Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THERMAL ANALYSES OF POLYMERS. XI
CORRELATION AMONG SEVERAL MODES OF THERMAL ANALYSIS FOR THE TRANSITIONAL BEHAVIOR OF BLOCK COPOLYMERS *

G. W MILLER
Owens-Illinois 1700 N. Westwood, Toledo, Ohio 43651 (U. S. A.)

and R. V. FITZSIMMONS
Amoco Chemical corporation, Naperville, Illinois 60540 (U. S. A.)

(Received April 3rd, 1972)

ABSTRACT

Data describing the transitional behavior of SBS, SIS and poly(ester–urethane) block copolymers are presented for a number of thermal techniques, *i.e.*, DTA, dilatometry, torsional modulus, dynamic mechanical analysis, and thermal depolarization. Accurate correlations were observed among these techniques for the major transition temperatures, whereas other significant transitions were observed mainly by volumetric and depolarization techniques.

The depolarization behavior of these elastomers offered a more vivid description of crystalline or molecular order than that afforded by DTA or dynamic mechanical analysis. The SBS and SIS elastomers have been described as completely amorphous, while poly(ester–urethanes) can exhibit small amounts of non-spherulitic molecular order. Apparently, each of these elastomers has some amount of microstructure.

INTRODUCTION

The developing technology of thermoplastic elastomers received a giant thrust with the commercialization of the styrene–isoprene–styrene (SIS) and styrene–butadiene–styrene (SBS)triblock polymers, and these materials have been the subject of at least two major symposia. Morton, *et al.*[1] have postulated that the triblock polymers exhibit domain formation by aggregation of the polystyrene segments, forming a two-phase system. However, at high polystyrene contents (about 40%), the polystyrene domains form a continuous phase. Useful block ranges have been postulated in the 10–20,000 molecular weight range for polystyrene and 40–80,000 molecular weight range for the polydiene.

---

*Presented before the Third Annual Meeting of the North American Thermal Analysis Society in Waco, Texas, on February 7–8, 1972.

Beecher, *et al.*[2] have reported on the morphological and mechanical behavior of these block copolymers. With the use of dynamic mechanical and DTA measurements for SIS, they found a transition at −64°C and another in the range of 65–92°C, attributing these independently to the polyisoprene and polystyrene segments, respectively. In another study Cooper and Tobolsky[3] were the first to show that these segmented elastomers (SBS) had two distinct transition temperatures, and in the same work, showed a similar type behavior for a poly(ester–urethane) elastomer.

The influence of isocyanate structure and the ratio of hard to soft block content in a polyurethane elastomer have been shown to be the major factors in determining the mechanical properties of the polymer[4–6]. The soft block in these elastomeric materials usually consists of a polyether or polyester diol of one to two thousand number average molecular weight, whereas the hard block is usually made from the condensation between the various diisocyanates and monomeric diols (*e.g.*, butanediol). The hard block sequences maintain the integrity of the polymer above the melting temperature of the soft block segment, whereas the soft block segment is responsible for the low temperature behavior of the elastomer and bonding with urethane blocks. In this latter case, poly(ester–urethanes) are, for the most part, tougher and more abrasion resistant than poly(ether–urethanes) of the same composition. The segmented urethane block copolymers show two major transitions when there is a sufficient content of the urethane hard block. For example, for a polyurethane made from an aliphatic polyester, MDI (4,4′-diphenylmethane diisocyanate), and an aromatic glycol in the ratio of 100 parts polyester to 50 parts MDI, a thermoplastic elastomer is made which has two major transition temperatures. The major lower transition temperature is characteristic of the polyester segment, and the higher temperature transition is typical of the urethane hard block. However, each of these segments has been shown to shift temperature according to the influence of the hard and soft blocks, respectively. As the ratio of isocyanate to polyester or polyether soft block increases, these transition temperatures for the hard block usually increase. By annealing the polyurethane elastomer in the temperature range 110°–140°C, changes in mechanical properties are also possible. The major transitional change for the soft block seems to shift to higher temperatures on copolymerization with urethane blocks, whereas the major change for the urethane hard block shifts to lower temperatures under the influence of the soft block[7].

Since the polybutadiene segment of the SBS elastomer can exist in three stereoregular forms, the influence of the stereoregularity could well change the properties of the elastomer under study. By analogy with the segmented poly(ester–urethanes), if the soft block has a low melting temperature, the elastomer will usually have good low-temperature flexibility. On the other hand, if the low temperature segment melts considerably above room temperature, then the elastomeric features of the segmented elastomer may decrease. This would be particularly true in the formation of a polymer from styrene and *trans*-polybutadiene, since *trans*-polybutadiene melts in the range of 100°C.

This report correlates the thermal response of three stereoregular polybutadienes and SBS, SIS, a poly(ester–urethane) (EU) block copolymers when viewed with four independent thermoanalytical techniques. Correlations between static and dynamic measurements for transitional changes are made, and the use of these transitional changes for predicting mechanical properties and behavior of these segmented elastomers are illustrated.

EXPERIMENTAL

Materials

The polyurethane elastomer used in this study was a sample of Texin 480A, a poly(ester–urethane) (EU), from the Mobay Chemical Company. The SIS and SBS elastomers were graciously supplied by Professor M. Morton of the University of Akron. The styrene–diene–styrene number average molecular weights were 13,000–64,000–13,000 for each elastomer. Stereoregular polybutadienes were obtained from the Phillips Petroleum Company, and their analyses are given in Table I.

TABLE I

GEOMETRIC RATIOS OF STEREOREGULAR POLYBUTADIENES

Sample	*Trans*	*Cis*	*Vinyl*
Trans	88.5	8.9	2.6
Cis	1.4	95.3	3.3
Vinyl	1.5	7.0	91.5

Methods

Dynamic mechanical analyses were carried out on the Toyo Rheovibron Viscoelastometer (Model DDV II), measuring the damping factor in the tensile mode at a heating rate of 2° per min.

DTA and DSC measurements were made with the duPont 900 system at a heating rate of 10° per min, and dilatometric measurements on the duPont 941 TMA at a heating rate of 2° per min as previously described[8].

Thermal depolarization analyses (TDA) were carried out as previously described at a heating rate of 5° per min[9]. Measurements of the torsion modulus *vs.* temperature were carried out on a Clash–Berg apparatus at a heating rate of 2° per min, using silicone oil as the heat transfer medium.

RESULTS

Stereoregular butadienes

Since in many block copolymers the thermal response is apparently additive, we examined the DSC response for *trans*, *cis* and vinyl polybutadienes, and the results are shown in Fig. 1. The *trans* isomer (TBD/ exhibited a change in heat capacity at

−81 °C followed by two endotherms beginning at 36° and 94 °C. The *cis* isomer (CBD) had a heat capacity change at −104 °C, followed by a recrystallization exotherm, beginning at −60 °C and peaking at −42 °C. The melting of these crystallites then occurs at −18 °C. The curve for the vinyl or 1,2-polybutadiene (VBD) shows two small heat capacity changes at −4° and 63 °C. The glass transition temperature for TBD has been reported[10] to occur at −18 °C. There is no evidence of this in the DSC scan. The glass transition for CBD has been reported[10,11] to occur at −108 °C, and a drastic change in the heat capacity is observed in Fig. 1 at −104 °C for the CBD,

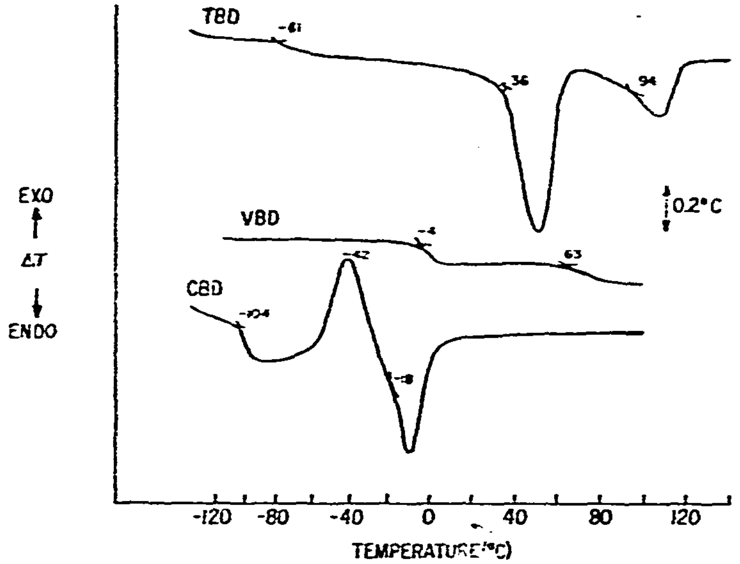

Fig. 1. DSC response of *trans*, *cis* and vinyl polybutadienes.

showing reasonable correlation. The glass transition for VBD has been reported[12] to occur at −9 °C, and in this work we see a change in the heat capacity at −4 °C. The temperature differences here appear to be due to the mode of determination, for in examining the dilatometric behavior of the VBD (Fig. 2), volumetric changes occur at −137°, −100°, −72 °C with a very large volumetric change at −9 °C. The TBD shows a change in the coefficient of expansion at −69°, −19°, 44° and 92 °C, offering rather good correspondence with the changes observed by DSC. Two large changes in the volume for CBD are observed at −15° and −4 °C with a small change at −66 °C.

The changes in the thermal depolarization behavior are shown in Fig. 3, illustrating a rather complex curve for the TBD with significant changes at −76°, 36°, 92° and 114 °C, where final fusion of the *trans* form occurs. The CBD shows only apparent fusion at −5 °C. The peak just prior to this temperature, beginning at −17 °C, is probably due to the crystalline segments of the elastomer as they begin to increase in order prior to final fusion. The onset of fusion at −17 °C corresponds well with a change in heat capacity at −18 °C and the volumetric displacement at −15 °C. However, one would normally expect that the recrystallization exotherm in

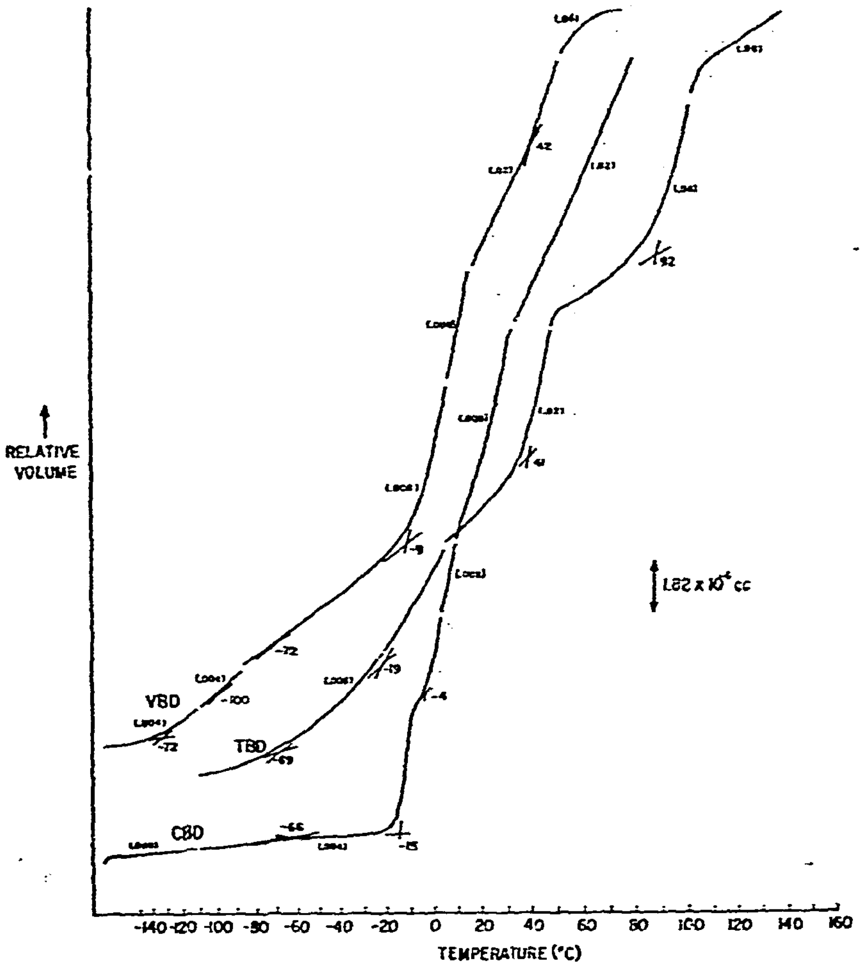

Fig. 2. Dilatometric behavior of *trans*, *cis* and vinyl polybutadienes.

Fig. 1 beginning near $-60\,°C$ should also be present in the depolarized light trace in Fig. 3, and there is a small increase in light intensity at this temperature.

The VBD, on the other hand, shows the onset of change at $-10\,°C$, followed by a larger increase in order at $+10\,°C$ and final fusion at 30 °C. The beginning of an increase in molecular order at $-10\,°C$ corresponds well with the large increase in volume at $-9\,°C$ for the VDB. The latter part of the VBD curve above 90 °C indicates the changes in depolarization that may accompany thermal degradation of a polymer, suggesting the use of thermal depolarization for the measurement of the rate of degradation of certain polymer systems. Increases in depolarized light transmission have been noted with non-stabilized elastomeric systems as well as those of the SBS and SIS triblock systems as thermal degradation occurs.

Dynamic mechanical properties of the CBD and TBD are shown in Fig. 4 in which the onset of the mechanical loss peak for the *trans* isomer occurs at $-77\,°C$ with a peak maximum at $-40\,°C$. The onset of a higher temperature peak occurs at 70 °C, with a diffuse peak in the vicinity of 35 °C. The CBD shows the onset of the

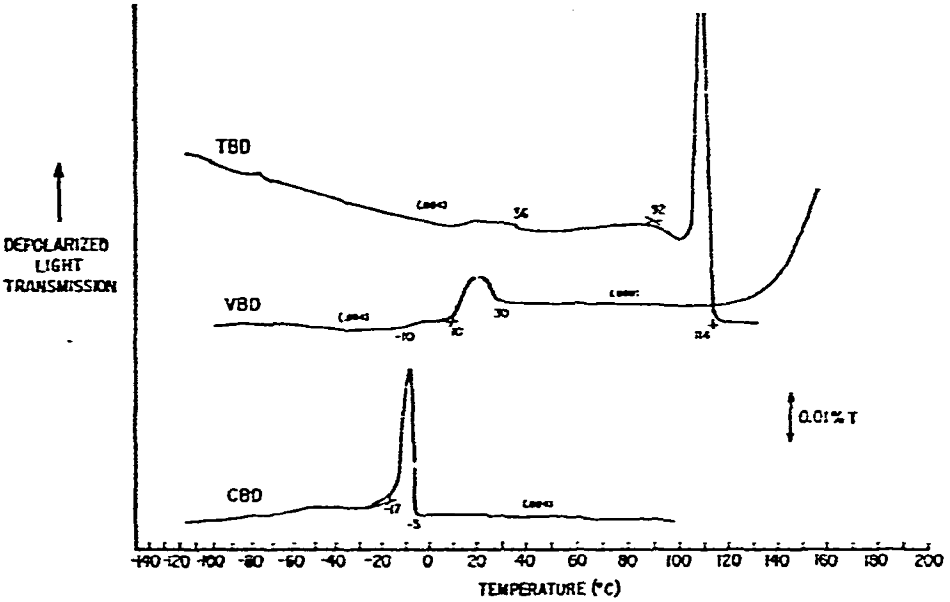

Fig. 3. TDA curves for *trans*, *cis* and vinyl polybutadienes.

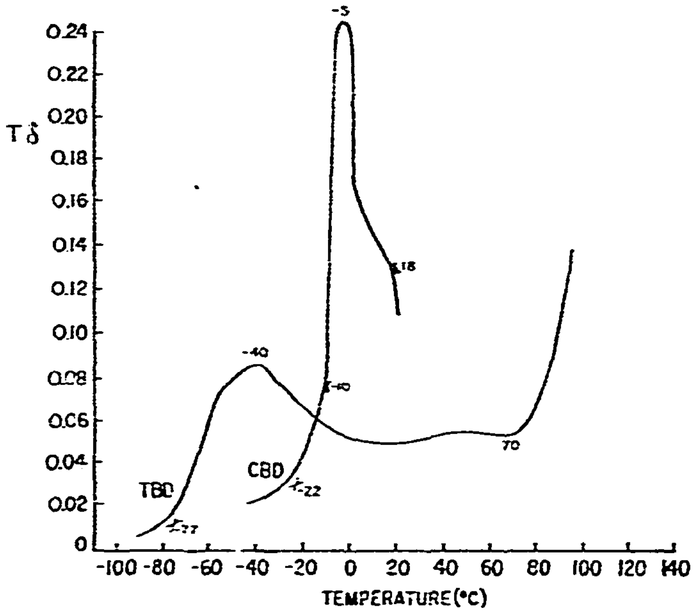

Fig. 4. Dynamic mechanical behavior of *trans* and *cis* polybutadienes.

mechanical loss peak near −22 °C, followed by a more rapid change in the mechanical loss at −10 °C. The peak maximum occurs at −5 °C with a small knee at 18 °C. The onset of the damping peak for the TBD corresponds well with changes observed by DSC, depolarization and dilatometry, whereas the peak maximum at −40 °C is not observed in any of the other three techniques. The diffuse maximum in the vicinity of 35 °C correlates well with the first endotherm at 36 °C by DSC and the small change in depolarized light level at 36 °C as well as the abrupt change in the dilatometric scan at 44 °C. The onset of the higher temperature peak is displaced somewhat from the values observed by DSC, TDA and dilatometry. For the CBD the onset of the mechanical change at −22 °C corresponds well with the changes observed by other techniques in this temperature range. In the case of the CBD material the cessation of fusion by TDA at −5 °C correlates well with the change in relative volume at −4 °C, whereas the peak maximum occurs at −5 °C as well. In this case, apparently the DMA peak maximum corresponds to the fusion temperature.

The report[10,11] of the glass transition near −108 °C for CBD is verified within this study. Apparently the glass transition of the TBD is in the range −76° to −81 °C. Correlations for the VBD only occurred near −9 °C, and this has been reported as a glass transition[12]. It would appear from the data that this may not be the glass transition but a first-order phenomenon.

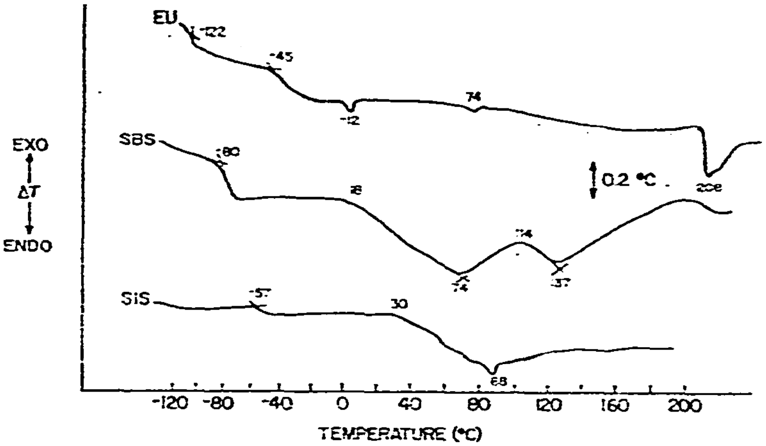

Fig. 5. DTA response of EU, SIS and SBS block copolymers.

Block copolymers

Beecher, *et al.*[2] have illustrated the DTA characteristics for an SIS copolymer, illustrating an endotherm at −64 °C. The SBS copolymer on the other hand showed a transition at −80 °C with apparent changes[13] in the heat capacity at 30° and 95 °C. The three DTA scans in Fig. 5 show our results for the SIS, SBS, and poly(ester–urethane) elastomer (Texin 480A). The SIS copolymer in this study shows a heat capacity change at −57 °C which is approximately 7° higher than that of Beecher. The onset of fusion for the SIS elastomer appears to begin at 30 °C with a definite endotherm at 88 °C, showing the fusion of the polystyrene domains. The SBS scan shows the first change at −80 °C, followed by small transitions at 18°, 74° and 137 °C. The transition at −80 °C approximates the ΔT change for polybutadiene. The change at 18 °C lies between the second major transitional change for each stereoregular isomer at −18° (*cis*), and 36 °C (*trans*). The fusion at 74 °C is that for the polystyrene domains, and the change at 137 °C cannot be readily assigned. The poly(ester–urethane) shows a very small change in heat capacity at −122 °C, followed by an abrupt drop at −45 °C and small endothermal transitions near −12° and 74 °C. Terminal fusion occurs at 208° C. The causes for these changes have been reported[4].

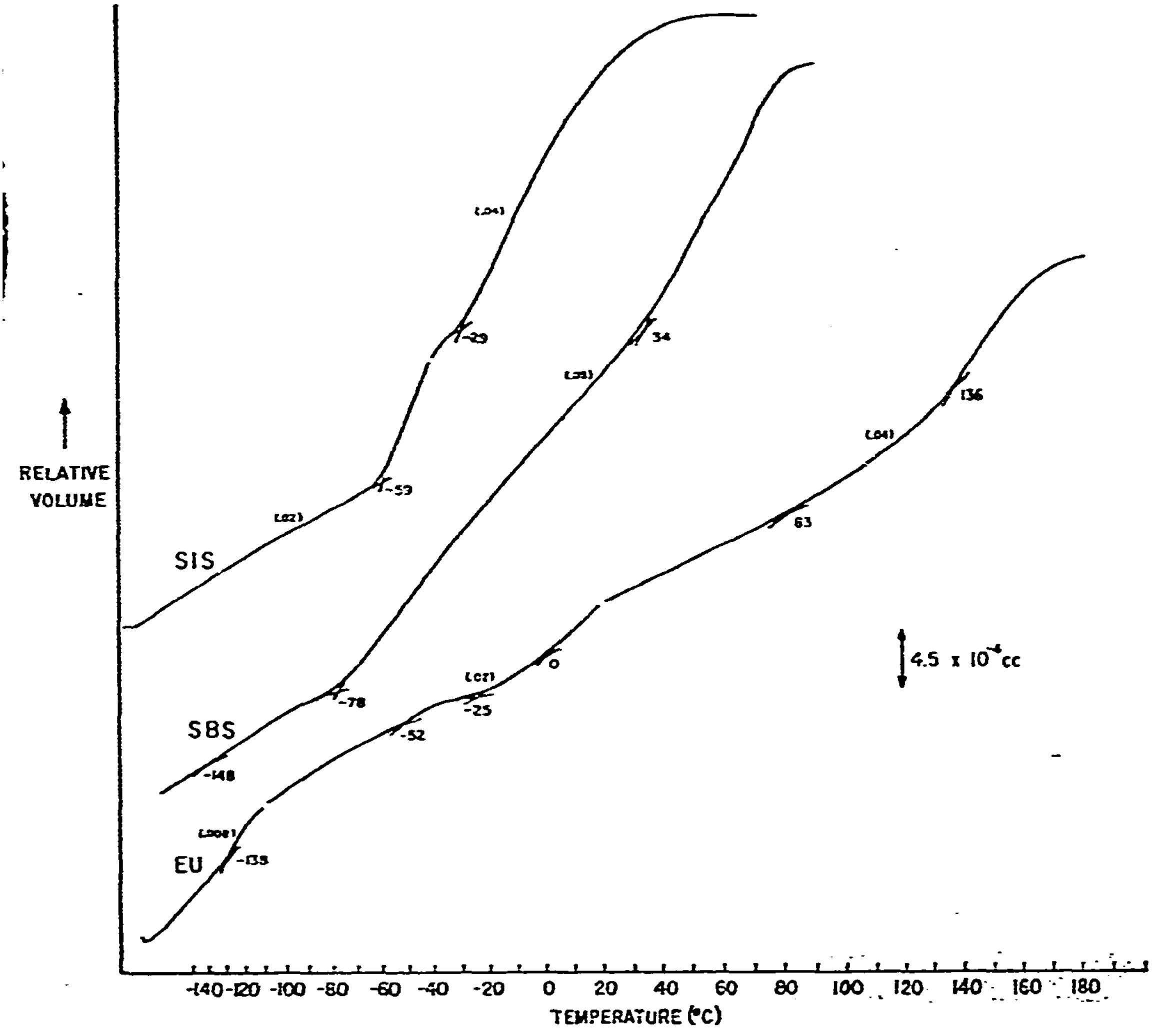

Fig. 6. Volumetric behavior of EU, SIS and SBS block copolymers.

In Fig. 6 are shown the dilatometric responses of each of the segmented elastomers at a heating rate of 2° per min. The volume–temperature curve for SBS shows a second-order change, according to Bekkedahl[14] at −148 °C and an abrupt transition at −78 °C, with a very small change in expansion coefficient at 34 °C. The SIS copolymer showed only two transitions occurring at −59° and −29 °C. The −59 °C-transition appears to be a first-order transition as does the −29 °C-transition. However, no change in the coefficient of expansion was apparent at temperatures below −59 °C under the conditions of this experiment.

The dilatometric response for the poly(ester–urethane) shown in Fig. 6 has a second-order change at −138 °C which agrees with the mechanical data published previously[12]. There is a small change in the coefficient of expansion at −52 °C, followed by the beginning of a first-order transition at −25 °C. The torsion modulus curve in Fig. 7 showed a small change at −130 °C, followed by the onset of a very large modulus change beginning at −56 °C, while the extrapolated onset occurs as high as −24 °C. These data agree well with the volumetric results shown in Fig. 6, and apparently the large modulus change is a result of these first-order phenomena. Other changes are also noted in the linear expansion and the volumetric data at 83° and 136 °C, which correspond reasonably well with the torsion modulus changes at 89° and 130° C, for the beginning of the modulus slope change and extrapolated onset of the modulus change, respectively. The change at −130 °C had previously been postulated[4] as arising from the glass transition within the polyester backbone, whereas the change at −56 °C is that due to the first-order fusion occurring within the polyester backbone, resulting mainly from ester–ester segment separation, a translational movement. The change in linear expansion and in the slope of the torsion modulus curve at 89 °C has been associated with the cleavage of hydrogen bonds between the polyurethane hard block and the polyester soft block, while the final fusion beginning near 130 °C is due to the cleavage of hydrogen bonding between urethane hard segments within the elastomer[4].

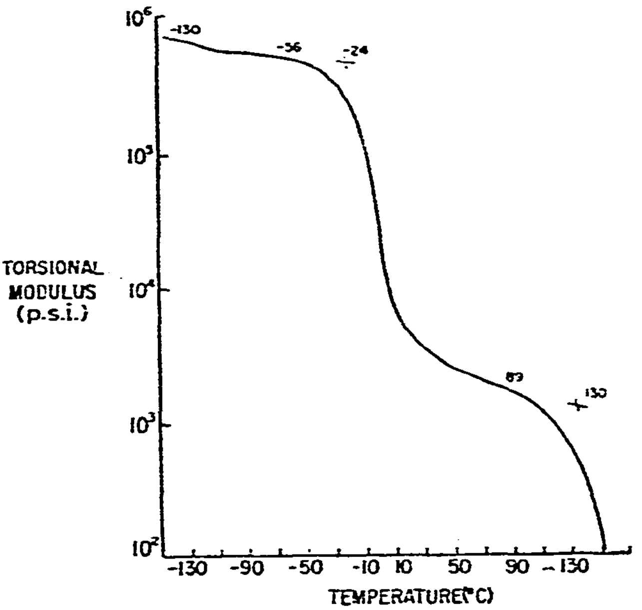

Fig. 7. Plot of torsional modulus *vs.* temperature for EU.

As the birefringence of a material changes with temperature, an increase in light level has been interpreted as that due to the recrystallization or more perfect ordering of areas within a polymer, whereas a decrease in the light level or birefringence is usually associated with the fusion or melting of an ordered area[9]. The generation of peaks in the continuous plot of depolarized light transmission *vs.* temperature is a frequent occurrence, and these peaks are due, for the most part, to increasing crystalline order during the small temperature range just prior to final fusion. For example, it has been shown[15] that the size of a crystal can be visibly measured to increase as a peak occurs just prior to final fusion. A peak may also arise when a material scatters most of the transmitted light, and a change in depolarization is noted only as the material melts and the light level for the isotropic state has the same value as that prior to the fusion phenomena[8]. The changes in birefringence shown in Fig. 8, as a function of temperature, illustrate a change beginning at −95 °C

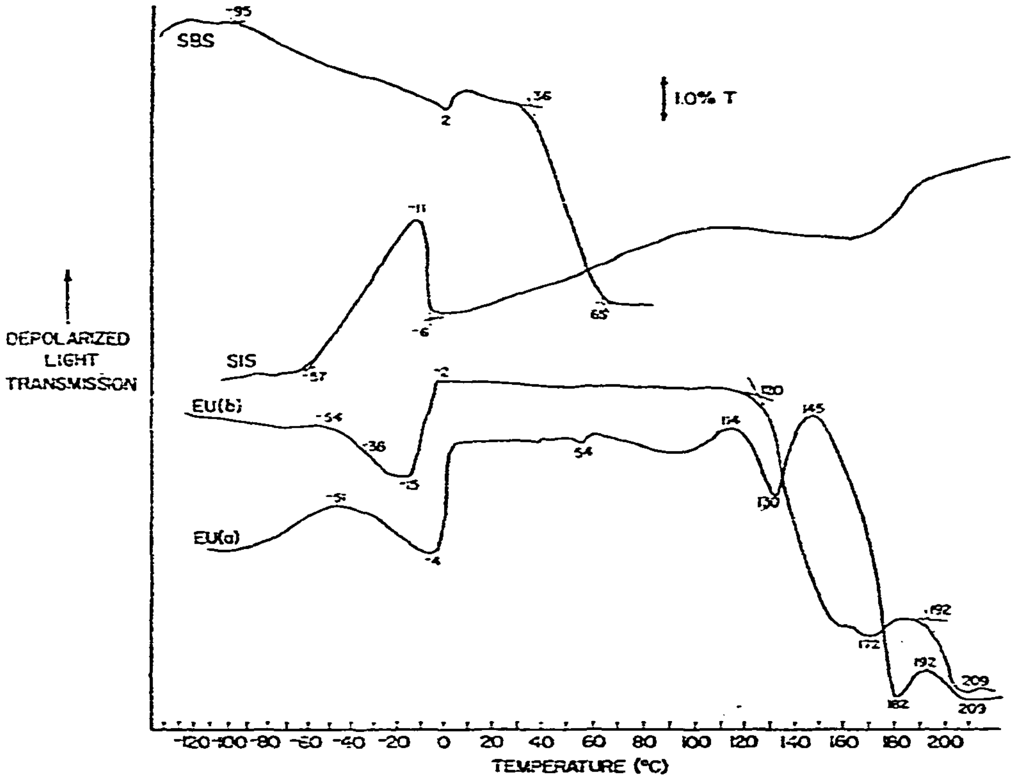

Fig. 8. TDA curves for EU, SIS and SBS block copolymers.

(SBS), where the light transmission begins to steadily decrease. A small amount of rearrangement of further molecular ordering begins at 2 °C, followed by the onset of final fusion, beginning at 36 °C and terminating at 65 °C. The SIS scan shows the onset of reordering or an increase in molecular order at −57 °C, with a total fusion of that order at −6 °C. Since the SIS elastomer was transparent and showed very little scattering, the peak observed for the SIS material is probably that due to further molecular ordering. There are no apparent transitional changes until 160 °C, at which point the SIS begins to decompose.

The change at −95 °C, observed by most thermal techniques, indicates the beginning of motion in the polybutadiene segment of the polymer, and at a programming rate of 5° per min continues until the temperature of 2 °C is reached. The beginning of motion for the polystyrene domains begin at 36 °C and terminates at 65 °C. This latter behavior of the polystyrene domains was also apparent in the DTA scans, but the beginning of fusion at 34 °C in the volume–temperature curves was apparent, agreeing well with the observation by TDA. The depolarization data, however, are apparently much more definitive than either the volumetric or thermometric data in showing the fusion of polystyrene domains. While the transition at −57 °C for the SIS block polymer is usually associated with the glass transition of the polymer, apparently an increase in birefringence or molecular order is occurring within the polymer which seems to manifest itself both in the volumetric and thermometric determinations as a fusion phenomenon. The depolarized light data apparently conflict with the idea of the glass tansition for SIS existing near −57 °C.

The two TDA scans for EU in Fig. 8 illustrate the effects of annealing. The unannealed specimen, curve (a), shows the onset of a further increase in molecular order at −51 °C followed by a second reordering phenomenon at −4 °C. A small change occurs at 54 °C with three fusion phenomena beginning at 114°, 145° and 192 °C. On annealing EU at 110 °C for 16 h, no change in birefringence is noted near −122 °C, but fusion begins at −51 °C and is completed at 75 °C, prior to recrystallization to a higher birefringent level at −2 °C. Major fusion begins at 130 °C with the melting of more ordered polymer from 202° to 209 °C, the latter fusion being in good agreement with the DTA and TDA for unannealed Texin 480A. For the annealing procedure it is easy to visualize the enhancement of urethane–ester hydrogen bonding by annealing at a temperature just slightly above this transition. Furthermore, the temperature of birefringence change usually associated with some degree of crystalline melting or with some degree of molecular disordering is increased on annealing, a behavior similar to the annealing of crystalline polymers. The elucidation of all of these changes are brought about by the extremely high sensitivity of the TDA measurement and the good resolution which is possible with this measurement. It is also selective for changes in crystallinity or molecular order for areas of less than 100 Å[16,17].

Stein[18] has shown that polystyrene rods in SBS exist in the polybutadiene matrix, giving rise to high amounts of form birefringence. Extension of the SBS elastomer orients primarily the polybutadiene segments. The H_v scattering is due to the grains within the SBS matrix, and the birefringence value calculated for this polymer is comparable to the values for spherulitic birefringence, leading to this type of H_v scattering.

The dynamic mechanical properties of the poly(ester–urethane) are shown in Fig. 9 at sub-ambient temperatures for three different frequencies. As the frequencies increase from 3.5 to 110 Hz, the peak temperatures change from −30° to −27° to −20 °C. However, the onset temperature changes from −55° to −50 °C, producing a slightly smaller temperature spread than the temperatures of the peak maxima, and the onset of the damping peaks at 11 and 110 Hz corresponds very well with the measured transition temperatures by linear expansion, torsional modulus and depolarized light techniques. These techniques yielded values in the range −45° to −52°C for the same transition. The temperatures of the peak maxima do not correlate with the DSC curve, but do show a correlation with the extrapolated onset of the torsion modulus curve as well as a correspondence with the end of a first-order transition beginning at −52°C and ending at −25°C, in the volume–temperature curve. The fact that the onset temperature for dynamic mechanical analysis (DMA) damping data corresponds so well with the low-frequency data (DSC, linear expansion and depolarization) as well as the beginning of change in the torsion modulus, could make the assignment of the onset of the dynamic mechanical peak more meaningful than the peak maximum, though the maximum represents a temperature at which the greatest amount of stored energy is lost from the sample.

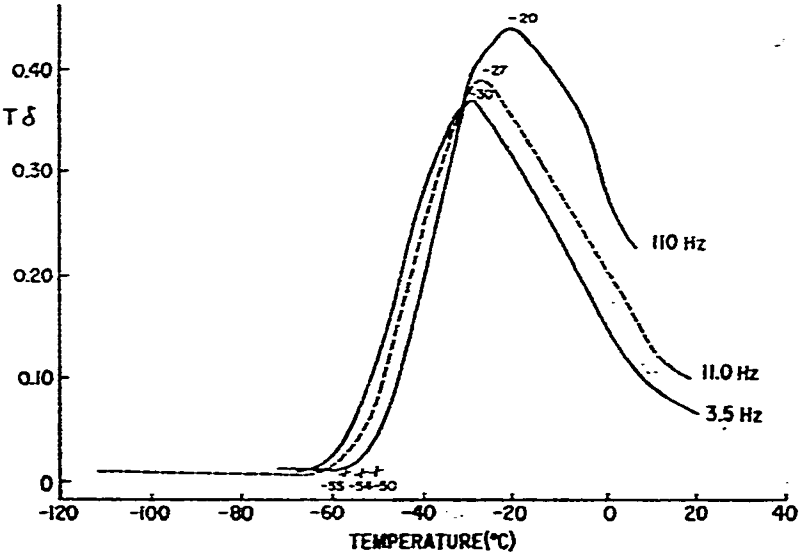

Fig. 9. Mechanical loss characteristics of EU at frequencies of 3.5, 11.0 and 110 Hz.

The dynamic mechanical behavior in Fig. 10 for the SBS and SIS copolymers show that the peak maxima at −72° and −40°C, respectively, do not correspond with any of the values determined by other thermal methods. However, as with the case of the poly(ester–urethane), the onset of the mechanical loss peak at −57° (SIS) and −95°C (SBS) correspond very well with changes by DSC, TDA and volume changes. From these data it might be reasonable to assume then, that the onset of the mechanical loss peak is the more reliable measurement of the temperature of the transition for these elastomers.

The assignment of the transition temperature to the onset of the dynamic mechanical loss peak may be further justified by comparing the DMA curve to a DSC curve. It is well known that DSC curves are usually heating rate from the thermal lag in the cell, and that the peak of the DSC curve changes with heating rate. If we invert the mechanical loss peak, its shape appears the same as a DSC endotherm, and when viewed with the same assignment of temperature change as the onset of a DSC curve, then these temperatures are very likely to correspond.

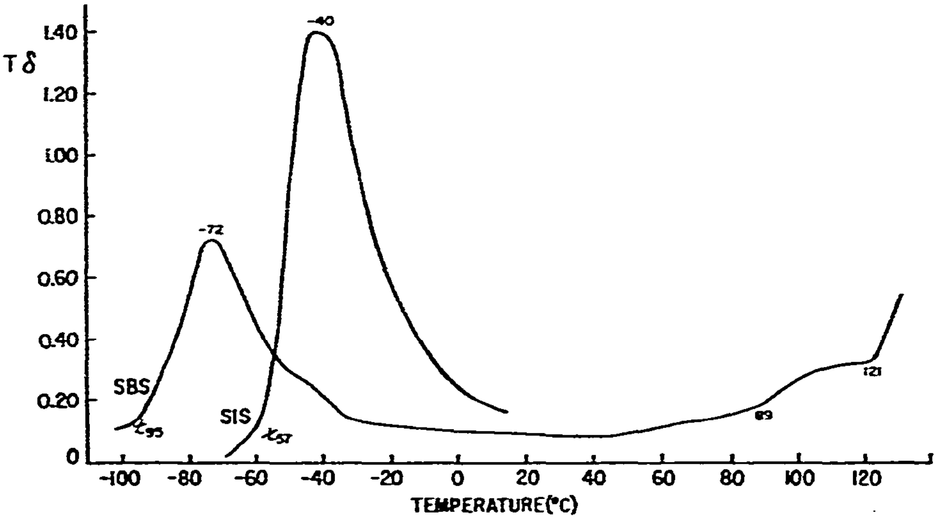

Fig. 10. Dynamic mechanical behavior of SIS and SBS block polymers.

This becomes even more obvious when considering the thermal resistance between the temperature sensing element and the sample for the measurement of DSC and DMA. If the measuring thermocouple is immersed in the sample, then when the property changes as a function of time, the most drastic change in the derivative of the time measurement will occur at the true melting temperature. However, if there is a thermal lag, that is, when the thermocouple is placed at some distance from the sample rather than in the sample, then the peak of this derivative will not be the temperature at which the transition occurs, but more likely the onset of the peak will be the more accurate temperature. The analogy between DMA, DTA, and DSC curves and their temperature assignments should promote the view of needed thermocouple coupling with the sample as well as its reduced sample size.

CONCLUSIONS

Examining the thermal response of segmented elastomers by thermal techniques, whose transducers are significantly different, provides a clearer interpretation of the morphological changes that may occur in block copolymers as a function of temperature. Both the dynamic mechanical analyses (DMA), DTA and DSC respond to properties which are more easily identified than those from the volumetric and depolarization analyses (TDA). However, the volumetric and TDA techniques clearly illustrate ordering or disordering processes that occur at temperatures above the glass transition, and in this sense are more indicative of the morphological change than DSC or DMA. All of the transition temperatures determined in this work appear in Table II.

TABLE II

TRANSITION TEMPERATURES BY VARIOUS THERMAL METHODS

Polymer	*Transition temperature (°C)*					
	DTA	*TDA*	*DMA*[a]	*Volume*	*Lit.*	*Ref.*
Poly(ester-urethane)	−122			−130	−125	7
	−45	−48	−50	−52		
	−12		(−20)	−26		
		1		0		
	74			83		
				136		
	208	209				
Poly(styrene-butadiene-styrene)				−148		
	−80	−95	−95	−78	−80	2
		36	(−72)	34		
		65	89			
			121			
Poly(styrene-isoprene-styrene)	−57	−57	−57	−59	−64	2
		−6	(−40)	−29		
	88					
Trans polybutadiene	−81		−77	−69		
			(−40)	−19	−18	10
	36	36	30	41		
	94	114	70	92		
Cis polybutadiene	−104		−22	−66	−108	10, 11
	−18	−17	−10	−15		
		−5	(−5)	−4		
			18			
1,2-Polybutadiene				−122		
				−72		
	−4	−10		−9	−9	12
		10				
	63	30		42		

[a] Temperatures in parenthesis are damping maxima.

The glass transition for the poly(ester–urethane) may be assigned the value of −122°C while that for the SBS triblock is shown to occur at −110°C, in good agreement with the polybutadiene changes. Because of the TDA response near −57°C for the SIS triblock, the assignment of the T_g for the SIS triblock appears questionable.

The value of −18°C as the glass transition reported in the literature[10] for TBD is quite questionable since a rather large transition occurs in the range −77° to −81°C. This latter low-temperature change is more typically that of a glass transition for TBD, since there is no apparent relaxation or distinct change in the depolarization level in this temperature range. The CBD assignment of −108°C for the glass transition is in good agreement with this work. The changes near −17°C for CBD are first-order transitions as are those occurring at higher temperatures. The very large and abrupt change occurring in the volumetric determination of VBD lends doubt to its assignment at −9°C as a glass transition, since large changes in depolarization also occur in this temperature range. The temperature of −100°C is more likely that of the glass transition for VBD since it corresponds well with the glass transition temperatures noted for the other two stereoregular polybutadienes.

The data from the six elastomers in this work by DMA indicate that the onset temperature of the mechanical loss peak may in many cases be more indicative of the transitional change than the temperatures of the loss peak as they correspond well with low-frequency measurements. In some cases, the peak maximum may be the temperature of fusion as observed by dilatometry, DSC and depolarization techniques. The correlation of DMA transition temperatures with those occurring by a variety of other thermal analytical techniques are indeed necessary for proper assignment.

Ferry[19] has reported that the T_g values for polybutadienes, whose *trans*:*cis*: vinyl contents are 50:43:7, 1.9:96.5:1.6 and 1.5:7:91.5 have T_g values of −101°, −112° and −12°C, respectively. It seems strange that while the high-*trans* and high-*cis* polybutadienes have glass transitions below −100°C, a high-vinyl polybutadiene should have a glass transition temperature about 100° higher. Rather one would expect that with a high-vinyl content most of the possibility for crystallization is lost, and the T_g for high-vinyl polybutadiene should be even lower than the partially crystalline *trans* and *cis* isomers. It has been shown in the literature that increasing crystallinity in a polymer tends to influence the glass transition so that it may occur at a higher temperature than the polymeric form in which no crystallinity is present. The data from this study support this conclusion.

These results support the proposition that the soft blocks in SIS, SBS and EU contribute a major amount to the molecular order within the microstructure of the polymers, and the hard blocks constitute domains within the matrix of the soft block. Stereoregular effects govern the transitional aspects of the soft blocks. Though SIS, SBS and EU have been treated as amorphous polymers, the order present in each of the domains as well as their grain boundaries contribute to large amounts of birefringence which changes on heating.

REFERENCES

1 M. Morton, J. E. McGrath, and P. C. Juliano, *J. Polym. Sci.*, C26 (1969) 99.
2 J. F. Beecher, L. Marker, R. D. Bradford, and S. L. Aggarwal, *J. Polym. Sci.*, C26 (1969) 117.
3 S. L. Cooper and A. V. Tobolsky, *J. Appl. Polym. Sci.*, 10 (1966) 1837; *Text. Res. J.*, 36 (1966) 800.
4 G. W. Miller and J. H. Saunders, *J. Polym. Sci.*, 8 (1970) 1923.
5 G. W. Miller, *J. Appl. Polym. Sci.*, 15 (1971) 39.
6 R. W. Seymour, G. M. Estes, and S. L. Cooper, *Macromol.*, 3 (1970) 579; *Am. Phys. Soc. Meet.*, Cleveland, April, 3 (1971) 365.
7 G. W. Miller, *J. Appl. Polym. Sci.*, 13 (1969) 1277.
8 G. W. Miller, *J. Appl. Polym. Sci.*, 15 (1971) 1985.
9 G. W. Miller, in R. S. Porter and J. F. Johnson (Eds.), *Analytical Calorimetry*, Vol. II, Plenum, New York, 1970, p. 397.

10 J. Brandrup and E. H. Immergut, *Polymer Handbook*, J. Wiley and Sons, New York, 1966, III-73.
11 M. L. Dannis, *J. Appl. Polym. Sci.*, 1 (1959) 121.
12 R. R. Garrett, *Rubber Plast. Age*, 46 (1965) 915.
13 R. A. Robinson and E. F. T. White, in S. L. Aggarwal (Ed.), *Block Copolymers*, Plenum Press, New York, 1970, p. 123.
14 N. Bekkedahl, *J. Res. Nat. Bur. Stand.*, 13 (1934) 411.
15 G. W. Miller, unpublished data.
16 G. S. Y. Yeh, *Am. Phys. Soc. Meet.*, Cleveland, March, 3 (1971) 411.
17 G. W. Miller, *3rd. Int. Conf. Therm. Anal.*, Davos, Switzerland, August, 1971.
18 R. S. Stein, *Polym. Lett.*, 9 (1971) 747.
19 J. D. Ferry, *Viscoelastic Properties of Polymers*, J. Wiley and Sons, New York, 1970, p. 316.