Molecular Dynamics of Polystyrene Model Molecules; Reorientational Correlation Times of Phenyl Groups of 2,4-Diphenylpentane

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The reorientational correlation times of phenyl groups in 2,4-diphenylpentane in solution were measured as a function of the temperature by means of Raman line-shape analysis. The reorientational correlation times of both isomers increase as the temperature increases, that is, the reorientational motion of phenyl groups in molecules gradually become active. In the low-temperature region, the reorientational correlation times of the meso 2,4-diphenylpentane are longer than those of the racemic one. This fact that the molecular motion of phenyl groups of the racemic isomer rotates more easily than that of the meso one is in agreement with the results obtained from ultrasonic study by Monnerie *et al.* On the other hand, in the higher-temperature region, the reorientational correlation times of the meso isomer are shorter than those of the racemic one. In addition, the potential barriers for the reorientational motion of phenyl groups are found to be (3.3±0.3) kcal/mol for the meso isomer and (2.0±0.3) kcal/mol for the racemic isomer.

Ultrasonic absorption studies of vinyl polymers in solution, especially of polystyrene, have shown that local segmental motions of the backbone and motions of the side chains themselves were observed for the ultrasonic relaxation phenomena in the megahertz region.

Recently, in order to clarify the nature of the elementary motion of polymer chains in solution, Monnerie *et al.*[1] have reported very interesting results on the ultrasonic relaxation of 2,4-diphenylpentane in solution. The 2,4-diphenylpentane is the simplest polystyrene model molecule; two configurational isomers are present of the racemic and meso types. Monnerie *et al.* have indicated that the single relaxation observed for both racemic and meso types of 2,4-diphenylpentane in solution is due to the equilibrium reaction of the rotational isomers between g^-t and tt, and between tt and g^-g^-, conformations for the meso and racemic isomers respectively. Though they have suggested that the observed ultrasonic relaxation can be explained by taking into account the rotational motions of phenyl groups, the ultrasonic studies did not give any detailed information.

In our previous papers,[2,3] we reported that the reorientational correlation times of phenyl groups in polystyrene chains in solution could be determined by means of laser Raman spectroscopy. The same quantities can also, in principle, be determined by means of NMR relaxation experiments, infrared-band-shape analysis, and depolarized Rayleigh scattering. Compared with these methods, however, Raman studies can give information of interest more directly.

In the present paper, we will report on the temperature dependence of the reorientational correlation times of phenyl groups in *racemic-* and *meso*-2,4-diphenylpentane in solutions and will discuss the molecular motions of the phenyl groups in these molecules in solution.

Experimental

The apparatus used consisted of an argon-ion laser (800 mW at 488 nm) manufactured by the Coherent Radiation Co., Ltd. and a JRS-U1 Laser Raman Spectrometer of the Japan Electron Laboratory Co., Ltd. The Raman spectrum was observed at 90° with respect to linearly polarized incident light. In the analysis of the Raman line shape of the $\nu_2(a_{1g})$ mode of the phenyl group, all the experiments were carried out with a fixed slit width (40 μm).

The measuring temperatures were in the range from −90 °C to 40 °C. A variable-temperature Raman cell of the Harney-Miller type was used. The details of the experimental procedures were described previously.[4]

The meso and racemic 2,4-diphenylpentane, abbreviated *m*-DPP and *r*-DPP respectively, were kindly provided by Prof. Monnerie; these samples were the same as those used for ultrasonic studies. The detailed properties of the samples used have been given in detail in the literature.[5,6,7] By means of NMR and IR studies, the samples used have been confirmed for the following points; for *m*-DPP, the twofold degenerated g^- t (or tg^+) state is predominant, and the other conformations of *r*-DPP are 75% in the tt state and 25% in the g^-g^- state at room temperature.

The chloroform used as a solvent was commercial product, a spectral-grade regent. The concentrations of *m*-DPP and *r*-DPP were both 20.0 wt %.

Results and Data Analysis

Before we determined the reorientational correlation times of phenyl groups of *m*- and *r*-DPP in solution, we confirmed that the Raman spectra of DPP did not change in the pure liquid state nor in chloroform solutions over the whole temperature range. This fact clearly indicate that the conformational changes of *m*- and *r*-DPP in solution do not occur in these experiments.

The reorientational correlation times (τ(or)) of the phenyl group of DPP were determined by means of the Raman-line-shape analysis of stretching mode. For example, the Raman-line-shapes of $I_{\parallel}(\omega)$ and $I_{\perp}(\omega)$ of the $\nu_2(a_{1g})$ band are shown in Fig. 1, where $I_{\parallel}(\omega)$ and $I_{\perp}(\omega)$ represent the paralleled and polarized Raman intensities respectively with respect to the linearly polarized incident light.

As the ν_2 band of DPP shown in Fig. 1 overlapped the other bands, it was extracted by resolving these Raman lines into their components with Lorentzian functions, using the non-linear least-mean squares method of

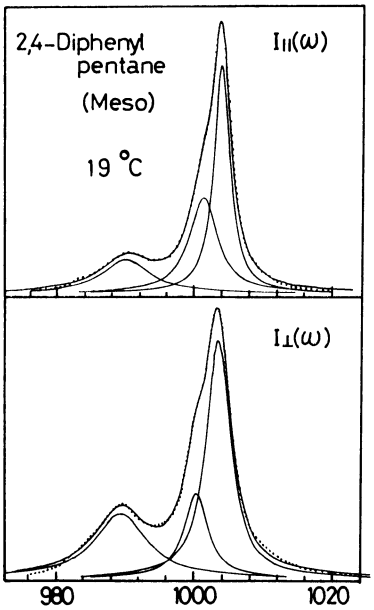


Fig. 1. Raman line shape of ν_2 band meso 2,4-diphenylpentane at 19 °C. Dotted line; observed, solid line; composed and decomposed with Lorentzian functions.

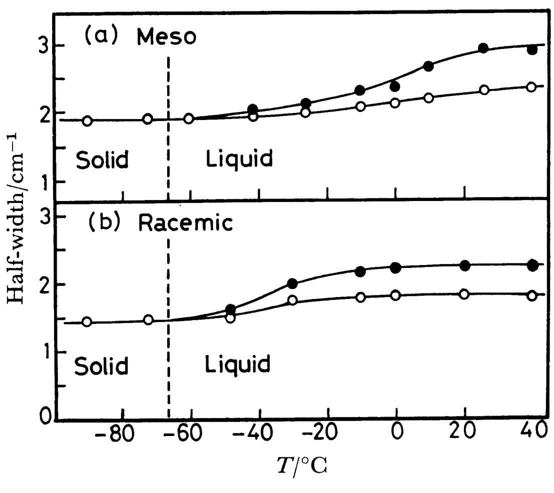
Fletcher-Powell.[8] After the correction for the line-boading effects of the instrumental slit width,[9] the true half-widths were determined for each one, $I_{\parallel}(\omega)$ and $I_{\perp}(\omega)$. As we found the depolarization ratio, $\rho_s(=I_{\perp}(\omega)/I_{\parallel}(\omega))$, to be about 0.02 for each isomer in throughout the temperature range, the intrinsic vibrational line shape, $I_{\text{isot}}(\omega)$, and the measured line shape, $I_{\parallel}(\omega)$, can be considered to be the same without the introduction of any significant errors.

The temperature dependences of the half-width of the isotropic and anisotropic parts of the Raman scattering, $\omega_{1/2}(\text{isot})$ and $\omega_{1/2}(\text{anis})$, are shown in Fig. 2. As was seen in Fig. 1, the Raman line shapes of $I_{\parallel}(\omega)$ and $I_{\perp}(\omega)$ can be represented by the Lorentzian curve within the limits of experimental error, also, we can estimate the reorientational correlation times, $\tau(\text{or})$, by means of the following relations;

$$\omega(\text{or}) = \omega_{1/2}(\text{anis}) - \omega_{1/2}(\text{isot}), \tag{1}$$

$$\tau(\text{or}) = (\pi c\omega(\text{or}))^{-1}, \tag{2}$$

where c is the velocity of light.



Dig. 2. Temperature dependence of $\omega_{1/2}(\text{isot})$ (○) and $\omega_{1/2}(\text{anis})$ (●) for each isomer. a); Meso isomer, b); racemic isomer.

The molecular symmetries of *r*- and *m*-DPP are C_1 and C_2 respectively. As has clearly been mentioned by Nafie and Peticolas,[10] in the DPP molecule the reorientational correlation time obtained from the $\nu_2(a_{1g})$ band of the ring-stretching vibration of phenyl groups should be related to a set of motions about the axes which diagonalize the moment-of-inertia tensor and also diagonalize the rotational diffusion tensor. However, the reorientation about the axis of the phenyl group, C–C$_{\text{ring}}$, will be faster than those about the other axes, taking into account the moment-of-inertia of each axis in the *m*- and *r*-DPP molecules. Accordingly, we may consider that the reorientational correlation time obtained from the $\nu_2(a_{1g})$ mode of the phenyl group is mainly concerned with the motion about the C–C$_{\text{ring}}$ axis.

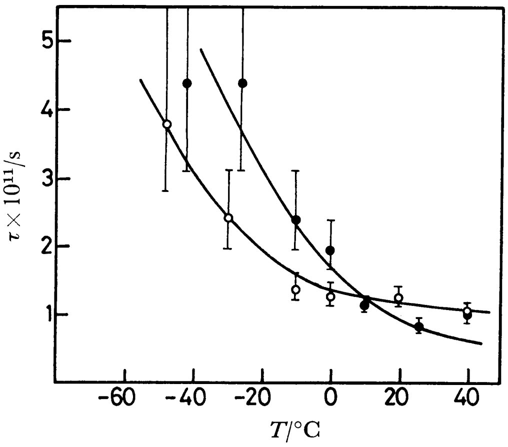


Fig. 3. Temperature dependence of the reorientational correlation time. ○; Racemic isomer, ●; meso isomer.

The temperature dependence of $\tau(\text{or})$ for each isomer of DPP in solution shown in Fig. 3. In the low-temperature region, the reorientational correlation times, $\tau(\text{or})$, of both isomers decrease sharply with an increase in the temperature and the values of $\tau(\text{or})$ of the racemic-type DPP are longer than those of the meso-type DPP at the same temperature. On the contrary, with an increase in the temperature, the temperature dependences of their $\tau(\text{or})$ become smaller and the $\tau(\text{or})$ values of meso-type DPP are longer than those of the racemic-type one.

Discussion

At the lowest temperature measured (−90 °C), of course, the solution was in a solid state (the melting point of chloroform is −63.5 °C), therefore, all the molecular reorientational motions were frozen out, that is, $\omega_{1/2}(\text{anis}) \simeq \omega_{1/2}(\text{isot})$.

Even in the liquid state, below temperatures of about −30 to −40 °C, the differences between $\omega_{1/2}$(isot) and $\omega_{1/2}$(anis) can hardly be distinguished, taking the experimental accuracy into account. This fact clearly indicated that the reorientational motion of phenyl groups in *m*- and *r*-DPP is frozen out and/or is extremely slow. In both isomers, as the temperature inceases, the differences between $\omega_{1/2}$(isot) and $\omega_{1/2}$(anis) increase. The reorientational motion of phenyl groups in a molecule gradually becomes active.

In the low-temperature region, the reorientational correlation times, τ(or), of *m*-DPP are longer than those of *r*-DPP; that is, the molecular motion of phenyl groups of the latter in the tt state rotates more easily than that of the former in the tg$^-$ state. This fact is in agreement with the results obtained by ultrasonic study.

However, at higher temperature, it seems that the reorientational motion of the phenyl groups of *m*-DPP becomes faster than that of racemic ones. As has been mentioned above, the conformational changes in each isomer could not be observed at any temperature. This suggests that there are some changes in the intermolecular relations in solution and open the way to further investigation of this subject.

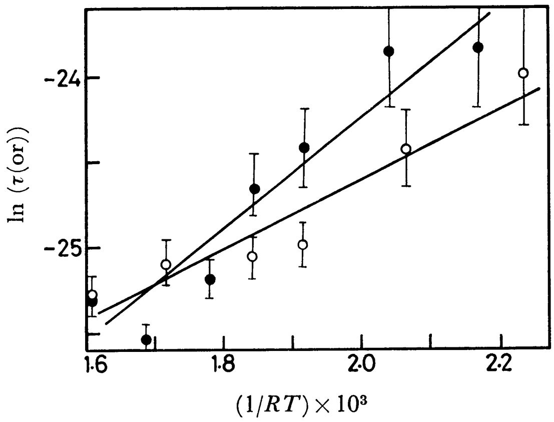


Fig. 4. Natural logarithmic reorientational correlation time *versus* $1/RT$. ○; Racemic isomer, ●; meso isomer.

The potential barrier for the reorientational motin of phenyl groups can be estimated from the following equation;[11]

$$\tau(\text{or}) \propto \exp\,(U_r/RT) \qquad (3)$$

where R is the gas-constant, T is the absolute temperature, and U_r is the potential barrier. Figure 4 shows the relationship between ln (τ(or)) and $1/RT$. As may be shown in Fig. 4, the difference between the meso and racemic isomers can be observed. The values obtained are (3.3±0.3) kcal/mol and (2.0±0.3) kcal/mol for the meso and racemic isomers respectively.

Usually, in solution the rotational relaxation time can be expressed by the Debye-Einstein relation;

$$\tau(\text{or}) = 4\pi a^3\eta/(3RT) \qquad (4)$$

where η is the viscosity coefficient of the solvent in a dilute solution. For chloroform, the activation energy obtained from the viscosity data[12] is 1.65 kcal/mol. This value is comparable to that obtained from the plot of ln(τ(or)) *vs.* $1/RT$ for *r*-DPP. The value of U_r for *m*-DPP is larger than that for the racemic one. The intramolecular interaction of phenyl groups in *m*-DPP may contribute to this difference in the rotational potential barrier. This fact shows that the rotational molecular motion of phenyl groups in *m*-DPP is hindered more than that of *r*-DPP.

TABLE 1. REORIENTATIONAL CORRELATION TIME

Sample	τ(or)/s
Toluene	0.60×10^{-11}
1,2-Diphenylethane	0.96
2,4-Diphenylpentane	2.4
Polystyrene M_w = 600	4.6
2200	6.4

(20 wt % in $CHCl_3$).

In Table 1, the τ(or) of DPP at room temperature is compared with those of several other molecules.[2,3] As the two phenyl groups in DPP are located at the 2 and 4 positions in normal pentane, the interaction between phenyl groups in DPP is much stronger than that of the 1,2-diphenylethane, where the two phenyl groups are located at the terminal carbon atoms. Therefore, the τ(or) of DPP is much longer than those of 1,2-diphenylethane and toluene, in which the phenyl group rotates freely. Moreover, the τ(or) values of polystyrene are longer than that of DPP and increase with the molecular weights, because of the short-range interaction between phenyl groups in the polymer chain.

In conclusion, the molecular motion of phenyl groups in DPP is very slow, and the rotation is almost completely hindered at low temperatures, where the single relaxation has been observed by ultrasonics. Accordingly, the single relaxation observed by ultrasonics should be considered to be due to the chain-conformational change in the molecule, as has mentioned by Monnerie *et al.* This is because the reorientational relaxation time of phenyl groups is of an order of 10^{-11} s, therefore, this motion should not be coupled with the rotational motion of the alkyl chain itself.

In addition, we can not consider that the elementary motion of polymer chains in solution is a conformational change, tt and tg$^+$ and/or tg$^-$ and g$^-$g$^-$, observed in 2,4-diphenylpentane. Usually in polystyrene solutions, the ultrasonic relaxations have been observed in the regions of MHz and several hundred MHz at room temperature.[13] Extrapolating the data obtained by Monnerie *et al.* to room temperature, the relaxation should be observed at 204 MHz in the tg$^-$(tg$^+$)$\rightarrow$tt process and at 575 MHz in tt$\rightarrow$g$^-$g$^-$. Besides, the relaxation amplitude, A, in those frequency regions is of an order of 1—2×10^{-17} neper/s^2 cm^{-1}; this value can hardly be detected at higher frequencies by means of present-day experimental techniques. Therefore, the unit of elementary motion of polymer chains in solution must be longer than the 2,4-diphenylpentane molecule.

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