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tions of the functions which have newly appeared in eq A.1 are required. A set of functions $\zeta_m(x)$ ($m = 0, 1, 2, ...$) is defined by

$$\zeta_m(x) \equiv \sum_{n=1}^{\infty} \frac{x^n}{n(n+m)^{3/2}} \qquad \text{(A.2)}$$

in the form of a power series in x.

Another set of functions $h_m(x)$ ($m = 0, 1, 2$) is defined as

$$h_0(\delta) \equiv -\chi_{AB}x(1 - 2x + C_2x\delta)\delta \qquad \text{(A.3a)}$$

$$h_1(\delta) \equiv \chi(x) + C_2x\delta(-\chi'(x) + \chi_{AB}(1 - 2x)) + 2C_3\chi_{AB}x^2\delta^2 \qquad \text{(A.3b)}$$

$$h_2(\delta) \equiv -C_2\chi(x) + C_3\chi'(x)x\delta - C_4\chi_{AB}x^2\delta^2 \qquad \text{(A.3c)}$$

where

$$\chi(x) \equiv \chi_{AP}(1 - x) + \chi_{BP}x - \chi_{AB}x(1 - x) \qquad \text{(A.4)}$$

and $\chi'(x)$ is the derivative of $\chi(x)$. Numerical constants C_m ($m = 2, 3, 4, ...$) are defined by $C_m \equiv 1/m^{3/2}$.

Appendix B. Explicit Forms of the Functions $g_{nm}(x)$

Expanding eq A.1 in double powers of ϕ_0 and δ and comparing it with the definitions of eq 3.2 and 3.4, we obtain the following functions:

$$g_{01}(x) = -(x + \ln x)/n + \ln(1 - x) + 1 - \chi_{AB}(1 - 2x)$$

$$g_{02}(x) = C_2[(2 - x)/n + x/(1 - x) - 2\chi_{AB}x]/2$$

$$g_{03}(x) = C_3[(3 - 2x)/n + (x/(1 - x))^2]/6$$

$$g_{11}(x) = C_2[-2(1 - 1/n) + (\ln x)/n - \ln(1 - x) + \chi_{AP} - \chi_{BP} + 2\chi_{AB}(1 - 2x)]$$

$$g_{12}(x) = C_3[(1 - 1/n) - 1/(1 - x) + 4\chi_{AB}x]/2$$

$$g_{20}(x) = C_2[x(2 - x)/2n + (1 - x)/2 - \chi_{AP}(1 - x) - \chi_{BP}x + \chi_{AB}x(1 - x)]$$

$$g_{21}(x) = C_3[(1 - 1/n)/2 - \chi_{AP} + \chi_{BP} - \chi_{AB}(1 - 2x)]$$

$$g_{30}(x) = C_3[x(3 - 2x)/n + 1 - x]/6$$

Registry No. PTHF (homopolymer), 24979-97-3; PTHF (SRU), 25190-06-1; CH_3OH, 67-56-1; cyclohexane, 110-82-7.

References and Notes

(1) Dondos, A.; Izumi, Y. *Makromol. Chem.* **1980**, *181*, 701.
(2) de Gennes, P. G. *J. Phys. (Les Ulis, Fr.)* **1976**, *37*, L59.
(3) Williams, C.; Brochard, F.; Frisch, H. L. *Annu. Rev. Phys. Chem.* **1981**, *32*, 433.
(4) Tanaka, T. *Sci. Am.* **1981**, *244*, 124. *Phys. Rev. Lett.* **1978**, *40*, 820.
(5) Dondos, A.; Benoit, H. *Makromol. Chem.* **1970**, *133*, 119.
(6) de Gennes, P. G. *J. Phys. Chem.* **1984**, *88*, 6469.
(7) Tanaka, F. *J. Chem. Phys.* **1983**, *78*, 2788.
(8) Tanaka, F. *J. Chem. Phys.* **1985**, *82*, 2466.
(9) Ushiki, H.; Tanaka, F. *Eur. Polym. J.* **1985**, *21*, 701.
(10) Lerman, L. S. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 1886. Laemmli, U. K. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 4288.
(11) Post, C. B.; Zimm, B. H. *Biopolymers* **1979**, *18*, 1487.
(12) Frisch, H. L.; Fesciyan, S. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 309.
(13) Nose, T. *J. Phys. (Les Ulis, Fr.)* **1986**, *47*, 517.
(14) Flory, P. J. *Principle of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1966.
(15) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303.
(16) Shultz, A. R.; Flory, P. J. *J. Polym. Sci.* **1955**, *15*, 231.
(17) Ptitsyn, O. B.; Kron, A. K.; Eizner, Y. Y. *J. Polym. Sci., Part C* **1968**, *16*, 3509.
(18) de Gennes, P. G. *J. Phys. (Les Ulis, Fr.)* **1975**, *36*, L55.
(19) Joanny, J. F.; Brochard, F. *J. Phys. (Les Ulis, Fr.)* **1981**, *42*, 1145.
(20) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1977.
(21) Gordon, M.; Kapadia, P.; Malakis, A. *J. Phys. A: Math. Gen.* **1976**, *9*, 751.

How Does the Polymer Main Chain Influence the Side-Chain Mobility? A Fluorescence Probe Study by Means of Twisted Intramolecular Charge-Transfer Phenomena

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ABSTRACT: ω-[[4-(*N,N*-Dimethylamino)benzoyl]oxy]alkyl methacrylates where alkyl is dodecyl, octyl, butyl, and ethyl were prepared and copolymerized with a large excess of methyl methacrylate. The content of the 4-(dimethylamino)benzoate (DMAB) as a fluorescence probe is less than 0.04 wt %. Fluorescence spectra of the samples were studied in dilute ethyl acetate (a good solvent) or *n*-butyl chloride (a poor solvent) solution. When rotation of the dimethylamino group is possible within the excited state lifetime, fluorescence from DMAB group is in part converted to twisted intramolecular charge-transfer (TICT) fluorescence. This fluorophore can therefore probe local segment mobility in the polymer. It was found that the ratio (*R*) of TICT emission intensity to the emission intensity from the local excited state of DMAB decreased with decreasing the alkyl spacer length. Together with the results of red edge excitation effects it was concluded that the local segment motion of side group was subjected to restriction by the polymer main chain as a function of separation from the main chain. Solvent and molecular weight effects were also discussed.

Introduction

The fluorescence method in polymer science is becoming increasingly popular because of its handiness and the possibility of obtaining detailed molecular information on the local environment.[2] When a small molecular fluorescence probe is simply mixed with a polymer to study averaged bulk properties of the polymer, one has to worry about the binding site or the position where the probe locates.[3] The demerit of probing a particular site could turn out to be a merit when one intends to study the distribution of the molecular environment in a polymer. We are now reporting a novel example providing the information on the distribution of segment mobility in a polymer side chain in dilute solution.

In view of recent advancement in time-resolved measurements of various rate constants, evidence is being

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accumulated in support of state distribution in solid polymers.[4] A number of years ago, it was demonstrated that anthryl groups attached to polymer chain ends showed distinctively different reactivities in photodimerization depending upon the state of aggregation.[5] The degree of photoreaction is often a function of temperature. At a certain temperature, molecules surrounded by a free volume larger than the threshold value required for the particular reaction can only react. Such microscopic inhomogeneity depends on the scale of domain size concerned. When one looks at a polymer molecule with an extremely high magnification, one will see the main chain, the side chain, and the empty space in between them independently. The mobility of various parts of polymer is certainly site dependent and therefore the available free volume will also be different from site to site.

Although various methods are available such as mechanical property measurements, calorimetry, and others to estimate segment motion or free volume as a function of temperature, it is rather difficult to focus on the information from a particular site. Because of its high sensitivity, high time resolution, and the small volume of probing, the fluorescence probe method is best suited for the purpose. An extremely small portion of a fluorescence probe molecule ($\ll 1\%$) incorporated in a polymer chain is sufficient to provide the local molecular information. The ^{13}C NMR can also pinpoint a specific site of a polymer. However, the sensitivity is much lower than that of the fluorescence probe method.

We chose 4-(dimethylamino)benzoate (DMAB), a twisted intramolecular charge-transfer (TICT) compound, as the probe. The usefulness has been reported in the study on free volume change under high pressure[6] and as a function of polymer concentration.[7] This type of probe exhibits dual fluorescence, one from the non-charge-transfer state appearing at high energy (b* band) and another from the twisted charge-transfer state in which the plane of dimethylamino group is perpendicular to the benzoate plane. This emission appearing at lower energy (a* band) is sensitive to local polarity and segment mobility. The ratio of these two fluorescence peaks is therefore a measure of segment mobility, while the position of the a* band provides information on local polarity.

This type of fluorescence has been a point of interest for over 10 years.[8] The TICT hypothesis has been first introduced by Grabowski[9] and is now widely recognized. When an electron-donating substituent and an electron-accepting substituent are conjugated in a molecule, two molecular planes, one containing the donor group and another having the acceptor group, are coplanar in the ground state. In the excited state, these two planes are twisted perpendicular to each other so that the positive charge on the amino group and the negative charge on the carbonyl group are separated. The charge-transferred state is stabilized by interactions with surrounding molecules, in general solvent molecules. If molecular twisting is not permitted during the excited-state lifetime, the a* emission does not appear.

While a great number of compounds fall in the category of a TICT compound,[8] the compounds exhibiting dual fluorescence are rather limited. These two emission bands are often not separated and change in the fluorescence quantum yield as well as the wavelength shift result. Those belonging to this type are triphenylmethane dyes, dicyanoethylene derivatives, rhodamines, and many others and have been widely used as fluorescence probes[10] since the pioneering work by Oster and Nishijima.[11] Obviously, the available information is more fertile if two peaks appear in a fluorescence spectrum.

Few years ago, we demonstrated that exciplex formation by a small amount of 1-(1-pyrenyl)-3-[4-(dimethylamino)phenyl]propane attached to the side chain of polymer was strongly affected by the rest of polymer chain even in dilute solution,[12] which is rather difficult to be interpreted on the basis of presently available polymer solution theories. In the present study, we prepared poly(methyl methacrylate) (PMMA) containing a very small amount of DMAB chromophore attached to the side chain via an alkyl chain of variable length. Close study of TICT fluorescence in dilute solution revealed that the fluorescence behaviors are dependent on the length of spacer as well as on the chain conformation. It is apparent that small rotational motion in the side chain is controlled by the polymer main chain even in very dilute solutions.

Experimental Section

Materials. Dodecyl 4-(dimethylamino)benzoate (**1a**) was obtained by esterification of 4-(dimethylamino)benzoyl chloride with dodecyl alcohol, purified by column chromatography (eluent, chloroform/*n*-hexane (3/1)), and recrystallization from *n*-hexane. NMR ($CDCl_3$) δ 1.30–1.41 (m, 23 H, $C_{11}H_{23}$), 3.03 (s, 6 H, $(CH_3)_2N$), 4.28 (t, 2 H, $CH_2OC(=O)$), 6.6–8.05 (dd, 4 H, Ar). Anal. Calcd: C, 75.62; H, 10.58; N, 4.20. Found: C, 75.21; H, 11.03; N, 4.15.

Other model compounds having octyl (**1b**) and butyl (**1c**) substituents were also prepared. **1b**: NMR ($CDCl_3$) δ 1.33 (m, 15 H, C_7H_{15}), 3.05 (s, 6 H, $(CH_3)_2N$), 4.30 (t, 2 H, $CH_2OC(=O)$), 6.6–8.0 (dd, 4 H, Ar). Anal. Calcd: C, 73.61; H, 9.81; N, 5.01. Found: C, 73.85; H, 9.58; N, 4.86. **1c**: NMR ($CDCl_3$) δ 1.34 (m, 7 H, C_3H_7), 3.05 (s, 6 H, $(CH_3)_2N$), 4.30 (t, 2 H, $CH_2OC(=O)$), 6.6–8.0 (dd, 4 H, Ar). Anal. Calcd: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.60; H, 8.74; N, 6.34. The ethyl derivative (**1d**) was reported previously.[7]

12-Hydroxydodecyl 4-(dimethylamino)benzoate (**2**) was similarly prepared from the acyl chloride and an excess amount of 1,12-dodecanediol. NMR ($CDCl_3$) δ 1.35 (m, 20 H, 10 CH_2), 2.70 (br s, 1 H, OH), 3.06 (s, 6 H, $(CH_3)_2N$), 3.63 (t, 2 H, CH_2OH), 4.30 (t, 2 H, $CH_2OC(=O)$), 6.6–8.05 (dd, 4 H, Ar). Anal. Calcd: C, 72.16; H, 10.09; N, 4.04. Found: C, 72.40; H, 9.89; N, 4.04.

12-[[4-(Dimethylamino)benzoyl]oxy]dodecyl methacrylate (**3**) was obtained by further esterification of **2** with excess methacryloyl chloride at room temperature. The product was purified by column chromatography and recrystallization from *n*-hexane. NMR ($CDCl_3$) δ 1.35 (m, 20 H, $10 \times CH_2$), 1.88 (s, 3 H, $CH_3C=C$), 3.05 (s, 6 H, $(CH_3)_2N$), 4.17 (q, 4 H, $2 \times CH_2OC(=O)$), 5.5–6.20 (2 s, 2 H, $CH_2=C$), 6.6–8.05 (dd, 4 H, Ar). Anal. Calcd: C, 71.91; H, 9.41; N, 3.35. Found: C, 71.72; H, 9.23; N, 3.28.

A series of the methacrylate monomers, 8-[[4-(dimethylamino)benzoyl]oxy]octyl methacrylate (**4**) and 4-[[4-(dimethylamino)benzoyl]oxy]butyl methacrylate (**5**), were similarly prepared. Analytical data agreed. 2-[[4-(Dimethylamino)benzoyl]oxy]ethyl methacrylate (**6**) was reported previously.[7]

Poly[(methyl methacrylate)-*co*-[12-[[4-(dimethylamino)benzoyl]oxy]dodecyl methacrylate]] (poly(MMA-*co*-12)) was synthesized by radical copolymerization of **3** with methyl methacrylate ($[\mathbf{3}]/[MMA] = 6.6 \times 10^{-5}$). Polymerization was carried out under nitrogen atmosphere at 70–75 °C in benzene by using azobis(isobutyronitrile) as an initiator. The copolymer was reprecipitated from benzene solution into methanol 3 times. The number-averaged molecular weight of polymer was determined to be 1×10^5 by GPC (HLC-802 (Toyo Soda) gel permeation chromatography). The standard was monodispersed polystyrene. The chromophore unit content is about 0.04 wt % as determined by UV absorption spectroscopy. Other copolymers, poly(MMA-*co*-8) and poly(MMA-*co*-4), were similarly prepared by copolymerization of MMA with **4** and **5**, respectively. Characterizations of the copolymers are shown in Table I. Poly(MMA-*co*-2) (copolymer of MMA with **6**)[7] was fractionated by a Toyo Soda HLC-802 using a TSK-gel (HG type) fractionation column.

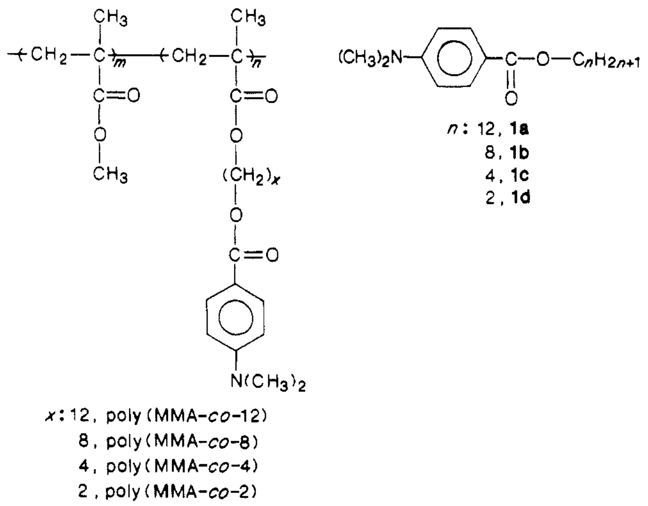
Solvents for spectroscopy were purified as follows. Ethyl acetate (EAc) was washed successively with 5% aqueous sodium carbonate and saturated sodium chloride solution several times, dried over magnesium sulfate, and fractionally distilled over calcium hydride

Table I
Some Properties of Polymer Samples

polymer	M_n[a]	wt % chromophore[b]
poly(MMA-*co*-12)[c]	1.0×10^5	0.04%
poly(MMA-*co*-8)	1.0×10^5	0.02%
poly(MMA-*co*-4)	5.5×10^4	0.01%
poly(MMA-*co*-2)	1.0×10^5	0.01%

[a] M_n was determined by GPC measurement with monodispersed polystyrenes as standard. [b] The chromophore content was determined by absorption spectroscopy. [c] The number in parentheses indicates the number of carbon atoms in the alkanediyl group connecting the TICT chromophore to the polymethacrylate main chain.

Chart I



several times. *n*-Butyl chloride (BuCl) was washed repeatedly with sulfuric acid, water, sodium carbonate solution, and water. After drying over magnesium sulfate and phosphorus pentoxide, BuCl was fractionally distilled over phosphorus pentoxide twice.

Spectroscopy. Fluorescence spectra were recorded under an argon atmosphere on a Hitachi MPF-4 fluorescence spectrophotometer. Spectroscopic data were transferred to an Oki IF-800 microcomputer and corrected for the instrumental response. Excitation spectra were measured by a Hitachi F-4000 spectrofluorimeter. Absorption spectra were recorded on a Hitachi 320 spectrophotometer. All measurements were performed at room temperature.

Results and Discussion

Effects of Spacer Length between TICT Chromophore and the Polymer Main Chain on Fluorescence in Dilute Ethyl Acetate Solution. The general formula of polymers and the model compounds are shown in Chart I.

The absorption spectra of polymer-bonded DMAB groups are nearly identical regardless of the length of spacer as shown in Figure 1. However, a slight broadening is observed when the chromophore is close to the main chain, which will be discussed later. Since the content of DMAB in copolymers is less than 0.04%, bulk physical properties of PMMA will not be affected by copolymerization. All polymer samples exhibit dual fluorescence with varying relative intensity of the a* band to the b* band.

It is rather surprising to find strong polymer effects on TICT fluorescence as a function of spacer length. The TICT chromophore separated from polymer main chain by a long spacer behaves still differently from the monomer model. Furthermore, the difference between polymer and monomer systems is underestimated owing to the different kinetic expressions at room temperature for polymers and monomer models.[7,13] Although we have not yet completed lifetime analysis of all samples, the lifetime of the a* band is comparable for **1d** and poly(MMA-*co*-2), indicating that the low value of R in polymers is due to the slow rate of the a* state formation in the polymer; that is, the rate of twisting in the polymer is slow.[14]

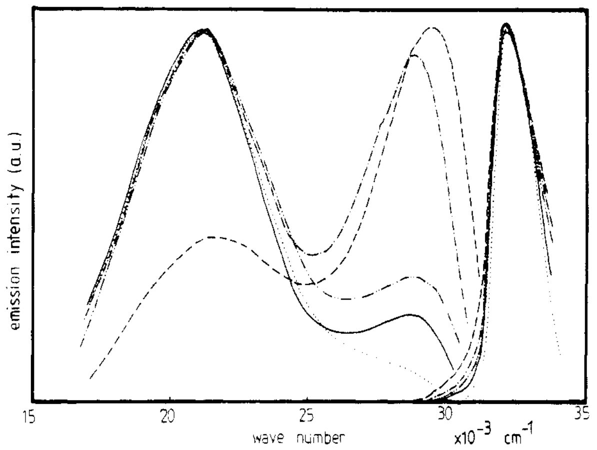


Figure 1. Absorption and emission spectra of poly(MMA-*co*-12) (—), poly(MMA-*co*-8) (- - -), poly(MMA-*co*-4) (– – –), poly(MMA-*co*-2) (— — —), and **1d** (···) in EAc. Concentration: 1 wt % for polymers, 2.1×10^{-5} M for **1d**. Excitation at 3.33×10^4 cm^{-1} (300 nm).

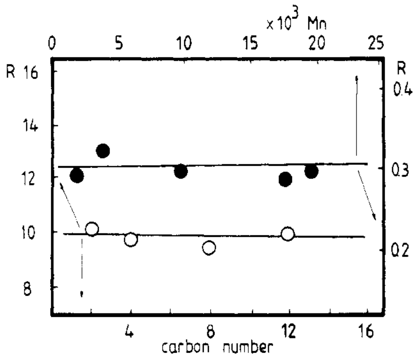


Figure 2. Emission intensity ratio (R) of the monomer model compounds versus alkyl chain length (○) and molecular weight dependence of R for poly(MMA-*co*-2) (●). Solvent, EAc.

While the segment motion relevant to the formation of TICT state is under the control of the polymer main chain, the energy of the TICT state is the same for all samples, indicating that the interaction between DMAB and solvent molecules is not affected either by the spacer length or by the polymer chain. Since the a* state is of charge transfer nature comparable to an exciplex, the energy level is sensitive to the local polarity. The results indicate that the DMAB group is similarly exposed to solvent, regardless of the polymer structure. It was also confirmed that the monomer model compounds with different alkyl chains (**1a–d**) show identical R values. Consequently, the observed polymer effect is attributable to polymer main chain effects. For poly(MMA-*co*-2) which showed the strongest effect on TICT fluorescence relative to monomer models, the polymer was fractionated and the molecular weight effect was examined. The R value is unaffected when the molecular weight ranges from 1.1×10^4 to 2.0×10^5 as shown in Figure 2.

The present results are difficult to be interpreted in the light of the theories of dilute polymer solution. All results demonstrate that the polymer main chain extends its effect to the remote end of the side groups and imposes re-

Table II
Properties of EAc and *n*-BuCl

solvent	ε[a]	n^2[a]	η (15 °C)[a]	Δf[b]	α (PMMA)[c]
EAc	6.02	1.88	0.473	0.200	0.64
BuCl	7.39	1.96	0.469	0.219	0.50

[a] ε, *n*, and η are dielectric constant, refractive index, and viscosity of solvents, respectively. Data from: *Organic Solvents*, 3rd ed.; Weissberger, A., Ed.; Wiley Interscience: New York, 1970. [b] Δf is defined as $\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)$. [c] α is defined by Sakurada-Mark-Houwink equation $[\eta] = KM^{\alpha}$. Data from: *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley Interscience: New York, 1970. Temperature: 35 °C for BuCl; 20 °C for EAc.

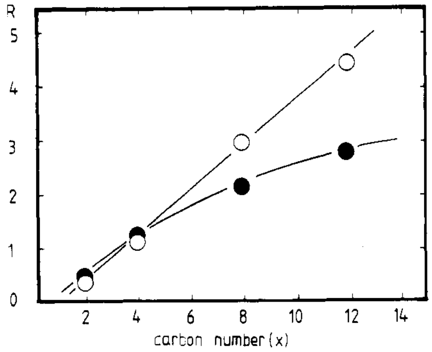


Figure 3. Emission intensity ratio (*R*) of copolymers as a function of the carbon number (X) of side chain in EAc (○) and in BuCl (●). Excitation at 3.33 × 10^4 cm^{-1} (300 nm).

strictions on the rotational motion of the dimethylamino group in DMAB. Ethyl acetate (EAc) is a good solvent for PMMA so that the end-to-end distance of PMMA is larger in this solvent and therefore the polymer main chain effect will be reduced in comparison with that in a poor solvent. To gain an inside look into the polymer chain effect, we examined the effect of solvent.

Polymer Effects on TICT Phenomena in Dilute *n*-Butyl Chloride Solution. We chose *n*-butyl chloride (BuCl) as a poor solvent. Physical constants of BuCl and EAc are compared in Table II. Dielectric constant, refractive index, and viscosity are comparable for these two whereas the exponential term (α) in the Sakurada-Mark-Houwink equation ($[\eta] = KM^{\alpha}$) is 0.5 for BuCl and 0.64 for EAc. Qualitatively, BuCl is a poorer solvent for PMMA than EAc. Different solvent effects on the present series of polymers are therefore primarily attributed to the difference in polymer chain expansion.

The relation between the *R* value and the length of side chain is depicted in Figure 3. When the side chain is short and close to the main chain, the solvent effect is comparable for EAc and BuCl. However, with increasing the length of alkyl chain, the *R* value in BuCl does not increase much and seems to level off. Side-chain mobility should therefore be a function of chain conformation. In a poor solvent where the polymer chain shrinks, the side chain would be entrapped in the shrunken polymer chain. In this case, liberation of the side-chain terminal group from the effect of main chain will be difficult even if the side chain is extended.

Polymer Structure and Red Edge Effect (REE) on TICT Fluorescence. The REE is a terminology given to the excitation wavelength dependence of fluorescence appearing when the conformational motion is slow enough to be comparable to the excited-state lifetime.[15] Rettig and co-workers have studied the relation between the rate of TICT state formation and the ground-state twist angle of DMAS group against the benzene ring for 4-(dimethylamino)benzonitrile.[16] In a previous work,[7] we reported for the first time that poly(MMA-*co*-2) exhibited a distinct red shift of the b* band and an enhanced a* emission intensity upon excitation at the absorption red edge even in fluid solution. While on the other hand, no REE was observed for **1d** under the same condition.[7] When microviscosity is low and the twisting rate of the b* state forming the a* state is much faster than the discipation rate of the a* state, fracturing of ground-state conformation of DMAB does not affect the *R* value. Namely, excitation of the ground-state conformers which are already partially twisted and absorb at the red edge of absorption band does not bring about any change in fluorescence spectrum. This is, however, not the case for the present polymers. Examples of excitation wavelength dependence are shown in Figure 4.

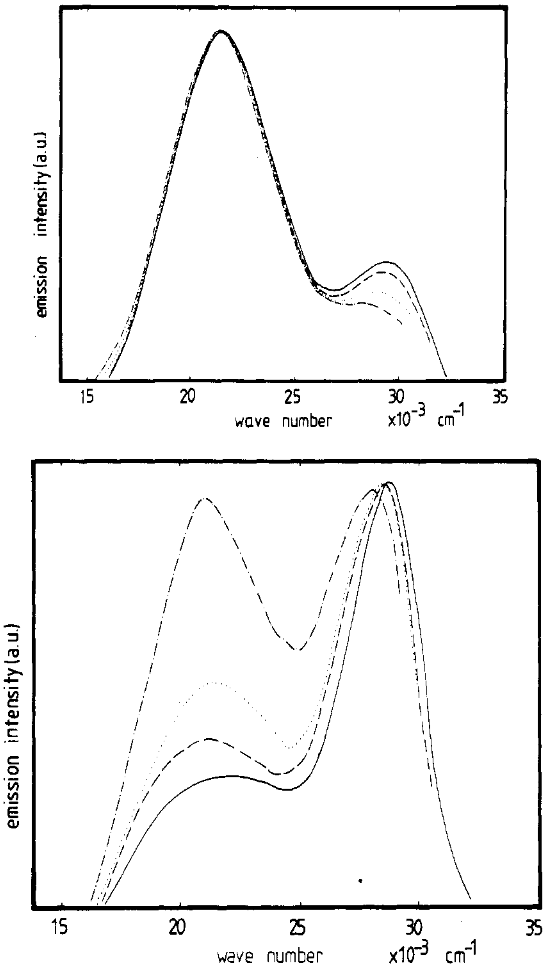


Figure 4. Excitation wavelength dependence of fluorescence spectra of poly(MMA-*co*-12) (top) and poly(MMA-*co*-2) (bottom) in EAc. Excitation at 34480 cm^{-1} (290 nm) (—), 33330 cm^{-1} (300 nm) (- - -), 32250 cm^{-1} (310 nm) (···), and 31250 cm^{-1} (320 nm) (-·-).

For poly(MMA-*co*-2) in EAc solution, excitation at the longer wavelength region brings about a red shift of the b* band (~10 nm for the excitation at 320 nm) and a prominent gain in the a* band intensity as compared with the fluorescence excited at 290 nm. On the other hand, the dilute solution of poly(MMA-*co*-12) exhibits a weaker REE, that is, a slight red shift of the b* band (~4 nm for the excitation at 320 nm) and a small increase in the a* emission intensity upon excitation of the absorption red edge.

Difference in REE among four polymer samples can be evaluated by introducing a parameter, η_R, given by

$$\eta_R = (R_\lambda - R_{290})/R_{290}$$

where R_λ and R_{290} are the *R* values with the excitation at

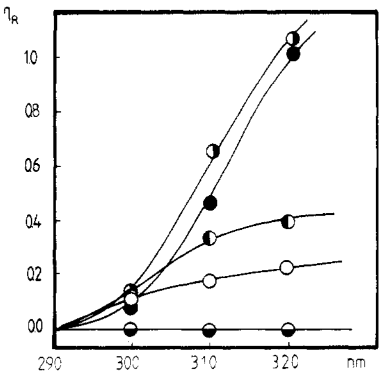


Figure 5. η_R (see text) as a function of excitation wavelength for poly(MMA-*co*-**12**) (○), poly(MMA-*co*-**8**) (◐), poly(MMA-*co*-**4**) (●), poly(MMA-*co*-**2**) (◑), and **1d** (⊖) in EAc.

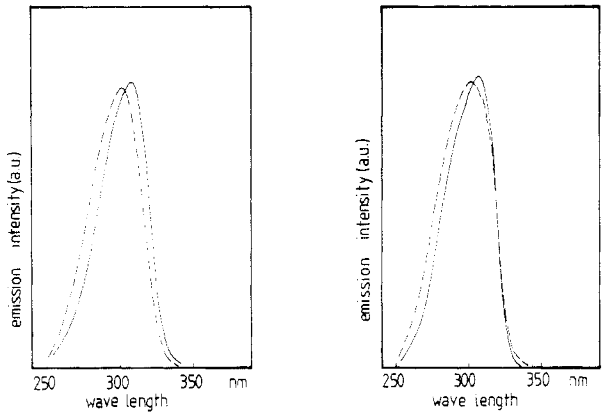


Figure 6. Fluorescence excitation spectra of poly(MMA-*co*-**2**) (left) and poly(MMA-*co*-**12**) (right) in EAc: (—) monitored at the a* emission maximum (430 nm); (- - -) monitored at the b* emission maximum (350 nm).

λ and 290 nm, respectively. Dependence of η_R on the wavelength of excitation is given in Figure 5. As we can see in Figure 1, the absorption spectrum becomes broader with decreasing spacer length between the polymer main chain and DMAB. This is the manifestation that restricted side-chain mobility leads to a broader distribution of the ground-state conformers. In a fluid system of low local viscosity when the rate of twisting is much faster than the overall decay rate of the excited state, excitation of different ground-state conformers brings about the a* state with same probability, whereas in a congested medium having a high friction coefficient, the TICT excited state is more readily formed by the excitation of twisted ground-state conformers absorbing at the red edge of absorption spectra. The sequence of excitation wavelength dependence of η_R is as follows, which agrees with the discussion mentioned above: poly(MMA-*co*-**2**) > poly(MMA-*co*-**4**) > poly(MMA-*co*-**8**) > poly(MMA-*co*-**12**).

The same line of discussion can be applied to the interpretation of excitation spectra, which depend on the monitoring wavelength. As shown in Figure 6, the excitation spectra of both poly(MMA-*co*-**12**) and poly(MMA-*co*-**2**) exhibit monitoring wavelength dependence. When the a* band is monitored, the excitation spectrum is red-shifted. The shift is larger for poly(MMA-*co*-**2**) than for poly(MMA-*co*-**12**). In particular, the excitation spectrum of poly(MMA-*co*-**2**) when the a* band is monitored is discretely different from that monitoring the b* band, indicating that the TICT state is formed exclusively by the excitation of a somewhat twisted ground state. Excitation spectra of the rest of the polymers fall in between the two.

The discussion on the relation between the angular distribution in the ground state and the TICT state formation has been presented by Rettig in small molecular systems.[17] He suggested that an increase in the twist angle between the DMA group and the aromatic ring facilitated the TICT formation on the basis of a MIM (molecules in molecules) calculation. The present results are in support of the concept of REE, indicating that the local viscosity in the vicinity of the polymer main chain is very high and comparable to that of glassy matrices.

Conclusion

Observation of REE together with broadening of absorption spectra convinces us of the polymer main chain effects on angular distribution of the ground-state conformation of the side chain. In other words, this represents the thermodynamic control of conformational equilibrium of a side chain by the bonded polymer main chain. There should also be the case of kinetic control of side-chain motion by the polymer main chain as revealed by the decreasing sequence of *R* values with decreasing spacer length in the polymer. Direct determination of the rate of twisting is now under way by means of a fluorescence lifetime measurement determining the rise profile of the a* band in the picosecond time region.

The present results suggest the importance of free volume distribution in the polymer depending upon the site of probing. Accumulation of experimental data on the correlation of local segment mobility with polymer structure will provide valuable information for the design of reactive polymers.

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Registry No. **1a**, 77016-80-9; **1b**, 58817-05-3; **1c**, 57754-81-1; **1d**, 10287-53-3; **2**, 112925-57-2; **3**, 112925-58-3; (**3**)(MMA) (copolymer), 112925-63-0; **4**, 112925-59-4; (**4**)(MMA) (copolymer), 112925-62-9; **5**, 112925-60-7; (**5**)(MMA) (copolymer), 112925-61-8; **6**, 79984-80-8; (**6**)(MMA) (copolymer), 105058-53-5.

References and Notes

(1) Visiting scientist from Institute of Photographic Chemistry, Academia Sinica, Beijing.
(2) *Photophysical and Photochemical Tools in Polymer Science*: NATO ASI series; Winnik, M. A, Ed., Reidel: Dordorecht; 1986, p C182.
(3) Tazuke, S.; Winnik, M. A., ref 2, pp 15–42.
(4) Richert, R. *Chem. Phys. Lett.* **1985**, *118*, 534. Richert, R.; Baessler *Chem. Phys. Lett.* **1985**, *118*, 235. Horie, K.; *Funct. Mater.* (*Tokyo*) **1986**, *6*, 41.
(5) Tazuke, S.; Tanabe, T. *Macromolecules* **1979**, *12*, 853.
(6) Hayashi, R.; Tazuke, S.; Frank, C. W. *Chem. Phys. Lett.* **1987**, *135*, 123.
(7) Hayashi, R.; Tazuke, S.; Frank, C. W. *Macromolecules* **1987**, *20*, 983.
(8) For recent review, see: Rettig, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971. Lippert, E.; Rettig, W.; Bonačić-Koutecký, V.; Heisel, F.; Miehé, J. A. *Adv. Chem. Phys.* **1987**, *67*, 1.
(9) Rotkiewicz, K.; Grellmann, K.; Grabowski, Z. R. *Chem. Phys. Lett.* **1973**, *19*, 315. Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A.; Cowley, D. J.; Baumann, W. *Nouv. J. Chim.* **1979**, *3*, 443.
(10) Loutfy, R. O., ref 1, p 429.
(11) Oster, G.; Nishijima, Y. *J. Am. Chem. Soc.* **1957**, *78*, 589.
(12) Tazuke, S.; Iwasaki, R.; Ikeda, T. *Japan-US Polym. Symp.* Kyoto, 1985, Preprints 199.
(13) The kinetics of TICT state formation is comparable to that of excimer or exciplex formation. The Arrhenius plot of the *R* value is bell-shaped, indicating that the a* and b* states are equilibrated at high temperature. The *R* value decreases with temperatures in this region (high-temperature region) while the formation of the a* from the b* is irreversible at low temperature and the *R* value increases monotonously in this region (low-temperature region). At room temperature, polymers are in the low-temperature region whereas monomer models are

already in the high-temperature region. Consequently, for comparison of the rates of $b^* \rightarrow a^*$ in polymers and monomer models, R value should be compared at a much lower temperature where both polymers and monomer models are in the low-temperature region. From the discussion above, the differences in R values between polymers and monomer models should be larger at low temperature. Details of temperature dependence will be published elsewhere.

(14) While the decay of the b^* band is multiexponential and the exact kinetic solution is difficult to obtain, the decay of the a^* band is nearly constant at ~5 ns for both **1d** and poly(MMA-*co*-**2**) in EAc at 25 °C. Preliminary study on the temperature dependence of R value reveals that back-reaction from the b^* state is negligible in these polymers at room temperature.

(15) Al-Hassan, K. A.; El-Bayoumi, M. A. *Chem. Phys. Lett.* **1980**, *76*, 121.

(16) Rettig, W. *J. Lumin.* **1980**, *26*, 21. Rettig, W.; Marschner, F. *Nouv. J. Chim.* **1983**, *7*, 415.

(17) Rettig, W.; Rotkiewicz, K.; Rubaszewska, W. *Spectrochim. Acta, Part A* **1984**, *40A*, 241.

Adsorption of Block Copolymers in Selective Solvents

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ABSTRACT: We study the adsorption of A–B diblock copolymers on a solid plane in a highly selective solvent. The A part is in a poor solvent and forms a molten layer on the solid wall where the solvent does not penetrate. The B part, in a good solvent, forms a brush grafted on this molten layer. The structure of the adsorbed copolymer film is governed by the chemical potential in the solution in contact with the wall. Copolymer chains have a tendency to self-aggregate in this solution forming several different mesophases. We present first a scaling theory of micelle and lamella formation and then study the geometry of the adsorbed film in equilibrium with these two phases. An important issue of this work is the role of the van der Waals interaction between the wall and the adsorbed A layer. If the copolymer asymmetry is large enough, i.e., if the B part has a higher molecular mass than the A part, in a wide range of concentration, and this quite independent of the phase behavior of the solution, the thickness of the molten A layer results from a balance between the van der Waals energy and the stretching energy of the brush. The B chains are almost fully extended in the brush. Various other adsorption regimes are found when the asymmetry of the copolymer is decreased.

I. Introduction

Block copolymers provide a simple and versatile method for steric stabilization of colloidal particles suspended in a solution.[1,2] The most direct scheme for colloid protection amounts to adsorbing a diblock chain from a solution in a selective solvent. Then the insoluble block A (which we sometimes call the "anchor") precipitates near the particles surface and adsorbs on it forming a dense film, whereas the soluble block B (called the "buoy") extends into the solution and forms an external layer ("brush"). For example,[3] for particles suspended in water, A may be an aliphatic chain, while B may be a water-soluble polymer such as POE or polyacrylamide. The relevant parameter for steric stabilization is then the density of chains in a "brush" σ or equivalently the area per copolymer junction Σ. For small Σ (i.e., $\Sigma < N_B^{6/5}a^2$ where N_B is the "buoy" polymerization index and a the monomer length) the chains in the brush are stretched and when two protected surfaces are brought together they repell each other. Such interactions have been studied by using Israelachvili force measurement apparatus for model block copolymers, polystyrene–polyvinylpyridine in cyclohexane, by Hadzioannou et al.[4] The aim of the present work is to estimate Σ, assuming that the protective layer is obtained by equilibrium adsorption from a solution of diblock copolymers in a selective solvent. In particular, we study the role of the molecular parameters of the chains, such as their composition or molecular weight, and of the solution concentration on the structure of the protective layer.

The structure of a protective layer in equilibrium with a reservoir containing copolymer chains is determined not only by the free energy of a chain in the layer but also by the external chemical potentials of the chains and the solvent. Hence adsorption processes are complicated by the tendency of copolymer chains to self-associate and form organized structures (micelles, lamellas, ...).[5,6] For a description of the adsorption we thus need a model for both the protective layer and the solution of copolymer chains.

We shall simplify the description by considering the case of a highly selective solvent, very poor for A and very good for B. Then the solvent does not penetrate the A layer precipitated against the solid surface, which is essentially a molten A film. We shall also neglect the concentration gradients in the copolymer layer. An important issue of this work is the role of long-range forces.[7] We will consider the simple case of van der Waals forces and neutral polymers, but the results could easily be extended to different kinds of long-range forces. In such a highly selective solvent, we have constructed a simple model of self-association of the copolymer solution. We consider two simple limiting cases, that of spherical micelles and that of lamellar structures; we limit our considerations to dilute solutions and situations close to the critical micelle concentration.

The paper is organized as follows: In the next section, we study the spreading of a copolymer droplet of finite volume on the wall; in section III, we derive the general properties of the adsorbed copolymer layer when the chemical potentials in the solution are known. These chemical potentials are calculated in section IV for micellar phases and lamellar phases and adsorption in equilibrium

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