quoted per gram of the individual block. For the central (E/B) block, $\Delta C_p(T_g^R)$ shows a slight trend with casting solvent and decreases from 0.263 J K^{-1} g^{-1} (E/B) to 0.167 J K^{-1} g^{-1} (E/B) as the casting solvent δ increases. No obvious trend in $\Delta C_p(T_g^s)$ could be detected and any internal variations are most likely a reflection of the difficulty in making accurate measurements of this transition.

In both cases the ΔC_p values are much lower than that expected for the free component. The value for a pure sample of polystyrene was found to be $\Delta C_p = 0.291$ J K^{-1} g^{-1} for quenched samples. The reason for this is not immediately obvious although it suggests that both blocks do not take part wholly in the glass-transition process. Whether this means that interfacial areas or other mixed phases account for this is open to speculation, nor is it known if this is a general feature of all block copolymers. These points are being investigated further.

To highlight the significant effect the crystallinity in Kraton-G has on the DSC thermogram, a sample of SBS copolymer was also studied and included in Figure 4 for comparison. The glass transitions for the two blocks can be detected, but there is now no evidence of any crystallinity in the intervening region.

Conclusions

It is established that the choice of solvent used to cast films of Kraton-G can have a significant influence on the complex modulus E^* measured at 298 K. The variation in $E^*(298)$ is found to be almost 2 decades within the limits of solubility of the copolymer and corresponds to a modulus change which otherwise could only be achieved by a significant alteration in the weight percent ratios of the component blocks in the copolymer.

The modulus changes arise from the difference in the way in which the polystyrene domains are distributed in the matrix. Good solvents for polystyrene disperse this phase more effectively and the glassy polystyrene domains tend to become connected forming a more continuous phase within the film. This increases the stress bearing capacity of the system. If the films are cast from solvents which are poor dispersers of polystyrene, these domains are much more compact and tend to form a discontinuous glassy phase throughout the matrix. This structure is less capable of carrying the stress and so the modulus drops, as most of the stress passes through the rubbery phase.

The observation that there was a small amount of crystallinity present in the Kraton-G did not affect the $E^*(298)$ to any extent as most of this has disappeared through melting at lower temperatures. It is unlikely that this would play a significant role in the physical response even at lower temperatures, however, as the extent of crystallinity associated with the central block is no more than 10%.

Heat capacity changes ΔC_p, calculated at each glass transition, indicate that either not all of the relevant block component takes part in the transition or that the presence of another block in the matrix alters ΔC_p in some way as yet undetermined. Further work of this kind on other block copolymer systems might be informative.

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Observation of a Super-Glass-Transition Event in the Damping Spectra of Amorphous Block Copolymers

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ABSTRACT: The dynamic thermomechanical spectra of several block copolymer systems have been studied in the frequency range 3.5 to 110 Hz. The samples were either ABA triblock copolymers or cruciform block copolymers, where A is polystyrene and B is either polybutadiene or an ethylene–but-1-ene random copolymer. Specimens for measurement were prepared from films cast using different solvents, either in the presence or absence of a cross-linking agent, di-*tert*-butyl peroxide. It was observed that when uncross-linked films were cast from solvents which had solubility parameters similar to polystyrene, the films had sufficient mechanical strength to allow dynamic mechanical measurements to be made at temperatures up to 60 K higher than the glass-transition temperature of the polystyrene block. This revealed the existence of a super-glass-transition process which is termed T_{ll}. Lightly cross-linked samples also exhibited this process but the intensity of the damping associated with T_{ll} decreased with increasing cross-link density. Measurements of the apparent activation energies ΔH^* for the glass- and super-glass-transition processes showed that ΔH^* for the latter was consistently lower. While the existence of a T_{ll} is confirmed, its molecular origins remain obscure.

The existence of a damping maximum which lies above the glass transition in the dynamic mechanical spectra of some amorphous polymers has been attributed to a "liquid–liquid" transition T_{ll}.[1] This event was first re-

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ported by Boyer from an analysis of a variety of data obtained for several polymer systems. Subsequently the phenomenon became the subject of an extensive study by Boyer, Gillham, and their co-workers[2–5] who detected a loss peak above T_g in polystyrene, using torsional braid analysis. The presence of such an event in this temperature region has been confirmed from dynamic mechanical data for other amorphous polymer composite systems[6] and there appears to be general agreement that it is observed when an inert polymer support is employed in the measurements.

Several workers[7–9] have voiced the criticism that the damping maximum is a consequence of having to use an inert support and that no transition is detected when measurements are made which involve only the polymer. The T_{ll} process has been variously ascribed to flow of the polymer melt within the support matrix, to changes in capillary interaction with the matrix, or to some other interaction between the polymer and the matrix. Since it is extremely difficult to apply dynamic mechanical methods to amorphous polymers in temperature ranges above T_g without the aid of some mechanical support, this widely expressed criticism, that T_{ll} is an artefact introduced by the support and not a true transition or relaxation process, would seem almost impossible to refute directly.

Accordingly, recent studies of the phenomenon have tended to concentrate on nonmechanical measurements which are not subject to the presence of a support medium,[10,11] but we have attempted to focus our attention on the original problem and use a dynamic mechanical approach. Gillham and Boyer[12] detected the presence of a T_{ll} in di- and triblock copolymers of styrene containing a rubbery center block of butadiene, hydrogenated butadiene, or hydrogenated isoprene, using torsional braid analysis with glass fiber supported systems. The observed damping peak lay above the T_g of the polystyrene block and was attributed to a relaxation in the polystyrene regions of the melt. It is now well established that films of block copolymers cast from different solvents have a two-phase structure resulting from microphase separation of the component blocks. It has also been demonstrated[13,14] that a suitable choice of solvent can alter the mechanical strength of the film, within certain limits. Thus one can ensure that the hard plastic phase is more widely dispersed throughout the matrix, thereby raising the modulus, by casting films from a solvent which is a good solvating medium for polystyrene but a poor solvent for the other component. It may then be possible to impart sufficient strength to a block copolymer film in this way and so permit investigation of the dynamic mechanical response above the glass-transition temperature of the styrene block (T_g^s). Alternatively, light cross-linking of the central block could also provide the necessary mechanical strength to the film, leaving the polystyrene segments free to move, except where tied to the central block. It might be suggested that the cross-linked central block was a support system but as the components are believed to reside in different and discrete domains in the matrix the internal response of the polystyrene block ought to remain unaffected.

Both approaches are examined here using two linear styrene–butadiene–styrene (SBS) triblock copolymers, a star-shaped (SBS) copolymer, and a styrene triblock copolymer, in which the central block is a random copolymer of ethylene and but-1-ene.

Experimental Section

Table I
Characteristics of the Block Copolymers

copolymer	type	10^{5} M_n	wt % polystyrene	10^4 M_n^s (polystyrene block)
TR1101-S	linear SBS	1.19	33.6	2.0
TR1102-L	linear SBS	0.83	24.7	1.03
Solprene 406	star SBS	2.10	36.9	1.94
Kraton G-1650	linear S(E/B)S	0.70	26.8	0.95

Samples. The characteristics of the block copolymers used are given in Table I. The samples are all commercially available, but the reported molecular weights and analyses were carried out in this laboratory or taken from GPC measurements carried out for us at RAPRA. Three SBS samples, two linear and one a four-arm cruciform (Solprene 406), were used, as well as a triblock, Kraton G1650, which has a random copolymer of ethylene and but-1-ene as the center block.

Films were cast from 10% polymer solutions, prepared using reagent grade solvents, at 298 K, on a clean poly(tetrafluoroethylene) surface. The solvent was allowed to evaporate slowly in a controlled manner in a nitrogen chamber so that each film took at least 24 h to form. The films were stripped from the PTFE surface and dried under vacuum at 333 K for 12 h. Film thicknesses were in the range 0.2 to 0.4 mm.

Cross-Linking. Several samples of the copolymers were cross-linked by incorporating a known amount of di-*tert*-butyl peroxide (DTBP) in the film. Subsequent treatment of the dried film at 423 K for 50 min led to sample cross-linking, the extent of which was dependent on the amount of DTBP contained in the film. As only lightly cross-linked samples were required the amount of DTBP varied from 1 to 15%, but no higher.

Dynamic Mechanical Measurements. The temperature dependence of the complex modulus, E^*, and mechanical damping, tan δ, were examined over the temperature range 300–500 K and at frequencies of 3.5, 11.0, 35.0, and 110.0 Hz, using a Rheovibron viscoelastometer, Model DDV-II-C. Spectra were obtained at a heating rate of approximately 2 K min^{-1}. Sample strips were cut from the cast films and the dimensions were established by means of a micrometer. When E^* values of less than 10^6 N m^{-2} were to be recorded, it was necessary to restrict the sample length to less than 5 mm. The data were uncorrected for compliance in the holding chucks.[15]

Results and Discussion

Uncross-Linked Samples. As one is primarily interested here in the dynamic mechanical behavior of the block copolymers at temperatures above T_g^s, the spectra are restricted to the temperature range 300–500 K. The tan δ–temperature curves, measured at 11 Hz, for Kraton-G strips cut from films cast using four different solvents, chloroform, tetrahydrofuran, toluene, and *n*-bromobutane, are shown in Figure 1. Two main features are obvious, a large damping maximum centered around 385 K which can be identified as the glass-transition region for the polystyrene block, and a second smaller peak around 435 K occurring in the temperature range one would expect to observe the T_{ll} event. The intensity of this second peak is found to be a function of the casting solvent. When the dispersing medium is a good solvent for polystyrene, e.g., $CHCl_3$, THF, and toluene, the T_{ll} damping is quite pronounced, but as the solvent quality changes and becomes poorer with respect to the polystyrene block, there is a corresponding decrease in the damping intensity of the T_{ll} which matches a similar decrease in the T_g^s peak area.[14] The change in area of the tan δ curves encompassing the damping maxima has been found to be related to the casting solvent and to the extent of the dispersion of the polystyrene phase throughout the

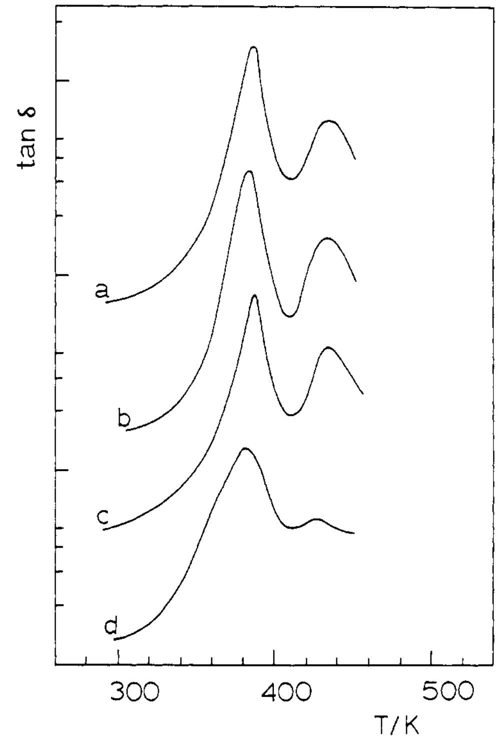

Figure 1. Damping curves measured at 11 Hz for Kraton-G films cast from: (a) chloroform, (b) tetrahydrofuran, (c) toluene, and (d) *n*-bromobutane. Curves are displaced vertically for clarity.

matrix. Thus, there is a tendency for the polystyrene component to be restricted to limited domains in the solid by the presence of a poor solvent for polystyrene as casting medium, and the damping peaks for both T_g^s and T_{ll} show a corresponding decrease in intensity. Regrettably, the somewhat surprising ability to cast copolymer films which maintain dimensional stability at temperatures well above T_g^s is restricted to solvents which show a preference for dissolving the polystyrene component in the case of the copolymer samples used in this study. If films are cast from solvents whose solubility parameter is closer to the rubbery central block, the modulus of the film is found to be lower at room temperature. This is caused by the improved dispersion of the rubber-like material throughout the matrix at the expense of the polystyrene phase. The loss in mechanical strength also means that the films tend to break in the instrument before the temperature range of interest is reached. Several films were cast from solvents such as hexane, which disperse the rubbery block but are not compatible with polystyrene. These were tested with little success. Most broke down about 10 K above T_g^s, often because the holding chucks simply bit through the film at the clamping points, where tension is applied to the sample. The greater dispersion of the polystyrene in the films we were able to study imparts the stability required to penetrate to temperatures above T_{ll} and allows one to observe the phenomenon.

Similar behavior was observed when the damping response of a dioxan cast film of TR1101 and a toluene cast film of Solprene 406 were recorded. Both of these liquids are poor solvating media for the polybutadiene block but readily dissolve polystyrene. The curves, displayed in Figure 2, are essentially the same as those for Kraton G. It should be noted that the damping maxima for the glass-transition temperature (T_g^R) of the central blocks would be observed at much lower temperatures: 190–200 K for polybutadiene and 230–240 K for the ethylene-but-1-ene block in Kraton-G.[14] The mechanical strength of the copolymer films was decidedly weaker above T_g^s when the block length of the styrene component was reduced. This is clearly demonstrated from the spectra shown in Figure 2 where the dioxan cast film of TR1101 (with M_n^s for the styrene block estimated to be 2.0×10^4) exhibits the T_{ll} damping peak, whereas the TR1102 film ($M_n^s = 1.03 \times 10^4$) broke before the required temperature range was reached. The copolymer apparently needs a certain minimum polystyrene block size to ensure that the matrix is reinforced sufficiently to allow dimensional stability at temperatures well above T_g^s.

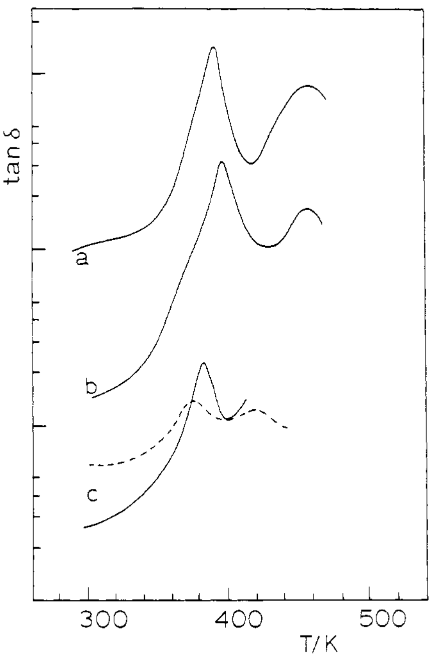

Figure 2. Damping curves measured at 11 Hz for: (a) TR1101 cast from dioxan, (b) Solprene 406 cast from toluene; and (c) TR1102 cast from dioxan, full line uncross-linked sample and broken line cross-linked with 15% DTBP. Curves are displaced vertically for clarity.

Table II
Values of T_g^s and T_{ll} for Copolymer Systems at 11 Hz

polymer	casting solvent	T_g^s, K	T_{ll}, K	T_{ll}/T_g^s 11 Hz	T_{ll}/T_g^s 0.3 Hz
Kraton-G	$CHCl_3$	386	434	1.12	
	THF	385	435	1.13	1.09
	toluene	387	435	1.12	
	n-bromobutane	381	426	1.12	
Solprene 406	dioxan	395	453	1.15	1.12
TR1101	dioxan	390	456	1.17	1.12
TR1102	dioxan	380			
TR1102 (cross-linked)	dioxan	372	416	1.12	

The relevant data for T_g^s and T_{ll} are collected in Table II, where the ratio of (T_{ll}/T_g^s) can be seen to be ~1.13 at 11 Hz. This is in good agreement with that calculated for supported systems.[2,12]

Inspection of the complex modulus–temperature curves in Figure 3 shows a two-step reduction in the value of E^* for Kraton-G films. The first, of almost two decades, corresponds to T_g^s. This is followed by a brief plateau region which is approximately the same for all samples at $\sim 2 \times 10^6$ N m^{-2}, and finally the decrease due to the T_{ll} can be seen before film failure occurs.

Cross-Linked Samples. The additional mechanical strength imparted to the copolymer films by a judicious

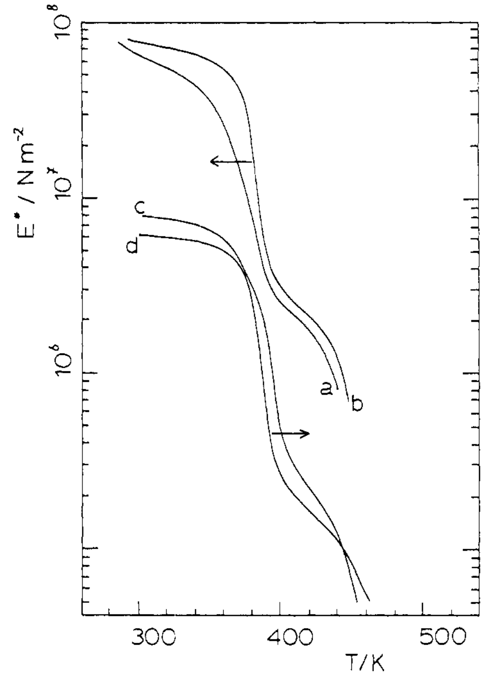

Figure 3. Temperature dependence of complex modulus E^* for: (a) Kraton-G cast from *n*-bromobutane, (b) Kraton-G cast from chloroform, (c) Solprene 406 cast from toluene, and (d) TR1101 cast from dioxan.

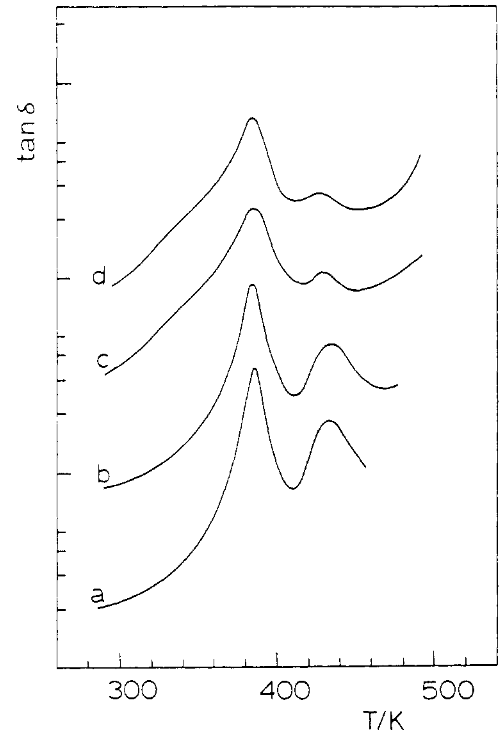

Figure 4. The influence of cross-linking on the damping behavior of Kraton-G films cast from toluene: (a) uncross-linked, (b) cross-linked with 1% DTBP, (c) cross-linked with 5% DTBP, and (d) cross-linked with 10% DTBP. Curves are measured at 11 Hz and displaced vertically.

choice of casting solvent has certain limitations as we have seen, particularly if the polystyrene blocks have low molecular weights. This can be overcome by introducing a limited number of cross-links into the sample, preferably between the central blocks of the copolymers. Cross-linked Kraton-G films were prepared from toluene solutions of the copolymer containing various quantities of DTBP. The nature and the extent of the cross-linking was only investigated in a qualitative manner. The samples prepared from solutions containing 5 and 10% DTBP were found to be only partially soluble in chloroform at 298 K, indicating the presence of cross-links in the films. It was also noted that T_g^R was raised to 231–237 K for the polybutadiene blocks, whereas the absolute values of T_g^s remained largely unaffected, suggesting that the cross-links were mainly located in the central blocks.

The effect of cross-linking on the dynamic mechanical damping spectra is illustrated in Figure 4. Films containing increasing amounts of DTBP, and by inference having an increasing cross-link density, show a lowering in the intensity of both the T_g^s and T_{ll} damping peaks. In addition the position of the T_{ll} peak is altered slightly to lower temperatures. The decreasing intensity of the damping can perhaps be attributed to a restriction in the motion of the polystyrene segments by the interchain cross-linking.

While the molecular origin of T_{ll} remains speculative at present, one suggestion is that it arises from the onset of cooperative motion of the complete chain. In a block copolymer, this would mean the entire polystyrene block, as the central rubber-like block would already possess that freedom. If, however, molecular motion in the central block was impeded by crosslinking, the movement in the polystyrene region would also be affected and the T_{ll} damping reduced in intensity. This implies that at sufficiently high levels of cross-linking no T_{ll} would be observed and this may account for the fact that there appears to be no equivalent T_{ll} associated with the central block in these samples. Presumably the restrictions imposed by the glassy blocks are equivalent in effect to a high cross-link density in the sample. This explanation does not account for the decrease of 7 K in the T_{ll} for a sample cross-linked with 10% DTBP, as one would expect intuitively that the temperature of the damping maximum would increase. Oddly, both the T_g^s and T_{ll} in a TR1102 film, cross-linked with 15% DTBP, also showed a decrease compared with uncross-linked samples.

The increased stability of the cross-linked films enabled the reversible nature of T_{ll} to be demonstrated. The Kraton G film containing 1% DTBP was heated to 450 K and the damping curve was recorded at a cooling rate of 5 K min^{-1}. The data obtained were found to be superimposable on the spectrum produced from the usual heating cycle. Cross-linked samples were also prepared from the TR1102 copolymer with the short polystyrene block; the broken-line curve in Figure 2 represents the response of this sample and shows the presence of a T_{ll}. Relatively high levels of DTBP (15%) had to be used to obtain the necessary strength in this film to reach temperatures above T_{ll}, and the resolution of the damping spectra is impaired somewhat.

Frequency Dependence of T_{ll}. The frequency dependences of the damping behavior of Kraton G, TR1101 and Solprene 406 films were measured and typical curves obtained at 3.5, 11.0, 35, and 110 Hz are shown in Figure 5. It can be seen quite clearly that an increase in frequency moves T_{ll} to higher temperatures much faster than T_g^s. Apparent activation energies (ΔH^*) for both processes were obtained by plotting log (frequency) against $(T_{max})^{-1}$, where T_{max} is the temperature of the maximum in either the glass-transition or super-glass-transition damping curves. Relevant data are collected in Table III. The rather restricted frequency range and the limitations in locating T_{max} with any degree of certainty make the estimated values of ΔH^* accurate to no better than ±15%. The results indicate, nevertheless, that in relative terms the process occurring above T_g, at what we term T_{ll}, has

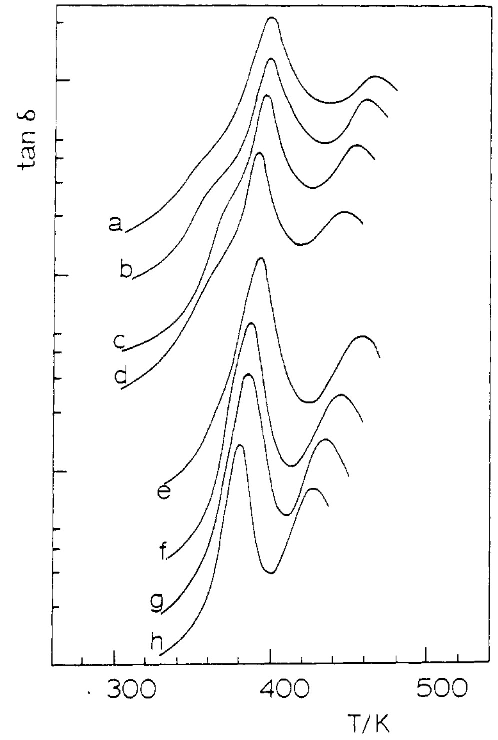

Figure 5. Frequency dependence of damping response for Solprene 406 cast from toluene (a–d) at frequencies 110, 35, 11, and 3.5 Hz, respectively. Curves (e–h) are for Kraton-G films cast from tetrahydrofuran again decreasing in frequency.

Table III
Frequency Dependence of T_g^s, and T_{ll}

polymer/casting solvent	frequency, Hz	T_g^s, K	T_{ll}, K	$\Delta H^{\ddagger}$, kJ mol^{-1}	
				T_g^s	T_{ll}
Kraton-G/THF	110	392	461	380	290
	35	387	445		
	11	385	435		
	3.5	380	427		
Solprene 406/toluene	110	400	467	470	290
	35	397	459		
	11	395	453		
	3.5	390	446		
TR1101/dioxan	110	402	483	285	165
	35	396	470		
	11	390	456		
	3.5	387	446		

a significantly lower $\Delta H^{\ddagger}$ than that for the glass transition. Values for the apparent activation energy of the glass transition in atactic polystyrene, quoted in the literature,[16] lie in the range 330–360 kJ mol^{-1}. The results we have obtained from the block copolymers are not wholly in accord with this, particularly in the case of Solprene 406. It is possible that the structural differences may account for some of this variation as the environment of the polystyrene block will be different in each sample and the restricting influence of the rubbery blocks will differ. This could be most pronounced in the Solprene sample which has a cruciform configuration. In each case the apparent activation energies for the T_{ll} process show comparable trends so that the ratio of (T_{ll}/T_g^s) remains remarkably constant. This would support the general conclusion that the molecular origins of T_{ll} are similar to those giving rise to the glass transition. The ratio (T_{ll}/T_g^s) at 0.3 Hz was also calculated to allow comparison with results reported by Gillham and Boyer[12] for block copolymers studied by torsional braid analysis. The agreement is good.

Other Evidence. Finally it can be noted that Gouinlock and Porter[17] measured the dynamic shear moduli of an SBS copolymer, with a polystyrene block size similar to TR1102, using the eccentric rotating disk mode. They observed a high-temperature transition at 415 K which resembled an actual phase change; this is in good agreement with the T_{ll} for the cross-linked TR1102 sample.

Conclusions

There seems to be little doubt that an event exists above the glass transition which can be seen as a maximum in the damping spectra. For convenience we have chosen to call this T_{ll} as it occurs in the same region as damping peaks observed in supported systems and labeled T_{ll} by several workers. The fact that this can also be observed in the dynamic mechanical damping spectra of unsupported block copolymer samples must surely dispel doubts that it is an artefact introduced by the use of mechanical supporting devices. We are grateful to one of the reviewers for drawing our attention to a recent paper by MacKnight and co-workers,[18] who used a steel spring as a polymer support.

When the dynamic mechanical response of this polymer/support system was examined only a large damping maximum in the T_{ll} region was detected, which these authors consider to be a result of the composite and not of molecular origin. We also have attempted to use spring supports but found them to be unsatisfactory. They are too insensitive to allow location of T_g and the mechanics of this system are such that above T_g the spring no longer appears to behave as part of the composite. This means that the viscous polymer and the spring support move out of phase leading to an alternative source of damping. We do not believe that this occurs in other support systems such as glass or cellulose fiber mats nor in the unsupported copolymer systems examined here.

Independent evidence from other types of measurement is beginning to accumulate in favor of the existence of T_{ll} and the potential importance of being able to locate T_{ll} accurately has been highlighted by Maxwell and Nguyen.[11] These workers, while studying the recoverable strain characteristics of polymer melts, located a T_{ll} transition and have proceeded to point out that when a plastic item is molded at temperatures below T_{ll} it will contain large internal strains, but that these may be removed by molding at temperatures above T_{ll}.

The molecular origins of T_{ll} are more difficult to identify with certainty. There is evidence from modulus–frequency data[19] that a damping maximum ought to appear above T_g, as we have now shown. The suggestion is that this would arise from long-range slippage of entanglements. The present data are insufficient to allow us to comment on that proposal and all we are able to say is that T_g and T_{ll} appear to have similar origins.

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A Transition above T_g in Amorphous Polymers as Shown by the Spin-Probe Technique

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ABSTRACT: Samples of 50% plasticized polystyrene were studied at temperatures $>T_g$ by the nitroxide spin-probe BzONO (Tempol benzoate). Correlation times, τ_c, were calculated by line-width analyses. Arrhenius plots showed a break in slope and this break is considered to occur at the liquid–liquid transition, T_{ll}, observed by other methods (with due allowance for increased frequency of the spin-probe measurements). $T_{ll}/T_{50G} = 1.15 \pm 0.03$ (T_{50G} is the temperature at which the extreme separation is 50 G), and the ratio of the activation energies below and above the transition = 1.7 ± 0.2, in good agreement with previous data. The transition is observed in atactic polypropylene, but not in isotactic polybutene-1. The character of the spectra change on going above T_{ll} is much more liquid-like than below T_{ll}. The plot of log $(T\tau_c)$ is linear in T^{-1} for polybutene-1 with an activation energy of 47 k J mol^{-1}.

The use of spin probes is proving a new and useful tool for the study of polymer relaxations. A stable free radical, normally of the nitroxide family, is added to the polymer matrix and the motion of the radical is studied by analysis of its electron spin resonance (ESR) spectrum. In particular, the broad-line solid-state ESR spectrum of a magnetically dilute nitroxide changes to the narrower three-line spectrum as the radical begins to move because of the motional averaging of the anisotropic hyperfine and g tensors; the temperature at which the extrema are separated by 50 G (T_{50G}) has been quantitatively related to the glass transition temperature (T_g) of the polymer.[1-3]

The present work reports an extension of the spin-probe technique to the study of those temperature regions above T_g where polymers exhibit rubbery or melt properties. There is considerable evidence for the existence of a transition in amorphous polymers in this region.

Relaxations have been found in plasticized anionic polystyrenes and in atactic polypropylene. The only known relaxation in amorphous polymers above T_g is the controversial T_{ll} relaxation which is thought to mark the change from limited ordering of the polymer chains to true liquid-like behavior.[4] Using automated Torsional Braid Analysis (TBA),[5] Gillham, Benci, and Boyer have studied the dependence of T_{ll} for mol wt 37 000 anionic PS on plasticizer content.[6] Variation of T_{ll} with molecular weight is discussed in ref 4. We have identified the ESR relaxation process with T_{ll} for reasons to be presented later, although such identification is not completely proven.

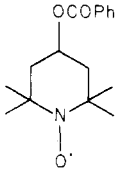
At temperatures $>T_g$, a spin probe is relatively fast moving, and it is possible to calculate the rotational correlation time τ_c for isotropic diffusion of the probe molecule by an analysis of the line widths of the ESR spectra.[7] The following experiments were undertaken to see if the motion of the probe was sensitive to transitions $>T_g$.

Experimental Section

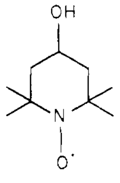
From the work of Gillham et al. on anionic polystyrene (PS), it was found that the T_{ll} occurs at 424 K for PS of mol wt 37 000 and T_g at 380 K.[6] However, spin probes are unstable at temperatures >430 K and, moreover, the increased frequency of the ESR measurements (~10^{10} Hz) above those used in TBA (~1 Hz) would also raise the expected value of T_{ll}. Plasticizing PS lowers the transitions: 50% plasticizer lowers T_{ll} by ~100 °C and T_g by ~90 °C for mol wt 37 000.[6] If it is assumed that a similar lowering would occur for other molecular weights, the temperature region around the expected T_{ll} could be studied comfortably by spin probes using plasticized PS. The plasticizer chosen was *m*-bis(*m*-phenoxyphenoxy)benzene, $(C_6H_5OC_6H_4O)_2C_6H_4$, obtained from Eastman Kodak Co., the same plasticizer as used in the TBA experiments.[6]

In addition to PS, a sample of low molecular weight atactic polypropylene (PP) was studied. This material had a below-ambient T_g (estimated as 211 K from T_{50G} vs. T_g correlation[2]) and was studied by two different probes. Isotactic PP is of course crystalline and spin-probe studies of isotactic PP show evidence of ordering in the polymer up to high temperatures (460 K) with the probe BzONO used in the present work.[8] To show the effect of crystallinity, a sample of commercial isotactic polybutene-1 (PB-1) was studied, because with PB-1 the ordering effect observed in PP was absent.

The spin probe chosen for most of this work was 2,2,6,6-tetramethyl-4-hydroxypiperidinyl-1-oxy benzoate, BzONO, which has been widely used in spin-probe studies (especially in the T_{50G} vs. T_g work[2]). A smaller probe, 2,2,6,6-tetramethyl-4-hydroxypiperidinyl-1-oxy, Tempol, was also used in PP.



BzONO



Tempol

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