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Indication of an order-order-transition by a partial disordering in ABC-triblock copolymers

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Dedicated to Prof. W. Borchard on the occasion of his 60th birthday

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Summary

Poly(ethylene-alt-propylene)-block-polyethylethylene-block-polystyrene (PEP-b-PEE-b-PS) triblock copolymers were synthesized by anionic polymerization and subsequent hydrogenation of poly-1,4-isoprene-block-poly-1,2-butadiene-block-polystyrene triblock copolymers (1,4PI-b-1,2PB-b-PS). Differential scanning calorimetry and dynamic mechanical spectroscopy reveal an order-order transition which is induced by the mixing of PEP and PEE above their respective order-disorder transition (ODT).

Introduction

In the last three decades block copolymers have attracted considerable attention both experimentally and theoretically. The behaviour of AB diblock and ABA triblock copolymers was the main focus. Leibler was the first to describe the order-disorder transition of these systems in the framework of the so called random-phase-approximation (RPA) (1). At present there is some discussion about the distinction between the "weak" and the "strong" segregation limit. Weak segregated systems show a rather broad interphase while this interphase is rather sharp for strongly segregated systems, i. e. the width of the interphase δ is of the same dimension as the periodicity of the characteristic long period d ($\delta \approx d$).

Besides small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS), dynamic mechanical analysis (DMA) is a sensitive method to probe microphase separation in block copolymers (2,3,4,5,6,7). Bates et al. and Han et al. have used DMA to determine the order-disorder transition temperature in different diblock copolymers (3,8,9,10,11,12,13).

While AB diblock copolymers show morphologies, which depend only on the composition and the thermodynamic interaction between the two comonomers, the situation is more complex in ABC triblock copolymers. There are two independent composition variables ϕ_A, ϕ_B and three independent binary interactions between the different components which control the morphology of the material (14). Based on a simple model the stability of different symmetric morphologies has been calculated (15). The free energy of the system is composed of two contributions. One is originating from the surface energies expressed in terms of Flory-Huggins-Staverman interaction parameters (χ_{AB}, χ_{BC}, χ_{AC})(16,17,18) while the other contribution originates from the conformational entropy of the different blocks. In our previous work no attempt was made to describe order-disorder transitions; only the stability regions of different ordered morphologies were considered, where all three blocks remain phase separated.

In this paper we will present first experiments on ABC-triblock copolymers, which show a partial disordering in such materials. This is due to an intermixing of two of the three blocks by varying the temperature.

Experimental

Materials

Cyclohexane (Riedel de Häen) was purified by distillation from CaH_2 and subsequently potassium under purified nitrogen atmosphere. **Styrene** (BASF) was distilled from CaH_2 under nitrogen, stirred over Bu_2Mg and condensed into storage flasks. **Butadiene** (Linde) was passed over columns with molecular sieve and activated alumina, followed by storage over Bu_2Mg under purified nitrogen before use. **Isoprene** (Fluka) was distilled from CaH_2, condensed from Bu_2Mg and treated as butadiene before use. **1,2-Dipiperidinoethane (DIPIP)** (Acros) was stirred over CaH_2 under vacuum for several days followed by two distillations from CaH_2 and subsequent storage under nitrogen. **s-Butyllithium** was used as received from Acros. Active initiator concentration was determined by the Gilman double-titration method (19). **Methanol** (Riedel de Häen) and **2-propanol** (Merck) were used as received. **Toluene** (Riedel de Häen) was purified by distillation from potassium after several days of reflux under purified nitrogen. **Cobalt(II)acetylacetonate** and **n-butyllithium** were used as received from Merck.

Synthesis

The 1,4PI-b-1,2PB-b-PS tribock copolymers were prepared by sequential anionic polymerization in a BÜCHI reactor system (20) using cyclohexane as solvent. All reaction components were added under dry nitrogen after purification. The polymerization was initiated by sec-butyllithium which was added to the reactor by means of a gas-tight syringe. Isoprene was polymerized at 50°C. By application of 1,2-dipiperidinoethane (DIPIP) occurs mainly 1,2-addition of butadiene (21). After addition of the modifing agent, butadiene was polymerized at 20°C, followed by polymerization of styrene at 50°C. During the reaction polyisoprene and polyisoprene-block-polybutadiene precursors were taken preceeding to the next monomer addition. The reaction was terminated by adding 2ml degassed methanol to the solution. The polymer was precipitated directly from the reaction solution in 2-propanol.

For the hydrogenation the dried 1,4PI-b-P1,2B-b-PS triblock copolymer was dissolved in toluene under nitrogen. The polymer solution was placed in a stainless steel reactor (BÜCHI). After several subsequent evacuations and flushing with hydrogen, the catalyst solution was added from a teflon sealed glass tube. Hydrogenation was carried out according to a method developed by Falk *et al* (22).

Molecular characterization

Molecular weights and polydispersity index of the precursors and the triblock copolymers were determined by size exclusion chromatography (SEC) in THF at 40°C. All measurements were done on an instrument fitted with PLGel-columns (Bischoff). Refractive index and UV-absorption were monitored with a differential refractometer and UV-detector (Waters).

^1H- and ^{13}C-NMR spectra were obtained from $CDCl_3$ solutions at room temperature on a Bruker AC-200 spectrometer.

Physical characterization

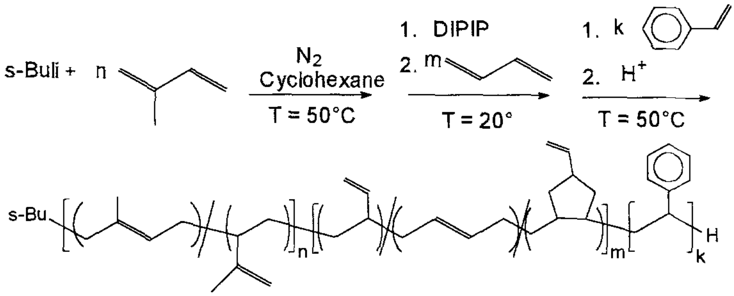
DSC measurements were done with the PEP-b-PEE-b-PS triblock copolymers on a Perkin Elmer DSC 7. The Tg of PEP and PEE was monitored by scanning within a temperature range between -100° and 30°C after annealing the samples below Tg for several hours. The polystyrene was examined by scanning between -20° and 120°C. Scans were taken at different heating rates to allow extrapolation of the received data to a heating rate of 0°/min.

Dynamical mechanical data were obtained with a Rheometrics RDAII rheometer equipped with a 25 mm parallel plate test fixture. The samples used for the measurements were prepared by melt pressing of the dry polymer at 150°C under vaccum for about 25 to 45 minutes. Isothermal frequency sweeps were employed for the testing of the materials over a wide temperature range and isochronal temperature sweeps were conducted at diffrent frequencies. The strains to which the samples were deformed during isothermal tests were determined for every temperature by individual strain sweeps.

Results and Discussion

By sequential anionic polymerization of isoprene, butadiene and styrene as shown in scheme 1 four 1,4PI-b-1,2PB-b-PS triblock copolymers were synthesized. The sequence isoprene→butadiene→styrene has been chosen to have the 1,4PI-b-1,2PB diblock copolymer respectivly their hydrogenated analogues as reference. The SEC traces of the PI and 1,4PI-b-1,2PB and of the resulting triblock copolymer as illustrated in Figure 1 show that the synthesis proceeds without noticeable termination after addition of monomer or DIPIP which is a result of the very pure reaction conditions.

The molecular weight of the polyisoprene precursor molecules was detemined by SEC with a universal calibration for polyisoprene. The integration of the ^{1}H-NMR spectra provided the composition of the triblock copolymers, which is presented in Table 1 where a simplification of the nomenclature of triblock copolymers is introduced: in brackets the sequential order of the blocks is given by the first letter of the monomer and the weight per cent added as subscript. The molecular weight of the polymer is given by the number following the bracket.



Scheme 1. Reaction path for the synthesis of Poly(1,4 I-b-1,2 B-b-S) triblockcopolymer.

sample	M_n	M_w/M_n	wt%	wt%	wt%	PI-Block		PB-Block		
description	[10^3 g$*$mol^{-1}]		PI	PB	PS	%1,4	%3,4	%1,2	%1,4	%cycl.
$(I_{50}B_{44}S_6)48$	48	1.03	50	44	6	92	8	90	2	*8*
$(I_{45}B_{45}S_{10})60$	60	1.07	45	45	10	85	15	92	-	*8*
$(I_{46}B_{38}S_{16})74$	74	1.05	46	38	16	84	16	88	6	*6*
$(I_{37}B_{37}S_{26})70$	*70*	*1.03*	*37*	*37*	*26*	*90*	*10*	*83*	*8.5*	*8.5*

Table 1. Molecular weight characterization and microstructure of 1,4PI-b-1,2PB-b-PS triblock copolymers.

The microstructure of the 1,4PI-b-1,2PB-b-PS triblock copolymers was determined by ^{1}H-NMR (Table 1). The content of 3,4 units in the PI-block of $(I_{46}B_{38}S_{16})74$ and $(I_{45}B_{45}S_{10})48$ is higher than it is supposed to be in cyclohexane as solvent. This might be due to traces of DIPIP which were sticking to the reactor and were not eliminated completely by several cleaning cycles with cyclohexane. The 1,2 content of PB varies from 83 to 92 %, which is less than reported by others (21). The lower 1,2-content coincides with the formation of cyclopentane units, which occurs in anionic butadiene polymerization with polar additives like DIPIP or TMEDA under monomer starved conditions (23). In our reactions this is due to the fact that a 100 % conversion had to be achieved in order to add styrene in the last polymerization step. Nevertheless, SEC reveals no molecular weight broadening or termination that could be affected by the cyclisation reaction (Figure 1). The small amount of cyclopentane units can be distinguished in the ^{1}H-NMR spectra at 5.8 ppm (Figure 3). Hydrogenation of the 1,4PI-b-1,2PB-b-PS triblock copolymers to the corres-ponding poly(ethylene-alt-propylene)-block-polyethylethylene-block-polystyrene triblock copolymer was achieved with a catalyst system described by Falk *et al* (22).

As the cobalt(II) salt which was used by Falk was not attainable we used cobalt(II)-acetylacetonate and modified the hydrogenation conditions in a way that resulted in complete hydrogenation of the double bonds without any hydrogenation of the aromatic ring in the styrene repeating units. The result of this hydrogenation can be seen in Figure 3 which compares the original to the hydrogenated block copolymer. The comparison of the SEC traces of these systems in Figure 2 proves that hydrogenation did not affect the molecular weight distribution.

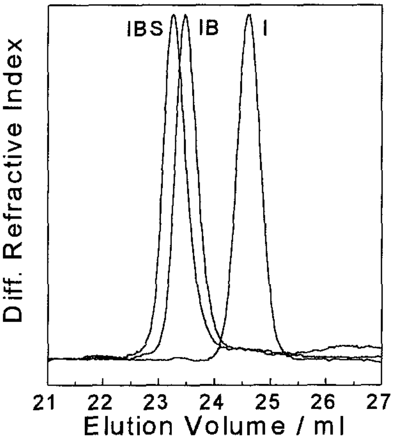


Figure 1. SEC traces of poly(1,4 I), poly(1,4 I-b-1,2 B) and poly(1,4 I-b-1,2 B-b-S)

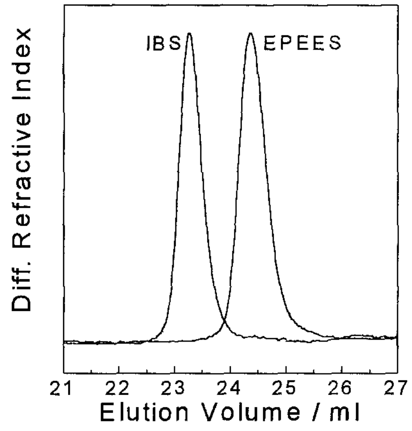


Figure 2. SEC traces of poly(1,4 I-b-1,2 B-b-S) and poly(EP-b-EE-b-S)

Differential scanning calorimetry was done with the hydrogenated samples at three different heating rates. All samples were annealed below the Tg of the PEP component for several hours before monitoring the behaviour of the elastomer blocks. All of the four samples obviously showed two glass transitions (Figure 4). This property can be attributed to a microphase separation between PEP and PEE, as it is known from the corresponding diblock copolymers examined by Bates *et al* (2,8).

In contrast to the procedure employed in the case of the elastomer blocks of the tri- block copolymers the glass transition of polystyrene was monitored by temperature scans at three different heating rates after simply quenching the samples to -20°C. Typical measurements as those presented in Figure 5 reveal an increasing Tg with increasing styrene content in the block copolymer. The results of all DSC examinations are summarized in Table 2.

The dynamic mechanical behaviour was examined by isothermal frequency sweeps over a wide temperature range and isochronal temperature sweeps at different frequencies. It is known from investigations in P(EP-b-EE) block copolymers by Bates et al (8) that the order-disorder transition (ODT) can be monitored by a distinct change in dynamic mechanical behaviour. Especially the slope of the dynamic moduli G' and G" changes in the low frequency region from $G' \sim G'' \sim \omega^{0.5}$ below the system's ODT to $G' \sim \omega^2$ and $G'' \sim \omega$ above this temperature. Isochronal temperature sweeps conducted at appropriate low frequencies show a sharp decrease in the modulus within a small temperature range at the

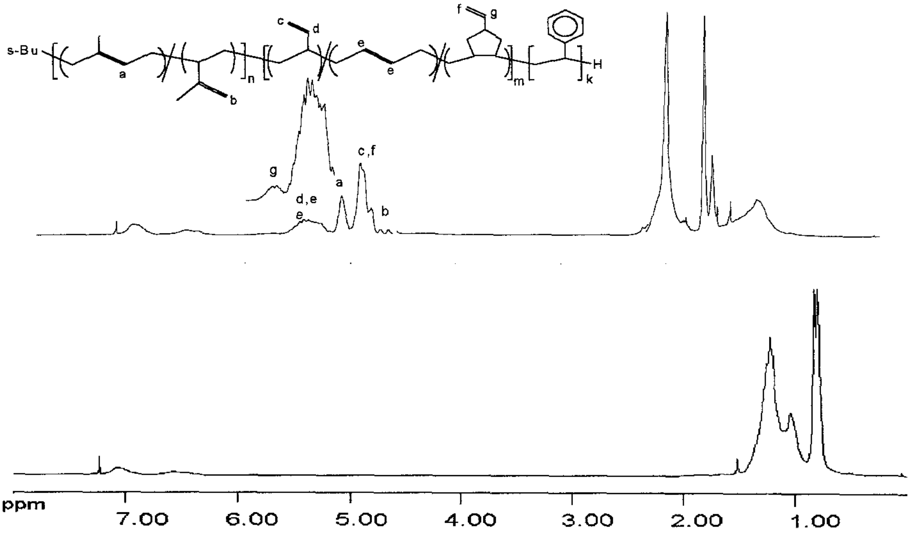
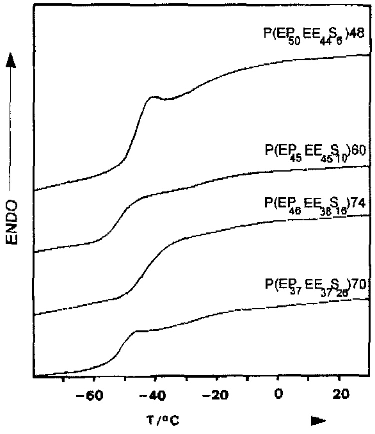


Figure 3. ^{1}H-NMR spectra of $(I_{45}B_{45}S_{10})60$ and $(EP_{45}EE_{45}S_{10})60$ in $CDCl_3$



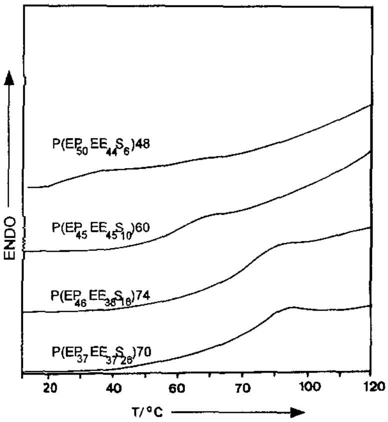


Figure 4. DSC traces of the PEP- and PEE-glass transitions in Poly(EP-b-EE-b-S) triblock co-polymers at a heating rate of 20°/min

Figure 5. DSC traces of Polystyrene glass transition in Poly(EP-b-EE-b-S) triblock co-polymers at a heating rate of 20°/min

Table 2. DSC results of Poly(EP-b-EE-b-S) triblock copolymers after extrapolation to a heating rate of 0°/min

Sample	Tg (PEP) [°C]	Tg(PEE) [°C]	Tg(PS) [°C]
$(EP_{50}EE_{44}S_6)48$	-54	-28	25
$(EP_{45}EE_{45}S_{10})60$	-56	-32	52
$(EP_{46}EE_{38}S_{16})74$	-47	-27	70
$(EP_{37}EE_{37}S_{26})70$	-57	-35	75

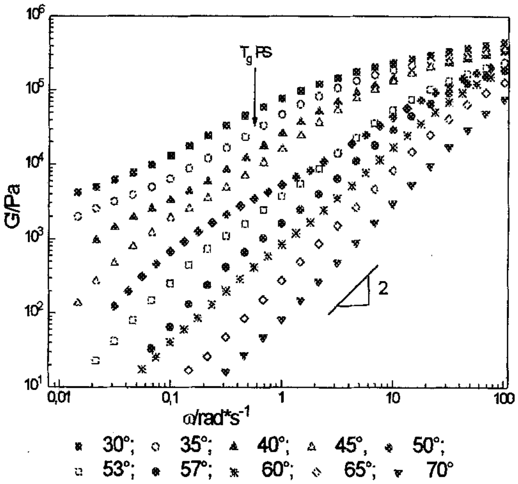


Figure 6. Isothermal frequency sweeps of $(EP_{50}EE_{44}S_6)48$

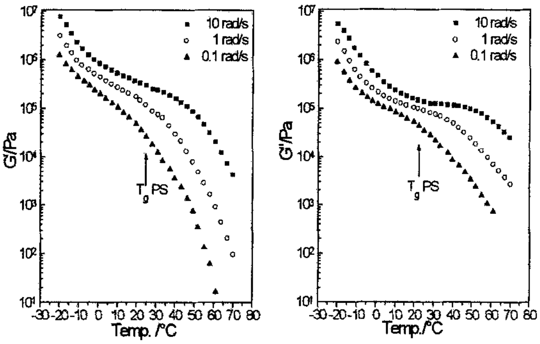


Figure 7 Isochronal temperature sweeps of $(EP_{50}EE_{44}S_6)48$

ODT. In asymmetric diblock copolymers this change at the ODT is not as pronounced (4).

The isothermal frequency sweeps of $(EP_{50}EE_{44}S_6)48$ in Figure 6 show the glass transition of polystyrene as a week step in the frequency sweeps. For the measurement at 40° the inflection is located at about 1 rad/s (see arrow). At this temperature as well as at lower temperatures a plateau is reached in the low frequency region which is due to the segregation of the three blocks. At 45° the modulus starts droping with increasing temperature. At 50° G' differs from the measure-ment at 40° over the whole measurement range. This diffe-rence is larger at higher tempe-ratures. Recent investigations in the ordering behaviour of PEP-PEE diblock copolymers have demonstrated the molecular weight dependence of the ODT (11). For a diblock copolymer with a molecular weight of 47800 and 54 % of PEP the ODT was located at 16°C. According to this result it can be concluded that in $(EP_{50}EE_{44}S_6)48$ the PS block must undergo the glass transition before the hydrocarbon blocks can mix. Due to their connection to the PS-block a sharp decrease in G' within a few degree cannot be observed. Although a slope of $G' \sim \omega^{1.8}$ at 70° indicates that the system is close to a behaviour characteristic for terminal flow it must be noted that the polystyrene block does not mix with the hydrocarbon blocks as SAXS investigations reveal (24). The occurence of a disordering process between the hydrocarbon blocks is also apparent in the temperature sweeps carried out at three different frequencies as shown in Figure 7. At temperatures about 20° to 30° the glass transition of the styrene block can be seen most clearly for the 0.1 rad/s sweep. The drop of the modulus according to the mixing of PEP

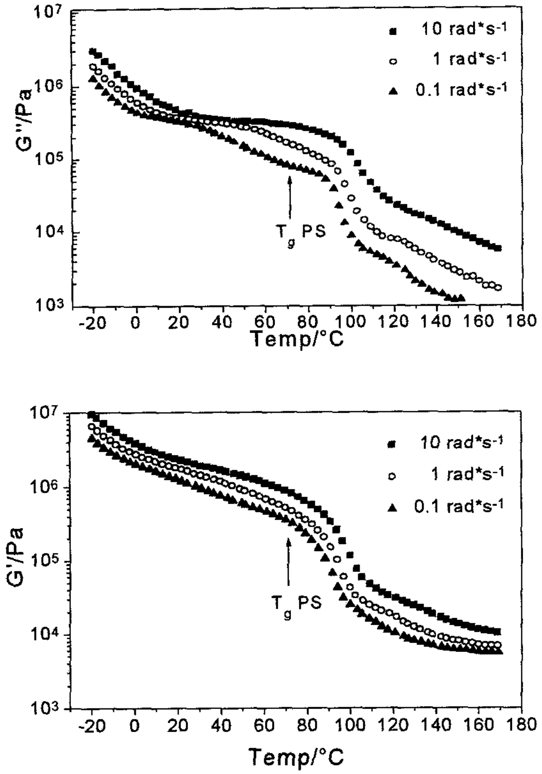


Figure 8 Isochronal temperature sweeps of (EP$_{37}$EE$_{37}$S$_{26}$)70

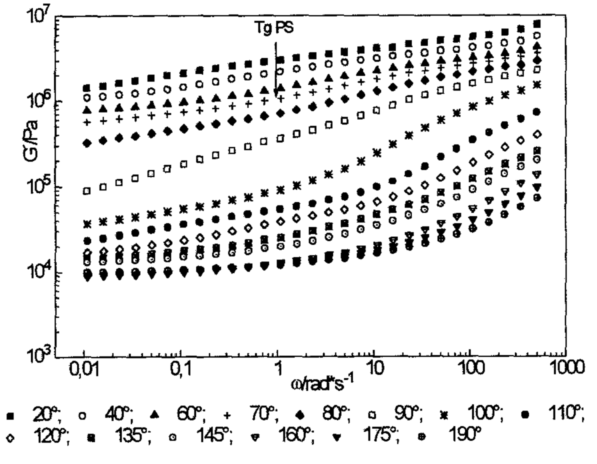


Figure 9. Isothermal dynamic frequency sweeps of (EP$_{37}$EE$_{37}$S$_{26}$)70

and PEE above 40° is obvious and becomes more pronounced at lower frequencies as has been observed in diblock copolymers showing an order-disorder transition. Again there is not a sharp drop within two or three degrees because of the segregated styrene block.

When the styrene block is enlarged the behaviour of the block copolymer changes drastically as can be seen from the DMA measurements of (EP$_{37}$ EE$_{37}$S$_{26}$)70. Figure 8 shows G'' and G' vs tempe-rature at three frequencies. At 1 rad/s the glass tran-sition of PS can be loca-lized at 75° in G'' whereas it is not so pronounced in G'. The drop in the modulus between 80° and 100° can be attributed to the mixing of the hydrocarbon blocks but in contrast to (EP$_{50}$EE$_{40}$S$_{6}$) 48 a plateau is reached. This is due to the phase separation between PS and the mixed PEP/PEE which means that the polymer behaves like an AB diblock copolymer where the mixed PEP/PEE forms one of the blocks. The similar result can be drawn from the frequency sweeps (Figure 9). The glass transition of PS appears as a week inflection at 1 rad/s in the frequency sweep at 70°. Between 80° and 100° a significant decrease in the modulus occurs which is due to the mixing of PEP and PEE. At higher temperatures a pla-teau is reached. Further heating of the sample does not induce a transition into the terminal flow and the plateau can be attributed to a persistent microphase seperation between the mixed PEP/PEE blocks and the PS block. In that regard the behaviour of the triblock differs from a diblock copolymer undergoing an order-disorder transition (3,7,10). According to these observations the experiments demonstrate that the increasing styrene content in poly(EP-b-EE-b-S) significantly influences the rheological behaviour of the system and shows the appearance of an order-order transition within the triblock copolymer. This transition is induced by the mixing of two blocks of the system.

Acknowledgments

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