Morphology and Molecular Miscibility of Segmented Copoly(ether ester)s with Improved Elastic Properties As Studied by Solid State NMR

Wouter Gabriëlse,*,† Viola van Guldener,† Holger Schmalz,‡ Volker Abetz,‡ and Ronald Lange†,§

DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands, and Makromolekulare Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany

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ABSTRACT: The morphology of copoly(ether ester) elastomers, based on poly(butylene terephthalate) (PBT) hard blocks and poly(ethylene oxide)-*block*-poly(ethylene-*stat*-butylene)-*block*-poly(ethylene oxide) (PEO-*b*-PEB-*b*-PEO) soft blocks, has been investigated by various solid-state NMR methods. ^{13}C IRCP and ^{1}H $T_{1\rho}$ NMR experiments show a heterogeneity in molecular motions for the PEO and PBT segments, indicating the presence of a PEO-rich phase and a PEO/PBT mixed phase. In contrast, for the PEB segments a homogeneous NMR relaxation behavior is observed, indicating the presence of a separate pure PEB phase. Deuterium NMR spectra recorded of block copolymers with selectively deuterated PBT clearly show at least two distinct motional environments of PBT already at room temperature: a broad peak which is assigned to PBT segments in a crystalline phase and an extremely narrow peak which is assigned to highly mobile PBT segments embedded in an amorphous matrix (PBT/PEO mixed phase). For copoly(ether ester)s with a relatively high PBT content (45% (w/w)), ^{2}H T_1 inversion−recovery experiments even reveal the presence of a "pure" amorphous PBT phase next to the PBT/PEO mixed phase. Hysteresis experiments show that copoly(ether ester)s based on PEO-*b*-PEB-*b*-PEO soft blocks have a significantly improved elastic behavior, i.e. lower plastic set, compared to that of PTMO-based copoly(ether ester)s.

Introduction

One of the goals in polymer science is to gain control over the relation between the molecular structure, the morphology, and the resulting mechanical properties. This is especially true for thermoplastic elastomers or TPE's. The aim in these TPE's is to obtain a well-defined two-phase morphology in which the elastomeric properties are fully exploited with the preservation of the thermoplastic processing characteristics. In this paper the relation between the morphology and the elastic properties of one class of TPE's, i.e., copoly(ether ester)s or TPE-E's, is described. TPE-E's consist in general of a poly(butylene terephthalate) or PBT hard phase and a poly(tetramethylene oxide) or PTMO soft phase.[1,2] Because of the partial immiscibility of the PBT and the PTMO segments, a co-continuous two-phase morphology is obtained.[3−7] It was assumed that this co-continuous two-phase morphology consists of crystalline PBT and a homogeneous amorphous PBT-PTMO phase. A recent study, using among others various solid-state NMR techniques, demonstrated the existence of a nonhomogeneous amorphous soft phase consisting of a PTMO-rich and a mixed amorphous PBT−PTMO phase.[8]

It is generally accepted that the presence of a co-continuous crystalline PBT phase causes the significant plastic deformation and hence minor elastic properties of TPE-E's upon relative large elongations. Orientation studies have shown that upon deformation the soft segments orient parallel to the stress direction,[9] whereas the hard segments initially orient transverse to the stress direction and only at higher elongations parallel to the stress direction.[10] This process of alignment of the crystalline polymer chains with the direction of stress continues up to 300% elongation and results in irreversible disruption of the crystalline matrix. In addition, it has been shown that the degree of crystallinity is of importance for the elastic properties.[11] The general idea is that the elasticity of copoly(ether ester)s could be improved by changing the co-continuous PBT hard phase into a disperse phase. This can be achieved by increasing the phase separation as was demonstrated in thermoplastic polyurethanes or TPE-U's[12,13] and in strongly phase-separated copoly(ether ester aramide)s.[14] Recently, we reported the successful synthesis of hydrogenated polybutadiene (PEB) containing PBT-based copolyesters.[15] Preliminary studies using TEM, SFM, DSC, DMA, and melt rheology showed that the incorporation of the nonpolar PEB soft block in PBT-based copoly(ether ester)s resulted in an extreme phase separation.[16] To elucidate the obtained morphology in more detail, the PEB containing copolyesters have been analyzed using solid-state NMR spectroscopy, which is a powerful tool to study the microphase structure of polymers.[17] NMR relaxation experiments are of special interest, since changes in molecular mobility are accompanied by changes in NMR relaxation times. ^{13}C inversion−recovery cross-polarization measurements (IRCP) and proton $T_{1\rho}$ relaxation experiments have been performed. In addition, selectively deuterated PBT homopolymer and selectively deuterated PBT copoly(ether ester)s have been prepared and analyzed using ^{2}H solid-state echo and inversion−recovery T_1 techniques. On the basis of the results of these NMR studies, a model is proposed in which the morphology of this novel type of TPE-E is related to the elastic properties of this material.

† DSM Research.
‡ Universität Bayreuth.
§ Present address: BASF Aktiengesellschaft, ZKS/B1, 67056 Ludwigshafen, Germany.

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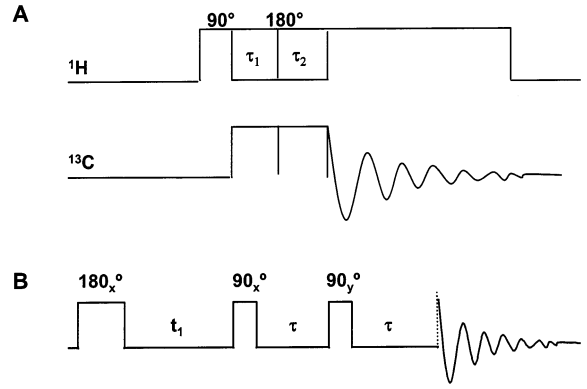

Figure 1. (A) Pulse sequence of ^{13}C IRCP experiment with spin temperature inversion on the proton reservoir. (B) Pulse sequence of ^{2}H T_1 inversion−recovery quadrupole echo deuterium experiment.

Table 1. Composition of the PEB-Based Copoly(ether ester)s

sample	amount of PBT (% (w/w))	P_n (PBT)	P_n (soft block) PEO-*b*-PEB-*b*-PEO
PBT25-1000	25	10	23−64−23
PBT35-1000	35	15	23−64−23
PBT45-1000	45	22	23−64−23

Experimental Section

Samples. The copoly(ether ester)s studied in this paper consist of PBT hard blocks and PEO-*b*-PEB-*b*-PEO soft blocks. The soft block is synthesized by chain extension of hydroxy-terminated hydrogenated polybutadiene by means of anionic ring-opening polymerization of ethylene oxide. The synthesis of the copolymers and the molecular characterization are described in detail by Schmalz et al.[15] We investigated three types of copoly(ether ester)s varying in the amount and block length of PBT. The designation code for the samples is PBT*x*−*y*, in which *x* is the amount of PBT (in % (w/w)) and *y* is the molecular weight of PEO in the soft block (in g/mol). The composition of the samples and the average block lengths (in number of monomer units, P_n) of the hard and soft blocks are given in Table 1. The hydrogenated polybutadiene has a molecular weight of 3600 g/mol. The total molecular weight of the soft block was 5600 g/mol, which was kept constant. The PBT concentration was varied between 25 and 45% (w/w). All samples were melt-pressed into plates.

Selectively labeled PBT homopolymer and selectively labeled PBT-containing copoly(ether ester)s were synthesized using 2,2,3,3-d_4-butylene glycol as the starting diol. The selectively deuterated copoly(ether ester) has the same composition as PBT45-1000.

NMR. ^{13}C solid-state NMR experiments were carried out on a Varian Inova 400 (400 MHz for ^{1}H) and on a Varian Unity 200 (200 MHz for ^{1}H) spectrometer using the 7 mm Jacobsen style VT CP-MAS probe. The ^{13}C cross-polarization magic angle spinning (CP-MAS) and ^{13}C inversion−recovery cross-polarization (IRCP) experiments were performed on the Inova 400, while the ^{1}H $T_{1\rho}$ experiments were performed on the Unity 200. The 90° pulse width was 5 μs for protons and carbons. Adamantane was used as an external chemical shift reference (38.3 ppm for the methylene resonance relative to TMS). All experiments were performed under magic angle spinning conditions. The spinning rate was 7 kHz for experiments carried out on the 400 MHz spectrometer and 4 kHz for experiments performed on the 200 MHz spectrometer. A recycle time of 2 s was used in all cross-polarization experiments. The ^{13}C IRCP pulse sequence is given in Figure 1a. The first step is a classical cross-polarization step, during which magnetization is transferred from the abundant ^{1}H spins to the dilute ^{13}C spins for a contact time τ_1. During the second part of the experiment (τ_2), the proton magnetization is inverted by applying a 180° phase shift on the proton spin locking field. The cross-polarization time τ_1 was set to a fixed value of 1 ms for the PEB containing copoly(ether ester)s. The inversion time τ_2 was varied between 0.005 and 20 ms. The $T_{1\rho}$ decay of protons was measured from the decay of carbons attached to them by using cross-polarization. By applying spectral deconvolution, the integral peak intensities of the various peaks could be determined as a function of the decay time. In the ^{1}H $T_{1\rho}$ experiments the spin lock time on protons was varied between 10 μs and 30 ms.

Solid-state ^{2}H spectra were recorded on a Varian Inova 400 (400 MHz for ^{1}H) using a wide-line probe. Spectra were obtained using the standard quadrupole echo pulse sequence[18] ($90_x-\tau-90_y-\tau$). The τ value was 20 μs, the recycle delay was 2 s, and the 90° pulse width was 2.5 μs. Inversion−recovery T_1 deuterium NMR spectra were obtained by using a 180° pulse followed by a variable delay t_1 and followed by the standard quadrupole echo pulse sequence (Figure 1b). The t_1 time varied between 1 μs and 1, and the τ value was set to 20 μs.

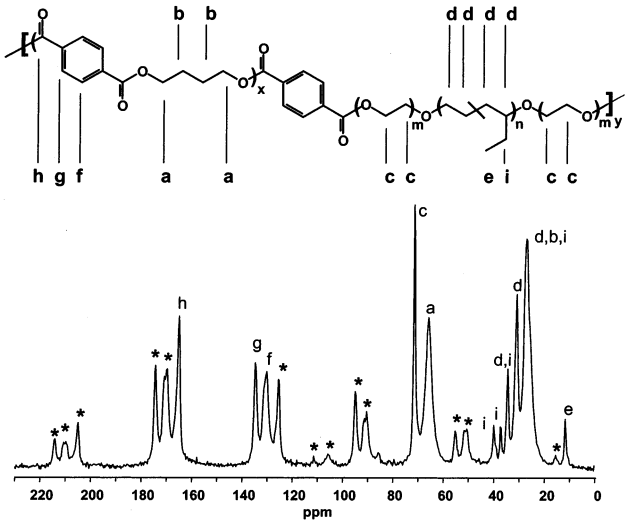

Figure 2. ^{13}C CP-MAS spectrum of PBT45-1000 at a spinning rate of 4 kHz and a contact time of 1 ms, recorded at 400 MHz for ^{1}H. Peaks marked with an asterisk are spinning sidebands. Note that the OCH_2 carbons of the first PEO unit directly connected to the terephthalate group belong to resonance a and not to c.

Results and Discussion

^{13}C CP-MAS Spectrum. Figure 2 shows the ^{13}C CP-MAS NMR spectrum of PBT45-1000 recorded at 400 MHz for ^{1}H. In addition to the spinning sidebands (marked by an asterisk), nine resonances (a−i) are observed, which are assigned to structural units shown in Figure 2. The spectrum shows four PBT resonances of the carbonyl carbons at 165.1 ppm (h), the protonated aromatic carbons at 130.7 ppm (g), the nonprotonated aromatic carbons at 134.7 ppm (f), and the PBT−OCH_2 groups at 65.9 ppm (a). For the soft block a resonance for the OCH_2 groups of PEO at 71.7 ppm (c) is observed. The ^{13}C NMR spectrum of the PEB block, which appears between 25 and 40 ppm, is rather complex since there are many overlapping lines originating from the sequence distribution in the soft PEB block. These lines can be resolved in a liquid-state spectrum but show severe overlapping in a solid-state spectrum. The assignments of the resolved peaks to the various structural units in the PEB block are indicated in Figure 2. It is noted that the main peak of the PEB unit shows severe overlapping with the CH_2 resonance of PBT at 27 ppm (b).

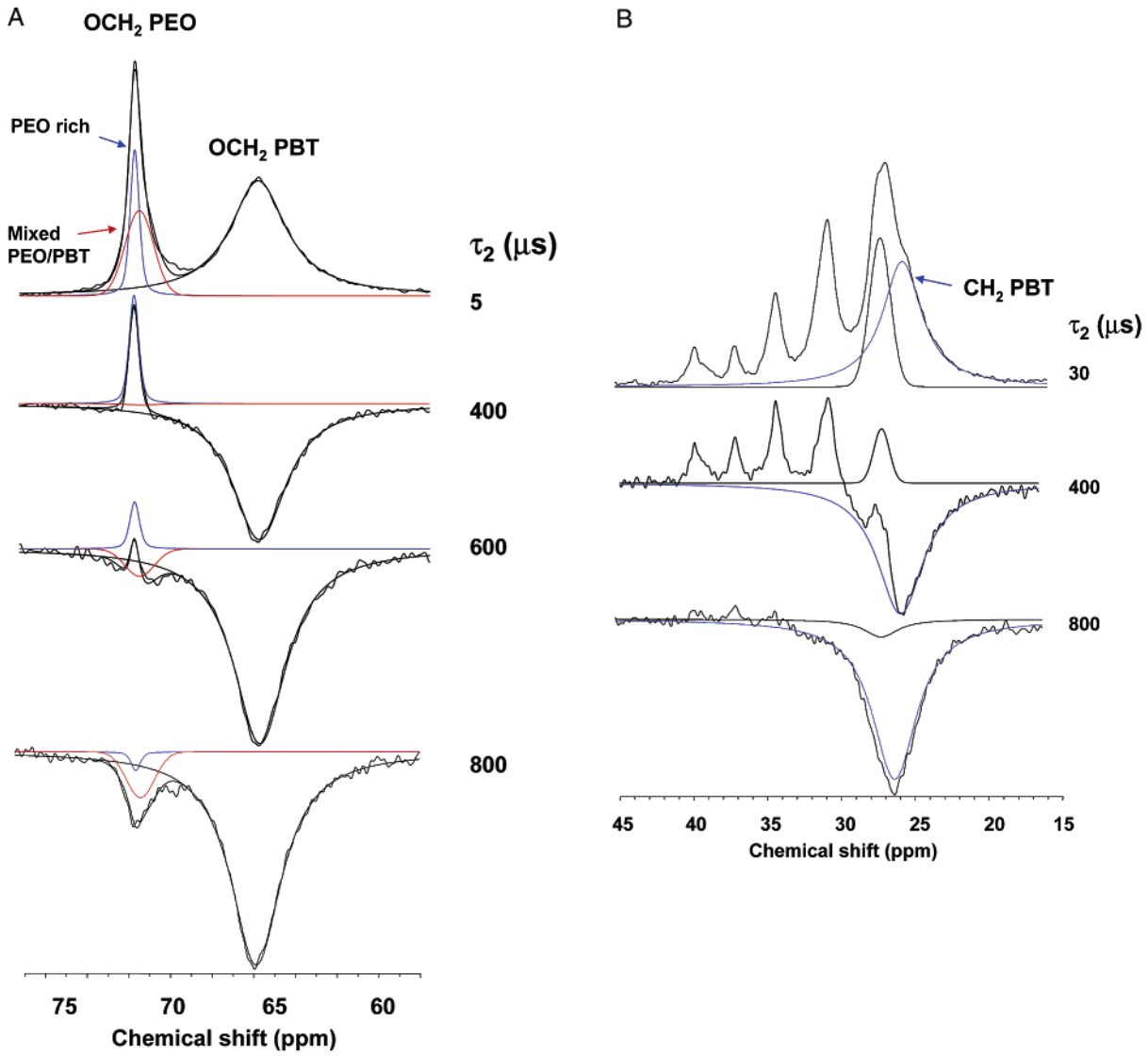

Figure 3. (A) ^{13}C IRCP spectra of PBT45-1000 showing the OCH_2 resonances of PBT and PEO. The PEO resonance is fitted with two lines: a narrow red peak and a blue broader peak. (B) ^{13}C IRCP spectra of PBT45-1000 showing the CH and CH_2 groups of the PEB soft block. Note the overlapping CH_2 resonance of PBT at 27 ppm, shown in blue. The black line is fitted to the resonances of the PEB soft block, whereas the blue line indicates the overlapping CH_2 of PBT. The rest of the fitted lines is left away for clarity.

^{13}C Inversion−Recovery Cross-Polarization (IRCP) Experiments. To study the molecular mobility of the hard and soft segment in more detail, we applied a ^{13}C IRCP experiment.[19] The IRCP experiment is composed of two contiguous parts. The first step is a classical cross-polarization step, during which magnetization is transferred from the abundant ^1H spins to the dilute ^{13}C spins for a contact time τ_1. During the second part of the experiment (τ_2), the carbon magnetization is inverted. The rate of this inversion process or depolarization process is determined by the cross-polarization dynamics. The cross-polarization or depolarization rate depends on the strength of the magnetic dipole−dipole coupling between ^{13}C and ^1H spins, which is affected by molecular motions. In the case of slow motions or low-amplitude motions cross-polarization is a relatively fast process; in the case of fast motions or high-amplitude motions, cross-polarization is a relatively slow process. We expect therefore the magnetization of the hard block to invert faster than that of the soft block. By using this IRCP pulse sequence, one component can be selectively nulled to yield a spectrum of the other. This experiment has been successfully applied before on copoly(ether ester)s based on PBT hard blocks and PTMO soft blocks.[8] On the basis of this experiment, it could be clearly shown that the amorphous phase is not a homogeneous mixture of hard and soft segments but is phase-separated in a "PTMO-rich" phase and a mixed "PBT/PTMO" phase.

The results for sample PBT45-1000 are shown in parts a and b of Figure 3 for respectively the OCH_2 carbons of the PEO and PBT segment (58−77 ppm) and the CH and CH_2 groups of the PEB between 15 and 45 ppm. The spectra recorded at different τ_2 are presented. The spectra are fitted with Lorentzian and/or Gaussian lines. In Figure 3a we see that the OCH_2 resonances of the "hard" PBT segment invert, as expected, faster than those of the PEO groups. Most interesting is the inversion of the OCH_2 groups of PEO at an inversion time (τ_2) of 600 μs. Here we clearly see that the PEO−OCH_2 resonance at 71.7 ppm is actually composed of two resonances: a narrow peak (blue line), which is still

positive and not yet inverted, and a broader peak (red line), which is already inverted. The broader peak is slightly shifted upfield (~0.3 ppm) with respect to the narrow line. For all samples we observe for the PEO−OCH_2 peak this splitting into two resonances. These two lines are almost individually observed at 400 μs (narrow line) and 800 μs (broad peak). These two lines, with different line width and cross-polarization behavior, are attributed to PEO segments with different molecular mobility. The narrow line, which inverts slow, can be assigned to PEO segments with relatively high mobility, whereas the broad line corresponds to PEO segments with more restricted mobility. These results indicate that the PEO segments do not form a completely demixed separate phase. Instead, we assign the narrow peak to highly mobile PEO segments in a PEO-rich phase and the broad peak to PEO segments with more restricted mobility due to partial mixing with more rigid PBT segments. These assignments are in agreement with previous studies on similar copoly(ether ester)s.[8]

For all PEB resonances (Figure 3b) we observe almost identical cross-polarization and depolarization behavior. At 800 μs all signals are at their "crossover point". This indicates that there is no heterogeneity in mobility for the PEB segment. It should be noted that the resonance at 27 ppm inverts faster, but this peak originates from the CH_2 carbons of PBT.

In summary, these results already indicate that the amorphous phase is composed of a highly mobile PEO-rich phase, a PEO/PBT mixed phase, and a pure PEB phase. These assignments are also in agreement with DMTA results[16] that are discussed in more detail in a separate contribution, in which for all samples two distinct T_g's are observed; a first T_g at −60 °C (PEB-pure phase) and a second T_g at −10 °C (PBT/PEO mixed phase). Furthermore, DSC measurements reveal the presence of a pure PEO phase[16] since in a DSC curve a clear melting peak at about 5 °C is observed.

^{1}H $T_{1\rho}$ Experiments. The ^{13}C IRCP experiments discussed above are sensitive to local motions of individual C−H groups. Hence, the heterogeneity in cross-polarization behavior, as determined for the various groups, does not necessarily reflect different domains (phases) with different molecular mobility. Here ^{1}H $T_{1\rho}$ experiments can provide valuable information. ^{1}H $T_{1\rho}$ relaxation times in solids usually represent averaged values over the relaxation behavior of the ensemble of protons. This is due to the strong dipolar coupling between protons, which gives rise to spin diffusion. When domains with different molecular mobility are relatively small (<ca. 5 nm), the relaxation behavior is averaged out to give a single value. Only for larger domains (>ca. 5 nm), a heterogeneity in the ^{1}H $T_{1\rho}$ relaxation behavior is observed.

The ^{1}H $T_{1\rho}$ decay curves are plotted in Figure 4 for sample PBT45-1000 at different temperatures (room temperature, 50 °C, and 80 °C). The solid lines represent least-squares fits of a mono- or biexponential decay function to the experimental data points. Only the experimental data and fits for the PEO−OCH_2 groups, the PBT−OCH_2 groups, and the CH_2 and CH groups of PEB are given. The relaxation time constants obtained from the fits are given in Table 2. At room temperature (Figure 4A) we observe a biexponential decay for the OCH_2 groups of PEO and for the OCH_2 groups of PBT and a monoexponential decay for the CH and CH_2 groups of PEB. For PEO, the slow decaying component

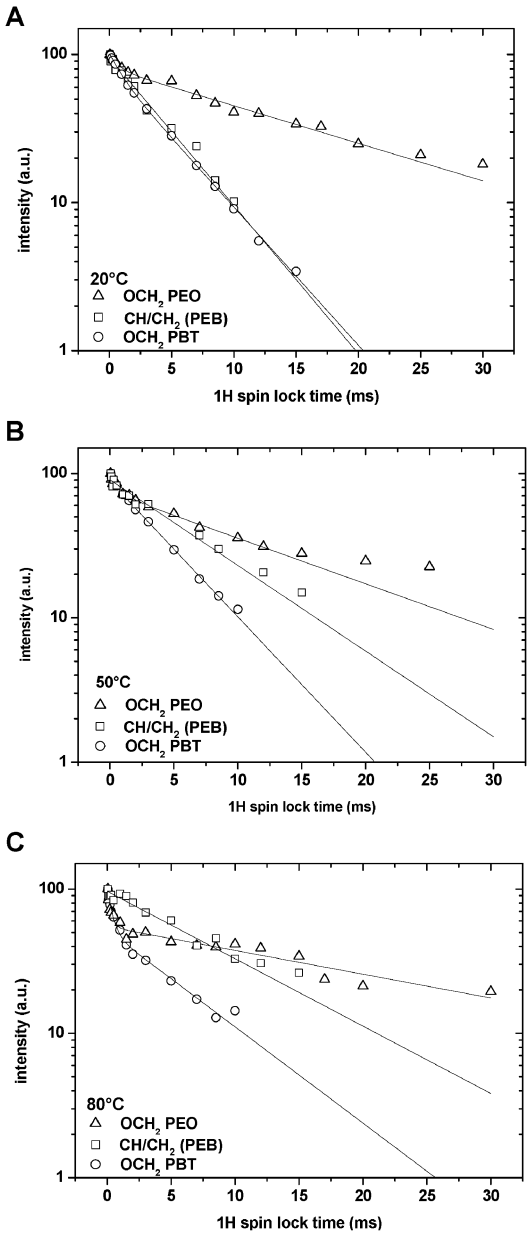

Figure 4. ^{1}H $T_{1\rho}$ decay of the OCH_2 (PEO), OCH_2 (PBT), and CH_2 (PEB) carbons of PBT45-1000 at different temperatures: (A) room temperature, (B) 50 °C, and (C) 80 °C. The solid lines represent least-squares fits of the experimental data using a biexponental decay function.

Table 2. ^{1}H $T_{1\rho}$ Relaxation Time Constants for PBT45-1000 Measured at 200 MHz for ^{1}H at Different Temperatures

PBT45-1000	carbons	$T_{1\rho}(^1H)^A$ [ms]	$T_{1\rho}(^1H)^B$ [ms]	I^A [%]	I^B [%]
RT	PEO (OCH_2)	0.69 ± 0.25	17.1 ± 1.3	21 ± 3	79 ± 3
	PEB (CH and CH_2)	4.34 ± 0.26			
	PBT (OCH_2)	1.02 ± 0.17	4.66 ± 0.14	22 ± 3	78 ± 3
T = 50 °C	PEO (OCH_2)	0.74 ± 0.38	13.74 ± 2.1	25 ± 5	75 ± 5
	PEB (CH and CH_2)	7.31 ± 0.76			
	PBT (OCH_2)	0.33 ± 0.10	4.63 ± 0.13	14 ± 2	86 ± 2
T = 80 °C	PEO (OCH_2)	0.24 ± 0.06	26.38 ± 3.54	48 ± 6	52 ± 2
	PEB (CH and CH_2)	9.3 ± 0.8			
	PBT (OCH_2)	0.39 ± 0.09	6.51 ± 1.0	49 ± 5	51 ± 5

is assigned to the highly mobile PEO-rich phase since at higher temperatures this relaxation time increases (Table 2), which is typical for highly mobile segments.

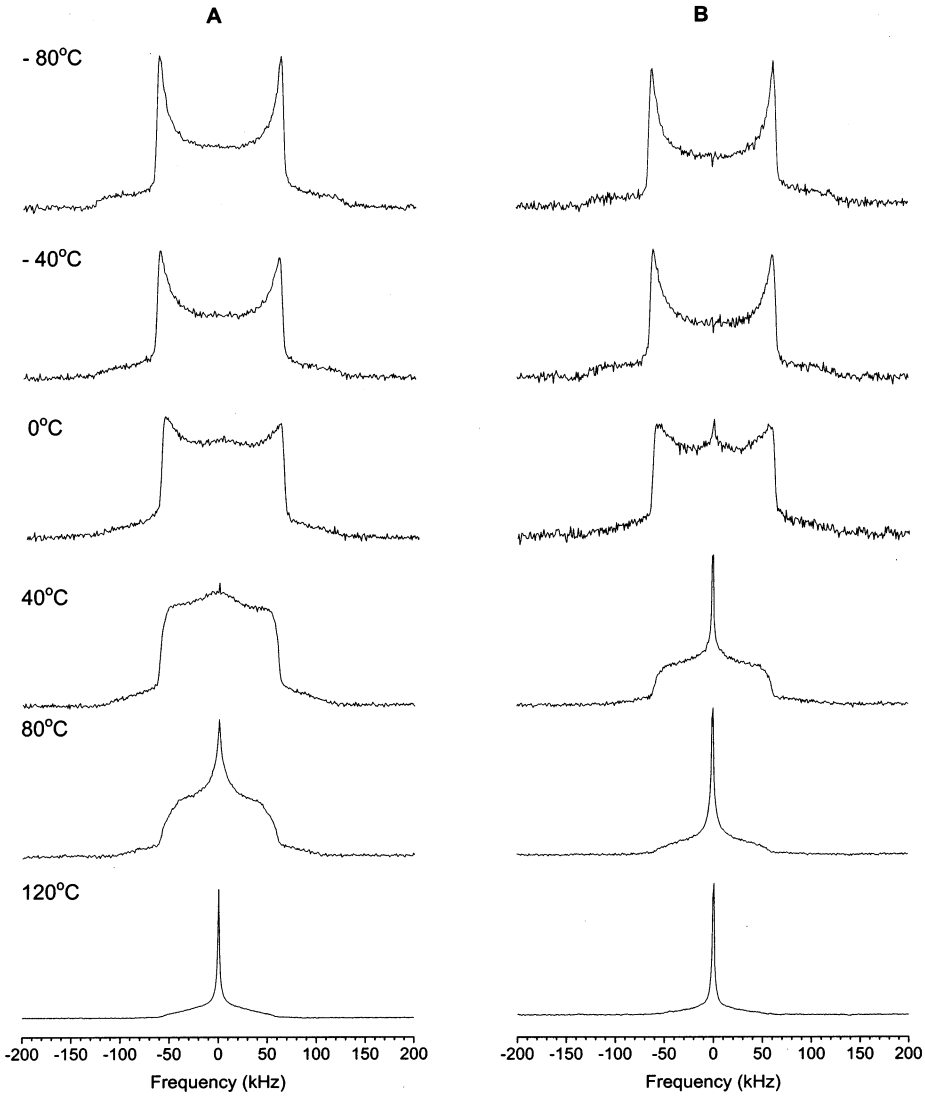

Figure 5. Temperature-dependent solid-state deuterium spectra for PBT (A) and PEB-based copoly(ether ester) (B). The spectra are scaled arbitrarily.

The fast decaying component is assigned to PEO segments with the more restricted mobility, mixed with PBT. For PBT the fast relaxing component is assigned to amorphous PBT segments with a relatively high mobility and the slow relaxing component to rigid crystalline PBT segments. Most interestingly, the relaxation time of the fast decaying component of PBT is of the same order of magnitude as the fast decaying component of PEO. Therefore, the short ^{1}H $T_{1\rho}$ relaxation times of PEO and PBT are assigned to an amorphous PEO/PBT mixed phase.

The monoexponential relaxation behavior of the CH and CH_2 groups of PEB indicates that the PEB forms a homogeneous amorphous phase without mixing with PEO or PBT segments. Also at elevated temperatures, the relaxation behavior of the PEB phase is clearly different from the relaxation behavior of PEO and PBT.

Deuterium NMR Experiments. ^{2}H NMR spectra provide detailed information about the type of molecular motions of specific groups. In fact, for PBT−PTMO block copolymers it has been reported[20] that deuterium NMR experiments showed two distinct motional environments for the hard PBT segments (at room temperature). One of the environments is identical to that observed in the PBT homopolymer, whereas the other motional environment is nearly isotropic. The isotropic motions of PBT segments are attributed to short blocks of hard segments residing in the soft segment matrix.

Figure 5 shows solid-state ^{2}H NMR spectra of selectively labeled PBT homopolymer (Figure 5A) and a selectively labeled PBT-based copoly(ether ester) (Figure 5B). For both systems the 2,3 methylene groups of the butanediol were deuterated. The spectra were recorded at temperatures between −80 and 120 °C. At low temperatures (−80 °C) the mobility is frozen; therefore, we observe for both polymers a typical Pake pattern.[17] At 40 °C a narrow peak superimposed on a broad line shape is observed for the PBT homopolymer. This narrow peak becomes more pronounced in the spectrum recorded at 80 °C. This narrow peak is assigned to amorphous PBT segments, which is in agreement with Jelinski et al.[21] For the PEB-based copoly(ether ester), a narrow peak appears already at 0 °C. In agreement with DMTA measurements,[16] in which a second T_g at −10 °C is observed, this narrow peak can be assigned to the PBT segments with a relatively high mobility, i.e., PBT segments that are embedded in a highly mobile soft matrix (amorphous PBT/PEO mixed phase).

It might be further discussed whether all amorphous PBT is mixed with PEO or partly resides in a separate

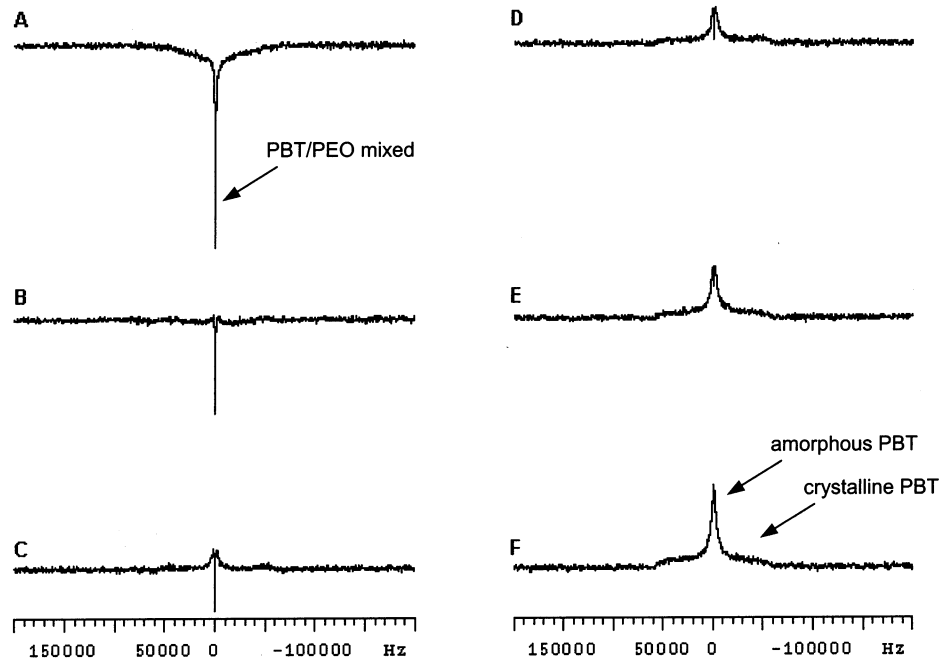

Figure 6. Inversion−recovery solid-state deuterium NMR spectra of a PEB-based copoly(ether ester) containing 45% (w/w) PBT at 80 °C. Spectra A−H are obtained with increasing t_3: spectrum A at 6 ms, B at 8 ms, C at 9 ms, D at 10 ms, E at 11 ms, and F at 12 ms.

amorphous phase. A first indication for a separate amorphous PBT phase was obtained in a DMTA curve, which showed a glass transition temperature at 50 °C. This transition was most pronounced for a sample containing 45% (w/w) hard blocks.[16] Indications for the presence of a pure amorphous PBT phase can be derived from ^{2}H T_1 inversion−recovery experiments. Some of the ^{2}H spectra recorded in ^{2}H T_1 experiments are shown in Figure 6. The first spectrum (Figure 6A), which is plotted negative, resembles the spectrum of the PEB-based copoly(ether ester) recorded at 80 °C as shown in Figure 5B. At an inversion time of 8 ms (Figure 6B) we see that the narrow peak is still negative while the broad component is nulled. At 9 ms (Figure 6C), a "less narrow" peak becomes positive, while the narrow peak is still negative. This peak becomes more pronounced in the spectra depicted in Figure 6D−F. Especially in Figure 6F, the extremely narrow peak is nulled, yielding a spectrum composed of two resonances: a relatively broad peak due to crystalline PBT and a relatively narrow peak, which is assigned to amorphous PBT. In fact, this spectrum resembles (only the relative intensities are different) the spectrum of the homopolymer PBT at 80 °C (Figure 5A). Summarizing, we conclude that, for samples with a relatively high PBT content (45% (w/w)), a "pure" amorphous PBT phase exists besides the amorphous PBT/PEO mixed phase. It is stressed that this conclusion cannot be drawn from ^{2}H NMR experiments alone, but is based on the combined results obtained from ^{2}H NMR experiments and DMTA experiments,[16] which reveal a T_g at 50 °C, which is typical for amorphous PBT.

Hysteresis Experiments. The NMR experiments described above unambiguously demonstrate that the PEB-containing copoly(ether ester)s possess an increased phase separation compared to the conventionally used PTMO containing copoly(ether ester)s. To show that this increased phase separation results in an improved elasticity, hysteresis experiments are performed. Figure 7 shows a comparison of hysteresis

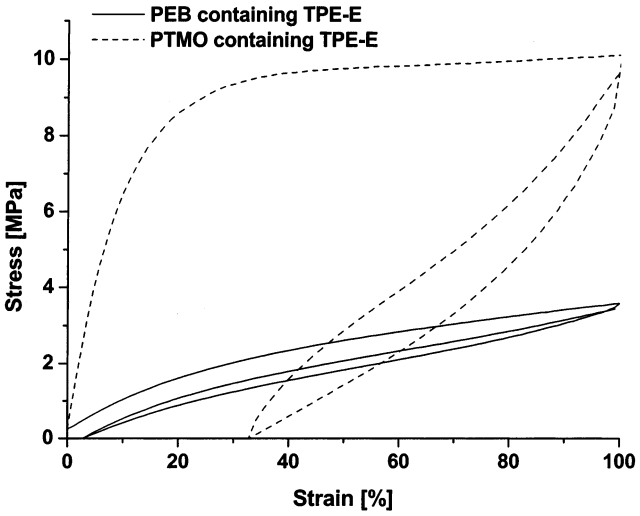

Figure 7. Hysteresis curves showing the first hysteresis cycle to a strain of 100% for a PTMO-based copoly(ether ester) containing 40% (w/w) PBT (dashed curve) and a PEB-based copoly(ether ester) containing 20% (w/w) PBT (solid curve).

measurements up to 100% strain for PBT20-1000 and the PTMO containing PBT1000-50 (possessing 50% PTMO with a molecular weight of 1000 g mol^{-1}). The curves underline the existence of the disperse and co-continuous morphology found for PBT20-1000[16] and PBT50-1000,[8] respectively. Comparing the obtained plastic deformations after elongation to 100%, which are 6 and 33% for PBT20-1000 and PBT50-1000, respectively, it is clearly demonstrated that an increased phase separation results in an improved elastic behavior. This significantly increased elastic behavior results not only from the increased amount of soft block (due to the less extreme phase separation between PBT and PTMO, incorporation of a higher amount of PTMO will prevent a phase separation and is hence not possible), but mainly from the difference in hard segment structure.

The co-continuous hard phase in PBT1000-50 is much easier irreversibly disrupted upon elongation, resulting in a much higher plastic deformation, compared to the disperse hard phase in the PEO-*b*-PEB-*b*-PEO-based copoly(ether ester)s.

Conclusion

Using various solid-state NMR techniques, detailed information on the phase behavior and molecular miscibility was obtained on copoly(ether ester)s based on PBT hard blocks and PEO-*b*-PEB-*b*-PEO soft blocks. Besides a crystalline PBT phase, we conclude that several phases with different molecular mobility are present in the amorphous phase, including a PEO-rich phase, a mixed PEO/PBT phase, and a pure PEB phase. This microphase separation was found in all samples investigated. In addition, it was found that, at least for samples with 45% (w/w) of hard block, a "pure" amorphous PBT phase is present. Hysteresis experiments showed that the copoly(ether ester)s with the PEO-*b*-PEB-*b*-PEO soft blocks have better elastic properties, i.e., a lower plastic deformation, compared to the conventionally used PBT−PTMO copoly(ether ester)s. Apparently, incorporation of a predominantly nonpolar soft block leads to a better phase-separated structure in which the PBT crystallites form dispersed domains in a mobile amorphous matrix. This dispersion of hard PBT domains in an amorphous matrix results in improved elastic properties compared to conventional copoly(ether ester)s with a co-continuous morphology.

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