assess the influence of the different types, amounts, and distribution of the short- and long-chain branching on the polymer properties. A study of the specific influence of these factors on the morphology and related properties,[22] similar to that recently reported for linear polyethylene,[23] will be presented shortly.

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(24) We wish to thank Dr. M. E. A. Cudby and Dr. T. Hama for providing us with these samples.
(25) The data of Hama et al.[1] have been corrected such that the major recurring CH_2 resonance has the same value as found in the present study.
(26) The data for the very low molecular weight sample, 13, have been ignored for obvious reasons.
(27) We wish to thank Dr. L. Westerman of Exxon Chemical Corporation, Baytown, Texas for kindly supplying us with these results. We also wish to thank him for most helpful discussions of this part of the problem and his valuable contribution to the interpretation of the results.

Dynamic Mechanical Behavior of Polystyrene–(Ethene-*co*-butene)–Polystyrene, Triblock Copolymer Films Cast from Various Solvents

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ABSTRACT: Films of Kraton G-1650, a styrene–(ethene-*co*-butene)–styrene triblock copolymer, have been cast from a variety of solvents with solubility parameters in the range 15.1 to 20.5 $(\mathrm{J\ m^{-3}})^{1/2}$. The complex modulus E^*, measured at 298 K, was found to vary from 4.4×10^6 N m^{-2} for films cast from low δ solvents to 2.05×10^8 N m^{-2} for films cast from high δ solvents. The areas under the damping peaks in the dynamic mechanical spectra were also altered by the casting solvent, which influences the manner in which the two component blocks are distributed in the solid state. Evidence of limited crystallinity in Kraton-G was found using differential scanning calorimetry and this was also used to estimate the heat capacity changes ΔC_p for the glass transitions associated with each block. These were always found to be less than that expected for the pure component.

It is now well documented that cast films of many block copolymers will exhibit a two-phase morphology which arises from the microphase separation of incompatible blocks into clearly defined regions or domains in the solid state.[1] The extent and nature of this separation will depend on a number of factors. Molau[2] showed that in an (AB) type diblock copolymer, five morphological states can be distinguished which depend on the molecular weight ratio of block B to block A. The shape of these various domain structures can be predicted using a statistical thermodynamic theory of microphase separation developed by Meier[3-5] who has shown that the final structure of a copolymer film will depend not only on the block composition but also on the casting solvent. The importance of the casting solvent in exercising substantial control on the morphology of the cast film was first recognized by Aggarwal et al.[6] and elaborated on by Kawai and co-workers.[7] The latter showed that a systematic change in structure could be detected in diblock copolymer films by changing the nature of the casting medium.

If the casting solvent can affect the sample morphology then it is likely that it will also change the dynamic mechanical response of the film. Miyamoto et al.[8] examined the physical properties of styrene–butadiene–styrene (SBS) films cast from four solvents and observed significant differences in behavior. During the course of this work Hourston et al.[9,10] extended the solvent range and found differences in the longitudinal sonic velocities, densities, and equilibrium swelling behavior of several SBS copolymer films cast from different solvents.

A systematic study of the dynamic mechanical behavior of films of Kraton G-1650, cast from solvents covering a wide range of polarity, is reported here. Kraton G-1650 is a triblock copolymer of styrene–(ethene-*co*-butene)–

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Table I
Characteristics of Kraton G-1650

			wt %		
sample	$10^{-5}M_n$	M_w/M_n	styrene	ethene	butene
Kraton G-1650	0.75	1.36	27	41	32

styrene, S(E/B)S, in which the central block differs from but is similar to that of butadiene in the SBS block copolymers. This should allow one to determine the extent of property variation in a different system and whether the solvent effects are of a general nature.

Experimental Section

Polymer Sample. A specimen of Kraton G-1650 was obtained from Monsanto (Shell), Canada. The material was used unfractionated but was first examined by gel permeation chromatography to determine its purity. The level of contamination from diblock polymer was found to be negligible and the sample was also free of other impurities. Material to be used was dissolved and reprecipitated to ensure this freedom from contamination was maintained, prior to measurements. Analysis of the molecular weight, molecular weight distribution, and structure produced the data shown in Table I and suggests that the block molecular weights are [9450/51000/9450].

Film Preparation. Copolymer films were cast from various solvents either on a clean mercury surface inside a Teflon restraining ring or directly on a Teflon surface inside a rectangular metal form. It has been demonstrated by Lewis and Price[11] that a slow rate of solvent evaporation from the films is required if the film morphology is to remain essentially unaffected by the process. Controlled evaporation rates of 48 to 72 h were used in all film preparation for solution volumes of 10 to 20 cm^3. This was slow enough to ensure that well-defined structures were obtained. Final drying was carried out under vacuum for a 24-h period at temperatures well below the glass-transition temperature of the polystyrene block, T_g^s.

Dynamic Mechanical Measurements. The complex modulus (E^*) and the damping characteristics (tan δ) for the various films were measured in the temperature range 150 to 400 K. Spectra were recorded at a frequency of 11 Hz using a Rheovibron viscoelastometer Model DDV II-C enclosed in an environmental chamber.

Differential Scanning Calorimetry. Glass-transition temperatures (T_g) and melting transitions were established by means of a Perkin-Elmer DSC-2 differential scanning calorimeter. The instrument was equipped with a low-temperature accessory and also with scanning auto zero to correct for base line irregularities. Scan rates of up to 20 K min^{-1} were used normally but in certain cases an improved definition was obtained if this was raised to 40 K min^{-1}. For low-temperature work, helium was used as purge gas. Quantitative measurements were made by weighing film samples of 14.0 to 17.0 mg into container pans which were then sealed; to ensure uniformity of thermal treatment in each run samples were quenched consistently from 330 to 150 K prior to each measurement. The enthalpy change ΔH for the melting transition was measured directly from the area under the thermogram curve, using a calibration constant derived from the melting endotherm of a known quantity of indium as standard. Heat capacity changes ΔC_p were estimated for the glass transitions by direct measurement from the thermograms.

Results and Discussion

Dynamic Mechanical Behavior. Films of Kraton-G were cast from a wide variety of liquids which were selected with solubility parameters (δ) ranging from 15.1 (J m^{-3})$^{1/2}$ to 20.5 (J m^{-3})$^{1/2}$. This ensured that the ability of the liquid to solvate the styrene block (δ = 18.7) ranges from very poor (hexane) to excellent (chloroform and dioxan). With similar crude limits the ability of the liquids to solvate the central block, estimated to have δ = 16.5 from Small's data,[12] decreased with increasing δ for the liquids. All were capable of dissolving the block copolymer completely, but the extent of dispersion of the individual phases within the films will be controlled to some extent by the solvating ability of the casting liquid for each individual block and the relative proportion of each block in the copolymer.

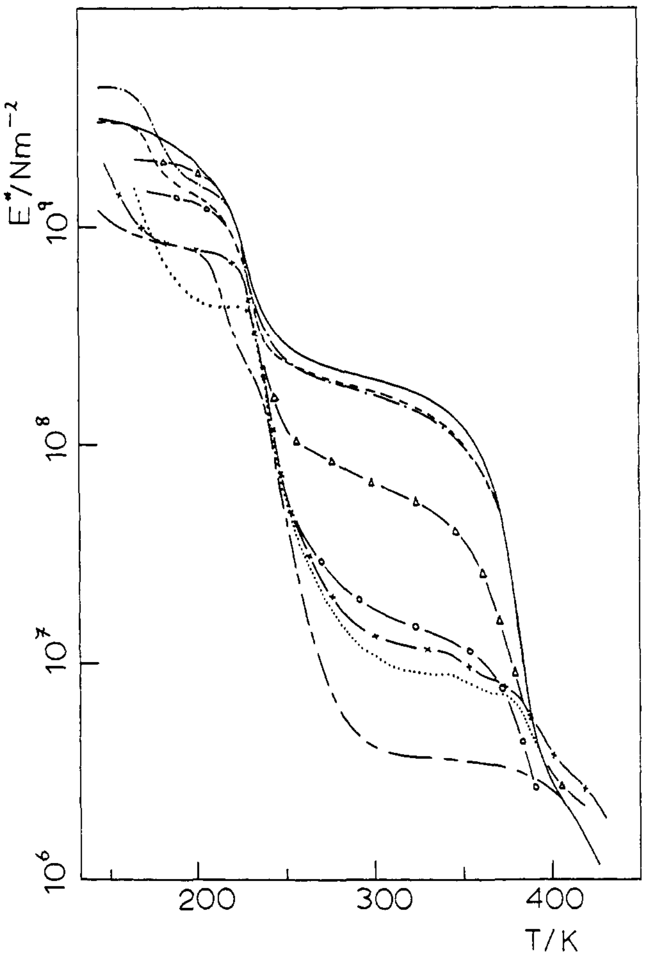

Figure 1. Temperature dependence of the complex modulus E^* for films of Kraton G-1650 cast from the solvents: (—) tetrahydrofuran; (-·-) chloroform; (- - -) toluene; (O) cyclohexene; (Δ) bromobutane; (×) "pressed"; (···) cyclohexane; (— - —) *n*-heptane.

This ought to be reflected in the dynamic mechanical response of each film and a series of E^*–temperature curves obtained for films cast from eight solvents are shown in Figure 1, while the corresponding damping behavior is shown in Figure 2. It is immediately obvious that while the modulus is altered slightly in the completely glassy state, T < 200 K, by the casting solvent, the effect is much more dramatic in the rubbery plateau region lying in the temperature range 240–370 K, between the glass transitions of the two blocks. As a measure of these differences one can select a value of E^* at 298 K as an arbitrary reference and indicator of the mechanical stiffness of these films in this ambient temperature range. Values of E^*(298) are recorded in Table II. When the casting solvent has a δ of greater than 18.0 the E^*(298) are in excess of 10^8 N m^{-2}, but this drops rapidly down to about 4 × 10^6 N m^{-2} when δ decreases to 15.1.

These observations agree with the results of previous workers who studied SBS[8-10] and SIS[9,10] block copolymers, although in the Kraton-G case the wider range of solvents used helps to demonstrate a distinct trend in behavior which was not so obvious in earlier work. In the absence of electron micrographs, one cannot comment on the precise morphologies of our films. The data do, however,

Table II
The $E^*(298)$ Moduli and Glass-Transition Temperatures for Kraton-G Films Cast from Several Solvents

			T_g^R		T_g^S
casting solvent	δ, $(\mathrm{J\,m^{-3}})^{1/2}$	$E^*(298)$, N m^{-2}	tan δ (11 Hz)	DSC	tan δ (11 Hz)
n-heptane	15.1	4.4×10^6	244	206	407
cyclohexane	16.8	1.2×10^7	241	207	393
"pressed"	(17.4)	1.4×10^7	240	206	392
cyclohexene	17.5	1.9×10^7	238	206	381
bromobutane	17.8	6.5×10^7	235	210	387
toluene	18.2	1.75×10^8	231	209	385
tetrahydrofuran	18.6	2.05×10^8	232	206	380
chloroform	19.0	1.70×10^8	233	205	382
dioxan	20.5	1.03×10^8	230		383

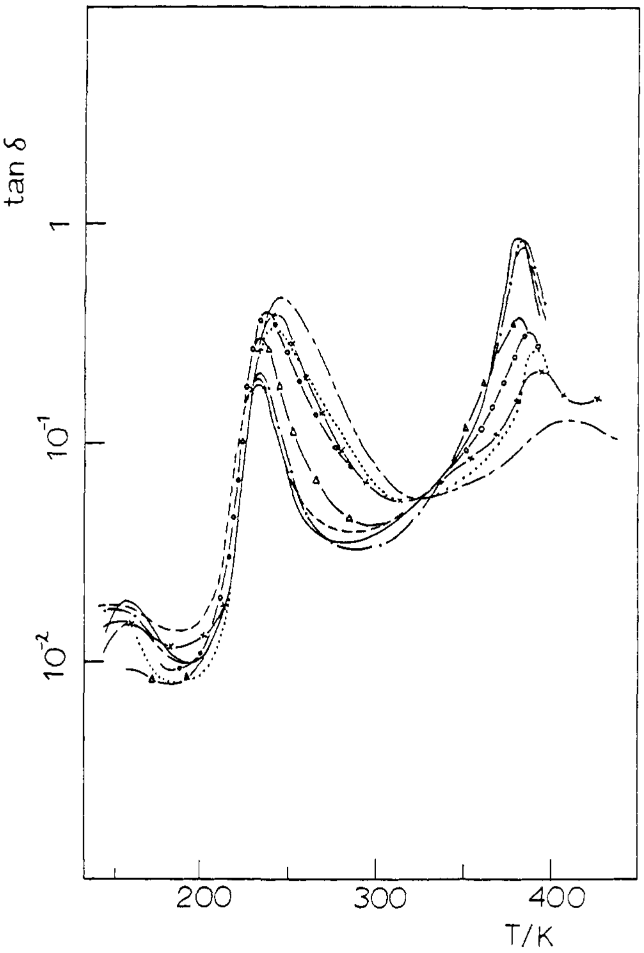

Figure 2. Temperature dependence of tan δ for films of Kraton G cast from various solvents. Key as for Figure 1.

support the explanations proposed by others concerning the relationship between film modulus and the extent of dispersal of the polystyrene phase.[1] Information relating to this phase dispersal is obtained from the damping spectra which exhibit three main features. In each there is a large damping peak centered around 230–240 K which can be assigned to the glass transition of the (E/B) block T_g^R; a second large damping peak, corresponding to the glass transition of the polystyrene block (T_g^S), normally has its maximum located in the temperature range 380–400 K, and a minor peak is found in the vicinity of 150 K.

As the areas under the appropriate glass transition damping maxima can be used as a measure of the solvent quality for each block, and will indicate the extent of dispersion of the component phase in the film, it is instructive to examine these trends in more detail. The analysis is summarized in Figure 3 where a sigmoidal dependence of both E^* and peak area on δ is clearly seen.

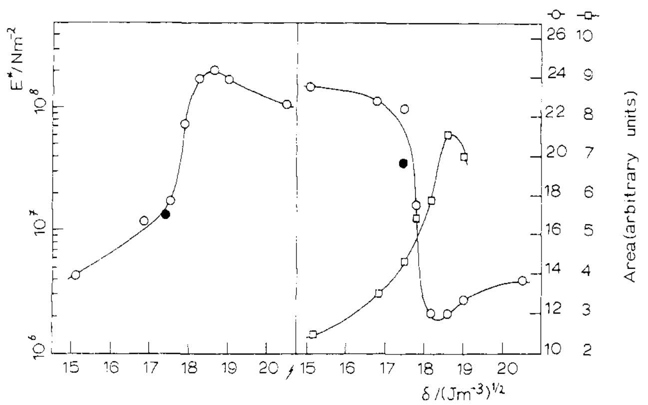

Figure 3. (a) Variation of $E^*(298)$ for Kraton G films, with the solubility parameter of the casting solvent (δ). The point marked with a solid circle is for a film pressed in the absence of a solvent. (b) *Area under the tan δ damping of the* (E/B) block (○) plotted as a function of the δ parameter of the casting solvent; (□) the curve for the area under the tan δ damping peak of the polystyrene block. Areas are measured in arbitrary units.

The curves could be used to predict $E^*(298)$ for any film of Kraton-G cast from a liquid lying within this range of δ parameters, or to predict the response of a hot pressed Kraton-G film prepared in the absence of any solvent. The latter can be achieved by assigning an approximate solubility parameter on the basis of a proportional contribution from the individual components. This gives a value of $\delta = 17.4\ (\mathrm{J\,m^{-3}})^{1/2}$. If this represents the interaction of the two blocks and controls the morphology then one would expect, by reference to the curve in Figure 3, a plateau modulus $E^*(298)$ of 1.6×10^7 N m^{-2}. This is in remarkably good agreement with the experimental value of $E^*(298) = 1.4 \times 10^7$ N m^{-2}. The area under the (E/B) block T_g^R damping peak also matched the curve in Figure 3 reasonably well.

The maximum for the damping peak associated with the (E/B) block, i.e., T_g^R, varied from 230 to 244 K when measured at 11 Hz, but this is dictated by the broadening of the damping peak rather than to a real increase in glass-transition temperature. The changing distribution of the (E/B) phase in the sample results in a changing spectrum of relaxational modes in the sample and a change in the area of the damping peak. The essentially constant value of T_g^R, obtained when measured by DSC, suggests that no fundamental change in T_g^R is brought about by varying the casting solvent.

The small damping peak, seen at 150 K in most samples of Kraton-G, is absent in the damping spectra of SBS block copolymers. One can then assume that it originates in the central (E/B) block and has its origins in one of two possible molecular mechanisms.

It was demonstrated previously[13] that a similar damping peak developed in this temperature region, during the hydrogenation of polybutadiene. It was suggested that

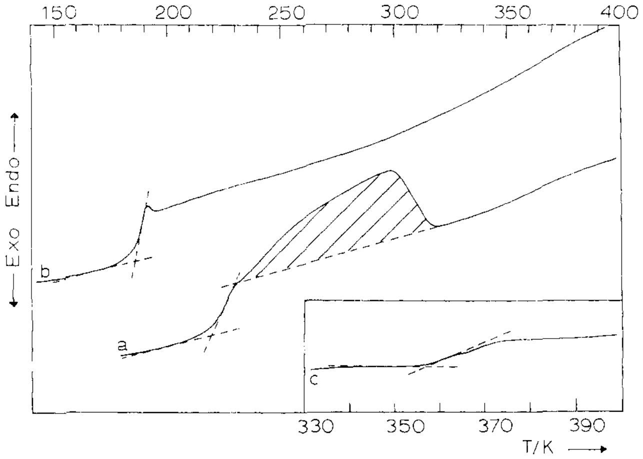

Figure 4. DSC thermograms for a Kraton G film, curve (a), and a styrene-butadiene-styrene block copolymer film, curve (b). The inset (c) is an enlargement of the glass-transition region of the polystyrene block in Kraton G showing the two-step behavior. Only the first step is marked with the broken lines.

once sequences of six to eight methylene units were formed in the polybutadiene chain, they would be capable of undergoing a "crankshaft" motion. As the (E/B) block is a random copolymer of ethene and but-1-ene, with a preponderance of the former, then this block will contain sequences of methylene units in the chain backbone which will be of an appropriate length to undergo a crankshaft movement of either the Boyer[14] or Schatzki[15] type. This seems to be the most likely explanation and the one which we favor, although there is a possibility that the small quantity of ethyl side chains present in the central block would also be capable of rotation in this temperature range. Indeed if both processes are present the damping could overlap and be indistinguishable.

DSC Thermograms. The DSC spectra which are obtained from the Kraton-G films are essentially identical in shape and number of prominent features. The curve (a) shown in Figure 4 is typical of all those measured for the films cast from different solvents, and three main events are obvious. At low temperatures there is a pronounced base line shift characteristic of a glass transition, which can be identified as the T_g^R of the (E/B) block. The value of T_g^R was found to be constant at 209 ± 2 K. Above the glass transition of the (E/B) block there is a broad, ill-defined, melting endotherm, shown as the shaded area in Figure 4. This tends to reach a diffuse maximum around 285 K in all cases although the definition is relatively indistinct. This suggests that the polymer possesses a small number of poorly defined crystalline regions within the matrix associated with the (E/B) block. The breadth of the endotherm implies the presence of small irregular crystallites varying greatly in both size and perfection. It is instructive to compare these thermograms with a similar series obtained previously when studying the hydrogenation of polybutadiene.[13] Here crystallinity developed gradually as hydrogenation progressed and at about 40-45% hydrogenation similar broad endotherms were detected, with peaks around 250-260 K. The general shape and temperature range covered were similar to those obtained for Kraton-G. This would suggest that the endotherm arises from the melting of small ordered ethylenic sequences present in the central block of the copolymer but that the butene units prevent this from developing further.

While the endotherms look very much alike in the various Kraton-G films, a quantitative estimate of the enthalpy of melting ΔH from the area under each curve reveals a definite trend with casting solvent. This can be seen in Table III, where ΔH decreases as the solubility parameter of the casting solvent increases. If it is assumed that this crystallinity arises exclusively from the central block, then ΔH, expressed as J g^{-1} of (E/B), varies from 23.5 J g^{-1} (E/B) for *n*-heptane cast films to 17.1 J g^{-1} (E/B) for chloroform cast films. This suggests that less of the central block is available to enter into an ordered structure in films formed using high δ solvents, perhaps because restriction of the (E/B) domains by the more effectively dispersed polystyrene impairs the ability of the (E/B) to crystallize.

Table III
Enthalpy Change for Melting of the Crystalline Portion of Ethene-Butene Block and Changes in Heat Capacity Associated with the Glass Transitions of Each Block

casting solvent	ΔH, J g^{-1} (E/B)	ΔC_p, J K^{-1} g^{-1} (E/B)	ΔC_p, J K^{-1} g^{-1} (PS)
n-heptane	23.5	0.246	0.117
cyclohexane	22.9	0.263	0.125
"pressed"	23.0	0.250	0.109
cyclohexene	19.0	0.175	0.063
bromobutane	18.3	0.167	0.088
toluene	17.4	0.175	0.121
tetrahydrofuran	17.2	0.167	0.096
chloroform	17.1	0.167	0.134
dioxan			0.121

This crystalline order does not appear to influence the magnitude of the modulus in the plateau region where the melting occurs, as the greatest tendency to form an ordered structure involving the (E/B) blocks is found in the low modulus films. The observed change in modulus with casting solvent must then be due entirely to the way in which the polystyrene phase is distributed throughout the film and is unrelated to the crystalline content of the polymer which might have been expected to enhance the mechanical stiffness. This is perhaps not too surprising as the percentage crystallinity can be estimated to be less than 10%, if the value of 240 J g^{-1} for the enthalpy of fusion of polyethene is used as a comparison.[16]

The third feature of the thermograms is the glass transition associated with the polystyrene block. This is relatively indistinct compared with the other two features but can be enhanced by increasing the scan rate to 40 K min^{-1} and by using a shorter and higher temperature scan range with nitrogen as purge gas. The base-line shift associated with the glass transition takes place over a somewhat extended range of temperature, usually about 345 to 370 K. There is also the suggestion of a two-step movement in this range but this was difficult to define accurately. A polystyrene sample with a chain length comparable with that of the polystyrene block in Kraton-G exhibited a clear, sharp, one-step transition at 364 K when measured at the same scan speed and under similar conditions. Thus the first step may represent the glass transition of polystyrene in the mixed phase at the edges of the pure polystyrene domains, where there is a partial dilution by the (E/B) blocks causing a small depression of T_g^s. The second step then corresponds to the glass transition of the polystyrene domains themselves. As the transitions are relatively weak because of the low styrene content of the Kraton-G, more conclusive evidence may be obtained if a copolymer with a larger styrene content is studied. This transition was not subject to changes brought about by varying the casting solvent.

Heat capacity changes ΔC_p, associated with each of the blocks in the copolymer, were estimated from the thermograms and are listed in Table III. Again values are 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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