Super-glass transition processes in amorphous polymers: fact or artefact?

J. M. G. Cowie* and I. J. McEwen
Department of Chemistry, University of Stirling, Stirling FK9 4LA, UK
(Received 4 December 1978)

Evidence for the existence of a damping process above the glass transition in amorphous polymers has been obtained for a number of different polymers supported on inert media. Several different support systems were tested including cellulose or glass fibre mats or braids and reproducible results were obtained irrespective of the supporting medium. The question of whether this is a spurious damping event introduced by the presence of a supporting medium is fully discussed.

INTRODUCTION

The merits of dynamic mechanical investigations of polymeric systems have been recognized for many years, providing as they do information on moduli, damping characteristics, phase changes, molecular relaxations and kinetic data. Mechanically weak polymers present a problem when preparing suitable specimens for such measurements, while low molecular weight and amorphous polymers cannot normally be studied at temperatures above their glass transition temperature T_g, because of loss of dimensional integrity in the sample. Some of these drawbacks can be overcome by using an inert support medium for these weaker polymer samples and a number have been investigated and developed[1–8].

The inert nature of the support medium is of prime importance and several attempts to use a second polymer as the support have met with limited success. Polystyrene supports have been used to study alkanes, in regions where polystyrene itself shows little or no response[1,3] and can be considered inert, but the use of Melinex as a support for urethane copolymers led to unacceptable interactions between the support and the polymer[4]. Greater success has been achieved with support systems comprising substances such as cellulose blotter, glass cloth[2], asbestos paper[2], steel mesh[7] and light spiral springs[5], but undoubtedly the most successful has been Gillham's use of glass braids in his torsional braid analyser[8].

The thermomechanical response of an amorphous polymer in the temperature region above T_g is important, particularly to rheologists, and the ability to determine whether there are significant transitions or relaxations occurring in the melt is of considerable interest. The use of supported systems does lend itself to this type of investigation and we have tested a number of different types of support in the Rheovibron viscoelastomer which allows a range of frequencies to be explored between 3.5 and 110 Hz.

Excluding the primary transitions normally associated with amorphous or semicrystalline polymers, namely T_g and the melting point, T_m, a substantial number of secondary transitions or relaxation processes have been located in the glassy state. Fewer have been authenticated above T_g. Some years ago, Boyer[9], in a review article, drew attention to evidence derived from studies on polystyrene, indicating that a superglass transition process, which he termed a 'liquid–liquid' transition, T_{ll}, could also be identified. This was based on observations by Spencer and Dillon[10] who reported that the zero shear viscosity of polystyrene exhibited a discontinuity around 560K, and by Flory and Fox[11] who found a similar effect in specific volume–temperature measurements in the region of 530K. Concurrently, Kargin and Malinskii[12a,b] presented deformation–temperature curves for polystyrene which pointed to the fact that the temperature characterizing the onset of flow in the system (T_f) was molecular weight dependent and Boyer suggested that T_f and T_{ll} could be identified with each other, as they displayed the same characteristics. . Further evidence for the existence of T_{ll} in polystyrene was obtained by Krimm and Tobolsky[13] from X-ray data and more recently by Gillham and his coworkers[14,15] who presented an extensive range of data showing evidence of a T_{ll} process in a series of 'monodisperse' polystyrene samples.

The presence of a T_{ll} transition in polystyrene has not been universally accepted and a number of workers cite data which do not support previous conclusions concerning its existence and the proposed molecular origins. For example, recent high temperature studies of the volumetric properties of polystyrene[16] have failed to detect indications of a second order transition in the 530–550K range.

The torsional braid technique used by Gillham has itself been criticized by Nielsen[17] who asserts that the observed damping peak associated with T_{ll} is an artefact of the method and merely reflects the behaviour of a glass braid impregnated with a viscous liquid. Patterson *et al.*[18] have pointed out that there is no quantitative agreement between T_{ll} values reported by Gillham[14] and the T_f values of Kargin and Malinskii[12], but Glandt *et al.*[15] have noted that the location of T_{ll} is sensitive to changes in molecular weight and polydispersity. It has also been suggested that the glass braid support used by Gillham introduces the transition artificially by reflecting either polymer flow within the support matrix or changes in capillary action or surface tension in the polymer–matrix system when the polymer is above T_g.

Such criticisms could be countered if the support medium is varied or eliminated all together and T_{ll} is still observed and if the phenomenon is demonstrated to be of a more general nature. To this end we have examined the dynamic mechanical behaviour of a number of polymers using a variety

0032–3861/79/060719–06$02.00

of supports and present evidence for the existence of a super-glass transition in amorphous polymers. In addition, the existence of this transition in unsupported copolymer systems is also demonstrated in order to remove doubts concerning the part played by the inert support medium.

EXPERIMENTAL

Polymer samples

Narrow molecular weight distribution polystyrene samples were obtained from Pressure Chemical Co. with molecular weights of 2030, 10 300, 20 400, and 390 000 g mol^{-1}. Poly(α-methylstyrene) fractions were prepared and characterized as described previously[19]. Oligomers of poly(propylene glycol) were supplied by Union Carbide (UK) Ltd; their number-average molecular weights were determined by vapour pressure osmometry and found to be 2615, 1710, and 990 g mol^{-1}. Polybutadiene oligomers were kindly donated by Dr E. G.Lovering of Polymer Corp. Sarnia, and were of mixed microstructure (60% *trans*, 20% *cis*, 20% vinyl) with allylic bromine end-groups. Previously characterized poly(dimethyl siloxane) samples[20] were obtained from Hopkin and Williams Ltd. The triblock copolymer of styrene/isoprene/styrene (SIS) was manufactured by Shell.

Sample preparation:

Filter paper strips with approximate dimensions (1.5 x 0.5) cm^2 were cut from Whatman No. 1 qualitative filter paper, then predried at 450K, for 24 h in a vacuum oven before being stored in a dessicator until required. This was the main type of support system used, but others were tried. These included strips of similar size cut either from glass fibre circles or a steel mesh support cut at 45° to the warp and weft. The latter was kindly given by Dr D. Meier of Midland Macromolecular Institute. When the polymer sample was a liquid, the composite samples were prepared by direct immersion of the supporting strips into the polymer, and after impregnation the excess was removed prior to measurement. For solid polymer samples [e.g. polystyrene and poly(α-methylstyrene)], chloroform solutions (15–20 wt %) of the polymers were prepared and support strips were immersed in these for 30 min, followed by drying in a vacuum oven at 373K for 12 h. These composites were also preheated in the instrument to 400K prior to measurement, to ensure that the last traces of solvent had been removed. Samples of SIS copolymer were cut from films cast from dioxane solutions. The copolymer was a triblock with $M_n = 1.96 \times 10^5$. The central isoprene block ($M_n = 1.43 \times 10^5$) had a predominantly 1,4- microstructure 70% *cis*, 25% *trans* and 5% 3,4- addition. Each polystyrene end block had a molecular weight of about 26 500.

Dynamic mechanical measurements

Measurements of the composite mechanical damping (tan δ) as a function of temperature were made using a Rheovibron viscoelastometer DDV-IIC, capable of operating at frequencies of 3.5, 11, 35, and 110 Hz. Spectra were measured at a heating rate of 2K min^{-1} and for all measurements the instrument was contained in a nitrogen dry box.

Values of tan δ were measured as a function of temperature and were, of course, for a composite when the sample is a supported polymer system. The most satisfactory support system was found to be the cellulose strips, as lubrication of the non-woven glass fibres by the liquid polymer in these composites sometimes resulted in specimen failure at temperatures above T_g. Use of the steel mesh was excellent for the location of major transitions, such as T_g, but was less sensitive to the detection of the minor damping features. In all cases, however, the three support media gave identical and reproducible results with similar polymer samples. Examination of the support media in the absence of polymer revealed no damping features in the temperature range covered by this study.

Differential scanning calorimetry (d.s.c.)

Thermograms were obtained using a Perkin–Elmer DSC-2 fitted with a low temperature accessory. Helium was used as purge gas. Baseline reproducibility was aided by using a scanning autozero.

RESULTS

Location of a super-glass transition damping process in supported systems

Polystyrene. Previous work on the dynamic mechanical behaviour of polystyrene, made use of the torsional braid technique at a nominal frequency of ~0.5 Hz[14]. These results showed the presence of a T_{ll} damping peak occurring at temperatures which increased as the molecular weight of the sample increased. It is thus easier to locate the T_{ll} damping in short chain length samples. The thermomechanical spectra measured at frequencies of 3.5, 11, 35 and 110 Hz for four polystyrene fractions supported on cellulose strips are shown in *Figure 1*. In the fractions with molecular weights lower than $M_n = 3.9 \times 10^5$ a major damping peak, associated with the glass transition process is clearly seen, and above this a smaller damping maximum is evident. The temperature of the maximum of this latter damping peak moves to higher temperatures as the sample chain length increases and eventually exceeds the temperature range of our measurements in the case of the fraction, $M_n = 3.9 \times 10^5$. In this sample only the T_g and the beginnings of a T_{ll} can be located. Both T_g and T_{ll} processes are found to be frequency dependent and extrapolation of the data to 0.5 Hz allows comparison to be made with Gillham's measurements using a different technique. The results are shown in *Table 1*, and are in reasonably good agreement with these workers, confirming their results and the comparability of the two techniques. Small differences in the absolute values are believed to arise from the use of a shearing force in Gillham's technique as opposed to a tensile force in the Rheovibron work. The super-glass transition peak can be identified with the Boyer T_{ll} and is quite pronounced particularly in the samples with $M_n = 1.03 \times 10^4$ and 2.04×10^4.

Poly(propylene glycol) (PPG). Dilatometric measurements on fractions of amorphous PPG indicate that the T_g lies between 195 and 200K, while mechanical measurements show the T_g of partly crystalline, stereoregular, PPG to be 211K. The tan δ–temperature spectra of cellulose filter paper composites of three amorphous, low molecular weight PPG samples are shown in *Figure 2*. These clearly display two distinct damping maxima lying between 200 and 300K. The peaks are close together for these short chain samples but the resolution is improved as both the frequency of measurement and the molecular weight of the sample increase. The peak appearing at the lower temperature, which is also the most prominent, lies around 210K–213K (0.5 Hz) and can be assigned to the glass transition process. The damping peak at the higher temperature is believed to be the T_{ll} event in PPG.

Poly(α-methyl styrene). The glass transition temperature of poly(α-methyl styrene) is approximately 75K higher than polystyrene because of the increased chain rigidity arising from the presence of the α-methyl group. Consequently, a T_{ll} event in this polymer, if it exists, would only be seen in low molecular weight samples as the expected temperature region for T_{ll} in high molecular weight materials is beginning to border on the degradation temperatures for this polymer. (It was also noted that these composites tended to break down above 500K). The damping characteristics of two fractions, measured at 3.5 Hz, are shown in *Figure 3.* A pronounced maximum, corresponding to the glass transition, appears in each sample and this contains an ill-resolved shoulder at higher temperatures which can be identified as a T_{ll} process. Measurements at other frequencies failed to improve the resolution to any significant extent.

Polybutadienes. Three samples of low molecular weight polybutadiene were studied and the damping response of each is shown in *Figure 4.* A narrow peak, which centres on 205K, can be identified with the glass transition and a much broader peak occurs at higher temperatures. The super-glass transition damping process in this system is best resolved for the lowest molecular weight fraction and became much more diffuse as the chain length increased. The maxima of these broad peaks are more difficult to locate with accuracy but do appear to be molecular weight dependent. The more diffuse nature of the damping maxima may be a consequence of a broader molecular weight distribution in these samples.

Poly(dimethyl siloxane). The polymers examined above are predominantly amorphous and all appear to demonstrate

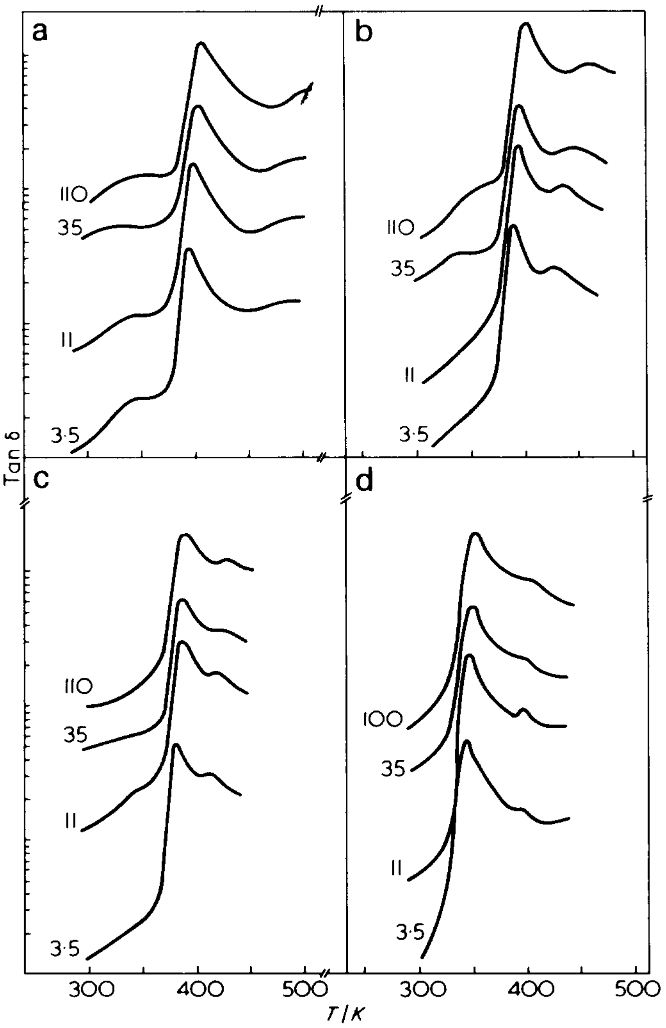

Figure 1 Damping spectra for four polystyrene samples: (a) 3.0 x 10^5, (b) 2.04 x 10^4, (c) 1.03 x 10^4, (d) 0.203 x 10^4. Frequencies as indicated on each curve and tan δ scales are displaced vertically

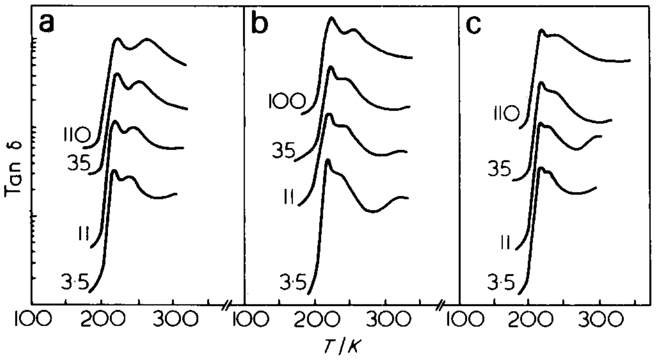

Figure 2 Tan δ composite as a function of temperature for poly(propylene glycols): (a) 2615; (b) 1710; (c) 990. Frequencies as indicated with all curves displaced vertically

Table 1 Glass transition temperature T_g, T_{ll} and apparent activation energies for both processes

Polymer	$10^3 Mn$	T_g (0.5 Hz) (K)	T_{ll} (K) (0.5 Hz)	$\frac{T_{ll}}{T_g}$	$\Delta H^{\ddagger}_{Tg}$ (kJ/mol^{-1})	$\Delta H^{\ddagger}_{Tll}$ (kJ/mol^{-1})
Polystyrene	390.00	388	–	–	380	–
	20.40	385	414	1.08	430	210
	10.30	378	401	1.06	420	252
	2.03	339	387	1.14	390	–
Poly(propylene glycol)						
1025	0.90	213	221	1.04	300	170
2025	1.70	210	220	1.05	250	110
4025	2.60	212	228	1.07	210	100
Poly(α-methylstyrene)						
LMG	3.60	427 (3.5 Hz)	439	1.03	550	200
LMB	10.00	451 (3.5 Hz)	478	1.06	–	–
Polybutadiene						
A	14.00	206 (3.5 Hz)	382	1.4	–	–
C	6.30	204 (3.5 Hz)	265	1.3	–	–
E	3.90	204 (3.5 Hz)	253	1.2	–	–

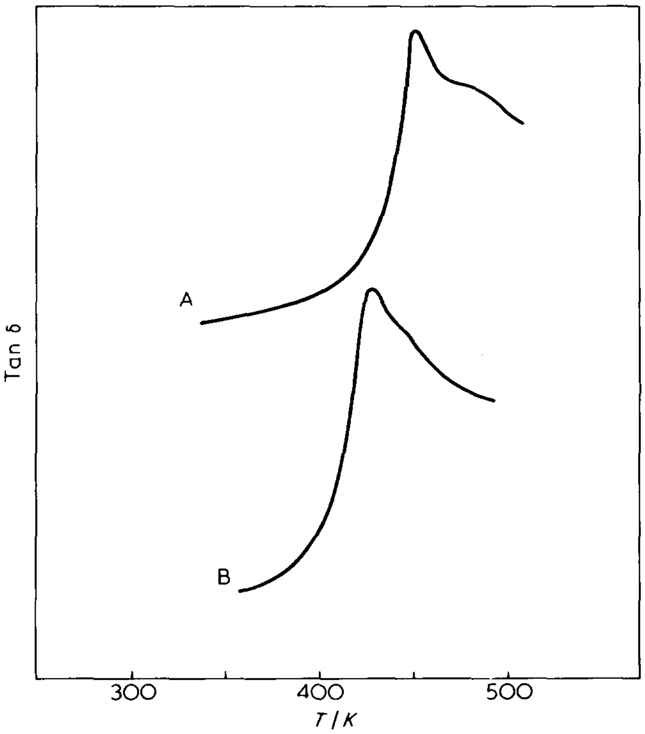

Figure 3 Damping spectra for poly(α-methylstyrene) samples (a) 10.0×10^3 and (b) 3.60×10^3, as a function of temperature

the existence of a super-glass transition process which we have termed T_{ll}. It is instructive to examine the behaviour of a semicrystalline polymer in order to effect comparison. A sample of poly(dimethyl siloxane) was selected and studied both by d.s.c. and dynamic mechanical techniques, the results of which are displayed in *Figures 5a* and *5b*. The damping spectrum *Figure 5a* has two main damping peaks, a lower one at 154K and an upper one which exhibits maximum damping at a temperature of 232K. In addition a distinct shoulder can be seen on the lower peak at about 170–180K. Comparison with the d.s.c. thermogram displayed in *Figure 5b* on the same temperature scale, allows us to assign the lower damping maximum to the glass transition and the upper to the melting transition. The latter appears as a double endotherm in the d.s.c. curves. The d.s.c. thermogram also shows the presence of a cold crystallization exotherm around 184K which corresponds closely to the shoulder above the glass transition damping peak. If the T_{ll} process exists in this sample then it will be effectively masked by the cold crystallization. The sample was annealed at approximately 200K for 10 min, then both the damping and d.s.c. thermograms were remeasured. The annealed sample spectra are shown as the broken curves in *Figures 5a* and *5b*. The spectra are now greatly simplified; the glass transition and cold crystallization features have been effectively eliminated and a single melting endotherm is observed in the d.s.c. curves. This is matched by a single damping maximum in the tan δ-temperature spectrum. Thus if the cold crystallization is reduced by annealing, the amorphous portion of the sample is also decreased and it becomes less likely that the T_{ll} process could then be observed if it is present. Boyer[9] has suggested that a T_{ll} process would not be observed in a semicrystalline polymer as the restriction of molecular motion by the crystallites would impede the molecular mechanism responsible for T_{ll}. Our observations do not disagree with this suggestion.

There is no possibility that the damping observed above T_g in the other polymers could also be a result of crystallization, as the d.s.c. thermograms in each case showed no evidence of this whatsoever.

Unsupported systems

Strips of SIS copolymer, unsupported by any mechanical device, were examined in the Rheovibron over a wide temperature range extending as far beyond the T_g of polystyrene as possible before sample failure was encountered. We have noted elsewhere[21] that sample stability in other copolymer systems was a function of the solvent used to cast the film. For the SIS samples it was observed that if dioxane was the casting solvent, then measurements of the sample damping were possible up to temperatures of about 500K before the specimen ruptured or flowed. Films cast from other solvents with lower solubility parameters did not exhibit this dimensional stability. The tan δ–temperature curve measured at 11 Hz for the most stable film is shown in *Figure 6*. There is a clearly defined damping peak shown above T_g of polystyrene, with a maximum centred around 450K. This is the temperature range one would expect to observe a T_{ll} process for a polystyrene sample of molecular weight approximately 25 000, which is the size of the polystyrene block in the SIS copolymer.

DISCUSSION

There is now overwhelming evidence, both in the literature and in the data presented here, for the existence of a damping maximum located above T_g in amorphous polymers. While

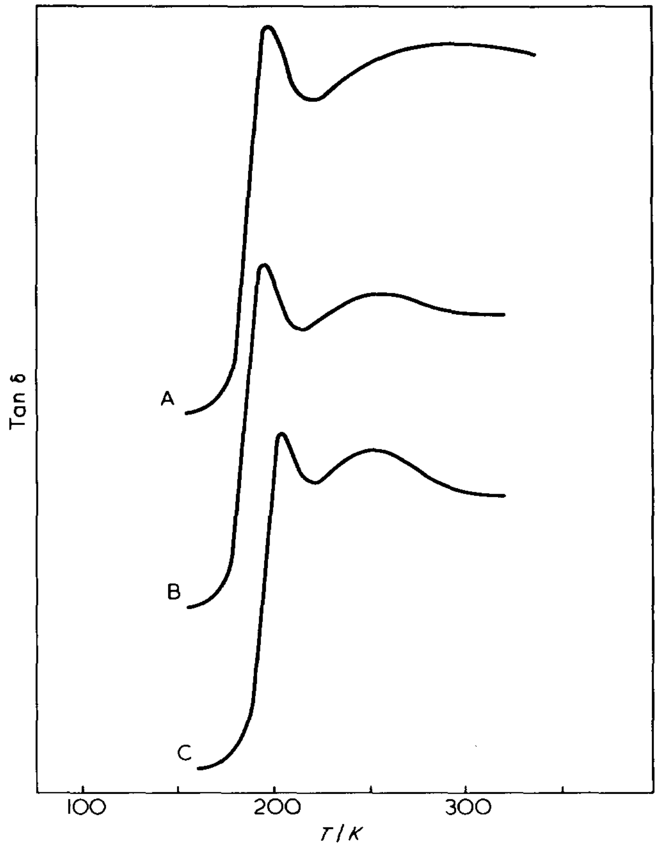

Figure 4 Temperature dependence of damping for polybutadiene fractions (a) 14.0×10^3, (b) 6.3×10^3 and (c) 3.9×10^3. Curves displaced vertically for clarity

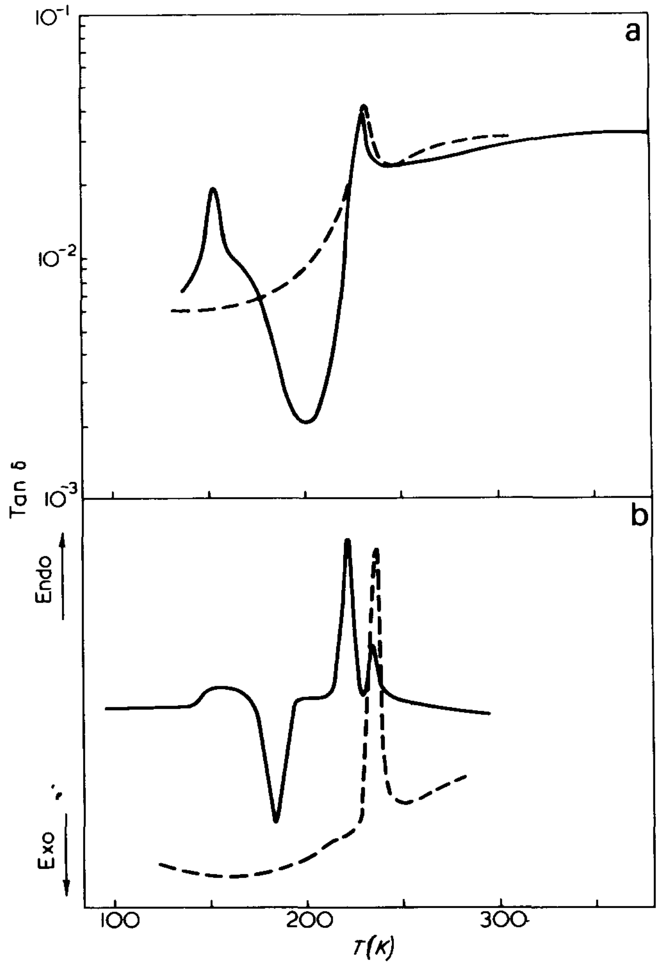

Figure 5 Thermal behaviour of poly(dimethyl siloxane) (a) damping curves, (b) d.s.c. thermograms. Solid lines represent quenched sa samples and broken curves are responses after annealing at 200K

most of the dynamic mechanical measurements have been made on supported systems, even those who dispute that the process is a true transition or relaxation, do not deny that such a damping peak does exist in such systems. Some argue, however, that it is introduced by the presence of the inert support and as such should be considered an artefact. One criticism is that surface tension effects or capillary action in the composite results in spurious damping above T_g, but we have have found that use of different support systems, which would alter such effects, has no influence on the detection or position of this damping process.

A more serious criticism has been voiced by Nielsen[17]. He observed that in a polymer–glass braid composite, one could expect to see two effects; above T_g the damping in the polymer will increase with temperature as viscous flow becomes important, but the braid, with a relatively constant modulus, will show a decrease in damping when impregnated with viscous polymer. The super position of these two effects will result in a damping maximum in the system which arises from the nature of the composite and not the polymer. This is difficult to counter, although it assumes that polymer and braid impregnated with polymer may act independently above T_g, which is not necessarily the case. Our work with the unsupported copolymer sample removes this doubt. If Nielsen is correct then we should see a constant increase in the damping above the polystyrene T_g, instead of which a damping maximum in the expected temperature region is again observed.

Neumann, Senich and MacKnight[6] have analysed data for polystyrene supported on a steel spring. They were unable to locate a glass transition, but reported a substantial damping peak in the T_{ll} region which they interpreted as an artefact of the spring–polymer composite system. Their arguments are based on a spring–dashpot model which predicts a maximum in tan δ corresponding to T_{ll}. This suggests T_{ll} corresponds to an isoviscous state and hence will be a function of the composite characteristics. We believe that for this particular support their analysis may be partly correct, but that a spring will respond differently in a composite compared with the supports used in this work. Above T_g the spring will tend to move through the viscous polymer rather than with it, and damping will occur because of this out of phase motion. This would be an artefact of the composite, but similar behaviour would not be experienced with support media such as cellulose and glass fibre mats. In the latter, the fibres of the support are randomly distributed and associated with a thin film of the polymer rather than with an independent bulk phase. Thus the behaviour of the composite will not result in the out-of-phase movement of polymer and support, as may be experienced with the spring. The observed damping then reflects a real process in the polymer rather than a spurious interaction of polymer and support. Again the data from the unsupported systems answer this comment most effectively.

There is also some reluctance to accept T_{ll} as real among workers who have been unable to detect comparable evidence for its presence in rheological measurements. Richardson and Savill[16] performed careful volume–temperature measurements on anionic polystyrene and found no evidence for a second order transition. However, Boyer has developed techniques for computer analysis of such data and has observed a T_{ll} in similar measurements by Hocker, Blake and Flory[22].

Other techniques have revealed the existence of a superglass transition process: infra-red[23], thermally stimulated discharge studies[24], thermal diffusivity[25] and elastic recovery studies[26] all support the dynamic mechanical work and reduce doubt about it being an artefact of the system. What does

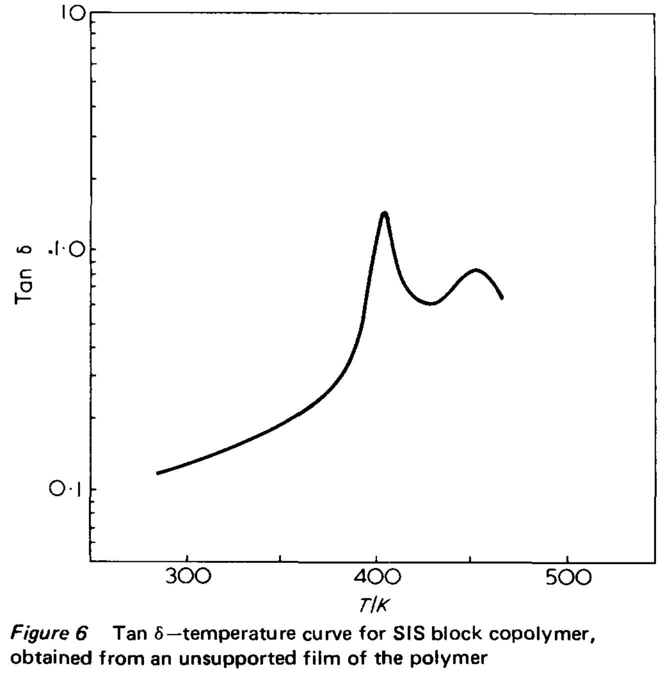

Figure 6 Tan δ–temperature curve for SIS block copolymer, obtained from an unsupported film of the polymer

remain to be determined is the exact nature of the process. The measurements are reversible and reproducible, suggesting that it is not an order–disorder process. The process seems to involve long range forces and bears some similarity to the glass transition, only the relaxation times appear to be longer. Entanglement slippage could be ruled out, as the event is seen in low molecular weight polymers. Cooperative motion of the whole polymer chain is a possibility, but more work is necessary if the mechanism is to be finally established.

The data are presently insufficient to allow one to do more than speculate on the precise nature of the process, and work is now proceeding in an attempt to arrive at a sound explanation of the phenomenon.

REFERENCES

1 Illers, K. H. *Rheol. Acta.* 1964, **3**, 195
2 Faucher, J. A., Koleske, J. V., Santee, E. R., Stratta, J. J. and Wilson, C. W. *J. Appl. Phys.* 1966, **37**, 3962
3 Crissman, J. M. *J. Appl. Phys.* 1974, **45**, 4190
4 Konshik, C. V. *MSc Thesis* Strathclyde University (1975)
5 Naganuma, S., Sakurai, T., Takahashi, Y. and Takahashi, S. *Kobunshi Kagaku*, 1972, **29**, 105
6 Neumann, R. M., Senich, G. A. and MacKnight, W. J. *Polym. Eng. Sci.* 1978, **18**, 624
7 Boyer, R. F. and Burmester, A. unpublished work
8 Gillham, J. K. and Lewis, A. F. *J. Appl. Polym. Sci.* 1963. **7**, 2293
9 Boyer, R. F. *Rubber Revs.* 1963, **34**, 1303
10 Spencer, R. S. and Dillon, R. E. *J. Colloid Sci.* 1949, **4**, 241
11 Fox, T. G. and Flory, P. J. *J. Appl. Phys.* 1950, **21**, 581
12 (a) Kargin, V. A. and Malinskii, U. M. *Doklady Akad Nauk SSSR*, 1950, **72**, 725; (b) *Ibid.* 1950, **72**, 915
13 Krimm, S. and Tobolsky, A. V. *J. Polym. Sci.* 1951, **6**, 667
14 Stadnicki, S. J., Gillham, J. K. and Boyer, R. F. *J. Appl. Polym. Sci.* 1976, **20**, 1245
15 Glandt, C. A., Toh, H. K., Gillham, J. K. and Boyer, R. F. *J. Appl. Polym. Sci.* 1976, **20**, 1277
16 Richardson, M. J. and Savill, N. G. *Polymer,* 1977, **18**, 3
17 Nielsen, L. E. *Polym. Eng. Sci.* 1977, **17**, 713
18 Patterson, G. D., Bair, H. E. and Tonelli, A. E. *J. Polym. Sci. (C)* 1976, **54**, 249
19 Cowdie, J. M. G., Bywater, S. and Worsfold, D. J. *Polymer,* 1967, **8**, 105
20 Cowie, J. M. G. and McEwen, I. J. *Polymer* 1973, **14**, 423
21 Cowie, J. M. G. and McEwen, I. J. *Macromolecules* 1979, **12**, 56
22 Hocker, H., Blake, G. J. and Flory, P. J. *Trans. Faraday Soc.* 1971, **67**, 2251
23 Enns, J. B., Boyer, R. F., Ishida, H. and Koenig, J. L. *ACS preprints, Org. Coat. Plast. Chem.*, 1978, **38**, 373
24 Marchal, E., Benoit, H. and Vogl, O. *J. Polym.Sci. (Polym. Phys. Edn)* 1978, **16**, 949
25 Ueberreiter, K. and Naghizadeh, J. *Kollois. Z. Z. Polym.* 1972, **250**, 927
26 Maxwell, B. and Nguyen, My. *SPE, Ann. Tech. Conf. Preprints* 1978