Effect of casting solvents on certain physical properties of ABA poly(styrene-*b*-butadiene) copolymers

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The effects of casting solvent and, to a limited extent, solvent evaporation rate have been investigated for ABA poly(styrene-*b*-butadiene) copolymers. The solvents investigated were cyclohexane, CCl_4, toluene, ethyl acetate, tetralin and cyclohexanone which cover a range of solvent qualities for the respective blocks of this copolymer. The properties measured were density, sonic velocity and absorption of a swelling agent (2,2,4-trimethylpentane) plus dynamic and thermomechanical measurements. The latter techniques indicated that as well as the glass transitions of the blocks, there was a shoulder at around 50°C. It was thought likely that the origin of this minor transition was a mixed phase. It was found that the properties of sheet cast from toluene were dependent on evaporation rate, but that there was no evaporation rate dependence when the casting solvent was cyclohexane.

INTRODUCTION

A number of papers[1–3] concerned with the physical properties of solvent cast styrene–butadiene–styrene block copolymers have now been published. As a consequence of the mutual incompatibility of the blocks, polymers of this type form regular phase-separated domains[4,5]. One of the major factors in governing the solid state structure is the styrene to butadiene ratio. Meier[6–8] has successfully predicted the shape of these domains using thermodynamic arguments. There is also conclusive evidence that different solvents[1], as well as solvent evaporation rate[2,3], can influence the resulting morphology.

Miyamoto, Kodama and Shibayama[1] have discussed the influence of four different casting solvents on the dynamic mechanical and thermal properties of a styrene–butadiene–styrene block copolymer. In this paper we report on a more extensive series of physical measurements made on sheet cast from six different solvents covering a wider range [8.2–9.9 $(\mathrm{cal/cm^3})^{1/2}$] of solubility parameter. The solvents investigated were cyclohexane, carbon tetrachloride, toluene, ethyl acetate, tetralin and cyclohexanone. The copolymer blocks are, of course, soluble to differing extents in each of the solvents. *Table 1* details the effect of these solvents on the polystyrene and polybutadiene blocks.

A study of the effect of changing the evaporation rate was restricted to sheet cast from toluene and cyclohexane only.

EXPERIMENTAL

The polymer used was unfractioned ABA poly(styrene-*b*-butadiene) copolymer manufactured by Shell Chemical Co. Characterization data are shown in *Table 2*. Approximately 8% w/v solutions in redistilled solvents were cast onto clean plate-glass trays where the rate of evaporation could be controlled by varying the rate of flow of air over the surface of the evaporating liquid. The evaporation rate was kept low (<10 ml/h) in order to eliminate the effect of this variable. Considerable care was taken to remove the last traces of solvent before any physical measurements were undertaken.

Density measurements were made in a Davenport density apparatus at 23°C using a calibrated ethanol/water column. Dynamic mechanical measurements were made using a Rheovibron Dynamic Viscoelastometer (Model

Table 1 Characteristics of casting solvents

Solvent	Solubility parameter* $(\mathrm{cal/cm^3})^{1/2}$	Comments
Cyclohexane	8.2	Dissolves polybutadiene; θ-solvent for polystyrene at 34°C
Carbon tetrachloride	8.6	Good solvent for both blocks
Toluene	8.9	Good solvent for both blocks
Ethyl acetate	9.1	Good solvent for polystyrene; non-solvent for polybutadiene
Tetralin	9.5	Good solvent for both blocks
Cyclohexanone	9.9	Good solvent for polystyrene; poorer solvent for polybutadiene

* The solubility parameters of polybutadiene and polystyrene are 8.4 and 9.1 $(\mathrm{cal/cm^3})^{1/2}$, respectively

Table 2 Polymer characterization data

Sample	SBS-1	SBS-2
Weight % polystyrene*	32	26
$\bar{M}_n \times 10^{-3}$	86	67
Configuration analysis†		
% *Cis*	38	38
% *Trans*	57	57
% 1,2	6	5
Density (kg/m³)	938	934

* Calculated from 100 MHz n.m.r. spectra; †calculated from 220 MHz n.m.r. spectra

Table 3 Densities at 23°C of cast SBS-1 sheet

Casting solvent	Density (kg/m^3)*
Cyclohexane	943.5
Carbon tetrachloride	943.9
Toluene	943.4
Ethyl acetate	942.9
Tetralin	944.6
Cyclohexanone	946.6

* Error ±0.5 kg/m^3

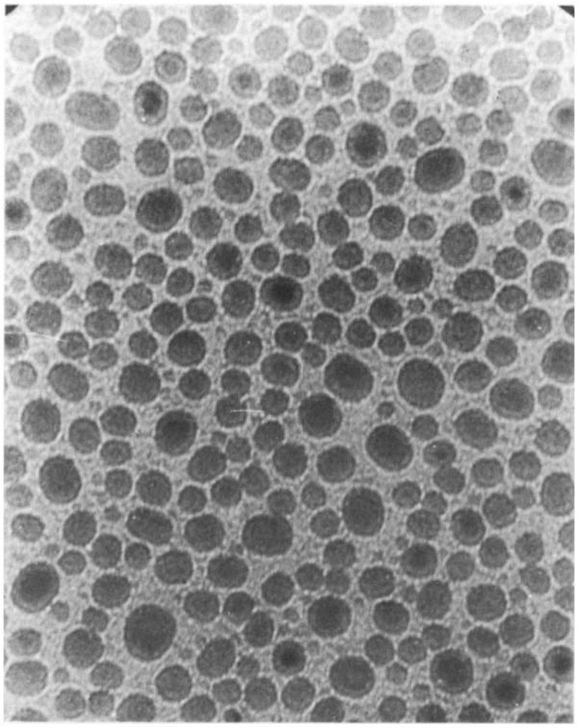

Figure 1 Electron micrograph (160 000x) of SBS-2 cast from ethyl acetate

DDV-II), whilst the longitudinal sonic velocity values were obtained with a Morgan Pulse Propagation Meter (PPM-5B) supplied by H. M. Morgan Co. Ltd, Cambridge, Massachussetts, USA. This instrument transmits sound pulses through the material, directly measuring the time taken to traverse a pre-set distance. A Perkin–Elmer Thermomechanical Analyser (Model TMS-1) was used in the penetration mode to study transitions in the cast sheet. The swelling measurements were made by immersing weighed test-pieces which were ~2.5 cm square and ~0.05 cm thick in redistilled 2,2,4-trimethylpentane, which swells the polybutadiene block only. The test-pieces were carefully reweighed at approximately 24 h intervals until equilibrium swelling had been reached and maintained for 3–4 days. The test-pieces were dried and weighed to constant weight at the end of the experiment to check for any extraction of material. At least three test-pieces were used from each sheet. Samples for electron microscopy were prepared by casting onto a clean mercury surface using a new method developed for these materials[9]. The material was stained by suspending the grids over a 1% w/v aqueous solution of osmium tetroxide in a closed vessel. Electron micrographs were obtained using a Siemens Elmiskop 1A electron microscope with an accelerating voltage of 80 kV.

RESULTS AND DISCUSSION

Influence on properties of casting solvent

Density. It is clear from *Table 3* that the sheets cast from cyclohexanone and tetralin are significantly more dense than those cast from the other four solvents where there are no meaningful differences in density. Of these six solvents ethyl acetate is the only one which does not lead to a regular array of polystyrene domains (spheres or cylinders) in a rubbery matrix. SBS-1 and SBS-2 in ethyl acetate form a multimolecular spherical micellar suspension in which the polybutadiene regions are precipitated and aggregated being held in solution by the soluble end-blocks alone. *Figure 1* shows an electron micrograph of SBS-2 in which a spherical structure of this type persists into the solid state. The aggregates have a range of diameters and seem to be mixed into a matrix of possibly monomolecular micelles. A possible structure for this system is shown schematically in *Figure 2*. Here the dark centres of the multimolecular micelles shown in the electron micrograph are precipitated polybutadiene blocks. The next lighter area is essentially polystyrene, but also seems to contain some polybutadiene. The outer dark ring is again precipitated polybutadiene which gives way to an outer fringe of polystyrene. It is known that the size of these micelles in ethyl acetate solutions depend upon both temperature and the age of the solution. In *Figure 2* an equilibrium process is shown and it is envizaged that the position of the equilibrium will depend on these factors amongst others. Clearly these postulated structures would have low strength. There has been some discussion in the literature[10] about the nature of these micelles. It is clear from this work that for the polymers used under these conditions the aggregates are polydisperse with respect to mass.

As far as trends in density and other physical and mechanical properties are concerned, it would seem reasonable to consider ethyl acetate cast material separately because of its quite distinct morphology. It is, perhaps, not surprising that cyclohexanone and tetralin give the highest densities because these solvents have solubility parameters which differ most from that of polybutadiene (8.4). They should give a more compact rubbery block conformation in solution which seems to persist into the solid state. In the case of cyclohexanone (density 947.8 kg/m^3) it was found virtually impossible to remove the final traces of solvent. So it must be concluded that the presence of residual solvent is making a minor contribution to the measured density value.

Longitudinal sonic velocity (V_L). The data in *Table 4* shows that the V_L values of the ethyl acetate cast sheets are substantially higher than the others. This is what would

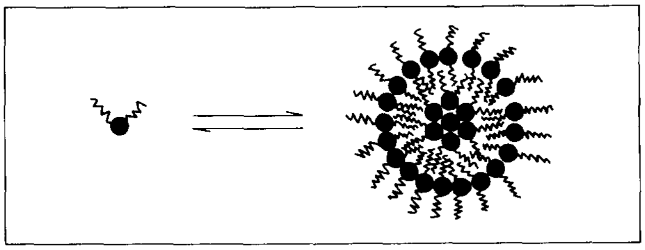

Figure 2 Schematic representation of the structure of a multimolecular micelle of SBS-2 cast from ethyl acetate. ●, Precipitated polybutadiene; 〰, soluble polystyrene

Table 4 Comparison of experimental and calculated longitudinal sonic velocities (V_L) at 20°C

	SBS-1			SBS-2		
Solvent	$E' \times 10^{-8}$* (N/m^2)	V_L (Expt) (km/sec)	V_L (Calc) (km/sec)	$E' \times 10^{-8}$* (N/m^2)	V_L (Expt) (km/sec)	V_L (Calc) (km/sec)
Cyclohexane	0.152	0.16	0.15	0.138	0.15	0.14
Carbon tetrachloride	0.165	0.16	0.15			
Toluene	0.20	0.17	0.17	0.15	0.16	0.15
Ethyl acetate	3.30	0.68	0.68	1.40	0.42	0.45
Tetralin	0.30	0.21	0.21			
Cyclohexanone	1.60	0.46	0.48			

* Dynamic storage modulus at 20°C and 110 Hz

Table 5 Equilibrium swelling data of SBS-1 in 2,2,4-trimethylpentane

Solvent	Weight (polymer + liquid)* / Weight polymer (equilibrium)	Polymer extracted (%)	Equilibrium weight after 24 h† (%)	$M_c \times 10^{-3}$ ‡
Cyclohexane	1.40	1.2	93.5	15.6
Carbon tetrachloride	1.41	1.0	95.7	15.7
Toluene	1.30	0.9	92.1	14.1
Ethyl acetate	1.28	1.8	70.2	13.9
Tetralin	1.27	7.4	91.6	14.7
Cyclohexanone	1.31	2.1	90.6	14.3

* Based on final weight of polymer; †based on initial weight of polymer; ‡the densities of the polystyrene and polybutadiene phases were taken to be 1050 and 899 kg/m^3, respectively

be expected if the structure of this material is as shown in *Figure 1*, where the polystyrene is much more nearly a continuous phase than it is in any of the sheets cast from the other solvents. Again, with the exception of the ethyl acetate cast material, it is the cyclohexanone and tetralin cast sheets which have significantly greater longitudinal sonic velocities than the others, which again are, within experimental error, the same.

Equation (1) holds for homogeneous, isotropic sheets.

$$E = \rho V_L^2 (1 - \nu^2) \qquad (1)$$

where E is the elastic modulus, ρ is the overall density and ν is the Poisson ratio. If the latter is assumed to be 0.5, which is a typical value for a rubber and experimentally determined values of dynamic storage modulus (E') are used for the elastic modulus, equation (1) may be used to predict values of V_L. This assumes that the elastic modulus is independent of frequency over the range covered by the two instruments, i.e. 110 to ~10 000 Hz. If the assumptions incorporated in equation (1) are valid for this system then the calculated and observed values should be in accord. It is clear from *Table 4* that agreement is well within usual experimental error (±8%) for the measurement of V_L in such systems. The wavelengths of the sound used in these experiments is ~2 cm, so that even the large composite structures thought to be present in the ethyl acetate cast sheets are vastly smaller than this, so the material will appear homogeneous in this experiment. The now proven assumption that ν equals 0.5 is again reasonable in that it is the continuous rubbery matrix which is being strained to low levels. The fact that in the ethyl acetate cast sheet the predicted values also agree with the experimental ones would indicate that here too the rubbery phase is continuous.

As this technique is sensitive to minor morphological and compositional variations[11] it is useful in the rapid characterization of such block copolymer systems.

Equilibrium swelling. As it is known that 2,2,4-trimethylpentane swells polybutadiene but not polystyrene it may then be used to ascertain whether casting solvent has any significant effect on equilibrium swelling and on M_c, the molecular weight between crosslinks. The data in *Table 5* clearly shows that there are only minor differences between sheet cast from cyclohexanone, tetralin, ethyl acetate and toluene, but that the cyclohexane and CCl_4 cast sheets absorb distinctly more of the swelling liquid. In every case there was a loss in weight (average ~2%) during swelling. In the data presented this was 7.4% for the tetralin cast sheet. In this case the material extracted was analysed by g.p.c. and found to consist substantially of the diblock contaminant known[12] to exist in these commercial copolymers. *Table 5* also indicates that the rate of absorption of 2,2,4-trimethylpentane during the first 24 h shows only small variations with solvent with the exception of the sheet cast from ethyl acetate. This sheet took substantially longer to reach equilibrium. This is by no means surprising as it would appear from *Figure 1* that in order to swell all the polybutadiene it is necessary for the liquid to diffuse through regions of polystyrene.

The listed values of M_c were calculated using the Flory–Rehner equation derived for conventional vulcanizates:

$$M_c = \rho_2 \bar{V}_1 (\phi_2{}^{1/3} - \phi_{2/2}) / \ln(1 - \phi_2) + \phi_2 + \chi_1 \phi_2{}^2 \qquad (2)$$

where ρ_2 is the density of the unswollen elastomer phase, $\bar{V}_1$ is the molar volume of the swelling agent, ϕ_2 is the volume fraction of elastomer in the swollen elastomeric phase and χ_1 is the polymer–solvent interaction parameter. This latter parameter was calculated from $\chi_1 = 0.406 + 0.522\ \phi_2$[13]. It is quite clear that equation (2), which is intended to describe the swelling of conventional vulcanizates, is not ideally suited to situations where the crosslinks are, in fact, polystyrene domains. It is thought, however, that although it cannot be regarded as a method yielding absolute values of M_c, it should be capable of ranking

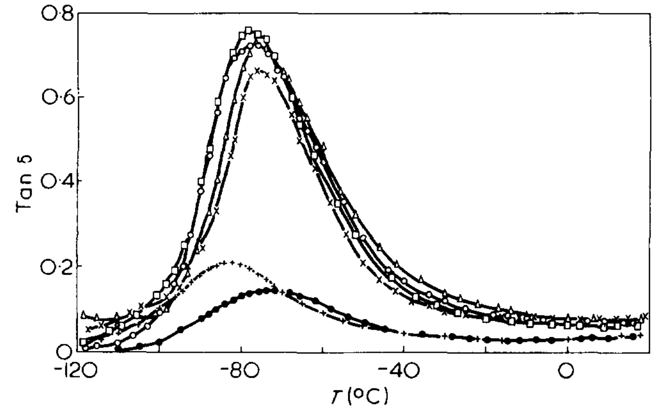

Figure 3 Tan δ *versus* temperature plot for SBS-1 sheet cast from cyclohexane (△), CCl_4 (○), toluene (□), ethyl acetate (●), tetralin (X) and cyclohexanone (+). Frequency, 110 Hz

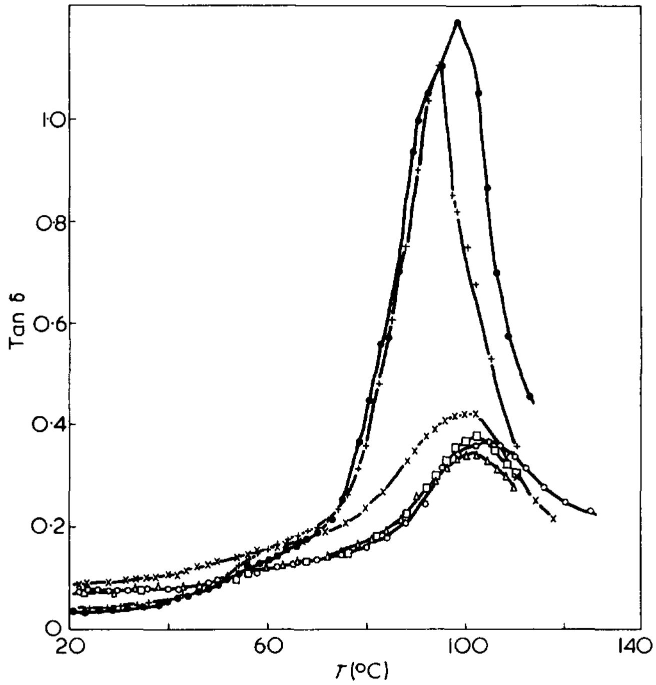

Figure 4 Tan δ *versus* temperature plot for SBS-1 sheet cast from cyclohexane (△), CCl_4 (○), toluene (□), ethyl acetate (●), tetralin (X) and cyclohexanone (+). Frequency, 110 Hz

very similar materials in order to crosslink density. In these SBS materials the ends are trapped in domains, so M_c may be regarded as an approximate measure of the number of permanent entanglements per mid-block.

In SBS-1 the rubbery mid-block has a molecular weight of 59 000 indicating that in all cases there are about 3 entanglements per mid-block. The error involved in this measurement is around ±500, so that there appears to be significantly less entanglement in the cyclohexane and carbon tetrachloride cast sheets. These are the solvents with solubility parameters most remote from that of polystyrene. It can be envizaged that in the concentrated solution the polystyrene is in compact domains with little mixing with polybutadiene and that this structure should persist into the solid state. Such a material should swell more than one in which the two phases are less clearly resolved.

Dynamic and thermomechanical studies. Miyamoto *et al.*[1] have investigated a similar SBS block copolymer cast from carbon tetrachloride, toluene, ethyl acetate and MEK which covers the solubility parameter range 8.6–9.3 $(cal/cm^3)^{1/2}$ by dynamic mechanical and d.s.c. techniques. Our work extends this solubility parameter range to cover values from 8.2 to 9.9 $(cal/cm^3)^{1/2}$ but includes only one micellating solvent whereas in the previous study[1] MEK is also a solvent in which multimolecular micelles are known to exist.

Figures 3–6 show tan δ, dynamic storage modulus (E') and dynamic loss modulus (E'') *versus* temperature. Clearly, as with Miyamoto *et al.*[1] the principal features of these dispersion curves are the glass transitions of the individual blocks which occur at the temperatures shown in *Table 6. Table 6* also show the influence of solvent on the peak height. This tan δ_{max} data shows that the height order for

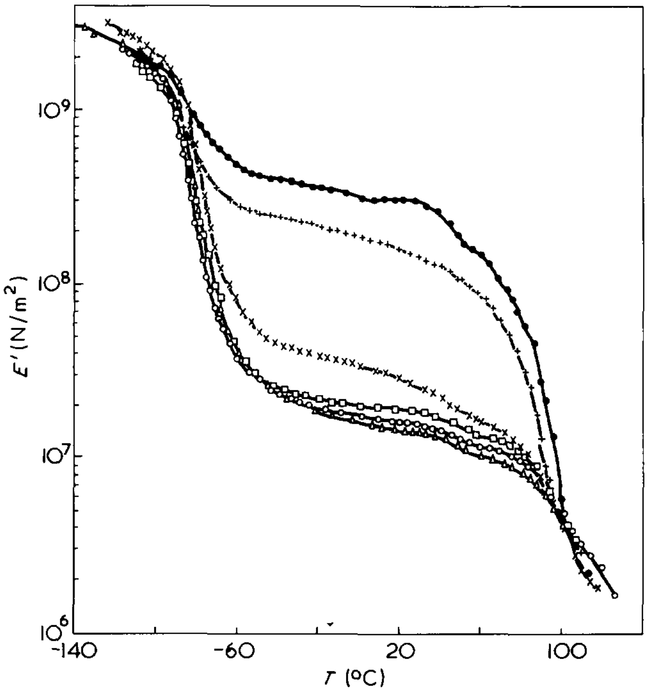

Figure 5 Dynamic storage modulus (E') *versus* temperature plot for SBS-1 sheet cast from cyclohexane (△), CCl_4 (○), toluene (□), ethyl acetate (●), tetralin (X) and cyclohexanone (+). Frequency, 110 Hz

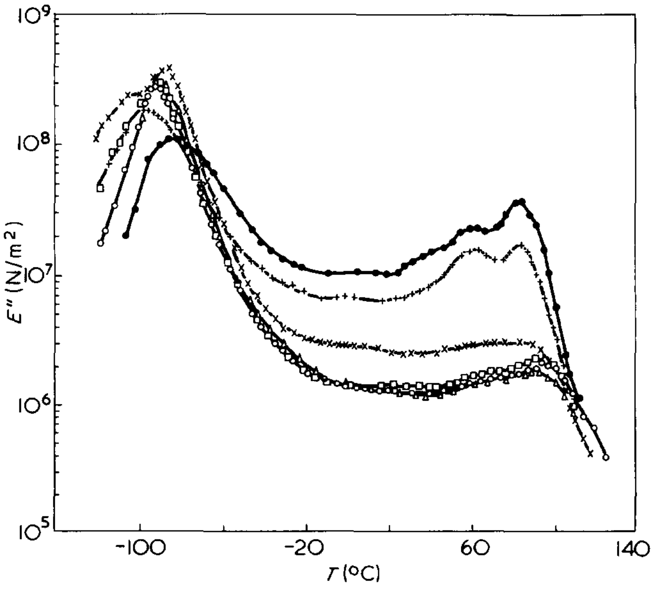

Figure 6 Dynamic loss modulus (E'') *versus* temperature plot for SBS-1 sheet cast from cyclohexane (△), CCl_4 (○), toluene (□), ethyl acetate (●), tetralin (X) and cyclohexanone (+). Frequency, 110 Hz

Table 6 Block glass transition temperatures* and maximum values of tan δ (tan δ_{max}) for SBS-1 cast from a range of solvents

Solvent	Polybutadiene		Polystyrene	
	T_g (°C)	tan δ_{max}	T_g (°C)	tan δ_{max}
Cyclohexane	–76	0.73	102	0.35
Carbon tetrachloride	–76	0.73	105	0.37
Toluene	–78	0.76	102	0.38
Ethyl acetate	–73	0.14	98	1.19
Tetralin	–76	0.66	101	0.42
Cyclohexanone	–83	0.21	95	1.11

* 110 Hz

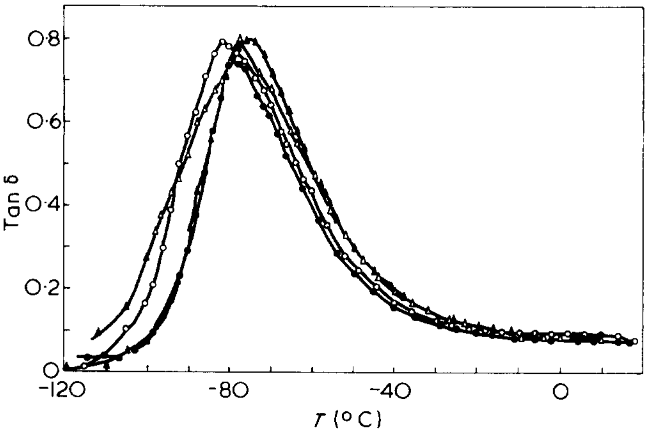

Figure 7 Tan δ *versus* temperature plot for SBS-2 cast from toluene at 10 ml/h (○) and 25 ml/h (●) and from cyclohexane at 10 ml/h (△) and 22 ml/h (▲). Frequency, 110 Hz

polybutadiene and polystyrene glass transitions respectively are toluene > cyclohexane ≃ CCl_4 > tetralin > cyclohexanone > ethyl acetate and ethyl acetate > cyclohexanone > tetralin > toluene > CCl_4 > cyclohexane. This is in good agreement with the previous[1] findings which also indicate that the temperature at which tan δ reaches a maximum is essentially constant. The only discrepancy being that in this work the tan δ_{max} for the polybutadiene block glass transition is greater in the toluene than in the CCl_4 cast sheet. The position of the peak is regarded as being accurate to ±2°C showing that for the Miyamoto *et al.*[1] solvents, our data is also essentially constant. For both blocks the glass transition temperatures in the sheet cast for cyclohexanone are distinctly lower than the others. As already mentioned, this sheet contains some residual solvent which proved impossible to remove. It is likely that the cyclohexanone is acting as a plasticizer for both phases.

Miyamoto *et al.*[1] observed a minor transition at 10°C for sheets cast from ethyl acetate and MEK which they tentatively ascribed to a mixed phase. On annealing, Miyamoto *et al.*[1] found that the magnitude of both major transitions (tan δ) decreased with a concomitant increase in E'. The minor dispersion changed from a resolved peak to a shoulder starting at ~0°C and running into the polystyrene α-transition. In effect the annealing process reduced, but did not eliminate, the differences caused by the differing casting solvents.

In this work a distinct shoulder on the polystyrene α-transition is observed. The magnitude of this shoulder changes (see *Figure 4*) in the following order: cyclohexanone > ethyl acetate > tetralin > toluene > CCl_4 ≃ cyclohexane. For the first three of these solvents this shoulder is very distinct and for the sheet cast from ethyl acetate and cyclohexanone the dynamic loss modulus *versus* temperature curves show a resolved peak at ~60°C. Lowering of the impressed frequency to 11 and 3.5 Hz did not lead to the resolution of these shoulders into distinct peaks.

Schneider and Wolf[14] have observed a small shoulder at 50°C (0.9 Hz) for atactic polystyrene. Illers and Jenckel[15,16], Illers[17] and Sinnott[18] have also reported this β-mechanism in atactic polystyrene. It is clear from n.m.r. evidence that the polystyrene blocks in SBS-1 are atactic. It has been shown[16,17] that this β-transition is only resolvable at low frequencies and merges into the α-peak at frequencies greater than 40 Hz. Takayanagi[19], however, observed this mechanism at 100 Hz as a shoulder on the α-peak at ~50°C. The apparent activation energy of this β-mechanism has been reported[16,17] as 146–167 kJ/mol and has been ascribed either to chain motion where phenyl groups meet less steric hindrance[16,17] or to twisting motions of the chains[19].

Another possible origin for this shoulder is, of course, a mixed phase. To test this latter possibility, samples were annealed under high vacuum at 153°C for 1 week. Annealing will result in better phase separation and a consequent reduction in the magnitude of this shoulder if it has its origin in a mixed phase. Thermomechanical analysis (t.m.a.) experiments were performed before and after annealing. This technique gave a very clear indication of the polybutadiene glass transition, but, especially for the annealed samples, the penetration *versus* temperature slope changes in the region of the polystyrene T_g were not particularly clear cut. However, the evidence from these experiments suggest that the transition at ~50°C is reduced by annealing. However, this cannot be taken as conclusive evidence for the presence of a mixed phase which would have to consist substantially of polystyrene to have a transition at 50°C.

Influence on properties of the rate of solvent evaporation

A very limited investigation into the influence of solvent evaporation rate on the resulting physical properties of the cast sheet (SBS-2) was undertaken for cyclohexane and toluene as casting solvent. In the case of cyclohexane a change in solvent evaporation rate from 10 to 22 ml/h left the measured properties unchanged. This is, perhaps, not surprising for with this solvent the polystyrene blocks will tend to be rather compact domains (see *Table 1*) even in solution. With solvents which are good for both blocks there will be more of a tendency for some interblock mixing in solution, more of which may persist into the solid at fast evaporation rates. In the case of toluene, sheet cast at 10 and 25 ml/h do show significant differences. The sonic velocities and the polybutadiene glass transition temperatures for the 10 and 25 ml/h cast sheets are 0.156 and 0.189 km/sec and –82° and –78°C respectively.

Figure 7 shows the interesting point that the width of the tan δ–temperature dispersion is sensitive to solvent evaporation rate for both of these casting solvents. In both cases the distribution of relaxation times is extended towards lower temperature for the slower rate of evaporation. This phenomenon will be further investigated.

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