polymers, T_g could no longer be regarded as a useful index for elucidating experimental results.

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Functionality and Structure of Polymers. 4. Photochemical and Photophysical Behavior of Polymers Having a Dianthracene Main Chain with Special Reference to Terminal Segment Mobility in the Solid State

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ABSTRACT: Polyesters (PADE-12, PATE-8, and PATE-12) and polyester urethanes (PAEU-6 and PAEU-10) having dianthracene units in their main chain (presented in Table I) were spectroscopically studied in the solid state. By photoirradiation at 300 nm at −196 °C, a small fraction (<5%) of dianthracene units was photolyzed to anthroate groups. The terminal anthroate groups were produced in a form of sandwich dimer, which gradually dissociated to the monomeric state upon warming. The mobility of the terminal segments depended on the polymer structure. In PAEU polymers in which hydrogen bonding was confirmed, the sandwich dimer structure was well retained at room temperature, whereas the polyesters could not hold the paired structure. From fluorescence spectroscopy, the sandwich dimer was shown to emit broad structureless fluorescence peaking around 500 nm. Also, the fluorescence spectra of isolated terminal anthroate groups indicated that the rotational freedom of the fluorophores in PAEU polymers was less than that in PATE or PADE polymers. Such minute mobility of terminal groups was not determined by glass-transition temperature alone. Another controlling factor was concluded to be hydrogen bonding. The restricted mobility of terminal groups reflected on the remaking of dianthracene units by irradiating at the ^1L_a band of the anthroate group. The reaction profile was distinctively different for PAEU polymers and for PADE-12, PATE polymers revealing intermediate behaviors. The remaking of dianthracene in PAEU polymers was efficient at low temperature and quickly leveled off at an early stage of photoirradiation. This was due to efficient photoreaction of sandwich dimers and other aggregated states of anthroate groups. However, the paired terminal anthroate groups were once annealed, and then remaking of dianthracene did not proceed in PAEU polymers so that the efficiency decreased at elevated temperatures. In PADE-12, although the fraction of the reactive sandwich dimer was small, the unpaired anthroate groups could react to form dianthracene units via the migration process. Consequently, the remaking process proceeded slowly and steadily and was accelerated at elevated temperatures. These effects of main-chain structure were comparable to the previously reported results on photodimerization of anthryl groups attached to polyesters and polyester urethanes as side groups. Dianthracene derivatives were proved to be versatile spectroscopic as well as reactive probes to envisage the minute segment mobilities in polymer matrices.

The synthesis and thermal properties of various polymers consisting of rigid and bulky dianthracene units and variable spacing segments were discussed in the previous article.[1] In spite of the fact that the polymer main chains are constructed mostly of soft aliphatic esters, the glass-transition temperatures (T_g) are considerably higher than the values reported for ordinary aliphatic polyesters.[2] The rigid dianthracene units are apparently responsible for the high T_g, while the soft spacing chains would control local segment mobility. Since dianthracene units are easily photolyzed to anthracene by irradiating at the wavelength below 300 nm, the state of terminal anthryl groups will be readily followed spectroscopically.

Photophysical information on anthracene derivatives in aggregated states has been provided by spectroscopic studies in glass-matrix solvents.[3,4] Consequently, spectroscopic investigation on photolyzed dianthracene polymers would inform us of the pairing of anthroate terminal groups produced from dianthracene units in the polymer matrix. The stability of the paired terminal

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Table I
Structures of Dianthracene Polymers[1]

abbreviation	structure[a]	T_g, °C
PADE-12	[-A A-COO(CH$_2$)$_{12}$OCO-]$_n$	(135)
PATE-8	[-A A-COO(CH$_2$)$_4$OCO(CH$_2$)$_8$COO(CH$_2$)$_4$OCO-]$_n$	86
PATE-12	[-A A-COO(CH$_2$)$_4$OCO(CH$_2$)$_{12}$COO(CH$_2$)$_4$OCO-]$_n$	72
PAEU-6	[-A A-COO(CH$_2$)$_4$OCONH(CH$_2$)$_6$NHCOO(CH$_2$)$_4$OCO-]$_n$	106
PAEU-10	[-A A-COO(CH$_2$)$_4$OCONH(CH$_2$)$_{10}$NHCOO(CH$_2$)$_4$OCO-]$_n$	108

[a] -A A-, dianthracene-9,10′-diyl.

groups (i.e., sandwich dimer and other aggregated structures of anthracene) must be a function of segment mobility and therefore of the structure of spacing segments. In addition, photoirradiation at the ^1L_a band of the terminal anthroate groups will induce the reverse process, giving dianthracene units again, if the terminal anthroate groups retain enough mobility to meet the reaction partner within the lifetime of the singlet excited state or the aggregated structures as precursors of dianthracene are preserved under the condition of remaking dianthracene units. Since the information on the behaviors of terminal groups is available both from photophysical and photochemical measurements, it is expected to provide an inside look into the role of the main-chain structure on segment mobility.

In the following sections, the dependence of segment mobility on main-chain structure well below T_g will be demonstrated. Although T_g is an approximate measure for rigidity of polymers determined by stiffness and bulkiness of segments and molecular interactions, any events relevant to minute segment mobility could not be estimated from T_g alone. We have already shown that bimolecular reactivities of polymer side groups to the solid state are sharply influenced by the polymer structure.[5] The bimolecular reactivities certainly increase above T_g. However, the change in the reactivities below and above T_g is again characteristic of polymer structure.

To determine the structural effects on terminal segment mobilities, a series of well-designed dianthracene polymers are needed. We chose therefore three polyesters and two polyester urethanes, each of which contains dianthracene units with designed intervals. Furthermore, the polyester urethanes are the isostructural family of relevant polyesters having the identical number of atoms connecting dianthracene units. The outline of investigation is shown in Scheme I.

Experimental Section

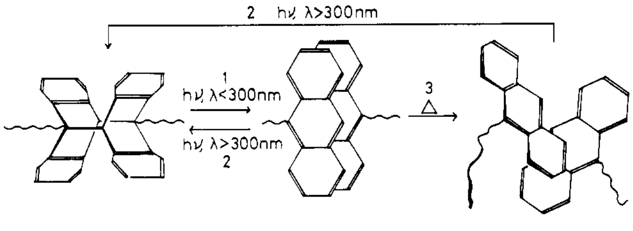
Materials. The five polymer samples (PADE-12, PATE-8, PATE-12, PAEU-6, and PAEU-10) were those already reported.[1]

Spectroscopy. The polymer sample was used as a thin film cast from chloroform solution on a quartz plate (1 × 4 cm) and placed in a Dewar flask equipped with parallel quartz windows. The temperature of the sample was controlled by a stream of thermostated nitrogen gas or kept at the liquid-nitrogen temperature. Both absorption and emission spectroscopy were carried out by installing this devise in the sample compartment of the spectrometer. A Shimadzu UV-200S spectrometer and a Hitachi MPF-4 spectrofluorometer were used for absorption and emission spectroscopy, respectively.

Photoreaction. The same thermostated Dewar flask was used for photoreaction. The light source was a JASCO CRM-FA spectroirradiator. Photolysis of dianthracene units and remaking of dianthracene were followed spectroscopically. Photoirradiation was operated in a nitrogen atmosphere to avoid oxidation of anthroate groups.

For the sample preparation for photoremaking of dianthracene units, polymer samples were first annealed at 80 °C for 2 h and cooled gradually overnight. The samples were then irradiated at 300 nm at 20 °C. The degree of photolysis was kept constant for each polymer. After photolysis, the absorbance at 365 nm (^1L_a band of the anthroate group) was 0.5 for PATE-12, PAEU-6, and PAEU-10, 0.4 for PADE-12, and 0.3 for PATE-8, which correspond to less than 5% decomposition of dianthracene units. The latter two polymers could not be photolyzed further within a reasonable time of irradiation owing to the inner filtering effect by the initially existing anthroate groups. The same equipment as that used for photolysis experiments was used for the remaking experiments with the irradiation wavelength of 365 nm. The light intensity at 365 nm was 11.3 W/m^2.

Scheme I



1: photolysis of dianthracene main chain
2: remaking of dianthracene units
3: thermal destruction of sandwich dimer structure

Results and Discussions

Structures and Properties of Dianthracene Polymers. The abbreviations, structures, and glass-transition temperatures (T_g) determined by the TBA method are tabulated in Table I.[1] The film-forming properties are generally good. The PADE-12 film looses transparency and cracks when the film thickness increases.

Absorption Spectroscopy of Anthroate End Groups Produced by Photolysis at −196 °C. The polymer samples show weak absorption due to anthroate groups remained unreacted or formed during polymer synthesis and subsequent handling. When polymers were prepared by photocycloaddition polymerization (PADE-12, PATE-8, and PATE-12), a part of the anthroate groups inevitably remained unreacted. Although PAEU polymers prepared by polyaddition of dianthracene units should not contain anthroate groups, there seems to be slight thermal decomposition during polyaddition polymerization. These initially existing anthroate groups in PADE-12 and, to a lesser extent, in PATE-8 somewhat interfere with the photolysis experiments. The molecular weight of PADE-12 is supposedly lower than that for PATE polymers, as judged by viscosity measurements. The inner filtering effect by the unreacted anthroate groups in PADE-12 caused a decrease in photolysis rate, and a longer period of photolysis was required.

At first we investigated the state of anthroate groups when the polymer was photolyzed at liquid-nitrogen temperature where all molecular motions were frozen. After about 1 h of photolysis of 300 nm, less than 5% of the dianthracene units was converted to anthroate groups.

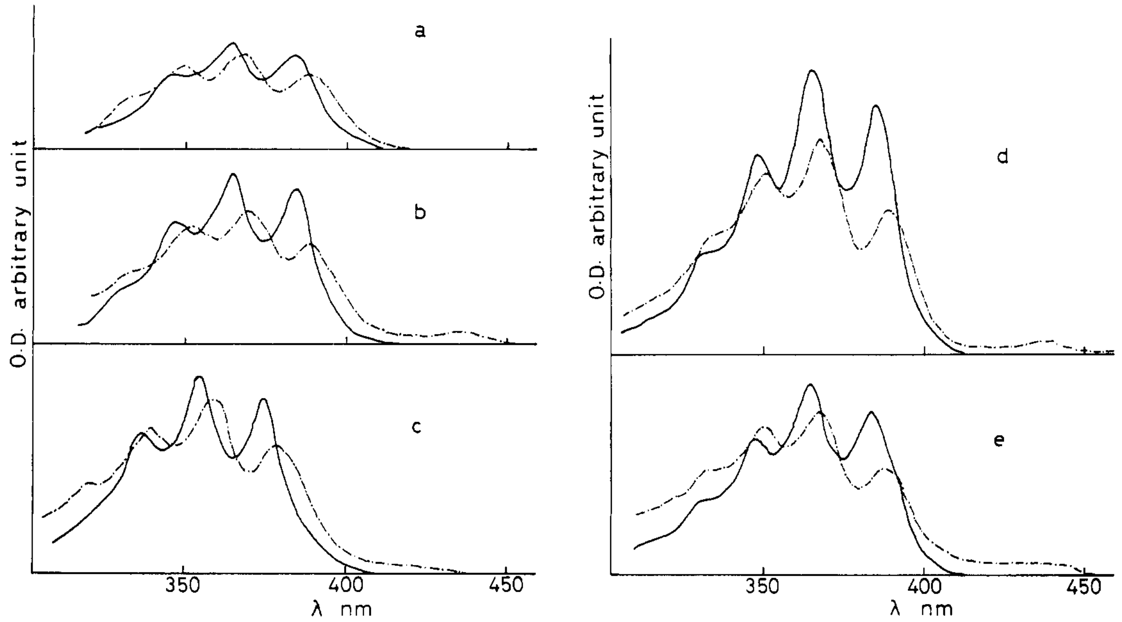


Figure 1. The S_0–S_1 absorption spectra of photolyzed dianthracene polymers. Photolysis at liquid nitrogen temperature and measurements at −189 °C (–··–) and at 60 °C (—): (a) PADE-12, (b) PATE-8, (c) PATE-12, (d) PAEU-6, and (e) PAEU-10.

Table II
Absorption Characteristics of Dianthracene Polymers After Photolysis

	absorption peaks (nm) after photolysis at −196 °C				
polymer	at −189 °C	after annealing at 60°C	$A(-189°)/A(60)$[a]	valley/peak at −189 °C[b]	valley/peak at 60 °C[c]
PADE-12	390, 368, 350	384, 365, 345	0.53	0.75	0.62
PATE-8	389, 370, 352	385, 365, 348	0.58	0.84	0.66
PATE-12	389, 369, 351	385, 365, 347	0.56	0.78	0.66
PAEU-6	389, 368, 351	385, 366, 349	0.50	0.73	0.66
PAEU-10	389, 368, 350	384, 365, 347	0.55	0.81	0.69
	absorption peaks (nm) after photolysis at −196 °C				
	sandwich dimer at − 196 °C	monomer	A_d/A_m[d]	valley/ peak of sandwich dimer	valley/ peak at room temp
anthracene[e]	383, 362, 344	380, 361, 344	0.4	0.3	0.28

[a] The ratio of peaking intensity at −189 °C to that at 60 °C. [b] Peak at 389 nm, valley at 381 nm. [c] Peak at 385 nm, valley at 375 nm. [d] Intensity ratio at 383 nm of sandwich dimer to that at 380 nm after decomposition of sandwich structure. [e] Data from ref 3.

Examples of absorption spectra depicted by broken lines in Figure 1a–e indicate that the terminal anthroate groups are in a paired state. Various aggregated states on anthracene derivatives such as sandwich dimer, stable dimer, and others have been proposed based on spectroscopic investigations.[3,4,6-13] Even if two anthryl groups are not chemically bound, the ground-state interactions bring about characteristic photoabsorption. The sandwich dimer corresponds to a paired anthracene in which two molecular planes are in a face-to-face stack. In the stable dimer, the parallel stacking is distorted, and the angle between two anthracene molecular planes is said to be 55°. When dianthracene is photolyzed in a rigid glass matrix, the sandwich dimer is formed initially and gradually converted to the stable dimer and other loose aggregate states by softening the glass matrix at higher temperatures.

The absorption spectra at −189 °C in Figure 1 agree with the reported spectrum of sandwich dimer, whereas the small absorbance of 440 nm would suggest the minor contribution of stable dimer structure. The spectrum shifts toward blue with warming, and an intensity enhancement was observed. The change in spectrum is completed after 30 min at 60 °C. These spectra are shown in Figure 1 by solid lines. The blue shift of the peaking wavelength and the enhanced intensity are characteristic of conversion from sandwich dimer to free anthroate groups.

In Table II, data of absorption spectra are summarized. The ratios of absorbance, $A(-189)/A(60)$, were obtained by comparing the absorbance at 384 nm (i.e., the peaking wavelength of free anthroate group) at −189 °C immediately after photolysis and at 60 °C after warming up. In comparison with Chandross's data obtained for unsubstituted anthracene,[3] a blue shift of ~10 nm is observed for each relevant peak attributable to the substitution at the 9 position. The values of $A(-189)/A(60)$ will correspond to that of A_d/A_m which is the intensity ratio of sandwich dimer to isolated anthracene at the peaking wavelength of the latter at 381 nm. Since the absorption spectra of anthroate groups attached to polymers are broader than those of the monomeric model compounds, as already reported[11] and also shown by the valley/peak ratios of the absorption spectra in Table II, the molar absorbance of polymer-bound anthryl groups (i.e., $A(60)$) is smaller, and consequently $A(-189)/A(60)$ is larger than A_d/A_m. If the integrated intensity ratios were compared, the values of $A(-189)/A(60)$ and A_d/A_m would have been closer.

The difference between the sandwich dimer at −189 °C and the free monomer state at 60 °C can also be seen from

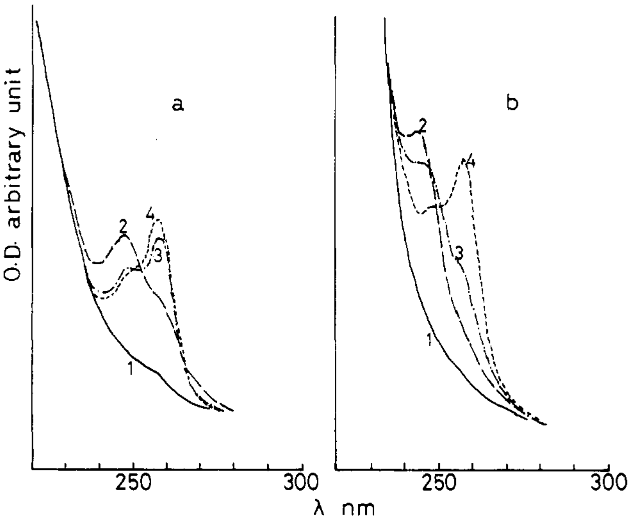


Figure 2. The S_0–S_2 absorption spectra of photolyzed PATE-12 (a) and PAEU-6 (b). Photolysis at liquid-nitrogen temperature. Before photolysis, 1; after photolysis, measurement at −189 °C (2), 0 °C (3), and 60 °C (4).

the $S_0 \rightarrow S_2$ absorption as depicted in Figure 2. The temperature-dependent spectra indicated that the sandwich dimer structure is retained at 0 °C in PAEU-6, whereas it disappeared considerably at the same temperature in PATE-12.

Knowing the absorbances of sandwich dimer and monomer, it is now possible to determine the fraction (x) of sandwich dimer during conversion from sandwich dimer to monomer. Let the number of anthroate groups produced by photolysis by N_0 and the absorption cross sections of monomer and sandwich dimer be σ_m and σ_d, respectively. The absorbance by anthroate groups exclusively in a form of sandwich dimer (A_d) or monomer (A_m) is given as follows.

$$A_m = N_0\sigma_m \tag{1}$$

$$A_d = \frac{N_0}{2}\sigma_d \tag{2}$$

When both components are mixed, the observed absorbance is given by

$$A_{obsd} = N_0(1 - x)_m + \frac{N_0}{2}\sigma_d x \tag{3}$$

Therefore,

$$x = \frac{(A_{obsd}/A_m) - 1}{(A_d/A_m) - 1} \tag{4}$$

In this derivation, the contribution of the stable dimer and other aggregated states was not considered.

The relaxation of the structured terminal groups is shown to be within a measurable time scale even below T_g, although the relaxation time of main-chain segment mobility is immeasurably long below T_g. When the decrease in the sandwich dimer fraction is followed at a constant temperature, the behaviors of anthroate terminal groups are shown to depend very much on polymer structure. Decomposition of sandwich structure is much faster in PADE or PATE polymers than in PAEU polymers. As shown in Figure 3, a part of the sandwich dimer disappears quickly, and then slow decomposition follows, indicating the presence of mobile and immobile sites in a polymer. Such inhomogeneity will be a characteristic of the polymer matrix in comparison with normal glass solvents consisting of small molecules. The sandwich dimers in PATE-12 disappear completely within 90 min.

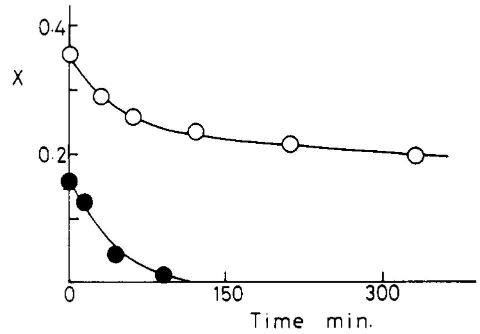


Figure 3. Disappearance of the sandwich dimer structure at 20 °C. The sample was photolyzed at 20 °C for 15 min and kept at the temperature: PAEU-6 (○) and PATE-12 (●).

These structure-dependent phenomena seem to be closely related to the behaviors of anthracene groups in photochemical remaking of dianthracene units, as will be discussed in the following sections.

Fluorescence Spectroscopy of Anthroate End Groups. The excited-state interactions of anthroate groups are much stronger than the ground-state interactions discussed above. Before photolysis, weak emissions due to anthroate end groups originally existing in the polymer samples are observed. The anthroate end groups produced by photolysis provide, however, entirely different fluorescence spectra extending over 500 nm at −196 °C as shown in Figure 4. This new species is likely to be a sandwich dimer[13] since the excitation spectra with the monitoring wavelength at 530 nm agree with the absorption spectra of the sandwich dimer. On the other hand, the excitation spectra either before or after photolysis coincide with the monomeric absorption spectra when the emission is monitored at 413 nm which is the peaking wavelength of monomeric emission from anthryl groups. Since the emission intensity at 413 nm is not much altered before and after photolysis, the newly produced anthroate groups by photolysis are mostly in the form of the sandwich dimer. This is the same conclusion as that derived from absorption spectroscopy.

The fraction of originally existing anthroate groups after photolysis was determined as 6% for PAEU-6 and PAEU-10, 12% for PATE-12, 30% for PATE-8, and 60% for PADE-12 by absorption spectroscopy. Although the sandwich dimer is the predominant species immediately after photolysis at −196 °C except for PADE-12, the fluorescence is very weak, and a clear peak of the sandwich dimer emission is not observed. This is due to the fact that the sandwich dimer structure is a precursor of remaking dianthracene units, and consequently the quantum efficiency of fluorescence is much smaller than that for free anthroate groups (i.e., originally existing ones). Even if photodimerization is sterically hindered, the sandwich dimer of 9,10-dichloroanthracene fluoresces with an efficiency of about 10% of the monomer,[4] indicating that radiationless deactivation is also facilitated in the sandwich dimer. The participation of cycloaddition would further decrease the fluorescence efficiency. In fact, [2,n]-(9,10)-anthracenophanes (n = 2 and 3) which are subject to reversible photoisomerization are nonfluorescent.[6] When n is 2, the fluorescence quantum efficiency has been estimated to be less than 0.001 while the photoisomerization quantum efficiency is 0.36.[11]

When the photolyzed sample is warmed up to room temperature (16–18 °C) for 30 min and fluorescence is measured again at −196 °C, the sandwich dimer emission

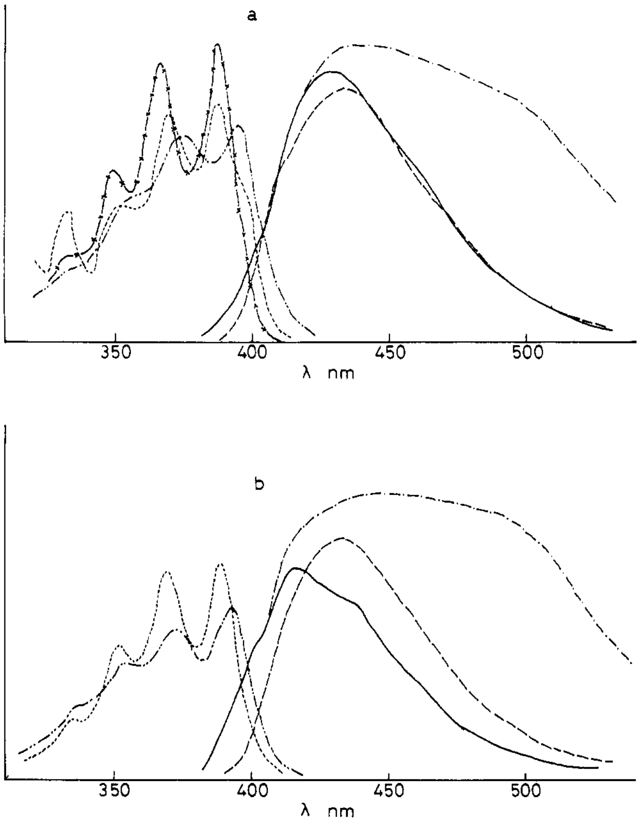


Figure 4. Fluorescence spectra of PATE-12 (a) and PAEU-6 (b) before and after photolysis. Emission spectra (excitation at 365 nm): both PATE-12 and PAEU-6 before photolysis (—), after photolysis at −196 °C (-··-), after warming up the photolyzed sample to 16 °C (---). Excitation spectra (emission monitored at 430 nm): PATE-12 both before and after photolysis at −196 °C (---), after warming up the photolyzed sample to 18 °C (-×-); PAEU-6, the shape of the excitation spectra was identical for all cases (···). Excitation spectra (emission monitored at 530 nm): PATE-12 before photolysis (---), after photolysis at −196 °C (-··-), after warming up the photolyzed sample to 18 °C (-×-); PAEU-6 after photolysis at −196 °C (-···-). If the photolyzed PAEU-6 was once warmed up to room temperature, the excitation spectrum (···) was independent of the monitoring wavelength.

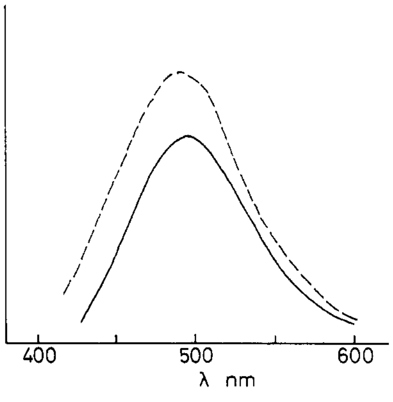
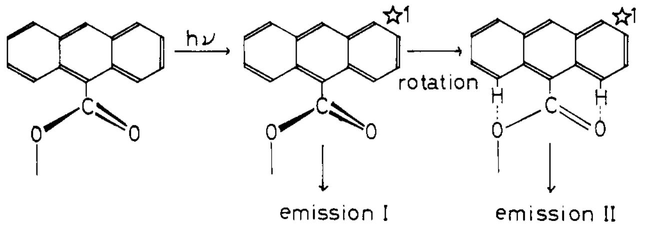


Figure 5. Emission spectra of the sandwich dimer pair. The monomeric emission was subtracted from the total emission measured immediately after photolysis at −196 °C: PATE-12 (—) and PAEU-6 (---).

is greatly diminished. The paired anthroate groups stable at liquid-nitrogen temperature are apparently destroyed at room temperature. The true shape of fluorescence spectrum of the sandwich dimer is depicted in Figure 5 by subtracting the monomeric fluorescence from the total fluorescence. When the monomeric emission overlaps the sandwich dimer emission considerably, as in the case of PADE-12 and PATE-8, this subtraction procedure is not applicable.

Scheme II



Comparison of fluorescence spectra from the originally existing anthroate groups in PAEU-6 and PATE-12 (Figures 4a and 4b, respectively) reveals that the environments of anthroate groups in these polymers are different. Fluorescence from PATE-12 is entirely structureless, whereas that from PAEU-6 retains the vibrational structure to some extent reflecting the structure of the absorption spectrum. This is an indication that the former is excimeric, whereas the latter is from the locally excited state. It has been reported that anthroic acid and its esters form intramolecular excimer depending upon the freedom of rotation.[14] When the rotation of the anthroate group is allowed, the molecular plane of the excited anthroate group is stabilized by the interaction between carboxylate oxygen atoms and hydrogen atoms at the 1,8 positions of anthracene, as shown below. Consequently, the emission shifts toward red and tends to be structureless (emission II, Scheme II). If such stabilization is not available, the emission from the locally excited state gives structured fluorescence (emission I). The emission from methyl anthroate in fluid solution is broad, and the Stokes shift is large, whereas the emission in rigid matrices is structured. The position and shape of emission is therefore reminiscent of the environment of the fluorophore. Applying these discussions to the present polymer systems, PAEU polymers provide a more rigid and restricted environment to anthroate groups than do PADE or PATE polymers. Incidentally, the shape of fluorescence from PAEU-10 is identical with that from PAEU-6, and that from PATE-8 or PADE-12 is identical with that from PATE-12. The restricted rotation of anthroate groups in PAEU polymers is explainable as the result of hydrogen bonding.

In comparison with those of glass-forming solvents, for example, EPA glass, the polyester matrices seem to be softer. PATE and PADE polymers show the emission peak due to originally existing anthroate groups at 430–433 nm at −196 °C, whereas methyl anthroate emits at 415 nm in EPA glass at the same temperature.[14]

From the microscopic viewpoint, the polymer matrix is not homogeneous at all. When photolyzed polymers are annealed above room temperature for 30 min and the fluorescence is determined at −196 °C, the peaking wavelength of monomer emission shifts toward blue, as shown in Figure 6. The higher the annealing temperature, the shorter the peaking wavelength. The anthroate end groups will migrate to more stable sites during annealing so that the mobility is reduced. A distinct difference is again found between PATE and PAEU polymers. The results in Figure 6 show that relaxation of PATE polymers is nearly completed at 60 °C, whereas the emission from photolyzed PAEU polymers after annealing at 60 °C is still red shifted by ~15 nm from that from the originally existing anthroate groups, indicating that annealing is not completed at this temperature. The annealing effect is also remarkable in the photoremaking of dianthracene to be discussed in the next section.

Table III
Summary of Electronic Spectroscopy of Photolyzed Polymers

(i) Spectral Characteristics

	aggregates (sandwich dimer)	monomeric
absorption peak	389 nm	385 nm
absorption intensity	weak	strong
emission peak	490 ± 10 nm (green)	430 ± 10 nm (blue)
emission intensity	weak	strong
excitation peak	394, 374 nm	389, 369 nm
effect of increasing temperature	decrease	increase
effect of annealing	decrease	increase

(ii) Environment of the Monomeric Terminal Anthroate Group

	environment	
	mobile	inmobile
position of emission spectra	low energy	high energy
shape of emission spectra	structureless	structured
favored temperature	high	low
matrix	PADE and PATE polymers	PAEU polymers, glass solvents

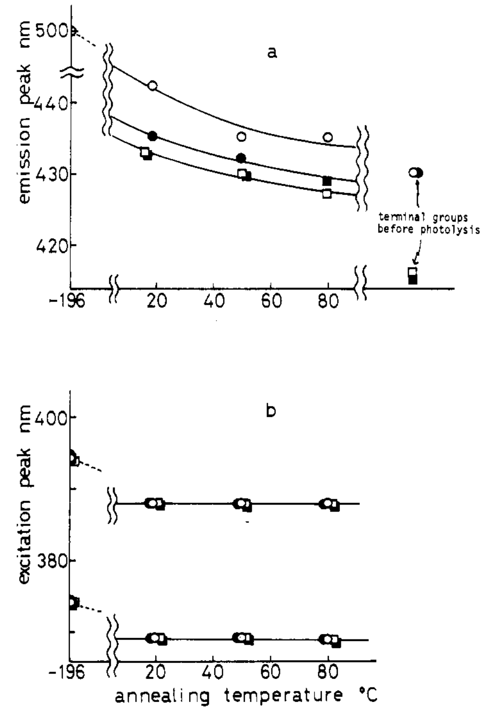


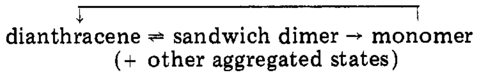
Figure 6. Temperature-dependent fluorescence maximum of terminal anthroate groups. After photolysis at −196 °C, the sample was annealed at a desired temperature for 30 min and then cooled quickly to −196 °C for fluorescence measurements: (a) emission maximum, excitation at 365 nm; (b) excitation maximum, monitoring emission at 530 nm; PATE-8 (○), PATE-12 (●), PAEU (□), PAEU-10 (■).

Characteristics of absorption and fluorescence spectra of anthroate groups are summarized in Table III.

Remaking of Dianthracene Units by Photocycloaddition of Polymer End Groups. General Comments. This is the reverse process of photolysis of dianthracene units. To make the remaking process possible, the reacting anthroate groups should be either mobile or in a pair. The sandwich dimer structure is said to be a precursor of dianthracene formation, which is supported by the absence of excimer emission from anthracene in solution.[15] Although excimer may lead to dianthracene, recent results have indicated[11] that excimer is not necessarily an intermediate for dianthracene formation. Since the biradical mechanism is claimed instead of the concerted one, parallel arrangement of two anthryl groups is seemingly not required. Instead, "edge-to-edge" arrangements of proximal anthryl groups are claimed as precursors of dianthracene. In addition to the sandwich dimer structure, other aggregated states would thus participate in the cycloaddition reaction.

Photodecomposition and remaking of dianthracene units incorporated in the polymer matrix have been described briefly for the copolycondensate of photodimerized 2-(2′,5′-dimethylpiperazinecarbonyl)anthracene, ethylene glycol bis(chloroformate), and dimethylpiperazine. The reaction profile of the polyurethane having no active hydrogens for hydrogen bonding resembles the behaviors of the present polyesters.[16]

Photolysis Experiments. The samples for remaking experiments were prepared by controlled photolysis of polymers. Dianthracene units are decomposed to anthroate groups with irradiation at 300 nm. Since the absorption spectra of the anthroate and the dianthracene unit overlap at the wavelength of irradiation, photolysis and remaking of the dianthracene compete, and the photoreaction reaches a photostationary state. The pairing state of produced anthroate groups affects the ultimate degree of photolysis. When anthroate groups cannot migrate and stay as a pair, the reverse process is fast, and the overall photolysis rate is slow. Although quantitative rate study of photolysis is difficult because of the difference in photoenergy absorption depending on the thickness of each polymer sample, the photolysis rate of polymers containing a small amount of casting solvent is faster than that of the completely dried sample by a factor of over 2. The casting solvent plays a role of plasticizer so that anthroate groups are mobile, and the sandwich dimer structure would be diminished to reduce the remaking rate. The same line of observation is obtained for the temperature effect on photolysis. The degree of photolysis at −196 °C where the sandwich dimer is the exclusive species is about one tenth of that at 20 °C. Since it is a photoreversible process, the difference in the degree of photolysis at −196 and 20 °C is not equivalent to the difference in the rate of photolysis. These qualitative observations are understood based on the following reaction scheme.



Annealing Effects on Remaking of Dianthracene Units. The initial absorbance of samples at 365 nm was kept constant at least for a polymer to ensure identical energy uptake by each sample. Nevertheless, the remaking rate depends considerably on the thermal history of the

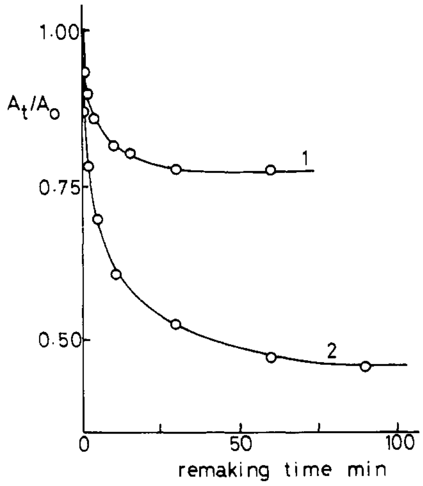


Figure 7. Effects of thermal history of PAEU-6 on remaking of dianthracene units. Irradiation wavelength: 365 nm at room temperature. (1) The sample was annealed at 80 °C for 2 h and quickly cooled then photolyzed at 20 °C until $A_0 = 0.5$. (2) The sample was annealed at 80 °C for 2 h and slowly cooled then photolyzed at 20 °C until $A_0 = 0.5$.

samples before photolysis. An example for the PAEU-6 polymer is presented in Figure 7. The degree of remaking is expressed by A_t/A_0 at 365 nm, where A_0 and A_t are the initial absorbance of anthroate groups and the absorbance after remaking reaction for t min. Curve 1 is for the sample which is heated at 80 °C for 2 h and then cooled quickly, and curve 2 is for the sample cooled gradually after the same heat treatment. The slower remaking rate of the former sample will be attributed to the strain remaining due to quick cooling. When a sample is not well annealed, the remaining strain will be relaxed during photolysis as motions of anthroate groups so that the anthroate groups will no longer stay in the position convenient for remaking dianthracene units. If the relative conformation of pairing anthroate groups is once distorted unfavorably, the following remaking process is particularly inefficient in PAEU polymers.

Annealing is usually carried out above T_g. The values of T_g of the present polymers are above 80 °C, except for PATE-12. Consequently, the heat treatment at 80 °C will not release the macroscopic strains involved in the main-chain conformation. The present results indicate that the local strains related to minor transitions below T_g influence the reactivity of anthroate groups. Such transitions were, however, not detected by the TBA analysis.

Temperature Effects on Remaking Dianthracene. The samples annealed at 80 °C for 2 h were photolyzed at 20 °C by irradiating at 300 nm. The photolyzed samples were immediately set at a desired temperature, and remaking of the dianthracene was spectroscopically followed

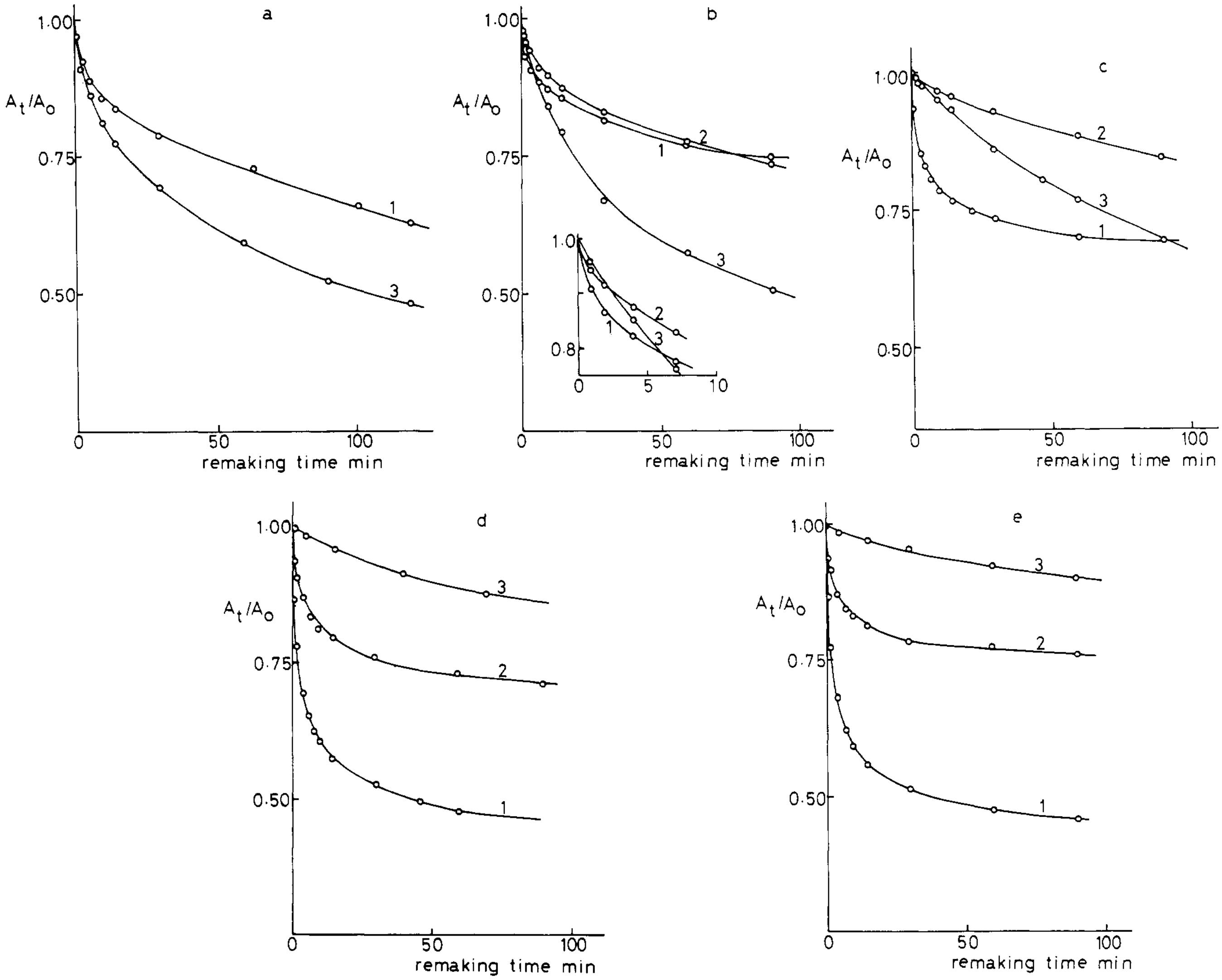


Figure 8. Temperature effects on remaking of dianthracene units: remaking temperature 20 °C (1), 40 °C (2), 60 °C (3); (a) PADE-12, (b) PATE-8, (c) PATE-12, (d) PAEU-6, and (e) PAEU-10.

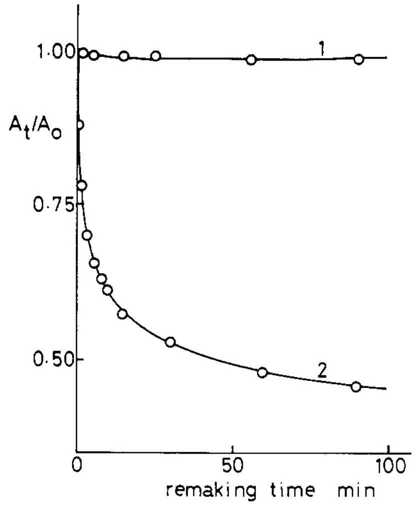


Figure 9. Effects of annealing photolyzed PAEU-6 on remaking of dianthracene units. (1) PAEU-6 was photolyzed at 20 °C until $A_0 = 0.5$ then heated to 80 °C to dissociate sandwich dimer before remaking of dianthracene units at 20 °C. (2) Reference sample without heat treatment.

under irradiation at 365 nm. The results are depicted in Figure 8.

The reaction profiles are divided into two groups. One is for the PAEU series and another is for the PADE and PATE series. The remaking time–conversion curves for the former series (Figure 8d,e) are characterized by an initial rapid reaction followed by a very slow process. The degree of initial rapid reaction decreases with increasing reaction temperature and totally disappears at 60 °C for both PAEU-6 and PAEU-10. The rate of the later slow stage increases only slightly with increasing temperature. The initial rapid reaction is attributed to dimerization of paired anthroate groups, including sandwich dimer and other aggregated states. Evidence is as follows. First, when the polymer is heated to 80 °C prior to the remaking experiment, photodimerization at 20 °C does not proceed at all as shown in Figure 9. We showed already that the sandwich dimer and other detectable aggregates dissociate completely at 60 °C. Second, the fraction of initial fast reaction within 10 min consumes about 45% of the anthroate groups, whereas the initial sandwich dimer fraction was determined as 34% using eq 4. These figures are reasonable since, in addition to sandwich dimer, loose aggregates of anthroate groups will participate in the initial fast photodimerization. When two anthryl groups are forced to locate close to each other by linking with a spacing group, the photodimerization quantum efficiency depends sharply on the length and structure of the spacing group, whereas the absorption spectra are nearly identical with that of unlinked anthracene derivatives with the exception of anthracenophanes.[11] Also, in the present polymer systems, loose aggregates like "edge-to-edge" arrangements will not be detected spectroscopically.

The subsequent slow process is attributed to photodimerization of unpaired or dissociated anthroate groups. The process including segment mobility is obviously very slow in PAEU polymers. Results of both fluorescence and absorption spectroscopy are in support of this conclusion.

Another type of remaking process represented by PATE-8, PATE-12, and PADE-12 (Figure 8a–c) is characterized by the small contribution of the initial fast process. Even at 20 °C where the participation of the sandwich dimer may be expected, the fast initial process is clearly observed only for PATE-12. At 40 °C, the initial fast process disappears for all polymers. These behaviors are closely related to the unstability of the sandwich dimer in the polyester environments as demonstrated in the previous sections, in particular by Figure 4. On the contrary, the later slow process is much faster in these polyesters than in PAEU polymers. This is again in good agreement with the spectroscopic findings that segment mobility is facilitated in the polyesters in comparison with PAEU polymers. The remaking rate increases with increasing temperature, and the shapes of the time–conversion curves are very much different from those for PAEU polymers. It will be concluded that polyesters as reaction media have more fluidity than polyester urethanes.

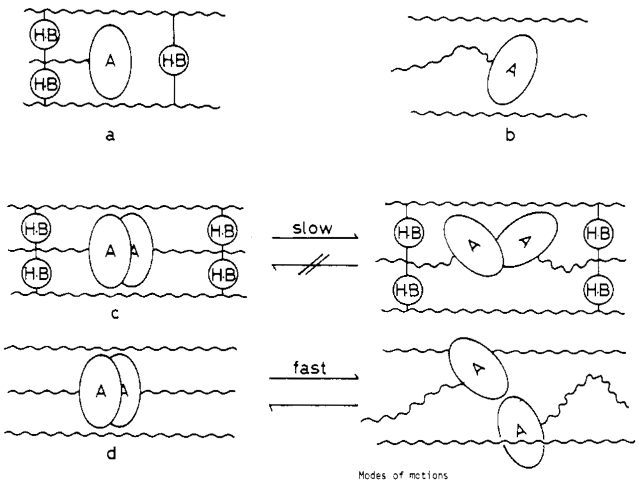
Segment Mobility and Polymer Structure. All results on the thermal stability of dianthracene polymers,[1] the amount and stability of the sandwich dimer structure, rotational freedom of anthroate groups, and ease of remaking dianthracene after photolysis, which are summarized in Table IV, support the conclusion that minor changes in polymer structure bring about remarkable change in segment mobility. From the comparison of isostructural polymer pairs, PAEU-6/PATE-8 and PAEU-10/PATE-12, it is surprising to find the restricted segment mobility in PAEU polymers. For example, the repeating unit of PATE-12 is different from that of PAEU-10 only by two methylene groups which are substituted by two imino groups in PAEU-10, the number of atoms spacing dianthracene units being the same at 28 for both polymers. The differences in atomic composition look marginal when considering one repeating unit expressed by $C_{52}H_{58}O_8$ for PATE-12 or by $C_{50}H_{56}N_2O_8$ for PAEU-10. Nevertheless, their photophysical and photochemical properties are much different.

The marked differences between polyesters and polyester urethanes are attributed to hydrogen bonding. The differences in T_g, in the length of spacing segments between dianthracene units, and in the number of ester groups per one repeating unit are not major influential factors. From the present results, we have learned that end-group mobility is not frozen even below T_g and is furthermore strictly controlled by the main-chain structure. It was reported that the segment mobility of the polymer end groups is more than five times faster than that of the segment incorporated in the middle of the polymer chain as a side group in the case of ethylenic polymers.[17,18] These results indicate that good free volume is available for a terminal segment to rotate, vibrate, or swing around.

Comparing photodimerizability of pendant anthryl groups in polyesters and polyester urethanes,[5] side-chain mobility is more restricted in the latter polymers. The change in side-chain reactivity around T_g is gradual for polyesters, and a certain reactivity remains below T_g, whereas the reactivity of polyester urethanes is negligible at T_g and released at 20–30 °C above T_g. There seems to be a good parallelism between end-group and side-group mobilities with respect to the effects of polymer structure. However, side-group dimerization of polyesters requires high temperature close to T_g, whereas end-group dimerization of unpaired anthroate groups in the present polyesters could proceed well below T_g. Besides higher mobility of terminal groups than side groups, a specific factor in the present polymers is the geminate production of terminal groups. Even if the spectroscopically detectable paired states disappear before the remaking experiment, terminal groups are expected to stay closer to each other than the statistic separation, assuming homogeneous distribution of terminal groups. Consequently, minute mobility of terminal groups will be suf-

Table IV
Qualitative Correlation between Terminal Segment Mobility and Polymer Structure

information	procedure of measurement	PADE-12	PATE-8	PATE-12	PAEU-6	PAEU-10	controlling factors
T_g	TBA	high	low	low	medium	medium	the length of spacer between dianthracenes, hydrogen bonding
hydrogen bonding	infrared spectroscopy	none	none	none	yes	yes	difference between ester and urethane linkage
rotational freedom of anthroate group	fluorescence spectroscopy	high	high	high	low	low	hydrogen bonding
stability of paired states (sandwich dimer) at 20 °C	relaxation of sandwich dimer, remaking of dianthracene	poor	poor	fair	good	good	hydrogen bonding
diffusion of terminal anthroate group	remaking rate of dianthracene after the initial fast reaction of sandwich dimer	fast	moderate	moderate	slow	slow	hydrogen bonding
efficiency of remaking dianthracene at 20 °C	total amount of dianthracene formation	fair	low	fair	high	high	balance between the stability of sandwich dimer and the diffusion of terminal anthroate groups
at 60 °C		high	high	fair	low	low	



			Modes of motions	
	Terminal species	Matrix	Rotational at -196°*	Swinging at room temperature**
a	originally existing	PAEU	not allowed	------------
b	originally existing	PATE, PADE	allowed	------------
c	photolytically formed	PAEU	allowed	scarcely allowed
d	photolytically formed	PATE, PADE	allowed	allowed

Sorces of information: *; Figures 4 and 5, **; Figures 3, 8, and 9.

Figure 10. Schematic depiction of structural effects on the terminal segment mobility: A, anthroate group; HB, hydrogen bonding.

ficient to remake dianthracene units.

The imino groups in polyester urethanes are separated from the anthryl end group by eight atoms, and the minute motions of the terminal anthryl group are not likely to be directly affected by the urethane linkage of relevant main chain. A better explanation is to consider the network structure of hydrogen bonding so that the free volume available for an end group is reduced. When the network is destroyed at elevated temperatures, segment mobility is released, and the bimolecular reaction involving the diffusion process would become possible. The reactions at elevated temperatures could not be examined with the present polyester urethanes due to thermal decomposition, however. The presence of hydrogen bonding would also affect the secondary and higher order polymer structures, which were not dealt with in this article. As the thermal history of the polymer is an important factor in deciding terminal group reactivities, orientation by stretching would alter the reaction behaviors as well. This is an interesting future subject.

We will next discuss the contents of "segment mobility" which is a vague expression including vibrational, rotational, and translational motions. As far as terminal segment mobility below T_g is concerned, translational motion accompanying the motions of total polymer molecules will be excluded, and instead swinging motion should be considered. The results in Figure 6 suggest that the rotational mobilities of the originally existing anthroate groups and that of the terminal groups formed by photolysis are different. The difference is particularly prominent in PAEU polymers. Even after sufficient annealing, the fluorescence maximum of photolytically formed anthroate groups locates at a longer wavelength region than that of the originally existing ones, indicating more restricted mobility of the latter species. Since the entire separation of paired anthroate groups by translational motion is not expected below T_g, the originally exisiting terminal groups will locate in more tight networks, as is schematically depicted in Figure 10. The situation is much the same for PATE or PADE polymers although the difference between originally existing and photolytically formed anthroate groups is small. This is a reasonable consequence since the compartmentalization of paired anthroate groups will not be as rigid as in the PAEU polymers.

Now the differentiation between rotational and swinging motions of terminal groups is possible. The former is allowed for polyesters but not for polyester urethanes at −196 °C. The latter, which is responsible for remaking dianthracene units from unpaired anthroate groups, is released well below T_g for polyesters but not for polyester urethanes. Although the present information is qualitative, the good parallelism among all pieces of information on various terminal segment mobilities would be a manifestation that the freedom of various mobilities is governed by the same structural factors.

Conclusion

We observed directly the mobility of terminal anthroate groups in polyesters and polyester urethanes. The finding that the terminal group mobility is not related to T_g is worth being emphasized. Very small mobilities are responsible for characteristic photochemical and photophysical properties of terminal groups, which are most strongly affected by inter- or intrapolymer hydrogen bonding.

The information on structural factors influencing terminal and pendant segment mobilities will be useful in the molecular engineering of photoresponsive polymers, although the present polymers themselves will have no practical values due to poor reversibility of photochromism.

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Conformational Characteristics of Poly(methyl acrylate). 1. Dipole Moment Measurements

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ABSTRACT: A sample of poly(methyl acrylate) with $M_v = 4.57 \times 10^5$ has been synthesized via free-radical polymerization. Six fractions having molecular weights $M_v = 4.70 \times 10^5$, 10.12×10^5, 6.90×10^5, 4.99×10^5, 4.49×10^5, and 3.33×10^5 were isolated, and their dipole moments in benzene solution were determined at different temperatures in order to study the effect of molecular weight and temperature on the dipole moment. The plot of dipole moment ratio against temperature exhibits a minimum at $T \simeq 35$ °C that, to our knowledge, has not been reported before; however, this ratio does not depend on molecular weight.

The published data concerning experimental dipole moment measurements of poly(methyl acrylate) (PMA) in solution are scarce;[1-3] the dependence of dipole moment on temperature has not yet been investigated. The aim of the present paper is to elucidate the dependence of PMA dipole moment on temperature from an experimental point of view in order to expand the knowledge on this topic. The experimental values of dipole moment will help, with an adequate theoretical interpretation, us to a better understanding of the conformation of PMA in solution. Our results show that the variation of dipole moment with temperature exhibits a transition, similar to the one found for some other polymers,[4,5] that indicates a change in short-range interactions at a given temperature.

For the present work, a sample of PMA has been synthesized, fractionated, and characterized (both the raw sample and the fractions) by viscometry. The dipole moment, evaluated according to the method of Guggenheim and Smith,[6,7] has been determined as a function of temperature and of molecular weight.

Experimental Section

(a) Materials. The monomer (methyl acrylate, Fluka, pure) was distilled under reduced pressure just before utilization in order

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