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Twisted Intramolecular Charge-Transfer Phenomenon as a Quantitative Probe of Polymerization Kinetics

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Introduction

The study of the behavior of excited states in polymer matrices is becoming increasingly important. Changes in fluorescence yields,[2,3-7] the position of the fluorescence maximum,[8] changes in polarization,[4,8] and the efficiency of intramolecular[9,10] and intermolecular[11] excimer formation have all been related to the changes in viscosity occurring during the polymerization.

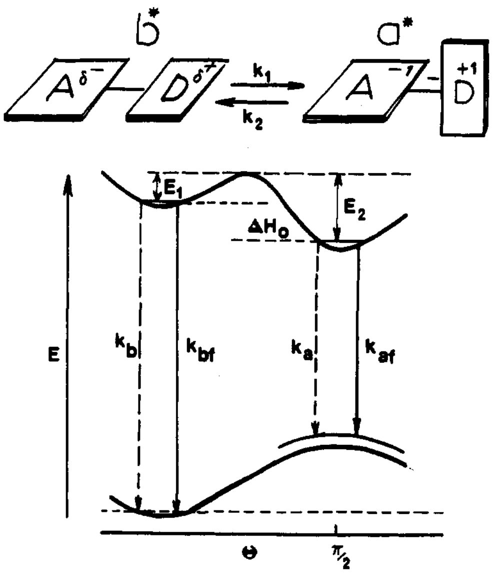
Aromatic systems possessing both a strong donor and acceptor substituent often exhibit anomalous emission properties, i.e., a large Stokes shift or dual luminescence, which are related to internal charge-transfer properties. In rigid molecules an *unusually* large Stokes shift, which is explained by the increase of the excited-state dipole moment and the theory of solvent shifts,[12-16] is observed. In flexible molecules, only one fluorescence band is found, possibly due to internal relaxation channels, which involve several kinds of rotations around molecular bonds.[17,18] Flexible systems are useful for the study of polymeric systems[2-4,8,19,20] because of their high sensitivity to the viscosity and the polarity of surrounding solvent molecules.[12-16] It has been known for some time[21,22,23] that a certain series of 4-(*N,N*-dimethylamino)benzonitriles (DMABN) or 4-(*N,N*-dimethylamino)benzoates exhibits a characteristic double fluorescence corresponding to two kinds of singlet excited states (see Scheme I). According to the twisted intramolecular charge-transfer (TICT) hypothesis proposed by Grabowski and co-workers,[21,24] the short-wavelength (b*) band is said to be due to coplanar molecule while the long-wavelength (a*) band origiantes from a molecule with perpendicular conformation, which causes full charge separation. Thus, the fluorescence spectra of these molecules strongly depend not only on the solvent polarity, but also on the medium viscosity,[25,26] and the molecules are expected to act as molecular probes sensing their microscopic microenvironment.[27-30]

To our knowledge, there are no published reports on the use of the TICT phenomenon for the quantitative measurements of polymerization rates. We have investigated this and report on it herein. As a model system, we have studied the thermal polymerization of methyl methacrylate initiated by benzoyl peroxide and measured the polymerization rate by monitoring the changes in the fluorescence emission spectra of series of 4-(*N,N*-dialkylamino)benzoates.

Experimental Section

Methyl methacrylate (MMA) was purified by distillation before use. Benzoyl peroxide (BP) was recrystallized from methanol–chloroform (1:1). Ethyl 4-(*N,N*-dimethylamino)benzoate (DMB) (Aldrich) was recrystallized from methanol. Fluorescence measurements were performed at ambient temperature in a SPEX 212-Fluorolog spectrofluorometer. Emission was measured by using front-face detection.

Scheme I



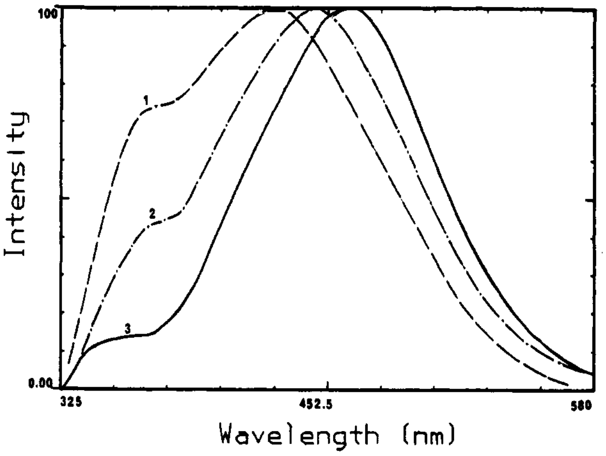


Figure 1. Fluorescence spectra of (1) BMB, (2) BPB, and (3) DBEM in MMA (λ_{ex} 300 nm).

Polymerization was carried out in Pyrex cylindrical tubes at 60 °C. Samples containing MMA, BP, and the spectroscopic probe were purged with argon for 15 min. As polymerization was continued, successive samples were removed from water bath and quenched at 0 °C. After warming to ambient temperature, the fluorescence spectra of the probe was measured. For gravimetric measurements the polymer was precipitated in an excess of methanol, filtered, and dried to constant weight.

Butyl 4-(*N,N*-diethylamino)benzoate (BDEB) was prepared from the potassium salt of 4-(*N,N*-diethylamino)benzoic acid and *n*-butyl bromide in DMF with tetrabutylammonium bromide (TBAB) as a catalyst. The reaction was carried out at 60 °C for 24 h, the resulting solution was put into water, and the organic layer was separated, washed, dried, and distilled in vacuum.

2-[[4-(*N,N*-Dimethylamino)benzoyl]oxy]ethyl methacrylate (DBEM) was prepared from 2-bromoethyl methacrylate (Polysciences) and the potassium salt of 4-(*N,N*-dimethylamino)benzoic acid in DMF in the presence of TBAB at 60 °C. The product was precipitated in water, filtered out, and purified by repeated crystallization.

Butyl 4-(*N*-piperidino)benzoate (BPB) was prepared by using a sequence of reactions starting from 4-fluorobenzoic acid through buty 4-fluorobenzoate to yield the final product, using the general procedure given by Suhr.[25,31] Butyl 4-(*N*-morphilino)benzoate (BMB) was prepared by a similar procedure. Structures were confirmed from their NMR spectra.

Results and Discussion

The structures of the probes used in our study along with their basic spectroscopic properties are shown in Table I. Figure 1 shows the fluorescence spectra of DBEM, BPB, and for BMB at ambient temperature in methyl meth-

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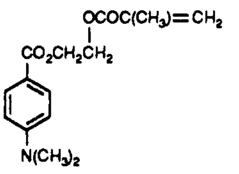
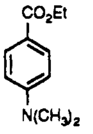
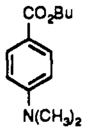
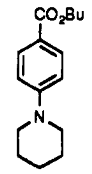
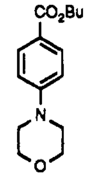
Table I
Structures, Abbreviations, and Basic Spectroscopic Properties of Probes Evidencing TICT Properties

	 DBEM	 DMB	 DBEB	 BPB	 BMB
λ_A^{max}, nm	310	306	312	308	300
R^a	0.16	0.26	0.08	0.46	0.75

[a] R, ratio of the fluorescence intensities from planar form (b*) and from TICT state (a*) in MMA.

acrylate solution. The dual nature of fluorescence spectra is clearly demonstrated by the fluorescence curves.

The specific compounds listed in Table I were chosen to test certain aspects of the probe chemistry for the following reasons: (1) DMB and DBEM represent molecules "rotating part" is of the "same size". However, whereas DMB reacts as a free molecule in polymer–monomer solution, DBEM can copolymerize and be incorporated to the polymeric chain. According to Tazuke et al.,[26-29] this may change the photophysical properties of the 4-(*N*,*N*-dimethylamino)benzoate molecule; (2) BDEB, BPB, BMB, and DMB represent molecules with various sizes of the rotating species. This may cause differential "sensitivity" of the probes to local viscosity changes, because of their different activation energies required for the rotation of donor substituent.[31]

According to Scheme I, the kinetic analysis based on the photostationary-state approximation[31] leads to the following expressions:

$$\Phi_B = [k_{bf}(k_2 + k_a)]/k_b(k_2 + k_a) + k_1k_a \qquad (1)$$

$$\Phi_A = k_{af}k_1/k_b(k_2 + k_a) + k_1k_a \qquad (2)$$

and

$$R = \frac{\Phi_B}{\Phi_A} = k_{bf}(k_2 + k_a)/k_{af}k_1 \qquad (3)$$

The twisting relaxation rates k_1 and k_2 are known to be temperature dependent.[20,32] For the polymeric system[27] while the 4-(*N*,*N*-dimethylamino)benzoate moiety is attached to the polymeric chain, the R can be simplified to eq 4.

$$\frac{\Phi_B}{\Phi_A} = R = k_{bf}(k_1 + k_a)/k_{af}k_1 \qquad (4)$$

With the assumption of the microviscosity concept[33-36] and on the basis of the above kinetic analysis one can conclude that molecules demonstrating the TICT phenomenon might be a good probe for monitoring the polymerization rate.

Figure 2 shows the changes in the fluorescence spectra for the BPB probe (2×10^{-4} M) observed after 55 min of MMA polymerization and Table II summarizes the data obtained for compounds tested in our experiments. Data from Table II show the following: (1) there is a relationship between the "sensitivity" of the probe (monitored by value of the slope) and the "size" of the rotating part of molecule. This can be easily explained by the Gierer and Wirtz microviscosity theory;[36] (2) incorporation of the probe into the polymeric chain increases the "sensitivity" of the probe. This observation is in a very good agreement with the data obtained by Hayashi et al.[27] for DBM and poly-DBM.

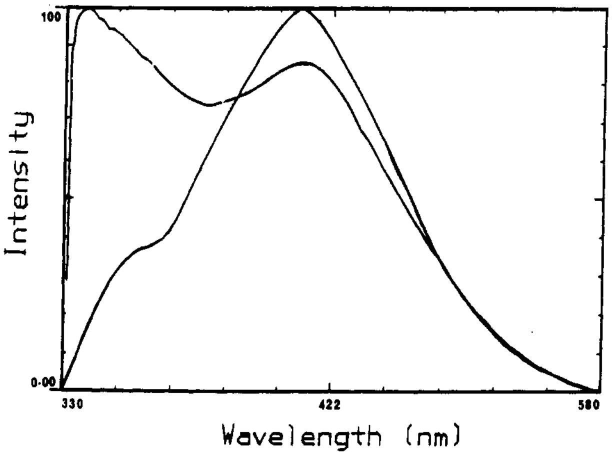


Figure 2. Change in the fluorescence spectra for BPB in MMA (λ_{ex} = 300 nm) (1) before polymerization and (2) after 50 min of thermally initiated polymerization.

Table II
Sensitivity Factors (Slopes from Figure 3) as a Function of the Structure and Concentration of Probe

concn, M/L	slope				
	DBEM	DMB	DBEB	BPB	BMB
2×10^{-4}	1.37×10^{-2}	1.18×10^{-2}	0.39×10^{-2}	3.16×10^{-2}	1.75×10^{-2}
4×10^{-4}	1.53×10^{-2}	1.10×10^{-2}			
6×10^{-4}	1.79×10^{-2}	1.17×10^{-2}			

It was found that the activation volume for the formation of the TICT state is 2.9 cm^3/mol for DMB, and 5.5 cm^3/mol for poly-DMB. On the basis of the literature data[28-30] the "sensitivity" of the attached probe can be increased by employing a longer spacer separating the probe from the polymeric chain. The attachment of pyrene to the polymeric chain disqualifies the former as a probe because of intramolecular excimer formation.[37]

In principle, the ratio of the b* and a* fluorescence intensities can be used to determine the progress of the polymerization but only when the linear relationship between the increase in R and the amount of obtained polymer is observed. The experimental results are shown in Figure 3.

The rate of MMA polymerization (R_p) in the presence of probes was determined gravimetrically at four benzoyl peroxide concentrations. The results can be represented by eq 5. The experiments also showed that there is no

$$R_p = -d[\text{MMA}]/dt = 1.33 \times 10^{-3}[\text{BP}]^{0.5}[\text{MMA}] \text{ M min}^{-1} \qquad (5)$$

influence of probe concentration on R_p. The results in Figure 3 indicate a linear relationship between the changes of ratio (R) value for the probe and the amount of polymer

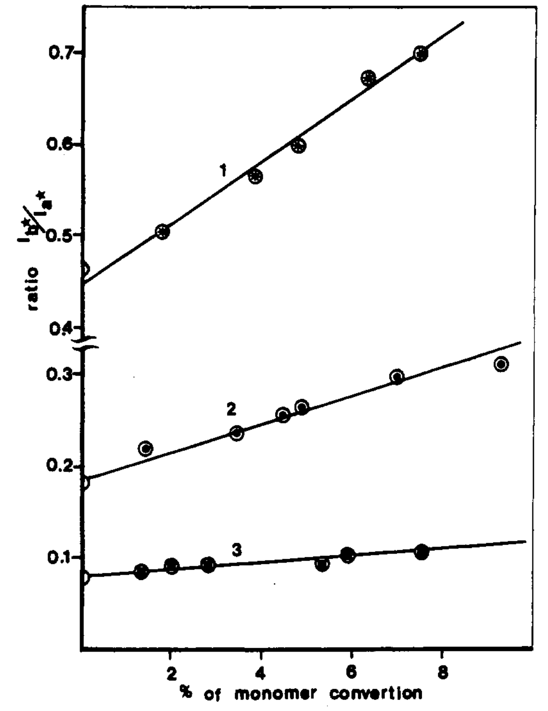


Figure 3. Increase in the fluorescence ratio during polymerization of MMA at 60 °C. Concentration of probes $c = 2 \times 10^{-4}$ M [BP] = 0.7%; (1) BPB, (2) DBEM, (3) BDEB. Fluorescence intensities monitored at λ_{max} for the A band and a wavelength of λ_{max} for the B band after polymerization.

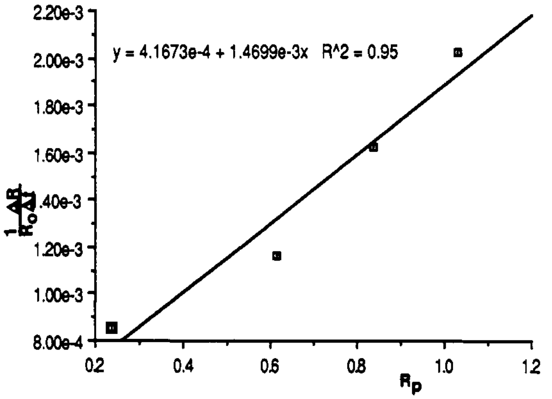


Figure 4. Correlation between the rate of increase in the fluorescence ratio and the rate of polymerization measured gravimetrically.

obtained. By analogy to the study on pyrene as a probe[11] one can conclude that for low conversion the following expression characterizes the changes in the fluorescence ratio and the rate of polymerization:

$$[1/R_0]\, dR/dt = [(1/\eta_0)\, d\eta/dc - (1/D_0)\, dD/dc]R_p \qquad (6)$$

where D is density, c is the polymer concentration, and η viscosity subscript 0 indicates the value in the absence of polymer. The correlation described by eq 6 is presented in Figure 4. The relationship from Figure 4 clearly shows that the rate of increase in fluorescence ratio is a measure of the rate of polymerization. The $(1/D_0)\, dD/dc$ value is equal to 1.2×10^{-3} L/g (3.8×10^{-3} L/g for pyrene[10]). This value indicates that the TICT phenomenon can detect the motion of a longer polymeric chain segment at the microscopic level than the pyrene probe.

Conclusions

We have shown that the TICT phenomenon can be applied as a spectroscopic probe for direct measurements of the rate of polymerization. The sensitivity of the probe depends on two factors: (i) the size of the rotating part of the molecule and (ii) whether the probe is attached to the polymeric chain or not. Incorporation of the probe increases its sensitivity.

Before the technique can be applied, it is necessary to realize that the ratio of the emissions from the b* and a* states is not only viscosity dependent. The polarity of the solvent changes the positions and relative intensities of the b* and a* bands. Also temperature can effect the changes in the ratio b* and a* band intensities.

Compounds evidencing TICT properties can operate at low concentrations, because the relative intensities of fluorescence from the b* and a* states are not concentration dependent (at least at low concentration). A low concentration of the probe allows the use of various fluorescence techniques, which can make it possible to probe the whole volume of the tested sample.

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Registry No. MMA, 80-62-6; DMB, 10287-53-3; BDEB, 132884-53-8; DBEM, 79984-80-8; BPB, 132884-54-9; BMB, 132884-55-0; DBEB, 57754-81-1; 4-(*N*,*N*-diethylamino)benzoic acid potassium salt, 132884-56-1; 2-bromoethyl methacrylate, 4513-56-8; 4-fluorobenzoic acid, 456-22-4; butyl 4-fluorobenzoate, 3888-64-0; *n*-butyl bromide, 109-65-9; 4-(*N*,*N*-dimethylamino)benzoic acid potassium salt, 68494-10-0.