Relaxations in lamellar polystyrene–polybutadiene diblock copolymer. Thermally stimulated depolarization current study

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Abstract

The samples of the polystyrene-polybutadiene (PSPB) diblock copolymers with lamellar structure were investigated by integral and partial thermally stimulated depolarization current (TSDC) measurements in the 160–303 K range, and compared to the analogous investigation performed on a homopolymer sample of polystyrene (PS). The current peak, which appeared at 187 K, was found to be a dipolar relaxation α peak caused by the glass transition in the PB phase. The space-charge relaxation, distributed in the 220–260 K range and split into two parts – denoted as β_1 and β_2, was attributed to the possible local motion of the phenyl rings in the PS phase. The current maxima of the β relaxations significantly increased and shifted to the lower temperatures in the copolymer samples due to the PS–PB interfaces. The occurrence of doubleness and the relative distance between β_1 and β_2 was discussed. The relative numbers of the relaxing dipoles (N) *vs.* E_a were approximated. The energy width (ω) was significantly increased in the copolymers due to the released motions at the glass–liquid PS–PB interfaces. © 1998 Elsevier Science B.V.

Keywords: Activation energy; Lamellar structure; Polystyrene polybutadiene copolymer; Thermally stimulated current

1. Introduction

Block copolymers due to their blocks incompatibility, are able to segregate and form microdomains under the condition $\chi N \gg 10$ (strong segregation limit), where χ is the Flory–Huggins segment–segment interaction parameter, and N the degree of polymerisation [1,2]. The size and shape of ordered microdomain structures characterized by narrow interfaces are determined by molecular weight and composition, respectively. Among various possible structures, the lamellar structure is highly interesting because of its anisotropic physical properties [1,2]. During the process of block segregation, the chains extended in the direction perpendicular to the lamellae [3] and contracted parallel to the lamellae in order to maintain the uniform density. This deviation from the random-coil conformation has an influence on the local dynamic behaviour of chain segments. It has been shown recently on a macroscopically oriented diblock copolymer, by deuterium NMR spectroscopy, that chain segments undergo uniaxial reorientations around the symmetry axis of the system (the direction perpendicular to the lamellae); an order parameter, $S \approx 10^{-4}$, has been measured [4,5].

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In this paper, we report the first results observed by thermally stimulated depolarization current (TSDC) on a lamellar structure of polystyrene–polybutadiene (PSPB) diblock copolymer. Two samples have been used: the macroscopically oriented sample (OR) and the sample consisting of randomly oriented lamellar microdomains (NO).

Concerning the TSDC on PSPB systems, one literature source dealing with triblock copolymer was found [6] covering the 120–350 K range. Only one peak was observed due to the glass transition of the PB phase. In a recent work [7], the cross-linking in PB rubber was studied by integral and partial TSDC showing glass-transition relaxation at 180–205 K.

TSDC measurement is a very powerful method for studying the relaxation phenomena in non-conductive polymers. The review for the 1972–1977 period is given in [8]. Various aspects of the theory and the experimental techniques can be found in [9–12]. Special progress has been made by fractional polarization which enables one to divide the relaxation process into a series of elementary processes [13–21]. New approaches in the analysis of TSDC are proposed in [22–24].

2. Experimental

A symmetric PSPB diblock copolymer was synthesized by anionic polymerization in benzene, using *s*-butyl-lithium as initiator. M_w was 84000 (42000 per block); the M_w/M_n value of the PS chains was 1.03. DSC, performed with the powder at heating rate of 10 K min^{-1}, showed two glass transitions at 180 and 378 K, corresponding to T_g of PB and PS, respectively. More about preparation can be found in [5]. In the experiments with homopolymer, the PS of M_w=60 000 was used. The preparation of samples for the TSDC measurements was carried out in two steps. First, the powder was compressed at 298 K under $4.81\times10^6 \text{ Nm}^{-2}$ in vacuum and heated, at 10 K h^{-1}, up to 393 K. The sample was then held at 393 K for 2 h and then cooled, at 10 K h^{-1}, to 298 K. Second, the 1 mm thick disc-like samples with diameters of 18 mm were formed by flow under constraint. At this stage, two different procedures were carried out. The samples with macroscopically oriented lamellar structure were obtained by pressure

of $1.47\times10^5 \text{ Nm}^{-2}$ and by heating up to 423 K, at 3 K h^{-1}. Then the sample was annealed at 423 K for 4 h and, subsequently, cooled to 298 K at 10 K h^{-1}. The final thickness of the disc was controlled by a 1-mm thick metallic ring. Small-angle X-ray scattering (SAXS) data performed on a similarly prepared sample confirmed that the block lamellae were strictly parallel to the sample surfaces [4]. This was also proved by deuterium NMR. The periodicity measured by SAXS was 497 Å. Randomly oriented lamellar structure was prepared under a pressure of $4.41\times10^5 \text{ Nm}^{-2}$ and by heating at a rate of 20 K h^{-1}. Annealing at 423 K was avoided. A simplified diagram of OR and NO is shown in Fig. 1.

For the TSDC measurements, the discs with silver evaporated electrodes, 13.6 mm in diameter, were placed in the cell filled with dry nitrogen. For integral measurements the polarization was performed by the electric field, E_p=12 kV cm^{-1}, at a temperature T_p=303 K, unless otherwise stated, for 10 min. The cooling to the storage temperature, T_o=173 K, under E_p was at the rate of ca. 2 K min^{-1}. The storage in the short-circuited state (SCS) at T_o was 30 min. Depolarization by heating was at the rate of 4 K min^{-1}. The runs with the partial polarization (thermal sampling) were carried out by E_p at various T_p for 10 min. Further, the sample was cooled down to T_p−5 K under E_p for 4 min. The cooling to T_o in SCS and the storage at T_o in SCS took altogether 30 min. The current was measured by a Keithley 617 electrometer and the temperature was controlled by an LFE model 2012 controller.
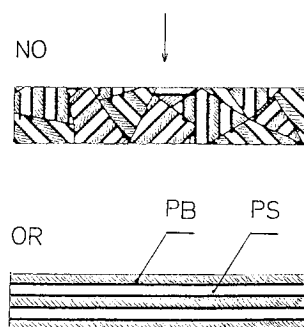

Fig. 1. Simplified diagram of samples with lamellar structure: NO, non-oriented; OR, oriented; PS polystyrene; PB, polybutadiene. Arrow shows the direction of electrical measurements.
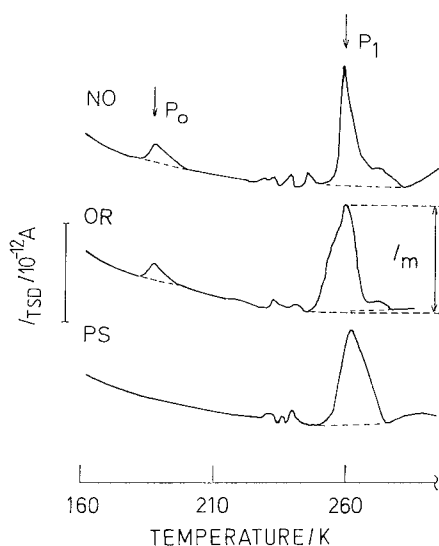
Fig. 2. Integral measurements of TSDC vs. temperature, for different samples: NO, non-oriented PSPB; OR, oriented PSPB; PS, pure PS; P_0, α relaxation peak; P_1, space charge relaxation peak; I_m, maximum current; E_p=12 kV cm^{-1}; and T_p=303 K.

Fig. 3. Plot of I_m vs. E_p for different peaks. (○) Related to P_0 and (●) related to P_1.

3. Results and discussion

3.1. Integral measurements

The results for integral measurements are shown in Fig. 2. In the cases of NO and OR one can find two peaks and a group of small peaks, respectively. Small peak P_o at 187±0.5 K is obviously caused by the glass transition of the PB phase (α peak) [6]. This is in agreement with the result for the PB rubber [7] and approximately with the DSC measurements (T_g appears at 180 K). Theoretically, the dipolar peak should not exist as a PB phase is an non-polar substance. The peak in question appears due to the presence of polar impurities depolarized by the glass-transition motions. The group of small peaks appear in the 230–248 K range. Moreover, one dominant peak is recorded at ca. 259±2 K. For the PS samples, the occurrence of P_1 is practically the same but with no P_0 which is specific just for the PB phase.

In order to examine the electric origin of the P_0 and P_1 peaks, the dependence of the maximum current I_m of the peaks vs. E_p was investigated and the results for one of the copolymer sample are shown in Fig. 3. The I_ms for P_0 are linear against E_p for the positive as well
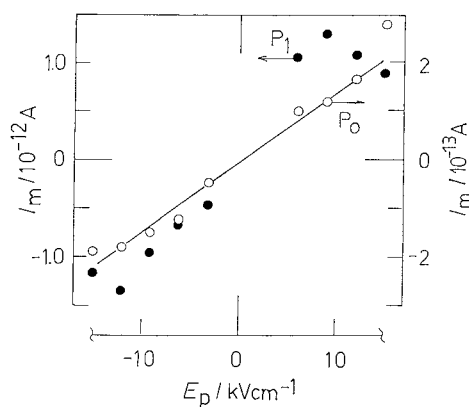
as for the negative E_p, and equal to zero when E_p equals zero. This behaviour is characteristic of dipolar peaks ([10], p. 100). According to [6], the α peak of the PB phase appears even with no poling at all. However, it happens with the freshly prepared sample only due to the charge incorporated during the preparation. As regards P_1, I_ms are not linear against E_p and less reproducible, which is typical for the space-charge peaks; namely they are influenced by the kind and concentration of the charge carriers.

3.2. Partial polarization measurements

The measurements with partial polarization gave much more reliable results. Fig. 4(a) contains the elementary peaks for OR in the temperature range of P_0 which had been confirmed as the α relaxation. P_0 is divided into five elementary peaks. Fig. 4(b and c) show comparison between NO and OR. For practical reasons, the partial peaks are presented only by their main parameters, i.e. temperature of the peak maximum T_m and I_m. No difference between the two systems was observed except for the negligible variation in the activation energy distribution.

The application of the partial technique was very important for the space-charge phenomena. In Figs. 5–7 one can see the main parameters of the partial peaks for the PS, NO and OR samples in the 214–260 K range. Instead of only one P_1 with some small satellite peaks, obtained by the integral technique, the space-charge relaxation appears to be much
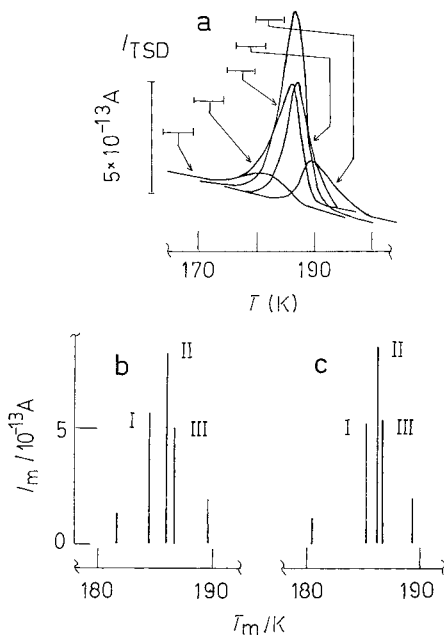
Fig. 4. Elementary peaks obtained by partial polarization across the α relaxation. (a) Fully shaped peaks, obtained with OR sample; (b) main parameters of peaks related to NO sample; and (c) main parameters related to OR sample. Horizontal lines show the temperature of the E_p application. $E_p=15$ kV cm^{-1}. (I), (II) and (III) the parameters of peaks used for the approximation of energy distribution.
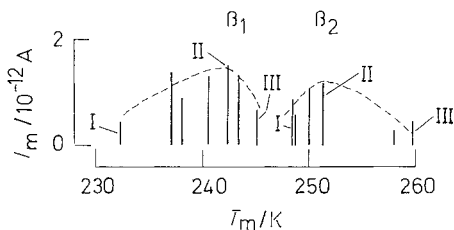

Fig. 5. Parameters of elementary peaks for PS in the range of space-charge relaxation. $E_p=12$ kV cm^{-1}; and (– – –) represents the course of the peak maxima. The process is splitting into two parts β_1 and β_2 relaxations.

more complex. Obviously, filling up the traps with charge during the poling in the integral procedure was
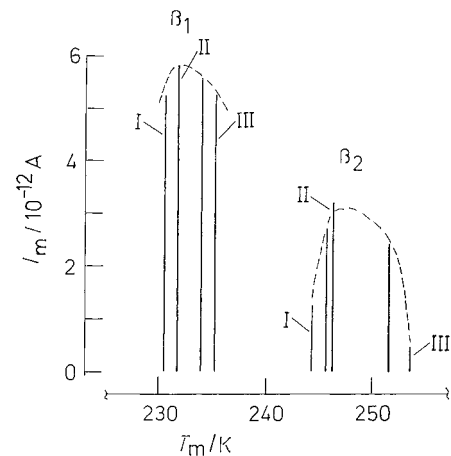

Fig. 6. Parameters of elementary peaks for NO in the range of space-charge relaxation.
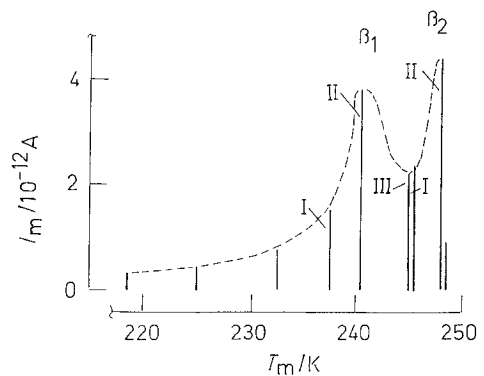

Fig. 7. Parameters of elementary peaks for OR in the range of space-charge relaxation.

not sufficient to exhibit the complete space-charge events. If we analyze the relation between T_p and T_m in the partial runs for the space-charge relaxation in OR (as an example, Table 1), T_m is always at a temperature lower than the applied T_p, except for some low temperature runs. This is another evidence that the peaks in question are caused by the space charge. On the contrary, in the cases of dipolar peaks, T_ms appear

Table 1
Main parameters of the partial TSDC peaks caused by the space-charge relaxation in OR sample.

T_p/K	301	293	283	271.5	261	250.5	246	241	231	225.5	220
T_m/K	248.5	245.5	248	245	240.5	240.5	232.5	237.5	237.5	225	218.5
$I_m/(10^{-12}$ A)	0.9	2.36	4.4	2.2	1.64	3.83	0.76	1.53	0.48	0.44	0.29

at higher temperatures than T_ps [25] (see Fig. 4). Fig. 5 contains I_m vs. T_m for the PS sample. Considering that the T_g for PS appears at much higher temperature, this relaxation in the glassy state of PS could be attributed to some local motions labelled as β relaxation. One could propose the motions of styrene phenyl rings, which interfere with the charge trapped into the PS, thus causing the charge release like the 'wet-dog effect' [26]. As the reproducibility of the space-charge peaks is moderate, the elementary peaks of the β mode are considered by drawing an approximate course of the peaks maxima (dashed lines in Fig. 5). One might say that the β relaxation appears in at least two steps, denoted as β_1 and β_2. It might indicate the presence of two locally different surroundings around the phenyl rings. It is known that dynamics of polymer chains is inhomogeneous along the chain [27]. One could assume the existence of at least two quasi-phases.

Figs. 6 and 7 relate to different copolymer samples. In all the cases, β relaxation appeared to be split into two parts. The released charge increased significantly, and the maxima are shifted towards lower temperatures. Obviously, the presence of interface plays an important role. The copolymer with the oriented structure shows the decrease in the temperature distance between β_1 and β_2 due to the increase of global homogeneity. The dielectric phenomena are an indicator of the events proceeding in the polymer structure.

3.3. Distribution of activation energy

For further characterization of the observed relaxations, the energy distribution $N(E_a)$ was approximated as follows. N is the relative number of electric dipoles which take part in the relaxation. It can be approximated for any of the partial peaks by the equation [28]:

$$N = I_m \times T_m \qquad (1)$$

The corresponding E_a was obtained by the initial-rise method. In order to approximate the energy distribution, three extreme partial peaks for one relaxation were chosen [25]. Peak (I) obtained with the relatively low T_m, when I_m was still high enough to apply the initial-rise method for determination of E_a (I). Peak (II) was the maximum amplitude peak for determination of E_a (II). Peak (III) was a high-energy

Table 2
The parameters of the extreme partial peaks and activation energy distribution $N(E_a)$ for α, β_1 and β_2 in different samples

	(I)	(II)	(III)	ω/eV
	T_m/K $\ln N$ E_a/(eV)	T_m/K $\ln N$ E_a/(eV)	T_m/K $\ln N$ E_a/(eV)	
PS				
α	—	—	—	—
β_1	232.3 8.49 2.18	242.8 9.74 2.33	245 9.00 2.44	0.26
β_2	248.7 8.85 2.44	251.3 9.58 2.55	259.7 8.65 2.82	0.42
NO				
α	184.5 8.55 0.84	186.0 8.95 1.26	186.7 8.44 1.70	1.71
β_1	230.5 11.01 3.21	231.7 11.12 3.74	235.3 11.04 5.50	[a]
β_2	244.3 9.64 3.08	246.3 10.58 4.74	253.5 8.67 7.04	3.15
OR				
α	185.3 8.46 0.93	186.3 8.98 1.36	186.7 8.51 1.83	1.66
β_1	237.5 9.81 0.96	240.5 10.74 1.64	245 10.20 3.46	4.43
β_2	245 10.20 3.46	248 10.91 5.00	248.5 9.44 2.54	2.38[b]

[a] Unreal value.
[b] Partial value.

peak, obtained with the highest T_m which was still suitable for determination of E_a (III). The chosen partial peaks (I), (II) and (III) are denoted in Figs. 4–7 and the corresponding I, II and III values for T_m, E_a and N are listed in Table 2

Fig. 8 contains the $N(E)$ approximations for the α process in samples NO and OR. By using logarithmic values for N, the exponential shape of the distribution can be transformed into a linear one [28]. This enables to draw the distribution triangles with the help of the related points I, II and III. All the values of $\ln N$ were
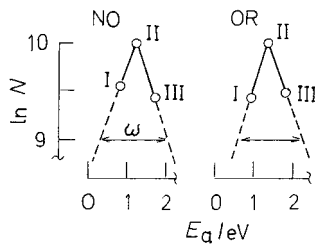
Fig. 8. Activation-energy distribution in the glass transitions of PB phase in the PSPB systems: N, approximate number of dipoles; ω, distribution width at 90% of maximum value; (I), (II) and (III) extreme values according to Table 2. $E_p=15$ kV cm^{-1}.

normalized to ln (II)=10. The distributions were characterized by widths ω at heights equal to 90% of the maximum value. The comparison between ω for NO and OR shows that the difference is as small as 0.05 eV and can be neglected.

The analogous characterization of β_1 and β_2 relaxations of all the examined samples are shown in Fig. 9. Determination of ω for β_1, sample NO, is not reliable because the peaks I, II and III are too close. In the case of β_2 relaxation for sample OR, w is only partial because peak III is too low for a correct determination of E_a. In spite of these exceptions, one can see that ωs
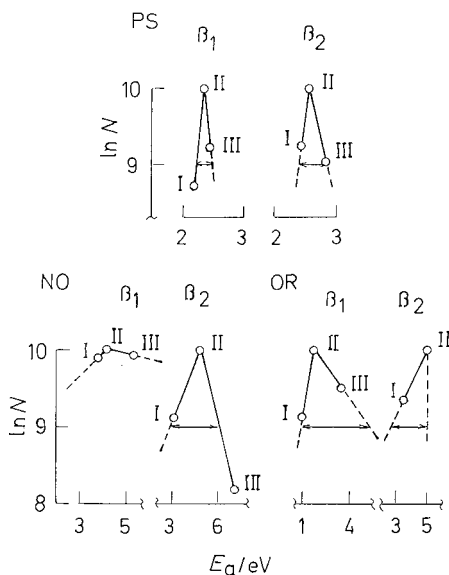

Fig. 9. Activation-energy distribution of the space-charge relaxation in different samples. $E_p=12$ kV cm^{-1}.

for copolymers significantly increase, when compared to ω in pure PS.

The width in distribution of the activation energy is an indicator of the relaxation dynamics. The systems with the hindered motions show the decrease in variety of E_a [29,30]. An increase in ω shows that the β_1 and β_2 motions in the PS phase are highly influenced and become more intense in the presence of liquid PB phase at the interfaces.

4. Conclusions

The integral TSDC measurements in the 160–303 K range for the copolymer samples with the oriented and the non-oriented lamellar structure result in two current peaks. The same measurements with the pure PS give only one higher temperature peak. The analysis of the electric origin of the peaks shows that the low-temperature peak at 187 K is a dipolar one, caused by glass transition in the PB phase, whereas the higher temperature peak is due to the space charge relaxation probably caused by the local motions of the phenyl rings in the PS phase, i.e. β relaxation.

The partial measurements with the 'thermal window' of 5 K shows that the β relaxation is distributed in the 220–260 K range and split into two parts, β_1 and β_2, probably due to the existence of two quasi-phases in PS. The current maxima in the β relaxations of copolymers significantly increase and shift towards the lower temperatures because of the PS–PB interfaces. The temperature distance between β_1 and β_2 in the oriented structure in relation to the non-oriented one decreases due to the increase in the global homogeneity.

The characterization of the α process by the approximate distribution $N(E_a)$ indicates that the orientation of the lamellae in the PSPB does not influence the distribution width ω. The same characterization of β indicates that ω in copolymers greatly increases. It is caused by the released motions and by the increase in variety of E_a at the PS–PB interfaces.

References

[1] G.H. Fredrickson, F.S. Bates, Annu. Rev. Mater. Sci. 26 (1996) 501.

[2] A. Halperin, M. Tirrell, T.P. Lodge, Adv. Polym. Sci. 100 (1992) 31.

[3] F.S. Bates, Science 251 (1991) 898.

[4] S. Valić, B. Deloche, Y. Gallot, A. Skoulios, Polymer 36 (1995) 3041.

[5] S. Valić, B. Deloche, Y. Gallot, A. Skoulios, J.P. Lingelser, in preparation.

[6] R. Capelletti, Proc. 6th International Symposium on Electrets, Oxford, 1988, pp. 510–14. Cited according to Phys. Abstracts 92 (1989) 95333.

[7] J. Pospišil, J. Honskus, R. Capelletti, Proc. 9th International Symposium on Electrets, Shangai, 1996, pp. 564–9.

[8] J. Vanderschueren, J. Gasiot, in: P. Braunlich (Ed.), Topics in Applied Physics, vol. 37, Springer, Berlin, 1979, pp. 159, 160.

[9] Y. Wada, M.M. Perlman, H. Kokado (Eds.), Charge Storage, Charge Transport and Electrostatics with their Applications, Elsevier, Amsterdam, 1979, Chap. 5.

[10] J. Van Turnhout, in: G.M. Sessler (Ed.), Topics in Applied Physics, Vol. 33, Springer, Berlin, 1980, p. 100.

[11] R. Chen, Y. Kirsh, Analysis of Thermally Stimulated Processes, 1st edn., Pergamon Press, Oxford, 1981, Chap. 3.

[12] G.A. Lushcheikin, Metody Issledovaniya Elekstricheskikh Svoistv Polimerov, Khimiya, Moscow, 1988, pp. 118–126.

[13] C. Lacabanne, D. Chatain, J. Guillet, G. Seytre, J.F. May, J. Polym. Sci. Polym. Phys. Edn. 13 (1975) 445.

[14] J. Vanderschueren, A. Linkens, B. Haas, E. Dellicour, J. Macromol. Sci., Phys. (B) 15 (1978) 449.

[15] K. Nishinari, D. Chatain, C. Lacabanne, J. Macromol. Sci. Phys. (B) 22 (1983) 529.

[16] A. Bernes, R.F. Bojer, D. Chatain, C. Lacabanne, J.P. Ibar, in: S.E. Keinath, R.L. Miller, J.K. Rieke (Eds.), Order in the Amorphous State of Polymers, Plenum, New York, 1987, pp. 305–326.

[17] J.P. Ibar, Polym. Eng. Sci. 31 (1991) 1467.

[18] J.P. Ibar, R.L. Gray, Proc. Am. Chem. Soc., Div. Polym. Mater.: Sci. Engin., Fall Meeting, Chicago, 1993, vol. 69, pp. 76–77.

[19] M. Topić, Z. Katović, Polymer 35 (1994) 5536.

[20] M. Topić, Thermochim. Acta 285 (1996) 231.

[21] H.S. Faruque, J. Mater. Sci. 30 (1995) 5210.

[22] M. Aldana, E. Laredo, A. Bello, N. Suarez, J. Polym. Sci. Polym. Phys. Edn. 32 (1994) 2197.

[23] A. Alegria, L. Goitiandia, J. Colmenero, Polymer 37 (1996) 2915.

[24] H. Ponevski, Bulgarian J. Phys. 22 (1995) 26.

[25] M. Topić, Z. Veksli, Polymer 34 (1993) 2118.

[26] M. Kryszewski, J. Ulanski, J.K. Jeszka, M. Zielinski, Polym. Bull. 8 (1982) 187.

[27] J.A. Kornfield, G.-C. Chung, S.D. Smith, Macromolecules 25 (1992) 4442.

[28] A.L. Komarski, S.A. Mansimov, A.L. Buchachenko, Polymer 27 (1986) 1014.

[29] M. Topić, A. Moguš-Milanković, Z. Katović, Polymer 32 (1991) 2892.

[30] M. Topić, Thermochim. Acta 294 (1997) 187.