^{1}H N.m.r. relaxation and molecular motion of polyethylene in solution as studied by the isotopic dilution technique

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The molecular motion of polyethylene has been studied in decalin-d$_{18}$ solution by ^{1}H n.m.r. relaxation with the isotopic dilution technique which can separate the proton spin–lattice relaxation times into the intra- and intermolecular contributions, intra T_1 and inter T_1. The temperature dependences of intra and inter T_1s show that the intra- and intermolecular motions are in the extreme narrow region. These results, also, were compared with the results of molten polyethylene reported in our previous work.

Keywords Molecules; motion; polyethylene; isotopic dilution; nuclear magnetic resonance; relaxation

INTRODUCTION

The segmental motion of a polymer chain in concentrated solution and melt consists of several components, such as micro-Brownian motion, rotation about a main chain and diffusion etc., and is also affected by the surrounding molecules. However, the overlapping of these different motions makes it difficult to understand the details of chain dynamics. If these different kinds of motion can be experimentally separated quantitatively, the mechanism of chain dynamics can be understood.

For this purpose, n.m.r. relaxation has provided useful information on molecular motion of a polymer chain[1]. The isotopic dilution technique in n.m.r. relaxation is useful because it eliminates the proton–proton dipolar interaction between protons at neighbouring polymer chains and simplifies the behaviour in n.m.r. relaxation in molten polyethylene (PE) put forward by the present authors[2] and Collignon and Sillescu[3], which separated the ^{1}H intra- and inter-spin–lattice relaxation time (T_1) of a protonated PE chain by dilution of PE with fully deuterated polyethylene (DPE). This technique makes it possible to discuss slower modes of polymer motion by means of the separation of intra and inter T_1's, although such slower modes of motion do not effectively contribute to T_1.

The isotopic dilution technique is a useful technique of separating both contributions of intra- and intermolecular magnetic dipole–dipole interactions to T_1[4–12]. The observed spin–lattice relaxation rate, $(1/T_1)$, is usually made up from the intra- and intermolecular interactions as follows

$$\frac{1}{(T_1)_{\rm obs}} = \frac{1}{(T_1)_{\rm intra}} + \frac{1}{(T_1)_{\rm inter}} \qquad (1)$$

where $(T_1)_{\rm obs}$ is the observed T_1 and $(T_1)_{\rm intra}$ and $(T_1)_{\rm inter}$ are the intra and inter T_1's, respectively. On dilution of protonated polymer with a deuterated one, the intermolecular H–H interaction is replaced by the very small H–D interaction, which makes $1/(T_1)_{\rm inter}$ small. As $1/(T_1)_{\rm inter}$ can be negligible in the limit of infinite deuterium dilution, observed T_1 can be interpreted as intra T_1, which has information about the motion of an individual protonated polymer chain in surrounding molecules such as concentrated solution of melt. Then, the inter T_1 can be obtained by the following equation.

$$\frac{1}{(T_1{}^1)_{\rm inter}} = \frac{1}{(T_1)_{\rm obs}} - \frac{1}{(T_1)_{\rm intra}} \qquad (2)$$

The purpose of this work is to determine the ^{1}H intra and inter T_1's of a PE chain by the isotopic dilution technique and to discuss the molecular motion of a PE chain in concentrated solution compared with that in melt.

EXPERIMENTAL

Sample preparation

Isotopic mixtures of high density PE ($M_w = 8.7 \times 10^4$, $M_w/M_n = 10.3$) obtained from Rubber and Plastics Association and DPE ($M_w = 3.0 \times 10^5$, $M_w/M_n = 2.78$. 90 at% D) obtained from Merck Co. were prepared by reprecipitation from p-xylene solution by adding

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0032–3861/82/040598–03$03.00

Table 1 Observed ^1H T_1's of PE in solution as functions of temperature and X_d

T_1	X_d	Temperature (°C)							
		94	103	112	121	130	139	148	158
T_1 (s)	0	1.05	1.15	1.30	1.50	1.59	1.73	1.88	2.02
	0.2	1.11	1.24	1.38	1.51	1.70	1.80	1.98	2.20
	0.4	1.17	1.30	1.34	1.51	1.77	1.93	2.10	2.11
	0.6	1.27	1.38	1.51	1.69	1.85	2.00	2.16	2.26
	0.8	1.38	1.41	1.60	1.70	1.90	2.01	2.20	2.25
Extrapolated intra T_1 (s)	1.0	1.35	1.48	1.64	1.80	1.93	2.12	2.26	2.43
Inter T_1 (s)		4.73	5.22	6.32	9.00	8.84	9.46	11.11	12.04

Table 2 Apparent activation energies, E_a, obtained from the plots of intra and inter T_1's against temperature

Nucleus	E_a (kJ mol^{-1})
^1H (intra)	12.13
^1H (inter)	21.17
^{13}C	11.55

methanol, and dried in vacuum. The weight fractions of DPE, X_d (=DPE/(DPE+PE)), were 0.0, 0.2, 0.4, 0.6 and 0.8. The solutions were obtained by adding the reprecipitated sample to fully-deuterated decalin-d$_{18}$ (obtained from Merck Co.) placed in the n.m.r. sample tube. Every sample tube was sealed under nitrogen atmosphere after degassing.

N.m.r. measurement

Proton and ^{13}C T_1 values were measured at 100°–170°C with a JEOL JNM PS-100 NMR spectrometer equipped with the PFT-100 Fourier transform system operating at resonance frequencies of 100 MHz for proton and 25.15 MHz for ^{13}C nucleus using the inversion recovery method. The 90° r.f. pulse used was 20.5 μs duration in most cases. The pulse repetition time was 10 s and equal to approximately five times the measured T_1.

RESULTS AND DISCUSSION

The temperature dependence of proton T_1 of PE samples in 20% w/v decalin-d$_{18}$ solution is listed as a function of X_d in *Table 1*. ^1H T_1 values increase with increasing temperature. According to BPP theory[13], the behaviour of these T_1's suggests that the motion of a reference site is fast compared with the measurement frequency. Further, *Table 1* shows that the T_1 values of protonated PE increase with dilution by deuterated PE at each temperature (the inverse of T_1 decreases linearly with dilution). A deuterium of deuterated PE should be about fifty times less effective than a hydrogen of protonated PE in promoting the relaxation of neighbouring hydrogen nuclei due to the smaller gyromagnetic ratio of deuterium. Thus, the above observed facts verify the view that the contribution of intermolecular interaction to ^1H T_1 decreases upon the addition of deuterated PE. ^1H intra T_1 values are determined by extrapolating the inverse T_1's to infinite deuterium dilution, namely $X_d = 1$, where each protonated PE chain can be assumed to be surrounded by deuterated PE chains. However, the inter T_1 values can be estimated from the difference between T_1 values at $X_d = 0$ and $X_d = 1$ using the following relation.

$$(T_1)^{-1}_{\mathrm{obs}} = (T_1)^{-1}_{\mathrm{inter}}(1 - X_d) + (T_1)^{-1}_{\mathrm{intra}} \tag{3}$$

The temperature dependence of intra T_1's of PE in solution obtained using equation (3) is shown in *Table 1*. The intra T_1 values increase with increasing temperature within the range of measurement temperature. The segmental motion of the backbone of a polymer which controls intra T_1 is in the extreme narrow region. It is convenient to discuss the degree of freedom in the segmental motion in terms of the apparent activation energy E_a, estimated from an Arrhenius plot of intra T_1 against temperature. The E_a values are listed in *Table 2*, compared with those in melt. The value in solution is somewhat lower than that in melt (17.93 kJ mol^{-1}). This supports the view that mobility in solution is higher than in melt. There are two principal factors controlling the rate of conformational transition in short segments, which lead to the interpretation of local mode magnetic relaxation. One of them is the intramolecular bond rotational potential energies and another is viscous forces hindering the segmental motion through the medium or the effect of entanglement. The activation energy of the intramolecular motion obtained from ^{13}C T_1's is nearly equal to the above value. This supports the view that the intra T_1's obtained from the isotopic dilution technique are reasonable.

The temperature dependence of inter T_1's of PE obtained using equation (3) is shown in *Table 1*. The inter T_1 data increase with increasing temperature. This indicates that the motion fulfils the extreme narrow case, namely, the corresponding motion to the inter T_1 in the system is very rapid compared with the molten PE case in which the inter T_1's in melt decrease with increasing temperature. The inter T_1 arises from fluctuations in the local field caused by relative translation of a polymer segment in different chains. Thus, the chains in molten PE approach closely with each other including entanglement so that the translation of the chain segments would be highly restricted and is in the slow molecular motion retion. In solution such restraint for molecular motion is diminished and therefore the motion becomes very rapid. However, the activation energy of intermolecular motion supports the above suggestion. In solution the E_a value is 21.17 kJ mol^{-1}, while that in melt is 50.90 kJ mol^{-1}. This indicates that intermolecular motion in the former is more rapid compared with that in the latter. The large decrease of activation energy in intermolecular motion between solution and melt compared with that in in intramolecular motion supports the idea that the addition of solvents has a great influence on the intermolecular motion.

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