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Molecular Order and Dynamics in Block Copolymers of Poly(oxybutylene) and Poly(oxyethylene)

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Summary: Broadband dielectric spectroscopy (10^{-2}-10^9 Hz) was employed to investigate the dynamics of poly(oxybutylene) chains in solid semicrystalline poly(oxybutylene)-poly(oxyethylene)-poly(oxybutylene) (BEB) triblock copolymers. The results are compared with those obtained for B homopolymers, EB diblocks and EBE triblocks. The B blocks were dipole-inverted in the homopolymers and the EBE triblocks, however not in the EB and the BEB copolymers. The segmental α relaxation, caused by local chain motion, and the normal mode relaxation, due to chain motions of larger length scale, were studied in detail with respect to time scale, relaxation strength and shape of the response. The α relaxation in the BEB copolymers shows similar behavior to that in the other three systems, whereas the normal mode relaxation shows characteristic differences in the four systems.

Keywords: α relaxation; block copolymers; dielectric properties; normal mode relaxation; polyethers

Introduction

Dielectric spectroscopy (DS) has been widely employed to investigate molecular mobility in polymeric systems over wide ranges of frequency and temperature in relation to conformational properties of the chains and molecular order in complex systems[1]. Polymers having dipole moments aligned in the same direction parallel to the chain contour (so-called type-A polymers) are of particular importance for such studies. They show, in addition to the common α or segmental relaxation, which covers only a few segments, the specific so-called normal mode relaxation (n relaxation), which is related to the fluctuation and orientation of the end-to-end polarisation vector of the chain and, thus, involves the whole of the polymer chain.

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Cis-polyisoprene (PI) is the polymer most extensively employed in dielectric studies of the n process, starting in the mid-1980s[2,3]. It possesses dipole moments both parallel and perpendicular to the chain contour and exhibits both the n process and α process, associated with the parallel and the perpendicular dipole moments, respectively. The molar mass dependence of the time scales of the two processes is fundamentally different and, thus, by varying the molar mass, the two processes could be distinguished from each other and studied in detail[3]. Samples investigated include pure PI in the bulk amorphous state[4-8] and in solutions[9], PI/PI blends[10], polyisoprene/polybutadiene blends[11], di- and triblock copolymers with PI as a component[12-14] and star polymers with PI arms[15]. Results from these and similar studies were used to test several proposed theories and models of polymer chain dynamics in homopolymers, blends and block copolymers.

Polyethers also possess dipole moments along the chain contour and DS was employed by Stockmayer and co-workers already in the 1960s to investigate the n and α processes in bulk polypropylene oxide (PPO)[16]. In two previous papers[17,18] we studied in detail, by broadband DS, the molecular mobility in diblock copolymers of poly(oxybutylene) and poly(oxyethylene) (in the following denoted by B and E, respectively), both A-type polymers. At temperatures lower than about 40-60°C the E blocks crystallise into lamellar crystals and do not exhibit long scale molecular mobility, so that DS probes selectively the mobility of the B chains. The molar mass of the B subchain was systematically varied and the results were compared with those of similar systematic studies on B homopolymers and of preliminary studies on two EBE triblock copolymers. They suggested effects of fixed chain ends (tethering) and of confinement on the mobility and the conformational properties of the B subchains in the block copolymers[17,18].

In this paper we extend the above studies and report the results of detailed investigations of molecular mobility in several BEB triblock copolymers by broadband DS (10^{-2}-10^{9} Hz) and of preliminary investigations by thermally stimulated depolarisation current (TSDC) techniques. As in the case of the EB diblocks[17,18], in the temperature range of measurements the E blocks are in the crystalline state and only the mobility of the B subchains is probed. The results for the n and α processes are analysed in detail to extract information from the frequency position (time scale), the relaxation strength and the shape of the corresponding loss peaks. This information refers to the structure and conformation of the B subchains in the triblocks and complements that obtained for the same samples by investigations of the overall solid-state structure by means of small-angle X-ray scattering (SAXS), differential scanning calorimetry (DSC) and Raman spectroscopy[19-21]. The results obtained for the BEB triblocks are compared with those obtained for the B homopolymers, the EB diblocks and the EBE triblocks, and are discussed in terms of constraints imposed on the amorphous B-blocks by tethering on the crystalline E-blocks and by confinement. One more point is considered here for the longer block copolymers, chain folding. For short B blocks the structural studies[19-21] show that both the crystalline E-blocks and the amorphous B-blocks remain unfolded. For longer B-blocks the unfolded conformation becomes unstable, leading to the formation of one or more folds of the E-blocks. This is due to the difference in cross-sectional area of the two chains (0.21nm^2 for E against 0.34nm^2 for B) and the need to fill space at approximately the same density[19-21]. Folding of the E-blocks reduces the effects of confinement of the B-blocks and this should be reflected in the conformational properties and the mobility of the B subchains. Folding of the B-blocks in the BEB triblocks has also been suggested by Raman spectroscopy studies[21].

Background

By expanding the local correlation function for a chain of N monomers[22] with respect to its eigenfunctions f_p (p=1,...,N), the dielectric loss for the n process, normalised to the relaxation strength $\Delta\varepsilon$, can be written in the form

$$\frac{\varepsilon''(f)}{\Delta\varepsilon}=\sum_{p=1}^{N} g_p(n)\frac{2\pi f\tau_p}{1+(2\pi f)^2\tau_p{}^2}$$
$$g_p(n)\propto\left[\int_0^N \xi(n)f_p(n)dn\right]^2 \qquad (1)$$

In these equations f is the frequency of measurement, τ_p is the relaxation time of the p-th mode and $\xi(n)$ is a parameter specifying the direction of the dipole along the chain contour of the n-th segment with respect to the bond vector $\mathbf{u}(n, t)$ of that segment at time t: $\xi(n) = 1$ and -1 for dipoles parallel and antiparallel to $\mathbf{u}$, respectively.

For low molar mass (un-entangled) polymers the modified Rouse model[23] predicts that $f_p \propto \sin(p\pi n/N)$ and $\tau_p \propto p^{-2}$, so that the dielectric loss, for a linear chain with $\xi(n) = 1$ for all segments, can be written as

$$\frac{\varepsilon''}{\Delta\varepsilon}=\frac{8}{\pi^2}\sum_{p:odd}\frac{2\pi f\tau_p}{p^2[1+(2\pi f)^2\tau_p{}^2]} \qquad (2)$$

Table 1. Structural characteristics of the BEB copolymers. M_n is the molar mass of the whole chain and M_B that of the B subchain, ϕ_B is the volume fraction of B in the copolymer melt, X_c is the degree of crystallinity of the E-block and k the number of folds of the crystalline E-block[19,21]

	M_n (g/mol)	M_B (g/mol)	ϕ_B	X_c	k
$B_{14}E_{56}B_{14}$	4500	1008	0.486	0.68	1
$B_{17}E_{201}B_{17}$	11300	1224	0.242	0.76	2
$B_{19}E_{58}B_{19}$	5300	1368	0.553	0.74	1
$B_{25}E_{90}B_{25}$	7600	1800	0.512	0.64	2
$B_{26}E_{95}B_{26}$	7900	1872	0.508	0.66	1-2
$B_{27}E_{105}B_{27}$	8500	1944	0.493	0.72	2
$B_{37}E_{77}B_{37}$	8700	2664	0.645	0.69	2
$B_{37}E_{150}B_{37}$	11900	2664	0.483	0.73	3

For the shape of the dielectric loss peak the Rouse model predicts[23]

$$\varepsilon''(f) \propto \begin{cases} 2\pi f\tau_1 \sum_{p:odd} p^{-2} & 2\pi f\tau_1 \ll 1 \\ (2\pi f\tau_1)^{1/2} & 2\pi f\tau_1 \gg 1 \end{cases} \tag{3}$$

For the molar mass dependence of the longest relaxation time τ_1 the Rouse model predicts $\tau_1 \propto M^2$ for un-entangled flexible linear chains. For longer chains in the entanglement regime the reptation model predicts[23] $\tau_1 \propto M^3$.

Dielectric studies of the n process can be carried out with both regular chains (i.e. having dipoles aligned in the same direction along the chain contour from one end to the other) and dipole-inverted chains. In the latter dipole inversion occurs at a particular point in the chain contour and then the dielectric n process reflects fluctuation of the difference vector $\Delta\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$ where $\mathbf{R}_1$ and $\mathbf{R}_2$ connect the dipole inversion point and the two chain ends[14,18,22]. Molecular motion remains the same, but the dielectric loss spectra change with dipole inversion[14,18]. For dipole inversion in the middle of the chain, only even eigenmodes contribute to dielectric losses (Equation (1)), so that the frequency of maximum loss f_{max} becomes 4 times higher than for the regular chain[22].

Experimental Part

The preparation[19] and the structural characterisation[19-21] of the BEB copolymers have been described elsewhere. The copolymers are denoted by $B_nE_mB_n$, where E is an oxyethylene unit, OCH_2CH_2, B an oxybutylene unit, $OCH_2CH(C_2H_5)$, and m, n the number-average block lengths in chain units. Table 1 lists structural characteristics of the BEB copolymers studied. The BEB copolymers were not dipole-inverted, as is also the case for the EB copolymers they

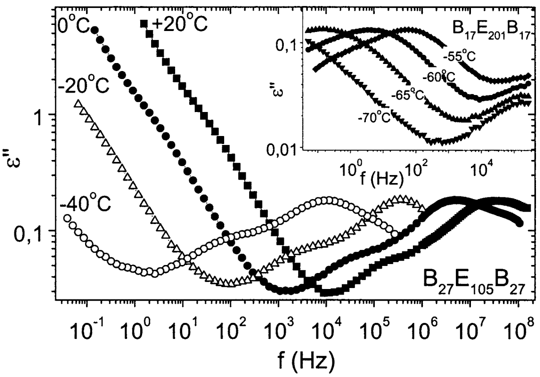

Figure 1. Dielectric loss ε'' against frequency f for the $B_{27}E_{105}B_{27}$ copolymer at selected temperatures. The inset shows a part of similar spectra for the $B_{17}E_{201}B_{17}$ copolymer.

are compared with. The B homopolymers and EBE copolymers were dipole-inverted in the middle of the B chain.

Broadband dielectric spectroscopy (DS) measurements were carried out in the frequency range 10^{-2}-10^{9} Hz, using equipment and cells already described[17,18]. A description of the method and the equipment used for thermally stimulated depolarisation currents (TSDC) measurements has been given elsewhere[24]. Dielectric measurements were carried out at temperatures lower than T_m, the melting temperature of the E-blocks. T_m was in the range 35-55°C, increasing with increasing m.

Results and Discussion

Figures 1 and 2 show the typical overall dielectric behavior of the BEB copolymers recorded by DS and TSDC. The TSDC technique (Figure 2(b)) corresponds to measuring dielectric loss against temperature at a fixed frequency in the range of about 10^{-3} Hz and it is characterised by high sensitivity and high resolving power[24]. In agreement with measurements on B homopolymers, EB and EBE copolymers[17,18], the high-frequency loss peak, at about 10^{4} Hz at –40°C in Figure 1 is due to the segmental α relaxation of the B subchains, whereas the weaker peak at lower frequencies, at about 10^{2} Hz at –40°C in Figure 1, is due to the n relaxation of the B subchains. In the TSDC plot of Figure 2(b) the loss peak at about –70°C is due to the α relaxation, whereas it is not clear at this stage whether the n relaxation makes a contribution to that peak. This is related to the question of merging of the α and n relaxations at low temperatures/frequencies, which has been discussed in detail for

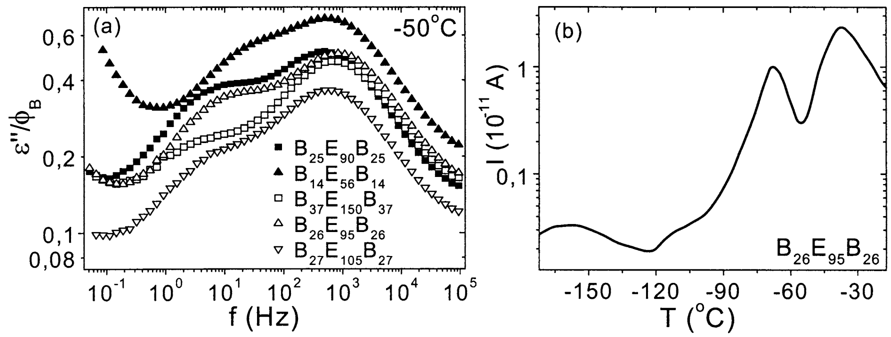

Figure 2. (a) Normalised dielectric loss ε''/ϕ_B against frequency f in the region of the α and the n relaxation for several BEB copolymers indicated on the plot at –50°C. (b) TSDC thermogram for the $B_{26}E_{95}B_{26}$ copolymer.

the B and the EB systems[17]. The steep increase of ε'' at low frequencies/high temperatures is due to conductivity. The shoulder on the ε'' swing, at about 10^2 Hz at 20°C, and the TSDC peak at about –40°C reflect the Maxwell-Wagner-Sillars interfacial polarisation, related to the heterogenous character of the samples[25]. The characteristics of the DS shoulder and the TSDC peak can be discussed in terms of morphology, this point being left out of the scope of the present paper. The TSDC peak at about –160 °C and the corresponding loss peak in the inset to Figure 1 at about 10^5 Hz at –70°C, not further studied here, are due to a secondary relaxation, probably related to the motion of chain ends[26]. Finally, the small TSDC peak at about –110°C, not resolved in the DS measurements, is related to traces of moisture in the samples[24].

In the following, attention is focused on the α and n relaxations. In Figure 2(a) we compare the behavior of several BEB samples in the frequency region of the two relaxations at –50°C. ε'' has been normalised to the same ϕ_B value by simply dividing by ϕ_B. Effective medium theory should be used for this in the future. The α loss peak is at approximately the same frequency, whereas the n loss peak (shoulder) shifts to lower frequencies with increasing molar mass of the B subchain and the two peaks are better resolved. This was already indicated in Figure 1 by comparing the behaviour of the two samples.

In order to extract quantitative information from the loss spectra, all the $\varepsilon''(f)$ data were subjected to a fitting procedure using the two-shape-parameter Havriliak-Negami[27] function,

$$\varepsilon^*(f) = \varepsilon' - i\varepsilon'' = \sum_{k=1}^{2}\left\{\varepsilon_{\infty k} + \frac{\Delta\varepsilon_k}{\left[1+(if/f_{0k})^{1-\alpha_k}\right]^{\gamma_k}}\right\} - i\frac{\sigma_{dc}}{\varepsilon_o f^s} \tag{4}$$

The second term on the right-hand side of Equation (4) quantifies the contribution of dc conductivity to the relaxation spectrum. ε_0 is the vacuum permittivity, ε_∞ is the limiting high-frequency permittivity, $\Delta\varepsilon$ is the relaxation strength, and f_0 is the position on the frequency scale of the relaxation process. The index k (k = 1, 2) refers to the two processes that contribute to the dielectric response: normal mode (k = 1) and segmental (k = 2) relaxation, in order of increasing frequency. The exponents α and γ ($0<(1-\alpha)$, $(1-\alpha)\gamma \leq 1$) define the symmetrical and asymmetrical broadening of the loss peaks, respectively, with respect to the Debye peak ($(1-\alpha) = \gamma = 1$). The frequency f_0 is directly related to the frequency of the maximum of dielectric loss, f_{max}[27].

Figures 3 and 4 refer to the time scale of the two relaxations. The Vogel-Tammann-Fulcher-Hesse (VTFH) equation[28]

$$f_{\max} = A\exp\left(-\frac{B}{T-T_0}\right) \tag{5}$$

with temperature-independent empirical parameters A, B, T_0 (Vogel temperature), was fitted to the data, the fit parameters being given in Table 2. We observe in Figure 3 that the behavior of the samples is similar with respect to the α relaxation, whereas the n relaxation becomes slower with increasing molar mass of the B-blocks. Extrapolation of the fits to the α data to f_{max} = 1.6mHz, corresponding to a relaxation time of τ = 100s, gives values of $T_{g,diel}$[17], which are in rather good agreement with corresponding TSDC and DSC data.

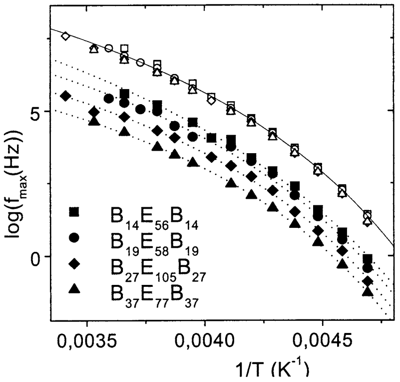

Figure 3. Arrhenius plot for the α (open symbols) and the n relaxation (filled symbols) for selected BEB copolymers. The lines are fits of Equation (5) to the data.

Figure 4 shows the dependence of the nominal relaxation time τ ($\tau = 1/(2\pi f_{max})$) of the α and the n relaxation on molar mass M_B for the BEB copolymers at –30°C. We have also included data for B homopolymers and EB copolymers[17,18].

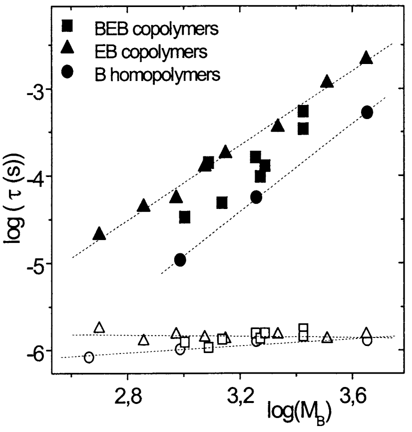

Figure 4. Nominal relaxation time τ at 30°C of the α (open symbols) and the n relaxation (filled symbols) against molar mass M_B, for the systems indicated on the plot. The lines are best linear fits to the data.

For the same molar mass M_B the α relaxation is slightly faster in the homopolymers than in the copolymers, particularly for smaller M_B. This is attributed to constraints imposed by the fixed chain ends[17]. The n relaxation is slower in the EB copolymers than in the B homopolymers. For the BEB copolymers τ values are between those for B and EB. This point can be discussed in terms of fixed chain ends and confinement of the B subchains in the copolymers[17], dipole inversion in the homopolymers and folding of the E-blocks for the BEB copolymers, which provides more space for the B subchains. The latter is characteristic for the BEB samples (Table 1) but not for the EB copolymers studied[17]. The exponent s in the relation $\tau \propto M_B^{\,s}$ is $s = 2.50 \pm 0.05$ for the homopolymers and $s = 2.0 \pm 0.1$ for the EB copolymers, this result suggesting stronger interactions in the homopolymers. The data for the BEB copolymers in Figure 4 scatter a lot, which can be attributed to differences among samples in chain folding (Table 1) and to the fact that, in contrast to B and EB, the BEB systems do not anneal after crystallisation[20].

Table 2. VTFH fit parameters for the segmental and the normal mode relaxation of the BEB copolymers.

	normal mode relaxation			segmental relaxation		
	log$A$	B(K)	T_0(K)	log$A$	B(K)	T_0(K)
$B_{14}E_{56}B_{14}$	10.33	1172	164	13.22	1738	149
$B_{17}E_{201}B_{17}$	9.76	1154	167	12.17	1272	164
$B_{19}E_{58}B_{19}$	8.99	842	174	12.02	1352	158
$B_{25}E_{90}B_{25}$	9.42	1143	165	11.27	1112	166
$B_{26}E_{95}B_{26}$	8.35	859	172	10.72	997	166
$B_{27}E_{105}B_{27}$	8.96	1008	169	11.64	1235	162
$B_{37}E_{77}B_{37}$	8.90	1194	162	11.39	1179	163
$B_{37}E_{150}B_{37}$	8.91	1124	164	11.48	1182	163

Figure 5 refers to the dependence of the dielectric strength $\Delta\varepsilon$ on M_B. For the α relaxation the three systems show comparable behavior and the dependence can be understood in

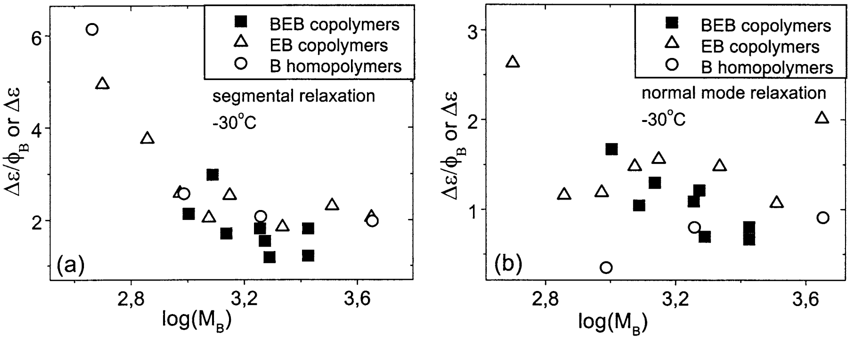

Figure 5. Dielectric strength $\Delta\varepsilon$ and normalised dielectric strength $\Delta\varepsilon/\phi_B$ for the α relaxation (a) and the n relaxation (b) of the systems indicated on the plot at –30°C.

terms of free chain ends[17]. For the n relaxation the results for the B homopolymers and the EB copolymers with short chains (i.e. without chain folding) have been previously used to calculate the end-to-end distance of the B-blocks and to show that these are more expanded and oriented in the copolymers than in the homopolymers[17,18]. This is not possible for the longer EB systems in Figure 5, $E_{31}B_{30}$ (1 fold), $E_{209}B_{45}$ (2-3 folds) and $E_{47}B_{62}$ (1 fold), or for the BEB copolymers (with the number of folds being given in Table 1). The decrease of $\Delta\varepsilon$ in Figure 5(b) with chain folding reflects the fact that the B subchains experience less spatial constraints in that case and can be quantitatively evaluated for chain conformation studies.

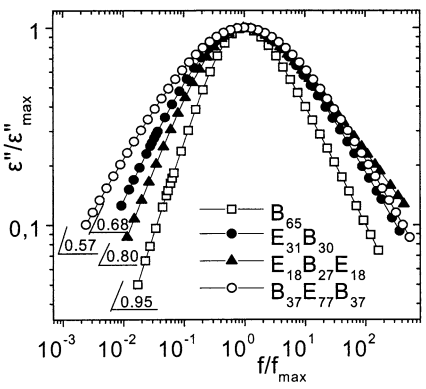

Figure 6. Scaling plot for the dielectric loss spectra of the n relaxation for the samples indicated on the plot at –30°C. The slopes on the low frequency side of the loss peaks are also indicated on the plot.

Figure 6 refers to the shape of the n relaxation in the systems B, EB, BEB and EBE. For that comparison we have selected from each class the sample with the longest B chain. The asymmetry parameter γ in Equation (4) is 0.68 for B_{65}, 0.72 for $E_{18}B_{27}E_{18}$ and ~1 for the EB and BEB samples, i.e. for the regular B chains. For the latter samples the deviation of the slopes from the value of 1 suggested by the theory (Equation (3)) may suggest that it is not the first mode in Equation (2) which is the most intensive one but other eigenmodes of higher order. The similar asymmetry parameter for the B and EBE samples, i.e. the dipole inverted samples, on the other hand, suggest that chain motions contributing to the second and other even modes are not significantly affected by fixing both chain ends. To further check this hypothesis experiments on more EBE samples are in progress.

Conclusions

The main results of this work, summarised in Figures 4-6, suggest that the segmental α relaxation of poly(oxybutylene) chains is similar in the four different environments (architectures) studied, whereas the normal mode relaxation, due to chain motions of larger length scales than the α relaxation, is affected by several factors, including fixed chain ends, geometrical confinement, chain folding, dipole inversion and annealing.

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