Allylic Prepolymers from Brassylic and Azelaic Acids*

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Synopsis

Diallyl brassylate (DAB), a new monomer, and diallyl azelate (DAA) were converted to new prepolymers for comparison with analogous commercial products from diallyl o- and m-phthalate (DAMP). Respective prepolymers from DAB and DAA had $\bar{M}_n$ 28,000 and 40,000 and contained approximately 0.8 free allyl moiety per repeating unit. Only the DAB prepolymer exhibited crystallinity at low temperatures as detected by differential scanning calorimetry and x-ray diffraction. Aliphatic prepolymers have greater heat stability than aromatic ones and evolve fewer calories per double bond during curing than reported for DAMP prepolymer. Low shrinkage (<1%) on curing and clear, hard end products indicate the potential of aliphatic prepolymers as thermosetting plastics. Their liquid state at room temperature should be advantageous in many applications.

INTRODUCTION

Prepolymers from diallyl esters are predominantly linear polymers with molecular weights low enough to permit solubility in many organic solvents; these polymers have pendent chains that bear allyl groups available for subsequent intermolecular crosslinking during curing.[1] Since the patent granted to Pollack et al. in 1942,[2] isomeric diallyl phthalate prepolymers have enjoyed increasing commercial use in molding compounds, reinforced plastics, decorative laminates, sealants, and coatings.[3] Such applications are favored by the long shelf life of the prepolymers[4]; the low mold shrinkage during curing[5]; and the useful physical, chemical, and electrical characteristics of the cured products.[3]

While these thermosetting products from aromatic monomers have well-established properties, analogous prepolymers from allylic esters of aliphatic dibasic acids have been investigated less thoroughly. Furthermore, the tendency of intramolecular cyclization involving pendent chains[6] reportedly decreases with increasing distance between the two allyl groups.[7,8] Theoretically ideal prepolymers, i.e., completely linear polymers formed through one allyl group of each monomer, might be prepared from allylic esters of dibasic acids with long chain lengths. Accordingly, we polymerized allylic esters of azelaic (nonanedioic) and of brassylic (tridecanedioic)

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acid derivable from high-erucic oil from such plants as crambe.[9]   We compared the properties of two new prepolymers from these monomers with Dapon M and Dapon 35, commercial products manufactured from diallyl *m*-phthalate (DAMP) and diallyl *o*-phthalate (DAOP), respectively.

EXPERIMENTAL

Monomer Preparation

Brassylic acid, from a pilot-plant ozonolysis of erucic acid,[10] contained 95.2% C_{13}, 3.3% other dicarboxylic acids, and 1.5% unknowns.   Azelaic acid, purchased as Emerox 1144 from Emery Industries, contained 90% C_9 and 10% other dicarboxylic acids according to GLC.   Into a 2-liter, single-necked flask equipped with a Barrett moisture trap and a condenser were introduced 1 mole of acid (either 244.32 g brassylic acid or 188.22 g azelaic acid) and 4 moles allyl alcohol (272 ml; a 100% excess) along with 0.03 mole *p*-toluenesulfonic acid monohydrate (5.71 g; 3% based on the acid) as catalyst and 750 ml benzene as entraining agent.   This mixture was refluxed and magnetically stirred until no more water collected.   After the product was washed with water to remove excess alcohol and catalyst, the crude ester was recovered in yields of 98% for diallyl brassylate (DAB) and 99% for diallyl azelate (DAA).

In an ASCO falling-film molecular still, 300 g crude ester mixed with 0.3 wt.-% Ionox 330 (1,3,5-trimethyl-2,4,6-tris[3,5-di-*tert*-butyl-4-hydroxybenzyl]benzene; mp 244°C; Shell Chemical Co.) was distilled under vacuum.   Pressures and jacket temperatures during the first passage to remove the volatiles and the second passage to distill the ester were 0.05–0.07 torr/135°C and 0.03 torr/175–185°C for DAB; 0.05–0.07 torr/90°C and 0.03 torr/150°C for DAA.   The recovery of purified monomer was 88.8% for DAB and 91.2% for DAA.   (Attempted conventional distillation of a sample of DAB without the inhibitor led to spontaneous polymerization at a nearly explosive rate.)

Prepolymer Preparation

Rates of polymerization were measured as follows: A mixture (10 g) of monomer and benzoyl peroxide (BPO, 2 mole-%, recrystallized from a chloroform solution by addition of methanol) was heated at 76°C.   A 0.5-ml sample was taken every 30 min.   After each sample was quickly cooled to 25°C, its refractive index and iodine value were determined; the unreacted monomer in the weighed remainder of the sample was removed by washing with methanol and centrifuging.   The methanol insolubles were dried, in vacuo, and weighed.   They were then extracted with acetone to give the prepolymer that was also dried and weighed.   The quantity of acetone-insoluble crosslinked polymer[1] was calculated from the methanol-insoluble and prepolymer fraction weights by difference.

On the basis of preliminary rate studies, the reaction was scaled up to prepare larger quantities of prepolymer. Into a 1-liter, three-necked flask equipped with a thermometer, nitrogen inlet, and mechanical stirrer was introduced 240 g of a mixture containing 98 mole-% distilled ester and 2 mole-% BPO. The mixture was allowed to polymerize at 76°C. When the refractive index (n_D^{25}) reached 1.4630 (a value selected from the rate studies that was reached in approximately 270 min for DAB and 220 min for DAA), the reaction was stopped by cooling the flask in a refrigerator.

The reaction products were warmed to room temperature and poured into four 250-ml centrifuge bottles. Into each bottle, 150 ml methanol was added. After the mixture was stirred for half an hour with a magnetic bar, it was centrifuged at 2500 rpm for 30 min, and the supernatant was decanted. This manipulation was repeated four times after which unreacted monomer was completely removed. The mass was dried under vacuum and dissolved in 500 ml acetone. The solution was filtered to remove the crosslinked polymer.

Prepolymer was recovered by stripping almost all the acetone with a rotating evaporator at room temperature, after which residual solvent was removed by a modified freeze-drying procedure as follows: The prepolymer was frozen ($-25°C$) in a flask connected to a high-vacuum (0.02 torr) system through a flexible hose. The flask was manually gyrated to produce a thin film during warming to room temperature. This freeze-drying procedure was repeated until the contents of the flask became constant in weight.

Materials recovered by stripping solvent from the decanted methanol layers were recycled at 65°C with or without additional BPO following the same procedure. Since these recovered materials contained oligomers as well as unreacted monomers and had higher refractive indexes than the original monomer–initiator mixtures, the lower reaction temperature was selected to permit better control of the polymerizations. The cutoff n_D^{25} was reached in 150–180 min.

Gelation Measurements

Monomer gel time was determined as follows: A total of 10 g monomer and initiator of different concentrations was weighed into a test tube (18 × 150 mm), i.e., 0.25 to 8 mole-% BPO or 1 to 8 mole-% azobisisobutyronitrile (AIBN). The mixture was swirled 5 min in a Vortex-Genie mixer (Fisher Scientific Company) to attain complete solution. The time to gelation was then measured with a gel time meter (Sunshine Scientific Instrument, Inc.). This instrument indicates when the viscosity reaches 320 P.[11] Boiling chloroform, carbon tetrachloride, and water were used as bath media.

Gel time of prepolymers was obtained similarly but without addition of a catalyst. Their shelf life at room temperature, i.e., 25°C, was estimated by extrapolation of a straight line of log (gel time) versus $1/T$, where T is the boiling point of bath medium in °K.[12]

Thermal Analysis

Samples were examined with a Perkin-Elmer differential scanning calorimeter, Model 1B, under the following conditions: appoximately 15 mg weighed to the nearest 0.01 mg; nitrogen flow in the housing, 30 ml/min; sensitivity range (mcal/sec, full scale), 4 for monomer and 8 for prepolymer; recorder chart speed, 1 in./min for monomer, 0.13 in./min for prepolymer without catalyst, and 0.50 in./min for prepolymer with catalyst (2 mole-% t-butyl perbenzoate); programming rate, 2.5°C/min for monomer and 10°C/min for prepolymer. Liquid nitrogen was the coolant. Benzene (mp 5.4°C), lead (mp 327°C), and indium (99.999% pure, mp 156°C, ΔH_f 6.79 cal/g,[13] K and K Laboratories, Inc.) served as standards. Areas of differential scanning calorimetry (DSC) thermogram peaks are directly related to enthalpies of transformations responsible for the process.[14] For calculation of ΔH values in kcal/repeating unit (RU), the following equation was used:

$$\Delta H = \frac{(6.79)(\text{indium wt})(\text{sample peak area})(\text{RU formula wt})}{(\text{indium peak area})(\text{sample wt})(1000)}.$$

Peak areas were measured with a planimeter. Those for calculating heats of curing were determined as shown in Figure 1, where the thermogram for prepolymer without catalyst served as the baseline. Small contributions from exotherms due to thermal crosslinking in the uncatalyzed sample were discounted graphically as indicated.

Thermogravimetric analysis (TGA) was conducted with a Cahn RG electrobalance under nitrogen flowing at 50 ml/min, sensitivity range 2 (full scale of 10 in. = 2 mg weight loss) and chart speed of 4 in./hr. The sample size was 1.8 ± 0.2 mg weighed accurately to 0.01 mg. For de-
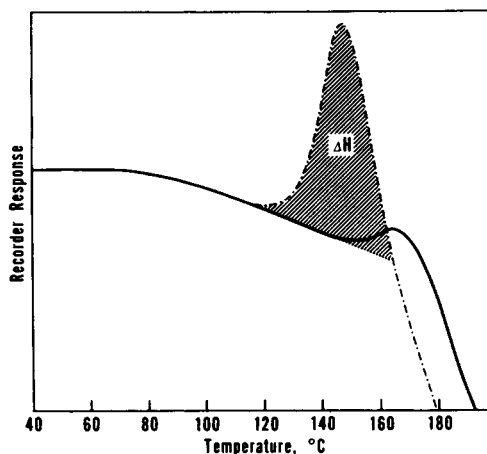

Fig. 1. Differential scanning calorimetry of diallyl brassylate (DAB) prepolymer with (broken line) and without (solid line) catalyst (2 mole-% t-butyl perbenzoate). Positive peaks represent exotherms. Programmed temperature rate, 10°C/min.

termination at programmed temperature, the scan rate was 5°C/min from 25° to 500°C. For isothermal determination, the temperature was raised rapidly, at 80°C/min, to the desired 200°, 300°, or 400°C and then held for 5 hr.

Physicochemical Properties

NMR spectra of carbon tetrachloride solutions were measured with a Varian HA-100 spectrometer. Chemical shifts are expressed in ppm from the TMS standard. IR spectra of neat films and Nujol mull between sodium chloride discs were determined in a Perkin-Elmer Model 137 spectrophotometer.

X-Ray diffraction was conducted at room ($+25°C$) and at low ($< -25°C$) temperatures in an enclosed system consisting of a capillary, an x-ray pin-hole, a flat film camera, a thermocouple, and a nitrogen gas inlet with a Mylar cylinder to cover the capillary. The low temperature was reached by a stream of dried (through a $CaCl_2$ tube) nitrogen gas that had passed through a copper coil immersed in a Dewar flask containing a Dry Ice-butanol mixture. The prepolymer sample was sealed in a capillary and exposed to CuK_α radiation (Ni filter) for 1 hr. The error of measurement is approximately 0.1 Å.

Iodine values[15] were determined for monomers in carbon tetrachloride and for prepolymers in chloroform because aromatic prepolymers are not completely soluble in carbon tetrachloride. Conclusions regarding solubility (0.1 g/ml for monomer and 0.05 g/ml for prepolymer) were drawn after agitating sample–solvent combinations for 5 min with a Vortex-Genie mixer. Viscosity was measured at 25°C in a LVT Model Brookfield Synchro-Lectric viscometer with a No. 4 spindle rotating at 1.5 rpm.

Purity of the starting acids as methyl esters from reaction with diazomethane in ethyl ether, as well as the distilled diallyl esters, was determined by GLC isothermally at 192°C on a Packard 7401 chromatograph equipped with a flame ionization detector, 5% Apiezon L on 60–80 Chromosorb W (AW-DMCS) 4 ft × ¼ in. column (0.1 μl sample), and 5% LAC-2-R 446 on 60–80 Chromosorb W (AW-DMCS) 12 ft × ¼ in. column (0.5 μl sample). Homologs were identified by their equivalent chain lengths based on methyl n-alkanoates as references.[16] Residual monomer in the isolated prepolymer fractions and absence of impurities other than diallyl esters in distilled monomers were determined by TLC on Silica Gel G plates with n-hexane:ethyl ether:acetic acid (60:40:1) as developing solvent and chromic acid (1 g $K_2Cr_2O_7$:50 g H_2SO_4:10 g H_2O) a charring reagent. Plates were heated for 30 min at 160°C for visualization.

A Mechrolab Model 301 A vapor pressure osmometer with acetone as solvent was used for $\bar{M}_n$ determinations. The molecular size distribution was measured with an Ana-Prep gel permeation chromatography apparatus (Waters Associates) containing columns packed with 10^4 and 10^7 Å (normal exclusion limit) Styragels. Samples were prepared by shaking 40 mg prepolymer in 50 ml dimethylformamide (0.08% w/v) for 16 hr,

TABLE I

Properties of Monomers and Prepolymers

Property	Monomers[a]		Prepolymers[a]	
	DAB	DAA[b]	From DAB	From DAA
Purity,[c] % by GLC	95.0	89.9		
Glass transition, °C			−63	−70
Mp, °C	14.1	−29.8	21.0	
Bp, °C/torr	149–150/0.2	111–114/0.2		
Sp. gr$_{25}^{25}$	0.9517	0.9844	1.0269	1.0767
n_D^{25}	1.4555	1.4533	1.4839	1.4882
$\bar{M}_n$			28,000	40,000
$\overline{DP}$			86	149
Apparent polydispersity ratio[d]			25.57	18.47
Apparent $\bar{M}_w$[d]			716,000	739,000
Viscosity (25°C), P × 10^{-2}			9.6	39
Iodine value				
Calculated	156	189	78[e]	95[e]
Observed	157	190	65	74
Saponification equivalent				
Calculated	162	134		
Observed	164	134		
C, %				
Calculated	70.33	67.14		
Observed	70.33	66.63		
H, %				
Calculated	9.94	9.01		
Observed	10.18	9.24		
Solubility[f]				
A	soluble	soluble	soluble	soluble
B	soluble	soluble	insoluble	insoluble
C	insoluble	insoluble	insoluble	insoluble
D	soluble	soluble	partially soluble	soluble
E	soluble	soluble	insoluble	partially soluble

[a] DAB = Diallyl brassylate; DAA = diallyl azelate.

[b] Reported values[18]: bp, 13°C/3 torr; d_{20}, 0.980; n_D^{25}, 1.4550; bromine number, 117.

[c] Contaminants were homologous diallyl esters. No other contaminants were detected by TLC.

[d] The qualification "apparent" is applied to polydispersity ratio $\bar{M}_w/\bar{M}_n$ and $\bar{M}_w$ because of the marked difference in three-dimensional structure between prepolymers containing long, pendent chains and the polystyrenes used as standards in gel permeation chromatography.

[e] Calculated on the basis of one allyl group per repeating unit (RU).

[f] A = Acetone, benzene, carbon tetrachloride, chloroform, 1,4-dioxane, ethyl acetate, ethyl ether, or tetrahydrofuran; B = cyclohexane, dimethylformamide, or methanol; C = water; D = acetonitrile; E = dimethyl sulfoxide.

followed by consecutive filtration through fine, very fine, and ultrafine sintered glass discs. Upon injection into the column, the sample was eluted with hot (65°C) dimethylformamide at a flow rate of 1 ml/min. The molecular size parameter A (equivalent to extended chain length of polystyrene with the same retention volume) was calculated by an empirical equation derived by Mr. C. L. Swanson of the Northern Regional Research Laboratory from least-squares fit of the linear relationship between log (chain length) and retention volume for polystyrene standards:

$$\log A = K_1 - K_2 \text{ (retention volume, ml)}$$

where the constants K_1 (10.605) and K_2 (0.08914) were derived from a curve for polystyrene standards (480, 1220, 9800, 20,200, and 48,000 Å furnished by Waters Associates). With the columns used, the lower limit of effective resolution was $A = 230$ Å (polystyrene of molecular weight approximately 4500).

Volume change during curing was measured by a displacement method: The volume of a marked test tube was calculated from the weight and density $(d_4^{25} \ 0.78659)$[17] of methanol required to fill it to the mark. After the mixture of prepolymer and catalyst (2 mole-% t-butyl perbenzoate) was carefully introduced below the mark on the empty tube and the tube plus contents weighed, methanol was added to the mark, and gross weight again was determined. Methanol was completely removed under vacuum, and the prepolymer was heated in an oven at 180°C for 2 hr. Then the volume of the cured polymer was similarly determined after cooling to room temperature.

RESULTS AND DISCUSSION

Monomer Purity and Properties

Whereas DAA had been prepared by Minokurov et al.[18] as early as 1963, DAB is a new monomer. We made both by p-toluenesulfonic acid-catalyzed esterification in quantitative yields. Purities of the distilled monomers were 95.0% for DAB and 89.9% for DAA. Thermograms showed a sharp melting peak for DAB and a peak with a shoulder for DAA. Selected physicochemical properties are listed in Table I; found compositional values agreed well with calculated ones.

Polymerization

Gel time is the elapsed time for growing polymers to reach that point at which large networks of crosslinked polymer molecules are formed and a sudden rise in viscosity to above 320 P[11] occurs. Figure 2 shows the effect of initiator on gelation. For polymerization with BPO, the reciprocal of gel time versus the concentration of initiator gave a straight line except at low concentrations, where gel times for 0.25 mole-% BPO-initiated DAB and 0.125 mole-% BPO-initiated DAA reactions were still not reached
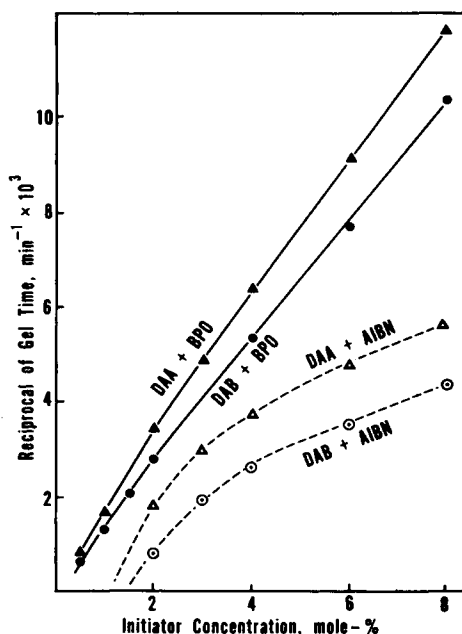
Fig. 2. Effects of initiator type and concentration on reciprocal gel time at 76°C. DAA = Diallyl azelate; BPO = benzoyl peroxide; AIBN = azobisisobutyronitrile.

after seven days. A linear relation for DAOP at 100°C has been reported, also with a deviation at low BPO concentration.[11] This deviation suggests that the rate of termination exceeds the combined rates of initiation and propagation. The termination involves degradative chain transfer in allylic polymerization.[19] For polymerization with AIBN, reciprocal gel time was clearly a nonlinear function of initiator concentration below 4 mole-%. This nonlinearity perhaps indicates different reaction kinetics than in the BPO-initiated reaction. Products from the AIBN runs were yellow and contained less prepolymer, e.g., 17.5% from DAB with 2 mole-% AIBN after 10 hr of reaction, in comparison with 21.4% from DAB with 2 mole-% BPO after 5.5 hr of reaction.

The relationship between gel time and reaction temperature for polymerization of monomers with 2 mole-% BPO is shown in Figure 3. From the monomer-plus-catalyst plots, 76°C (boiling carbon tetrachloride heating bath) was selected as a suitable temperature for preliminary rate studies and larger-scale preparative runs because it allowed convenient polymerization times. (The half-life of BPO at 76°C is 350 min, estimated from a semilog plot of half life versus temperature based on available data.[20,21]) Changes in refractive index and iodine value at this temperature (Fig. 4) were noticeably faster for DAA than for DAB. In agreement with these nearly linear n_D^{25} and iodine value plots (until gelation was approached), prepolymer content increased linearly to 22% for DAB and
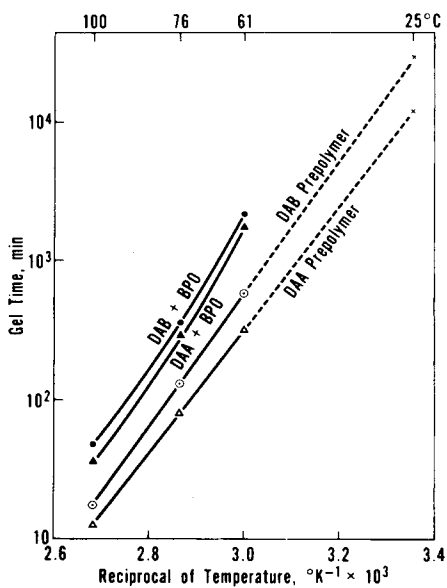
Fig. 3. Gel time as a function of reciprocal of temperature for monomers (DAA and DAB) with 2 mole-% BPO and for prepolymers without catalyst. Broken lines represent extrapolations to $10^3/298°K$ at point x (12,000 min for DAA prepolymer and 28,000 min and DAB prepolymer).

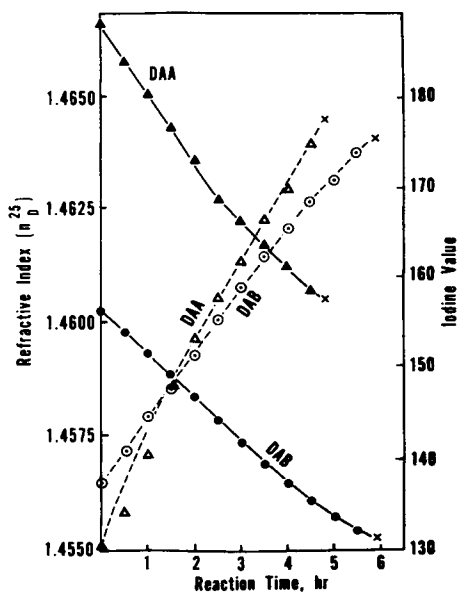Fig. 4. Changes in refractive index, (△) and (⊙), and iodine value, (▲) and (●), during polymerization of monomers (DAA and DAB) at 76°C with 2 mole-% BPO added; x = gel point.
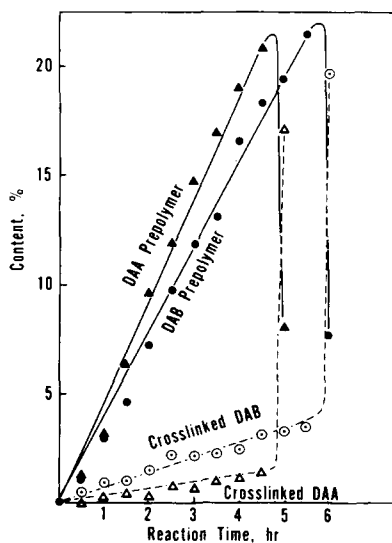
Fig. 5. Formation of prepolymer (solid lines) and crosslinked polymer (broken lines) during polymerizations represented in Fig. 4.

21.5% for DAA at gel point, and it decreased precipitously thereafter as soluble prepolymer crosslinked to form insoluble gel (Fig. 5). Conversely, the crosslinked polymer formed slowly at first but rapidly after the gel point. Patterns were similar when DAB was recycled at 65°C. The recovery of prepolymer, however, was proportional to the amounts of supplemental initiator. With 0, 0.5, or 2 mole-% additional BPO, the respective yields were 15.9, 17.4, and 18.5%. For recycled DAA without addition of BPO, the yield was 14.5%.

Since Figures 4 and 5 represent data taken from the same small-scale polymerizations of DAB and DAA, it was possible to select an index of refraction indicating formation of substantial prepolymer yields but safely ahead of the gel point. Accordingly, larger-scale (preparative) reactions were stopped when n_D^{25} reached 1.4630. In general, predictions from the rate studies were borne out, but less efficient dissipation of heat from the larger mass of reactants resulted in an initial rise in temperature. In an early preparation of DAB prepolymer (500 g reactants) before proper controls were incorporated, the reaction temperature rose to 87°C within the first hour. Afterward it returned to 76°C, and polymer content increased linearly with time as in the preliminary rate studies. Average yields for DAB prepolymer were 17.5%; for DAA prepolymer, 15.0%. The prepolymer fractions contained no residual monomer detectable by TLC.

Prepolymer Properties

Prepolymer fractions were clear, colorless liquids. Selected physicochemical properties of them are given in Table I. Spectroscopy reflected
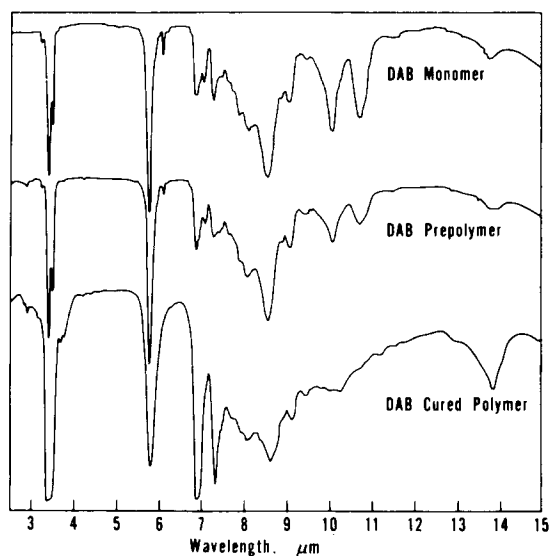
Fig. 6. Infrared spectra. Thin film between sodium chloride discs for DAB monomer and prepolymer; Nujol mull for the cured polymer.

the presence of polymer chains and unreacted allyl groups. The former were represented by a broad NMR band centered at 3.95 ppm and by appreciable loss of absorption fine structure for protons alpha (2.24 ppm, triplet) and beta (1.58 ppm, multiplet) to ester moieties. This decrease in resolution relative to the same parts of corresponding monomer spectra is attributable to slow rotation of the polymer chains. Allyl group signals[22] (and apparent multiplicities) centered at 4.46 ppm (doublet) for the allylic protons, 5.20 ppm (multiplet) for methylene protons, and 5.90 ppm (multiplet) for the single vinyl proton were about half as intense in the prepolymer spectra as in those of the monomers. A comparison of DAB monomer and prepolymer IR spectra (Fig. 6) reveals intensity decreases (in relation to C—H and C=O stretching bands near 3.4 and 5.8 μm) of more than 50% for bands at 6.10, 10.12, and 10.78 μm, attributable to allylic groups.[23] This decrease indicates the proportion of these groups that react during prepolymer formation.

By saponification and reesterification, Simpson et al.[6] demonstrated that intramolecular cyclization occurred in allylic prepolymers. They also observed that the cyclization tendency decreased with increasing distance between the two allyl groups in the monomer. Almost 20 years later, Matsumoto et al.[8] confirmed this observation. Table II gives percentages of cyclization of pendent allyl groups calculated from iodine values. As expected, the DAB prepolymer had the lowest value of the four prepolymers listed, but the differences among DAB, DAA, and DAMP prepolymers are small. The much higher cyclization value for DAOP prepolymer perhaps may result from imposition by the ortho monomer of geometry that substantially shortens interallylic distance over that in the meta analog.

TABLE II
Properties Relevant to Curing of Prepolymers

Prepolymer from:	DAB	DAA	DAMP[a]	DAOP[a]
Prepolymer reactive groups				
Allyl/RU[b]	0.83	0.78	0.76	0.53
Cyclization, %[c]	17	22	24 (16)	47 (44)
Curing				
Heat evolved, kcal/DB[a]	11.2[d]	15.5[d]	—	19.4[e]
Shrinkage, %	0.7[d]	0.3[d]	<1.0[f]	<1.0[f]

[a] DAMP = Diallyl m-phthalate; DAOP = diallyl o-phthalate; DB = double bond.

[b] Calculated by dividing the found iodine value by the theoretical value assuming one unreacted allyl group per RU.

[c] Previously reported[24] values given in parentheses.

[d] DAB and DAA prepolymers were cured after addition of 2 mole-% t-butyl perbenzoate. Calculation of heat evolved per DB is based on the assumption—supported by IR evidence—that all available allylic DB in these two prepolymers reacted in the curing process.

[e] From reference 25.

[f] From reference 3.

Figure 7 shows curves from gel permeation chromatography. Number-average and weight-average molecular sizes were calculated by the usual method[26] from the data represented: $\bar{A}_n$ 1082 for DAB prepolymer and 1980 for DAA prepolymer; $\bar{A}_w$ 27,678 for DAB prepolymer and 36,591 for DAA prepolymer. Multiplication of $\bar{M}_n$ from vapor pressure osmometry by the polydispersity ratio $(\bar{A}_w/\bar{A}_n)$ gave the $\bar{M}_w$. The high polydispersity ratio (Table I) may be ascribed to long pendent chains and formation of intramolecularly cyclized structures, both of which increase markedly the cross-sectional dimension relative to that of the polystyrene standards. Because of this poor comparability between prepolymers and polystyrene standards, curves in Figure 7 indicate that relative degrees of heterogeneity and dimensional variation in the prepolymers but not necessarily the absolute molecular size distribution.

Representative DSC thermograms are given in Figure 8. Indicated glass transition[28] temperatures were verified by exact reproductions in repetitive runs through the −90°C to +25°C range for each sample. DAB prepolymer was unique in showing an acute melting endotherm (from −7° to 25°C, with peak temperature at +21°C). This DSC evidence of crystallinity was confirmed by x-ray analysis. The reflection of the DAB prepolymer covered a range of 4.2 to 4.6 Å (main diffraction spacing 4.4 Å) at room temperature but became a distinct diffraction line with a spacing of 4.1 Å when the temperature was lowered below −25°C, clearly showing the crystallinity of the sample. Because crystallinity was apparently one-dimensional, calculating the degree of crystallinity and the size of crystallites was impossible. In contrast, the DAA prepolymer gave a broad diffraction spanning from 4.1 to 4.7 Å (main diffraction spacing 4.5 Å) at room temperature and from 4.1 to 4.6 Å (main diffraction

spacing 4.4 Å) at low temperature.   These data indicated the amorphous
nature of the prepolymer regardless of temperature.

The broad exotherms in Figure 8 near 175°C for the aliphatic prepoly-
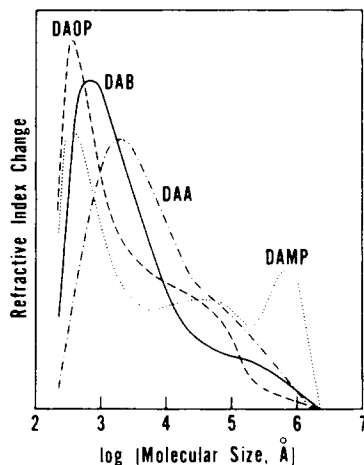mers and 275°C for DAMP reflect thermally induced crosslinking.   When

Fig. 7. Gel permeation chromatography of prepolymers from monomers indicated
(DAOP = diallyl o-phthalate; DAMP = dially m-phthalate). "Molecular size"
(designated A in text) is the extended chain length in Å based on calibration with poly-
styrene standards.
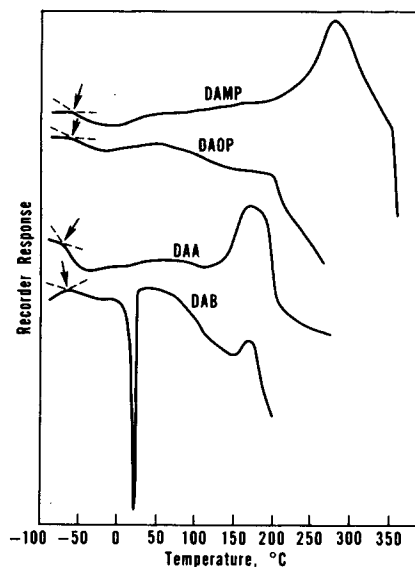
Fig. 8. Differential scanning calorimetry of prepolymers from monomers indicated.
Positive peaks represent exotherms.   Programmed temperature rate, 10°C/min.   Glass
transition points indicated by arrows were located on the thermograms by the procedure
illustrated in reference 27.

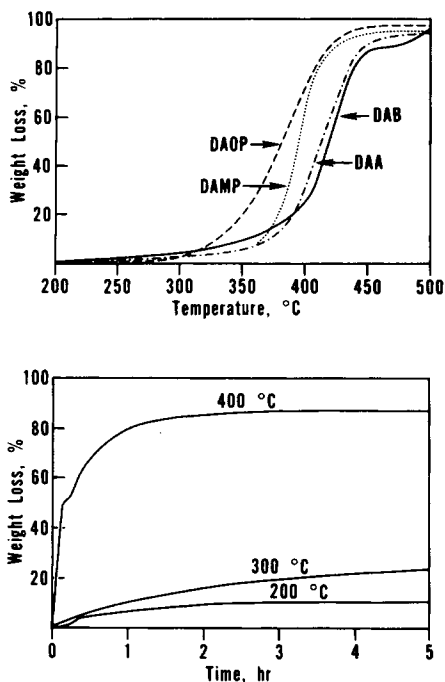Fig. 9. Thermogravimetric analysis (nitrogen atmosphere). Upper curves: pro-grammed-temperature (5°C/min, 25 to 500°C) decomposition of prepolymers from monomers indicated. Weight loss between 25° and 200°C was less than 1.0% for all four prepolymers. Lower curves: isothermal decomposition of DAB prepolymers at temperatures indicated.

heating was stopped after these peaks appeared, the samples were no longer soluble in the prepolymer solvents listed in Table I (solvent group A). Moreover, initial addition of 5% by weight of Ionox 330 inhibitor to DAB prepolymer prevented appearance of its DSC exotherm at 170°C.

Interpretation of the pronounced negative recorder responses after the crosslinking exotherms is complicated by changes in heat transfer efficiency and specific heat of the samples. These recorder responses may partially reflect decomposition—especially for DAMP after the inflection near 350°C—but a better indication of thermal stability was provided by TGA (Fig. 9). At programmed temperatures, decomposition started at 200°C and became drastic around 400°C, with our aliphatic prepolymers exhibiting greater stability than the commercial products prepared from aromatic diallyl esters. At isothermal temperatures, a drastic increase in weight loss occurred at 400°C, wlch leveled off after 3 to 4 hr of heating. Additional information regarding stability of prepolymers without added catalyst is given in Figure 3, where extrapolated shelf times of 28,000 min for DAB prepolymer and 12,000 min for DAA prepolymer are indicated.

Thermal and volume changes accompanying curing of prepolymers with added catalyst are summarized in Table II. For the aliphatic prepoly-

mers, enthalpies of crosslinking were determined as illustrated in Figure 1. The ΔH values so obtained were corrected for allylic double bonds removed by cyclization in the prepolymers. Absence of IR bands at 6.10, 10.12, and 10.78 μm in the cured product from DAB (Fig. 6) support the assumption that all available allyl moieties participated in the catalyzed crosslinking reaction. Specific gravity increased from 1.0237 and 1.0732, respectively, for DAB and DAA prepolymers (plus 2 mole-% t-butyl perbenzoate) to 1.0307 and 1.0763 for the hard transparent cured products from them.

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