High Terminal Segment Mobility in Poly(methyl methacrylate) As Studied by Fluorescence Probe Method

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ABSTRACT: Poly(methyl methacrylate) (PMMA) in which the terminal group was 4-(*N*,*N*-dimethylamino)benzoate (DMAB) was prepared. Fluorescence from the terminal group both in solutions and solid provided a sensitive measure of rotational segment mobility, reflecting the ease of the rotating dimethylamino group to form the twisted intramolecular charge-transfer (TICT) state. Thus, the ratio (R) of emission from the TICT state (a* band) to that from the untwisted locally excited state (b* band) was taken as an index. Comparison of the R value for the end-capped polymer with those for monomer model compound (ethyl 4-(*N*,*N*-dimethylamino)benzoate; EtDMAB) and PMMA bearing a trace amount of DMAB on the side chain revealed that the twisting motion at the polymer end group was more facile than that of the polymer side chain and comparable to that of EtDMAB. When the degree of polymerization is increased, the end-group motion is suppressed slightly in a good solvent (ethyl acetate) and strongly in a poor solvent (*n*-butyl chloride).

Introduction

Direct measurement of polymer segment mobility at specific sites is a point of current interest.[2-4] Such information is of primary importance when one aims at design and synthesis of specialty polymers where dynamic behaviors of polymer determine the functions. Polymers falling into this category are macromonomer,[5] cross-linkable polymers,[6] material-transporting membranes with fixed carriers,[7] polymer-bonded reagents such as immobilized biocatalysts,[8] and so forth. The understanding of segment motion as a function of polymer main chain, as well as side-chain structure, molecular weight, temperature, and solvent, will benefit the development of specialty polymers. Fluorescence probe method will be best suited for this investigation, owing to its high sensitivity, site selectivity, and versatility of the information including dynamic measurement.

Recently we have shown that the present twisted intramolecular charge-transfer (TICT) chromophore is a handy and sensitive fluorescence probe to monitor the segment mobility and steric constraint at a specific site in a polymer in a relativistic scale and that the mobility of polymer side group is dependent on the polymer main chain as well as the neighboring side chains.[9] Furthermore, the effects of polymer main chain on side-chain mobility are a function of the length of the particular side chain bearing the TICT probe.[9b] For the side chain of a fixed length, the main-chain conformation (i.e., the end-to-end distance) in solution and the length of neighboring side chains have to be taken into account.[9c] Demonstration of fluorescence behaviors subjected to minute changes in molecular environment encourages us to use this probe for more detailed study. Recently, Sung et al. have shown the greater chain-end mobility in comparison with the side chain for a growing epoxy–diamine network by site-specific labeling with azobenzene chromophore.[10] They suggested that the free volume for a dangling chain is similar to that for the free-probe molecule. It is consequently timely to extend our recent study to estimate the relative segment mobility at a polymer terminal group.

Experimental Section

Preparations of Materials. (Methylthio)ethyl 4-(dimethylamino)benzoate (I) was prepared by the reaction of 4-(dimethylamino)benzoyl chloride with (methylthio)ethanol in the presence of pyridine. The product was purified by column chromatography (eluent: benzene) and recrystallization from *n*-hexane. ^{1}H NMR ($CDCl_3$): δ 2.3 (s, 3 H, CH_3S), 2.74 (t, 2 H, SCH_2–), 2.95 (s, 6 H, $(CH_3)_2N$), 4.30 (t, 2 H, OCH_2–), 6.6–8.05 (dd, 4 H, Ar). Anal. Calcd: C, 60.25; H, 7.11; N, 5.86; S, 13.39. Found: C, 60.35; H, 7.30; N, 5.91; S, 13.38.

Poly(methyl methacrylate) (PMMA) bearing a 4-(dimethylamino)benzoate (DMAB) group on the polymer chain end was prepared by radical polymerization in the presence of mercaptoethanol. A total of 30 g of MMA added with 16 mg of azobis(isobutyronitrile) and 40 mg of mercaptoethanol as a chain-transfer agent was polymerized under nitrogen atmosphere at 60 °C for 10 h after repeated freeze–pump–thaw cycles. The polymer was precipitated from benzene into methanol three times; yield 33%. Then polymer was fractionated by a Toyo Soda HLC-802 using a TSK-gel (HG type) fractionation column (eluent: chloroform).

Each fraction of polymer with a terminal hydroxyl group was esterified with an excess amount of 4-(dimethylamino)benzoyl chloride in benzene for 12 h. Unreacted acyl chloride was removed by repeated reprecipitation. The content of bonded DMAB chromophore was determined spectroscopically. The molar extinction coefficient of the end group was assumed to be the same as that of ethyl 4-(dimethylamino)benzoate (EtDMAB) ($\epsilon = 3.3 \times 10^4$ L/mol·cm at 306 nm in ethyl acetate (EtAc)). The content of the terminal hydroxyl group was determined from the sulfur content of the polymer. The molecular weight of the polymer was determined by GPC using monodispersed polystyrenes as the standard. The glass transition temperature (T_g) was measured by a differential scanning calorimeter (DSC) (Seiko I&E DSC-5000 calorimeter, operating at a heating rate of 10 °C/min). The T_g of the polymer having the highest molecular weight is very similar to the value for PMMA, but the T_g's of two others are lower, probably owing to the decreased molecular weight and a relative increase in the role of end groups which may act as a plasticizer in this molecular weight region. The abbreviations and characterization of the polymers are summarized in Table I.

The chemical structures of the samples are given in Scheme I.

Polymer films were prepared by casting from EtAc solution on a quartz plate.

Spectroscopy. Absorption and fluorescence spectra were measured by a UV-320 spectrometer (Hitachi) and a F-4000 spectrofluorometer (Hitachi). Emission spectra were corrected by means of a homemade program on a PC 9801 computer. The sample solution for fluorescence spectroscopy was purged by bubbling argon gas for 20 min in an ice bath. Temperature-

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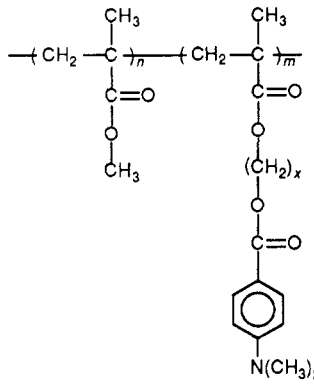
Table I
Properties of the End-Capped Polymers

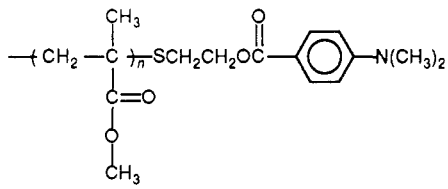
polymer	M_n,[a] × 10^4	M_w,[a] × 10^4	M_w/M_n	chromophore content [DMAB]/[MMA][b]	OH content [OH]/[MMA][c]	T_g, °C
PMMA	40.0					122.2
PMMA-S-DMAB1	4.8	7.8	1.62	0.8×10^{-3}	2.9×10^{-2}	119.3
PMMA-S-DMAB2	2.3	3.7	1.63	2.1×10^{-3}	3.2×10^{-2}	79.5
PMMA-S-DMAB3	1.3	1.8	1.38	4.0×10^{-3}	3.2×10^{-2}	68.3

[a] M_n and M_w were determined by GPC. [b] Content of DMAB was obtained by UV spectroscopy. [c] Content of OH was determined by elemental analysis monitoring the content of the S atom.

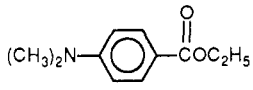
Scheme I



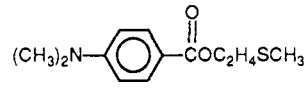
x = 2 poly (MMA-*co*-2), 12 poly (MMA-*co*-12).



M_w = 7.8 x 10^4 PMMA-S-DMAB1, 3.7 x 10^4 PMMA-S-DMAB2, 1.8 x 10^4 PMMA-S-DMAB3.



EtDMAB



MeSDMAB

controlled experiments were carried out in a cryostat (DN 1704, Oxford). The purification of solvents was reported previously.[9b,c]

Results and Discussion

Sample Preparation. Use of mercaptoethanol as a chain-transfer agent is a convenient way to introduce hydroxyl terminal groups. Since stoichiometric end capping by the DMAB group is not necessary, the present method is superior to the polymerization with a radical initiator bearing DMAB group. Although we tried photoinduced polymerization of MMA with photolysis of 1,6-bis[4-dimethylamino)benzoyl]-3,4-dimercaptohexane-1,6-diyl, some photodecomposition of the chromophore as well as probable radical attack on the chromophore caused contamination of the end-capped PMMA.

It is preferable to fractionate PMMA with a hydroxyl terminal group before labeling with DMAB. The long-term stability of a DMAB group in contact with chloroform as the eluent for GPC is doubtful.

An absorption spectrum of the end-capped polymer agrees very well with that of the monomer model compound EtDMAB except for a slight red shift in the polymer. A small red shift seems to be a common phenomenon when the chromophore is bonded to polymethacrylates as discussed previously for polymethacrylate with DMAB side groups.[9]

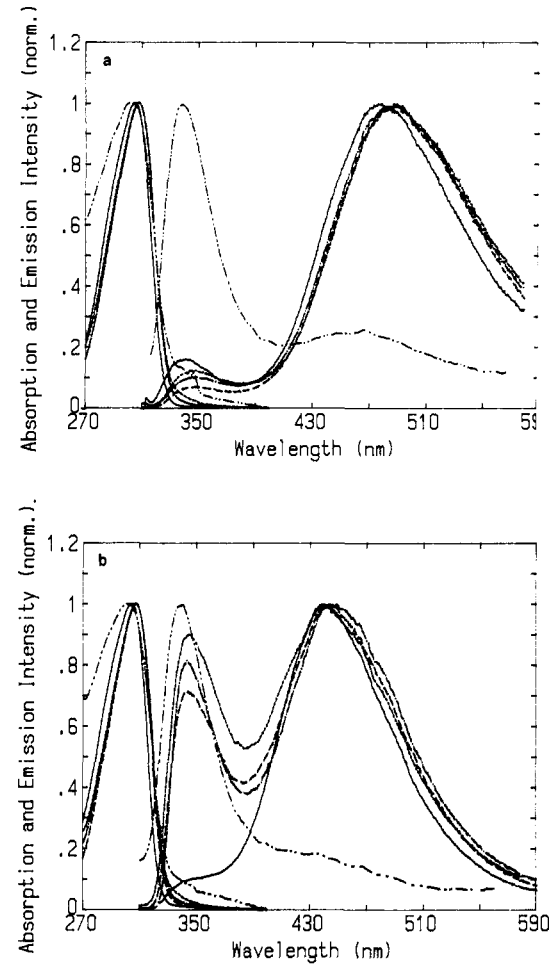


Figure 1. Absorption and fluorescence spectra of PMMA-S-DMAB1 (- - -) (0.2 wt %), PMMA-S-DMAB2 (– · –) (0.2 wt %), PMMA-S-DMAB3 (– –) (0.2 wt %), poly(MMA-*co*-2) (- · · ·) (1 wt %), and EtDMAB (—) (2×10^{-5} M) in EtAc at 234 K (a) and in BuCl at 200 K (b). Excitation at 300 nm.

Surprisingly Strong TICT Fluorescence from the Terminal DMAB Group. Fluorescence and absorption spectra of four polymers and the monomer model compound EtDMAB are shown in Figure 1.

The difference in fluorescence between poly[(methyl methacrylate)-*co*-[2-[[4-(dimethylamino)benzoyl]oxy]-ethyl methacrylate]] [poly(MMA-*co*-2)] and the present end-capped polymers is obvious. For the end-capped polymer, the emission is mostly from the TICT state (a* band, at 450 nm) similar to the case of the monomer model, whereas the emission from the locally excited state (b* band, at 350 nm) predominates in poly(MMA-*co*-2). On the widely accepted assumption that the a* band appears as a result of charge-transfer state formation by twisting the dimethylamino group from the π-conjugated planar structure to the position where the plane of the dimeth-

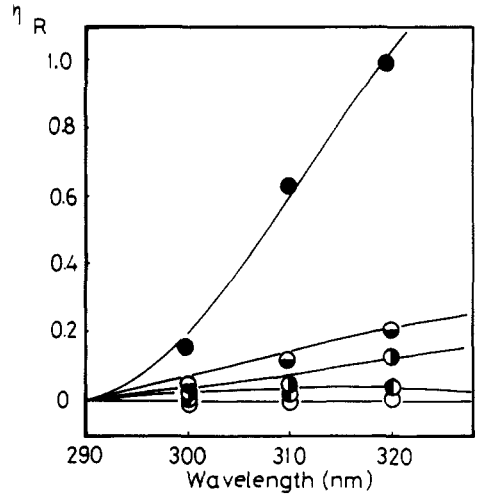


Figure 2. η_R as a function of excitation wavelength for poly(MMA-*co*-2) (●), PMMA-S-DMAB1 (◒), PMMA-S-DMAB2 (◑), PMMA-S-DMAB3 (◐), and EtDMAB (○) in EtAc, at 293 K.

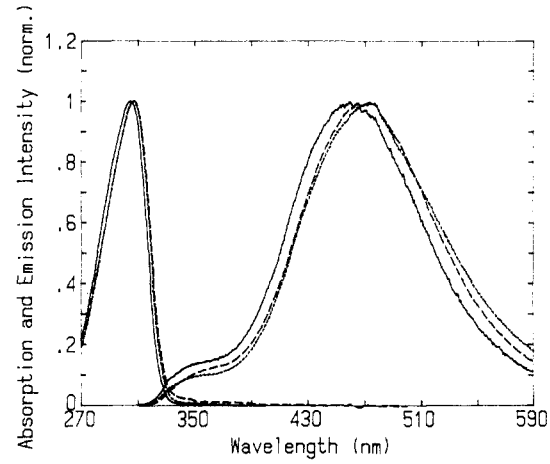


Figure 3. Absorption and fluorescence spectra of PMMA-S-DMAB3 (– –) (0.2 wt %), EtDMAB (—) (2×10^{-5} M), and MeSEt-DMAB (· · ·) (1×10^{-5} M) in EtAc at 295 K. Excitation at 300 nm.

ylamino group is perpendicular to benzoate group, the magnitude of the a* band/b* band intensity ratio (R value) is a measure expressing the ease of bond rotation. However, the role of solvent assisting the rotation is still controversial.[11,12]

As the following discussion shows, there is no doubt that the motion of a terminal group is much freer than that of a side chain.

The kinetics of TICT state formation is generally treated under two extreme conditions. One is to assume no back-reaction from the a* state to the b* state in the low-temperature region; another is for the condition when the a* and b* states are in equilibrium at higher temperature. The Arrhenius plots are therefore similar to those of excimer and exciplex formation within the frame work of Birks' kinetics[13] and are bell-shaped. Although the temperature corresponding to the maximum R value is different from system to system, the present fluorescence measurements conducted at 234 K in EtAc and at 200 K in BuCl are both in the low-temperature region.[14] Consequently, the backward reaction b* ← a* is negligible, and the R value can be considered as a direct measure of the rate of TICT state formation.

In the previous papers,[9] we have noticed that not only the rotational motion leading to the TICT state formation but also the ground-state distribution of twisted angle is controlled by polymer microenvironment. When the rate of conformation change is slow relative to the a* excited-state lifetime, the R value is also dependent on the twisting angle of the ground-state conformers and hence the excitation wavelength. Excitation at the longer wavelength which excites conformers already twisted to some extent in the ground state brings about a higher R value. This REE (red edge effect) expressed by a parameter η_R ($\eta_R = (R_\lambda - R_{290nm})/R_{290nm}$) has been used to evaluate the influence of polymer chains as well. The results shown in Figure 2 indicate that the η_R is rather small for the end-capped polymers and the distribution of the terminal DMAB conformer is unimportant. The state of the terminal DMAB group is more similar to that of the monomer model in solution than that of the side-chain DMAB group.

Effect of the Sulfur Atom of the Alkylthio Group. For strict comparison of the end-capped polymer with the side-chain polymer, a small difference in the probe structure should be discussed. For preparative convenience a sulfur atom was introduced in the end-capped polymer. Effects of the sulfur atom in the ester alkyl group are observed as a small red shift of both absorption and emission spectra as shown in Figure 3 by comparing MeSEtDMAB with EtDMAB. Since through-bond interaction of the sulfur atom with the carbonyl or the phenyl group is unlikely, the most probable effect is the interaction of sulfur with the ester carbonyl, forming a five-membered ring. This interaction is further supported by FT-IR spectra of DMAB. The C=O stretching vibration of the (methylthio)ethyl ester appears at 1689.4 cm^{-1} whereas that of ethyl ester and dodecyl ester appears at 1699.0 or 1696.1 cm^{-1}, respectively. An enhanced electron density of the carbonyl group owing to the presence of an electronegative methylthio group in the vicinity will be the origin of the red shift.[15] Other absorption peaks are not affected much by the change in ester alkyl groups.

Small differences in both absorption and emission spectra in Figure 1 for the end-capped polymer compared with EtDMAB will be attributed to this sulfur effect. However, the R value is not influenced in the presence of sulfur as shown in Figure 2, and therefore the preceding discussion on the polymer effect is not affected.

Effect of Molecular Weight. Figure 4 shows that the R value decreases as a function of weight-averaged molecular weight for the end-capped PMMAs. When the degree of polymerization (DP) is increased, the R value decreases gradually in a good solvent (EtAc) and sharply in a poor solvent (BuCl). These results are in contrast to the previous results of poly(MMA-*co*-2) for which no molecular weight effect was found when the molecular weight ranges from 1.1×10^4 to 2.0×10^5.[9b] In poly(MMA-*co*-2), the chromophore is located rather close to the main chain and its mobility seems to be controlled by its relatively close neighbors. Consequently, the molecular weight effect will saturate at a much lower molecular weight region. The terminal TICT chromophore stretches out of the polymer chain and in principle is independent of the rest of the polymer chain. However, if the polymer chain becomes long enough for another chain end to come around to the terminal chromophore, the polymer chain effect will become operative. It is very reasonable that the polymer effect appears at a much smaller molecular weight region in BuCl in which the end-to-end distance is shorter than that in EtAc.

Mobility of the Terminal Group in the Solid State. We have found a good correlation between the

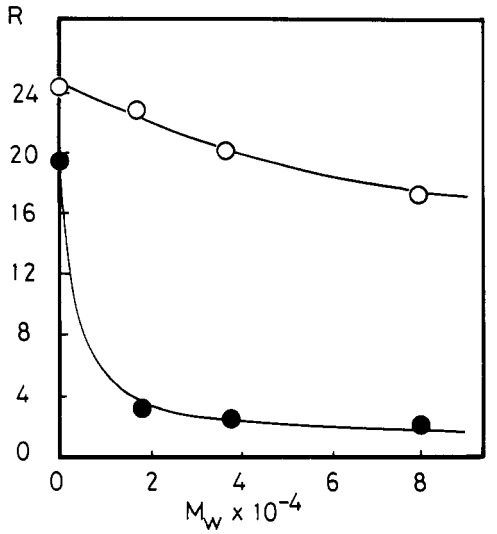


Figure 4. Emission intensity ratio, R, of the end-capped polymers as a function of weight-averaged molecular weight (M_w) in BuCl (●) and in EtAc (○). Excitation at 300 nm and data from Figure 1.

fluorescence behaviors in dilute solutions and in solid state when the TICT chromophore is bonded to the side chain of various methacrylate polymers. Although the intensity of the a* band is considerably limited in solid polymer, the sequence of the R value depending on polymer structure is identical in solution and in solid.[9d] A similar relation has been found for the end-capped polymers. The emission spectra of four polymers in solid are given in Figure 5. Corresponding to the surprisingly high segment mobility in solutions, the end-capped polymer exhibits stronger TICT fluorescence than poly(MMA-*co*-2) and poly[(methyl methacrylate)-*co*-[12-[[4-(dimethylamino)benzoyl]oxy]dodecyl methacrylate]] [poly(MMA-*co*-12)] in solid state. Among the side-chain TICT polymers, poly(MMA-*co*-12) was shown to provide the highest molecular mobility to the TICT chromophore. The DMAB chromophore in poly(MMA-*co*-12) is even more mobile than a free monomer model compound doped in polyMMA.[9d] The present results indicate that the terminal part of a polymer chain creates a large free volume.

In the solid state, the TICT fluorescence is not clearly separated from the b* emission and may not indicate the formation of a genuine TICT state. Nevertheless, reasonable correlation of the R value with polymer structure is a manifestation that the spectral change is related to a certain molecular motion in polymer solid.

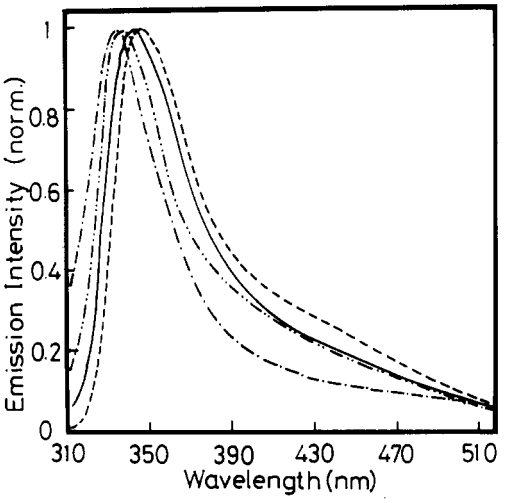


Figure 5. Fluorescence spectra of poly(MMA-*co*-2) (- · -), poly(MMA-*co*-12) (- · · -), PMMA-S-DMAB1 (—), PMMA-S-DMAB2 (- - -), in solid state. Excitation at 300 nm.

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