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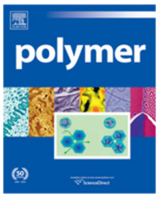

Dynamic mechanical study of molecular dynamics in ethylene–norbornene copolymers

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ABSTRACT

Dynamic mechanical studies of molecular dynamics have been performed for two ethylene–norbornene copolymers. The analysis of data indicates the existence of three relaxation processes: a primary (α) and two secondary (β and γ) ones. It was found that the secondary processes β and γ are connected with the local motions of ethylene and norbornene groups, respectively and that their rates follow the Arrhenius relation. Moreover, the β process was recognized as the Johari–Goldstein process acting as the precursor of the cooperative structural α-relaxation. Contrary to γ and β processes, the motional rate of α-one follows the Vogel–Fulcher–Tammann equation indicating the cooperative nature of motions involved in this process. An increase in norbornene content in copolymer slows down the molecular dynamics of both norbornene fragments and whole chains, and in consequence shifts these relaxation processes into higher temperatures. Using the Havriliak–Negami formalism the motional parameters for the processes mentioned above were estimated.

1. Introduction

Ethylene/norbornene copolymers (Scheme 1) are representatives of cyclic olefin copolymers (COC) belonging to amorphous thermoplastics. The excellent transparency, characteristic of single-phase thermoplastics, is the main advantage of these copolymers. The exceptional optical properties in the visible and near-UV-regions, combined with the shatter resistance better than that of glass, as well as half-glass density create demand for these materials, especially for applications such as precision optics and optical storage media [1]. An understanding of the relation between molecular dynamics and physical properties is crucial for engineering and use of these materials. Many studies concerning their synthesis, thermal behavior, morphology, microstructure and molecular dynamics were reported [2–13]. It was found that the glass transition temperature rose almost linearly with the increase in NB content in copolymer [6–8], although recently some exceptions were reported [9]. The synthesis of ethylene–norbornene copolymers using metallocene-based catalysts was first reported by Kaminsky [14]. Extensive investigations into the influence of different catalyst symmetries on the microstructure of these copolymers using ^{13}C NMR high resolution solution experiments were performed [8], [15]. Bergström et al. [16] in the 2D NMR study of microstructure of the alternating copolymers revealed that copolymers with a small amount of norbornene contained isolated NB units, while blocks of norbornene units of varying lengths appeared in materials with a norbornene content of more than 50% mol. Block sequences of norbornene units, mainly dyads, were observed when NB content was 45% mol, whereas triads appeared in copolymers having a higher norbornene content (66% mol).

The first dynamic mechanical study of ethylene/norbornene copolymers undertaken by Wilson et al. [11] indicated the existence of the two relaxations termed β and γ. The γ relaxation was considered to represent the onset of motions such as kinks, crankshafts, or other motions of the methylene units, while β relaxation was claimed to be originating in the motion of norbornene multiplets. Scrivani et al. [12] evidenced the existence of α and γ relaxations. The γ relaxation was attributed to the motions of methylene units sequence, that is, kink formation, inversion, and migration, whereas the α relaxation was attributed to glass transition motions. All three relaxations were observed by Ekizoglou et al. [13]. It was also found that the viscoelastic and rheological properties of COC's are influenced by molecular weight and depend strongly on the type of polymer chain conformation.

All three relaxation processes mentioned above were evidenced in our recent paper [17] reporting the result of NMR, dielectric and mechanical studies of the copolymer containing 35% of norbornene. It was found that the temperature dependences of motional rates associated with both the α process and the γ process follow the Vogel–Fulcher–Tammann (VFT) equation indicating a cooperative nature of these motions. However, such a character of motions

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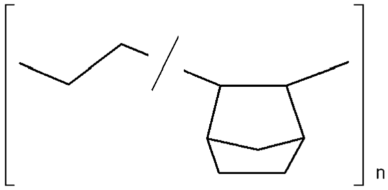

Scheme 1.

involved in the γ process was revealed only when the data obtained from all three methods, which cover the range of correlation times from 10^{-10} to 10^{-1} s, were considered together, whereas, the analysis of correlation times derived from each method alone seems to follow the Arrhenius law.

The aim of this work was to investigate molecular dynamics in two cycloolefin copolymers with a different content of norbornene. The oscillatory shear measurements were performed at three frequencies in a wide temperature range. The results were analyzed according to the Havriliak–Negami model, using the approach proposed by Szabo at al. [18]. This allowed us to characterize the motions responsible for all relaxation processes.

2. Experimental part

2.1. Materials

The materials used in this study are commercially available polymers of brand name Topas® (*Thermoplastic Olefin Polymer of Amorphous Structure*) produced by Ticona. The copolymers were obtained by means of metallocene-catalyzed copolymerisation. The two grades of ethylene–norbornene copolymers, of serial numbers 8007 and 6013, investigated in the frame of this work, were designated as EN35 and EN51. These acronyms include the information on a molar norbornene content, which according to Poulsen et al. [19] is of 35% and 51% mol for the polymers mentioned above, respectively. The values of weight average molar masses are very similar for both copolymers being 116 kg/mol for EN35 and 102 kg/mol for EN51, while their polydispersity indexes are 3.4 and 2.0, respectively. The samples were used as received.

2.2. Experimental techniques

Differential Scanning Calorimetry measurements were performed using a Netzsch 204 Phoenix apparatus. Heating and cooling cycles covered the temperature range between 173 K and about 50° above respective glass transition temperature for each copolymer. The temperature was changed at the rate of 20 K/min. Glass temperatures determined from the second heating cycle were equal to 354 K and 421 K for EN35 and EN51, respectively. A thermal annealing test for both ethylene–norbornene copolymers was carried out and contrary to the results obtained by Chu [20] the influence of annealing on the value of T_g was not observed.

Oscillatory shear measurements were carried out on films prepared by hot-pressing using SPECAC heated platens. The polymer pellets were heated to about 50 K above glass transition, kept 3 min to reach a suitable plastic state and pressed using a 2-ton load for a further 3 min. The 0.5 mm thick films were then quenched in water-cooled plates. The samples were cut into bars of about 15 × 6 × 0.5 mm dimensions. The measurements were made in oscillatory mode by means of the rheometer ARES (Rheometric Scientific). The complex shear moduli were collected at three frequencies of 0.1, 1, and 10 Hz from 138 K up to 20° above respective glass transition temperatures, at a heating rate of 2 K/min. Prior to the temperature/frequency measurements, the dynamic strain sweep tests at a frequency of 0.1–10 Hz were performed in order to have the measurements in the linear response regime.

3. Results and discussion

The complex shear dynamic modulus G^* consists of its real (storage modulus, G') and imaginary (loss modulus, G'') components:

$$G^* = G' + iG'' \tag{1}$$

The ratio of the loss modulus to the storage modulus is known as the “loss factor”:

$$\tan\varphi = \frac{G''}{G'} \tag{2}$$

and describes the ratio of the dissipated and the reversibly exchanged work [21].

In dynamic mechanical measurements the occurrence of molecular motions manifests itself in a step-like and bell-shaped form in the G' and G'' temperature dependencies, respectively. For a simple motion (Debye-process) both effects occur when $\omega\tau = 1$, where $\omega = 2\pi\nu$ is the angular frequency of the applied oscillation, while τ denotes relaxation time describing the motion. The behavior of tan φ temperature dependence is similar to that of G'', but the observed maxima are more pronounced and shifted up to higher temperatures.

The temperature dependences of G' and G'' for both copolymers at 1 Hz, shown in Fig. 1, reflect three relaxation processes denoted as γ, β and α following an increase in temperature. The γ relaxation appears as maximum of G'' at the temperature around 134 K for both copolymers. The process is more distinct for the polymer with a lower norbornene content. The α relaxation is manifested by a distinct maximum of loss modulus G'' and an abrupt decrease in storage modulus G'. The temperatures at which these features are observed are 363 K and 429 K for EN35 and EN51 copolymers, respectively, and are in good agreement with the glass transition temperatures observed in DSC measurements. The β process appears as a weak shoulder on the low temperature side of the peak of G'' connected with α relaxation. This effect is less visible for the copolymer with a lower norbornene content.

An analysis of rheological data was carried out using the approach proposed by Szabo [18]. A similar procedure has been used to analyze the dynamic mechanical relaxation of copolyester based layered silicate nanocomposites [22].

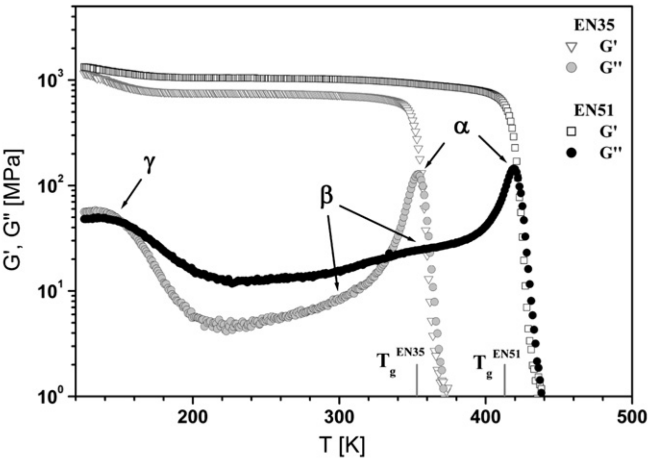

Fig. 1. Isochronal temperature dependences of storage modulus (G') and loss modulus (G'') at 1 Hz for EN35 and EN51. The vertical solid lines mark the glass transition temperatures for both copolymers.

The description of the experimental results comprises an analysis of the shape of the G'' versus G' dependence (Cole–Cole plot) and the determination of the appropriate temperature dependences of relaxation time for particular processes. It has to be noticed that for such a representation the experimental points form a unique curve whose shape is independent of temperature and frequency. This allows deriving the parameters δ, ε, G_o and G_∞ without the knowledge of the temperature dependence of relaxation times.

There are many model functions used to describe experimental data [23]. The most versatile one is the model function proposed by Havriliak and Negami [24], which for the complex shear modulus is defined as:

$$G^*(\omega,\tau,\delta,\varepsilon) = G_\infty - \frac{G_\infty - G_o}{\left(1+(i\omega\tau)^{\delta}\right)^{\varepsilon}} \tag{3}$$

where G_∞ and G_o denote "unrelaxed" and "relaxed" limiting values of the storage shear modulus, which can be estimated at its low and high temperature limit, respectively. The δ and ε, ranging between 0 and 1 are the shape function parameters related to the width and asymmetry of the loss peak, respectively. For δ and ε equal to 1 the equation (3) corresponds to the simple Debye-process, while their values lower than 1 indicate the existence of relaxation times distribution and/or the presence of correlated motions.

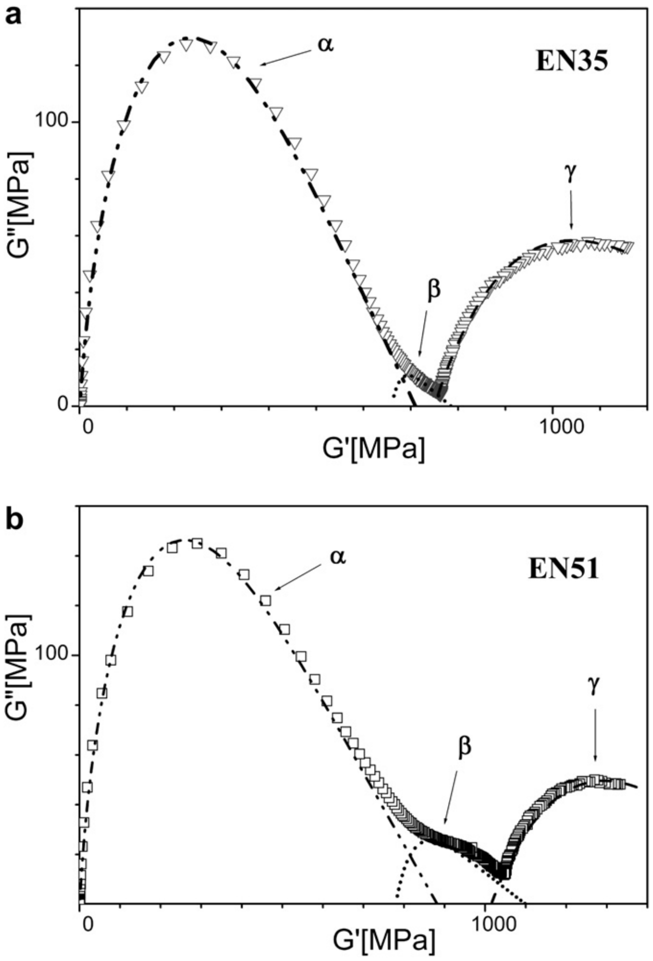

Fig. 2. Cole–Cole plot at 1 Hz for a) EN35, b) EN51. The dash double dotted, dotted and dashed lines show the contributions due to existence of α, β and γ processes, respectively. The Havriliak–Negami parameters obtained from the fitting are listed in Tables 1 and 2.

The Cole–Cole plots for EN35 and EN51 at 1 Hz are shown in Fig. 2. In the regions of high and low G' values, two distinct asymmetric semicircular arcs are observed, corresponding to γ and α processes, respectively. The β process is much weaker and for EN51 it is visible in the G' mid-region, whereas for EN35 it is hidden by an intense α-process located nearby.

The derived parameters δ, ε, G_0, and G_∞, used to fit the experimental data for each relaxation mechanism, are presented in Table 1. The theoretical dependences of G'' versus G' (at 1 Hz) obtained with these parameters are shown in Fig. 2. The non-solid lines represent the best fits to the experimental data for each of the three particular relaxations. Due to the low intensity of β process its parameters were estimated after the preliminary fitting of the more pronounced γ and α processes. The values of G' and G'' used through the fitting procedure were found from the equation (3) as real and imaginary parts of G^*, respectively. Finally, the derived values of δ, ε, G_0 and G_∞ were used in the fitting procedure of the temperature dependences of tan φ.

It was found that the relaxations connected with γ- and β-process followed well the Arrhenius equation

$$\tau = \tau_o \exp\left(\frac{E_a}{RT}\right), \tag{4}$$

where R is the gas constant, E_a denotes the activation energy and τ_o is a pre-exponential factor.

For the α-process, associated with correlated motions, the mean relaxation time above the so-called Vogel temperature T_0 was well described by the Vogel–Fulcher–Tammann (VFT) equation [25]:

$$\tau = \tau_o \exp\left(\frac{D\cdot T_0}{T-T_0}\right), \tag{5}$$

where τ_o is a pre-exponential factor, T_0 is the temperature at which the relaxation time diverges to infinity (usually its value is 40–60 K below T_g), while the fragility parameter D describes a departure of τ from the exponential temperature dependence [26] and can be interpreted in terms of intermolecular cooperativity [27].

Temperature dependences of tan φ were fitted for all three frequencies simultaneously. The best fits of the data at 1 Hz are shown in Fig. 3, while the derived parameters are listed in Tables 1 and 2.

In the glassy state the large-scale conformational changes are inhibited and the applied mechanical force induces local transitions only [21]. The observed low temperature process γ occurs at the same temperature/frequency range as the one observed for the polyethylene [28], which was interpreted as very local motion of ethylene units corresponding to the trans-gauche isomerization [29,30]. As it is seen from Fig. 1 and from Table 1 the strength of γ-relaxation for copolymer EN35 is higher than that for copolymer EN51, which corroborates the assumption that this relaxation is connected with the motion in which ethylene groups are involved. A similar effect was observed in mechanical studies into other ethylene–norbornene copolymers [12]. The activation energy for this motion is equal to 48 and 46 kJ for EN35 and EN51, respectively, showing a similar character of motions in both polymers. The effect

Table 1
Havriliak–Negami parameters determined from the rheological data analysis for secondary processes in EN35 and EN51.

		δ	ε	ΔG (Pa)	E_a [kJ/mol]	τ_o [s]
EN35	process γ	0.31	0.25	9×10^8	48	3×10^{-18}
	process β	0.5	0.18	1.3×10^8	100	4×10^{-15}
EN51	process γ	0.26	0.38	7.5×10^8	46	1×10^{-17}
	process β	0.5	0.16	3.2×10^8	100	5×10^{-13}

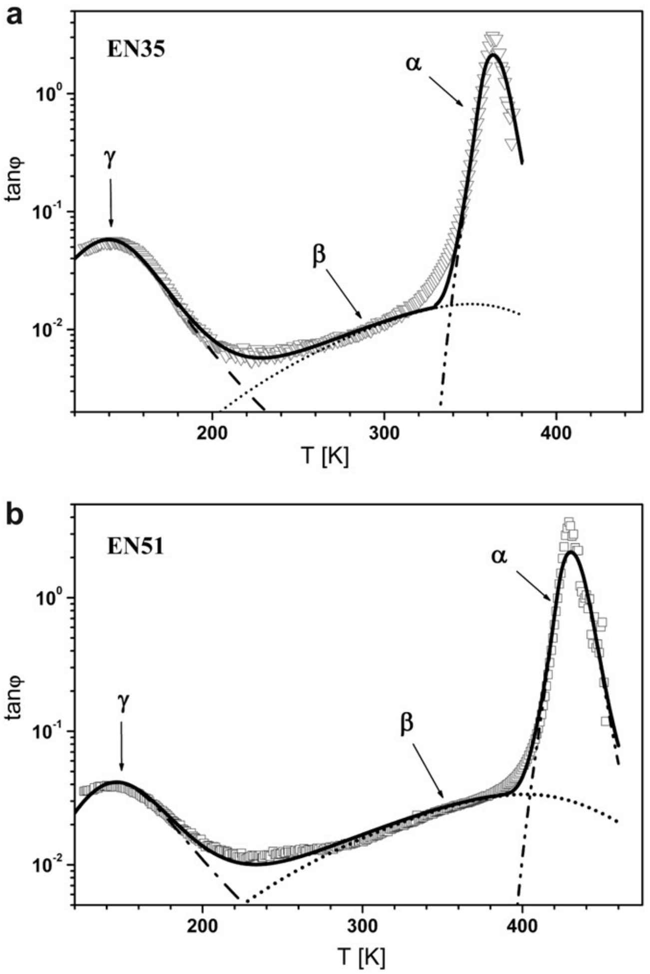

Fig. 3. Isochronal temperature dependences of loss tangent at 1 Hz in a) EN35 and b) EN51. The lines show the contributions due to existence of α (— · · —), β (• • • • •) and γ (— • —) processes discussed in text. The best fit Havriliak–Negami parameters are collected in Tables 1 and 2.

of the increase in norbornene incorporation results in the slowing down of the rate of exchange motion between conformational states. The estimated relaxation times at room temperature, as found using the parameters mentioned above, fall into the nanoseconds range, which is consistent with PALS measurements made by Poulsen at al [19]. The derived values of activation energy are slightly lower than the apparent activation energies obtained from other DMTA studies [12,13,17]. It has to be noticed that these literature values were estimated on the basis of temperature position of G'' or tan δ maxima at few frequencies only, whereas our values were derived from the fitting of experimental data in the broad temperature range for all three frequencies studied.

The most distinct relaxation observed in the studied copolymer is the α-relaxation, associated with the glass transition process. It is well established that the motions, which are responsible for this transition have a cooperative character and their rates are well described by VFT relation. The VFT parameters (Table 2), derived from the fitting of loss tangent temperature dependences, are very similar for both copolymers, with the exception of the Vogel temperature (T_o) which was found to be 62 K higher for norbornene-rich copolymer. This indicates that a higher content of norbornene in copolymer makes the chains much stiffer and moves the segmental motions to higher temperatures. The observed increase in T_o agrees very well with the increase in the glass transition temperature obtained in DSC measurements. The fragility parameters D derived from the fitting of α-process were estimated to be 6.0 for copolymer EN35 and 4.6 for EN51, locating these materials in the middle of the range of the fragile glass formers. They are slightly higher compared to parameters found by Blochowiak [31] which (expressed as D values) are 4.5 and 3.5 for the above mentioned systems, respectively. The decrease in the $\delta\varepsilon$ product for α-process from 0.22 for copolymer EN35 to 0.18 for EN51 may imply an increase in the structure disorder for the copolymer with higher contents of stiff norbornene units. This is in accordance with findings [27] that for a wide range of glass formers an increase in non-exponentiallity of the structural response, resulting from structural inhomogeneity, is correlated with the increase in fragility.

Table 2
Havriliak–Negami parameters determined from the rheological data analysis for α-process in EN35 and EN51 copolymers.

	δ	ε	D	τ_o [s]	T_o [K]	ΔG (Pa)
EN35	0.76	0.29	6	4.5×10^{-14}	300	7.3×10^8
EN51	0.77	0.24	4.6	7×10^{-14}	364	8.3×10^8

The β-relaxation observed in the studied copolymers is less pronounced as compared to α- and γ-relaxation. Unlike the γ process the β-one is more intense for the copolymer with higher norbornene contents, which suggests that norbornene units are involved in this relaxation. The activation energy for the motion responsible for that process is found to be equal to 100 kJ/mol in both copolymers, which settles it in the upper limits of the energy barrier for rotational motion derived from the atomistic simulation of the polynorbornenes (from 35 to 110 kJ/mol) [32]. Although the derived activation energy is rather high, it seems to be reasonable if one takes into account the size of moving elements, that is, high volume of norbornene group. Similar values were also observed for other polymers having a more rigid backbone or sterically hindered pendant groups [33–36]. Thus, undoubtedly, this relaxation is associated with the motion of fragments of copolymer chains containing norbornene units. An observed slowing down of this type of motions for copolymer containing a larger amount of norbornene (Table 2) may result from a growth in intermolecular (interchain) interactions. It was indicated that a high value of activation energy of such processes as compared to low molecular weight substances [37,38] may need some cooperativity of motions of bulky groups [33–35]. Moreover it was found that in the vicinity of glass transition the rates of the motions involved in α and

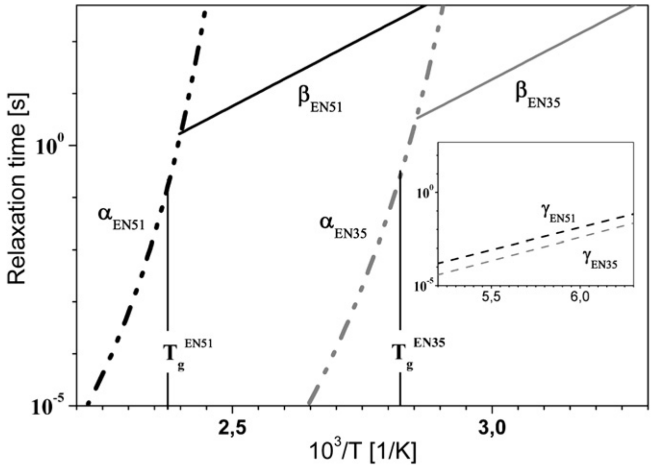

Fig. 4. Temperature dependences of relaxation times in EN35 and EN51. The lines represent the curve fits to the experimental data. The vertical arrows mark the glass transition temperatures for both copolymers.

β processes are very close to each other (Fig. 4). This suggests that the motion responsible for β-relaxation acts as the precursor of the motions associated with the α-relaxation. Both intermolecular origin of β process and close proximity of motional rates of α and β processes near T_g indicate that the observed secondary β-relaxation can be regarded as Johari–Goldstein relaxation [39,40]. Similar conclusions have been drawn for other polymers containing bulky groups [38]. Pressure dependent studies would provide evidence for this suggestion [41].

4. Conclusions

Oscillatory shear measurements have been used to determine relaxation processes and to examine the influence of copolymer composition on the molecular dynamics of ethylene–norbornene copolymers. This study confirms the existence of the three relaxation processes γ, β, and α connected with the motions of ethylene and norbornene fragments of chains as well as the chains as whole, respectively. The parameters of motions have been established based on the analysis of Cole–Cole diagrams and isochronal temperature dependences of the mechanical loss tangent. It has been found that an increase in the number of norbornene groups incorporated into the polymer chain does not change the character of the motions, but slows them down. It is assumed that the β process acts as the precursor of the global motion and can be treated as the Johari–Goldstein one.

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References

[1] Lamonte RR, McNally D. Plast Eng 2000;56:51–5.
[2] Arndt-Rosenau M, Beulich I. Macromolecules 1999;32(22):7335–43.
[3] Tritto I, Marestin C, Boggioni L, Zetta L, Provasoli A, Ferro DR. Macromolecules 2000;33(24):8931–44.
[4] Tritto I, Marestin C, Boggioni L, Sacchi MC, Brintzinger H-H, Ferro DR. Macromolecules 2001;34(17):5770–7.
[5] Boggioni L, Bertini F, Zannoni G, Tritto I, Carbone P, Ragazzi M, et al. Macromolecules 2003;36(3):882–90.
[6] Benedikt GM, Elce E, Goodall BL, Kalamarides HA, McIntosh LH, Rhodes LF, et al. Macromolecules 2002;35(24):8978–88.
[7] Thorshaug K, Mendichi R, Boggioni L, Tritto I, Trinkle S, Friedrich C, et al. Macromolecules 2002;35(8):2903–11.
[8] Rische T, Waddon AJ, Dickinson LC, MacKnight WJ. Macromolecules 1998;31(6):1871.
[9] Forsyth J, Pereña JM, Benavente R, Pérez E, Tritto I, Boggioni L, et al. Macromol Chem Phys 2001;202(5):614–20.
[10] Maiti P, Okamoto M. J Appl Polym Sci 2004;91(6):3421–7.
[11] Wilson TP, Von Dohlen WC, Koleske JV. J Polym Sci Polym Phys 1974;12(8):1607–18.
[12] Scrivani T, Benavente R, Pérez E, Pereña JM. Macromol Chem Phys 2001;202(12):2547–53.
[13] Ekizoglou N, Thorshaug K, Cerrada ML, Benavente R, Pérez E, Pereña JM. J Appl Polym Sci 2003;89(12):3358–63.
[14] Kaminsky W, Bark A, Arndt M. Macromol Chem Macromol Symp 1991;47:83–93.
[15] Ruchatz D, Fink G. Macromolecules 1998;31(15):4674.
[16] Bergström CH, Sperlich BR, Ruotoistenmäki J, Seppälä JV. J Polym Sci A Polym Chem 1998;36(10):1633.
[17] Makrocka-Rydzyk M, Orozbaev B, Nowaczyk G, Głowinkowski S, Jurga S. Acta Phys Pol A 2005;108(2):385–93.
[18] Szabo JP, Keough IA. Thermochim Acta 2002;392–393:1–12.
[19] Poulsen L, Zebger I, Klinger M, Eldrup M, Sommer-Larsen P, Ogilby PR. Macromolecules 2003;36(19):7189–98.
[20] Chu PP-J, Cheng M-H, Huang W-J, Chang F-C. Macromolecules 2000;33(25):9360–6.
[21] Strobl G. The physics of polymers. Berlin Heidelberg: Springer–Verlag; 1996.
[22] Kalgaonkar RA, Nandi S, Tambe SS, Jog JP. J Polym Sci B Polym Phys 2004;42(14):2657–66.
[23] Beckmann PA. Phys Rep 1988;171(3):85–128.
[24] Havriliak S, Negami S. Polymer 1967;8:161–210.
[25] (a) Vogel H. Phys Z 1921;22:645;
(b) Fulcher GS. J Am Chem Soc 1925;8:339;
(c) Tammann G, Hesse G. Annorg Allg Chem 1926;156:245.
[26] Angell CA. J Non-Cryst Solids 1991;131–133(1):13–31.
[27] Böhmer R, Ngai KL, Angell CA, Plazek DJ. J Chem Phys 1993;99(5):4201–9.
[28] Stehling FC, Mandelkern L. Macromolecules 1970;3(2):242–52.
[29] Hentschel D, Sillescu H, Spiess WH. Macromolecules 1981;14(5):1605–7.
[30] Głowinkowski S, Makrocka-Rydzyk M, Wanke S, Jurga S. Europ Polym J 2002;38(5):961–9.
[31] Blochowiak M, Pakula T, Butt HJ, Bruch M, Floudas G. J Chem Phys 2006;124(1):134903–8.
[32] Haselwander ThFA, Heitz W, Krügel StA, Wendorff JH. Macromolecules 1997;30(18):5345–51.
[33] Hardy L, Stevenson I, Boiteux G, Seytre G, Schönhals A. Polymer 2001;42(13):5679–87.
[34] Hardy L, Fritz A, Stevenson I, Boiteux G, Seytre G, Schönhals A. J Non-Cryst Solids 2002;305(1–3):174.
[35] Hardy L, Stevenson I, Fritz A, Boiteux G, Seytre G, Schonhals A. Polymer 2003;44(15):4311.
[36] Wübbenhorst M, de Rooij AL, van Turnhout J, Tacx J, Mathot V. Colloid Polym Sci 2001;279(6):525–31.
[37] Nogales A, Denchev Z, Šics I, Ezquerra TA. Macromolecules 2000;33(25):9367–75.
[38] Ngai KL, Capaccioli S. Phys Rev E 2004;69(3):0315011–5.
[39] Johari GP, Goldstein M. J Chem Phys 1970;53(6):2372–88.
[40] Ngai KL, Paluch M. J Chem Phys 2004;120(2):857–73.
[41] Ngai KL. Phys Rev B 2005;71(2):2142011–9.