NANOSTRUCTURE- DIAMAGNETIC SUSCEPTIBILITY CORRELATIONS IN REGULAR ALTERNATING TERPOLYMERS OF ETHENE AND PROPENE WITH CARBON MONOXIDE

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ABSTRACT

A series of regular alternating terpolymers of ethene, propene and carbon monoxide with different Et/CO content was characterized by wide- and small-angle X-ray scattering, differential scanning calorimetry and diamagnetic susceptibility measurements. All terpolymers proved to be amorphous at room temperature. The occurrence of multiple endothermic effects appearing at T_m , above the glass transition temperature T_g , extending over a fairly broad temperature range is discussed on the basis of a three-dimensional network of Et/CO nano-crystals spanning the continuous, non-crystalline Pr/CO matrix in the initial samples. Magnetic susceptibility data obtained in the temperature range studied confirm our previous findings: Accordingly, it is the onset of large-scale (segmental) mobility, rather than the density variations, the one responsible for the discontinuous changes of diamagnetic susceptibility observed, both, at T_g and T_m . The unusual large differences found between absolute χ -values for samples with different chain composition are interpreted in the light of the classical theory of random copolymerization, assuming that ter-polymer chains are made up of two randomly distributed "virtual co-monomers", (Et/CO) and (Pr/CO).

Key words: Terpolymers of ethane and propene with carbon monoxide, small angle and wide angle X-ray scattering, diamagnetic susceptibility, heat capacity.

INTRODUCTION

Regular alternating ter-polymerization of ethene (Et), propene (Pr) and carbon monoxide (CO) has proven to be efficient for the preparation of thermoplastic elastomers that are comparable in their mechanical performance to cross-linked rubbers. However, they are superior to the latter in their ability to be melt-reprocessed and/or recycled [1, 2]. The unique mechanical properties of these terpolymers at room temperature originate from "self-reinforcement" of the highly elastic, continuous amorphous matrix of Pr/CO by ordered, nano-size domains of Et/CO blocks [3-5]. As inferred from dielectric [5] and viscoelastic [6] measurements, nanocrystallinity of this kind persists over a surprisingly broad temperature interval above the glass transition temperature $T_g \approx 290$ K. Moreover, the Newtonian viscosity of terpolymers in the molten state exhibits a surprisingly strong dependence on chain microstructure. This dependence could be quantitatively reproduced by classical copolymerization theory assuming the strictly alternating Et/CO and Pr/CO copolymers as "virtual homopolymers" 11 and 22, and the strictly alternating (Et/CO)/(Pr/CO) ter-polymer as an "alternating virtual copolymer" 12 [6]. The high sensitivity of the diamagnetic susceptibility as a technique capable of detecting a variety of changes both in polymer chain microstructure (*intramolecular effects*) as well as on the local packing density of polymers (*intermolecular effects*) is well established [7-10]. In particular the detection of intermolecular effects by means of magnetic susceptibility measurements offers additional applications for the investigation of the nano-structure and properties of polymers [8]. The aim of the present paper is to extend the above investigations by examining the diamagnetic susceptibility of terpolymers in a broad temperature interval spanning from the glassy to the rubbery states.

EXPERIMENTAL

Materials

Alternating terpolymers of ethene, propene and carbon monoxide with varying Et/CO content w_1 (in weight %) = 14.2, 30.7, 31.9, 33.2, 35.3, 39.6 and 52.9 (hereafter referred to as Et/CO = 14.2, ..., 52.9) were prepared by a pulse-feed polymerization technique based on a discontinuous injection of Et to a running Pr/CO copolymerization [3, 4]. Their chemical composition and chain microstructure were controlled by the chemical analysis and NMR [3]; the number-average ($\langle M_n \rangle$) and weight-average ($\langle M_w \rangle$) molar masses (determined by gel-

permeation chromatography using standard polystyrene samples for calibration) are shown in Table 1.

Techniques

Wide-angle X-ray scattering (WAXS) patterns (2θ range of scattering angles from 5 to 40°) were measured using a DRON-2,0 diffractometer. Small-angle X-ray scattering (SAXS) data (2θ -range from $3'$ to 5°) were obtained with a standard Kratky camera (KRM-type diffractometer) as described elsewhere [11].

The specific heat capacity c_p was measured with the custom-made differential calorimeter with diathermal shells (DCDS) [12] (temperature interval: 150-550 K, heating rate: 2 K/min) (relative error of a single run about 3 %). Standard samples of sapphire and benzoic acid were used for c_p calibration.

The diamagnetic susceptibility (χ) was determined in the temperature interval 273-430 K by the relative Faraday method described elsewhere [9, 10]. For calibration, standard ionic crystals of NaCl, KCl and KJ with the room-temperature diamagnetic susceptibilities χ (here and thereafter expressed in the CGS units) of -0.518×10^{-6} , -0.519×10^{-6} and -0.384×10^{-6} , respectively [13], were used. As checked by repeated calibrations, as well as by control measurements of χ for a series of chemical-grade organic liquids ($10^6 \chi = -0.713$, -0.433 and -0.520 for toluene, formic and acetic acids, respectively [14]), the maximum deviations from tabulated values did not exceed 0.5- 0.7 %, while the relative error of measurement was below 0.3 %.

RESULTS AND DISCUSSION

Figure 1a illustrates some representative WAXS patterns for selected samples (Fig. 1a). Similarly to the case of terpolymers with higher Et/CO content [5], the diffraction patterns are characterized here by the absence of distinct crystalline reflections. This result is in accordance with their essentially non-crystalline (i.e., "X-ray amorphous") character, showing a diffuse maximum around $2\theta \approx 18^\circ$ corresponding to the short-range order on the scale of about 0.49 nm (presumably, intermolecular spacings).

Evidence for long-range order could not be detected from the SAXS curves of the studied samples, except for the one having the highest Et/CO content. Fig.1b illustrates for this sample a slight excess of the scattering intensity at $2\theta < 1^\circ$ suggesting the existence of a weak structural heterogeneity.

The main feature of the c_p vs. T plots from the first heating runs of all studied samples (Fig. 2a) are the prominent jumps ΔC_p at the glass transition temperature T_g , and the subsequent weak (tending to increase with the Et/CO contents from ~ 4 J/g for Et/CO=14.2 up to ~ 8 J/g for Et/CO=52.9), multiple endothermic effects setting-on at $T_m \approx 325$ K and extending over broad temperature intervals. As discussed elsewhere [5, 6], these effects support the concept of a three-dimensional network of Et/CO nano-crystals spanning the continuous, non-crystalline Pr/CO matrix in the initial samples. During the second heating run (Fig. 2b) the thermograms remain essentially the same, except for the change of the multiple endotherms showing weak deviations from linearity in the temperature intervals above T_g . This result suggests a very slow kinetics of recovery of the initial nano-crystallinity in the studied terpolymers.

As illustrated more in detail in Fig. 3a for the ter-polymer Et/CO=31.9, all terpolymers exhibit two stepwise jumps in χ (see Fig. 3b): the largest one (corresponding to a change $\Delta\chi \approx 1.5$ %) located at T_g ; and the much weaker one ($\Delta\chi \approx 0.3$ %) corresponding to T_m . These results confirm our previous contention [9] that basically the onset of large-scale (segmental) mobility, rather than density variation is the one, which is responsible for the stepwise changes of diamagnetic susceptibility at both T_g and T_m . However, in the present case the unusually large difference between absolute χ -values for samples with different chain composition (Fig. 3b) is the issue of more immediate concern.

We wish to discuss next, as done before [6], the composition dependence of χ within the frame of the classical theory of random copolymerization [15, 16] assuming that the ter-polymer chains are made up of two randomly distributed “virtual co-monomers”, 1 (Et/CO) and 2 (Pr/CO). Within this context, χ is expected to depend on the molar fractions of different diads, f_{ij} , as

$$\chi = \chi_{11}f_{11} + \chi_{12}f_{12} + \chi_{21}f_{21} + \chi_{22}f_{22}, \quad (1)$$

(where χ_{ij} are the “partial” susceptibilities of corresponding diads). The fractions of **similar** (f_{11}, f_{22}) and **unlike** ($f_{12} = f_{21}$) diads were calculated [6] as:

$$f_{11} = r_1 F/K, f_{22} = r_2/FK, f_{12} + f_{21} = 1/K, \quad (2)$$

where $F = [M_1]/[M_2]$ is the initial molar ratio of virtual comonomers in the reactor, $K = r_1 F + 2 + r_2/F$ (for illustrative purposes, $r_1 = 5.6$ and $r_2 = 0.14$ were assumed as the relevant reactivities of Et and Pr, respectively [6]).

As can be seen from Fig. 4, the variation of χ with composition for ter-polymers can be reasonably reproduced (dashed line) by substituting $\chi_{11} = \chi_{22} = -0.120 \times 10^{-6}$ and $\chi_{12} = \chi_{21} = -0.750 \times 10^{-6}$ into eq. (1). The latter fitting parameters are comparable in magnitude to Langevin's diamagnetism contributions for the virtual "homopolymers" of Et/CO ($\chi_d = -0.714 \times 10^{-6}$) and Pr/CO ($\chi_d = -0.737 \times 10^{-6}$) respectively, estimated using the semi-empirical Kirkwood's equation [13]

$$\chi_d = -3.11 \times 10^{-6} (z\alpha)^{1/2}, \quad (3)$$

where z is the total number of electrons in the chain repeating unit, and α is the electronic polarizability (calculated by the Lorenz-Lorentz formula using the tabulated increments [17] for molar refraction). In terms of the general relationship [14]:

$$\chi = \chi_d + \chi_p, \quad (4)$$

(where χ_d and χ_p are respectively the diamagnetic and paramagnetic contributions to the molecular diamagnetism), the above result reveals a negligible (if any) contribution of the "paramagnetic" (Van Vleck's) term, χ_p , to the total susceptibility χ . In other words, the best-fit values of $\chi_{12} = \chi_{21} = -0.750 \times 10^{-6}$ imply the least distortion of the spherical symmetry of electron density distribution in the strictly alternating (Et/CO)/(Pr/CO) ter-polymer. Within this context, the very low values of $\chi_{11} = \chi_{22} = -0.120 \times 10^{-6}$ can be regarded as evidence for unusually strong distortions of electron shells (i.e., dominant contribution of the paramagnetic term χ_p) for strictly alternating (Et/CO) and (Pr/CO) copolymers. However, this preliminary conclusion requires further experimental verification.

CONCLUSIONS

1. WAXS analysis shows that alternating ter-polymers of ethane, propene and carbon monoxide are amorphous at room temperature. However, multiple endothermic effects setting at T_m , above the glass transition temperature T_g , extending over relatively broad temperature intervals are

considered as evidence for a spatial network of Et/CO nano-crystals spanning the continuous, non-crystalline Pr/CO matrix in the initial samples.

2. The obtained data confirm the previous finding that it is basically the onset of large-scale (segmental) mobility, rather than density change the one that is responsible for stepwise changes of diamagnetic susceptibility at, both, T_g and T_m .
3. The unusually large differences between absolute χ -values for samples of different chain composition is explained within the frame of the classical theory of random copolymerization assuming that the ter-polymer chains are made up of two randomly distributed “virtual co-monomers”, 1 (Et/CO) and 2 (Pr/CO).

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REFERENCES

1. Belov, G.P. Alternating copolymers of carbon monoxide. *Polymer Sci. C*, **2001**, *43*, 1651-1666.
2. Mueller, G. ; Rieger, B. Propene based thermoplastic elastomers by early and late transition metal catalysts. *Prog. Polymer Sci.* **2002**, *27*, 815-851.
3. Huhn, W.E. ; Hollmann, F. ; Hild, S. ; Rieger, B. Nanostructured Alkene-Carbon Monoxide Terpolymers: New Materials via a Pulse-Feed-Polymerization Technique. *Makromol. Mater. Eng.* **2000**, *283*, 115-119.
4. Hollmann, F. ; Muecke, A. ; Hild, S. ; Rieger, B. A New Family of Polyketone Block-Terpolymers Showing Elastic Properties. *Polym. Mater. Sci. & Eng.* **2001**, *84*, 101-102.
5. Privalko, V.P. ; Pissis, P. ; Polizos, G. ; Korskanov, V.V. ; Privalko, E.G. ; Dolgoshey, V.I. ; Kramarenko, V.Yu. ; Huhn, W. ; Hollmann, F. ; Rieger, B. Dielectric relaxation of the alternating terpolymers of ethene, propene and carbon monoxide. *J. Macromol. Sci. Phys.* **2002**, *B41*, 99-116.
6. Privalko, V.P. ; Dolgoshey, V.B. ; Privalko, E.G. ; Shumsky, V.F. ; Hollmann, F. ; Rieger, B. Viscoelastic behaviour of the regular alternating terpolymers of ethen and propene with carbon monoxide. *J. Macromol. Sci. Phys.* **2002** (accepted for publication).
7. Baltá Calleja, F.J. Magnetic susceptibility as an application to the study of order-disorder phenomena in polymers. *J. Polymer Sci. C* **1969**, *16*, 4311-4322.
8. Ania, F. ; Baltá Calleja, F.J. Principles and applications of diamagnetism in polymers. In : "Computational Chemistry : Structure, Interactions and Reactivity", part B (ed. by S. Fraga), Elsevier, Amsterdam (1992), p. 527-554.
9. Sobolev, V.B. ; Privalko, V.P. Technique to study temperature dependence of magnetic susceptibility of polymers. *Komposits. Polimer. Mater.* **1992**, N 53, 54-57.
10. Privalko, V.P. ; Sobolev, V.B. ; Rekhteta, N.A. ; Sichko, V.N. Structure-dependent magnetic susceptibility of sharp poly(ethylene oxide) fractions. *J. Macromol. Sci. Phys.* **1998**, *B37*, 765-771.
11. Lipatov, Yu.S. ; Shilov, V.V. ; Gomza, Yu.P. ; Kruglyak, N.E. X-Ray Methods of Characterization of Polymer Systems. *Naukova Dumka, Kyiv*, 1982 (in Russian).
12. Privalko, V.P. ; Titov, G.V. Heat capacity of filled amorphous polymers. *Vysokomol. Soed.* **1979**, *A21*, 348-354.
13. Dorfman, Ya. G. Diamagnetism and the Chemical Bond. *Fizmatgiz, Moscow* (1961) (in Russian).

14. O'Sullivan, P. S. ; Hammett, H.F. A semiempirical theory of diamagnetic susceptibilities with particular emphasis on oxygen-containing organic molecules. J. Am. Chem. Soc. **1970**, *92*, 25-32.
15. Alfrey, T., Jr. ; Bohrer, J.J. ; Mark, H. Copolymerization. Interscience, New York, 1952.
16. Ito, K. ; Yamashita, Y. Copolymer composition and microstructure. J. Polymer Sci. **1965**, *A3*, 2165-2187
17. Fricke, R. ; Stemming, B. ; Haberdietzl, W. Die Stellung der Inkrementsystematik in der theoretischen Chemie. II. Mitteilung : Bindungsinkremente fuer Molsuszeptibilitaet, Molrefraktion, Parachor, Verbrennungswaerme und Atomisierungsenthalpie. Z. phys. Chem. **1970**, *245*, 81-103.

Table 1. Average number, M_n , and weight molecular weight, M_w , glass transition temperature, T_g , and specific heat capacity, Δc_p , of the terpolymers investigated

w_1	$10^{-5} \langle M_n \rangle$	$10^{-5} \langle M_w \rangle$	T_g / K	$\Delta c_p / \text{J (g K)}^{-1}$
14.2	9.78	17.03	293	0.415
30.7	12.12	21.11	291	0.460
31.9	12.18	22.51	290	0.485
33.2	12.19	20.46	290	0.425
35.3	3.79	7.08	287	0.455
39.6	10.73	16.22	287	0.475
52.9	12.89	18.14	283	0.455

Figure captions

Fig. 1. WAXS (a) and SAXS (b) patterns for terpolymers. Curves in Fig. 1b, (from bottom to top) refer to samples with increasing Et/CO content, as in Table 1.

Fig. 2. Variation of specific heat capacity with temperature for the first (a) and the second (b) heating runs. The curves (from top to bottom) refer to samples with increasing Et/CO content (see Table 1).

Fig. 3. Plot of the diamagnetic susceptibility vs. temperature for sample Et/CO=31.9 (a) and for other terpolymers (b). In Fig. 3b, the curves (from bottom to top) refer to samples with increasing Et/CO content (see Table 1).

Fig. 4. Plot of diamagnetic susceptibility as a function of composition (from bottom to top) for terpolymers measured at 275 K (opened squares) and 375 K (filled squares).

Fig. 3a

Fig. 3b

Fig. 4