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Thermally Stimulated Discharge Current and Dynamic Mechanical Investigation of Polyisobutylene−Polybutylene Terephthalate Thermoplastic Multiblock Copolymers

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ABSTRACT: Characterization of polyisobutylene (PIB)−polybutylene terephthalate (PBT) multiblock copolymers by thermally stimulated discharge (TSD) current and dynamic mechanical analysis (DMA) methods is described. Both the length of the PIB segments (2200−10000 g/mol), and the overall composition (30−80 wt %) of the multiblock copolymers were varied. Both methods support the block structure of the multiblock copolymers investigated. Despite the apolar nature of the PIB segments, they proved to be detectable by the TSD method. The relaxation times and the mobility of the chain length were also determined.

Introduction

Thermoplastic elastomers (TPEs) represent one of the most important classes of copolymers.[1] The importance of these materials is demonstrated by the commercial introduction of different types of TPEs in the early 1970s. TPEs, consisting of a PIB soft segment connected to a polyester hard segment, possess good thermal stability and processing.[2] The synthesis of well-defined (PIB-*b*-PBT)$_n$ multiblock copolymers can be achieved by reaction of dihydroxy telechelic PIB with dimethylterephthalate plus butanediol.[3] The synthesis of dihydroxy telechelic PIB with controlled M_n and M_w/M_n can be achieved by living cationic polymerization, which yields polymers with very narrow molecular mass distribution ($M_w/M_n < 1.1$). If the length of the PIB segments and the overall composition are varied, the lengths of the polyester segments can be changed. The resulting copolymers were thermally stable up to 260 °C.

Our goal was to study (PIB-*b*-PBT)$_n$ multiblock copolymers by TSD[4−8] and DMA in order to get insight into the relaxation processes of multiblock copolymers, and to support the block structure of (PIB-*b*-PBT)$_n$ copolymers. Another goal was to prove the applicability of TDS to block copolymers containing apolar segments.

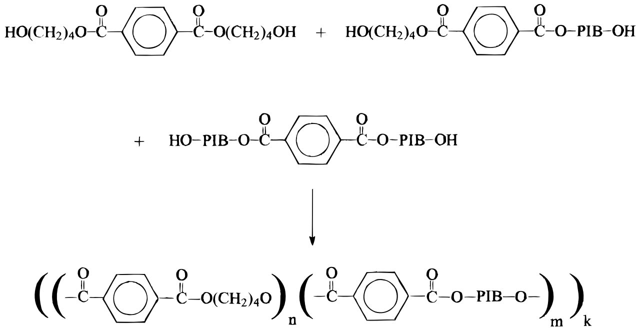
Experimental Section

Synthesis of (PIB-*b*-PBT)$_n$ Multiblock Copolymers. The synthesis of the copolyesters investigated has been described in a previous paper.[3] The synthesis route is shown in Scheme 1.

The molecular mass of PIB soft segments were 2200, 4800, and 10000 g/mol. The overall composition of the copolymers with respect to PIB were varied in the 30−80 wt % range.

Sample Preparation for TSD and DMA Measurements. Plates of 0.2 mm and 1 mm were compression molded at 160 °C and 2.5 MPa. Disks of 53 mm diameter were cut for TSD experiments. The plates were supplied with sputter-coated gold on both sides of the electrodes of 38 mm diameter.

Scheme 1. Schematic Synthesis Route for the (PIB-*b*-PBT)$_n$ Multiblock Copolymers



Strips of 30 × 10 × 1 mm were cut for DMA measurements. Samples containing 30 and 50 wt % PIB of $M_n = 2200$ g/mol were not suitable for sample preparation because of rigidity and brittleness.

Apparatus and Experimental Conditions. A detailed description of the TSD method has been published.[6] The scheme of the TSD apparatus used is shown in Figure 1.

Because of the thin samples, a relatively low 600 V polarizing voltage was applied and the heating rate was 1 K/min. This voltage produces about 3 kV/mm polarizing field. After 10 min polarization at 110 °C, the samples were cooled to −120 °C at 1 K/min. The recorded depolarization current values were transformed to 1 kV/mm electric field and 30 cm^2 electrode area.[6]

DMA measurements were carried out with a Rheomertics MK−III DMA system at 1 Hz frequency and 32 μm deformation amplitude in a dual cantilever mode ranging from −90 to +140 °C at 2 K/min heating rate.

Theoretical Background of TSD

The initial polarization (P_0) is proportional to the E_p forming (polarizing) the electric field. In case of the "short circuit" method, the external field (E) is zero during depolarization; i.e., eq 1 is valid. The heating rate

$$\int_0^1 E\,dx = 0 \quad j \neq 0; \qquad (1)$$

of the sample was constant (b) during the measurement

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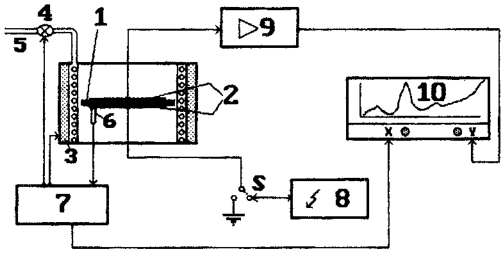


Figure 1. Schematic representation of TSD instrument: 1, sample; 2, electrodes; 3, heating and cooling block; 4, liquid N$_2$ valve; 5, liquid N$_2$ inlet; 6, temperature sensor; 7, temperature programmer; 8, high voltage supply; 9, current amplifier; 10, X−Y recorder.

of the current density (j)

$$T = T_0 + bt \tag{2}$$

where T = absolute temperature and T_o = initial temperature.

The relaxation time of dipoles can be described by the Arrhenius-type equation

$$\tau_{(T)} = \tau_o e^{-A/RT} \tag{3}$$

where τ = relaxation time at T, τ_o = preexponential factor, and A = activation energy.

Assuming a single relaxation process, the depolarization current density ($j_{(T)}$) at temperature T produces an asymmetrical peak in the temperature function and can be calculated by eq 4, where P_o = initial polarization.

$$j_{(T)} = -\left(\frac{P_o}{\tau_o}\right) \exp\left[-\frac{A}{RT} - \frac{1}{b\tau_o}\int_{T_o}^{T} \exp\left(-\frac{A}{RT}\right) \mathrm{d}T\right] \tag{4}$$

The total current is obtained by simplifying eq 4, by using $C = AP_0/\tau_0$, $B = A/Rb\tau_0$, and $s = A/RT$ (where A = area of the electrode) and integrating by using a series expansion of eq 4 with respect to s.

$$I(s) = C \exp\{-s - B[e^{-s}(s^{-2} - 2s^{-3} + 6s^{-4} + ...]_{s_o}^{s}\} \tag{5}$$

Thus, τ_0 can be calculated by eq 6, where T_m =

$$\tau_0 = \frac{RT_m^{\,2}}{bA \exp(A/RT_m)} \tag{6}$$

temperature at the maximum of the current peak. The activation energy can be obtained from the half width of either the lower (eq 7) or the upper peak (eq 8),

$$A = 1.443R\frac{1}{\frac{1}{T_l} - \frac{1}{T_m}} \tag{7}$$

$$A = 0.962R\frac{1}{\frac{1}{T_m} - \frac{1}{T_u}} \tag{8}$$

where T_l = the lower half temperature of a current peak and T_u = the upper half temperature of a current peak.

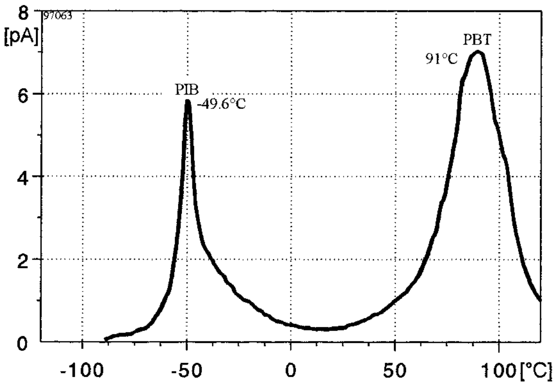


Figure 2. TSD trace of sample containing 75 wt % PIB of M_n = 4800 g/mol.

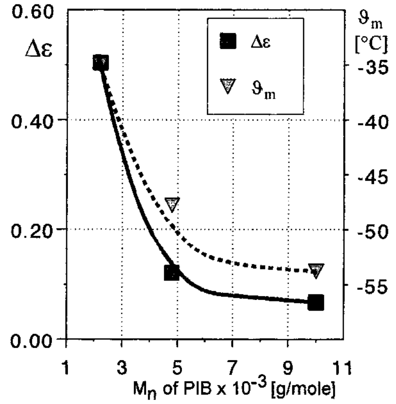


Figure 3. The change of the $\Delta\epsilon$ relaxation strength and the ϑ_m peak temperature values of samples containing 75 wt % PIB of (PIB-*b*-PBT)$_n$ multiblock copolymers on the molecular mass of PIB blocks.

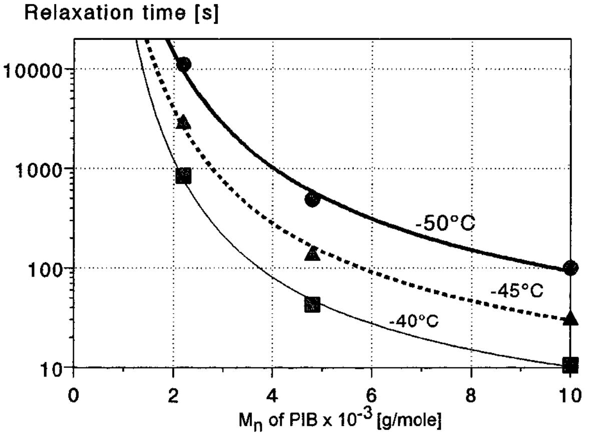


Figure 4. Relaxation time of PIB segment motions vs molecular mass of PIB segments at different temperatures.

The total charge of the transition (Q) is given by

$$Q = \int_{t_o}^{t} I\,\mathrm{d}t = \frac{1}{b}\int_{T_1}^{T_2} I\,\mathrm{d}T \quad (T_1 \ll T_m \text{ and } T_2 \gg T_m) \tag{9}$$

The relaxation strength ($\Delta\epsilon$) can be calculated as

$$\Delta\epsilon = \sigma/E\epsilon_0 \tag{10}$$

where $\sigma = Q/A$ is the charge density of the surface and ϵ_o = permittivity of vacuum.

Since the conditions in eq 1 are fulfilled, multiple transitions can be regarded as the sum of currents of

Table 1. Resolved Peaks of TSD[a]

sample	parameters	1 PIB	2 PBT1	3 PBT2	4 PBT3	5 PBT4
wt $\%_{PIB} = 30$ $M_{n,PIB} = 10000$ g/mol	ϑ_m (°C)	−55	79	85	50.9	
	I_m (pA)	1.6	20	30	5	
	A (kJ/mol)	95	159	105	105	
	τ_0 (s)	4.48−21	1.01−21	2.96−13	5.92−15	
	$\Delta\epsilon$	0.039	0.769	1.775	0.243	
wt $\%_{PIB} = 50$ $M_{n,PIB} = 10000$ g/mol	ϑ_m (°C)	−53	79.9	88.5	23.6	
	I_m (pA)	2.75	32	32	0.86	
	A (kJ/mol)	94	185	126	43	
	τ_0 (s)	1.28−20	1.43−25	3.28−16	2.76−05	
	$\Delta\epsilon$	0.070	1.068	1.62	0.0814	
wt $\%_{PIB} = 75$ $M_{n,PIB} = 10000$ g/mol	ϑ_m (°C)	−53.8	86.9	96	19	
	I_m (pA)	3.55	8.2	13	0.44	
	A (kJ/mol)	97	175	75	46	
	τ_0 (s)	1.97−21	1.51−23	2.21−23	5.52−06	
	$\Delta\epsilon$	0.0675	0.300	1.026	0.038	
wt $\%_{PIB} = 30$ $M_{n,PIB} = 4800$ g/mol	ϑ_m (°C)	−48.5	52	89.4	10.8	
	I_m (pA)	1.78	4.38	17	0.95	
	A (kJ/mol)	90	84	77	40	
	τ_0 (s)	3.32−19	1.01−11	6.86−09	4.41−05	
	$\Delta\epsilon$	0.049	0.265	1.38	0.0883	
wt $\%_{PIB} = 75$ $M_{n,PIB} = 4800$ g/mol	ϑ_m (°C)	−47.2	85	99		−35
	I_m (pA)	5	4	4		1.6
	A (kJ/mol)	105	99	95		40
	τ_0 (s)	1.29−22	2.35−12	3.37−11		1.19−06
	$\Delta\epsilon$	0.120	0.250	0.28		0.106
wt $\%_{PIB} = 70$ $M_{n,PIB} = 2200$ g/mol	ϑ_m (°C)	−35	72	97.6		
	I_m (pA)	20	3.5	3		
	A (kJ/mol)	111	78	63		
	τ_0 (s)	1.15−22	1.20−09	1.45−06		
	$\Delta\epsilon$	0.504	0.255	0.296		

[a] ϑ_m = temperature in °C at the maximum of the current peak. I_m = maximum of the current peak.

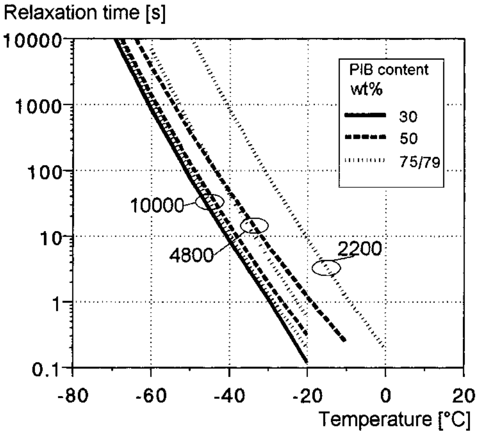


Figure 5. Relaxation time map of PIB segments of the (PIB-*b*-PBT)$_n$ multiblock copolymers. The numbers refers to the molecular mass of PIB segments.

individual transitions given by eq 11, where $I_{d(T)}$ = total

$$I_{d(T)} = \sum_{i=1}^{n} I_{d(T)i} \tag{11}$$

current; $I_{d(T)i}$ = current of individual transitions. Equation 11 cannot be applied for layered samples or for samples possessing a rough phase structure. In the latter case current inversion may occur, which can easily be recognized by the negative peaks in the TSD spectrum.

Results and Discussion

Thermally Stimulated Discharge (TSD). A typical TSD spectrum of the (PIB-*b*-PBT)$_n$ multiblock copolymer is shown in Figure 2, demonstrating that there are two well-distinguished regions in the TSD spectra of the samples.

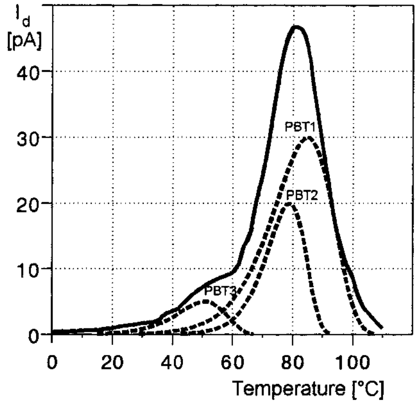


Figure 6. High-temperature part of the resolved depolarization spectrum of the (PIB-*b*-PBT)$_n$ multiblock copolymer containing 30 wt % PIB of M_n = 10 000 g/mol. Solid line represent the measured, while the dashed lines the resolved transitions listed in Table 1.

To evaluate these spectra, the individual transitions were considered as a single relaxation process and approximated by eq 5. The peaks of the lower and higher temperature region can be assigned to the PIB and polyester segments, respectively. The appearance of the lower peak referring to the PIB segments is unexpected since these segments are nonpolar. A possible explanation for the occurrence of the lower peak is that the polar polyester chain environment induces polarization of the soft apolar segments. The activation energy was determined from the width of the TSD current peak, and the

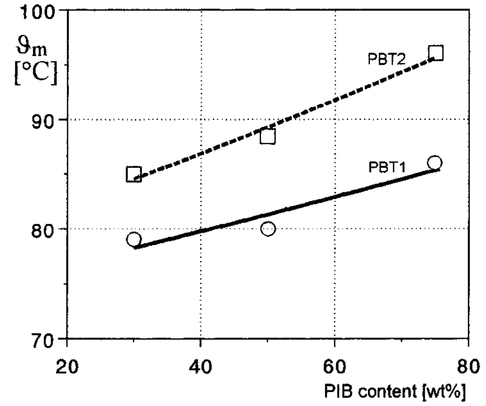


Figure 7. Depolarization current peak maxima of PBT1 and PBT2 transitions vs PIB content (M_n of PIB segments is 10 000 g/mol).

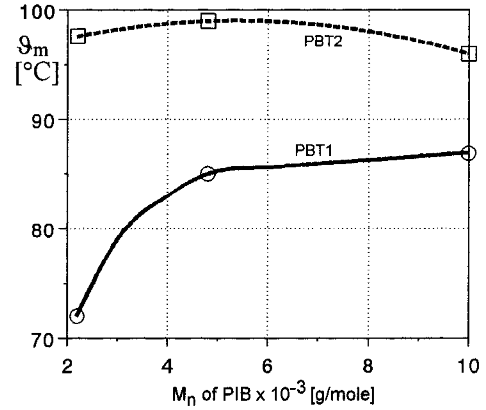


Figure 8. Depolarization current peak maxima of PBT1 and PBT2 transitions vs molecular mass of PIB (PIB content = 75 wt %).

Table 2. Results of DMA, Giving ϑ_{max} and tan δ_{max} Values for the (PIB-*b*-PBT)$_n$ Multiblock Copolymer

	peak 1 (PIB)		peak 2 (PBT)	
sample	ϑ_{max} [°C]	tan δ_{max}	ϑ_{max} [°C]	tan δ_{max}
wt %$_{PIB}$ = 30 $M_{n,PIB}$ = 10000 g/mol	−58.4	0.155	68.2	0.134
wt %$_{PIB}$ = 50 $M_{n,PIB}$ = 10000 g/mol	−33.9	0.781	91.2	0.283
wt %$_{PIB}$ = 75 $M_{n,PIB}$ = 10000 g/mol	−34.2	0.911	*a*	*a*
wt %$_{PIB}$ = 30 $M_{n,PIB}$ = 4800 g/mol	−26.0	0.307	71.4	0.171
wt %$_{PIB}$ = 75 $M_{n,PIB}$ = 4800 g/mol	−33.3	0.912	92.1	0.144

[a] Not detectable.

resolved and identified peaks are summarized in Table 1.

However, the TSD spectra clearly demonstrated that all samples were block copolymers. Figure 3 shows the ϑ_m peak maxima and $\Delta\epsilon$ relaxation strength values of high PIB-containing copolymers as a function of the molecular mass of the PIB segments.

The change of $\Delta\epsilon$ is significant. Interestingly, both values decrease by increasing the PIB chain length. The PIB peaks are not the direct responses of the PIB segments, thus, no proportionality is expected between the PIB concentration and the peak intensities ($\Delta\epsilon$). This means that the polar blocks may polarize the PIB segments; in other words, the dependence of $\Delta\epsilon$ and ϑ_m on the molecular mass of PIB segments can be explained by considering a polarization of the PIB segments by the polar hard segments.

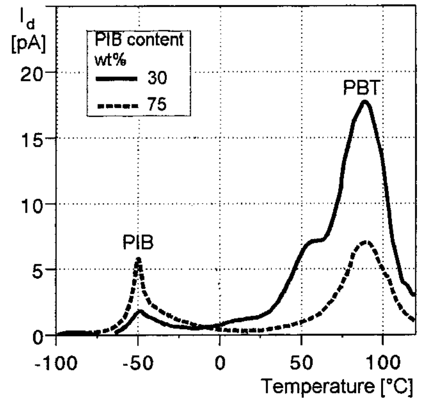


Figure 9. Depolarization spectra of (PIB-*b*-PBT)$_n$ copolymers containing 30 and 75 wt % PIB of M_n = 4800 g/mol.

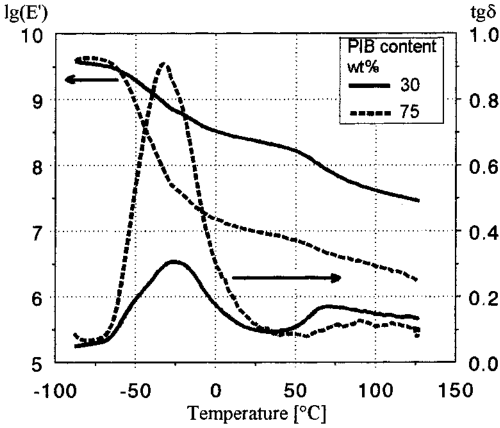
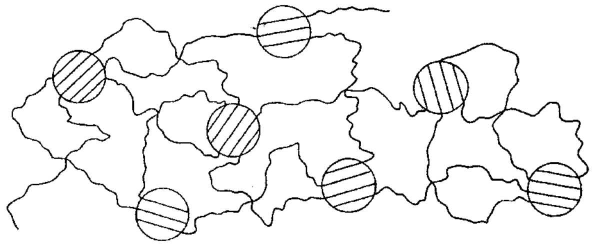


Figure 10. The results of dynamic mechanical analysis obtained on the (PIB-*b*-PBT)$_n$ multiblock copolymers (M_n of PIB segments is 4800 g/mol).

Scheme 2. Schematic Representation of the Microdomains of the (PIB-*b*-PBT)$_n$ Multiblock Copolymer



Upon calculation of relaxation times for PIB transitions, a strong dependence on the molecular mass of the PIB segments can be observed (see Figure 4), but the relaxation time is independent of the PIB-content, as shown in Figure 5.

A split transition is assigned to the PBT polyester segments in the range 20−120 °C. Typical resolved high-temperature TSD transitions of a sample containing 30 wt % PIB segment of M_n = 10 000 g/mol is shown in Figure 6.

The multiple TSD transitions can be attributed to the multimodal distribution of the PBT segments in domains of the thermoplastic multiblock copolymer.

The values of ϑ_m as a function of PIB-content, and M_n of the PIB blocks are plotted in Figures 7 and 8, respectively.

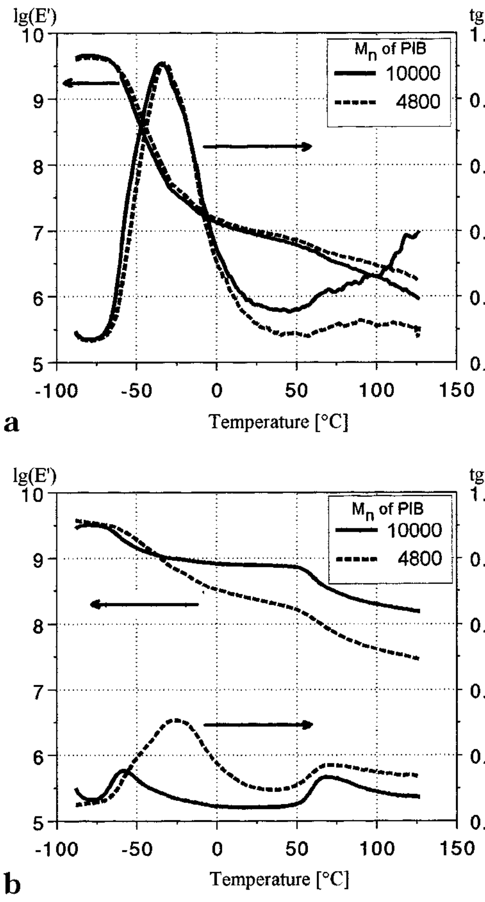


Figure 11. (a) Results of dynamic mechanical analysis obtained on the (PIB-*b*-PBT)$_n$ multiblock copolymers containing 75 wt % PIB of M_n = 4800 and 10000 g/mol. (b) Results of dynamic mechanical analysis obtained on the (PIB−PBT)$_n$ multiblock copolymers containing 30 wt % PIB of M_n = 4800 and 10 000 g/mol.

The length of the PBT blocks is dependent on the number of the active endgroups of PIB; therefore, a high PIB-content yields short PBT blocks, and the shorter the PBT block- length, the lower is the mobility (higher ϑ_m; see Figure 9). However, the ϑ_m of PBT2 does not depend on the M_n of the PIB blocks.

Dynamic Mechanical Analysis (DMA). DMA results also indicate a block structure of the copolymers investigated. The presence of the PIB and the PBT segments are signaled both in the modulus (E') and in the loss factor (tan δ). DMA results are summarized in Table 2.

The multiblock (PIB-*b*-PBT)$_n$ forms microcrystalline microdomains during microphase separation as shown in Scheme 2.

The flexibility of the rubbery PIB chains is reduced by the microcrystalline PBT microdomains. By increasing the PIB content the number of PBT domains decreases, i.e., the PIB chains move more freely. Therefore, the lower the PIB content the higher is the tan δ_{max} (see Figure 10). The chain-length of PIB has little effect on the mechanical behavior at high PIB concentrations (see Figure 11a). By increasing the length of PIB, a significant shift of tan δ_{max} to lower temperatures can be noticed at low PIB contents (see Figure 11b). This shift can be explained by considering that in the presence of shorter PIB chains crystalline PBT microdomains are more frequent than that of the longer PIB chains.

Conclusions

The TSD and DMA results support the block structure and phase separation of the copolymers investigated. TSD proved to be very useful for characterizing block copolymers. The polar blocks may induce polarization of the soft, nonpolar segments. TSD can be utilized to obtain information on the relaxation processes of different copolymer segments. This technique is also useful to investigate the modality of polar and nonpolar segments in block copolymers.

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