Vinyl-Terminated Oligomeric Ethers: A Study of the Crosslinking Process

S. J. BARTON, J. S. GHOTRA, A. E. MATTHEWS,* and G. PRITCHARD

School of Applied Chemistry, Kingston Polytechnic, Kingston upon Thames, Surrey KT1 2EE, UK

SYNOPSIS

A thermosetting resin consisting of a mixture of vinyl-terminated oligomeric ethers was prepared by a two-step synthesis. This required the reaction of 1,4-bis(chloromethyl) benzene with the potassium salt of bisphenol A, and subsequent vinylation of the chloromethyl end groups by means of a Wittig reaction. The linear vinyl prepolymers were thermally crosslinked through their reactive styryl end groups (without the addition of catalyst) to produce castings and woven glass laminates. A study of the crosslinking process was carried out by differential scanning calorimetry (DSC). The water absorption and the thermooxidative stability of the crosslinked polymer were investigated. A styrene solution of the oligomeric ethers was also crosslinked, using benzoyl peroxide as a catalyst. The moisture absorption characteristics of the crosslinked styrene copolymer were compared with those of the crosslinked homopolymer. Both substances showed hydrophobic character.

INTRODUCTION

The synthesis and characterization of linear vinyl-terminated oligomeric ethers has been described in an earlier publication.[1] These oligomeric ethers undergo crosslinking through their terminally situated unsaturation on heating, without releasing volatile products liable to generate voids. The crosslinked network structure, being free of hydrophilic groups, such as esters, carbonyls, and hydroxyl groups, is expected to have a low water uptake. It was one of the objectives of this study to confirm the hydrophobic character of the crosslinked polymer.

The present communication also reports on the crosslinking of these oligomeric ethers, the thermooxidative stability of the crosslinked products, and the effects of the initial stages of thermooxidative degradation on water absorption. Finally, it reports on the glass transition temperature, heat distortion temperature, and some mechanical properties of the crosslinked network polymers.

EXPERIMENTAL

Synthesis of Vinyl-Terminated Ether Oligomers

Vinyl-terminated ether oligomers were prepared as previously reported.[1] Briefly, the following two reactions were performed (Fig. 1). In the first stage, two mol 1,4-bis(chloromethyl)benzene were reacted with one mol bisphenol A in dimethyl acetamide, using anhydrous potassium carbonate as the base, to obtain a mixture of chloromethyl-terminated ether oligomers. In the second stage, Wittig vinylation of the chloromethyl-terminated oligomers was achieved by preparing their diphosphonium derivatives in dimethyl formamide, then passing formaldehyde gas through the cooled contents and adding methanolic sodium hydroxide as the base.

Crosslinking Process

Curing of the oligomeric ethers was carried out both in air and under an atmosphere of nitrogen. Castings of the oligomeric ethers were made by melting the powder into silicone molds preheated to 200°C, or into closed molds of stainless steel treated with a release agent. Cure temperatures of 200°C were maintained for 1 h. The crosslinked products made
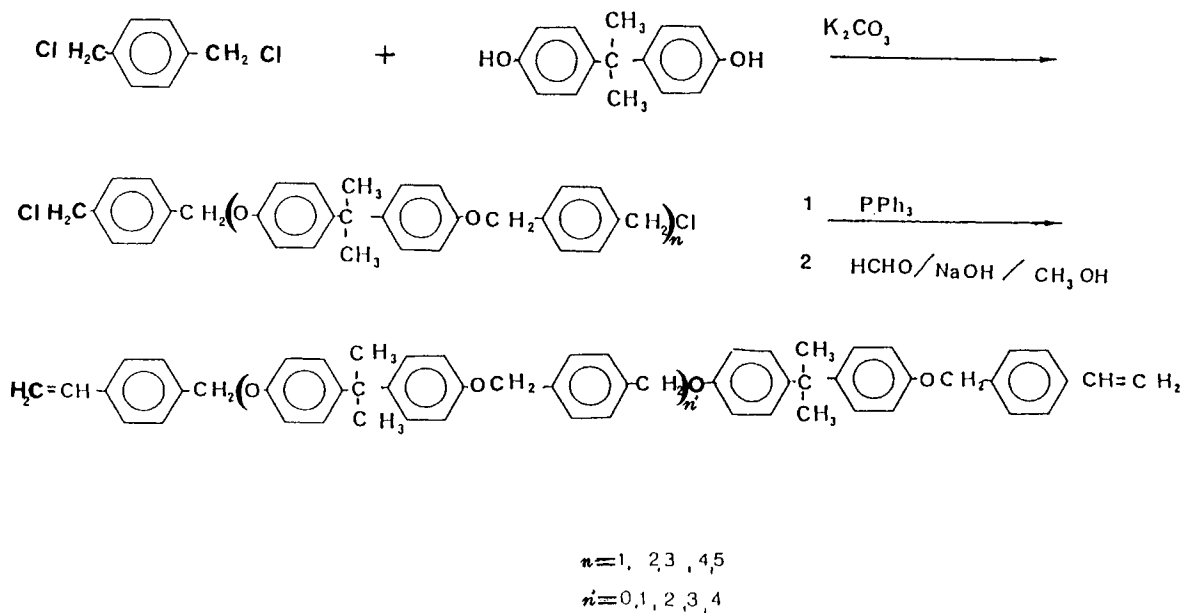
Figure 1   Synthesis of vinyl-terminated oligomeric ethers using the Wittig reaction.

in this way will be described as homopolymers, in contrast to those made by crosslinking styrene solutions (see later), which will be termed copolymers, by analogy with unsaturated polyesters.

Laminates were prepared by impregnating the woven roving glass reinforcement with the ether oligomers, i.e., the homopolymer. Stacks of three plies were placed in a picture frame mold between two aluminium plates pretreated with release agent. The laminates were cured in an electrically heated hydraulic press at 200°C for 1 h. Solutions of the oligomeric ethers in styrene (50 : 50 w/w) were cured in closed molds at 90–100°C using 1% w/w active benzoyl peroxide as catalyst.

Solvent Extraction

Three samples of the cured homopolymer were ground to coarse powders. In each case, a known amount of the powder was extracted for three weeks at 20°C with dichloromethane. The swollen particles were filtered off, washed repeatedly with dichloromethane, and dried to constant weight at 100°C. On average, 94.3% of the polymer was insoluble. The solid recovered from the extract was mainly insoluble in methanol.

Differential Scanning Calorimetry (DSC)

Five-mg samples of uncrosslinked polymer were sealed in aluminium dishes, and DSC thermograms were obtained using a Mettler DSC 20 system fitted with a nitrogen purge. The temperature was increased from 25 to 350°C at a rate of 15°C/min. Isothermal traces were also produced at several temperatures between 100 and 180°C.

Water Absorption Studies

Cast homopolymer discs 1.5 mm thick and 40 mm in diameter were prepared by heating the powder in open silicone molds at 200°C under an atmosphere of nitrogen for 1 h. The discs were sanded to a smooth finish and dried to constant weight prior to their immersion in distilled water at 70°C.

Similar discs were cured in the same way at 200°C using closed steel molds; they were sanded to a thickness of 0.75 mm and heated again in air at 160°C for 68 h. The discs warped during this treatment. They were immersed in water at 70°C.

Square water absorption specimens (50 × 50 × 1.5 mm) were machined from a sheet of the styrene copolymer. The specimens were dried to constant weight and immersed in water at 50°C.

Laminate specimens (50 × 50 × 1.5 mm) were also used for water absorption. They were cured under pressure for 30 min at 210°C. Some of these specimens were then further heated in air at 80 and 120°C for 70 h prior to their immersion in water.

All water absorption specimens were immersed in water in sealed glass containers that were them-

selves stored in constant temperature cabinets. On the first day of immersion, changes in weight were recorded every hour, and then at progressively longer periods. The specimens were dried with an absorbent cloth and cooled in a desiccator before weighing.

Measurements of Physical and Mechanical Properties

The heat distortion temperature was determined in accordance with BS2782 Part 1 (1970), Method 102G. The glass transition temperature (T_g) was determined by three different methods:

1. *Torsional pendulum.* An automated torsional pendulum[2] was used, and the T_g taken as the temperature at which the modulus dropped to half of its value at ambient temperature.
2. *Thermomechanical analysis (TMA).* A Mettler TMA 40 Thermal Analysis System was used to follow the expansion of a homopolymer sample with increasing temperature. The T_g was taken as the crossover point of two regression lines drawn from two points adjacent to the kink in the expansion curve.
3. *DSC.* The T_g was determined by dynamic runs with a heating rate of 10°C/min, from 40°C upward.

The Barcol hardness of homopolymer castings was determined using a Barber Colman impressor (GYZJ934-1). Flexural strength and modulus were measured using an Instron (Model 1114) in a three-point bending mode according to ISO 178 (1975) with a crosshead speed of 2 mm/min.

RESULTS AND DISCUSSION

No catalyst was necessary to cure the homopolymer. Previously, Steiner[3] reported crosslinking the bis(vinylbenzyl) ether of bisphenol A with 1% benzoyl peroxide to produce a tough horny resin. The temperature and curing cycle details were not given. The fact that no catalyst was necessary to cure the longer chain vinyl-terminated oligomeric ether resins described here eliminates the possibility of catalyst residues likely to increase water absorption.

Curing reactions were conducted either under an atmosphere of nitrogen or in closed steel molds. Although the mixture of vinyl-terminated oligomeric ethers appeared to be completely fluid at 130°C, we found that a cure temperature of 180–200°C was preferable. This ensured that a homogeneous mix-

ture was obtained rapidly, and that the resin was of sufficiently low viscosity to flow easily within the mold.

Processing Window

The dynamic DSC thermogram of the vinyl-terminated oligomeric ethers is shown in Figure 2. The presence of the crystalline first oligomer is shown by the melting endotherm at 95°C. Further melting points could just be detected in the temperature range 120–150°C, while the exotherm of the curing reaction commenced at 170°C. The heating rate used was 10°C/min. Clearly, a very small processing window was available. (The processing window can be defined in two ways. One definition equates it with the difference between the lowest temperature, T_1, at which sufficient flow occurs to enable the resin to adopt the mold shape, and the lowest temperature, T_2, at which the curing reaction starts. The other considers the window as the period of time during which the resin is still capable of flow at a given fixed temperature. T_1 depends on the shape of the mold and the pressure applied.)

Figure 2 suggests that T_1 could not be less than

HEAT FLOW
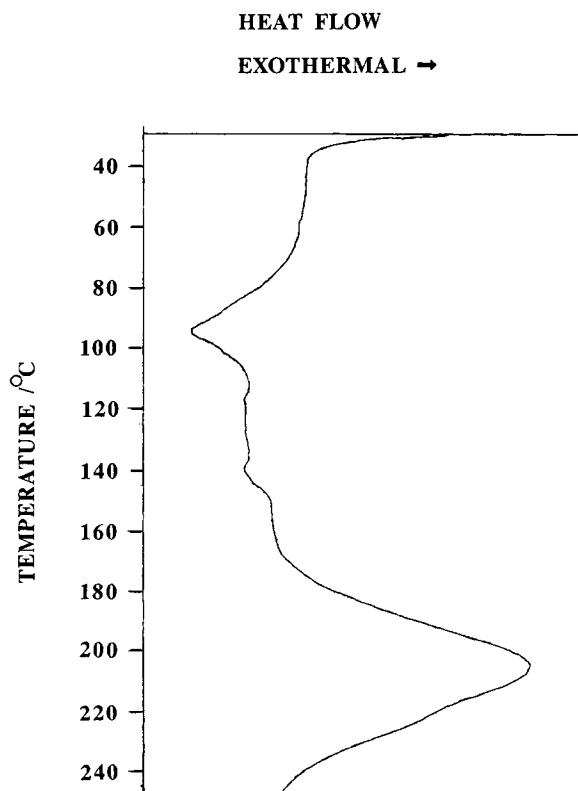
EXOTHERMAL →

Figure 2 Dynamic DSC thermogram of the vinyl-terminated ether (heating rate, 10°C/min).
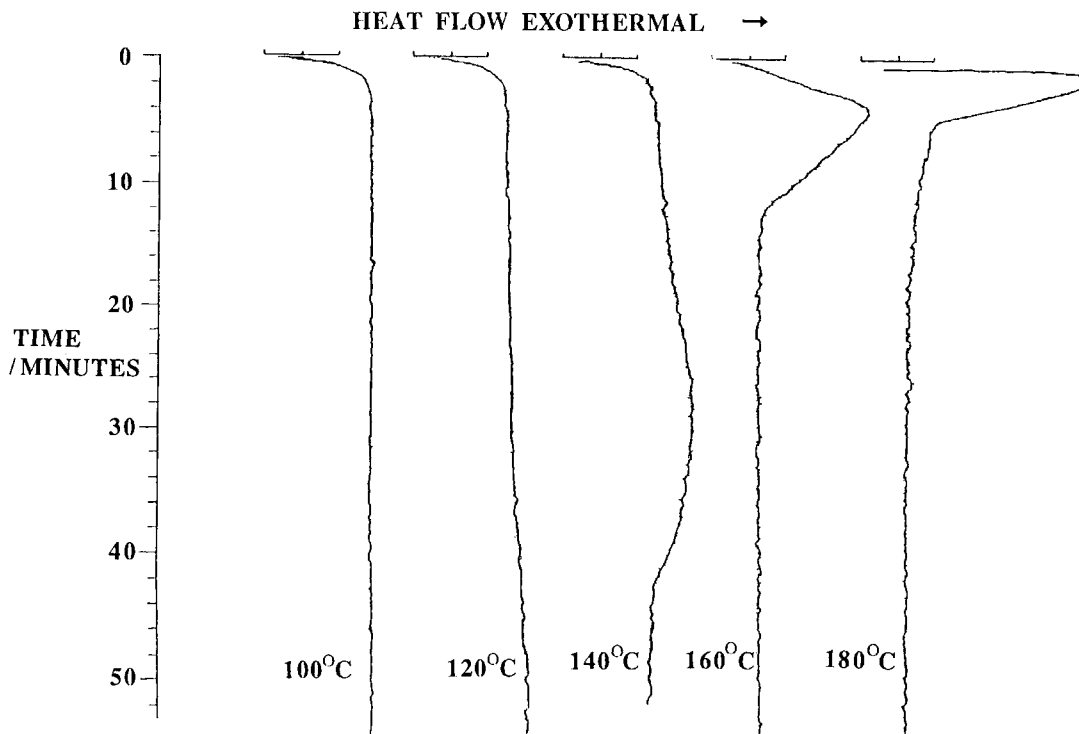
Figure 3 Isothermal DSC plots for vinyl-terminated oligomeric ether at various temperatures.

150°C, but T_2 is more difficult to define from a dynamic thermogram. Isothermal DSC plots (Fig. 3) showed that at 100°C there was no noticeable exotherm for up to 1 h, suggesting that little or no crosslinking was taking place. At 120°C there was a very slight exotherm but the sample remained soluble after 1 h at this temperature. At 140°C the polymer was substantially cured (i.e., the exotherm ceased) in approximately 40 min, and the sample became insoluble and infusible. No investigation was made of the homogeneity of the product crosslinked below the melting point of the highest oligomer. The curing became more rapid at higher temperatures, with the exotherm complete within 12 min at 160°C and 6 min at 180°C. Therefore, the processing window must be regarded as zero by the first definition, but the second definition gives useful values based on the flow time as a function of temperature.

Percec and Auman[4] studied the curing reaction of various vinyl-substituted polymers using DSC. They also observed that no free radical initiator was necessary for crosslinking these polymers. They identified curing exotherms at temperatures as low as 114°C. The reaction of styryl groups can occur readily at fairly low temperatures, given sufficient chain mobility.

Moisture Absorption Characteristics

The water absorption parameters of various specimens are listed in Table I and illustrated in Figures 4 and 5 for castings and laminates, respectively. The equilibrium water absorption of the cast homopolymer immersed in distilled water at 70°C was 0.28% by weight, an exceptionally low value for a crosslinkable laminating resin. This supports the view that one of the major factors affecting water absorption is the presence or absence of hydrophilic groups in the crosslinked network. The structure of the crosslinked vinyl-terminated ethers contains only very weakly hydrophilic sites (i.e., methylene ether groups), so low water absorption figures would be expected. However, there are other relevant factors to consider, notably free volume, which generally increases with crosslink density, because of the development of a rigid macromolecular framework.

The diffusion coefficient of the cast homopolymer was of similar magnitude to that of an epoxy resin, even though M_{max} was much lower. There is not necessarily a simple linear relationship between the water absorption maximum and the diffusion coefficient. A low value of M_{max} does not necessarily imply a low value of D. This fact has also been observed

Table I   Water Absorption Parameters

Specimen	Temperature (°C)	Water Uptake (%)	Diffusion[1] Coefficient $(m^2 \ s^{-1})$
Cast homopolymer	70	0.28	4×10^{-12}
Cast homopolymer after 68 h in air at 160°C	70	0.91	2.5×10^{-12}
Cast homopolymer	50	0.32	1.7×10^{-12}
Styrene copolymer (50 : 50 w/w)	50	0.17	7.3×10^{-12}
Homopolymer laminate[2]	50	0.28	7.3×10^{-13}
Homopolymer laminate after 70 h in air at 80°C	50	0.27	4.3×10^{-13}
Homopolymer laminate after 70 h in air at 120°C	50	0.34	1.5×10^{-12}

[1] Diffusion coefficients (D) were calculated from the initial slope of the Fick's Law plot, using the expression:

$$D = \pi\left(\frac{h}{4M_{max}}\right)^2\left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}\right)^2,$$

where h = thickness, M_1 and M_2 are the percentage water absorptions at times t_1 and t_2, and M_{max} is the equilibrium water uptake.
[2] 57% w/w glass woven roving reinforcement.

by Barrie and Machin[5] and by Johncock and Tudgey.[6]

The low water absorption of the styrene copolymer can be explained by the hydrophobic character of its aromatic hydrocarbon content and by the dilution of the methylene ether groups. The copolymer was 98.1% insoluble after 24 h in refluxing toluene,

suggesting that styrene molecules were firmly bonded into the crosslinked network.

The water absorption of the laminate homopolymer after 40 d immersion in water was 0.28%. By this point, the equilibrium had been almost reached, but a further small increase probably took place after this time.
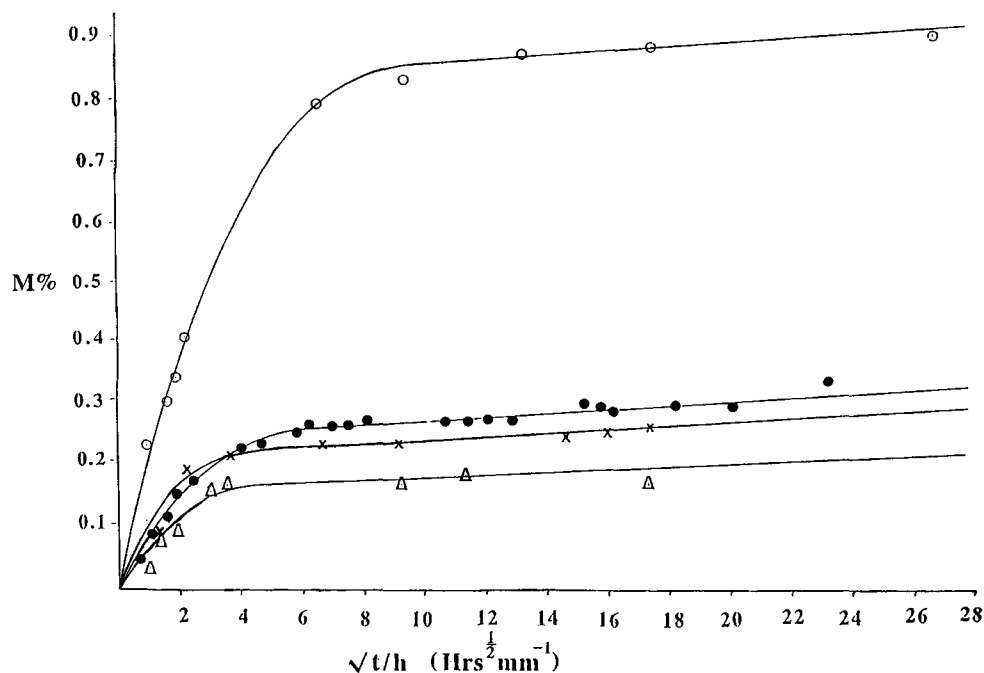
Figure 4   Sorption curves for various unreinforced polymers immersed in distilled water: homopolymer, 50°C - ● -; homopolymer, 70°C - X -; homopolymer, 70°C (after 68 h in air at 160°C) - ⊙ -; copolymer, 50°C - △ -. Thickness, 1.5 mm with the exception of the oxidized sample; which was 0.75 mm.
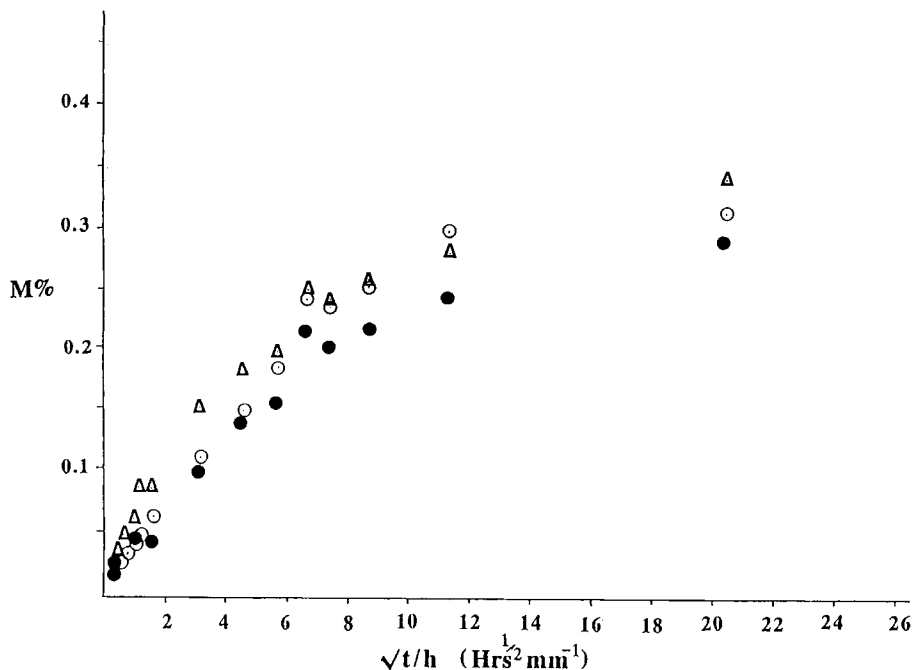
Figure 5   Sorption curves for various glass laminates immersed in distilled water: homopolymer glass laminate, 50°C - ⊙ -; homopolymer glass laminate, 50°C (after 70 h in air at 80°C) - ● -; homopolymer glass laminate, 50°C (after 70 h in air at 120°C) - △ -; Specimen thicknesses, all 1.5 mm.

Glass fibers do not absorb moisture and so the expected moisture absorption value would in theory be much lower than that of the unreinforced polymer; however, in practice, laminates often have a higher moisture absorption value caused by small voids associated with the fiber wetting process. As expected, the diffusion coefficient of the laminates was smaller than that of the castings.

There was a tendency towards pseudo-Fickian sorption (Fig. 5) insofar as the initial, linear part of the absorption graph of mass absorbed vs. $(t^{0.5})/h$ was anomalously short. Other criteria of Fickian behavior, such as adherence to the film thickness scaling law, the coincidence of the sorption and desorption curves, and the Arrhenius relationship between diffusivity and temperature, have not yet been fully applied.

A cast homopolymer sample 0.75 mm thick was heated in air at 160°C for 68 h and immersed in water at 70°C. The water absorption maximum of the heat-aged sample rose to 0.91% and the diffusion coefficient to 2.5×10^{-12} m²s^{-1}, indicating that oxidation had occurred. A similar phenomenon was observed but to a much lesser extent with a laminate heat aged at 120°C for 70 h. A plot of log M against log t no longer had a slope of 0.5, suggesting either that interactions between the moisture and polymer

oxidation products were occurring, or that surface changes such as microcracking had begun.

Thermooxidative Behavior

Water absorption curves for the homopolymer castings and laminates aged in air at 120°C (i.e., 15° above the glass transition temperature of the dry polymer) for 70 h showed only a slight increase in both M_{max} and D, while cast samples aged in air at 160°C ($T_g + 55$°C) showed large increases in both parameters. Samples aged at 80°C showed the same water absorption characteristics as the unaged specimens. The samples aged at 160°C changed from colorless to pale brown. An investigation of the reaction was carried out to determine whether oxidation had occurred.

The infrared spectra of heat-aged and virgin samples of the crosslinked product were obtained by curing thin films of the polymer onto a sodium chloride plate under an atmosphere of nitrogen, recording the IR spectra, and then heating the films at 200°C in a circulating air oven for 6 h. The principal difference after heat aging was the appearance of a new peak at 1735 cm^{-1}, presumably caused by the oxidation of benzyl ether groups to phenyl ben-

zoate type structures. A peak associated with hydroxyl groups was also present at 3450 cm^{-1}.

The oxidation of methylene groups to ketonic ones is well known.[7] The oxidation of ethers to produce hydroperoxides and finally peroxides is widely attributed to the formation of a hydroperoxide on the methylene group, followed by decomposition to ketonic species. The ketonic group can be oxidized further, with chain cleavage to an acid and a diketonic species.

To examine the mechanism of the oxidation more closely, the bis(benzyl) ether of bisphenol A was adopted as a model compound and produced by the reaction of benzyl chloride with bisphenol A using the potassium carbonate/dimethyl acetamide system. The NMR spectrum had peaks at $\delta = 1.6$ ppm (isopropylidene group), $\delta = 5.0$ ppm (methylene ether), $\delta = 6.7$–7.3 ppm (phenylene protons of bisphenol A), and $\delta = 7.4$ ppm (aromatic protons from the terminal phenyl groups). The IR spectrum contained peaks from the benzyl ether at 1010 and 1240 cm^{-1}. The mass spectrum showed a peak from the parent molecular ion at $m/e = 408$. The melting point of the white crystalline compound was 127–127.5°C.

The bis(benzyl) ether of bisphenol A was heated and stirred at 180°C for one week. It yielded white crystals of a sublimate, and a dark brown residue. The white crystals of the sublimate were identified as those of benzoic acid, according to the melting point and the IR spectrum. The NMR spectrum of the residue had changed radically. The peak from the isopropylidene group had been split into three, and the size of the benzyl ether peak was much reduced. Although the aromatic region was highly complex, new peaks were observed at $\delta = 8.2$ ppm and $\delta = 8.3$ ppm. The IR spectrum of the residue contained a broad new peak at 3450 cm^{-1}, characteristic of hydroxyl absorptions. The IR spectrum also showed a strong peak at 1735 cm^{-1}, attributed to a carbonyl absorption from an aromatic ester (cf. phenyl benzoate). The ether group peaks were still present in the IR spectrum.

The mass spectrum of the oxidized residue showed peaks at $(m/e) = 436$, 422, 332, and 318. However, these peaks were absent from the mass spectrum of the unoxidized sample. The peak at $m/e = 408$ was still present. The new peaks were attributed to parent molecular ions of the bis(benzoyl) ester of bisphenol A ($m/e = 436$), the benzyl ether–benzoyl ester ($m/e = 422$), the monobenzoyl ester of bisphenol A ($m/e = 332$), and the analogous monobenzyl ether ($m/e = 308$), as shown in Figure 6.
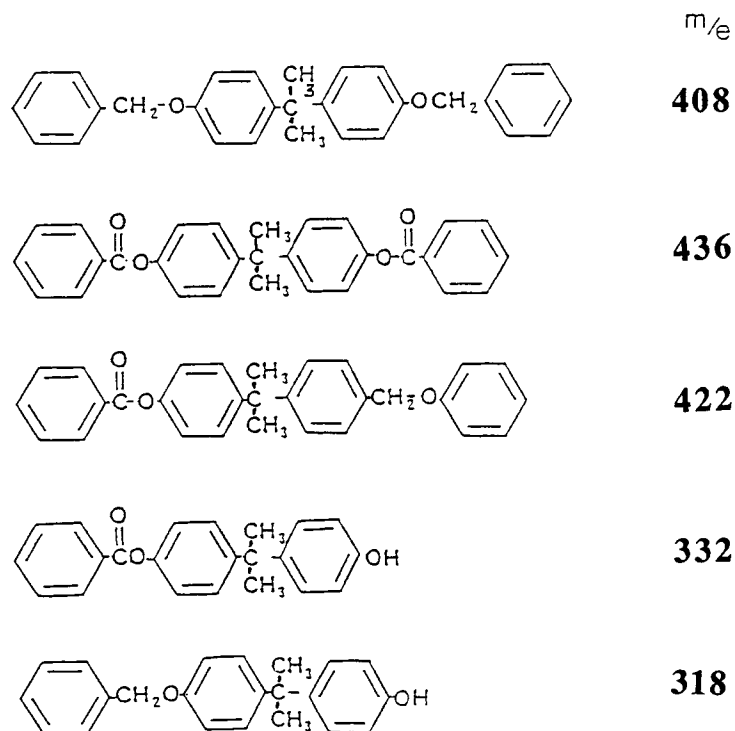

Figure 6 Mass spectrum peak assignments for the oxidation products from the bis(benzyl) ether of bisphenol A.

Thin layer chromatography of the oxidized residue suggested that there were three major components in the mixture, and that some of the original bis(benzyl)ether of bisphenol A was still present. The ^{1}H NMR spectrum of an aqueous sodium hydroxide extract of the oxidized sample showed no peak at $\delta = 5.0$ attributable to methylene ether protons, but it contained peaks from bisphenol A units and further peaks at $\delta = 8.2$, $\delta = 8.3$, and $\delta = 7.2$–7.6 ppm associated with benzoate aromatics, suggesting the presence of the monobenzoic ester.

It is proposed that the initial stage of oxidation involves proton abstraction by radical species from the labile methylene ether group, followed by the addition of oxygen to form a peroxide radical. This can abstract a proton from another benzyl ether group to form a hydroperoxide and an oxidizable radical R$^\bullet$ that can reenter the cycle, as shown in Figure 7.

The hydroperoxide and the peroxide are both thermally unstable. On decomposition they produce RO$^\bullet$ and hydroxyl radicals, which can further enter the autooxidation cycle. The hydroxyl radicals readily abstract protons to form water, i.e.

$$OH^\bullet + RH \rightarrow H2O + R^\bullet$$
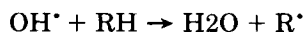
and again a reactive radical species is produced. The peroxide intermediates formed during the oxidation of the bis(benzyl)ether of bisphenol A decompose either to ester molecules or to phenolic-hydroxyl-containing species and benzoic acid through the prior formation of benzaldehyde (Fig. 8). The breakdown of peroxy radicals to yield benzoic ester and hydroxyl radicals is another alternative mechanism. Prolonged heating of the polymer in air
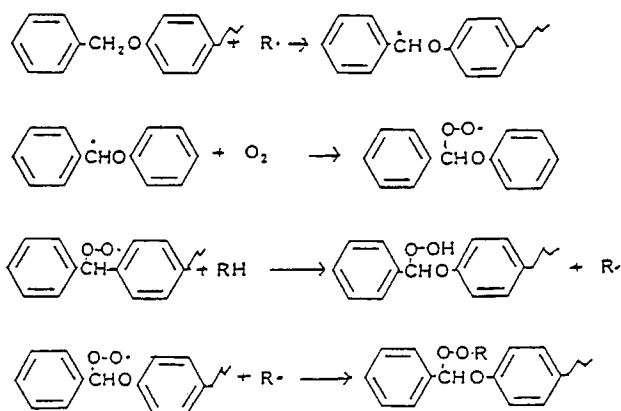
Figure 7 Proposed mechanism of thermooxidative degradation of vinyl-terminated oligomeric ethers.
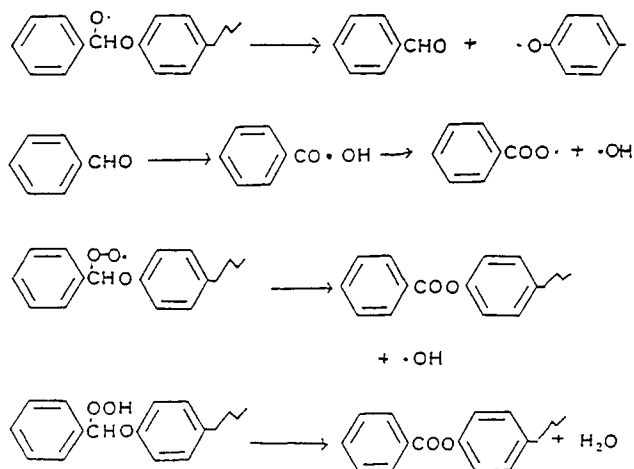
Figure 8 Proposed mechanism of peroxide intermediate degradation.

would, therefore, introduce hydrophilic carbonyl groups, and promote chain cleavage, with the emission of water molecules. Each factor would increase the rate of water absorption and the amount of water absorbed.

Mechanical Properties

Some mechanical properties of the castings and laminates were measured. The flexural strength of the castings (80 MPa) and the flexural modulus (3.3 MPa) were as expected for a thermosetting resin; the flexural strength (342 MPa) of the laminate was higher than expected.

The flexural modulus (7.9 GPa) was low for a 57% w/w glass roving laminate. The average Barcol hardness of a cast homopolymer specimen was 40. The heat distortion temperature and the glass transition temperature, determined by three different methods, were 115 and 105–107°C, respectively.

CONCLUSIONS

The vinyl-terminated ether oligomers were prepared by the condensation reaction of 1,4-bis(chloromethyl)benzene and bisphenol A, followed by the Wittig reaction. The crosslinking reaction of these oligomeric materials was studied using differential scanning calorimetry. The castings and laminate specimens were prepared by thermal crosslinking at temperatures up to 200°C. The unreinforced and reinforced specimens had exceptionally low water absorption maxima, although the diffusion coefficients were comparable with those of typical epoxy

resins. Thermooxidative degradation introduced hydrophilic groups into the crosslinked network, increasing the rate of absorption and the amount of water absorbed. The change in the water absorption properties of the thermally aged specimens has been explained in terms of oxidation leading to the formation of hydrophilic centers, with accompanying chain scission. The mechanism of thermal oxidation was investigated by means of a model compound. In summary, the crosslinked network investigated combines reasonable mechanical properties with one of the lowest water absorption maxima yet reported for crosslinkable, nonfluorinated laminating resins.

REFERENCES

1. S. J. Barton, J. S. Ghotra, A. E. Matthews, and G. Pritchard, *Polymer*, **30**, 1546 (1989).
2. P. Z. Xieng, I. A. Ansari, and G. Pritchard, *Polym. Test.*, **5**, 321 (1985).
3. E. G. Steiner, U. S. Pat. 4,116,936 (1978).
4. V. Percec and B. C. Auman, *Polym. Preprints*, **25**, 122 (1984).
5. J. A. Barrie and D. Machin, *J. Macromol. Sci.*, **B-3**, 645 (1969).
6. P. Johncock and G. F. Tudgey, *Br. Polym. J.*, **15**, 14 (1983).
7. J. P. Critchley, G. J. Knight, and W. W. Wright, *Heat-Resistant Polymers*, Plenum Press, New York (1983).