

Dynamic Mechanical Analysis and Interpretation of Molecular Motions in Polyarylates*

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SYNOPSIS

Molecular motions in polyarylates synthesized from substituted bisphenols have been investigated by dynamic mechanical analysis. Substitution at the ring carbon atom results in a more pronounced enhancement in glass transition temperature (T_g) as compared to substitution at the bridge carbon atom. The enhancement in mono and disubstituted polyarylates is more consistent than that in the case of polycarbonates and polysulfones. The β transition has been shown to result from defects in the polymer samples. The molecular motion responsible for the τ transition in polyarylates has been shown to be more localized than in the case of polycarbonates. Introduction of the phthalide ring in the isopropylidene unit of bisphenol-A molecule results in splitting of the τ transition peak into two. The results have been compared with those reported for other bisphenol-based polymers, viz. polycarbonates and polysulfones, and explained on the basis of the structural attributes of the polymers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In an earlier communication from our group, the results of the wide angle X-ray diffraction (WAXD) analysis of a series of polyarylates were discussed.¹ Three types of polyarylates were synthesized. In the first series, the substituents at the bridge carbon atom of the bisphenol moiety were varied. In the second series, methyl substituents were incorporated at the ring carbon atom. The third series was based on phenolphthalein as the aromatic diol. It was observed that in the series comprising bridge-substituted polyarylates, the average intersegmental chain spacing (d spacing) was almost constant but the chain flexibility varied as reflected in the values of T_g .

In order to obtain further insight into the contribution of various subgroups/bonds on chain flexibility, conformational analysis of three polyarylates was carried out using a molecular modelling approach.² A correlation was shown to hold between the values of glass transition temperatures (T_g) and

the conformational entropies calculated for the independent rotation of various bonds. It also emerged that in these polyarylates, the bonds involving the bridge carbon atom in bisphenol-A and the phenyl rings play a major role in governing the chain conformation and rigidity; whereas the bonds around the ester linkages are relatively flexible.

The relaxations in polymers arise from the cooperative main chain motion as well as the motion of subgroups. The results of such studies have been correlated in the past with the properties of the polymer, such as impact strength, permeability, etc. Techniques such as nuclear magnetic resonance (NMR),³⁻⁵ dielectric measurements^{6,7} and dynamic mechanical analysis (DMA)⁸ have been widely used to investigate the molecular relaxations in polymers. In particular, detailed DMA studies for various polycarbonates have been reported.⁹⁻¹² In comparison, excepting investigations on polyarylates based on phenolphthalein by Nurmukhametov et al.¹³ and bisphenol-A based polyarylates reported by Starkweather et al.,¹⁴ molecular motions in polyarylates have not been extensively investigated. Recently it has been suggested that the scale of molecular motions associated with the τ transition in polycarbonates, polysulphones, and polyarylates could be different.^{10,15} A detailed investigation of the τ tran-

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sition in a number of polyarylates, wherein the nature and site of substitution is systematically varied, would clarify the origin of molecular motion responsible for the τ transition in polyarylates vis-à-vis polycarbonates and polysulphones.

In this paper, the results of dynamic mechanical analysis of a series of substituted polyarylates are reported and compared with those for polycarbonates and polysulphones. The differences in the molecular motions responsible for the τ transition in these polymers have been highlighted.

EXPERIMENTAL WORK

The syntheses of the polyarylates characterized by DMA in this work were reported earlier.¹ The structures are shown in Figure 1.

Preparation of Samples for DMA

Samples were prepared by solution casting as well as by compression molding in order to study the effect of specimen preparation on the dynamic mechanical behavior of polymers.

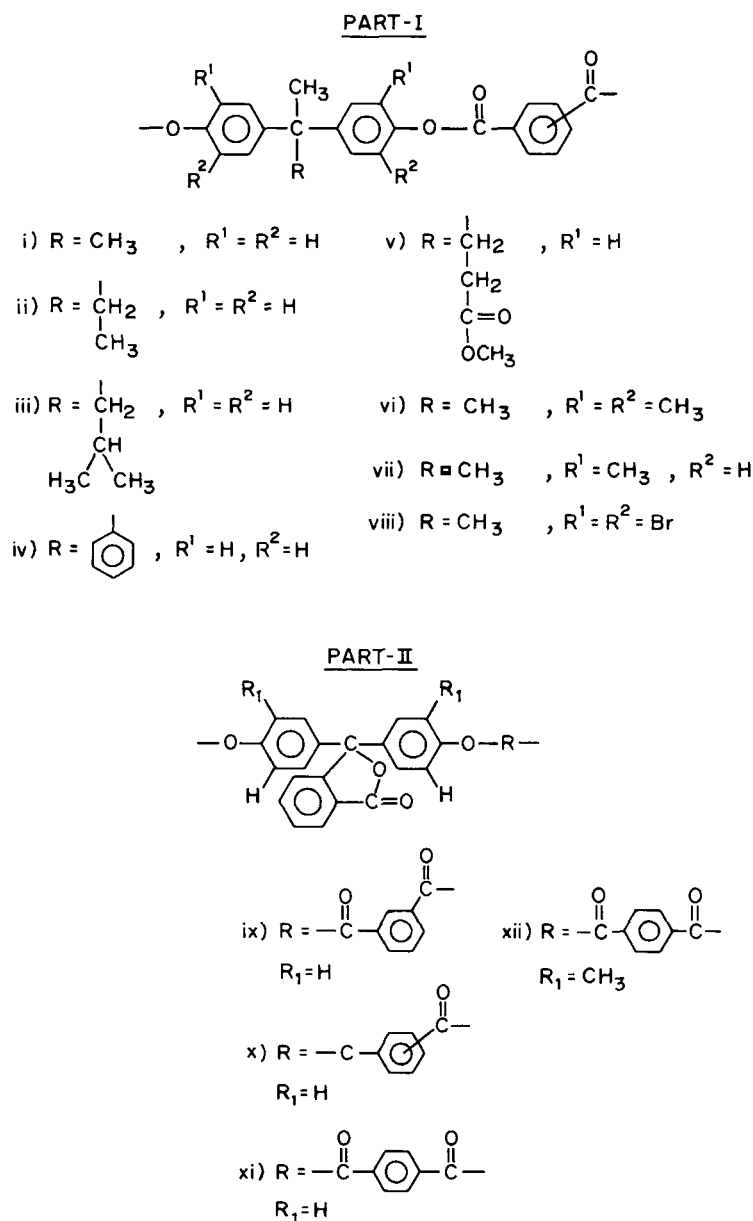


Figure 1 Repeat unit structures of polyarylates synthesized and characterized by dynamic mechanical analysis (DMA). Identification corresponds to Table I.

Compression Molding

The polyarylates as synthesized were either in the form of powder or fibers. In order to facilitate compression molding, the polymers were initially cold-pressed. Bars of dimensions $1.6 \times 12.7 \times 64$ mm were formed by keeping these cold-pressed specimens in a mold which was placed in the hydraulic press and preheated in all cases to about $T_g + 60^\circ\text{C}$.

Solution Casting

Ten-percent solutions of the polyarylates in chloroform were cast onto clean glass plates and slowly evaporated to form a thick sheet. Strips of standard dimensions were then cut and dried under vacuum at 80°C for 48 h. Some solution-cast specimens were further heated at 160°C for 12 h. The evacuation time was adequate to ensure complete removal of chloroform. This was verified by subjecting the sample to thermogravimetric analysis up to 600°C , which did not show any solvent loss. The specimens were stored in a vacuum desiccator until measurements were done, to prevent moisture sorption during storage.

Dynamic Mechanical Analysis

A Rheometrics Dynamic Mechanical Spectrometer Model 7700, with a rectangular fixture, was used to measure the shear storage modulus G' , the loss modulus G'' , and $\tan \delta$ as a function of temperature. A uniform strain of 0.5% and frequency of 10 rads/s (1.59 Hz) were used in all the measurements. The

temperature range scanned was from -150°C to $T_g + 20^\circ\text{C}$. The activation energy was determined for the polyarylates based on Bis-A/IPC:TPC and Bis-MIBK/IPC:TPC by making measurements at various frequencies between 1 rad/s and 500 rads/s.

RESULTS AND DISCUSSION

A typical dynamic mechanical spectrum for the polyarylate Bis-A/IPC:TPC is shown in Figure 2. Three different peaks are observed and are denoted as α , β and τ as per the nomenclature followed by Yee and Smith.⁹ Various transition temperatures observed for the polyarylates studied are listed in Table I. The following sections discuss the effects of various experimental parameters, polymer structure, and specimen history on the transitions investigated.

The α Transition (T_g)

From Table I it is observed that the α transition is influenced by both the nature and site of substitution. It has been shown by us earlier that in the case of polyarylates, the molecular motions in the main chain as well as the side chain contribute to T_g .² Thus T_g decreases marginally as a result of enhanced side chain mobility when flexible groups such as ethyl or valeric ester are substituted for the methyl group in bisphenol-A. Substitution by bulky groups results in an increase in T_g , as in the case of polyarylates based on Bis-MIBK and bisacetophenone. These results are similar to those reported by Yee and Smith⁹ for polycarbonates and by Aitken et al.¹⁵

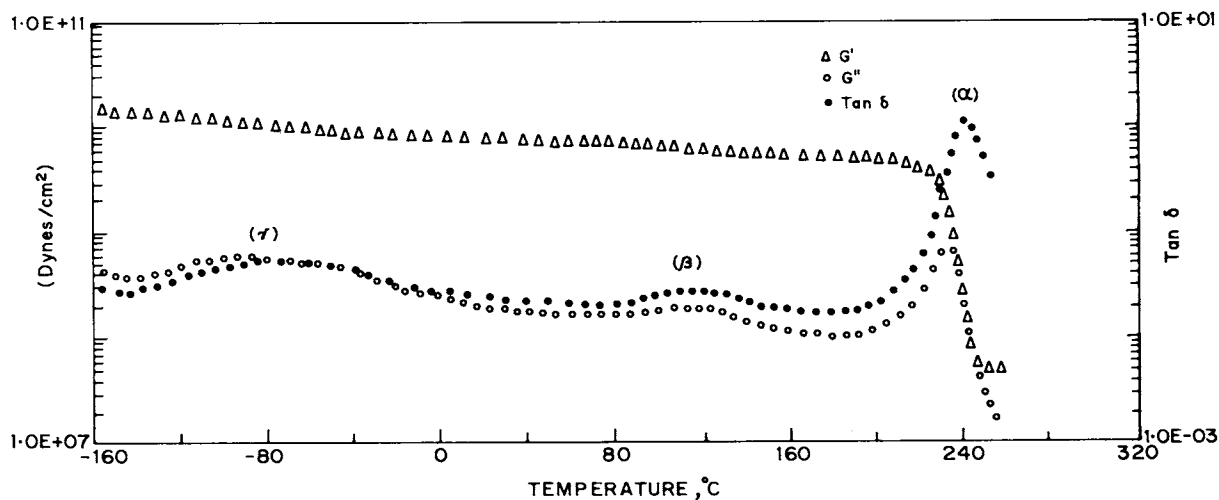


Figure 2 Dynamic mechanical spectrum for the annealed specimen of Bis-A/IPC:TPC (1:1).

Table I Dynamic Mechanical Transitions in Polyarylates

Polymer	α , °C	β , °C	τ , °C	d , Å
A) Compression Molded Samples				
Lexan (PC)	150	80	-101	5.21
i) Bis-IPC : TPC	198	84	-84	5.15
ii) Bis-MEK/IPC : TPC	192	—	-92	5.18
iii) Bis-MIBK/IPC : TPC	216	94	-72	5.21
iv) Bis-Aceto/IPC : TPC	267	—	-85	5.09
v) Bis-valeric/IPC : TPC	183	114	-93	5.03
vi) TMBis-A/IPC : TPC	274	129	43	5.74
vii) DMbis-A/IPC : TPC	234	—	32	5.21
B) Solution Cast Samples				
ii) Bis-A/IPC : TPC	182	82	-90	—
v) Bis-valeric/IPC : TPC	165	114	-100	—
viii) TMBis-A/IPC : TPC	248	124	43	—
viii) Tetra bromo Bis-A/IPC : TPC	285	220	110	4.14
ix) PPha/IPC	258	170	-100, -50	—
x) PPha/IPC : TPC	278	183	-100, -50	—
xi) PPha/TPC	300	191	-100, -50	—
xii) O-cresolphthalein/TPC	314	215	38	5.34

for polysulphones. Molecular modelling analysis shows that the substitution of a bulky group at the bridge carbon atom restricts the motion of the phenyl ring in bisphenol-A. Substitution of a methyl group on the phenyl ring has an even greater effect on the main chain motion as reflected in T_g .

In the case of the polyarylates based on mixed dicarboxylic acids, the T_g is enhanced by 36°C when bisphenol-A is replaced by 3,3' dimethyl bisphenol-A; by 76°C when replaced by 3,3',5,5' tetramethyl bisphenol-A; and by 87°C when replaced by tetra-bromo bisphenol-A. In contrast, in the case of polycarbonates, substitution of bisphenol-A by 3,3' dimethyl bisphenol-A leads to a decrease in T_g from 150°C to 98°C, while substitution by 3,3',5,5' tetramethyl bisphenol-A leads to an enhancement in T_g to 191°C.¹⁷ Similar substitutions in the case of polysulphones lead initially to a small decrease in T_g from 186°C to 180°C and subsequently to an increase to 242°C. It was argued that monosubstitution leads to a less efficient packing and higher free volume as compared to that for an unsubstituted or symmetrically substituted molecule.⁹ However, a comparison of the densities and fractional free volumes reported by Aitken et al.¹⁵ indicates that as bisphenol-A is replaced by dimethyl bisphenol-A and tetramethyl bisphenol-A, the density decreases consistently while the fractional free volume first decreases and then increases. In either case, the T_g variations in the polycarbonates and polysulphones are not consistent with the above results. It therefore

appears that the intermolecular interactions at the local segmental levels in the two cases are different and are responsible for variations in T_g .¹⁸ As expected from the reduced conformational entropy,² the phenolphthalein-based polyarylates exhibit higher T_g . The measured T_g values for the phenolphthalein-based polyarylates reported here are within $\pm 10^\circ\text{C}$ of those reported by Nurmukhametov et al.¹³ Substitution at the bridge as well as the ring carbon atom, as in the case of *o*-cresolphthalein-based polyarylates, results in further enhancement in T_g to 314°C.

The method of specimen preparation also affects α transition. In comparison to compression-molded specimens, specimens prepared by solution casting exhibit: (i) a more diffuse α peak which appears at lower temperatures; (ii) foaming in all cases immediately after the β relaxation peak, resulting in an increase in G' ; and (iii) a decrease in the height of the α transition peak [see Fig. 3(a)]. Foaming does not appear to be caused by the residual solvent alone, since it is also observed in some of the specimens prepared by compression molding. Further, foaming is eliminated on annealing near T_g of the solution-cast as well as compression-molded specimens. This also leads to an increase in the glass transition temperature and peak height [Fig. 3(b)].

A logarithmic plot of frequency vs. reciprocal temperature is shown in Figure 4. The activation energies calculated for the α transition for bisphenol-A and Bis-MIBK-based polyarylates are 252 and

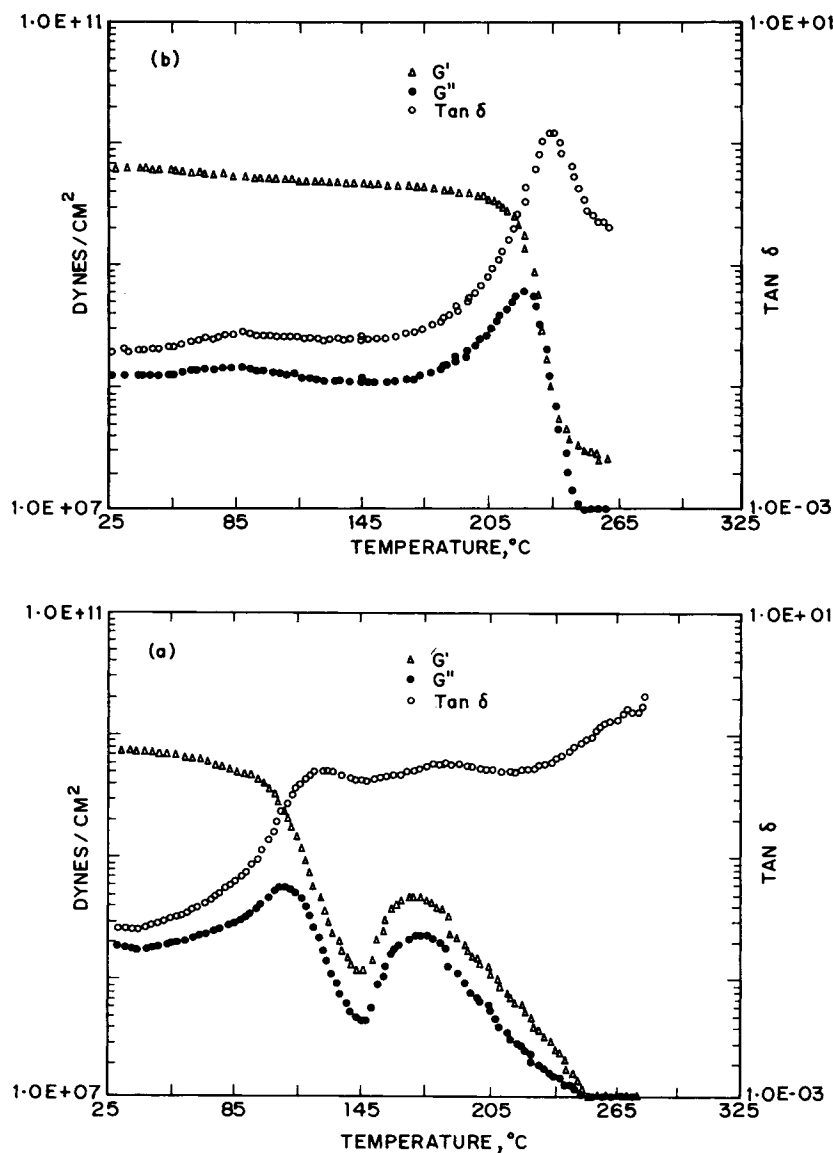


Figure 3 Effect of foaming of specimen on the storage modulus (G'), the loss modulus (G'') and $\tan \delta$ in the solution cast specimen Bis-A/IPC:TPC. (1 : 1) (a) Unannealed specimen; (b) Specimen annealed at 160°C for 8 hours.

273 kcal/mol, respectively. These values are reasonable in comparison to the activation energy (219.7 ± 55.2 kcal/mol) recently reported by Fried et al.¹⁹ for polysulfone based on bisphenol-A.

The β Transition

In this paper, β transition denotes the transition which may appear between the α and the τ transition temperature. β transition is not observed in all specimens (see Table I). Boyer²⁰ studied molecular motions in a number of amorphous and semicrystalline

polymers using DMA. The β transition was assigned to the onset of motions which are precursors to the long-range segmental motions occurring at T_g . It is possible that this precursor motion can be executed only when sufficient defects are present in the polymer sample. Yee and Smith⁹ identified two types of β transitions. The transition of the first type does not disappear on annealing, while that of the latter type does. The β transition observed by us belongs to the latter category and has its origin in defects.

We now present the results of (a) the effect of specimen annealing, and (b) activation energy

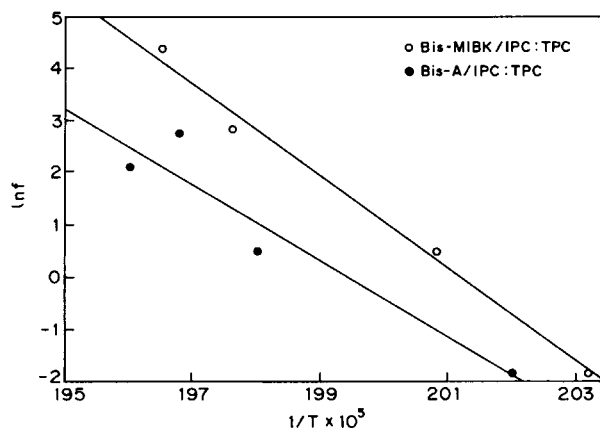


Figure 4 Arrhenius plot for α transition in Bis-A/IPC:TPC (1 : 1) and Bis-MIBK/IPC:TPC (1 : 1).

measurements, to show that the β transition in the case of polyarylates does in fact originate from defects.

Annealing at temperatures below T_g resulted in either a decrease in the magnitude of or the disappearance of the β transition peak in the case of the polyarylates, viz Bis-A/IPC:TPC and TMBis-A/IPC:TPC (Fig. 5), depending on the temperature and time of annealing. Similar results have been reported by Illers and Breuer²¹ for polycarbonate and by Fried et al.⁸ for polysulfones.

The activation energy of 88 kcal/mol. for the β transition in polyarylate based on bisphenol-A is too high to be assigned to the motion of individual subgroups, typical values for which are around 10–12 kcal/mol.¹⁴ This further indicates that the β transition does not have its origin in the motion of monomer subgroups. The activation energy for the β transition in polyarylate based on bisphenol-A is close to that for bisphenol-A-based polysulfone (67.3 ± 35.7 kcal/mol) reported by Fried et al.⁸ β transition was always observed in the case of specimens prepared by solution casting (Table I). However, as it was also observed in some specimens prepared by compression molding, the transition cannot be attributed to the presence of residual solvent.

The τ Transition

The τ transition in polycarbonates has been extensively investigated in the past, as it is believed to be related to its impact strength. Yee and Smith,⁹ investigated the effects of substitution at the bridge and ring carbon atom of bisphenol-A on τ transition

in polycarbonates. The transition was always observed as a single peak, regardless of whether the substitution was at the bridge or the ring carbon atom. This was attributed to the fact that the transition involved the motion of the monomer unit as a whole. NMR studies on polycarbonate also indicate that the τ transition arises from the cooperative motion of various subgroups, viz. $>C=O$, $>C(CH_3)_2$ and the phenyl ring flip.¹⁰ The τ transition for the symmetrically substituted Cl_2BPA polycarbonate was shifted to $50^\circ C$ as against at $-100^\circ C$ in the case of bisphenol-A based polycarbonate. For the asymmetrically substituted CIBPA polycarbonate, only one peak was observed at $5^\circ C$ rather than two peaks at $50^\circ C$ and $-100^\circ C$, respectively. A single τ transition peak was also observed in the case of copolymers based on tetramethyl bisphenol-A, as well as bisphenol-A. Two distinct transitions corresponding to the individual polycarbonates were observed only when the individual

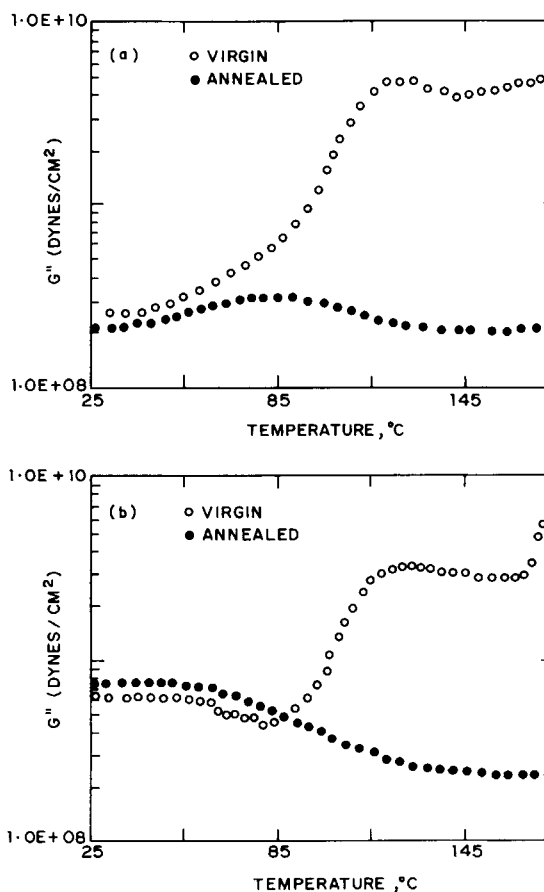


Figure 5 Effect of annealing on β transition in (a) Bis-A/IPC:TPC (1 : 1) and (b) TMBis-A/IPC:TPC (1 : 1).

block lengths in the block copolymers comprised more than six monomer units.¹⁰ This has been attributed to the hyperconjugation effect.¹¹

In contrast, the τ transition in polysulphones comprises two peaks corresponding to the motion of bisphenol-A unit and the diphenyl sulphone unit, respectively; indicating that the molecular motions responsible for τ transition in the case of polysulphones are more localized.¹⁵ In the case of polysulphone based on dichlorodiphenyl sulphone and bisphenol-A, only one transition at -80°C is observed, since the motion associated with each unit appears at the same temperature. Substitution of bisphenol-A by tetramethyl bisphenol-A leads to two peaks at temperatures corresponding to the motion of tetramethyl bisphenol-A and dichlorodiphenyl sulfone moieties, respectively. Substitution at the bridge and the ring carbon atoms in bisphenol-A as well as the replacement of bisphenol-A by naphthalene-based diols resulted in two distinct peaks corresponding to the motion of each unit.

As in the case of polycarbonates, the τ transition in polyarylates (see Fig. 2) is very broad. While this indicates that the τ transition in polyarylates may arise from more than one type of molecular motion, there is evidence that a major contribution comes from the phenyl ring mobility. For all the polyarylates based on bridge-substituted bisphenols (Table I, section A), the variation in τ transition temper-

ature is relatively small. If the τ transition were to result from the cooperative motion of all the monomer subgroups ($> \text{C}=\text{O}$, $> \text{C}(\text{CH}_3)_2$, and phenyl flip), the substitution of one of the methyl groups in polyarylate based on bisphenol-A by a bulky phenyl ring, as in the case of polyarylate based on bisacetophenone, should have affected the τ transition more drastically. In contrast, substitution on the phenyl ring by methyl groups, as in the case of polyarylates based on dimethyl bisphenol-A and tetramethyl bisphenol-A, shows a single peak resulting from the shift in the τ transition to higher temperature by approximately 150°C , as compared to that in the case of the bridge-substituted polyarylates. Molecular modelling studies also indicate that the bond rotations around the ester group and around the bridge carbon are relatively facile as compared to phenyl ring rotation.² These factors lead to the conclusion that the major contribution to τ transition comes from the phenyl ring mobility. NMR data on these polyarylates would further confirm this hypothesis.

Indirect evidence in support of the role of localized molecular motion (especially the phenyl ring mobility) in governing the τ transition is seen in Figure 6, in which the low-temperature dynamic mechanical spectra for bisphenol-A and phenolphthalein-based polyarylates are compared. The τ transition peaks in the three phenolphthalein-

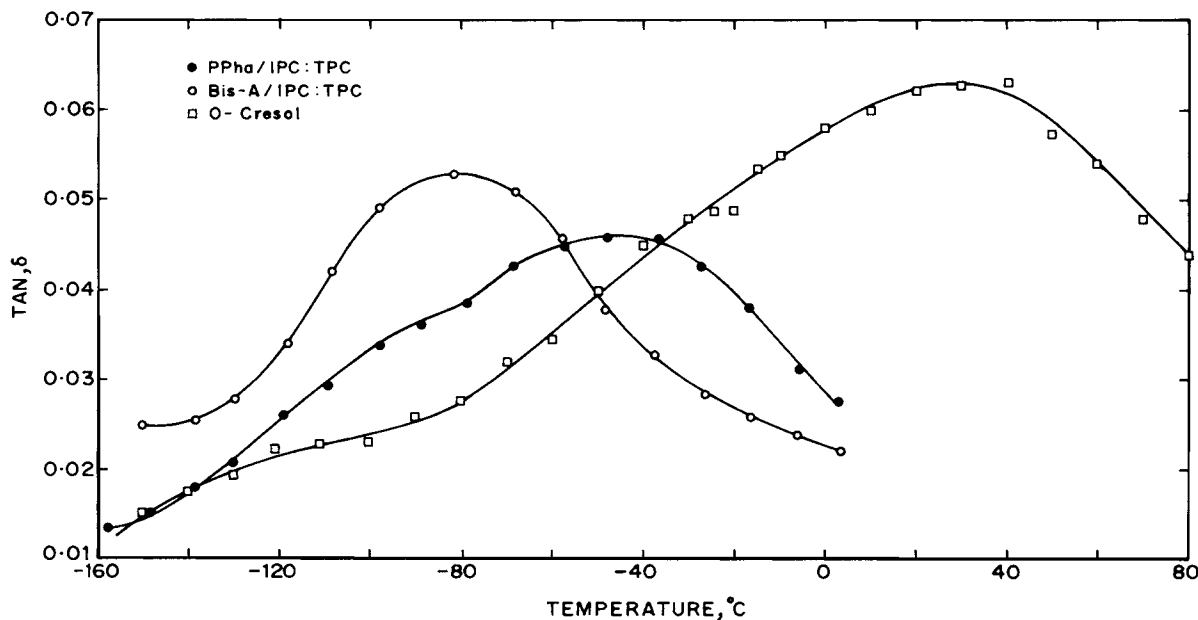


Figure 6 τ transition in (●) PPha/IPC:TPC (1 : 1); (○) Bis-A/IPC:TPC (1 : 1); and (□) *O*-cresolphthalein/TPC.

based polyarylates, viz. PPha/IPC, PPha/IPC:TPC (50 : 50) and PPha/TPC consist of a shoulder around -100°C , which is close to the peak maximum for the bisphenol-A polyarylate. This is accompanied by another peak maximum at -50°C (see Table I). In contrast, in polycarbonates, substitution by rigid and bulky groups in the isopropylidene unit of bisphenol-A results in a single peak close to -100°C , as in the case of bisphenol-A based polycarbonate. We believe that the τ transition temperature is determined mainly by the mobility of the phenyl ring. The resolution of the τ transition into the main peak and a shoulder results from the flip of the phenyl rings in two different environments caused by the orientation of the phthalide group toward one of the two phenyl rings in the bisphenol moiety. The rotation of the phenyl ring which is closer to the phthalide would be more restricted and result in τ transition at a higher temperature. The other peak would be close to the τ transition temperature observed in the case of the polyarylate based on bisphenol-A. This interpretation is also supported by the molecular modelling studies.²

In order to confirm that the splitting of the τ transition peak results from the incorporation of the phthalide ring and to verify the effect of ring substitution on the shift in τ transition temperature, DMA spectra of polyarylates based on *o*-cresolphthalein-TPC and tetrabromo bisphenol-A-IPC/TPC were investigated. Comparison of the DMA spectrum of *o*-cresolphthalein-based polyarylate with that of the polyarylate based on dimethyl bisphenol-A reveals that in both cases the τ transition is observed in the range of $32\text{--}38^{\circ}\text{C}$. This peak arises from the motion of the phenyl ring on which the methyl group is substituted and has therefore shifted to higher temperature. In the case of polyarylates based on tetrabromo bisphenol-A, the polarity of the bromo group results in a decrease in the *d* spacing to 4.14 \AA and a decrease in mobility. This peak is therefore shifted even further upwards, to 110°C .

In view of the flexibility of the ester linkage and the molecular size of the aromatic dicarboxylic acid unit, the transition corresponding to the motion of the acid unit is expected to appear below -100°C . This, however, was not detected; perhaps because it lies below -150°C , i.e., outside the temperature range over which the measurements could be made. It should be possible to identify these peaks if a bulkier dicarboxylic acid were to be used. Indeed, two sub- T_g peaks have been reported for naphthalene-based polyesters by Blundell and Buckingham.²²

CONCLUSIONS

The detailed study of molecular motions in polyarylates chosen on the basis of the site and the nature of the substituents is reported in this work. The variation in T_g can be correlated with the changes in the degrees of freedom in both the main chain as well as the side chain of the polymer, as predicted from the molecular modelling studies.²

The origin of the β transition in polyarylates has been established by studying the effects of specimen annealing and by activation energy measurements. It has been shown that the β transition originates from the defects in the polymer specimen.

The molecular motion responsible for τ transition in polyarylates is more localized than in the case of the polycarbonates. The major contribution to this transition comes from the motion of phenyl rings in the bisphenol moiety. The τ transition is shifted to higher temperature as a result of substitution on the phenyl ring and by the incorporation of the phthalide ring in the isopropylidene unit. The latter results in the splitting of the peak into two. The onset of pendent chain motions at the bridge carbon in polyarylates appears to be at temperatures below -150°C , which is beyond the temperature range scanned. The characterization of these motions by solid-state NMR would provide additional insight into the origin of molecular motions in polyarylates.

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