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Dielectric relaxation of poly(*n*-hexyl isocyanate) in concentrated solutions of polybutadiene

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Abstract

We report the dielectric relaxation in a ternary system in which a trace amount of poly(*n*-hexyl isocyanate) (PHIC) is dissolved in concentrated toluene solutions of polybutadiene (PB). The dielectric response is due to the rod-like PHIC molecules having high dipole moment along its chain contour. Solutions of PB form entanglement networks which retard the reorientation of the PHIC molecules. With increasing concentration (C_{PB}) of PB from 0 to 40 wt% the relaxation behaviour changed at a crossover concentration C^{+}_{PB}. In the range below C^{+}_{PB}, the relaxation time τ for reorientation of the PHIC molecules increased on account of the effect of entanglement. However above $\mathrm{C}^{+}_{\mathrm{PB}}$, τ decreased and at the same time the relaxation strength decreased with increasing C_{PB}. The crossover concentration C^{+}_{PB} depended on the molecular weight M of the PHIC, i.e. $\mathrm{C}^{+}_{\mathrm{PB}} = 0.13$ at $M = 29,000$, and $C^{+}_{\mathrm{PB}} = 0.25$ at $M = 20,000$. The decrease of the relaxation strength can be attributed to the reduction of the effective dipole moment due to the restriction of motions of the PHIC chains in entanglement networks of PB chains. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Entanglement; Rod-like chain; Flexible chain

1. Introduction

Although effects of entanglement on chain dynamics of rod-like polymers have been studied both theoretically and experimentally by many authors [1–4], studies of entanglement effects between a rod-like chain and flexible chains are relatively rare [5–7]. When a trace amount of a rod-like polymer is dissolved in an entanglement network of flexible chains, overall rotational motion of the rod-like chain is expected to be heavily damped. Gupta et al. [5] reported the dielectric relaxation of ternary systems composed of polystyrene, solvent and a trace amount of rod-like molecules having a strong dipole moment; poly(γ-benzyl-L-glutamate) (PBLG) and poly(hexyl isocyanate) (PHIC). They reported that the relaxation time τ for reorientation of the rod-like molecules increased monotonously with increasing concentration of polystyrene and that the dielectric behaviour did not agree with the theories [8,9] for dilute solution of rod-like molecules if the viscosity of the polystyrene solution was taken as the medium viscosity. De Gennes [6] proposed a theory of rotational diffusion D_{r} of a rod-like chain having the length L in an entanglement network of flexible chains with the distance between entanglements of R_{e}, assuming that the rod-like chain is allowed to move only in the direction of the rod and that it changes the orientation angle by an order of R_{e}/L when the rod moves by L. The relaxation time $\tau(= 1/2D_{\mathrm{r}})$ is given by [6]

$$\tau \propto L^5 M_{\mathrm{e}}^{-1} \tag{1}$$

where M_{e} ($\sim R_{\mathrm{e}}^2$) denotes the molecular weight between entanglements of the flexible chains. In concentrated solution of a flexible polymer, M_{e} is proportional to the inverse of the concentration C_{fp}^{-1} of the flexible polymer [10] and hence Eq. (1) predicts that τ is proportional to C_{fp} in concentrated solution. Hill and Sonne discussed the dynamics of a rod-like chain dissolved in a semidilute solution of a semiflexible polymer with the persistence length L^* [7]. They predicted that τ is proportional to $L^7 C_{\mathrm{fp}}^2$.

Guputa et al. [5] reported that the dielectric relaxation strength decreased as well as τ with increasing concentration of flexible chains. They attributed the result to the aggregation of the PBLG or PHIC molecules. When the paper by Gupta et al. was published, the stiffness of the PHIC molecules had not been well characterised. Later, Teramoto et al. [11,12] studied the characteristics of PHIC and determined the persistence length q to be 37 nm at 25 °C in toluene. The corresponding molecular

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weight is 27,000. The molecular weights of the PHIC samples used by Gupta et al. were higher than q indicating that their samples were not rod-like. The above mentioned theory by de Gennes also published after the paper by Gupta et al. was published. Thus it is needed to reexamine the dynamics of rod-like molecules in flexible chains. In this view, we carried out dielectric measurements on a ternary system in which a small amount of (PHIC) is dissolved in concentrated toluene solutions of polybutadiene (PB). The reason for the use of PB is that M_e of PB is much lower than that of polystyrene [10].

The theories of de Gennes [6] and Hill and Soane [7] deal idealised systems in which the chain length L of a rod-like polymer is much longer than the mesh size of entanglement networks. However in the present system, the molecular weight of the rod-like chain is limited. Therefore our objective is not to compare the experimental results with those theories, but is to examine the dynamical behaviour of PHIC molecules in a system containing relatively short PHIC chains. We will firstly examine the dynamics of PHIC molecules in dilute solution in toluene and then will examine the effect of adding PB chains to dilute PHIC solutions.

2. Experimental

PHIC was synthesised at −20 °C in toluene by using a titanium compound ($TiCl_3OCH_2CF_3$) reported by Patten and Novak [13] as the catalyst. The PHIC samples were characterised by using vapour-phase osmometry, membrane osmometry (Mechrolab Inc Model 502), and gel permeation chromatography (GPC) equipped with light scattering detector (Tohso LS-8000) [14]. The characteristics are shown in Table 1. As described in Section 1, the molecular weight corresponding to the persistence length q of PHIC is 27,000. The molecular weights of the three PHIC samples used here are approximately equal or less than q and therefore the conformation of the present PHIC samples is approximately rod-like. The lengths L of the PHIC molecules are calculated according to the data of molecular weight per unit contour length M_L (=740 nm^{-1}) reported by Teramoto et al. [11] (Table 1). Narrow distribution PB was prepared by anionic polymerisation in heptane with *s*-butyllithium as the catalyst. PB was characterised with GPC. The characteristics is also shown in Table 1. The solvent toluene used for preparation of sample solutions was of the grade of 99.9% purity and was produced by Dojin Chemicals (Kumamoto, Japan).

Table 1
Characteristics of sample

Code	$10^{-4}M_n$	L (nm)	M_w/M_n
PHIC-13	1.25	17	1.2
PHIC-20	1.95	26	1.18
PHIC-28	2.80	37	1.24
PB-79	7.90	–	1.05

Dielectric measurements were carried out on an RLC bridge (QuadTech Model 1693, Maynard, USA) in the range 0.015–200 kHz.

3. Results and discussion

3.1. Dielectric behaviour of PHIC/toluene binary system

The frequency f dependence of the dielectric loss factor ε'' for a dilute toluene solution of PHIC-20 is shown in Fig. 1 where ε'' is normalised by the concentration C (=0.00030 g ml^{-1}) of PHIC-20. As is observed usually the loss peak shifts to higher frequency and intensity decreases approximately in proportion to the inverse of temperature T. Similar behaviour was observed for the other two PHIC samples. The relaxation time $\tau (= 1/2\pi f_m)$ at 290 K is plotted against the number average molecular weight M in Fig. 2, where f_m denotes the loss maximum frequency. For solutions of PHIC-20 and PHIC-13, the loss peaks at 290 K locate above the highest frequency (200 kHz) used in the present measurements and therefore f_m was determined by extrapolation of the Arrhenius plots, namely the $\log f_m$ vs. $1/T$ plots. According to Kirkwood and Auer [9] the relaxation time of a rod-like molecule with length L and diameter b is given by

$$\tau = \frac{\pi \eta_s L^3}{6k_B T\left[\ln\left(\frac{L}{b}\right) - \delta\right]} \qquad (2)$$

where η_s is the solvent viscosity and δ the small collection term depending on the shape of the ends. This equation predicts that the slope of the double logarithmic plots of τ vs. L is close to 3 but slightly smaller than 3. The slope of

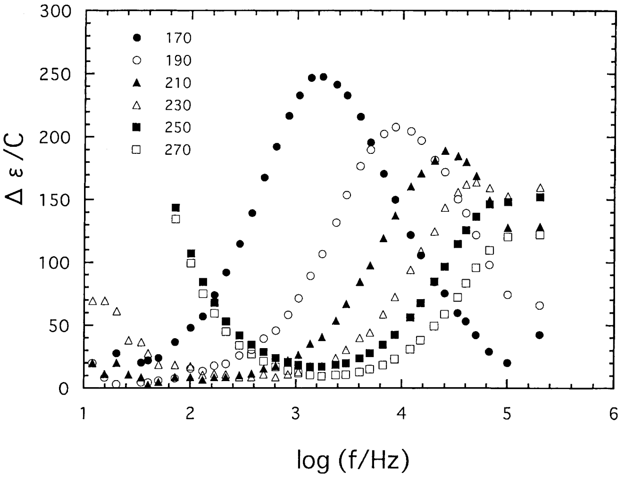

Fig. 1. Frequency f dependence of the normalised dielectric loss factor ε''/C for PHIC-20 dilute solution ($C = 0.00030$ g cm^{-3}) in toluene. Temperatures of measurement are indicated in the figure.

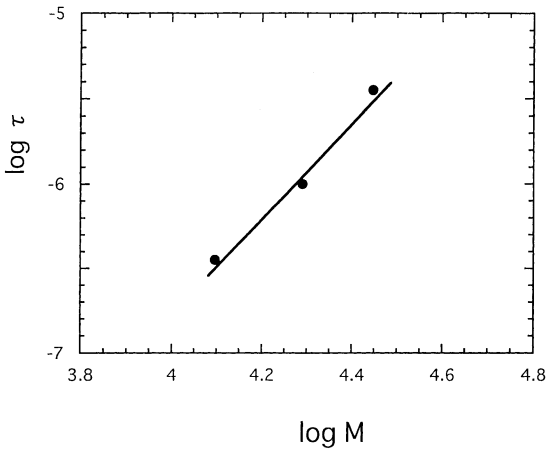

Fig. 2. Molecular weight dependence of relaxation time τ for dilute PHIC solutions in toluene.

the plot shown in Fig. 2 is 2.90 and agrees well with this theory. The L dependence of τ was already examined in detail by Takada et al. [15] and present result agrees well with their data. Eq. (2) predicts that the temperature dependence of the relaxation time is totally due to that of the viscosity of toluene. However, the activation energy for τ of PHIC-20 at 280 K is 14 kJ mol^{-1} and is higher than the activation energy (8.8 kJ mol^{-1}) of the viscosity of toluene. In Fig. 1, we see that the half width of the ε'' curve is independent of temperature and is 1.60 decades. This value is larger than the half width (=1.14) for the single dispersion and is mostly due to the distribution of molecular weight.

The dielectric relaxation strength $\Delta\varepsilon$ divided by the PHIC concentration C in the unit of g cm^{-3} was determined by the Cole–Cole plot. Generally $\Delta\varepsilon/CM$ of a rod-like molecule with the dipole moment p and length L is given by

$$\frac{\Delta\varepsilon}{CM} = \frac{4\pi N_A \mu^2}{3k_B T M_L^2} F \tag{3}$$

where M is the molecular weight, N_A is the Avogadro number, μ the dipole moment per unit contour length ($p = \mu L$), M_L the molecular weight per unit contour length, and F the internal field factor. Here only F is not well defined. Takada et al. [15] reported that F is closer to unity than the familiar factor given by Onsager [16] and is given by the Buckingham equation [17]. Adachi et al. also indicated that F for the normal mode relaxation exhibited by flexible chains having the dipole moment aligned parallel to the chain contour (Type A chains) is close to unity [18]. Thus F for dipoles extending over a long distance is close to unity irrespective of the conformation. Eq. (3) indicates that $\Delta\varepsilon/(MC)$ is independent of molecular weight. This value is 0.0165 for PHIC with M less than q and is shown later in Fig. 6. The value of μ is calculated to be 1.20×10^8 D cm^{-1} ($= 4.00 \times 10^{-20}$ C).

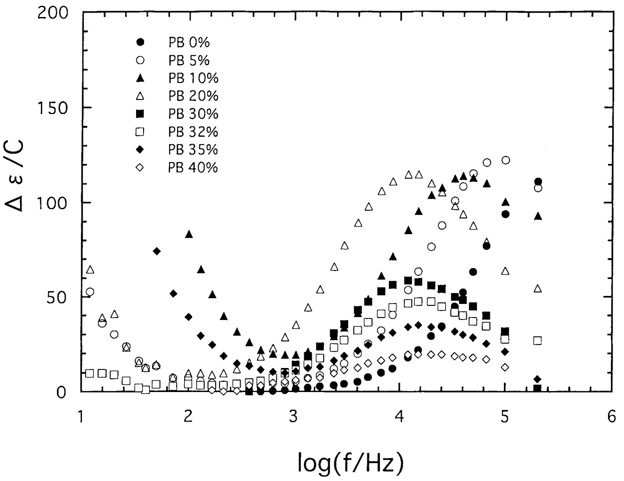

Fig. 3. Frequency f dependence of the normalised dielectric loss factor ε''/C for PHIC-20/PB/toluene ternary system. Concentration of PHIC-20 is fixed to be 0.00030 g cm^{-3} (0.035 wt%) and concentration of PB is changed from 0 to 40 wt% as indicated in the figure.

3.2. Dielectric behaviour of PHIC/PB/toluene ternary system

Fig. 3 shows the frequency f dependencies of the dielectric loss ε'' divided by concentration C of PHIC for the ternary system composed of PHIC-20, PB, and toluene. The concentration C of PHIC-20 was ca. 0.00030 g cm^{-3} and concentration of PB (C_{PB}) was changed from 0 to 40 wt%. Hereafter we represent the experimental data with C_{PB} given by weight fraction of PB. In this figure, we recognise two characteristic features. With increasing C_{PB} the loss maximum frequency f_m shifts to lower frequency but with further increase of C_{PB}, f_m decreases no more but increases slightly. The crossover concentration C_{PB}^+ between those different behaviour is ca. 20 wt%. The second feature is that the intensity ε''/C is almost independent of C_{PB} below C_{PB}^+ but above C_{PB}^+ it decreases with increasing C_{PB}. We will call the former the regime I and latter the regime II. It is expected that in the range of very low C_{PB}, there exists another regime where both f_m and the intensity are independent of C_{PB}. In the present study, we did not examine such a low C_{PB} range. Fig. 4 shows the frequency f dependence of ε''/C for the ternary system containing 0.030 g cm^{-3} of PHIC-28. We see very similar behaviour to the PHIC-20/PB/toluene system. The C_{PB}^+ is ca. 10 wt% indicating that C_{PB}^+ is sensitive to the molecular weight of PHIC.

Fig. 5 shows the C_{PB} dependencies of the relaxation time τ defined by $1/(2\pi f_m)$. Here the arrows indicate the relaxation times at $C_{PB} = 0$. In the regime I, τ increases with C_{PB} but in the regime II it decreases with increasing C_{PB}. In these two regimes the plots conform approximately to straight lines. The crossover concentration C_{PB}^+ may be defined by the concentration at which the two lines intersect. The values of C_{PB}^+ thus determined are 25 and 15 wt% for PHIC-20 and PHIC-28, respectively. The slope of the plot

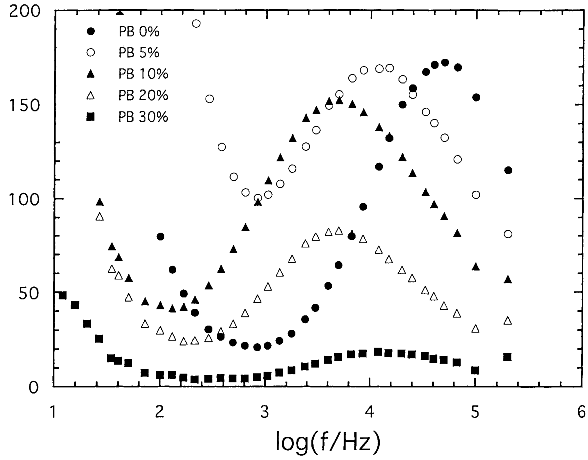

Fig. 4. Frequency f dependence of the normalised dielectric loss factor ε''/C for PHIC-28/PB/toluene ternary system. Concentration of PHIC-28 is fixed to be 0.00030 g cm^{-3} (0.035 wt%) and concentration of PB is changed from 0 to 30 wt% as indicated in the figure.

in the regime I is 1.46 and will be discussed later. It is interesting to see that the slope for PHIC-28 is also ca. 1.4 although the number of the data points is not enough.

Fig. 6 shows the normalised relaxation strength $\Delta\varepsilon/CM$ for the two systems. The arrows have the same meaning as Fig. 5. The crossover concentration C_{PB}^{+} was determined in the same manner as in Fig. 5; $C_{PB}^{+} = 20$ and 13 wt% for PHIC-20 and PHIC-28, respectively. The slight discrepancy between the values of C_{PB}^{+} determined in Figs. 5 and 6 may be ascribed to experimental error and will not be discussed further.

Gupta et al. [5] reported that the relaxation strengths for PHIC/poly-styrene/toluene and PBLG/polystyrene/dioxane systems decrease monotonously with increasing concentration of polystyrene in the range of polystyrene concentration from 0 to 20 wt%. They did not find the two regimes having different concentration dependence. They ascribed their result to aggregation of the rod-like molecules. The origin of this discrepancy between the present data and those of Gupta et al. is not clear at the present stage. However, we suspect that there was systematic error in the determination of $\Delta\varepsilon$ in the work of Gupta et al. as the determination of the static and high frequency dielectric constants needs extrapolation of the dielectric constants measured in a finite range of frequency. They did not describe the method of determination of $\Delta\varepsilon$ in detail.

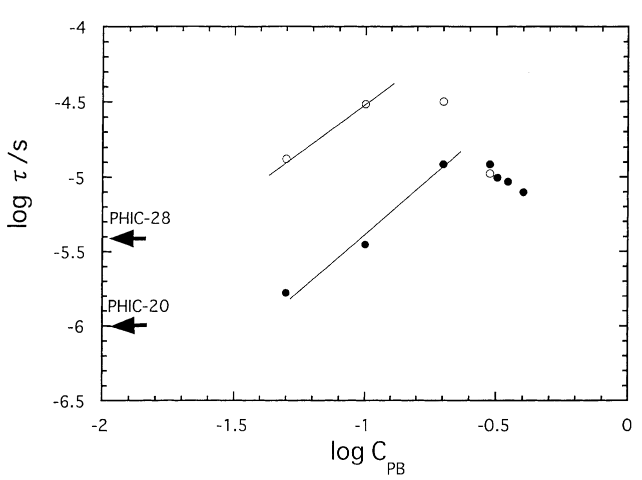

Fig. 5. Dependence of relaxation time τ for reorientation of PHIC molecules on concentration C_{PB} of PB.

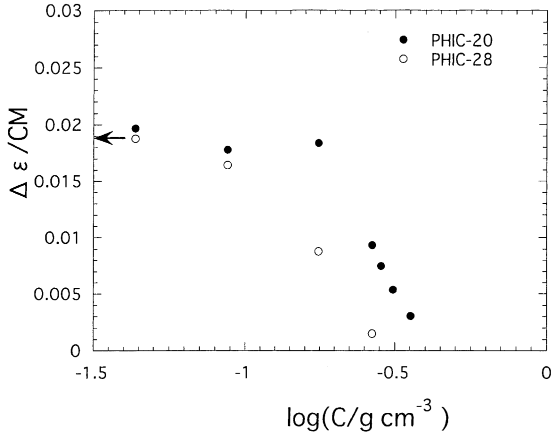

Fig. 6. Dependence of dielectric relaxation strength $\Delta\varepsilon$ normalised by CM for PHIC-28/PB/toluene ternary system. The arrow indicates the value for the PHIC dilute solution in toluene.

3.3. Dynamics of PHIC chains in regime I

In the concentration range of $C_{PB} < C_{PB}^{+}$, the relaxation strength $\Delta\varepsilon/C$ is independent of C_{PB} and the relaxation time of the PHIC chains increases with increasing C_{PB}. This behaviour indicates that the PHIC molecules rotate fully but their motions are retarded by entanglement effects. Thus the behaviour must be closely related to the sizes of the PHIC molecules and the entanglement networks. The lengths L of the PHIC-20 and PHIC-28 molecules are 26 and 37 nm, respectively, as listed in Table 1. On the other hand, the distance R_e between entanglements of PB chains decreases with increasing concentration.

Generally, polymer solutions are classified into dilute, semidilute, semiconcentrated, and concentrated regimes [19–23]. For the sake of simplicity, we neglect here the semiconcentrated regime and estimate the C_{PB} dependence of R_e as follows. The crossover concentration C_s^* from dilute to semidilute regimes (overlapping concentration) is estimated to be 0.012 g ml^{-1} for the present PB sample from the intrinsic viscosity in heptane [23]. According to the scaling theory by de Gennes [24], R_e in semidilute solution is given by the correlation function ξ of segment density C_s. Thus the concentration dependence of C_s is given by [19]

$$\xi \propto \left(\frac{C_s}{C_s^*}\right)^{\frac{-\nu}{3\nu-1}} \tag{4}$$

where ν is the Flory excluded volume parameter and for the present PB solution $\nu = 3/5$ as toluene is a good solvent for

PB. The assumption that ξ is similar to R_e was examined by rheological methods and was indicated that R_e approximately scales as Eq. (4) [25]. Thus we assume that R_e in PB/toluene simidilute solutions is proportional to $C_{PB}^{-0.75}$.

In the concentrated regime M_e is proportional to C_{PB}^{-1} as mentioned earlier. Thus R_e in the concentrated regime scales as $C_{PB}^{-0.5}$. Here we encounter a difficulty in determination of the crossover concentration C^{**} between the semidilute and concentrated regimes. According to Daoud and Jannink [20], C^{**} is given by $(T - \theta)/\theta$ where θ is the theta temperature. For the present PB/toluene solution, θ is not known and therefore we roughly assumed that C^{**} is 0.20. The reason is that for polyisoprene in benzene the crossover from semidilute to semiconcentrated solution was observed around 0.20 g ml^{-1} [22].

In the bulk state, the molecular weight M_e^0 between entanglement points was reported to be 1900 [10] and the relationship between the end-to-end distance R_0 and molecular weight for PB containing 60% *cis*-linkage is given by [26]

$$R_0 = 0.0825\sqrt{M}\ (\text{nm}) \tag{5}$$

Thus R_e of the bulk PB is calculated to be 3.59 nm.

From above mentioned arguments the C_{PB} dependence of R_e is calculated and plotted in Fig. 7. In the same figure, L's of PHIC-20 and PHIC-28 are indicated by dotted lines. We see that L is longer than R_e but is not sufficiently longer than R_e for the all solutions examined in the present study. Thus the present system is far from the model used in the theories [6,7]. In the regime I, the PHIC molecules reorient in a loose entanglement network in which L is several times longer than the mesh size.

As is seen in Fig. 5, the relaxation time τ increases with C_{PB} in the regime I. From the slope of the plot we see that $\tau \propto C_{PB}^{1.46}$. This exponent is higher than that predicted by Eq. (1) but is lower than the theory proposed by Hill and Soane [7]. It is noted that the friction coefficient for motion of molecules also increases with increasing C_{PB}. Thus the exponent of 1.46 is not totally due to the entanglement effect. In the present study only two PHIC samples were used for the test of C_{PB} dependence. Therefore it is difficult to examine whether τ satisfies the scaling form of $\tau \propto L^{\alpha}$.

3.4. Dynamics of PHIC chains in regime II

In the regime II, the intensity decreased with increasing C_{PB}. Several origins may be raised. As the first possibility, we consider that the solubility of PHIC in PB solutions becomes low and hence in the regime II, the excess PHIC molecules above the solubility precipitate and do not contribute to the dielectric relaxation. The second probability is aggregation of more than two PHIC molecules as assumed by Gupta et al. [5]. If the aggregation occurs so that the dipoles orient antiparallel in the cluster, the intensity decreases. The third possibility is the frozen-in of overall rotation of the PHIC molecules due to constraint by PB chains. In this case only the rotational oscillation is allowed and the effective dipole moment decreases.

Now we check these possibilities. If the first mechanism is true, we can estimate the solubility of PHIC in the PB solution by comparing $\Delta\varepsilon/C$ in the regimes I and II. It is noted that in the above mentioned experiments we used the PHIC concentration $C = 0.035$ wt% ($= 0.00030$ g ml^{-1}). For PHIC-20/PB/toluene solutions of $C_{PB} = 35\%$ the hypothetical solubility is estimated to be ca. 0.01% since the relaxation strength is ca. 1/3 of $\Delta\varepsilon/C$ in the regime I. Therefore if the first possibility is true, solutions of PHIC-20 with C less than 0.01 wt% should exhibit high normalised strength $\Delta\varepsilon/C$. This is tested in Fig. 8 where the ε''/C curves for PHIC-20/PB/toluene solutions of $C_{PB} = 35\%$ with varying PHIC concentration are shown. It is seen that the peak value of ε''/C even at $C = 0.003$ wt% is much smaller than the value of ε''/C in the regime I. Thus the first possibility is ruled out.

The result shown in Fig. 8 also rules out the second possibility. If aggregates of the PHIC molecules are formed, the association equilibrium is attained. Therefore if the

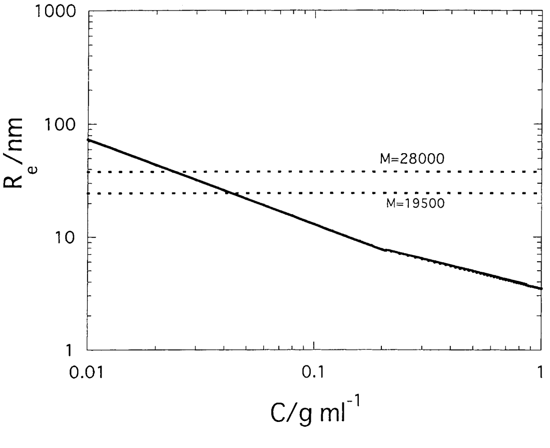

Fig. 7. Theoretical estimation of the mesh size of entanglement network R_e for concentrated PB solutions (solid line) and the level of the length of PHIC molecules (dotted line).

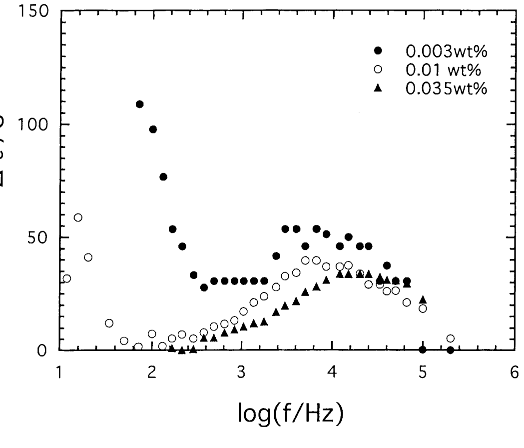

Fig. 8. Frequency f dependence of the normalised dielectric loss factor ε''/C for PHIC-20/PB/toluene ternary system. Concentration of PB is fixed to be 35 wt% and concentration C of PHIC is changed from 0.003 to 0.035 wt%.

second possibility is true, the ratio of the free PHIC molecules and hence $\Delta\varepsilon/C$ should increase with decreasing C. As is seen in Fig. 8, the intensity is almost independent of C and hence the experimental result is not harmony with the second possibility. In the regime II, the relaxation time decreases with increasing C_{PB} (Fig. 5). The size of aggregates is expected to increase with increasing C_{PB}. However the relaxation time decreases with increasing C_{PB} in the regime II. This fact also rules out the second possibility.

From the above discussion we consider that the most probable mechanism of the decrease of intensity is the restriction of the overall rotation of the PHIC molecules: the PHIC molecules cannot rotate in an entanglement network formed by PB chains. The oscillation (liberation) of the PHIC molecules is allowed in the range of angle of $\theta = R_e/L$ where R_e is the distance between the entanglement. If the dipole moment of the PHIC chain is μL, the effective dipole moment reduces to $\mu L \sin(\theta/2)$. Since the range of angle for rotational motion is less than 180° the relaxation time also decreases in the regime II.

However, this explanation has a difficulty. The dielectric relaxation due to overall rotation should be observed in low frequency region. As seen in Figs. 3 and 4, ε'' increases due to the dc conduction in the low frequency region and we could not observe such relaxation. We also expect that if this mechanism is true bimodal peak should be observed around the crossover PB concentration. In Figs. 2 and 3 no such peaks are seen. We speculate that the overall rotation is governed by the mechanism given by Eq. (1), and the translational diffusion coefficient D_{trans} decreases suddenly in the regime II. The interaction between relatively long hexyl groups of PHIC chains and PB chains will result in slow down of D_{trans} in the regime II. This speculation must be tested by measurement of diffusion in future.

4. Conclusion

The dielectric relaxation of rod-like poly(*n*-hexyl isocyanate) (PHIC) molecules in concentrated toluene solutions of polybutadiene (PB) has been studied. In dilute solution of PHIC in toluene, the dielectric relaxation time τ is proportional to $L^{2.90}$ in agreement with the Kirkwood–Auer theory, where L denotes the length of the PHIC molecules. In concentrated toluene solutions of PB, L is found to be longer than the mesh size of entanglement networks formed by PB chains, and the relaxation behaviour depends strongly on the PB concentration C_{PB}. There exist the regime I and II where the C_{PB} dependence of τ differ. In the regime I, τ increases with increasing C_{PB} of PB but above a crossover concentration C_{PB}^{+}, τ decreases (the regime II). The crossover concentration C_{PB}^{+} increases with decreasing molecular weight M of the PHIC, i.e. $C_{\mathrm{PB}}^{+} = 0.13$ at $M = 29,000$, and $C_{\mathrm{PB}}^{+} = 0.25$ at $M = 20,000$. In the regime I, τ is proportional to $C_{\mathrm{PB}}^{1.46}$. In the regime II the relaxation strength $\Delta\varepsilon$ decreases with increasing C_{PB}. The decrease of $\Delta\varepsilon$ is explained by considering the restriction of motions of the PHIC chains in entanglement network of PB chains.

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