

Effect of Chemical Structure of Allyl Ethers on Polymerization and Properties of Multifunctional Acrylate Systems

EIRIK S. JENSEN,^{1,*} PAUL GATENHOLM,¹ SRIKANTH R. NANGUNERI,² and LON J. MATHIAS^{2,†}

¹Nordic Institute for Coatings Research, Agern Alle 3, DK-2970 Hoersholm, Denmark and ²Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406-0076

SYNOPSIS

Allyl ether resins with various chemical structures and degrees of functionality were used as promoters and cross-linkers for polymerization of acrylic oligomers at room temperature in air. Thin films were prepared to allow monitoring of polymerization via disappearance of acrylate and allylic unsaturation by FTIR. The effect of air upon curing of films was investigated; excluding air from the surface of the film had a much greater effect than did addition of allyl ether. In air, the curing rate and extent of cure were found to be dependent upon molecular weight M_n and degree of functionality of the allyl compounds. At high allyl monomer concentrations, homopolymerization of the allyl groups occurred. The mechanical properties (tensile strength, Young's modulus, and elongation at break) of films were evaluated on an Instron, whereas viscoelastic properties, transition temperatures, and cross-link densities of polymer bars were studied by dynamic mechanical analysis and relaxation measurements. The study showed that addition of highly functional allyl ethers combines the advantages of an air-curable system with those of highly cross-linked materials, allowing ultimate properties to be tailored.

INTRODUCTION

In recent years, regulations restricting the emission of organic solvents from coatings have accelerated work on new coating systems with low levels of volatile organic compounds (VOC). Acrylates are one such polymer resin group demonstrating excellent outdoor durability,¹⁻³ although they are used mainly in the form of high molecular weight latices in emulsion paints. During the last 10 years, the use of reactive acrylic oligomers in UV-cured coating systems has dramatically increased. One drawback to such use is that polymerization in air of acrylates is retarded by oxygen,^{4,5} which can also lead to chain transfer, low molecular weight contaminants, and tacky surfaces. Adding tertiary amines to UV-curable systems shortens the induction time through

generation of α -amino radicals that consume oxygen by a chain peroxidation process.^{6,7} A comprehensive study of the effect of oxygen on light-induced polymerization of acrylates⁸ showed that one molecule of tertiary amine ties up ca. 16 molecules of oxygen. Tertiary amines are, however, only used as oxygen scavengers to decrease the concentration of oxygen in the film so that polymerization of reactive vinyl monomers can take place; in too high concentrations, they can themselves inhibit radical polymerization.

Multifunctional allyl ether resins have unique properties because they form polymers through an autoxidation process^{9,10} and can also polymerize through the double bond.^{4,5,11} Homopolymerization, however, involves extensive degradative chain transfer reactions.^{12,13} A recently published study on the polymerization of unsaturated esters in the presence of allyl ethers confirmed two different cure mechanisms in films, with an autoxidative polymerization at the surface and a free radical polymerization occurring in the bulk.¹⁴⁻¹⁶ The radical

* Present address: Technical University of Denmark, Kemiteknik Byg. 227, DK-2800 Lyngby, Denmark.

† To whom correspondence should be addressed.

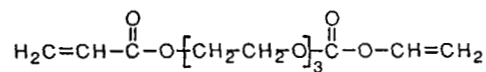
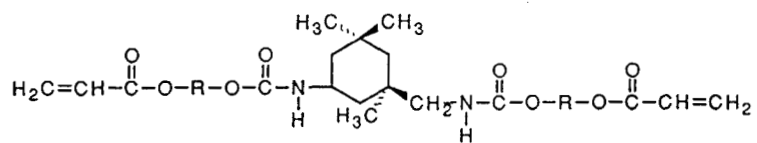
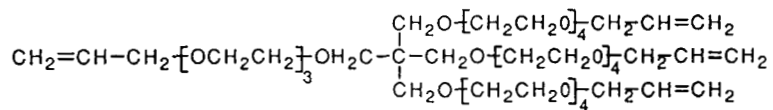
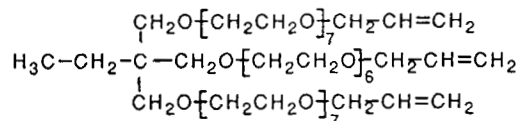
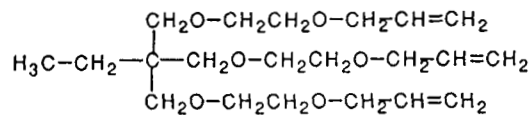
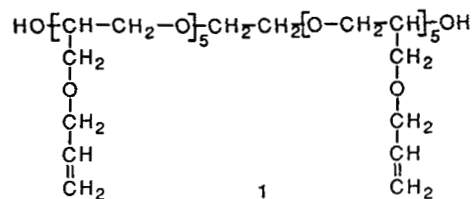


Figure 1 Structures of allyl ether resins 1–4 and acrylates 5 and 6.

polymerization was much faster than was the autoxidative polymerization. We found in an earlier study¹¹ that the polymerization rate of added acrylate decreases with increasing surface/bulk ratio, which confirms the above. Allyl ethers have been the subject of other polymerization studies with acrylates,^{17,18} which demonstrated the commercial utility of this approach. The proposed reaction scheme for the promotion of acrylate polymerization involves generation of peroxy radicals through α -hydrogen abstraction with sequential oxygen radical formation through a redox process with catalytic cobalt salts. These allyl oxygen radicals act as both initiators and cross-linking agents for acrylates.⁵

The objective of the present work was to investigate the effect of added allyl ethers on multifunctional acrylate polymerization rate, degree of cure, and physical properties.

EXPERIMENTAL

Materials

Four different allyl ethers with a high degree of functionality were used. Poly(allyl glycidyl ether) (PAGE-10, **1** in Fig. 1) was donated by Monsanto Chemical Company, Springfield, MA. Other allyl ethers were synthesized from trimethylolpropane and pentaerythritol by Perstorp Polyols, Perstorp AB, Sweden. Compounds **2**, **3**, and **4** in Figure 1 were obtained by polyaddition of ethylene oxide¹⁹ with termination by allyl chloride.²⁰⁻²³ Average molecular weights and functionalities of the allyl ethers used are summarized in Table I. The acrylate mixture used contained 80% Actilane 20 (**5**), manufactured by the Societe Nationale de Poudres et Explosifs (SNPE, France), and 20% triethylene glycol diacrylate (TEGDA, **6**). *t*-Butyl peroxide was used at 100 ppm as initiator in all polymerizations in conjunction with a commercial cobalt catalyst at 600 ppm (Sevosyn Combi LS from Servo Delden, The Netherlands).

Film Preparation and IR Spectroscopy

Films were obtained by casting the reaction mixture onto a KBr pellet at 23°C and 50% relative humidity (RH) with a 100 μm aluminum tape ring used to assure constant thickness of the film. Measurements without air present were made by sandwiching a film between two tablets with a 100 μm aluminum ring in between. A Nicolet 5-DX FTIR spectrometer was used with 10 scans taken at a resolution of 4 cm^{-1} . Rapid analysis was done to minimize flowing of the wet film. To insure accurate quantitation of the acrylate peak at 810 cm^{-1} , solutions of tripropylene glycol diacrylate in THF were analyzed to give a calibration plot of concentration vs. peak height after base-line correction.

NMR Characterization

Test pieces were oven-treated at 80°C to give uniformly cured samples for mechanical testing. The cross-linked products were then swelled in DMSO-*d*₆, and solution ¹³C-NMR spectra were obtained on a Bruker 300 MHz spectrometer with integration to estimate unreacted acrylate and allyl ether group concentrations. This method only allows evaluation of those groups that are not tightly held in the cross-linked matrix.

Mechanical Testing

Films were drawn on a glass plate with a bar applicator from a 100% mixture (no solvent). After tack free time (TFT) plus 14 days, the plate was put into water and the film removed and dried for 3–4 days. Young's modulus, tensile strength, and elongation were measured on the 90 μm films obtained using an Instron 1193. The strain rate was $2.67 \times 10^{-2} \text{ s}^{-1}$, and the temperature, 23°C \pm 0.5. All results given are an average of eight measurements.

Table I Molecular Weight (M_n) and Functionality (F_a) in mol/mol and mmol/g Compound

	Compound					
	1	2	3	4	5	6
M_n	1200	380	1200	950	1000	246
F_a (mol/mol)	10	2.4	2.4	3.3	2	2
F_a (mmol/g)	8.3	6.3	2	3.5	2	8.1

Dynamic Mechanical Analyses (DMA)

DMA measurements of the series of cross-linked systems containing **1–4** were performed using three different experimental schemes involving temperature sweep, frequency sweep, and stress relaxation above the estimated glass transition temperature (T_g). All samples tested were fabricated by curing the components in a mold (dimensions $3.1 \times 12.8 \times 63.0$ mm). Samples were then cured at room temperature in the presence of air, released from the mold, and postcured in an oven at 80°C for 24 h for better comparison between the systems. A Rheometrics mechanical spectrometer (RMS-800) was used in torsional mode for DMA data acquisition. To ensure linear viscoelastic behavior, strain sweep measurements were performed to estimate ranges of adjustable strains for temperature sweep studies (estimated linear viscoelastic [LVE] region between 0.08 and 1.0%) and to maintain constant strains (chosen from LVE to be 0.3%) for frequency sweep and stress-relaxation studies.

For temperature sweep studies, a constant frequency of 3.15 rad/s (~ 0.5 Hz) in the adjustable strain and tension mode was employed. A 15°C interval for each measurement was used from -150 to -50°C , followed by 5° intervals until the sample reached 100°C or the plateau region for the sample. An equilibration time of 2 min was used to achieve thermal equilibrium before each measurement.

Frequency sweep studies were performed at 60°C (above T_g) at a constant strain of 0.3% (adjusted according to the stiffness of each sample in the LVE

region) in the frequency range 0.1–100 rad/s. Stress-relaxation studies were performed to supplement the temperature sweep data in determining the plateau modulus (G_N) for estimation of M_c . The appropriate strains were chosen similar to those in the frequency sweep studies for testing at 60°C .

RESULTS AND DISCUSSION

Conversion of Acrylates

Conversion was measured using base-line correction of the acrylate band at 810 cm^{-1} and the allyl band at 925 cm^{-1} . The band at 767 cm^{-1} from the acrylate was used as an internal reference for calculating acrylate and allyl group conversions. Figure 2 shows the IR spectrum of the acrylate mixture with an expanded section ($750\text{--}850\text{ cm}^{-1}$) used for monitoring acrylate conversion.

Polymerization of the acrylic oligomer was carried out with the different allyl ethers at various concentrations between 10 and 40 wt %. Figure 3 shows conversion plots of acrylate double bonds at 10 wt % of the allyl ethers. More than half of the acrylate double bonds reacted after 4 h at 23°C and 50% RH, whereas only 5% of the double bonds were converted when no allyl ether was added. Increasing the amount of allyl ether to 20 wt % and then 40 wt % further increased the initial polymerization rate for **1** and **3**. It nearly tripled with 40% **3**, but gave a lower overall conversion than for the 10% mixture.

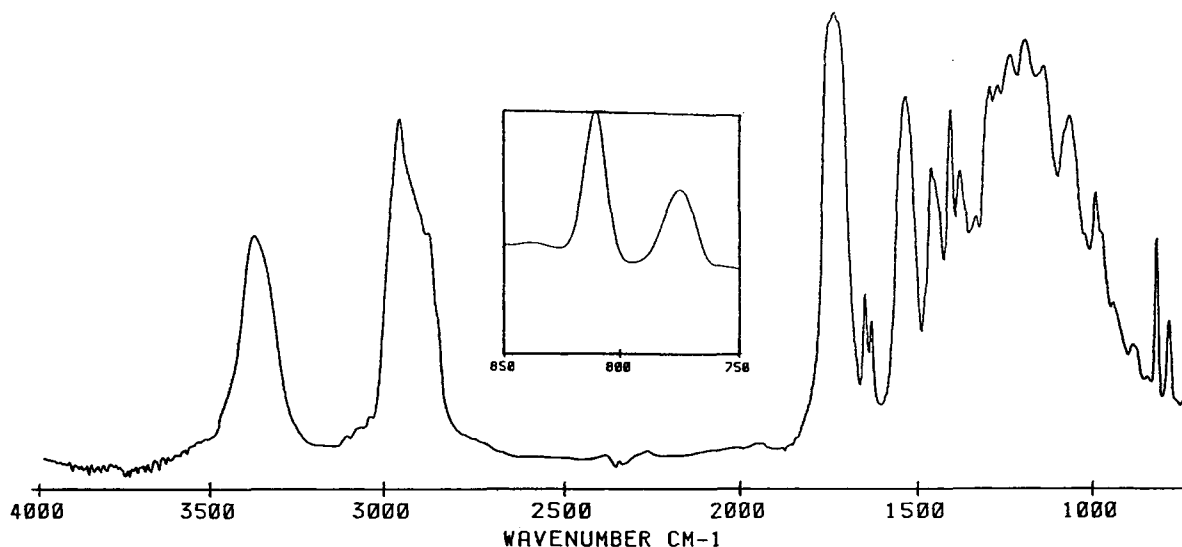


Figure 2 IR spectrum of **5** plus **6** with enlarged inset of $750\text{--}850\text{ cm}^{-1}$ region showing the internal standard at 775 cm^{-1} and the acrylate peak at 810 cm^{-1} .

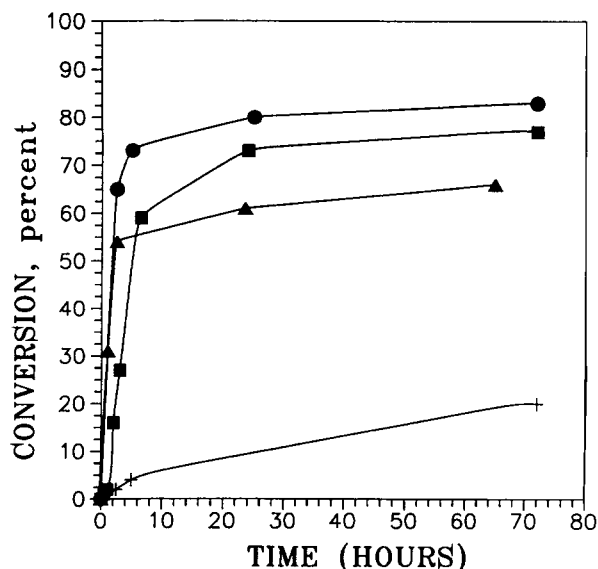


Figure 3 Conversion of acrylate vs. time at 10 wt % allyl ether resin: (●) 1; (▲) 2; (■) 3. (+) Conversion of acrylate when no allyl ether is added.

Compound 1 showed the highest efficiency for rate and conversion, probably due to fast uptake of oxygen dissolved in the film. Compound 3 gave an optimum rate of reaction at about 20 wt % with a slight decrease at higher concentrations.

Compound 2 was the least efficient of the allyl additives in terms of both rate and conversion (Figs. 4 and 5). The initial polymerization rate and the overall conversion is greater for 3 than for 2 even though the functionality in mmol allyl double bonds

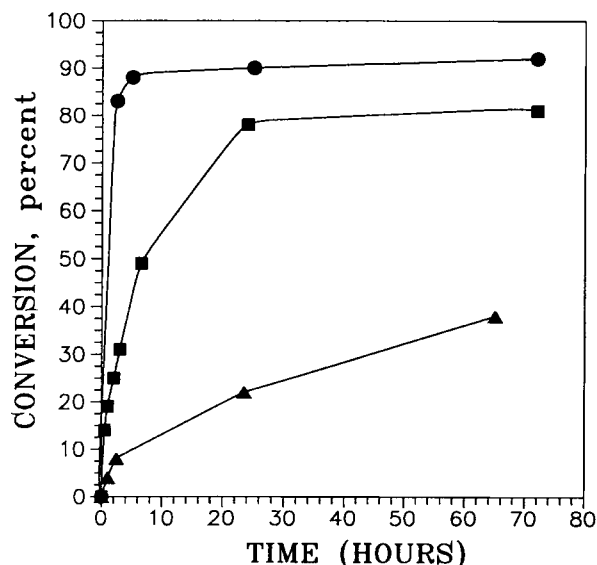


Figure 4 Conversion of acrylate vs. time at 40 wt % allyl ether resin: (●) 1; (▲) 2; (■) 3.

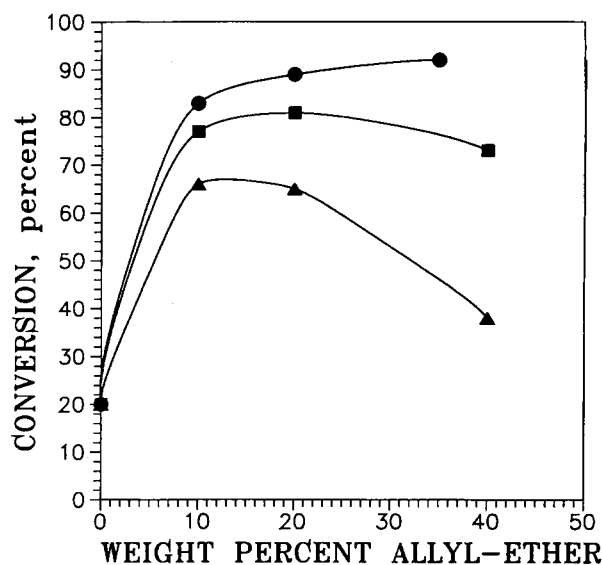


Figure 5 Conversion of acrylate after 3 days of polymerization vs. wt % allyl ether resin: (●) 1; (▲) 2; (■) 3.

per gram of compound is three times smaller for 3. However, the polymerization and overall conversion appears to be proportional to the combination of molecular weight and functionality of the allyl ether. The values of functionality (in mol $\text{CH}=\text{CH}_2/\text{mol}$ product and mmol $\text{CH}=\text{CH}_2/\text{g}$ product), together with molecular weights, are shown in Table I.

Another possible explanation for the differences in promoting the polymerization of acrylate double bonds could be differences in spatial arrangement of the terminal allyl ether groups. Ethylene oxide oligomers adopt a 7_2 helix conformation in condensed states, which may increase the intramolecular distance between allyl ether end groups in 3 and allow each to act independently of the others. The allyl ether groups of 2 may be held so close together that initial α -hydrogen abstraction is followed by rapid intramolecular chain transfer reactions that consume allyl groups without generating additional peroxide moieties capable of initiating acrylate polymerization. Others have observed similar low activity for low molecular weight allyl ether compounds as promoters for curing of unsaturated polyesters.¹⁶ In contrast, the allyl ether groups in 1 are pendent from the backbone of the polymer and, despite being in relatively close proximity, their much higher concentration leads to the highest rates and overall conversion of acrylate units.

Conversion of Allyl Unsaturation

In general, it is thought that there are two possible reaction paths for the polymerization of allyl ether

(Fig. 6). One is addition to the double bond through radical polymerization. The second involves abstraction of α -hydrogens to give stabilized radicals that are not reactive enough to initiate polymerization,¹³ but generate peroxy radicals in the presence of oxygen. These undergo redox reaction with added cobalt salts to give reactive oxygen radicals (Fig. 6). The second reaction path is of great importance for acrylate polymerization in both reducing or eliminating the inhibiting effect of oxygen and in generating peroxide initiator moieties. In any event, the overall conversion of allyl double bonds were unaffected by the amount and type of allyl ether present. In contrast to acrylate conversions that ranged between 35 and 90%, allyl conversion was relatively constant at 50–70% (Fig. 7).

Polymerization Conditions

Polymerizations of the acrylic-co-allylic systems were greatly affected by air. Figure 8 shows the conversion of acrylate groups as a function of time at different concentrations of allylic resin 3 in the presence of air and when air was excluded from the surface. Reactions summarized in Figure 8 involve room temperature cure with added *t*-butyl peroxide as coinitiator with the cobalt complex. For reactions in the absence of air, conversion occurred very rapidly and completely independent of the amount of allyl ether used. In the presence of air, the conversion of acrylate was somewhat inhibited even with added allyl ether, and an earlier study showed that the polymerization of this system was affected by the thickness of the film.¹¹ It can be concluded that addition of allyl ethers almost overcomes the oxygen

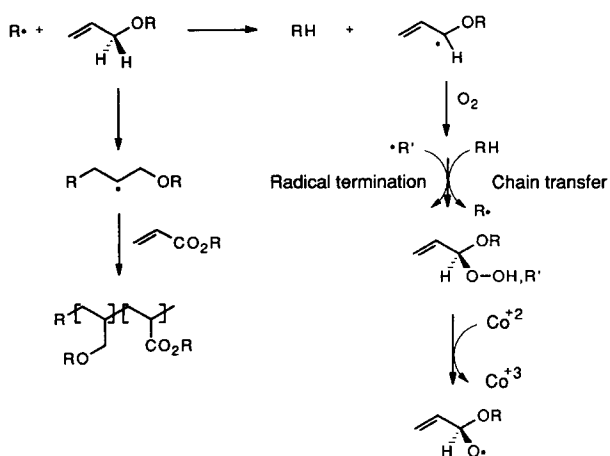


Figure 6 Reaction scheme for polymerization of allyl ether resin through radical and autoxidative mechanisms.

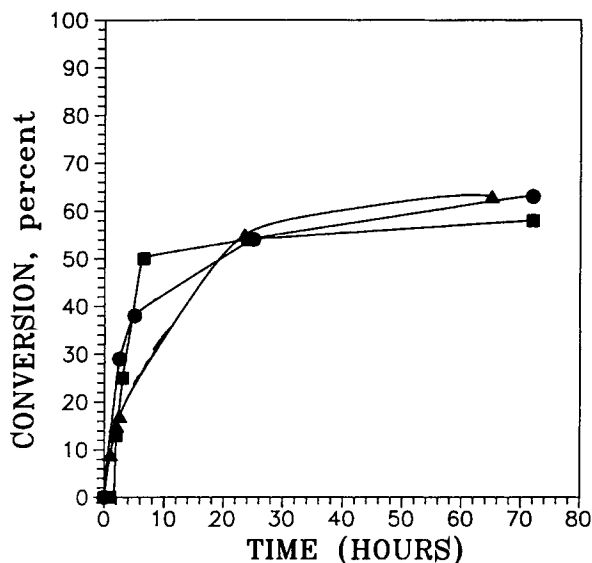


Figure 7 Conversion of allyl unsaturation vs. time for (●) 1; (▲) 2; (■) 3.

inhibition effect on acrylate polymerization in air and that the effect of oxygen inhibition increases with decreasing film thickness.

Mechanical Properties of Films

Tensile strength, elongation at break, and Young's modulus were evaluated for films containing 25 wt

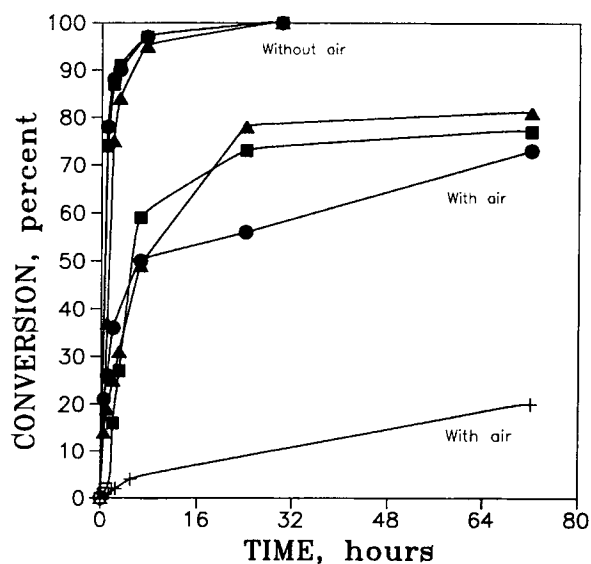


Figure 8 Conversion of acrylate vs. time: polymerization in presence of air and in absence of air at 10 (■), 20 (▲), and 40 wt % (●) added 1 vs. polymerization in the presence of air without allyl ether (+).

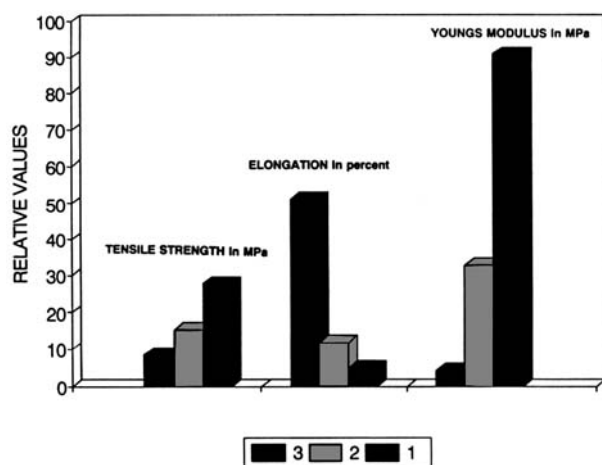


Figure 9 Relative values of tensile strength, elongation at break, and Young's modulus on films of 25 wt % allyl ether and 75 wt % acrylate (80% **5** and 20% **6**).

% allyl ether. Relative values are shown in Figure 9. As expected, **1** produces a very strong but brittle coating, whereas **3** gives a more flexible and tougher coating. Elongation at break was 10 times higher for **3** than for **1**, whereas the Young's modulus was almost 20 times lower. Compound **2** gave films that possessed intermediate values of modulus and elongation. Selection of individual allyl ether components alone or in combination should thus allow development of desired levels of modulus and flexibility.

Temperature Sweep

T_α , T_β , and G_N (average plateau modulus) were determined from plots of G' and $\tan \delta$ (G''/G') vs. temperature at 0.5 Hz. From G_N , the number average molecular weights of the segments between cross-

links (M_c) were estimated using the relationship based on the theory of elasticity (used previously on highly cross-linked materials²⁴): $G_N = \rho RT/M_c$, where ρ is in g/cm^3 , T in K, R in $\text{erg}/\text{mol K}$, G_N in dynes/cm^2 , and M_c in g/mol .

Table II summarizes the results of the temperature sweep and stress-relaxation studies. Solution NMR analysis of the DMA samples containing **1**–**4** at 10 wt % allyl ether was also carried out and showed no residual allyl groups, although this method will show only highly mobile components under the conditions used. At 25 wt %, **4** did not show any residual allyl groups, while all other allyl ethers did. The T_g and G_N values decreased with increasing content of the ethoxylated trimethylolpropane and pentaerythritol derivatives. The decrease in properties for **2** is dramatic compared to the other samples, whereas samples with **4** possessed good properties considering the low degree of functionality. Values of M_c for **4** do not change as much as for **2** and **3**, going from 10 to 25 wt %, which, combined with the NMR results, indicates that **4** is more efficient as a cross-linking agent than is **2** or **3**. Compound **1** showed an optimum G_N at 25 wt %, in accordance with an earlier study on the elastic moduli and tensile strengths of films containing **1** in a range of concentrations.¹¹ Samples with 25 wt % **2** showed similar properties to those with 100% acrylates, but with the advantage of being air-curable.

Typical temperature sweep curves are shown in Figure 10 for material with **3** at 40 wt % (see also Table III). The $\tan \delta$ curve reveals a β -transition at about -85°C and a third transition at -30°C . The β -transition occurs at the same temperature for all samples and with decreasing strength proceeding from 10 to 40 wt % added allyl compound. Samples with 10 wt % **1**, **2**, and **4** all showed the same T_g

Table II Average Plateau Storage Modulus (G_N in MPa) from Temperature Sweep and Stress-Relaxation Measurements and Molecular Weight Between Cross-links (M_c in g/mol)

Compound	% Allyl							
	0		10		25		40	
	G	M_c	G	M_c	G	M_c	G	M_c
1			750	410	900	348	660	474
2			760	425	470	650	380	846
3			450	722	400	828	330	860
4			690	479	640	506	—	—
5 + 6	440	650						

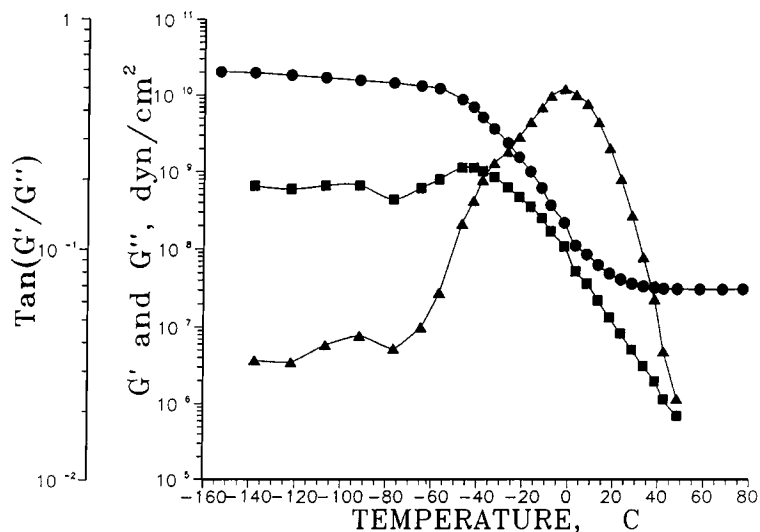


Figure 10 Storage (●) and loss (■) modulus together with $\tan \delta$ (▲) for 40 wt % **3**.

(39°C) as the sample with 100% acrylate, indicating that addition of small amounts allyl ether does not significantly alter this transition. Increasing the amount of allyl ether gradually moves T_g to lower values for samples with **2**, **3**, and **4**, with **2** and **4** (with the lowest functionalities) showing the least efficiency as cross-linking agents. Using **1** gave good copolymerization and cross-linking since T_g increased to 48°C.

A third transition was also seen for most samples. This third transition was very broad for **1** at 40 wt % (ranging from -20 to 60°C) and could be due to segments of **1**. The transition is not nearly as pronounced for **3** as for **1** and occurs at -30° (see Fig. 10). A weak transition at -30°C is seen for **2** at 25 and 40 wt % and also for **4** at 25 wt %. This transition is probably due to movement of the ethylene

oxide segments of these two compounds in the cross-linked matrices.

Frequency Sweep

The frequency sweep evaluations were made to directly measure the stiffness of the sample. From the plot of G' vs. ω , the relative elasticities of the materials were compared. Plots of G' and G'' gave indications of polydispersity in the samples, with a higher slope indicating a higher dispersity in M_c . Polydispersities of **1** samples were almost equal, whereas values differed considerable for **2** and **4**. The polydispersity increased with the amount of allyl ether from 10 to 25 wt % of **4**, but decreased for increasing **2**.

Table III Transition Temperatures from DMA

System	T_g (°C)	T_β (°C)	T_γ (°C)
5 + 6 alone	39	-92	None
10% 1	39	-85	None
25% 1	48	-85	25
40% 1	48	-85	25
10% 2	39	-85	None
25% 2	28	-85	-30
40% 2	18	-85	-30
10% 3	18	-85	None
25% 3	18	-85	-30
40% 3	-2	-85	-30
10% 4	38	-85	None
25% 4	19	-85	-30

CONCLUSIONS

Allyl ether resins (in combination with initiator and catalyst) promote curing of multifunctional acrylates in the presence of air. The structure and functionality of the allyl ethers have a significant effect on acrylate conversion: **1** was the most efficient promoter of acrylic polymerization, followed by **3** and **2**. The conversion of acrylate units was unchanged for **1** above 25 wt % and was maximum for **3** and **1** at 20–25 wt %. The overall conversion of acrylates was approximately proportional to the combination of molecular weight (M_n) and functionality of the added allyl ether resin. Addition of allyl ethers almost overcomes the oxygen inhibition effect on acrylate polymerization in air, although the effect of

oxygen inhibition increased with decreasing film thickness. Reaction of allyl ether resins through the double bond was almost unaffected by the amount of added allyl ether.

Varying the type of allyl ether in coating films also affected the properties of the coatings. Consistent with good incorporation of the allyl ether in the copolymer were DMA results that did not show any transitions due to the allyl ethers at low concentrations. Using **1** (with a functionality of 10 mol/mol and $M_n = 1200$) in a coating formulation gave a strong but more brittle film than with **3** (with a functionality of 3 mol/mol and $M_n = 1200$), which gave a more flexible film. The degree of cross-linking decreased with increasing allyl ether content, except for **1**, which had an optimum at 25%. Addition of large amounts of allyl ether gave additional transitions in the cured samples, which could be due to segments in **1-4** incorporated in the tightly cross-linked systems.

This work was made possible by a grant from Nordisk Industri Forsker Komite and Perstorp AB. We thank Kathe Ogemark (Perstorp AB) for synthesis of the allyl ether. E. S. J. wishes to thank all the members of the Department of Polymer Science at University of Southern Mississippi for hospitality and assistance during his visit.

REFERENCES

- W. C. Feist, *Am. Paint Coat. J.*, **November 21**, 36 (1989).
- M. L. Jansen, *J. Oil Chem. Col. Assoc.*, **5**, 117 (1986).
- W. C. Feist, *Annu. Rep. Br. Wood Preser. Assoc.*, 13 (1984).
- T. Karotkki, *M. Eng. Thesis* (in Danish), Technical University of Denmark, 1989.
- J. Knapczyk, *J. Coat. Techn.*, **61**, 756 (1988).
- C. L. Osborn, *J. Rad. Cur.*, **3**, 2 (1976).
- K. J. Kim and C. E. Hoyle, *J. Appl. Polym. Sci.*, **33**, 2985 (1987).
- C. Decker and A. Jenkins, *Macromolecules*, **18**, 1241 (1985).
- H. J. Toivonen, *Acta Chem. Scand.*, **B38**, 63 (1984).
- H. J. Toivonen, *Acta Chem. Scand.*, **B38**, 37 (1984).
- E. S. Jensen and P. Gatenholm, in *Proceedings of the Seventeenth Water-borne and Higher Solids Coatings Symposium*, University of Southern Mississippi Press, Hattiesburg, MS, 1990, pp. 325-340.
- P. Bartlett and R. Altschul, *J. Am. Chem. Soc.*, **67**, 812 (1945).
- G. Odian, *Principles of Polymerization*, 2nd Ed., Wiley-Interscience, New York, 1981, p. 250.
- H. J. Traencker and H. U. Pohl, *Angew. Makromol. Chem.*, **98**, 1 (1981).
- H. U. Pohl, H. J. Traencker, and H. J. Rosenkranz, *Angew. Makromol. Chem.*, **108**, 61 (1981).
- M. Johansson and A. Hult, *J. Polym. Sci.*, to appear.
- J. Knapczyk, in *XIX FATIPEC Congress*, Aachen, 1988, Vol. 1, p. 139.
- M. Ojunga-Andrew, in *Proceedings of the Seventeenth Water-borne and Higher Solids Coatings Symposium*, University of Southern Mississippi Press, Hattiesburg, MS, 1990, pp. 164-186.
- G. Dittus, H. Kroeper, and H. Meerwein, *Sauerstoff Verbindungen I*, teil 3, George Thieme Verlag, Stuttgart, 1965, p. 485.
- V. Chernaya and S. Kovtun, *Vestn. Khark. Politekh. Inst.*, **76**, 87 (1973); *Chem. Abstr.*, 18681a (1973).
- H. Haupt, Ger. Offen. 2,437,789 (February 19, 1976); *Chem. Abstr.*, **84**, 135113u (1976).
- N. Krishnamurti, M. Shirsalkar, and M. Sivarsamba, *J. Oil Colour Chem. Assoc.*, **63** (12), 474 (1980); *Chem. Abstr.*, **94**, 121983x (1980).
- Fujiwara, Kunihiko, Japanese Kokai 77,73,806 (June 21, 1977); *Chem. Abstr.*, **87**, 151701b (1977).
- A. V. Tobolsky, D. Katz, M. Takahashi, and R. Shauffhauser, *J. Polym. Sci. A*, **2**, 2749 (1964).

Received July 20, 1990

Accepted August 13, 1990