# Curing Reaction and Product Properties of Polysulfones Terminated with Active Functional Groups

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## SYNOPSIS

The curing processes of maleimide-terminated polyether sulfone oligomers ($M_n$ from 1100 to 3000) and ethynyl-terminated polysulfone prepolymers ($M_n$ from 2600 to 12000) were investigated by means of DSC. The initial temperature of cure reaction is increased, and the apparent activation energy $E_a$ of cure reaction is decreased as the $M_n$ of the uncured prepolymer increases. On the basis of the $T_g$ changes during the curing process, the kinetics of cure is proposed to be similar to a stepwise reaction, although the curing reaction is believed to proceed via a free radical chain mechanism. In this proposed reaction some initial reaction products with many branches and one remaining active functional group are formed first. The more these products occur, the more likely they can interreact to form a network. During the curing process the mobility of the active end group is restricted by the rigid polysulfone chain. Therefore, the reaction is mainly controlled by the movement of polymer, i.e., by the kinetics of diffusion. Films of these cured polymers were made by casting from solution. Their $\beta$ relaxation peaks at low temperatures were examined by dielectric and dynamic mechanical measurements. The films made of the prepolymer with $M_n > 3000$ are flexible and foldable.

## INTRODUCTION

Bismaleimides (BMI), though not a new class of materials, show generally higher cured glass transition temperatures and less environmental sensitivity than state-of-the-art epoxies. They suffer, however, from brittleness due to their high crosslink density. Various attempts have been made to improve the impact and fracture toughness of BMI materials. One possible modification involves the introduction of long chains in the backbone of BMI to reduce crosslink density. If these chains are too flexible, however, they tend to decrease the $T_g$ of the network. On the other hand, polysulfones or polyether sulfones[1] and polyether–ether ketone, etc.[2] are excellent engineering thermoplastics. They have higher $T_g$'s and are mechanically stronger than commodity thermoplastics. They also have improved solvent resistance and better high-temperature dimensional stability as required in aerospace applications. Therefore, there is merit in the idea of synthesizing bismaleimide-terminated polysulfone (or other polyaryl ether) oligomers containing suitable long chains for providing product toughness and having terminal functional groups by which the polymer can be crosslinked and/or chain extended. Once cured, these materials may have better toughness, better mechanical properties, but still possess high $T_g$ and good resistance to creep at high temperatures. To this end many oligomers have been prepared.[3-5] Besides maleimide, the terminal functional group can also be ethynyl,[6] allyl,[7] cyanato, etc.

It is also essential to develop resin systems that combine ease of processing with desirable physical properties. Thus, knowledge of the relationship between the reactivity of the functional group, the oligomer molecular weight, and the changes in the physical properties during curing process becomes very critical.

In this work the curing reactions of two kinds of polysulfone oligomers are described. One is maleimide-terminated polyethersulfone (MTPES); an-
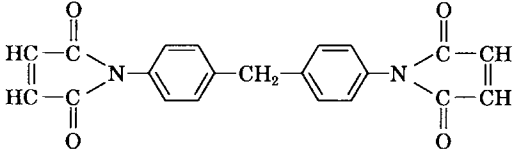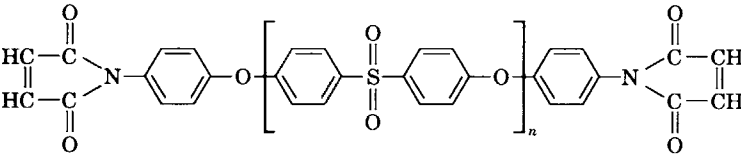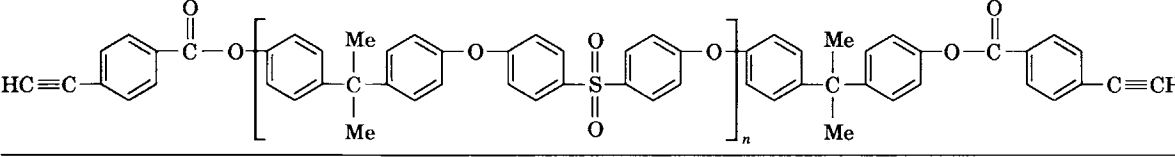
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other is ethynyl-terminated polysulfone (ETPS). Each type of oligomer was synthesized with several different molecular weights. Thermal characterization of these materials was achieved by using DSC, and the activation energies for the curing reactions were determined. The molecular mobilities of the cured products are investigated by dielectric and dynamic mechanical measurements. The effect of structure on the properties is discussed.

## EXPERIMENTAL

Two kinds of polyaryl sulfone oligomers or prepolymers with terminal functional groups used in this work are listed in Table I. The ethynyl-terminated polysulfones were obtained from Hergenrother of the NASA-Langley Research Center.

Their syntheses and characterization were reported by Hergenrother.[8,9] The maleimide-terminated poly(oxy-1,4-phenylene sulfonyl-1,4-phenylene) oligomers (MTPES) were prepared in our laboratory. The synthetic approach and structural characterization are described in detail in a separate paper.[10] Matrimid 5292 part A (BMI resin from CIBA-GEIGY) was also examined to compare its curing mechanism with that of the MTPES system. All of these prepolymers and oligomers are in the powder form at room temperature. It is not easy to consolidate well and form a transparent sample from these powders by compression molding, but good films can be obtained by solution casting. Thus, MTPES and ETPS were dissolved in dimethylacetamide (DMAc) and the solutions were centrifuged and subsequently cast onto plate glass. The wet films were dried in stages: 50°C for 4 h and 120,

**Table I  Chemical Structure and Molecular Weight of Resins**



| BMI-5292 (A) | | $M_n = 358$ |
| --- | --- | --- |



| No. | $n$ | $M_n$ |
| --- | --- | --- |
| MTPES-2 | 2.8 | 1010 |
| MTPES-6 | 4.5 | 1400 |
| MTPES-8 | 6.8 | 1900 |
| MTPES-9 | 9 | 2500 |
| MTPES-12 | 12 | 3000 |



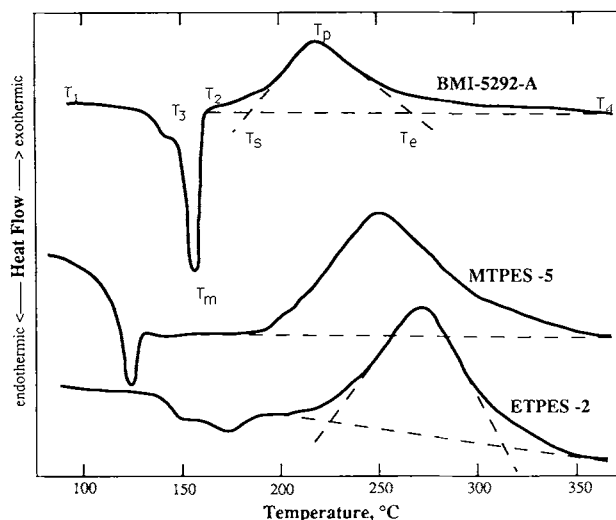| No. | $n$ | $M_n$ |
| --- | --- | --- |
| ETPS-2 | 4.8 | 2600 |
| ETPS-5 | 11 | 5360 |
| ETPS-9 | 19 | 8890 |
| ETPS-12 | 26 | 12000 |

**Figure 1** DSC traces for several oligomers.

150, 170, and 210°C for 1 h each to remove solvent. Then it was cured at 250°C for 4 h. Finally, MTPES needed postcuring at 280°C (or higher temperatures) for 1 h in nitrogen. The film was removed from the glass with boiling water. Attempts to make a cured film from the lowest molecular weight MTPES oligomers often failed because they were very brittle and always broke when cooling from the curing temperature. However, a film could be made successfully on aluminum foil for dielectric loss measurements.

A differential scanning calorimeter (Perkin-Elmer Series 7 DSC) was used for investigating the cure reactions of these oligomers and characterizing their $T_g$'s. The dynamic mechanical spectra (DMS) of crosslinked polymer films (about $45 \times 5 \times 0.05$ mm) were determined using a dynamic viscoelas-

tomer at four frequencies (1, 3.3, 11, and 90 Hz) and approximately 1°C/min heating rate. The viscoelastometer consisted of solid-state transducer conditioners, a digital oscilloscope for capturing the signals, and a computer employing correlation analysis for determining the dynamic moduli and phase angle. The dielectric loss of the cured films was measured as a function of temperature using an automatic dielectric measurement system from General Radio at frequencies of 0.234, 1, 2.5, 6, and 20 kHz.

## RESULTS AND DISCUSSION

### Cure Reaction

The structure and molecular weight of difunctional polysulfones are given in Table I. A highly crosslinked network structure was obtained by heating these oligomers at 200–300°C. The curing reaction is believed to proceed via a free radical mechanism. Thermal scans of these oligomers were performed by using differential scanning calorimetry in nitrogen atmosphere. Some of the DSC traces are summarized in Figure 1. Before 200°C a sharp endothermic peak associated with melting of the oligomer was observed only in BMI-5292A and MTPES-5. For other samples only a broad endothermic peak or a shift of the trace in the endothermic direction was observed. These are probably associated with the softening or glass transition of the uncured oligomer. This transition occurs over a wide range of temperatures and shifts toward high temperatures with increasing oligomer molecular weight, as expected. The crosslinking reaction is responsible for the exothermic peak above 200°C. However, defining

**Table II    Results of DSC Analysis$^a$ of Various Resins**

| | Melt or Soften | | | Cure Reaction | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Resin | $T_1$ (°C) | $T_m$ (°C) | $T_2$ (°C) | $T_3$ (°C) | $T_s$ (°C) | $T_p$ (°C) | $T_e$ (°C) | $T_4$ (°C) | $H$ (J/g | kJ/mol) |
| BMI-5292A | 120 | 156 | 165 | 150 | 175 | 214 | 257 | 390 | 295 | 105 |
| MTPES-5 | 110 | 122 | 125 | 167 | 201 | 248 | 328 | 360 | 91 | 92 |
| MTPES-6 | 117 | 159 | 187 | 190 | 204 | 251 | 311 | 318 | 72 | 100 |
| MTPES-12 | 111 | 166 | 189 | 205 | 211 | 270 | 344 | 350 | 29 | 87 |
| ETPS-2 | 120 | 157 | 180 | 184 | 226 | 273 | 317 | 360 | 97 | 251 |
| ETPS-9 | 160 | 180 | 220 | 220 | | 256 | | 340 | 32 | 288 |
| ETPS-12 | 169 | | 180 | 231 | 252 | 297 | | 360 | 17 | 204 |

$^a$ Heating rate: 20°C/min.
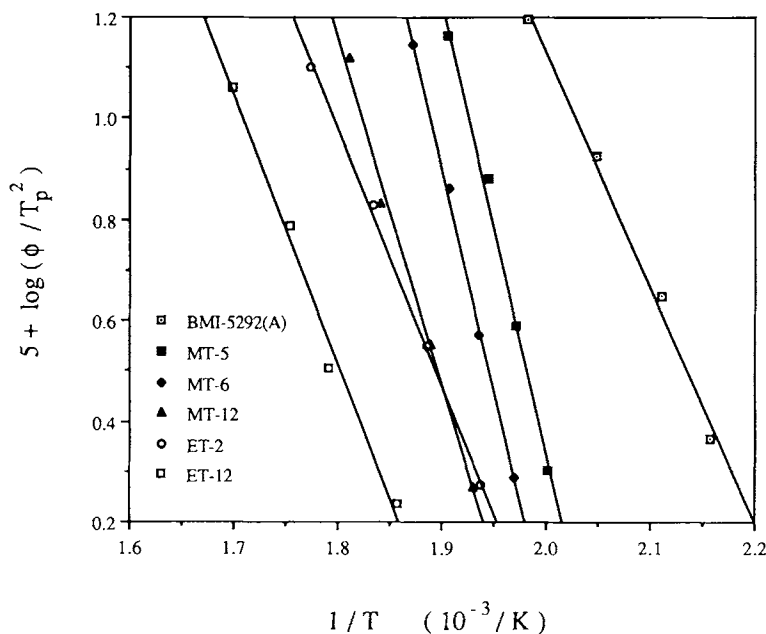
**Figure 2** Arrhenius plots of the cure reactions.

the $T_g$ of uncured prepolymers and the baseline of the exothermic peak created some difficulty in some samples where the end of the fusion endotherm and the beginning of the curing exotherm were not clearly distinguishable. The onset and ending temperature $T_s$ and $T_e$ were obtained by extrapolating the low- and high-temperature sides of the exothermic peak to the base line. $T_s$ and $T_e$ were designated as starting and ending temperatures for the curing reactions although in fact the curing reaction initiated at $T_3$ and continued until $T_4$ (see Fig. 1). Thermodynamic quantities such as the heat of reaction $\Delta H$, exothermic peak temperature $T_p$ and $T_s$, $T_e$ were measured and the results are shown in Table II. It is obvious that $T_s$ and $T_p$ increase with the

molecular weight of the uncured prepolymers, as expected. Considering the difficulty of quantifying the DSC data, the heats of polymerization of each functional prepolymer with different $M_n$'s are reasonably similar. However, it should be noted that the molecular heats of polymerization of the ethynyl-terminated oligomers are higher than those of BMI.

## Kinetics of the Cure Reaction

The following studies were undertaken further to analyze the effect of molecular weight on the kinetics of polymerization. The rate of polymerization can be described by $-(dX/dt)$, thus

$$-\frac{dX}{dt} = k_T(1 - X)^n \qquad (1)$$

where $X$ is fractional conversion (dimensionless), $k_T$ is specific rate constant at temperature $T$, and $n$ is reaction order. In the case where both the temperature and time are variables, the rate of reaction is given as follows:

$$-\frac{dX}{dt} = \left(\frac{\partial X}{\partial t}\right)_T + \left(\frac{\partial X}{\partial T}\right)_t \frac{dT}{dt} \qquad (2)$$

At the exothermic peak the term $\partial X/\partial T$ is equal to zero, and the heating rate is $\phi$. When temperature effects are taken into account, Eq. (2) becomes

**Table III  Peak Temperatures (°C) of Exothermal Reaction for Various Resins**

| Resin | Heating Rate (°C/min) | | | | $E_a$ (kJ/mol) |
|---|---|---|---|---|---|
| | 5 | 10 | 20 | 40 | |
| BMI-5292A | 190.5 | 200.7 | 215.4 | 231.4 | 89.4 |
| MTPES-5 | 226.4 | 234.0 | 241.0 | 252.0 | 171.5 |
| MTPES-6 | 234.5 | 243.8 | 251.0 | 261.5 | 168.1 |
| MTPES-12 | 244.8 | 256.0 | 270.1 | 279.2 | 130.7 |
| ETPS-2 | 243.2 | 257.2 | 272.5 | 290.7 | 97.3 |
| ETPS-12 | 265.4 | 285.3 | 297.2 | 316.0 | 101.7 |

$$\frac{dX}{dt} = A(1 - X)^n \exp\left(-\frac{E_a}{RT}\right) \qquad (3)$$

where $E_a$ is the apparent activation energy of the cure reaction. If the equation is differentiated again with time, we obtain

$$\frac{d(dX/dt)}{dt}$$

$$= \frac{dX}{dt}\left\{\frac{E_a\phi}{RT^2} - An(1 - X)^{n-1}\exp\left(-\frac{E_a}{RT}\right)\right\} \qquad (4)$$

At $T_p$ the maximum of reaction rate is reached, where $d(dX/dt)/dt = 0$. Thus,

$$\frac{E_a\phi}{RT_p^2} = An(1 - X)_p^{n-1}\exp\left(-\frac{E_a}{RT_p}\right) \qquad (5)$$

However, the value of $n(1 - X)_p^{n-1}$ is almost constant in spite of the changing heating rate,[11] so

$$\frac{d[\ln(\phi/T_p^2)]}{d(1/T)} = -\frac{E_a}{R} \qquad (6)$$

The apparent active energy, $E_a$, can then be calculated[12] from the slope of the straight line when plotting $\log(\phi/T_p^2)$ vs. $1/T$.

The exothermic peaks of various resins shifted toward high temperatures when elevating the heating rate from 5°C/min to 40°C/min. The Arrhenius plots are shown in Figure 2, and the data are summarized in Table III.

Varma and co-workers[13] investigated the effect of structure on cure reactions for six bismaleimide resins and proposed that the presence of an electron withdrawing group in the backbone of the bisimide increased the curing temperature and reduced the reactivity of the maleimide bond. We found that the $E_a$ of ETPES-5, -6, and -12 are higher than that of BMI-5292A. This is consistent with the thesis of Varma et al. because sulfone is a strong electron withdrawing group.

**Table IV  Elevation of Glass Transition Temperature of Resins in Curing Process[a]**

| Resins | $T_{max}$ (°C) | Partial Exotherm Area (J/g) | Converted (%) | $T_g$ (°C) |
|---|---|---|---|---|
| BMI-5292 | 214.9 | 106.0 | 35 | 116 |
| | 250 | 208.3 | 70 | 127.5 |
| | 390 | 295.7 | 100 | > 290 |
| MTPES-5 | 183 | 0.038 | 0.04 | 115 |
| | 204.8 | 2.07 | 2.3 | 115 |
| | 224.8 | 14.17 | 15.5 | 121 |
| | 255.3 | 42.05 | 46 | 139 |
| | 284.7 | 69.01 | 75 | 163 |
| | 300.8 | 77.95 | 85.3 | 177 |
| | 317.7 | 84.48 | 92.4 | 189 |
| | 335.8 | 89.03 | 97.4 | 215 |
| | 360 | 91.41 | 100 | 254 |
| MTPES-6 | 180 | 0 | 0 | 161 |
| | 230 | 11.21 | 15.6 | 167.6 |
| | 240 | 18.35 | 25.6 | 177.5 |
| | 250 | 26.96 | 37.6 | 184.6 |
| | 260 | 36.08 | 50.3 | 195 |
| | 280 | 54.158 | 75.6 | 219.4 |
| | 360 | 71.63 | 100 | 229.9 |
| MTPES-12 | 200 | 0 | 0 | 198 |
| | 225 | 0.80 | 2.8 | 200 |
| | 250 | 6.19 | 21.3 | 208 |
| | 271 | 13.32 | 45.9 | 218 |
| | 300 | 22.247 | 76.7 | 225 |
| | 325 | 27.55 | 94.9 | 226 |
| | 350 | 29.00 | 100 | 227 |

[a] Heating rate: 20°C/min.
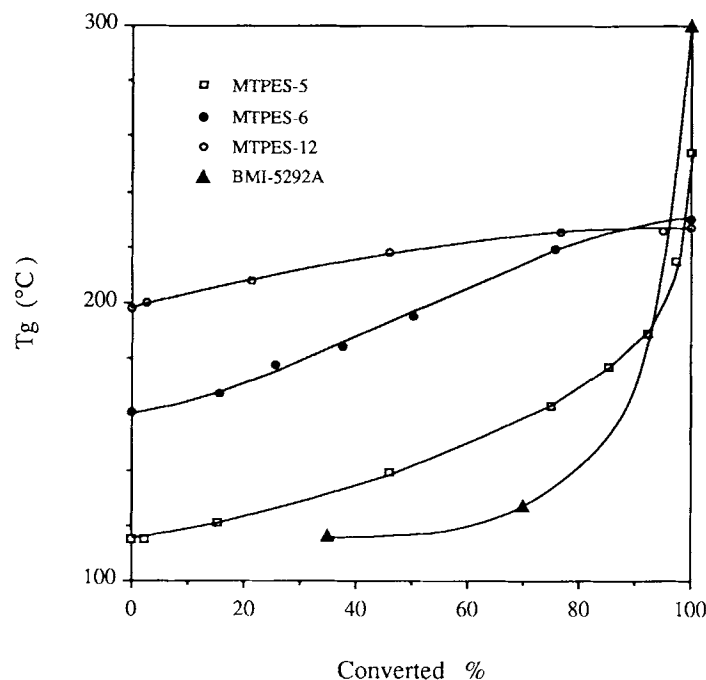
**Figure 3**  $T_g$ elevation during the curing process of various resins.

It is interesting to note that for the same backbone structure, $E_a$ decreases as the backbone chain length increases. $E_a$ decreases to a stable value if the prepolymeric chain is long enough. This is evidenced by the fact that both $E_a$'s of ETPS-2 and -12 are almost the same even though their molecular weights are quite different but are both greater than 2000.

The resin curing process is very complicated. The activity of the functional group, which is located at the end of the polymer chain, is influenced by the nearest neighbor unit, and the mobility of this group is restricted by the connected segments, perhaps even the entire prepolymer chain. A phenomenon that often occurred in the curing process was that the curing reaction stopped at a certain degree even though there were still very many active functional groups in the system. The reason for the inability to complete the reaction is that the bulk viscosity becomes so high with the increase in crosslink density that the mobility of functional groups is frozen. The kinetic action is usually the main factor controlling the curing process.

In our systems the cure reaction must await the

**Table V  Physical Properties of Various Resins**

| Oligomer or Prepolymer | $M_n$ (uncured) | $T_g$ (°C) | Physical Properties (cured) | | | | Film |
| | | | $E'$ (GPa) | | | | |
| | | | 25°C | 100°C | 150°C | 200°C | |
|---|---|---|---|---|---|---|---|
| MTPES-6 | 1400 | 277 | 2.6 | 2.5 | | 2.3 | Clear, brittle |
| MTPES-8 | 1900 | 272 | 2.5 | 2.4 | | 2.2 | Clear, brittle |
| MTPES-9 | 2400 | 253 | 2.3 | 2.2 | | 2.0 | Clear, brittle |
| MTPES-12 | > 3000 | 253 | 2.05 | 2.0 | | 1.9 | Clear, foldable |
| ETPS-2 | 2600 | 224 | 1.95 | 1.9 | 1.85 | | Clear, foldable |
| ETPS-5 | 5360 | 215 | 1.72 | 1.67 | 1.62 | | Clear, foldable |
| ETPS-9 | 8900 | 212 | 1.6 | 1.5 | 1.45 | | Clear, foldable |
| ETPS-12 | 12000 | 211 | 1.6 | 1.5 | 1.45 | | Clear, foldable |
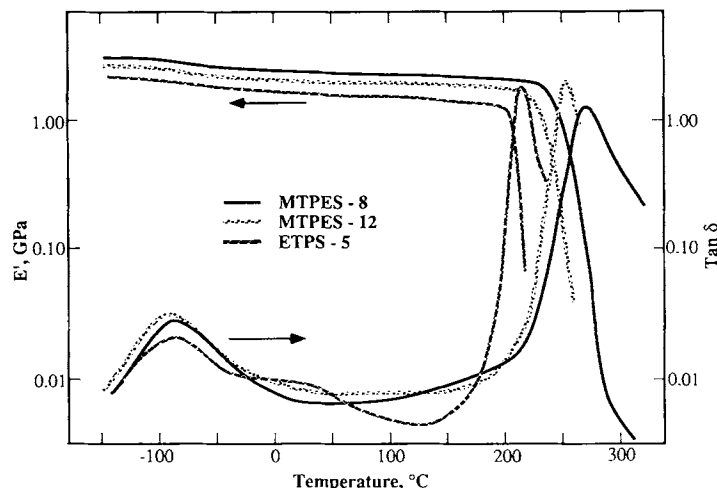
**Figure 4** Dynamic mechanical spectra of several cured films.

onset of mobility of the chains at temperatures higher than their respective $T_g$'s. Therefore, $T_s$, $T_p$, and $T_e$ increase as the oligomer or prepolymer molecular weight increases. However, the measured activation energy is lower as the uncured prepolymer molecular weight becomes higher. The reduction in $E_a$ is due to the fact that the movement of functional groups located at the ends of longer polymer chains is less restricted to react further than others with lower molecular weights. These relationships will become more distinct upon further examination of the change of the $T_g$ of the system during the cure process.

## Behavior of Crosslinking Polymerization

The change of the $T_g$'s of the resin during curing was examined by means of DSC to help understand the crosslinking behavior. The exothermal trace was divided into several parts and the degree of conversion of each part can be calculated from the ratio of the exothermic area to that of the entire peak. The resin was cured in a sample pan by first scanning at 20°C/min until the temperature reached $T_{max}$, and quenched to 80°C (at 200°C/min) and then the $T_g$ was determined immediately by a second scan. The results are summarized in Table IV. The curves
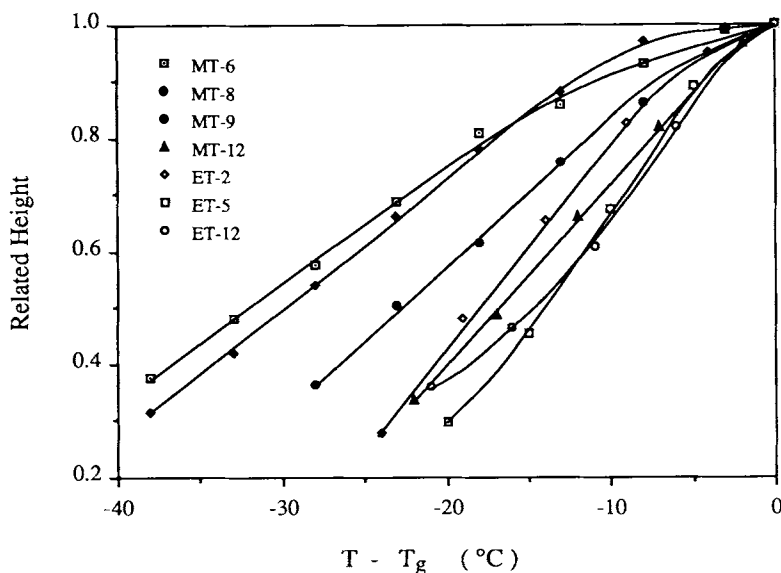


**Figure 5** A comparison of the $T_g$ peak profiles reduced to the same temperature difference from $T_g$.
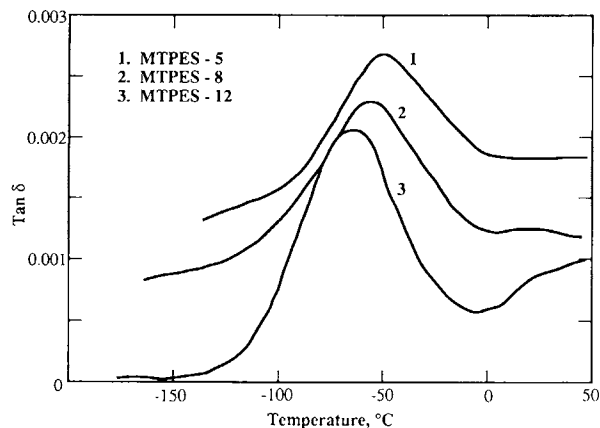
**Figure 6** Dielectric loss (234 Hz) in cured MTPES films. The traces for MTPES-5 and MTPES-12 have been shifted by +0.0005 and −0.0005 for clarity.



**Figure 7** Dielectric loss (234 Hz) in cured ETPS film. The traces for ETPS-5 and ETPS-12 have been shifted by 0.0005 for clarity.

showing how the $T_g$'s change with the degree of conversion for various MTPES are shown in Figure 3. For a low molecular weight oligomer, its $T_g$ changes very slowly at short cure times. For example, the $T_g$ of the BMI-5292A resin almost does not go up until the converted degree or conversion runs to 70%. But, as the cure stage reaches completion, $T_g$ rises very rapidly. For MTPES-12, which has a long chain between both terminal functional groups, its $T_g$ is elevated gradually before 50% cured and is nearly constant after 70% cure. For MTPES-6 with an intermediate chain length, its trace has a sigmoidal shape.

These results indicate that though the cure reaction of BMI is a radical chain reaction, its kinetics is similar to that of stepwise polymerization. The following mechanism of cure is therefore proposed: A radical formed from the opening of the double bond of the maleimide group is always located on a rigid polymer chain. Further chain polymerization is difficult to occur. On the other hand, when one end group of a bis-terminated functional oligomer reacts, the mobility of the other end is restricted at once and the probability of reaction becomes smaller immediately, particularly if the polymer chain is short. Therefore, in this case, short polymer chains with several short branches are probably formed during the early stages of the cure process. Both the polymer chains and branch chains are shorter if the oligomer molecular weight is lower. Thus the movement of the whole polymer molecule is relatively easy for lower molecular weight and shorter branches, resulting in lower $T_g$. But the active end group has low mobility; consequently the apparent activation energy becomes higher. On the other
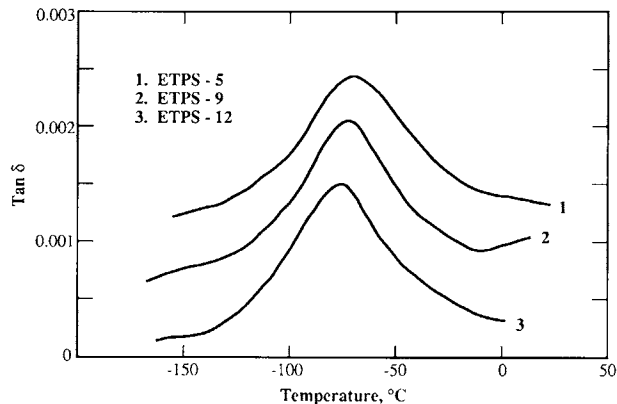
hand, for another oligomer with a longer chain between the terminal functional groups, once the reaction occurs, the molecular weight will rise rapidly and the $T_g$ goes up accordingly. Because the longer chains are more flexible than the short ones, movement of the functional groups located at the ends of long chains is easier. This appears to be a reasonable explanation for the lower apparent $E_a$. At the end of curing, the chain length between both crosslinking points is sufficiently long that the $T_g$ changes no further even though the crosslinking reaction continues to approach completion.

## Mechanical Properties of Products

The films (thickness 0.05–0.06 mm) were made by solution casting and postcured completely near
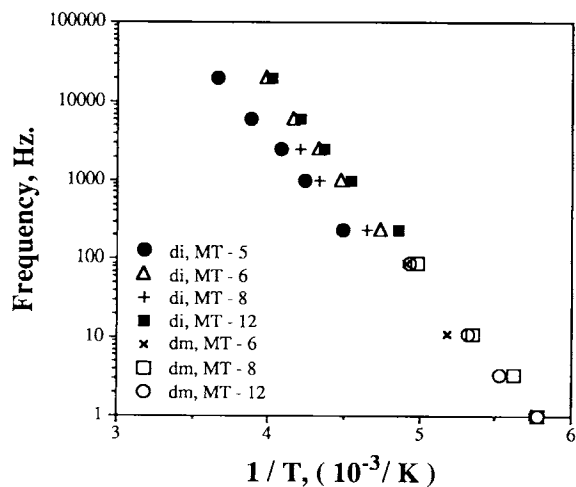


**Figure 8** The Arrhenius plots of $\beta$ relaxation for MTPES resins.

**Table VI   The $\beta$ Peak Shift of Resins in Dielectric Spectrum**

| Resins | Frequency (Hz) | | | | | $E_a$ (kJ/mol) |
|---|---|---|---|---|---|---|
| | 234 | 1000 | 2500 | 6000 | 20000 | |
| MTPES-5 | −50°C | −37°C | −28°C | −15°C | 0°C | 44.42 |
| MTPES-6 | −62°C | −52°C | −42°C | −33°C | −22°C | 48.62 |
| MTPES-8 | −58°C | −42°C | −35°C | | | 42.61 |
| MTPES-12 | −67°C | −53°C | −44°C | −35°C | −24°C | 43.71 |
| ETPS-5 | −62°C | −52°C | −43°C | −34°C | | 48.28 |
| ETPS-9 | −66°C | −55°C | −46°C | −39°C | | 47.71 |
| ETPS-12 | −70°C | −57°C | −51°C | −42°C | | 45.37 |

280°C for 1 h. Some results from dynamic mechanical analysis are shown in Table V and Figure 4. The data indicate that they have high $T_g$'s. The film formed from $M_n$ prepolymer with $M_n > 3000$ are more flexible and foldable.

## $\alpha$ Relaxation ($T_g$)

The $\alpha$ relaxation peak ($T_g$) of cured products increase in temperature and width as the molecular weight of the corresponding oligomers decrease, as expected. The widths of the relaxation peaks are compared by normalization, in which the relative magnitude (tan $\delta$/tan $\delta_{max}$) is plotted against ($T - T_g$). The results are given in Figure 5. The change of half peak width with $M_n$ of oligomers obviously exhibits a sigmoidal shape. This could mean that a highly crosslinked network has a broad relaxation time spectrum or that the relaxing segments are strongly coupled to each other. When considered together with the results of the kinetics studies, this could also be interpreted as support for the idea that the crosslink reaction occurred incompletely and many surviving functional groups remain in the

cured products, especially when the molecular weight of the uncured prepolymer is very low.

## $\beta$ Relaxation

The ductility of glassy polysulfone polymers was discussed in terms of the $\beta$ relaxation at about −100°C, which is thought to be related to the local motion of the aryl ether and sulfone groups.[14,15] It is also well known that this $\beta$ peak is affected by the absorption of small amounts of water.[16] To understand the molecular weight effect of the prepolymer on the mechanical relaxation of cured products at low temperatures, the specimens were dried at 120°C for several days before the measurements. The $\beta$ relaxation peaks of various resins determined by dynamic mechanical analysis and dielectric analysis with different frequencies are shown in Figures 4, 6, 7, and Tables VI and VII. The activation energies in these tables are obtained by plotting the peak frequencies vs. reciprocal peak temperatures according to an Arrhenius-type equation. These plots are shown in Figs. 8 and 9 for MTPES and ETPS, respectively. If the $\beta$ relaxation involves several re-

**Table VII   The $\beta$ Peak Shift of Resins in DMS**

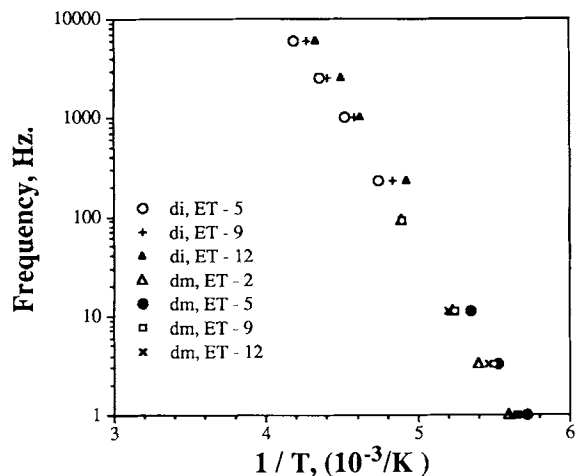| Resins | Frequency (Hz) | | | | $E_a$ (kJ/mol) |
|---|---|---|---|---|---|
| | 1 | 3.3 | 11 | 90 | |
| MTPES-6 | −99°C | −95°C | −80°C | −69°C | 40.35 |
| MTPES-8 | −100°C | −95°C | −86°C | −72°C | 45.95 |
| MTPES-12 | −100°C | −92°C | −85°C | −70°C | 44.23 |
| ETPS-2 | −95°C | −88°C | −82°C | −69°C | 52.78 |
| ETPS-5 | −98°C | −92°C | −86°C | −76°C | 54.44 |
| ETPS-9 | −96°C | −91°C | −83°C | −69°C | 49.02 |
| ETPS-12 | −96°C | −90°C | −81°C | | 44.81 |

**Figure 9** The Arrhenius plots of $\beta$ relaxation for ETPS resins.

peat units, as was found to be the case in BPA-polycarbonate,[15] then the $\beta$ peak should shift to higher temperature as the crosslink density increases. As shown in the results, the dielectric loss data are consistent with this expectation; however, the DMS data show no change. It is obvious that the data from DMS do not correlate well with those from the dielectric analysis. We have to discuss the reason why such is the case.

If we assume that the cured product is an incomplete network with many shorter branches, then many of these observations can be explained. The $\beta$ relaxation peak from DMS can then be due to local motions of the main chain. The differences in the networks formed from various oligomers is not so large that changes in the $\beta$ peaks can be observed within the experimental accuracy. However, dielectric analysis is more sensitive to the motion of the side branches. Therefore, the effect of different molecular weight oligomers on the $\beta$ relaxation of the cured products can be observed. If the molecular weight of the difunctional oligomer is lower, then there can be many short side branches in the network and if higher the converse is true. We note that the differences in the $\beta$ relaxations determined by DMS and DS are less for the ETPS systems as shown in Figure 9. The absence of a difference is probably due to the fact that the ETPS have higher molecular weights.

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