal and the THF- d_6 was permitted to evaporate. Risk of hazardous peroxide formation on the plate was considered very low as the quantity of material was small and the phenolic model compounds could also act as stabilizers for the THF- d_6 . The solvent was allowed to evaporate until an opaque film formed on the ATR crystal and FTIR data acquisition was initiated.

5.3. Results and discussion

Results are presented for ATR-FTIR spectroscopy of the carbamic acid side reaction, baseline spectra of the model compounds, spectra of the reaction products of the model compounds with phenyl isocyanate, and catalyzed reactions of pMDI with the model compounds in THF. The discussion reflects on the potential significance of the carbamic acid reaction to the cross catalyzed PF-pMDI system. It also considers the catalyst directing effects on the reaction products generated by the reactions of the model compounds with phenyl isocyanate or pMDI.

5.3.1. Carbamic acid side reaction

When pMDI and water come in contact, they react to form carbamic acid, with subsequent release of carbon dioxide and formation of an aryl amine as shown in Figure 5.1. The aryl amine then reacts with other isocyanate groups to form a urea.

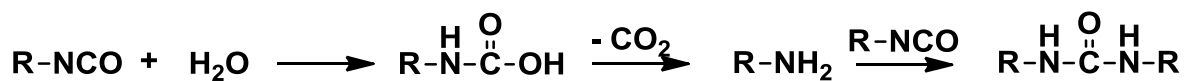


Figure 5.1. The carbamic acid reaction pathway to urea formation

ATR-FTIR spectra of deionized water and pMDI are shown in figure 5.2. Isocyanates with functionality value greater than two form polyureas.

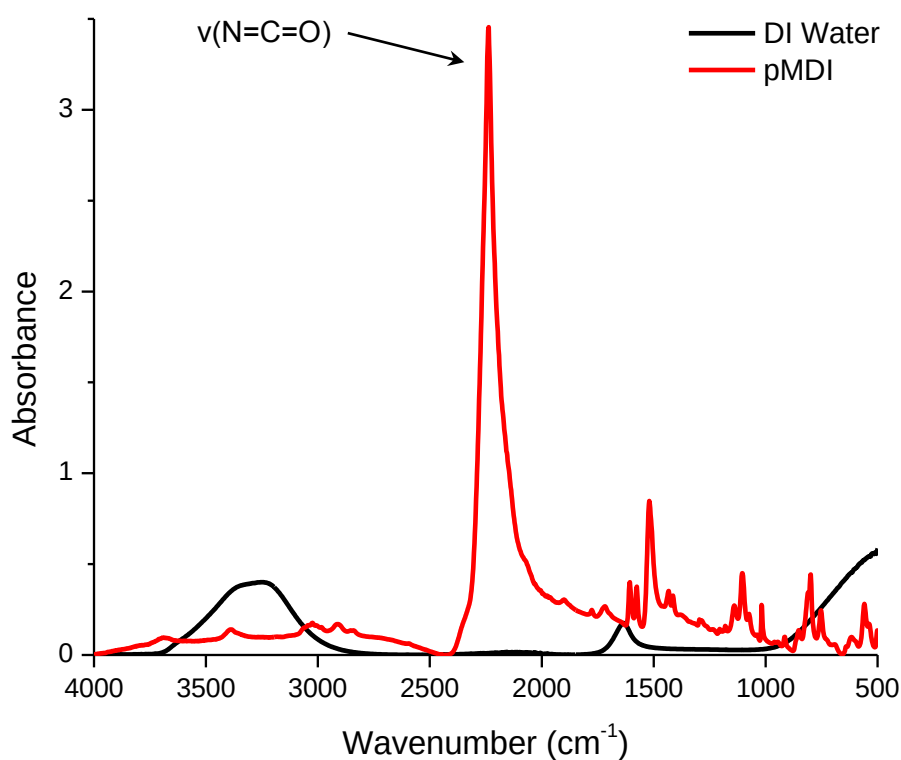


Figure 5.2. ATR-FTIR spectra of the carbamic acid reactants: pMDI ($f = 2.22$) and water

The ATR-FTIR spectra in Figure 5.3 show the reaction progress of pMDI with water over approximately 40 minutes at ambient temperature. The spectra indicate that new peaks form at 1638, 1596, 1555, 1307, 1231, 1204, and 1017 cm^{-1} . Important aryl urea peak regions have been identified in the reference literature: ν_s (NH) (3360-3320 cm^{-1}), solid phase amide I ν_s (C=O) (1670-1615 cm^{-1}), amide II band δ (NH) (1605-1515 cm^{-1}), ν_{as} (N-C-N) (1360-1300 cm^{-1}) and ν_s (N-C-N) (1190-1140 cm^{-1}).^{9,18} These regions correspond with the following polyurea

peaks that would be expected to form during the carbamic acid reaction: 1638 cm^{-1} amide I ν_s (C=O), 1596 cm^{-1} and 1555 cm^{-1} amide II band δ (NH), 1307 cm^{-1} ν_{as} (N-C-N), and 1231 cm^{-1} or 1204 cm^{-1} may possibly represent ν_s (N-C-N). The identity of the peak at 1017 cm^{-1} is uncertain. The strongest spectral peak for carbon dioxide from the reaction at 2345 cm^{-1} is not apparent as it is either masked by the ν_s (N=C=O) peak or is not present due to off-gassing. The ν_s (N=C=O) peak remained strong after 40 minutes reaction time, indicating that little had been consumed, with relatively slow reactivity. This observation is consistent with the data provided in Table 2.9.¹⁹

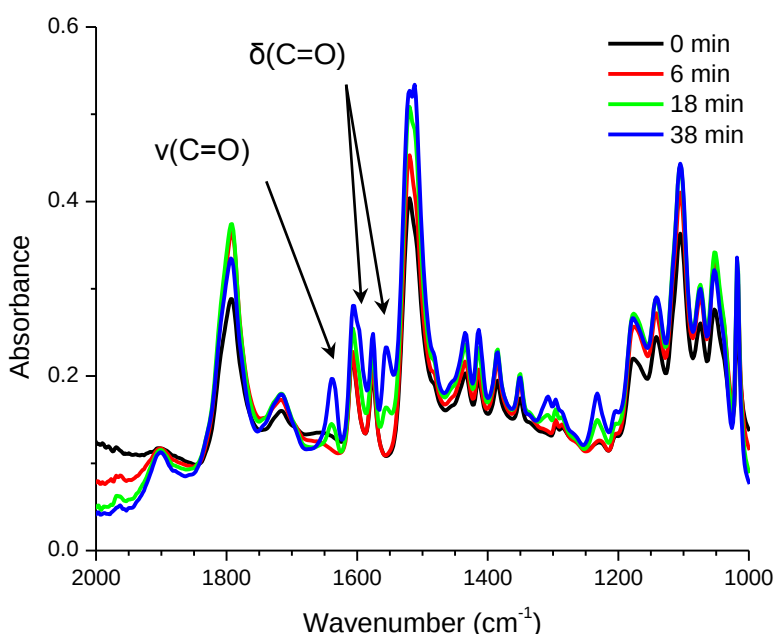


Figure 5.3. ATR-FTIR spectra from 2000 to 1000 cm^{-1} of carbamic acid reaction for pMDI and water with subsequent polyurea formation over about 40 minutes at ambient temperature

The ATR-FTIR spectra of 1,3-DPU, a diaryl urea model compound, is given in Figure 5.4. Key peaks are assigned as follows: 1645 cm^{-1} amide I C=O stretching, 1595 cm^{-1} and 1557 cm^{-1} amide II band NH deformation, 1315 cm^{-1} asymmetrical N-C-N stretching, and 1156 cm^{-1} for symmetrical N-C-N stretching. These peaks are very close to the peaks generated by the reaction of the pMDI with the DI water, suggesting that the carbamic acid reaction has occurred, with resulting polyurea formation.

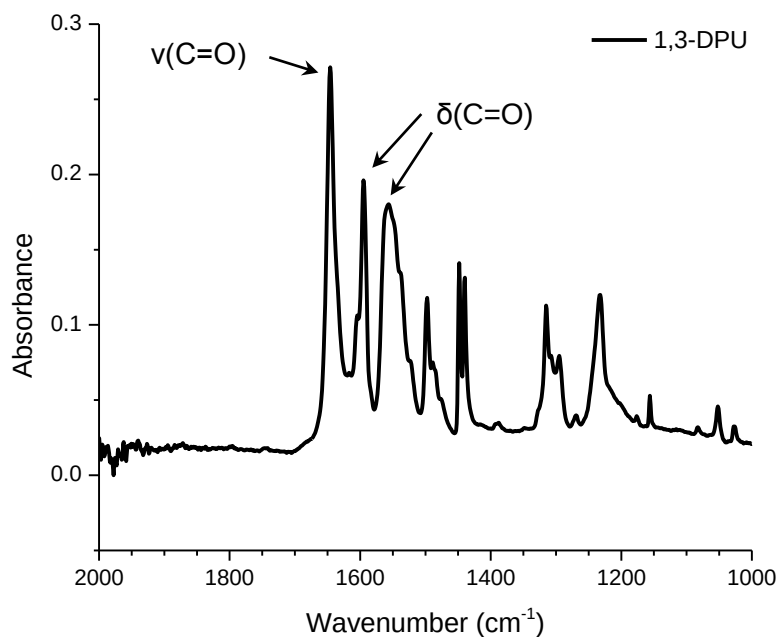


Figure 5.4. ATR-FTIR Spectrum of 1,3-diphenylurea prepared by evaporative deposition from CHCl₃ between 2000 and 1000 cm⁻¹ (1024 scans)

Taken together, the spectral data for the 1,3-DPU supports the conclusion that the reaction of the pMDI and DI water has formed a urea due to the carbamic acid reaction. These spectral peaks should prove useful for identifying the presence or absence of the carbamic acid reaction in the cross-catalyzed reactions of PF and pMDI.

5.3.2. Urethane forming reactions of model compound by ATR-FTIR

Copolymerization reactions of the monomers and oligomers of PF and pMDI isocyanates can occur at either the phenolic hydroxyl or benzylic hydroxymethyl groups. The impact of structural selectivity for either phenyl or benzyl urethanes would mean that copolymer formation would result in different thermal stabilities.²⁰ Based on the thermal dissociation temperatures of polyurethane linkages found in Table 2.12 of section 2.2.6, the mechanical performance of the copolymer could be compromised.

Thus, understanding the ATR-FTIR spectral peaks of each of these reaction types will be important for interpreting the spectra of the more complex cross-catalyzed PF-pMDI system.

This study focuses on acquiring baseline spectra for the model compounds, the products of their reactions with phenyl isocyanate, and their dynamic reactions with oligomeric pMDI.

5.3.2.1. Model compound baseline spectra

The ATR-FTIR spectra of the model compounds phenol, benzyl alcohol, 2-HMP, and 4-HMP were acquired at ambient temperature and are shown in Figure 5.5. The ATR-FTIR spectra of the oligomeric pMDI ($f = 2.22$) at ambient temperature and the spectrum of 4,4'-MDI in CHCl_3 is shown in Figure 5.6. Spectra of the catalysts DBTL and TEA were also acquired to determine their potential contributions to the dynamic reaction spectra. The ATR-FTIR spectra of the catalysts DBTL and TEA at ambient temperature are shown in Figure 5.7.

5.3.2.1.1. Results for phenolic model compound baselines

The most important FTIR vibrational bands for the phenolic model compounds involved in urethane formation reactions would be those structural features most directly associated with the hydroxyl functional groups involving either the O-H bonds or the adjacent C-O bonds. Table 5.1 provides an overview of expected vibrational modes of benzene, phenol, and benzyl alcohol, and based on the reference literature.^{1,21} The vibrational mode peak values are for 2-HMP from this study.

Table 5.1. Infrared vibrational modes of phenolic model compounds (cm^{-1})

Vibrational mode	Benzene ²¹	Phenol – melt ¹	Benzyl alcohol ¹	2-HMP
ν O-H	---	3244	3329	3252, 3167
ν C-H (aromatic)	3100-3000	3052	3100-3000	3100-3000
ν C-H (methylene)	---	---	2940-2860	2957, 2875
ν C=C	1500	1601, 1501, 1478	1501, 1455	1610-1596, 1504, 1457
δ C-H bending in plane	1000	999 ³	1007 ³	1002
δ CH ₂ scissoring (bending)	---	---	1471	1482
δ C-H bending out of plane	675	815, 753	745	775, 749, 733
δ O-H bending in plane	---	1378	1368 ³	1365
δ C=C bend	---	699	707	713
δ O-H bending out of plane	---	650	1209	1217, 667
ν C-O (Aryl alcohol)	---	1231	---	1244
ν C-O (1° alcohol)	---	---	1023	1049

The important vibrational modes typically encountered are $\nu(\text{O-H})$ (3330 to 3170 cm^{-1}), $\delta(\text{O-H})$ in plane bending (1378 to 1365 cm^{-1}), $\delta(\text{O-H})$ out of plane bending (667 to 650 cm^{-1} for aryl alcohols, 1217 to 1209 cm^{-1} for benzylic alcohols), $\nu(\text{C-O})$ (1244 to 1231 cm^{-1} for aryl alcohols and 1049 to 1023 for primary alcohols). Peaks based on these vibrational modes would be expected to decrease and or shift due to urethane formation reactions with isocyanates. For phenol, benzyl alcohol, 2-HMP, and 4-HMP, the O-H stretching peaks were centered at 3337 , 3292 , $3418/3251$, $3377/3321\text{ cm}^{-1}$ respectively. The differences in the FTIR spectra of 2-HMP and 4-HMP at high wavenumbers can be attributed to the intramolecular hydrogen bonding of 2-HMP. The 4-HMP, with a structure constrained by the planar aromatic ring, would be limited to intermolecular hydrogen bonding. The significance for interpretation was that the phenolic hydroxyl appeared at higher wavenumbers, while the benzylic hydroxyl appeared at lower wavenumbers. The FTIR spectra for these four model compounds are shown in Figure 5.5.

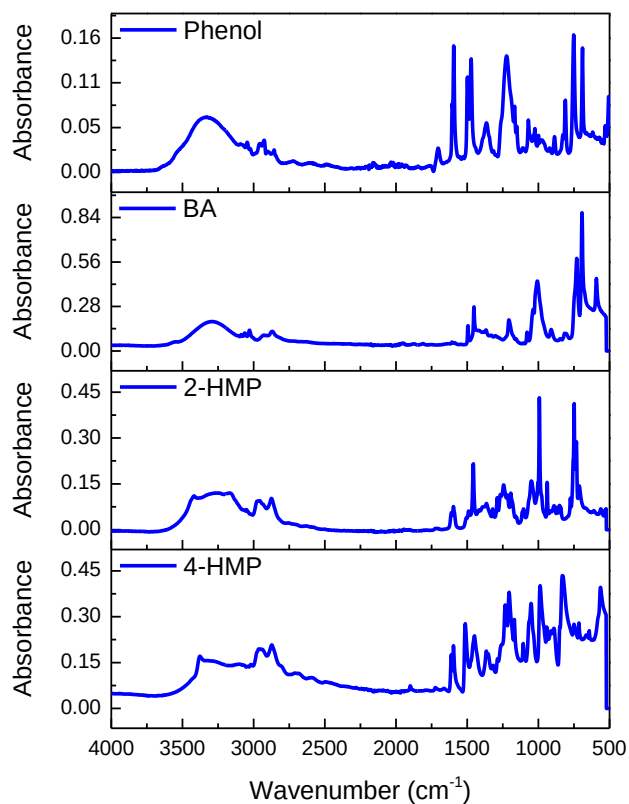


Figure 5.5. ATR-FTIR spectra of phenol, benzyl alcohol, 2-HMP, and 4-HMP

5.3.2.1.2. Results for isocyanate model compound baselines

The spectrum for 4,4'-MDI in CHCl_3 gave a $\nu(\text{N}=\text{C}=\text{O})$ peak at 2250 cm^{-1} while the spectrum for pMDI ($f = 2.22$) gave a $\nu(\text{N}=\text{C}=\text{O})$ peak at 2238 cm^{-1} . This slight difference of 12 cm^{-1} may be due to the presence of 2,4'-MDI and other oligomers in the pMDI. The isocyanate model spectra are shown in Figure 5.6.

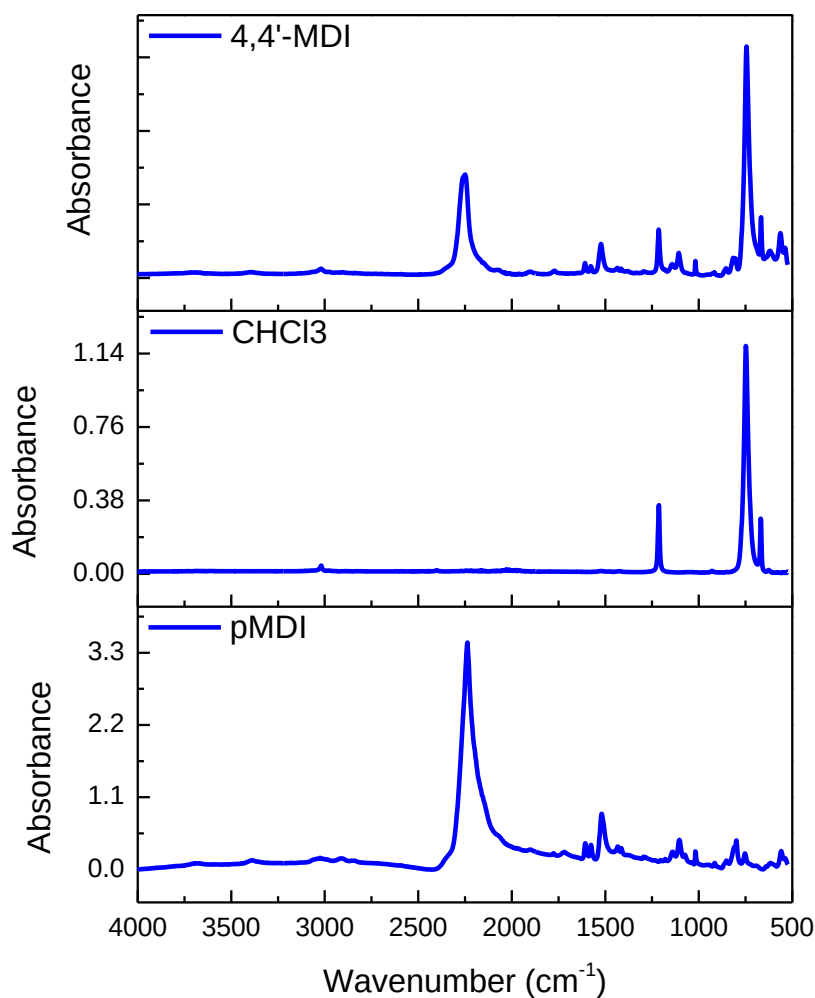


Figure 5.6. ATR-FTIR spectra of the isocyanate model compounds 4,4'-MDI and pMDI ($f = 2.22$) with CHCl_3 solvent used for 4,4'-MDI

5.3.2.1.3. Results for catalyst baselines

The spectra for DBTL and TEA exhibit many of the characteristic peaks of compounds containing alkyl hydrocarbon chains (i.e. stretching at 3000-2750 cm^{-1}) and are shown in Figure 5.7. In addition, the DBTL spectrum has carbonyl bands due to its two laurate residues with peaks at 1738 and 1711 cm^{-1} . These peaks have the potential to overlap with urethane amide I bands formed by DBTL catalyzed reactions of isocyanates and phenolics. The potential for overlap, however, is mitigated by the low sample concentration of DBTL when it is used as a catalyst. The peaks for TEA are found mostly from 3000 to 2800 cm^{-1} and 1500 to 1000 cm^{-1} , with a few bands from 800 to 700 cm^{-1} . Thus, neither catalyst should interfere with peaks for OH, NH, or NCO stretching, with only negligible DBTL overlapping of the amide I carbonyl stretching.

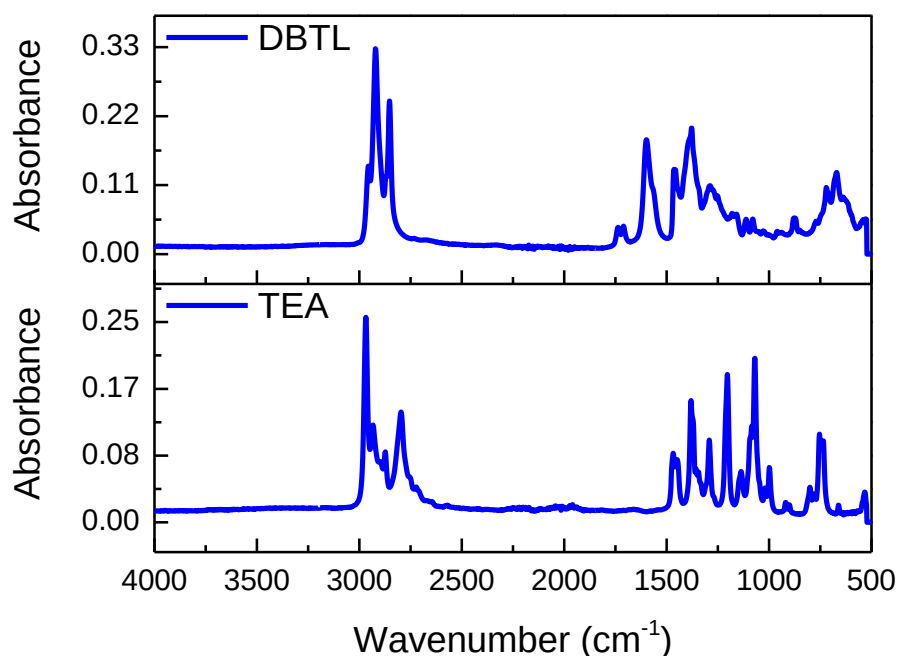


Figure 5.7. ATR-FTIR spectra of the model compounds dibutyltindilaurate and triethyl amine

5.3.2.2. Real time reactions of PF model compounds with pMDI ($f = 2.22$) in THF

The model compounds phenol and benzyl alcohol were reacted with oligomeric pMDI ($f = 2.22$) in the presence of DBTL or TEA catalyst at ambient temperature and monitored by real time ATR-FTIR. Reactions with these two model compounds assured exclusive formation of phenyl or benzyl urethanes respectively for easier distinction and spectral interpretation. Both model compounds reacted with the pMDI in the presence of TEA and DBTL catalysts to form of benzyl and phenyl urethanes.

In the OH and NH stretching region, the phenol peak wavenumber was greater than benzyl alcohol (See figures 5.8 and 5.9). Inspection of the peak shape revealed that phenol had more absorbance in the 3450 to 3350 cm^{-1} range than benzyl alcohol. The peak for benzyl alcohol reaction products was the narrower than phenol. Reactions of phenol with pMDI in the presence of TEA resulted in a stronger left shoulder around 3400 cm^{-1} than DBTL, like due to the preference for the formation of phenyl urethanes (Figure 5.8.). Reactions with benzyl alcohol in the presence of TEA showed higher peaks just above 3300 than DBTL (Figure 5.9).

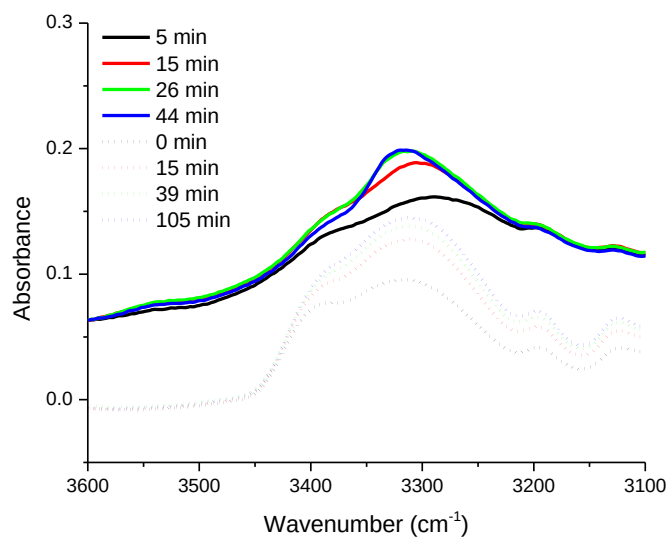


Figure 5.8. Normalized real time reactions of phenol with pMDI ($f = 2.22$) for the $\nu(\text{OH})$ and $\nu(\text{NH})$ region (3600 to 3100 cm^{-1}) in THF at ambient temperature catalyzed by DBTL (solid lines) or TEA (dotted lines)

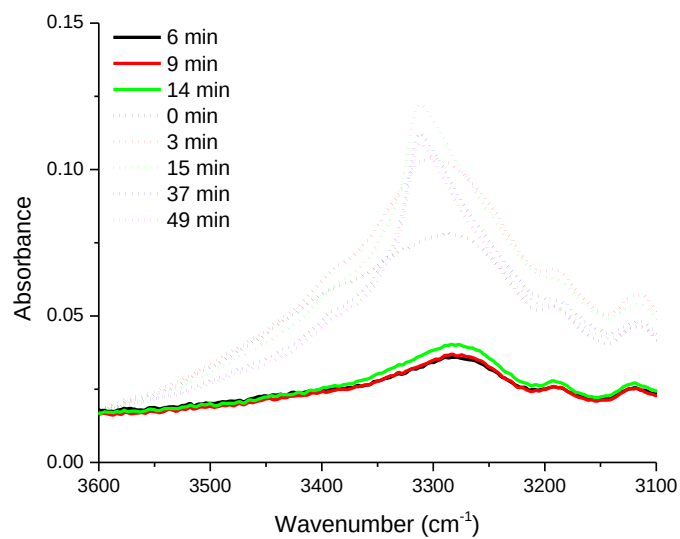


Figure 5.9. Normalized real time reactions of benzyl alcohol with pMDI ($f = 2.22$) for the $\nu(\text{OH})$ and $\nu(\text{NH})$ region (3600 to 3100 cm^{-1}) in THF at ambient temperature catalyzed by DBTL (solid lines) or TEA (dotted lines)

In the $\nu(\text{N}=\text{C}=\text{O})$ region, the peak wavenumber for the benzyl alcohol reaction was greater (2280 cm^{-1}) than for phenol (2272 cm^{-1}) in Figures 5.10 and 5.11. The peak shapes showed that the intensity decreased more on the lower wavenumber side of the peaks as the reaction progressed. One possible explanation of this phenomena is that the pMDI may have contained different isomers such as 2,4'-MDI and 4,4'-MDI with varied reactivity, leading to the shifts in peak values as well as decreasing intensity. In Figure 5.10, the reaction of pMDI with phenol in the presence of DBTL results in the residual isocyanate having a higher wavenumber than the same reaction performed in the presence of TEA. This observation raises the possibility that the catalyst type may also be directing towards different isocyanate isomers; the data generated in this study, however, are insufficient to draw any firm conclusions. In figure 5.11, most of the isocyanate was clearly consumed in the reactions with benzyl alcohol, likely more so than with phenol. Again, since concentrations were unknown and reaction times varied, this is another potential area for future investigation.

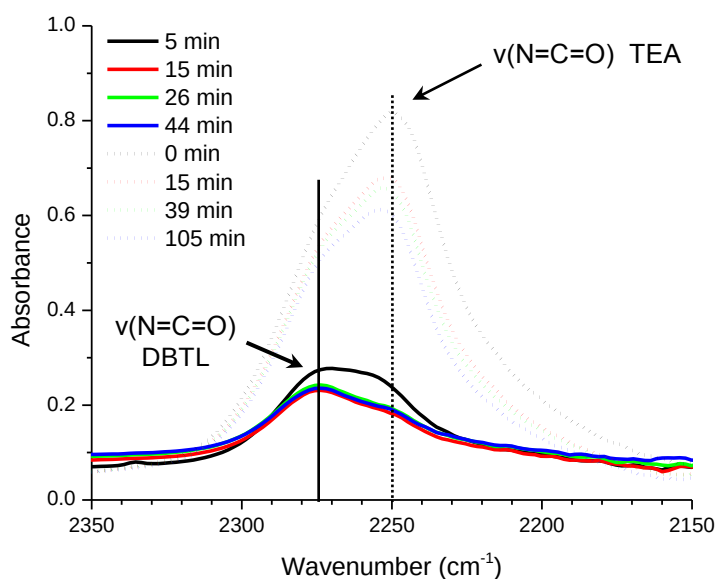


Figure 5.10. Real time reactions of phenol with pMDI ($f = 2.22$) for the $\nu(\text{N}=\text{C}=\text{O})$ region (2350 to 2150 cm^{-1}) in THF at ambient temperature catalyzed by DBTL (solid lines) or TEA (dotted lines)

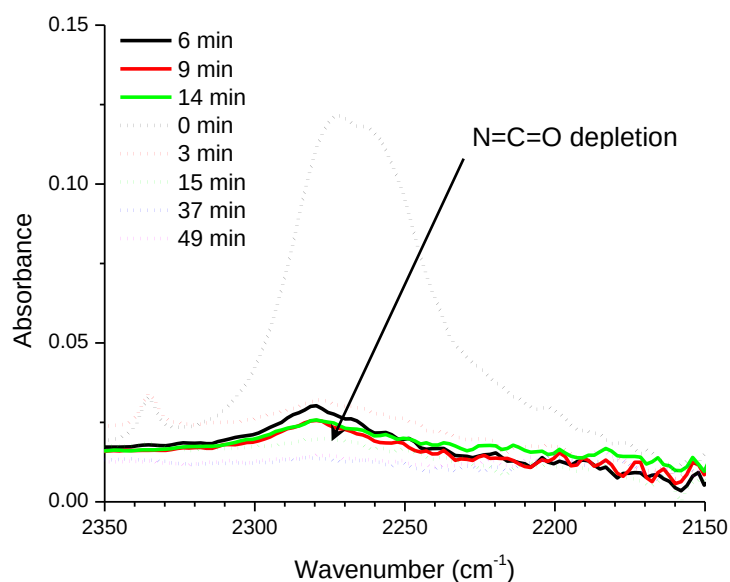


Figure 5.11. Real time reactions of benzyl alcohol with pMDI ($f = 2.22$) for the $\nu(\text{N}=\text{C}=\text{O})$ region (2350 to 2150 cm^{-1}) in THF at ambient temperature catalyzed by DBTL (solid lines) or TEA (dotted lines)

The amide I $\nu(\text{C}=\text{O})$ carbonyl is characterized by two different forms, an unassociated peak and a hydrogen bonded peak.⁹ In the dynamic spectra, the unassociated peaks would form at relatively low concentrations due to formation of urethane linkages. As concentrations of these urethane groups increased, however, more of their NH groups would begin to associate through hydrogen bond formation, with resulting peak shifts. Table 5.2 provides the amide I peaks for phenyl and benzyl urethane reaction products in their free (unassociated) and hydrogen bonded (associated) forms.

Table 5.2. FTIR wavenumber (cm^{-1}) of the amide I carbonyl $\nu(\text{C}=\text{O})$ band for catalyzed reactions of PF model compounds with phenyl isocyanate in THF at ambient temperature

Catalyst	PF Model Compound			
	Phenol		Benzyl Alcohol	
	unassociated	associated	unassociated	associated
DBTL	~1745	1717-1711	1732	~1710
TEA	~1745	1721-1715	1728	1709-1700

For unassociated amide I carbonyls, the estimated peak wavenumber for phenol (1745 cm^{-1}) was greater than for benzyl alcohol ($1732\text{--}28\text{ cm}^{-1}$). The hydrogen bonded phenol amide I carbonyl had a peak wavenumber of $1721\text{--}11\text{ cm}^{-1}$, while benzyl alcohol was about $1710\text{--}1700\text{ cm}^{-1}$. Dynamic spectra of the amide I carbonyl region may be seen in Figures 5.12 through 5.15. Real time reactions of phenol with pMDI ($f = 2.22$) in THF at ambient temperature catalyzed by TEA had more free amide I than by DBTL (Figure 5.12), while benzyl alcohol reactions had the reverse, where catalysis by DBTL resulted in more free amide I than by TEA (Figure 5.13). Visual comparison of the spectra for the amide I region of phenol (Figure 5.14) and benzyl alcohol (Figure 5.15) with each catalyst clearly showed that the unassociated amide I for phenol was greater than that for benzyl alcohol, and likewise for the associated amide I peaks. This observation was consistent with the data from Table 5.2. These findings are also consistent with Zhuang and Steiner's earlier IR results with phenyl urethanes at $1723\text{--}16\text{ cm}^{-1}$ and benzyl urethanes at $1704\text{--}3\text{ cm}^{-1}$.¹² The most important difference between phenyl and benzyl urethanes was the higher phenyl urethane wavenumber that should prove useful for future identification purposes with the cross-catalyzed system.

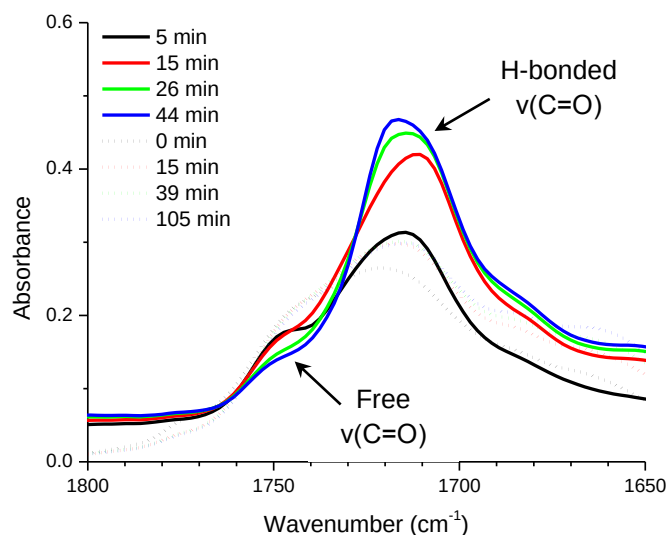


Figure 5.12. Real time reactions of phenol with pMDI ($f = 2.22$) in THF at ambient temperature catalyzed by DBTL (solid lines) or TEA (dotted lines) from 1800 to 1650 cm^{-1}

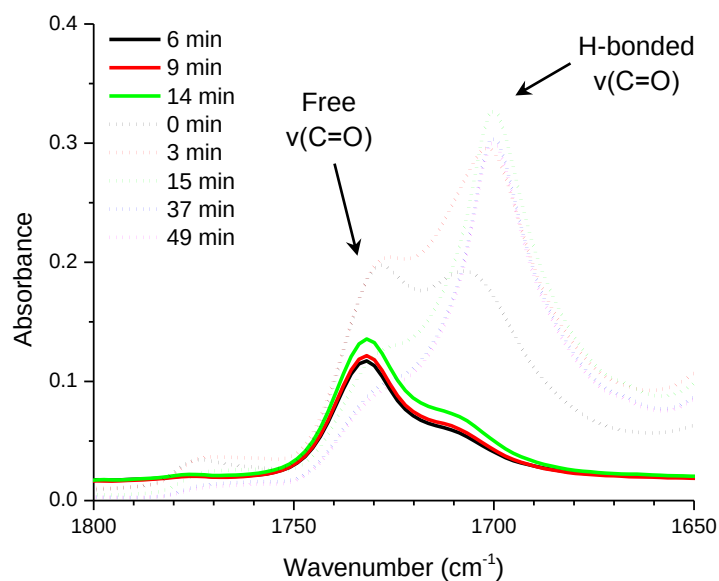


Figure 5.13. Real time reactions of benzyl alcohol with pMDI ($f = 2.22$) in THF at ambient temperature catalyzed by DBTL (solid lines) or TEA (dotted lines) from 1800 to 1650 cm^{-1}

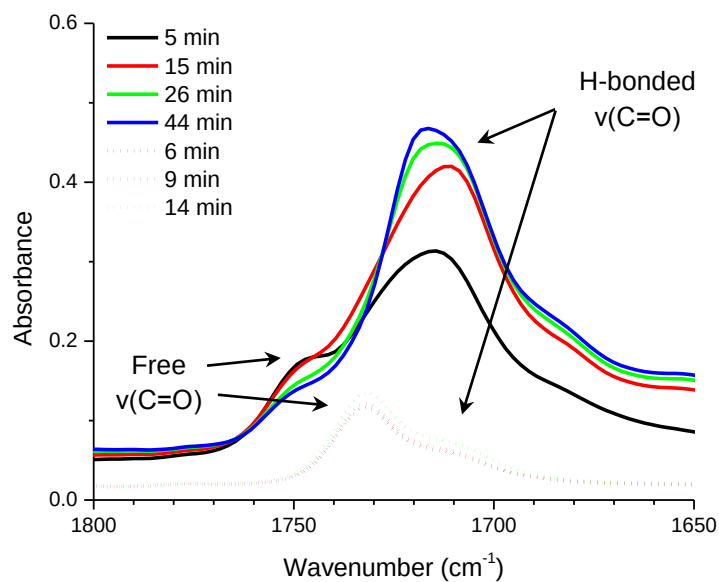


Figure 5.14. Real time reactions of phenol (solid lines) or benzyl alcohol (dotted lines) with pMDI ($f = 2.22$) in THF at ambient temperature catalyzed by DBTL from 1800 to 1650 cm^{-1}

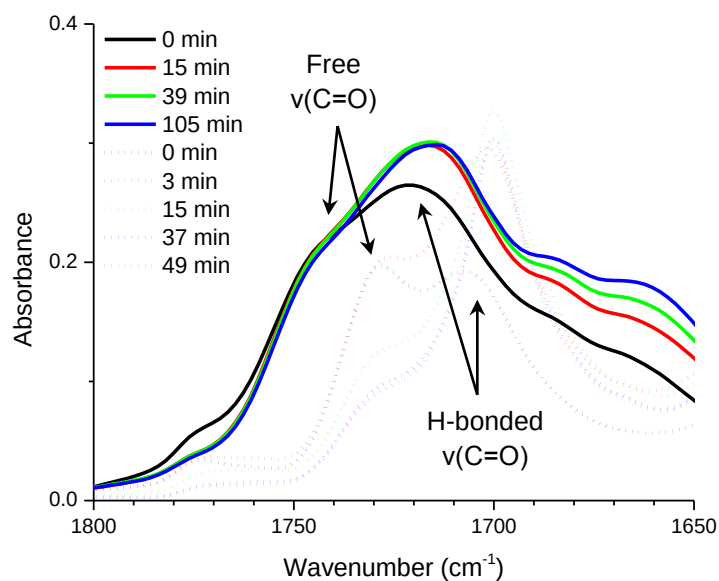


Figure 5.15. Real time reactions of phenol (solid lines) or benzyl alcohol (dotted lines) with pMDI ($f = 2.22$) in THF at ambient temperature catalyzed by TEA from 1800 to 1650 cm^{-1}

5.3.2.3. Reactions of PF model compounds with phenyl isocyanate in THF- d_6

The samples of PF model compounds reacted with phenyl isocyanate in THF- d_6 that were prepared for the NMR studies in chapter 4 were ideally suited for the evaporative deposition sample preparation technique. The samples used were the model compounds phenol, benzyl alcohol, 2-HMP, and 4-HMP that were reacted with phenyl isocyanate using DBTL or TEA as the catalyst. The ATR-FTIR experiments were prepared by evaporation of the THF- d_6 in situ from the ATR diamond crystal. The FTIR results for the most intense peak in the OH/NH/CH stretching region are provided in Table 5.3.

Table 5.3. FTIR wavenumber (cm^{-1}) of the most intense peak in the OH/NH/CH stretching region for reactions of PF model compounds with phenyl isocyanate at ambient temperature in THF- d_6

Catalyst	PF Model Compound			
	Phenol	Benzyl Alcohol	2-HMP	4-HMP
Model (v OH)	3337	3292	3418/3251	3377/3321
DBTL	3344 (sharp)	3268 (v. sharp)	3286 (broad)	3303 (broad)
TEA	3345 (sharp)	3268 (v. sharp)	3289 (v. broad)	3302 (sharp)

The $\nu(\text{OH})$ and $\nu(\text{NH})$ bands were relatively sharper for the monofunctional compounds, but broader for the difunctional model compounds. The ranking of the average peak wavenumber was phenol > 4-HMP > 2-HMP > benzyl alcohol; the catalyst type had no apparent effect on the OH and NH stretching peaks. The results for the hydrogen stretching region were indicative of the reactions that took place; the phenolic urethanes gave a sharp peak at $3344\text{--}5\text{ cm}^{-1}$ while benzylic urethanes had a very sharp peak at 3268 cm^{-1} (Figure 5.16). The difunctional hydroxy compounds 2-HMP and 4-HMP, however, had mostly broader peaks as a result of reactions that formed both phenolic and benzylic urethanes, with the most intense peaks appearing at $3286\text{--}9\text{ cm}^{-1}$ and $3302\text{--}3\text{ cm}^{-1}$ respectively (Figure 5.17). Interestingly, the hydrogen stretching peak of the TEA catalyzed reaction was sharper than the other hydrogen stretching peaks for 2-HMP and 4-HMP, suggesting that the reaction product may have been more highly directed than the other three catalyst/model combinations for these two compounds. This inference was partially supported by the results for the amide I carbonyl band (*vide infra*).

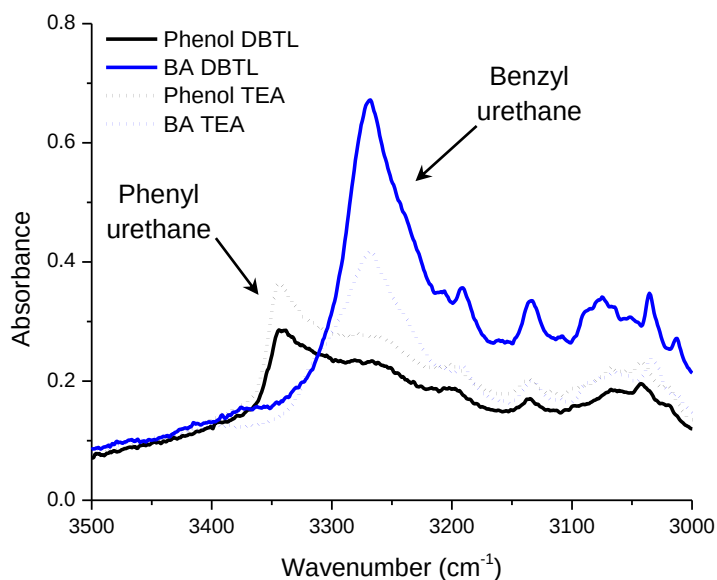


Figure 5.16. ATR-FTIR spectra from 3500 to 3000 cm^{-1} for DBTL and TEA catalyzed reactions of phenol and benzyl alcohol with phenyl isocyanate at ambient temperature in THF-d₆

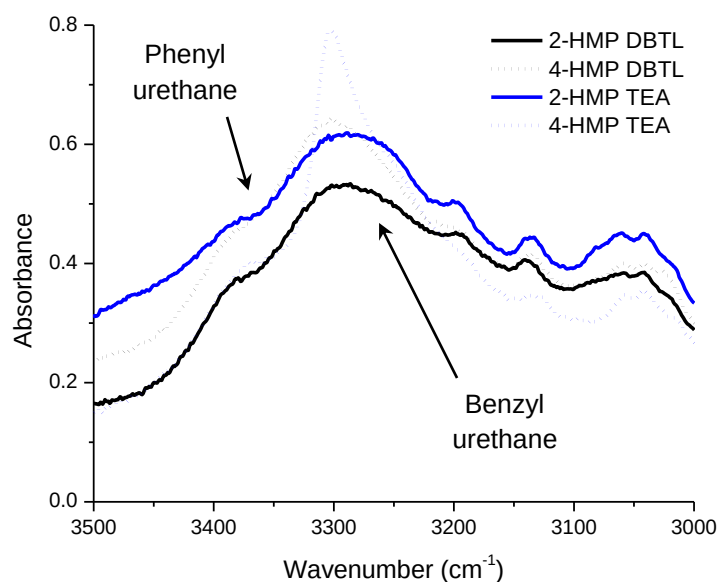


Figure 5.17. ATR-FTIR spectra from 3500 to 3000 cm^{-1} for DBTL and TEA catalyzed reactions of 2-HMP and 4-HMP with phenyl isocyanate at ambient temperature in THF-d_6

For the amide I carbonyl band with free NH groups, the peak wavenumber order was phenol (1748 cm^{-1}) > benzyl alcohol (1712 cm^{-1}); no clear peaks were observed for unassociated urethanes formed from 2-HMP or 4-HMP. The catalyst type had no effect on peak position. For the amide I carbonyl band with hydrogen bonded NH groups, the peak wavenumber order was phenol (1715 cm^{-1}) > 4-HMP (1701 cm^{-1}) > 2-HMP (1694 cm^{-1}) > benzyl alcohol (1687 cm^{-1}) for DBTL catalyzed systems, while it was phenol (1716 cm^{-1}) > 2-HMP (1713 cm^{-1}) > 4-HMP (1709 cm^{-1}) > benzyl alcohol (1688 cm^{-1}) for TEA catalyzed reactions. Catalyst had no effect on phenol or benzyl alcohol carbonyl peak position (Figure 5.18), but resulted in the TEA catalyzed products of 2-HMP and 4-HMP having peaks at +19 and +8 cm^{-1} respectively (Figure 5.19). These results are consistent with the directing effects of DBTL and TEA observed in the ^{13}C NMR experiments discussed in Chapter 4, where DBTL resulted in the formation of benzyl urethanes, while TEA led to the formation of phenyl urethanes.

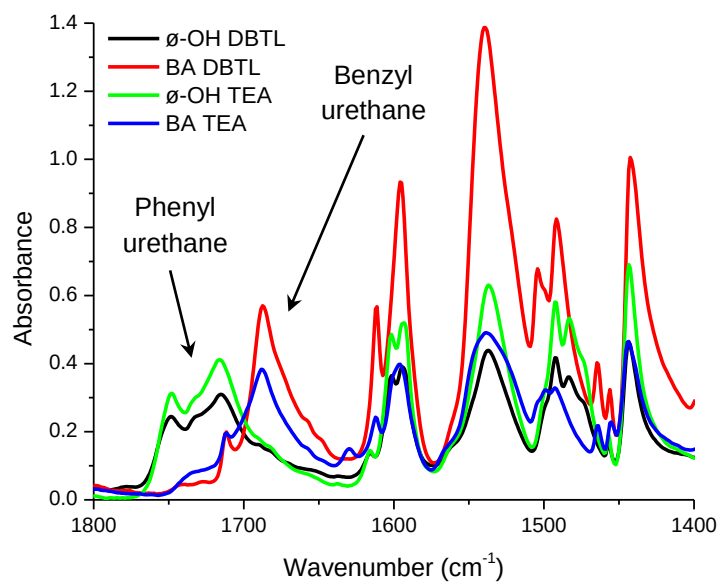


Figure 5.18. ATR-FTIR spectra from 1800 to 1400 cm^{-1} for DBTL and TEA catalyzed reactions of phenol (ϕ -OH) and benzyl alcohol (BA) with phenyl isocyanate at ambient temperature in THF-d_6

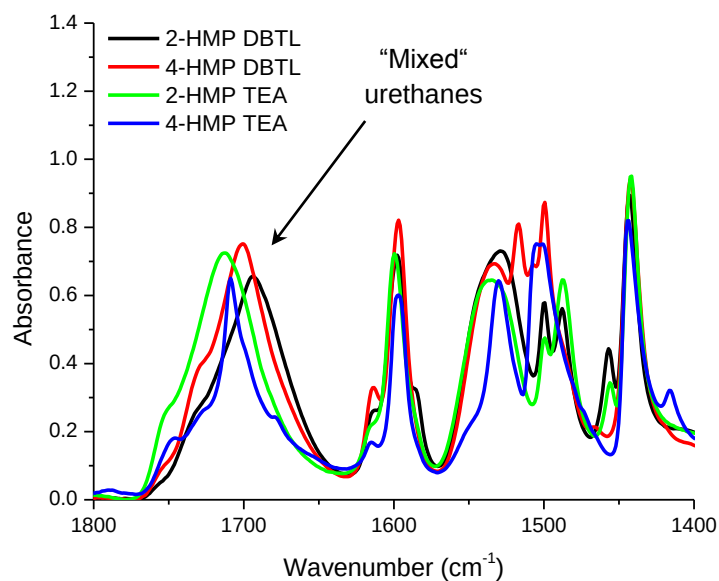


Figure 5.19. ATR-FTIR spectra from 1800 to 1400 cm^{-1} for DBTL and TEA catalyzed reactions of 2-HMP and 4-HMP with phenyl isocyanate at ambient temperature in THF-d_6

The FTIR results for the peaks in the Amide I $\nu(\text{C}=\text{O})$ region are provided in Table 5.4. The amide I carbonyl band gave two distinct peaks for each of the reaction products of phenol and benzyl alcohol. These distinct peaks were attributed to the unassociated or free urethane and the associated or hydrogen bonded urethane as had been done in the literature.⁹ The free urethane peak was of lower intensity than the hydrogen bonded peak, indicating that the bulk of the urethane was present in the hydrogen bonded form.

Table 5.4. FTIR wavenumber (cm^{-1}) of the amide I carbonyl ($\text{C}=\text{O}$) stretching band for reactions of PF model compounds with phenyl isocyanate at ambient temperature in THF- d_6 (free/hydrogen bonded)

Catalyst	PF Model Compound			
	Phenol	Benzyl Alcohol	2-HMP	4-HMP
DBTL	1748/1715	1712/1687	none/1694	none/1701
TEA	1748/1716	1712/1688	none/1713	none/1709

The two peaks for associated and unassociated phenolic urethanes were found at higher wavenumbers, 1748 and $1715\text{-}6\text{ cm}^{-1}$, than those for the benzylic urethanes which were observed at 1712 and $1687\text{-}8\text{ cm}^{-1}$ (see Figure 5.20). This observation should prove important for application of ATR-FTIR data to interpretation of the copolymer structure of the complex cross-catalyzed systems. The results for 2-HMP and 4-HMP were indicative of the catalytic directing effect towards hydroxyl selectivity (Figure 5.21). The ATR-FTIR results indicated that DBTL catalyzed 2-HMP yielded the most benzyl urethane as shown by its amide I band at 1694 cm^{-1} , while its TEA catalyzed version was at 1713 cm^{-1} , yielding more phenyl urethane. Similarly, the 4-HMP catalyzed by DBTL yielded more benzyl urethane as shown by its amide I band at 1701 cm^{-1} , while its TEA catalyzed version was at 1709 cm^{-1} , yielding more phenyl urethane. Neither the 2-HMP nor 4-HMP had much urethane in its free form present, unless it was present as a minor shoulder to the peak of the hydrogen bonded form.

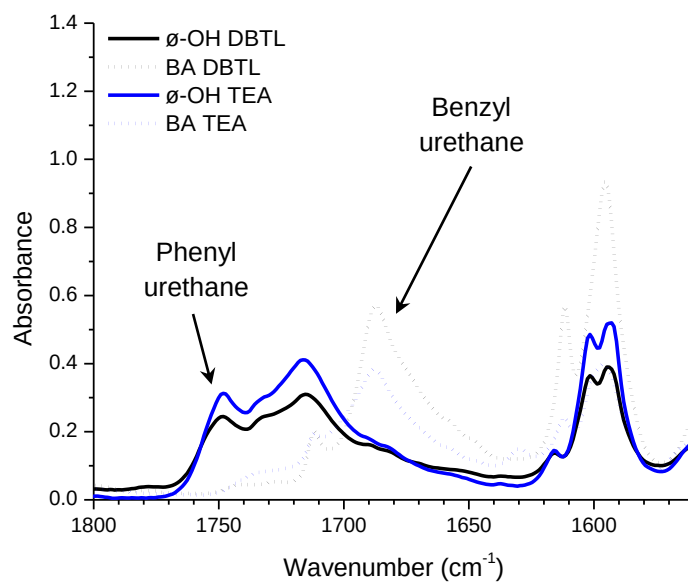


Figure 5.20. ATR-FTIR spectra from 1800 to 1560 cm^{-1} for DBTL and TEA catalyzed reactions of phenol (ϕ -OH) and benzyl alcohol (BA) with phenyl isocyanate at ambient temperature in THF- d_6

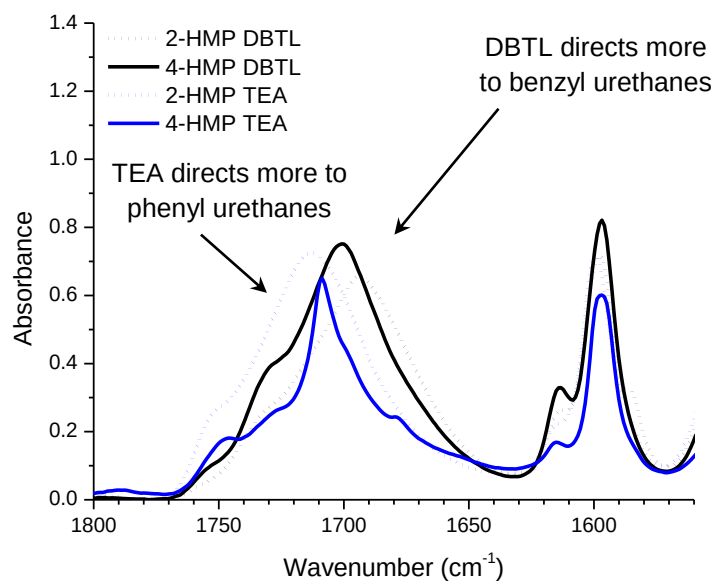


Figure 5.21. ATR-FTIR spectra from 1800 to 1560 cm^{-1} for DBTL and TEA catalyzed reactions of 2-HMP and 4-HMP with phenyl isocyanate at ambient temperature in THF- d_6

Table 5.5 provides a compilation of the reaction mix composition for 2-HMP and 4-HMP found by ^1H NMR in chapter 4. Careful inspection of the spectra of Figure 5.10 and comparison with this data table show that the directing effects of the TEA and DBTL towards phenyl and benzyl urethanes respectively. The FTIR method, however, is not able to distinguish the identity of BPDU in contrast to the NMR method.

Table 5.5. Composition of reaction mix components (%) for catalyzed reactions of 2-HMP and 4-HMP with phenyl isocyanate at ambient temperature in THF- d_6 by ^1H NMR (from section 4.3.2.3 and .4.)

Reaction Mix Component	DBTL		TEA	
	2-HMP	4-HMP	2-HMP	4-HMP
Monomer	0.80	2.10	18.70	13.00
BU	83.10	67.50	14.70	3.00
PU	0.00	0.00	48.70	73.50
BPDU	16.10	30.40	18.00	10.40

Table 5.6 gives the average peak wavenumbers, $\nu(\text{OH})$ and $\nu(\text{C=O})$, for reactions of phenol, and benzyl alcohol with pMDI ($f = 2.22$) in THF with DBTL catalyst at ambient temperature. There is also in the table a comparison to values from Tables 5.3 and 5.4, for the OH and NH stretching and amide I stretching carbonyl peaks. The OH and NH stretching peaks were broader for the reactions of pMDI with the models than those of phenyl isocyanate (see section 5.3.2.3). The reactions of pMDI would have generated more isomers than those of the phenyl isocyanate. Also, the THF solution may have allowed the formation of more types of hydrogen bonded isomers leading to the band broadening and the different peak intensity.

Table 5.6. Average wavenumber (cm^{-1}) for real time reactions of PF model compounds with pMDI ($f = 2.22$) at ambient temperature in THF with DBTL catalyst (Amide I is free/hydrogen bonded)

Region	PF Model Compound	
	Phenol	Benzyl Alcohol
OH/NH stretching	3302 (broad)	3282 (broad)
Δ from Table 5.3	42	-14
C=O amide I	1747/1715	1732/none
Δ from Table 5.4	1/0	-20/none

5.4. Conclusions

This study has demonstrated that ATR-FTIR spectroscopic techniques can differentiate among specific functional groups for the reaction peaks generated by the carbamic acid side-reaction, phenyl urethane formation, and benzyl urethane formation. The amide I $\nu(\text{C}=\text{O})$ peaks are most useful for interpretative purposes, as they are found in a spectral region with little interference from the peaks of other functional groups. The carbamic acid side-reaction forms an amide I $\nu(\text{C}=\text{O})$ peak at 1638 cm^{-1} . Phenyl urethane forms amide I $\nu(\text{C}=\text{O})$ free and associated peaks at 1748 and 1715 cm^{-1} respectively. Benzyl urethane forms amide I $\nu(\text{C}=\text{O})$ free and associated peaks at 1712 and 1687 cm^{-1} respectively. Knowledge of this structural information will permit effective interpretation of the complex FTIR spectra for cross-catalyzed reactions of PF and pMDI.

5.5. References

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Chapter 6: FTIR Studies of Accelerated Reactions of PF Model Compounds

6.0. Overview

The objective of this investigation was to determine the best FTIR peaks for monitoring the propylene carbonate accelerated condensation reactions of alkaline PF resoles. Due to the complexity involved in PF acceleration, model compound experiments were used to aid in FTIR peak identification for the various potential reactions. All reactions were monitored by ATR-FTIR. Baseline model compound spectra were acquired, and propylene carbonate hydrolysis was modeled by reactions with sodium hydroxide and ammonium hydroxide in an aqueous environment. Real time condensation reactions of the phenolic models 2-HMP and 4-HMP accelerated by propylene carbonate were monitored in the presence of ammonium hydroxide or sodium hydroxide in an aqueous environment. The real time accelerated condensation of an alkaline PF resole by propylene carbonate was also investigated and interpreted based on the model compound studies.

The hydrolysis of propylene carbonate by sodium hydroxide and ammonium hydroxide differentiates among their reaction products. Accelerated condensation of 2-HMP and 4-HMP by propylene carbonate in the presence of ammonium hydroxide or sodium hydroxide formed methylene bridges. These model compound studies identified changes during propylene carbonate hydrolysis, formation of hydroxypropyl carbamate, and methylene bridge formation. The data provided FTIR peaks useful for monitoring the accelerated condensation reactions of alkaline PF resoles at ambient temperature.

6.1. Introduction

Accelerated PF resole condensation reactions result in the formation of methylene bridges between the phenolic aromatic rings and hydrolysis of the accelerant. Kamo et al. investigated the cure accelerating effects of propylene carbonate on phenolic resins¹ and the catalytic effect of sodium bicarbonate on condensations of hydroxymethylphenols². The principal techniques employed were ¹³C NMR and HPLC analysis. Conner et al. characterized the condensation reactions of 2-HMP and 4-HMP with ethyl formate, propylene carbonate, γ -butyrolactone and

triacetin accelerators using HPLC and ^{13}C NMR.³ They used a 5:1 (v:v) mixture of DMF and water with sodium hydroxide as an ionizing agent at a 0.50 NaOH to phenol molar ratio.³ They found that while without acceleration that the 4-HMP self -condensation was faster than 2-HMP, with acceleration the 2-HMP was more reactive than the 4-HMP.³ What neither research group attempted was to monitor the accelerated reactions using FTIR. Poljanšek and Krajnc, however, monitored the reaction progress of a PF pre-polymer using in-line FTIR spectroscopy, but did not study acceleration.⁴

The present study attempts to monitor acceleration reactions using FTIR to complement these earlier acceleration studies. To characterize the complex cross-catalyzed reactions of PF and pMDI by FTIR, an understanding of what spectral peaks and regions will change during polymerization is necessary. By studying the accelerated condensation reactions of phenolic model compounds and PF resoles in isolation from the pMDI components, specific peaks and trends may be identified for interpretation of the more complex reactions among multiple components.

6.2. Experimental

6.2.1. Materials

6.2.1.1. Materials for model compound studies

Samples of the model compounds 2-hydroxymethyl phenol (99%), 4-hydroxymethyl phenol (99%), propylene carbonate (99%), and 1,2-propanediol (99%) were purchased from Sigma-Aldrich. The model compounds were used as received. Sodium bicarbonate (Fisher certified ACS grade) was used to model one of the reaction products for propylene carbonate hydrolysis. Ammonium hydroxide (25 %, Acros Organics) and sodium hydroxide prills (98% Sigma-Aldrich, reagent grade) were used as reagents. Deionized (DI) water (Millipore Direct Q 3 UV with pump) and N,N-dimethylformamide (DMF, Sigma-Aldrich) were used as solvents in these experiments.

6.2.1.2. PF resin materials

The materials used for preparation of PF resins were phenol (Sigma-Aldrich, $\geq 99\%$), NaOH prills (Sigma-Aldrich, $\geq 98\%$), aqueous ammonium hydroxide (Acros Organics, 25%), deionized (DI) water (Millipore Direct Q 3 UV with pump), paraformaldehyde (Sigma-Aldrich, 95%), tin(II)chloride dihydrate (Sigma-Aldrich, 98%). The materials were used as received.

6.2.2. Methods

6.2.2.1. PF resin preparation apparatus

The PF Resin preparation apparatus comprised a 1000-mL glass reaction kettle with a four-neck glass top, a reflux condenser connected via a two-way glass adapter, a glass stirring rod assembly with a Teflon stir blade, and a rubber stopper fitted with an electronic thermocouple. Exothermic heat was controlled with an ice water bath or vacuum reflux condenser connected to a water aspirator. The heating ramp and reaction temperature were controlled with an infrared lamp connected to a Barnant Temperature Controller Model R/S with feedback from the electronic thermocouple. Temperature control was within ± 0.1 °C. The glass stirring rod was connected via a flexible rotating joint to a BDC 2002 variable speed motor.

6.2.2.2. Synthesis of PF resin with sodium hydroxide

PF resin was prepared with phenol, NaOH prills, DI water I, paraformaldehyde I, paraformaldehyde II, DI water II, and tin(II)chloride dihydrate. Phenol (255.6 g, 2.72 mol), NaOH prills (21.7 g, 0.54 mol), and DI water I (123.5 g, 6.85 mol) were added to the 1000-mL reaction kettle and dissolved with stirring. Paraformaldehyde I (50.9 g, 1.61 mol) was added in increments over 5 minutes to the kettle through a funnel, allowing it to dissolve and react. The reaction mix was heated to 47.0 °C to completely dissolve the reactants. Heat generated was controlled with cooling as needed to avoid a potentially hazardous reflux. The remaining paraformaldehyde II (99.3 g, 3.14 mol) was added over 51 min, using a powder addition funnel equipped with an auger feed for delivery of free-flowing prills to the reaction. The reaction temperature was 76.0 °C upon completion of the addition. DI water II (50.2 g, 2.78 mol) was used to rinse residual materials into the reaction vessel. Temperature was raised to 85.0 °C and

was held for 60 min to produce a PF condensate, and then the reaction mixture was cooled to 25.0 °C over 22 min. The resin was split into two portions. Tin(II)chloride dihydrate (0.9225 g, 4.08 mmol) dissolved in DI water (1.0690 g, 59.32 mmol) was added to one portion of the PF condensate (300.17 g). Each resin portion was placed in a glass bottle and stored at 4 °C. The formulated F:P molar ratio was 1.75 and the NaOH:P molar ratio was 0.20.

6.2.2.3. Synthesis of PF resin with sodium hydroxide and ammonium hydroxide

PF resin was prepared with phenol, aqueous ammonium hydroxide, DI water I, paraformaldehyde I, NaOH prills, paraformaldehyde II, and DI water II. The phenol (257.2 g, 2.73 mol), aqueous ammonium hydroxide (76.8 g, 0.55 mol), and DI water I (65.4 g, 3.63 mol) were added to the 1000 m reaction kettle and dissolved with stirring. The paraformaldehyde I (51.2 g, 1.70 mol) was added in increments over 4 minutes to the kettle through a funnel, allowing it to dissolve and react. The reaction mix was heated to 36.0 °C promote dissolution; any exothermic reaction was controlled with cooling as needed to avoid a hazardous reflux while the temperature was allowed to rise to 70.0 °C. Since the materials would not go into solution, NaOH prills (21.7 g, 0.54 mol) were added to the reactor. The paraformaldehyde II (100.1 g, 3.33 mol) was added over approximately 60 minutes using a powder addition funnel. The DI water II (50.0 g, 2.77 mol) was used to rinse residual materials into the reaction vessel. Heat was applied to reach 85.0 °C and that temperature was held for 67 minutes when cooling to 25.0 °C commenced over 33 minutes. The resin was split into two portions, one of PF condensate (300.06 g) to which tin(II)chloride dihydrate (0.9137 g, 0.405 mmol), dissolved in DI water (1.08 g, 5.993 mmol), was added to it. Both resin portions were placed in glass bottles and stored at 4 °C. The formulated F:P molar ratio was 1.75, the NH₄OH:P molar ratio was 0.20, and the NaOH:P molar ratio was 0.20.

6.2.2.4. ATR-FTIR technique

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was performed using a Nicolet 8700 spectrometer equipped with a Pike Technologies Gladiator ATR accessory. The ATR had a diamond crystal with dimensions of 2.2 x 3.0 mm. Absorbance was measured

between 4000 and 500 cm^{-1} , using 32 scans at 4 cm^{-1} resolution unless otherwise specified, and ATR correction.

For neat liquids such as propylene carbonate, or samples in aqueous solution, a droplet of the liquid was placed on the surface of the ATR diamond crystal and covered with either an inverted watch glass or a covered solvated sample holder to prevent evaporation and contamination. A droplet of the solution was dispensed onto the ATR crystal from a glass pipette or a 1.0 mL microliter syringe and FTIR data acquisition was begun after a background scan was completed.

6.2.2.4.1. ATR-FTIR experiments

The ATR-FTIR experiments were run qualitatively to provide information on the types of structures produced due to reaction. The inability to precisely quantify the amount of material deposited and the possibly incomplete nature of micro-mixing on the ATR diamond crystal made quantitative experimentation extremely difficult to perform.

6.2.2.4.2. Sodium hydroxide hydrolysis of propylene carbonate

Propylene carbonate and an aqueous sodium hydroxide solution were reacted in situ on the ATR diamond crystal using a liquid sample holder over approximately 15 minutes at ambient temperature.

6.2.2.4.3. Ammonium hydroxide hydrolysis of propylene carbonate

Propylene carbonate and a 25% aqueous ammonium hydroxide solution were reacted in situ on the ATR diamond crystal using a liquid sample holder over approximately 95 minutes at ambient temperature.

6.2.2.4.4. Accelerated reactions of PF model compounds at ambient temperature

The experimental conditions of Conner et al.³ were repeated on the ATR diamond crystal using a series data acquisition scan with propylene carbonate as the accelerant. Two experiments were run: hydrolytic acceleration of 2-HMP and 4-HMP condensation by propylene carbonate.

The solvent for the 2-HMP and 4-HMP was H₂O:DMF 5:1 (v:v) ratio, in the presence of sodium hydroxide at a 0.50 NaOH to HMP molar ratio. The propylene carbonate to HMP molar ratio was 0.375. The reaction proceeded for over 60 minutes at ambient temperature (22 to 25 °C).

6.2.2.4.5. Accelerated reactions of oligomeric PF resoles at ambient temperature

The PF resin prepared with sodium hydroxide and the PF resin prepared with sodium hydroxide and ammonium hydroxide were reacted on the ATR diamond crystal with propylene carbonate added in a molar ratio of 0.25 to the calculated amount of phenol in each PF resole. A background scan was acquired, and then sufficient quantities of each PF resole and propylene carbonate were mixed on a glass slide in the calculated ratios just prior to data acquisition. Immediately upon combination, enough droplets of the mixture were applied from a glass pipette to the ATR diamond crystal to completely wet and cover it. Data acquisition was commenced immediately and the material was covered with a watch glass to minimize evaporation of water from the sample. The ambient temperature of the ATR stage was 26 °C.

6.3. Results and discussion

6.3.1. Hydrolytic side-reactions

6.3.1.1. Propylene carbonate hydrolysis by sodium hydroxide

To understand the role of propylene carbonate as a specific PF accelerator in cross-catalyzed PF-pMDI systems and for potential identification of reactants and products, the hydrolysis reactions of propylene carbonate were studied with ATR-FTIR. Propylene carbonate is subject to hydrolysis under alkaline conditions present in PF resins. The reaction products of propylene carbonate and aqueous sodium hydroxide are 1,2-propanediol and sodium bicarbonate as shown in Figure 6.1.

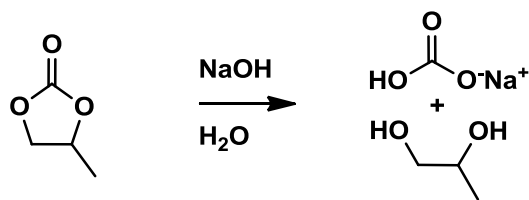


Figure 6.1. Hydrolysis of propylene carbonate under aqueous alkaline conditions

FTIR spectra were acquired for propylene carbonate, an aqueous sodium bicarbonate solution, and 1,2-propanediol as shown in Figure 6.2. The propylene carbonate spectrum was characterized by its $\nu(\text{C}=\text{O})$ peak at 1779 cm^{-1} . It also had weaker methylene and methyl $\nu(\text{C}-\text{H})$ peaks in the 3000 to 2800 cm^{-1} range and peaks below 1500 cm^{-1} representing various C-H and C-O bond vibrations. The spectrum of the 1,2-propanediol model compound indicated the type of spectral changes that should be expected during the hydrolytic decomposition of propylene carbonate. The $\nu(\text{O}-\text{H})$ and $\nu(\text{C}-\text{H})$ stretching peaks of 1,2-propanediol were in the 3600 to 3000 cm^{-1} and 3000 to 2800 cm^{-1} ranges respectively. Thus, reduction in the PC carbonyl peak should be expected to parallel growth in the O-H and C-O-H related peaks during hydrolysis due to formation of 1,2-propanediol and bicarbonate.

A background scan of deionized water indicated a broad $\nu(\text{OH})$ band between 3700 and 3000 cm^{-1} and an additional broad band with a symmetrical bending peak at 1635 cm^{-1} . Infrared peak values for water in the literature are $\nu_{\text{as}}(\text{OH})$ at 3756 cm^{-1} , $\nu_{\text{s}}(\text{OH})$ at 3652 cm^{-1} , and $\delta_{\text{s}}(\text{OH})$ at 1596 cm^{-1} .⁵ These bands were also present in an aqueous solution of sodium bicarbonate. Since the water bands may have obscured bicarbonate peaks in those two regions, their peaks locations were checked by subtracting the deionized water spectrum from the bicarbonate. This subtraction showed that sodium bicarbonate had a characteristic peak at 1359 cm^{-1} with an associated shoulder at about 1311 cm^{-1} .

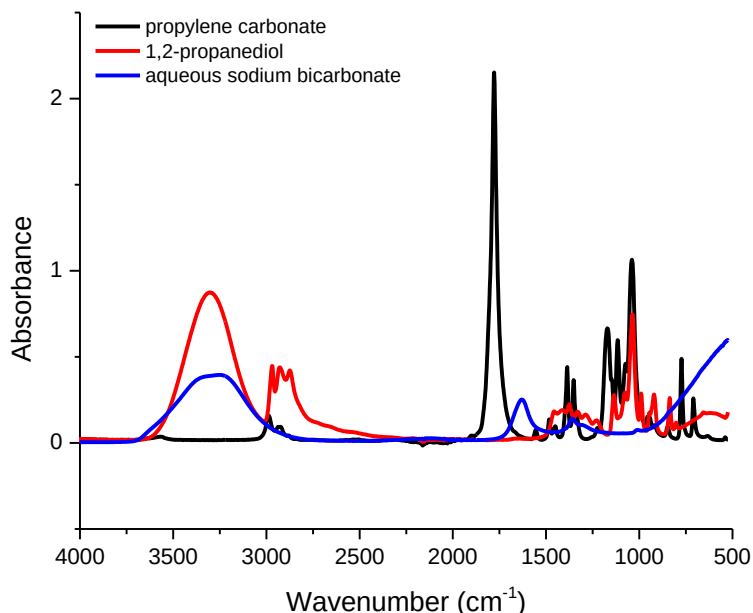


Figure 6.2. FTIR spectra of the model compounds propylene carbonate, 1,2-propanediol, and sodium bicarbonate in aqueous solution from 4000 to 500 cm^{-1}

The spectral results of the reaction between propylene carbonate and aqueous sodium hydroxide reaction are shown in Figure 6.3. The PC carbonyl peak at 1778 cm^{-1} was the most useful peak for monitoring the reactant hydrolysis and showed that essentially all the reactant was consumed within 15 minutes. The peaks at 1615 and 1353 cm^{-1} illustrated the accumulation of the bicarbonate reaction product. The peak at 1291 cm^{-1} was more useful for monitoring the accumulation of 1,2-propanediol than the $\nu(\text{C-H})$ peaks between 2900 and 2800 cm^{-1} , due to the overlap of the $\nu(\text{C-H})$ peaks of propylene carbonate and 1,2-propanediol. The peaks at 1171 and 1116 cm^{-1} , likely due to symmetric and asymmetric stretching of the C-O-C bonds, further depicted the decrease in propylene carbonate. The peaks in the 1075 to 1040 cm^{-1} region represented both decreasing propylene carbonate bands (1073 and 1040 cm^{-1}) and increasing 1,2-propanediol peaks (1072 and 1040 cm^{-1}). This competing effect rendered these peaks less useful for interpretation of the dynamic spectra and the more complex reaction systems.

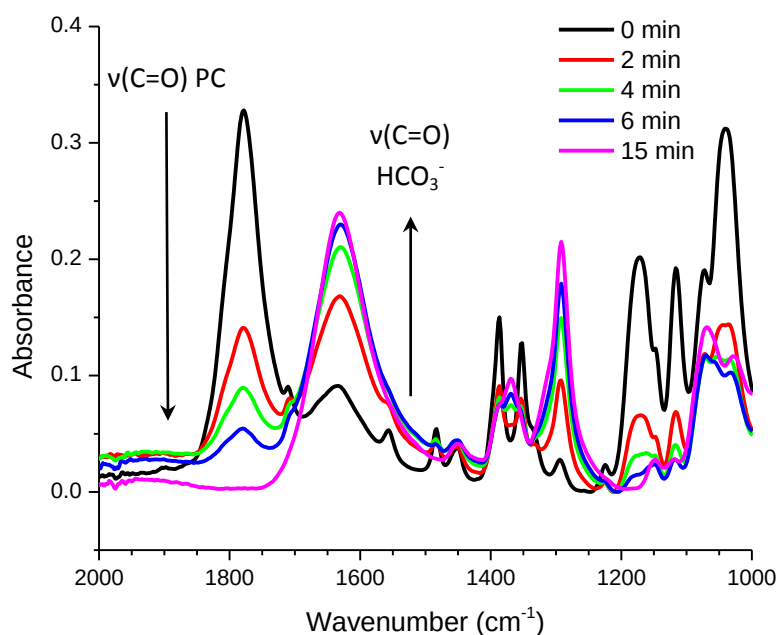


Figure 6.3. Real time FTIR spectra for propylene carbonate hydrolysis by sodium hydroxide at ambient temperature over approximately 15 minutes from 2000 to 1000 cm^{-1}

6.3.1.2. Propylene carbonate hydrolysis by ammonium hydroxide

Reaction of propylene carbonate and ammonium hydroxide will produce two isomers of hydroxypropyl carbamate (HPC) as depicted in Figure 6.4. This potential side-reaction is important for understanding cross-catalyzed PF-pMDI systems involving an ammonium hydroxide catalyst and alkylene carbonate, ester, or lactone type PF accelerators.

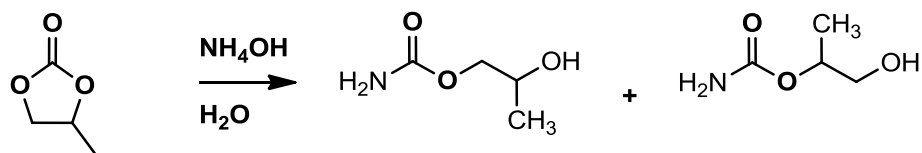


Figure 6.4. Hydrolysis of Propylene Carbonate and formation of hydroxypropyl carbamate

As mentioned earlier, the spectrum of deionized water had a broad $\nu(\text{OH})$ band between 3700 and 3100 cm^{-1} and an additional broad $\delta(\text{OH})$ band with a peak at 1635 cm^{-1} , bands that were also present in aqueous solutions of ammonium hydroxide. Since the water bands may have obscured ammonium hydroxide peaks in those two regions, their peaks locations were checked by subtracting the deionized water spectrum from the ammonium hydroxide spectrum. The ammonium hydroxide had characteristic peaks at 3391 cm^{-1} for $\nu(\text{N-H})$ and 1100 cm^{-1} for $\delta(\text{N-H})$ that were not present in the DI water spectrum.

The control reaction of propylene carbonate with aqueous ammonium hydroxide is important to understand, since it is a potential sub-reaction among accelerated condensation reactions of PF model compounds. The spectral results of this reaction are shown in Figure 6.5. The PC carbonyl peak at 1778 cm^{-1} showed that the reactant was not consumed within 95 minutes. Carbamate amide I carbonyl peaks formed and accumulated at 1711 cm^{-1} (free), 1637 cm^{-1} (associated isomer), and 1604 cm^{-1} (associated isomer).

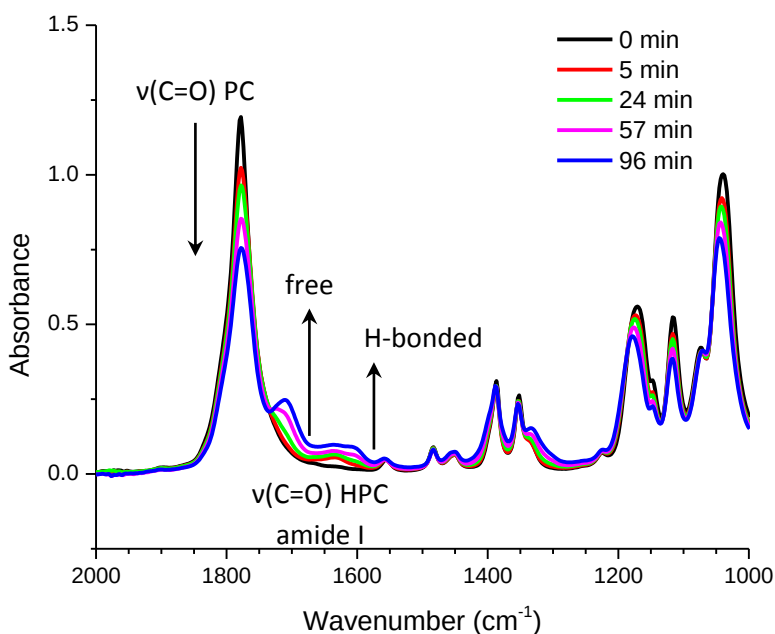


Figure 6.5. Real time FTIR spectra for propylene carbonate hydrolysis by ammonium hydroxide at ambient temperature over approximately 95 minutes from 2000 to 1000 cm^{-1}

The two hydrogen bonding peaks were attributed to the two hydroxypropyl carbamate isomers anticipated from formation of HPC. The assignment of the growing shoulder at 1606 cm^{-1} was uncertain; though it may have been a carbamate related band, perhaps one of the isomers, or from a deformational vibration. Methylene peaks were observed at 1483 cm^{-1} and 1451 cm^{-1} . The peak at 1483 cm^{-1} showed little dynamic change, while the peak at 1451 cm^{-1} showed a very slight change in intensity. Peaks at 1388 cm^{-1} and 1353 cm^{-1} exhibited little change, while a peak at 1334 cm^{-1} started as a shoulder to the 1353 cm^{-1} peak, but eventually formed a distinct peak, possibly due to a methyl group from either propylene carbonate or 1,2-propanediol.

Significantly, no peak was detected at 1291 cm^{-1} for the accumulation of 1,2-propanediol; it was likely replaced by the peak at 1334 cm^{-1} due to the effect of the carbamate substituent. The peaks at 1178 , 1148 , 1117 , 1071 , and 1045 cm^{-1} all reflect the ring opening consumption of propylene carbonate and its hydroxypropyl reaction products similarly to the aforementioned alkaline hydrolysis reactions with sodium hydroxide. The peaks at 1178 and 1117 cm^{-1} , likely due to symmetric and asymmetric stretching of the C-O-C bonds, further depicted the decrease in propylene carbonate. The peaks in the 1075 to 1040 cm^{-1} region again represented both decreasing propylene carbonate bands (1073 and 1040 cm^{-1}) and increasing 1,2-propanediol peaks (1072 and 1040 cm^{-1}). Dynamic changes in the C-O-C stretching region were not as useful for interpretive purposes as the PC carbonyl and HPC amide I peaks, since the C-O-C stretching peaks of the reactants and products overlapped.

6.3.2. Accelerated PF condensation

6.3.2.1. Accelerated reactions of PF model compounds

6.3.2.1.1. PF model compounds

The phenolic model compounds 2-HMP and 4-HMP provide hydroxymethyl functional groups in the ortho and para positions. Since their condensation will form methylene bridges, time sequenced reactions should provide useful information regarding their development. Figure 6.6 details the ATR-FTIR spectra for 2-HMP and 4-HMP as acquired by evaporative deposition from THF as described in Chapter 5.2.2. Important features of the spectra included the O-H

stretching region where 2-HMP had two sharp peaks at 3418 and 3167 cm^{-1} outside of a broad rounded peak at 3252 cm^{-1} , while 4-HMP had two sharp peaks at 3377 and 3101 cm^{-1} outside of a broad rounded peak at 3288 cm^{-1} . The in phase $\nu_{\text{ip}}(\text{C-H})$ and out of phase $\nu_{\text{oop}}(\text{C-H})$ for C-H stretching were at 2957 and 2975 cm^{-1} for 2-HMP and at 2956 and 2973 cm^{-1} for 4-HMP.

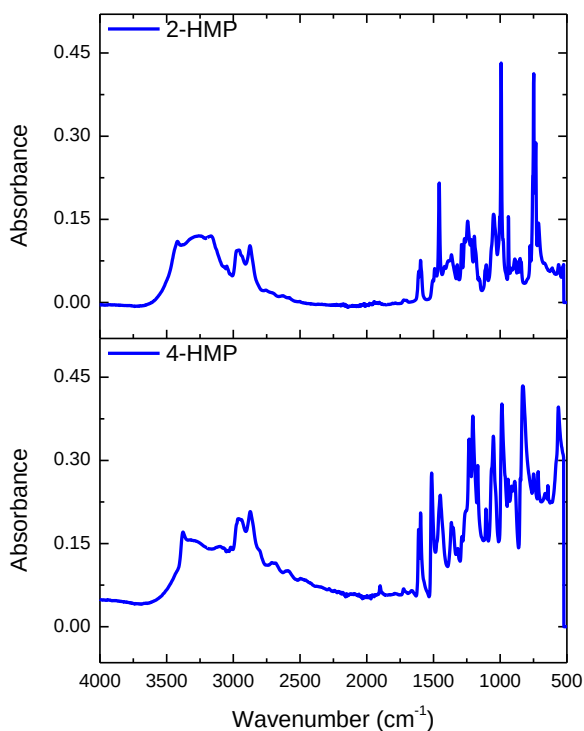


Figure 6.6. FTIR spectra of 2-HMP and 4-HMP

The FTIR spectra of propylene carbonate and its 1,2-propanediol hydrolysis reaction product are shown in Figure 6.7. The key features of the PC spectra included its strong carbonyl peak at 1779 cm^{-1} , which was its clearest indicator of consumption during reaction, and its $\nu(\text{C-H})$ related peaks at 2988, 2936, 2924, and 2881 cm^{-1} , and its $\delta(\text{C-H})$ related peaks at 1483 and 1450 cm^{-1} . The 1,2-propanediol had a strong O-H stretching band at 3305 cm^{-1} and $\nu(\text{C-H})$ related peaks at 2969, 2929, 2874 cm^{-1} , and a $\delta(\text{C-H})$ peak at 1457 cm^{-1} . The presence of PC and 1,2-propanediol in the accelerated PF reaction system may have overlapped with peaks from the PF hydroxymethyl groups and methylene bridges.

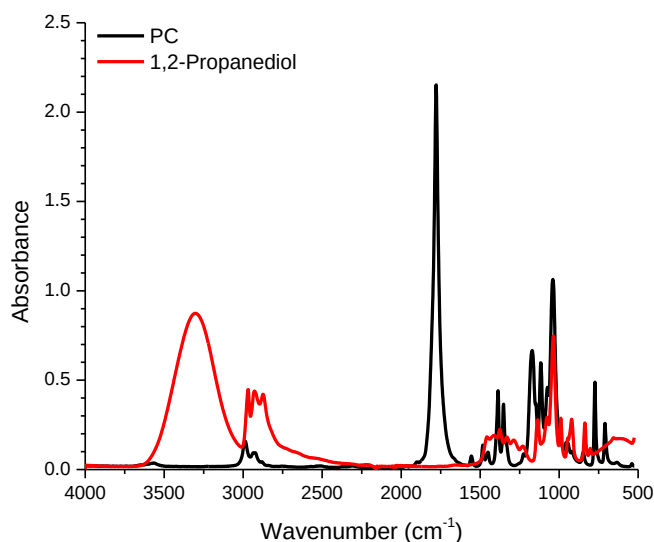


Figure 6.7. FTIR spectra of propylene carbonate and 1,2-propanediol

Bicarbonate anion is another reaction product of propylene carbonate hydrolysis. Its spectra was recorded in aqueous solution and determined by subtraction of the spectra of deionized water from its spectra. Its main peaks were observed at 1615 and 1359 cm^{-1} . These peaks should not interfere with methylene peak detection. Since ammonium hydroxide can act as a catalyst for the cross-catalyzed PF-pMDI system and it can react with propylene carbonate to form hydroxypropyl carbamate, its spectrum was recorded in 25% aqueous solution and also analyzed by subtraction of the spectra of deionized water from its spectra. Its main peaks were observed at 3391 and 1100 cm^{-1} . These peaks should also not interfere with methylene peak detection either. Subtraction spectra for sodium bicarbonate and ammonium hydroxide are shown in Figure 6.8.

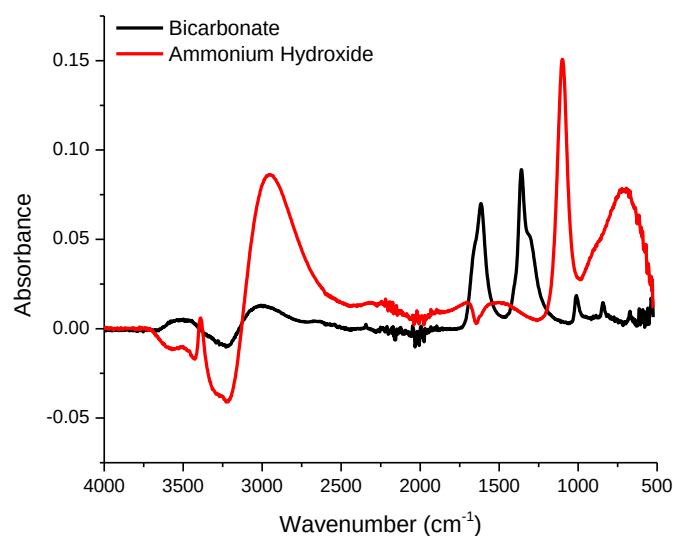


Figure 6.8. FTIR spectra for DI H₂O solutions of sodium bicarbonate and ammonium hydroxide by spectral subtraction of DI H₂O

6.3.2.1.2. Accelerated reactions of PF model compounds at ambient temperature

Accelerated reactions of 2-HMP and 4-HMP model compounds were studied to understand the effects of condensation on the FTIR spectra. The aqueous ammonium hydroxide solutions of 2-HMP and 4-HMP were reacted with propylene carbonate on the ATR-FTIR diamond crystal. A control reaction of ammonium hydroxide solution with propylene carbonate was also studied. Important spectral results from the fingerprint region are shown in Table 6.1 with the following discussion.

Table 6.1. FTIR peaks and assignment for accelerated reactions of PF models dissolved in aqueous NH_4OH

Model Reaction Peaks (cm^{-1}) from 1800 to 1300 cm^{-1}			Proposed Peak Assignment ⁶
$\text{NH}_4\text{OH} \times \text{PC}$ (control)	2-HMP $\times$ $\text{NH}_4\text{OH} \times \text{PC}$	4-HMP $\times$ $\text{NH}_4\text{OH} \times \text{PC}$	
1778	1779	1781	PC $\nu(\text{C}=\text{O})$
1711	1700	1693	Amide I unassociated
1637	1636	1637	Amide I H-bonded (1)
1604	1608	1612	Amide I H-bonded (2)
1558	1558	1558	PC (???)
---	---	1517	ring C=C stretching
1483	1483	1483	δ - CH_2 -
---	1456	1455	δ - CH_2 - bridge
1451	---	---	- CH_2 - scissor vibration
1388	1388	1400	Sym. - CH_3 aliphatic
1353	1354	1356	tertiary CH
1334	1330	1328	tertiary CH

6.3.2.1.2.1. Accelerated reactions of 2-HMP with NH_4OH and PC at ambient temperature

The reaction of 2-HMP with propylene carbonate in the presence of aqueous ammonium hydroxide is important to understand, since it is also indicative of accelerated condensation reactions of ortho hydroxymethyl substituted PF resoles. This reaction exhibited several important peaks indicative of carbonate hydrolysis with subsequent carbamate formation (Figure 6.9). The carbonate carbonyl at 1779 cm^{-1} decreased in intensity, while carbamate amide I carbonyl peaks formed at 1700 cm^{-1} (free), 1636 cm^{-1} (associated isomer), and 1608 cm^{-1} (associated isomer). Two hydrogen bonding peaks may be attributed to the two hydroxypropyl carbamate isomers that can be anticipated from formation of hydroxypropyl carbamate. Methylene peaks were observed at 1483 cm^{-1} and 1456 cm^{-1} . Most importantly, the differences from the control reaction peak for propylene carbonate and ammonium hydroxide that was discussed in section 6.3.1.2 indicated that condensation occurred. The peaks at 1483 cm^{-1} and at 1451 cm^{-1} showed dynamic change in intensity in addition to a peak shift from 1451 cm^{-1} (see Figure 6.10). Peaks at 1388 cm^{-1} and 1354 cm^{-1} exhibited less change, while a peak at 1330 cm^{-1} started as a shoulder to the 1354 cm^{-1} peak, but eventually formed a distinct peak. Although some concentration of solids in the sample may have occurred during analysis, those changes likely occurred due to condensation of 2-HMP.

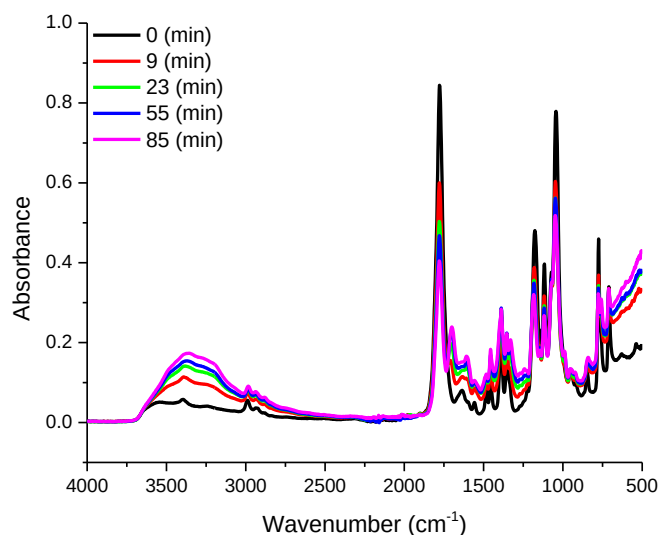


Figure 6.9. FTIR of the reaction of 2-HMP with propylene carbonate in the presence of NH_4OH over 85 minutes at ambient temperature. Spectral range is from 4000 to 500 cm^{-1}

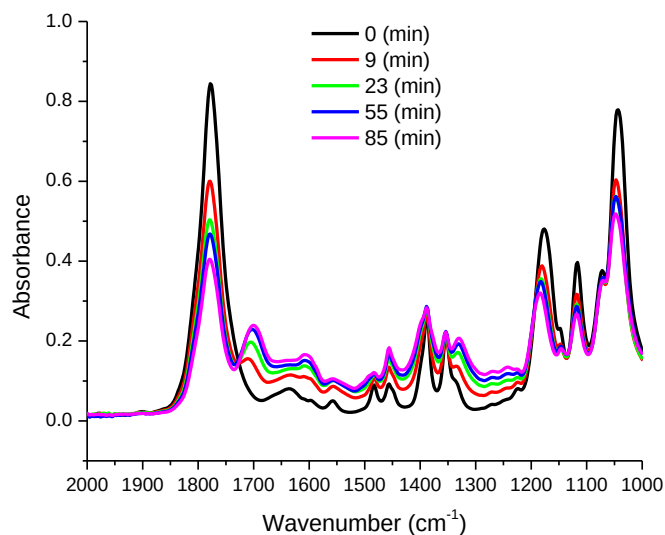


Figure 6.10. FTIR of the reaction of 2-HMP with propylene carbonate in the presence of NH_4OH over 85 minutes at ambient temperature. Spectral range is from 2000 to 1000 cm^{-1}

6.3.2.1.2.2. Accelerated reactions of 4-HMP with NH_4OH and PC at ambient temperature

The reaction of 4-HMP with propylene carbonate in the presence of aqueous ammonium hydroxide is important to understand, since it is also indicative of accelerated condensation

reactions of para hydroxymethyl substituted PF resoles. This reaction also exhibited several important peaks indicative of the hydrolysis of the carbonate with subsequent carbamate formation (see Figure 6.11). Conner et al. had earlier concluded that 2-HMP and 4-HMP had different reactivity in accelerated reactions.³ The carbonate carbonyl at 1781 cm^{-1} decreased in intensity, while carbamate amide I carbonyl peaks formed at 1693 cm^{-1} (free), 1637 cm^{-1} (associated isomer), and 1612 cm^{-1} (associated isomer). Two hydrogen bonding peaks may be attributed to the two hydroxypropyl carbamate isomers that can be anticipated from formation of hydroxypropyl carbamate. A peak that was unique to 4-HMP was found at 1517 cm^{-1} and appears to have been aromatic ring C=C stretching. Methylene peaks were observed at 1483 cm^{-1} and 1455 cm^{-1} that showed dynamic change in intensity. Most importantly, the differences from the control reaction peak, with a shift from 1451 cm^{-1} and a dynamic increase in intensity over time indicated that condensation occurred. A peak that began at 1388 cm^{-1} shifted strongly to 1400 cm^{-1} . The peak at 1356 cm^{-1} exhibited less change, while a peak at 1328 cm^{-1} started as a shoulder to the 1356 cm^{-1} peak, but eventually formed a distinct peak. Similar to 2-HMP, some concentration of solids in the sample may have occurred; those changes likely occurred due to condensation reactions.

The most important conclusion for these model compound reactions of was that they provide evidence for the accelerated methylene bridge formation of both 2-HMP and 4-HMP when compared to the control reaction of propylene carbonate with NH_4OH . The key peak was at $1455\text{-}6\text{ cm}^{-1}$ which was a shift from the 1451 cm^{-1} peak of the control reaction of propylene carbonate with ammonium hydroxide (see Figures 6.12 to 6.14). To confirm these changes in peak intensity for these weaker signals, the spectra for 2-HMP and 4-HMP were normalized against the 0 minute sample of 2-HMP at 1470 cm^{-1} (see Figure 6.15). This spectral graph shows that the 2-HMP had a sharper methylene peak at 1456 cm^{-1} while 4-HMP had a flatter methylene peak at 1450 cm^{-1} .

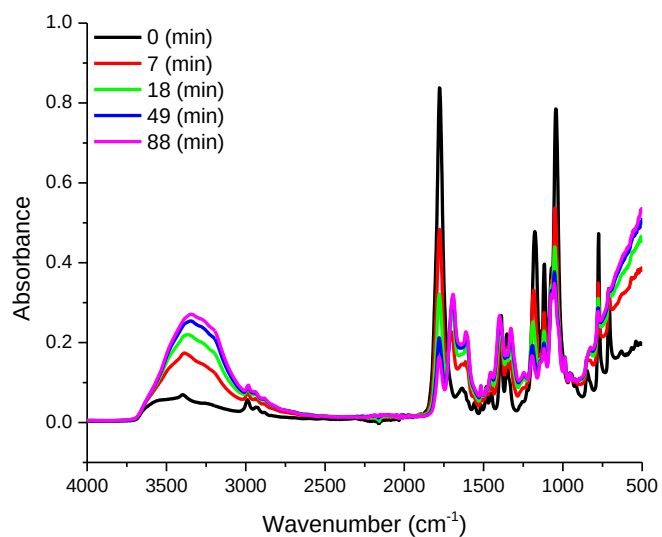


Figure 6.11. FTIR of the reaction of 4-HMP with propylene carbonate in the presence of NH_4OH over 88 minutes at ambient temperature. Spectral range is from 4000 to 500 cm^{-1}

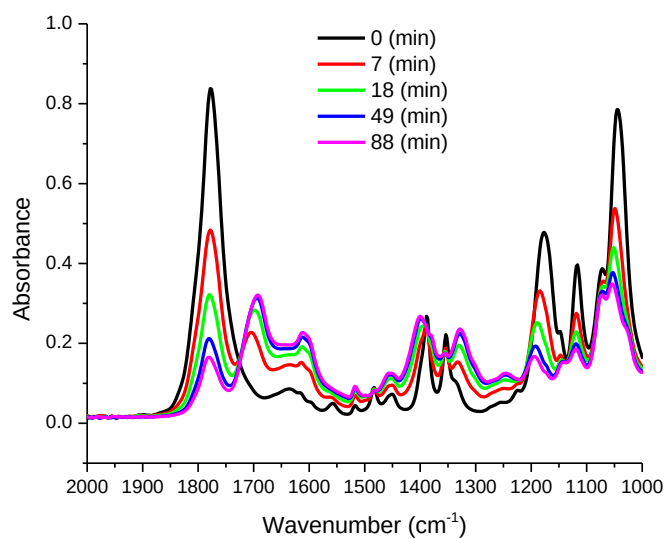


Figure 6.12. FTIR of the reaction of 4-HMP with propylene carbonate in the presence of NH_4OH over 88 minutes at ambient temperature. Spectral range is from 2000 to 1000 cm^{-1}

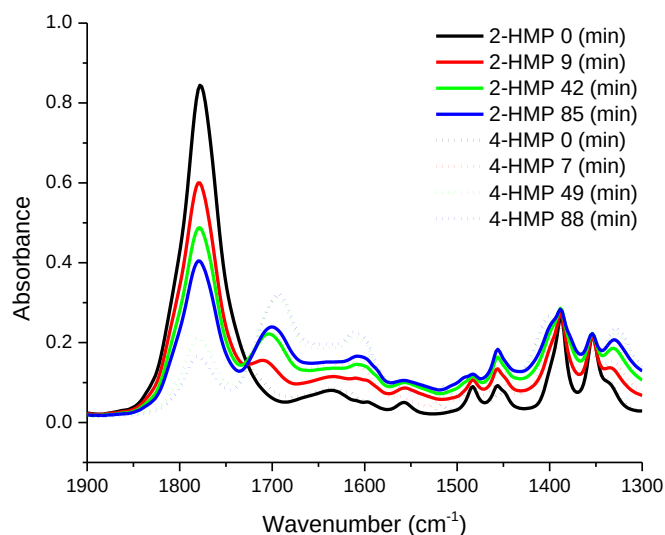


Figure 6.13. FTIR comparison of the reactions of 2-HMP and 4-HMP with propylene carbonate in the presence of NH_4OH over 88 minutes at ambient temperature. Spectral range is from 1900 to 1300 cm^{-1}

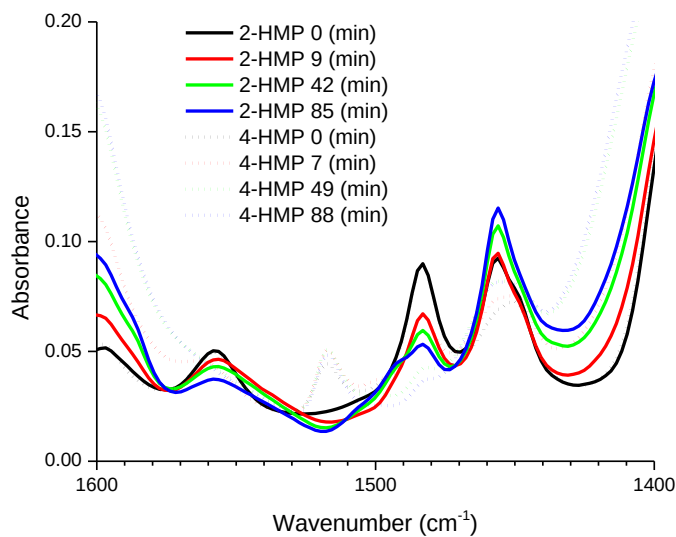


Figure 6.14. FTIR comparison of the reactions of 2-HMP and 4-HMP with propylene carbonate in the presence of NH_4OH over 88 minutes at ambient temperature. Spectral range is from 1600 to 1400 cm^{-1}

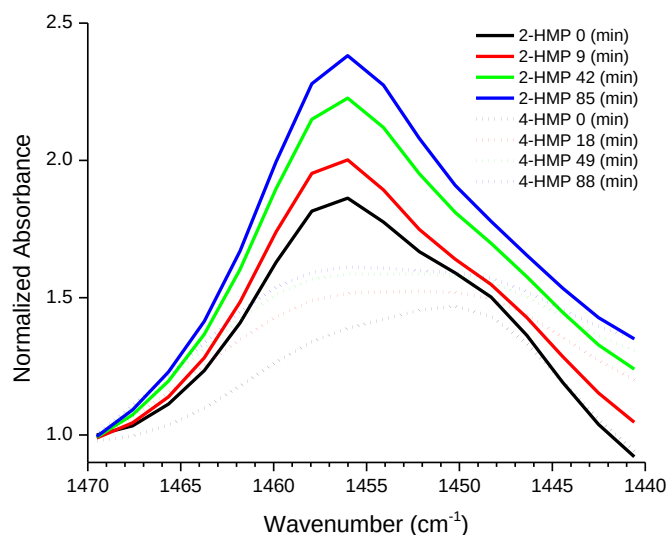


Figure 6.15. FTIR comparison of the reactions of 2-HMP and 4-HMP with propylene carbonate in the presence of NH_4OH over 88 minutes at ambient temperature. The spectral range is 1470 to 1440 cm^{-1} and is normalized to the absorbance of 2-HMP at 0 min. for 1470 cm^{-1}

6.3.2.1.3. Accelerated reactions PF model compounds dissolved in $\text{H}_2\text{O}/\text{DMF}$ in the presence of NaOH

The experimental conditions of Conner et al.³ were repeated on the ATR diamond plate with 2-HMP and 4-HMP using a series data acquisition scan. This method allowed comparison of these FTIR results to the NMR and their chromatographic results to provide additional interpretive information for the characterization of accelerated PF model compound reactions. Figures 6.16 through 6.18 show plots for the $\nu(\text{C-H})$ peak at 2955 cm^{-1} (Figure 6.16) and for the $\delta(\text{C-H})$ peaks at 1455 and 1446 cm^{-1} (Figures 6.17 and 6.18) as a function of time as the best mapping of the different possible methylene bridge formation reactions. A graph of the $\nu(\text{C=O})$ carbonyl peak at 1779 cm^{-1} of the propylene carbonate as a function of time illustrates the hydrolysis reaction (Figure 6.19). The graphs at 2955 (Figure 6.16) and 1455 cm^{-1} , (Figure 6.17) show the apparent development of methylene bridges for both 2-HMP and 4-HMP. The graph at 1446 cm^{-1} had the interesting development that while the peak for 4-HMP showed increasing concentration, the 2-HMP peak initially decreased, then increased in concentration (Figure

6.18). This observation may be attributed to overlapping peaks signifying initial hydrolysis of the propylene carbonate with formation of hydroxypropyl carbamate, followed by methylene bridge formation, similar to what was seen in Figures 6.14 and 6.15. What is interesting, is that the reaction of the 4-HMP did not exhibit this trend, consistent with the findings of Kamo et al. and Conner et al. regarding the reactivity of hydroxymethyl groups in the 2 and 4 positions,^{1,3} which appeared to have been the case in these reactions. From the relative intensities of these spectra, the extinction coefficient of the 4-HMP solution must have been lower than for the 2-HMP, since both solutions were prepared at the same concentration. Clearly, the propylene carbonate was consumed faster by reaction with 2-HMP than 4-HMP as seen in Figure 6.19, also consistent with the results in the literature.^{1,3} These results confirm the finding that propylene carbonate acceleration reactions prefer hydroxymethyl groups in the ortho positions rather than the para positions.¹ A further implication is that alkaline PF resoles with their higher free 2-hydroxymethyl content, as discussed in 2.1.2.2. regarding PF condensation reactions, are well suited for acceleration by propylene carbonate.

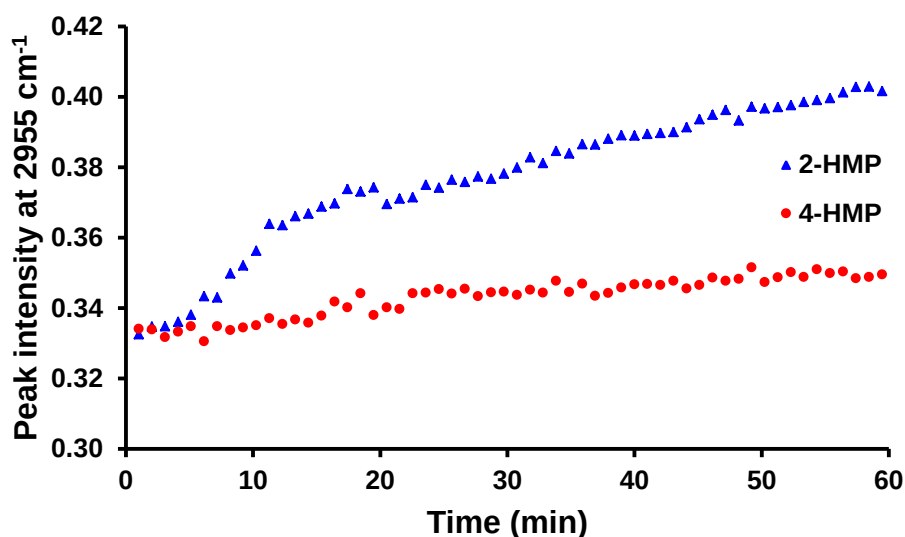


Figure 6.16. Hydrolytic acceleration of 2-HMP and 4-HMP condensation by propylene carbonate in H₂O:DMF 5:1 ratio, with NaOH, over 60 minutes at ambient temperature. FTIR spectral data is for intensity of the methylene $\nu(\text{C-H})$ peak at 2955 cm^{-1} from a baseline set from 3700 to 1900 cm^{-1}

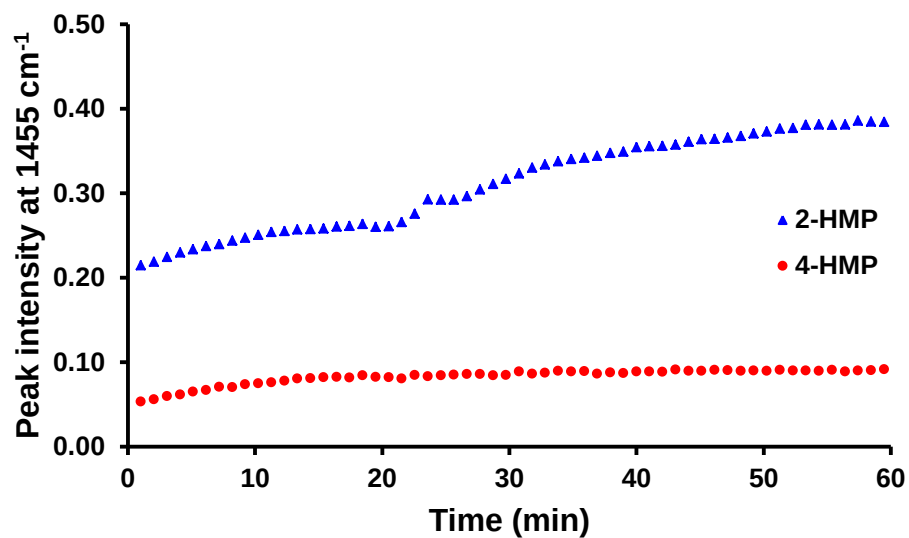


Figure 6.17. Hydrolytic acceleration of 2-HMP and 4-HMP condensation by propylene carbonate in H₂O:DMF 5:1 ratio, with NaOH, over 60 minutes at ambient temperature. FTIR spectral data is for intensity of the methylene δ (C-H) peak at 1455 cm⁻¹ from a baseline set from 1900 to 900 cm⁻¹

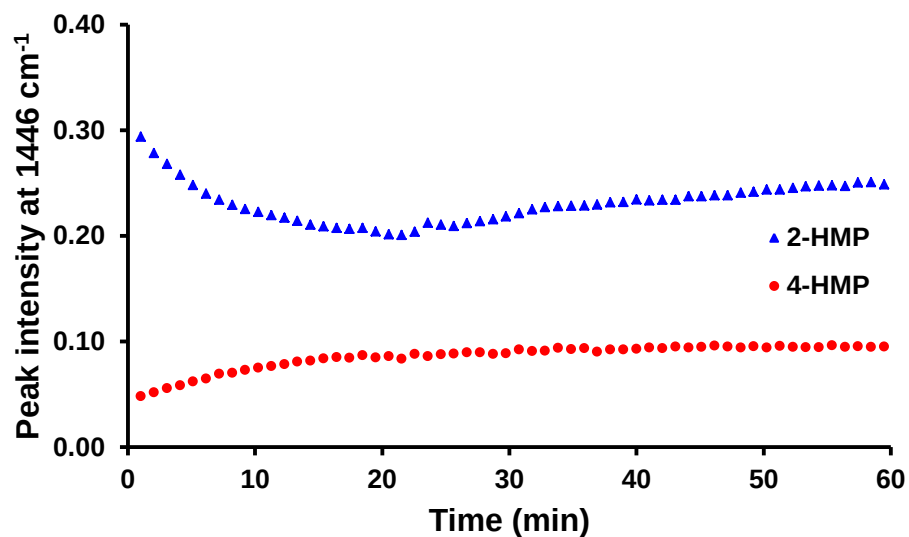


Figure 6.18. Hydrolytic acceleration of 2-HMP and 4-HMP condensation by propylene carbonate in H₂O:DMF 5:1 ratio, with NaOH, over 60 minutes at ambient temperature. FTIR spectral data is for intensity of the methylene δ (C-H) peak at 1446 cm⁻¹ from a baseline set from 1900 to 900 cm⁻¹

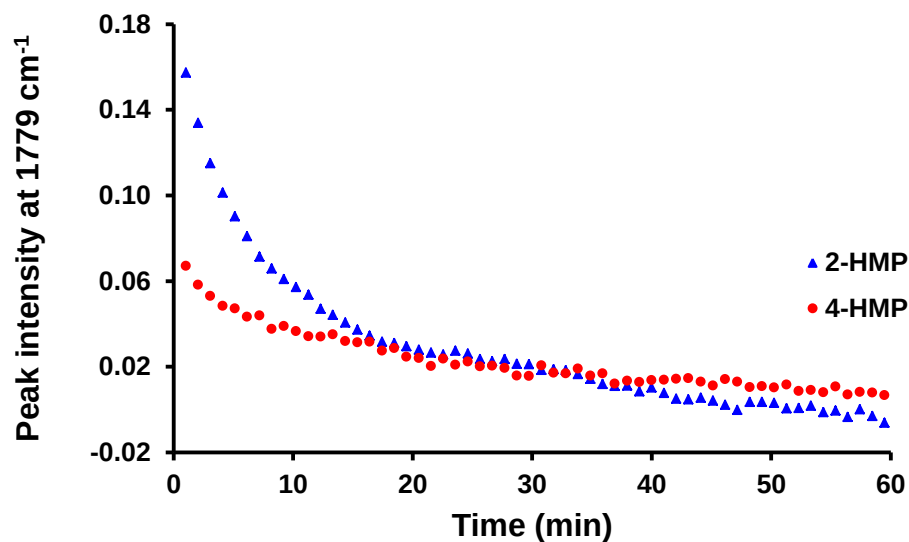


Figure 6.19. Hydrolytic acceleration of 2-HMP and 4-HMP condensation by propylene carbonate in H₂O:DMF 5:1 ratio, with NaOH, over 60 minutes at ambient temperature. FTIR spectral data is for intensity of the carbonyl $\nu(\text{C}=\text{O})$ peak at 1779 cm^{-1} from a baseline set from $1900\text{ to }900\text{ cm}^{-1}$

6.3.2.1.4. Accelerated reactions of oligomeric PF resoles at ambient temperature

6.3.2.1.4.1. FTIR spectra of oligomeric PF resoles

The FTIR spectra of oligomer PF resoles under four different polyurethane catalyst treatments were acquired for baseline purposes. An example spectrum is shown in Figure 6.20. The PF resole oligomers were prepared in a 2 x 2 factorial experimental design with variables of NH₄OH (0 and +) and SnCl₂ (0 and +). The SnCl₂ did not have a strong effect on the FTIR spectra. The NH₄OH, however, did lead to some shifts in spectral peaks, which are listed in the next chapter; the ammonium hydroxide reacted into the PF oligomer, altering its chemical structure.

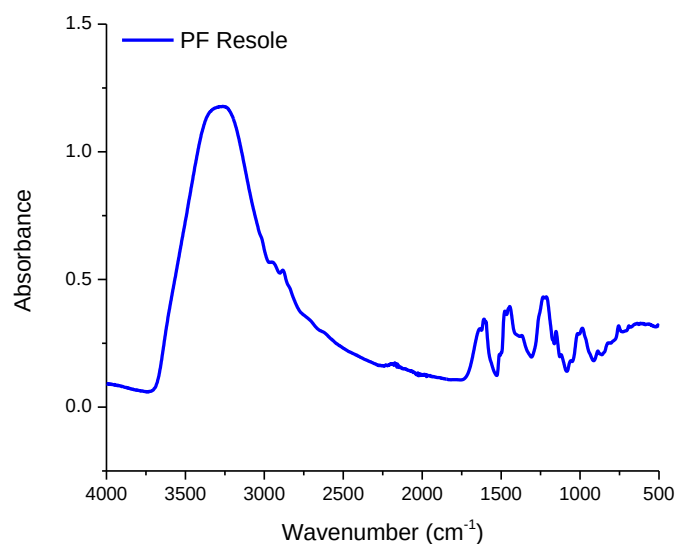


Figure 6.20. FTIR spectra of PF resole (no NH_4OH /no SnCl_2) from 4000 to 500 cm^{-1}

The challenge in studying reactions of PF resins by FTIR is that both the PF oligomer and its PC accelerator have methylene groups in their structure. In order to identify a peak that might specify the formation of methylene bridges without being obscured by other types of methylene present, the aliphatic C-H FTIR peaks of several model compounds and oligomeric PF resoles were compared as shown in Table 6.2. The best peak available without a close overlapping peak from the accelerator or its reaction products was at approximately 2955 cm^{-1} . This peak at 2955 cm^{-1} as well at peaks at 1455 and 1446 cm^{-1} were selected as the best potential representatives of methylene bridge formation and the propylene carbonate carbonyl peak at 1779 cm^{-1} was selected for accelerator hydrolysis.

Table 6.2. Important FTIR peaks of aliphatic C-H groups for PF models and PF resoles (cm⁻¹)

Models	alkane $\nu(\text{CH}_2)$				aliphatic $\delta(\text{C-H})$	$\delta(\text{CH}_2)$	
	in phase	out of phase				I	II
PC	2988	2936	2924	2881	1483	1450	
1,2-Pdiol	2969		2929	2874		1457	
2-HMP		2957		2875	1482	1457	
4-HMP		2956		2873			1449
PF resoles							
NH ₄ OH SnCl ₂							
o	o	2947		2884	1476		1445
+	o	2957		2885	1476	1458	1447
o	+	2957		2884	1476	1454	1446
+	+	2957		2986	1476	1458	1447
Literature ⁴		2953		2895	1478	1451	

6.3.2.1.4.2. FTIR spectra of the acceleration of oligomeric PF resoles by propylene carbonate

With a better understanding of the potential reaction peaks that could form in a dynamic system, the condensation reactions of an oligomeric PF resole with propylene carbonate were studied by ATR-FTIR at ambient temperature over 34 minutes. Spectral results tracking the progress of this reaction are shown in Figures 6.21 through 6.23, covering the range from 4000 to 500 cm⁻¹, 1900 to 900 cm⁻¹, and zoomed in to 1500 to 1400 cm⁻¹. In Figure 6.21 a clear decrease in the O-H stretching region is evident, however an unexpected increase in the propylene carbonate region was observed, as seen in Figure 6.22. Observation of the reacting sample showed that it formed an emulsion. The condensing PF polymer phase separated from the aqueous solvent, resulting in a denser polymeric phase that deposited on the ATR crystal, resulting in an interpretive artifact. Efforts to normalize the data gave no different results, thus, caution was necessary in interpreting these experimental results. Nonetheless, dynamic peak wavenumber shifts should still prove useful in detecting changes due to reactions.

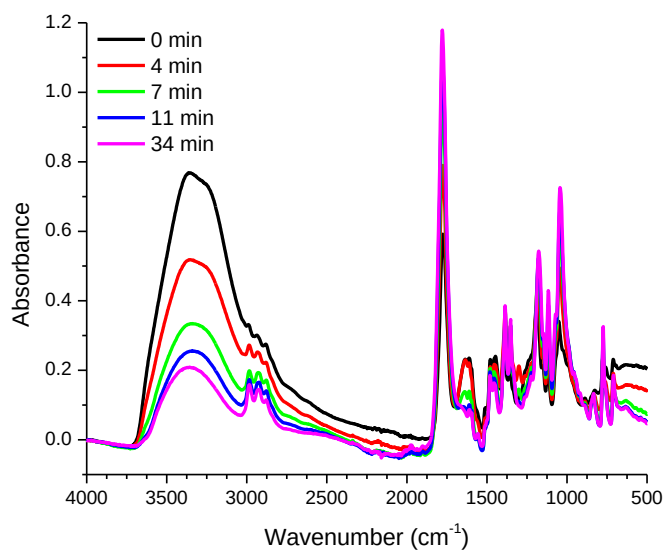


Figure 6.21. FTIR spectra for the reaction of a PF resole (no NH_4OH /no SnCl_2) with propylene carbonate from 4000 to 500 cm^{-1} over 34 minutes at ambient temperature

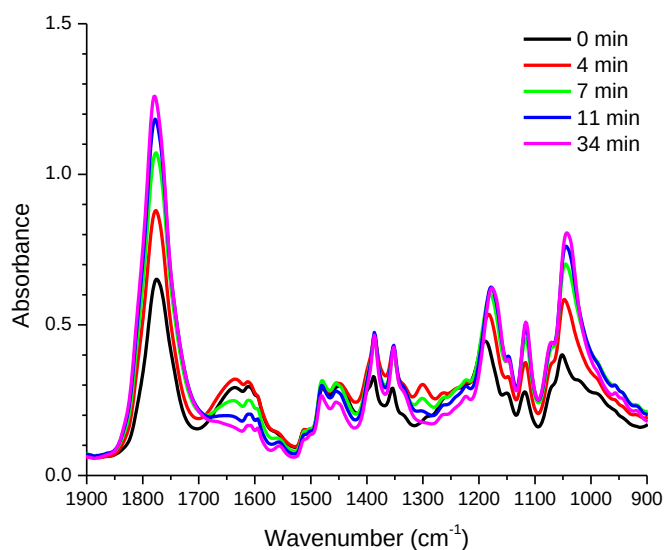


Figure 6.22. FTIR spectra for the reaction of a PF resole (no NH_4OH /no SnCl_2) with propylene carbonate from 1900 to 900 cm^{-1} over 34 minutes at ambient temperature

The zoomed spectra of Figure 6.23 show that the first and second peaks around 1445 cm^{-1} shift to 1455 cm^{-1} due to likely methylene bridge formation reactions taking place. The spectra at 0 and 4 minutes have a peak near 1445 cm^{-1} that initially increases, becoming the most

substantial methylene peak. At 7 minutes it diminished and the peak at 1455 cm^{-1} displays greater intensity for the rest of the reaction until 34 minutes reaction time. This peak shift is the strongest indicator of the methylene bridge formation by propylene carbonate acceleration.

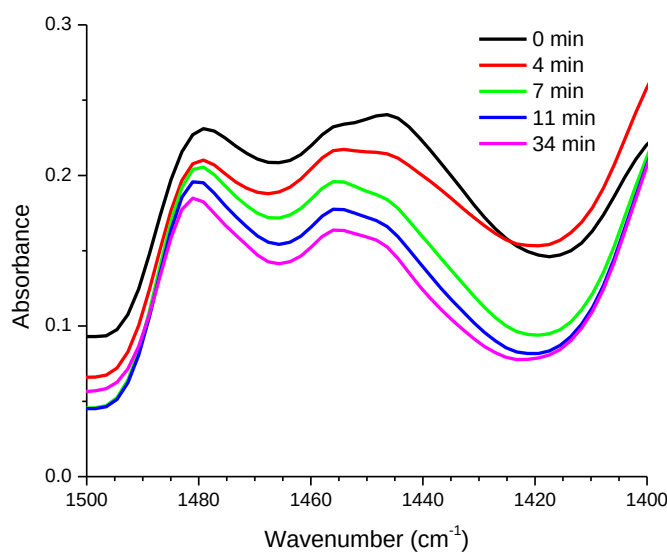


Figure 6.23. FTIR spectra for the reaction of a PF resole (no NH_4OH /no SnCl_2) with propylene carbonate in the methylene bridge region from 1500 to 1400 cm^{-1} over 34 minutes at ambient temperature

6.4. Conclusions

Monitoring the reactions of compounds modeling the hydrolysis of propylene carbonate and the accelerated condensation of PF monomers by ATR-FTIR revealed important peaks for interpreting the FTIR spectra of accelerated alkaline PF resoles condensation reactions. Real time hydrolysis of propylene carbonate by sodium hydroxide and ammonium hydroxide differentiated between their reaction products and provided reference peaks for future use. Real time acceleration condensation of 2-HMP and 4-HMP by propylene carbonate in the presence of ammonium hydroxide or sodium hydroxide provided reference information regarding methylene bridge formation. ATR-FTIR studies of previous research using NMR and

liquid chromatography regarding acceleration of 2-HMP and 4-HMP confirmed and augmented the earlier conclusion that propylene carbonate had a greater acceleration effect on 2-HMP than 4-HMP. The results of the model compound studies were useful for identifying changes that took place in the dynamic spectra for propylene carbonate hydrolysis, formation of hydroxypropyl carbamate, and for methylene bridge formation during PF condensation. Although the data was not unambiguous, the peaks in the 1445 to 1455 cm⁻¹ region were most useful for monitoring the accelerated condensation reactions of alkaline PF resoles at ambient temperature.

6.5. References

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Chapter 7: Structural Determination of Cross Catalyzed Reactions of PF and pMDI During Reaction and of their Copolymer in the Solid State

7.0. Overview

The objective of the investigation covered in this chapter was to determine the structure of the polymer generated by the cross catalyzed reactions of PF and pMDI. The approach had three major elements. First, the cross catalyzed reactions were followed with ATR-FTIR and interpreted on the basis of the earlier model compound studies. The effects of the stoichiometry of reactants on the structures produced during these cross catalyzed reactions were also probed with ATR-FTIR. Second, the solid polymeric reaction products were characterized by transmission FTIR. Third these same solid reaction products were studied by solid state ^{13}C CP/MAS NMR for correlation with the transmission FTIR results.

The results indicated that the reactions formed a copolymer comprising phenyl and benzyl urethanes, as well as methylene bridged phenolic condensates. Among the catalysts, ammonium hydroxide favored formation of phenyl urethanes, while tin(II)chloride may have favored formation of benzyl urethanes. The PF acceleration was more difficult to detect due to weaker peak intensity in FTIR and band broadening in CP/MAS NMR. The copolymerization was dependent on the reaction stoichiometry, requiring sufficient ratios of isocyanate to hydroxyls for effective co-reaction. Comparison of the CP/MAS results with the results for ^{13}C NMR of phenolic model compound reactions with phenyl isocyanate under alkaline conditions confirmed that the hydroxide to phenol molar ratio is directing the ratio of benzyl to phenyl urethanes formed in the copolymer.

7.1. Introduction

Determination of polymer structure in the solid state is more challenging than in solution. Due to solubility issues, solution NMR will not work with thermosets, so other methods are necessary. Solid state NMR is a suitable method for structural determination of these insoluble polymers. Cross polarization combined with magic angle spinning minimize band spreading due to lattice relaxation effects.

Some of the work using solid state NMR for wood bonding thermosets has focused on the interphase between the adhesive and wood.¹⁻⁷ Ni and Frazier studied the effects of high 2,4'-MDI and 4,4'-MDI contents in pMDI on the cured properties of wood bonded with pMDI with CP-MAS NMR. Isocyanates reacted with moisture present in the wood to form polyurea, with isocyanate dimerization and biuret formation also occurring. Urethane functional groups may have also formed, but were not clearly detected due to overlap of urea and urethane signals. The 2,4'-MDI was slower curing than the 4,4'-MDI.² Zhou and Frazier investigated urethane bonds to wood using pMDI resins doubly labeled isocyanate groups with ¹³C and ¹⁵N and solid-state NMR to minimize carbonyl carbon signal overlap.⁴ Using both ¹³C and ¹⁵N resulted in partial resolution of the urethane and urea carbonyl carbons.

Other solid state NMR has focused on the PF polymer structure and formation.⁸⁻¹¹ Beyond a few model compound studies,¹²⁻¹⁵ however, the literature on the solid state structure of PF-pMDI copolymers, is scant. Although Riedlinger studied PF-pMDI hybrid systems,¹⁶ he did not provide any data on the solid state chemical structure of the polymerized adhesive. Zheng et al. studied the bondlines of flakes bonded with neat PMDI and three aqueous PF/PMDI blends at 33/67, 50/50, 75/25 ratios. They concluded that the combination resulted in emulsions that would result in nano-scale phase separated morphology of the dispersed phase material within the continuous phase material. This phase separation could have resulted in toughening of the material in fracture toughness testing, with potential implications for bond performance. Zheng et al. also did not provide specific information on the structures formed.¹⁷

The technical challenge with identifying the structural reaction products of cross-catalyzed reactions of PF and pMDI is the complexity created by the number of reactants and reactions involved. The starting materials, an aqueous PF resole with a polyurethane catalyst and pMDI with propylene carbonate accelerator, contribute to the total number of peaks present. The possible reactions include catalyzed phenyl and benzyl urethane formation, accelerated phenolic self-condensation, the carbamic acid reaction, and propylene carbonate hydrolysis. The number of signals caused by these reactants and products present renders structural identification very difficult in either FTIR or NMR techniques.

As we have seen in Chapter 5, FTIR is able to differentiate among phenyl and benzyl urethanes in the carbonyl region. Although ATR-FTIR worked well with liquids and solutions, good results with solids were more difficult to obtain. Transmission FTIR with KBR pellets is a more suitable method for determining the functional groups present in such polymeric solids. Thus, using transmission FTIR along with solid state CP-MAS NMR should prove useful in identifying the structural components of the PF-pMDI copolymer. This study will investigate the structure of the accelerated PF-pMDI copolymer using CP-MAS NMR and transmission FTIR in the solid state after following dynamic reactions of the cross-catalyzed PF-pMDI reactions with ATR-FTIR

7.2. Experimental

7.2.1. pMDI

Two pMDI oligomers, Rubinate M and Rubinate 1245 were supplied by Huntsman Polyurethanes. Rubinate M has an isocyanate functionality of 2.70, an isocyanate content of 31.2%, and an equivalent weight of 135 g/mol. Its specific gravity is 1.23 at 25 °C, and nominal viscosity is 190 mPa·s at 25 °C. Rubinate 1245, a low viscosity pMDI, had a specified isocyanate functionality of 2.22, an isocyanate content of 32.8%, and an equivalent weight of 128 g/mol. Its specified specific gravity was 1.23 at 25 °C, and its nominal viscosity was 25 mPa·s at 25 °C.¹⁷ The pMDI was stored under a dry nitrogen blanket and used as received.

7.2.2. PF resin materials

The materials used for preparation of PF resins were phenol (Sigma-Aldrich, ≥ 99%), NaOH prills (Sigma-Aldrich, ≥ 98%), aqueous ammonium hydroxide (Sigma-Aldrich, 25%), deionized (DI) water, paraformaldehyde (Sigma-Aldrich, 95%), tin(II)chloride dihydrate (Sigma-Aldrich, 98%). The materials were used as received.

7.2.3. PF resin preparation apparatus

The PF Resin preparation apparatus comprised a 1000-mL glass reaction kettle with a four-neck glass top, a reflux condenser connected via a two-way glass adapter, a glass stirring rod assembly with a Teflon stir blade, and a rubber stopper fitted with an electronic thermocouple.

Exothermic heat was controlled with an ice water bath or vacuum reflux condenser connected to a water aspirator. The heating ramp and reaction temperature were controlled with an infrared lamp connected to a Barnant Temperature Controller Model R/S with feedback from the electronic thermocouple. Temperature control was within ± 0.1 °C. The glass stirring rod was connected via a flexible rotating joint to a BDC 2002 variable speed motor.

7.2.4. PF resin preparation

7.2.4.1. Synthesis of PF resin with sodium hydroxide

PF resin was prepared with phenol, NaOH prills, deionized (DI) water I, paraformaldehyde I, paraformaldehyde II, DI water II, and tin(II)chloride dihydrate. Phenol (255.6 g, 2.72 mol), NaOH prills (21.7 g, 0.54 mol), and DI water I (123.5 g, 6.85 mol) were added to the 1000-mL reaction kettle and dissolved with stirring. Paraformaldehyde I (50.9 g, 1.61 mol) was added in increments over 5 minutes to the kettle through a funnel, allowing it to dissolve and react. The reaction mix was heated to 47.0 °C to completely dissolve the reactants. Heat generated was controlled with cooling as needed to avoid a potentially hazardous reflux. The remaining paraformaldehyde II (99.3 g, 3.14 mol) was added over 51 min, using a powder addition funnel equipped with an auger feed for delivery of free-flowing prills to the reaction. The reaction temperature was 76.0 °C upon completion of the addition. DI water II (50.2 g, 2.78 mol) was used to rinse residual materials into the reaction vessel. Temperature was raised to 85.0 °C and was held for 60 min to produce a PF condensate, and then the reaction mixture was cooled to 25.0 °C over 22 min. The resin was split into two portions. Tin(II)chloride dihydrate (0.9225 g, 4.08 mmol) dissolved in DI water (1.0690 g, 59.32 mmol) was added to one portion of the PF condensate (300.17 g). Each resin portion was placed in a glass bottle and stored at 4 °C. The formulated F:P molar ratio was 1.75 and the NaOH:P molar ratio was 0.20.

7.2.4.2. Synthesis of PF resin with sodium hydroxide and ammonium hydroxide

PF resin was prepared with phenol, aqueous ammonium hydroxide, DI water I, paraformaldehyde I, NaOH prills, paraformaldehyde II, and DI water II. The phenol (257.2 g, 2.73 mol), aqueous ammonium hydroxide (76.8 g, 0.55 mol), and DI water I (65.4 g, 3.63 mol)

were added to the 1000 m reaction kettle and dissolved with stirring. The paraformaldehyde I (51.2 g, 1.70 mol) was added in increments over 4 minutes to the kettle through a funnel, allowing it to dissolve and react. The reaction mix was heated to 36.0 °C promote dissolution; any exothermic reaction was controlled with cooling as needed to avoid a hazardous reflux while the temperature was allowed to rise to 70.0 °C. Since the materials would not go into solution, NaOH prills (21.7 g, 0.54 mol) were added to the reactor. The paraformaldehyde II (100.1 g, 3.33 mol) was added over approximately 60 minutes using a powder addition funnel. The DI water II (50.0 g, 2.77 mol) was used to rinse residual materials into the reaction vessel. Heat was applied to reach 85.0 °C and that temperature was held for 67 minutes when cooling to 25.0 °C commenced over 33 minutes. The resin was split into two portions, one of PF condensate (300.06 g) to which tin(II)chloride dihydrate (0.9137 g, 0.405 mmol), dissolved in DI water (1.08 g, 5.993 mmol), was added to it. Both resin portions were placed in glass bottles and stored at 4 °C. The formulated F:P molar ratio was 1.75, the NH₄OH:P molar ratio was 0.20, and the NaOH:P molar ratio was 0.20.

7.2.5. Copolymer preparation

A mix of Rubinate M and Propylene Carbonate (PC, Sigma Aldrich 99%) was prepared at a 9 to 1 weight ratio of pMDI:PC. Using 5 mL syringes, 2 mL and 4 mL of each PF resin-catalyst combination was put into a 20 mL glass vial and weighed, to which 2 mL of the pMDI-PC mix was added and weighed, for a total of 8 combinations. Weights were measured to 0.1 mg accuracy. After addition, the components were stirred together with a Teflon coated stirring rod at ambient temperature (25 °C) and allowed to stand overnight. The samples were vacuum dried for 6 days using a Fisher Isotemp Vacuum Oven (Model 281) set at -94 kPa using a BOC Edwards XDS 5C vacuum pump. Vacuum drying was done at ambient temperature. Upon removal the samples were desiccated over calcium chloride for another for at least another 9 to 11 days until they were dry enough to pulverize with a mortar and pestle. The pulverized samples were placed into separate glass vials and stored in the dessicator for solid state NMR and FTIR analysis.

7.2.6. ATR-FTIR

Dynamic ATR-FTIR scans were performed using a Nicolet 8700 spectrometer equipped with a Pike Technologies Gladiator ATR accessory. The ATR had a diamond crystal with dimensions of 2.2 x 3.0 mm. Absorbance was measured between 4000 and 500 cm^{-1} , using 32 scans at 4 cm^{-1} resolution unless otherwise specified, and ATR correction. A background scan was completed prior to FTIR data acquisition.

The reactants were the mixture of the PF resin as prepared in sections 7.2.4. and 7.2.5. and the Rubinate M and PC prepared at 9 to 1 weight ratio of section 7.2.6. A droplet of each liquid was placed on a glass slide from a glass pipette or a 1.0 mL microliter syringe prior to mixing. The droplets of each solution were mixed quickly with a glass stirring rod and a small amount of the mixture sufficient to cover the surface of the ATR crystal was placed onto it. The sample on the ATR diamond crystal was covered with an inverted watch glass to prevent evaporation or contamination.

7.2.7. FTIR

Potassium Bromide (KBr) pellets of the dry copolymer samples prepared were made from ~200 mg KBr and ~3 mg of copolymer sample weighed to 0.1 mg accuracy. The KBr was Acros IR grade. FTIR was run on a Nicolet 8700 FTIR in transmission mode. A total of 64 background scans and 1024 sample spectral scans were acquired over the range from 4500 to 500 cm^{-1} . Resolution was 4 cm^{-1} and the aperture setting was 100. Data was analyzed using OMNIC software by Thermo Electron Corporation.

7.2.8. CP/MAS NMR

Solid state CP/MAS ^{13}C was run on a 300 MHz Bruker Avance II NMR spectrometer operating at 75.47 MHz for ^{13}C using 4-mm zirconium rotors. Magic Angle Spinning was at 9 KHz. The contact time was X milliseconds. About 2000 scans were run for the ^{13}C CP/MAS analysis using a standard cross polarization pulse sequence.

7.3. Results and discussion

7.3.1. FTIR studies of catalyzed and accelerated reactions of PF and pMDI oligomeric prepolymers

Time dependent vibrational spectroscopy has aided the understanding of the dynamic transformations that occur during chemical reactions and polymerization.¹⁸⁻²³ Thus, this technique should also be useful for studying the catalyzed and accelerated reactions of PF and pMDI oligomeric prepolymers. Acquisition of spectra for the PF and pMDI oligomers, NH_4OH catalyst, and propylene carbonate accelerator was necessary for to provide a baseline for comparison of the effects of mixing and of changes due to reactions. With baseline spectra available, the dynamic reaction of PF and pMDI was studied as a control for reactions of PF and a pMDI/PC blend catalyzed either with NH_4OH or the combination of NH_4OH and SnCl_2 . These reactions yielded detailed spectral information regarding not only the reaction products, but equally as important for understanding structure, the pathway to those products.

Two further studies on the spectra of those reaction products provided information linking the dynamic reaction pathways to the polymer structure. The first investigation related the ratio of PF and pMDI components to the polymeric structure generated and to stoichiometric effects that would be expected with step growth polymerization. The second study researched the effects of the PF catalyst combinations and the ratio of PF and pMDI components on the structure of the solidified polymer formed using transmission FTIR of solid polymer samples embedded in KBr pellets. This second set of samples was also the subject of the solid state NMR study. Together, these studies aided in connecting the studies on the overall reaction chemistry from raw materials through the reactive process to their polymeric products.

7.3.1.1. Reference spectra for base materials

The ATR-FTIR spectra of the PF base oligomers had significant differences due to treatment with NH_4OH as shown in Figure 7.1, but not due to treatment with SnCl_2 (not shown).

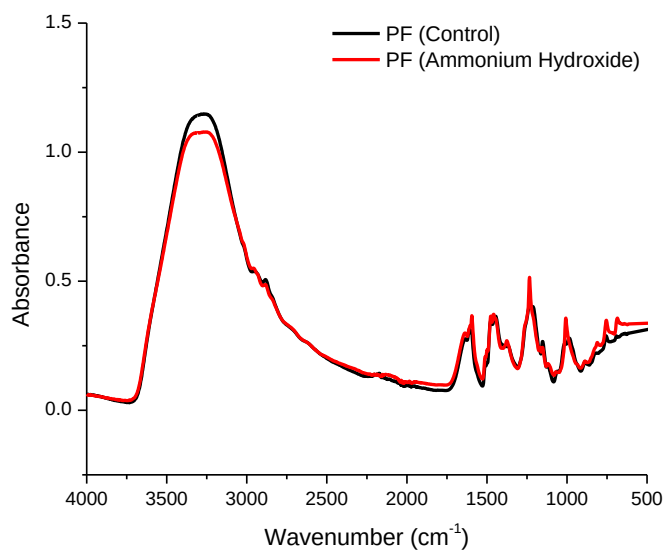


Figure 7.1. FTIR spectra of PF resin prepared with and without NH_4OH from 4000 to 500 cm^{-1}

The distinctive difference among the NH_4OH modified PF resins was the sharper single peaks in the fingerprint region as seen in Figure 7.2.

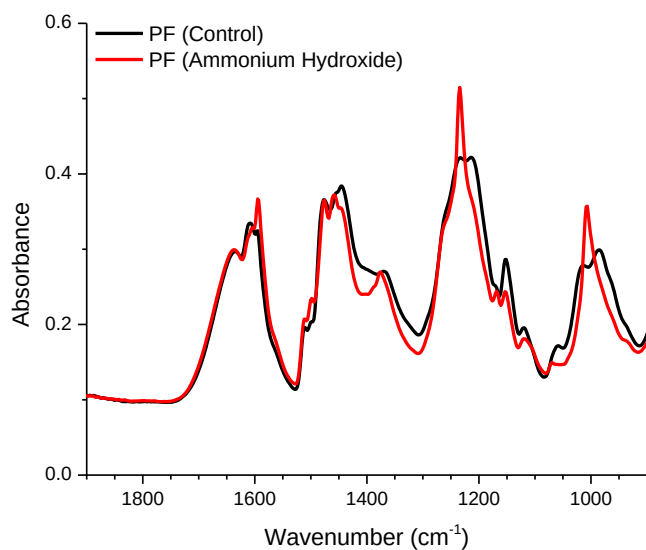


Figure 7.2. FTIR spectra of PF resin prepared with and without NH_4OH from 1900 to 900 cm^{-1}

7.3.1.2. Reaction of PF and pMDI

A reaction of uncatalyzed PF and pMDI oligomers at ambient temperature for over 20 minutes provided a control baseline for any reactions of the two components that may occur in the absence of catalyst or accelerator. Spectra representative of the dynamic changes taking place during the reaction are shown for the range of 4000 to 500 cm^{-1} in Figure 7.3. Clearly reactions occurred among the components of the mixture as seen in the O-H/N-H stretching region in Figure 7.4. Although the N=C=O peak intensity at 2243 cm^{-1} decreased slightly, most of the isocyanate functional groups remained after 25 minutes reaction time.

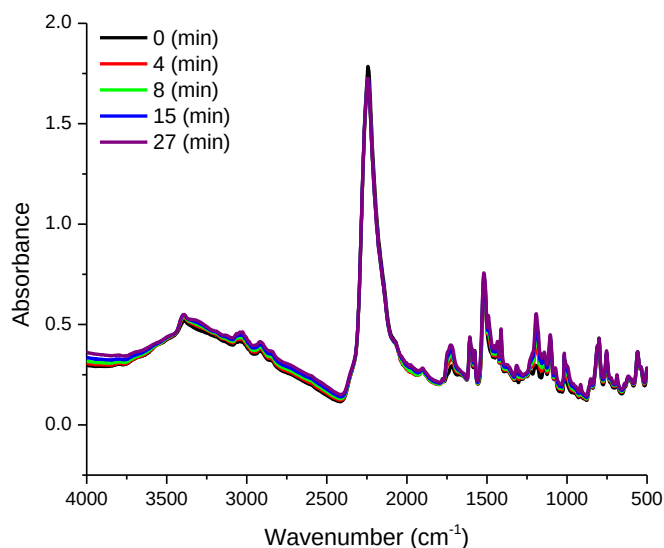


Figure 7.3. Real time FTIR of the uncatalyzed reaction between PF and pMDI at ambient temperature from 4000 to 500 cm^{-1}

In the hydrogen stretching region for O-H, N-H, and C-H from 3700 to 2800 cm^{-1} shown in Figure 7.4, the peak at 3390 cm^{-1} increased with time and a new rounded peak formed as a shoulder to it in the range of 3350 to 3225 cm^{-1} .

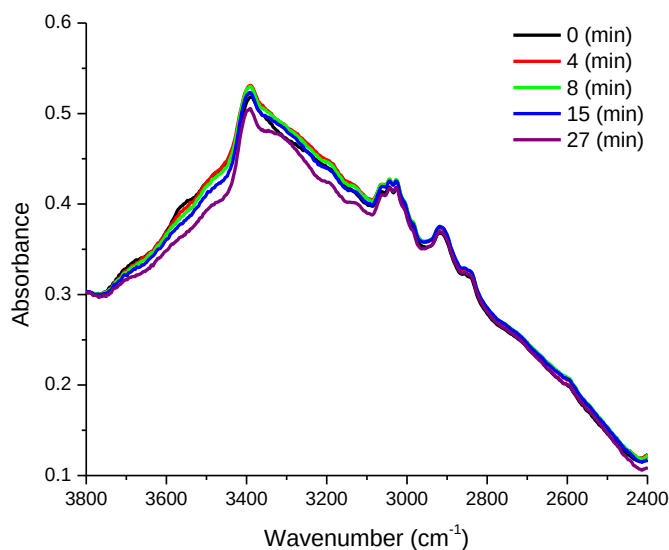


Figure 7.4. Real time FTIR of the uncatalyzed reaction between PF and pMDI at ambient temperature for the O-H, N-H, and C-H stretching region from 3800 to 2400 cm⁻¹

These developing peaks are suggestive of the formation of N-H groups within a urethane or a urea structure when compared to the peaks for the model urethane compounds and 1,3-DPU.

In the fingerprint region from 1800 to 600 cm⁻¹ shown in Figure 7.5, the results indicated two important trends. One, most of the reaction products formed in the phenyl urethane region with peaks at 1745 cm⁻¹ and 1725 to 1719 cm⁻¹; rather than the benzyl urethane region at lower wave numbers. Two, the minimal peak changes at 1638, 1555, and 1512 cm⁻¹ indicated that the carbamic acid reaction was limited.

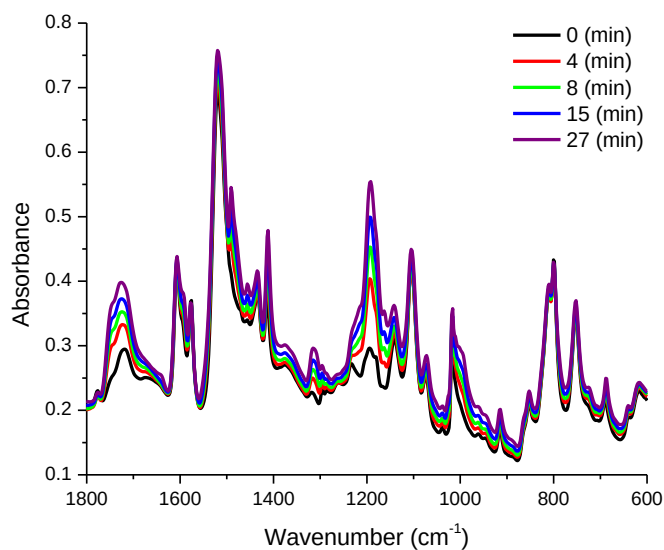


Figure 7.5. Real time FTIR of the uncatalyzed reaction between PF and pMDI at ambient temperature for the fingerprint region from 1800 to 600 cm^{-1}

The growing peak at 1192 cm^{-1} is likely due to $\nu(\text{C-O-C})$ as a result of phenyl urethane formation. A similar peak was present at 1193 cm^{-1} in the reaction products of phenol and pMDI in the presence of DBTL or TEA, but not for reactions of benzyl alcohol and pMDI in the presence of DBTL or TEA. Also, reactions of phenol with phenyl isocyanate had peaks at 1195 and 1196 cm^{-1} , while reactions with benzyl alcohol did not. This additional data lends evidence to the case for $\nu(\text{C-O-C})$ identification.

The initial carbonyl observed may be due to the lag time involved in the data acquisition for the first spectra, as each spectra required about one minute real time to run. Mixing time and application time also would have permitted some reactions to occur. Furthermore, since the carbonyl peak is an intense peak, even low concentrations could be observed. Another increasing peak is present at 980 cm^{-1} . Although its identity is not certain, Poljansek attributed a PF peak at 976 to 1,2,4 substituted benzene rings,¹⁹ which would represent the presence of 2,4-DHMP and 2,4 substituted phenolic oligomers, both likely to be present in this PF resole.

7.3.1.3. Cross-catalyzed reactions

The real time series of ATR-FTIR spectra for the combination of PF modified by NH_4OH and reacted with a mixture of pMDI and PC ($[\text{PF} + \text{NH}_4\text{OH}] \times [\text{pMDI} + \text{PC}]$) are shown in Figures 7.6 through 7.9. Key features of these spectra worth noting are the buildup of the hydrogen bonding material due to urethane formation and PC hydrolysis in the 3300 cm^{-1} region shown in Figure 7.6. Also to be noted in Figure 7.7 is the decrease in the intensity of the $\nu(\text{N}=\text{C}=\text{O})$ peak ranging from 2243 to 2246 cm^{-1} during the course of the reaction.

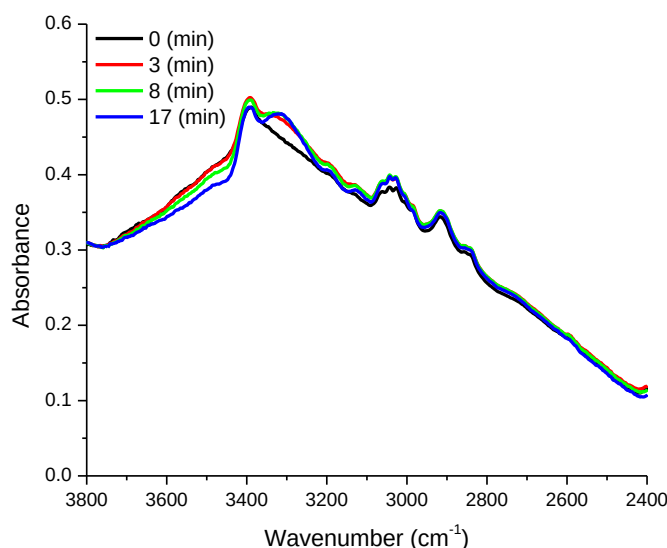


Figure 7.6. Real time FTIR of the cross-catalyzed reactions of (PF + NH_4OH) and (pMDI + PC) at ambient temperature over 17 min. for the O-H and N-H stretching range of 3800 to 2400 cm^{-1}

The spectra in Figure 7.8 show the dynamic changes occurring in the fingerprint region with a closer zoom to the range from 1900 to 1300 cm^{-1} in Figure 7.9. The shoulder at 980 cm^{-1} that was evident in uncatalyzed phenyl urethane forming reactions of PF and pMDI, is present in these reactions also as seen in Figure 7.8. The PC carbonyl $\text{C}=\text{O}$ stretching peak at 1779 cm^{-1} is clearly decreasing in intensity due to its consumption under hydrolysis. The amide I peaks between 1750 to 1650 cm^{-1} are simultaneously increasing, with the peak at 1722 cm^{-1} also being indicative of phenyl urethane formation. The peak forming at 1490 cm^{-1} is possibly an

amide II peak and it was also present in the uncatalyzed phenyl urethane forming reactions of PF and pMDI. The peak at 1455 cm^{-1} for the aliphatic methylene deformation is increasing suggesting that methylene bridge formation is indeed occurring. To further check whether this increase in intensity was due to methylene bridge formation, the increase in intensity was compared to that for several other reaction systems, including some of the model compound reactions as controls, shown in Table 7.1. For the control reactions, the change in intensity was fairly similar, about 17%, while for the cross-catalyzed reactions it was substantially higher: 23% for NH_4OH catalysis and 45% for combined NH_4OH and SnCl_2 catalysis. Though not conclusive, these results point towards accelerated methylene bridge formation induced by the hydrolytic reaction of PC.

Table 7.1. Percent increase in peak intensity for methylene group peaks in the $1455\text{ to }1450\text{ cm}^{-1}$ range

Reaction System	$\Delta I/I_0 \times 100\%$
PC x NaOH (control)	18.4%
PC x NH_4OH (control)	17.2%
PF x pMDI (control)	16.2%
[(PF + NH_4OH) x (pMDI + PC)]	23.0%
[(PF + NH_4OH + SnCl_2) x (pMDI + PC)]	45.0%

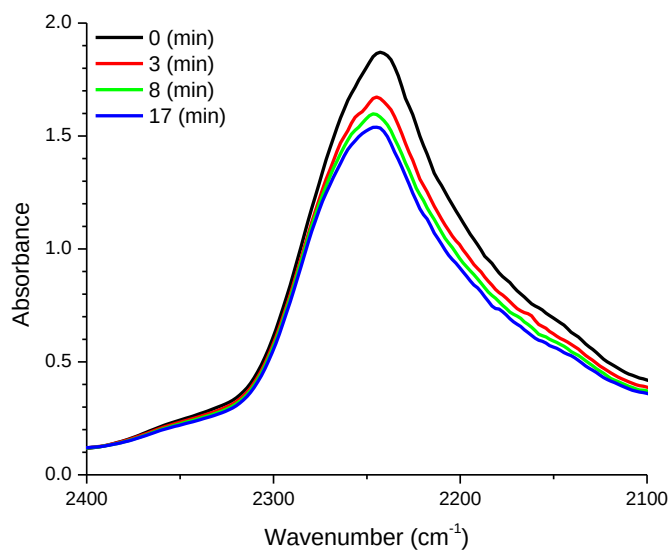


Figure 7.7. Real time FTIR of the cross-catalyzed reactions of (PF + NH₄OH) and (pMDI + PC) at ambient temperature over 17 min. for $\nu(\text{N}=\text{C}=\text{O})$ from 2400 to 2000 cm⁻¹

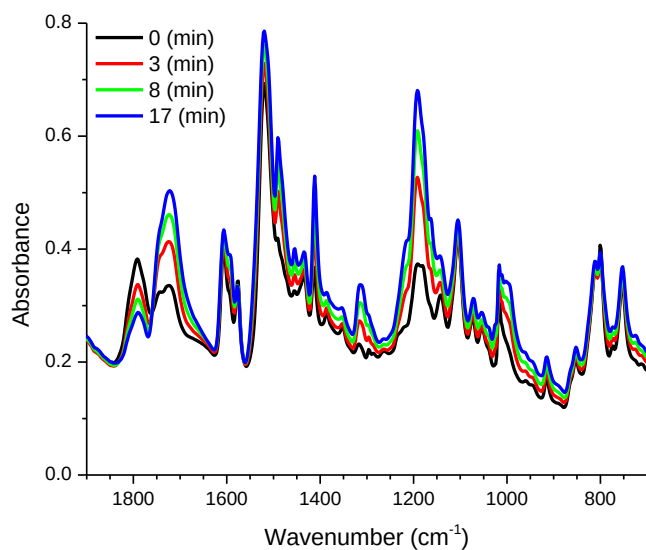


Figure 7.8. Real time FTIR of the cross-catalyzed reactions of (PF + NH₄OH) and (pMDI + PC) at ambient temperature over 17 min. for the fingerprint region of 1900 to 700 cm⁻¹

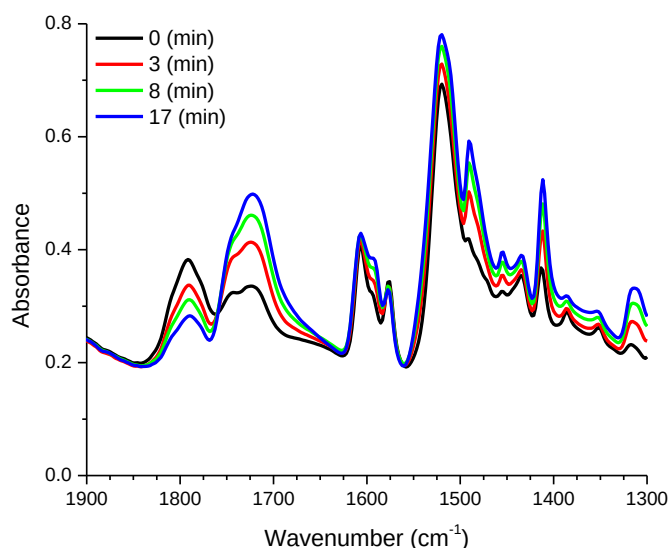


Figure 7.9. Real time FTIR of the cross-catalyzed reactions of (PF + NH₄OH) and (pMDI + PC) at ambient temperature over 17 min. for the carbonyl and amide bands from 1900 to 1300 cm⁻¹

Figure 7.10 shows the spectral results for the time lapse study of the PF-pMDI reaction cross-catalyzed with the NH₄OH/ SnCl₂ combination. Several important features were indicative of benzyl urethane formation. First, the amide I peak region between 1700 and 1650 cm⁻¹ showed more material accumulated in this region than the NH₄OH only catalyzed system, which, as was pointed out earlier in Chapter 5, is associated with the formation of benzyl urethanes. Second, peaks at 1593 and 1512 cm⁻¹ are distinctly present, paired with peaks at 1604 and 1520 cm⁻¹ that are not clearly seen in the NH₄OH only catalyzed system, though they are likely present as shoulders. Since the NH₄OH only catalyzed system is known to favor formation of phenol urethanes, this data is the first clear evidence that the SnCl₂ influences and favors the formation of benzyl urethanes. Also, the dual NH₄OH/ SnCl₂ catalyst system was observed in other experiments to lead to the most complete isocyanate reactions.

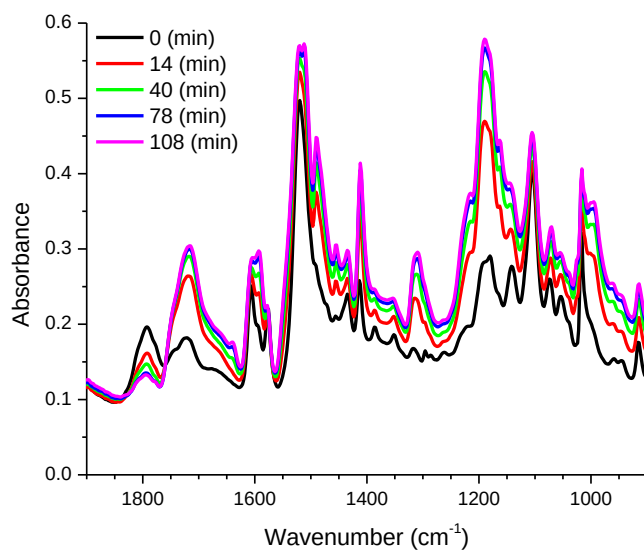


Figure 7.10. Real time FTIR of the cross-catalyzed reactions of (PF + NH₄OH + SnCl₂) and (pMDI + PC) at ambient temperature over 110 min. for the carbonyl and amide bands between 1900 to 900 cm⁻¹

Figure 7.11 shows the O-H/N-H/C-H stretching region for the time lapse study of the PF-pMDI reaction cross-catalyzed with the NH₄OH/SnCl₂ combination. The key feature to note in these spectra is the relative intensity of the peak at 3304 cm⁻¹ is greater than its surrounding peaks than the NH₄OH only catalyzed system. This observation is another indication of the more complete reaction fostered by the NH₄OH/ SnCl₂ catalyst combination.

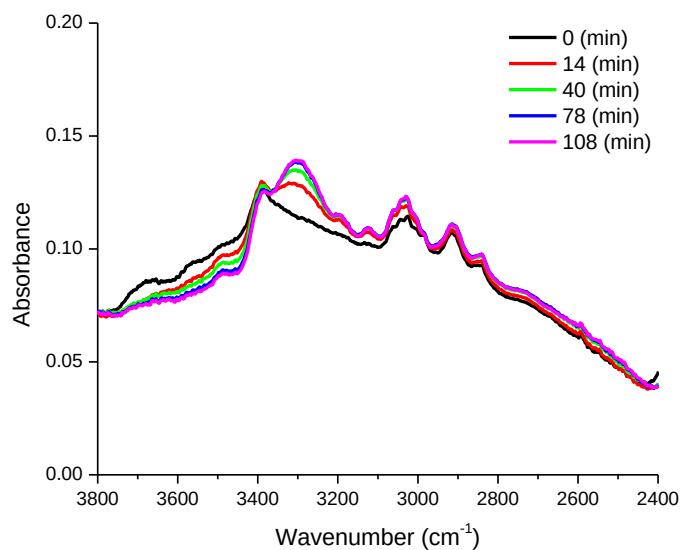


Figure 7.11. Real time FTIR of the cross-catalyzed reactions of (PF + NH₄OH + SnCl₂) and (pMDI + PC) at ambient temperature over 110 min. for the O-H and N-H stretching range from 3800 to 2400 cm⁻¹

7.3.1.4. PF-pMDI stoichiometry reactions

PF condensation and urethane formation reactions are classic examples of step growth polymerization. As such, these reactions should be subject to limitations based upon stoichiometric ratios for complete reaction. In order to test this sub-hypothesis, a series of cross-catalyzed reactions were run to demonstrate the effect of material proportions on urethane formation. The (wt./wt.) ratios of PF to pMDI were 20:80, 40:60, 50:50, 60:40, and 80:20 based on liquid weight. The materials were pre-dissolved in THF in order to ensure complete mixing and reaction, as earlier experiments had shown that mixing might be diffusion limited due to the rapid polymer formation and solidification. ATR-FTIR was run on gels from these mixes as well as supernatant liquids that separated from the gels over time.

Table 7.2. Calculated molar ratios of reactants for the FTIR study of the stoichiometric effects on the cross catalyzed reactions of PF and pMDI

Weight ratios of the THF solutions		Quantity of reactants in mmol						Calculated molar ratios		
PF with NH ₄ OH	pMDI-PC	Φ-OH	CH ₂ -OH	Total OH	1245	M	total NCO	PC	(total) OH:NCO	PC:CH ₂ OH
80	20	7.384	12.923	20.307	1.158	0.275	1.433	0.203	14.173	0.016
60	40	5.175	9.057	14.232	2.216	0.526	2.742	0.388	5.190	0.043
50	50	4.803	8.405	13.208	2.855	0.678	3.533	0.499	3.739	0.059
40	60	3.698	6.472	10.170	3.481	0.827	4.308	0.609	2.361	0.094
20	80	1.732	3.031	4.763	4.506	1.070	5.576	0.788	0.854	0.260

Figure 7.12 illustrates the effect of the PF component on the O-H/N-H stretching region for the gels; the higher the PF concentration, the stronger the signal from 3600 to 3100 cm⁻¹.

Conversely, the higher the pMDI concentration, the weaker the signal was from 3600 to 3100 cm⁻¹. These spectra also exhibited a strong signal in the C-H stretching region from 3000 to 2800 cm⁻¹ due to their THF content. The fingerprint region from 1900 to 1100 cm⁻¹ is shown in Figure 7.13 provided great detail regarding the effects of these varied ratios. The propylene carbonate peak at 1779 cm⁻¹ was present in all spectra except the 20:80 mix, where it must have been completely consumed, due to the relatively low amount of PC present. Urethane related peaks were evident around 1725, 1658, 1538, 1509, and 1190 cm⁻¹. PF related peaks were evident around 1475, 1457, 1365, and 1234 cm⁻¹, with aromatic stretching peaks at 1606 and 1594 cm⁻¹ and at 1512 cm⁻¹. Figure 7.14 shows how the peak intensities for the maximum amide I peak and the 1538 cm⁻¹ peak vary as a function of weight percent PF resin. In this experiment, the 40% PF to 60% pMDI ratio gave the highest proportion of urethane reaction products. Ratios lower or higher than this amount dropped systematically, indicating that the maximum formation of polymer depends on the proportion of functional groups present in each system. The spectra of the supernatant floating on the top of the gel in Figure 7.15 shows the effects of residual PF and any 1,2-propane diol formed by hydrolysis in the O-H stretching region. Figure 7.16 shows that PC, PF and possibly NaHCO₃ were present in solution within the supernatant.

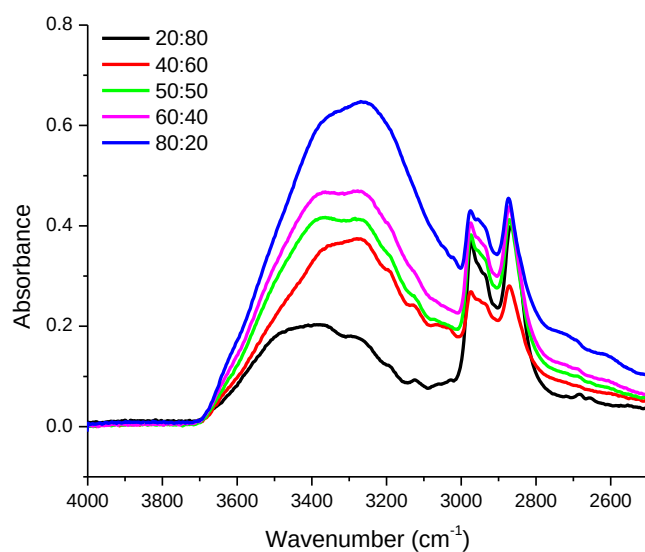


Figure 7.12. Stoichiometry blends PF:pMDI (wt.:wt.) gels in H₂O/THF from 4000 to 2500 cm⁻¹

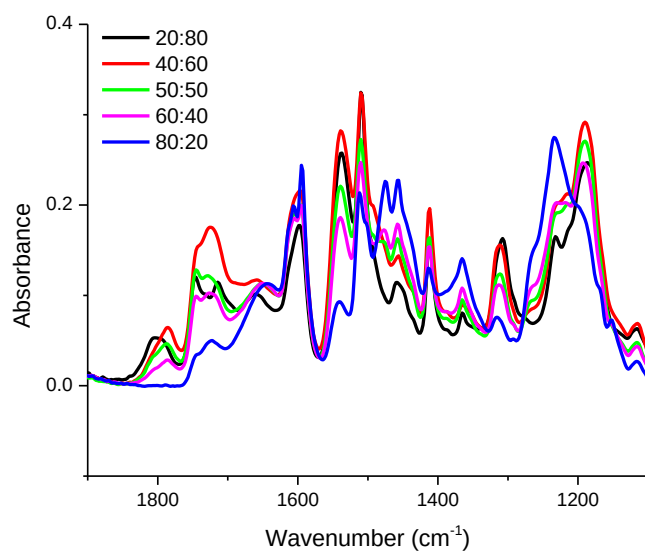


Figure 7.13. Stoichiometry blends PF:pMDI (wt.:wt.) gels in H₂O/THF from 1900 to 1100 cm⁻¹

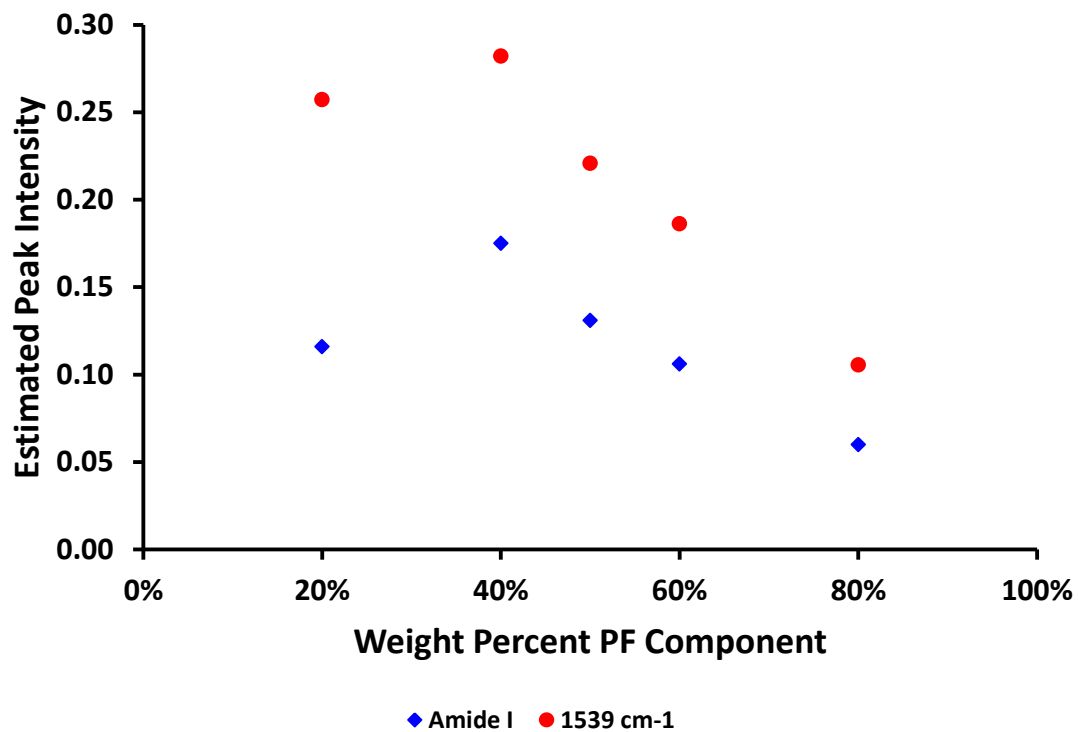


Figure 7.14. Peak intensities as a function of PF weight percent in the reaction mix with a pMDI/PC blend for five different PF to pMDI mix ratios

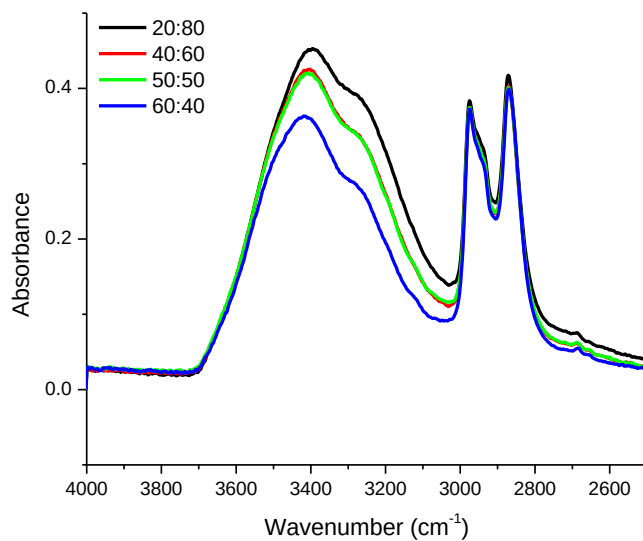


Figure 7.15. Stoichiometry blends PF:pMDI (wt.:wt.) supernatant (sol) in H₂O/THF from 4000 to 2500 cm⁻¹

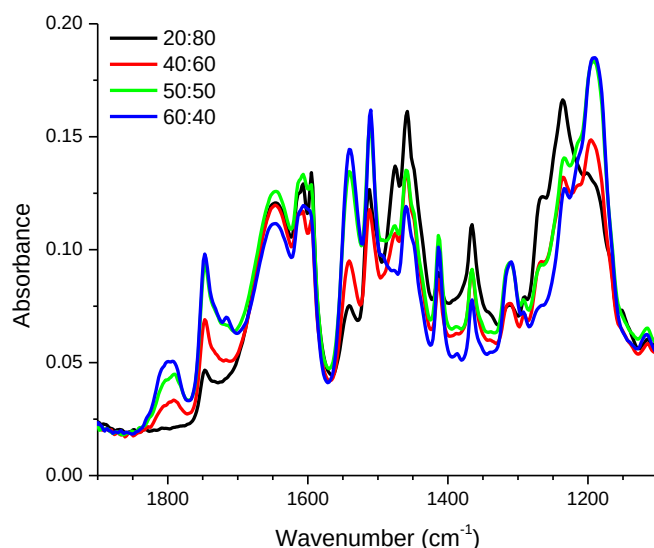


Figure 7.16. Stoichiometry blends PF:pMDI (wt.:wt.) supernatant (sol) in H₂O/THF from 1900 to 1100 cm⁻¹

7.3.2. Transmission FTIR results

7.3.2.1. Solid state transmission spectroscopy

The dynamic scans following the polymerization reactions with ATR-FTIR method provided insight into the reaction pathway due to the ability to apply the reactive liquids directly to the ATR crystal. For the solid polymer product, however, transmission spectroscopy using KBr pellets proved to be a better means of acquiring detailed spectra in the solid state with less spectral noise than the ATR method would permit with the solid powders. Table 7.3 shows the molar quantities of these reactants. Spectral data was compiled and averages were calculated for each of the main factor effects and for the catalyst sub-combinations.

Figure 7.17 compares the averages for the effects of PF to pMDI ratios over the entire FTIR frequency range from 4000 to 500 cm⁻¹. Inspection of these averages from 4000 to 2000 cm⁻¹ (Figure 7.18.) revealed that the higher ratio of PF to pMDI resulted in lower isocyanate content,

due to lower starting proportions and possibly due to reaction. Figure 7.19 shows how the higher levels of pMDI led to more urethane formation via the amide I bands. Also, the proportion of the amide I bands above 1700 cm^{-1} suggests that more phenyl urethanes were formed by this combination.

The presence of NH_4OH catalyst led to a more complete reaction of the phenolic hydroxyls and/or hydroxymethyl groups with the pMDI isocyanate functional groups, as seen from Figure 7.20. Again Figure 7.21 illustrates in the amide I region that the NH_4OH preferred the formation of phenol urethanes while systems without it had somewhat more benzyl urethanes. The presence of SnCl_2 catalyst also resulted in more consumption of the phenolic hydroxyls and/or hydroxymethyl groups as seen in Figure 7.22. The effect of SnCl_2 catalyst on benzyl urethane formation was obscured from the averaged spectra as seen in Figure 7.23; its effect was made clearer by examining the averages of each of the catalyst factor combinations. Figure 7.24 shows a clear effect on the consumption of hydroxyl and isocyanate groups in the ranked order of $\text{NH}_4\text{OH} \cdot \text{SnCl}_2 > \text{SnCl}_2 > \text{NH}_4\text{OH} > \text{no catalyst}$. The dual peaks due to SnCl_2 observed earlier at 1604 and 1593 cm^{-1} and at 1520 and 1512 cm^{-1} showed up in the catalyst combination average spectra for the fingerprint region (Figure 25) from 1800 to 1100 cm^{-1} . Again the NH_4OH catalysis appeared to favor phenol urethane formation, while the SnCl_2 favored benzyl urethane formation based upon the proportions of the peaks in the amide I region.

Table 7.3. Molar quantities of functional groups for transmission FTIR spectra and CP/MAS ^{13}C NMR of PF-pMDI copolymer calculated from sample weights and formulations

Sample	Experimental variable			Quantity of functional groups present (mmol)					
	NH_4OH	SnCl_2	PF/pMDI	OH	NCO	PC	2x PC	ϕOH	CH_2OH
1	-	-	2:2	30.62	16.62	2.44	4.88	11.14	19.49
2	-	-	4:2	61.52	16.83	2.47	4.94	22.37	39.15
3	-	SnCl_2	2:2	30.72	16.80	2.47	4.93	11.17	19.55
4	-	SnCl_2	4:2	59.54	16.57	2.43	4.86	21.65	37.89
5	NH_4OH	-	2:2	28.70	16.95	2.49	4.98	10.44	18.26
6	NH_4OH	-	4:2	58.33	17.01	2.50	5.00	21.21	37.12
7	NH_4OH	SnCl_2	2:2	29.31	16.75	2.46	4.92	10.66	18.65
8	NH_4OH	SnCl_2	4:2	57.39	16.79	2.47	4.93	20.87	36.52

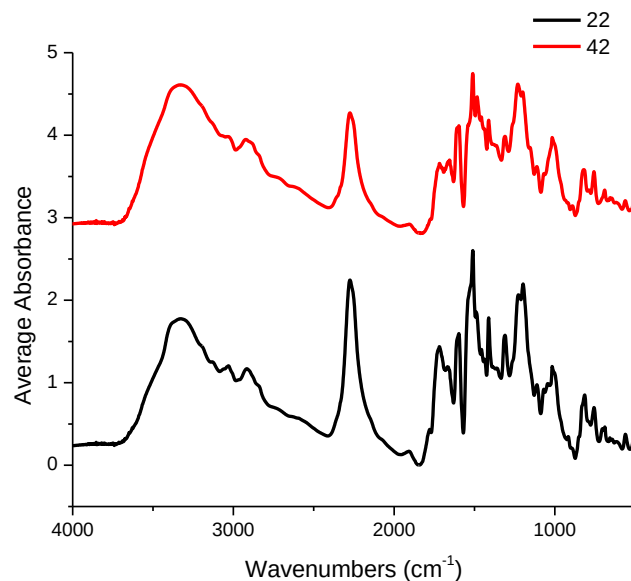


Figure 7.17. Average of transmission FTIR spectra for the cross catalyzed reaction products of PF and pMDI from 4000 to 500 cm^{-1} for the mix ratios of 2 mL:2 mL and 4 mL:2 mL PF:pMDI

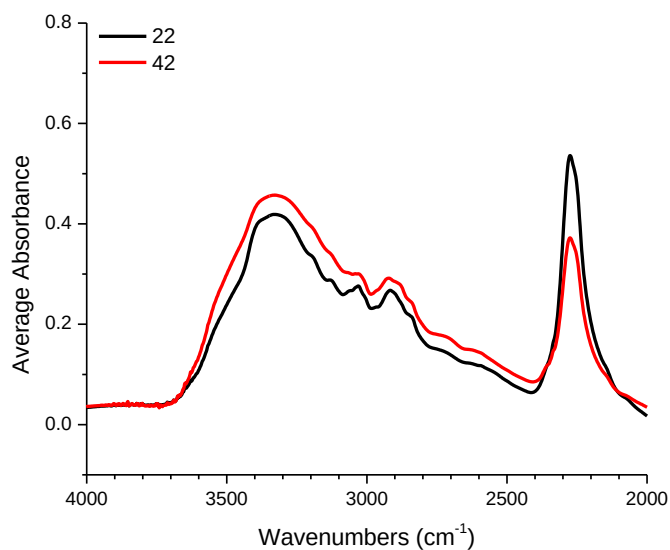


Figure 7.18. Average of transmission FTIR spectra for the cross catalyzed reaction products of PF and pMDI from 4000 to 2000 cm^{-1} for the mix ratios of 2 mL:2 mL and 4 mL:2 mL PF:pMDI

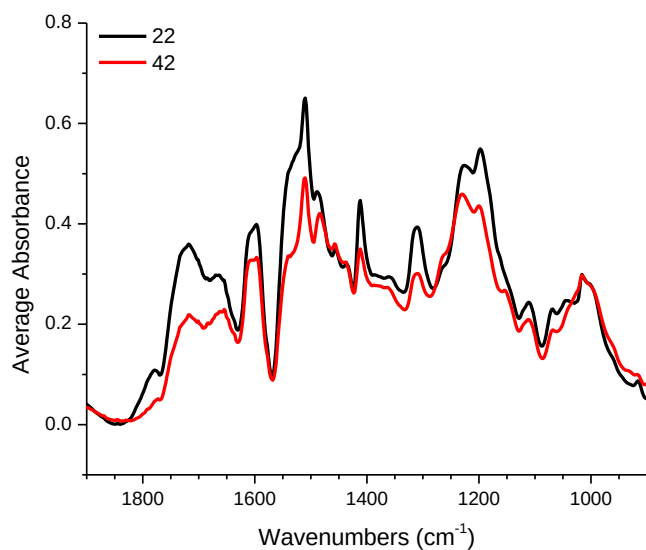


Figure 7.19. Average of transmission FTIR spectra for the cross catalyzed reaction products of PF and pMDI from 1900 to 900 cm^{-1} for the mix ratios of 2 mL:2 mL and 4 mL:2 mL PF:pMDI

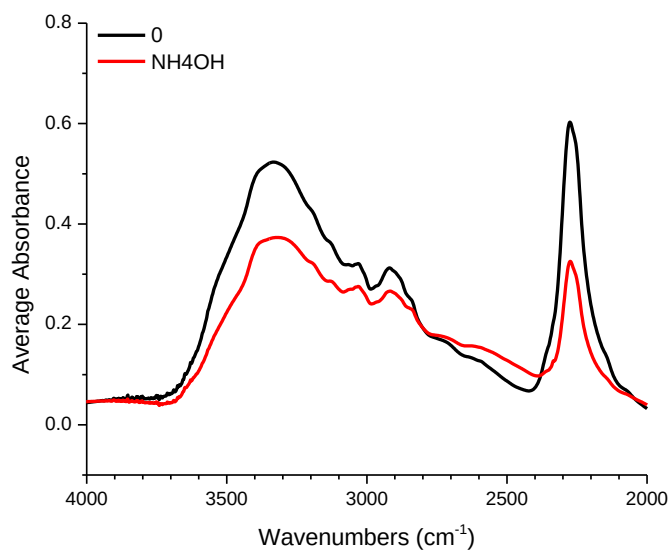


Figure 7.20. Average of transmission FTIR spectra for the cross catalyzed reaction products of PF and pMDI from 4000 to 2000 cm^{-1} for the mixes with and without ammonium hydroxide

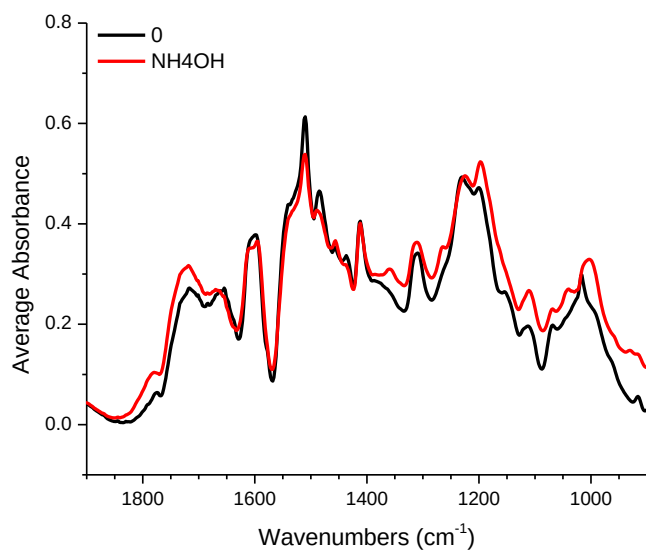


Figure 7.21. Average of transmission FTIR spectra for the cross catalyzed reaction products of PF and pMDI from 1900 to 900 cm^{-1} for the mixes without and with ammonium hydroxide

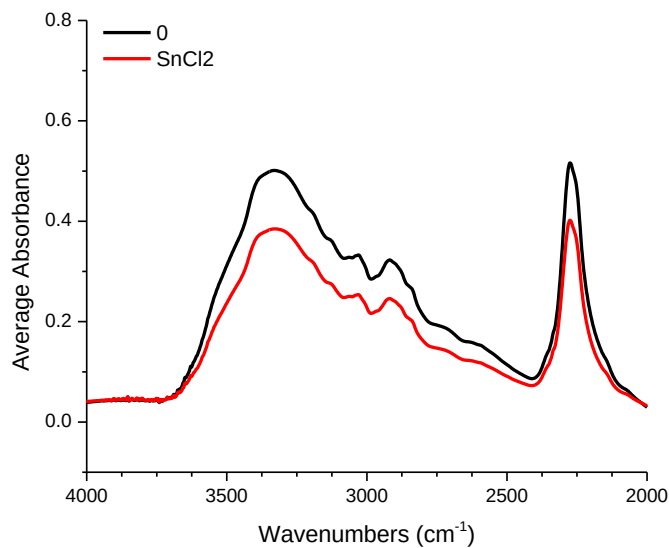


Figure 7.22. Average of transmission FTIR spectra for the cross catalyzed reaction products of PF and pMDI from 4000 to 2000 cm^{-1} for the mixes without and with tin(II) chloride

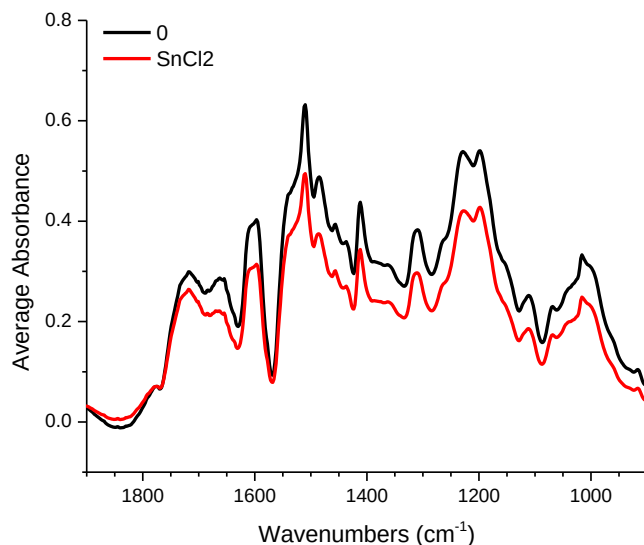


Figure 7.23. Average of transmission FTIR spectra for the cross catalyzed reaction products of PF and pMDI from 1900 to 900 cm^{-1} for the mixes without and with tin(II) chloride

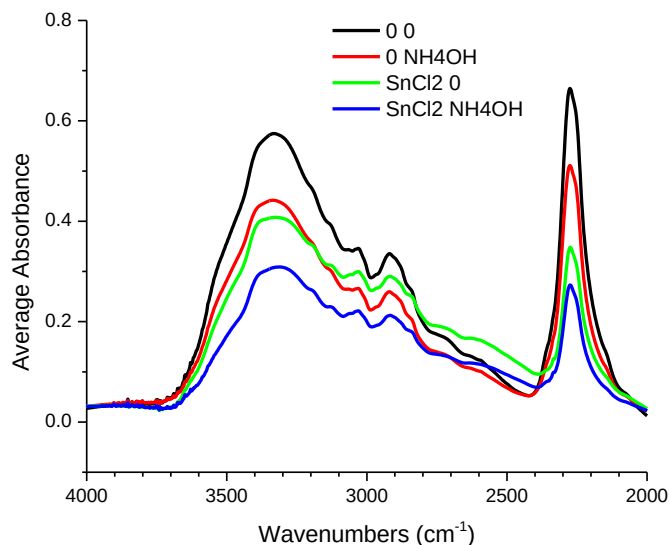


Figure 7.24. Average of transmission FTIR spectra for the cross catalyzed reaction products of PF and pMDI from 4000 to 2000 cm^{-1} for the 2 x 2 factorial experimental design of mixes with four different combinations of ammonium hydroxide and tin(II) chloride

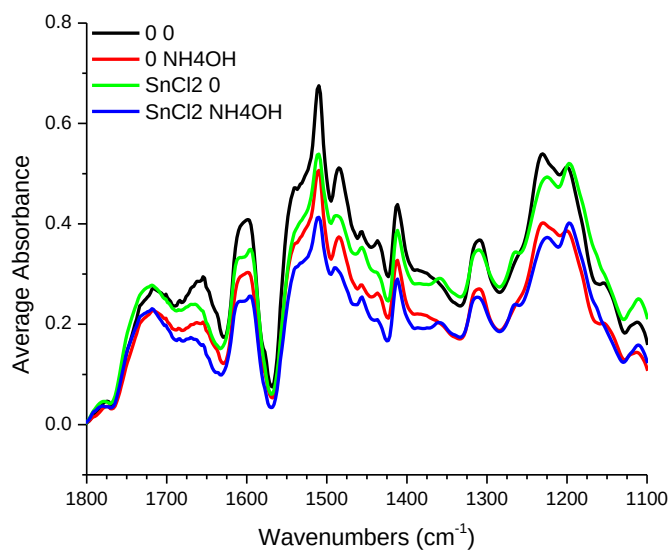


Figure 7.25. Average of transmission FTIR spectra for the cross catalyzed reaction products of PF and pMDI from 1800 to 1100 cm^{-1} for the 2 x 2 factorial experimental design of mixes with four different combinations of ammonium hydroxide and tin(II) chloride

Comparisons of the normalized individual spectra are shown in Figure 7.26 for the range from 1500 to 1400 cm^{-1} and in Figure 7.27 for the range from 1900 to 1500 cm^{-1} respectively. In Figure 7.26., The peaks at 1410 cm^{-1} show that the lower 2 mL:2 mL stoichiometric ratio of PF to pMDI produced more of this peak, meaning it was probably an amide related peak. The relatively stronger peaks at 1455 cm^{-1} indicated a higher concentration of methylene bridges at the 4 mL:2 mL stoichiometric ratio of pF to pMDI, possibly due the presence of NH_4OH . The peaks between 1490 to 1480 cm^{-1} exhibited substantial shifting as well as intensity variation; the lower 2 mL:2 mL stoichiometric ratio of pF to pMDI was more intense and the NH_4OH resulted in a shift from 1483 cm^{-1} to 1490 cm^{-1} . This shift was indicative of a different reaction product due to the presence of NH_4OH . Interestingly, this shift was not evident at the higher 4 mL:2 mL stoichiometric ratio of pF to pMDI in the presence of NH_4OH . In Figure 7.27 detailing the amide I $\nu(\text{C}=\text{O})$, the strongest amide I peak was at 1722 cm^{-1} . It was related to the stronger, more complete reactions of PF and pMDI that occurred at the lower 2 mL:2 mL stoichiometric ratio, likely phenyl urethane. The identity of the peak at 1655 cm^{-1} was uncertain, as it was too

low compared to the an expected peak for benzyl urethane around 1690 cm^{-1} , based on the on the earlier model compound studies.

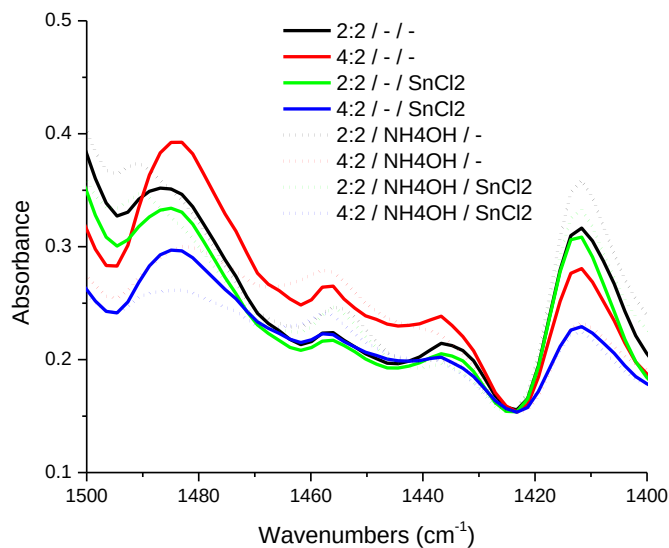


Figure 7.26. Transmission FTIR spectra from 1500 to 1400 cm^{-1} for the cross catalyzed reaction products of PF and pMDI normalized to the minima at 1423 cm^{-1}

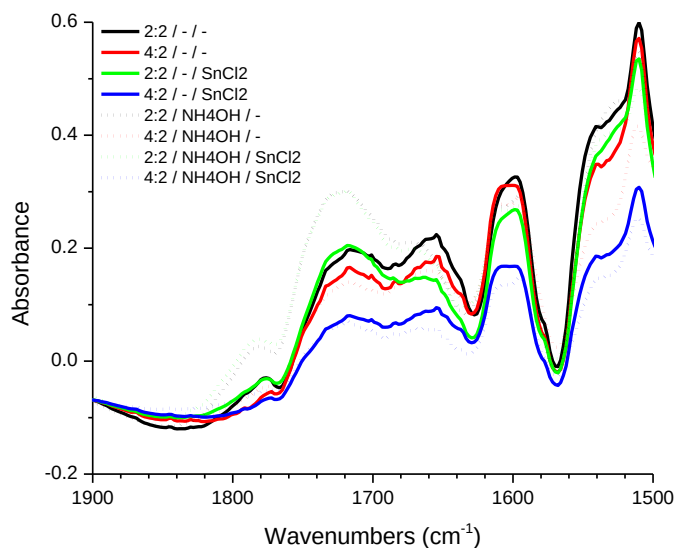


Figure 7.27. Transmission FTIR spectra from 1900 to 1500 cm^{-1} for the cross catalyzed reaction products of PF and pMDI normalized to the minima at 1900 cm^{-1}

It could have been due to the formation of hydroxypropyl carbamate from the NH_4OH and propylene carbonate with an expected peak near 1635 cm^{-1} . Its higher proportion in the slower gelling systems where NH_4OH was absent associated this peak with incomplete reactions.

7.3.2.2. Analysis

The peak height intensities were used for analyzing the effects of the experimental variables (catalyst, accelerator, and stoichiometry) on copolymer structure (Table 7.4). Since different weight ratios of the eight samples to KBr were used, these weights were normalized for the set. The sample weight percent was calculated as the sample weight divided by the total weight of the sample and the KBr. The normalized sample weight percent was the sample weight percent divided by the lowest weight percent sample among the eight samples. The normalized intensities were calculated by dividing the measured peak intensity by its normalized sample weight percent.

Table 7.4. Normalized peak intensities for FTIR peaks of cross catalyzed PF-pMDI copolymer

Variable				Normalized peak intensities (at peak in cm^{-1})				
Sample	NH_4OH	SnCl_2	PF/pMDI	3330	2275	1716	1655	1716/1655
1	-	-	2:2	0.433	0.592	0.250	0.271	0.924
2	-	-	4:2	0.524	0.508	0.213	0.228	0.932
3	-	SnCl_2	2:2	0.388	0.549	0.255	0.208	1.230
4	-	SnCl_2	4:2	0.461	0.406	0.191	0.205	0.932
5	NH_4OH	-	2:2	0.395	0.460	0.415	0.325	1.276
6	NH_4OH	-	4:2	0.261	0.151	0.148	0.160	0.926
7	NH_4OH	SnCl_2	2:2	0.258	0.264	0.282	0.211	1.340
8	NH_4OH	SnCl_2	4:2	0.210	0.143	0.135	0.124	1.088

7.3.2.2.1. $\nu(\text{OH})/\nu(\text{NH})$ at 3330 cm^{-1}

The OH and NH stretching in the region from approximately 3500 to 3200 cm^{-1} was characterized by a broad band attributed to a variety of chemical environments from hydrogen

bonding. The effect of both the NH_4OH and the SnCl_2 was to reduce the peak intensity, implying that both materials catalyzed the reaction of the reactive groups of the starting material (see Figure 7.28). The combination of both catalysts reduced peak intensities the most and may have had a synergistic effect. Although the reduction due to the NH_4OH was greater than for the SnCl_2 , their concentrations were not comparable, thus no direct comparison of catalytic effect was possible. The ratio of PF to pMDI had little effect on this peak, possibly due to the fact that reacting hydroxyl groups would be replaced by N-H groups of urethanes, which would be found in the same broad hydrogen bonding band.

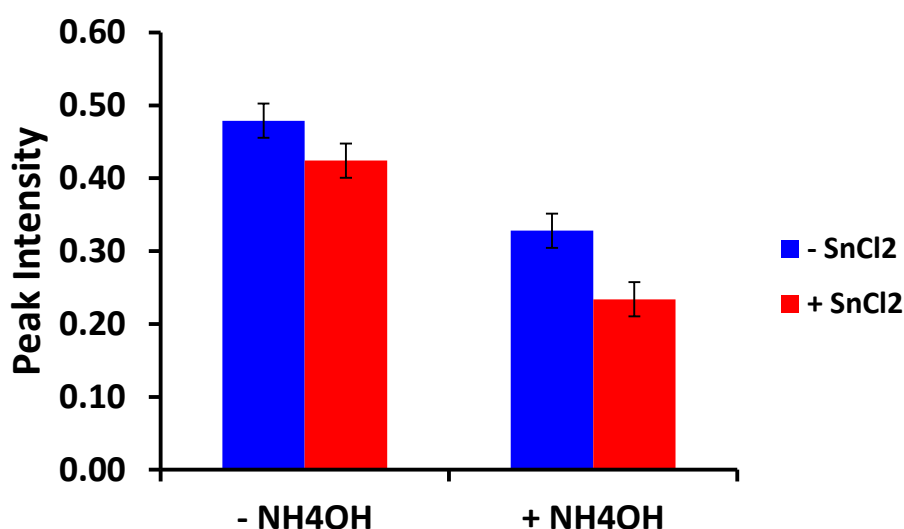


Figure 7.28. Average of $\nu(\text{OH})/\nu(\text{NH})$ with standard error at 3330cm^{-1}

7.3.2.2.2. $\nu(\text{N}=\text{C}=\text{O})$ at 2275 cm^{-1}

The NCO stretching band at 2275 cm^{-1} was characterized by a narrow, sharp band. The effect of both the NH_4OH and the SnCl_2 was to reduce the peak intensity, implying that both materials catalyzed the reaction of the active hydrogen groups of the starting material (see Figure 7.29). The reduction due to the NH_4OH was greater than for the SnCl_2 , although their concentrations were different and their catalytic effect was not directly comparable. The higher ratio of PF to pMDI substantially reduced this peak due to the reduced proportion of isocyanate present and its more complete reaction.

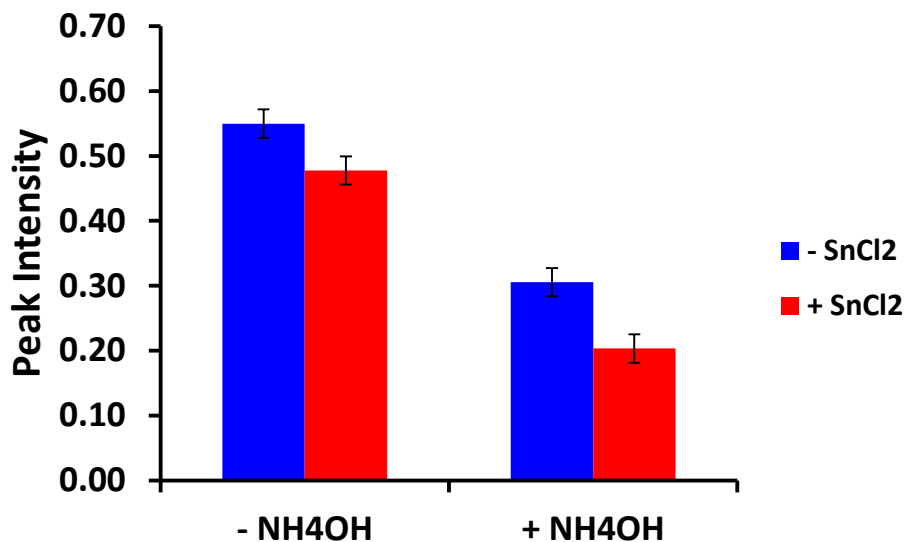


Figure 7.29. Average of $\nu(\text{N}=\text{C}=\text{O})$ with standard error at 2275 cm^{-1}

7.3.2.2.3. Amide I $\nu(\text{C}=\text{O})$ at 1716 cm^{-1}

The results for the phenyl urethane $\nu(\text{C}=\text{O})$ band at 1716 cm^{-1} were more complex as they displayed an apparent interaction between the NH_4OH and the SnCl_2 (see Figure 7.30). When no NH_4OH was present, the effect of SnCl_2 was negligible. In the presence of NH_4OH , however, the samples had higher peak intensity without SnCl_2 , but lower peak intensity with it. Thus, the effect of NH_4OH alone was to enhance phenyl urethane formation, but in combination with SnCl_2 it actually decreased phenyl urethane formation, possibly producing more benzyl urethane instead. The higher ratio of PF to pMDI substantially reduced this peak. The higher proportion of pMDI in the 2:2 ratios meant that more urethane functional groups could be formed, leading to higher peak intensity than for the 4:2 ratios.

The high level of residual isocyanate in the solid state polymer is undesirable for composite wood and must be eliminated for practical applications. One possible cause is that when the PF-pMDI system begins to gel, access of the NCO functional groups becomes diffusion limited. Over time, residual moisture present in the solidified material may reduce the NCO content via the carbamic acid reaction, though its mobility may be limited by the effects of hydrogen bonding in the copolymer.

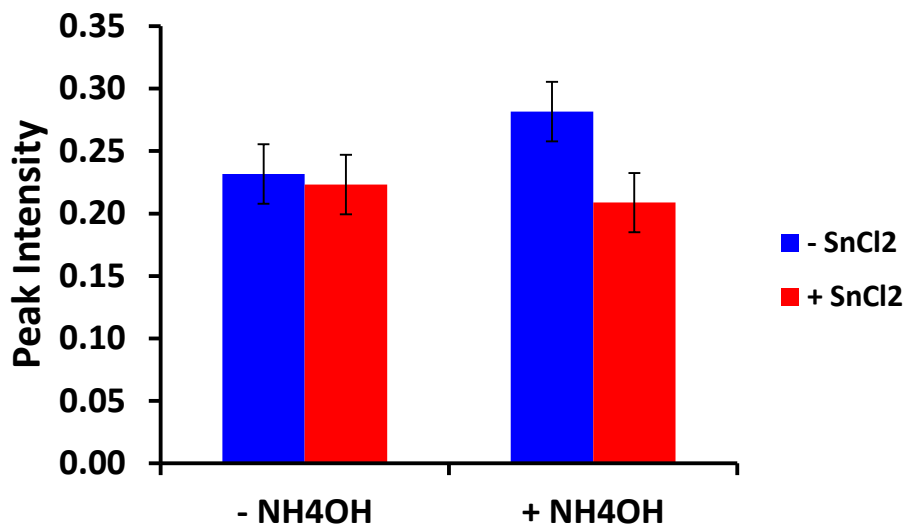


Figure 7.30. Averages of amide I $\nu(\text{C}=\text{O})$ bands with standard error at 1716 cm^{-1}

7.3.2.2.4. Amide I $\nu(\text{C}=\text{O})$ at 1655 cm^{-1}

The normalized peak intensity results for the C=O stretching band at 1655 cm^{-1} of benzyl urethane were less complex than for phenol urethane (see Figure 7.31). The highest benzyl urethane peak intensity was found when neither catalyst was present.

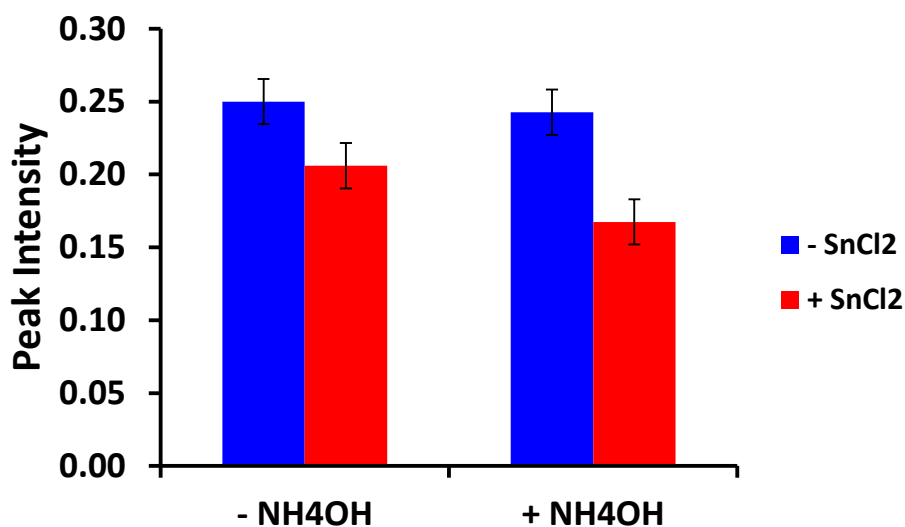


Figure 7.31. Average of amide I $\nu(\text{C}=\text{O})$ bands with standard error at 1655 cm^{-1}

The effect of both the NH_4OH and the SnCl_2 was to decrease the intensity of the benzyl urethane peak. The SnCl_2 had the stronger effect on the normalized peak intensity of benzyl urethane, decreasing it on average by 0.060, while NH_4OH decreased it on average only by 0.023. The absolute concentrations of the phenol and benzyl urethane are not comparable, since there was no information on their extinction coefficients. The 4:2 ratio of PF to pMDI substantially reduced this peak. Again, the higher proportion of pMDI in the 2:2 ratio meant that more urethane functional groups could be formed, leading to higher peak intensity than for the 4:2 ratio.

7.3.2.2.5. Ratio of amide I $\nu(\text{C}=\text{O})$ ($1716/1655\text{ cm}^{-1}$)

The ratios for the normalized peak intensities of the amide I bands at 1716 and 1655 cm^{-1} were calculated to understand the effect of the catalysts on the relative proportion of these peaks. Higher concentrations of phenyl urethanes than phenyl urethanes may have predominated for ratios above 1 (see Figure 7.32). These results may be questionable as the benzyl urethane model reaction amide I peaks were found closer to 1700 cm^{-1} . The peak at 1655 cm^{-1} could have been from formation of hydroxypropyl carbamate had a peak at 1637 cm^{-1} .

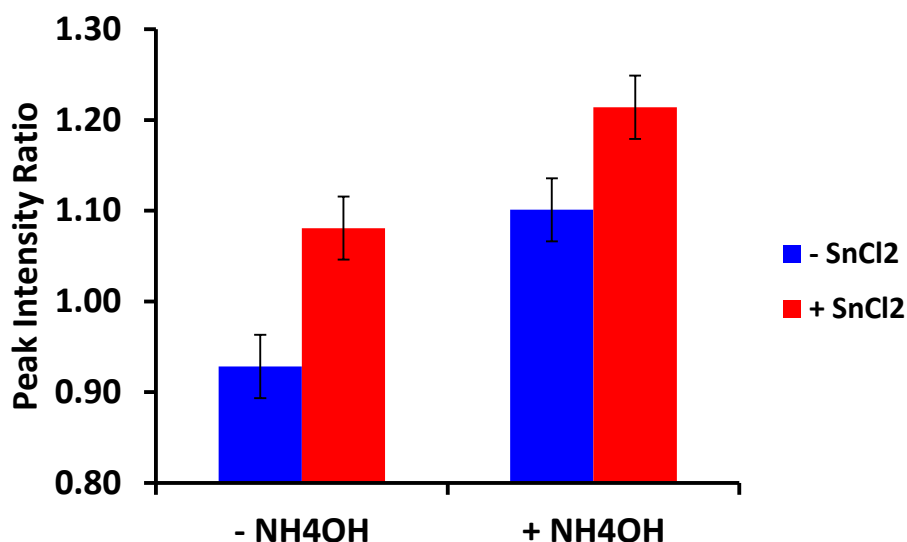


Figure 7.32. Ratios of amide I bands ($1716\text{ cm}^{-1}/1655\text{ cm}^{-1}$) with standard error

The addition of either the NH_4OH or the SnCl_2 had the effect of increasing this ratio above 1.0, with the greatest predominance of the phenyl urethane occurring when both catalysts were present, in the most reactive system. The higher ratio of PF to pMDI substantially reduced this ratio, meaning that a lower proportion of phenyl urethanes to benzyl urethanes were produced.

7.3.3. CP/MAS ^{13}C NMR results

The CP/MAS ^{13}C NMR results were indicative of effects of the experimental parameters as detailed in Table 7.3 and are illustrated in Figure 7.33. Aliphatic hydrocarbons from the pendant methyl group of propylene carbonate and 1,2-propane diol appeared in peaks at 10 and 18 ppm. The $-\text{CH}_2-$ methylene bridge carbons of condensed phenolic monomers occurred at 35.2 to 35.9 ppm for 2,4' bridges and at 39.8 to 40.0 ppm for 4,4' bridges respectively. The 2,4' bridges were most evident at the 2:1 ratio of PF to pMDI, when no NH_4OH catalyst was present; these methylene bridges were least apparent when both NH_4OH and SnCl_2 catalysts were used in the system as seen in Figure 7.34. The 4,4' bridges were observed in similar ratios under all conditions and may have been present in the starting PF oligomers or an reaction product accelerated by the propylene carbonate or its hydrolysis product sodium bicarbonate. No 2,2' bridges were evident. Hydroxymethyl and benzyl urethane $-\text{CH}_2\text{O}-$ groups appeared in the ranges of 60-65 ppm and 64 -70 ppm respectively. Although these carbon peaks overlapped, some trends were still evident, as the highest proportions of benzyl urethanes were observed at the 2:2 PF:pMDI ratio, with NH_4OH and SnCl_2 catalysts present, as seen in Figure 7.34 and 7.35.

The aromatic ring carbons of either phenol or pMDI generally were observed between 115 and 140 ppm. More specifically, the tertiary aromatic or unsubstituted C-2, C-4 and C-6 ring carbons appeared as a broad shoulder in the 115 to 120 ppm range. The 4:2 ratio treatment resulted in the right side of the shoulder being slightly more upfield than the 2:2 ratio, consistent with the expectation that higher PF content would result in a higher concentration of unsubstituted C-2, C-4 and C-6 ring carbons in the copolymer. The strongest single peak in all spectra was observed in the 129.1 to 129.4 ppm range and was attributed to the C-3 and C-5

peaks that would be present in either of the PF and pMDI copolymer components. The most distinct peaks, however, were found in the 135 to 140 ppm range, representing the C-2, C-4 and C-6 ring carbons of phenyl urethanes, the C-2, C-4 and C-6 ring carbons of benzyl urethanes, and the C-1 carbon of the pMDI attached to the urethane nitrogen. Due to the band broadening and overlap, no specific assignments were possible, but several general trends emerged. The sharpest peaks occurred when NH_4OH and SnCl_2 catalysts were present at the 2:2 PF:pMDI mix ratio. Moderate shoulders were observed at 4:2 with NH_4OH and 2:2 with no NH_4OH combinations. Almost no shoulder was observed for the 4:2 ratio when NH_4OH was absent.

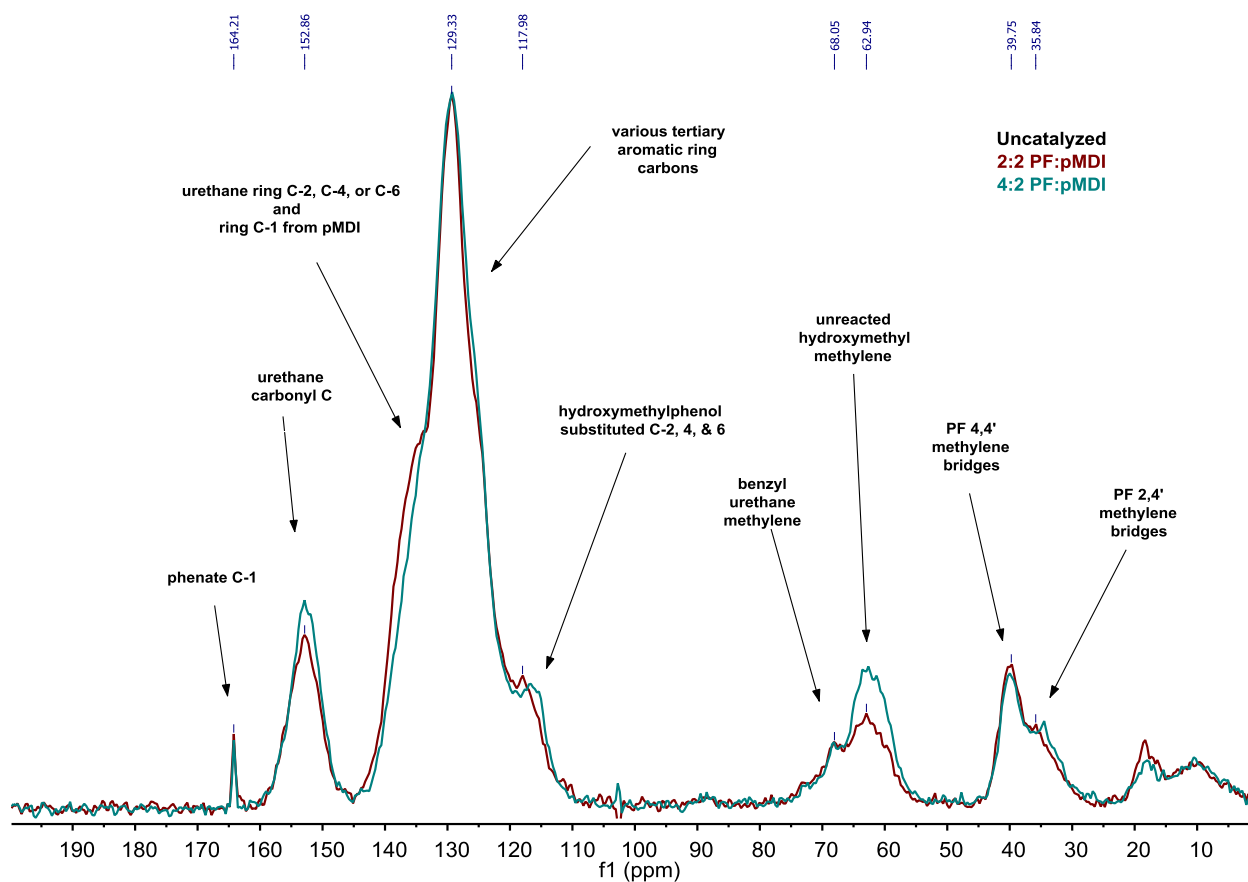


Figure 7.33. Typical CP/MAS ^{13}C spectra of PF-pMDI copolymers with peak identification

The urethane carbonyl and phenolic C-1 carbon peaks appeared down field, with the phenate anion presenting a sharp peak at 164 ppm (Figure 7.34). This peak was relatively small, corresponding to the approximately 20% phenate that could be expected from the formulated

OH:P molar ratios of 0.20. The phenolic C-1 carbon and urethane carbonyl peaks showed up as a broadened peak between 150 and 155 ppm. The carbonyl peak of 1,3-DPU would be expected to appear at about 152.5 ppm as found in Chapter 4. These peaks did exhibit some differentiation among themselves as the conditions without NH_4OH were centered at 152.6 to 152.9 ppm, while those peaks from copolymers prepared with NH_4OH were found at 153.9 to 154.4 ppm. The lower ppm peaks were attributed to phenol urethanes and the peaks at 154 ppm to higher proportions of benzyl urethanes. The lack of NH_4OH catalyst led to the formation of relatively more phenol urethanes.

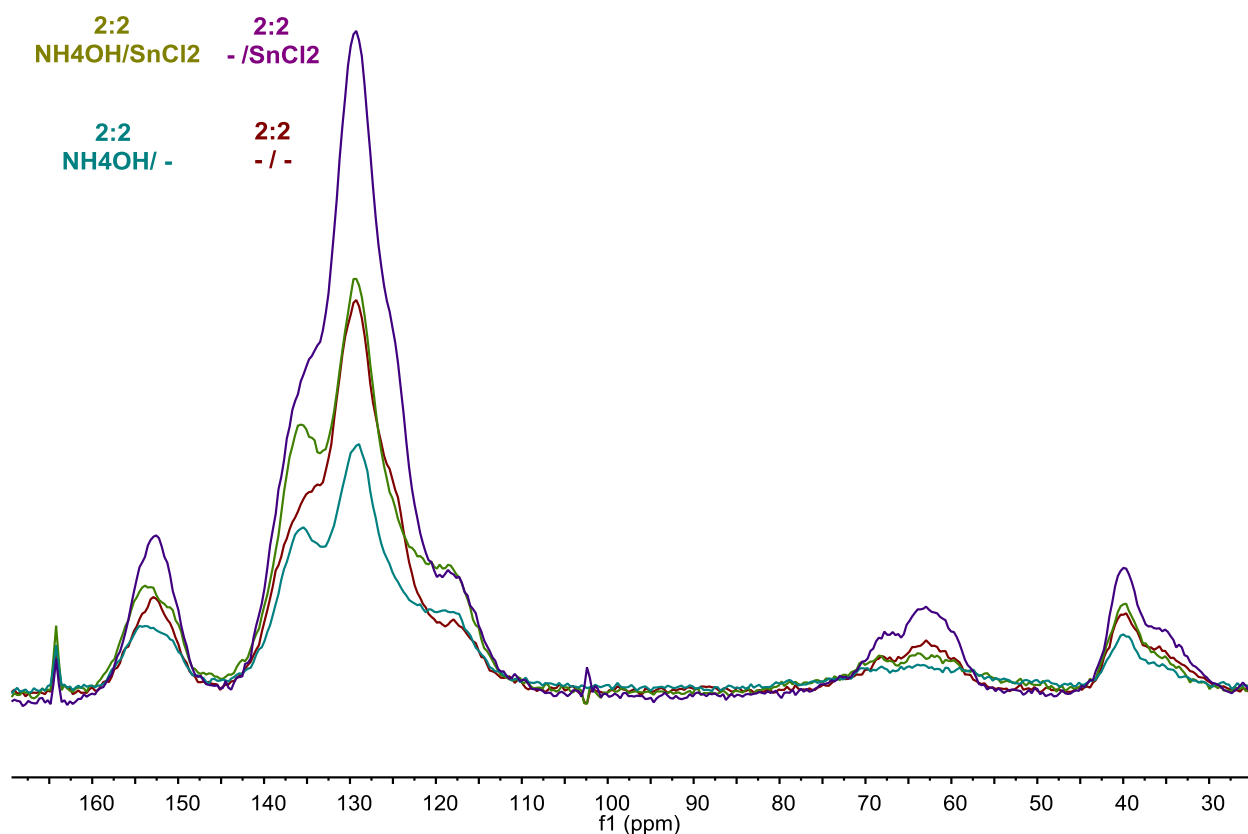


Figure 7.34. CP/MAS ^{13}C NMR of the 2:2 PF:pMDI (vol:vol) ratio for four catalyst combinations

The picture that emerged is that in the presence of NH_4OH catalyst with a relatively balanced PF to pMDI stoichiometry, a higher proportion of benzyl urethanes formed from C-2 hydroxymethyl groups, while SnCl_2 had a minor effect (See Figures 7.34 and 7.35). This conclusion is supported by three separate spectral observations: (1) the reduction of 2,4' PF

methylene linkages that formed in the presence of NH_4OH , (2) the observations of benzyl urethane formation at 65 to 75 ppm and 135 to 140 ppm, correlated with the presence of the catalyst, and (3) the shift of the carbonyl carbon peaks from 153 to 154 ppm because of NH_4OH . Taken together, the NH_4OH is enhancing the reaction of the 2 and 6-hydroxymethyl groups with the isocyanate leading to higher proportions of benzyl urethanes in the copolymer.

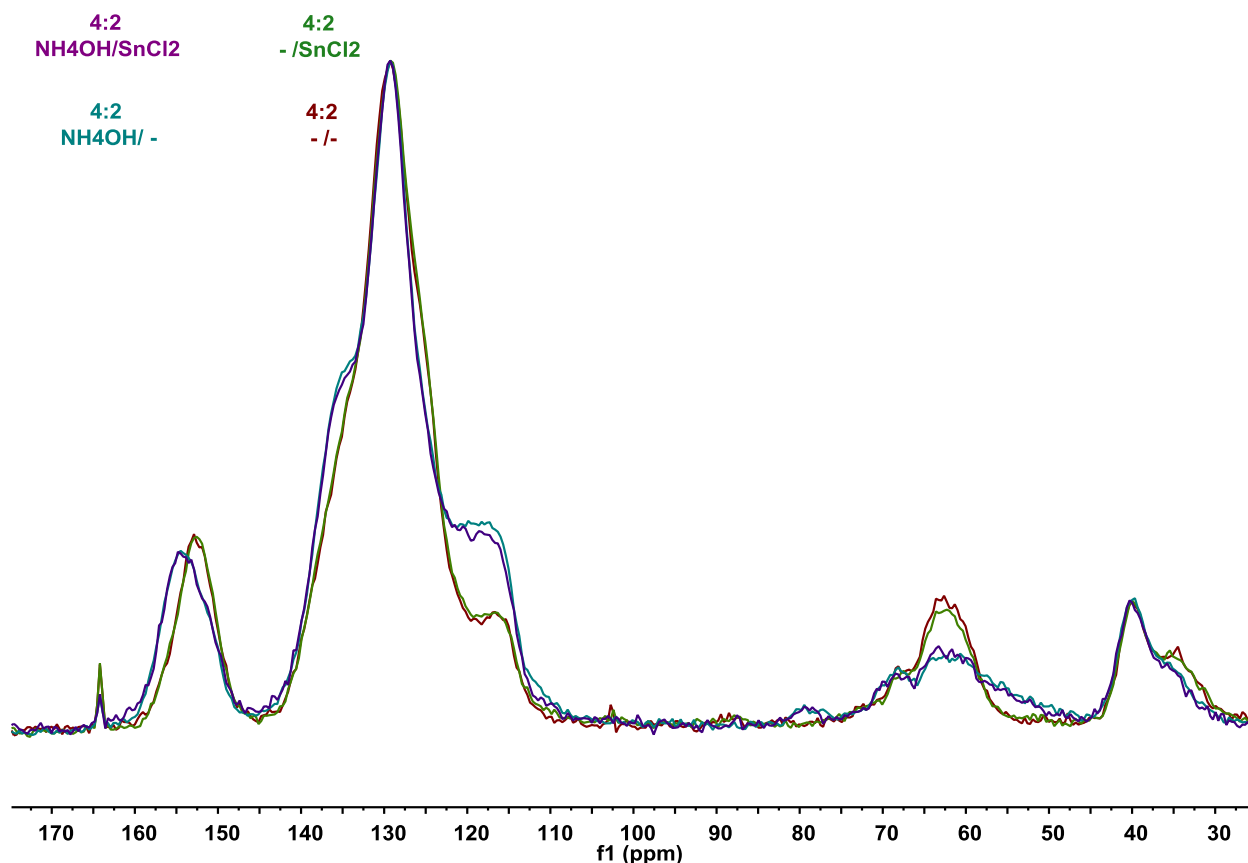


Figure 7.35. CP/MAS ^{13}C NMR of the 4:2 PF:pMDI (vol:vol) ratio for four catalyst combinations

As additional verification of these conclusions, the CP/MAS spectra were compared against spectra from the reactions of phenolic model compound with phenyl isocyanate from Chapter 4. As solution NMR, these spectra would provide much sharper peaks for identification of contributing structures to the CP/MAS spectra. Figure 7.36 illustrates the peaks for the reactions of phenol and benzyl alcohol with phenyl isocyanate in the presence of DBTL catalyst. These two reactions produced either phenyl urethane or benzyl urethane respectively and therefore provide a clear indication of the type of urethane formed in the 155 to 150 ppm

region. The other peaks in the aromatic ring carbon region give a clear indication of the source of the broadened peaks of the CP/MAS spectra.

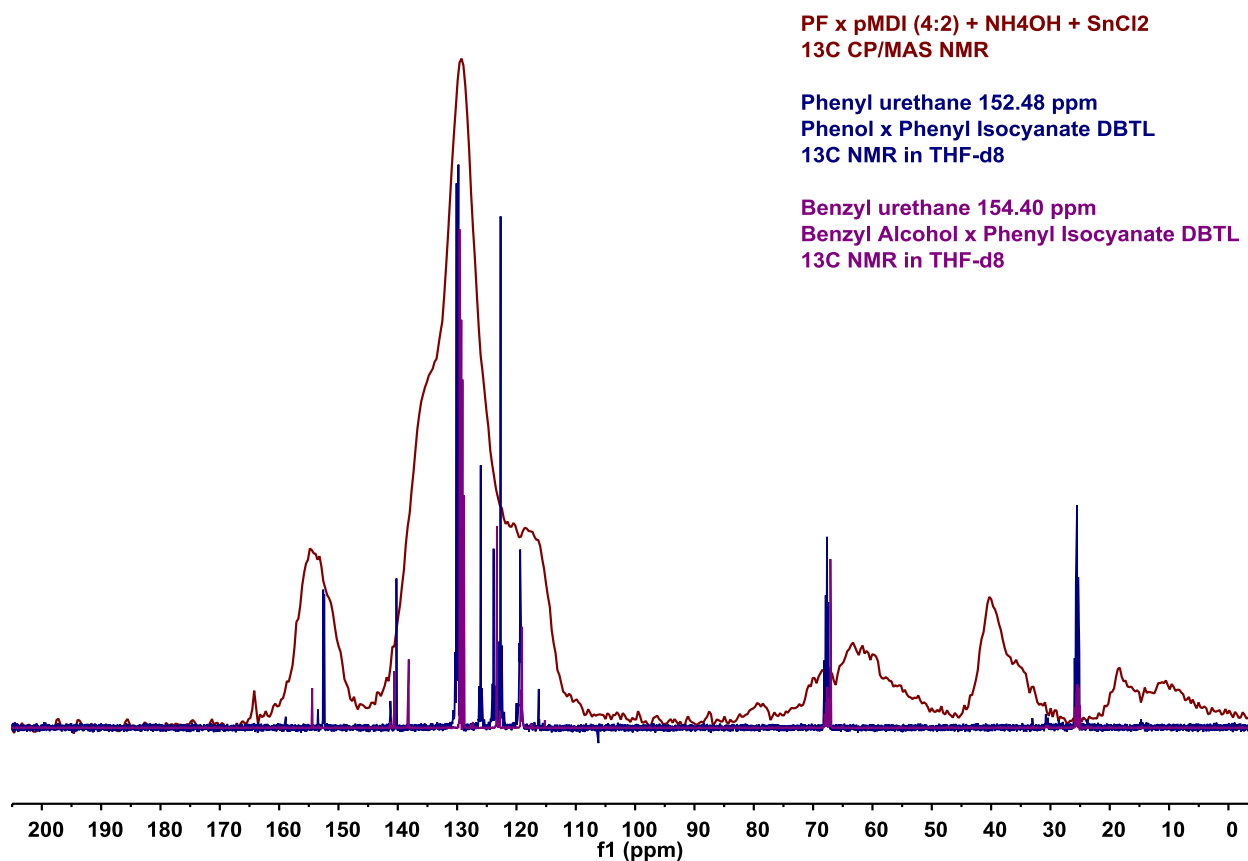


Figure 7.36. Comparison of CP/MAS ¹³C NMR spectrum for the 4:2 PF:pMDI (vol:vol) ratio with NH₄OH and SnCl₂ catalysts against ¹³C NMR spectra of phenol and benzyl alcohol reacted with phenyl isocyanate in the range from 205 to -5 ppm

The spectra for the reactions of 2-HMP and 4-HMP in the presence of TEA and DBTL were compared against the spectra of the 4:2 PF:pMDI ratio with NH₄OH and SnCl₂ present. The results for comparison of three separate spectral regions are shown in Figures 7.37 to 7.39. Figure 7.37 illustrates the phenolic C-1 and urethane carbonyl region from about 160 to 148 ppm. The various possible chemical structures cover the entire range, but the peak for the CP/MAS spectra correlates best with the DBTL reacted peak of 2-HMP, a reaction that was shown in Chapter 4 to highly favor the formation of benzyl urethane.

PF x pMDI (4:2) + NH₄OH + SnCl₂
13C CP/MAS NMR

2-HMP x Phenyl Isocyanate TEA
13C NMR in THF-d₈

4-HMP x Phenyl Isocyanate TEA
13C NMR in THF-d₈

2-HMP x Phenyl Isocyanate DBTL
13C NMR in THF-d₈

4-HMP x Phenyl Isocyanate DBTL
13C NMR in THF-d₈

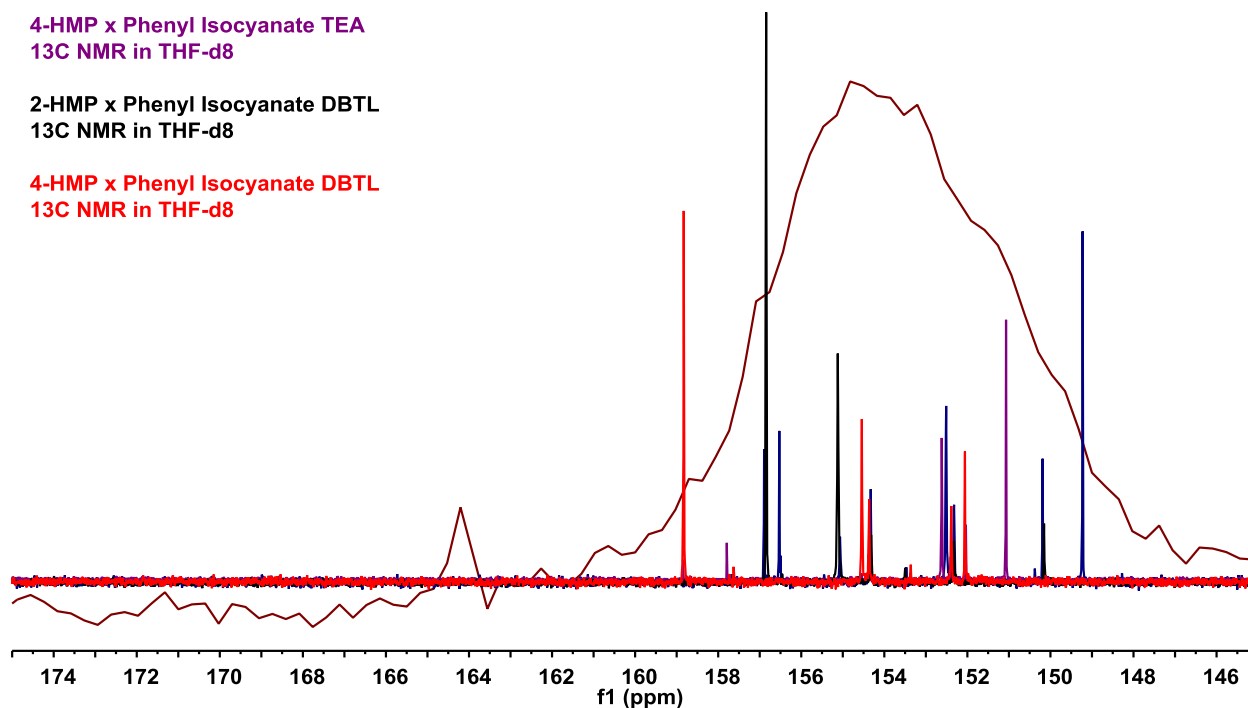


Figure 7.37. Comparison of CP/MAS ¹³C NMR spectrum for the 4:2 PF:pMDI (vol:vol) ratio with NH₄OH and SnCl₂ catalysts against ¹³C NMR spectra of 2-HMP and 4-HMP reacted with phenyl isocyanate in the range from 175 to 145 ppm

Figure 7.38 illustrates the aromatic ring carbon region from about 142 to 112 ppm. The many possible chemical structures cover the entire range again here, but the most interesting CP/MAS spectra peak was the broad shoulder between 139 and 133 ppm, that resulted from the formation of benzylic urethanes in the catalyzed model compound reactions with 2-HMP and 4-HMP.

PF x pMDI (4:2) + NH₄OH + SnCl₂
13C CP/MAS NMR

2-HMP x Phenyl Isocyanate TEA
13C NMR in THF-d₈

4-HMP x Phenyl Isocyanate TEA
13C NMR in THF-d₈

2-HMP x Phenyl Isocyanate DBTL
13C NMR in THF-d₈

4-HMP x Phenyl Isocyanate DBTL
13C NMR in THF-d₈

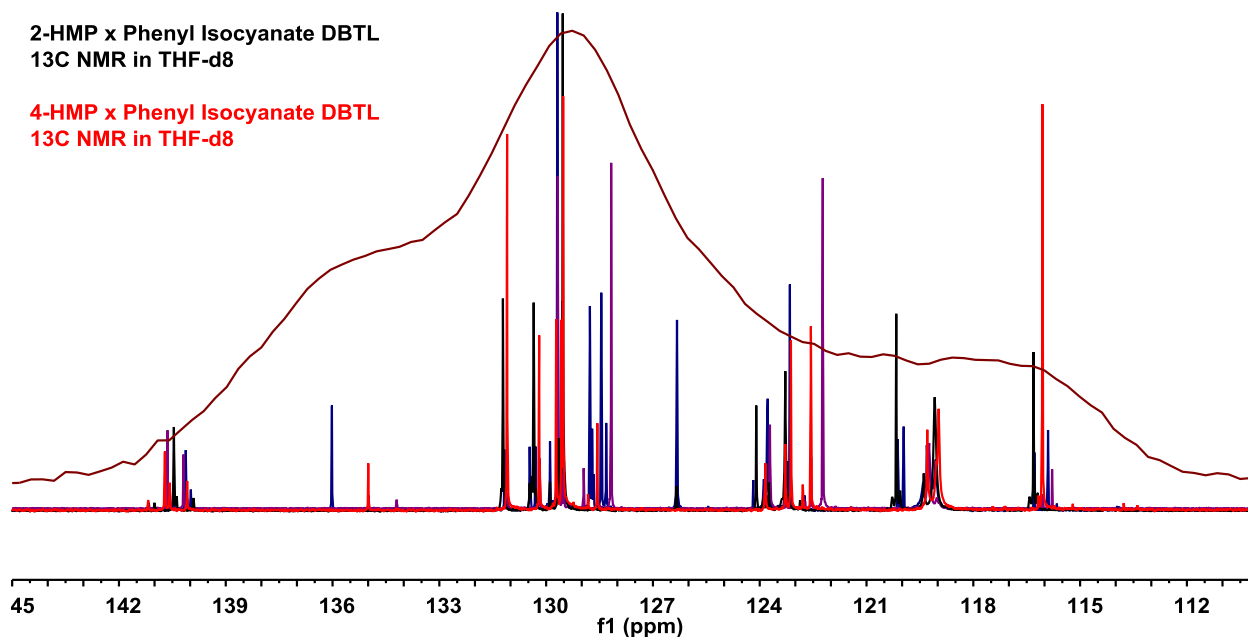


Figure 7.38. Comparison of CP/MAS ¹³C NMR spectrum for the 4:2 PF:pMDI (vol:vol) ratio with NH₄OH and SnCl₂ catalysts against ¹³C NMR spectra of 2-HMP and 4-HMP reacted with phenyl isocyanate in the aromatic ring carbon range from 145 to 110 ppm

Figure 7.39 illustrates the methylene carbon region from about 72 to 52 ppm. The peaks of the reactions of 2-HMP or 4-HMP with phenyl isocyanate that resulted from the urethane formation were found in the same range as the broad CP/MAS spectra peak. Again the CP/MAS peak appeared nearest the peak of the reaction product for 2-HMP with phenyl isocyanate which was almost entirely benzyl urethane in the 2 position. The interesting question that arises from this data is why the NH₄OH favored formation of the benzyl urethane when the TEA catalyzed reactions in Chapter 4 favored phenyl urethane formation.

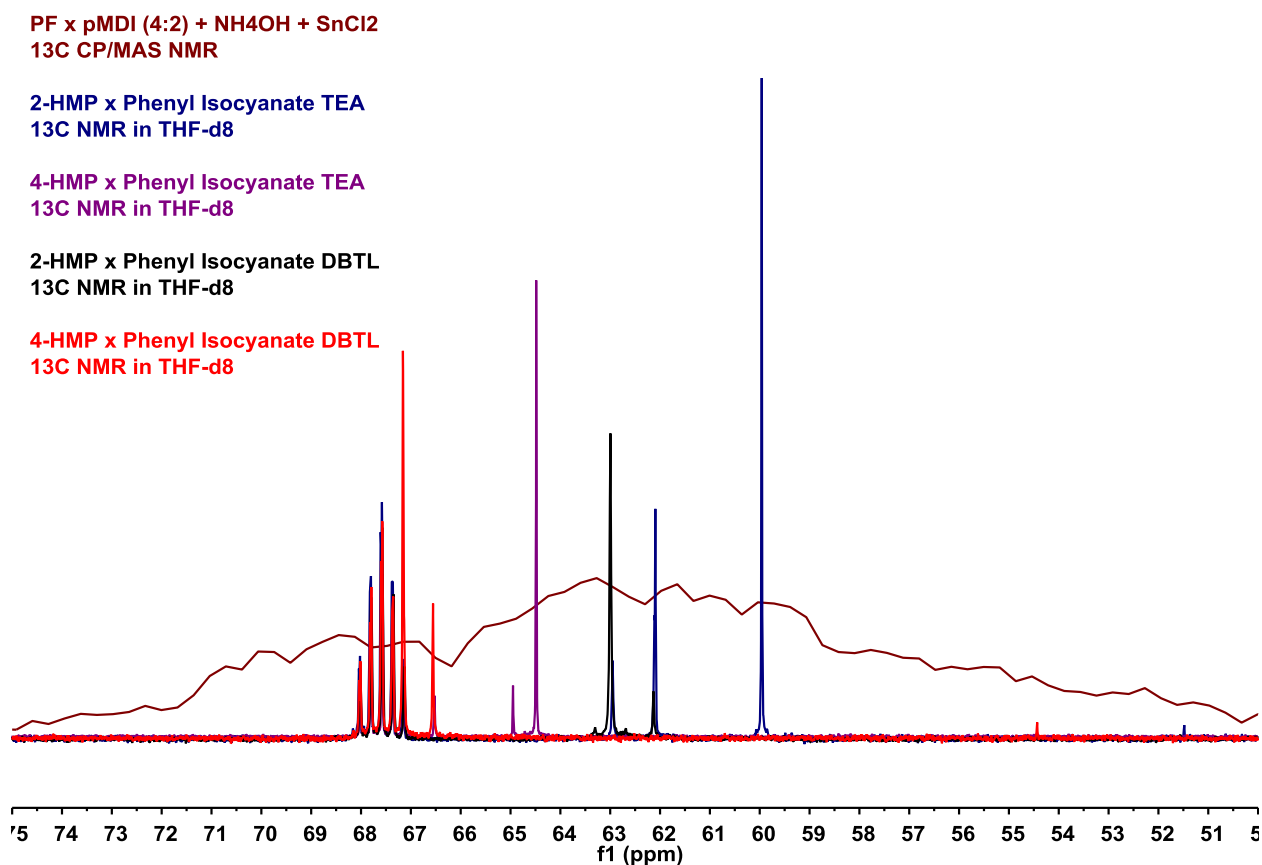


Figure 7.39. Comparison of CP/MAS ¹³C NMR spectrum for the 4:2 PF:pMDI (vol:vol) ratio with NH₄OH and SnCl₂ catalysts against ¹³C NMR spectra of 2-HMP and 4-HMP reacted with phenyl isocyanate in the hydroxymethyl and benzylic methylene range from 75 to 50 ppm

A review of the data for the alkaline environment reactions in Chapter 4, showed that under neutral conditions for 2-HMP benzyl urethane formation was favored, while under alkaline or anionic conditions phenyl urethane formation was favored. If the PF reaction component is considered on the basis of its hydroxide to phenol molar ratio, approximately 20 % is in the anionic phenate form, while 80 % is in the neutral form. Thus, this particular formation probably favored formation of benzyl urethanes more than a PF resole with a much higher hydroxide to phenol molar ratio would. Furthermore, this inference leads to a hypothesis for future testing predicting that a series of cross-catalyzed PF-pMDI copolymers having the PF component hydroxide to phenol molar ratio ranging between 0.01 and 1.00 should show varied

ratios of benzyl and phenyl urethanes that could be confirmed by the chemical shifts of ^{13}C CP/MAS NMR and the spectral peaks of transmission FTIR in material in the solid state.

7.4 Conclusions

The cross-catalyzed polymerization of PF and pMDI results in a copolymer possessing a combination of phenyl urethane, benzyl urethane, and methylene bridges.

The following trends were evident in FTIR of the copolymer in the solid state:

- The presence of ammonium hydroxide and tin (II) chloride and the higher PF:pMDI ratio resulted in lower residual isocyanate, with higher urethane formation. The relative proportions of phenyl urethane to benzyl urethane were uncertain due to overlapping peaks.
- Overall a relatively high percentage of free isocyanate was present, likely due to the removal of water that would have initiated isocyanate consuming carbamic acid reactions.
- The combination of ammonium hydroxide and tin (II) chloride synergistically enhanced the reactivity of the materials and reduced the amount of residual NCO

The following trends were evident from ^{13}C CP/MAS NMR of the copolymer in the solid state:

- The presence of ammonium hydroxide and tin (II) chloride and the higher PF concentration resulted in urethane formation.
- The presence of ammonium hydroxide favored formation of benzyl urethane mostly from the 2-hydroxymethyl groups, while phenyl urethane formed in its absence.
- The higher ratio of PF to pMDI resulted in higher proportions of 2,4' phenolic methylene bridges, especially in the absence of ammonium hydroxide.
- Comparison of the CP/MAS results with the results for ^{13}C NMR of phenolic model compound reactions with phenyl isocyanate under alkaline conditions confirmed that the hydroxide to phenol molar ratio is directing the ratio of benzyl to phenyl urethanes formed in the copolymer.

The overall reaction stoichiometry is likely driving the type of co-polymer forming. A benzylic urethane pathway predominates under balanced stoichiometric conditions in the presence of ammonium hydroxide, phenolic urethanes are favored in its absence, and accelerated phenolic condensation with methylene bridge formation is most important when the PF component is in excess compared to the pMDI component, granted sufficient accelerator is available. Based on these considerations, this cross catalyzed system is eminently tunable by formulation for type of co-polymer (benzylic urethane vs. phenolic urethane vs. phenolic methylene bridged), reactivity, and cost of the composition.

7.5. References

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Chapter 8: Summary, Conclusions, and Future Research

The objective of this research to elucidate the polymer structure generated by the cross-catalyzed reactions of PF and pMDI prepolymers. Initial research on phenolic model compounds identified the fundamental importance and effect of electrostatic interactions on the electronic structure of the substituted or unsubstituted phenolic aromatic rings. These effects were related to the reactivity of those compounds previously published in the literature. These effects were determined in part by the solvated ionic radius, solvent dielectric constant, and their effect on ionic generated electric field strength, which in turn was predicted to affect PF reactivity due to variation of electronic structure in the aqueous alkaline environment. NMR chemical shifts were used to predict relative electron density and order of reactivity with reasonable success for phenolic model compounds towards formaldehyde addition, self-condensation, and urethane formation with isocyanates. 2-HMP hydroxymethyl groups were predicted to be more reactive than 4-HMP in forming urethane bonds under neutral conditions; 2-HMP hydroxymethyl groups would be more reactive than those of 4-HMP in forming urethane bonds under alkaline conditions. The reactivity of neutral model compounds was predicted to be faster than the alkaline reactivity for 2- and 4- HMP.

Alkali metal cations acted as an electron withdrawing force on a phenolic monomer's electronic structure, with the strength of this effect mostly dependent on their proximity to the phenoxide anion and resonance effects. The effect of the cation was related to the dielectric screening of their inner shell electrons and the local dielectric effects of the solvation shell. Solvents also affected electron density, likely due to hydrogen bonding, and thus also should have a slight effect on reactivity. From the NMR data, the order of formaldehyde addition reactivity found in the literature was predicted for 4 of 5 reactions.

The reactions of phenolic model compounds with phenyl isocyanate were studied with ^1H and ^{13}C NMR and the structure of their reaction products was determined under neutral organic and aqueous alkaline conditions. Reactions of phenyl isocyanate with the phenolic model

compounds phenol, benzyl alcohol, 2-HMP, and 4-HMP in THF- d_8 under neutral conditions, without catalyst, were relatively slow. The result was residual monomer and the precipitation of 1,3-diphenyl urea due to the carbamic acid reaction of phenyl isocyanate with water. The reaction of phenyl isocyanate with the phenolic model compounds phenol, 2-HMP, and 4-HMP in the presence of TEA catalyst favored the formation of phenyl urethanes, while reactions with benzyl alcohol, 2-HMP, and 4-HMP in the presence of DBTL catalyst favored the formation of benzyl urethanes. Reactions of 2-HMP and 4-HMP with phenyl isocyanate resulted in formation of BU, PU, and BPDU. DBTL catalysts favored formation of BDPU strictly by the benzyl urethane pathway, while TEA favored formation of BDPU mostly by the phenyl urethane pathway, although some BU was also present. The favored formation of BU in the presence of TEA was attributed to the formation of nucleophilic phenoxides due to deprotonation of the phenolic hydroxyl group.

Under aqueous alkaline conditions, 2-HMP was more reactive than 4-HMP, with the alkaline conditions favoring PU formation over BU formation for 2-HMP, while neutral conditions favored BU formation over PU formation, especially when no catalyst was present. For 4-HMP, however, under neutral conditions when no catalyst was present, no BU and only modest amounts of PU formed. Small amounts of BDPU formed with 2-HMP, but essentially none formed with 4-HMP. The enhanced reactivity of the 2-HMP was attributed to intramolecular hydrogen bonding and a resulting resonance stabilization of the phenolic aromatic ring. A higher reactivity of the 2-hydroxymethyl group towards isocyanates was considered beneficial, as typical alkaline PF resoles contain high proportions of 2- and 6-hydroxymethyl groups. Benzyl urethane formation would also be beneficial, due to conservation of mass during polymerization instead of loss due to formaldehyde emission during condensation.

The goal of ATR-FTIR spectroscopic studies was to generate real time structural information using model compounds to permit effective interpretation of the complex FTIR spectra for cross-catalyzed reactions of PF and pMDI. The research demonstrated the ability to differentiate among specific functional groups for the reaction peaks generated by the carbamic acid side-reaction, phenyl urethane formation, and benzyl urethane formation.

Amide I $\nu(\text{C}=\text{O})$ peaks were identified for the carbamic acid side reaction, as well as for phenyl and benzyl urethane formation. These amide I $\nu(\text{C}=\text{O})$ peaks were most useful for interpretative purposes, as they were found in a spectral region with little interference from the peaks of other functional groups.

Reactions modeling the hydrolysis of propylene carbonate and the accelerated condensation of PF monomers were monitored by real time ATR-FTIR, revealing important peaks for spectral interpretation of accelerated alkaline PF resoles condensation reactions. The real time hydrolysis of propylene carbonate by sodium hydroxide and ammonium hydroxide differentiated between their reaction products, providing reference peaks for interpretation of the complex cross-catalyzed reactions. Real time accelerated condensation of 2-HMP and 4-HMP by propylene carbonate in the presence of ammonium hydroxide or sodium hydroxide provided information regarding methylene bridge formation. ATR-FTIR studies of the acceleration of 2-HMP and 4-HMP confirmed and augmented earlier conclusions in the literature that propylene carbonate affected acceleration of 2-HMP more than 4-HMP. The results of the model compound studies were useful for identifying changes that took place in the dynamic spectra for propylene carbonate hydrolysis, formation of hydroxypropyl carbamate, and for methylene bridge formation during PF condensation.

The overall reaction stoichiometry between the PF and pMDI components drove copolymer formation. A benzylic urethane pathway predominated under balanced stoichiometric conditions in the presence of ammonium hydroxide, while phenyl urethane formation was favored in its absence. Accelerated phenolic condensation with methylene bridge formation became more important when the PF component was in excess compared to the pMDI component, granted sufficient accelerator was available. Based on these considerations, cross catalyzed systems are eminently tunable by formulation for type of co-polymer (benzylic urethane vs. phenolic urethane vs. phenolic methylene bridged), reactivity, and cost of the composition.

FTIR identified a relatively high percentage of free isocyanate present in copolymer formed at ambient temperature due to the removal of water that would have otherwise initiated

isocyanate consuming carbamic acid reactions. The combination of ammonium hydroxide and tin (II) chloride synergistically enhanced the reactivity of the materials and reduced the amount of residual isocyanate.

From ^{13}C CP/MAS NMR of the copolymer in the solid state, the presence of ammonium hydroxide and tin (II) chloride, and the higher PF concentration resulted in substantial urethane formation. The presence of ammonium hydroxide favored formation of benzyl urethane mostly from the 2-hydroxymethyl groups, while phenyl urethane formed in its absence. The higher ratio of PF to pMDI favored formation of 2,4' phenolic methylene bridges, especially in the absence of ammonium hydroxide. Comparison of the CP/MAS results with the results for ^{13}C NMR of phenolic model compound reactions with phenyl isocyanate under alkaline conditions confirmed that the hydroxide to phenol molar ratio directed the ratio of benzyl to phenyl urethanes formed in the copolymer.

All research is constrained by the limitations of time and resources and the need to focus on a particular area in depth. This research was no exception and had to be limited from many other related topics that should prove interesting and fruitful fields of research in the future. The application of NMR chemical shifts and its relationship to chemical kinetics and reactivity should be worthy of further investigation. In the area of accelerated PF condensation, further work is needed to clearly distinguish the formation of methylene bridges using in situ spectroscopic methods. Such study should more clearly demonstrate the parallel reactions of accelerated condensation and urethane formation investigated in this research. This work has identified the effect of phenolic oligomers in the neutral and anionic state on reaction product structure; however, this particular field of investigation also needs more extensive work to confirm the validity of the hypotheses identified herein.

Furthermore, if a technology is to be developed for the practical utilization of cross-catalyzed reactions of PF and pMDI for commercial purposes, several obstacles need to be overcome. The first is the limited phase miscibility of an aqueous PF component in an organic pMDI and liquid accelerator composition. The dynamic effects that would limit diffusion and cause phase separation due to rapid gelation and polymerization must be taken into account in any practical

application. In addition the sheer rapid reactivity of the cross-catalyzed chemistry lays out a challenge to devise means for latent delivery of this reactivity in a manner that can be triggered on demand and with a completeness of reaction leaving no residual monomers, especially isocyanate. Microencapsulation is one method that has been proposed as a vehicle for latent delivery of the reactivity that merits further research. The possibility of delivering a two-component system to a substrate such as wood where a rapid reaction could be initiated under pressure and optional heat would be a tremendous advance over current technologies.