(24) Yoshimura, M.; Nogami, T.; Yokoyama, M.; Mikawa, H.; Shirota, Y. *Macromolecules* **1976**, *9*, 211.
(25) Yoshimura, M.; Mikawa, H.; Shirota, Y. *Macromolecules* **1978**, *11*, 1085.
(26) Shirota, Y.; Takemura, K.; Mikawa, H.; Kawamura, T.; Matsuzaki, K. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 913.
(27) Jiang, G.-J.; Shirota, Y.; Mikawa, H. *Polym. Bull.* **1985**, *14*, 447.
(28) Yokoyama, M.; Tamamura, T.; Atsumi, M.; Yoshimura, M.; Shirota, Y.; Mikawa, H. *Macromolecules* **1975**, *8*, 102.
(29) Fox, R. B.; Price, T. R.; Cozzens, R. F.; Echols, W. H. *Macromolecules* **1974**, *7*, 937.
(30) Vala, Jr.; M. T., Haebig, J.; Rice, S. A. *J. Chem. Phys.* **1965**, *43*, 886.
(31) Yabumoto, S.; Ishii, K.; Arita, K. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 1577.
(32) Srivastava, A. K.; Mathur, G. N. *Polymer* **1982**, *23*, 20.
(33) Phillips, D., Ed. *Polymer Photophysics*; Chapman and Hall: New York, 1985.
(34) Fox, R. B.; Price, T. R.; Cozzens, R. F.; McDonald, J. R. *J. Chem. Phys.* **1972**, *57*, 534.
(35) David, C.; Piens, M.; Gueskens, G. *Eur. Polym. J.* **1972**, *8*, 1019.
(36) Somersall, A. C.; Guillet, J. E. *Macromolecules* **1973**, *6*, 218.
(37) Kyle, B. R. M.; Kilp, T. *Polymer* **1984**, *25*, 989.
(38) Reid, R. F.; Soutar, I. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 153.
(39) Harwood, H. J.; Ritchey, W. M. *J. Polym. Sci., Polym. Lett. Ed.* **1964**, *2*, 601.
(40) Arita, K.; Ohtomo, T.; Tsurumi, Y. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 211.
(41) Kuran, W.; Pasynkiewicz, S.; Nadir, R. *Makromol. Chem.* **1977**, *178*, 411.

^{13}C Spin-Lattice Relaxation and Chain Local Motions of Poly(β-hydroxybutyrate) in Tetrachloroethane Solution

Photis Dais*

Department of Chemistry, University of Crete, P.O. Box 1470, 71110 Iraklion, Crete, Greece

Maria Elena Nedea, F. G. Morin, and R. H. Marchessault*

Department of Chemistry, McGill University, 3420 University Street, Montreal, Quebec, Canada. *Received January 17, 1989; Revised Manuscript Received April 5, 1989*

ABSTRACT: Carbon-13 spin-lattice relaxation times and NOE factors were measured as a function of temperature in two magnetic fields for poly(β-hydroxybutyrate) in 1,1,2,2-tetrachloroethane-d_2. The relaxation data were interpreted in terms of chain segmental motion and methyl internal rotation by using the sharp cutoff model of Jones and Stockmayer (JS) and the Hall-Weber-Helfand (HWH) correlation function. Both models describe in a satisfactory and comparable manner the chain local motions of PHB resulting in approximately similar correlation times (1×10^{-10} s at 20 °C) and activation energy (22 kJ/mol) for cooperative segmental motions in the chain. They differ, however, in the time scale of methyl motion, which was found to be about 3-4 times faster with the JS description as compared to that using the HWH model, although both models give a comparable activation energy for methyl rotation. The latter motion is relatively fast and comparable to that observed in small and medium sized molecules in solution. The present results indicate that type 2 short-range motion, according to Helfand's terminology, is likely to occur in the PHB chain.

Introduction

Determination of ^{13}C relaxation parameters has proven to be a very powerful tool for elucidating the nature of local motions of polymer chains in solution. A number of models have been developed[1] for interpretation of nuclear spin relaxation data. Among these, the three-bond jump model of Jones and Stockmayer[2] (JS) and that of Hall, Weber, and Helfand[3,4] (HWH) have proven to be successful in describing polymer dynamics in solution. Both models will be used to describe the segmental mobility of a high molecular weight sample of the optically active poly(β-hydroxybutyrate), PHB (1), in 1,1,2,2-tetrachloroethane-d_2

$$[-OCH(CH_3)CH_2C(=O)-]_n$$

1

(TCE) solvent. On the basis of the present relaxation data, comparison of the two models will be made as well in terms of their ability to describe local motions in the PHB chain.

Experimental Section

The PHB sample used in this study was obtained from ICI Agricultural Division, Billingham, U.K. The weight-average molecular weight of the PHB sample (M_w = 400 000 g/mol) was determined by the relation[5]

$$[\eta] = 7.7 \times 10^{-5} M_w^{0.82} \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity in chloroform at 30 °C. The latter quantity of PHB in TCE solution was determined by using a Cannon-Ubbelohde type dilution viscometer. The intrinsic viscosity and Huggins constant, k', in eq 2 were found to be 0.685

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \qquad (2)$$

dL/g and 1.72, respectively. ^{13}C nuclear magnetic resonance experiments were conducted on Varian XL-200 and XL-300 spectrometers operating at 50.3 and 75.4 MHz for the carbon nucleus. The temperature was controlled to within ±0.1 °C by means of a precalibrated copper-constantan thermocouple in the probe insert. The relaxation times were measured by the standard inversion recovery technique with a repetition time longer than $5T_1$. A total of 100-200 acquisitions were accumulated for each set of 11-15 "arrayed" τ values. Values of T_1 were determined by a three-parameter nonlinear procedure with a rms error of ±5% or better. The experiments were repeated until reproducibility of the data was better than ±5%. ^{13}C NOE experiments were carried out by gated decoupling, at least three experiments being performed for each temperature value. Delays of at least 10 times the longest T_1 were used between 90° pulses. Samples of PHB, 6% (w/v) in TCE-d_2, were degassed by bubbling with nitrogen gas for 2 min before use. Nevertheless, measurements with undegassed samples did not show any measurable change in the T_1 and NOE values relative to those of degassed samples.

Results and Discussion

Table I summarizes the ^{13}C T_1 values and NOE factors for the protonated carbons of PHB as a function of temperature in two magnetic fields. As can be seen in Figure 1, the T_1 values of the backbone carbons change monotonically in both fields over the whole temperature range measured and they increase with increasing magnetic field.

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* Authors to whom correspondence should be addressed.

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Table I
Carbon-13 Spin-Lattice Relaxation Times (T_1, in ms) and NOE Factors[a] of Protonated-Carbons in PHB in TCE-d_2 as a Function of Temperature and Magnetic Field

	300 MHz			200 MHz		
temp, °C	CH	CH_2	CH_3	CH	CH_2	CH_3
-10	186 (1.77)	110 (1.75)	256 (2.51)	160 (2.61)	92 (2.45)	237
0	213 (1.92)	127 (2.00)	316 (2.59)	192 (2.80)	111 (2.81)	279
10	235 (2.19)	139 (2.21)	358 (2.65)	230	137	317
20	285 (2.36)	170 (2.40)	447 (2.74)	275	164	400
30	353 (2.56)	209 (2.61)	547 (2.78)	324	191	535
40	430 (2.63)	259 (2.68)	663 (2.91)	383	228	631
50	524 (2.70)	323 (2.85)	813	448	271	729
60	642 (2.80)	392	967	527	324	835

[a] Values in parentheses; full NOE is considered when parentheses are omitted.

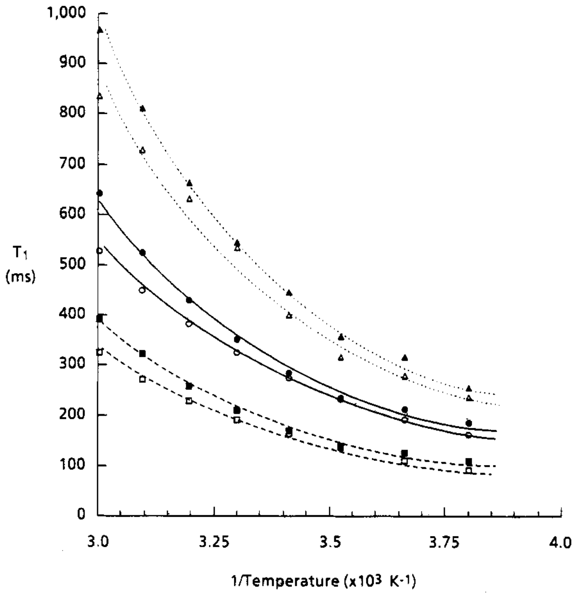

Figure 1. Plot of ^{13}C spin-lattice relaxation times, T_1 (ms), versus reciprocal temperature for PHB in TCE-d_2. Solid lines, CH; dashed lines, CH_2; dotted lines, CH_3. Solid symbols, 300 MHz; open symbols, 200 MHz.

Doi et al.[6] have analyzed some ^{13}C T_1 data for PHB in solution in terms of isotropic motion and concluded that the chain is rather flexible. Nevertheless, the NOE factors of Table I, which are invariably below the extreme-narrowing limit in almost the whole temperature range at 300 MHz and at low temperatures at 200 MHz, indicate that a single exponential function, i.e., isotropic motion, is inadequate to account for these relaxation data.

Another interesting feature of the data in Table I is that the ratio of T_1 values, $T_1(CH)/T_1(CH_2)$, is fairly constant at 1.65, rather different from the value of 2 expected from the number of directly bonded protons. As it will be seen later, it may be assumed that both atoms move in concert in the segmental rearrangement process and NT_1 for the two carbons, where N is the number of directly attached protons, should be equal. Accordingly, part of the NT_1 differences can be attributed to a differential in the dipolar interactions of the backbone carbons with protons other than those directly attached to the carbons within the same monomer unit. A simple examination of molecular models reveals that the methine carbon receives additional relaxation contributions from the two protons of the nearby methylene group at a distance of ca. 2.2 Å, whereas the methylene carbon interacts only with the single methine proton at a similar distance of ca. 2.2 Å. The methine carbon will therefore relax at a slightly enhanced rate relative to the methylene carbon. These nonbonded C–H dipolar interactions were included in the analysis of the relaxation data that follow. Due to the relatively fast methyl internal motion (see below), which presumably makes no contribution to the relaxation, dipolar contributions from the methyl protons to the backbone carbons were not considered. It should be pointed out that PHB assumes a right-handed 2_1 helical conformation[7,8] in the solid state and if that conformation is retained in solution, additional dipolar interactions could occur between the backbone carbons of a monomer unit and protons from neighboring monomer units within a fiber period. However, these contributions are considered to be too small ($r_{CH} \cong 3$ Å) to be involved in the present analysis. Exact values of the various C···H distances were obtained from the crystal structure of PHB obtained from X-ray diffraction studies.[7,8]

Modeling the Motions of PHB in Solution. The correlation time of the overall tumbling motion, τ_R, was estimated at infinite dilution as a function of the molecular weight, M, and the intrinsic viscosity $[\eta]$ of the polymer solution in a given solvent of viscosity η_0 through the hydrodynamic equation[9]

$$\tau_R = 2M[\eta]\eta_0/3RT \tag{3}$$

and found to be 1.1×10^{-5} s in TCE at 30 °C. This value changes only slightly, considering a solution of finite concentration (6% w/v) and the effect of the molecular weight distribution of the PHB sample.[10] This long correlation time guarantees the preponderance of the local motions as the major relaxation source for the protonated carbons of PHB.

The second type of motion modulating the dipolar interactions is backbone rearrangement, which will be described by the JS model, in which the motion is modeled as a three-bond jump on a tetrahedral lattice, i.e., as a "crankshaft" motion. The time scale of the segmental motion is described by a harmonic mean correlation time, τ_h, and the breadth of the distribution of correlation times is characterized by the number of bonds, m, involved in the cooperative motion or the quantity, $2m - 1$, which stands for the chain segment expressed in bonds that are coupled to the central bonds. In addition to segmental motion, internal motions such as methyl rotation are added as independent local motions, in the form of an appropriate correlation function describing either diffusional stochastic motion or jumps among energy minima in the potential energy curve with a correlation time τ_{ir}.[11] The JS composite spectral density is

$$J(\omega_i) = 2\sum_{k=1}^{s} G_k \left(\frac{A\tau_{k0}}{1+\omega_i^2\tau_{k0}^2} + \frac{B\tau_{bk0}}{1+\omega_i^2\tau_{bk0}^2} + \frac{C\tau_{ck0}}{1+\omega_i^2\tau_{ck0}^2} \right) \tag{4}$$

$$A = (3\cos^2\theta - 1)^2/4 \qquad B = 3(\sin^2 2\theta)/4$$
$$C = 3(\sin^4\theta)/4 \tag{5}$$

Table II
Simulation Parameters for PHB Using JS and HWH Models[a]

	JS			HWH		
temp, °C	$2m - 1$	$10^{-9}\tau_h$, s	$10^{-11}\tau_{ir}$, s	$10^{-9}\tau_0$, s	$10^{-9}\tau_1$, s	$10^{-11}\tau_{ir}$, s
−10	9	0.205	2.75	10.00	0.328	9.13
0	13	0.148	2.09	5.14	0.182	7.82
10	9	0.113	1.85	4.83	0.140	7.11
20	9	0.076	1.44	1.24	0.100	5.80
30	9	0.052	1.18	0.67	0.079	4.88
40	9	0.039	0.99	0.55	0.056	4.28
50	9	0.029	0.81	0.41	0.042	3.64
60	9	0.023	0.72	0.24	0.033	3.30
E_a, kJ/mol		23	14	40	22	12
$10^{14}\tau_\infty$, s		2	5	79	1	24
corr coef		0.999	0.998	0.980	0.999	0.996

[a] The $2m - 1$ and τ_h parameters of the JS model and the τ_0 and τ_1 correlation times of the HWH model were calculated from the relaxation data of the backbone methine and methylene carbons. The τ_{ir} values were calculated from the relaxation data for the methyl group, while holding the appropriate parameters for the backbone constant.

where θ = the angle between the internuclear interaction and the axis of rotation for the fast internal motion and $s = (2m + 1)$. The weighting functions are given by

$$G_k = 1/s + (2/s)\sum_{q=1}^{s-1} \exp(-\gamma q) \cos\left(\frac{(2k-1)\pi q}{2s}\right); \quad \gamma = \ln 9 \qquad (6)$$

For overall molecular motion of a polymer chain given by τ_R and a threefold jump by a methyl group among three minima at Φ and $\Phi \pm 120°$:

$$\tau_k^{-1} = \omega\lambda_k; \qquad \lambda_k = 4\sin^2\left(\frac{(2k-1)\pi}{2(m+1)}\right) \qquad (7)$$

$$\tau_{k0}^{-1} = \tau_R^{-1} + \tau_k^{-1} \qquad (8)$$

$$\tau_{bk0}^{-1} = \tau_{ck0}^{-1} = \tau_R^{-1} + \tau_k^{-1} + \tau_{ir}^{-1} \qquad (9)$$

where w is the rate of occurrence of the three-bond jump of the polymer backbone usually expressed as the harmonic mean, $\tau_h^{-1} = 2w$.

Theoretical calculations,[12-16] as well as experimental findings,[17,18] have questioned the presence of the crankshaft motions involved in the JS model. Recent computer simulations[12,13] and kinetic theory analysis[14] of conformational transitions in polyethylene-type chains support the idea that the rate-controlling step of the chain motion is the surmounting of but a single bond internal rotational barrier, which is accompanied by librational fluctuations in neighboring bonds in such a way as to localize the motion, preventing the unfavorable movement of the whole polymer chain. Corresponding analytical theories for the time correlation function, describing conformational transitions of this type, have been offered by Hall, Weber, and Helfand (HWH).[3,4] For the segmental description developed by the HWH model, the time scale is set by two parameters: τ_0, the correlation time for single conformational transitions, and τ_1, the correlation time for cooperative or correlated transitions. This segmental description is then combined with the correlation time for methyl internal motion, τ_{ir}.[19] The HWH composite spectral density function is

$$J(\omega_i) = AJ_a(\tau_0,\tau_1,\omega_i) + BJ_b(\tau_{b0},\tau_1,\omega_i) + CJ_c(\tau_{c0},\tau_1,\omega_i) \qquad (10)$$

The parameters A, B, and C are functions of the angle θ as before. The form of J_a, J_b, and J_c is the same as J given below with τ_0 replaced by τ_0, τ_{b0}, and τ_{c0}, respectively.

$$J(\omega_i) = 2\{[(\tau_0^{-1})(\tau_0^{-1} + 2\tau_1^{-1}) - \omega_i^2]^2 + [2(\tau_0^{-1} + \tau_1^{-1})\omega_i]^2\}^{-1/4} \times \cos\left[\tfrac{1}{2}\arctan\{2(\tau_0^{-1} + \tau_1^{-1})\omega_i/[\tau_0^{-1}(\tau_0^{-1} + 2\tau_1^{-1}) - \omega_i^2]\}\right] \qquad (11)$$

As above, for a threefold jump of a methyl group

$$\tau_{b0}^{-1} = \tau_{c0}^{-1} = \tau_0^{-1} + \tau_i^{-1} \qquad (12)$$

Assuming purely ^{13}C–^1H dipolar relaxation, the spin–lattice relaxation time and NOE may then be calculated from the following well-known equations from the above expressions for $J(\omega)$

$$1/T_1 = \frac{\hbar^2\gamma_C^2\gamma_H^2}{10r_{CH}^6}[J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)] \qquad (13)$$

$$\text{NOE} = 1 + \frac{\gamma_H}{\gamma_C}\left[\frac{6J(\omega_H + \omega_C) - J(\omega_H - \omega_C)}{J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)}\right] \qquad (14)$$

Numerical Calculations. The correlation times were calculated by using the MOLDYN program,[20] modified to include the JS and HWH motional models plus a fast internal motion. The T_1 values and NOEs for both the CH and CH_2 groups at both field strengths for a given temperature were used as input, and the best-fit correlation times from each model were calculated by using a Simplex routine to vary the parameters until the sum of squares of deviations of the calculated relaxation times and NOEs from the observed was a minimum. Values for the sum of squares of the order 0.01–0.001 were observed in the present calculations, reflecting a good fit (T_1s and NOEs were reproduced generally to within 10%). Although the deviation of the ratio of observed T_1s from the theoretical value of 2 is sizable and cannot be completely accounted for by including nonbonded dipolar relaxation mechanisms, fitting the CH and CH_2 relaxation data separately gave correlation times and activation energies that were not significantly different. The τ_{ir} correlation times in both models were subsequently determined for a given temperature by adjusting them to account for the methyl carbon relaxation data, while holding τ_h and $2m - 1$ (or τ_0 and τ_1) at the values determined from the relaxation data of the backbone carbons.

Comparison of the Simulation Parameters. The simulation parameters of the JS and HWH models which reproduce the relaxation data of PHB are summarized in Table II. A salient feature of the simulation parameters is that τ_h and τ_1, the correlation times for cooperative segmental motions in the two models, are comparable. In fact, τ_1 values are longer than τ_h by a factor of 1.2–1.6. This is quite apparent in the Arrhenius summaries in Table II, where both activation energy and prefactor are rather similar for τ_h and τ_1. The similarity between τ_h and τ_1 has been rationalized[21,22] on the basis that both models derive correlation functions for cooperative local motions in terms of conformational diffusion, although these models were developed from quite different starting points. The activation energies for local motions calculated from the two models are essentially equal (22–23 kJ/mol) and somewhat higher than for most vinyl polymers. A comparable investigation of the relatively rigid polycarbonates in the same solvent[22] yielded an activation energy close to that found here for PHB.

The time constant τ_0 in the HWH model is more than an order longer than τ_1 (Table II), indicating that single-bond conformational transitions play a lesser role than the cooperative transitions for PHB in solution, as was noted by Lin et al.[21] for polymer chains of greater complexity than polyethylene. This conclusion is further supported by the much higher activation energy accompanying a single-bond transition compared to that obtained for cooperative transitions (40 versus 22–23 kJ/mol, Table II).

The correlation times, τ_{ir}, for methyl internal rotation are three to four times longer for the HWH model that those for the JS model. This different time scale for methyl motion was not apparent in a similar study[22] on polycarbonates, where τ_{ir} was relatively constant upon changing the description of segmental motion. Both models should be further tested against a few more sets of data to draw definite conclusions, since the HWH model was derived on a very local molecular basis, considering conformational jumps on a polymethylene chain without pendant groups.[23] The calculated activation energy of 12–14 kJ/mol for the methyl group rotation reflects a rather fast motion typical of that observed in most small molecules but contrasts with the higher activation energy value of 17–18 kJ/mol obtained for the hindered methyl internal rotation in polycarbonates.[22]

Possible Modes of Chain Local Motion in PHB. It is of interest to discuss these results in terms of particular local motions that may occur in the PHB chain. ^{13}C spin–lattice relaxation studies[24,25] in polyesters that contain aryl and aliphatic chain segments have shown that the most reasonable mode of motion for polyesters with an even number of methylene carbons between the ester groups is a crankshaft conformation about the coaxial CH_2–carbonyl bonds. This cooperative transition is a type 1 motion according to Helfand's classification of polymer motion[13] and leaves the chain ends in the same position at the start and end of the transition. On inspection, the 2_1 helix found in the solid state for PHB (Figure 2b) is a suitable conformation to allow for type 1 motions, since any given bond within the backbone is parallel with the same bond two monomer units distant.

Simultaneous rotations around these bonds would result in type 1 motion. Because the chains ends are not involved, these motions are particularly favorable in a hydrodynamic sense, but on the other hand they involve a barrier of ca. 20 kJ/mol, twice the height of the trans–gauche transition. (Although the number of bonds involved in the crankshaft motion depicted in Figure 2b does not correspond exactly to the number $2m - 1$ from the fit, this parameter is of secondary importance in the calculation and its value is more useful as an indicator of degrees of freedom available in the polymer chain. A large value for the $2m - 1$ parameter would represent relatively few degrees of freedom.)

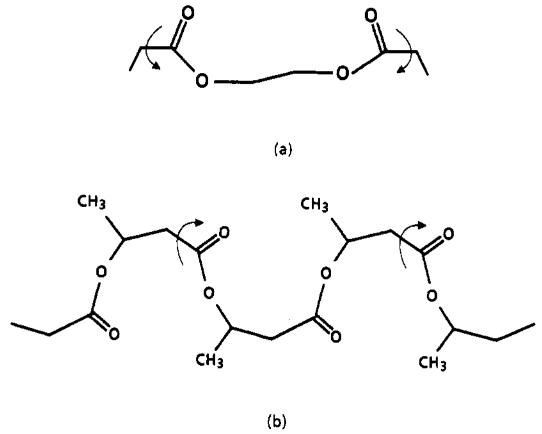

Figure 2. Conformation that allows for (a) the crankshaft motion of a typical polyester involving two methylene carbons between ester groups and (b) a type 1 motion available to the PHB chain, which locally assumes the crystalline 2_1 helical conformation. Four monomer units are shown.

A second type of local motion, which may contribute to the relaxation of polyesters,[24,25] is the type 2 motion according to Helfand's terminology.[13] In type 2 processes, the chain ends are translated relative to each other by the motion, but the angular orientation of the two is unaffected. Although the displacement of the chain ends makes type 2 motion less favorable than type 1 motion, the former motion requires a smaller activation energy than the latter, i.e., only slightly more than the barrier separating the trans and gauche states.[12] Both types of motions could occur in the PHB chain.

With these two potential modes of motion outlined, it is necessary to determine which is more likely to occur in PHB. Assume the observed activation energy can be written as[26,27]

$$E_a = \Delta H_\eta + E^* \tag{15}$$

where ΔH_η is the activation energy for the solvent viscosity and E^* is the potential barrier for the local motions. ΔH_η for TCE was determined to be 12 kJ/mol over the temperature range 0–80 °C from a plot of ln η versus $1/T$, where η is the viscosity of TCE.[28] Results in Table II lead to $E^* \simeq$ 10–11 kJ/mol for τ_h and τ_1 and $E^* \simeq 28$ kJ/mol for τ_0. Considering that type 1 motions require two barrier crossings and type 2 motions slightly more than one ($E^* \simeq 20$ versus 10 kJ/mol), the present results for τ_h and τ_1 indicate that only a single barrier is being crossed in the segmental motions and therefore type 2 motions occur more readily in PHB.

In summary, we have shown that relaxation times of PHB in solution cannot be adequately explained assuming isotropic motion and that the activation energy for segmental motions is more typical of fairly rigid polymers. Both the Jones–Stockmayer and Hall–Weber–Helfand models accurately describe the local motions in PHB. Further studies of spin–lattice relaxation of PHB as a function of solvent and molecular weight are currently in progress, along with similar studies of the bulk polymer.

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Registry No. 1 (SRU), 26744-04-7; 1 (homopolymer), 26063-00-3.

References and Notes

(1) Heatley, F. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *13*, 47. Schaeffer, J. *Top. Carbon-13 NMR Spectrosc.* **1974**, *1*, 150.

(2) Jones, A. A.; Stockmayer, W. H. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1347.

(3) Hall, C. K.; Helfand, E. *J. Chem. Phys.* **1982**, *77*, 3275.

(4) Weber, T. A.; Helfand, E. *J. Phys. Chem.* **1983**, *87*, 2881.

(5) Marchessault, R. H.; Okamura, K.; Su, C. J. *Macromolecules* **1970**, *3*, 735.

(6) Doi, Y.; Kunioka, M.; Nakamura, Y.; Soga, K. *Macromolecules* **1986**, *19*, 2860.

(7) Cornibert, J.; Marchessault, R. H. *J. Mol. Biol.* **1972**, *71*, 735.

(8) Yokouchi, M.; Chatani, Y.; Tadokoro, H.; Teranishi, K.; Tani, H. *Polymer* **1973**, *14*, 267.

(9) Riseman, J.; Kirkwood, J. G. *J. Chem. Phys.* **1949**, *16*, 442. Isihara, A. *Adv. Polym. Sci.* **1958**, *5*, 531.

(10) Dais, P. *Carbohydr. Res.* **1987**, *160*, 73.

(11) Jones, A. A.; Lubianez, R. P. *Macromolecules* **1978**, *11*, 126.

(12) Helfand, E.; Wasserman, Z. R.; Weber, T. A. *Macromolecules* **1980**, *13*, 526.

(13) Helfand, E. *J. Chem. Phys.* **1971**, *54*, 4651.

(14) Skolnick, J.; Helfand, E. *J. Chem. Phys.* **1980**, *72*, 5489.

(15) Helfand, E. *J. Chem. Phys.* **1978**, *69*, 1010.

(16) Helfand, E.; Wasserman, Z. R.; Weber, T. A. *J. Chem. Phys.* **1979**, *70*, 2016.

(17) Baysal, B.; Lawry, B. A.; Yu, H.; Stockmayer, W. H. In *Dielectric Properties of Polymers*; Karasz, F. E., Ed.; Plenum Press: New York, 1972. Jones, A. A., Matsuo, K.; Kuhlman, K. F.; Geny, F.; Stockmayer, W. H. *Polym. Prepr.* **1975**, *16*, 578.

(18) Morawetz, H. *Science* **1975**, *203*, 405. Chen, D. T.-L.; Morawetz, H. *Macromolecules* **1976**, *9*, 463. Liao, T. P.; Okamoto, Y.; Morawetz, H. *Macromolecules* **1979**, *12*, 535.

(19) Roy, A. K.; Jones, A. A. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1793.

(20) Craik, D. J.; Kumar, A.; Levy, G. C. *J. Chem. Inf. Comput. Sci.* **1983**, *1*, 30.

(21) Lin, Y. Y.; Jones, A. A.; Stockmayer, W. H. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 2195.

(22) Connoly, J. J.; Gordon, E.; Jones, A. A. *Macromolecules* **1984**, *17*, 722.

(23) Viovy, J. L.; Monnerie, L.; Brochon, J. C. *Macromolecules* **1983**, *16*, 1845.

(24) Henrichs, P. M.; Hewitt, J. M.; Russel, G. A.; Sandhu, M. A.; Cranshot, H. R. *Macromolecules* **1981**, *14*, 1770.

(25) Tekely, P.; Lauprêtre, F.; Monnerie, L. *Macromolecules* **1983**, *16*, 415.

(26) Kramers, H. A. *Physics* **1940**, *7*, 284.

(27) Mashimo, S. *Macromolecules* **1976**, *9*, 91. Friedrich, C.; Lauprêtre, F.; Noël, C.; Monnerie, L. *Macromolecules* **1980**, *13*, 1625.

(28) National Research Council *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; Washburn, E. W., Ed.; McGraw-Hill Inc.: New York, 1930; Vol. VII, p 213.

Exciton Migration on Polymers

E. J. Janse van Rensburg,* J. E. Guillet, and S. G. Whittington

Department of Chemistry, University of Toronto, Toronto, Ontario, M5S 1A1, Canada.

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ABSTRACT: The properties of migrating excitons on chromophores substituted along a polymer chain are considered. The mean survival time of the excitons and the survival function of an exciton are studied in the presence of an exciton trap on the chain. A postulate that the mean survival time τ_n scales with the length n of the chain as n^μ is studied. It is found that for singlet (fast) diffusion $\mu = 2$ while for triplet (slow) diffusion $\mu = 1$. The methods used are a nonrigorous scaling argument and Monte Carlo calculation for singlet migration of excitons on linear polymers and stars, while a perturbative calculation proves successful for the triplet exciton diffusion case.

1. Introduction

Energy transfer within single molecules or between different molecules is of particular significance in polymer chemistry. Energy donors and acceptors (chromophores) in the molecules may be excited by incoming photons of a sufficient wavelength to form a localized excitation in a chromophore (usually called an exciton). Polymer chains may have chromophores substituted at intervals along the chains, and it is of particular interest that transfer of the exciton may occur between two of these chromophores under suitable conditions. For the sake of simplicity, it is assumed that chromophores will always be spaced at *regular* intervals along the chains.

There is experimental evidence for the transfer of excitons between chromophores in the same molecule or even between different molecules.[1] The mechanisms for these transfers have been investigated in detail (see, for example, the books by Guillet[2] and Phillips[3]). Briefly, they are (1) the induced dipole interaction (or the Förster process[4]), which is a long-ranged, nonradiative, single-step process with a range between 15 and 100 Å, and (2) the exchange mechanism (or Dexter transfer[5]), which is a short-ranged, nonradiative, single-step process with a range of about 15 Å. Furthermore, there is a distinction between excitons in the singlet or triplet state. The singlet exciton is a spin zero excited state of the chromophore with a lifetime of between 10^{-11} and 10^{-7} s and a transfer rate typically shorter than the conformational relaxation time of a polymer (say, 10^{-4}–10^{-3} s, which is typical for a crankshaft motion). The triplet exciton is a metastable spin 1 state that has a lifetime of between 10^{-6} and 10^{1} s.[2,3] Typically, the triplet state would have a transfer time longer than the conformational relaxation time of a polymer.

In a molecule where the chromophores are sufficiently close together, the transfer of excitons from one chromophore to another can be viewed as a random walk on the chromophores. Energy transfers between chromophores substituted along a polymer happen between nearest-neighbor chromophores and can also occur between any two chromophores that are close together in space in a particular conformation but are far removed from each other along the chain. This situation is illustrated in Figure 1. Experimental evidence for these processes is readily available.[1] The problem is now reduced to one of diffusion of the exciton along the polymer. This diffusion process is strongly influenced by the distribution of

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