

Twisted Intramolecular Charge-Transfer Behavior of a Pre-Twisted Molecule, 4-Biphenylcarboxylate Bonded to Poly(Methyl Methacrylate)

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A trace amount of 4-biphenylcarboxylate having a pre-twisted biphenyl moiety was attached to a poly(methyl methacrylate) side chain and the fluorescence properties of the chromophore were investigated in various solvents such as ethyl acetate and butyl chloride. At room temperature, the polymer exhibited a distinct red shift of the short wavelength emission (325 nm) and an enhanced emission intensity around 430 nm upon excitation at the absorption red edge. The temperature dependence of the intensity ratio (*R*) of the 325 nm emission to the 430 nm emission was observed when exciting at the red edge over the temperature range between -20 and 60 °C. However, the temperature dependence was not observed when exciting at the shorter wavelength. The Arrhenius plot of the *R* value shows the activation energy of 6.0 kJ/mol which is in good agreement with the energy required for the twist of the biphenyl moiety. Together with the results of red edge excitation effects it was concluded that the pre-twisted geometry of the biphenyl moiety is preserved by the restriction of the polymer chain to facilitate the formation of the twisted intramolecular charge transfer (TICT) state upon excitation.

Introduction

The photo-induced intramolecular charge transfer (ICT) is currently one of the most attractive topics as a basis function for photoelectronic devices¹ as well as a basic mechanism of biological and chemical energy conversion.²⁻⁵ The photo-induced charge separation is maximized when the donor and acceptor groups are mutually perpendicular to minimize the electronic coupling between the two groups. The resulted state is known as a twisted intramolecular charge transfer (TICT) state. The TICT process results in the observation of an extraordinarily large Stokes-shifted band (a-band) as well as a normal Stokes-shifted band (b-band). The formation of the excited TICT state is followed by solvent relaxation which is important in determining the overall charge-transfer process.⁶⁻¹⁰ For the solvent relaxation the solvent polarity has been reported to be the most important parameter. In fact, it has been demonstrated^{11,12} that with increase in the polarity of the media the energy barrier for the TICT (ICT) process decreases, causing an increase in the solvent relaxation time and the TICT (ICT) rate. Thus, the large class of TICT molecules have proven to be a fluorescence probe of solvation dynamics.

Furthermore recent studies have shown that a TICT molecule, dimethylaminobenzoate (DMAB), is a useful fluorescence probe to study polymer segment mobility in solution.^{13,14} This molecule consists of two planar chromophores, the dimethylamino substituent and the para-substituted benzene ring, linked by a σ -bond between the nitrogen atom of the amino group and a carbon atom of the benzene ring. In the ground electronic state, the electronic conjugation between the π orbitals of the benzene ring and the lone-paired electrons on the nitrogen tends to favor a coplanar configuration. Upon excitation, a partial ICT occurs, and followed by twist-

ing of the $C_{\text{aryl}}-N$ bond so that the further stabilized TICT state is formed. Thus, this type of molecule must overcome the conjugation in the locally excited state by the twisting. The twisting is usually facilitated and stabilized by restructuring of solvent molecules in polar solvent. However, as Guo reported,^{13,14} in the presence of polymer the probability of solvation is suppressed by surrounding polymer chains, reducing the probability of TICT state formation. Consequently Guo proposed that the polymer microenvironmental effect on TICT formation in solution was mainly attributed to the change in the solvation dynamics in the course of the TICT formation process.¹⁵ However, the steric effects of bulky neighboring side chains to reduce the ground-state twisting still cannot be ruled out. Thus, Guo's proposal should be further investigated by looking at the polymer environmental effects on the TICT of the pre-twisted molecule in the ground state. This is because the twisting relaxation to reach the TICT state is not necessary in the pre-twisted molecule as in the case of 9,9'-bianthryl, and their overall ICT rate is determined only by the solvent relaxation dynamics.^{16,17}

We have previously investigated the solvent effects on the photophysical properties of a pre-twisted molecule, 4-biphenylcarboxylic acid (4BPCA).¹⁸ It has been shown that upon excitation the pre-twisted biphenyl moiety becomes coplanar in nonpolar solvent, but the pre-twisted conformation is preserved in polar solvents exhibit ICT interaction. However the barrier height for further twist relaxation is relatively high so that the TICT formation is not feasible even in polar solvents. Also it has been observed that the excited-state ICT and geometry change are competitive and affected by the restriction environment such as cyclodextrin cavity.¹⁹ Thus this molecule would be a good model to study the polymer environmental effects on the TICT of the pre-twisted molecule in the ground state. In the present study we prepared a poly(methyl methacrylate) (PMMA) containing

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a trace amount of 4-biphenylcarboxylate linked to the side chain. The excitation-wavelength dependences of fluorescence properties of the chromophore revealed that the TICT is facilitated in the presence of the polymer enthalpically in contrast to the suppression of TICT in DMAB-bound PMMA.

Experimental

Materials. 4-biphenylcarboxy methacrylate (4-BPCMA) was prepared by mixing 4-biphenylcarboxylic acid with methacryloyl chloride in dry dioxane containing trace amount of triethylamine as a catalyst. Nitrogen was purged through the mixture solution for overnight. The solid product was obtained by evaporating solvent under reduced pressure and purified by recrystallizing with ethanol.

Poly(methyl methacrylate) having biphenylcarboxylate in a side chain was prepared by radical copolymerization of methyl methacrylate with 4-BPCMA. Polymerization was carried out under a nitrogen atmosphere at 70 °C, using thiophene-free dry benzene as a solvent and azobis(isobutyronitrile) as an initiator. The copolymer was reprecipitated several times from benzene-methanol. The structure was confirmed by ¹H NMR (CDCl₃); δ 0.8-1.1 (s, s 3H, -CH₃), 1.5-2.0 (s, 2H, -CH₂), 3.5-3.8 (s, 3H, -OCH₃), 7.5-7.8 (s, 9H, C₁₂H₉). The number-average molecular weight of the polymer was determined to be 1 × 10⁵ by gel permeation chromatography (GPC) measurement using a Waters HPLC system fitted with a refractive index detector and a Waters Ultrahydrogel 250 column. Approximate calibration of the column was accomplished by using poly(ethylene glycol) as a standard. BCMA content is about 0.05% as determined by UV absorption spectroscopy (Beckman UV-5260 spectrophotometer). All the sample solutions were degassed by freeze-pump-thaw technique before the spectral measurements.

Spectral measurements. Fluorescence spectra were measured on a scanning SLM-AMINCO 4800 spectrofluorometer, which makes it possible to obtain corrected spectra using Rhodamine B as a quantum counter. The optical density at an excitation wavelength was held constant when different solutions were compared. Fluorescence quantum yields were determined by comparison with a reference of known quantum yield (Indole in ethanol, (0.32) or quinine

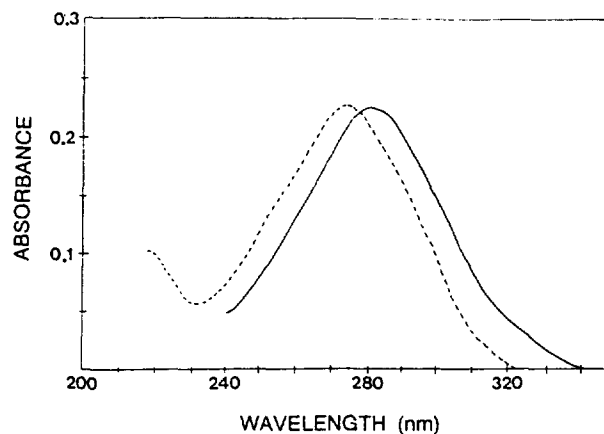


Figure 1. Absorption spectra of 4BPC-bound PMMA (—) and free 4BPCA (---) in EAc or BuCl.

bisulfate).²⁰ Fluorescence lifetimes were measured by a time-correlated single photon counting (TCSPC) method, using a dual-jet picosecond dye laser (Coherent; Model 702) synchronously pumped by a mode-locked Ar ion laser (Coherent; Innova 200) as described in the previous paper.¹⁹ The cavity-dumped beam had 1 ps pulse width, the average power of ca 40 mW at 3.8 MHz dumping rate, and the tunability of 560-620 nm when Rhodamine 6G for gain dye and DODCI (diethyldicyanine) for saturable absorber were used. To excite the sample, the dye laser pulse was frequency-doubled by β-BBO (β-barium borate) crystals. All the standard electronics used for the TCSPC were from EG&G Ortec. This method allows a time resolution of about 20 ps by deconvolution.

Results and Discussion

The general formula of 4BPC-bound PMMA copolymer is shown in Chart I. Since it is known that the polymer effect on the TICT is the stronger as the chromophore is closer to the main chain,^{13,14} the carboxyl group was directly bound to the main chain without a -(CH₂)_x- spacer. Thus, with this structure the π-conjugation of biphenyl ring is further extended by the additional carbonyl group of the main chain.

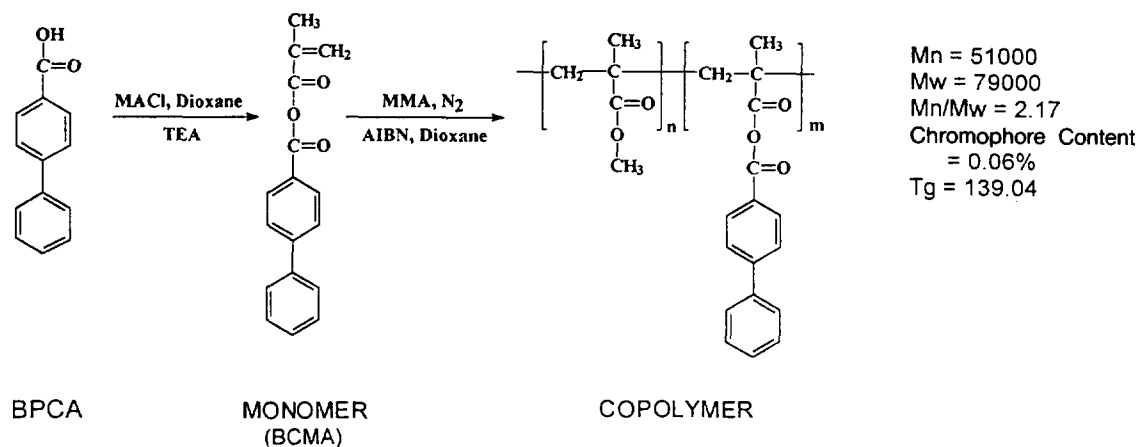


Chart I.

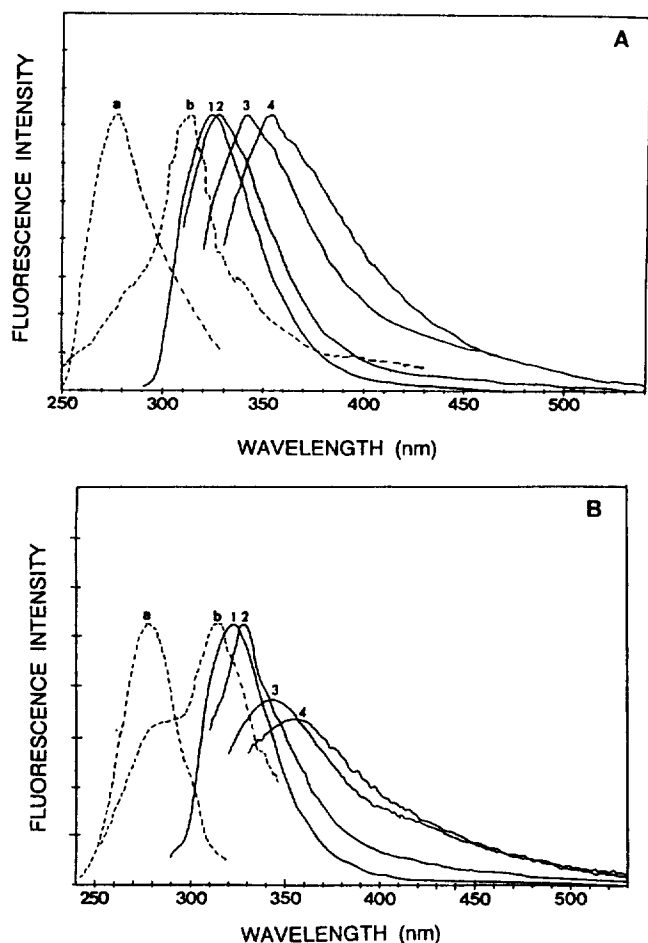


Figure 2. Fluorescence emission spectra of 4BPC-bound PMMA in EAc (A) and BuCl (B) measured by excitation at different wavelengths; (1) 270-290 nm, (2) 300, (3) 310 and (4) 320 nm. The dotted spectra represent the fluorescence excitation spectra measured by monitoring the emission wavelengths at 330 nm (a) and 430 nm (b).

Because of this the absorption maximum of the 4BPC-bound polymer in ethyl acetate (EAc) or butyl chloride (BuCl) was red-shifted by 10 nm in comparison with that of the free 4BPCA as shown in Figure 1, indicating the electronic interaction of 4BPCA group with the polymer main chain and solvent molecules.

Figure 2 shows the fluorescence spectra of the 4BPC-bound PMMA dissolved in good solvent, EAc, and poor solvent, BuCl. It is interesting to note that upon excitation at the absorption red edge (320 nm) in both solvents exhibited a distinct red shift of the 330 nm emission band and an enhanced emission band around 430 nm. Figure 3 shows the enhancement of the ratio of 430 nm emission to 330 nm emission of 4BPC-bound PMMA as the excitation wavelength increases. This excitation-wavelength dependence of the dual emission is the same as the typical red edge effect^{21,22} observed for TICT fluorescence which is usually observed under the condition of restricted molecular mobility as in the polymer system.^{13,14} When conformational change is restricted, a number of independent conformers absorbing different wavelengths exist within the time-scale of the excited-

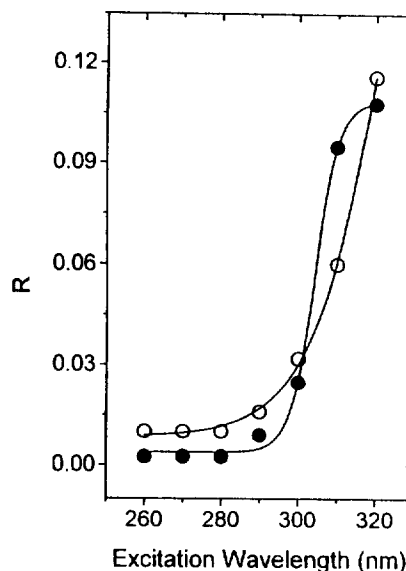


Figure 3. Fluorescence intensity ratio (R) of 430 nm emission to 330 nm emission of 4BPC-bound PMMA in EAc (closed circles) and BuCl (open circles) as a function of excitation wavelength.

state lifetime. The partially pre-twisted conformer in the ground state can be excited by the red edge absorption and undergoes more facile conversion to the TICT state (a^*) because the necessary angle for the twist relaxation is smaller. When considering these facts, the newly enhanced 430 nm emission should be originated from the TICT state (a^*) formed exclusively by the excitation of a somewhat twisted ground-state molecules, while 330 nm emission is attributed to the locally excited state (b^*). Supporting this implication, the excitation spectra exhibit monitoring wavelength dependence as shown in Figure 2. When the 430 nm emission is monitored, the excitation spectrum is distinctively different from the 330 nm emission. Excitation spectrum monitoring the 380 nm emission fall in between the two. Of course the slight red edge effect was also observed for the free 4BPCA in the same solvent. This is because a partial hindrance of the internal rotation around the central C-C bond of the biphenyl moiety is inhibited by the molecule-solvent interaction to keep the pre-twisted conformation in the ground-state as reported¹⁸ previously. Nevertheless the ratio of the a^* emission to b^* emission is much smaller than in the polymer system, indicating that the polymer segment motion plays an important role in undergoing a facile conversion to the a^* state by maintaining the pre-twisted conformation to minimize the angle of rotation.

In order to further confirm the dual emission, the fluorescence lifetimes were measured by monitoring the different emission bands. As shown in Table 1, the fluorescence monitored at 300 nm showed biexponential decay with the short component (100 ps) and the long component (780 ps). The decay times for these two components are similar to those of noncoplanar conformer and coplanar conformer of free 4BPCA, respectively which are observable in nonpolar solvents.¹⁸ This indicates that the excited-state geometry change of the biphenyl moiety from the pre-twisted form to the cop-

Table 1. Fluorescence decay times of 4BPCA-bound PMMA polymer in EAc monitored at different wavelengths*

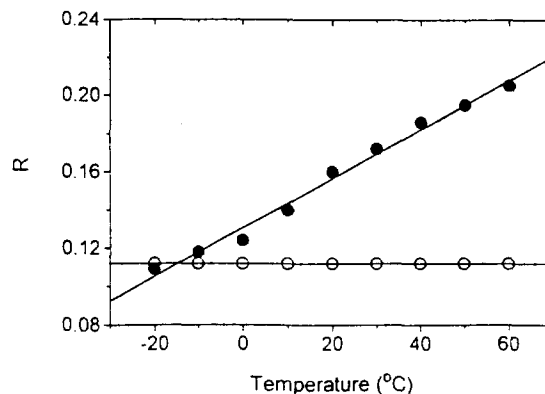
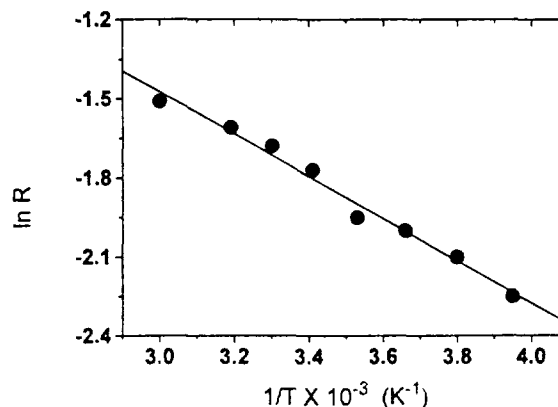
Monitoring Wavelength (nm)	Decay times (ps)
300	100 (22%)
	780 (78%)
360	2100 (7%)
	760 (54%)
	80 (39%)
400	2320 (15%)
	740 (43%)
	60 (42%)

*Excitation wavelength was 295 nm since it was difficult with our laser system to get 310 or 320 nm laser pulse which would have enhanced TICT emission around 430 nm by the red edge effect.

lanar one is still possible in the polymer segmental restriction. Thus, the fast decay component is attributed to the emission from locally excited-state noncoplanar conformer whereas the slow decay is attributed to the intramolecular charge transfer (ICT) emission from the coplanar conformer. However, as the monitoring wavelength increases, the fluorescence decay is analyzed to fit the triexponential functions with the third component (2 ns) in addition to the short and long components. It is also interesting to note that as the emission wavelength increases the amplitudes of the third 2ns component increases while that of the 780 ps component decreases. This should be due to the increase of the TICT emission at the expense of the ICT emission, being consistent with the previous discussion that the 430 nm emission is from the further twisted a^* state.

This is rather surprising observation when considering the following two facts. Firstly in the case of DMAB-bound PMMA the conformational motion of DMAB is subjected to restriction by the polymer main chain so that the formation of TICT state is inhibited.¹⁴ Secondly it has been previously observed that even in polar solvent TICT emission from the free 4BPCA was not observed although the intramolecular charge transfer state is formed with the inhibition of the excited-state geometrical change toward coplanarity of biphenyl moiety.¹⁸ This is because the internal rotation of biphenyl moiety is still competitive with the intramolecular charge transfer. Thus the present results lead us to conclude that the conformational change of the 4BPC is inhibited in the polymer matrix by the restriction of the polymer main chain and the twist angle of the biphenyl moiety is rather preserved. Consequently the formation of TICT state is more feasible in the polymer matrix. This is consistent with the Rettig's suggestion that the TICT formation is facilitated by the increase in the ground-state twist angle between the electron donating group and electron accepting group.¹⁹

In order to determine the activation energy for the formation of the TICT state, we have made the Grabowski's TICT kinetic analysis^{23,24} of the temperature dependence of the fluorescence spectrum of 4BPC-bound PMMA in EAc. The Grabowski's kinetic model is based on photostationary approximation, leading to the derivation of the following equations.

**Figure 4.** Temperature dependences of R value of 4BPC-bound PMMA in EAc monitored by excitation at 260 nm (open circles) and 320 nm (closed circles).**Figure 5.** Arrhenius plot of R value of 4BPC-bound PMMA in EAc monitored by excitation at 320 nm.

$$\text{The } a^* \text{ emission quantum yield, } \Phi_a = \frac{k_{fa}k_1}{k_b(k_2+k_a)+k_1k_a} \quad (1)$$

$$\text{The } b^* \text{ emission quantum yield, } \Phi_b = \frac{k_{fb}(k_2+k_a)}{k_b(k_2+k_a)+k_1k_a} \quad (2)$$

$$R = \Phi_a/\Phi_b = \frac{k_{fa}k_1}{k_{fb}(k_2+k_a)} \quad (3)$$

Here, $k_a = k_{fa} + k_a^*$ and $k_b = k_{fb} + k_b^*$ where k_{fa} (k_{fb}) and k_a^* (k_b^*) are the rate constants of the radiative and nonradiative transition from the a^* state and b^* state, respectively. k_1 and k_2 are the twisting relaxation rate constant of $b^* \rightarrow a^*$ and the backward-reaction rate constant of $a^* \rightarrow b^*$, having the activation energy E_1 and E_2 , respectively. It is known that in the low-temperature region k_{fa} , k_{fb} and k_a are temperature-independent and k_2 is negligibly small as compared with k_a . Under these conditions, the temperature-dependence of a measurable quantity, R , is expressed by equation (4) in the low-temperature region (250 K-330 K).¹⁴

$$R = A \exp(-E_1/k_BNT) \quad (4)$$

k_B is the Boltzman constant.

Figure 4 shows the temperature-dependence of the R

value for the 4BPC-bound PMMA with an excitation wavelength 320 nm, exhibiting the increase of R value as the temperature increases. The Arrhenius plot according to eq. (4) (Figure 5) gives the activation energy of 6.0 kJ/mole. This value is the same as that for the internal rotational barrier energy of the biphenyl moiety.¹⁹ Of course this value is similar to the activation energy for the solvation measured from the temperature dependence of solvent viscosity (6.8 kJ/mole in EAc²³). However, it should be noteworthy that the temperature dependence was not observed for the free 4BPCA in EAc even when excited at the red edge wavelength. These observations imply that the enhanced TICT emission in the PMMA polymer is due to the polymer segmental motion-associated twist of biphenyl moiety. Thus, the present results confirm again that molecular twisting plays an important role in the TICT in the polymeric environment. It is known that the solvation is retarded in the polymer matrix. However, if the polymer effect is the retardation of solvation only, the observation of the TICT emission of the 4BPC-bound PMMA, which is not observed from the free 4BPCA in polar solvents,¹⁸ would be impossible in contrast to the present results. Besides it is also important to note that for the DMABN-bound PMMA the temperature dependence of R value is independent of the excitation wavelength.^{15,23} This is attributed to the barrierless process of the $b^* \rightarrow a^*$. However, in the present case the temperature dependence of the R value was observed to be dependent on the excitation wavelength; the R is independent of temperature when exciting at the blue edge absorption (Figure 4) whereas it is sensitively dependent on the temperature change when exciting at the red edge absorption. This result indicates that the $b^* \rightarrow a^*$ is not a barrierless process in contrast to the case for DMAB-bound PMMA.¹⁵ In other words, even if the ground-state conformation is already twisted, a difference appears in the enthalpy term of producing the perpendicularly twisted TICT state. Namely further-molecular twisting is primarily important to be stabilized regardless with solvation.

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