Inter- and Intramolecular Interactions of Polymers as Studied by Fluorescence Spectroscopy. II. Excimer Formation of Polyesters Having Pendant 1-Naphthylmethyl Groups

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ABSTRACT: Intra- and intermolecular interactions of polyesters with (1-naphthyl)methyl side groups were investigated by means of fluorescence spectroscopy. Following polyesters, their dimer and monomer model compounds were prepared. Polyesters: poly{[2-(1-naphthyl)methylpropane-1,3-diyl]oxy[(1-naphthyl)methylmalonyl]oxy} (PN-1N), poly{[2-(1-naphthyl)methylpropane-1,3-diyl]oxysuccinyloxy} (PN-2), poly{[2-(1-naphthyl)methylpropane-1,3-diyl]oxyadipyloxy} (PN-4), poly{[2-(1-naphthyl)methylpropane-1,3-diyl]oxysebacyloxy} (PN-8). Dimer model compounds: di[3-(1-naphthyl)propyl] succinate (DN-2), di[3-(1-naphthyl)propyl] adipate (DN-4), di[3-(1-naphthyl)propyl] sebacate (DN-8). Monomer model compounds: 1,3-bisacetoxy-2-(1-naphthyl)methylpropane (MN-II), 3-(1-naphthyl)-1-acetoxypropane (MN-I). From the measurements of the ratio of excimer emission to monomer emission (F_e/F_m) as a function of concentration and temperature, the effects of polymer structure on the intra- and intermolecular interactions and also on the thermodynamic parameters of these molecular interactions were investigated. The results were compared with those of monomer and dimer model compounds. The excimer formation by polymers was found to be entropically more favorable than that for corresponding dimer model compounds whereas the excimer formation by MN-I and MN-II was not observed in the concentration range studied ($<10^{-2}$ M). The sequence of F_e/F_m for polymers was PN-1N < PN-2 $\simeq$ PN-4 $\simeq$ PN-8 at 21 °C. The prominent concentration dependence of F_e/F_m indicated the association of polymer molecules even in dilute solutions.

In the study of polymer effects upon interactions between functional groups either attached or unbound to a polymer, the nature and extent of the interactions should be treated as a function of the molecular structure of the polymer. For the purpose of designing functional polymers such as polymer catalysts, photopolymers, and many other reactive polymers, understanding of the molecular interactions in polymeric systems should be the basis of research, since the origin of so-called polymer effects is to be explained by the peculiarities of intra- and intermolecular interactions in polymeric systems compared with the relevant monomer and/or dimer model compounds.

Fluorescence spectroscopy is a potential technique to study the structure–molecular interaction relationship in polymeric systems, since fluorescence is very sensitive to the environment in which the fluorophore locates. For example, when fluorophores known to form excimers are built in a polymer, the fluorescence spectroscopy of the polymer as a function of concentration and temperature enables us to have an inside look into the inter- and intramolecular interactions. In the preceding article,[1] the exciplex formation between carbazyl and terephthalate groups was taken as an index of interaction and the specific nature of the intra- and intermolecular interactions of poly{[2-(ω-carbazylbutyl)-2-methylpropane-1,3-diyl]-oxy-terephthaloyl-oxy} was discussed. Strong exciplex fluorescence in the polymer system, compared to that in monomer model systems, was attributed to specific interpolymer interactions.

The aim of the present article is to study the interactions between like molecules by excimer formation and to look for the correlation of these molecular interactions with the polymer structure. For this purpose, use of ethylenic polymers is out of the question because of the limited choice of molecular design. Consequently, a number of new polyesters with (1-naphthyl)methyl side groups and their monomer and dimer model compounds were prepared for spectroscopic measurements.

Results

Preparation of Samples. Structures and abbreviated nomenclatures are summarized in Table I.

These polymers can be prepared by the ester exchange or by the diacyl chloride method. Although the later procedure provides comparatively high molecular weight polymers, polycondensation of diol (**2**) with succinyl chloride and adipoyl chloride resulted in intensive coloration of products. For the present purpose of spectroscopic study the ester exchange method conducted at a lower temperature than that usually employed in polyester syntheses[2] was used at the expense of molecular weight. The diacyl chloride method was conveniently applied for the preparation of PN-8 polymer.

Absorption and Fluorescence Spectra of Naphthalene Derivatives. The absorption spectra of naphthyl groups attached to polymer, dimer, or monomer are almost identical indicating that the specific molecular interactions in the ground state is negligibly weak. However, the fluorescence spectra shown in Figure 1 are considerably different from each other. Except for the monomer model compound (MN-II), excimer emission with varying intensity is observed as a broad shoulder. Excitation spectra measured by varying the wavelength of monitoring emission shown in Figure 2 are identical when the monomer emission at 325 nm and the long wavelength limit of assumed excimer emission at 450 nm are monitored. Furthermore, the shape of the excitation spectra reflects the absorption spectrum of PN-1N very well. This is good evidence for the broad emission around 400 nm to be excimer emission. The relative intensities of excitation and absorption spectra do not run parallel when scanning the wavelength, since the excitation spectra are not corrected for the wavelength dependence of the photomultiplier and also for the emission characteristics of the exciting light source.

When the long wavelength limit of absorption is irradiated at 315 nm, the emission spectrum shows an enhanced emission intensity around 350 nm, as shown in Figure 2. Dependence of the shape of fluorescence spectra on the exciting wavelength is an indication that the emission originates from more than two absorbing species. A recent report[3] showed that the dimer naphthyl groups in polyvinylnaphthalene fluoresces peaking at 342, 360, and 378 nm. In the present systems, naphthyl groups are widely separated from each other in comparison to polyvinylnaphthalene and consequently, the contribution of dimer emission would be smaller.

Table I
Structures of Various Naphthalene Derivatives

Abbreviation	Structure	$\overline{DP}$
	(i) Polymers	
MN-I	$CH_3COCH_2CHCH_2OCCH_3$ (O; H_2C-Np; O)	
PN-1N	$+CH_2CHCH_2OC-CH-CO+_n$ (Np-CH_2; O; CH_2; Np; O)	~3
PN-2	$+CH_2CHCH_2OC(CH_2)_2CO+_n$ (Np-CH_2; O; O)	3–4
PN-4	$+CH_2CHCH_2OC(CH_2)_4CO+_n$ (Np-CH_2; O; O)	8–9
PN-8	$+CH_2CHCH_2OC(CH_2)_8CO+_n$ (Np-CH_2; O; O)	>10
	(ii) Dimers	
MN-II	$CH_3CO(CH_2)_3$-Np (O)	
DN-2	Np-$(CH_2)_3OC(CH_2)_2CO(CH_2)_3$-Np (O; O)	
DN-4	Np-$(CH_2)_3OC(CH_2)_4CO(CH_2)_3$-Np (O; O)	
DN-8	Np-$(CH_2)_3OC(CH_2)_8CO(CH_2)_3$-Np (O; O)	

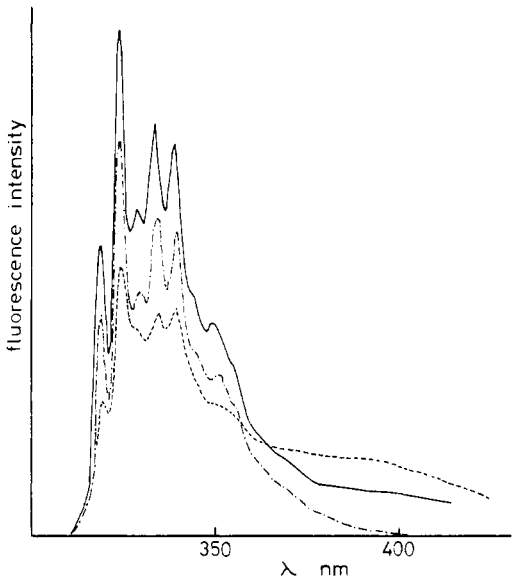

Figure 1. Fluorescence spectra of naphthyl groups in THF. [fluorescer] = 10^{-4} M, excitation at 280 nm. (—) DN-2 at −78 °C; (- - -) PN-1N at −33 °C.

Since the value of F_e/F_m, where F_e and F_m are intensities of excimer and monomer emission, respectively, is independent of the solute concentration around 10^{-4} M, the broad shoulder at about 400 nm ought to be attributed to intramolecular excimer formation. The value of F_e/F_m is considered as an approximate measure of the ease of excimer formation. There seems to be a small contribution of the monomer emission to F_e since a small apparent value ($\lesssim$0.01) of F_e/F_m was observed for MN-I and MN-II at the infinite dilution. There might be also a small contribution of the excimer emission at 324 nm where the F_m was determined. In the following discussions on the relative magnitude of F_e/F_m, the fluorescence intensity data are not corrected for the mixing

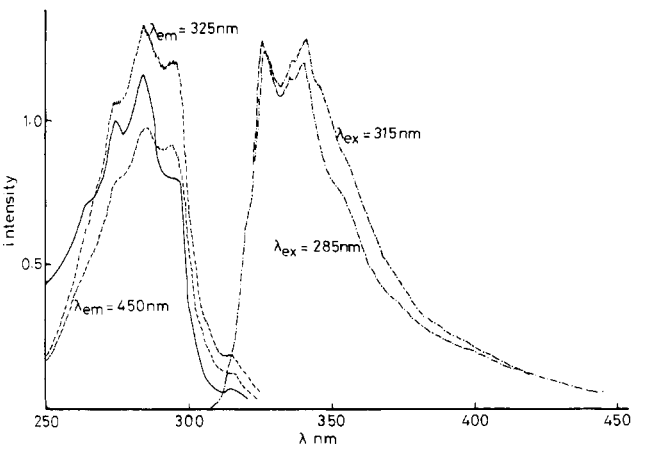

Figure 2. Absorption, emission, and excitation spectra of PN-1N in THF: (—) absorption; (- · -) emission; (- - -) excitation.

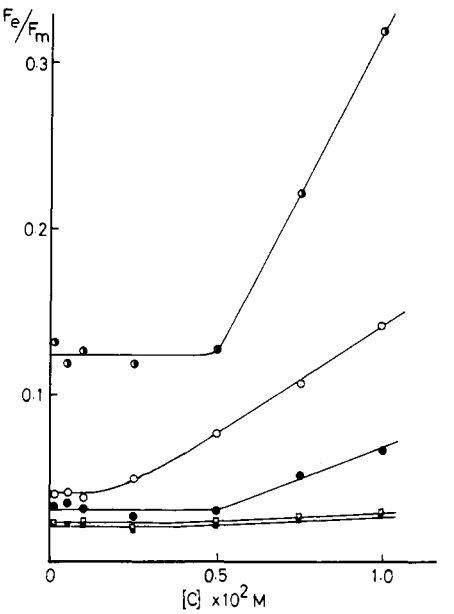

Figure 3. Concentration dependence of F_e/F_m in THF: (◑) PN-1N; (○) PN-2; (●) PN-4; (□) DN-2; (■) DN-4, at room temperature.

of excimer emission with monomer emission and vice versa.

Concentration Dependence of F_e/F_m. The values of F_e/F_m were plotted as a function of concentration in Figure 3. A prominent difference between polymers and dimers is observed. The tendency of intermolecular excimer formation of DN-2 and DN-4 is negligible. The excimer emission from MN-I and MN-II is not observed in the concentration region studied in Figure 3.

The reason for the nonlinear dependence of F_e/F_m on the solute concentration is not clear at the present stage of study. A similar trend of the F_e/F_m vs. [C] plots was reported for ethylene dichloride or cyclohexane solution of polystyrene.[4] The values of F_e for DN-8 and PN-8 are too small to be determined accurately at room temperature and are not included in Figure 3.

Temperature Dependence of F_e/F_m. Assuming the following elementary processes and stationary concentrations for the excited states of the naphthyl group ([M*]) and the excimer ([D*]), a kinetic expression (eq 8) is derived where M denotes the ground state of the naphthyl group.

$$M \xrightarrow{h\nu} M^* \quad I_{abs} \tag{1}$$

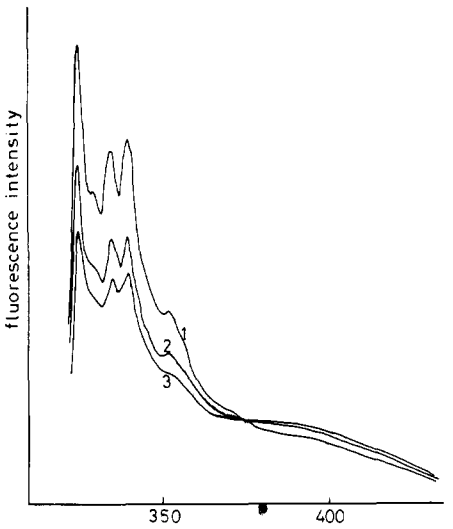

Figure 4. Temperature dependence of fluorescence spectrum of PN-1N in THF: (1) at −78 °C; (2) at −57 °C; (3) at −33 °C.

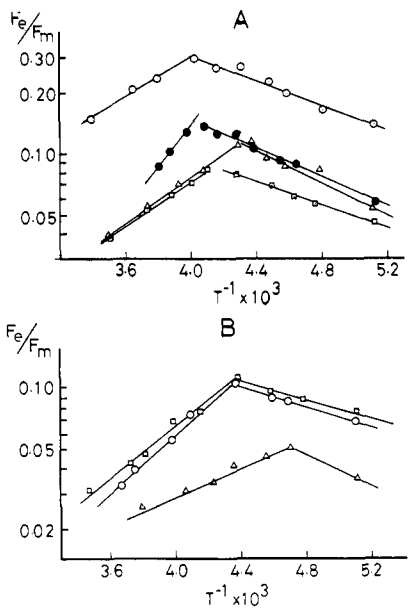

Figure 5. Temperature dependence of F_e/F_m in THF. [fluorescer] = 10^{-4} M. A for polymers: (○) PN-1N; (●) PN-2; (□) PN-4; (△) PN-8. B for dimers: (○) DN-2; (□) DN-4; (△) DN-8.

$$M^* \longrightarrow M + h\nu_f \quad k_{Mf} \tag{2}$$

$$M^* \longrightarrow M \quad k_{IC} \tag{3}$$

$$M^* + M \longrightarrow D^* \quad k_{Da} \tag{4}$$

$$D^* \longrightarrow 2M + h\nu_f' \quad k_{Df} \tag{5}$$

$$D^* \longrightarrow M^* + M \quad k_{Dd} \tag{6}$$

$$D^* \longrightarrow 2M \quad k_{DIC} \tag{7}$$

$$F_e/F_m = k_{Df}k_{Da}[M]/k_{Mf}(k_{Df} + k_{Dd} + k_{DIC}) \tag{8}$$

To derive thermodynamic parameters, we put the following assumptions: (i) $k_{Dd} \gg k_{Df} + k_{DIC}$ at a high temperature range; (ii) $k_{Dd} \ll k_{Df} + k_{DIC}$ at a low temperature range; and (iii) $k_{Df} + k_{DIC}$ is independent of temperature. These assumptions are the same as those put forward by Geuskens.[5] Examples of the temperature dependence of fluorescence spectra at a low temperature range are shown in Figure 4. The presence of an isoemissive point at 374 nm indicates that assumption (iii) is applicable to the present systems. The validity of assumptions (i) and (ii) is also verified as follows. The linear relation found for the plots log (F_e/F_m) vs. $1/T$ (Figures 5 and 6) requires either k_{Dd} or $k_{Df} + k_{DIC}$ to be negligible, k_{Mf} and k_{Df} being independent of temperature. The constancy of k_{Mf} over a wide range of temperature is an established fact and k_{Df} of many aromatic molecules are known to be temperature independent.[6] When excimer formation occurs, $\Delta H_{Dd}^{\ddagger}$ ought to be larger than $\Delta H_{Da}^{\ddagger}$, the difference being the binding energy of the excimer. The assumptions (i) and (ii) would result in a negative and a positive slope for log (F_e/F_m) as a function of $1/T$ at a low temperature range and a high temperature range, respectively, as observed experimentally. The slope of the plots in higher temperature regions thus represents the enthalpy change of the monomer–excimer equilibrium expressed by (9) whereas the slope in lower temperature regions corresponds to the activation energy of excimer formation given by (10).

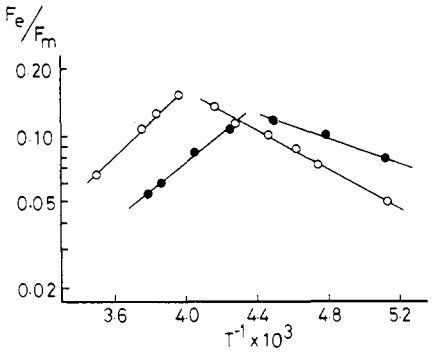

Figure 6. Temperature dependence of F_e/F_m in ethyl acetate. [fluorescer] = 10^{-4} M. (○) PN-2; (●) DN-2.

$$\ln (F_e/F_m) = \ln (k_{Df}[M]/k_{Mf}) + \ln (k_{Da}/k_{Dd})$$
$$= (\Delta H_{Dd}^{\ddagger} - \Delta H_{Da}^{\ddagger})/RT - (\Delta S_{Dd}^{\ddagger} - \Delta S_{Da}^{\ddagger})/R + \text{constant} \tag{9}$$

$$\ln (F_e/F_m) = \ln ([M]/k_{Mf}) + \ln (k_{Da})$$
$$= -\Delta H_{Da}^{\ddagger}/RT + \Delta S_{Da}^{\ddagger}/R + \text{constant} \tag{10}$$

Thermodynamic parameters determined are tabulated in Table II. Although the absolute values of entropy terms cannot be calculated, the relative values may be obtained taking $\Delta S_{Da}^{\ddagger}$ for DN-2 as standard ($\Delta\Delta S_{Da}^{\ddagger}$ in Table II).

Discussions

Comparison of the fluorescence data in Table II for the monomer model compounds, the dimer model compounds, and the polymers immediately indicates the following points.

(i) Intramolecular excimer formation occurs to a noticeable extent even for a pair of the naphthyl groups separated by 16 carbon atoms and 2 oxygen atoms (DN-8 and PN-8). (ii) The value of F_e/F_m extrapolated to 21 °C is higher for the polymer system than that for the relevant dimer system. This is understandable since the local concentration of ground state naphthyl groups in the vicinity of an excited naphthyl group should be higher in a polymer system than in the corresponding dimer system. (iii) As a matter of course, excimer formation by MN-I or MN-II was not detected in the concentration region studied. (iv) The activation energies (about

Table II
Excimer Formation of Naphthalene Derivatives

Sample	Solvent[a]	T_c,[b] °K	$(F_e/F_m)^{max}$	$\Delta H_{Da}^{\neq}$, kcal/mol	$\Delta\Delta S_{Da}^{\neq}$, eu	$\Delta H_{Dd}^{\neq} - \Delta H_{Da}^{\neq}$, kcal/mol
Naphthalene	THF		0.01			
MN-I	THF		0.01			
PN-1N	THF	250	0.300	1.4	2.8	2.2
PN-2	THF	248	0.140	1.6	2.1	4.4
PN-2	EA	251	0.156	2.0	4.1	3.5
PN-4	THF	241	0.086	1.3	0.2	2.1
PN-8	THF	252	0.110	1.8	3.2	3.1
MN-II	THF		0.01			
DN-2	THF	229	0.102	1.1	0.0	3.3
DN-2	EA	229	0.128	1.2	1.1	3.0
DN-4	THF	228	0.110	1.0	−0.1	2.9
DN-8	THF	210	0.05[c]	1.6[c]	1.4[c]	1.6[c]

[a] THF, tetrahydrofuran; EA, ethyl acetate. [b] Temperature at which F_e/F_m is maximum. [c] Approximate values.

2 kcal/mol) determined for the excimer formation of polystyrene[7,8] and polyvinylnaphthalene[5,7] are not much different from the present results. The activation energy of excimer formation is nearly independent of polymer structure whereas T_c depends strongly on the kind of polymer. No general trend of $\Delta H_{Da}^{\neq}$ determined for the present series of polymers could be found. Probably, the effect of main chain structure on the activation energy of intramolecular excimer formation is not large. (v) Comparing the dimers and the polymers, the excimer formation by polymers is energetically not advantageous. Consequently, the higher efficiency of excimer formation in the present polymer systems is attributed to a small entropy loss brought about by excimer formation. Naphthyl groups in a polymer molecule are under a sterically restricted condition and therefore the entropy loss caused by taking a face-to-face arrangement with the adjacent naphthyl groups would be smaller in polymer systems. The profile is depicted in Figure 7.

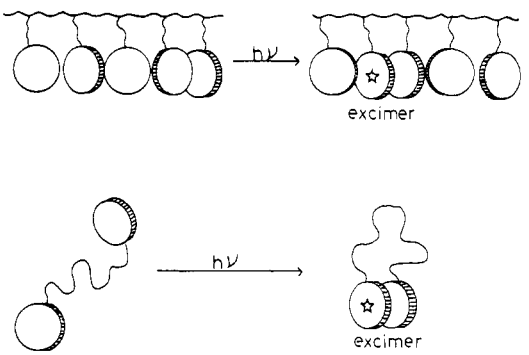

Figure 7. Schematic sketches showing the difference between polymer and dimer in excimer formation. Polymer: Both rotation and translation of the fluorophores are restricted. Dimer: Rotation of the fluorophores is free. The translational freedom of the fluorophores will also be more than that for polymers.

Since excimer formation is a diffusion controlled process, the small $\Delta H_{Da}^{\neq}$ values are considered to be the activation energy of segmental diffusion. Slightly higher values of $\Delta H_{Da}^{\neq}$ for a polymer than that of the corresponding dimer model compound would suggest the restricted mobility of the fluorophore attached to the polymer chain. The thermodynamic parameters are, however, gross quantities, including the effects of temperature on the conformation of polymer molecules in solution, which is not taken into account in the present discussions.

When two fluorophores are connected by methylene groups, separation by three methylene groups brings about the strongest molecular interactions regardless of the fluorophores.[9-11] For example, 1,3-di(9-carbazolyl)propane is capable of forming the intramolecular excimer whereas 1,4-di(9-carbazolyl)butane is not.[11] Even in DN-2, in which the closest approach of the naphthyl group is expected among the present series of dimers, two naphthyl groups are separated by eight methylene groups and two carboxylate groups. The detection of slight but definite excimer formation in all of three dimer model compounds is an unexpected result compared with the information available for α,ω-disubstituted polymethylenes. Specific interactions between ester groups were suspected to participate in enhancing intramolecular excimer formation. However, the intensity of excimer emission was not significantly affected by changing the solvent from THF to ethyl acetate which was expected to destroy any ester–ester interactions.

The difference in concentration dependence of F_e/F_m for the polymers and the dimers is remarkable. As shown in Figure 3, there is a broad correlation between the value of F_e/F_m at infinite dilution and the slope of F_e/F_m vs. [C] plots at concentration over 5×10^{-3} M for the polymer systems. On the other hand, the intermolecular excimer formation in the dimer systems does not exist, at least in the concentration region up to 10^{-2} M, indicating that the intermolecular excimer formation in very dilute solution is a specific feature of the polymers. In the preceding article,[1] results were presented concerning a similar interpolymer association forming an exciplex between the singlet state of carbazole and the ground state of terephthalate. The proposal of polymer association prior to photoexcitation would be applied to the present systems as well. Without the assumption of polymer preassociation, the rate of encounter between polymers (eq 4) would have to be faster than that between smaller molecules since a change in k_{Da} is the most likely reason for the polymer effect. This is a serious contradiction to the known lower translational diffusion constants of polymers than those of smaller molecules.

Experimental Section

Materials. Diethyl[(1-naphthyl)methyl]malonate (1) was prepared by condensation of 1-chloromethylnaphthalene with diethyl malonate.[19] The fraction distilled at 171–2°/0.2 mm was collected.

2-[(1-Naphthyl)methyl]-1,3-propanediol (2). 1 (0.5 g) in 10 ml of dry ether was added dropwise to 0.95 g of lithium aluminum hydride suspended in 15 ml of dry ether. After refluxing 3 h, the crude 2 was separated (3.2 g, 89%). Recrystallization from hot benzene gave colorless plates (3.0 g): mp 80–81 °C; ir (KBr disk) 3340, 2900 cm^{-1}; NMR (acetone-d_6) δ 2.15 (1 H, m, –CH–), 3.20 (2 H, d, $CH_2C_{10}H_7$), 3.60–4.10 (6 H, m, CH_2OH), 7.40–8.50 (7 H, m, aromatic H). Anal. Calcd for $C_{14}H_{10}O_2$: C, 77.75; H, 7.46. Found: C, 77.90; H, 7.53.

2-[(1-Naphthyl)methyl]-1,3-diacetoxypropane (MN-I). The diol (2) was acetylated by refluxing with acetic anhydride. Viscous oil: bp 182 −4 °C (0.5 mm); ir (neat) 1750 cm^{-1}; NMR ($CDCl_3$) δ 2.00 (6 H, s, CH_3), 2.50 (1 H, m, –CH–), 3.10 (2 H, d, $CH_2C_{10}H_7$), 4.07 (4H,

d, $-CH_2O-$), 7.23–8.05 (7 H, m, aromatic H). Anal Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.36; H, 6.85.

3-(1-Naphthyl)-*n*-propanol (3). To suspensions of lithium aluminum hydride (7.1 g) in THF, 14.6 g of β-(1-naphthyl)propionic acid was added dropwise. The product obtained after refluxing for 16 h was separated and distilled at 151–152 °C (0.4 mm) (10.7 g, 83.1%) (lit.[20] 125–127 °C (0.01 mm)).

3-(1-Naphthyl)-*n*-propyl Acetate (MN-II). The alcohol **3** was acetylated by the same method as the preparation of MN-I: bp 182 °C (0.2 mm); ir (neat) 1740 cm^{-1}. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.05; H, 6.98.

Dimer Model Compounds: DN-2, DN-4, and DN-8 were prepared by reactions of **3** with succinyl chloride, adipoyl chloride, and sebacyl chloride, respectively, in benzene and recrystallized from *n*-hexane. DN-2: mp 58–59 °C; ir (KBr disk) 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.90 (4 H, m $-CH_2CH_2CH_2C_{10}H_7$), 2.63 (4 H, s, $-C(=O)CH_2CH_2C(=O)-$), 4.33 (4 H, t, $CH_2C_{10}H_7$), 7.40–8.30 (14 H, m, aromatic H). Anal. Calcd for $C_{30}H_{30}O_4$: C, 79.27; H, 6.65. Found: C, 79.22; H, 6.47. DN-4: mp 66–67 °C; ir (KBr disk) 1732 cm^{-1}. Anal. Calcd for $C_{32}H_{34}O_4$: C, 79.64; H, 7.10. Found: C, 79.41; H, 7.15. DN-8: mp 52–53 °C; ir (KBr disk) 1740 cm^{-1}. Anal. Calcd for $C_{36}H_{42}O_4$: C, 80.26; H, 7.86. Found: C, 80.46; H, 7.69.

Solvents. THF and ethyl acetate were purified by accepted procedures.

Polycondensation. (i) An equimolar mixture of **2** and a dimethyl or diethyl ester of dicarboxylic acid together with a small amount of catalyst was heated gradually in a stream of nitrogen bubbled through the reaction mixture with such a rate that the reaction temperature reached 150–160 °C after 3 h. When the viscosity of the reaction mixture began to increase, the vessel was gradually evacuated to the final pressure of 0.02–0.05 mm during a period of 10 h. The polycondensate was reprecipitated from THF–*n*-hexane.

(ii) An equimolar mixture of **2** and sebacyl chloride was reacted without catalysts or acid acceptors. The evolved hydrogen chloride was removed by bubbling nitrogen through the reaction mixture. The reaction conditions were the same with (i) except for a shorter reaction period of 4–6 h.

Determination of the Degree of Polycondensation. The number of repeating units in a polymer was estimated by GPC using a Toyo Soda HIC-801A (eluting solvent; THF). The molecular weight–count number relation was calibrated for the monomer and dimer model compounds. The determined molecular weight of polymers agreed well with the values determined by means of vapor pressure osmometry.

Fluorescence Spectroscopy. The fluorescence spectra were measured by a Hitachi MPF-4 fluorescence spectrometer. In the concentration region of the present measurements, any corrections for the reabsorption of fluorescence by solutes were not required. As a measure of excimer formation, the ratio of fluorescence intensity at 400 nm (excimer emission, F_e) to the value at 324 nm (monomer emission, F_m) was determined.

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Properties of Monomeric Paramyosin Using Transient Electric Birefringence Techniques[1]

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ABSTRACT: Paramyosin samples obtained from the chowder clam, *Mercenaria mercenaria*, by different extraction techniques were studied using transient electric birefringence techniques. The proteins remain monomeric (unaggregated) in 1 mM buffer solution at pH 3.1 to 3.8 and near pH 10. At pH 3.2, the molecules obtained by different extraction techniques exhibit rotational diffusion constants that indicate a 5% difference in length between them, with the probable native form of paramyosin being the longer species. This difference in rotational diffusion constant disappears at higher pH, and, in addition, a large difference in dipole moment between the molecules observed at pH 3.2 also disappears at high pH. These results are used to hypothesize that the rodlike native paramyosin molecules have one or two partly flexible portions on their ends; at one end of each molecule this portion probably contains excess basic amino acids which are charged at low pH to account for the higher dipole moment of this form of paramyosin at these low pH values. At pH 3.2, these portions of the macromolecule are not flexible and act as stiff parts of the rodlike molecules, but they gradually become flexible at higher pH. Possible mechanisms for this change in flexibility are discussed.

In addition to the myosin and actin that are found in most muscle tissue, molluscan muscles contain large amounts of another fibrous protein, paramyosin. In these muscles, the paramyosin is located in large filaments that are analogous to the myosin-containing filaments found in skeletal muscle. The role of paramyosin in these muscles is thought to be purely structural by some[3] while others have proposed that it plays a major role in the "catch contractions" peculiar to molluscan muscle.[4,5] The "catch contraction" is characterized by the ability of these muscles to contract for long periods of time with the utilization of little or no energy.

It has been shown that paramyosin is a rod-shaped protein with a two-chain α-helical coiled coil structure.[6,7] The two chains, which appear to be identical,[8] probably both run in the same direction giving rise to a molecular polarity. The length of the molecule determined by light scattering[9] and electron microscopy[10] is in the range of 1200 to 1300 Å with some differences between species. The molecular weight lies in the range of 190 000 to 220 000 also with some interspecies differences.[10]

It has been known for some time that different procedures for extracting paramyosin from molluscan muscle result in samples whose properties are appreciably different. One such procedure is the ethanol extraction procedure as developed by Bailey[11] and modified by Johnson et al.[4] In this technique, the paramyosin, along with actin, myosin, and tropomyosin, is extracted from the muscle using a 0.6