Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Thermomechanical Behavior of an Aromatic Polysulfone

John K. Gillham[a]; George F. Pezdirtz[b]; Lionel Epps[b]
[a] Department of Chemical Engineering, Princeton University, Princeton, New Jersey [b] Chemistry and Physics Branch, NASA-Langley Research Center, Hampton, Virginia

To cite this Article Gillham, John K. , Pezdirtz, George F. and Epps, Lionel(1969) 'Thermomechanical Behavior of an Aromatic Polysulfone', Journal of Macromolecular Science, Part A, 3: 6, 1183 — 1195
To link to this Article: DOI: 10.1080/10601326908051944
URL: http://dx.doi.org/10.1080/10601326908051944

J. MACROMOL. SCI.–CHEM., A3(6), pp. 1183-1195, October, 1969

Thermomechanical Behavior of an Aromatic Polysulfone

JOHN K. GILLHAM

Department of Chemical Engineering
Princeton University
Princeton, New Jersey

and

GEORGE F. PEZDIRTZ and LIONEL EPPS

Chemistry and Physics Branch
NASA-Langley Research Center
Hampton, Virginia

SUMMARY

The thermomechanical behavior (less than 1 Hz) of a newly available, high temperature, aromatic polysulfone has been investigated by the technique of torsional braid analysis (TBA). Speculations concerning the synthesis and structure are discussed in terms of NMR and infrared spectroscopy, elemental analysis, and a review of the general literature on polysulfones. In addition to the glass transition at 287°C, a secondary relaxation was detected in the glassy state at -100°C by a mechanical loss maximum and change in modulus. The stability of the polysulfone at elevated temperatures in air and nitrogen as monitored by TBA, DTA, and TGA is reported. The influence of heat to 500°C, high doses of ionizing radiation, and water on the transitions of the polymer is discussed.

INTRODUCTION

An essentially aromatic, thermoplastic material which is reported to be structurally useful for prolonged periods in air at 260°C, has recently been introduced commercially by the 3M Company [1, 2]. This material appears to have chemical, mechanical, and electrical properties that would be potentially suitable for use in previously excluded hostile environments, particularly as a replacement for die-cast metals. For a high-temperature polymer, its ease of melt processability is unusual. The relative lack of shear-rate sensitivity results in injection-molded specimens of good quality. An important detrimental property is the severity of environmental stress-cracking that occurs with ketones.

Previous work with high-temperature heterocyclic aromatic polymers, such as the polybenzimidazoles [3], has indicated that thermal reactions (cross-linking and/or intramolecular chain-stiffening) are responsible for the increase in modulus with temperature at elevated temperatures. Should these reactions occur in aromatic polysulfones, the polymers might well be converted to materials which would be mechanically useful to temperatures well above their original and limiting glass transition temperatures. The present report deals with the thermomechanical behavior of the 3M polysulfone; its thermal conversion to a different material which essentially retains its room-temperature modulus to temperatures above 500°C; and the stability in air of the derived product. The effect of high-energy electron and gamma radiation in doses of more than 2000 Mrads on the thermomechanical spectra is also reported.

STRUCTURE

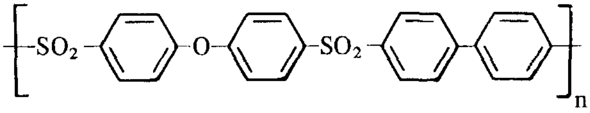
The structure of the polysulfone used in this study has not been disclosed by the manufacturer* but is reported to be composed of phenylene and biphenylene units linked only by oxygen and sulfone groups [1, 2]. The number average molecular weight is of the order of 30,000 [4]. Biphenyl, diphenyl ether, and phenol were reported to be the main detected volatile products of pyrolysis at 475°C.

The NMR spectrum in deuterated dimethyl sulfoxide substantiates the absence of aliphatic hydrogens, and the aromatic region (1.7-3.2 τ) (Fig. 1) confirms the aromatic nature of the polymer. The infrared spectrum (Fig. 4)

---

*Additional description of the synthesis of the 3M polysulfone appeared after completion of the present report; H. A. Vogel, *Am. Chem. Soc. Polymer Preprints,* **10**, 160 (1969).

also substantiates this absence of aliphatic protons. The reported constituents and linkages [1, 2]; the reported pyrolysis products [1, 2]; and a comparison of the NMR spectrum (Fig. 1) with that of essentially structure (**I**) (Ref. [7], p. 273, Fig. 8; see insert of Fig. 1) suggest that the latter is structurally related to the 3M polysulfone. The intense resonances in the region of 2.1 τ



(I)

may then be attributed to protons of the p,p′-diphenyl disulfonyl group and to the protons ortho to the sulfone groups in the p,p′-diphenyl ether units. The resonances at 2.8 τ have been assigned to the protons ortho to the oxygen in the p,p′-diphenyl ether group and are split into a doublet by the presence of protons meta to the oxygen [7]. The ratio of the area of the resonances at 2.8 τ to the integrated area in the vicinity of 2.1 τ is that expected (1:3) for the structure (**I**). The main differences between the NMR spectrum of the 3M polysulfone (Fig. 1) and that referred to above [7] (Fig. 1, insert) lie in the additional resonances in the latter (particularly at 1.8, 2.15, 2.3-2.5, and 3.1 τ) which arise from additional structural complexity.

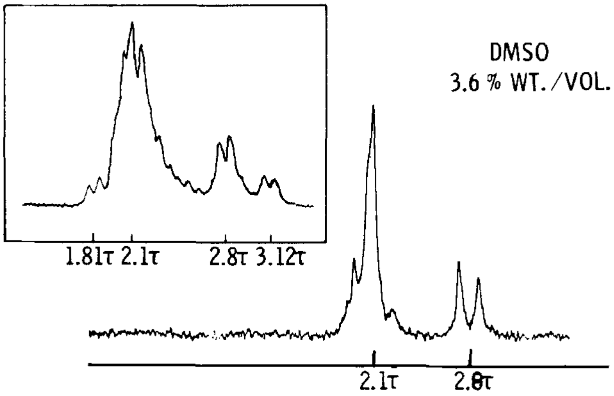


Fig. 1. Comparison of NMR spectrum of the 3M polysulfone with that of an aromatic polysulfone [7] (insert); 60 MHz, 25°C, 3.6% polymer.

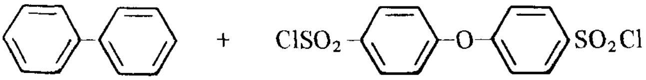
A copolymer structure with ortho- and para-substituted aromatic nuclei and branching would contribute to this complexity.

Elemental analyses of untreated samples of the 3M polysulfone gave an average carbon-to-sulfur ratio of 4.51 (variance of 0.05) compared with a value of 4.50 calculated for the above structure (**I**).

Although these are exceptions [5], the absence of crystallinity in aromatic polysulfones is common even for those polymers with symmetrical structures. The 3M polysulfone forms amorphous materials.

SYNTHESIS

The industrial synthesis of the 3M polysulfone has not been divulged; however, general methods of synthesis of aromatic polysulfones have been reviewed [5-8]. Polymer with a structure essentially that of structure (**I**) can be prepared by forming sulfone linkages via electrophilic sulfonylation of aromatic nuclei using small amounts of catalyst such as $FeCl_3$. The particular reaction could then involve the following monomers:



The other main route to aromatic polysulfones involves linking monomers which contain sulfone linkages by, for example, ether linkages. The specific structure (**I**) cannot be conveniently formed by this particular method.

TRANSITIONS

Since the material is an amorphous thermoplastic polymer, its utility at elevated temperatures is based on the high glass transition temperature of about 287°C [2] which was obtained from dilatometric experiments. This is in agreement with values obtained herein by differential thermal analysis (Fig. 2) and with a torsion pendulum (less than 1 Hz) (Fig. 5, curve 1). The low-frequency (100 Hz) dielectric loss increases drastically [2] at temperatures approaching the glass transition temperature, as is to be expected. The transitions other than T_g are reported to be absent, in spite of the highly commendable property of impact resistance at room temperature (e.g., notched Izod impact strength up to 4 ft lb/in. of notch [2]) and some ductility at -196°C [2]. The engineering properties of aromatic polysulfones are reviewed in Refs. [1, 2, and 8].

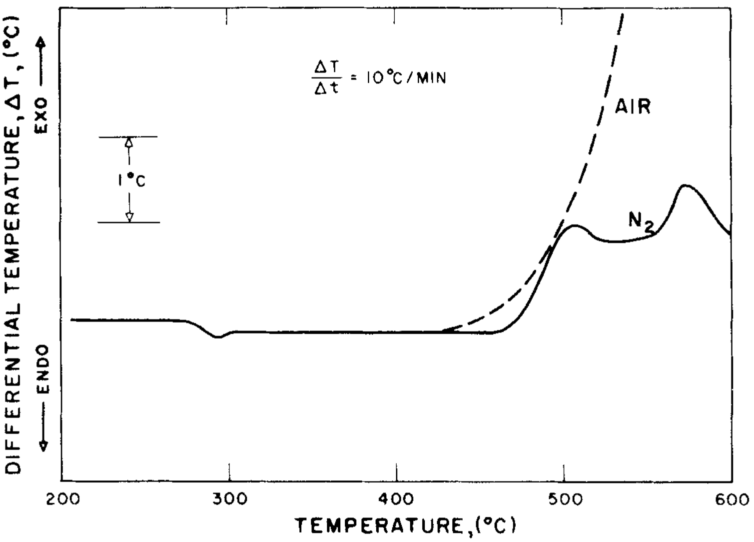


Fig. 2. DTA of the 3M polysulfone. Films were prepared in situ from DMSO solutions by heating to 340°C ($\Delta T/\Delta t$ = 2°C/min) in nitrogen and cooling. The duPont thermo analyzer (Model 900) with the DSC attachment was used.

STABILITY

Thin films of the dry polymer (prepared by heating to 340°C in nitrogen at 2°C/min and then cooling) lose very little weight in either nitrogen or air below ca. 450°C ($\Delta T/\Delta t$ = 5°C/min), as shown in Fig. 3. Contrary to a previous report [2], for which the rate of temperature rise was not designated, we observed a region above 450°C where the weight loss in air was less than that in dry nitrogen or under a vacuum of 10^{-6} Torr. The apparent higher stability in air presumably results from a slight gain in weight due to oxidation which offsets loss in weight in the region from 450 to 580°C.

Exotherms due to degradation were observed (Fig. 2) to begin at 460°C ($\Delta T/\Delta t$ = 10°C/min) in nitrogen and in air, the latter being larger. An infrared spectrum of a solvent-free film (prepared by heating in vacuo to 340°C at 2°C/min and then cooling) is shown in Fig. 4. Infrared spectra of films which had been heated in vacuo at 2°C/min showed no appreciable change up to 450°C; at higher temperatures, increased absorption developed at 870 cm^{-1}. When the initially clear film was heated at 10°C/min to 500°C

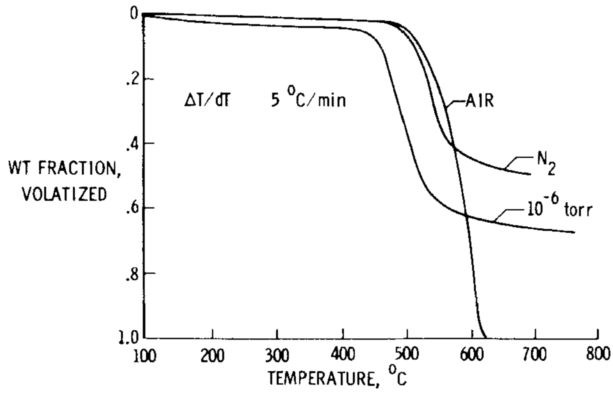


Fig. 3. Thermogravimetric analysis of the 3M polysulfone.

in nitrogen, it was converted to a smooth, glossy, black, opaque film which superficially appeared to be free of bubbles or voids.

The films were initially soluble in dimethyl formamide, but after heating to 500°C in nitrogen (ΔT/Δt = 10°C/min) they were insoluble. When the films were heated to only 450°C they colored only slightly and were found to swell, but not to dissolve in dimethyl formamide at 25°C, indicating that cross-linking had occurred.

The absence of aliphatic hydrogen and the fact that the sulfur in the chain is in its highest oxidation state are considered to be responsible for the good aging and self-extinguishing characteristics of the polymer in air at elevated temperatures. The tensile strength at 260°C decreased only 2% after 1000 hr in air at 260°C [1].

THERMOMECHANICAL BEHAVIOR

The thermomechanical behavior of the polymer in nitrogen was determined over the range -190 to 500°C by the technique of torsional braid analysis [3], which uses a modified torsion pendulum operating at about 1 Hz. Curve 1 in Fig. 5 shows the initial behavior of the polymer after it had been preheated to 340°C (ΔT/Δt = 2°C/min) in an attempt to remove the dimethyl formamide solvent. The glass transition is readily detected by the drastic drop in modulus and sharp damping maximum at 290°C. A broad damping maximum was observed in the region of -100°C. This and other lower-temperature relaxation processes could be responsible

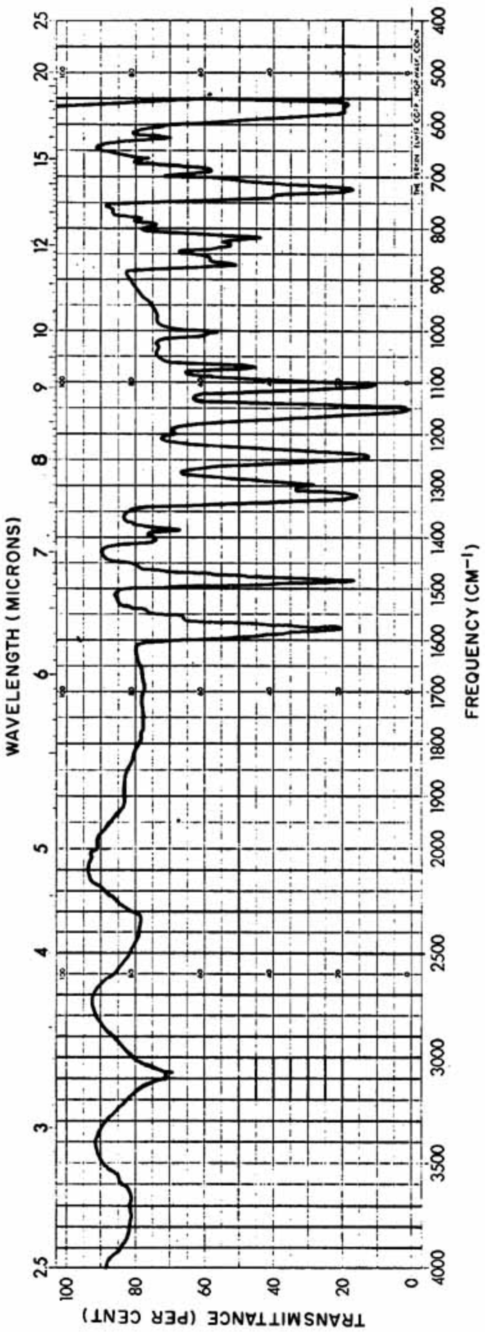


Fig. 4. Infrared spectrum of the 3M polysulfone.

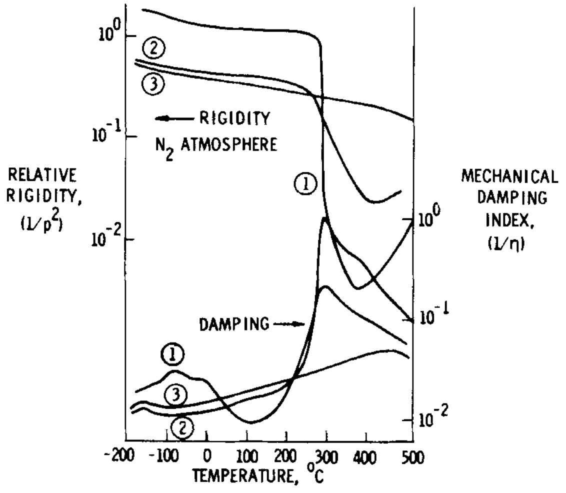


Fig. 5. Effect of thermal treatment on the thermomechanical behavior of the 3M polysulfone.

for the reported [2] impact properties at room temperature and for the low-temperature ductility of the films. The increase in modulus and concomitant decrease in mechanical loss above 380°C are the consequence of chemical reactions and lead to the formation of a new material. After the heating cycle (Fig. 5, curve 1) the specimen was cooled immediately and then recycled to give curve 2 of Fig. 5. The specimen was then held at 500°C for 1 hr, cooled, and reheated to 500°C to give curve 3. The successive thermal treatments in nitrogen result in conversion of the thermoplastic polymer, with a well-defined glass transition temperature (290°C), to a material which displays only minor thermal softening and low mechanical loss from -190 to 500°C. The well-resolved damping peaks of the original material contrast with the essentially monotonic mechanical loss of the pyrolyzed product. These changes would be expected from the conversion of a thermoplastic to a thermoset material by the process of thermal cross-linking. It might be noted that whereas cross-linking increases the glass transition temperature of the polymer, cross-linking appears to decrease the temperature of the loss maximum in the glassy phase. The latter phenomenon presumably arises from the preferential freezing-out-by-cross-linking of longer range motions which without cross-linking display dissipation at higher temperatures.

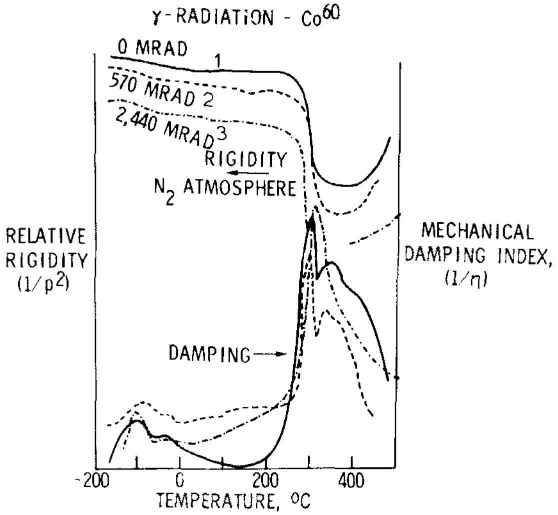


Fig. 6. Effect of γ radiation on the thermomechanical behavior of the 3M polysulfone. (Rigidity curves have been displaced vertically.)

The material which had been formed by pyrolysis at 500°C for 1 hr in nitrogen displays modest mechanical stability in air above 400°C. The samples for these oxidative experiments were polymer-coated glass braids of diameter ca. 0.03 in. and were completely oxidized within 1000 min at 400°C.

RADIATION EFFECTS

Glass braids coated with polymer, which form the samples for torsional braid analysis, were subjected to various doses of electron and gamma radiation. All samples were preheated to 340°C ($\Delta T/\Delta t$ = 2°C/min) to remove solvent. Several braids were placed in glass tubes and heated in vacuo (10^{-6} Torr) at 150°C overnight. The tubes were cooled and then sealed at 10^{-6} Torr and irradiated with ^{60}Co at 2 Mrads/hr at 47°C. These samples showed no appreciable change in their thermomechanical spectra for doses up to 2500 Mrads except for an apparent increase in damping between 0 and 200°C, which is indicative of a lightly cross-linked system (Fig. 6). This increase in damping between 0 and 200°C is also shown by unirradiated samples which have been heated to 500°C ($\Delta T/\Delta t$ = 2°C/min) and immediately cooled (Fig. 5, curve 2).

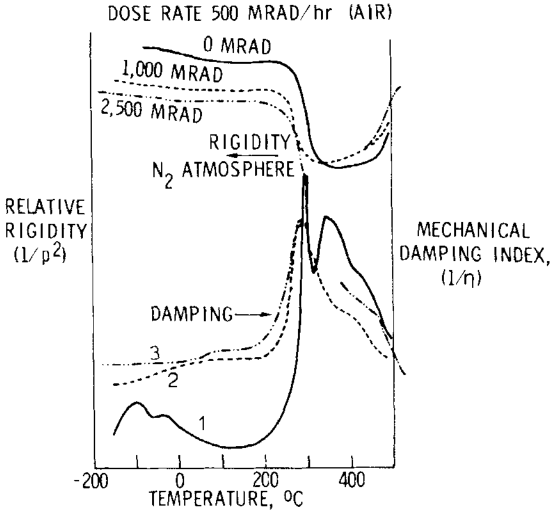


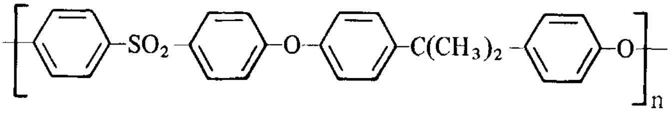
Fig. 7. Effect of 1-MeV electrons on thermomechanical behavior of the 3M polysulfone. (Rigidity curves have been displaced vertically.)

To compare the effects of 1-MeV electrons with those of cobalt-60 gamma rays, several samples were subjected to electron irradiation in air, immediately following solvent removal and cooling to room temperature. The radiation source was a Dynamitron accelerator with the dose rate at 500 Mrads/hr. The temperature was not controlled. The -100°C transition defined by the maximum in the mechanical damping (Fig. 7, curve 1) was not detected after 1000 megarads under these conditions (Fig. 7, curves 2 and 3). Since this peak remained after 2500 Mrads of gamma radiation at the lower dose rate (Fig. 6), its destruction is believed to be a consequence of the combination of thermal and some oxidative effects which occur at the high electron dose rate in air. In a separate experiment (not shown) the specimens were irradiated with electrons in a vacuum at a lower dose rate of 50 Mrads/hr. Total doses were up to 2500 Mrads and temperatures were below 50°C. At the lower dose rate the low-temperature damping peak remained and the thermomechanical spectra (not shown) appeared to be the same as those resulting from the same dose of gamma irradiation.

EFFECT OF WATER ABSORPTION

When the low-temperature portion (25 to -195°C) of the thermomechanical spectra (not shown) of the 3M polysulfone was not obtained immediately after preparing the solvent-free specimens, a damping peak was found at ca. 0°C. This peak was not present when the sample was held at 150°C in nitrogen for an hour or longer before cooling immediately to -195°C. Since the polymer is hygroscopic, the 0°C "transition" shown by samples which had not been preheated was ascribed to water absorbed at room temperature. Exposing a sample to a high relative humidity and cooling from room temperature to -195°C resulted in a thermomechanical spectrum in which the 0°C peak was greatly enhanced but the -100°C damping maximum was unaffected.

Dynamic mechanical (5000-50,000 Hz) studies [9] of a polysulfone, available commercially from the Union Carbide Corporation, with the structure II:



(II)

had indicated that a secondary relaxation at ca. -43°C (6100 Hz) involved absorbed water molecules. However, subsequent work [10] with the above Union Carbide polymer using a torsion pendulum showed a well-defined loss transition at ca. -100°C for the polymer in the "pure state". The impact resistance of the polymer was shown [10] to be related to the magnitude of the -100°C transition which was varied by antiplasticization with such additives as N-phenyl-2-naphthylamine.

A comparison of the structure of the Union Carbide polysulfone (II) with that proposed for the 3M polysulfone (I) suggests that the 3M polymer molecule would be less flexible and would give rise to a higher glass transition temperature. However, localized motions at low temperatures are likely to be centered about the common ether linkages and could lead to each polymer displaying similar properties in the glassy state. The dynamic mechanical results appear to be consistent with the structure proposed for the 3M polymer.

REFERENCES

[1] B. A. Benson, R. P. Bringer, H. A. Vogel, and N. L. Watkins, *SPE Ann. Techn. Conf., Detroit, Mich., May 1967,* **13**, 612.

[2] G. A. Morneau and R. P. Bringer, "Behavior of a 500°F. Thermoplastic under Various Environmental Influences," Regional Conf., Baltimore-Washington SPE Section, September 8, 1967.

[3] J. K. Gillham, *Polymer Eng. Sci.,* **7(4)**, 225 (1967).

[4] R. P. Bringer, private communication.
[5] J. B. Rose, *Chem. and Ind.*, **15**, 461 (1968).
[6] M. E. A. Cudby, R. G. Feasey, B. E. Jennings, M. E. B. Jones, and J. B. Rose, *Polymer*, **6**, 589 (1965).
[7] M. E. A. Cudby, R. G. Feasey, S. Baskin, V. Kendall, and J. B. Rose, *Polymer*, **9**, 265 (1968).
[8] H. Lee and K. Neville, *New Linear Polymers*, McGraw-Hill, New York, 1967, Chap. 5.
[9] M. Baccaredda, E. Butta, V. Frosini, and S. DePetris, *J. Polymer Sci.*, **A-2(5)**, 1296 (1967).
[10] L. Robeson, and J. Faucher, *J. Polymer Sci.*, **B(1)**, 35 (1969).

Accepted by editor May 22, 1969
Received for publication July 3, 1969

Discussion of Paper by John K. Gillham et al.

Thermomechanical Behavior of an Aromatic Polysulfone

M. Shen:	Is the polymer the degrading or cross-linking type as far as the effect of radiation is concerned?
G. Pezdirtz:	Radiation causes both chain scission and cross-linking to occur simultaneously, but the high concentration of aromatic rings in the main chain provides a high degree of radiation stability, and cross-linking is the predominant reaction.
M. Price:	Can you speculate on the actual reaction which occurs to alter T_g? Does the TGA of the polymer change after radiation or heat treatment?
J. Gillham:	The glass transition temperature is raised presumably by formation of cross-links between the phenyl residues. We would not expect the thermal treatment to change the form of the TGA at elevated temperatures. The effect of irradiation has yet to be examined.
H. Levine:	Did you examine the effect of varying cooling rate from 500°C to room temperature on the shape or intensity of the −100°C damping peak?

J. Gillham: No, we did not for the reason that quenching would produce stresses which might result in fractures in the composite samples.

E. Scalca: What was the environmental stress-crack behavior after your thermal treatment?

J. Gillham: The original polysulfone undergoes environmental stress-cracking in the presence of ketones [2]. This appears to be an important limitation which may well be alleviated by some process. We have not investigated the effect of thermal or irradiative treatment on this phenomenon.