3.4. Synthesis and Characterization of a New Vinyl Ester Oligomer

3.4.1. Introduction

A range of alternate candidates structurally analogous to bisphenol A-based vinyl esters were synthesized and characterized in Dr. J. E. McGrath's research group in order to decrease the water absorption and cure shrinkage of bisphenol-A based vinyl ester resins for dental applications.[1, 2] It was reported that these novel vinyl ester oligomers showed improvements in properties such as lower initial viscosities. One of these new vinyl ester oligomers, the dimethacrylate of bisphenol A propoxylate, (Figure 3.4.1) is potentially interesting for application in composite matrix resins. The viscosity of this vinyl ester oligomer at room temperature is only 300 cps and it can be processed into composites without dilution. The object of this research is to study the polymerization and copolymerization of this new resin under typical conditions for on-line composite processing and to examine the mechanical properties of the cured networks. In this chapter, syntheses, cure reactions, and toughness of this new vinyl ester are presented.

3.4.2. Synthesis of Oligomers

The methacrylation of propoxylated bisphenol-A (Schemes 3.4.1 & 3.4.2) was carried out by reacting it with methacryloyl chloride in the presence of triethylamine in dichloromethane at room temperature.[1. 3, 4] The yield of this reaction is around 80%. The propoxylated bisphenol-A is commercially available. However, ^{1}H-NMR shows that the commercial product has some unknown impurities which cannot be removed by drying under vacuum or washing with dilute basic or acid solutions. Thus the propoxylated bisphenol-A used in this

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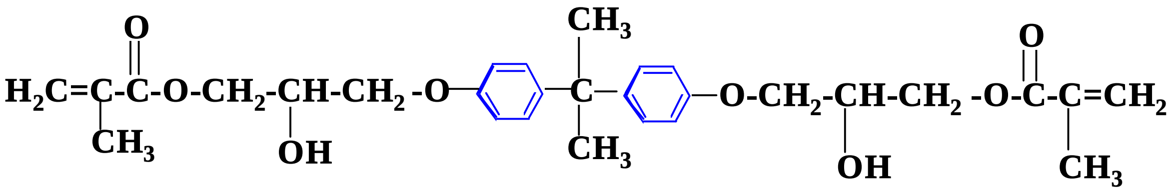
[1] S. Kalachandra, D. F. Taylor, C. D. DePorter, H. J. Grubbs, J. E. McGrath, *Polymer*, 34, 778, 1993.

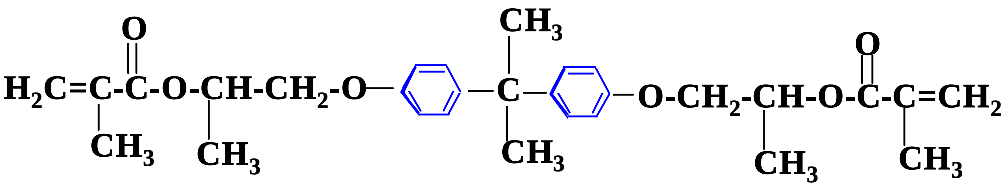
[2] H. K. Shobha, M. Sankarapandian, A. R. Shultz, and J. E. McGrath, S. Kalachandra and D. F. Taylor, *Macromol. Symp*., 111, 73, 1996.

[3] S. Kobayashi, E. Masuda, and S. I. Shoda, *Macromolecules*, 22, 2878, 1989.

[4] J. E. Dietz, and N. A. Peppas, *Polymer*, 38(15), 3767, 1997.



Tg = -6 ^{o}C, η = 1.2 x 10^{6} cps at 25 ^{o}C



Tg = -27 ^{o}C , η = 300 cps at 25 ^{o}C

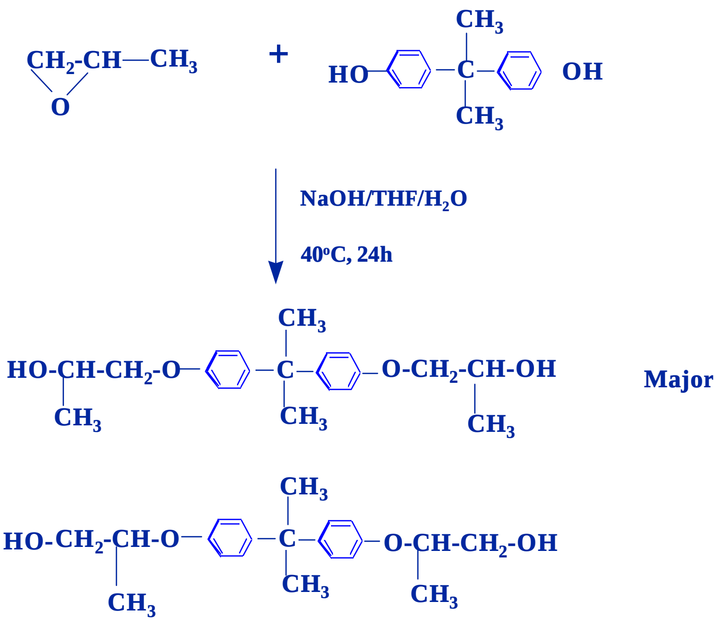
Figure 3.4.1. Structure comparison of two vinyl ester resins. Top structure: dimethacrylate of diglycidyl ether of bisphenol A; Bottom structure: dimethacrylate of propoxylated bisphenol A.

work was prepared in house from bisphenol-A and propylene oxide (Scheme 3.4.1) and the ^{1}H-NMR spectrum shows no unknown impurities in the structure (Figure 3.4.2). The structures of the propoxylated bisphenol-A and the dimethacrylate of bisphenol A propoxylate vinyl ester after esterification with methacryloyl choride were confirmed by ^{1}H-NMR and IR spectroscopy (Figures 3.4.3 and 3.4.4). The ^{1}H-NMR spectroscopic analysis shows that the number of methacrylate endgroups per vinyl ester molecular is nearly 2 as determined by comparing the peak area of the methylene protons adjacent to the oxygen atom of the ester group (5.3 ppm) and the vinyl protons of the methacrylate group (5.5 + 6.1 ppm).

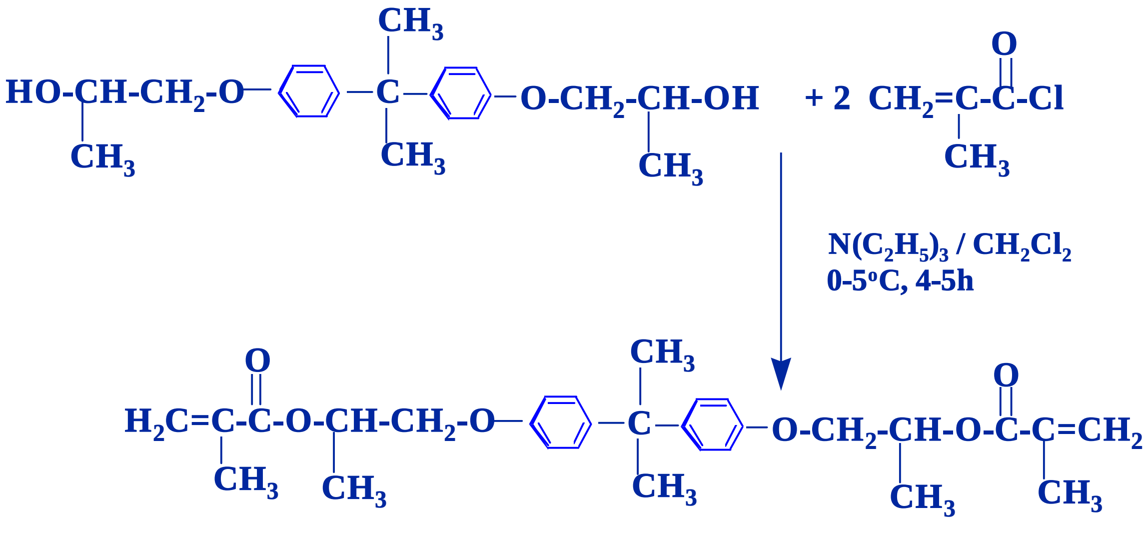
3.4.3. Polymerization And Copolymerization

Polymerization of the di-methacrylate of bisphenol A propoxylate neat resin was studied using FTIR at high temperatures which are typical conditions for an on-line process. Figure 3.4.5 shows the IR spectra of the new resins during cure at 160 ^{o}C. The peak at 1635 cm^{-1} corresponding to the double bond of the new resins was used to calculate conversion of C=C double bonds corresponding to the vinyl ester endgroups. The peak at 1610 cm^{-1} was used as the reference peak. Figure 3.4.6 shows the results of FTIR analyses at cure temperatures of 120, 140 and 160^{o}C using two initiators (1% benzoyl peroxide and 0.2% t-butylperoxybenzoate). Conversion of the final methacrylate end groups increases with temperature and conversion at 160^{o}C was 85%. Figure 3.4.7 shows the ^{13}C-NMR spectrum of the neat network cured at 160^{o}C for one hour. The carbonyl groups (167 ppm) attached to unreacted vinyl groups are around 10 percent, therefore the conversion is around 90%. The FTIR results on conversion of methacrylaye endgroups at 160 ^{o}C (85%, Figure 3.4.6) are in fairly good agreement with the ^{13}C-NMR results (90%, Figure 3.4.8). It was reported that conversion of this new vinyl ester was only 51% at a cure temperature of 80 ^{o}C using AIBN as the initiator.[2] Copolymerization of the dimethacrylate of bisphenol A propoxylate with styrene was also studied by FTIR. The heights of the infrared absorbancies at 946 cm^{-1}

Scheme 3.4.1.



Scheme 3.4.2.



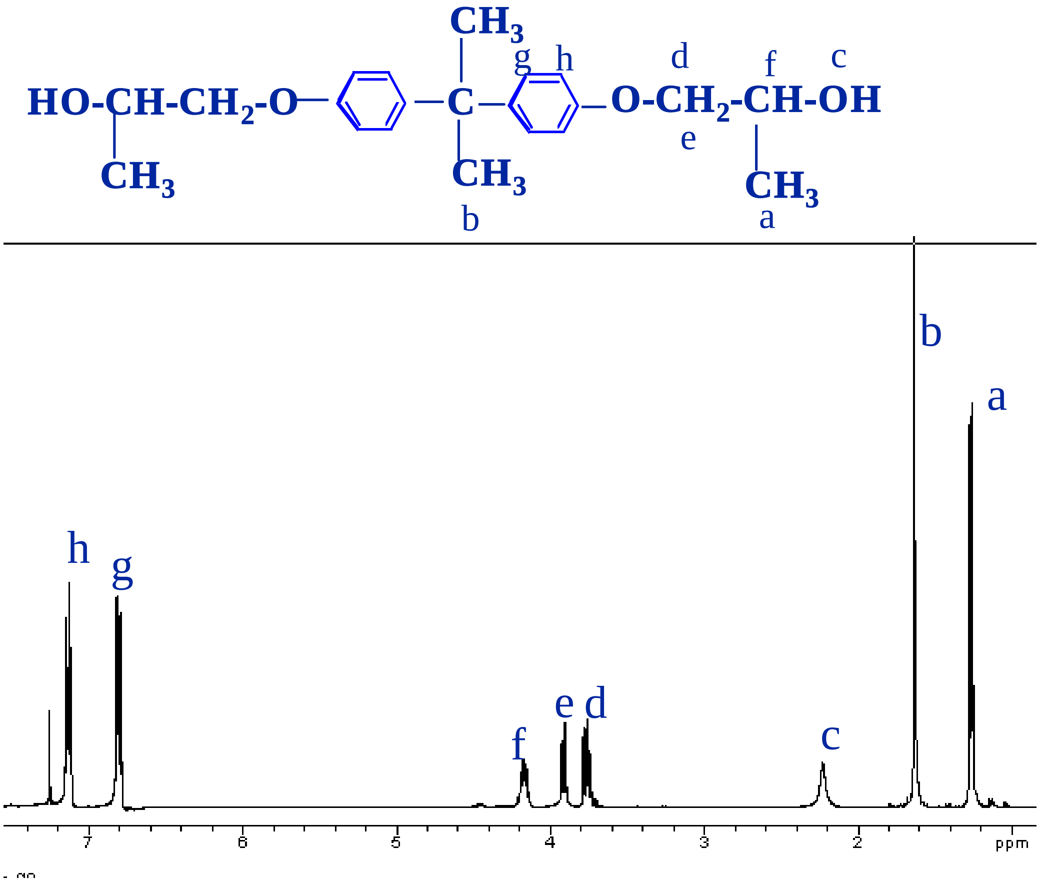


Figure 3.4.2. ^{1}H-NMR spectrum of [2,2-bis(4-(2-hydroxyprop-1-oxy)phenyl] propane or bisphenol A propoxylate synthesized in our laboratory.

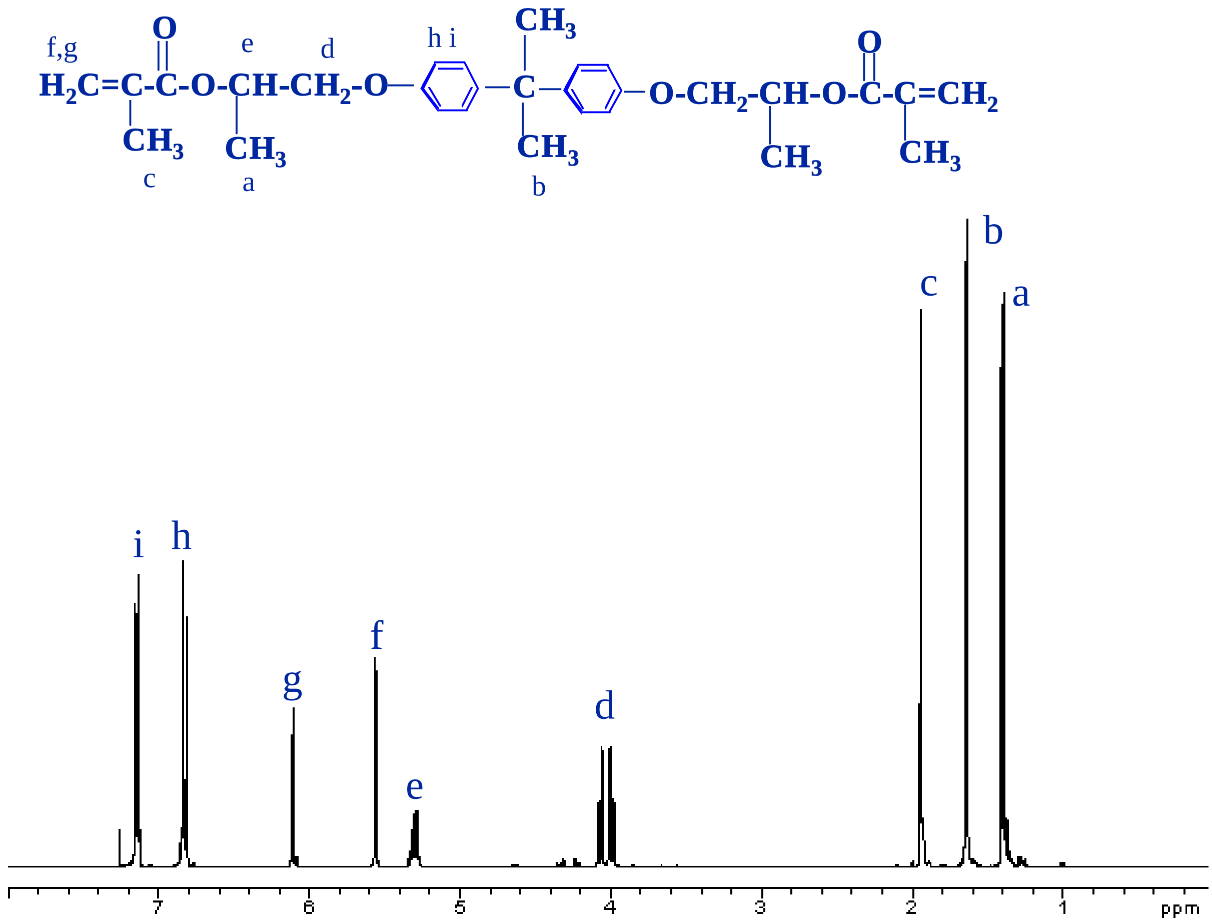


Figure 3.4.3. ^{1}H-NMR spectrum of dimethacrylate of bisphenol A propoxylate. Bisphenol A propoxylate was synthesized in our laboratory.

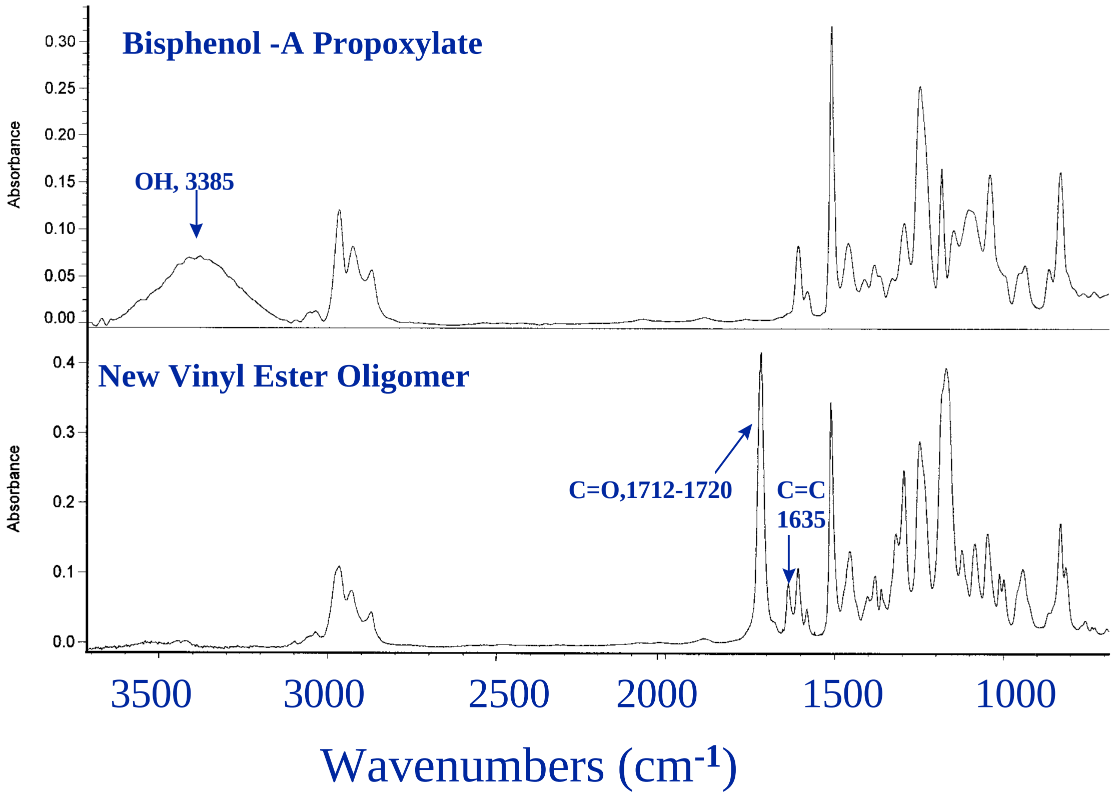


Figure 3.4.4. IR spectra of propoxylated bisphenol-A and dimethacrylate of bisphenol A propoxylate.

and 910 cm^{-1} corresponding to methacrylate and styrene double bonds respectively were monitored quantitatively and used to calculate reaction conversions. There was a background peak that overlapped the absorbance at 946 cm^{-1} and needed to be subtracted from the conversion spectra to analyze the data appropriately. Figure 3.4.9 shows the FTIR results for the cure reaction of the dimethacrylate of bisphenol A propoxylate diluted with 30 wt% styrene at 140 °C (two initiators : 1 % benzoyl peroxide and 0.2 % t-butylperoxybenzoate). The final conversion of methacrylate endgroups at 140°C was determined to be 96% by FTIR. The residual methacrylate endgroups of a network from the dimethacrylate of bisphenol A propoxylate diluted with 30 wt % styrene (cured at 140 °C) was determined to be 7% by ^{13}C-NMR spectroscopy (Figure 3.4.8). Results obtained by FTIR and ^{13}C-NMR spectroscopy both show that the final conversion of methacrylate endgroups at 140 °C was close to 100%.

The kinetics of the cure reactions of these resins were also studied using both isothermal and dynamic DSC.[5] Figure 3.4.10 shows DSC thermograms for the isothermal polymerization of the dimethacrylate of bisphenol A propoxylate at 120°C, 140°C and 160°C. The isothermal cure was followed by a dynamic scan, so the heat of isothermal cure and the residual heat of reaction could be determined. The final conversion was calculated from equation (1) and listed in Table 3.4.1.

$$\text{Conversion} = \frac{\text{Heat of isothermal cure}}{(\text{Heat of isothermal cure}+\text{Heat of residual peak})} \qquad (1)$$

As the data shown in Table 3.4.1, the initiator has a significant effect on the conversion at certain temperatures. When 1% benzoyl peroxide is used as the initiator, a complete cure can

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[5] M. S. Hong and I. J. Chung, *Polymer J.,* 23, 747, 1991.

[6] W. D. Cook, G. P. Simon, P. J. Burchill, M. Lau, and T. J. Fitch, *J. Appl. Polym. Sci*., 64, 759, 1997.

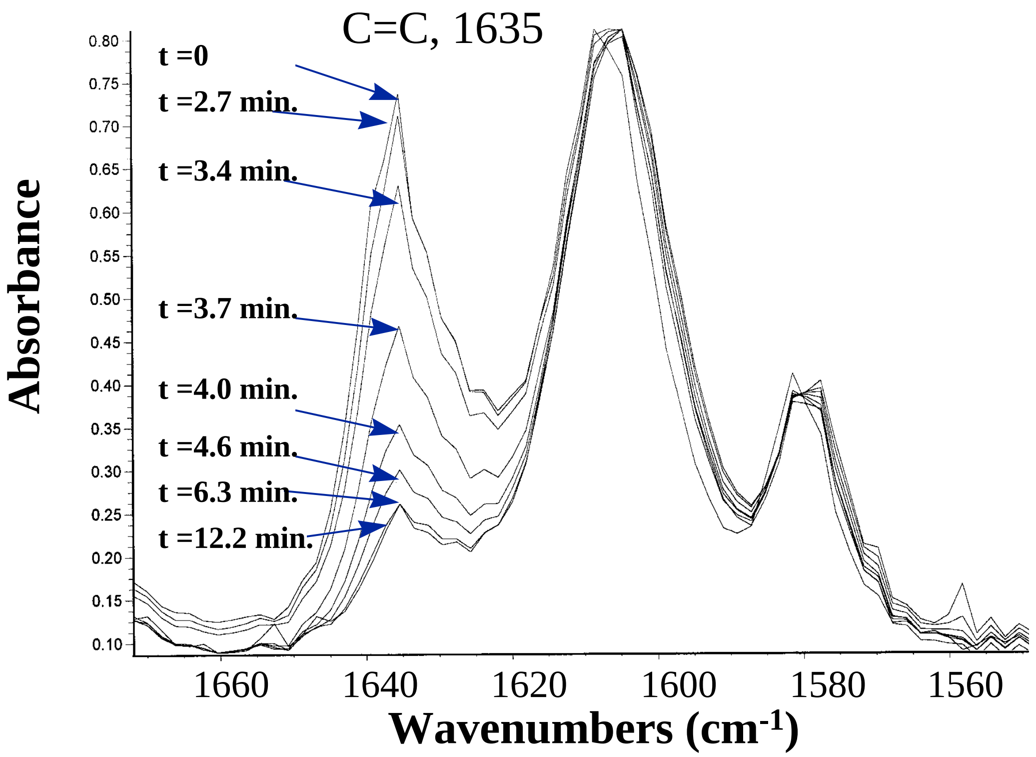


Figure 3.4.5. IR spectra of dimethacrylate of bisphenol A propoxylate resins during cure reaction (160 ^{o}C).

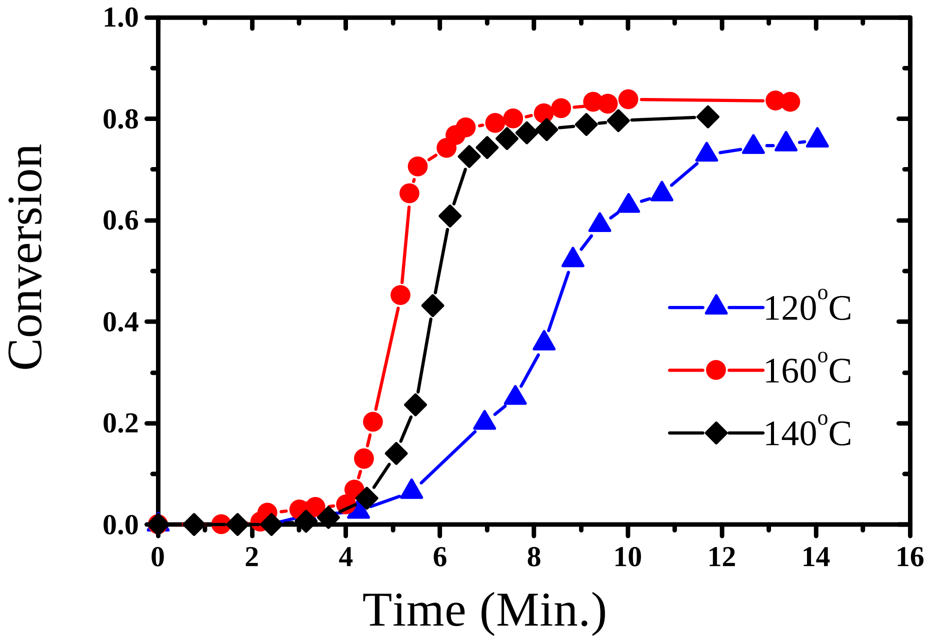


Figure 3.4.6. Double bond conversion of the dimethacrylate of bisphenol A propoxylate resins at different cure temperatures (1% benzoyl peroxide and 0.2% t-butyl peroxybenzoate).

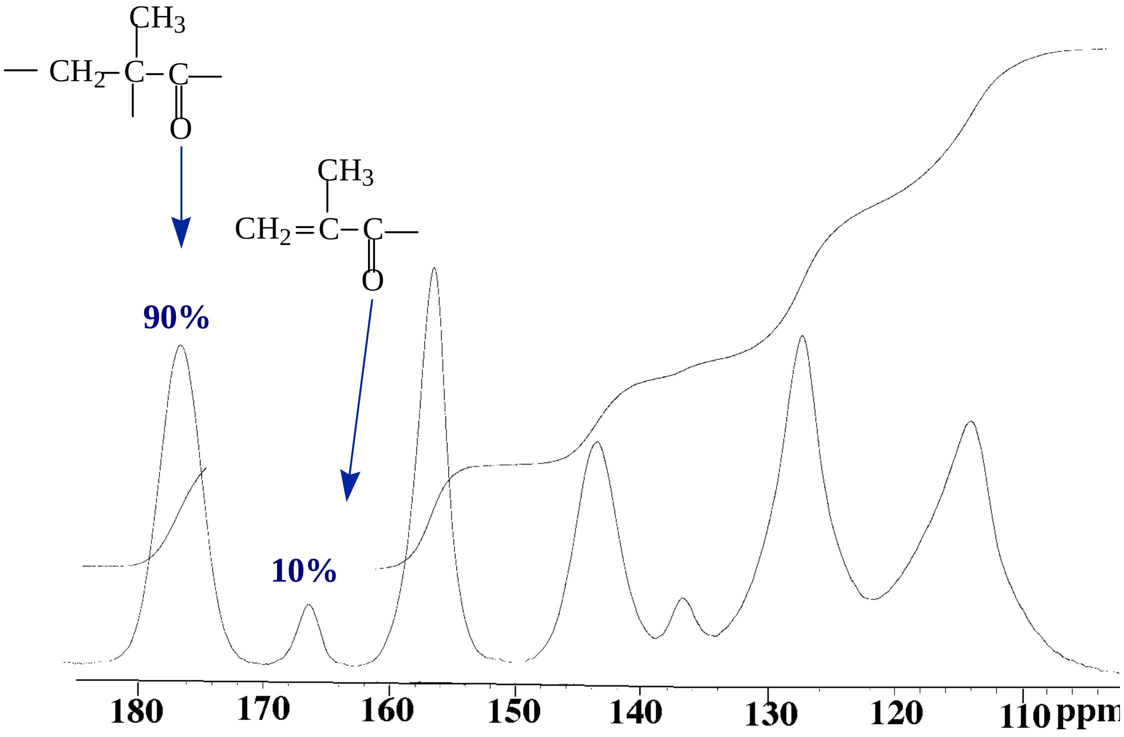


Figure 3.4.7. ^{13}C-NMR spectrum of the dimethacrylate of bisphenol A propoxylate network.

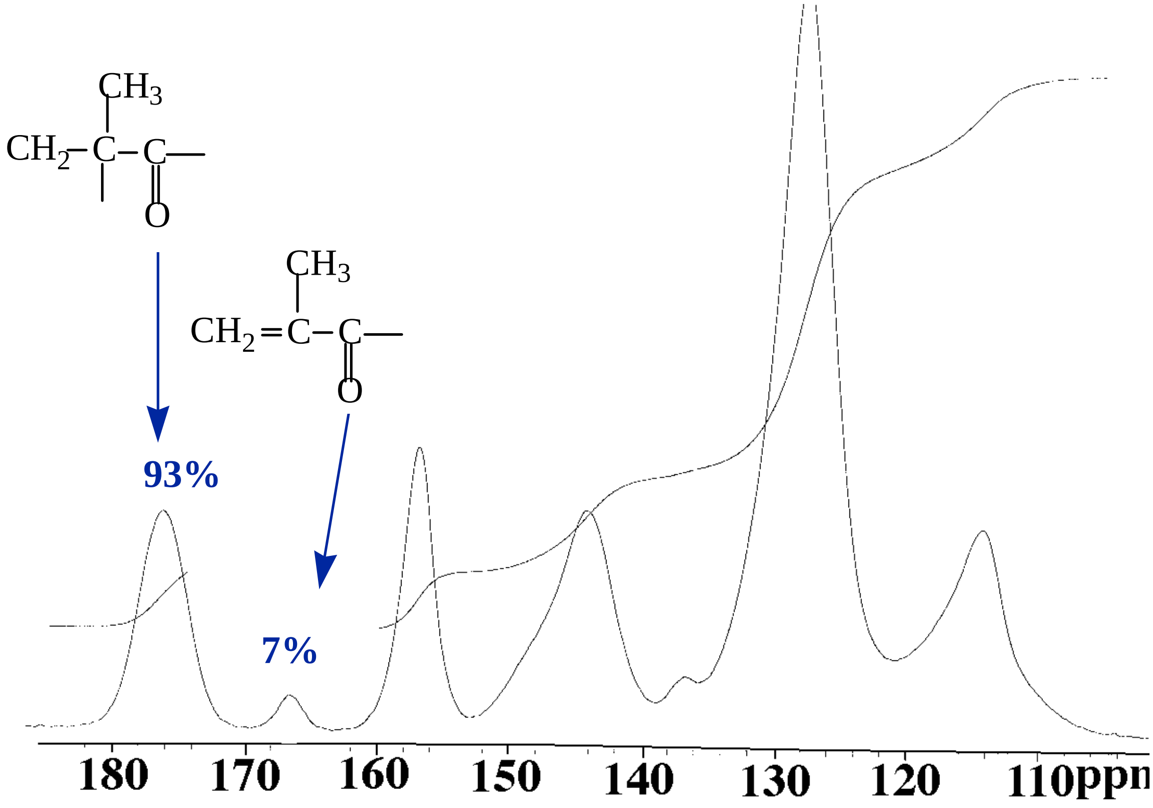


Figure 3.4.8. ^{13}C-NMR spectrum of a network from the dimethacrylate of bisphenol A propoxylate diluted with 30 wt% styrene.

Table 3.4.1. Final conversion of double bonds for the dimethacrylate of the propoxylated bisphenol-A By DSC.

	100°C	120°C	140°C	160°C
BPO	50	75	~100	---
t-BPB	---	61	89	~100

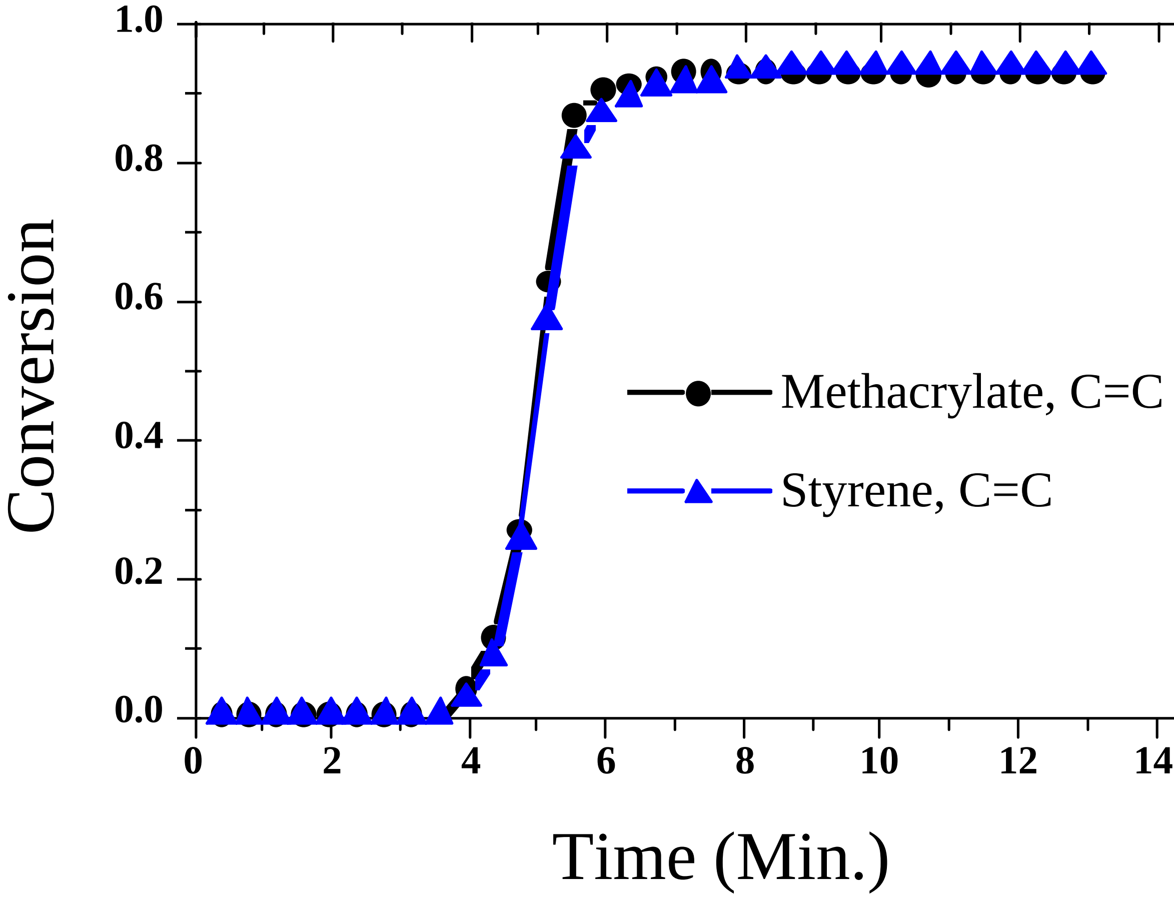
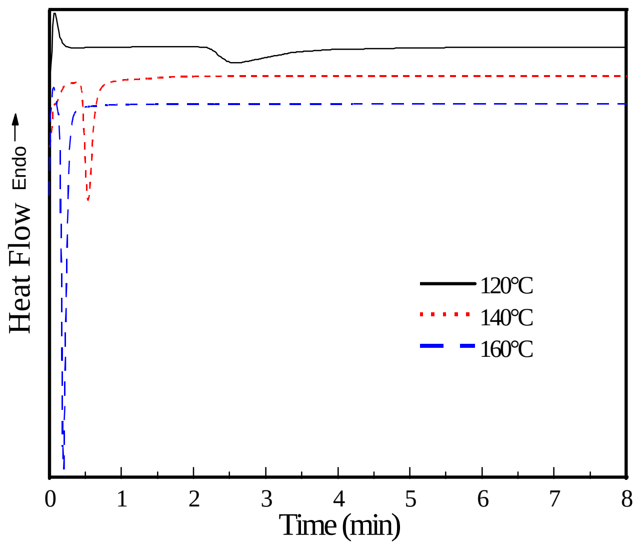


Figure 3.4.9. Conversion as a function of time studied by FTIR at 140°C for the dimethacrylate of bisphenol A propoxylate diluted with 30 Wt% styrene.

(a)



(b)

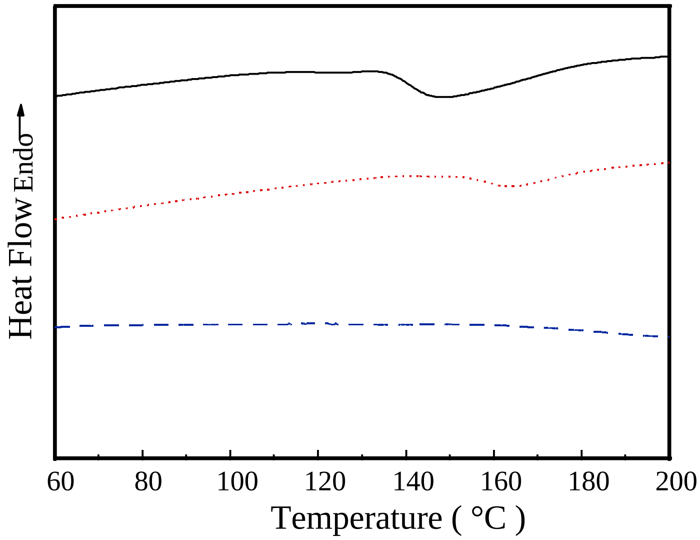


Figure 3.4.10. (a) Isothermal cure of the dimethacrylate of bisphenol A propoxylate at various temperatures; (b) dynamic scan after the isothermal cure. 1% of t-BPB was used as initiator.

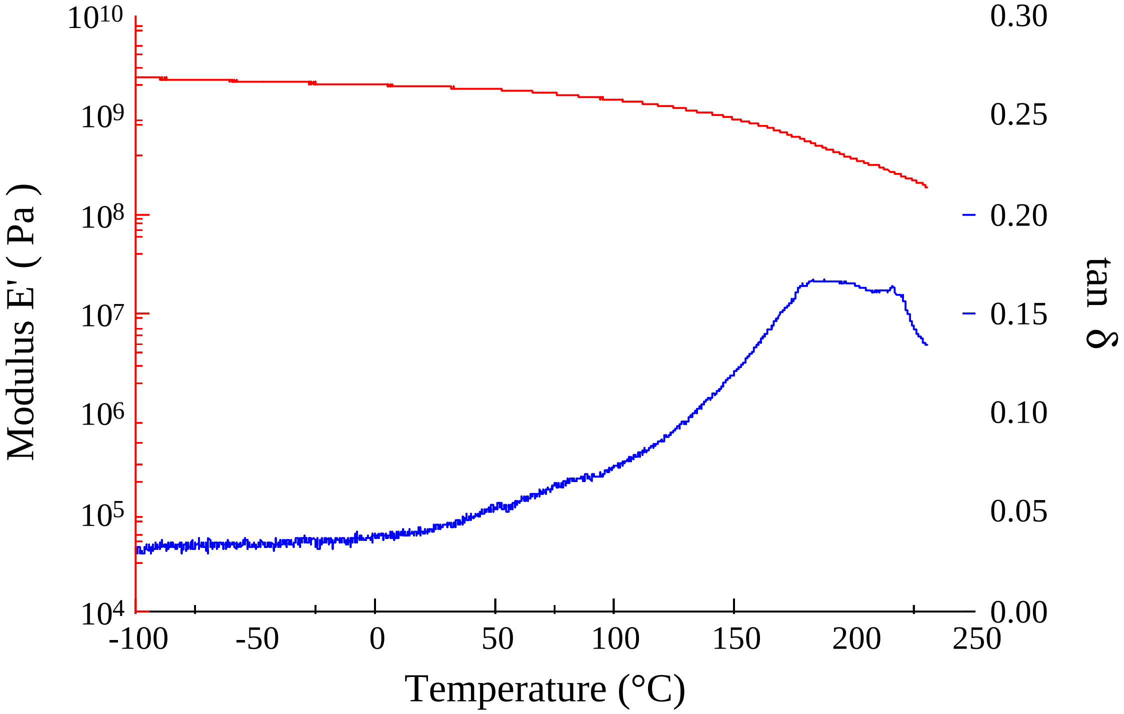


Figure 3.4.11. DMA of a network prepared by curing the dimethacrylate of bisphenol A propoxylate resins.

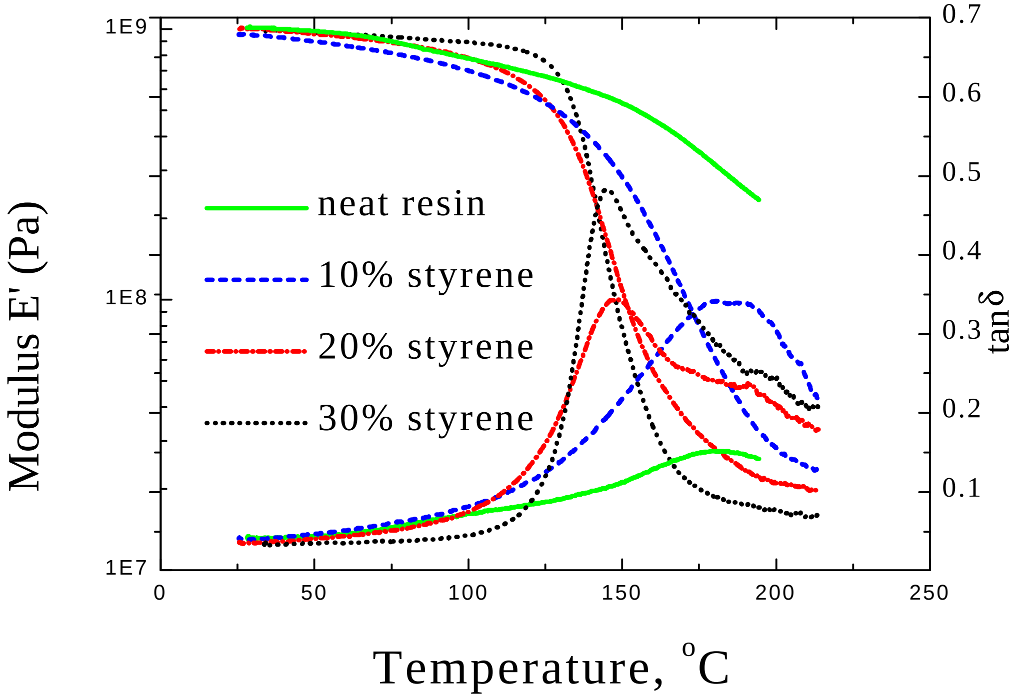


Figure 3.4.12. DMA of networks prepared by co-curing the dimethacrylate of bisphenol A propoxylate diluted with 10, 20, and 30 wt% styrene.

be obtained at 140^{o}C. However, when 1% t-butylperoxybenzoate is used as the initiator, only 89 % conversion is obtained, approaching completion at 160 ^{o}C.

Both DSC and DMA were used to determine the T_g of the dimethacrylate of bisphenol A propoxylate network. DSC is not sensitive enough to detect the T_g of the neat network due to its highly crosslinked structure. Figures 3.4.11 and 3.4.12 show the DMA results of the cured neat resin. The storage modulus decreases continuously with increases in temperature and a very broad T_g was observed.

Thermal stability under N_2 of the dimethacrylate of bisphenol A propoxylate networks was examined by TGA. There was a 5% weight loss at 310^{o}C for the new netwotks compared to 326 ^{o}C for the bisphenol-A based vinyl ester (M_n = 690 g/mol) (Figure 3.4.13). Thus, it was concluded that the thermal stability of these materials was similar.

Toughness of the networks from the dimethacrylate of bisphenol A propoxylate was tested using ASTM Standard D 5045-91, in terms of the critical-stress intensity factor, K_{1c}. The results are summarized in Table 3.4.2. The neat dimethacrylate of bisphenol A propoxylate network has a low K_{1c} value (0.52 MN/m$^{3/2}$) probably due to the highly crosslinked structure resulting from the low molecular weight (M_n = 480 g/mol) precursor. The netwrok from the dimethacrylate of bisphenol A propoxylate diluted with 30 wt% styrene had a K_{1c} of 0.60 MN/m$^{3/2}$ - very close to that of the 35 wt% styrene/vinyl ester resin (M_n = 690 g/mol) (K_{1c} = 0.63 MN/m$^{3/2}$). Another interesting result concerning these new networks is the influence of styrene on toughness. The toughness of the bisphenol-A/epichlorohydrin network decreases when styrene concentration is increased from 20 to 60 wt%, and there is an optimum styrene concentration (between 0-20%) in the resin to obtain the highest K_{1c} value. However, the data in Table 3.4.2 indicate that addition of styrene increases the toughness of these new materials. More work is needed to improve toughness of these materials either through chain extension or by other approaches. Results on systematically varied network compositions with bisphenol

A-epichlorohydrin based materials indicate that an <Mn> of around 1000 g/mol is needed to obtain good network toughness.

The use of the new resin as a comonomer to improve other resins properties were also examined. This new resin was mixed with a 1000 g/mol <Mn> bisphenol A/epichlorohydrin dimethacrylate and styrene and cured. A network comprised of 25 wt% styrene, 25 wt% of new resin and 50 wt% of the 1000 g/mol oligomer had a K_{1c} value of 0.87 $MN/m^{3/2}$ and T_g value of 145 ^{o}C. Commercial Derakane 441-400 containing 30wt% styrene has a K_{1c} value of 0.72 and Tg of 146^{o}C. This mixed resin has a lower styrene concentration (25%), a higher K_{1C} value and almost same Tg as compared to Derakane 441-400. Although the viscosity of the mixed resin was higher than Derakane 441-400, it can still flow well. The viscosity of the mixed resin need to be measured in the future work. Preliminary results suggest that the new resin has the potential to improve other resins properties.

Table 3.4.2. Comparison of K_{1c} of dimethacrylate of bisphenol A propoxylate resin and other vinyl ester resins.

Samples	T_g, °C	K_{1c}, MN/m$^{3/2}$	Density of Resins, g/ml	Density of Networks, g/ml	Shrinkage, %	Gel Fraction, %	Swelling Index in Water	Swelling Index in CH_2Cl_2
Pure dimethacrylate of bisphenol A propoxylate resin	Broad 120-200	0.52±0.03	1.090	1.152	5.3	97.0	1.01	1.47
30 wt%styrene/ dimethacrylate of bisphenol A propoxylate resin	145	0.60±0.05	1.072	1.140	5.9	97.8	1.01	1.42
25 wt%styrene 25wt%dimethacrylate of bisphenol A propoxylate resin,	145	0.87±0.08	1.091	1.160	5.9	96.6	1.01	1.52
28 wt% styrene/vinyl ester (Mn=690g/mol)	146	0.72±0.11	1.087	1.177	7.6	98.5	1.02	1.48
35 Wt% styrene/vinyl ester (Mn=690g/mol)	144	0.63±0.11	1.070	1.168	8.4	98.3	1.02	1.59
28 wt% styrene/vinyl ester (Mn=1000g/mol)	128	2.03±0.04	1.095	1.159	5.5	96.7	1.02	1.83

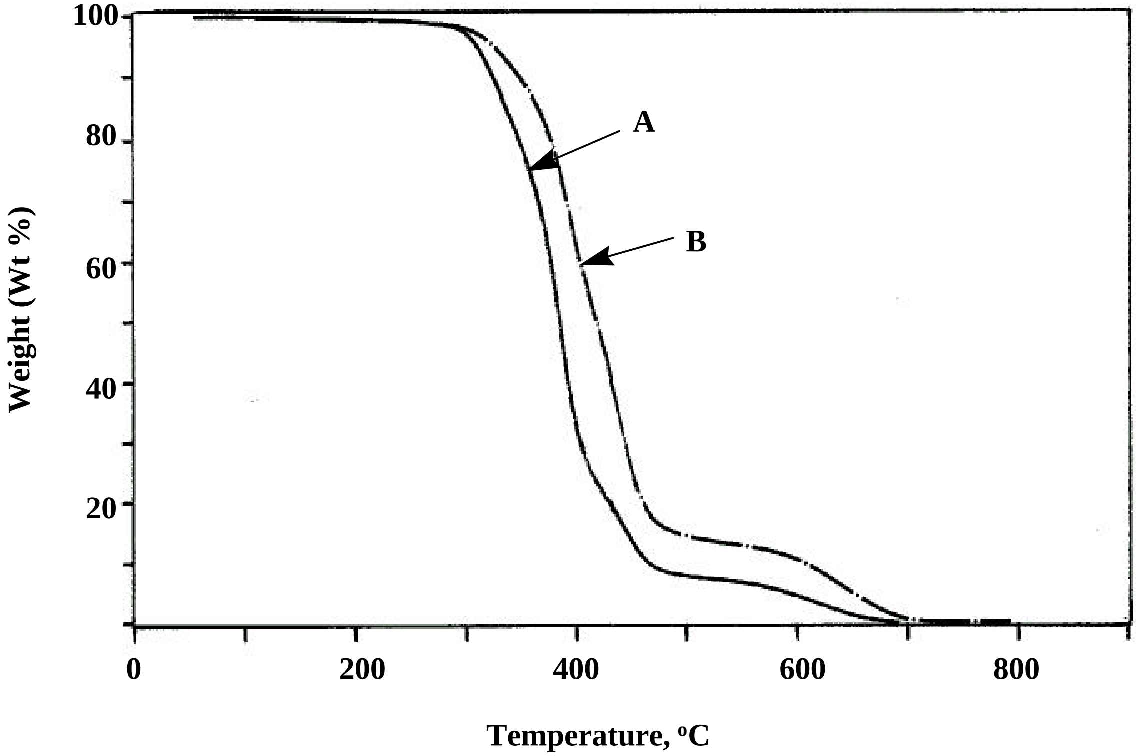


Figure 3.4.13. TGA of cured neat dimethacrylate of bisphenol A propoxylate resin (A) and neat vinyl ester resin (B) (M_n = 690 g/mol).