

STUDY OF THE MOLECULAR MOTION IN POLYEPICHLOROHYDRIN BY HIGH RESOLUTION NMR

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ABSTRACT

The molecular motion in polyepichlorohydrin (PEPCH), in solution and bulk, was studied by high resolution NMR by means of line width, spin-lattice relaxation time T_1 and nuclear Overhauser effect NOE. The results show that the VJGM model can describe the main chain motion of PEPCH in solution perfectly. In bulk state, the relationship between the line width and the temperature is consistent with WLF equation, but that between the high frequency molecular motion correlation time (in T_1 scale) and temperature is consistent with Arrhenius equation. The motion parameters of PEPCH in both states were calculated. The internal rotation motion of side $-\text{CH}_2\text{Cl}$ group was analyzed by using equal three-site jump and diffusion internal rotation model in both states.

INTRODUCTION

For total amorphous and semi-crystalline polymers, high resolution ^{13}C spectra can be obtained even under normal condition when the measuring temperature is much higher than the glass transition temperature ($T = T_g + 50 \sim T_g + 100^\circ\text{C}$) because the fast molecular motion diminished the dipole-dipole interaction and chemical shift anisotropy. As a consequence, high resolution ^{13}C NMR finds wide applications in studying the molecular motion in rubber, elastomer and semi-crystalline polymers^[1-3]. The results of studying on the molecular motion in polyisobutylene in bulk state showed that T_1 's do not depend on the molecular weight above the critical molecular weight^[4,5]. This means that the segmental motion is still dominating the relaxation process in bulk state elastomer and the relaxation does not depend on the chain entanglement and bulk viscosity. So we can use the molecular motion model in polymer solution to describe the molecular motion of polymer in bulk state.

Polyepichlorohydrin is a kind of special synthetic rubber with good oil resistance, fire resistance and ozone resistance properties. The results of dielectric relaxation study showed that there were two transitions in amorphous PEPCH, located at -16°C and -120°C , respectively^[6]. There are also two transitions in NMR second order dipole moment measurements^[7,8]. The location is $-10 \sim +20^\circ\text{C}$ and -110°C , respectively. The former corresponds to the glass transition and the latter to the second transition, the internal rotation of side $-\text{CH}_2\text{Cl}$ group. The activation energy of glass transition is $15.8 \text{ Kcal} \cdot \text{mol}^{-1}$, that of second transition $8.4 \sim 8.5 \text{ Kcal} \cdot \text{mol}^{-1}$.

In this paper, high resolution NMR was used to analyze the molecular motion of PEPCH in solution and bulk state.

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THEORY

Under the condition of polymer solution, the protonated ^{13}C nuclei are relaxed exclusively by a dipole mechanism, therefore, the following relations can be applied

$$\frac{1}{nT_1} = \frac{\gamma_H^2 \gamma_C^2 \hbar^2}{20r^6} \cdot [J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)] \quad (1)$$

$$\text{NOE} = 1 + \frac{\gamma_H}{\gamma_C} \cdot \frac{6J(\omega_H + \omega_C) - J(\omega_H - \omega_C)}{J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)} \quad (2)$$

Among the models describing the molecular motion of polymers in solution, the most successful model to describe the segmental motion of polymer in solution is VJGM model^[9,10]. The correlation function corresponding to the VJGM model is

$$G_{\text{VJGM}}(t) = \exp(-t/\tau_0) \exp(t/\tau_d) \text{erfc}[(t/\tau_d)] \quad (3)$$

where the erfc is error supplement function. The corresponding spectra density function is

$$J_{\text{VJGM}}(\omega) = \frac{2\tau_0\tau_d(\tau_0 - \tau_d)}{(\tau_0 - \tau_d)^2 + \omega^2\tau_0^2\tau_d^2} \cdot \left\{ \left(\frac{\tau_0}{2\tau_d} \right)^{1/2} \cdot \left[\frac{(1 + \omega^2\tau_0^2)^{1/2} + 1}{1 + \omega^2\tau_0^2} \right]^{1/2} \right. \\ \left. \cdot \left(\frac{\tau_0}{2\tau_d} \right)^{1/2} \frac{\omega\tau_0\tau_d}{\tau_0 - \tau_d} \cdot \left[\frac{(1 + \omega^2\tau_0^2)^{1/2} - 1}{1 + \omega^2\tau_0^2} \right]^{1/2} - 1 \right\} \quad (4)$$

where τ_0 characterizes long-scale tumbling motion, and τ_d characterizes local segmental motion.

For the side group, the relaxation was influenced by both main chain motion and side group internal rotation. The total correlation function can be expressed as the product of correlation function for main chain and that of the side group assuming the motion being independent with each other. So the total correlation function for the side group can be expressed as

$$G(t) = G_{\text{VJGM}}(t) * G_i(t) \quad (5)$$

By assuming the model of side $-\text{CH}_2\text{Cl}$ group rotation being equal to three site jumping or diffusion internal rotating, the spectra density function can be expressed as follows, respectively.

For equal three site jump^[11], the spectra density function is

$$J(\omega) = AJ_{\text{VJGM}}(\tau_0, \tau_d, \omega) + 2(B + C)J_{\text{VJGM}}(\tau_1, \tau_d, \omega) \quad (6)$$

where the $\tau_1^{-1} = \tau_d^{-1} + \tau_i^{-1}$, $A = 1/4(3\cos^2\Delta - 1)^2$, $B = 3/4\sin^2 2\Delta$, $C = 3/4\sin^4\Delta$, Δ is the angle between a C—H vector and rotation axis, τ_i is the correlation time of the rotation of side group.

For diffusion internal rotation^[11], the spectra density function is

$$J(\omega) = AJ_{\text{VJGM}}(\tau_0, \tau_d, \omega) + 2BJ_{\text{VJGM}}(\tau_0, \tau_d, \omega) + 2CJ_{\text{VJGM}}(\tau_0, \tau_d, \omega) \quad (7)$$

where $\tau_1^{-1} = \tau_0^{-1} + D_i$, $\tau_1^{-1} = \tau_0^{-1} + 4D_i$, D_i is the diffusion coefficient of side group internal rotation. The correlation time can be obtained by fitting the T_1 and NOE values to equations (1,2,4,6,7).

EXPERIMENTAL

(1) The Measurements of T_1 and NOE

The measurements of ^{13}C T_1 and NOE of PEPCH in CDCl_3 solution were carried out on Varian XL-200 spectrometer. The method used to measure the ^{13}C T_1 is inversion-recovery method. The NOE's were obtained by direct comparison of peak areas obtained with proton decoupling to the corresponding areas with inverse gate proton decoupling. The resonance frequency of ^{13}C is 50.3 MHz. The width of 180° pulse is $14.6\mu\text{s}$ and waiting delay $D_0=8\text{s}$.

The ^{13}C T_1 and NOE of PEPCH in bulk state were measured on BRUKER MSL-400 spectrometer. The resonance frequencies of proton and carbon are 400.13 MHz and 100.6 MHz, respectively. The line widths were got out from the spectra directly.

(2) Data processing

The fitting of T_1 and NOE to equations (1, 2, 4, 6, 7) were carried out on VAX-11-785 computer by using SIMPLEX program. The correlation times can be calculated by the data fitting, because the relationship between the motion correlation times or diffusion coefficients and temperature is consistent with Arrhenius equation,

$$\tau = \tau_0 \exp(E_a / RT) \quad (8)$$

$$D = D_0 \exp(-E_a / RT) \quad (9)$$

$$\ln \tau = \ln \tau_0 + \frac{E_a}{RT} \quad (10)$$

$$\ln D = \ln D_0 + \frac{E_a}{RT} \quad (11)$$

the motion activation energy can be obtained from the slope of the straight line of $\ln \tau$ or $\ln D$ against $1/T$. This process and the processing of line width were carried out on IBM-PC computer by using TURBO PASCAL language program.

RESULT AND DISCUSSION

(1) Relaxation and motion of PEPCH in solution

The T_1 and NOE data of PEPCH in CDCl_3 solution measured on XL-200 spectrometer were listed in Table 1. It can be seen that $T_{1\text{CH}}/T_{1\text{CH}_2}$ is 1.82 ± 0.1 being nearly the same as the theoretical value 2.0. So the discussion about the main chain motion of PEPCH were based on the data of CH group. PEPCH's formula structure is $-\left[-\text{CH}_2 - \underset{\text{CH}_2\text{Cl}}{\underset{|}{\text{CH}}} - \text{O} \right]_n -$. The CH_2 ^{13}C resonance appears

as a doublet because there are two kinds of sequence distribution (mr, rr). As the difference in T_1 values is in the limit of the error of experiment, the average value

of the both has been used. The fact that the T_1 and NOE are increased as temperature rises implies that the correlation time is on the fast side of T_{1min} and that the molecular motion rate becomes faster as temperature rises. The nT_1 of $-\text{CH}_2\text{Cl}$

Table. 1 The values of ^{13}C T_1 and NOE of PEPCH in CDCl_3 solution (XL-200)

Temp. (K)	CH		CH_2		$-\text{CH}_2\text{Cl}$	
	$T_1(\text{s})$	NOE	$T_1(\text{s})$	NOE	$T_1(\text{s})$	NOE
288.4	0.44	2.84	0.25	2.84	0.27	2.89
293.5	0.49	2.87	0.27	2.88	0.29	2.92
298.4	0.53	2.89	0.29	2.91	0.32	2.93
303.2	0.57	2.90	0.32	2.92	0.35	2.94
308.3	0.66	2.92	0.35	2.93	0.40	2.95
313.2	0.73	2.93	0.38	2.94	0.44	2.95
318.2	0.81	2.95	0.42	2.95	0.48	2.96
323.2	0.89	2.95	0.49	2.96	0.54	2.97

group is longer than that of CH group shows that the internal rotation of $-\text{CH}_2\text{Cl}$ group is fast.

Table. 2 The motion and relaxation parameters of CH group of PEPCH in CDCl_3 solution. (XL-200)

Temp. (K)	Experiment. values		Calculated values		Correlation times	
	$T_1(\text{s})$	NOE	$T_1(\text{s})$	NOE	$\tau_0 \times 10^{10} (\text{s})$	$\tau_d \times 10^{11} (\text{s})$
288.4	0.44	2.84	0.44	2.84	3.90	6.20
293.5	0.49	2.87	0.49	2.87	3.49	5.38
298.4	0.53	2.89	0.53	2.88	3.16	4.96
303.2	0.57	2.90	0.57	2.90	2.87	4.47
308.3	0.66	2.92	0.66	2.92	2.52	3.69
313.2	0.73	2.93	0.73	2.93	2.28	3.27
318.2	0.81	2.95	0.81	2.94	2.00	3.03
323.2	0.89	2.95	0.89	2.95	1.86	2.58

The results of data fitting by VJGM model are listed in Table.2. It is clear from the table that the correlation times τ_0 , τ_d become shorter, that is, the rate of molecular motion becomes faster as the temperature increases and the fitting of the T_1 and NOE by VJGM model is very satisfactory. So the VJGM model describes the segmental motion in polymer solution very successfully. The activation energy of segmental motion of the main chain of PEPCH can be obtained from the slope of $\log \tau \sim 1/T$ straight line. $E_a(\tau_0)$ and $E_d(\tau_0)$ equal $16.7 \text{ KJ} \cdot \text{mol}^{-1}$ and $19.2 \text{ KJ} \cdot \text{mol}^{-1}$, respectively (see Figure 1). By comparing the activation energy with that of polypropylene oxide $E_a = 11 \pm 2 \text{ KJ} \cdot \text{mol}^{-1(12)}$, it can be concluded that the barrier for the segmental motion of main chain of PEPCH is higher than that of polypropylene glycol. Because the volume of side $-\text{CH}_2\text{Cl}$ group is larger than that of $-\text{CH}_3$, the substitution of $-\text{CH}_3$ by $-\text{CH}_2\text{Cl}$ made the flexibility of main chain of PEPCH become worse. So the flexibility of main chain depends strongly on the volume of side group.

To process the data of side $-\text{CH}_2\text{Cl}$ group measured on single magnetic field, we can assume the model of internal rotation of $-\text{CH}_2\text{Cl}$ being jumping in equal three site and rotating diffusively, respectively. The results of data fitting of T_1 and NOE of side $-\text{CH}_2\text{Cl}$ group by the above assumption are listed in Table 3. It can be seen that the fitting is very successful by comparing the experimental and

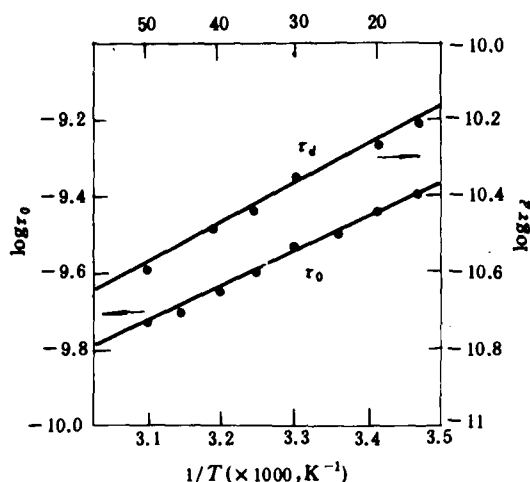


Fig.1 The semi-log plot of the correlation time of the main chain of PEPCH against $1/T$ in solution. (VJGM Model)

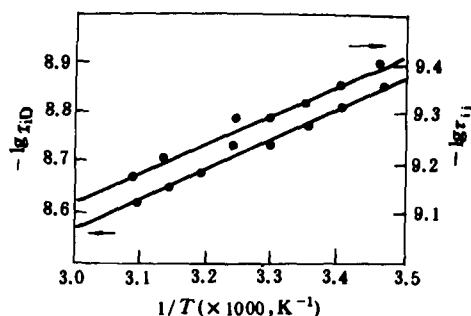


Fig.2 The relationship between the correlation time of the internal rotation of $-\text{CH}_2\text{Cl}$ in PEPCH in solution. τ_{ID} is the correlation time of the diffusion rotation and $\tau_{\frac{1}{3}}$ the correlation time of the equal three site jump

calculated data. The activation energy of internal rotation of $-\text{CH}_2\text{Cl}$ group can be calculated from the slope of the semi-log plot of internal rotation correlation time of $-\text{CH}_2\text{Cl}$ against $1/T$ (see Figure 2). The activation energy is $11.34 \text{ KJ} \cdot \text{mol}^{-1}$ (equal three site jump) and $11.29 \text{ KJ} \cdot \text{mol}^{-1}$ (diffusion rotation), respectively. The parameters are reliable because both are equal essentially. The internal activation energy of side $-\text{CH}_2\text{Cl}$ group is higher than that of $-\text{CH}_3$ of PPO ($E_a = 6.25 \text{ KJ} \cdot \text{mol}^{-1}$)^[3]. This is easy to understand because the volume of $-\text{CH}_2\text{Cl}$ is larger than that of $-\text{CH}_3$ group. So the restriction to the rotation of $-\text{CH}_2\text{Cl}$ is stronger than that of $-\text{CH}_3$ and the activation energy increased.

Table. 3 The relaxation and motion parameters of side $-\text{CH}_2\text{Cl}$ group of PEPCH in CDCl_3 solution. (XL-200)

Temp. (K)	Experi. values		Eq. three-site jump			Diffusion rotation		
			Calcul. values		Correl. time	Calcul. values		Correl. time
	$T_1(\text{s})$	NOE	$T_1(\text{s})$	NOE	$\tau_i \times 10^{10}(\text{s})$	$T_1(\text{s})$	NOE	$\tau_i \times 10^9(\text{s})$
288.4	0.27	2.90	0.27	2.90	7.57	0.27	2.90	2.15
293.5	0.29	2.92	0.29	2.92	7.05	0.29	2.91	2.00
298.4	0.32	2.93	0.32	2.93	6.59	0.32	2.93	1.87
303.2	0.35	2.94	0.35	2.94	5.80	0.35	2.94	1.64
308.2	0.40	2.95	0.40	2.95	5.74	0.40	2.95	1.63
313.2	0.44	2.95	0.44	2.96	5.33	0.44	2.95	1.52
318.2	0.48	2.96	0.48	2.96	4.96	0.48	2.96	1.41
323.2	0.54	2.97	0.54	2.97	4.47	0.54	2.97	1.27

(2) Relaxation and motion of PEPCH in bulk state

Even though the glass transition temperature of PEPCH is higher than that of most elastomers, the fast molecular motion can diminish the most part of the dipole-dipole interaction and chemical shift anisotropy. High resolution ^{13}C spectrum of PEPCH can be obtained under normal condition. The ^{13}C spectra of PEPCH

measured on MSL-400 spectrometer by using liquid broad band probe under different temperatures were shown in Figure 3. As the temperature rises, the line width of every peak becomes narrower and the molecular motion faster. The peaks separate completely at 45 °C. That makes us possible to study the molecular motion of PEPCH in bulk state under normal condition. The change of line widths with temperature can be seen in Table 4. Figure 4 can be drawn by plotting $\ln W$ against $1/T$. The plot of $\ln W \sim 1/T$ is not a straight line. That means the relationship between the correlation time corresponding to NMR line width and temperature is not consistent with Arrhenius equation. This result is reasonable because the

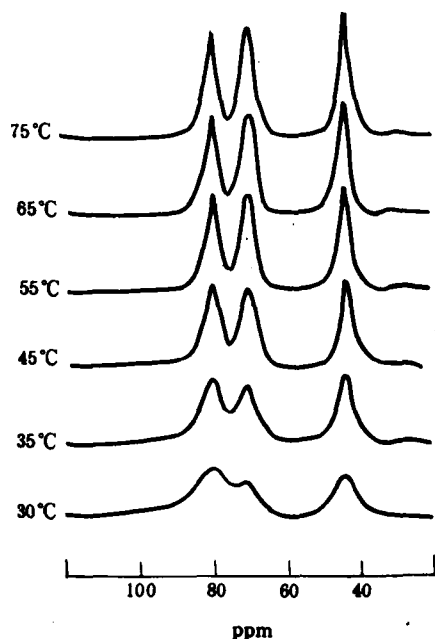


Fig.3 The ^{13}C spectrum of PEPCH at different temperatures in bulk state. (MSL-400)

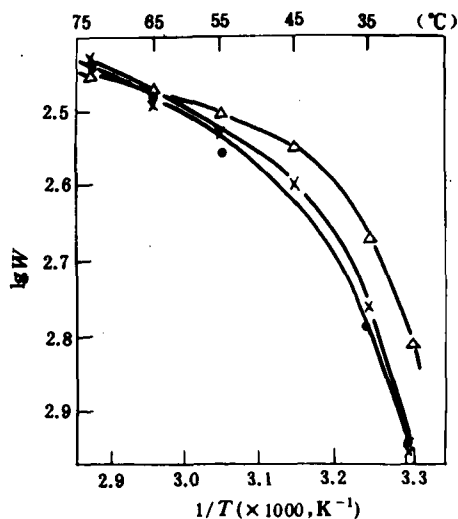


Fig.4 The relationship between ^{13}C line width of each group in PEPCH and $1/T$ in bulk state

(●) CH; (×) CH_2 ; (△) CH_2Cl

Table 4 The ^{13}C line widths of every group in PEPCH in bulk state at different temperatures.

Temp. (K)	Line Widths (Hz)		
	CH	CH_2	CH_2Cl
348	277	273	281
338	302	313	295
328	360	334	313
318	388	388	352
308	604	568	462
303	863	891	640

activation energy of long range molecular motion (T_2 scale) for polymer is not a constant but a function of temperature in the temperature range of $T_g \sim T_g + 100^\circ\text{C}$.

The relationship between the line width and the correlation time of long range molecular motion can be expressed as^[14]

$$\frac{W}{W_s} = \left(\frac{\tau}{\tau_s} \right)^k \quad (12)$$

according to Ni's results. Where W and W_s are the line widths at temperature T and reference temperature T_s , respectively. τ and τ_s are the motion correlation times at corresponding temperature. Then

$$\lg \frac{W}{W_s} = - \frac{KC_1(T-T_s)}{C_2+(T-T_s)} \tag{13}$$

where C_1 , C_2 are the coefficients in WLF equation. Equation (13) can be rewritten as

$$-1/\lg \left(\frac{W}{W_s} \right) = \frac{1}{KC_1} + \frac{C_2}{KC_1} \cdot \frac{1}{T-T_s} \tag{14}$$

Figure 5 can be drawn by plotting $-1/\ln \left(\frac{W}{W_s} \right)$ of every peak of PEPCH

against $1/T$. Obviously, the relationship between the line width and temperature is consistent with WLF equation. This means that the long range molecular motion of PEPCH depends on free volume because WLF equation reflects the dependence of molecular motion on the free volume. There is also such dependence of line width on temperature in poly-1,2-butadiene^[14]. Considering the great difference in the structure of poly-1,2-butadiene and PEPCH, equation (14) may be general to all polymers. The KC_1 and C_2 can be calculated from the slope and intercept of

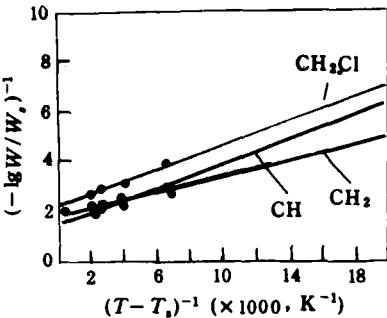


Fig.5 The plots of $[-\lg(W/W_s)]^{-1}$ of each carbon in PEPCH against $(T-T_s)^{-1}$ in bulk state

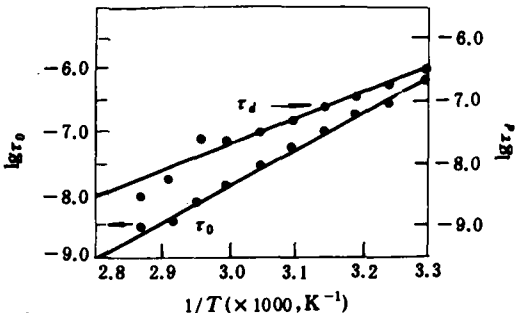


Fig.6 The relationship between the correlation time of main chain of PEPCH and $1/T$ in bulk state (VJGM model)

Table 5 The motion and relaxation parameters of CH group in the main chain of PEPCH in bulk state. (MSL-400, VJGM Model)

Temp. (K.)	Experiment. values		Calculated values		Correlation times	
	T_1 (s)	NOE	T_1 (s)	NOE	$\tau_0 \times 10^8$ (s)	$\tau_d \times 10^9$ (s)
303	1.34	1.39	1.34	1.39	125	218
308	0.98	1.41	0.98	1.40	62.8	108
313	0.78	1.46	0.78	1.41	38.6	61.9
318	0.63	1.47	0.63	1.42	25.8	37.2
323	0.49	1.50	0.49	1.44	15.5	18.8
328	0.40	1.50	0.40	1.48	10.2	8.94
333	0.35	1.54	0.35	1.51	8.39	5.23
338	0.31	1.54	0.31	1.58	8.91	2.53
343	0.28	1.58	0.28	1.64	2.12	1.25
348	0.26	1.64	0.26	1.64	1.02	1.05

the straight lines in Figure 5 as follows,

$$\begin{aligned} \text{CH: } KC_1 &= 0.654 & C_2 &= 155 \\ \text{CH}_2: KC_2 &= 0.610 & C_2 &= 106 \\ -\text{CH}_2\text{Cl: } KC_1 &= 0.435 & C_2 &= 104 \end{aligned}$$

The value of constant C_1 can not be calculated as the value of the constant K is unknown. The values of C_2 are not the same. Ni et al.^[14] also observed the same behavior in 1,2-PB. But no explanation has been presented.

The ^{13}C T_1 and NOE of PEPCH in bulk state measured on MSL-400 spectrometer are listed in Table 5. A smaller weight factor of NOE is selected in fitting the experimental data because the error of NOE is somewhat larger. Obviously, the T_1 decreased but NOE increased with temperature, so the correlation time of the segmental motion is on the slow motion side of $T_{1\min}$. As an attempt, VJGM model was used to fit the relaxation parameters of main chain. The results are also listed in Table 5. The results of T_1 fitting are very good but that of NOE is bad. From the slope of $\lg\tau \sim 1/T$ straight line, see Figure 6, the activation energy of main chain may be obtained $E_a(\tau_0)$ and $E_a(\tau_d)$ are equal to $80.2 \text{ KJ} \cdot \text{mol}^{-1}$ and $107.8 \text{ KJ} \cdot \text{mol}^{-1}$, respectively. These values are higher than $66.1 \text{ KJ} \cdot \text{mol}^{-1}$, reported in literature [7]. So the VJGM model may describe the molecular motion semi-quantitatively. Figure 7 can be drawn by plotting the $\lg\tau/\tau_s$ against $1/T_s$. Obviously, the relationship between the correlation time and temperature is not consistent with WLF equation. That is, the WLF equation is inadequate to describe the high frequency local molecular motion. It may be concluded from the above discussion that the relationship between the correlation time and temperature satisfies the WLF equation for long range, low frequency molecular motion (line width , T_2 scale) and Arrhenius equation for small scale, high frequency molecular motion (T_1 scale). The information about molecular motion in different frequency scale can be obtained by using line widths (or T_2) or T_1 .

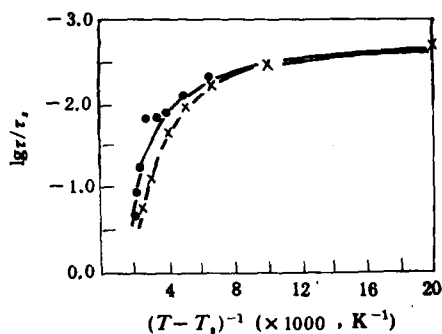


Fig.7 The relationship between the correlation time (T_1 scale) and $1/(T-T_s)$, WLF equation.

(●) τ_0 ; (×) τ_d .

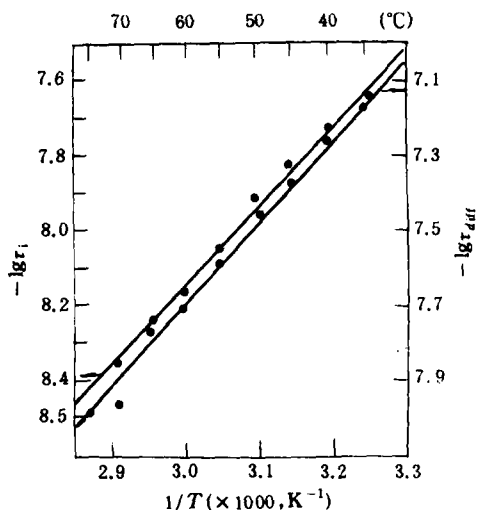


Fig.8 The curve of activation energy of side $-\text{CH}_2\text{Cl}$ group of PEPCH

The relaxation time and fitting data of side $-\text{CH}_2\text{Cl}$ group are listed in Table 6. The correlation time is also on the slow side of $T_{1\min}$. The data fitting used only the T_1 data. The activation energy of internal rotation of $-\text{CH}_2\text{Cl}$ is $40.5\text{KJ} \cdot \text{mol}^{-1}$ (see Figure 8). The difference between the values and that reported in literature is very small. There is no great difference between those obtained by the models (equal three site jump and diffusion rotation), even though the physical mean of equal three site jumping model is clearer than that of diffusion rotation. Because the results of data fitting are very similar to each other, the methods used to fit the data is reasonable. In other words, the models above can describe the internal rotation of the side $-\text{CH}_2\text{Cl}$ group correctly.

Table 6 The motion and relaxation parameters of side $-\text{CH}_2\text{Cl}$ group in PEPCH in bulk state. (MSL-400, the model describing the main chain motion in VJGM model)

Temp. (K)	Experiment. values		Eq. Three-site Jump			Diffusion rotation		
	$T_1(\text{S})$	NOE	$T_1(\text{S})$	NOE	$\tau_1 \times 10^9(\text{S})$	$T_1(\text{S})$	NOE	$\tau_{\text{diff}} \times 10^8(\text{S})$
303	0.40	1.42	0.40	1.30	29.9	0.40	1.30	8.93
308	0.30	1.45	0.30	1.31	22.4	0.30	1.31	6.68
313	0.24	1.49	0.24	1.32	18.2	0.24	1.32	5.45
318	0.20	1.51	0.20	1.33	14.5	0.20	1.33	4.23
323	0.17	1.53	0.17	1.36	12.0	0.17	1.36	3.52
328	0.14	1.59	0.14	1.40	8.71	0.14	1.40	2.57
333	0.12	1.61	0.12	1.44	6.92	0.12	1.44	1.96
338	0.12	1.63	0.12	1.51	5.75	0.12	1.52	1.68
343	0.11	1.68	0.11	1.59	4.36	0.11	1.61	1.10
348	0.11	1.75	0.11	1.63	3.24	0.11	1.69	0.65

CONCLUSION

The information about the molecular motion in different frequency scales can be obtained by line width, T_1 and NOE, respectively. The long range molecular motion is consistent with WLF equation but local scale molecular motion with Arrhenius equation. The molecular motion, both segmental motion of main chain and internal rotation of side group of PEPCH are slower than that of PPO because of the big side $-\text{CH}_2\text{Cl}$ group.

Keywords:

Polyepichlorohydrin; Molecular motion; NMR; NMR relaxation

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