# Thermoplastic toughened styrenic thermosets: synthesis, properties and consequences of radical based cure chemistry

**J. L. Hedrick*, J. G. Hilborn, R. B. Prime, J. W. Labadie, D. J. Dawson, T. P. Russell and V. Wakharker**
*IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099, USA*

*(Received 18 May 1992; revised 20 April 1993)*

A novel thermosetting resin based on vinylic end groups was prepared and its network formation investigated. 2,2-Bis(4-vinylbenzyloxyphenyl)hexafluoropropane was prepared by the condensation of vinylbenzyl chloride with Bisphenol-AF in the presence of $K_2CO_3$. This distyrenic monomer was cured thermally to produce a highly crosslinked network with $<0.5\%$ sol fraction. The networks prepared by this reactive monomer were brittle. However, their fracture toughness could be modified with the incorporation of vinylbenzyl end-capped perfluoroalkylene aryl ether oligomers. The thermoplastic component phase separated into discrete composite particles in the continuous network phase. The thermoplastic modified network showed improved fracture toughness without sacrificing the modulus or good dielectric characteristics.

**(Keywords: thermoset; network; cure chemistry)**

## INTRODUCTION

High performance polymers play an important role as packaging materials in the manufacture of microelectronic devices and components, and are finding applications as interlayer dielectrics for thin film wiring in multichip packages and chip interconnection, passivation layers and structural resins. The polymer requirements for these applications vary, but generally include high thermal and dimensional stability, low thermal expansion coefficient, low residual stress from thermal cycling, good mechanical properties and low dielectric constant. The dielectric constant is of particular importance, as the propagation varies with the inverse of the dielectric constant and a lower value also allows for denser wiring[1]. Other important characteristics of the polymer dielectric which contribute to the fabrication of multilayer structures include processability, planarization and auto-adhesion[1,2]. Both global and local planarization are critical for any polymer application. Global planarization reflects the ability of a polymer solution to coat the overall topography and is related to the solids content of the solution[1]. Local planarization is a measure of the manner in which the polymer fills gaps and holes on the underlying topography and is directly related to the viscosity of the polymer melt. As a class of materials, polyimides have best satisfied the material requirements for microelectronic applications[3]. However, as the material requirements for the microelectronic industry become more demanding, other polymers may outperform polyimides.

Research directed towards new materials which satisfy many of the requirements has led to the investigation of thermosetting polymer systems. Highly crosslinked networks generally show high tensile strength and modulus, excellent chemical resistance and good dimensional stability. Furthermore, since thermosetting resins involve the transformation of low molecular weight solids or oils to a high molecular weight glass, high solids compositions may be attained producing highly planar surfaces after cure. Epoxy resins are among the most commonly used thermosetting polymers due to their availability, cost, and ease of processing. These materials have found applications in composite circuit boards, cards and encapsulants. Other resins based on maleimide, norbornene (nadimide), cyanate and propargyl are also viable candidates for such applications[4–8]. However, drawbacks to the use of such materials as dielectric insulators result from their moderate thermal stability and the contributions of their polar end groups to both dielectric constant and water uptake. Recently, there have been several reports of thermosetting resins based on less polar crosslinking chemistry including a vinylic[9], benzocyclobutene[10], vinyl ether[11] and other reactive end groups. In most of these systems, formulations have been developed allowing B-staging (partial polymerization to afford highly viscous solutions). The high thermal stability of these structures is, in many respects, comparable to many of the conventional resins; however, the contribution of the reactive end group chemistry to

---

* To whom correspondence should be addressed

0032-3861/94/020291-09

the dielectric constant and water uptake is much less. Unlike the epoxy resins where the cure reactions with respect to time and temperature have been carefully mapped out in a time–temperature–transformation (TTT) diagram[12], there have been very few reports about the kinetics of such radical and cationic curing reactions. For the most part, the initial stages of an epoxy cure follow typical step growth condensation kinetics (i.e. dimers, trimers, etc.) to the point of gelation, where the polymerization becomes kinetically controlled. However, for the case of radical and cationic networking reactions, high molecular weights and gelation are achieved early in the reaction and as the polymerization proceeds, the monomer conversion to the network's structure increases. Due to the rapid onset of gelation, it is very difficult to prepolymerize or B-stage these resins with minimal gel content. In addition, toughening with either reactive thermoplastics or elastomers becomes complicated since the desired level of phase separation is dictated not only by thermodynamic but also kinetic factors.

The brittle mechanical properties of such networks are of concern particularly for the fabrication of multilayer components which undergo numerous thermal cycles resulting in high residual stress. Multiphase elastomeric materials in the form of block[13,14], graft[15] and ion containing[16] copolymers have been shown to be successful means of impact modifying brittle polymers. A classic example of an elastomeric toughened matrix is high impact polystyrene (HIPS) where styrene is polymerized in the presence of polybutadiene. This technology has been applied to epoxy resins through the utilization of low molecular weight liquid butadiene acrylonitrile copolymers having either carboxyl or amine reactive end groups[17–29]. The $K_{1,C}$ fracture toughness values of the rubber modified epoxy networks are considerably higher in some cases than those for the unmodified materials.

Recently, another approach has been used to modify epoxy networks and other brittle materials. The incorporation of tough–ductile engineering thermoplastics has been shown to produce a better balance of properties than that obtained with elastomeric materials (i.e. toughness *versus* stiffness). Hedrick *et al.*[30–32] have synthesized both amine and phenolic hydroxyl terminated aryl ether sulfone oligomers of various molecular weights to modify chemically epoxy resins. Upon curing, the polysulfone phase separated and interfacial adhesion was forced due to the chemical reaction. The polysulfone modified networks showed enhanced toughness at a minimal sacrifice to bulk properties. Kim and Brown[33] investigated the morphology in the polysulfone modified epoxy resin system, and found the morphology to be similar to the rubber toughened networks with a phase inversion occurring at a composition between 10 wt% and 30 wt% of the polysulfone modifier. Others have observed a bi-continuous morphology, characteristic of spinodal decomposition[34]. Spinodal decomposition was achieved by either varying the thermoplastic structure or composition. For this type of morphology, substantial improvements in fracture toughness were observed.

Apart from several sheet moulding compounds, there have been few reports on the toughening of resins which crosslink via addition polymerization kinetics. Furthermore, questions regarding the development of a phase separated morphology and the phase size required for optimum toughness of such radically cured systems which have been modified with either elastomers or thermoplastics have not been addressed. We have prepared a monomer, 2,2-bis(4-vinylbenzyloxyphenyl)-hexafluoropropane, with vinylic reactive end groups which polymerizes or cures via addition polymerization kinetics. In this paper, details regarding the synthesis, curing and mechanical properties of this vinylic monomer will be discussed as well as the investigations on the use of highly fluorinated thermoplastics to toughen the resulting network including the results from the morphological and mechanical analyses.

## EXPERIMENTAL

### *Materials*

*N*-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF) were distilled from $P_2O_5$ prior to use. The 4-vinylbenzyl chloride (Dow Chemical Co.), **1**, was used without further purification. 1,6-Bis(4-fluorophenyl)perfluorohexane was prepared as described in the literature[35]. 4,4′-(Hexafluoroisopropylidene)diphenol or Bisphenol-AF, **2**, was recrystallized from toluene/ethyl acetate.

### *Monomer synthesis*

*2,2-Bis(4-vinylbenzyloxyphenyl)hexafluoropropane,* **3**. A 3 l three-necked round-bottomed flask equipped with a mechanical stirrer, thermocouple temperature sensor, heating mantle and reflux condenser with nitrogen inlet was charged with 4,4′-(hexafluoroisopropylidene)diphenol (155.0 g, 461.0 mmol), acetone (1.5 l), **1** (151.0 g, 989.4 mmol, 2.15 eq.) and potassium carbonate (300.0 g, 2.17 mol), in that order. The flask was flushed with nitrogen and heated to reflux. The progress of the reaction was monitored by h.p.l.c. ($C_{18}$-reverse phase column, aqueous-$CH_3CN$ mobile phase, 230 nm detector). After 3 days of reflux, the starting materials were consumed and the bis-ether was the only material visible by h.p.l.c. The reaction mixture was diluted with $CH_2Cl_2$ (1.3 l) and filtered to remove the salts; the filter cake was washed with more $CH_2Cl_2$ (700 ml). The combined filtrates were stripped of solvents and the residue taken up in $CH_2Cl_2$ (2 l), washed with water (two × 1 l), dried ($Na_2SO_4$), filtered, and stripped to afford crude product (317.1 g). This material was triturated with hexanes (600 ml), filtered, and the solids washed with hexanes (300 ml) and dried overnight to yield **3** (177.7 g). A second crop (17.3 g) was obtained by stripping the filtrate and triturating the residue with hexanes (350 ml) and isolating as above. The combined yield was 74.4%.

### *Network formation*

Monomer **3** ($\sim$15 g) was placed in an Erlenmeyer flask containing a magnetic stir bar, sealed and flushed with oxygen to prevent the onset of gelation. The flask was then placed in a hot oil bath (130°C) where **3** melted. The monomer was then poured into a hot silicone mould (250°C), sealed and cured (2 h) to yield network **4**.

### *Polymer synthesis*

The phenolic hydroxyl terminated perfluoroalkylene aryl ether oligomers were prepared according to a published procedure[35]. A typical synthesis was conducted in a three-necked flask equipped with a nitrogen inlet, mechanical stirrer and Dean–Stark trap and condenser.

A detailed synthetic procedure designed to prepare a perfluoroalkylene aryl ether oligomer with a number-average molecular weight of ~5000 is provided. The flask was charged with Bisphenol-AF (6.7243 g, 20.000 mmol) and 1,6-bis(4-fluorophenyl)perfluorohexane (8.2963 g, 16.923 mmol) and carefully washed into the flask with NMP (50 ml). Toluene (35 ml) was then added, followed by $K_2CO_3$ (4.4200 g, 31.98 mmol). Note that $K_2CO_3$ was used in 40–50% excess. The reaction mixture was then heated until the toluene began to reflux. An optimum reflux rate was achieved when the oil bath was maintained between 140°C and 150°C. Toluene was periodically removed from the Dean–Stark trap and replaced with deoxygenated dry toluene to ensure dehydration. The oil bath was maintained at 140°C until the presence of water was no longer observed in the Dean–Stark trap, which took 4–8 h. The temperature was increased to 170°C and held for 20 h. The polymerization mixture was diluted with NMP, filtered hot to remove inorganic salts, cooled and treated with several drops of acetic acid. The polymer solution was coagulated in a 10× volume of 4/1 water/methanol, then stirred sequentially with 4/1 water/methanol and methanol. The polymer, **5**, was isolated by filtration and dried in a vacuum oven at 40°C to a constant weight. The yield was essentially quantitative.

### *End group derivatization*

The determination of the molecular weight of the perfluoroalkylene aryl ether oligomers was accomplished by silylating the phenolic hydroxyl end groups with dimethyl trimethylsilylamine and using $^1H$ n.m.r. to ratio the aromatic protons to the methyl protons of the end groups. This molecular weight value was used to derivatize the phenolic hydroxyl end groups with **1**. Derivatization of oligomer **5a** was accomplished by dissolving 10 g of the oligomer in DMF and adding in dry NaH. Once the evolution of gas had stopped, the solution was filtered into vinylbenzyl chloride (0.7100 g) and 18-crown-6 dissolved in DMF. The end-capping procedure took 24 h at 60°C.

### *Thermoplastic modification*

The thermoplastic modification of the styrenic resin was accomplished by mixing the oligomer powder with **3** in an Erlenmeyer flask with a stir bar. The flask was sealed with a rubber septum under an oxygen atmosphere, and placed in an oil bath (135°C) where the monomer melted and dissolved the oligomer. The solution was then poured into a hot silicone mould (250°C), sealed and cured (2 h). Alternatively, the powders could be deposited using an electrostatic powder coater (Model C-30 from Electrostatic Technology).

### *Characterization*

Glass transition temperatures ($T_g$s) taken as the midpoint of the change in slope of the baseline, were measured on a DuPont DSC 1090 instrument with a heating rate of 10°C min$^{-1}$. Thermogravimetric analysis (t.g.a.) of the polymer films was performed at a heating rate of 5°C min$^{-1}$ for the variable temperature scans, and the isothermal scans were taken at 400°C over an 8 h period. Mechanical property measurements were made on an Instron tensile tester at a strain rate of 10 mm min$^{-1}$. Dynamic mechanical behaviour was measured using a Polymer Laboratories dynamic mechanical thermal analyser in the tension mode with a heating rate of 10°C min$^{-1}$ (10 Hz).

The morphology of the toughened styrenic networks was characterized by small angle X-ray scattering (SAXS). SAXS measurements were performed on a Kratky camera using a 60 $\mu$m entrance slit and Ni filtered CuK$\alpha$ radiation (1.54 Å). The X-rays were supplied by a Rigaku rotating anode source operated at 50 kV and 200 mA. The polymer films were mounted in an evacuated chamber which was directly in line with the final collimation block and the flight path to the detector. The entire scattering profile was collected simultaneously using a TEC model 210 position sensitive detector situated at a distance of ~0.5 m from the specimen. The scattering profile was accumulated on an MCA after pulse height discrimination.

The value of $K_{1,C}$ (fracture toughness) indicates the critical stress intensity for a load which will cause catastrophic failure in the tension mode and, in this study, the three-point bend specimen geometry was used. For a three-point bend specimen:

$$K_{1,C} = \frac{3PLa^{1/2}Y}{Bw^2} \tag{1}$$

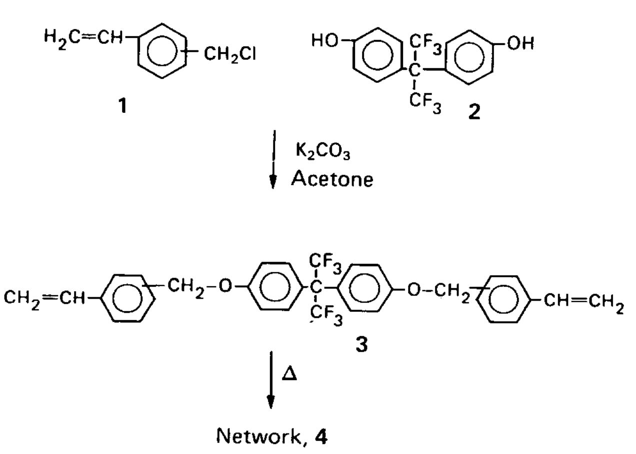
where $P$ is the load, $w$ is the width, $L$ is the length ($=2w$), $B$ is the thickness, $a$ is the crack length and $Y$ is a geometric factor given by:

$$Y = 29.6 - 186(a/w) + 656(a/w)^2 - 1017(a/w)^3 + 639(a/w)^4 \tag{2}$$

The criteria described in ASTM E394 were followed as closely as possible. The dimensions of the fracture toughness samples were ~3.2 × 6.4 × 38.1 mm. The precrack was introduced with a saw cut and then 'sharpened' with a new razor blade. The crosshead speed utilized was 0.5 mm min$^{-1}$ for all samples tested.

## RESULTS AND DISCUSSION

The styrenic end capped monomer, 2,2-bis(4-vinylbenzyloxyphenyl)hexafluoropropane (**3**), was prepared by the condensation of vinylbenzyl chloride (**1**) with Bisphenol-AF (**2**) (*Scheme 1*). It is important to note that **1** is a mixture of the 3- and 4-chloromethyl isomers, as



**Scheme 1**

denoted in *Scheme 1*, which were not separated prior to the reaction. The reaction was carried out in refluxing acetone in the presence of $K_2CO_3$ under a nitrogen blanket. Analysis of the reaction mixture by h.p.l.c. showed quantitative conversion of **2** with the formation of a single product peak. The product was isolated as a white crystalline solid with the spectral characteristics of **3**. The isomeric structures of **1** were maintained in **3**, yet were indistinguishable by h.p.l.c.

The network formation of **3** was accomplished by use of radical initiators and thermal curing. The curing of **3** was followed by calorimetry measurements (*Figure 1*), where the compound was observed to melt at ~75°C and react spontaneously between 170°C and 190°C to afford the desired network structure **4** (*Scheme 1*). The addition of 1 wt% di-tert butyl peroxide or benzoyl peroxide lowered the polymerization temperature to ~160°C or to just above the melting point (~80°C), respectively. For most of our experiments, **3** was cured without the use of an initiator; however, the cure time and temperature strongly influenced the network structure and subsequent properties. Curing **3** isothermally at temperatures ranging from 130 to 250°C by dynamic mechanical thermal analysis (d.m.t.a.) produced dramatically different behaviour. The $T_g$s, although broad, ranged from ~125 to 180°C depending on the curing temperatures. Samples cured isothermally at low temperatures produced low $T_g$s even if subsequent high temperature treatments were given. However, the high temperature cure (200–250°C) produced networks with high $T_g$s (180°C). The reason for differences in network properties obtained with different curing schedules is not understood. The heterogeneous course of the reaction involves events such as cyclization, microgel formation, gel particle precipitation or side reactions which are more or less dependent on heating rate or temperature and could account for the differences in final structure[36]. For our experiments we cured the samples at 250°C (2.0 h), sufficiently above the $T_g$ to produce the highest $T_g$ material.

The network structure prepared by this reactive monomer could be readily fabricated from the melt into a variety of shapes producing clear, void-free specimens. Many of the characteristics of the network are highlighted in *Table 1*. The calorimetry measurements showed no $T_g$ which was not unexpected for such a highly crosslinked structure. However, by the dynamic mechanical results shown in *Figure 2*, a broad relaxation characteristic of $T_g$ can be observed extending over 100°C. Furthermore, at $T_g$ the drop in modulus is minimal, indicative of a highly crosslinked structure. The modulus value above $T_g$ was used to estimate the molecular weight between crosslink junctions. While the conditions for the application of rubber elasticity theory, i.e. long chain flexible chains, were not satisfied, a value of 350 g mol$^{-1}$ was estimated which suggests an effective network formation. Consistent with these data, the swelling measurements showed only marginal solvent uptake (~10 wt% in chloroform) and no appreciable sol-fraction, indicative of full network formation (*Table 1*).

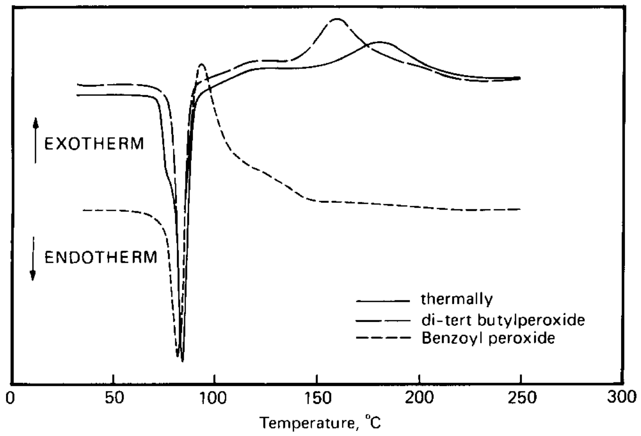


**Figure 1** D.s.c. thermograms of **3** cured thermally (——), with di-tert butylperoxide (– –) and benzoyl peroxide (- - -)

**Table 1** Characteristics of network **4**

| | |
|---|---|
| $T_g$ | –[a] |
| Sol fraction (%) | <0.5 |
| Polymer decomposition temperature (°C) | 390 |
| Isothermal weight loss (% h$^{-1}$) | |
| ($N_2$ atmosphere) 250°C | 0.05 |
| 300°C | 0.1 |
| Modulus (MPa) | 2300 |
| Solvent resistance | Exceptional (~10% swell in chloroform, 60 h) |
| Fracture toughness, $K_{1,C}$ (N m$^{-3/2}$) | $0.32 \times 10^6$ |
| Dielectric constant | 2.9 |

[a] Not detectable by d.s.c.

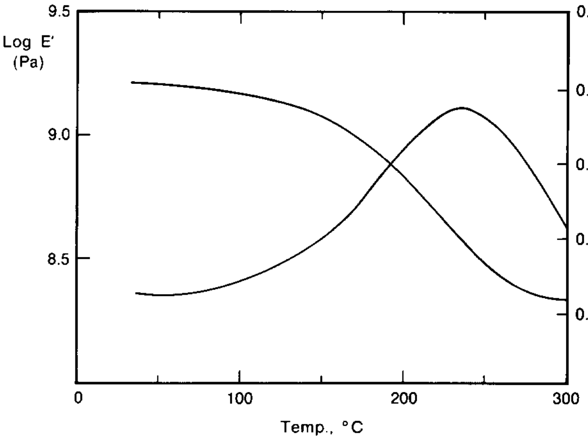


**Figure 2** Dynamic mechanical behaviour of network **4** cured isothermally at 250°C

The thermal stability, as determined by isothermal ageing and variable temperature scanning, was excellent with minimal weight loss upon isothermal ageing at 250 and 300°C and a decomposition temperature in excess of 390°C (*Table 1*). The mechanical properties, also shown in *Table 1*, were consistent with the highly crosslinked structure. The modulus was high, yet the toughness was extremely low as judged by fracture toughness measurements. For comparison, an epoxy network derived from diaminodiphenyl sulfone and diglycidylether of Bisphenol-A, has a $K_{1,C}$ fracture toughness value of $0.60 \times 10^6$ N m$^{-3/2}$, which is nearly twice that of the styrenic network. Finally, the dielectric properties were good with a value of 2.9 which was relatively insensitive to water uptake.

Although specimens for mechanical testing could be fabricated in a silicone mould from the monomer melt and subsequently cured, film processing by conventional methods (i.e. doctor blading, spin coating, etc.) was difficult. Film thickness was difficult to control, even though high solids compositions were possible, since the monomer was not of sufficient molecular weight to possess film forming properties. Furthermore, **3** tended to crystallize as the solvent evaporated. Attempts to 'B-stage' **3** to yield a viscous solution were unsuccessful since the monomer polymerizes via addition polymerization kinetics and gelation occurred early in the polymerization. Deposition of polymer films via a powder coating process appeared to be a viable alternative to solution processing. Powder deposition offers numerous advantages including solventless deposition, high efficiency deposition (compared to spin coating where ~95% of the polymer solution is lost), 100% solids composition for optimum global planarization and low melt viscosity for good local planarization. The requirements for a material to be deposited as a powder generally include brittle mechanical properties for powder formation, a melting or softening point substantially above room temperature for shelf-life, and polymerization temperature high enough to produce a processing window for planarization prior to vitrification or curing.

The styrenic resin appeared to satisfy many of the general requirements for powder deposition. The low molecular weight crystalline monomer could be milled readily into a fine powder (~10 μm particle size). The melting point of **3** is high enough above room temperature for shelf-life, yet provides a sufficient processing window for melt flow prior to the onset of network formation as demonstrated by the calorimetry measurements (*Figure 1*). An electrostatic powder coater was used to deposit **3** on silicon wafers containing 2 × 5 μm trenches designed to test for local planarization. The coated wafers were initially heated to 90°C to melt the resin and allow good flow prior to polymerization, and then ramped to 250°C to effect the network formation. An SEM micrograph of a cross-section of the coated wafer is shown in *Figure 3*. In the micrograph, a film of even thickness was observed with no evidence of the surface topography consistent with the high solids composition. In addition, the trenches were completely filled as a result of the low viscosity melt, characteristic of excellent local planarization.

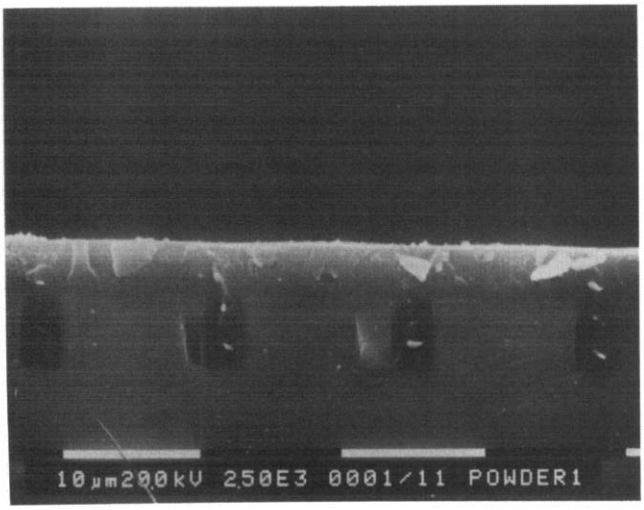


**Figure 3** SEM micrograph of silicon wafer containing 2 × 5 μm trenches with an overcoat of network **4**

The brittle mechanical properties of **4** were of concern. The strategy used to toughen the styrenic resin with minimal sacrifice of the modulus and dielectric properties was the incorporation of poly(perfluoroalkylene ether) (PFE). PFE is a tough ductile engineering thermoplastic with high elongation (50%) and modulus (1400 MPa), and shows many of the same characteristics as poly(aryl ether sulfone)[35]. In addition, since PFE has a low dielectric constant (~2.65), the modified styrenic resin should also have enhanced dielectric properties. Physical mixtures of PFE and the styrenic resins, **3**, resulted in large scale phase separation upon network formation and the modified network showed a reduction in properties. Therefore, reactive PFE oligomers were required to control the size scale of the phase separation.

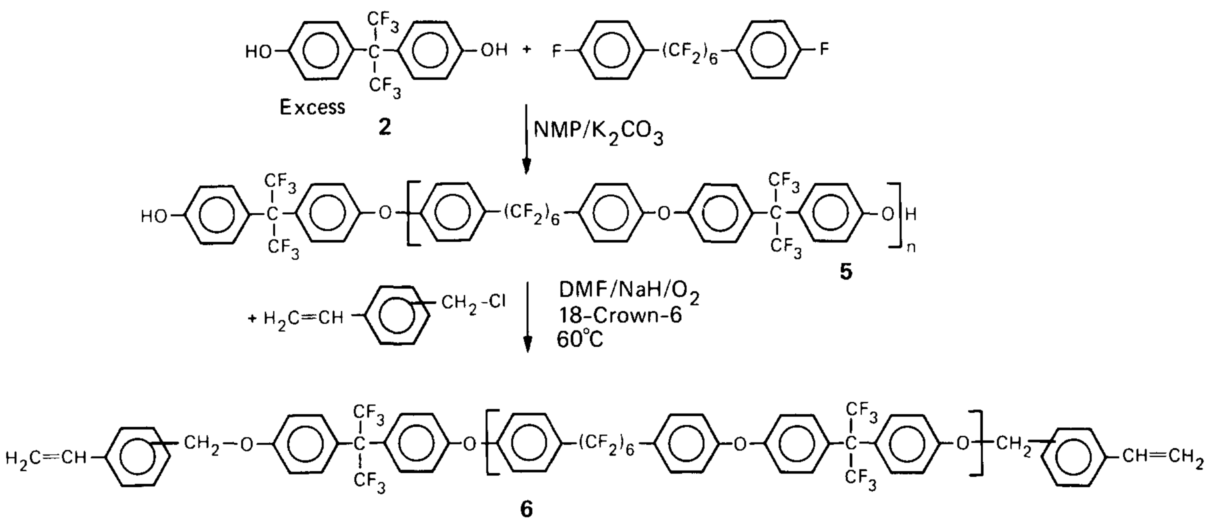
The preparation of vinyl end-capped oligomers was a two-step process which first involved the synthesis of phenolic hydroxyl terminated oligomers followed by end capping with vinylbenzyl chloride (*Scheme 2*). The phenolic hydroxyl terminated oligomers were prepared via a nucleophilic aromatic displacement polymerization of Bisphenol-AF with 1,6-bis(4-fluorophenyl)perfluorohexane according to a published procedure[35]. The perfluoroalkylene group has been demonstrated to be sufficiently electron withdrawing to activate the aryl halides towards displacement, analogous to a conventional activating group (e.g. sulfone) for the preparation of poly(aryl ether sulfone). An excess of Bisphenol-AF was used, according to the Carothers equation, to control both end-group functionality and oligomer molecular weight. The polymerization was carried out in NMP at 170°C in the presence of excess base to afford oligomers **5a–d**.

The characteristics of the phenolic hydroxyl PFE oligomers denoted **5a–d** are shown in *Table 2*. The number-average molecular weights, determined by end group analysis using $^1$H n.m.r., ranged from 2500 to 20 000 g mol$^{-1}$, and were in good agreement with the predicted values. However, it should be pointed out that the average degrees of polymerization are somewhat low since the fluorine in the polymer backbone contributed significantly to the molecular weight. The $T_g$s ranged from 50 to 90°C and increased with molecular weight.

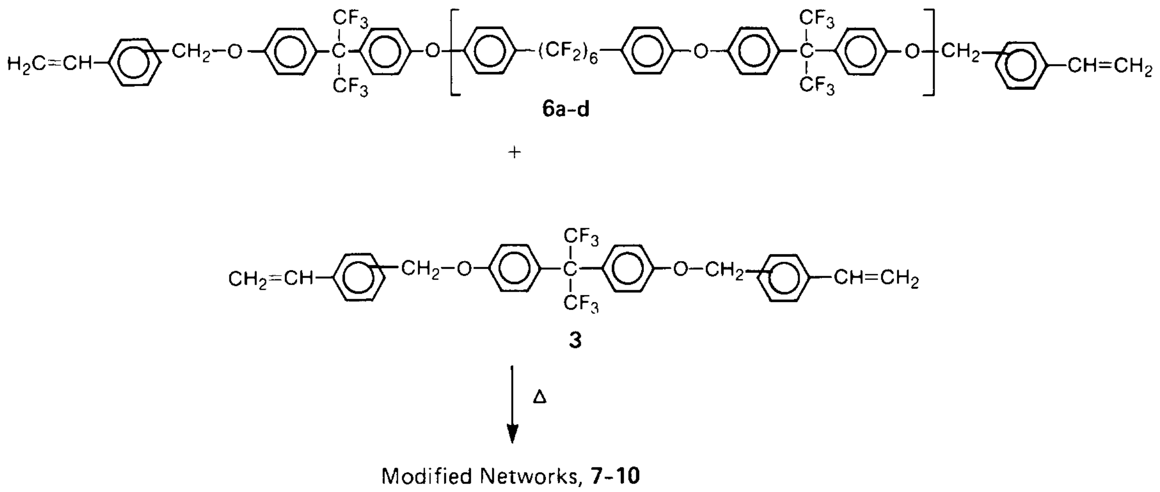
The vinyl end-capped monomers were readily prepared by reacting the phenolic hydroxyl oligomers with vinylbenzyl chloride (*Scheme 2*). The oligomers were dissolved in DMF and treated with sodium hydride to form the reactive bisphenoxide, filtered to remove excess sodium hydride, and added dropwise to vinylbenzyl chloride and 18-crown-6 at 60°C, to afford oligomers **6a–d**. The characteristics of the vinyl end-capped oligomers are also included in *Table 2*. The number-average molecular weights, determined by $^1$H n.m.r. end group analysis, ranged from 2650 to 19 100 g mol$^{-1}$.The molecular weight values of the vinyl end capped

**Table 2** Characteristics of perfluoroalkylene aryl ether oligomers

| Sample no. | Phenolic hydroxyl end-capped, $\langle M_n \rangle$ (g mol$^{-1}$) | Sample no. | Vinylbenzyl end-capped, $\langle M_n \rangle$ (g mol$^{-1}$) | $T_g$ (°C) |
|---|---|---|---|---|
| **5a** | 2500 | **6a** | 2650 | 58 |
| **5b** | 5000 | **6b** | 5100 | 70 |
| **5c** | 9800 | **6c** | 10 100 | – |
| **5d** | 20 000 | **6d** | 19 100 | 89 |



**Scheme 2**



**Scheme 3**

oligomers were close to the values of the parent oligomers, **5a–d**, indicating quantitative or near quantitative conversion of the phenolic hydroxyl to vinyl end groups.

One major consideration with the thermoplastic toughening of the styrenic resin is whether the appropriate morphology would be achieved for optimum mechanical property enhancement. During the cure of a thermosetting system, there are two phenomena of importance: gelation and vitrification. Gillham and co-workers have modelled these events using an isothermal TTT diagram, which has been extended to include the phase separation process in toughened systems[12,21,22]. The window for phase separation is fairly narrow and must occur early in the polymerization prior to gelation or in the liquid phase on a TTT diagram. The extent of phase separation is fixed once gelation begins. For the case of epoxy resins which follows typical condensation polymerization kinetics (i.e. the formation of dimers, trimers, etc.), sufficient time for the phase separation is achieved allowing the control of both the gel point and the resultant morphology. Conversely, the styrenic resin cures by radical or chain growth mechanisms and in such addition polymerizations, high molecular weight is achieved instantly and the conversion changes with time. Thus, gelation should occur early and the resultant morphology should be dictated by the kinetics rather than the thermodynamics[37].

Thermoplastic modification of the styrenic network **4** involved mixing the functional oligomers (**6a–d**) with **3** at compositions ranging from 10 to 30 wt% and heating to ~130°C (oxygen atmosphere) where **3** melted and served as a solvent for the oligomers (*Scheme 3*). This process usually took 3–10 min with the higher molecular weight oligomers and the higher compositions taking somewhat longer. The homogeneous solutions were then poured into a hot mould (250°C), sealed and cured (2.0 h). The resulting networks **7–10** were transparent with no evidence of large scale phase separation.

The characteristics of the thermoplastic modified networks and, for comparison, network **4** are shown in *Table 3*. The thermoplastic molecular weight varied from 2650 to 19 100 g mol$^{-1}$, denoted as networks **7–10**, and the thermoplastic composition ranged from 5 to 30 wt%, denoted as **a–d**. The thermal stability of the modified network, as judged by the polymer decomposition temperature, was comparable to that of the control **4**. The dielectric constants of several selected thermoplastic modified networks were measured and shown to be comparable or even somewhat lower than the unmodified network (*Table 3*). Therefore, both the

**Table 3** Thermal and electrical characteristics of thermoplastic modified networks

| Sample no. | PFE, $\langle M_n \rangle$ (g mol$^{-1}$) | Composition PFE (wt%) | Polym. decomp. temp. (°C) | Dielectric constant |
|---|---|---|---|---|
| **4** | – | – | 390 | 2.90 |
| **7a** | 2650 | 20 | – | – |
| **8a** | 5100 | 10 | – | 2.85 |
| **8b** | 5100 | 20 | 390 | 2.80 |
| **8c** | 5100 | 25 | – | – |
| **8d** | 5100 | 30 | 390 | – |
| **9a** | 10 100 | 10 | 385 | 2.86 |
| **9b** | 10 100 | 20 | 390 | – |
| **10a** | 19 100 | 10 | – | – |
| **10b** | 19 100 | 20 | 385 | – |

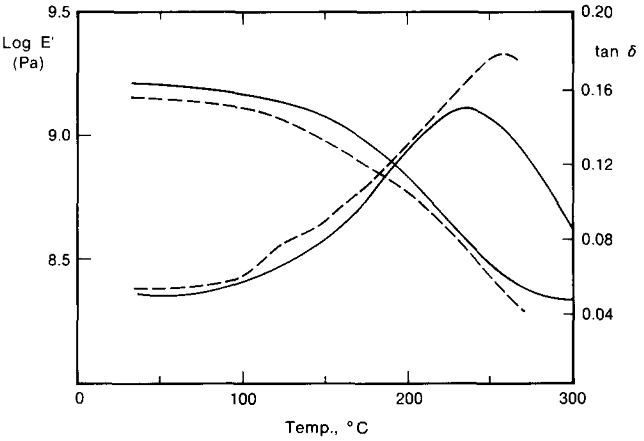


**Figure 4** Dynamic mechanical behaviour of network **4** (——) and modified network **8c** (– – –)

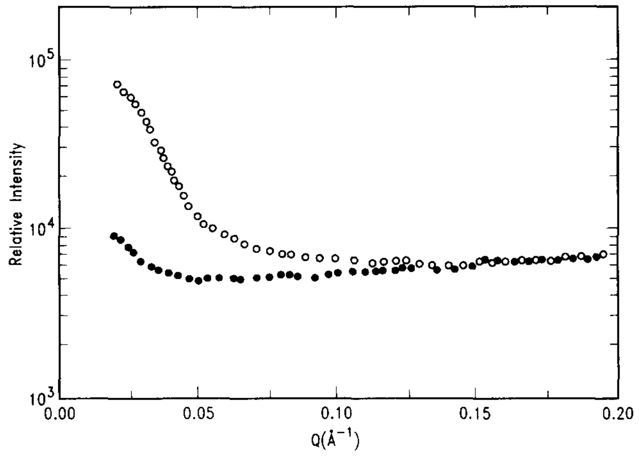


**Figure 5** SAXS of network **4** (●) and network **8b** (○)

thermal and dielectric properties were maintained with the incorporation of the PFE.

The dynamic mechanical behaviour for **4** and **8c** are shown in *Figure 4*. As previously mentioned, **4** shows a broad $T_g$ ranging from ~130 to 250°C with only a minimal drop in modulus. Likewise, network **8c** shows a similar transition corresponding to the network $T_g$ along with another transition at ~100°C which is believed to result from the PFE component or phase, indicative of a phase separated morphology. This transition is ~20 to 30°C higher than the parent oligomer, **6b**, and this shift may result from either phase mixing or from restriction of the chain ends. The latter is believed to be the most probable, due to the low degree of polymerization of the oligomer.

*Figure 5* shows the typical SAXS profiles for the fully cured styrenic network and the fully cured thermoplastically modified styrenic network (samples **4** and **8b**). The data are plotted as the log of the scattering intensity as a function of the scattering vector $Q$ [$Q=(4\pi/\lambda)\sin\theta$, where $\lambda=1.54$ Å and $2\theta$ is the scattering angle]. The scattering arising from the styrenic network is weak. However, the scattering from thermoplastically modified network shows more than an order of magnitude increase in intensity indicative of the phase separation that has occurred in the system.

For particles randomly dispersed in a matrix where the overall fraction of the particles is low and interparticle interferences are negligible, then the size of the particle can be estimated by use of Guiniers law where:

$$I(Q)=I(0)\mathrm{e}^{-Q^2R^2/3} \tag{3}$$

where $I(Q)$ is the intensity scattered at a scattering vector $Q$ from particles having a $z$-averaged radius of gyration $R_g$. $I(0)$ is the intensity at $Q=0$ and, if absolute units were used, would be related to the mass of the object. If it is assumed that the particles are spherical with a radius $R_s$, then:

$$R_s=\sqrt{\tfrac{5}{3}}R_g \tag{4}$$

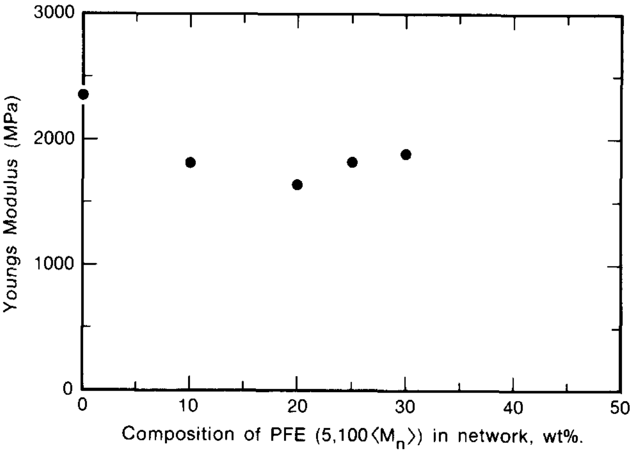


**Figure 6** Modulus *versus* wt% of PFE modifier, **6b**, in the networks (**8a–d**)

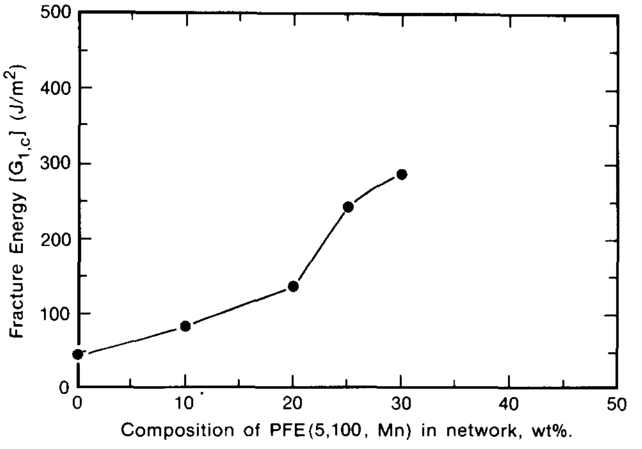


**Figure 7** Fracture energy, $G_{1C}$, *versus* molecular weight of PFE modifiers (**6a–d**) as a function of molecular weight at 20 wt% modifier (samples **7a**, **8b**, **9b** and **10b**)

The data in *Figure 5* were analysed to extract an $R_g$ of 80 Å which translates into the radius of a corresponding sphere of 103 Å. Similar analyses on the other data sets yielded basically the same result. Thus, the SAXS data suggest that the dispersed particles have a size of ~ 100 Å.

The phase separation in these systems was controlled by the competing effects of thermodynamics, kinetics and polymerization rate. Thermodynamics predicts phase separation with molecular weight build up or network formation. However, kinetic factors limit the equilibrium thermodynamic morphology due to insufficient time for diffusion. For thermosetting systems, further complications exist since both molecular weight and viscosity increase with conversion. Once the development of the network reaches the gelation stage, the phase separation process is over and the morphology fixed. In the case of the styrenic resin where high molecular weight or gelation is achieved early in the polymerization, the resultant morphology is kinetically controlled limiting the size of the domains[21,22]. It is important to note that the size scale of the phase-separated thermoplastic is substantially smaller than those of epoxy-based systems. However, it is interesting that the domain size is nearly the same as those of the polysulfone modified epoxy systems which form a co-continuous phase resulting from spinodal decomposition[34]. More importantly, those materials which form a co-continuous morphology show the highest fracture toughness values.

*Table 4* contains the mechanical properties of the thermoplastic modified networks. The molecular weights of the oligomers ranged from 2650 to 19 100 g mol$^{-1}$ (**5a**–**d**) yielding networks **7**–**10**, with PFE compositions as high as 30 wt% and for comparison the properties of network **4** are also shown. The modulus values for the modified network are lower than that of the neat resin; however, this drop is small in comparison to a rubber toughened system (*Figure 6* and *Table 4*). These data are consistent with other reports of thermoplastic toughened networks[31,32].

The fracture energy, $G_{1,C}$, values improved substantially with the incorporation of the PFE modifier. The improvement was greater with the higher PFE block lengths as graphically represented in *Figure 7*. Interestingly, the highest molecular weight oligomer **5d** is well above the entanglement molecular weight and, consequently, has good film forming characteristics, whereas the remaining oligomers (**5a**–**c**) are near their entanglement molecular weight. A similar effect on the toughness of the network by the molecular weight of the modifier was also observed in the polysulfone modified epoxy networks[30–32]. Furthermore, as expected, by increasing the fraction of the modifier from 10 to 30 wt% the fracture toughness increased as shown in *Table 4* and *Figure 8*. However, unlike other thermoplastic toughened systems, this improvement was modest since the morphology was essentially identical for all the samples (i.e. the network

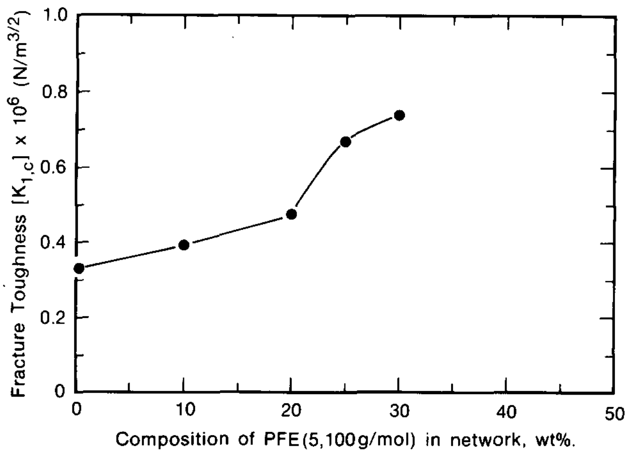


**Figure 8** Fracture toughness, $K_{1,C}$, *versus* wt% of PFE modifier (samples **8a**–**d**)

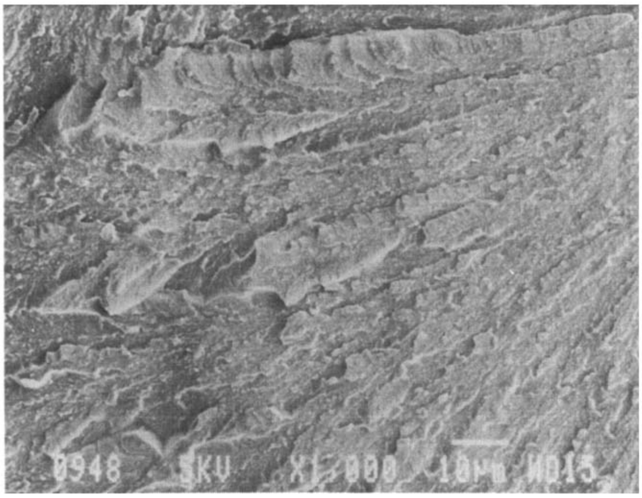


**Figure 9** SEM micrograph of the fracture surface of sample **10b**

**Table 4** Mechanical properties of thermoplastic modified networks

| Sample no. | PFE, $\langle M_n \rangle$ (g mol$^{-1}$) | PFE composition (wt%) | Modulus (MPa) | $K_{1,C}$ (× 10$^6$)(N m$^{-3/2}$) | $G_{1,C}$ (J m$^{-2}$) |
|---|---|---|---|---|---|
| **4**(Control) | – | – | 2.36 | 0.33 | 46.60 |
| **7a** | 2650 | 20 | 1.89 | 0.54 | 154.24 |
| **8a** | 5100 | 10 | 1.82 | 0.39 | 85.77 |
| **8b** | 5100 | 20 | 1.65 | 0.47 | 138.39 |
| **8c** | 5100 | 25 | 1.83 | 0.67 | 135.56 |
| **8d** | 5100 | 30 | 1.89 | 0.74 | 288.81 |
| **9a** | 10 100 | 10 | 1.88 | 0.41 | 89.41 |
| **9b** | 10 100 | 20 | 1.80 | 0.52 | 150.22 |
| **10a** | 19 100 | 10 | 1.80 | 0.55 | 168.05 |
| **10b** | 19 100 | 20 | 1.80 | 0.85 | 401.38 |

was always the continuous phase). It is noteworthy to point out that the improved fracture energy for this system is also small in comparison to that observed for most other rubber-toughened materials[18,23,24]. It is important to note, however, since the fracture energy is normalized by the modulus of the composite material, these values will always tend to be high for a rubber modified network due to the substantial drop in modulus.

The mechanism of toughening in these PFE modified styrenic networks is difficult to ascertain due to the small size of the domains. *Figure 9* is an SEM micrograph of the fracture surface of a typical test specimen which shows river deformation patterns associated with the generation of new surfaces, and local deformation processes. Conversely, the fracture surface of a rubber toughened network consists of holes ($\sim 5\,\mu$m) and the most accepted toughening mechanism incorporates the basic deformation processes and their interactions[23,24]. The first involves a dilatation or void formation at the particle or its interface produced by triaxial stress ahead of the crack tip along with the stresses at the particles. The second involves initiation of local shear deformations at the equator of the particles where the stresses are the greatest. This latter process is primarily responsible for the toughening of the resin networks. The fracture surface of a polysulfone modified epoxy network shows discrete composite particles of polysulfone in the epoxy matrix ($\sim 0.1\,\mu$m in size) and the toughening mechanism is believed to be two-fold. First, the sulfone having a different modulus served as a stress concentrator, initiating local plastic deformation in the epoxy in the vicinity of the particle[30–32]. This, however, was modest in comparison to a rubber particle since the modulus mismatch was not as great. Second, the polysulfone particles plastically deformed, and the toughness of the modified network improved with sulfone molecular weight. For each of these the discrete phase was of sufficient size to microscopically probe the area between the particles and to investigate the toughening mechanisms. The techniques available to investigate the deformation processes in the region between the PFE domains in the styrenic network were limited. It is believed that the discrete domains serve as sites of stress concentrations and, due to the small size and frequency of domains, the resulting stress fields couple, thereby magnifying the local stress. This, in turn, serves to initiate a local plastic deformation, the only deformation process available to such a highly crosslinked material, in the material between the domains[18]. Furthermore, due to the strong molecular weight dependence of the PFE block on the $K_{1,c}$ values, the deformation of the ductile PFE phase most likely contributes to the improved toughness also.

## CONCLUSIONS

A new thermosetting monomer, 2,2-bis(4-vinylbenzyloxyphenyl)hexafluoropropane, was prepared and the network chemistry, thermal and mechanical properties investigated. It was shown that the toughness could be enhanced by the incorporation of a tough engineering thermoplastic. Specifically, vinylbenzyl end-capped aryl ether perfluoroalkylene oligomers of various molecular weights were prepared and used to modify the thermosetting monomer. The resulting networks showed a two-phase morphology with domain sizes between 80 Å and 100 Å and significant enhancements in fracture toughness. The toughness was achieved without sacrificing the modulus, dielectric properties and thermal stability of the parent network.

## REFERENCES

1 Tummala, R. R. and Rymaszewski, E. J. 'Microelectronics Packaging Handbook', Van Nostrand Reinhold, New York, 1989, Ch. 1
2 Brown, H. R., Yang, A. C., Russell, T. P., Volksen, W. and Kramer, E. J. *Polymer* 1988, **29**, 1807
3 Sroog, C. E. *J. Polym. Sci., Macromol. Rev.* 1976, **11**, 161
4 Lyle, G. D., Senger, J. S., Chen, D. H., Kilic, S., Wu, S. D., Mohanty, D. K. and McGrath, J. E. *Polymer* 1989, **30**, 978
5 Cizmeciogln, M. and Gupta, A. *SAMPE Quart.* 1982, **13** (3), 16
6 Delano, C. and Harrison, E. *SAMPE* 1975, **20**, 243
7 Mallet, M. and Darmory, F. *Org. Coat. Plast. Prepr.* 1974, **34**, 173
8 Serafini, T. T., Delvigs, P. and Lightsey, G. R. *J. Appl. Polym. Sci.* 1972, **16**, 905
9 Zupanccic, J. J., Zweig, A. M., Conrad, J. P. and Dinkel, E. A. *Polym. Mater. Sci. Eng.* 1989, **60**, 610
10 Hahn, S. F., Townsend, P. H., Burdeaux, D. C. and Gilpen, J. A. *Polym. Mater. Sci. Eng. Proc.* 1989, **59**, 190
11 Crivello, J. V., Lee, J. L. and Conlon, D. A. *J. Radiat. Cur.* 1983, **10**, 6
12 Gillham, J. K. *Soc. Plas. Eng., Proc. Ann. Tech. Conf.* 1980, **38**, 268
13 Noshay, A., Matzner, M., Barth, B. P. and Walton, R. K. *Adv. Chem. Ser.* 1976, **154**, 302
14 Webster, D. C., Hedrick, J. L. and McGrath, J. E. *SAMPE Proc.* Reno, Nevada, 1984
15 Bucknall, C. B. 'Toughened Plastics', Applied Science, London, 1977
16 Campbell, J. R. *et al. US Pat. Appl. 528 189*, 1983
17 Lee, H. and Neville, K. 'Handbook of Epoxy Resins', McGraw Hill, New York, 1967
18 Kinloch, A. J. and Young, R. J. 'Fracture Behavior of Polymers', Applied Science, New York, 1983
19 Riew, C. K. and Gillham, J. K. *Adv. Chem. Ser.* 1983, **208**
20 Bauer, R. S. *Am. Chem. Soc. Symp. Ser.* 1983, **22**
21 Manzione, L. T., Gillham, J. K. and McPherson, C. A. *J. Appl. Polym. Sci.* 1981, **26**, 889
22 Manzione, L. T., Gillham, J. K. and McPherson, C. A. *J. Appl. Polym. Sci.* 1981, **26**, 907
23 Kinloch, A. J., Shaw, S. J., Tod, D. A. and Hunston, D. L. *Polymer* 1983, **24**, 1341
24 Kinloch, A. J., Shaw, S. J. and Hunston, D. L. *Polymer* 1983, **24**, 1355
25 Bucknall, C. B. and Yoshi, T. *Br. Polym. J.* 1978, **10**, 53
26 Pearson, R. A. and Yee, A. F. *Polym. Mater. Sci. Eng.* 1983, **49**, 316
27 Bitner, J. R., Rushford, J. L., Rose, W. S., Hunston, D. L. and Riew, C. K. *J. Adhesion* 1982, **13**, 3
28 Kunz-Douglass, S., Beaumont, P. W. R. and Ashby, M. F. *J. Mater. Sci.* 1980, **5**, 1109
29 Kunz, S. C., Sayre, J. A. and Assink, R. A. *Polymer* 1982, **23**, 897
30 Hedrick, J. L., Yilgor, I., Hedrick, J. C., Wilkes, G. L. and McGrath, J. E. 30th National SAMPE Symposium, March 1985
31 Hedrick, J. L., Jurek, M. J., Yilgor, I. and McGrath, J. E. *Polym. Prepr.* 1985, **26** (2), 293
32 Hedrick, J. L., Mohanty, D. K., Johnson, B. C., Viswanathan, R., Hinkley, J. A. and McGrath, J. E. *J. Polym. Sci., Polym. Chem. Edn* 1986, **23**, 287
33 Kim, S. C. and Brown, H. R. *J. Mater. Sci.* 1989, **22**, 2589
34 Yamanaka, K. and Inoue, T. *Polymer* 1989, **30**, 662
35 Labadie, J. W. and Hedrick, J. L. *Macromolecules* 1991, **23**, 5371
36 Dusek, K. in 'Developments in Polymerization-3' (Ed. R. N. Haward), Applied Science, London, 1982, Ch. 4