mer films are much smaller than that in homogeneous solutions of methylviologen ($>10^8$ M^{-1} s^{-1}).[27] This is attributed to the fact that, even though the redox species are close enough, they cannot necessarily achieve a proper juxtaposition for electron transfer because of their attachment to the polymer chains; i.e., the configurational constraints of the polymer would limit the mutual orientation of neighboring redox sites. Since this would involve an ordering process with an entropy loss, an exothermic interaction between redox centers, if any, may significantly favor the mutual orientation that would in turn favor electron exchanges.

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Registry No. PolyMPT, 25657-63-0; copolyMPT, 85709-38-2; I_2, 7553-56-2.

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Twisted Intramolecular Charge-Transfer Phenomenon as a Fluorescence Probe of Microenvironment. Effect of Polymer Concentration on Local Viscosity and Microscopic Polarity around a Polymer Chain of Poly(methyl methacrylate)

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ABSTRACT: A 4-(*N*,*N*-dimethylamino)benzoate group showing a twisted intramolecular charge transfer (TICT) was bonded to a poly(methyl methacrylate) side chain and the effects of polymer environment on fluorescence were investigated in ethyl acetate. The temperature dependence of the fluorescence behavior indicated restricted side chain rotation and reduced solvation in the polymer even under dilute conditions. With increasing polymer concentration, the TICT emission showed a blue-shift and decreased intensity up to a polymer concentration of 70%. Above this concentration, the activation energy to form the TICT state suddenly increased. The twisting motion of the dimethylamino group required a free volume of 5.4 cm^3/mol, which was in good agreement with the activation volume obtained from pressure effects on the TICT phenomenon. The TICT phenomenon is shown to be sensitive to both local polarity and local viscosity of the surroundings so that the TICT chromophore is expected to be a candidate for a fluorescence probe in polymer property studies.

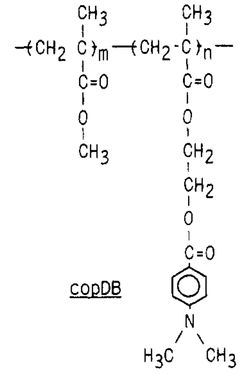
Introduction

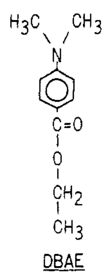
Fluorescence methods, such as steady-state fluorescence spectroscopy, excited-state decay analysis, time-resolved fluorescence spectroscopy, and fluorescence depolarization have been shown to be quite effective in the investigation of the microscopic environment around a chromophore. A number of studies have been reported on the use of excimer or exciplex formation in polymeric systems to examine local segment mobility, phase separation, or polymer compatibility.[1] The fluorescence depolarization method has been widely used to monitor molecular motion in polymers, molecular aggregates, and biological systems.[2]

A series of derivatives of 4-(*N*,*N*-dimethylamino)benzonitrile (DMABN) or 4-(*N*,*N*-dimethylamino)benzoate exhibits characteristic fluorescence spectra in polar solvents, showing two emission bands (dual fluorescence) corresponding to two kinds of excited states; i.e., a* and b* states. According to the twisted intramolecular charge-transfer (TICT) hypothesis first proposed by Grabowski and co-workers,[3] the dual fluorescence can be explained as follows. In the excited state, the donor part (dimethylamino (DMA) group) of the initially planar molecular rotates around the amino–phenyl bond; this is accompanied by the development of a charge separation between donor and acceptor moieties as shown in Scheme I. In polar solvents, the twisted and polar a* state can be stabilized by solvent reorientation, so that the a* band appears at a longer wavelength region relative to the planar non-CT b* band. (The TICT hypothesis has been widely checked and discussed by several authors.[4])

Thus, the fluorescence spectra of these molecules strongly depend not only on the solvent polarity but also on the medium viscosity.[5,6] In other words, the TICT chromophore is expected to act as a molecular probe sensing the microscopic environment. There are a number of compounds such as 9-(*N*,*N*-dimethylanilino)anthracene,[7] *p*-(dimethylamino)benzylidenemalononitrile,[8] and so forth, exhibiting TICT-like emission without clear separation of the a* and b* bands. The position, shape, and intensity of these TICT-like emission are sensitive to molecular mobility, solvation, and polarity of the microscopic environment around the chromophore so that they can be candidates for fluorescence probe for polymer study.[9] Dual fluorescence of the TICT compounds would provide much more detailed and fertile information. As a fluorescence probe, the TICT compound has much merit. It can probe both local viscosity and local polarity, and, furthermore, the mode of molecular motion necessary to the TICT phenomenon is well defined and limited to the rotation around a particular bond. This is a difference from intramolecular exciplex or excimer formation, in which multiple modes of bond rotation and bending are compounded.[10] Fluorescence polarization study also cannot be free from ambiguity of the mode of rotation.[11]

To decide the usefulness and limits of the TICT chromophore as a fluorescence probe, we need to study the basic photophysics of the chromophore in the polymer. The objective of this study is to examine the rotational motion of the amino group in a polymer-bonded 4-(*N*,*N*-dimethylamino)benzoate (copDB) chromophore in solution. The effects of polymer concentration and temperature on the TICT phenomenon of copDB were compared with those of a small-molecule model compound, ethyl 4-(*N*,*N*-dimethylamino)benzoate (DBAE), in solution. Our concern is to have an inside look into how the polymeric environment influences the TICT phenomenon.


copDB


DBAE

Experimental Section

Materials. Ethyl 4-(*N*,*N*-dimethylamino)benzoate was prepared by esterification of 4-(*N*,*N*-dimethylamino)benzoyl chloride (obtained from 4-(*N*,*N*-dimethylamino)benzoic acid according to ref 12, with ethanol. DBAE was purified by chromatography (Wakogel C-200 silica gel column using benzene as an eluent) followed by sublimation in vacuo. The structure was confirmed by both NMR and elemental analysis.

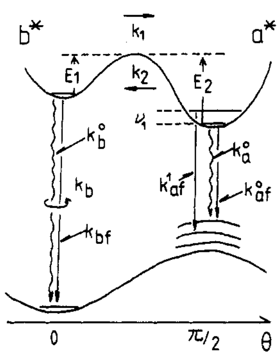
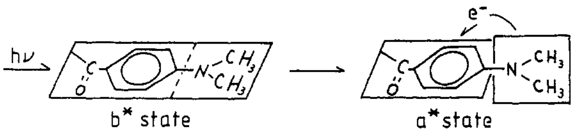


Figure 1. Kinetic scheme proposed by Grabowski.[3] θ represents the twist angle between the donor and acceptor planes.

Scheme I



[(4-(*N*,*N*-Dimethylamino)benzoyl)oxy]ethyl methacrylate (DBMA) was synthesized by esterification of 4-(*N*,*N*-dimethylamino)benzoyl chloride with hydroxyethyl methacrylate. The product was purified by column chromatography (silica gel with benzene as an eluent): NMR (CDCl$_3$) δ 1.95 (s, 3 H, CH$_3$), 3.05 (s, 6 H, CH$_3$N), 4.5 (s, 4 H, CH$_2$), 5.6–6.2 (s, s, 2 H, CH$_2$=), 6.6–8.05 (d, d, 4 H, aromatic). Anal. Calcd: C, 64.95; H, 6.92; N, 5.05. Found: C, 65.22; H, 6.93; N, 5.25.

Poly(methyl methacrylate) having DBAE in a side chain was prepared by radical copolymerization of methyl methacrylate with DBMA. Polymerization was carried out under a nitrogen atmosphere at 70 °C, using thiophene-free dry benzene as a solvent. Methyl methacrylate was distilled under reduced pressure before use. Azobis(isobutyronitrile) was used as an initiator. The copolymer was reprecipitated from benzene–methanol several times. The number-average molecular weight of the polymer was determined to be 3×10^5 by GPC measurement using a Waters Model 244 liquid chromatograph with monodisperse poly(methyl methacrylate) as a standard. DBMA content is about 0.01% as determined by UV absorption spectroscopy (Hitachi 320 spectrophotometer).

General Technique. Fluorescence spectra were recorded under aerobic conditions using a modular spectrofluorimeter that has been previously described.[13] The spectra were not corrected for instrumental response. Throughout this study, ethyl acetate (Aldrich spectrophotometric grade, Gold Label) was used as a spectroscopic solvent without further purification, and the excitation wavelength was 295 nm. The quantum yield ratio of two emission bands, *R*, was calculated from the intensity ratio at each emission band maximum with a correction for the contribution of the higher energy b* band to the a* band intensity.

For temperature-dependent fluorescence studies above room temperature, measurements were carried out with a specially designed electrically heated aluminum block, which was controlled by a Eurotherm Model 919 digital temperature controller (±0.5 °C). For the measurements below room temperature, the sample block was thermostated by cold nitrogen gas (±1 °C). Concentrated polymer solutions were inserted between two quartz disks to monitor the frontface fluorescence emission.[14]

Results and Discussion

Kinetic Treatment. The kinetic model for the TICT phenomenon proposed by Grabowski[15] is shown in Figure 1. According to the scheme, the planar non-CT b* state is directly produced by photoexcitation and then relaxes to the TICT state (a* state) with the torsional motion of the DMA group. The kinetic analysis based on the

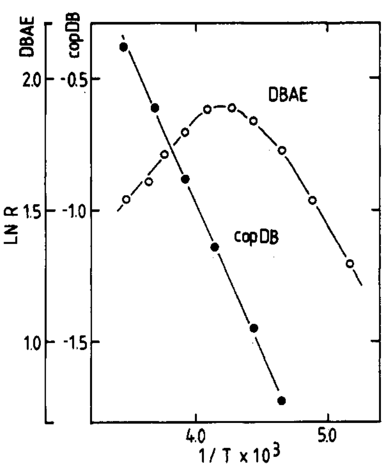


Figure 2. Temperature dependence of the intensity ratio R in ethyl acetate: (●) 1% solution of copDB, (○) 2×10^{-5} M solution of DBAE.

photostationary state approximation leads to the expressions for emission quantum yields ϕ_b and ϕ_a in eq 1 and eq 2, respectively.[5] The twisting relaxation rate k_1 and

$$\phi_b = \frac{k_{bf}(k_2 + k_a)}{k_b(k_2 + k_a) + k_1 k_a} \tag{1}$$

$$\phi_a = \frac{k_{af}k_1}{k_b(k_2 + k_a) + k_1 k_a} \tag{2}$$

$$R = \phi_a/\phi_b = \frac{k_{af}k_1}{k_{bf}(k_2 + k_a)} \tag{3}$$

its back-reaction rate k_2 are known to be temperature dependent as expressed in eq 4 and 5. k_{af} and k_{bf} are radiative rate constants of the a* and b* state, respectively.

$$k_1 = A_1 \exp(-E_1/RT) \tag{4}$$

$$k_2 = A_2 \exp(-E_2/RT) \tag{5}$$

$$k_{af} = k_{af}^0 + k_{af}^1 \exp(-h\nu_1/kT) \tag{6}$$

$$k_a = k_{af} + k_a^0 \tag{7}$$

$$k_b = k_{bf} + k_b^0 \tag{8}$$

The radiative transition from the vibrationally lowest TICT state is symmetry forbidden[6] because of its twisted geometry. As a consequence, the transition (k_{af}) occurs mainly from the less forbidden vibrationally activated TICT state with a twist angle of less than 90° between the donor and acceptor planes.[5,15] Thus, k_{af}^0 may be neglected as compared to k_{af}^1 in eq 6 such that k_{af} is dependent on temperature with the activation energy $h\nu_1$.

For various TICT chromophores such as DBAE, the ratio of the two fluorescence band intensities, $R = \phi_a/\phi_b$, increases with temperature and finally reaches a maximum value at T_{max}. A further increase in temperature leads to a decrease in R due to the contribution of the back reaction with rate constant k_2 as shown in Figure 2. Above T_{max} (the high-temperature region), an excited-state equilibrium should be established, while below T_{max} (the low-temperature region), k_2 should be negligibly small as compared with other deactivation processes represented by k_a from the TICT state ($k_a \gg k_2$). Thus, in the low-temperature region below T_{max}, eq 3 can be simplified to eq 9. The

$$R = \frac{k_{af}k_1}{k_{bf}k_a} \tag{9}$$

deactivation rate from the lowest excited TICT state, represented by k_a^0 in eq 7, which includes intersystem crossing, may be enhanced by the close-lying S_1 and T_1 states at the 90° twisted TICT geometry. Therefore, k_a^0 is much larger than k_{af}^1 in eq 7, as has been supported by experimental results reported by Grabowski et al.[15] and Rettig.[5]

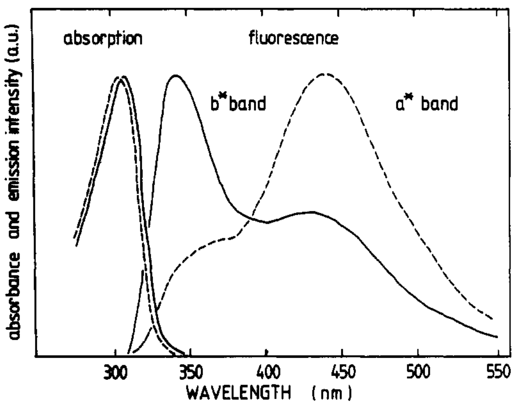


Figure 3. Absorption and emission spectra of copDB and DBAE in ethyl acetate at 25 °C: (—) 1 wt % copDB sol., (---) DBAE 2×10^{-5} M. Excitation wavelength at 295 nm.

By considering these conditions, we can calculate the sum of the activation energy for the formation of the TICT state (E_1) and the energy gap between the lowest and second lowest vibrational levels of the TICT state ($h\nu_1$) by means of an Arrhenius plot of R according to eq 9.

Polymer Effects on the TICT Phenomenon in Dilute Solution. In ethyl acetate, the absorption spectrum of copDB is almost identical with that of the monomeric model compound (DBAE) except for a slight red-shift (~3 nm) in copDB (Figure 3). Although ground-state dimer or solute–solvent complex formation of (*N*,*N*-dimethylamino)benzonitrile has been reported in several solvents by McGlynn et al.[16] and Mataga et al.,[17] there is no indication of distinct ground-state interaction for copDB.

On the other hand, copDB exhibits dual fluorescence around 350 and 450 nm as shown in Figure 3. In comparison with the fluorescence spectrum of DBAE,[18,19] the two fluorescence bands of copDB at 350 and 450 nm may be attributed to the fluorescence from the planar non-CT excited state (b* band) and that from the TICT state (a* band), respectively. Intramolecular charge transfer accompanied by torsional motion of the DMA group takes place in dilute solution of copDB. However, the fluorescence spectra of copDB are dependent on temperature and concentration, as discussed in the following section.

The Arrhenius plot has a negative slope for copDB solution as shown in Figure 2, indicating that the back reaction (k_2) is likely to be negligibly small as compared with k_a (the low-temperature region). The slope of the plot below room temperature, thus, represents $E_1 + h\nu_1$. On the other hand, DBAE shows a positive slope on the Arrhenius plot between room temperature and -30 °C, indicating that the excited-state equilibrium is established (the high-temperature region). The difference in temperature dependence of the TICT phenomenon between copDB and DBAE suggests that the torsional motion of the DMA group in a polymer side chain is more hindered than that of the low molecular weight model compound.

It is not well understood how torsional motion of a polymer side group is affected by the rest of the polymer chain in highly diluted solutions. In the case of intramolecular exciplex formation of 1-(1-pyrenyl)-3-(4-(*N*,*N*-dimethylamino)phenyl)propane bonded to a polymer side group,[20] the rate of exciplex formation in the polymer in dilute solution is much slower than that of the reference

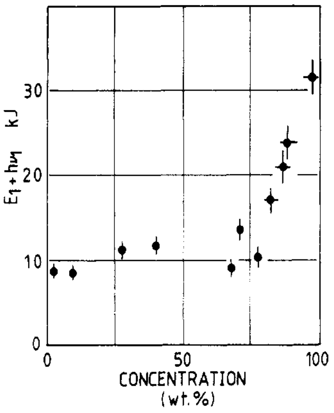


Figure 4. Concentration dependence of $E_1 + h\nu_1$ of copDB in ethyl acetate.

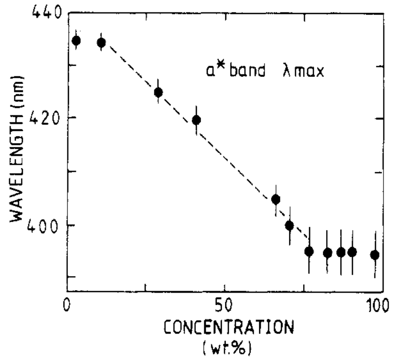


Figure 5. Emission band shift of a* fluorescence maximum of copDB as a function of the polymer concentration in ethyl acetate at 25 °C.

small-molecule system. The influence of the polymer main chain on small-molecule motions of the polymer side chain in dilute solution is an unsurveyed subject. Also the physics of dilute polymer solution provides no information on the side chain–main chain interactions.

Concentration Dependence of Fluorescence Behavior. The activation energies ($E_1 + h\nu_1$) ranged between ~10 kJ/mol for dilute solutions and ~30 kJ/mol for highly concentrated solutions of copDB in ethyl acetate, as shown in Figure 4. In addition, with the increase in the polymer concentration, the emission maximum of the a* band shifts very much to higher energy (Figure 5), indicating that the a* state is less stabilized by solvation with increasing the concentration. The vibrational level of the a* state ($h\nu_1$) may therefore be changed with the stability of the a* state. However, ν_1 is normally 100–250 cm^{-1} for DMABN derivatives[5] and 40 cm^{-1} for DBAE in nonpolar solvents,[21] which are negligible in comparison with E_1. Consequently, we will confine our discussions to E_1 in this study. The break point in Figure 4 clearly indicates that the TICT probe is not sensitive to the macroscopic viscosity of the polymer solution but rather is sensitive to local viscosity around the chromophore.

A similar phenomenon has been reported for polystyrene solutions using the fluorescence depolarization method by Nishijima et al.[22] They calculated the local viscosity and the rotational relaxation time of naphthacene in benzene solutions. According to their results, the local viscosity is independent of the polymer concentration below 15%, whereas it gradually increases from 15% to 60%. In the present case, however, E_1 shows an almost constant value up to about 70%, as shown in Figure 4. These results indicate that naphthacene is more sensitive to the packing or entanglement of the polymer chain than is the DBAE molecule because of the larger size of the molecular rotor of naphthacene compared with the DMA group. More specifically, below a bulk concentration of 70%, the DMA group of DBAE apparently can rotate almost as freely as in dilute solution.

On the other hand, in highly concentrated solutions, the local viscosity measured by Nishijima et al. markedly increases by a factor of 10 above 60%, whereas in the TICT case E_1 increases by a factor of 3 over the concentration range from 70% to 100% as shown in Figure 4. As a result of extensive overlap of the polymer chains in the highly concentrated solutions, the rotational motions of naphthacene and the DMA group are strongly restricted in highly concentrated solutions over 60% for naphthacene and over 70% for the DMA group. This difference corresponds to the difference in size between the DMA group and naphthacene molecule. From these results, the fluorescence behavior of the TICT chromophore represents less motion of molecules as compared with other fluorescence probes larger in size.

The blue-shift of the a* band with polymer concentration (Figure 5) provides further insight into the microscopic environment in the polymer solution. In semidilute solution below 10% (the overlap threshold c^* is approximately 0.01–0.02 g cm^{-3} for this polymer), the emission maximum of the a* band is independent of concentration, indicating that the change in solvation associated with the charge separation is not influenced by the polymer chain in this concentration region. For concentrations in the range from 10% to 75%, the a* band gradually shifts to the blue as the concentration increases, suggesting the formation of a less solvated TICT state than that in dilute solution. Although the probe size and the type of polymer are different from the Nishijima's experiments, the gradual blue-shift of the a* band corresponds qualitatively to the concentration dependence of local viscosity obtained by the depolarization measurement. The blue-shift would consequently be attributed to the effect of the polymer network on reorientational motion of solvent molecules around the chromophore, while the polymer network does not affect the friction factor of the torsional motion represented by E_1. Above 60%, the shape of the spectrum no longer depends on the concentration, indicating that the immediate environment of the chromophore consists primarily of polymer chain segments with minimal contribution from solvent molecules. In this concentration region, the fluorescence behavior seems to reflect the influence of the nature of the polymer matrix alone.

It is a difficult problem to describe the results in highly concentrated polymer solution in accordance with the existing theories. However the de Gennes' mesh model and scaling concept[23] might provide a qualitative explanation for these phenomena. According to this model, the molecular structure of a semidilute solution looks like a network with a certain average mesh size, ξ (i.e., correlation length). Inside this mesh, small spheres with diameter $D < \xi$ move easily with a friction coefficient relating to the viscosity of the pure solvent, while the spheres with diameter $D > \xi$ are trapped and the local or effective viscosity controlling the friction is closer to the viscosity of the entangled solution. From small-angle neutron scattering experiments on semidilute polystyrene solutions,[24] ξ was determined to be in the order of 10^1–10^2 Å in the concentration range 10^{-1} to 10^{-2} g cm^{-3}. This mesh size seems large enough to allow free rotation of the DMA group, so that the friction relevant to E_1 might be constant in this concentration region. Although it is outside the scope of the scaling treatment, it is reasonable to propose that ξ continues to decrease as the solution becomes more

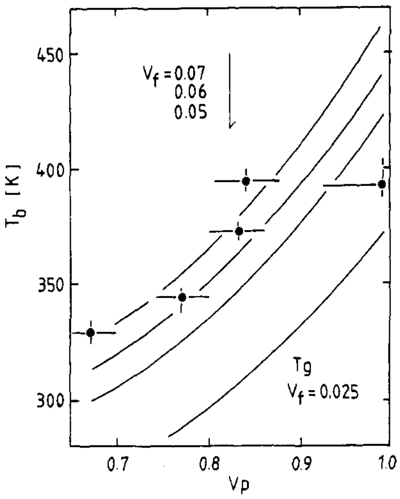


Figure 6. Concentration dependence of specific temperature, T_b (see text), and its interpretation by free volume fraction V_f.[26] The concentration dependence of T_g was obtained from eq 11 when the free volume fraction equals 0.025.

concentrated, eventually reaching the level of the probe size (~10⁰ Å). When the probe molecule motion requires more available space than is permitted by the mesh formed in the polymer matrix, the hindrance to motion is expected to increase. This could be the origin of the dramatic rise in E_1 shown in Figure 4.

Interpretation by Free Volume Theory. In the highly concentrated region above 70%, the fluorescence spectra no longer depend on temperature below a certain temperature T_b (the subscript stands for "break point"),[25] indicating that the motion of the DMA group is strongly hindered below this particular temperature. The concentration dependence of T_b runs parallel with that of the glass transition temperature T_g, while T_b is always higher than T_g by about 40 K, as shown in Figure 6.

The free volume fraction (V_f) may be correlated with the glass transition temperature by the well-known relation of eq 10 proposed by Williams, Landel, and Ferry[26]

$$V_f = 0.025 + 4.8 \times 10^{-4}(T - T_g) \qquad (10)$$

where 0.025 represents the free volume fraction at T_g. If the contribution of the solvent to the free volume of the polymer system is included, the free volume fraction at an ambient polymer concentration, C, may be expressed as follows:[27]

$$V_f = C[0.025 + 4.8 \times 10^{-4}(T - T_g)] + (1 - C)[0.025 + \alpha_s(T - T_g')] \qquad (11)$$

where α_s and T_g' are the thermal expansion coefficient and the glass temperature of the solvent. With eq 11, the concentration dependence of T_g can be described by a line for $V_f = 0.025$ in Figure 6. Similarly, the values of T_b fall in the region between two lines calculated for $V_f = 0.05$ and $V_f = 0.07$ as shown in Figure 6. The present results suggest that the rotational motion of the DMA group requires about 0.05–0.07 of free volume fraction.[28] This value corresponds to 5.4 ± 0.8 cm^3/mol of free volume at room temperature, which is calculated by multiplication of the volume for 1 mol of PMMA monomer unit by the free volume fraction. This value is in excellent agreement with the activation volume (5.5 cm^3/mol) independently derived from the pressure effect on TICT phenomenon to be reported in a forthcoming publication.[29]

The importance of the free volume consideration in interpreting the TICT phenomenon was recently suggested also by Al-Hassan and Rettig.[30] Their results on the excitation wavelength dependence of DMABN fluorescence in PMMA matrix revealed the presence of multiple ground-state species, each having a slightly different energy level from the other and, furthermore, after excitation, each relaxing to the TICT state with different probabilities. These phenomena would stem from a broad distribution of the twist angle of the DMA group both in the excited and ground states and be relevant to the free volume available to the chromophore. Our present results are consistent with the context.

For copDB, the fluorescence behavior is dependent on excitation wavelength even in very dilute solutions.[31] The TICT chromophore bonded to the polymer seems to be subject to a specific rotational barrier of surrounding polymer chain so that homogeneous distribution of various conformers in the ground state and in the excited state would be difficult even under dilute conditions. In order to understand polymer effects on the TICT phenomenon in detail, experiments are now in progress on the dynamics and temperature dependence of the TICT fluorescence as functions of excitation wavelength dependence.[32]

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Registry No. DBMA, 79984-80-8; DBAE, 10287-53-3; 4-$(CH_3)_2NC_6H_4COCl$, 4755-50-4; $H_2C{=}C(CH_3)CO_2(CH_2)_2OH$, 868-77-9; $(H_2C{=}C(CH_3)CO_2CH_3)$(DBMA) (copolymer), 105058-53-5.

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Dielectric Relaxation in Liquid Crystalline Poly(*p*-hydroxybenzoic acid-*co*-ethylene terephthalate)

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ABSTRACT: Dielectric constant and loss have been measured over the frequency range 1 Hz–100 kHz from −180 to +180 °C for liquid crystalline poly(*p*-hydroxybenzoic acid-*co*-ethylene terephthalate) (P(HBA–ETP)) with molar ratios (HBA–ETP) of 0.6–0.4 and 0.8–0.2. In order of decreasing temperature, there are three transitions in these copolyesters: α_{HBA}, the glass–rubber transition of the HBA-rich phase, α_{ETP}, the glass–rubber transition of the ETP-rich phase, and β, a sub-glass transition that can be assigned to both the HBA-rich and ETP-rich phases. The symmetrically broadened β process shows a close resemblance to the β process in poly(ethylene terephthalate) (PETP) with regard to activation energy and width, but it occurs at progressively higher temperatures (isochronically) with increasing HBA content. The α_{ETP} occurs at lower temperatures than in PETP and has a width similar to that of semicrystalline PETP. The 0.6–0.4 copolymer exhibits a double α_{ETP}, which may indicate the presence of two different ETP-rich phases in this polymer.

Introduction

Polymers exhibiting liquid crystalline behavior in the melt, so-called thermotropic liquid crystalline polymers, have received considerable attention during the past decade. The mesomorphic melt phase is highly shear-sensitive and gives injection-molded solidified specimens with highly anisotropic mechanical properties. The modulus along the direction of orientation approaches the values of glass-fiber-reinforced thermoplastics. A distinct advantage of the thermotropic liquid crystalline polymers is their low melt viscosity when sheared, which makes them considerably easier to process than glass-fiber-reinforced thermoplastics.

The first example of a thermotropic polymer was reported in 1975 by Roviello et al.[1] and consisted of polyesters derived from aliphatic diacyl chlorides and *p*,*p*′-dihydroxy-α,α'-dimethylbenzalanine. A year later, Jackson and Kuhfuss[2] reported a thermotropic liquid crystalline copolyester based on *p*-hydroxybenzoic acid (HBA) and ethylene terephthalate (ETP). This polymer has served as a model compound, and numerous papers on this polymer can be found in the literature, e.g., ref 2–10.

Jackson and Kuhfuss[2] have presented NMR and WAXS data in support of a random distribution of the comonomer units in P(HBA–ETP) with molar composition 0.6–0.4. Nevertheless, the occurrence of two distinct and separate glass transitions in this polymer is clear evidence of the existence of separate phases rich in HBA and ETP.[4,5] Furthermore, electron microscopy and ESCA provide evidence of such a two-phase structure in the 0.6–0.4 copolymer.[6–8] The ETP-rich phase is discontinuous, exhibiting a domain size of the order of 1 μm. The molecular structure and morphology of P(HBA–ETP) with molar composition 0.8–0.2 is less disputed. Zachariades et al.[9,10] have shown that the distribution of the comonomer units is not random but that there are blocks of comonomers. These authors have also found some evidence for the existence of a minor amount of homopolymer of PHBA in the 0.8–0.2 copolymer samples. Transmission electron microscopy, electron diffraction, and X-ray analysis of the 0.8–0.2 copolymer indicate that long HBA sequences are present in discrete domains with a well-defined lamellar structure with a thickness of 200–400 Å.[9,10]

Dielectric studies of thermotropic liquid crystalline polymers have been relatively few.[11–16] Only one of these studies[16] deals with the polymer treated in the present paper. The authors report two dielectric relaxations in P(HBA–ETP) with molar composition 0.6–0.4: a β relaxation peaking at −30 °C (1 kHz) with an activation energy of 21 kJ mol^{-1} and an α relaxation centered at about 70 °C (1 kHz) with an activation energy of 500 kJ mol^{-1}. The authors claim that these data show a close resem-

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