Table III
Conformational Parameters of Microphase Domains

designation	α_B	N, Å^{-3}	D_c, eq, Å	D_{EM}, Å	L_{eq}, Å
GBG-4	0.288	1430×10^{-8}	437	450	
GBG-2	0.494	2450×10^{-8}	334		377
GBG-1	0.589	2920×10^{-8}	306		316

to be the same as those for GBG-4. As a matter of course, $D_{c,eq}$ increases with increasing a, α, and ΔW. Among these parameters, the value of α for chloroform should be determined in further experiments.

For samples GBG-2 and GBG-1, we have no electron micrograph so far; however, from the values of φ_B for these samples, we may expect either cylindrical or lamella-like micelle. Thus, $D_{c,eq}$ and L_{eq} were estimated from eq 14 and 15, respectively. Table III summarizes the data on microheterophase structures for GBG-4, GBG-2, and GBG-1. In Table III, all the calculations were performed by assuming $\alpha = 1.2$ and $a = 7.5$ Å.

In conclusion, formation and structure of the microheterophase of rod-coil-rod type block copolymer were quantitatively analyzed as functions of conformational parameters and interfacial free energy, on the basis of the micelle formation mechanism at critical concentration.

Water permeability and mechanical properties of such novel block copolymer membranes will be reported in a succeeding paper.

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Functionality and Structure of Polymers. 3. Synthesis and Thermal Properties of Polymers Having a Dianthracene Main Chain

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ABSTRACT: Polyesters and polyester urethanes having dianthracene units as main chain components were synthesized either by photocycloaddition of α,ω-dianthryl compounds or polyaddition of a diol containing dianthracene units with diisocyanates. These polymers are soluble in EDC or methylene chloride, and transparent films can be cast. Thermal analysis by means of torsional braid analysis (TBA) indicated distinct structural effects upon transition temperature. Polyester urethanes have higher T_g than analogous polyesters, which was attributed to hydrogen bonding in the former polymers. A temperature-dependent IR spectrum of a polyester urethane showed the participation of hydrogen bonding. The effect of hydrogen bonding is not only to affect T_g but also to control minute segment mobility above T_g which reflects on the thermal cleavage of the dianthracene main chain. Thermal decomposition of polyesters proceeded gradually above 90 °C, whereas polyester urethanes were stable up to a higher temperature probably due to restricted segment mobility caused by hydrogen bonding even above T_g. When hydrogen bonding nearly disappeared at elevated temperatures, dianthracene units in polyester urethanes were thermally cleaved rapidly. These structure–reactivity correlations were compared with the behaviors of polyesters and polyester urethanes having pendant anthryl groups presented in the previous article of this series of publication.

Anthracene and its derivatives are unique spectroscopic as well as reactive probes owing to their spectroscopic sensitivity to the state of aggregation, molecular interaction, and photochemical dimerization. We have been investigating photophysical and photochemical behaviors of various chromophores and fluorophores attached to polymers having well-defined structures.[1-5] When polyesters having pendant anthryl groups are used, the rate of photodimerization of pendant anthryl groups depends strongly on the mobility of polymer chain both in solution[2] and solid.[3] It was also found that thermal dissociation of dianthracene units in the photocross-linked polymers

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proceeded with different rates reflecting the backbone polymer structure. Small differences in polymer main chain structure brought about distinct differences in both photodimerization and thermal dissociation processes.[3] Furthermore, absorption spectra indicated interchromophore interactions both in ground and excited states.[4,5] These preceding works demonstrated the usefulness of the anthryl group to the study of inter- and intramolecular interactions.

In this article, we intended the synthesis of polyesters and polyester urethanes having dianthracene main chain with regular intervals. These polymers are readily subject to thermolysis and photolysis, and the decomposition behaviors must be a function of polymer structure. If the reversible process, namely, photodimerization at longer wavelength irradiation and photodissociation at shorter wavelength irradiation, can be repeated, there is a possibility of reversible photomemory. The reversibility must also depend on polymer structure. When a pair of anthryl groups produced by the scission of polymer main chain can stay close to each other, the reverse process to dianthracene would proceed with high efficiency.

To obtain suitable polymer samples, careful molecular designing is required. Since dianthracene is notorious for its insolubility, a long and flexible spacer has to be inserted between dianthracene units. Although dianthracene polymers have been prepared by Smets and DeSchryver in the past,[6,7] their polymers were made of rather stiff and short spacing main chains and/or prepared by copolycondensation with soft segments. Consequently, their polymers are either not sufficiently soluble in common solvents or do not have well-defined repeating units. Furthermore, thermal analysis could not be applied to their polymers. We have now prepared soluble and flexible dianthracene polymers having well-defined structures and distinct transition temperatures to meet our purpose.

Experimental Section

Materials. 4-Hydroxybutyl 9-Anthroate. 9-Anthroic acid (5.0 g) and 25 mL of thionyl chloride were refluxed in 25 mL of dry benzene under stirring. After gas evolution subsided, the excess thionyl chloride was distilled off under reduced pressure. The yellow residue dissolved in 50 mL of dry THF was added dropwise to a large excess of 1,4-butylene glycol containing an equivalent amount of triethylamine to the acyl chloride. After the reaction mixture had been stirred for 2 h, the mixture was filtered and evaporated. After the usual workup, the product was chromatographed on silica gel (elutant, chloroform) and finally recrystallized from toluene: yield 4.0 g (61%); mp 70.5–71.5 °C; IR 3300 (ν_{OH}), 1720 cm^{-1} ($\nu_{C=O}$); NMR δ 1.63–2.16 (m, 4 H, $-CH_2-$), 3.03 (s, 1 H, $-OH$), 3.67 (t, 2 H, $-CH_2C=O$), 4.70 (t, 2 H, $-CH_2O$), 7.33–8.70 (m, 9 H, aromatic H). Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 76.64; H, 5.98.

9,10-Bis(4-hydroxybutyleneoxycarbonyl)dianthracene (2). 4-Hydroxybutyl 9-anthroate (5.6 g) in 60 mL of THF, deaerated by bubbling with a stream of nitrogen for 20 min, was irradiated for 15 h by a 300 W high-pressure mercury lamp through a filter solution (naphthalene in *n*-hexane) to cut off the wavelength below 320 nm. The solvent was distilled off and the residue was washed with toluene. Repeated recrystallization from THF–benzene mixture gave 4.8 g (86%) of the photodimer: mp 185.5–186.5 °C dec; IR 3400 (ν_{OH}), 1720 ($\nu_{C=O}$), 1450, 1470 cm^{-1} (δ_{OH}); NMR δ 1.36–2.06 (m, 8 H, $-CH_2-$), 2.89 (s, 2 H, $-OH$), 3.63 (t, $-CH_2C=O$), 4.59 (t, 4 H, $-CH_2O-$), 5.09 (s, 2 H, aromatic H), 7.03 (m, 16 H, aromatic H). Anal. Calcd for $C_{38}H_{36}O_6$: C, 77.53; H, 6.16. Found: C, 76.51; H, 6.15.

α,ω-Alkylene bis(9-anthroate) (**3**) was prepared by refluxing 9-anthroyl chloride with the corresponding α,ω-diol (feed ratio, 2.1/1.0) in anhydrous benzene. The product was chromatographed on silica gel (elutant, chloroform) and finally recrystallized from an *n*-hexane–toluene mixture. 1,8-Octylene bis(9-anthroate) (**3a**), mp 141–3 °C, 1,12-decamethylene bis(9-anthroate) (**3b**), mp 87–89 °C, and 1,8-(3,6-dioxaoctylene) bis(9-anthroate) (**3c**), mp 100–102 °C, were prepared by this procedure.

4,4′-Bis[(9-anthroyl)oxymethylene]diphenylmethane (3d). The dried potassium salt of 9-anthroic acid prepared from 3.5 g of the free acid in situ and 4,4′-bis(bromomethyl)diphenylmethane (1.85 g) were reacted in DMF (30 mL) for 10 h at 90–95 °C. Product (2.5 g, 75%) was obtained after recrystallization from toluene: mp 188–190 °C; IR 1730 cm^{-1} ($\nu_{C=O}$); NMR δ 3.97 (s, 2 H, Ph_2CH-), 5.57 (s, 4 H, $-OCH_2Ph$), 7.16–8.47 (s, 26 H, aromatic H).

Bis[(9-anthroyl)oxytetramethylene] Adipate (4a). The equimolar mixture of 4-hydroxybutyl 9-anthroate and triethylamine in anhydrous benzene was added with 0.5 mol equiv of adipoyl chloride as a benzene solution. After the usual workup, the product was purified by chromatography on silica gel (elutant, methylene chloride): viscous oil; yield 88%; IR 1700 cm^{-1} ($\nu_{C=O}$); NMR δ 1.33–2.50 (m, 16 H, $-CH_2-$, alkyl$-CH_2COO-$), 4.23 (t, 4 H, $-CH_2O-$), 4.67 (t, 4 H, $ArCOOCH_2-$), 7.36–8.57 (m, 18 H, aromatic H). Similarly, the following tetraester compounds were prepared: bis[(9-anthroyl)oxytetramethylene] sebacate (**4b**), yield 85%, mp 66–69 °C; bis[(9-anthroyl)oxytetramethylene] decamethylenedicarboxylate (**4c**), yield 90%, mp 84–86 °C.

Poly[oxycarbonyl(dianthracene-9,10′-diyl)carbonyloxytetramethyleneoxycarbonyldodecamethylenecarbonyloxytetramethylene] (PATE-12), poly[oxycarbonyl(dianthracene-9,10′-diyl)carbonyloxytetramethyleneoxycarbonyloctamethylenecarbonyloxytetramethylene] (PATE-8), poly[oxycarbonyl(dianthracene-9,10′-diyl)carbonyloxytetramethyleneoxycarbonyltetramethylenecarbonyloxytetramethylene] (PATE-4), poly[oxycarbonyl(dianthracene-9,10′-diyl)carbonyldodecamethylene] (PADE-12), poly[oxycarbonyl(dianthracene-9,10′-diyl)carbonyloxyoctamethylene] (PADE-8), and poly[oxycarbonyl(dianthracene-9,10′-diyl)carbonyloxymethylene(diphenylmethane-4,4′-diyl)methylene] (PADE-Ph) were prepared by the photocycloaddition reaction of corresponding monomers. The monomer solution was degassed by freeze–pump–thaw cycles and was irradiated at 50–60 °C by a 300 W high-pressure mercury lamp externally through a solution filter containing 2.5×10^{-2} M of naphthalene in *n*-hexane. The reaction mixture became viscous toward the end of the reaction. The polymer was precipitated in acetone and dried in vacuo. The reaction conditions were tabulated in Table I.

Poly[iminocarbonyloxytetramethyleneoxycarbonyl(dianthracene-9,10′-diyl)carbonyloxytetramethyleneoxycarbonyliminohexamethylene] (PAEU-6). Dioxane solution (35 mL) containing 2.1041 g of **2** and 0.6019 g of hexamethylene diisocyanate was stirred at 50–60°, and 1 mol % of dibutyltin dichloride in 5 mL of dioxane was added. After the solution had reacted for 5 h, two drops of the diisocyanate was added, and the reaction was continued for another 3 h. After the solution was left to stand overnight, a small amount of methanol was added to cap the isocyanate end groups, and the polymer was precipitated in benzene as white flakes. Poly[iminocarbonyloxytetramethyleneoxycarbonyl(dianthracene-9,10′-diyl)carbonyloxytetramethyleneoxycarbonyliminodecamethylene] (PAEU-10) was similarly prepared using decamethylene diisocyanate.

Torsional Braid Analysis (TBA).[8] The measurements were made by an apparatus determining the decrement of unrestricted torsional oscillation (Oyo Denki Co., Ltd.). A braid made of glass fibers was dipped in a chloroform solution of polymer, and then the relative rigidity of the braid was determined as a function of temperature. Since the absolute value was not available under the condition of TBA analysis, P^{-2} was considered as relative rigidity, P being the period of oscillation. The dynamic decrement index, $1/n$, was determined from the known relation, $\Delta = 1/n(\ln(A_0/A_n))$ where Δ is logarithmic decrement and A_0 and A_n are the distortions at 0th and nth vibrations. Setting the boundary condition of $A_0/A_n = 30/1$, we obtained n.

Infrared Spectroscopy. A thin film of PAEU-6 was cast on a NaCl plate from chloroform solution. The NaCl plate was attached to an aluminum block which was temperature controlled, and the IR spectrum was measured by a Perkin-Elmer 125 spectrometer as a function of temperature.

Thermal Decomposition. A known amount of polymer solution was evaporated in a test tube so that a thin polymer film was formed on the glass wall. The sample was thermolyzed at

Table I
Preparative Conditions for PADE and PATE Polymers

polymer	monomer	solvent[b]	[monomer], M	reaction time, h	precipitant[b]	polymer yield, %
PADE-8	**3a**	MC	0.1	36	A	80
PADE-12	**3b**	MC	0.2	36	A	82
PADE-TEG	**3c**	MC	0.2	(ppt)		
PADE-Ph	**3d**	EDC	0.1	9[a]	A	86
PATE-4	**4a**	MC	0.2	48	H	81
PATE-8	**4b**	MC	0.2	48	E	59
PATE-12	**4c**	MC	0.2	48	E	51

[a] Polymer precipitated. [b] Solvent and precipitant: MC, methylene chloride; EDC, ethylene dichloride; A, acetone; H, *n*-hexane; E, diethyl ether.

Table II
Structures and Properties of Dianthracene Polymers

polymer[a]	monomer structure[b]	method[c]	η_{sp}/c[d]	soluble in[e]	film[f]	elemental analysis found	elemental analysis calcd	peak of 1/*n*, °C[g]
PADE-8	(**3a**) $A-CO_2(CH_2)_8OCO-A$	3		MC	○[j]			
PADE-12	(**3b**) $A-COO(CH_2)_{12}OCO-A$	3	0.42[h]	MC, C	△	C, 82.98 H, 7.03	C, 82.59 H, 6.93	(135)
PADE-Ph	(**3d**) $A-COOCH_2(p-C_6H_4)CH_2(p-C_6H_4)CH_2COO-A$	3		hot EDC	△[j]			
PATE-4	(**4a**) $A-COO(CH_2)_4OCO(CH_2)_4COO(CH_2)_4OCO-A$	4	0.061[h]	MC, C	◎	C, 75.63 H, 6.06	C, 74.91 H, 6.30	
PATE-8	(**4b**) $A-COO(CH_2)_4OCO(CH_2)_8COO(CH_2)_4OCO-A$	4	1.38[h]	MC, C	◎	C, 75.81 H, 6.72	C, 76.37 H, 6.68	86
PATE-12	(**4c**) $A-COO(CH_2)_4OCO(CH_2)_{12}COO(CH_2)_4OCO-A$	4	0.81[h]	MC, C	◎	C, 76.14 H, 7.14	C, 77.01 H, 7.21	72
PAEU-6	(**2**) $HO(CH_2)_4OCO-\overset{\frown}{\underset{\smile}{A\;A}}-COO(CH_2)_4OH$ + $OCN(CH_2)_6NCO$	2	0.68[i]	MC, C	◎	C, 73.61 H, 6.46 N, 4.16	C, 73.00 H, 6.39 N, 3.70	106
PAEU-10	(**2**) $HO(CH_2)_4OCO-\overset{\frown}{\underset{\smile}{A\;A}}-COO(CH_2)_4OH$ + $OCN(CH_2)_{10}NCO$	2	0.37[i]	MC, C	◎	C, 72.86 H, 7.13 N, 3.54	C, 73.87 H, 6.94 N, 3.45	108

[a] The abbreviations stand for polymers of anthroate units linked by diester (DE), tetraester (TE), and ester urethane (EU) main chain. [b] A, 9-anthryl; $-\overset{\frown}{\underset{\smile}{A\;A}}-$, dianthracene-9,10′-diyl. [c] Corresponds to the synthetic route, see text. [d] In chloroform, 25 °C. [e] MC, methylene chloride; C, chloroform; EDC, ethylene dichloride. [f] Film was cast on a quartz plate: ◎ , tough and transparent film was easily cast; ○ , good transparent film was obtained by careful casting; △ , casting of transparent film was difficult. [g] Data of torsinal braid analysis. [h] *c* = 0.8%. [i] *c* = 1.0%. [j] Film had to be cast from hot solution.

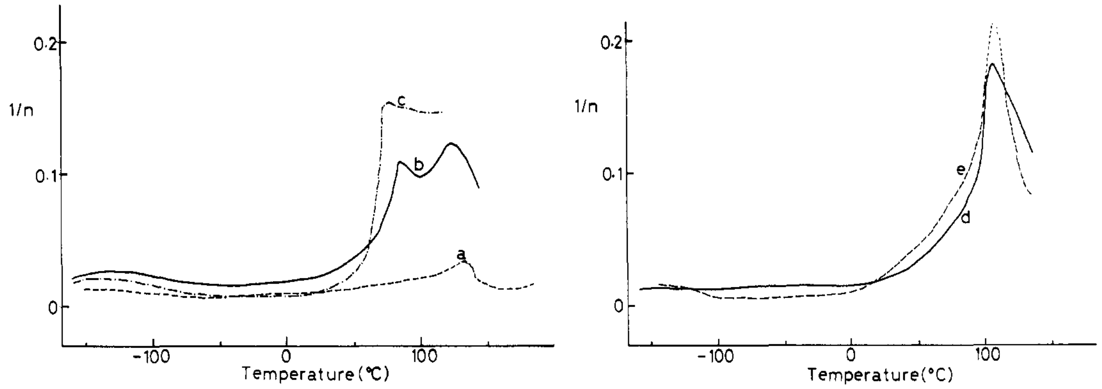


Figure 1. TBA curves of dianthracene polymers: (a) PADE-12, (b) PATE-8, (c) PATE-12, (d) PAEU-6, and (e) PAEU-10.

the desired temperature for 15 min. The polymer was then dissolved in chloroform to make up a 5×10^{-4} M solution based on the initial dianthracene unit. The decomposed amount of the dianthracene unit was determined by measuring the intensity of anthracene absorption.

Results and Discussion

Polymer Synthesis. The basic requirements for polymer designing are as follows. (i) Polymers are to be soluble in common solvents at room temperature. (ii) Transparent film can be obtained. (iii) Dianthracene units are to be arranged with regular intervals. To meet these requirements, we made the synthetic designs shown in Scheme I.

Scheme I

Route 1

$$C_{14}H_9CH_2OH \xrightarrow{h\nu} \underset{\mathbf{1}}{HOCH_2(C_{14}H_9)_2CH_2OH} \rightarrow \text{polyurethanes}$$

Route 2

$$C_{14}H_9COOH \xrightarrow{SOCl_2} C_{14}H_9COCl \xrightarrow{HO(CH_2)_nOH}$$

$$C_{14}H_9COO(CH_2CH_2)_nOH \xrightarrow[\lambda\ >300\ \text{nm}]{h\nu}$$

$$\underset{\mathbf{2}}{HO(CH_2)_nOCO(C_{14}H_9)_2COO(CH_2)_nOH} \rightarrow$$

polyesters or polyester urethanes

Route 3

$$C_{14}H_9COCl \rightarrow \underset{\mathbf{3}}{C_{14}H_9COO\text{-}R\text{-}OCOC_{14}H_9} \xrightarrow[\lambda\ >320\ \text{nm}]{\text{photocycloaddition}}$$

polyesters

Route 4

$$C_{14}H_9COO(CH_2)_4OH \xrightarrow{ClCO(CH_2)_nCOCl}$$

$$\underset{\mathbf{4}}{C_{14}H_9COO(CH_2)_4OCO(CH_2)_nCOO(CH_2)_4OCOC_{14}H_9}$$

$$\xrightarrow[\lambda\ >320\ \text{nm}]{\text{photocycloaddition}} \text{polyesters}$$

$C_{14}H_9$, 9-anthryl; $(C_{14}H_9)_2$, dianthracene-9,10′-diyl

Among these, route 1 was unsuccessful. The monomer 1 is poorly soluble in any solvent, and polycondensation with diisocyanates was not possible. To improve the solubility of dianthracene monomer, long flexible chains must be attached. In route 2, the half ester of ethylene glycol (n = 2) is not yet sufficiently soluble. Further extension of the alkyl group using butylene glycol (n = 4) brought about good solubility of the monomer in THF and dioxane. Polycondensation with hexamethylene or decamethylene diisocyanate produced high molecular weight polyester urethanes (PAEU-6 and PAEU-10). However, when polycondensation proceeded too far, the polymer began to precipitate. The once precipitated polymer during reaction was insoluble even in Me_2SO and HMPA. The polycondensation reaction has to be stopped before phase separation occurs.

For the synthesis of polyesters, the analogous polycondensation process cannot be applied since ester exchange during polycondensation randomizes the arrangement of dianthracene units and furthermore a part of the dianthracene units will be cleaved under the condition of polyester formation at elevated temperature. As alternative methods, routes 3 and 4 were proposed. Route 3 has been reported by Smets and DeSchryver.[6] Photoirradiation of degassed methylene chloride or ethylene chloride solution containing α,ω-dianthryl monomers at the wavelength region longer than 320 nm induces successive photodimerization of anthryl groups exclusively, giving high molecular weight polymers. When the spacing ester chain between anthryl groups is long and soft, photodimerization is generally facilitated. An exception is monomer 3c, which precipitates during photoirradiation in spite of its soft poly(ethylene oxide) chain. The precipitated product is insoluble in HMPA, Me_2SO, chloroform, THF, and others, indicating a cross-linked structure. Further investigation on this monomer was not attempted.

The dianthracene polymers were tabulated in Table II. We chose PADE-12, PATE-8, PATE-12, PAEU-6, and PAEU-10 for property study. It should be noted that PATE-8/PAEU-6 and PATE-12/PAEU-10 are isostructural pairs, in which two methylene groups in a repeating unit of polyester are substituted by two imino groups in relevant polyester urethane, the number of atoms between neighboring dianthracene groups being the same.

Thermal Analysis of Dianthracene Polymers. Transition temperatures of the polymers were determined by the TBA method. Results are shown in Figure 1, and the peaking temperatures are tabulated in Table II. Since previously reported dianthracene polymers[6,7] are of rigid structures, they decomposed below or at the transition temperature. The present polymers consisting of soft segments possess distinct transition temperatures.

The peak of $1/n$ corresponds to uncontineous change in rigidity. The true T_g has to be determined by the relation between specific volume and temperature and is in general slightly lower than the peaking temperature of $1/n$. Here we consider the peaking temperature $1/n$ as T_g. As expected from the accepted rule of T_g–structure correlation, T_g decreases with an increase in the number of ester groups in a repeating unit. The changes in the number of methylene groups from 8 to 12 for PATE polymers, and 6 to 10 for PAEU polymers, do not bring about much difference in T_g. When the number of methylene groups in the main chain increases, T_g would approach a limiting value as demonstrated for the change

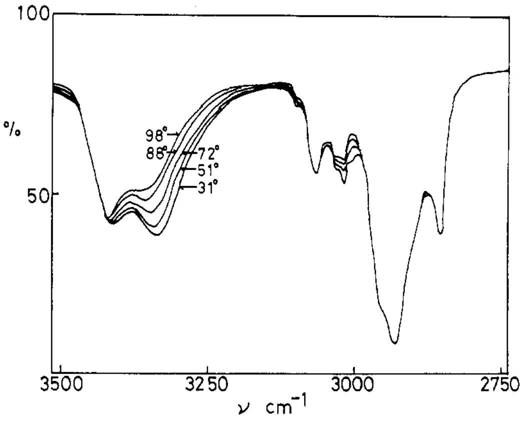


Figure 2. Temperature-dependent IR spectra of PAEU-6.

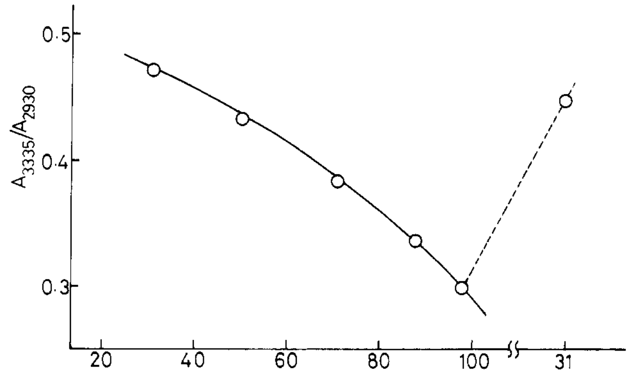


Figure 3. Relative amount of hydrogen bond in PAEU-6 as a function of temperature.

in T_g of poly(alkylene terephthalate) as a function of alkylene chain length.[9]

Comparing the isostructural pairs, PATE-8/PAEU-6 and PATE-12/PAEU-10, polyester urethanes have higher T_g than relevant polyesters. The difference is attributed to hydrogen bonding in polyester urethanes.

Hydrogen Bonding in Polyester Urethane. Differences between polyesters and polyester urethanes in T_g and in thermal decomposition behaviors to be discussed in the following section are attributed to the presence of hydrogen bonding of urethane groups. Temperature-dependent IR spectra of PAEU-6 are shown in Figure 2. The stretching vibration of free NH groups appears at 3430 cm^{-1}, whereas that of hydrogen-bonded groups is observed at 3335 cm^{-1}. As the temperature increases, the absorption at 3430 cm^{-1} decreases. Simultaneously, the stretching vibration of hydrogen-bonded carbonyl groups observed as a shoulder at 1700 cm^{-1} disappears, indicating the breakdown of hydrogen bonding at higher temperature. The ratio of absorbance at 3335 cm^{-1} to that at 2930 cm^{-1} (ν_{CH_2}) was plotted against temperature in Figure 3 as a relative measure of hydrogen bonding. All measurements were made under equilibrium conditions. Figure 3 shows good reversibility of hydrogen-bond formation and dissociation.

Thermal Decomposition of Dianthracene Polymers. The rates of thermal decomposition reflect polymer structure as shown in Figure 4. All polymers are stable up to 90 °C, and thermal decomposition is gradually accelerated with increasing temperature. The shapes of the decomposition curves will be classified into three types. PADE-12 begins to decompose just above 90 °C, and the rate increases steadily with temperature, whereas PAEU-6 and PAEU-10 are stable up to 100 °C, but the decomposition rate jumps suddenly between 120 and 130 °C. The behaviors of PATE-8 and PATE-12 are in between PADE and PAEU polymers. As the first approximation, the sequence of T_g may be a measure for the ease of thermolysis. In fact, the order of the rate of thermolysis at 130 °C, PATE > PAEU > PADE, agrees with the reversed order of T_g. T_g is a function of main-chain rigidity and interpolymer interactions, both of which control segment mobility. The above sequence of decomposition at elevated temperature would suggest the importance of segment mobility in the course of vibrational thermal activation of the dianthracene unit. However, such argument based on T_g will be valid only for a series of polymers consisting of identical functional groups. The stability of PAEU polymers below 120 °C is apparently larger than others. As shown in Figure 3, hydrogen bonding still participates above T_g, and the extra stability of PAEU polymers is attributed to the restriction of segment mobility due to hydrogen-bond formation.

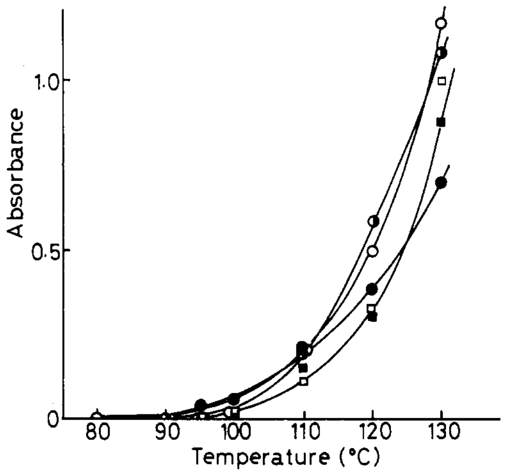
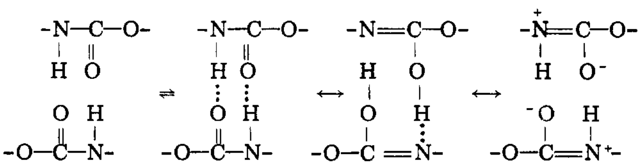


Figure 4. Thermal dissociation of dianthracene units in PADE-12 (●), PATE-8 (○), PATE-12 (◑), PAEU-6 (□), and PAEU-10 (■) at different temperatures. Reaction time, 15 min; absorbance monitored at the peaking absorption of the anthryl group.

Similar effects were observed for photodimerization of polyesters and polyester urethanes having pendant anthryl groups in the solid state.[3] The results indicated clearly that the segment mobility of polyester urethanes was not completely released at T_g, and consequently photodimerization did not occur at this temperature. On the other hand, the pendant anthryl groups in polyesters were reactive around T_g. Thermal cleavage of these polymers cross-linked by photodimerization of pendant anthryl groups was also found to be strongly structure dependent. The presence of the hydrogen bond would suppress segment mobility either by interchain interactions or by increasing the double bond character of the C–N bonds.



In conclusion, the rate-determining factor for thermal cleavage seems to be the local mobility of dianthracene units, whereas T_g is the temperature at which the main-chain mobility is liberated. As a consequence, the thermolysis rate and T_g are not necessarily correlated. In other words, T_g is a bulk quantity concerning the whole polymer molecule, whereas thermal cleavage relates to a specific site of a polymer molecule. When minute segment mobilities below T_g dominate the chemical and physical properties of polymers as will be discussed in the following article on photolysis and remaking of dianthracene 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