Study of the molecular mobility in swollen poly(epichlorohydrin): 1. Nonpolar swelling agent

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The broad line n.m.r. spectra of the amorphous fraction of poly(epichlorohydrin) have been analysed. Two motional transitions were observed and the T_g and a low temperature transition β assigned to the motion of the CH_2Cl groups. The study of the poly(epichlorohydrin) swollen by a low molecular weight liquid (deuterobenzene), has provided information about the influence of swelling on the molecular dynamics, and the participation of intermolecular interactions in the second moment of the resonance lines. The observed value of the second moment of the spectra is higher than that calculated for a planar chain conformation. This indicates that the chain conformation of the atactic, amorphous poly(epichlorohydrin) is different from the conformation observed in the crystalline, isotactic fraction of the polymer.

(Keywords: poly(epichlorohydrin); molecular motion; conformation; swelling; glass transition)

INTRODUCTION

The structure of poly(epichlorohydrin) $(CH(CH_2Cl)-CH_2O)_n$ (PECH) and the molecular dynamics of its chains are very important in determining the elastomeric properties of this polymer. The literature data concerning this subject are rather scarce. In particular there is no information about the chain conformation of amorphous PECH: which as an elastomeric polymer of some industrial importance[1].

X-ray diffraction study of the oriented fibres of crystalline, non-elastomeric PECH led to the determination of the parameters of the elementary cell and the spatial group of this polymer[2]. These studies indicated an almost planar conformation of PECH chains in the crystallite, similar to that found in crystalline poly(propylene oxide)[2,3].

The measurements of the dielectric relaxation in amorphous PECH[4] show two motional transitions: at −16°C and at −120°C, the first one being assigned to the glass transition. Two relaxation transitions have also been observed for other amorphous polyethers, like poly(propylene oxide)[6,7] and poly(epibromohydrin)[4].

The aim of the work presented here was to gain information about the molecular dynamics; inter- and intramolecular interactions; the chain conformation of the atactic PECH and also the influence of the swelling by a low molecular weight liquid upon these effects. In Part 1 studies of PECH with an unpolar swelling agent, benzene-d_6, are presented, so that the effects of the dipolar interactions between the swelling agent and the polar groups of the polymer have been avoided.

The dynamics of these systems were studied by n.m.r.

EXPERIMENTAL

Sample preparation

The synthesis and the fractionation of PECH was carried out according to the method of Vandenberg[8], using $Al(Bu)_3/(H_2O)$ (1:0.6) as initiator. The crude polymer was fractionated. An amorphous fraction ($M_\eta = 140000$), soluble in acetone at −30°C and crystalline fraction ($M_\eta = 430000$), insoluble at room temperature in any common solvent, (but soluble in boiling acetone or benzene), were isolated. G.p.c. analysis has shown a unimodal molecular weight distribution and the absence of low molecular oligomers in both fractions. The amorphous fraction was atactic, the crystalline isotactic[9]. The crystallinity was checked by X-ray diffraction.

The swollen samples were prepared by adding known weights of benzene-d_6 to known amounts of amorphous PECH. The system was then homogenized by storing it for 48 h at 60°C in a sealed vial. The samples contained 35 wt% and 50 wt% of the swelling medium.

Measurements

The wide-line n.m.r. spectra were recorded at 30 MHz using a Varian WL-109 spectrometer. The temperature was stabilized by the E-257/WL-257 built-in unit and measured using a Ni–CrNi thermocouple. The measurement conditions were selected to avoid any saturation or overmodulation of the spectra.

The numerical calculations were carried out using a Wang 2200 minicomputer.

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RESULTS AND DISCUSSION

Figure 1 shows the spectra (half of the derivative of the absorption line) of the unswollen samples of amorphous PECH at several temperatures. The spectra of the unswollen samples were recorded between −176°C and +30°C, the spectra of the swollen polymer between −176°C and −5°C. In a wide range of temperatures a narrow signal of the residual solvent is observed. This signal is of low intensity, heavily overmodulated and was not considered in the analysis of the spectra.

Line width

The line width was measured as the distance between the extremes of the derivative of the absorption curve. The temperature dependence of the line width is shown in *Figure 2*. The rather high line width for the amorphous, unswollen PECH at low temperatures (≈ 15.5 G) is worth noting. Two transitions were observed for this sample: at −110°C, accompanied by a decrease of the line width of 1.3 G (from 14.2 to 12.9 G) and at a temperature interval of −10°C to +20°C, at which the line width sinks from 11.9 G to 0.3 G. The last transition is explained as the glass transition of the polymer[4,5]. The origin of the β transition at −110°C, which is also observed in dielectric relaxation[5], is less clear. It seems that, as stated by Blyth and Jeffs[4], it is associated with the motions of the side groups CH_2Cl, bound by strong dipolar interactions with other CH_2Cl and with C–O–C groups. The β transition was also observed in an n.m.r. T_1 study of poly(propylene oxide)[7]. But it disappeared, however, when the hydrogen atoms in the side group CH_3 of this polymer are replaced by deuterium. This confirms the origin of the transition from the side group motion.

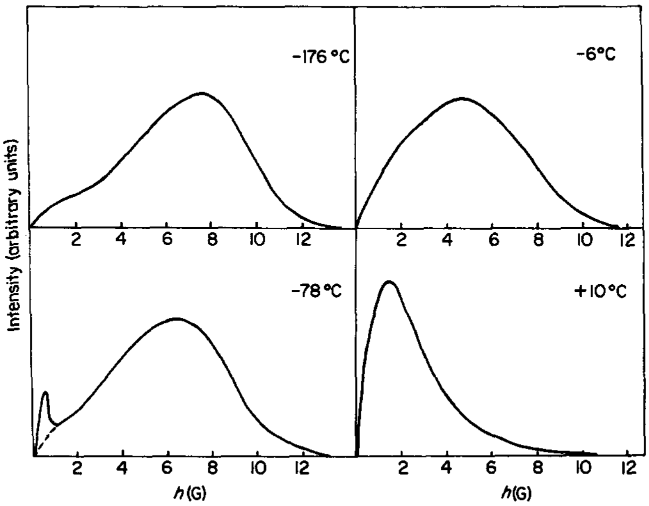

Figure 1 Wide line n.m.r. spectra of amorphous poly(epichlorohydrin)

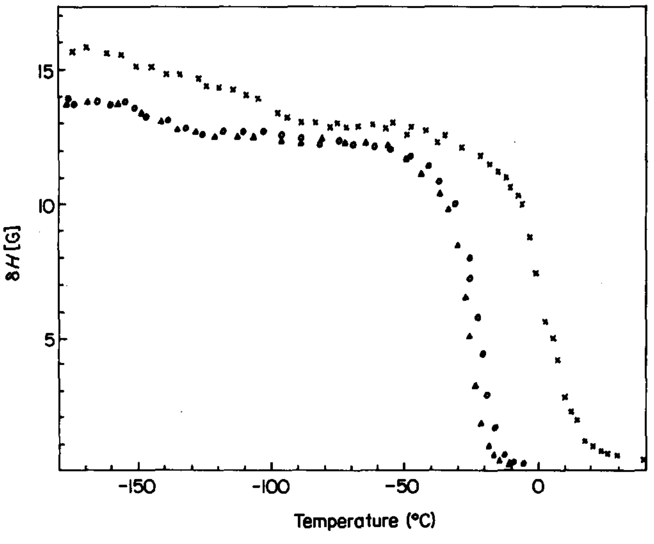

Figure 2 Line widths in n.m.r. spectra of amorphous poly(epichlorohydrin). (X): unswollen polymer; (O): polymer swollen with 35 wt% C_6D_6; (▲): polymer swollen with 50 wt% C_6D_6

The swelling of the polymer by a low molecular liquid is often applied for studying the dynamics and morphology of macromolecular systems[10–15]. It leads to an increase of the chain–chain distances, which lowers the intermolecular interactions. In the absence of specific interactions between the polymer and the low molecular swelling agent[10,11] the molecular motions may become active at lower temperatures, as it was frequently observed[12–16].

For swelling of PECH an unpolar agent, benzene-d_6, was chosen. Samples containing 35 wt% and 50 wt% of benzene-d_6 were studied.

The swelling shifts both transitions towards lower temperatures (*Figure 2*). The T_g is shifted by ≈ 20°C for samples containing 35% of the swelling medium, and by 25°C for samples containing 50% of the swelling medium. The β transition is shifted by 40°C for both degrees of swelling. The line-width for both swollen samples is equal to 13.8 G at −176°C. This allows the conclusion that a degree of chain separation was already reached in the sample containing 35% benzene-d_6, which to a great extent eliminates the influence of the intermolecular interactions. This conclusion is further supported by the study of the second moment of the sepctra, as shown later in this paper.

The swelling does not cause any significant changes of the line shape, except for its narrowing. The lack of a distinct separation of the resonance line into a broad and narrow component, often occurring in two-phase systems[15,17–19] confirms the amorphous structure of the polymer and its morphological homogeneity, unchanged upon swelling.

Correlation time and activation energy of the transitions

Using a modified theory of Bloembergen, Purcell and Pound (see refs. 20–22), Smith[23] described the correlation time τ_c as

$$\tau_c = \frac{8 \ln 2}{\gamma \delta H} tg\left[\frac{\pi}{2}\left(\frac{\delta H^2 - B^2}{C^2 - B^2}\right)\right] \qquad (1)$$

where γ is the gyromagnetic ratio of the studied nucleus, δH [G] is the line width in the transition range and B and C [G] are the line widths above and below the transition temperature.

The correlation times (*Figure 3*) yield the activation energy for a given transition according to the Arrhenius formula

$$\tau_c = \tau_0 \exp(E_A/RT) \qquad (2)$$

The obtained values for the activation energy of the glass transition are equal to 15.8 kcal mol^{-1} and are within the same limit of error for swollen and unswollen samples.

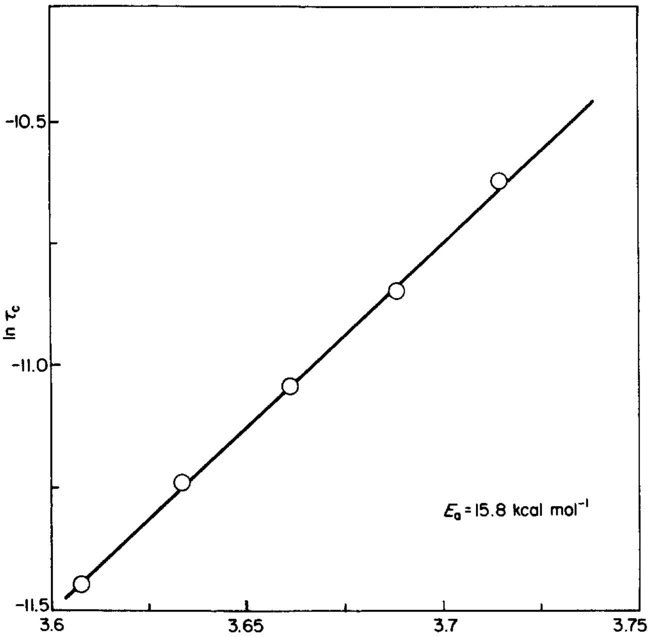

Figure 3 Correlation times τ_c vs. temperature for amorphous poly(epichlorohydrin)

The determination of the activation energy for the β transition is much more sensitive to experimental error, especially in the determination of the low and high temperature limits of the line width. The values obtained may be taken only as an approximate estimate. For unswollen samples we obtain 8.4 kcal mol^{-1} with $B = 12.8$ G and $C = 14.1$ G. This value agrees well with the activation energy of 8.5 kcal mol^{-1} found for this transition from dielectric relaxation data[4].

The swelling with benzene lowers the activation energy for the β transition to 4.5 kcal mol^{-1}. This indicates that the intermolecular interactions exercise a strong influence upon the molecular motion responsible for this transition.

Second moment of the lines

The second moment of the lines is given by the expression[19]:

$$\Delta H_2^2 = \int_{-\infty}^{+\infty} h^2 g(h) dh \tag{3}$$

where h is the external magnetic field deviation from the resonance value and $g(h)$ the absorption function.

The changes of the second moment of the spectra with temperature are shown for all studied samples in *Figure 4*. Qualitatively, they resemble the changes in the line width and confirm the occurrence of both earlier discussed transitions.

The second moment at lowest temperature reached (−176°C) is equal to 22 G^2 for the unswollen samples of amorphous PECH. Upon swelling this value is lowered to 19 G^2.

It is to be noted that the second moment of the spectra of unswollen, amorphous PECH is higher than for the crystalline fraction, which was measured as 19.5 G^2 at −170°C.

It is possible to calculate the value of the second moment of the n.m.r. spectrum, assuming a given, rigid conformation of the chain[24]:

$$\Delta H_2^2 = \frac{18}{5} \frac{\mu^2}{N} \sum_{j>k} r_{jk}^{-6} \tag{4}$$

where r_{jk} is the distance between the protons j and k, μ the magnetic moment of the proton and N the number of interacting protons.

According to this equation we calculated the second moment for an isolated, heteroatactic triad in the planar zigzag conformation. This conformation is assumed to prevail in the PECH[2] and poly(propylene oxide)[3] chains in crystallites. Taking the bond angles and distances from the X-ray studies on poly(propylene oxide)[3] and from tabulated data[25] we obtain values for the second moment between 13.8 G^2 and 15 G^2, depending upon the mutual position of the CH$_2$Cl groups. The assumption of free rotation of the CH$_2$Cl groups would lower this value by ≈ 3 G^2.

This calculated decrease agrees well with the value found experimentally for the β transition (*Figure 3*), which confirms its earlier given interpretation.

It is clearly seen that the calculated value of the second moment is much lower than found experimentally (15 G^2 *versus* 22 G^2). In the relationship[4] however only the intramolecular proton–proton interactions are accounted for. Therefore only after the contribution of the intermolecular interactions to the second moment has been estimated, does it become possible to decide whether the planar conformation is likely to occur in the amorphous polymer.

This estimation may be carried out on the basis of the results obtained for swollen samples. For an unpolar solvent like benzene no significant interactions between the swelling liquid and the polymer may be expected. The swelling-induced crystallization of the atactic PECH can also be excluded. Therefore the decrease of the second moment of the swollen samples at low temperatures must

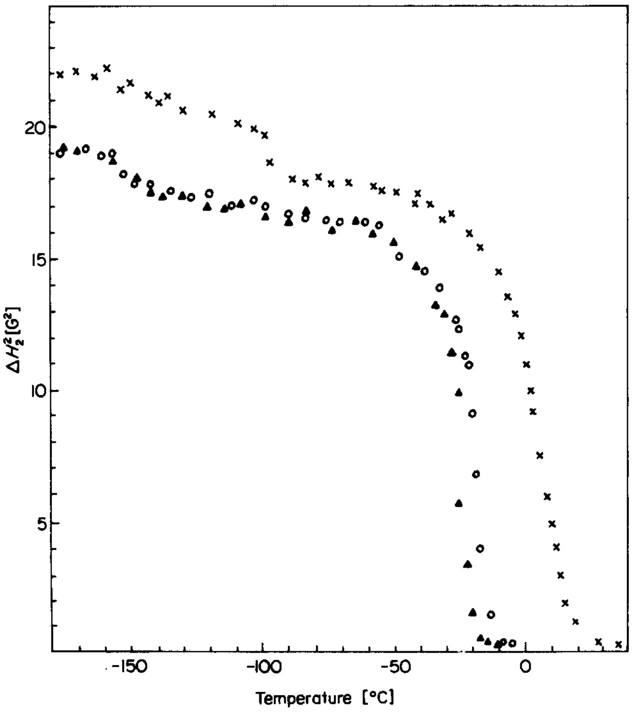

Figure 4 Second moment of the wide line n.m.r. spectra of amorphous poly(epichlorohydrin). (X): unswollen polymer; (○): polymer swollen with 35 wt% C$_6$D$_6$; (▲): polymer swollen with 50 wt% C$_6$D$_6$

be assigned to the lowering of the intermolecular interactions. The second moment for the sample containing 35% of deuterobenzene is the same as for the sample swollen with 50% of the solvent. The reached degree of swelling seems therefore to be sufficient to approximate the contribution of the intermolecular interactions to the second moment. Upon swelling the second moment is reduced from 22 G^2 to 19 G^2, which yields 3 G^2 as the approximate contribution of the intermolecular interactions. The remaining intramolecular contribution (19 G^2) still significantly exceeds (by 4 G^2 to 5 G^2) the value calculated for the planar chain conformation. This large discrepancy may be due to a non-planar chain conformation, different from that observed in crystallites.

The analysis of the possible chain conformations of atactic PECH and their comparison with experimental findings requires the calculation of conformational energies as functions of the bond angle rotation. Such an analysis will be discussed in a separate paper.

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