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Motional heterogeneity of polystyrene-*block*-polybutadiene: a spin probe study

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Abstract

Polystyrene-*block*-polybutadiene copolymers (SB) with 0.5 mass fraction of styrene were studied by electron spin resonance (ESR) of nitroxide spin probes. The influence of the block length ($\bar{M}_w = 12,000$, $\bar{M}_w = 48,000$ and $\bar{M}_w = 83,000$) and the solvation power of casting solvents on the motional dynamics of spin probe were measured over a wide temperature range. Two nitroxide radicals as spin probes were selected: 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl benzoate (BzONO) and 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (Tempol). Irrespective of the spin probe used two ESR spectral components differing in their motional properties above the phase transition of polybutadiene blocks (PB) were observed. The fast component was assigned to spin probes located in polybutadiene-rich domains and the slow component to spin probes in polystyrene-rich domains. The range of two spectral components and the phase transition of the slow ESR component, $T_{5\mathrm{mT}}$, depend on the block length. The influence of the interphase and accumulation of free volume in the interphase on the Tempol probe motion was investigated by changing copolymer morphology in the films casted from selective and nonselective solvents. The analysis of the motional heterogeneity from the ratio of the fast and slow motional component presents evidence that in the selective solvent for polystyrene (PS) blocks (2-butanone) the most irregular structure with a large interphase is formed. The difference in fast motion of spin probes indicates that the motional dynamic is related to the change of domain structure.

Keywords: ESR; Spin probes; Heterogeneity

1. Introduction

Block copolymers with their complex structure have received considerable attention over 30 years due to many useful and unique properties. Recent advances in synthetic chemistry and possibilities to tailor specifically structured block copolymers open a new field of application of these copolymer systems with new mechanical, optical, electrical and other properties [1–3]. The simplest and most studied are diblock copolymers made up of two polymerized blocks of monomers, A and B, chemically bonded to each other. Sufficient immiscibility between A and B blocks induces self-assembly into various well-ordered phase-separated pure microstructures with an intervening interfacial region of mixed composition. Phase behaviour is primarily determined by the overall degree of polymerization, N, interaction parameter, χ, copolymer composition, f, and two additional factors: conformational asymmetry [4–7] and fluctuation effects [4,8–11]. An understanding of dynamical properties of block copolymers has an important role in the manipulation of the block copolymer microstructure or microscopic anisotropy for their successful implementation [3]. This is specially referred to the area of rheology and alignment behaviour of strongly segregated copolymers. Since the dynamics is strongly coupled to the state of order the intercorrelations between molecular dynamics and morphology contributes to further understanding of copolymer behaviour.

The mobility of copolymer chains is commonly assessed by dynamic mechanical measurements [12], nuclear magnetic resonance [13–16], dynamic light scattering (DLS) [17], dielectric spectroscopy [18] and dynamic infrared linear dichroism spectroscopy [19]. However, one of the method which can also offer an insight into the dynamics properties and microphase separation of block copolymers is electron spin resonance (ESR) using nitroxide spin probes

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as molecular reporters [20,21]. Molecular motion of spin probe is sensitive to the local density of molecular packing (or free volume) and to local segmental dynamics of polymer chains. From the temperature dependent complex ESR spectra details of motional heterogeneity as a consequence of complex morphology and microphase separation can be obtained. The presence of more than one spectral component is an indication of microphase separation. The free volume approach in the complex ESR spectra may be useful in understanding low molecular mass compound penetration in block copolymers in order to control transport properties in membranes or in drug delivery devices.

The aim of present study is to explore molecular dynamics of symmetric diblock copolymers of styrene and butadiene depending on the block length. The attention is focused on the dynamical heterogeneity in a wide temperature range. The results were deduced by comparison with similar studies of the homopolymers of polybutadiene and polystyrene of similar molecular mass. To explore how the change of copolymer morphology influences motional heterogeneity or phase separation copolymers were casted from different solvents. Therefore three thermodynamically different solvent were chosen; good solvent for both component and selective solvents for PB and PS component, respectively. Two spin probes were selected to scan a wider free volume distribution.

2. Experimental

2.1. Sample preparation

Symmetric polystyrene-*block*-polybutadiene copolymers (PS-b-PB) of three different molecular masses were synthesized by anionic polymerization at the Charles Sadron Institute. Polybutadiene and polystyrene samples of similar molecular mass (Polymer Source Inc.) were used as received (Table 1).

2.2. Sample characterization

Differential scanning calorimetry measurements (DSC) were carried out with a Perkin–Elmer DSC7 calorimeter using a heating/cooling rate of 20 K/min. The molar-mass distributions were determined using size exclusion chromatography.

A Varian liquid chromatograph equipped with a refractive detector was used. Three columns from Supelco (G6000-4000-2000 HXL) were used with THF as the eluent. The molar-mass distributions were narrow and similar (Table 1).

2.3. ESR measurements

The polymers were doped with 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (Tempol) and 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl benzoate (BzONO) using three different solvents: benzene, 2-butanone and *n*-heptane. The samples were dissolved at a 5% concentration in a spin probe solution in one of the solvents. The solvent was slowly evaporated at 308 K and the resulting films thus obtained were annealed 48 h or longer in vacuum near the glass transition temperature until no changes were observed in the ESR spectra. The concentration of spin probes did not exceed 0.03 mass%.

The ESR spectra were recorded on a Varian E-109 X-band spectrometer operating at the same modulation of 0.1 mT and microwave power of 5 mW. A variable temperature unit controlled the temperature. The samples were allowed to equilibrate for at least 10 min after approaching the temperature of measurements. During data acquisition the number of scans were chosen according to the signal-to-noise ratio (10–100 scans).

The simulation of the two component spectra is made on the basis of a set of components derived from the experimental data. The subtraction of broad polystyrene component at various temperatures from the corresponding complex spectra resulted in a set of narrow components with rotational correlation times in the 0.1 ns range (Fig. 1). The fraction of each component in the simulated spectra is determined with the deviation of less than 3%.

Table 1
Sample characteristics

Sample	Code[a]	Mass fraction of styrene	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Polystyrene-*block*-polybutadiene	SB1-b, SB1-bt, SB1-h	0.50	12,000	1.05
Polystyrene-*block*-polybutadiene	SB2-b, SB2-bt, SB2-h	0.50	48,000	1.04
Polystyrene-*block*-polybutadiene	SB3-b, SB3-bt, SB3-h	0.50	83,000	1.03
Polystyrene	PS1	1.00	7,600	1.03
Polystyrene	PS2	1.00	20,800	1.07
Polystyrene	PS3	1.00	43,400	1.04
Polybutadiene	PB	0.00	41,000	1.03

[a] b-films cast from benzene; bt-films cast from 2-butanone; h-films cast from *n*-heptane.

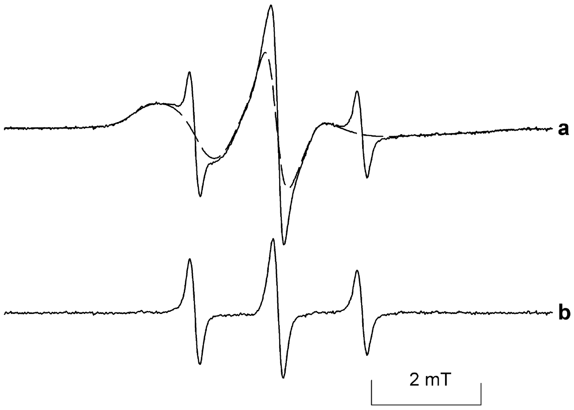

Fig. 1. An example of a semiquantitative analysis: (a) experimental complex ESR spectra of SB2-b (full line) and broad component PS2 (dashed line) probed with Tempol at 310 K; (b) narrow component obtained by subtraction of experimental data.

3. Results and discussion

3.1. ESR spectra of BzONO probe in block copolymers

The ESR spectra of block copolymers and pure block components (PS and PB) were measured in the temperature range 170–410 K at intervals of 5 K. As an example selected spectra of SB3 block copolymer with doped BzONO as a spin probe are shown in Fig. 2. Above ~370 K the intensity of the ESR signal was slowly disappearing. Below this temperature the ESR measurement were repeated after the heat treatment up to 370 K and cooling to 170 K. Changes in the spectra appeared to be very little influenced by repeated heating. BzONO probe was applied due to previous successful use in similar copolymers and in polystyrene homopolymer where this particular probe has demonstrated the best agreement of the T_{5mT} parameter and glass transition temperature [20,22] T_{5mT} is the temperature at which the width of the ESR spectrum is 5 mT. This parameter correlates with the glass transition temperature, T_g. However, transition temperature, T_{5mT}, for the two motional components will also be determined by the size and shape of the spin probe [22].

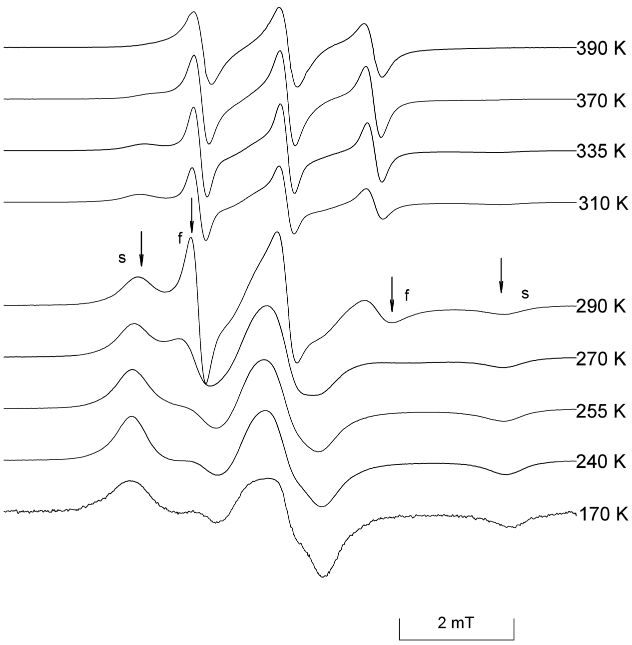

Fig. 2. Temperature dependent ESR spectra of SB3-b probed with BzONO. The low and high field fast and slow components are indicated by ‘s’ and ‘f’, respectively.

Contrary to the ESR spectra of the pure polystyrene and polybutadiene, block copolymers display two ESR spectral components in the given temperature interval irrespective of the block length. Two spectral components correspond to spin probes embedded in two different motional environments; an indication of microphase separation. The outer maxima separation, $2A_{zz}$, of the broad component shifts slowly inwards with increasing temperature. However, the linewidths of a broad component are similar to those of pure PS components of comparable molecular mass below the glass transition temperature. This behaviour suggests that the slow motion component is predominantly connected with spin probes embedded in the phase resembling restricted molecular motion of the polystyrene blocks. The narrow component corresponding to the spin probes in the mobile regions has a wider splitting as compared with the pure polybutadiene component. Above certain temperature when T_{5mT} is reached the mobility of probe molecules in each component becomes comparable and only fast motional spectrum is obtained.

The occurrence of two spectral components differing in their mobility and intensity ratio above the characteristic temperatures is influenced by the block length and block copolymer interphase. Characteristic temperatures where the fast motional component appears and the slow component reaches T_{5mT} are shown in Table 2. Fast motional domains seem to be insensitive to the BzONO probe depending on the block length. However, the disappearance of the slow motion component appears to be dependent on the molecular mass. T_{5mT} increases with an increase of block length. Similar results are observed by DSC measurements (Table 3). T_g values reveal a glass transition temperature depression of the PS component in block copolymers as already determined in other PS-b-PB and polystyrene-*block*-polyisoprene (PS-b-PI) copolymers [13,20,23,24]. For comparison an influence of molecular mass on T_g of pure PS is shown in Table 3. Smith et al. [19] have shown by selective deuterium labelling that in PS-b-PI copolymers styrene segments near the block junction mixed in the interphase region have a rubber-like mobility even at room temperature. The chain ends of lower molecular mass diblock and block-junctions demonstrate higher mobility at lower temperatures as compared with the copolymers of a higher molecular mass. In SB1 block copolymer with the lowest molecular mass slow component disappears at lower temperature. With increasing temperature the intensity of the fast component of complex spectra increases at the

Table 2
T_{5mT} values of fast and slow components of ESR spectra of samples probed with BzONO and Tempol

Sample	Spin probe	T_{5mT} (K) Fast component[a]	T_{5mT} (K) Slow component[a]
SB1-b	BzONO	265	315
SB2-b	BzONO	265	385
SB3-b	BzONO	265	385
PS1	BzONO	–	385
PS2	BzONO	–	395
PS3	BzONO	–	395
PB	BzONO	257	–
SB1-b	Tempol	245	305
SB2-b	Tempol	250	335
SB3-b	Tempol	255	345
PS1	Tempol	–	290
PS2	Tempol	–	295
PS3	Tempol	–	295
SB1-b:	Tempol	240	305
SB1-h	Tempol	245	305
SB2-bt	Tempol	245	315
SB2-h	Tempol	250	335
SB3-bt	Tempol	255	325
SB3-h	Tempol	265	350

[a] Error of measurements ±2 K.

expense of slow component much faster than in the case of SB2 and SB3. Such a free volume generation with temperature may be expected due to the larger interphase and increased segmental dynamics as the copolymer is approaching the order–disorder transition temperature (T_{ODT}). It is known that the PS-b-PB copolymer with the shortest block lengths, SB1, is phase separated [25] up to ~305 K, while the other two PS-b-PB samples having longer block are phase separated in the entire measured temperature interval and are composed of two domains of specific structure [3].

In the case of SB1 T_{ODT} is within the investigated temperature interval and close to the motional transition observed by spin probe method. The appearance of a motionally narrowed three lines ESR spectrum indicates that the both components of the block copolymer are in the fast motion regime. Although the other two copolymers SB2 and SB3 did not yet reach T_{ODT} according to the literature data [25], the appearance of a motionally narrowed spectrum at higher temperatures is connected with the cooperative motion of polystyrene chains reaching its glass transition.

Table 3
Glass transition temperatures

Sample	T_g (PS) (K)	T_g (PB) (K)
SB1-b	301	183
SB2-b	369	179
SB3-b	378	180
PS1	358	–
PS2	371	–
PS3	382	–

The details of the motional dynamics above and/or close to T_{ODT} were deduced from DLS experiments by Papadikis et al. [17] on the same symmetric diblock copolymer of low molecular mass. Above the T_{ODT} the copolymers melts exhibit more than one relaxation mode which reflect the inhomogeneity of the copolymer. The modes correspond to the segmental reorientational dynamics of the polystyrene blocks chain orientation and stretching in the compositional fluctuation field. In the polarized experiment additional modes due to the diffusive processes were observed. In the copolymer with the lowest molar mass the stretching mode disappears deep in the disordered state. The change of the molecular dynamics in the fast motion regime above T_{ODT} from the ESR spectra could not be detected due to the decay of the signal.

Contrary to the phase transition depression of the PS phase, T_{5mT} of the PB domains reveal a slight increase as compared with the pure PB component (Table 2). Similar effect is observed by NMR spin–spin relaxation, T_2, measurements [16]. The two T_2 relaxation times, characteristic for two motionally different phases reveal a lowering of T_2 of the PB phase. The second moment of the short T_2 corresponding to the PS blocks is smaller as compared with the pure PS phase. This is explained by the restricted motion of PB segments as a result of the interpenetration of some PB segments into the PS phase at the interphase. A very small ratio of mobile segments intermixed into the slow PS phase enhance the mobility of PS segments to a higher extent than the motion of mobile butadiene segments is reduced by the rigid PS chains [13].

3.2. ESR spectra of Tempol probe in block copolymers

The ESR spectra of smaller spin probe (Tempol) embedded in the block copolymers show similar behaviour to those of BzONO probe. Due to the size and shape of a probe molecule characteristic spectral changes appear at lower temperatures. For a comparison selected spectra of SB3 block copolymer doped with Tempol and measured in the temperature range from 170 to 410 K are shown in Fig. 3. T_{5mT} temperatures are lower than the corresponding T_{5mT} temperatures determined by the BzONO probe and glass transition temperatures determined by DSC measurements. The packing of chain within separated blocks and the corresponding segmental mobility may reduce the free volume available to the spin probe molecule depending on its size. The use of a Tempol probe enables to reach smaller vacancies and follow different rates of molecular motion of PS and PB blocks. The intensity of the fast component is changing with temperature and can be taken as a good measure of the free volume generation depending on the block length.

A full quantitative analysis of the motional dynamics would require a modelling of the spectra sensitive to a large

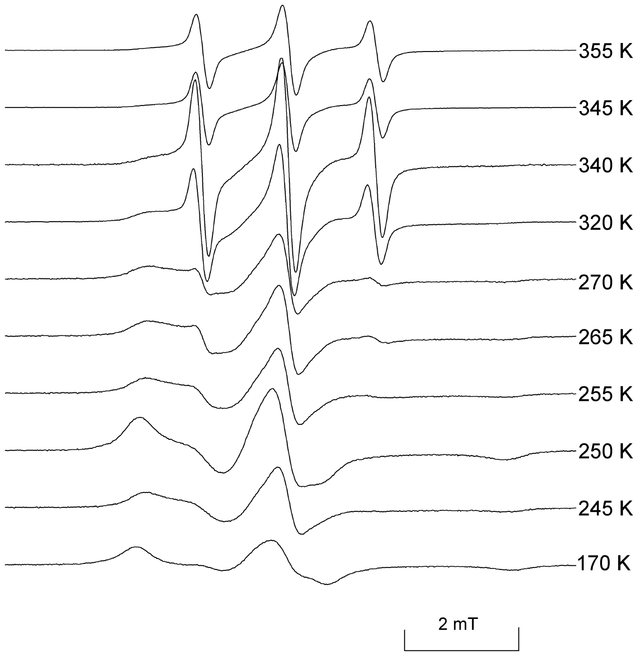

Fig. 3. Temperature dependent ESR spectra of SB3-b probed with Tempol.

number of parameters, which is not the purpose of the present paper. In order to obtain information about the relative component weight a 'semiquantitative' analysis of the experimental ESR spectra was performed [26,27]. Since the bimodal experimental spectra consist of clearly distinguished slow (10^{-7}–10^{-9} s) and fast components (10^{-10}–10^{-11} s), respectively, the complex spectra can be simulated by a superposition of broad experimental polystyrene spectra and the narrow components. The results are given in Table 4. The low molecular mass block copolymer, SB1, reveals rather fast increase of free volume with increasing temperature as the copolymer approaches order–disorder transition. The other two block copolymers change the free volume slowly. Since they are still far below the order–disorder transition obviously different relaxation times due to the structural organization are present. In other words free volume within the ordered domains is developing much slower at given temperatures as compared with the SB1 block copolymer. The length of blocks also changes the amount of interphase. Since the ESR spectra are not able to differentiate spin probes embedded only in the interfacial region, as already discussed in Section 3.1, an increase of fast motion is attributed to the motional dynamics of the interfacial chains and PB chains. In the case of copolymers with longer blocks or copolymers in the region of strong segregation with considerable smaller interfacial region a slight increase of free volume in the measured temperature interval shows continuous increase of the fraction of motional segments.

3.3. Effect of casting solvents on motional heterogeneity

Phase separated structures of block copolymers are known to depend upon the solvent selectivity used in the casting process [23,28–34]. We have carried out the analysis of molecular motion of spin probes embedded in the phase separated copolymers having different block length casted from benzene, 2-butanone and *n*-heptane. The unequal partition of solvent in the microdomains formed in the solution changes the 'effective' volume ratio of the microdomains and modifies the interphase of phase separated structures during the solvent evaporation [34]. It could be expected that the generation of free volume with temperature will be sensitive to the phase separated structures and their interphase developed from various solvents.

The smaller probe, Tempol, has shown to be more sensitive to the local free volume distribution and packing differences induced by casting from various solvents and was further used in this study. The $T_{5\mathrm{mT}}$ values of the slow motion ESR component of spin probed block copolymers with longer blocks (SB2 and SB3) casted from 2-butanone are shifted to lower temperatures as compared with the films casted from other two solvents, irrespective of the spin probe used in the experiment (Table 2). The lowering of $T_{5\mathrm{mT}}$ of the polystyrene component is an indication that the dynamical properties of spin probe molecules are different. The difference between $T_{5\mathrm{mT}}$ values of the same copolymers casted from different solvents should be looked for in the domain structure or copolymer morphology. Since 2-butanone is a good solvent for PS blocks the polymer–solvent interaction and diffusivity of solvent molecules would contribute to different microphase separation during the evaporation [28].

However, in a certain temperature region above the temperature at which two motional phases appear (Fig. 4),

Table 4
Fractions of the ESR fast components of films probed with Tempol

T (K)	Fractions of the ESR fast components								
	SB1-b	SB1-bt	SB1-h	SB2-b	SB2-bt	SB2-h	SB3-b	SB3-bt	SB3-h
270	0.15	0.26	0.16	0.05	0.21	0.06	0.04	0.18	0.02
280	0.25	0.34	0.28	0.06	0.23	0.07	0.05	0.20	0.03
290	0.34	0.40	0.34	0.07	0.26	0.09	0.07	0.22	0.04
300	0.40	0.45	0.41	0.09	0.30	0.12	0.08	0.26	0.05
310	1.00	1.00	1.00	0.11	0.35	0.13	0.10	0.30	0.06

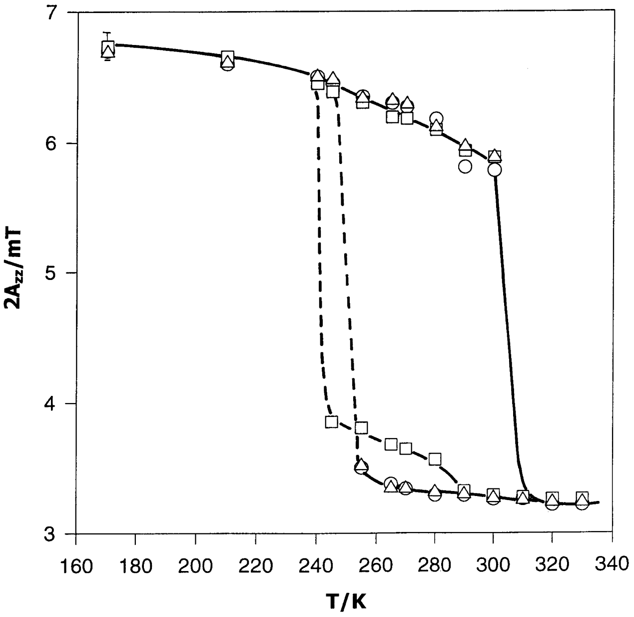

Fig. 4. The temperature dependence of the outer maxima separation, $2A_{zz}$, for both slow and fast component of SB1-b (○), SB1-bt (□) and SB1-h (△) probed with Tempol. The dashed line indicates motional behaviour of the PB phase and the full line at higher temperature corresponds to the slow PS phase.

the outer maxima separation, $2A_{zz}$, of SB1 casted from 2-butanone reveals slower mobility of fast component as compared with the same values of SB1 copolymer casted from benzene and *n*-heptane. The lowered mobility of predominantly polybutadiene chains could be explained with larger fraction of interphase and consequently stronger influence of still restricted polystyrene chains on PB segmental motion.

The influence of casting solvents on the molecular dynamics of motionally phase separated block copolymers is studied by comparing the fractions of a fast component of the complex ESR spectra (Table 4). The results reflect the fluctuation in the local chain density and the generation of free volume with temperature depending on the casting solvent. It should be noted that the ratio of probe molecules attaining fast and/or slow motion is only a relative measure. In most heterogeneous polymer systems a fraction of fast or slow component does not equal to the amount of a real phase [21]. A spin probe distribution in the phase separated symmetric block copolymers casted from the solvents is determined by several parameters; namely a solubility of polymer segments, interaction of spin probe with polymer segment, spin probe size and polarity and accessible free volume. Our experiments on the PS-PB mixtures of the same molecular mass as the corresponding blocks in the investigated block copolymers in benzene have shown that only ~25% of a probe partition in the polybutadiene phase. Therefore the fraction of a narrow component is a relative measure of motionally active spin probes determined by the polymer chain packing. Films casted from 2-butanone at low temperatures reveal in general higher fraction of ESR fast component compared with the films casted from other two solvents. However, this difference between the solvents slowly disappears in SB1 films at temperatures approaching T_{ODT}.

Block copolymers with longer blocks (SB2 and SB3) casted from 2-butanone exhibit significantly higher fraction of fast motion in the whole temperature range. The same copolymers casted from benzene and *n*-heptane do not show significant increase of fast motion in the same temperature interval. A considerably smaller fraction of the fast motion in those two copolymers suggest dynamically different environment due to the microdomain morphology. The results of free volume change confirm that the phase separation is affected by the solvent and molecular mass of the blocks. An increase of free volume of SB copolymers having higher molecular mass (SB2 and SB3) casted from benzene and *n*-heptane is considerably slower as compared with the films casted from 2-butanone. Benzene as a solvent seems to be responsible for faster free volume increase in SB3 copolymers compared to the *n*-heptane. However, the faster increase of free volume in SB2 copolymers is observed with *n*-heptane (Table 4). An increase of ESR fast motional component and $T_{5\mathrm{mT}}$ shifts to lower temperature of SB copolymers of higher molecular mass casted from selective solvent for PS phase could be explained with the larger fraction of interphase and consequently an increase of free volume. The increase of total interphase is a result of lower degree of phase separation. If the good solvent for PB blocks is applied there is a change in local free volume, however, those changes are considerably smaller than in the case of SB films prepared from nonselective solvent.

The common characteristic of all the films casted from selective solvents i.e. by swelling only one type of blocks and leaving the other block in a collapsed state results in a less regular structure and higher diffusivity between the domains. The difference of motional dynamic of spin probe incorporated into the copolymer matrix appears to be sensitive to interfacial changes due to the morphology. The spin probes within the segregated block may also account for conformational differences adapted in casted films.

4. Conclusions

The motional heterogeneity in SB copolymers has been studied by ESR of nitroxide spin probes. The results were compared with the homopolymers of PS and PB of similar molecular mass. Two spin probes, BzONO and Tempol, were selected to scan a wider free volume distribution.

The ESR components were detected in SB copolymers in contrast to one spectral component in homopolymers. The slow component is assigned predominantly to the PS phase while the fast component includes PB phase and spin probes located in the interfacial region. The temperature range in which two spectral components, resembling motionally different domains, appear depends on the block length. The free volume generation with temperature confirms that the block length has an effect on phase separation and interphase.

The ESR spectra of SB copolymers casted from different solvents have shown that the Tempol probe motion is sensitive to the domain morphology created by the solvent. The lowering of $T_{5\mathrm{mT}}$ of the slow component and larger fractions of fast motion in the films casted from good solvent for PS (2-butanone) is explained with the morphology which creates larger interphase or structures with less segregation and lower local density compared to the block copolymers prepared from nonselective solvent. The differences in the fraction of fast motion induced by different solvents are smaller in the copolymer with the shortest block length.

Since this study has shown that the spin probe molecules are very sensitive to the change of free volume induced either by the domain structure or temperature they can be successfully used as model molecules to probe the presence and penetration of small molecules into the complex polymer systems.

Acknowledgements

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References

[1] Hamley IW. The physics of block copolymers. Oxford: Oxford University Press; 1998.
[2] Bates FS, Fredrickson GH. Phys Today 1999;52:32–8.
[3] Fredrickson GH, Bates FS. Annu Rev Mater Sci 1996;26:501–50.
[4] Bates FS, Schulz MF, Khandpur AK, Förster S, Rosedale JH, Almdal K, Mortensen K. Faraday Disc 1994;98:7–18.
[5] Vavasour JD, Whitmore MD. Macromolecules 1993;26:7070–5.
[6] Bates FS, Fredrickson GH. Macromolecules 1994;27:1065–7.
[7] Khandpur AK, Förster S, Bates FS, Hamley IW, Ryan AJ, Bras W, Almdal K, Mortensen K. Macromolecules 1995;28:8796–806.
[8] Bates FS, Rosedale JH, Fredrickson GH, Glinka CJ. Phys Rev Lett 1988;61:2229–32.
[9] Rosedale JH, Bates FS. Macromolecules 1990;23:2329–38.
[10] Bates FS, Rosedale JH, Fredrickson GH. J Chem Phys 1990;92: 6255–70.
[11] Almdal K, Bates FS, Mortensen K. J Chem Phys 1992;96:9122–32.
[12] Colby RH. Curr Opin Coll Interf Sci 1996;1:454–65.
[13] Stöppelmann G, Gronski W, Blume A. Polymer 1990;31:1838–53.
[14] Kulik AS, Haverkamp J. Polymer 1995;36:427–9.
[15] Soltani R, Lauprêtre F, Monnerie L, Krause S. Polymer 1995;36: 275–82.
[16] Bershtein VA, Vilesov AD, Vinogradova LV, Volodin VP, Gotlib YuYa, Darinskii AA, Yegorova LM, Yegorov VM, Zhukov IYu, Zgonnik VN, Kenunen IV, Sinani AB, Terent'eva IV, Frenke SYa, Shevelev A. Vysokomol Soed 1990;32:2324–30.
[17] Papadikis CM, Brown W, Johnsen RM, Posselt D, Almdal K. J Chem Phys 1996;104:1611–25.
[18] Floudas G, Antonietti M, Förster S. J Chem Phys 2000;113:3447–51.
[19] Smith SD, Noda I, Marcott C, Dowrey AE. In: Noda I, Rubingh DN, editors. Polymer solutions, blends and interfaces. Amsterdam: Elsevier Science; 1992. p. 43–64.
[20] Kumler PL, Keinath SE, Boyer RF. Polym Engng Sci 1977;17: 613–21.
[21] Veksli Z, Andreis M, Rakvin B. Prog Polym Sci 2000;25:949–86.
[22] Kumler PL. Molecular motion in polymers by ESR. In: Boyer RF, Keinath SE, editors. MMI Press Symposium Series. New York: Harwood Academic Publishers; 1978. p. 189–222.
[23] Beecher JF, Marker L, Bradford RD, Aggarwal SL. J Polym Sci C 1969;26:117–34.
[24] Stühn B. J Polym Sci, Polym Phys Ed 1992;30:1013–9.
[25] Papadikis CM, Almdal K, Mortensen K, Posselt D. J Phys II 1997;7: 1829–54.
[26] Müller G, Stadler R, Schlick S. Macromolecules 1994;27:1555–61.
[27] Schädler V, Kniese V, Thurn-Albrecht T, Wiesner U, Spiess HW. Macromolecules 1998;31:4828–37.
[28] Inoue T, Soen T, Hashimoto T, Kawai H. J Polym Sci A2 1969;7: 1283–301.
[29] Hasegawa H, Hashimoto T. Polymer 1992;33:475–87.
[30] Hasegawa H, Tanaka H, Yamasaki K, Hashimoto T. Macromolecules 1987;20:1651–62.
[31] Turturro A, Gattiglia E, Vacca P, Viola GT. Polymer 1995;36: 3987–96.
[32] Cohen RE, Bates FS. J Polym Sci, Polym Phys Ed 1980;18:2143–8.
[33] Funaki Y, Kumano K, Nakao T, Jinnai H, Zoshida H, Kimishima K, Tsutsumi K, Hirokawa Y, Hashimoto T. Polymer 1999;40:7147–56.
[34] Lodge TP, Hamersky MW, Hanley KJ, Huang CI. Macromolecules 1997;30:6139–49.