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Molecular Dynamics in Cyclic Olefin Copolymer

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Nuclear magnetic resonance, broadband dielectric spectroscopy and dynamic-mechanical thermal analysis were employed to study molecular dynamics of ethylene-norbornene copolymer. The analysis of experimental data indicates existence of three motional processes denoted as α , β , and γ in order of decreasing temperature. The α relaxation is related to the dynamic glass transition, while the β relaxation, observed only for the untreated sample, is assigned to short range segmental motions involving norbornene units. The γ relaxation is due to very local motions of ethylene units e.g. trans-gauche isomerization, similar to those responsible for γ relaxation in polyethylene. The rate of motion accountable for γ process, follows the Vogel–Fulcher–Tammann equation, similarly to α transition, indicating cooperative nature of the motion.

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1. Introduction

Knowledge of the relation between structure and molecular dynamics in polymers is very important to understand their physical properties. One of the ways to obtain polymer with desired properties is copolymerization of composites having different dynamical properties. The cyclic olefin copolymers (COC) are polymers, which combine a flexibility of olefins with strength and rigidity of norbornene. Due to their excellent transparency, low density, and thermal and chemical resistance they are useful materials in optic industry [1, 2].

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In this paper we report NMR, dielectric, and rheological studies of metallocene catalyzed ethylene-norbornene copolymer with repeat unit as shown in Fig. 1. The aim of the work is to investigate molecular dynamics of linear copolymer containing ethylene and norbornene units in wide frequency and temperature ranges.

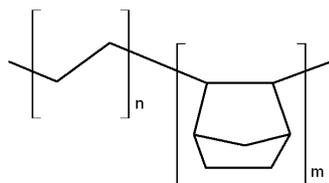


Fig. 1. Chemical structure of ethylene-norbornene copolymer.

The relatively high glass transition temperature of ethylene-norbornene copolymers (up to 180°C) can be altered linearly with increasing the norbornene (NB) comonomer content [3, 4]. The structure of these copolymers has been extensively studied using ^{13}C high resolution in solution [5–7]. It was found that in copolymer with low NB content the close vicinity of two or more NB groups is rather rare.

2. Experimental

The material used in this study is commercially available polymer of brand name Topas[®] (thermoplastic olefin polymer of amorphous structure) produced by Ticona (Germany). The samples were used in the form of pellets as received without any purification. According to Poulsen et al. [8] the studied sample Topas 8007 has 35 mol percentage of randomly distributed NB.

Differential scanning calorimetry measurements were done using Netzsch 204 Phoenix apparatus. Two cycles were performed, each consisting of heating and cooling of the sample with the rate 20 K/min. Glass temperature specified from the second heating cycle was of 353 K.

^1H NMR experiments were made for samples sealed under vacuum in glass tubes after air evacuation for few hours. Broad-line measurements were carried out with a home-made marginal oscillator spectrometer operating at 28 MHz. Second moment values were calculated by numerical integration of spectra and corrected for finite modulation amplitude. Spin-lattice relaxation times T_1 and $T_{1\rho}$ were measured at 200 MHz (BRUKER CXP spectrometer) and additional T_1 measurements were performed at 30 MHz (home-made spectrometer). T_1 values were determined with saturation recovery technique [9], while $T_{1\rho}$ by spin-locking the magnetization in the rotating field (of 68 kHz) [10]. Temperature of the sample was controlled using a conventional gas flow system and monitored with accuracy 1 K.

Dielectric and mechanical spectroscopies measurements were carried out on films obtained using a SPECAC hot-press system. The material was heated up 50°C above the glass transition, held 3 min to reach a suitable plastic state and pressed using 2 tons load during the next 3 min. Films were quenched in water cooled plates. Measurements of complex permittivity and loss tangent of copolymer that covered the frequency range 10^{-2} to 3×10^6 Hz and temperature interval 138 to 398 K (5 K step) were performed with the dielectric spectrometer BDS-80 (Novocontrol) using BDC-S (Alpha Analyzer) probe head. The gold-plated sample of 150 μm thickness was kept between electrodes of 20 mm diameter.

The study of viscoelastic properties was made in oscillatory mode by means of the rheometer ARES (Rheometric Scientific). The complex elasticity modulus and loss tangent of copolymer were determined for 10 frequencies ranged from 0.03 to 15 Hz in temperature range from 128 to 375 K.

3. Results and discussion

The temperature dependence of ^1H NMR line second moment M_2 is shown in Fig. 2. There are three regions where a decrease in the second moment is observed. The first one from 100 to 295 K with M_2 dropping from 0.23 to 0.167 mT^2 , the second from 330 to 350 K, where M_2 decreases to 0.148 mT^2 , and third region above 360 K where fast decrease to almost zero value appears. Such temperature behavior of the second moment indicates the existence of three different motional processes. The two first reductions of second moment similarly as in polyethylene [11] are connected with local motions, which involve (i) ethylene groups (e.g. trans-gauche isomerization) and (ii) short segments containing aliphatic fragments and norbornene units, respectively. The third one appearing just above glass transition temperature involves large scale rotational and translational motion (liquid-like motion).

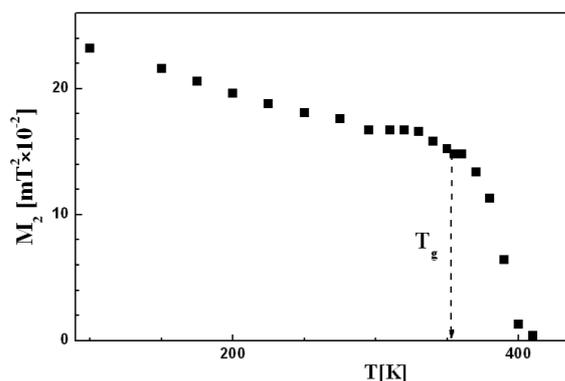


Fig. 2. Temperature dependence of the second moment of ^1H NMR line of ethylene-norbornene copolymer. Glass transition temperature is denoted by dashed line.

Molecular motions in studied copolymer are reflected in measurements of proton spin–lattice relaxation T_1 and $T_{1\rho}$ shown in Fig. 3. The observed minima for T_1 measured at 60 MHz (at 222 K) and $T_{1\rho}$ (at 192 K) indicate that reorientational motion takes place. The temperatures at which the minima appear are consistent with gradual decrease in the second moment observed at the lowest temperatures indicating that both features result from the same kind of motion. The qualitative analysis of the spin–lattice relaxation behavior was based on the assumption that temperature dependences of T_1 and $T_{1\rho}$, which are governed by dipolar interaction modulated by motional processes, can be approximated by [12]:

$$\frac{1}{T_1} = \frac{2}{3}\gamma^2\Delta M_2[J(\omega) + 4J(2\omega)], \quad (1)$$

$$\frac{1}{T_{1\rho}} = \frac{2}{3}\gamma^2\Delta M_2 \left[\frac{3}{2}J(2\omega_1) + \frac{5}{2}J(\omega) + J(2\omega) \right], \quad (2)$$

where ΔM_2 is defined as part of the second moment averaged by considered motion, and J 's denote the spectral densities of the correlation functions for the appropriate frequencies. The broad and asymmetrical shapes of T_1 and $T_{1\rho}$ minima, as well as their relatively large values reveal that the description of molecular motion with the use of a simple BPP model [13] is inadequate. The experimental data were fitted according to the Havriliak–Negami function [14], for which $J(\omega)$ is defined as follows [15]:

$$J_{\text{HN}}(\omega) = \frac{2}{\omega} \sin \left\{ \varepsilon \arctan \left[\frac{(\omega\tau)^\delta \sin(\delta\pi/2)}{1 + (\omega\tau)^\delta \cos(\delta\pi/2)} \right] \right\} \\ \times \left[1 + 2(\omega\tau)^\delta \cos \left(\frac{\delta\pi}{2} \right) + (\omega\tau)^{2\delta} \right]^{-\varepsilon/2}, \quad (3)$$

where the parameter δ is a measure of correlations of motions and the product of δ and ε describes distribution of correlation times, while τ is a correlation time, whose temperature dependence was approximated by the Arrhenius equation. The fitting of experimental data was performed for ΔM_2 giving the best agreement to T_1 data. The obtained fits, shown as solid lines in Fig. 3, were obtained for the activation energy of 27 kJ/mol. Distinct difference between theoretical and experimental value of $T_{1\rho}$ at minimum may be due to temperature dependence of parameter describing distribution of correlation times and/or the increase in number of ethylene groups involved in the motion when temperature rises up, which was observed in other polymers [11, 16–18].

Motional behavior of the studied copolymer observed in NMR is reflected in dielectric and mechanical studies. The temperature dependences of dielectric and mechanical loss tangent for different frequencies are shown in Fig. 4 and Fig. 5. Three relaxation processes labelled γ , β , and α in order of increasing temperature are evidenced, however in the case of mechanical data the β process is revealed

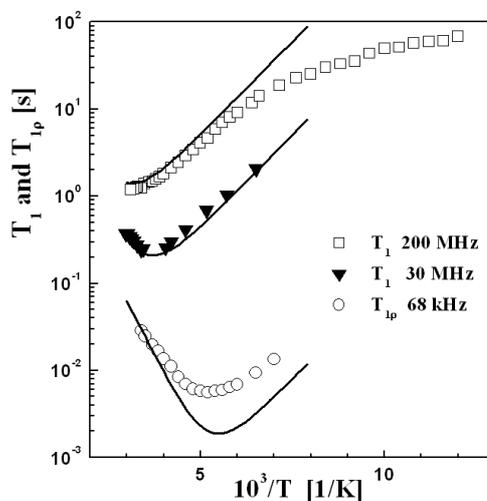


Fig. 3. Temperature dependences of the ^1H spin-lattice relaxation times T_1 and $T_{1\rho}$ of ethylene-norbornene copolymer. The solid lines represent fits according to the Havriliak-Negami function.

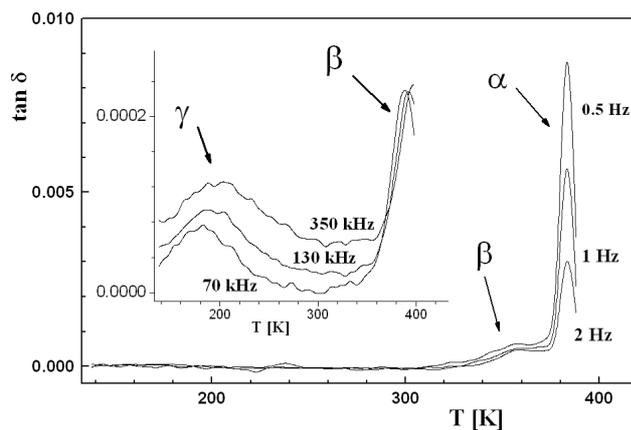


Fig. 4. Temperature dependence of dielectric loss tangent at selected frequencies (main plot — lower frequencies, inserted plot — higher frequencies) for ethylene-norbornene copolymer.

only as a very weak shoulder on the low temperature side of the α process. Taking into account the temperatures and frequencies at which the particular relaxation processes appear it can be stated that these relaxation processes originate from three types of motions, which were recognized in the second moment analysis, namely γ process reflecting the local motion of ethylene groups, β process resulting from short segmental motions, and α process associated with the glass transition motions.

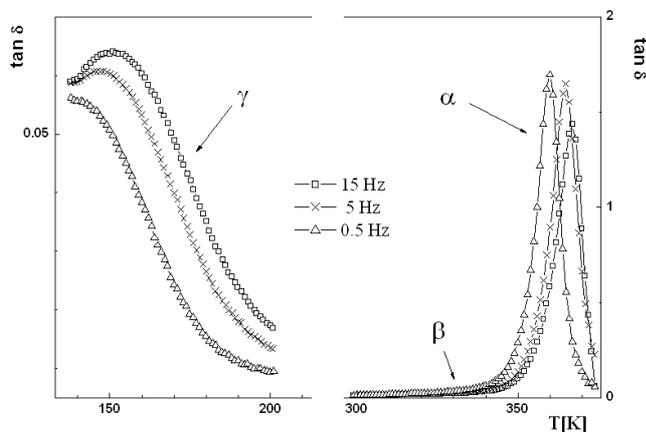


Fig. 5. Temperature dependence of mechanical loss tangent at selected frequencies for ethylene-norbornene copolymer.

The activation energies of considered motions obtained from analysis of frequency–temperature location of the loss maxima together with that obtained from fitting of NMR relaxation data are summarized in Table I.

TABLE I

The activation energies of considered motions. The parentheses involve the temperature ranges for which activation energies were derived.

	E_a [kJ/mol], α process	E_a [kJ/mol], γ process
NMR	–	27 (130 ÷ 330 K)
DS	380 (364 ÷ 393 K)	31 (146 ÷ 200 K)
MS	533 (355 ÷ 367 K)	64 (128 ÷ 143 K)

The obtained values are in good agreement with those derived by Poulsen et al. studies of oxygen diffusion [8] and by Scrivani et al. from dynamic-mechanical thermal analysis (DMTA) measurements [19].

The decrease in the apparent activation energy values for α and γ processes for higher frequency window suggests that the rate of motion for these processes can be described by the Vogel–Fulcher–Tammann (VFT) formula [20]:

$$\frac{1}{\tau} = \frac{1}{\tau_0} \exp\left(-\frac{DT_0}{T - T_0}\right), \quad (4)$$

where D is fragility parameter and T_0 is temperature corresponding to an infinite relaxation time.

The temperature dependence of motional frequencies derived from NMR, dielectric, and mechanical studies for α and γ process are shown in Fig. 6 and

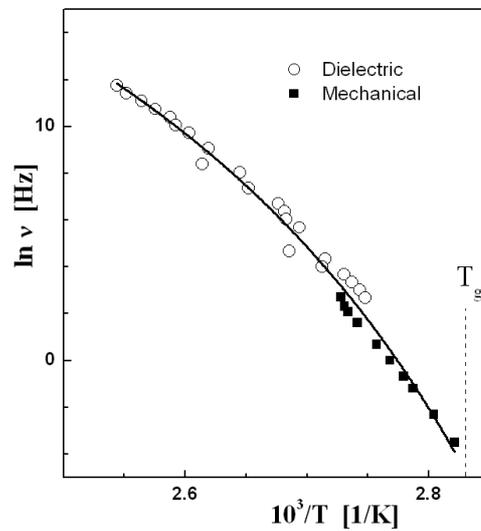


Fig. 6. Relaxation map for α process in ethylene-norbornene copolymer. The solid line represents the best fit according to VFT equation.

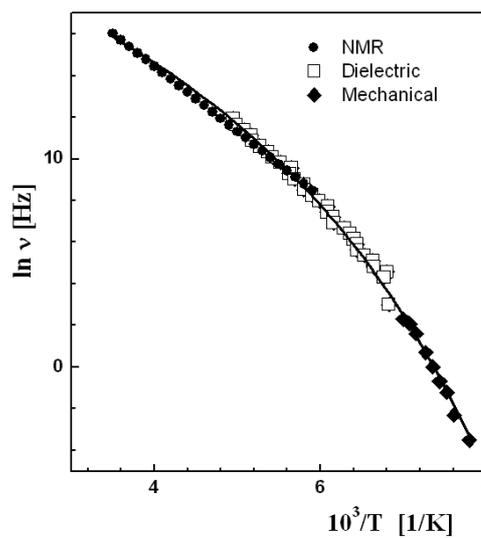


Fig. 7. Relaxation map for γ process in ethylene-norbornene copolymer. The solid line represents the best fit according to VFT equation.

Fig. 7, respectively, where the solid lines are fits to VFT equation for parameters presented in Table II.

Good agreement between experimental values and theoretical fits indicates that the motions responsible for α and γ processes are cooperative in nature. For α process the cooperative motion is well established phenomenon and can be imag-

TABLE II
Parameters of VFT fit for α
and γ processes.

	α process	γ process
D	6	15
T_0 [K]	310	80

ined as a move of selected segments with its environment. In the case of the γ process it seems that the local trans-gauche conformational transitions of methylene groups correlate with motion of next nearby unit, leading also to the non-Arrhenius relaxation. Such behavior was suggested for low temperature relaxation in polymers in molecular dynamics simulation studies [21, 22]. Comparison of fragility parameters for the two processes indicates that the low temperature one is less cooperative than that connected with glass transition.

At this stage of study we have not precisely analyzed the motional parameters of β process. We want only to mention that peak intensity depends on thermal treatment of sample which was also observed by Chu et al. [23].

4. Conclusions

NMR, dielectric, and mechanical spectroscopies were used to characterize in a broad frequency range the molecular dynamics of ethylene-norbornene copolymer. Three motional processes, denoted as α , β , and γ are detected. The γ and β processes are associated with local motion. The results show that γ relaxation has similar origin to that of polyethylene trans-gauche isomerization, while β process results from short range segmental motion in which norbornene units are involved. The α process is attributed to the large scale motions associated with the dynamic glass transition. Temperature dependences of frequencies of motion for α and γ relaxations are well described by the Vogel–Fulcher–Tammann equation indicating cooperative nature of the molecular motions.

Acknowledgments

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