Further, the relative orientation of the diffraction pattern with respect to the field is such that the molecular chains must either be parallel or perpendicular to the long axes of these crystals; the latter is assumed here, implying that the dipole vectors are then parallel to these long axes. The (200) planes are among the most densely packed in β-PVF$_2$; in common with the situation in other polymers[13], it is these densely packed planes that are nucleated by the substrate.

From *Figure 1*, *b* appears to be the preferred growth direction of these essentially two-dimensional crystals of β-PVF$_2$; this agrees with the radial growth direction of polyethylene with which β-PVF$_2$ shares a great similarity in unit-cell structure. However, if such were the case also in three-dimensional crystals, β-PVF$_2$ would differ from the α and γ polymorphs, since there the dipole vectors are normal to the radial growth direction[7]. However, it is probable that the preferred growth direction in three-dimensional crystals of the β phase is *a*, which happens to be restricted by the thinness of the sample; this would then make the radial orientation of unit cells and dipole vectors consistent among the α-, β-, and γ-polymorphs of PVF$_2$ (note that the *a*- and *b*-axial designations are reversed in β-PVF$_2$ from their assignments in the α and γ forms).

Investigations of the morphology and temperature-dependence of melt-grown β crystals are continuing.

REFERENCES

1 Hasegawa, R., Takahashi, Y., Chatani, Y. and Tadokoro, H. *Polym. J.* 1972, **3**, 600

2 Miller, R. L. and Raisoni, J. *J. Polym. Sci. (Polym. Phys. Edn)* 1976, **14**, 2325

3 Scheinbeim, J., Nakafuku, C., Newman, B. A. and Pae, K. D. *J. Appl. Phys.* 1979, **50**, 4399.

4 Lando, J. B. and Doll, W. W. *J. Macromol. Sci. (B)* 1968, **2**, 205

5 Farmer, B. L., Hopfinger, A. J. and Lando, J. B. *J. Appl. Phys.* 1972, **43**, 4293

6 Prest, W. M. Jr, and Luca, D. J. *J. Appl. Phys.* 1975, **46**, 4136

7 Lovinger, A. J. *J. Polym. Sci. (Polym. Phys. Edn)* 1980, **18**, 793

8 Morra, B. S. and Stein, R. S. *J. Polym. Sci. (Polym. Phys. Edn)* in press

9 Willems, J. and Willems, I. *Experientia* 1957, **13**, 465

10 Fischer, E. W. *Kolloid Z.* 1958, **159**, 108

11 Balik, C. M., Farmer, R. and Baer, E. *J. Mater. Sci.* 1979, **14**, 1511

12 Lovinger, A. J. and Keith, H. D. *Macromolecules* 1979, **12**, 919

13 Lovinger, A. J. *Polym. Prepr.* 1980, **21**, 253

Proton n.m.r. relaxation and molecular motion of liquid n-paraffin $C_{32}H_{66}$ as studied by isotopic dilution

Isao Ando

Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan

and Kazuo Sato

Central Research Laboratory, Idemitsu Kosan Co., Sodegaura-cho, Kimitsu, Chiba, Japan

(*Received* 22 *September* 1980; *revised* 18 *November* 1980)

INTRODUCTION

The proton spin-lattice relaxation time, T_1, gives useful information about the molecular motion of macromolecules[1]. However, there is some difficulty in understanding the mechanism of T_1 of macromolecules in concentrated solution and melt because of the effects of chain entangling. The isotopic dilution technique[2-11] is useful to overcome such problems, because it eliminates the proton–proton dipolar interaction on neighbouring polymer chains thus enabling the determination of the intramolecular and intermolecular T_1's by dilution of a molecule considered with a fully-deuterated analogue.

We have successfully applied this technique to the understanding of the mechanism of molecular motion of polyethylene (PE)[10,11]. In molten PE the molecular motion which contributes to intramolecular T_1, is in the extreme narrow region, $\omega\tau_c \ll 1$, however, the molecular motion contributing to intermolecular T_1 is in the slow motional region, $\omega\tau_c > 1$, where ω is the resonance frequency and τ_c is the correlation time. The intermolecular T_1 was influenced by the effect of chain entangling. In order to clarify this effect, liquid n-paraffin may be compared with PE, because the effect of chain entangling depends considerably on the chain length of the molecule considered.

The purpose of this work is to separate the observed proton T_1 of liquid n-paraffin, n-$C_{32}H_{66}$, into intra- and intermolecular contributions by the isotopic dilution technique, and to discuss the molecular motion of this molecule as compared with molten PE which we have reported in a previous paper[10].

ISOTOPIC DILUTION TECHNIQUE

The observed proton spin-lattice relaxation rate, $(1/T_1)_{\mathrm{obs}}$, is given by the sum of the following terms.

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

where $(1/T_1)_{\mathrm{intra}}$ and $(1/T_1)_{\mathrm{inter}}$ are the intra- and intermolecular relaxation rates respectively. The intramolecular relaxation depends on the segmental motions of the molecule whereas the intermolecular relaxation depends on the relative translational motions of different molecules. The general expressions for these contributions are given by Gutowsky and Woessner[12] as

$$\left(\frac{1}{T_{1_i}}\right)_{\mathrm{intra}} = \frac{2\pi\hbar^2\gamma^2\eta a}{3kT}\left(3\gamma_i^2\sum_j r_{ij}^{-6} + 2\sum_f^{*}\gamma_f^2 r_{if}^{-6}\right) \qquad (2a)$$

0032-3861/81/030413-03$02.00

$$\left(\frac{1}{T_{1_i}}\right)_{\text{inter}}=\frac{\pi^2\mathrm{h}^2\gamma_i^2\eta N_0 a}{kT}\left(3\gamma_i^2\sum_j r_{ij}^{\circ\,-1}+2\sum_f^{*}\gamma_f^2 r_{if}^{\circ\,-1}\right) \tag{2b}$$

where the summations $\sum_j$ are over nuclei of the same species and $\sum_f$ over all others. In equation (2a) the summations are over nuclei in the same molecule considered and in equation (2b) they are over nuclei of neighbouring molecules. r_{ij}° is the mean value of proton–proton distance, r_{ij}, belonging to different molecules. η is the viscosity, a the molecular radiusm N_0 the number of molecules per unit volume and T the absolute temperature. In this work the second term in equation (2a) is not applicable. Also the second term in equation (2b) may be neglected, since dipolar interaction between proton and deuterium is considerably smaller than that between protons, and the ratio of these interactions is given by

$$\frac{2\mu_D^2}{3\mu_H^2}\cdot\frac{I_D+1}{I_D}\cdot\frac{I_H}{I_H+1}=0.042 \tag{3}$$

where μ_x is the magnetic dipole moment of nucleus x and I_x the spin quantum number. Although equations (2a) and (2b) are approximate, significant information about the molecular motion of the molecule under consideration may be provided by determination of intra- and intermolecular T_1's together with the knowledge of other physical properties such as viscosity.

EXPERIMENTAL

Isotopic mixtures of n-$C_{32}H_{65}$ (from Tokyo Kasai Co.) and deuterated n-$C_{32}H_{66}$ (from Merk Co.) were prepared by a co-melting procedure. The weight fractions of n-$C_{32}D_{66}$, x_d = n-$C_{32}D_{66}$/(n-$C_{32}D_{66}$ + n-$C_{32}H_{66}$) were 0.0, 0.2, 0.4, 0.5, 0.7 and 0.9.

When a molten sample was prepared, it was placed in n.m.r. sample tubes of 2 mm outer diameter, and subjected to pumping, repeated freezing and melting. Finally, the sample tube was sealed off.

Proton T_1 values were measured at 98.5 to 165.2°C with a JEOL JNM PS-100 n.m.r. spectrometer equipped with the PFT-100 Fourier transform system operating at a resonance frequency of 100 MHz using the inversion recovery method with an accumulation of 50 scans. The 90° pulse was 20.1 μs duration. The pulse repetition time was 20 s which is five times greater than the measured T_1. The T_1 values were determined by least squares analysis of time-dependent peak intensities and were reproducible to 5–10%. *NOE*'s for $^{13}CH_2$ carbons were measured at 99 to 165°C with a JEOL FX-60 n.m.r. spectrometer operating at resonance frequency of 15.15 MHz using the gated decoupling method.

RESULTS AND DISCUSSION

The T_1^{-1} data of n-$C_{32}H_{66}$ are shown in *Table 1* as a function of x_d at each temperature. The T_1^{-1} values decrease linearly as x_d increases at each temperature. This suggests that the effect of the intermolecular interaction on T_1^{-1} decreases with increase in x_d. Also, the T_1^{-1} values decrease with increasing temperature at each x_d. This apparent behaviour of T_1^{-1} suggests that the molecular motion is in the extreme narrow region[13]. Also, maximum *NOE*'s of $^{13}CH_2$ carbons are observed for all temperatures within experimental error, and thus the molecular motion is in the extreme narrow region. However, in order to discuss the details of the molecular motion in the system, the observed relaxation rate should be separated into intra- and intermolecular T_1^{-1} contributions.

Extrapolation of the observed T_1^{-1} to $x_d = 1$ gives intramolecular T_1^{-1}. However, the intermolecular T_1^{-1} can be obtained from equation (1) using known values of observed T_1^{-1} and intramolecular T_1^{-1}. The intra- and intermolecular T_1 values obtained from a set of the observed data shown in *Table 1* are listed in *Table 2*. The intra- and intermolecular contributions decrease linearly with increasing $1/T$. Thus, both the intra- and intermolecular motions are in the extreme narrow region. In the intra T_1 case, the numerical values are near to those of molten PE at corresponding temperatures. However, the sign of the slope of the temperature dependence of the inter T_1's for both the samples are different from each other.

The slope of the plots of log $(1/T_1)$ against $1/T$ provides the activation energy, E_a, of the corresponding molecular motion. The values of activation energy for the intra- and intermolecular motions are 13.15 and 25.12 kJ mol^{-1}, respectively. The E_a value for the former is slightly smaller compared with that of molten PE, 17.93 kJ mol^{-1}, which we have reported previously, but they are close to each other. Therefore, the intramolecular motion which corresponds mainly to the segmental motion is not sensitive to chain length. Woessner *et al.*[14] have obtained an activation energy of 15.24 kJ mol^{-1} for the intramolecular motion of n-dodecane (n-$C_{12}H_{26}$) using the isotopic dilution technique together with an automatic data acquisition system. This value is near to that of n-$C_{32}H_{66}$. However, the E_a value of the intermolecular motion of the molecule considered is much smaller than that of molten

Table 1 Temperature dependence of observed proton T_1 of n–$C_{32}H_{66}$ as a function of x_d

Temperature (°C)	T_1 (s)					
x_d =	0.0	0.2	0.4	0.5	0.7	0.9
98.5	1.058	1.176	1.282	1.351	1.492	1.613
111.3	1.205	1.333	1.471	1.562	1.724	1.852
120.2	1.381	1.510	1.664	1.765	1.962	2.096
135.7	1.639	1.818	1.980	2.074	2.281	2.464
165.2	2.222	2.326	2.500	2.564	2.778	3.030

Table 2 Temperature dependence of intramolecular- and intermolecular-T_1's determined by isotopic dilution

Temperature (°C)	T_1 (s) intra-T_1	 inter-T_1
98.5	1.636	2.236
111.3	1.912	3.257
120.2	2.127	3.937
135.7	2.532	4.740
165.2	3.125	7.692

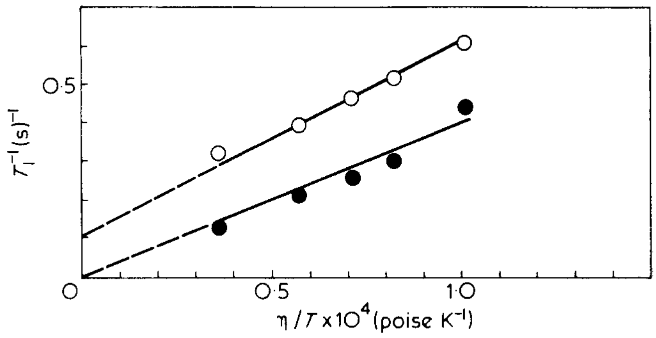

Figure 1 Dependence of proton T_1^{-1} of n–$C_{32}H_{66}$ as a function of η/T. Intramolecular-T_1 (○); intermolecular-T_1 (●)

PE, $E_a = 59.5$ kJ mol^{-1}. This means that the effect of entanglement on the molecular motion is smaller when compared with the case of molten PE.

According to equations (2a) and (2b), the rates of both translational and segmental motions are proportional to the η/T and the distance terms. In order to investigate the relationship between the molecular motions and the viscosity on molecular surroundings, the values of $1/T_1$ are plotted against η/T as shown in *Figure 1* where the values of η/T for n-$C_{32}H_{66}$ reported by Porter *et al.*[15] were used. The rates of both intra- and intermolecular T_1's increase linearly with increasing η/T. The positive sign of the slope of their straight lines comes from the increase in the distance between the protons in the same molecule or the protons in neighbouring molecules with increasing temperature. The value of intermolecular T_1^{-1} extrapolated to $\eta/T = 0$ is zero and that of intramolecular T_1^{-1} extrapolated to $\eta/T = 0$ deviates from zero. These values suggest that the intermolecular T_1 behaviour follows equation (2b), and the translational motion is isotropic and the effect of chain entangling can be neglected.

REFERENCES

1 (a) McCall, D. W., Douglass, D. C. and Anderson, E. W. *J. Polym. Sci.* 1962, **59**, 309;
(b) McBriety, V. J. *Polymer* 1974, **15**, 503;
(c) Folland, R. and Charlesby, A. *Radiat. Phys. Chem.* 1977, **10**, 61;
(d) Heatley, F. and Wood, B. *Polymer* 1978, **19**, 1405;
(e) Heatley, F. *Prog. NMR Spec.* 1979, **13**, 47
2 Bergmann, K. *J. Polym. Sci. Polym. Phys. Edn* 1968, **16**, 1611
3 Lee, A. G., Birdsall, N. J. M. and Metcalfe, J. C. *Biochemistry* 1973, **12**, 1650
4 Seiter, C. H. A. and Chan, S. I. *J. Am. Chem. Soc.* 1973, **95**, 7541
5 Natrajan, K. M., Samulski, E. T. and Cukier, R. I. *Nature* 1978, **275**, 527
6 Kroon, P. A., Kainosho, M. and Shan, S. I. *Biochem. Biophys. Acta* 1976, **433**, 282
7 Kimmich, R. and Voigt, G. *Z. Naturforsch.* 1978, **33A**, 1294
8 Kimmich, R. and Voigt, G. *Chem. Phys. Lett.* 1979, **62**, 181
9 Voelkel, R. and Sillescu, H. *J. Magn. Reson.* 1979, **34**, 559
10 Morita, M., Ando, I., Nishioka, A., Sato, K. and Suzuki, S. *J. Polym. Sci. Polym. Lett. Edn* 1980, **18**, 109
11 Ando, I., Morita, M., Nishioka, A. and Sato, K. to be submitted
12 Gutowsky, H. S. and Woessner, D. E. *Phys. Rev.* 1956, **104**, 843
13 Bloembergen, N., Purcell, E. M. and Pound, R. V. *Phys. Rev.* 1948, **73**, 679
14 Woessner, D. E., Snowden Jr., B. S., McKay, R. A. and Strom, E. T. *J. Magn. Reson.* 1969, **1**, 105
15 Porter, R. S. and Johnson, J. F. *J. Appl. Polym. Sci.* 1960, **3**, 194

Hydrogen ion equilibria in poly(methacrylic acid) and poly(ethacrylic acid) solutions

Desmond E. Joyce and Tomas Kurucsev
Department of Physical and Inorganic Chemistry, The University of Adelaide, Adelaide, South Australia 5001
(*Received* 29 *April* 1980)

INTRODUCTION

We described recently, results on hydrogen ion equilibria of weakly basic cationic polysoaps in their aqueous solution[1]. We have shown that the concept of hydrophobic interactions may be used effectively in the construction of feasible models to aid interpretation of experimental data obtained at different temperatures. Anomalous titration curves for poly(methacrylic acid), PMA, compared with poly(acrylic acid), PAA, in aqueous solution, have also been explained by invoking the hydrophobic effect[2-4], which results in the formation of a compact globular state for PMA at low degrees of ionization. Further support for this interpretation appears to be provided by a recent report concerning aqueous solutions of poly(ethacrylic acid), PEA[5].

In this work we determined the effect of temperature on the titration behaviour of the polyacids. Our primary aim has been to ascertain whether or not these materials are suitable for extending our previous work and conclusions concerned with the basicity of hydrophobic weak polyelectrolytes.

EXPERIMENTAL

Materials

The poly(acrylic acid) sample was obtained from Aldrich Chemical Co. (average molecular weight of 250 000). Poly(methacrylic acid) was prepared by polymerization of methacrylic acid in aqueious solution using benzoyl peroxide as initiator. The polymer was recovered from solution by precipitation with hydrochloric acid and by drying *in vacuo*. Ethacrylic acid was prepared according to the method of Böhme and Teltz[6]; it was polymerized in 5% aqueous solution using the intiator asobisisobutarymidine hydrochloride at about $\frac{1}{2}$% w/w of monomer. After approximately 12 h at 50–60°C a milky suspension was evident; the reaction mixture was kept in this temperature range for a further 2 days. Small molecular weight material was then removed by exhaustive dialysis against water.

Potentiometric titrations

An EIL Model 7050 pH meter (Electronics Instruments

0032-3861/81/030415-03$02.00