Intrachain Conduction and Main-Chain Conformation of Conducting Polymers as Studied by Frequency-Domain Electric Birefringence Spectroscopy

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The single-chain dynamics of a typical soluble conducting polymer, poly(3-hexylthiophene), has been studied in solutions by frequency-domain electric birefringence spectroscopy. From the results, we have obtained information on the intrachain conduction mechanism exclusively without the interference from the interchain one as well as information on a close correlation between the conduction mechanism and the main-chain conformation. It is clearly revealed that there exist two kinds of transport of carriers along the polymer chain with different diffusion distances and diffusion constants.

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For the last decade, conducting polymers with π-conjugated electronic structure have attracted the interest of physicists and chemists because of peculiar properties such as the high electric conductivity comparable to metals, the solubility in organic solvents, and the nonlinear optical property [1].

The transport mechanisms of the conducting polymers in the solid state (bulk or films) are classified into three categories, i.e., the intrachain (intramolecular), interchain (intermolecular), and interfibrillar hoppings. Since all of these three hopping mechanisms can contribute to the electric conductivity of the polymers in the solid state, it is difficult to distinguish each contribution by the experimental results of the conductivity in the solid state alone.

If the conducting polymer is dilutely dissolved in a solvent, the interchain hopping is inactivated and the motion of carriers is restricted within a single chain, since polymer chains are isolated from each other in the solvent as an insulator. Thus, we can obtain exclusively the information on the intrachain conduction mechanism, i.e., on the electric conductivity of a single chain by investigating the motion of carriers in the dilute solution of conducting polymers [2].

It is known that the conformational change of a polymer chain in the solution from a coiled form to an extended one has a strong correlation with the electronic structure of the polymer chain [3–6]. However, the intrachain transport mechanism of carriers on the polymer chain in the solution still remains obscure. When the external electric field is applied to the solution, the motion of carriers within a single chain contributes to the electric polarizability of the chain and consequently to the dielectric constant of the whole solution and not to the solution conductivity, because the carriers are bound to the single chain. In this case, two different types of dielectric responses are expected: One is due to the permanent (or quasipermanent) dipole moment that arises from carriers moving along a polymer chain much more slowly than the rotation of the chain. The external electric field produces a torque to orient the permanent dipole moment toward the direction of the electric field, which results in the electric polarization due to the rotation of the permanent dipole moment. The other is the case where the carriers move much faster than the rotation. Then, the external electric field induces a dipole moment due to the transport of carriers on the polymer chain, which results in a different type of electrical torque to orient the chain. These two different responses can be clearly distinguished by the frequency-domain electric birefringence (FEB) spectroscopy [7], which gives us the information on the mobility of carriers along the polymer chain as well as on the polymer conformation. The purpose of this study is to reveal the intrachain conduction and main-chain conformation of a typical soluble conducting polymer, poly(3-hexylthiophene) (P3HT), by using the FEB technique.

There are two kinds of electric birefringence techniques: the FEB spectroscopy and the transient electric birefringence (TEB) method [2,8]. The TEB method has been applied to the solution of poly(diacetylene) in order to study the rod-coil transition of the polymer conformation [4]. However, for investigation of the conducting polymers, the FEB spectroscopy is more adequate than the TEB method, since the FEB spectroscopy can give us the transport relaxation time and hence the mobility of the carrier along the polymer chain separately from the rotational relaxation time of the polymer chain. The comparison between the rotational and transport relaxation times leads to a detailed understanding of the correlation between the conformation and intrachain conduction of the conducting polymer.

The preparation methods of P3HT can be seen elsewhere [9(a)]. The P3HT material used in this study was

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lightly doped with $FeCl_2$ anions that neutralize the positive charges on the P3HT chains [9]. The elementary analysis indicates that the number ratio of the dopants of $FeCl_2$ to the monomer units of P3HT was ca. 1.5%. The weight-average molecular weight $\overline{M}_w$ of the sample was 2.5×10^5 g with $\overline{M}_w/\overline{M}_n$ of 5.5, where $\overline{M}_n$ is the number-average molecular weight. To dissolve the P3HT sample in solutions, we adopted two kinds of solvents, toluene and methylene chloride. The P3HT sample was highly soluble in toluene and less soluble in methylene chloride than in toluene. For the FEB measurement, we prepared the solutions of 0.01 wt% P3HT in mixtures of toluene and methylene chloride with various fractions. Incidentally, the experimental results showed that the rotational relaxation time was independent of the polymer concentration. This suggests that polymer chains are isolated from each other in the solution with no aggregation or entanglement.

By the FEB measurement, we obtain the Kerr response K, which is defined as the birefringence response Δn divided by the mean-square value of the applied electric field with the angular frequency ω, and is written as $K = K_{dc} + \mathrm{Re}[K^*_{2\omega}\exp(i2\omega t)]$, where K_{dc} corresponds to the dc component Δn_{dc} of Δn and $K^*_{2\omega}(=K'_{2\omega} - iK''_{2\omega})$ is the complex amplitude of the term corresponding to the 2ω component $\Delta n_{2\omega}$ of Δn. According to the theoretical treatment [7], K_{dc} affords the information on the anisotropy and dynamics of the electrical polarizability of the polymer chain. The relaxation time τ' of $K_{dc} \equiv \mathrm{Re}(\psi^*)$ is given by a harmonic mean of the rotational relaxation time τ_r of the polymer chain and the transport relaxation time τ_t of carriers along the polymer chain as

$$(\tau')^{-1} = (\tau_r)^{-1} + (\tau_t)^{-1}, \tag{1}$$

where ψ^* is the response function of the dc component. Thus, if the carrier transport along the chain is much faster than the rotation of the polymer chain, i.e., $\tau_t \ll \tau_r$, τ' approaches to τ_t, which indicates that we can obtain the transport relaxation time τ_t directly from K_{dc} in this case. Incidentally, τ' is identical with the relaxation time of the complex dielectric constant ε^* measured by the dielectric relaxation spectroscopy.

On the other hand, the 2ω component $K^*_{2\omega}$ is given by

$$K^*_{2\omega} = \psi^*\phi^* = \psi^*(1 + 2i\omega\tau_r/3)^{-1}, \tag{2}$$

and thus affords the rotational relaxation time τ_r through the data analysis combined with K_{dc}. We can obtain τ_t by introducing τ' from K_{dc} and τ_r from $K^*_{2\omega}$ into Eq. (1). The experimental data were fitted to the semiempirical formulas of the Havriliak-Negami type [10] in place of the Debye one given by Eq. (2) to take into account the distributions of the relaxation times τ_t and τ_r.

The FEB spectra were measured in the frequency range below 100 kHz at room temperature. The outline of the apparatus used in this study was described in the previous paper [7,11].

Figure 1 shows the FEB spectra of the solutions of P3HT in mixtures of methylene chloride and toluene with various weight ratios of (a) 100:0, (b) 90:10, and (c) 80:20, where the solid curves are best-fitting ones obtained from the semiempirical formulas of the Havriliak-Negami type. It is seen from K_{dc} in Fig. 1(a) that there exist three relaxations: the low-frequency (LF) one with a relaxation frequency of ca. 40 Hz, the middle-frequency (MF) one with a relaxation frequency of 1 kHz, and the high-frequency (HF) one with no dispersion in the frequency range below 100 kHz. Since the relaxation frequency of the LF relaxation is nearly equal to the rotational relaxation frequency f_r observed in $K^*_{2\omega}$, the LF relaxation is ascribed to the rotational motion of the permanent or quasipermanent dipole moments. On the other hand, the MF and HF relaxations with the relaxation frequencies much higher than the rotational one are ascribable to the induced dipole moments and the reciprocals of relaxation frequencies yield the transport relaxation times of carriers along the polymer chain. In addition, the comparison of Figs. 1(a)-1(c) exhibits that the relaxation strengths of the MF and HF relaxations decrease exponentially with increasing fraction of toluene; in particular the MF relaxation decreases most rapidly. At the same time, as the fraction of toluene increases, the rotational relaxation frequency shifts to the higher region while the MF relaxation frequency remains almost constant.

The decreases of the MF and HF relaxation strengths and the rotational relaxation time $\tau_r = (2\pi f_r)^{-1}$ with in-

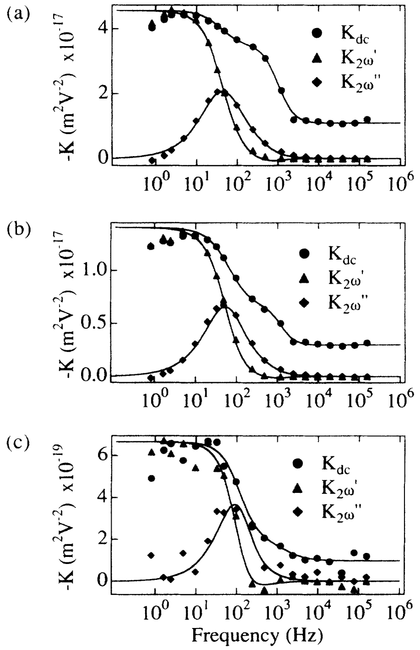

FIG. 1. The FEB spectra of the solutions of 0.01 wt% P3HT in mixtures of methylene chloride and toluene with weight ratios of (a) 100:0, (b) 90:10, and (c) 80:20.

creasing fraction of toluene suggest the rod-coil transition of the polymer conformation. As the polymer chain changes its conformation from an anisotropic extended form to an isotropic coiled one, the FEB signal arising from the optical anisotropy of the polymer conformation is reduced drastically and the shrinkage of the polymer size accelerates the overall rotation of the polymer chain. We confirmed the change of the main-chain conformation from a rodlike form to a coiled one with the increasing mixture ratio of toluene by the absorption spectra of the P3HT solutions.

If we approximate a semiflexible chain of P3HT as a rod with the effective length $L_{\rm eff}$ and the effective radius a, we can evaluate $L_{\rm eff}$ from the experimental results of the rotational relaxation time τ_r by using the following relation [12]:

$$\tau_r = \frac{\pi \eta L_{\rm eff}^3}{6 k_B T [\ln(L_{\rm eff}/a) - \gamma]} , \tag{3}$$

where $k_B T$ is the thermal energy, γ a correction term for the end effect, and η the solvent viscosity. Figure 2 shows the dependence of $L_{\rm eff}$ evaluated from τ_r on the fraction of methylene chloride in mixed solvents. It is seen from Fig. 2 that the increase of the fraction of methylene chloride results in the increase of the effective size of the polymer chain, namely, a crossover from a coiled form to an extended one. Incidentally, the value of $L_{\rm eff}$ in pure methylene chloride is evaluated to be 1.3 μm, which is about twice as long as a contour length of 0.59 μm calculated from the weight-average molecular weight $\overline{M}_w$. This discrepancy may be ascribed to a large polydispersity of P3HT sample.

When a conducting polymer chain has a coiled form, the conjugation of π electron is cut off at the defect points which yield the flexibility of the molecule. As the polymer chain changes the conformation from a coiled form to an extended one, the number of the defect points on the polymer chain decreases, and hence mobile carriers on the chain can transport along the polymer chain within a longer range up to the contour length of the chain. As shown in Fig. 1, the experimental results indicate that the MF relaxation can be clearly observed only for a highly extended form of P3HT. Thus, the MF relaxation is ascribable to the fluctuation of the mobile carriers along the polymer chain within the range of the order of the contour length. Since the transport relaxation time τ_t in the one-dimensional system is written with the diffusion distance L and the diffusion constant D as

$$\tau_t = L^2/2D , \tag{4}$$

we can evaluate the diffusion constant D ($\equiv D_M$) of the MF relaxation to be 1.1×10^{-9} m^{2}s^{-1} from the experimental value 1.02 kHz of the transport relaxation frequency $f_t = (2\pi\tau_t)^{-1}$ for the MF relaxation by using Eq. (4) with the assumption that the diffusion distance L ($\equiv L_M$) of the MF relaxation is equal to the effective rod length $L_{\rm eff}$.

On the other hand, the defect points may restrict the motion of the carriers on the polymer chain within a short range between two defects in a short time scale. Figure 1(a) shows that the HF relaxation coexists with the MF one, which suggests a possibility that the HF one is due to a much more localized transport of the mobile carrier along the P3HT chain in pure methylene chloride. In order to obtain more detailed information on the HF relaxation, we measured the dielectric relaxation of the solution of 0.13 wt% P3HT in pure methylene chloride with an impedance analyzer (HP 4191A) in the high-frequency range above 1 MHz at room temperature. The dielectric relaxation spectra of the P3HT solution are shown in Fig. 3, where the solid curves are the best-fitting ones obtained by using the semiempirical formula of the Havriliak-Negami type [10]. The figure exhibits a dielectric relaxation with a dielectric increment (relaxation strength) $\Delta\varepsilon$ of 0.58 and a relaxation frequency f_d of 26.0 MHz.

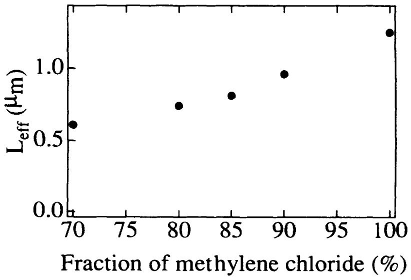

FIG. 2. Effective length of P3HT in 0.01 wt% solution as a function of the fraction of methylene chloride.

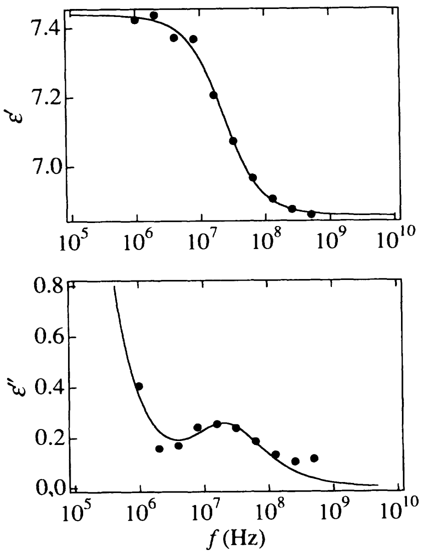

FIG. 3. The dielectric relaxation spectra of the solution of 0.13 wt% P3HT in methylene chloride.

When the dielectric relaxation arises from the induced dipole moments with the relaxation time τ_d much faster than the rotational relaxation time τ_r of the polymer chain, τ_d is identified with the transport relaxation time τ_t given by Eq. (4). Further, the dielectric increment $\Delta\varepsilon$ is related with the fluctuation distance L as

$$\Delta\varepsilon = C_N e^2 L^2 / 3\varepsilon_0 k_B T , \qquad (5)$$

where C_N is the number concentration of the mobile carriers contributing to the dielectric relaxation , e the elementary charge, and ε_0 the vacuum permittivity.

The mobile carrier is produced when the dopant extracts an electron from the polymer chain and becomes distant from the carrier. If the dopant is in the vicinity of the carrier, the carrier is pinned down to the dopant owing to the strong Coulombic attractive force from the dopant and thus becomes insensitive to the external electric field. The dopants distant from the polymer chain (free dopants) produce the solution conductivity σ and the concentration of the free dopants is considered to be equal to the concentration C_N of the mobile carriers. Hence, if the mobility μ of the dopant $FeCl_2$ in methylene chloride is known, we can evaluate C_N by measuring the solution conductivity $\sigma = C_N e \mu$.

To estimate μ, we measured the concentration dependence of the conductivity of methylene chloride solutions of several salts including ClO_4 or BF_4 as an anion, of which the size is close to $FeCl_2$. The results indicated that the mobilities of these anions in methylene chloride were nearly equal to each other, and hence μ of $FeCl_2$ may be also similar to them. Thus, C_N is evaluated from σ as ca. 2×10^{-3} mol/m^{-3} for the 0.13 wt% P3HT solution. Substituting this value of C_N and the observed value of $\Delta\varepsilon$ into Eq. (5), we obtain the diffusion distance L ($\equiv L_H$) of the HF relaxation as 5×10^{-2} μm, from which we have, in turn, the diffusion constant D ($\equiv D_H$) of the HF relaxation as 2×10^{-7} m^{2}s^{-1} by using Eq. (4) with the observed value of τ_t ($=\tau_d$). The value of D_H is 2 orders of magnitude larger than D_M and is of the same order as the diffusion constant (10^{-6}–10^{-7} m^{2}s^{-1}) of the neutral soliton in polyacetylene measured by NMR [13(a)] and ESR [13(b)] or the polaron in polyaniline by ESR [13(c)]. As a consequence, the HF relaxation is ascribable to the fluctuation of the mobile carriers along the polymer chain with the shorter fluctuation distance L_H and the faster diffusion constant D_H compared with the MF relaxation. Since the size of a thiophene monomer unit is 0.39 nm, the value of L_H implies that there is one defect point per ca. 100 monomers, which is consistent with the highly extended form of the P3HT chain in pure methylene chloride as mentioned before. In addition, the diffusion constant D_M of the MF relaxation much slower than D_H of the HF one is ascribable to the defects hindering the long-range hopping of the carriers along the polymer chain.

In summary, by the FEB and dielectric relaxation spectroscopies, we have obtained the information on the intrachain conduction and main-chain conformation of P3HT in the solution. As the fraction of toluene in mixed solvents increases, the polymer conformation changes from an extended form to a coiled one (the rod-coil transition). On the other hand, the intrachain conduction of P3HT in pure methylene chloride shows two kinds of transports of the mobile carriers with different diffusion distances and diffusion constants. Although the faster diffusion constant D_H within the shorter range has been reported for other conducting polymers by NMR and ESR measurements, the slower diffusion constant D_M within the longer distance up to the contour length is first revealed in the present study by the FEB technique. Thus, the FEB spectroscopy is a useful technique for the investigation of the conduction mechanism in the conducting polymers.

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