Study of molecular mobility in swollen poly(epichlorohydrin): 2. Polar swelling agent

B. Trzebicka, S. Śmigasiewicz and E. Turska
Institute of Polymer Chemistry, Polish Academy of Sciences, 41-800 Zabrze, Poland
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Broad line n.m.r. spectra of atactic, amorphous poly(epichlorohydrin) swollen with polar liquids: nitrobenzene-d$_5$ and nitromethane-d$_3$ were analysed. The influence of the swelling agent on the dynamics of molecular mobility was studied by comparison of the relaxations in swollen and pure polymer. In the system poly(epichlorohydrin)–nitrobenzene an antiplastification effect was observed. For a nitrobenzene content of 45 wt% an additional transition, not observed in unswollen PECH, occurs at −60°C. It was interpreted as an overlapping of a relaxation and a kinetic process. The results discussed were confirmed by studies of dielectric relaxation in these systems.

(Keywords: poly(epichlorohydrin); broad line n.m.r.; dielectric relaxation; swelling; chain dynamics)

INTRODUCTION

In spite of the wide industrial application of amorphous poly(epichlorohydrin) (PECH) owing to its elastomeric properties, there is little information concerning the morphology of this polymer and the dynamics and conformation of its chains. X-ray diffraction[2,3] led to the conclusion that the conformation of isotactic PECH chains is close to planar. The measurements of dielectric relaxation in amorphous PECH[4] indicates the occurrence of two relaxation transitions in this polymer, as observed for other polyethers[5,6]. The glass transition in amorphous PECH was also observed by d.s.c.[7]

Previously[8], we reported the results of broad line n.m.r. studies of amorphous, atactic PECH and of the system PECH–benzene-d$_6$. Two relaxation transitions were discovered in amorphous PECH, and it was shown that the chain conformation in this substance is significantly different from the conformation observed in crystalline, isotactic fractions of this polymer.

To gain some insight into the influence of the dipolar polymer–liquid interactions on the chain dynamics, these studies are extended in this paper to nitromethane-d$_3$ and nitrobenzene-d$_5$ as swelling agents for amorphous PECH. Broad line n.m.r. was used for this study, and in some cases (PECH–nitrobenzene-d$_5$) dielectric relaxation was measured to confirm the results obtained.

EXPERIMENTAL

Sample preparation

An amorphous, acetone-soluble fraction of PECH ($M_n = 140\,000$) synthesized as described by Vanderberg[9] was used. This fraction was shown to be atactic[10], and X-ray amorphous. The molecular weight distribution was unimodal (by g.p.c.).

Swollen samples were prepared by adding a known amount of liquid to a known amount of polymer and homogenizing the system in sealed vials for 48 h at −60°C. Samples containing 45 wt% nitromethane-d$_3$, and 25 wt% and 45 wt% nitrobenzene-d$_5$ were studied.

Measurements

The first derivatives of the broad-line n.m.r. absorption spectra were recorded by using a Varian WL-109 at 30 MHz, the temperature being stabilized by the built-in unit and measured with a Ni–CrNi thermocouple. Line width was measured as the distance between the extrema of the derivatives of absorption lines. The second moment of the spectra ΔH_2^2 was calculated according to ref. 11 as

$$\Delta H_2^2 = \int_{-\infty}^{+\infty} h^2 g(h) \mathrm{d}h$$

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

Correlation times and activation energies were calculated, as previously described[8], from the Arrhenius equation, based upon Smith's paper[12].

Dielectric relaxation was measured by using a three-electrode cell. The samples could be pasted directly over the electrodes because of their good adhesion. Dielectric parameters were measured by a General Radio bridge 1615A, excited by a 1316 generator from the same manufacturer. A selective nanovoltmeter type 233 from Unipan, Poland, was used as the zero inidicator.

RESULTS AND DISCUSSION

The broad line n.m.r. studies of swollen PECH were achieved by cooling the samples to −160°C, elevating the temperature and measuring the spectra at certain temperatures after thermal equilibrium was reached.

The swelling did not cause any significant changes in the shape of n.m.r. lines by comparison with unswollen samples[8], except for a narrowing of the lines. A narrow

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component, an overmodulated and distorted signal, observed over a wide range of temperatures, is due to the residual amounts of low molecular, non-deuterated swelling liquid and/or low molecular impurities. This line was not taken into account when analysing the spectra.

The influence of a low molecular liquid on the molecular mobility of polymer chains in the system polymer–low-molecular liquid causes a decrease in interchain interactions and in most cases lowers the temperatures of relaxation transitions[13–17]. This effect was also observed in benzene-swollen PECH[8]. In some cases, however, the interactions between the polymer and the swelling liquid lead to more complex effects[18–22].

The presence of two polar groups in the PECH chain (–CH_2Cl and C–O–C[4]) justifies the use of nitromethane (dipole moment $\mu = 3.02$ D (ref. 23)) and nitrobenzene (dipole moment $\mu = 4.01$ D (same reference)) as swelling agents.

Second moment of n.m.r. lines

Figures 1, 2 and *3* show the temperature dependence of the second moment of n.m.r. lines in the system PECH–nitromethane, and PECH–nitrobenzene. An analogous function for unswollen PECH is also indicated. Both the line width and the second moment of the lines supply, as far as the present discussion is concerned, the same information; therefore only the second moment will be shown in the rest of this work.

The results indicate that in systems containing 45 wt% nitromethane or nitrobenzene the chains are separated to an extent that practically completely eliminates the interchain interactions. At low temperatures (-160°C) the second moment is 3 G^2 lower (22 G^2 vs. 19 G^2) than in unswollen polymer. As shown previously, on studying the system PECH–benzene[8] this value corresponds to the situation in which the interchain interactions do not contribute significantly to the shape of n.m.r. lines. These conditions are not reached for swelling with 25 wt% nitrobenzene (*Figure 2*). In this system the second moment at -160°C is 19.5 G^2.

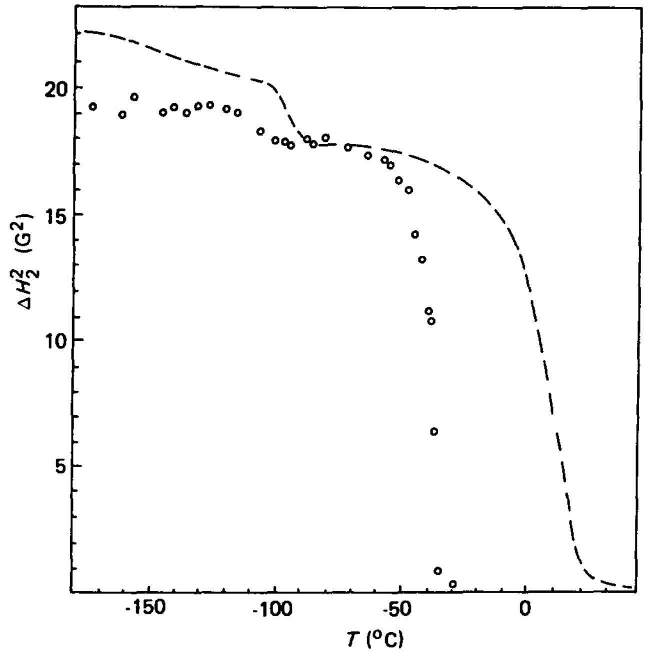

Figure 1 Second moment of the broad line n.m.r. spectra of amorphous poly(epichlorohydrin): ---, unswollen polymer; ○, polymer swollen with 45 wt% nitromethane-d_3

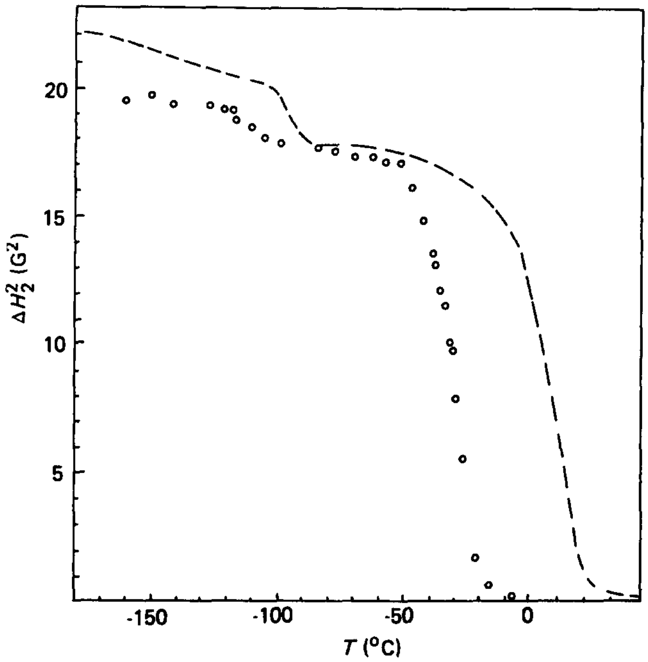

Figure 2 Second moment of the broad line n.m.r. spectra of amorphous poly(epichlorohydrin): ---, unswollen polymer; ○, swollen polymer with 25 wt% nitrobenzene-d_5

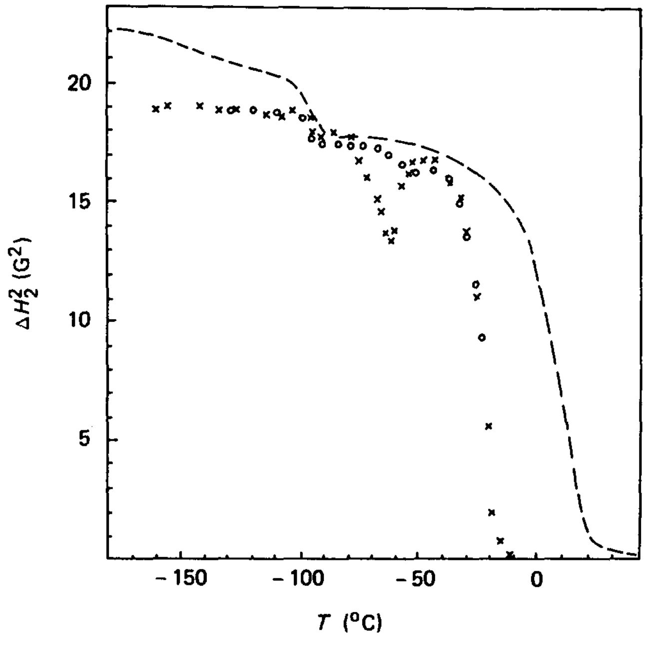

Figure 3 Second moment of the broad line n.m.r. spectra of amorphous poly(epichlorohydrin): ---, unswollen polymer; ×, polymer swollen with 45 wt% nitrobenzene-d_5 (increasing temperature); ○, polymer swollen with 45 wt% nitrobenzene (decreasing temperature)

In all swollen samples a low-temperature β-relaxation is observed, similar to that occurring in unswollen PECH[8]. This transition may be assigned to the onset of mobility of CH_2Cl side groups in the polyether chains[4]. The process depends very strongly on the swelling agent used. For benzene-swollen samples this transition was shifted downwards to -140°C.

Swelling with 45 wt% nitromethane shifts the transition to lower temperatures. It occurs at -118°C, *ca.* 15°C lower than in the unswollen sample. No shift of this transition to lower temperature could be detected, however, for swelling with nitrobenzene: in the system containing 25 wt% nitrobenzene β-transition occurs at -100°C to -115°C, the same temperature as in unswollen polymer. An increase of the nitrobenzene content to 45 wt% makes this transition less significant. The changes of second moment accompanying it are smaller and the transition seems to occur at a slightly higher temperature than is observed in unswollen PECH.

The swelling exercises a strong effect on the mobility of longer chain segments, which leads to the glass transition. In all studied cases swelling shifts the glass transition to lower temperatures. In the system PECH–nitromethane the glass transition is observed at -50°C to -35°C, i.e. 40°C lower than for unswollen PECH.

The swelling with nitrobenzene influences the glass transition temperature in a more complex way. In the sample containing 45 wt% of nitrobenzene T_g occurs at -35°C to -25°C, lower than in unswollen polymer, but almost 10°C higher than in a sample containing 25 wt% of nitrobenzene. A similar effect is observed for activation energies of glass transition: for the sample swollen by 45 wt% nitrobenzene we measured 28 kcal mol^{-1}, but for the sample swollen by 25 wt% nitrobenzene only 16 kcal mol^{-1}.

The above dependence of the transition temperature on the content of the swelling agent that has been discussed suggests the action of two competing effects in these systems. The first effect is the separation of the chains by the swelling liquid, which increases the free volume and lowers the interchain interactions. This effect mobilizes the side groups and chain segments and lowers the transition temperature, as measured for the PECH–benzene system[8].

In the system swollen by a polar liquid there is also another effect, competing with the first, that to some extent hinders the molecular mobility. It may be assumed that it has its source in the dipolar interactions of the polar liquids with chain elements.

The competing action of both effects causes, in the case of the swelling with nitromethane, the β-relaxation to be shifted less toward lower temperatures than for the PECH–benzene system[8]. In the system PECH–nitrobenzene the accumulation of both effects influences very significantly both β- and glass-transition. Although only some of the CH_2Cl side groups may be engaged in dipolar interactions with nitrobenzene, these interactions make the relaxation of these bounded groups more difficult and also hinder the mobility of the CH_2Cl groups not directly involved. The β-transition temperature is not shifted towards lower temperatures (hindered mobility). The decrease of the line width and the second moment accompanying this transition are, in the sample containing 45 wt% nitrobenzene, lower than for unswollen samples (only some of the CH_2Cl groups undergo transition).

Swelling with nitrobenzene leads to an antiplastification of the chains of PECH, observed for the glass transition and known also for other polymer systems[21,22,24]. Its source here may be next to effects described above, the solvation of polar groups in the main chain by nitrobenzene. Dipolar interactions seem to play an important role in the formation of such solvates.

Both the changes of the second moment (*Figure 3*) and of the line width indicate the occurrence of an additional transition in the sample containing 45 wt% nitrobenzene at about -70°C to -50°C. This transition is of a rather unusual character. The following observations characterize the behaviour of the sample in this temperature range.

(a) When the sample is placed in liquid N_2 vapours in the variable temperature probe of the spectrometer, allowed to cool to -160°C (it takes about 1 h) and then heated from -160°C to -50°C at a rate of *ca.* 10°C h^{-1}, a minimum of the second moment (and the linewidth) at -60°C is observed. The second moment falls from *ca.* 17.5 to 13 G^2 to grow again between -60°C and -50°C (*Figure 3*).

(b) While decreasing the temperature from above T_g to -70°C (with the same rate as in (a)) no such minimum is observed (open circles in *Figure 3*). The character of the changes is in this case typical for a relaxation transition.

(c) The process described at (a) is not quasistatic. When the minimum of the second moment is reached at -60°C, as described in (a), and the sample is kept at this temperature, the second moment (and the linewidth) grows slowly to reach, after *ca.* 3 h, the value 16.8 G^2.

(d) Very slow changes of the temperature from low to high (under 1°C/h) yield data, represented by open circles in *Figure 3* (no minimum).

(e) Slow cooling (*ca.* 10°C/h) of the sample from above T_g to below -70°C and subsequent measurements according to (a) lead to a transition shown by the data marked by crosses in *Figure 3*.

All these findings are confirmed by the dielectric relaxation results (see the next section).

The observations (a)–(e) indicate a complex character of the transition at -60°C. No plausible, unequivocal interpretation of these findings can be given at present. A possible rather rough explanation assumes a relaxation process that precedes a kinetic transformation. The relaxation process at this temperature may be due to the onset of the mobility of short chain segments rather than of nitrobenzene-solvated side groups. Since the line narrowing observed at -60°C is rather large, it may be assumed that the kinetic process responsible for this transformation engages a rather large quantity of chain segments and probably leads to a new chain conformation in which the mobility is hindered again (increase of the second moment at -50°C).

Dielectric measurements

The unusual behaviour of the system PECH–nitrobenzene, especially the antiplastification effect and the course of the transition at -60°C, caused us to make dielectric measurements in this system.

Figure 4 shows the changes of the loss factor $\tan\delta$ and of the capacity in the system PECH–nitrobenzene (45 wt%) with increasing temperature (from -140°C to -10°C) and with decreasing temperature (from -10°C to -70°C) at frequencies 10 kHz and 1 kHz. *Figure 5* shows the changes of $\tan\delta$ in the system PECH–nitrobenzene (25 wt% at 1 kHz (temperature increasing from -140°C to -10°C)).

A diffused area of β relaxation is observed in both samples at *ca.* -100°C, similar to that found by n.m.r. (*Figures 2* and *3*). The temperatures of glass transition differ in both samples: T_g in the system containing 25 wt% nitrobenzene occurs *ca.* 10°C lower than in the system with 45 wt% nitrobenzene (compare *Figure 4b* with *5*). This confirms the antiplastification effect in the 45 wt% sample and agrees with n.m.r. data.

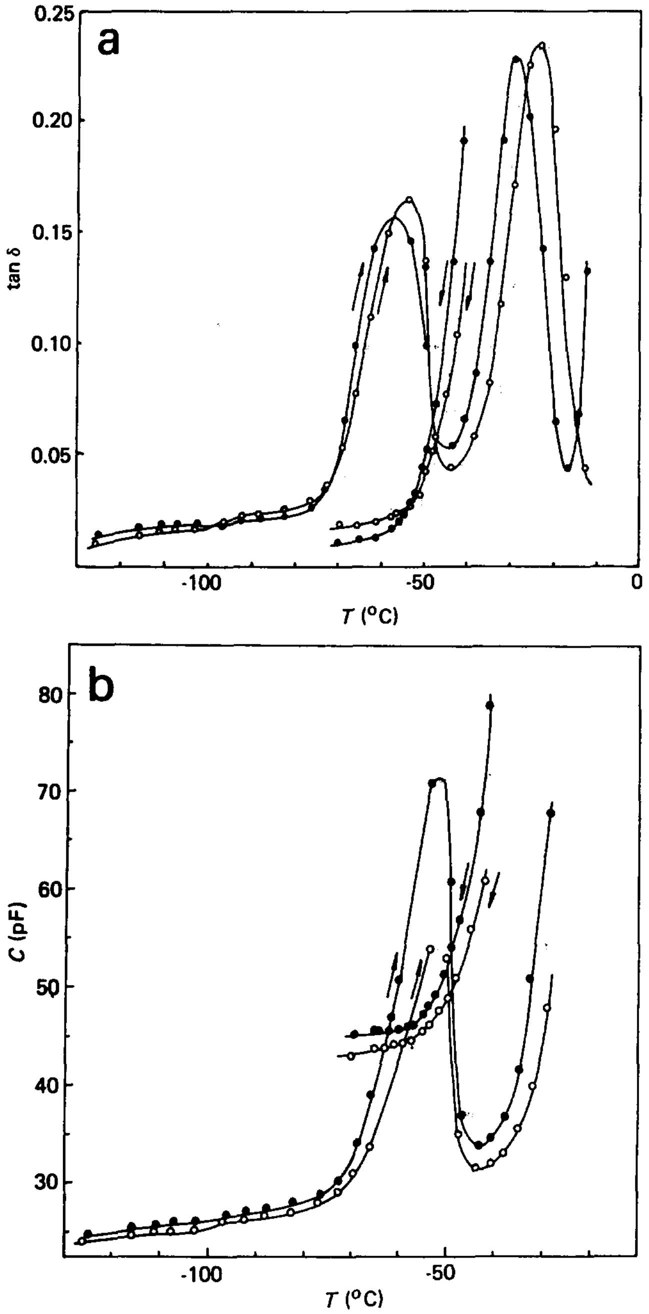

Figure 4 Loss factor tan δ (a) and capacitance (b) of poly(epichlorohydrin) swollen with 45 wt% nitrobenzene-d$_5$ measured at: ○, 10 kHz; ●, 1 kHz. Arrows indicate direction of temperature changes

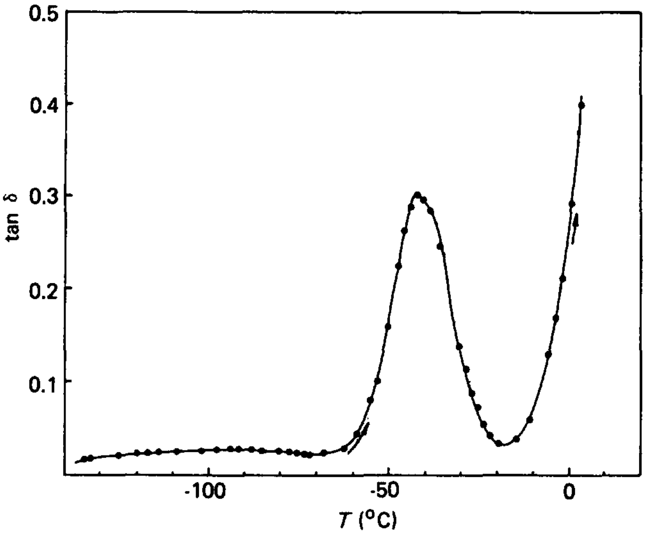

Figure 5 Loss factor tan δ at 1 kHz of poly(epichlorohydrin) swollen with 25 wt% nitrobenzene-d$_6$

The transition observed by n.m.r. at −60°C in the sample swollen by 45 wt% nitrobenzene (*Figure 3*) is also seen at this temperature in dielectric measurements (*Figure 4*). The capacitance runs at this temperature through a maximum whose height decreases with increasing frequency. Similar behaviour, unusual for relaxation transitions, was also observed for annealed polyimides[25]. Both capacitance and tan δ at the maximum decrease when the sample is held at −60°C for a prolonged time, as do the line width and the second moment of the n.m.r. lines. No maximum is observed when the measurements are made while cooling the sample.

All these observations agree well with n.m.r. data and confirm the discussion presented above.

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