Molecular mobility and phase structure of isotactic poly(epichlorohydrin) as revealed by broad-line nuclear magnetic resonance

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Isotactic partially crystalline poly(epichlorohydrin) (PECH) was studied by broad-line nuclear magnetic resonance in the temperature range from −170 to +40°C. The temperature dependence of the linewidth and the second moment, and the fractions of individual lines in the spectrum, obtained through decomposition of the total spectrum, were analysed. The derived data yield conclusions about the changes in molecular mobility in this polymer. The theoretical value of the second moment for the crystal lattice of isotactic PECH was calculated based upon known unit-cell parameters. Comparison of these data with the results of wide-line X-ray diffraction studies allowed conclusions to be drawn about the phase structure of isotactic PECH, and especially about morphological inhomogeneity in the rigid phase.

(Keywords: isotactic poly(epichlorohydrin); broad-line nuclear magnetic resonance; chain dynamics; structure; chain interactions)

INTRODUCTION

Data on the structure of isotactic, crystalline poly(epichlorohydrin) (PECH), a polymer with chain repeat unit $[CH_2–CH(CH_2Cl)–O]_n$, are very scarce in the literature. The space group and unit-cell parameters of this polymer are known($a = 12.16$ Å, $b = 4.90$ Å, $c = 7.03$ Å)[1,2]. Perego and Cesari[1] have shown that isotactic PECH crystallizes like isotactic poly(propylene oxide)[3] in the orthorhombic system. The chain conformation in the crystallites differs from planar only by ±15°.

Thermal crystallization of isotactic PECH was studied by X-ray diffraction[6]. The crystallization temperature was shown to influence the degree of order in the crystallites only insignificantly. The growth of spherulites during crystallization of isotactic PECH was also studied by optical methods[4].

The differential scanning calorimetry (d.s.c.) study of isotactic PECH[5] has shown multiple melting endotherms and yielded data on the glass transition temperature (−27.5°C). All the morphological studies of isotactic PECH carried out so far indicate the presence of ordered (crystalline) and amorphous regions in this polymer. Measurements of the degree of crystallinity yield values of 29% (d.s.c.)[5], 38% (wide-angle X-ray scattering, WAXS)[6] and 42% (density measurements)[6].

The aim of this work was to obtain information about the dynamics of chains of isotactic PECH and the supermolecular structure of this polymer by means of a broad-line nuclear magnetic resonance (b.l.n.m.r.) study. Analysis of the lineshapes of the b.l.n.m.r. spectra made it possible to determine the fractions of rigid and mobile phases. A model of the phase structure of this polymer was proposed, which attempts to account for the different morphological properties observed using different techniques.

EXPERIMENTAL

Sample preparation

The synthesis and fractionation of PECH was carried out according to the work of Vandenberg[7] using $Al(Bu)_3/H_2O$ (1:0.6) as initiator. The polymer obtained was fractionated and the fraction insoluble in acetone at room temperature (but soluble in boiling acetone) was used for further studies ($MW \approx 430\,000$ g mol^{-1}, unimodal molecular-weight distribution by gel permeation chromatography, g.p.c.). ^{13}C n.m.r. studies[8] indicated that the PECH so obtained is practically fully isotactic.

Żmudziński *et al.* used WAXS to determine the degree of crystallinity of this fraction as 38%[6]. The glass transition temperature was measured by d.s.c. as −27.5°C[5].

Measurements

B.l.n.m.r. measurements were carried out at 27.4 MHz using an autodyne n.m.r. spectrometer built in the Laboratory of Radiospectroscopy at the Adam-Mickiewicz University in Poznan (Poland). Temperature was stabilized using a 650H temperature regulator (Unipan, Poland) and measured with a Pt resistance thermometer to an accuracy of ±0.5°C. The spectra (first derivatives of absorption lines) were recorded under conditions appropriate to avoiding saturation. The narrow line in the spectra of isotactic PECH was overmodulated. The necessary numerical calculations were carried out using programs written in BASIC and run on a Zenith 140 microcomputer.

RESULTS AND DISCUSSION

Width and shape of the n.m.r. line of isotactic PECH

The n.m.r. spectra of isotactic PECH for some chosen temperatures are shown in *Figure 1*. In the temperature

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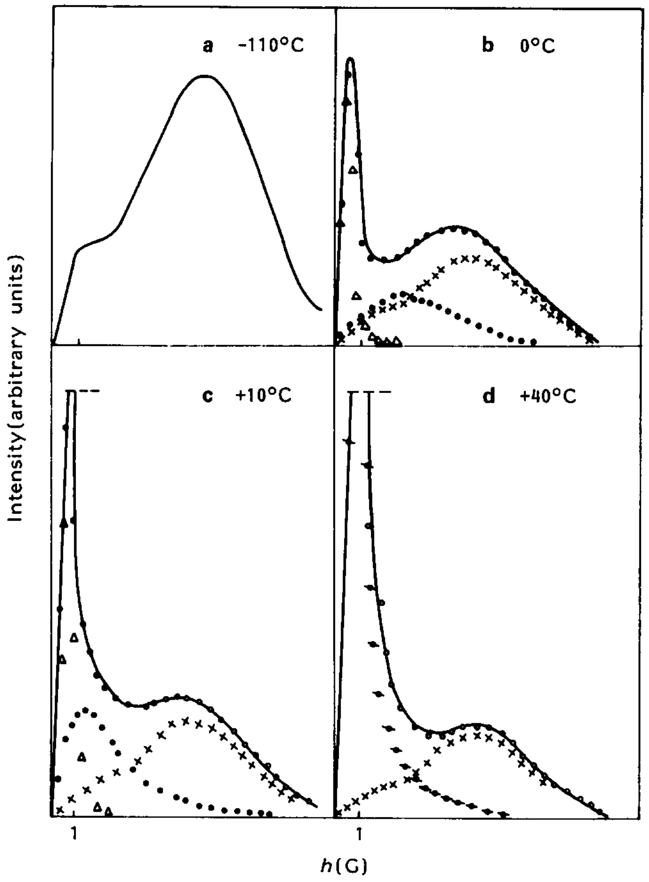

Figure 1 Lineshapes of the ^1H b.l.n.m.r. spectra of isotactic PECH: ×, α component; ●, β component; △, Γ component; —●—, β+Γ components; ○, calculated total spectrum; ——, experimental spectrum

range from −170 to −30°C, the lines are of similar shape and their widths change only slowly with increasing temperature. Already at −140°C a narrow line has appeared in the spectra. Such a line is generally due to low-molecular-weight impurities or an oligomeric fraction in the system. In our case g.p.c. allowed us to exclude the presence of a low-molecular-weight (oligomeric) fraction. The intensity of this line decreases with increasing duration of sample drying, but the line cannot be completely eliminated. This line is thus due to the presence of a low-molecular-weight liquid (the solvent used in polymer synthesis). In spite of the low integrated intensity of this line (less than 3%), it had to be taken into account when analysing the total lineshape.

When the temperature is increased above −30°C, the shape of the spectrum changes. There appears a component that in the first stage increases the intensity of the middle part of the spectrum (*Figure 1b*) and later causes a significant increase in the narrow component of the spectrum (*Figures 1c* and *1d*). The spectrum of isotactic PECH in the temperature range of the main transition consists of two lines of clearly different widths and intensities (*Figure 1d*). Such a spectrum is characteristic of heterophase polymers[9,10].

To obtain more detailed information about the transition temperatures and content of individual dynamically different regions in the polymer, it is necessary to separate the individual lines in the spectrum and to determine the intensities of the components. Such an analysis has been reported for many partially ordered polymeric systems[9–14]. An often applied method for such a separation, that due to Wilson and Pake[15], could not be used here.

A method proposed by Bergmann and Nawotki[16] is widely used. According to this method the total spectrum can be represented as the sum of components corresponding to the resonance of individual groups of spins, which may be treated as isolated. Several least-squares procedures were proposed to fit the experimental and calculated spectra by systematic changes in the parameters of the theoretically chosen components[17,18].

The decomposition of the n.m.r. spectra of isotactic PECH recorded above −30°C was carried out according to the method of Bergmann and Nawotki using the non-linear least-squares fitting algorithm of Marquardt[17]. Experimental spectra were derivatives of absorption lines; therefore, to obtain the real intensities of the decomposed lines and their fraction in the total absorption spectrum, the calculated lines were integrated numerically. The best fit was obtained when the spectra were separated into three components, called α, β and Γ.

Wide component, α. The problem of the separation of the line responsible for the resonance of rigid chains belonging to crystalline regions was not solved unequivocally. The shape of such a line differs from polymer to polymer and may also change with temperature, which is due to changes in the relaxation processes in the ordered regions. In most cases the shape of this line is described by a so-called low-temperature curve[11,16,19]. In most cases, too, the experimental spectrum of the polymer with the highest possible degree of crystallinity recorded at low temperature and low modulation amplitude is accepted as the low-temperature curve. In our case the spectrum of isotactic PECH at −110°C was chosen as the low-temperature line for fitting the α line in the spectra of the isotactic polymer at the main transition.

The β component. At a temperature of −30°C a line of medium width appears in the spectra. The best fit was obtained using a Gaussian curve below 0°C and a Lorentz curve above this temperature. At +40°C the width of this line is comparable with the width of the narrow component Γ and with the applied modulation amplitude; in that case the Γ line becomes identical with the β line.

Narrow component, Γ. The Γ component accounted for the resonance of protons of the low-molecular-weight liquid. This line was described using a function given by Eichoff and Zachmann for narrow overmodulated lines[20]:

$$g(h) \propto \frac{1}{[2a(ac^{1/2}+d)]^{1/2}} - \frac{1}{[2c(ac^{1/2}+d)]^{1/2}}$$

where

$$a = b^2(h - H_M)^2 + 1$$

$$c = b^2(h + H_M)^2 + 1$$

$$d = b^2(h^2 - H_M^2)^2 + 1$$

H_M is the modulation amplitude and b the width of the Lorentz line corresponding to the narrow component when recorded at low modulation amplitude.

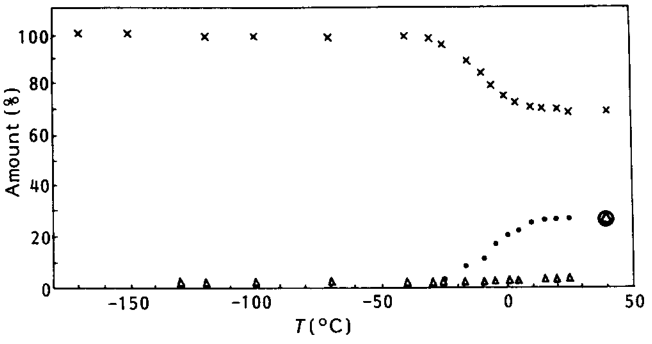

Figure 2 Fractions of components α (×), β (●) and Γ (△) in the spectrum of atactic PECH

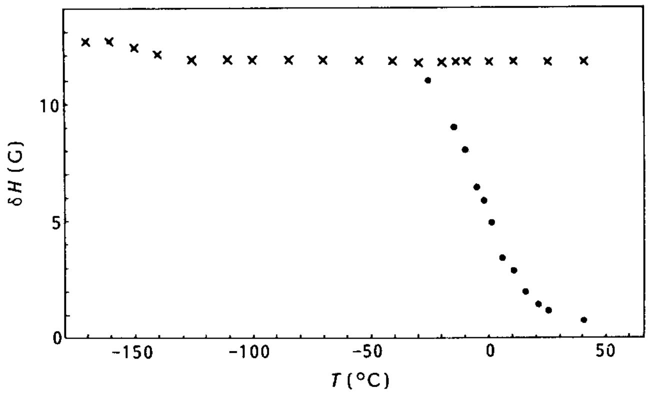

Figure 3 Linewidth of components α (×) and β (●) in the spectrum of isotactic PECH

The decomposition of spectra carried out in the way described above allows us to make conclusions about the dynamics and morphology of the polymer studied. The decomposed spectra of isotactic PECH are shown in *Figure 1*. *Figure 2* shows the fraction of individual lines, *Figure 3* the changes in the linewidths and *Figure 4* the changes in the second moment of the lines as a function of temperature.

The width of the line decreases slightly in the temperature range from −140 to −120°C. Above this temperature the width of the α component of the spectrum seems to be constant, as in the region of the main transition (−30 to +40°C). The wide component in the spectra has to be related to those polymer chains which from the n.m.r. point of view remain rigid in this range of temperatures. The slight decrease in the linewidth at about −130°C is probably due to isotropic rotation of the CH_2Cl side groups. A similar transition was observed previously in atactic PECH and was discussed earlier[21,22]. Above −110°C this line changes neither shape nor width, and the corresponding polymer chains therefore remain rigid. The fraction of this line in the total spectrum decreases when the temperature is increased above −30°C (*Figure 2*). This decrease is accompanied by the appearance of the β line. Numerical analysis reveals the presence of this line already at −30°C. Its shape is initially Gaussian, and its width at −30°C is ca. 11 G. With increasing temperature, this line becomes of Lorentz shape and its width decreases to 0.7 G at +40°C (*Figure 3*). The β component may therefore be assigned to those polymer chains whose mobility increases with increasing temperature from about −30°C.

Such a significant decrease in the linewidth as observed for the β component reflects the onset of cooperative translational and rotational movements involving long chain segments, typical of the glass transition[9]. The glass transition in this polymer measured by d.s.c. falls within the region of this transition determined by n.m.r. The fraction of the β component in the total spectrum reaches a constant value of ca. 27% above +10°C. The rest of the chains (ca. 70%) remain rigid at this temperature.

The fraction of rigid chains determined by n.m.r. is ca. 30% larger than the fraction of crystalline regions determined by X-ray diffraction[6]. It is obvious that the parts of the chains belonging to the X-ray amorphous regions remain rigid at the glass transition. Part of the chains in the disordered regions (27%) is mobile in the temperature range from −30 to +40°C; another part of the chains (30%), although not forming a crystal lattice, remains rigid.

The fraction of the narrow component Γ, related to the presence of low-molecular-weight liquid in the samples, remains constant. The true width of this line, measured when the spectrum is recorded without overmodulation of this component, is ca. 0.5 G at +20°C. The results of other n.m.r. studies on semicrystalline polymers[11,13] indicate that a small part of this line may be due to the fast motion of chain ends.

Second moment of the n.m.r. spectra of isotactic PECH

The changes in the second moment of the components of the spectrum of isotactic PECH are presented in *Figure 4*. At −170°C, when there is practically no mobility of the chains, the second moment reaches $18.9\,G^2$.

The transition related to the onset of mobility of part of the CH_2Cl groups occurs in isotactic PECH at −140 to −120°C, lower than the low-temperature transition observed in atactic PECH[23]. The decrease in the second moment at this transition equals $1.6\,G^2$ and is smaller than that observed in atactic PECH. It follows that only some of the chloromethylene groups are engaged in the rotational transition at this temperature.

In the temperature range from −120 to −30°C, the second moment remains practically constant. Between −30 and +40°C the second moments of both the total

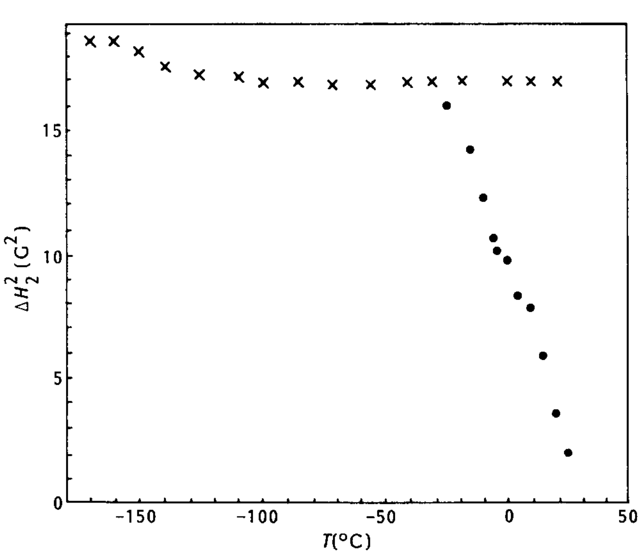

Figure 4 Second moment of components α (×) and β (●) in the spectrum of isotactic PECH

spectrum and the β line fall significantly, which is due to an increase in chain mobility at the glass transition.

The theoretical value of the second moment of any system of interacting protons may be calculated if their spatial arrangement is known. A comparison of values so calculated and measured allows conclusions to be made about the kind and order of the interactions between protons in the spatial structure assumed and allows one to compare an ideal crystalline structure with the real order observed.

Both inter- and intramolecular components of the second moment were calculated for isotactic PECH. The parameters of the unit cell and the chain conformation given in ref. 1 were assumed. Chain fragments consisting of two repeat units served to make up the unit cell of isotactic PECH. This cell was then extended into a structure of any size by translation of the chains along the x, y and z axes.

The second moment for the structure so generated was calculated by summing the interactions of the protons of the central chain among themselves (intramolecular component) and with the protons of other chains in the structure generated (intermolecular component). Simple considerations, based upon the elementary formula for the second moment of n.m.r. spectra[9]:

$$\Delta H_2^2 = \frac{9}{5}\frac{\mu^2}{n}\sum_{\substack{i,j\\ i\neq j}} r_{ij}^{-6}$$

where μ = magnetic moment of the nucleus, n = number of interacting protons and r_{ij} = distance between protons i and j, leads to the following equation:

$$\Delta H_2^2 = \Delta H_{2\,\mathrm{intra}}^2 + \Delta H_{2\,\mathrm{inter}}^2 = \frac{715.7}{N}\sum_{i>j} r_{ij}^{-6} + \frac{357.9}{N}\sum_{i,k} r_{ik}^{-6}$$

where N = number of protons in the central chain, i and j are protons belonging to the central chain, k are protons in the remaining part of the structure and r_{ij} = distance between protons i and j (Å).

The calculated values of the second moment depend initially for obvious reasons on the size of the structure generated, but with increasing size of the structure they quickly reach constant values:

$$\Delta H_{\mathrm{inter}}^2 = 3.3\ \mathrm{G}^2$$

$$\Delta H_{\mathrm{intra}}^2 = 16.0\ \mathrm{G}^2$$

$$\Delta H_{\mathrm{total}}^2 = 19.3\ \mathrm{G}^2$$

The calculated total value of the second moment equals 19.3 G^2 and is very close to the value found experimentally for isotactic PECH at −170°C (18.9 G^2). The second moment ΔH_2^2 for the non-crystalline regions of the isotactic polymer may be estimated better using the formula:

$$u_\mathrm{c}\Delta H_{2\mathrm{c}}^2 + u_\mathrm{n}\Delta H_{2\mathrm{n}}^2 = \Delta H_{2\,\mathrm{exp}}^2$$

where u_c and u_n are the fractions of crystalline and non-crystalline regions as revealed by X-ray studies, and $\Delta H_{2\mathrm{c}}^2$ and $\Delta H_{2\mathrm{n}}^2$ are values of the second moment for the crystalline and non-crystalline regions, respectively.

The value of the second moment of the non-crystalline regions, $\Delta H_{2\mathrm{n}}^2$, calculated from the above equation, equals 18.7 G^2. The proton–proton interactions at −170°C therefore differ only insignificantly in both phases. A similar finding was observed in polyethylene[11]. It cannot be excluded that both the microconformation and the chain interaction in the crystalline and non-crystalline regions are very similar.

Phase structure and dynamics in isotactic PECH

The dynamics of the macromolecules, their structure and conformation, and the phase structure of polymers are closely related to each other. The results discussed above yielded information about the mobility of isotactic PECH, confirmed the occurrence of the glass transition in this polymer in the temperature range −30 to +40°C[5,24], and allowed estimation of the fraction of chains engaged in this transition.

Deeper insight into the phase structure of isotactic PECH may be gained by comparison of these data with the results of X-ray diffraction analysis. X-ray diffraction data reveal that ca. 38% of the chains of this polymer belong to the crystalline regions, the remaining part being disordered (amorphous). In contrast, n.m.r. data indicate that 70% of the chains remain rigid at the glass transition. The fraction of ordered regions characterized by X-ray diffraction is very different from the fraction of rigid chains calculated from n.m.r. data. To account for this discrepancy, it is necessary to assume the presence of three kinds of morphologically different regions in isotactic PECH:

(a) regions consisting of chains forming the crystal lattice, rigid in the temperature range studied;

(b) regions consisting of chains rigid in this temperature range, but not ordered in a crystal lattice; and

(c) regions consisting of disorded chains, mobile above −30°C.

The experimental evidence presented here is not sufficient to make any conclusions about the structure of the regions consisting of rigid, X-ray amorphous chains. A comparison of the second moment of the spectrum calculated for a rigid lattice with its experimentally measured value indicates that the proton–proton interactions in the second and third regions are similar to that observed in the crystallites. The second moment, however, represents both inter- and intramolecular interactions, so that this does not indicate unequivocally a morphological similarity of these phases, although such a similarity cannot be ruled out.

Comparison of the data presented here for the isotactic polymer with those published earlier for atactic PECH[22,23] yields interesting results. The n.m.r. study of atactic PECH indicates that this polymer is fully amorphous and morphologically homogeneous (the b.l.n.m.r. spectrum at the glass transition consists of a single line), in contrast with isotactic PECH, which is a heterophase and shows complex structure in the n.m.r. spectrum at T_g.

The value of the second moment for atactic PECH measured at the lowest experimentally accessible temperature is 22 G^2 (ref. 23) and is larger than for the isotactic polymer (18.9 G^2). Similar behaviour was previously observed for some other polymers, e.g. poly(ethylene terephthalate)[25]. Detailed theoretical calculations of the second moment and comparison of the value so calculated with the experimental data and with the results of X-ray studies indicate that the proton–proton interactions in the disordered region of the isotactic polymer are also higher than in the atactic polymer. Some groups of protons in atactic PECH must therefore approach each other more closely than in the isotactic polymer, which is undoubtedly due to the different conformation of the atactic chains. Intermolecular interactions may also play a role here. The relaxation of the side groups, which in the atactic polymer seems to be determined by intermolecular dipolar interactions[21,22], occurs in isotactic PECH at a lower temperature. It may therefore also be assumed that intermolecular interactions between the polar groups in isotactic PECH are weaker in comparison with the atactic polymer.

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