

## Chapter 3. Results and Discussion

### 3.1. Network Formation of Vinyl Ester/Styrene Resins

#### 3.1.1. Introduction

Vinyl ester oligomers diluted with styrene are important matrix resins (Figure 3.1.1) for thermoset polymer matrix composites.<sup>1-3</sup> They react via free radical copolymerizations to form crosslinked composite matrices, similar to the curing reactions of unsaturated polyester-styrene resins. The network formation mechanism via free radical addition copolymerization is attractive for "on-line" processing because the chemistry allows for good resin stability at room temperature yet rapid reaction at elevated temperatures. The low room temperature viscosities of the vinyl ester-styrene mixtures coupled with rapid cure schedules and low cost make them prime candidates for use in composites for transportation or infrastructure applications.<sup>4</sup> As mentioned in Chapter 1, such applications include construction of parts for automobiles and other surface transportation vehicles, fascia for buildings, and reinforcements for bridges.

Vinyl ester oligomers have terminal reactive double bonds and can form a crosslinked network with or without the addition of a comonomer. It should be noted that the term *vinyl ester resin* can refer to a family of vinyl ester oligomer-styrene blends. The molecular weight of the vinyl ester oligomer, as well as the percentage of styrene varies. The unsaturated bonds on the termini of the vinyl ester oligomers copolymerize with the comonomer (styrene) to form a crosslinked network. Unfortunately, polymeric network formation via free radical

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<sup>1</sup> M. S. Hong and I. J. Chung, *Polym. J.*, 23, 747, 1991.

<sup>2</sup> J. J. Lesko and J. S. Riffle, *Proc. Am. Soc. Compos., 10<sup>th</sup> Tech Conf.*, 53, 1995.

<sup>3</sup> B. K. Larson and L. T. Drzal, *Composites*, 25, 711, 1994.

<sup>4</sup> R. E. Young in *Unsaturated Polyester Technology*, P. E. Bruins, Ed., Gordon and Breach, New York, 1976, p.315.

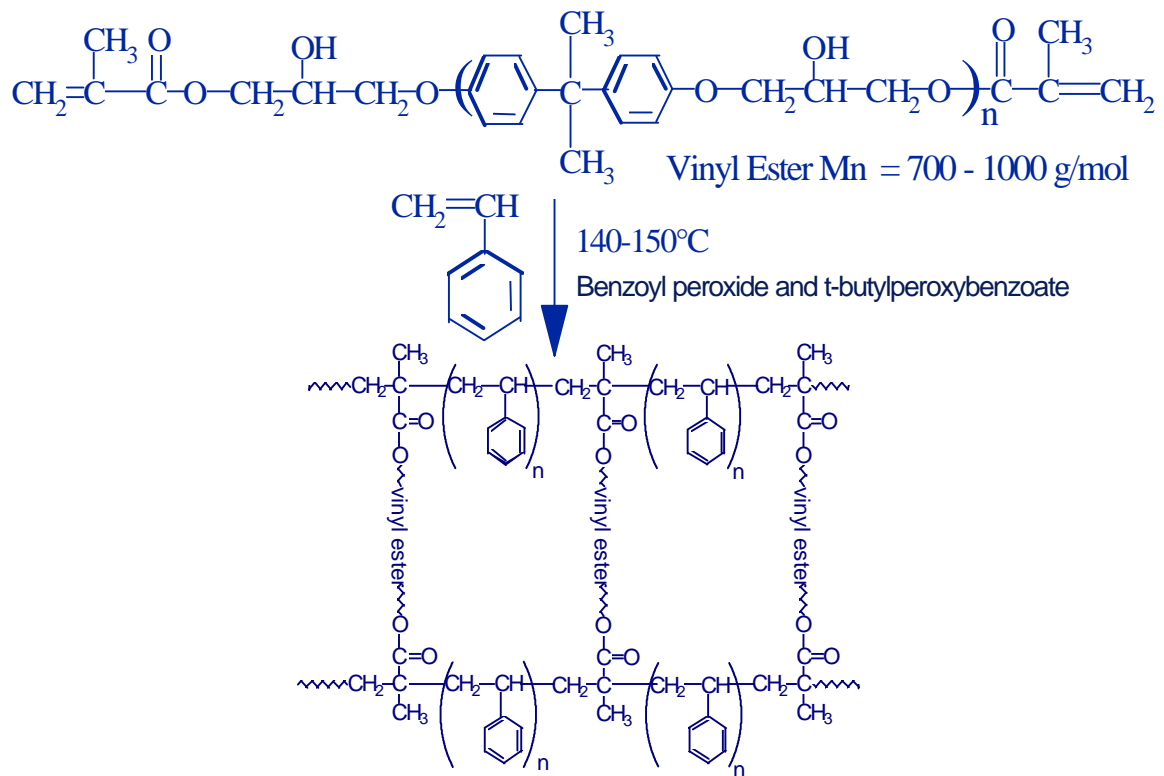


Figure 3.1.1. Typical conditions for free radical addition copolymerization of vinyl ester-styrene resins.

copolymerization is not well understood, and a better understanding of such reactions is desirable to design and control the properties of the networks.

Phenomenological models have been used to study the cure reactions of vinyl ester resins by DSC.<sup>5-7</sup> However, information on the reaction mechanism was difficult to obtain by the DSC studies. Infrared spectroscopy can provide detailed information with regard to free radical copolymerizations. Very fast cure reactions can be monitored, and different types of double bond conversion can be assessed independently and/or simultaneously. The reaction kinetics of selected vinyl ester resins have been investigated previously using FTIR at room temperature and interpreted based on copolymerization theory.<sup>8</sup> The room temperature cured systems were reported to have low conversions due to vitrification, although it is also believed by the author of this thesis that the conversion calculations from FTIR data need to be modified. However, when curing at high temperatures, high conversions can be obtained and the kinetics of the cure reactions may be very different from room temperature cures. Further studies on the kinetics of the cure reaction are also important for high temperature cures which are typical conditions for composite processing operations. This chapter focuses on the chemical reactions of vinyl ester-styrene resins to form thermoset copolymers. In this study the simple copolymerization equation is used to analyze the FTIR data. It has been reported that multifunctional monomer polymerization exhibits a diffusion-controlled termination mechanism due to the limited mobility of the macroradicals.<sup>9</sup> However, this study reveals a quite different picture for vinyl ester/styrene copolymerization systems at high temperatures. As will be discussed in the following sections, almost complete conversion (95-

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<sup>5</sup>J. H. Lee and J. W. Lee, *Polym. Eng. Sci.*, mid-May, 34, 1994.

<sup>6</sup>C. D. Han and K. Lem, *J. Appl. Polym. Sci.*, 29, 1879, 1984.

<sup>7</sup>B. Gaur and J. S. P. Rai, *Eur. Polym. J.*, 29, 1149, 1993.

<sup>8</sup>M. Ganem and B. Mortaigne, *J. M. S. Pure Appl. Chem.*, A30(11), 828, 1993.

<sup>9</sup>A. E. Hamielec, J. F. Macgregor, and A. Penlidis, in *Comprehensive Polymer Science*, Vol. 3, G. Allen and J. C. Bevington, eds., Pergamon Press, London, 17-31, 1989.

100%) can be obtained, and the polymerization becomes diffusion controlled only at very high conversion levels.

### 3.1.2. Cure Reactions Studied by FTIR

Methacrylate (vinyl ester) and styrene double bond conversions were monitored under conditions typical for composite processing operations such as pultrusion or resin transfer molding. Two free radical initiators were used simultaneously (1.1 wt.% benzoyl peroxide and 0.2 wt.% t-butylperoxybenzoate). This is common for continuous processes where, for example, the temperature of the material as it enters a die might be significantly lower than the temperature in the latter parts of the die. One initiator is used which initiates the reaction at the lower temperature while the other is designed to initiate chains as the temperature increases.

Copolymerizations were studied at 140°C using a vinyl ester oligomer with  $M_n = 690$  g/mol and terminal methacrylate groups diluted with systematically increasing amounts of styrene (Figures 3.1.2 and 3.1.3). Infrared absorbances at  $943\text{ cm}^{-1}$  (methacrylate) and  $910\text{ cm}^{-1}$  (styrene), after being normalized and corrected for the backgrounds of the fully cured materials, were used to quantify the conversion data (Figure 3.1.4). A small, but significant, absorbance at  $943\text{ cm}^{-1}$  corresponding to about 20% of the initial absorbance always remained in the fully cured samples. This was assigned to the vinyl ester backbone (and not to approximately 20% of the methacrylate groups which remained unreacted). Both solid state  $^{13}\text{C}$  NMR experiments and the infrared spectrum of a high molecular weight polyhydroxyether (Figure 3.1.5) with a repeat unit structure similar to the vinyl ester polymer backbone support this assignment. The ratio of the absorbances at  $943\text{ cm}^{-1}$  (vinyl ester backbone) vs.  $830\text{ cm}^{-1}$  in the polyhydroxyether was 0.11. Since this was close to the analogous ratio in the fully reacted vinyl ester networks (0.091), it was concluded that both absorbances were likely due to the vinyl ester backbone. The carbonyl regions of the  $^{13}\text{C}$  solid state NMR spectra of the networks were analyzed to confirm that the methacrylate

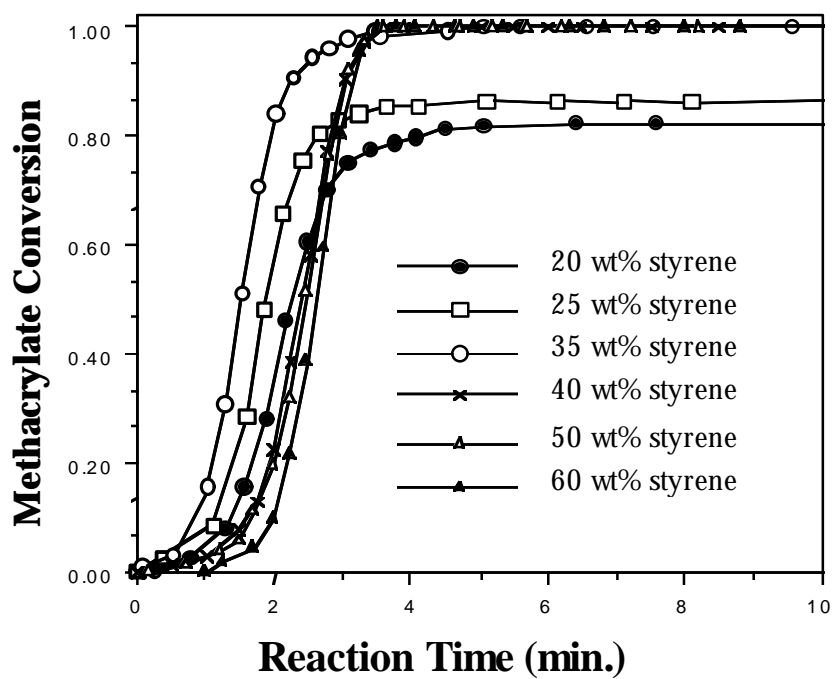


Figure 3.1.2. Styrene content effects on methacrylate conversion at 140°C (Raw data were listed in Tables 3.1.5 to 3.1.7).

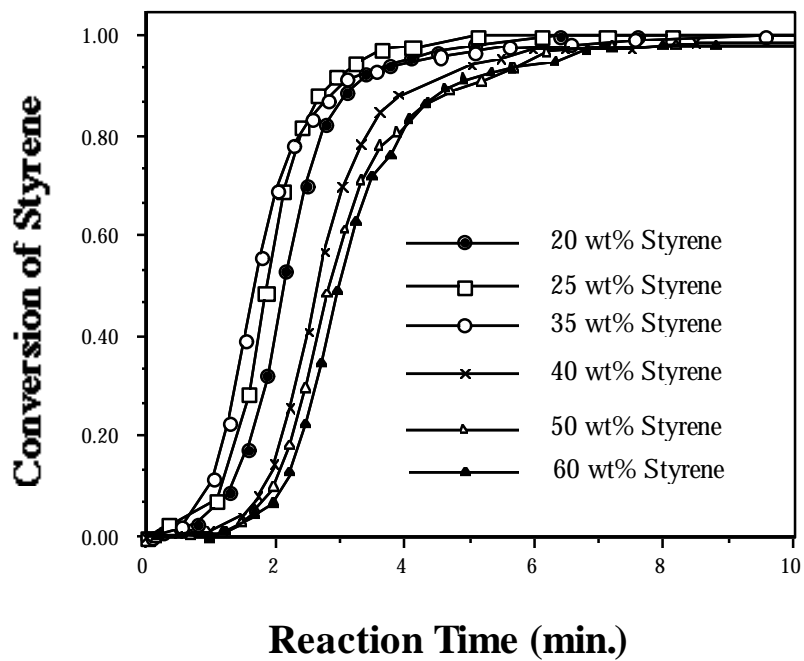


Figure 3.1.3. Styrene content effects on styrene conversion at 140°C (Raw data were listed in Tables 3.1.5 to 3.1.7).

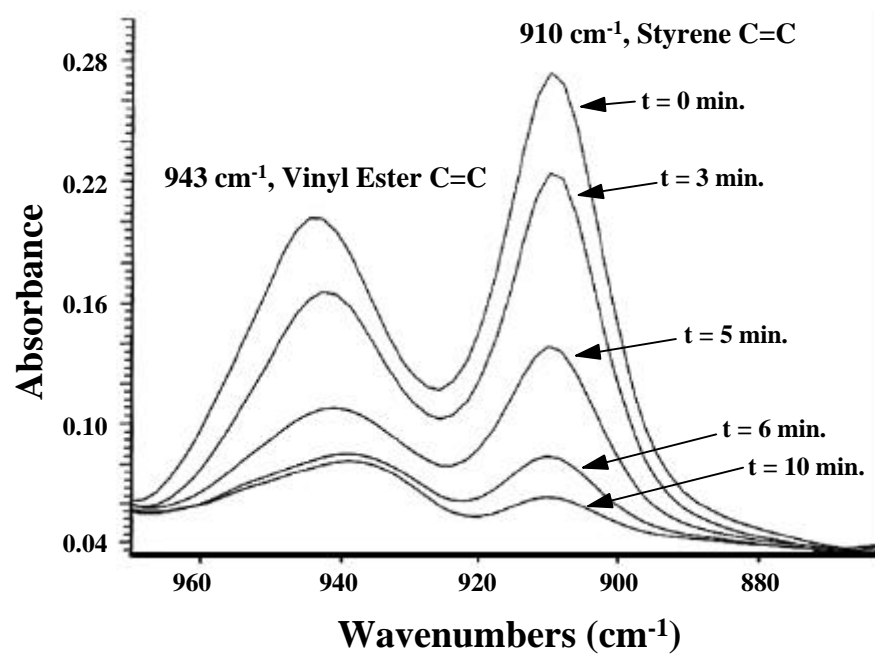


Figure 3.1.4. Infrared spectra of a vinyl ester resin during cure (120°C).

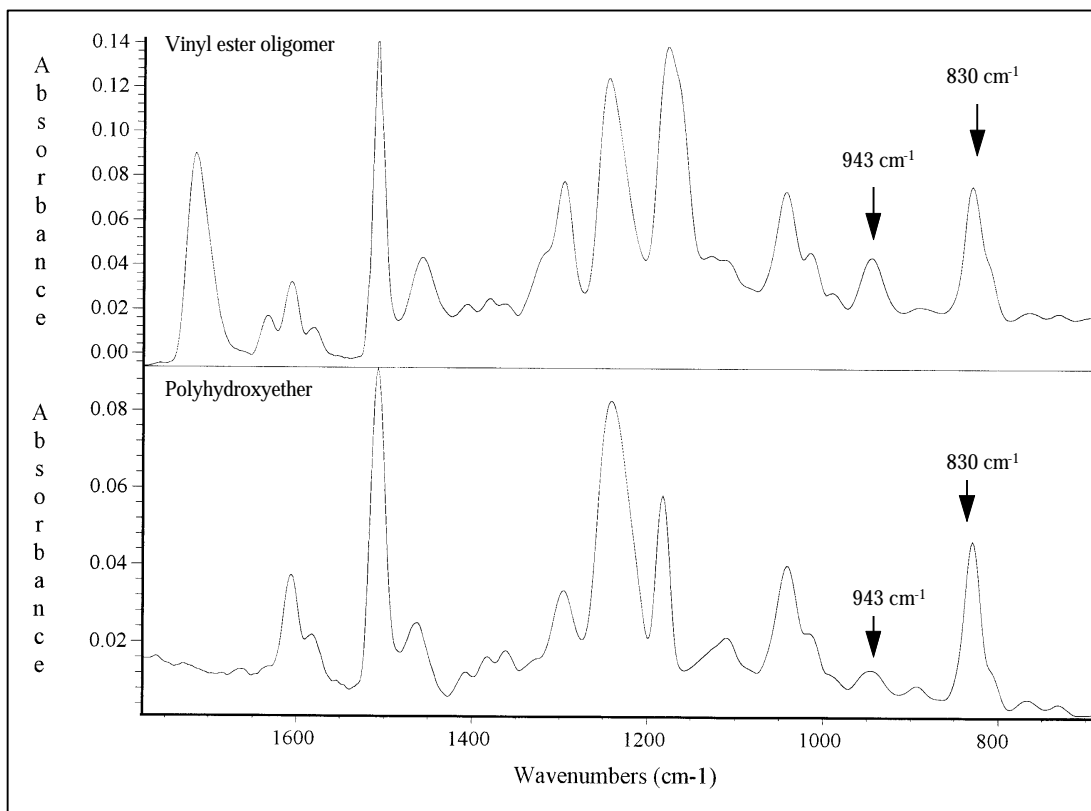


Figure 3.1.5. Infrared spectrum of a linear polyhydroxyether model with the same chemical structure as the vinyl ester backbone.



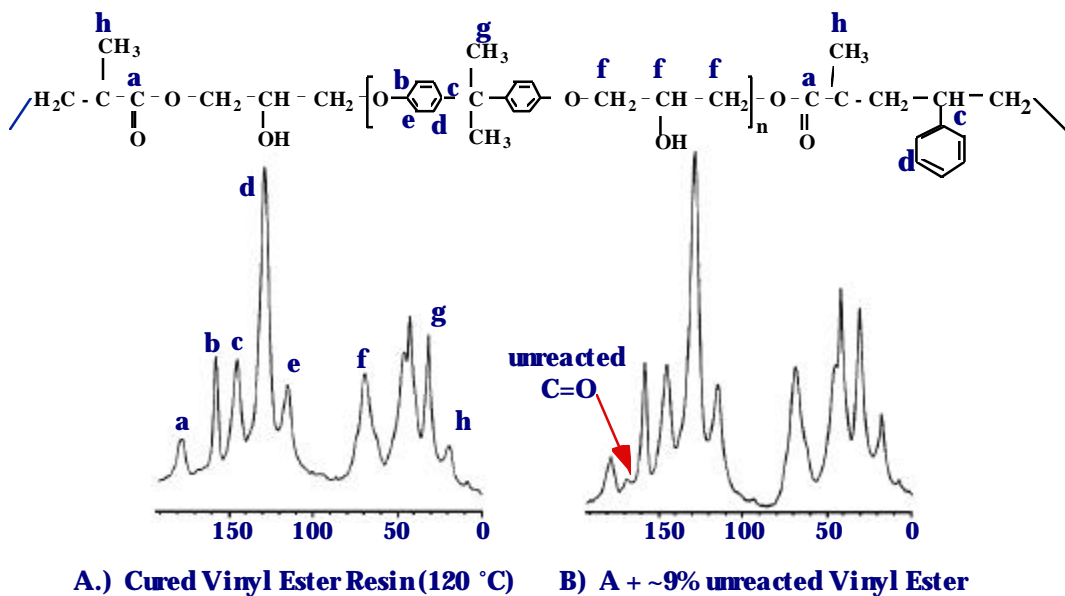


Figure 3.1.6.  $^{13}\text{C}$ -NMR spectra of (a) fully cured vinyl ester resin and (b) the fully cured resin with 9% unreacted methacrylate groups added.

Table 3.1.1. Analysis of methacrylate conversion by  $^{13}\text{C}$  solid state NMR.

Samples	Area of peak 167/Area of peaks (167+177)
Fully cured Derakane 441-400	~ 0
The cured sample + 2 mol% methacrylate from the uncured vinyl ester resin	~ 0
The cured sample + 5 mol% methacrylate from the uncured vinyl ester resin	3.5
The cured sample + 9 mol% methacrylate from the uncured vinyl ester resin	6.4
The cured sample + 20 mol% methacrylate from the uncured vinyl ester resin	16.0

groups reacted quantitatively.<sup>10</sup> A vinyl ester (690 g/mol plus 28 wt.% styrene) was reacted under conditions in which quantitative conversion was expected (120°C for 30 min.) and resonances due to unreacted (167 ppm) and reacted (177 ppm) methacrylate carbonyl carbons were assessed (Figure 3.1.6). No peak at 167 ppm was detectable, suggesting that all of the methacrylates had reacted, while the FTIR spectrum of the same sample exhibited about 20% of the initial absorbance at 943 cm<sup>-1</sup>. Subsequently, from 2-20 mole percent unreacted methacrylate was added into the fully cured sample and the integrals of the unreacted and reacted methacrylate carbonyl carbons were quantified (Table 3.1.1). Although the solid state NMR resonances are broad and approximately ± 4% error exists, the data clearly demonstrate that if a small percentage of unreacted methacrylate groups had remained in the cured samples, they would have been detectable by NMR.

It is recognized that subtracting the fully cured spectrum from the IR spectra to obtain reaction conversions may introduce an error in the conversion data since the background peak at 943 cm<sup>-1</sup> could not be assigned to a structure. It may result from the polyhydroxyether backbone structure of the vinyl ester oligomers (in which case the amount to be subtracted would essentially be a constant for a given sample thickness), or the background peak may change in intensity with conversion. Based on the spectrum for a high molecular weight polyhydroxyether (Figure 3.1.5), it was reasoned that at least most of this background was due to the backbone structure.

Monomer reactivity ratios were calculated from the FTIR data obtained at low conversions to predict the azeotropic feed composition (the monomer feed ratio where the copolymer composition should remain constant throughout the polymerization). The two double bonds in the vinyl ester oligomer were assumed to have the same reactivity. Thus, any terpolymerization effects due to pendent double bonds were neglected. Copolymerization was assumed to obey a terminal reactivity model, meaning that only the mer unit carrying the reactive free radical at the end of the propagating chain affects the kinetics.

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<sup>10</sup> R. H. Newman and K. H. Patterson, *Polymer*, 37(7), 1065, 1996.

These assumptions allowed the simplest copolymerization equations<sup>11</sup> to be employed (equation 1 which can algebraically be rearranged to equation 2). Note that [M] in equations 1 and 2 refers to the equivalent concentration of methacrylate double bonds instead of

$$\frac{d[S]}{d[M]} = \frac{[S]}{[M]} \times \frac{r_s [S] + [M]}{[S] + r_m [M]} \quad (1)$$

$$r_s = \frac{d[S]}{d[M]} \times \left[ \frac{[M]}{[S]} \right]^2 r_m + \left[ \frac{d[S]}{d[M]} - 1 \right] \times \frac{[M]}{[S]} \quad (2)$$

referring to the molar concentration of the difunctional vinyl ester oligomer.

The compositions of crosslinked copolymers ( $d[S]/d[M]$ ) at early reaction stages were determined from the styrene concentration consumption ( $d[S]$ ) and methacrylate consumption ( $d[M]$ ) (Table 3.1.2 and early conversion slopes from Figure 3.1.7). The reactivity ratios were estimated by using the copolymerization equation (equation 2) and plotting  $r_m$  vs.  $r_s$  (Figure 3.1.8).<sup>12</sup> The point of intersection for these six vinyl ester-styrene compositions represents the estimated reactivity ratio pair for the methacrylate endgroups on the vinyl ester oligomer and styrene. It was found that  $r_s \cong 0.36 \pm 0.05$  and  $r_m \cong 0.24 \pm 0.1$  for styrene and methacrylate, respectively. Reactivity ratios of corresponding small monomer systems, methyl methacrylate and styrene, previously measured at 60°C are  $r_s = 0.52$  and  $r_m = 0.46$ .<sup>13</sup>

Although these ratios are similar,  $r_s/r_m$  (1.5) for the thermosetting styrene/vinyl ester system is

<sup>11</sup> F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs and F. R. Mayo, *J.A.C.S.*, 70, 1519, 1948.

<sup>12</sup> D. Braun, H. Cherdron, and W. Kern, *Practical Macromolecular Organic Chemistry*, Harwood Academic Publishers, New York, 1984.

<sup>13</sup> G. Odian, *Principles of Polymerization*, John Wiley & Sons, New York, 1981.

significantly higher than for the linear copolymerization of styrene with methyl methacrylate where  $r_s/r_m$  equals 1.1.

The mole fractions of styrene in the feed vs. the mole fractions of styrene at early conversions in the copolymers for the vinyl ester-styrene networks and for styrene-methyl methacrylate copolymers are compared in conjunction with the azeotropic 45° line (Figure 3.1.9). The azeotropic point (where the experimental data crosses the azeotropic line in Figure 3.1.9) for the vinyl ester network with a 690 g/mol vinyl ester oligomer is 54 mole percent styrene which corresponds to 26 wt. % styrene. Thus, it is anticipated that this particular vinyl ester-styrene composition should yield networks in which the composition of the network formed in the early stages of polymerization have the same composition as the network formed in the latter stages. As is also indicated in Figure 3.1.9, for systems with lower percentages of styrene in the feed (below the azeotropic point), the network formed in the early stages of polymerization should have more styrene due to the higher value of  $r_s$  than  $r_m$ . Therefore, in the latter stages of polymerization, only the terminal double bonds of the vinyl ester continue

Table 3.1.2. Feed and copolymer (slopes of  $d[S]$  vs.  $d[M]$  at early conversion).

weight % styrene in feed	20	25	35	40	50	60
mole % styrene in feed	46	52	63	67	78	83
mole % styrene in copolymer	53	59	61	62	72	80

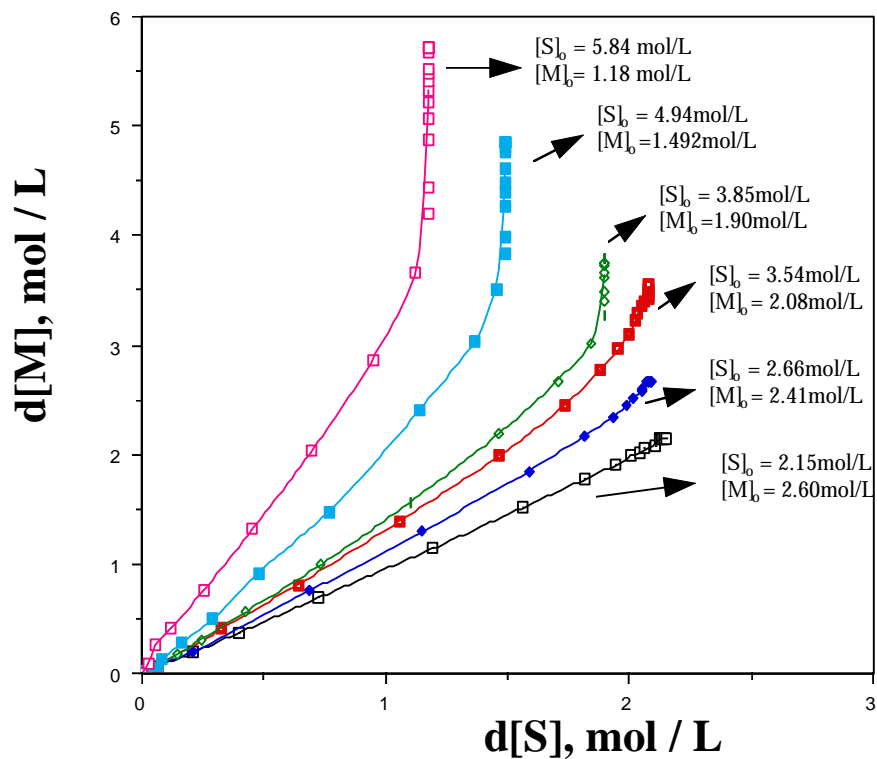


Figure 3.1.7. Styrene consumption as a function of methacrylate consumption.  
 $[S]_0$  and  $[M]_0$ : Concentration of feed. Copolymer compositions for assessing the reactivity ratios were calculated from the early conversion portions of the graphs.

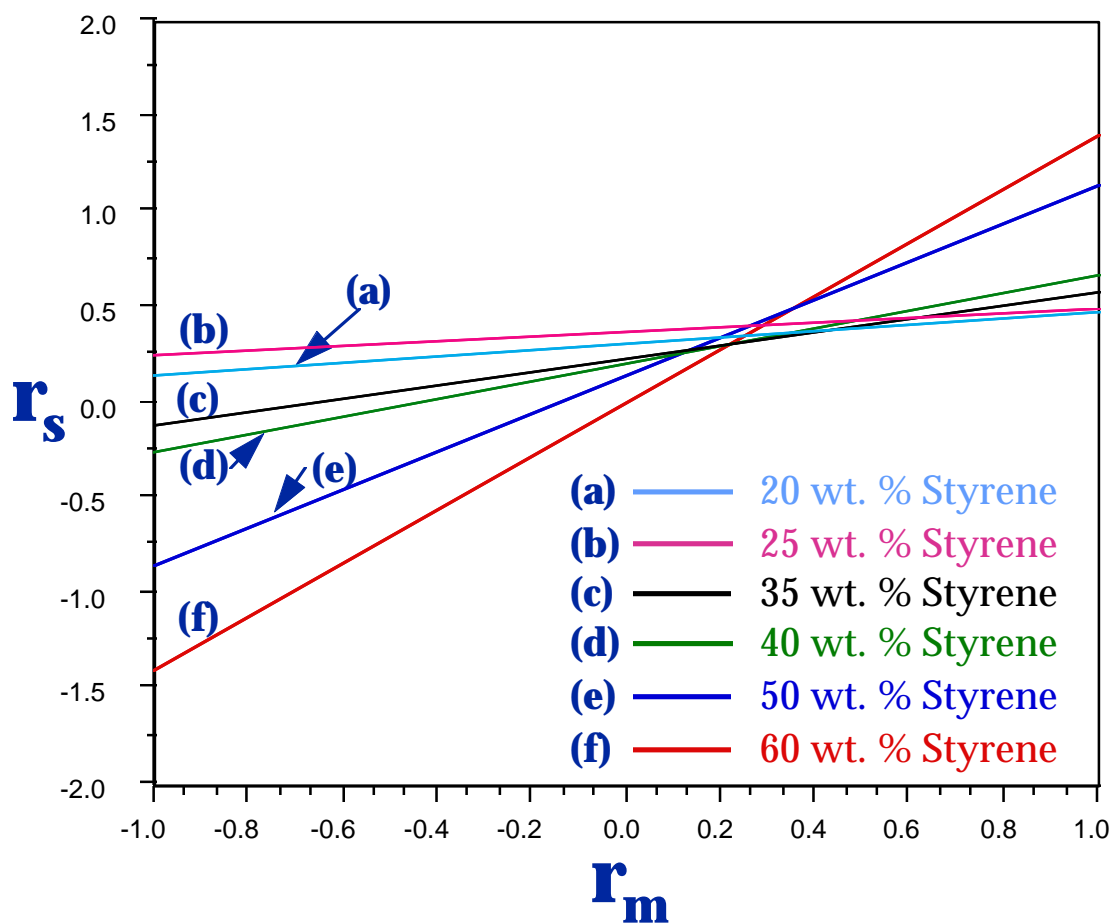


Figure 3.1.8. Graphical determination of  $r_s$  and  $r_m$ ,  $r_s = 0.36 \pm 0.05$ ,  $r_m = 0.24 \pm 0.1$

to react because all styrene has been consumed. On the other hand, for systems with higher percentages of styrene in the feed (above azeotropic point), the network formed in the early stages of polymerization should have less styrene. Only styrene is left in the latter stages of polymerization.

Besides compositions of crosslinked copolymers, cure reaction rates were also calculated based on the FTIR experimental data. Figure 3.1.10 shows a plot of cure reaction rate as a function of double bond conversion at three different cure temperatures. The onset of autoacceleration can immediately be observed. Shortly after the polymerization reaches its maximum rate, the reduced mobility in the system leads to diffusion-controlled propagation and autodeceleration occurs. Eventually polymerization stops when vitrification suppresses the propagation reaction. It was also found that the cure reaction rates at 120°C and 140°C cure temperatures were much faster than the reaction rate of the system at 100°C.

Using  $r_s = 0.36$  and  $r_m = 0.24$ , the experimental copolymer compositions were compared with those predicted by the Meyer-Lowry integrated copolymer composition equation (equation 3) (Figure 3.1.11).<sup>9</sup>  $X$  corresponds to total monomer conversion,  $f_{10}$  is the initial mole fraction

$$X = 1 - \left(\frac{f_1}{f_{10}}\right)^a \left(\frac{(1-f_1)}{(1-f_{10})}\right)^b \left(\frac{(f_{10} - d)}{(f_1 - d)}\right)^g \quad (3)$$

$$a = r_2/(1-r_2)$$

$$b = r_1/(1-r_1)$$

$$g = (1-r_1r_2)/((1-r_1)(1-r_2))$$

$$d = (1-r_2)/(2-r_1-r_2)$$



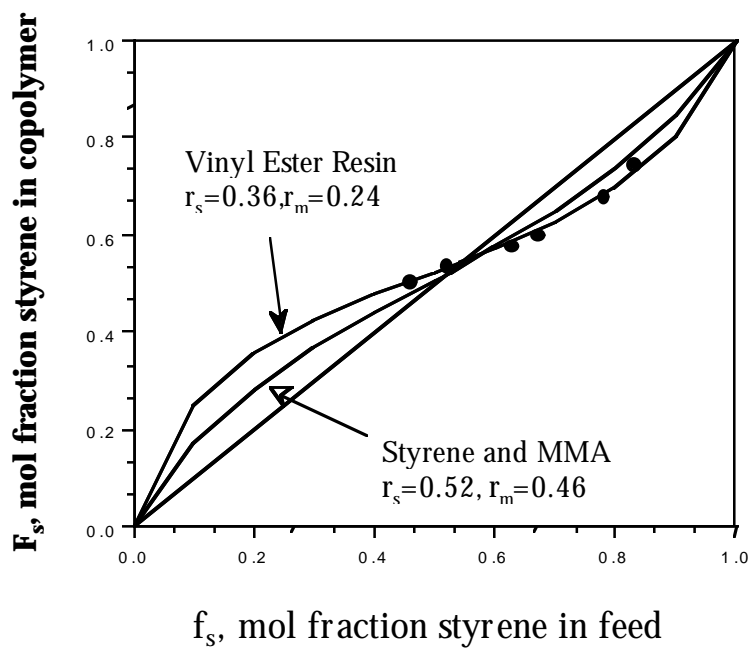


Figure 3.1.9. Comparison of copolymer compositions with feed composition for the vinyl ester-styrene thermoset relative to a linear methyl methacrylate-styrene composition.

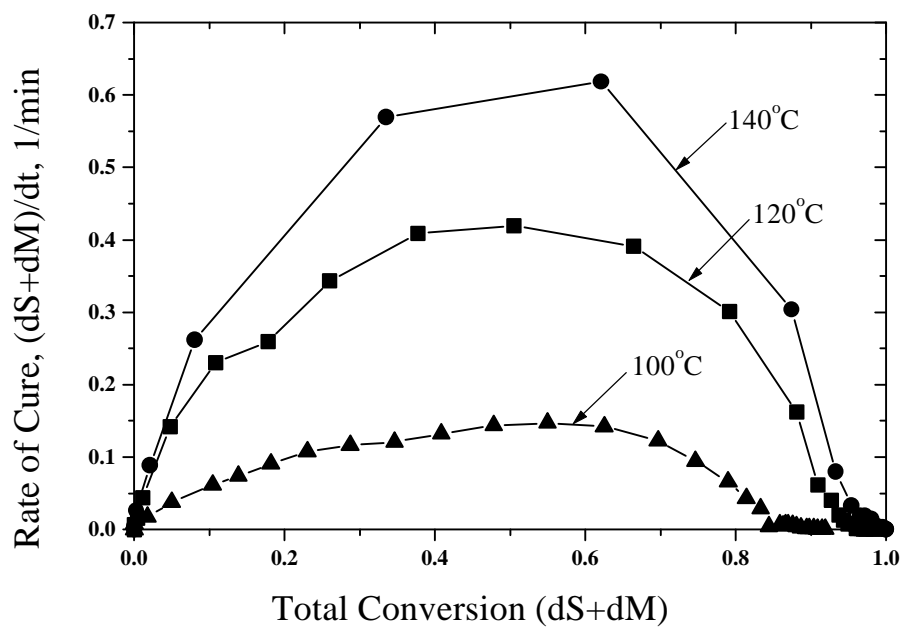


Figure 3.1.10. Cure reaction rate as a function of total double bond conversion for Derakane 441-400 (1.1 wt% benzoyl peroxide plus 0.2 wt% t-butyl peroxybenzoate, error  $\pm 4\%$ ).

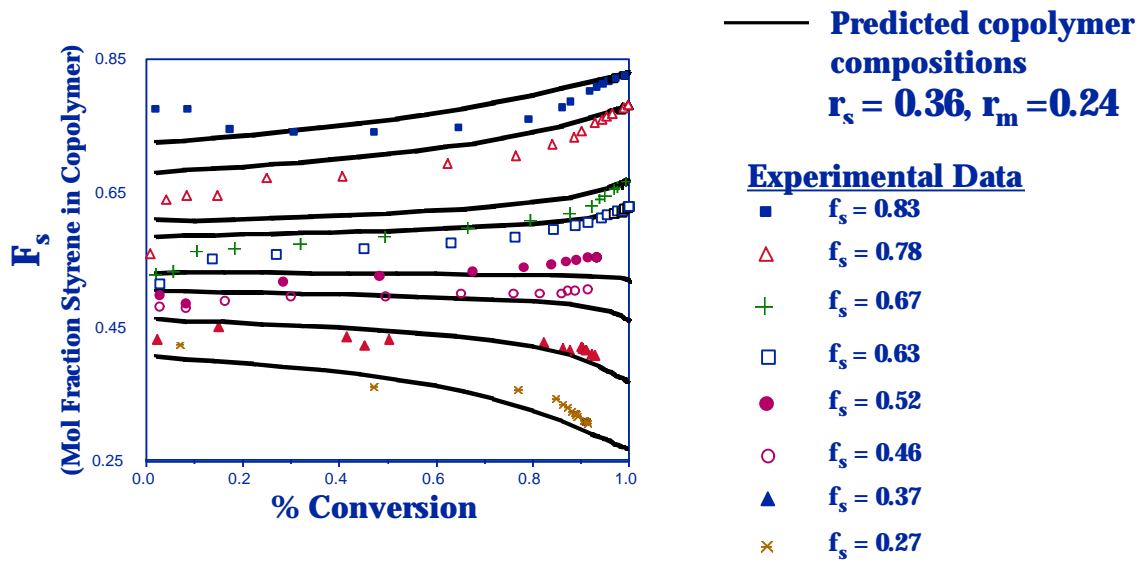


Figure 3.1.11. Copolymer compositions calculated using  $r_s = 0.36$  and  $r_m = 0.24$  and the integrated copolymer equation. Comparisons are made between experiments and prediction.

of monomer 1 (styrene) in the feed, and  $f_1$  is the mole fraction of monomer 1 in the feed at a given conversion ( $X$ ). Computer programs developed by Harwood<sup>14-15</sup> were used to predict copolymer compositions throughout the reactions, including the latter stages where significant gelation had occurred (Figure 3.1.10). The experimental vinyl ester network compositions were very close to those predicted by the integrated equation. As expected, both the experimental and predicted copolymer composition curves corresponding to feed compositions near the azeotropic point are nearly flat. Thus, it is concluded that the copolymerization equations designed for linear systems can be used to at least approximate the copolymerization of vinyl esters at high temperatures (above  $T_g$  corresponding to the fully converted material). Gelation apparently does not significantly alter the copolymer composition for this system. This is particularly important in light of the fact that phase separation of the gel from the sol occurs very early in these reactions (visual observation).

### 3.1.3. Sol/Gel Analysis

Network formation of a vinyl ester having a methacrylate/styrene composition very close to the azeotropic composition (Derakane 441-400, vinyl ester  $M_n = 690$  g/mol diluted with 28 weight percent styrene) was also studied by analyzing the soluble portions of the reaction mixture (the sol) and insoluble crosslinked copolymer (the gel) as a function of reaction time. Table 3.1.3 lists the compositions of the sol fractions determined by both FTIR in methyl ethyl ketone solution and  $^1\text{H}$  NMR. FTIR calculations were based on absorbances at  $830\text{ cm}^{-1}$  (vinyl ester backbone) relative to  $700\text{ cm}^{-1}$  (phenyl peak of styrene). It was not possible to evaluate the double bond absorbances using this method due to overlapping FTIR absorbances with the solvent. The compositions of the sol fractions (and hence, also, for the gel fractions) remained approximately constant until the final stages of gelation. During the final stage, the sol becomes enriched with styrene. This can be explained in light of the kinetic copolymerization results. Although the relative concentration of reacted methacrylate and

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<sup>14</sup> H. J. Harwood, N. W. Johnston, and H. Piotrowski, *J. Polym. Sci., Pt. C*, 25, 23, 1968.

<sup>15</sup> H. J. Harwood, *J. Polym. Sci., Pt. C*, 25, 37, 1968.

Table 3.1.3. Composition of sols as a function of cure time(Derakane 441-400).

Reaction Time (Min.)	Wt % Styrene in Sol (FTIR)	Wt% Styrene in Sol ( <sup>1</sup> H-NMR)	Gel Fraction (Wt. %)
0	30	30	0
2.80	29	33	12
3.00	29	34	19
3.20	28	34	33
3.33	30	35	42
3.40	33	34	55
4.00	32	36	77
4.53	43	39	95
4.75	100	100	100
4.88	100	100	100
5.50	100	100	100
8.00	100	100	100

Reaction conditions: 120 °C, 1.1 wt % benzoyl peroxide + 0.2 wt % t-butyl peroxybenzoate.

## Derakane 441-400 (28 wt% Styrene)

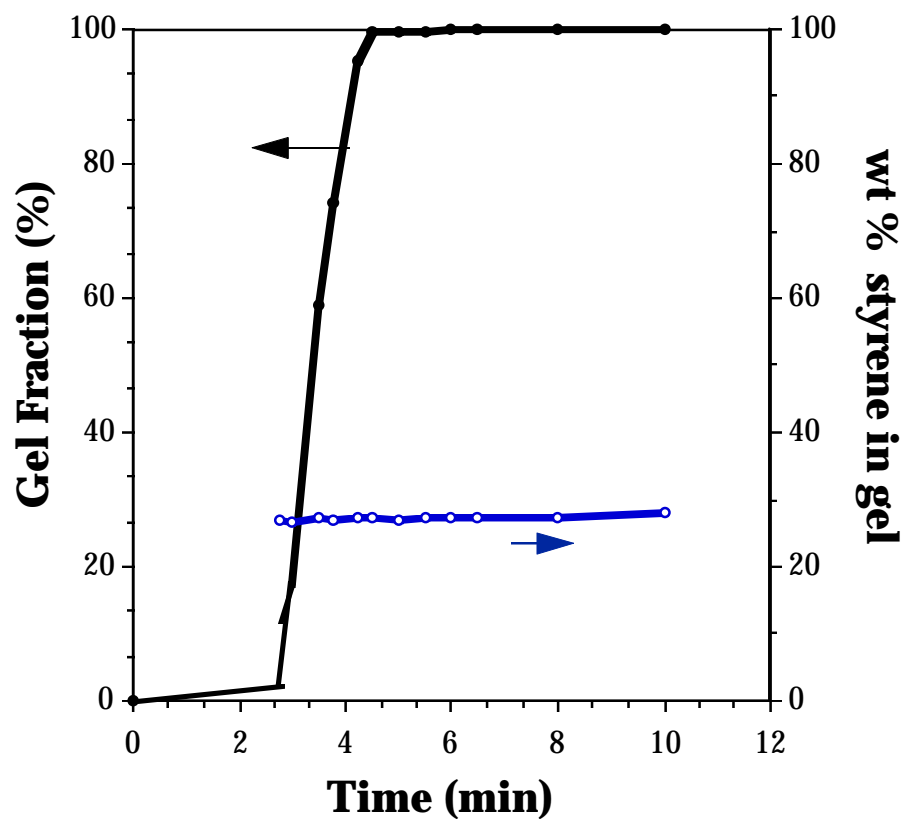


Figure 3.1.12. Gel composition during cure at 120 °C (Derakane 441-400,  $M_n$  of the vinyl ester oligomer equals 690 g/mol, 28 wt% styrene).

styrene double bonds should remain approximately constant throughout the reaction (because this vinyl ester composition is near the azeotropic point), unreacted methacrylate groups would be expected to be primarily pendent to the network chains toward the end of the reaction. Thus, unreacted styrene should remain in the sol but unreacted methacrylate should exist primarily in the gel.

The chemical compositions of the gels isolated during the cure of Derakane 441-400 were examined by FTIR using KBr pellets. Gel compositions were also calculated by ratioing the absorbances at  $830\text{ cm}^{-1}$  and  $700\text{ cm}^{-1}$  corresponding to the vinyl ester and styrene components, respectively. Unfortunately, the solid state IR measurements were not sufficiently sensitive to accurately monitor the double bond region. Thus, it was not possible to assess the amount of pendent unreacted methacrylate groups in the gel fractions. Gel formation was first detected at  $\cong 2.75$  minutes at  $120\text{ }^{\circ}\text{C}$  (immediately following the induction period caused by the inhibitors which were present) which corresponds to an overall double bond conversion of about 12%. During cure, the styrene composition in the gel remained constant at  $\sim 28$  weight percent after the gel fraction approached 20-30% (Figure 3.1.12). When the gel fraction was low (10-15%), the gel had a slightly lower styrene content (21-25%). Possibly at the early stages of the reaction, a significant fraction of the methacrylate groups in the gel was still unreacted.

The gel fractions were also analyzed by differential scanning calorimetry. The materials were first heated to  $200^{\circ}\text{C}$  at  $10^{\circ}\text{C}$  per minute to insure complete reaction, then cooled and reheated at  $10^{\circ}\text{C}$  per minute. Table 3.1.4 shows the reaction times of the gels and their corresponding glass transition temperatures. No residual heat of reaction was observed during the first heat for any of these gels. The  $T_g$ 's of these gels all ranged between  $125^{\circ}\text{C}$  to  $128^{\circ}\text{C}$ , supporting the infrared data that all of the gel compositions were nearly equal. The small increase in  $T_g$  at longer reaction times was probably due to an increase in the crosslink density.

The effect of temperature on the conversion of each type of double bond was examined using Derakane 441-400 vinyl ester/styrene resin (28 wt% styrene). Figure 3.1.13 summarizes the experimental results graphically at cure temperatures of 100°C, 120°C, and 140°C. Vinyl ester network formation is extremely fast under these conditions. At 140°C, the FTIR indicates that almost 100% conversion of vinyl ester and 90% conversion of styrene occurred within three minutes of the induction period and close to 100% conversion was obtained for this system at longer reaction times (25-30 min) at 120°C and 140°C. In examining the polymerization behavior of these systems (Figure 3.1.10), it was found that the cure reaction rates at 120°C and 140°C were much faster than the reaction rate of the system at 100°C. When the polymerization proceeds more rapidly than the volume relaxation, excess free volume is generated.<sup>16</sup> As discussed earlier, the final conversion of the reaction may be limited by the chain mobility. Excess free volume could provide the additional mobility needed for higher final conversion at higher cure temperatures. By contrast, at 100°C, only around 90% conversion was achieved even at reaction times of more than one hour. This is apparently due to vitrification ( $T_g$  of the cured 28 weight percent vinyl ester resin is 135-145°C). Cure temperatures lower than  $T_g$  would be expected to result in residual unsaturation.

The effect of styrene concentration on monomer conversion was also studied by FTIR at 140°C. Significant levels of methacrylate groups remain unreacted at 140°C with styrene compositions lower than about 28-30 weight percent. Since the  $T_g$  of the fully cured 28 weight percent styrene network is 135-145°C and higher  $T_g$ 's would be expected for lower styrene contents, this behavior may also be due to vitrification.

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<sup>16</sup> K. S. Anseth, L. M. Kline, T. A. Walker, K. J. Anderson, and C. N. Bowman, *Macromolecules*, 28, 2491, 1995.



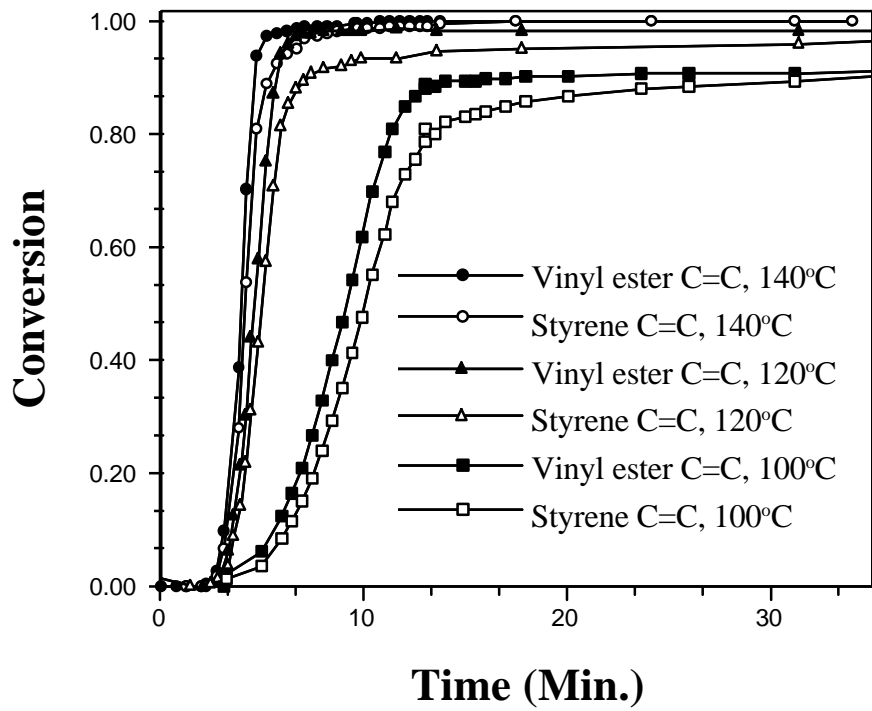


Figure 3.1.13. Reaction conversion at various cure temperatures.

Table 3.1.4. Analysis of gel by Differential Scanning Calorimetry

Reaction time (minutes)	T <sub>g</sub> (°C)
2.75	125
3.50	126
4.00	127
8.00	127
10.0	128

### 3.1.4. Conclusions

Reactivity ratios of styrene with terminal methacrylates on vinyl ester oligomers were estimated to be  $r_S = 0.36$  and  $r_M = 0.24$  at 140 °C. The azeotropic point for a vinyl ester resin having a backbone molecular weight of 690 g/mol occurs at approximately 26 weight percent styrene. Gelation occurs early in these reactions relative to networks such as epoxy resins which cure by step-growth mechanisms. The first gel was detected as early as 12% double bond conversion using Derakane 441-400 (140°C). Sols and gels isolated during a reaction with a feed composition very near the azeotropic point (Derakane 441-400) confirm that the composition of the gel remains nearly constant except for the very early and very late stages of reaction.

Table 3.1.5. Conversion data of Derekane 441-400 at various cure temperatures by FTIR (1.1 wt% benzoyl peroxide and 0.2 wt% t-butylperoxybenzoate).

Cured at 140°C			Cured at 120°C			Cured at 100°C		
Time (Min.)	$\alpha_{\text{MMA}}$	$\alpha_{\text{S}}$	Time (Min.)	$\alpha_{\text{MMA}}$	$\alpha_{\text{S}}$	Time (Min.)	$\alpha_{\text{MMA}}$	$\alpha_{\text{S}}$
0	0	0	0	0	0	0	0	0
0.78	0	0	1.05	0	0	3.23	0	0
1.28	0	0	1.50	0	0	4.93	0.024	0.011
1.98	0	0	1.62	0	0	5.90	0.063	0.037
2.28	0.005	0	2.12	0	0	6.42	0.125	0.083
2.70	0.025	0.017	2.43	0.005	0.003	6.95	0.163	0.114
3.15	0.096	0.065	2.83	0.011	0.012	7.43	0.212	0.151
3.80	0.389	0.281	3.35	0.060	0.035	7.93	0.269	0.191
4.18	0.702	0.540	3.63	0.126	0.090	8.43	0.332	0.242
4.70	0.939	0.810	3.92	0.214	0.142	8.93	0.399	0.293
5.20	0.974	0.892	4.22	0.302	0.218	9.43	0.466	0.350
5.70	0.982	0.926	4.50	0.439	0.314	9.92	0.543	0.413
6.18	0.986	0.945	4.82	0.577	0.433	10.43	0.620	0.479
6.67	0.989	0.955	5.18	0.753	0.576	10.95	0.697	0.553
7.02	0.992	0.969	5.55	0.874	0.709	11.42	0.769	0.624
7.67	0.993	0.975	5.90	0.945	0.817	11.95	0.813	0.681
8.17	0.995	0.979	6.32	0.964	0.855	12.43	0.851	0.729
8.68	0.995	0.983	6.65	0.974	0.881	12.95	0.870	0.758
9.53	0.996	0.987	7.03	0.979	0.896	13.45	0.880	0.786
9.70	0.996	0.987	7.45	0.980	0.907	13.92	0.889	0.812
10.20	0.996	0.989	7.98	0.983	0.916	14.95	0.894	0.823
10.72	1.00	0.991	8.90	0.984	0.923	15.42	0.894	0.832
11.20	1.00	0.992	9.37	0.986	0.933	15.92	0.894	0.838
11.70	1.00	0.993	9.85	0.985	0.937	16.93	0.899	0.840
12.20	1.00	0.994	11.60	0.987	0.934	17.95	0.899	0.852
12.72	1.00	0.995	13.63	0.986	0.947	20.08	0.904	0.858
13.17	1.00	0.995	17.75	0.985	0.954	23.68	0.905	0.869
13.67	1.00	0.996	31.47	0.985	0.962	26.00	0.907	0.882
17.40	1.00	1.00	39.50	0.984	0.974	31.17	0.908	0.887
24.15	1.00	1.00	40.68	0.985	0.978	35.43	0.910	0.897
31.12	1.00	1.00	49.70	0.985	0.981	44.18	0.913	0.904
33.95	1.00	1.00	50.80	0.985	0.982	52.88	0.914	0.915
			57.53	0.985	0.982	65.62	0.915	0.923
						74.25	0.916	0.931

$\alpha_{\text{MMA}}$  is the conversion of methacrylate end groups of vinyl ester oligomers.  $\alpha_{\text{S}}$  is the conversion of styrene. Error:  $\alpha_{\text{MMA}} \pm 4\%$ ,  $\alpha_{\text{S}} \pm 2\%$ .

Table 3.1.6. Conversion data of vinyl ester resins with various styrene contents cured at 140°C by FTIR (1.1 wt% benzoyl peroxide and 0.2 wt% t-butylperoxybenzoate).

20 wt% Styrene			25 wt% Styrene			35 wt% Styrene		
Time (Min.)	$\alpha_{\text{MMA}}$	$\alpha_{\text{S}}$	Time (Min.)	$\alpha_{\text{MMA}}$	$\alpha_{\text{S}}$	Time (Min.)	$\alpha_{\text{MMA}}$	$\alpha_{\text{S}}$
0	0	0	0	0	0	0	0	0
0.26	0.006	0.009	0.35	0.028	0.024	0.05	0.008	0.002
0.76	0.025	0.029	1.10	0.086	0.075	0.54	0.032	0.020
1.26	0.080	0.086	1.60	0.285	0.282	1.04	0.156	0.113
1.56	0.153	0.172	1.85	0.477	0.488	1.27	0.308	0.229
1.86	0.279	0.320	2.14	0.658	0.694	1.52	0.508	0.392
2.16	0.460	0.531	2.39	0.752	0.815	1.77	0.704	0.560
2.46	0.601	0.703	2.65	0.801	0.879	2.02	0.836	0.694
2.76	0.699	0.823	2.93	0.824	0.919	2.27	0.904	0.780
3.08	0.748	0.885	3.20	0.836	0.946	2.54	0.940	0.837
3.40	0.773	0.923	3.64	0.851	0.971	2.80	0.960	0.873
3.73	0.785	0.938	4.10	0.852	0.978	3.09	0.975	0.910
4.08	0.794	0.952	5.09	0.859	1.00	3.54	0.980	0.932
4.48	0.810	0.967	6.12	0.861	1.00	4.54	0.990	0.960
5.05	0.816	0.980	7.10	0.862	1.00	5.04	1.00	0.969
6.40	0.819	1.00	8.10	0.862	1.00	5.57	1.00	0.975
7.560	0.819	1.00	10.45	0.865	1.00	6.55	1.00	0.983
12.46	0.825	1.00	13.12	0.866	1.00	7.54	1.00	0.992
17.78	0.825	1.00	18.10	0.867	1.00	9.54	1.00	1.00
22.31	0.822	1.00	23.10	0.867	1.00	12.54	1.00	1.00
27.55	0.828	1.00	28.12	0.867	1.00	17.40	1.00	1.00
--	--		--	--	--	27.57	1.00	1.00

Table 3.1.7. Conversion data of vinyl ester resins with various styrene contents cured at 140°C by FTIR (1.1 wt% benzoyl peroxide and 0.2 wt% t-butylperoxybenzoate).

40 wt% Styrene			50 wt% Styrene			60 wt% Styrene		
Time (Min.)	$\alpha_{\text{MMA}}$	$\alpha_{\text{S}}$	Time (Min.)	$\alpha_{\text{MMA}}$	$\alpha_{\text{S}}$	Time (Min.)	$\alpha_{\text{MMA}}$	$\alpha_{\text{S}}$
0	0	0	0	0	0	0	0	0
0.48	0.014	0.003	0.17	0	0	0.23	0	0
0.98	0.027	0.015	0.70	0.014	0.005	1.00	0	0
1.48	0.074	0.042	1.20	0.042	0.009	1.23	0.019	0.014
1.73	0.128	0.082	1.47	0.056	0.028	1.71	0.046	0.044
1.98	0.223	0.145	1.70	0.111	0.057	1.98	0.098	0.070
2.23	0.385	0.257	1.97	0.194	0.099	2.21	0.216	0.129
2.50	0.581	0.408	2.22	0.319	0.185	2.46	0.386	0.225
2.77	0.770	0.568	2.47	0.514	0.299	2.71	0.595	0.350
3.03	0.899	0.695	2.80	0.764	0.488	2.96	0.804	0.491
3.32	0.973	0.786	3.07	0.917	0.616	3.24	0.954	0.626
3.60	1.00	0.849	3.32	0.972	0.711	3.51	1.00	0.720
3.90	1.00	0.882	3.62	1.00	0.777	3.78	1.00	0.760
4.62	1.00	0.902	3.90	1.00	0.806	4.06	1.00	0.836
5.00	1.00	0.940	4.30	1.00	0.863	4.34	1.00	0.869
5.48	1.00	0.952	4.70	1.00	0.891	4.63	1.00	0.893
5.97	1.00	0.970	5.20	1.00	0.910	4.93	1.00	0.913
6.47	1.00	0.973	5.70	1.00	0.934	5.33	1.00	0.928
7.48	1.00	0.973	6.20	1.00	0.967	5.64	1.00	0.937
8.48	1.00	0.988	7.20	1.00	0.976	6.31	1.00	0.947
10.48	1.00	0.988	8.20	1.00	0.981	6.81	1.00	0.974
13.47	1.00	0.988	10.30	1.00	0.981	7.99	1.00	0.981
15.00	1.00	0.988	13.25	1.00	0.981	8.79	1.00	0.981
22.00	1.00	0.988	18.25	1.00	0.981	10.73	1.00	0.981
--	--	--	23.20	1.00	0.981	13.74	1.00	0.981
--	--	--	28.35	1.00	0.981	28.79	1.00	0.981

$\alpha_{\text{MMA}}$  is the conversion of methacrylate end groups of vinyl ester oligomers.  $\alpha_{\text{S}}$  is the conversion of styrene. Error:  $\alpha_{\text{MMA}} \pm 4\%$ ,  $\alpha_{\text{S}} \pm 2\%$ .