Dynamic mechanical properties of a polycarbonate/polystyrene copolymer: Effects of casting solvent

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(*Received* 23 *November* 1982)

Dynamic mechanical properties of three polycarbonates, of polystyrene and of a blend and a copolymer of polystyrene with one polycarbonate have been investigated. While the properties of the blend were found to be a simple combination of those of the constituent homopolymers, modified α-relaxation behaviour was found for the polystyrene chains in the copolymer. The modifications, dependent on the casting solvent and thermal treatments used in sample preparation, were found to correspond to enhancement of the segmental motions in polystyrene chains, in spite of their attachment to more rigid polycarbonate. The modifications have been attributed to incorporation of excess free volume during solvent casting. A mechanism is proposed which correlates the excess free-volume fractions with the solubility parameters of the casting solvents.

Keywords Polycarbonate; polystyrene; copolymer; casting solvent; free-volume model; dynamic mechanical properties

INTRODUCTION

We have previously developed and described a general procedure for synthesizing non-linear block copolymers, termed AB-crosslinked polymers (ABCPs), with controlled structures by linking chains of preformed polymer A with chains of a chemically different polymer B, formed *in situ*[1]. These materials are blends of A_2BA_2-type block copolymers with unreacted polymer A. The A and B constituents are normally immiscible and the polymers undergo microphase separation and, depending on composition and solvent casting conditions, may also exhibit macroscopic phase separation[2,3].

Recently, we described the tensile properties of an ABCP of a polycarbonate (PCarb-2, see *Table 1*) as A component and high-molecular-weight polystyrene (PSt) as B component[4]; the overall composition was 75% (w/w) PSt. A sample was cast as a film from homogeneous solution in dichloromethane. Electron microscopy established its morphology as a uniform dispersion of spherical PCarb domains (44 nm diameter), with a few large domains of PCarb homopolymer, in a PSt matrix. Inclusion of the PCarb introduced a yielding process and slightly toughened the PSt at ambient temperature. At temperatures above the glass transition temperature (T_g) of PSt the polymer behaved in a similar manner to conventional thermoplastic elastomers at ambient temperatures, i.e. the PSt chains acted as the elastomer and the PCarb domains provided physical crosslinks.

We are currently investigating the dynamic mechanical properties of multicomponent polymers, including ABCPs with low degrees of crosslinking of A chains by B chains (no gel fraction), using a Rheovibron viscoelastometer. In view of the novel tensile properties of the PCarb/PSt ABCP, referred to above, and the toughening effect of the PCarb we studied its dynamic mechanical properties. Here we describe the properties of that polymer cast from a variety of solvents, together with data for a series of PCarbs of different structure. The relaxation behaviour and the T_g of the PSt chains vary with the casting solvent and subsequent thermal history. Modifications to the relaxation behaviour are discussed in terms of the free-volume model for segmental motions and the solubility parameters of the PCarb, PSt and casting solvents.

EXPERIMENTAL

Materials

Three polycarbonates were synthesized by condensation polymerization of the appropriate bisphenols with phosgene. The polymers were formed from bisphenol-A, from 1,1,1-trichloro-bis-2-(*p*-hydroxyphenyl)ethane and from an equimolar mixture of the two bisphenols; the polymers are designated in *Table 1*. The sample of PCarb-2 used in this investigation had $\bar{M}_n = 14$ kg mol^{-1} and $\bar{M}_w/\bar{M}_n = 2.1$. The PSt homopolymer had a number-average molecular weight of 150 kg mol^{-1}, approximately.

The PCarb-2/PSt ABCP used was the same polymer as used in a preceding study and had been prepared by crosslinking chains of PCarb-2 ($\bar{M}_n = 16$ kg mol^{-1}) with PSt ($\bar{M}_n \sim 257$ kg mol^{-1}); the synthetic procedure has been summarized elsewhere[5]. The relative crosslinking index (the number of junction points per weight-average A chain) was less than 0.7 and the overall composition was 75% (w/w) PSt.

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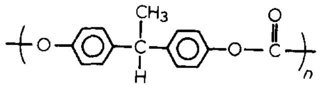
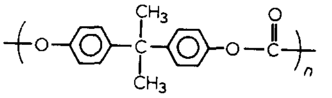
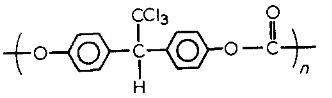
0032-3861/83/091171-09$03.00

Table 1 Structures and properties of polycarbonates

Structure	Code	Transition temperatures (°C)			Ref.
		T_α	T_β	T_γ	
 (I)	PCarb-1	130[a]	70[b]	−100[b]	8, 9
 (II)	PCarb-A	150[c]	80[c]	−100[c]	7
50:50 copolymer of (II) and (III)	PCarb-3	220	102	−76	This work[d]
 (III)	PCarb-2	240	138	−72	This work[d]

[a] Dilatometric measurements
[b] Tensile measurements, 35 Hz
[c] Torsion pendulum, 1 Hz
[d] Tensile measurement, 110 Hz ($T_{E''_{max}}$)

As in our previous study, samples were cast slowly from dilute (~2% (w/v)) homogeneous solution, to form films 0.15–0.2 mm thick; the initial rate of solvent loss was approximately 1% h^{-1}. In the later stages, samples were dried under vacuum (~1 Torr) at 25°C for 10 days, and the temperature was then increased gradually to and maintained at 90°C with the sample under vacuum for 24 h or until constant weight was achieved. To check on residual solvent content and to reveal any effects of annealing at higher temperature, some samples were further annealed under vacuum at 125°C.

Instruments

Electron micrographs were obtained using a JEM-7 transmission microscope (Nippon Denshi Ltd, Tokyo) operating at an accelerating voltage of 100 kV. Ultra-thin sections were cut on an ultramicrotome (LBK Mk III); the sections were unstained[3].

Dynamic mechanical properties (tensile storage (E') and loss (E'') moduli and tan δ) were measured using a Rheovibron viscoelastometer CCV-IIC (Toyo Baldwin Ltd, Tokyo). Samples (dimensions 0.15 × 2 × 30 mm, approx.) were cut from the cast films. Measurements were made at an operating frequency of 110 Hz over the temperature range −150° to 250°C using a heating rate of 1.5°C min^{-1} with the samples in a nitrogen atmosphere; some measurements were made using lower operating frequencies.

Tensile properties were also measured using an Instron TSM universal tensile tester as described previously[4].

RESULTS AND DISCUSSION

Dynamic mechanical spectroscopy

(i) *Pure polymers. Figure 1* shows the temperature dependences of storage modulus (E') and loss tangent (tan δ) at 110 Hz for PSt and three PCarbs. The glass transition temperature, defined as the maximum of the E''–temperature curve ($T_{E''_{max}}$), for PSt cast from dichloromethane solution was observed at 122°C; the maximum of the tan δ–temperature curve was not obtained. A small secondary transition, which has previously been observed and attributed to local oscillation modes of the backbone chain[6], is apparent at about 80°C.

In contrast to PSt, PCarbs, including PCarb-2 which has a very high T_g (*Table 1*), are tough polymers. For the PCarb-2 used in this work and cast from dichloromethane solution we obtained an ultimate tensile strength of 72.5 MN m^{-2} with 30% extension to break.

According to Yee and Smith[7], PCarbs normally exhibit three dynamic mechanical relaxation processes designated α, β and γ; the primary α-relaxation corresponds to the glass–rubber transition. We have also observed three relaxation processes in each PCarb; transition temperatures ($T_{E''_{max}}$) are quoted in *Table 1*, together with some literature data. Glass transition temperatures of the

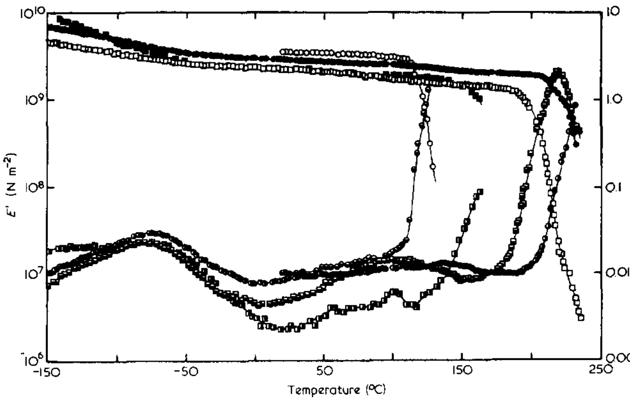


Figure 1 Dynamic mechanical properties of PSt (E', ○; tan δ, ◒), PCarb-A (E', ■; tan δ, ◨), PCarb-2 (E', □; tan δ, ⬓) and PCarb-3 (E', ●; tan δ, ◑) cast from dilute solution in dichloromethane

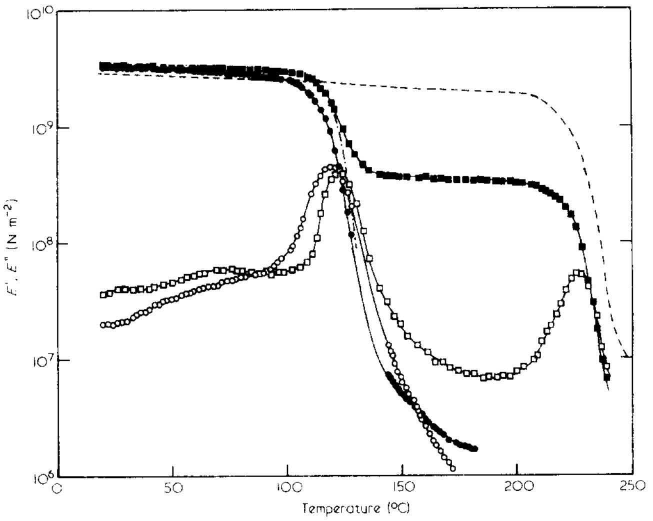


Figure 2 Dynamic mechanical properties of a PCarb-2/PSt blend containing 75% (w/w) PSt (*E'*, ■; *E''*, □) and for a PCarb-2/PSt ABCP of the same overall composition (*E'*, ●; *E''*, ○). Also indicated are *E'* data for PSt (–·–) and PCarb-2 (---) taken from *Figure 1*. All samples were cast from dilute solution in dichloromethane

chlorinated PCarbs (PCarb-2, PCarb-3) are very high compared with that of PCarb-A and other non-chlorinated PCarbs. The transition temperature for PCarb-2 at 110 Hz (240°C) is comparable to that determined by Wielgosz and Porejko[10] at low frequencies (~220°C). Dynamic mechanical measurements were also made at lower frequencies and, from transition maps, the apparent activation energies for the α-relaxations in PCarb-A and PCarb-2 were found to be 462 and 798 kJ mol^{-1}, respectively.

γ-relaxations in non-chlorinated PCarbs are normally observed at low temperatures, about −100°C, and the intermediate β-relaxations are normally small and broad[7]. We observed the γ-relaxations in chlorinated PCarbs at about −75°C and β-relaxations in PCarb-2 and PCarb-3 at 138° and 102°C, respectively. The secondary relaxations have been attributed to motions of phenyl groups[8], carbonate groups[11] or of the whole monomer unit[7]. Intensities of the secondary relaxation peaks in the chlorinated PCarbs are low, while the relaxation temperatures (peak maxima) increase with chlorine content. These facts, together with increased activation energies for α-relaxations, indicate that all molecular motions in the chlorinated PCarbs are more restricted than in the non-chlorinated PCarbs, probably because of steric hindrance associated with the trichloromethyl groups. PCarb chains constructed from space-filling models confirm the existence of severe steric hindrance in the vicinity of the chloromethyl groups.

(ii) *Blends.* Films of PCarb-2/PSt blends were prepared by mixing dilute solutions of individual polymers in dichloromethane; the initial mixtures were homogeneous. PCarb-2 and PSt are immiscible in bulk[3]. Consequently, as solvent was removed from the homogeneous solution and the total polymer content increased, macroscopic phase separation occurred and droplets readily coalesced. Because of the relative densities of the two polymers ($\rho_{PSt} = 1.04\,g\,cm^{-3}$; $\rho_{PCarb\text{-}2} = 1.43\,g\,cm^{-3}$) the final films consisted of an upper layer of PSt and a lower layer of PCarb-2.

Figure 2 presents dynamic mechanical data for a blend film containing 75% (w/w) PSt and shows transitions corresponding to the glass transitions of the constituents. The high moduli (*E'* and *E''*) between the primary transitions reflect the continuity of the PCarb in the stress direction in the laminated film. Experimental values of *E'* are consistent with values calculated from the moduli of the constituents using the Takayanagi parallel model[12]; at 140°C the observed and calculated moduli are 0.40 and 0.44 GN m^{-2}, respectively.

(iii) *ABCP.* Under the sample preparation conditions employed, the PCarb-2/PSt ABCP did not undergo macroscopic phase separation[3] but formed a macroscopically uniform, transparent film[4]. *Figure 3* is a transmission electron micrograph of an unstained, ultra-thin section of the ABCP and shows a PSt matrix with a dispersion of small, spherical PCarb domains (diameter ~45 nm); the apparently high volume fraction of PCarb (actual 19.6%) is a consequence of using relatively thick sections. This morphology is almost identical with that in the samples used previously to study the tensile properties of this ABCP (PCarb domain diameters, 44 nm).

Included in *Figure 2* are the variations in *E'* and *E''* with temperature for the PCarb-2/PSt ABCP cast from dichloromethane solution under conditions identical with those used to prepare the blend. The major relaxation at ~120° is attributed to the α-relaxation of the PSt matrix. A relaxation corresponding to the glass transition of the PCarb was not observed because of the dominating influence of the PSt and consequently low value of *E'* at high temperatures; the modulus–temperature curves are consistent with the observed morphology and continuity of a rubbery microphase above 140°C. Values of *E'* at temperatures between the T_gs of the constituents vary with both the overall composition of the ABCP[13] and the nature of the casting solvent (see also *Figure 5*).

It may be noted from *Figure 2* that, while $T_{E''_{max}}$ for the α-relaxation of PSt in the blend is at the same temperature as that in pure PSt, the temperature of the corresponding maximum for the ABCP is shifted. In effect, T_g of the PSt in the ABCP has shifted to a lower temperature and the breadth of the transition has increased.

The magnitudes of the modifications to the relaxation

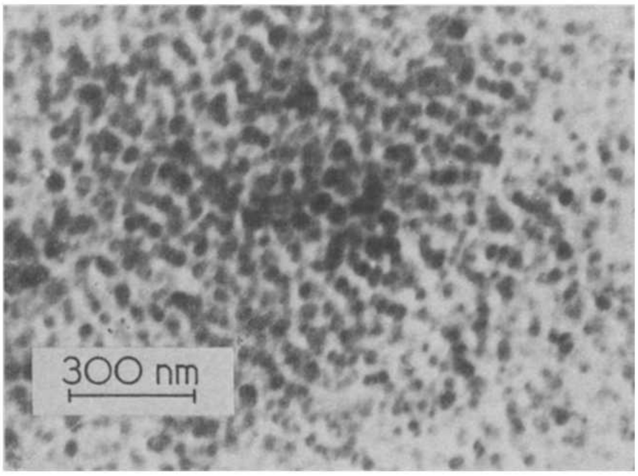


Figure 3 Transmission electron micrograph of an ultra-thin section (unstained) of the PCarb-2/PSt ABCP (75% w/w PSt). The spherical domains are PCarb

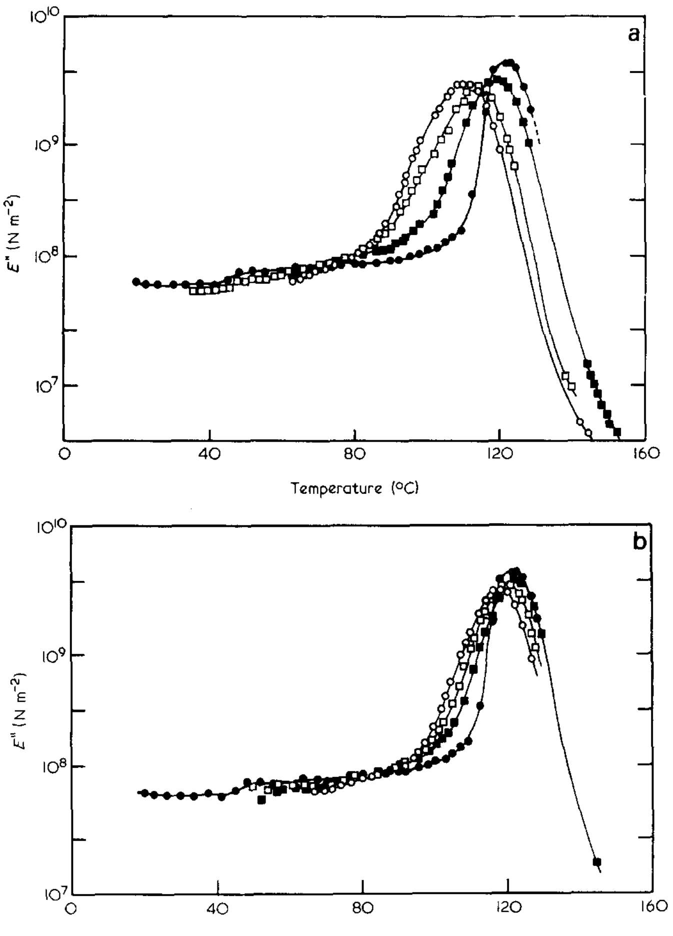


Figure 4 Variations in E'' with temperature for a PCarb-2/PSt ABCP cast from dichloromethane (■), butan-2-one (□) and tetrahydrofuran (○) and for PSt cast from dichloromethane (●). Samples were annealed at (a) 90°C and (b) 125°C

behaviour of the PSt chains are dependent on the casting solvent and on the annealing conditions. *Figure 4* presents variations in E'' with temperature, over a limited temperature range, for the ABCP cast from three different solvents and for two different annealing conditions for each solvent used. The solvents employed in preparing the samples responsible for the data in *Figure 4* are all good solvents for both PSt and PCarb and, qualitatively, all produce similar modifications to the relaxation behaviour.

In contrast, *Figure 5* shows variations of E' and E'' with temperature for the ABCP cast from a mixture of dichloromethane and acetone (30/70 v/v) which initially gives a homogeneous solution but during casting becomes a preferential solvent for PCarb as the dichloromethane evaporates at a faster rate than acetone. For this sample, annealed at 90°C, $T_{E''_{\max}}$ is identical with that of PSt homopolymer and of PSt in the blend (*Figure 2*). When annealed at 125°C there was no shift in $T_{E''_{\max}}$ from that of the blend or PSt homopolymer.

Modified relaxations in polystyrene chains

It is clear from the data in *Figures 2* and *4* that the relaxation behaviour and, hence, the development of segmental motions with temperature of the PSt chains in the ABCP are different to those of PSt homopolymer and of PSt in the blend. Irrespective of casting solvents or annealing conditions employed, the observed modifications correspond to reductions in $T_{E''_{\max}}$ and to increases in the breadth of the relaxation peak, extending the peaks to lower temperatures. That is, segmental motions in PSt chains occur at lower temperatures in the ABCP than in homopolymer or in the blend. A comparison of the data obtained from PSt homopolymer, from the blend and from the ABCP, all cast from dichloromethane under identical conditions, demonstrates that these changes in behaviour must, in some way, be a consequence of the attachment of PCarb and PSt chains.

The above observations contrast with the results of many other studies of multicomponent polymers. In the simplest systems the properties of composites are a superposition of the properties of the constituents; T_gs are at the same temperatures as in the pure constituents. Frequently, however, T_gs are shifted to intermediate temperatures between those of the constituents[14–18]. Such shifts have been attributed to partial mixing of the components[14–17]. Various relations exist for estimating glass transition temperatures of mixed regions and all predict transition temperatures between those of the constituents. Attempts have been made to estimate the compositions of mixed regions from the transition temperatures; in some cases distributions of compositions in the vicinities of interfaces have been suggested[15,17]. We have also observed enhanced segmental motions in chains when attached to a more mobile component (i.e. lower T_g) and retarded motions when attached to a more rigid component[19]. All these effects would be expected to increase T_g or otherwise reduce molecular motions of PSt chains in the ABCP. However, in this work we have observed enhanced molecular motions in PSt when attached to PCarb chains which have a higher T_g.

Before definitely attributing the enhancements in molecular motion in PSt chains to their attachment to PCarb we must exclude possible trivial reasons for these effects. Enhanced molecular motions are often attributed to inclusion of additional free volume and, in the present context, there are two potential trivial causes. The first is free volume associated with PSt chain ends. This effect can be discounted because the PSt is of high molecular weight ($\bar{M}_n = 175\,\mathrm{kg\,mol^{-1}}$)[4] and for most PSt chains both ends are attached to PCarb chains, because the propagating

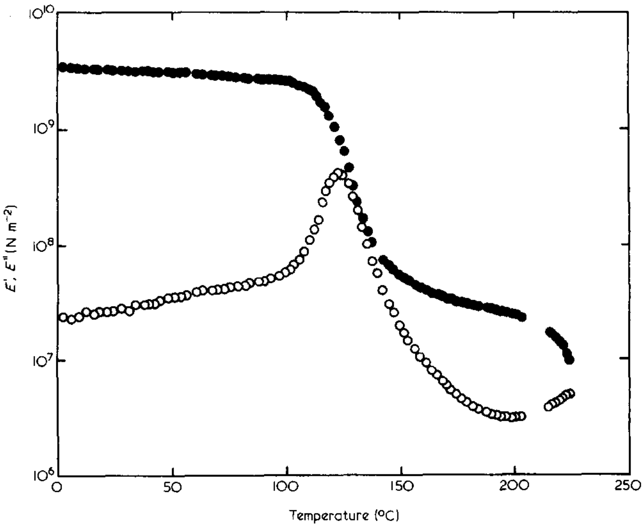


Figure 5 Variations in E' (●) and E'' (○) with temperature for a PCarb-2/PSt ABCP cast from dilute solution in acetone/dichloromethane (70/30 v/v)

Table 2 Influence of sample history on transition temperatures

Casting solvent	T_b (°C)	T_f (°C)	$\Delta T_{E''_{\max}}$ [a] (°C)	W_d	Δw_d Calc.	Δw_d Obs.[b]
Acetone	56.5	−94.7	–	–	–	–
Dichloromethane	39.8	−95.1	2.0	0.0034	0.0025	0
Butan-2-one	79.6	−86.4	6.5	0.0106	0.006	0.002
Tetrahydrofuran	66	−108.5	8.0	0.0140	0.007	0.002
Dichloromethane/acetone (30:70)	–	–	0	0	0	0

[a] Change produced by annealing at 125°C
[b] ±0.001

PSt radicals terminate by radical combination. Both effects would be expected to reduce available free volume. Also, the chains in the ABCP are identical irrespective of casting solvent.

The second effect to be discounted, which is of concern in all solvent-cast materials, is the presence of residual solvent. Care was taken to ensure that PSt homopolymer, the blend and the ABCP, cast from dichloromethane, were all cast under identical conditions so that their residual solvent contents should be comparable. Nevertheless, while the relaxation behaviours of PSt in the homopolymer and blend are the same, that of PSt in the ABCP is different. To verify that residual solvent was not responsible for the observed behaviour, samples were further annealed to constant weight at 125°C (3 h) under vacuum; no sample cast from dichloromethane showed any weight loss on annealing at 125°C. Additional annealing produced no change in relaxation behaviour in the PSt homopolymer or in the blend but in the ABCP $T_{E''_{\max}}$ increased and the breadth of the relaxation peak decreased (*Figure 4*).

Small weight losses associated with annealing the PCarb/PSt ABCP cast from other solvents are summarized in *Table 2*. Consequent modifications to molecular motions for samples cast from the non-selective solvents can be seen by comparing *Figures 4a* and *4b*; the additional annealing produces increases in the temperatures of $E''_{\max}$ ($\Delta T_{E''_{\max}}$ in *Table 2*) and decreases in the breadths of the transition. There was no change in behaviour when the sample cast from dichloromethane/acetone was annealed at high temperature.

Assuming free-volume additivity, the T_g of a polymer in the presence of a diluent may be estimated using the Kelley–Beuche equation[20]:

$$T_g = \frac{\alpha_p T_{gp} V_p + \alpha_d T_{gd} V_d}{\alpha_p V_p + \alpha_d V_d} \qquad (1)$$

where αs are the differences in coefficients of volume expansion of liquid and glass, *V*s are volume fractions and subscripts *p,d* refer to pure polymer and diluent respectively. For PSt we take $\alpha_p = 3\times10^{-4}\,^{\circ}\mathrm{C}^{-1}$,[21] $T_{gp} = 122°\mathrm{C}$ and for all solvents $\alpha_d = 10^{-3}\,^{\circ}\mathrm{C}^{-1}$.[22] As values of T_g for solvents we use melting points (T_f) quoted in the literature[23]; these are presented in *Table 2* along with the boiling points of the solvents (T_b). Using the above parameters we calculated the weight fractions of solvent which, according to equation (1), should have been retained (W_d) to reduce the T_g of PSt by the observed shifts in $T_{E''_{\max}}$, assuming uniform distribution of solvent in PSt and PCarb, and which should have been lost on subsequent annealing at 125°C (Δw_d) to produce the observed increases in $T_{E''_{\max}}$, assuming solvent was lost from the PSt regions only; these quantities are quoted in *Table 2*.

Although the small solvent losses detected on annealing some samples at 125°C might cause some increase in $T_{E''_{\max}}$, discrepancies between the observed weight losses and those calculated to be necessary to produce the observed shifts in $T_{E''_{\max}}$ suggest that residual solvent is certainly not the prime reason for the low values of $T_{E''_{\max}}$ observed. Calculated values actually underestimate amounts of solvent which would have had to have been lost on annealing since no account was taken of solvent loss necessary to decrease the width of the transition (assuming the intensity at the low-temperature side of the relaxation peak is due to additional free volume associated with excess solvent). Also, calculated values of Δw_d assumed solvent loss from PSt only with no solvent loss from the PCarb, which is probably unrealistic.

Had residual solvent been primarily responsible for the shifts in $T_{E''_{\max}}$, we might have expected that, in all cases, solvent would have been lost until the PSt glassified and, since solvent was removed under the same conditions in all samples, that the same T_g or rate of molecular motion would be observed in each sample, which is patently not true. Alternatively, it could be argued that it would be more difficult to remove the higher boiling solvents but the sample cast from dichloromethane/acetone mixture had a higher $T_{E''_{\max}}$ than the sample cast from dichloromethane alone. Therefore, we conclude that modifications to the molecular motions in PSt chains are, in some way, a consequence of their attachment to PCarb and that the extent of these modifications is dependent on sample history.

Free-volume model

In an attempt to identify the origin of enhanced molecular motions in the ABCP we shall adopt the free-volume approach to glass transitions. We are not justified in assuming that the T_g, however defined, corresponds to a state of iso-free volume universal for all polymers[24]. However, we might expect that, for our PCarb/PSt ABCP, T_g for the PSt chains at equilibrium should occur under iso-free-volume conditions, irrespective of the method of sample preparation. Further, because of the correspondence of T_gs ($T_{E''_{\max}}$) of PSt homopolymer, PSt in the blend and PSt in the ABCP cast from dichloromethane/acetone, we shall assume the iso-free-volume concept applies to all PSt chains encountered in this study. Shifts in T_g and modifications to relaxation behaviour will be considered in terms of additional free-volume fractions (Δv_f) relative to that at the normal T_g of PSt, T_{g0}.

Table 3 Influence of casting solvent on associated free volume

Casting solvent	Solubility parameter $(\mathrm{J\,cm^{-3}})^{1/2}$	Annealing temp. (°C)	$T_{E''_{max}}$ (°C)	$10^3\Delta v_f$ (for peak shift)	$10^3\Sigma\Delta v_f$ (from *Figure 8*)	Excess free volume lost on annealing at 125°C (%)
Acetone	20.25	–	–	–	–	–
Dichloromethane	19.84	90	119	0.9	1.67	58.1
		125	122	0	0.71	
Butan-2-one	19.02	90	113	2.7	3.5	58.1
		125	120	0.6	1.45	
Tetrahydrofuran	18.61	90	110	3.6	4.47	53.0
		125	118	1.2	2.10	
PCarb	20.35[a]					
PSt (cast from dichloromethane)	18.32[a]	90	122			
		125	122			

[a] Calculated according to Small's method[26]

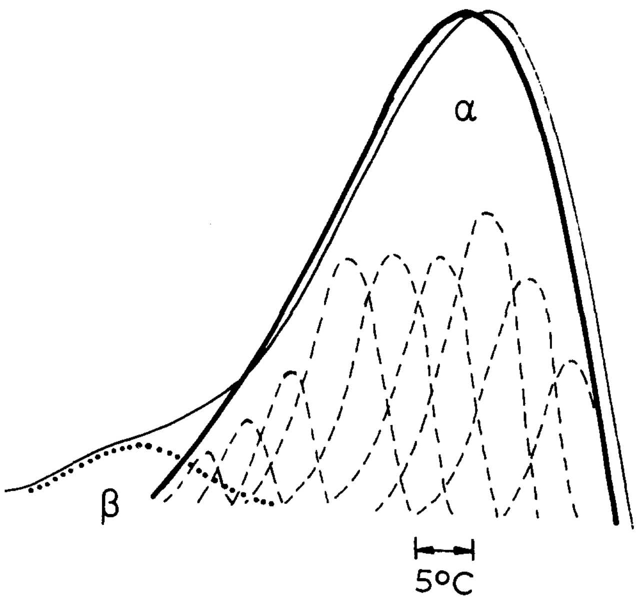


Figure 6 Schematic representation of the isolation of the α-relaxation peak of PSt in the ABCP, from the influence of the PSt β-relaxation and the influence of PCarb, and its decomposition into 'shifted' relaxation peaks as described in the text

Whichever definition of free volume V_f for the unperturbed polymer with glass transition temperature T_{g0} is employed[24], it can be shown that if additional free volume ΔV_f is added to the total volume V_g at T_{g0} then the glass transition temperature of the modified polymer (T_g') is related to the additional free-volume (Δv_f) by

$$\Delta v_f = \Delta V_f / V_g = \alpha(T_{g0} - T_g') \qquad (2)$$

assuming that coefficients of expansion of normal and modified polymers are identical both above and below T_g. On the basis of equation (2) the shifts in $T_{E''_{max}}$ for PSt chains in the ABCP cast from dichloromethane and from tetrahydrofuran, dried by heating to 90°C, correspond to $\Delta v_f = 9\times10^{-4}$ and 3.6×10^{-3}, respectively; these increases compare with the commonly assumed free-volume fraction at T_{g0} (V_f/V_g) of 2.5×10^{-2}. Values of $T_{E''_{max}}$ and corresponding values of Δv_f for various samples are collected in *Table 3*.

Small increases in free volume, as estimated above, might be expected to cause simple shifts of the α-relaxation peak if the additional free volume is uniformly distributed. However, the broadened relaxation peaks reflect a broader distribution of relaxation times for PSt chains in the ABCP than in the homopolymer. Manabe *et al.*[25] observed broader relaxation peaks in polyblends than in the constituent homopolymers and attributed the modified behaviour to changes in the free-volume distribution and, hence, to a distribution of T_gs. Following the same approach, we attribute the increased breadths to enhanced motions at low temperatures and consider the idea that this effect is a consequence of increased free volume resulting from less efficient packing of PSt chains in the ABCP than in homopolymer.

As a model, Manabe *et al.*[25] assumed that the blends were divided into a large number of small volume elements with different associated free volumes; minimum dimensions for the elements were taken to be those necessary for it to exhibit independent properties—probably several nanometres. We also assume that the PSt in the ABCP is divided into volume elements, the T_gs of which are determined by the local free-volume fraction according to equation (2), and that in each volume element the distribution of relaxation times is the same as that in PSt homopolymer at an equivalent temperature to its T_g.

If this model is realistic the PSt would probably have a continuous variation in local free volume. However, to simplify the estimation of excess free volumes involved, we assume that the free-volume changes are discontinuous and that the PSt is divided into distinct volume elements the T_gs of which are separated at intervals of 5°C. This situation is represented schematically in *Figure 6* which depicts a portion of the E''–temperature curve for an α-relaxation of PSt chains in an ABCP (thick solid line) and a series of superimposed curves (broken lines) which have the same shape as the E''–temperature curve for PSt, the peaks of which are separated at 5°C intervals and, in combination, give the thick curve. The relative heights of the small peaks are assumed proportional to volume fractions of PSt associated with the appropriate T_g and free volume.

To perform the analysis it was necessary to isolate the α-relaxation peak from other components. First, as depicted in *Figure 6*, the small β-relaxation for PSt (dotted line) was subtracted from the total E'' peak (thin solid line) assuming that the β-relaxation peak is approximately symmetrical. Secondly, it was necessary to remove the influence of the PCarb which causes a small apparent shift in peak temperature for PSt as an inevitable consequence of its inclusion, i.e. a blending effect of a polymer with a high T_g.

The properties of multicomponent polymers may be estimated from the properties of the components using procedures developed by Takayanagi[12] who proposed that the complex modulus E^* of a composite material formed from two polymers 1,2 is given by:

$$\frac{1}{E^*}=\frac{\phi}{\lambda E_2^*+(1-\lambda)E_1^*}+\frac{1-\phi}{E_1^*} \qquad (3)$$

where E_1^*, E_2^* are the complex moduli of the components and ϕ, λ are parameters determined by the morphology and composition of the composite. To effect the required separation we have applied the Takayanagi procedure in reverse. We determined the storage and loss moduli of the ABCP (E',E'') and subtracted the contribution for PCarb assuming 25% (w/w) spherical PCarb inclusions, i.e. $\phi=0.379$, $\lambda=0.52$, $\phi\lambda=0.25$. This calculation assumed that the relaxation behaviour of the PCarb in the ABCP is unmodified. As depicted in *Figure 6*, this procedure gave a peak for the PSt α-relaxation (thick solid line) the peak of which is shifted very slightly from that of the ABCP.

The above procedure gave a series of α-relaxation peaks for the PSt chains in the ABCP cast from different solvents. Representative results (for $E''>3\times10^7\,\mathrm{N\,m^{-2}}$) for samples cast from dichloromethane and tetrahydrofuran are shown in *Figure 7* (solid lines). The E'' peaks were then subdivided into smaller peaks with the same shape as the α-relaxation peak for PSt homopolymer, as outlined above and as depicted in *Figure 6*. Recombining the small peaks gave peaks (broken lines) in reasonable agreement with the originals, *Figure 7*. Better agreement could have been achieved by subdividing the originals into a larger number of peaks approximating to a continuous distribution.

In performing these calculations we assumed that the total E'' peak is a simple summation of all the separate, shifted E'' peaks. To be strictly consistent, since all these volume elements form part of the same composite structure, we should effect the subdivision of the E'' peaks using procedures based on mechanical models. At this stage we have insufficient information to do this reliably. Not only do we have no *a priori* knowledge of the volume fractions of the separate volume elements, we also have no knowledge of the location or form of those elements. Hence, we cannot assume realistic values of ϕ and λ for each element. However, we are currently only interested in producing a semi-quantitative estimate of the amounts of PSt which have modified properties and in identifying trends in behaviour. We can, therefore, only make comparisons between similar materials. Consequently, we have not performed the analysis on the sample cast from acetone/dichloromethane because its properties are quite different, in that values of E' above 120°C are high compared with other samples and this must be a consequence of some as yet unidentified morphological difference and connectivity of the PCarb component.

The estimated distributions of free volumes in PSt chains are presented in *Figure 8* where volume fractions of PSt (derived from peak heights) with appropriate T_g and free volume are plotted as a function of additional free-volume fraction Δv_f, expressed as a percentage of the volume of unmodified PSt at T_{g0}. Successive data points correspond to additional shifts of 5°C in T_g (assuming $\alpha=3\times10^{-4}$). Thus, *Figure 8* provides a semi-quantitative description of the amount and distribution of excess free volume in the PSt component of the ABCP cast from dichloromethane, butan-2-one and tetrahydrofuran and heated under different conditions.

In general, the volume fractions of PSt with excess associated free volume decrease monotonically as the additional free-volume fraction increases, except for low volume fractions associated with $\Delta v_f=1.5\times10^{-3}$. These low free-volume fractions may have been accentuated by the simplicity of the model adopted and may be less apparent if smaller increments of T_g, approximating to a continuous distribution of T_gs, had been used in the calculation.

For all samples the analysis indicates that some volume fraction of the PSt has no additional associated free volume. These volume fractions are very dependent on the casting solvent, especially for samples heated to 90°C (*Figure 8a*). The analysis also indicates that those samples which have the largest shift in T_g have some volume fraction associated with $\Delta v_f=10^{-2}$, almost a 50% increase over the associated free-volume fraction of 0.025 commonly attributed to polymers at T_{g0}. Total additional free-volume fractions ($\Sigma\Delta v_f$) associated with the PSt were

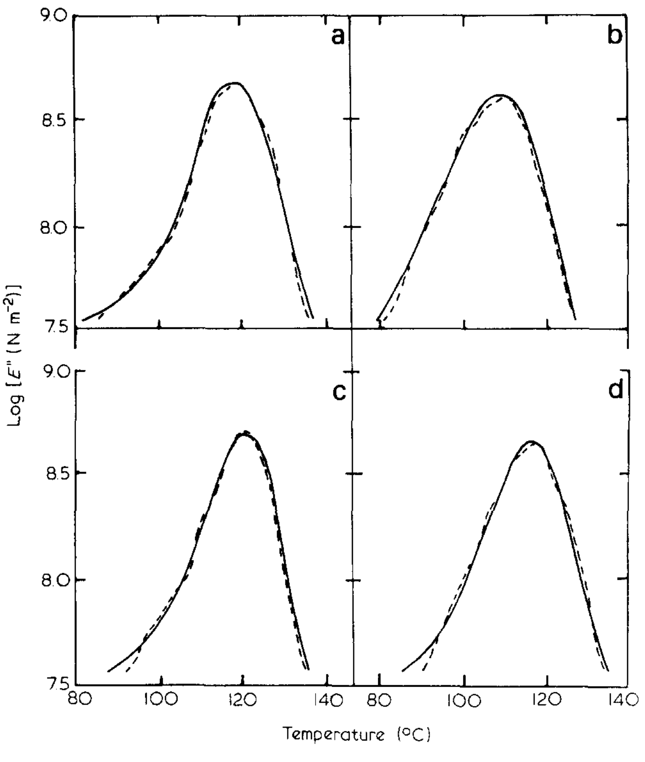


Figure 7 α-relaxations for PSt chains in the ABCP. Solid lines represent peaks isolated from the β-relaxation and from the influence of PCarb. Broken lines represent the sum of the 'shifted' α-relaxation peaks attributed to regions with different free volumes. Parts (a), (b) are for samples heated to 90°C and (c), (d) for samples annealed at 125°C; (a) and (c) are for the ABCP cast from dichloromethane and (b), (d) for the sample cast from tetrahydrofuran

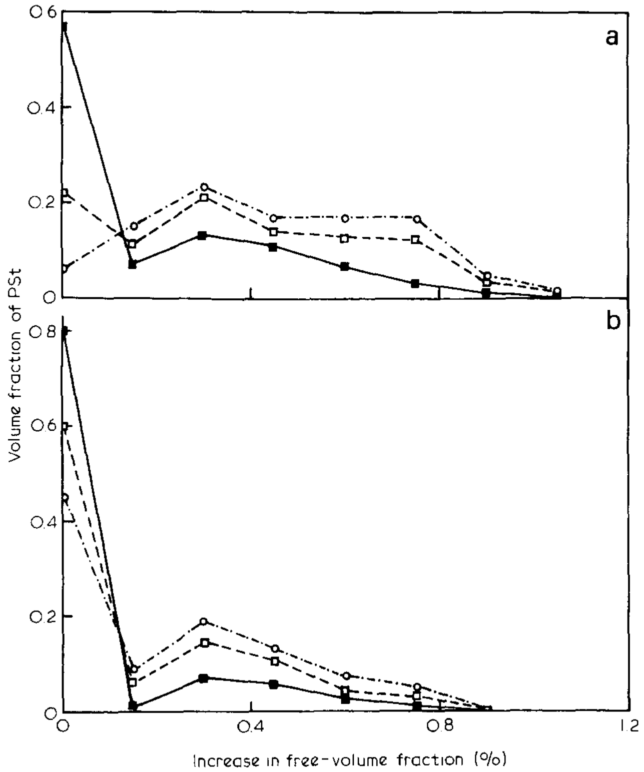


Figure 8 Volume fractions of PSt associated with excess free volume as a function of the percentage increase in free volume. (a) Samples heated to 90°C, (b) samples annealed at 125°C. Samples cast from dichloromethane (■———), butan-2-one (□– – –) and tetrahydrofuran (○–·–)

calculated from data in *Figure 8* and the results are collected in *Table 3*. While the total excess free-volume fractions vary considerably they are, in all cases, small compared with 0.025.

Heating samples at 125°C considerably reduces the additional associated free volume. From a comparison of *Figures 8a* and *b* it is obvious that the volumes of PSt associated with relatively large excess free volumes are decreased markedly and there are large increases in the volume fractions associated with no additional free volume. These effects combine to reduce the widths of the relaxation peaks and to shift $T_{E''_{\max}}$. Further, the values of $\Sigma\Delta v_f$ in *Table 3* show that for each solvent the estimated proportion of excess associated free volume lost is remarkably constant (53–59%) in view of the simplicity of the model used.

Solubility parameters

We note that solvent-cast ABCPs do not adopt equilibrium properties or, presumably, equilibrium morphologies in terms of chain packing because the properties and associated free volumes of the films (a) are dependent on the casting solvent and (b) may be modified by annealing. Departures of the relaxation behaviour of PSt chains in the ABCP from that in homopolymer or blend must be a consequence of their attachment to PCarb. It is widely accepted that the local environments of chains in the vicinities of interfaces in copolymers will be different to that in bulk homopolymer. Usually it is assumed that some mixing of the components will occur in the interfacial region. Interfacial thicknesses and compositions could, as required by the experimental observations, be expected to depend on the casting solvent. However, there is no evidence that PCarb is mixed with PSt in the interfacial regions because this would be expected to retard molecular motions in PSt chains, whereas enhanced motions are found experimentally.

A comparison of the solubility parameters of the casting solvents and the values of $T_{E''_{\max}}$ (*Table 3* and *Figure 4*) indicates a possible origin for the observed effects. Dichloromethane, butan-2-one and tetrahydrofuran are all reasonably good solvents for both components while acetone (and, presumably, the acetone-rich mixture produced during solvent casting from acetone/dichloromethane) is a selective solvent for PCarb-2. As we progress through the series tetrahydrofuran, butan-2-one, dichloromethane and acetone/dichloromethane we note that the solubility parameter increases, the breadth of the E'' peak and associated free volume decrease, $T_{E''_{\max}}$ increases and, generally, the relaxation behaviour of the PSt component becomes more like that of PSt even though the solubility parameter of PSt is lower than those of all solvents used and that of PCarb-2 is higher than that of all the solvents. That is, the worse the casting solvent is for PSt the more normal is the relaxation behaviour of the PSt.

We can reconcile the observed changes in free volume and relaxation behaviour with casting solvent in the following way. Consider, first, casting from tetrahydrofuran, which is the worst solvent for PCarb-2 and the best for PSt. As solvent is removed and the PSt and PCarb start to segregate we expect solvent to be preferentially associated with PSt. The PCarb chains will tend to aggregate into domains and become immobilized while the PSt chains will be solubilized and mobile. Thus, aggregation of PCarb will dominate the development of the morphology and will control the number of PSt–PCarb junction points per unit area of the domain–matrix interface. Therefore, as the remainder of the solvent is lost, primarily from the PSt, little if any reorganization of PCarb will be possible. Hence, the ends of the PSt chains will be fixed in space at predetermined points on the PCarb domains. We suggest that consequences are incomplete space-filling in the vicinity of the PSt–PCarb interface and incorporation of excess free volume in the PSt component.

Moving through butan-2-one, which represents an intermediate situation, to dichloromethane, a better solvent for PCarb than for PSt, the reverse situation applies. In this case the PSt chains will tend to aggregate first while the PCarb chains will be associated with relatively large proportions of solvent. The PSt chains will adopt the most favourable conformations possible, i.e. those closest to random coils; this process will be relatively unhindered because of the mobility of the PCarb chains and, hence, the junction points. Therefore, on aggregation, the PSt chains will incorporate less excess free volume and, in the dry film, will exhibit relaxation behaviour closer to that of normal PSt. We might anticipate that under these circumstances modifications to the relaxation behaviour of PCarb would be apparent. This is unlikely in the present study in view of the low content of PCarb and the fact that some of that PCarb is homopolymer, which would probably minimize such effects.

The above ideas reach an extreme situation in the acetone/dichloromethane cast sample. As the dichloromethane evaporates preferentially, the solvent system will become a non-solvent for PSt which will, essentially, precipitate, while the attached PCarb and PCarb homopolymer will remain in solution. Thus PSt chains will pack in their most favourable conformations, subject to slight residual constraints, while the volume fraction of the PCarb/acetone 'phase' might remain sufficiently high to bring about a change in morphology and some continuity of the PCarb component in the dry film.

CONCLUSIONS

The dynamic mechanical properties of three PCarbs and PSt and certain multicomponent polymers based on these components have been studied. The properties of a blend of PSt and PCarb-2, a chlorine-containing PCarb, are consistent with the properties calculated using the Takayanagi parallel model, applicable to the laminate formed as a result of phase separation during casting from dichloromethane solution.

A PCarb-2/PSt copolymer (75% w/w PSt) was cast from several solvents. Investigation of the dynamic mechanical properties of that polymer identified modifications to the relaxation behaviour of the PSt chains, compared with those in the homopolymer or in the blend.

Differences in the dynamic mechanical properties of multicomponent polymers cast from different solvents have been noted by other workers[27,28]. For example, Cowie *et al.* studied PSt–(ethene-*co*-butene)–PSt block copolymers cast from different solvents and found marked differences, almost two orders of magnitude, in the moduli of the polymers at temperatures between the T_gs of the constituents[27]. The range of solubility parameters used in that study was much greater than in our current investigation and it is probable that such large differences in moduli were due to major changes in morphology. Variations in morphology of block copolymers with casting solvent are well documented[29].

In our investigations a much smaller range of solubility parameters were involved, permitting identification of more subtle modifications in the relaxation behaviour without major change in morphology; only the sample cast from acetone/dichloromethane gave significantly different results which might be a consequence of a change in morphology. We observed that, compared with PSt in the homopolymer and the blend, segmental motions of PSt chains in the ABCP were enhanced even though those chains were attached to more rigid PCarb-2 chains. We conclude that the enhancement of segmental motions is a direct consequence of the attachment of PSt to PCarb. Further, we conclude that variations in the α-relaxation of PSt cast from different common solvents and with different thermal histories are an inevitable result of failure to establish equilibrium packing of PSt chains during solvent casting. We have recently discussed failure to establish equilibrium conditions in solvent-cast blends of PCarb and poly(methyl methacrylate)[30].

The possibility that the enhanced motions arose from incorporation of additional free volume during solvent casting was examined. The variations in E'' with temperature were analysed in a manner designed to provide a semi-quantitative estimate of additional free-volume fractions involved, which were found to be small compared with that present in a normal polymer at T_g. Variations in the estimated excess free volumes were correlated with casting solvent and thermal history. For samples cast from good solvents for both components, the additional free volume could be significantly reduced, but not removed, by thermal annealing.

Additional incorporated free-volume fractions decreased as the solubility parameter of the casting solvent increased from values close to that of PSt to that of the PCarb. A mechanism for solvent casting is proposed whereby this trend in behaviour is attributed to changes in the aggregation of chains during the casting process as a result of relative preferences for the solvents by the two polymers. It is suggested that the additional free volumes involved are situated close to the interface between PSt and PCarb and one might speculate that the excess free volume is, in some measure, responsible for the toughening effect of PCarb on PSt observed previously[4].

ACKNOWLEDGEMENTS

The authors wish to thank SERC for financial support for one of us (K.H.) and for funds to purchase the Rheovibron.

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