

**NMR Study of Molecular Motion in Poly(Ethylene oxide)**

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Proton second moment and spin-lattice relaxation times  $T_1$ ,  $T_2$  and  $T_{1D}$  for helical poly(ethylene oxide) 5000 over a wide temperature range are measured. The results of CW and pulse experiments corroborate the existence of a motional process in the crystalline region of the polymer interpreted as oscillation or rotation of molecules around their helical axes. The activation energy for this type of motion is found to be 12 kcal/mole.

INTRODUCTION

The chain conformation of poly(ethylene oxide) (PEO) with the chemical structure  $[-CH_2CH_2O-]_n$  is known to be helical (7, helix) (MIYAZAWA, 1961, MIYAZAWA et al., 1962). The maximal crystallinity of PEO appears at a molecular weight of about  $10^4$  (ALLEN et al., 1963).

CW NMR (SLICHTER, 1959, HIKICHI and FURUICHI, 1965) as well as dynamic mechanical (McCRUM, 1961, READ, 1962) and dielectric (McCRUM, 1961, ARISAWA et al., 1965) studies of PEO suggested the existence of two different motional processes. That revealed at low temperatures by the appearance of a narrow component in the proton NMR spectra was interpreted as molecular motion in the amorphous region of the polymer. The marked narrowing of the broad component of the NMR line observed at higher temperatures, however, well below the melting point, was assigned to motion in the crystalline region. The existence of two types of motion in PEO has found some confirmation in spin-lattice relaxation studies by CONNOR and HARTLAND (1969). The  $T_1$  measurements performed for PEO 6000 and PEO  $2.8 \times 10^4$  show a nonexponential magnetization decay allowing to obtain two relaxation times assigned to crystalline (longer  $T_1$ ) and amorphous (shorter  $T_1$ ) regions, respectively. Although  $T_1$  minima are observed, no correlation of the broadline transition and relaxation data has been found.

In order to decide conclusively whether the same motional process in the crystalline region is responsible for the broadline transition and spin-lattice relaxation and to determine its activation parameters, we proceeded to temperature measurements of the proton second moment  $M_2$  and spin-lattice relaxation times  $T_1$ ,  $T_2$  and  $T_{1D}$  for identical samples of PEO.

## EXPERIMENTAL

**Material:** The specimen used was commercially available PEO 5000 (SERVA, HEIDELBERG) with melting temperature 332-334 K. Samples were degassed and sealed in glass tubes under vacuum to prevent contact with atmospheric oxygen. Proton magnetic resonance spectra were recorded with a Bloch type RY 2301 (USSR) spectrometer. Spin-lattice relaxation times were measured using a pulse spectrometer constructed in this Laboratory, operating at a Larmor frequency of 25 MHz (PAJAK et al., 1974). Relaxation times  $T_1$  were measured applying  $90^\circ$ - $t$ - $90^\circ$  pulse sequences. Rotating frame data were obtained for a radiofrequency field of  $H_1 = 18.4$  G and 6.4 G, by the spin-locking method (HARTMANN and HAHN, 1962) and dipolar relaxation times were measured using a  $(90^\circ)_x$ - $t$ - $(45^\circ)_y$ - $t$ - $(45^\circ)_y$  pulse sequence (JEENER and BROEKAERT, 1967)<sup>p</sup>.

## RESULTS AND DISCUSSION

The proton magnetic resonance spectra of PEO 5000 recorded at lower temperatures consisted of one broad component. However, above 210 K up to the melting point, they moreover revealed a second narrow component. The temperature dependence of the second moment for the broad component after its separation from the experimental spectra is shown in Fig. 1. A marked decrease in second moment is observed in the temperature range from 273 K up to the melting point. This transition, confirming earlier studies (HIKICHI and FURUICHI, 1965, OLF and PETERLIN, 1966) is attributed to the onset of molecular motion in the crystalline region of the polymer. The activation energy of this motion calculated from the temperature dependence of the second moment (GUTOWSKY and PAKE, 1950) is close to 12 kcal/mole.

Two-phase structure of poly (ethylene oxide) is confirmed by spin-lattice relaxation times measurements. The free induction signal consisting of two components with short and long decay times characterizes the two-phase structure of PEO, composed of crystalline and amorphous regions. Since the intensity of the component with long-time decay was small, only measurements of relaxation times for the short-time decay component were made (with the exception of  $T_{1p}$  measurements in the melting region, where two relaxation times were determined, however, in this case the value of  $T_{1p}$  for the component with long-time decay is close to the  $T_{1p}$  value and one can assume that  $T_{1p}$  describes a relaxation process in the molten part of the polymer). The temperature dependences of the proton relaxation times  $T_1$ ,  $T_{1p}$  and  $T_{1D}$  are shown in Fig. 2. The minima observed for the relaxation times  $T_{1p}$  at 322 K ( $H_1 = 18.4$  G) and 307 K ( $H_1 = 6.4$  G) as well as for  $T_{1D}$  around 293 K (well below the melting point) suggest the existence of molecular motion in the crystalline region and permit the evaluation of the correlation times at temperatures where minima of  $T_{1p}$  occur. Assuming the Arrhenius relation as valid the activation energy of this motion was calculated as equal to 12 kcal/mole. Similar values are obtained from the slopes of  $\log T_{1p}$  vs.  $1/T$  and  $T_{1D}$  vs.  $1/T$ .

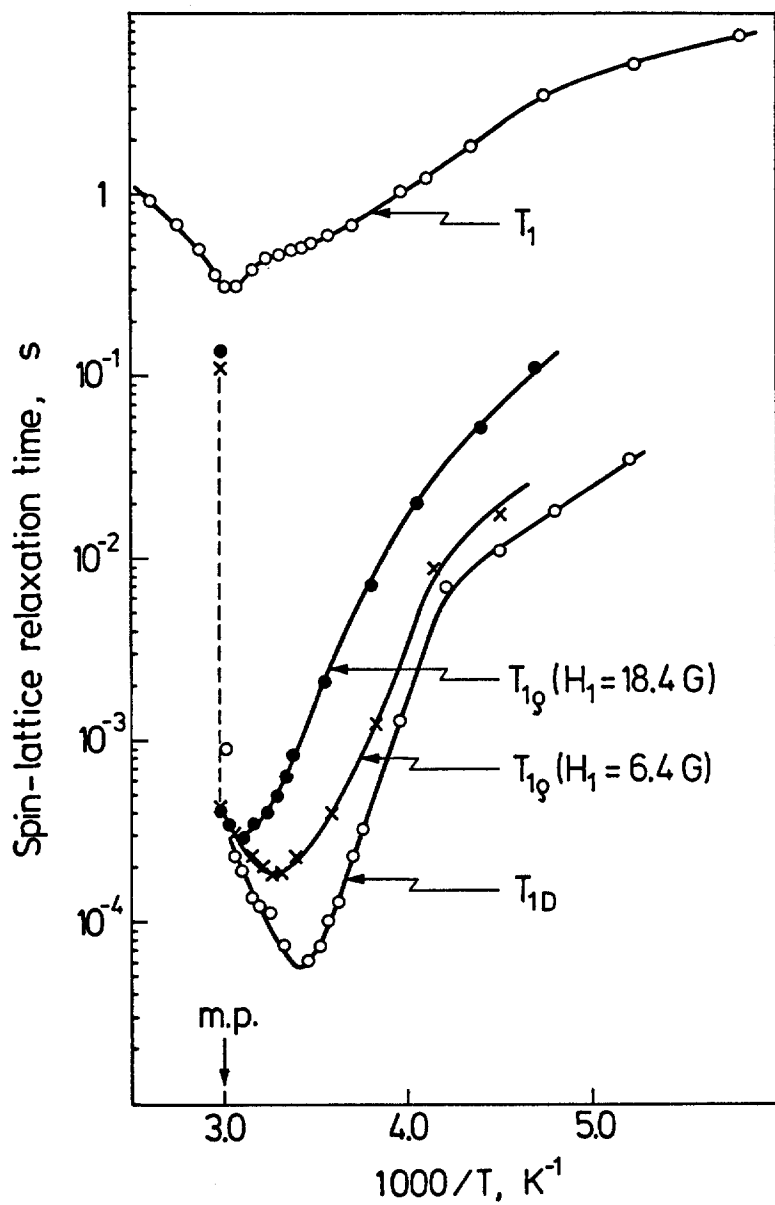


Fig.2. Temperature dependence of  $T_1$ ,  $T_{1\rho}$  and  $T_{1D}$  for PEO 5000

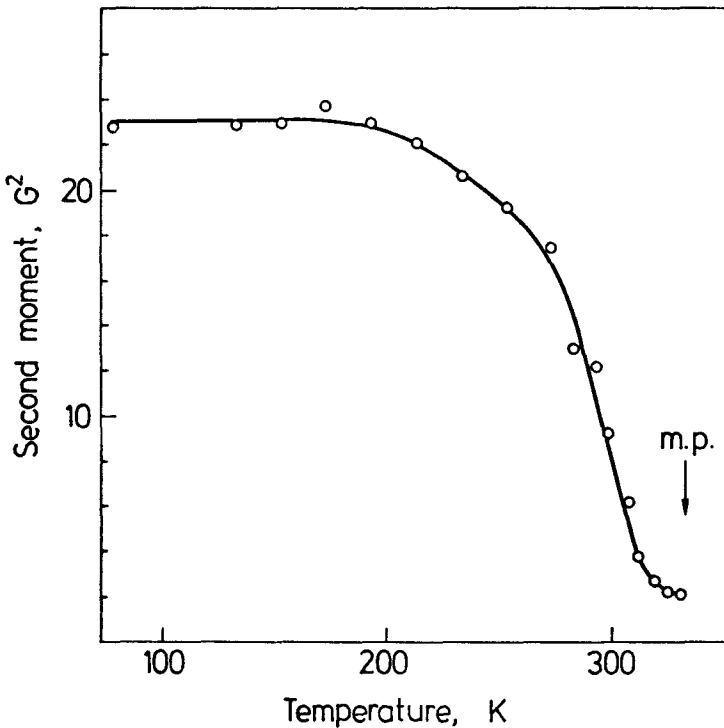


Fig.1: Temperature dependence of  $M_2$  for PEO 5000

A comparison of the temperatures for the second moment transition and spin-lattice relaxation minima leads to the conclusion that the same type of motion is responsible for both the line narrowing as well as  $T_{1p}$  and  $T_{1D}$  relaxation. Good agreement of the activation energies for this motion derived independently from CW and pulse experiments confirms the correctness of our statement. According to earlier CW NMR studies (HIKICHI and FURUICHI, 1965, OLF and PETERLIN, 1966) this motion involves an oscillation or rotation of helical molecules around their axes.

Let us add that the minimum of  $T_1$  observed close to 330 K is due to the melting process (CONNOR and HARTLAND, 1969) rather than to the considered above motion.

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