July, 1988] *Bull. Chem. Soc. Jpn.*, *61, 2443—2449 (1988)*

Intramolecular End-to-End Reactions of Photoactive Terminal Groups Linked by Poly(oxyethylene) Chains

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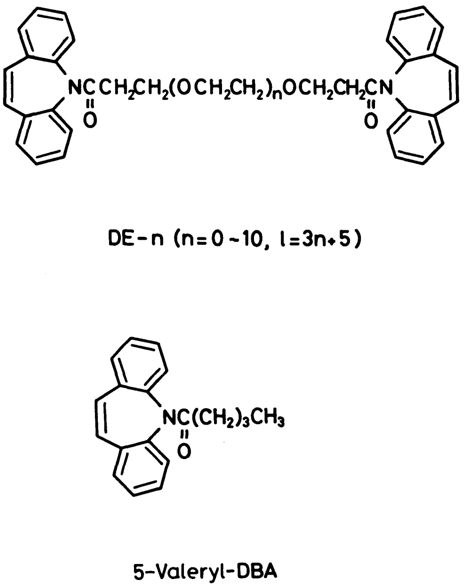
(Received January 8, 1988)

The triplet-sensitized photochemical reaction using a series of poly(oxyethylene) chains with a pair of photoactive terminal groups, dibenz[*b,f*]azepine (DBA) chromophores ($DBA-COCH_2CH_2(OCH_2CH_2)_nOCH_2$-$CH_2CO-DBA$, n=0—10) was examined. The photoirradiation of bichromophoric compounds caused either intra- or intermolecular reactions. These reactions were kinetically analyzed by two different methods: the measurement of deactivation processes of the reaction intermediates (excited triplet state of DBA) by nanosecond laser photolysis and the quantitative analysis of the reaction products by GPC. The intramolecular deactivation rate constant, k^{intra}, showed a remarkable chain-length dependence; the maximum k^{intra} value appeared at $n=5$ and it was found to be $5.9\times10^4\ s^{-1}$. On the other hand, the intramolecular cyclization rate also depends on the chain length; the maximum quantum yield, ϕ_d^{intra}, was given at $n=7$ ($\phi_d^{intra}=0.51$). The chain length for the maximum cyclization yield shifted slightly to the longer region than that for the maximum k^{intra} value due to the restriction of the terminal structure (anti-configuration). The results obtained for this reaction system are compared with those obtained for the previously reported polymethylene system and the effect of chain flexibility on the intramolecular ring-closure reaction is discussed.

Previously, we reported on the intra- and intermolecular end-to-end photochemical reactions of a pair of terminal dibenz[*b,f*]azepine (DBA) chromophores linked by polymethylene chains.[1,2] The probing DBA chromophore undergoes photodimerization via an excited triplet intermediate under the sensitized conditions and gives an anti-cyclobutane dimer as a unique reaction product.[3,4] In contrast with other intramolecular ring-closure reactions reported in the past,[5–15] these characteristics of DBA chromophore give the following features to this reaction system: (1) The reaction intermediate, the triplet state of DBA chromophore, has a long lifetime, 17 μs, so a wide range of chain lengths can be pursued for the cyclization reaction. (2) Ring-closure probability of specific chain conformation can be obtained, since two terminal DBA groups must approach each other from an opposite side for the cycloaddition reaction to make the anti-cyclobutane ring.

Our previous results, obtained for the polymethylene system, demonstrated that the intramolecular cyclization rate is pronouncedly controlled by the chain length connecting a pair of terminal DBA groups and that the terminal direction of a molecular chain exerts a great influence upon the chain-length dependence of the intramolecular ring-closure reaction.[1] That is, we concluded in the previous work that the intramolecular reaction yield is determined by the equilibrium ring-closure probability of a molecular chain. Generally, the cyclization reaction is considered to be affected not only by the chain length, but also by the chain nature. Sisido et al. carried out intrachain reactions of a pair of reactive groups attached to both ends of the polysarcosine chain,[16] and poly(oxyethylene) chain[17] and the intrachain reactivities were compared among the polymer chains. They showed that the intrachain reaction of the polysarcosine chain proceeds more effectively than that of the poly(oxyethylene) chain and that the intrachain reaction of the polysarcosine chain is more efficient than that of the polymethylene chain by two or three times. The flexibility of a molecular chain is expected to be one of the most important nature in determining the reaction yield of the cyclization; that is, a flexible molecular chain will show a higher cyclization yield than a rigid one.

In the present work, we investigated the intra- and intermolecular end-to-end reaction of bichromophoric poly(oxyethylene) compounds, as shown in Fig. 1. These compounds are denoted as DE-*n* (n=0—10, $l=3n+5$). Hereafter, "n" represents the number of



DE-n (n=0~10, l=3n+5)

5-Valeryl-DBA

Fig. 1. A series of poly(oxyethylene) compounds having a pair of DBA groups as the terminal reactants, DE-*n* (n=0—10). Monomeric compound, 5-valeryl-DBA, is also shown.

oxyethylene units, and "l" the number of atoms in the poly(oxyethylene) chain. The experimental results obtained for this system were compared with those obtained for the polymethylene system and the effect of chain nature on the intramolecular cyclization was examined.

Experimental

Materials. Bichromophoric Compounds: A series of poly(oxyethylene) compounds having a pair of dibenz[*b,f*]-azepine (DBA) as the terminal groups were synthesized according to the procedure reported by Kricka et al.,[18] i.e., by an acylation reaction of the corresponding poly(oxyethylene)dicarboxylic acid dichloride with 5*H*-DBA. For example, 5,5′-(4,7,10,13,16,19-hexaoxadocosanedioyl)bisdibenz[*b,f*]azepine (DE-5) was prepared as follows. Hexaoxadocosanedicarboxylic acid dichloride (1.1 g) in dry benzene was added dropwise to a stirred benzene solution of 5*H*-DBA (1.0 g, Aldrich) at room temperature. The reaction mixture was refluxed for 5 h, then cooled and washed with water. A solution of the reaction mixture was dried with calcium chloride, and evaporation of the solvent afforded a yellow oily product. The product was purified by column chromatography on neutral alumina eluted with the mixture of dichloromethane and methanol (500:3). A series of other bichromophoric compounds, except for DE-0, were prepared by the same procedure as DE-5. DE-0 was obtained by an acylation reaction of 5*H*-DBA with 3,3′-oxybis-(propanoyl chloride). All obtained compounds were identified by IR, UV, and NMR spectra. The spectra for the obtained bichromophoric compounds showed the same characteristic spectra. The data were as follows: IR (KBr); 3100, 2850, 1660, 1600, 1490, 1370, 1100, 800, and 760 cm^{-1}, UV (CH_2Cl_2); λ_{max}=287 nm, ^{1}H NMR (CD_2Cl_2); δ=1.8—2.8 (m, $-COCH_2CH_2-$), 3.2—3.8 (m, $-OCH_2CH_2O-$), 6.9 (s, $-CH=CH-$), 7.2—7.5 (m, aromatic). The reaction yields of all obtained compounds were about 60%. The purity of the compounds was confirmed by TLC (one spot, on neutral alumina).

Poly(oxyethylene)dicarboxylic Acid Dichlorides: Each poly(oxyethylene)dicarboxylic acid dichloride was prepared from the corresponding poly(oxyethylene)dicarboxylic acid by a reaction with thionyl chloride; e.g., 3,6,9,12,15,18-hexaoxaeicosanedicarboxylic acid dichloride was obtained as follows. 3,6,9,12,15,18-Hexaoxaeicosanedicarboxylic acid dissolved in thionyl chloride was heated at 50°C for 1 h under stirring. When the evolution of hydrogen chloride stopped, the excess thionyl chloride was removed by distillation and an acid chloride was obtained. A series of other acid chlorides were obtained by the same procedure as 3,6,9,12,15,18-hexaoxaeicosanedicarboxylic acid dichloride.

Poly(oxyethylene)dicarboxylic Acids: Each poly(oxyethylene)dicarboxylic acid was prepared by the hydrolysis of the corresponding poly(oxyethylene)dicarbonitrile with hydrochloric acid; e.g., 3,6,9,12,15,18-hexaoxaeicosanedicarboxylic acid was obtained as follows. 3,6,9,12,15,18-Hexaoxaeicosanedinitrile was dissolved in hydrochloric acid (12 M (1 M=1 mol dm^{-3})) and was refluxed for 5 min; then the water was removed by distillation. The residue was extracted by dichloromethane and the evaporation of dichloromethane afforded 3,6,9,12,15,18-hexaoxaeicosanedicarboxylic acid. A series of acids were obtained by the same procedure as 3,6,9,12,15,18-hexaoxaeicosanedicarboxylic acid.

Poly(oxyethylene)dicarbonitriles: Each poly(oxyethylene)-dicarbonitrile was prepared by an addition reaction of acrylonitrile to poly(ethylene glycol); e.g., 3,6,9,12,15,18-hexaoxaeicosanedinitrile was prepared as follows. Acrylonitrile in benzene was added dropwise to the benzene solution of pentaethylene glycol under stirring in the presence of potassium hydroxide as a catalyst. The reaction mixture was stirred for 1 h at room temperature. After the insoluble substance was filtered off, benzene was evaporated to yield 3,6,9,12,15,18-hexaoxaeicosanedinitrile. A series of other nitriles were obtained by the same procedure as 3,6,9,12,15,18-hexaoxaeicosanedinitrile.

Polyethylene Glycols: Commercial polyethylene glycols (Tokyo Kasei) were used for the shorter chains than tetraethylene glycol. A series of polyethylene glycols longer than tetraethylene glycol were prepared according to the procedure of Pedersen,[19] i.e., by the Williamson method. For example, pentaethylene glycol was prepared as follows. Potassium hydroxide was dissolved in excess ethylene glycol (Wako) under stirring. 1,2-Bis(2-chloroethoxy)ethane (Tokyo Kasei) was added to the solution and heated at 80 °C for 48 h. The reaction mixture was cooled to room temperature and potassium chloride was filtered off. After unreacted ethylene glycol was removed by distillation under reduced pressure, pentaethylene glycol was obtained by fractional distillation under highly reduced pressure. Other polyethylene glycols were obtained by a similar procedure.

Benzophenone (BP, Wako) used as the triplet sensitizer was purified by recrystallization from ligroin several times and dried in vacuo.

Dichloromethane used as the solvent was purified as follows. Dichloromethane was washed with sulfuric acid and water, and then washed with 10% sodium hydroxide aqueous solution and with water till it became neutral. Dried 1,2-dichloroethane with calcium chloride was distilled twice over calcium hydride.

Laser Photolysis. An NEC SLG 2009 ruby laser was used for laser photolysis.[20] The concentration of the deaerated sample solutions was in the range 5.0×10^{-4} to 2.0×10^{-3} mol l^{-1} in chromophore units. The concentration of BP used as the triplet sensitizer was 2.5×10^{-3} mol l^{-1} for all sample solutions. Samples were excited by the second-harmonic pulse (347 nm, 16 ns, 3.02×10^{-8} einstein/pulse). The laser power was attenuated by a suitable combination of filters, so that the absorbance of the $T_n \leftarrow T_1$ absorption was less than 0.2. Under such conditions, the T–T annihilation process became negligibly small.

Photoirradiation. Photoirradiation was carried out for 0.5 h in a thermostat kept at 25 °C. A Toshiba 300-W high-pressure mercury lamp was used as the excitation source. A 365-nm mercury line was selected through a combination of filters: a Toshiba UVD-2 and a Corning C.S. 0-52. The concentration of bichromophoric compounds in the deaerated solution was adjusted to be 2.0×10^{-3} mol l^{-1} with respect to the chromophore concentration. The concentration of BP was 2.5×10^{-3} mol l^{-1}. All sample solutions were filled in a 1-cm quartz cell and deaerated by several freeze-pump-thaw cycles at ca. 10^{-6} Torr (1 Torr=133.322 Pa).

The number of photons at 365 nm was measured to be 1.89×10^{-9} Einstein cm^{-2} s^{-1} by the potassium trioxalatoferrate(III) actinometry.[21)]

Product Analysis. Intra- and intermolecular photoreaction products were analyzed by a Toyo Soda HLC 802 UR gel permeation chromatograph with double G2000H columns eluted by THF. UV, IR, NMR spectra of the products were measured by a Shimadzu UV-200 S double-beam spectrophotometer, by a JASCO IR-G infrared spectrophotometer, and by a JEOL FX-90 Q NMR spectrometer using TMS as an internal standard, respectively. The spectroscopic data for the obtained products were as follows. The IR spectra for the intra- and intermolecular products showed the same characteristic spectra: IR (KBr); 1660 (s, C=O), 1450 $\mathrm{cm^{-1}}$ (m, CH). All intermolecular reaction products showed the same characteristic ^{1}H NMR spectra: ^{1}H NMR (CD_2Cl_2); δ=1.9—2.7 (m, methylene), 3.4—3.7 (m, oxyethylene), 6.9 (s, ethylenic), 7.1—7.5 (m, aromatic). For all intramolecular cyclomers the chemical shifts of the ^{1}H NMR spectra were as follows: ^{1}H NMR (CD_2Cl_2); δ=2.5—4.1 (m, oxyethylene), 4.0 (s, methine), 6.9—7.7 (m, aromatic).

Results and Discussion

Intra- and Intermolecular End-to-End Interactions Measured by Nanosecond Laser Photolysis. The absorption spectra of a series of bichromophoric compounds, DE-*n* (*n*=0—10), in dichloromethane were found to be independent of the chain length (*l*) and were identical with the monomeric compound, 5-valeryl-DBA (λ_{max}=287 nm).[4)] This fact shows that a pair of terminal DBA groups of these bichromophoric compounds do not have any specific interaction with each other in the ground state.

Intra- and intermolecular end-to-end interactions in the excited triplet state were examined by nanosecond laser photolysis through the kinetic analysis of the deactivation processes of the terminal DBA triplet. Benzophenone (BP) sensitized $T_n \leftarrow T_1$ absorption spectra of the bichromophoric compounds in dichloromethane at room temperature were independent of the chain length (*l*) and identical with those of the bichromophoric polymethylene compounds reported previously.[1)] The $T_n \leftarrow T_1$ absorption band of the DBA triplet for DE compounds (λ_{max}=420 nm) hardly overlaps with that of the BP triplet (λ_{max}=520 nm). Therefore, the decay curves at 400 nm and 520 nm were unambiguously analyzed. Figure 2 shows the scheme of BP sensitization and the deactivation processes of the sensitized DBA triplet in the bichromophoric compounds. In this figure, BP and ^{3}BP* represent benzophenone in the ground state and in the excited triplet state, respectively. DBA–DBA represents a bichromophoric molecule in the ground state and ^{3}DBA*-DBA in the excited triplet state of the bichromophoric molecule. The rate constant, k_n^s, is the sum of the rate constants for all unimolecular decay processes of the triplet BP, and k_t the rate constant for the triplet–triplet (T–T) energy transfer from BP to a terminal DBA group. The rate constant, k_n, is the sum of the rate constants for all unimolecular decay processes of the excited triplet state of DBA, k_n^{intra} the rate constant of the triplet deactivation by intramolecular quenching, and k_d^{intra} the rate constant of the intramolecular ring-closure reaction, and k_n^{inter} the rate constant of the deactivation by intermolecular quenching, k_d^{inter} the rate constant of intermolecular cycloaddition reaction. The decay processes are roughly divided into two routes: one is a decay path in which the excited triplet DBA group is self-quenched and gives no reaction product, a kind of genuine concentration quenching process; the other is a decay path in which the terminal DBA group in the excited state reacts with that in the ground state and gives the photoproducts. Each decay path consists of intramolecular and intermolecular processes.

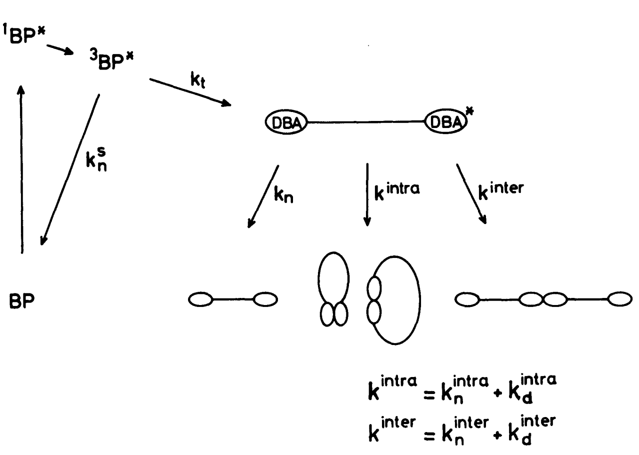


Fig. 2. T–T energy transfer from benzophenone to the bichromophoric compounds and deactivation processes of the excited triplet state of the bichromophoric compounds.

The lifetime of the BP triplet (τ^D) was measured at several concentrations of DE molecules which were the triplet energy acceptor. The Stern–Volmer equation for the lifetime of the BP triplet is expressed as follows:

$$\tau_0^D/\tau^D = 1 + \tau_0^D k_t[\mathrm{DBA}], \qquad (1)$$

where τ_0^D is the lifetime of the BP triplet in the absence of the DE molecule ($\tau_0^D = 3.6\times10^{-6}$ s),[4)] and [DBA] the concentration of DBA chromophore. The plot of τ_0^D/τ^D against the concentrations of DBA chromophore for all DE compounds showed a straight line, and from the slope of the line the rate constant for a T–T energy transfer, k_t, was estimated for each DE compound. Figure 3 shows the chain-length dependence of the k_t value. The k_t value is almost independent of the chain length of DE compounds and is close to the diffusion-controlled rate constant ($k_t \approx 2\times10^9\ \mathrm{M^{-1}\,s^{-1}}$). This tendency and the k_t value itself are almost the same as those for the polymethylene system.[1)] In this low-molecular-weight region, the diffusion rate constant is presumed to be independent of the molecular size.[22)]

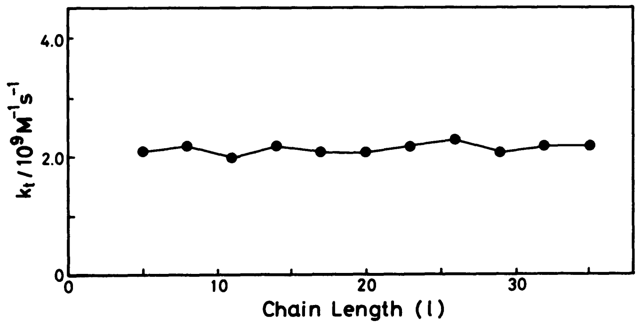


Fig. 3. Chain length dependence of the rate constant of T-T energy transfer, k_t, from benzophenone to a terminal DBA group of poly(oxyethylene) compound in dichloromethane at room temperature.

The lifetime of the terminal DBA triplet, τ^A, in this reaction system is represented by the following equation:

$$1/\tau^A = k_n + k^{intra} + k^{inter}[DBA], \qquad (2)$$

where k^{intra} is the sum of the rate constants of k_n^{intra} and k_d^{intra} ($k^{intra}=k_n^{intra}+k_d^{intra}$), k^{inter} the sum of k_n^{inter} and k_d^{inter} ($k^{inter}=k_n^{inter}+k_d^{inter}$). The lifetime of the terminal DBA triplet was measured for several concentrations of the DE compound, and the plot of $1/\tau^A$ against the concentration of the terminal DBA group gave a straight line for each compound. From the intercept in this plot, the k_n+k^{intra} value was obtained. The k^{intra} value for each bichromophoric compound was determined by subtracting the k_n value from the k_n+k^{intra} value, since the k_n value is considered to be inherent to the DBA chromophore. In this case, the k_n value is assumed to be equal to the k_n^A value obtained for the monomeric compound, 5-valeryl DBA, which was reported previously ($k_n=k_n^A=5.9\times10^4$ s^{-1}).[4] Figure 4 shows a plot of the k^{intra} value obtained in this reaction system against the chain length of the bichromophoric compounds, together with the results obtained in the previous polymethylene system. In this figure, it is apparent that the k^{intra} value is strongly dependent on the chain length. The peak of the k^{intra} value corresponding to the first peak in the polymethylene system was not observed in the poly(oxyethylene) system. In the present system, the shortest chain length (l) was 5 (n=0). Therefore, the first peak for intramolecular interaction exists presumably at a chain length shorter than l=5.

In the range of the chain length l=5 to 11, the k^{intra} values are very small compared with those of other chain lengths. This tendency in this system is almost the same as that in the polymethylene system reported previously. This means that poly(oxyethylene) chains in this region can hardly take a favorable or stable ring conformation intramolecularly.

On the other hand, the k^{intra} value increases with increasing chain length beyond l=11 and the maximum value appears at l=20. This indicates that a strong interaction occurs intramolecularly between a pair of terminal DBA groups with this extent of separation. At this chain length, the poly(oxyethylene) chain takes a favorable conformation for the terminal DBA groups to interact with each other. This experimental finding indicates that ring-closure probability of a poly(oxyethylene) chain reaches the maximum at the chain length l=20. For the poly(oxyethylene) system, the chain length which gives the maximum value of k^{intra} is slightly longer than that for the polymethylene system. This effect is due to an increasing contribution of k_d^{intra} to the k^{intra} value, which will be discussed in the following section. That is, the k_d^{intra} value increases sharply at l=20 in the poly(oxyethylene) system and the chain length for the maximum value of k^{intra} shifts to a longer region than that for the polymethylene system.

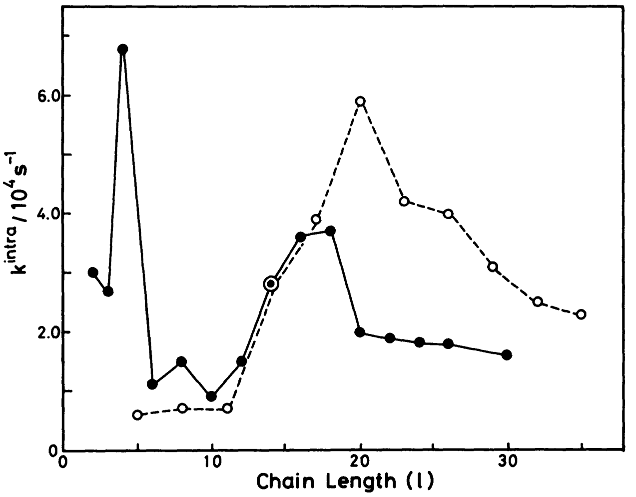


Fig. 4. Chain length dependence of the rate constant of intramolecular interaction, k^{intra}, for poly(oxyethylene) system (○), and polymethylene system (●) at room temperature.

A theoretical treatment for the intramolecular ring-closure probability of a poly(oxyethylene) chain (C-O-(-C-C-O-)$_m$-C, m=3—20) was carried out by Sisido et al.[23] They calculated the ring-closure probability of a poly(oxyethylene) chain by the Monte Carlo Method. In their calculation, the maximum ring-closure probability appears at m=4 or 5 (the number of atoms in the chain is 15 or 18) under the critical distance between the chain ends, r_0=6 or 4 Å, respectively. The calculated result is different from their experimental findings. They concluded that this discrepancy is attributed to the effect of the bulky terminal groups attached to the poly(oxyethylene) chain. In our experimental examination, the maximum k^{intra} value appears at n=5 (l=20). This chain length is also longer than the chain length of the maximum ring-closure probability calculated by the Monte Carlo Method. The difference between our experimental findings in the present system and their calculated results may be attributed to the effect of the terminal DBA groups.

In the region of the chain length $l \geqq 17$, the k^{intra} values in this system are larger than those in the polymethylene system. This indicates that the collisional frequency of the terminal reactants in the poly(oxyethylene) system is higher than that in the polymethylene system. The difference of collisional frequencies in the two systems is due to the difference of the flexibility between two molecular chains connecting terminal DBA groups. Yamakawa et al. have investigated the chain stiffness of flexible chain polymers on the basis of helical wormlike chains.[24,25] They defined the parameters λ^{-1} and τ/τ^0 as the static chain stiffness and the dynamic chain stiffness, respectively, where τ and τ^0 are the correlation time of a flexible chain and that of the monomer unit, respectively. The larger the parameter λ^{-1}, the statically stiffer the chain, and the larger the parameter τ/τ^0, the dynamically stiffer the chain. They showed that there is a good correlation between the dynamic stiffness τ/τ^0 and the static stiffness λ^{-1}; τ/τ^0 is a monotonically increasing function of λ^{-1}. According to their theoretical estimate, the value λ^{-1} is 14.5 and 12.0 Å for the polymethylene chain and for the poly(oxyethylene) chain, respectively. Hence, the poly(oxyethylene) chain is considered to be more flexible than the polymethylene chain from a dynamic standpoint as well as from a static one. Our experimental results agree well with their theoretical prediction.

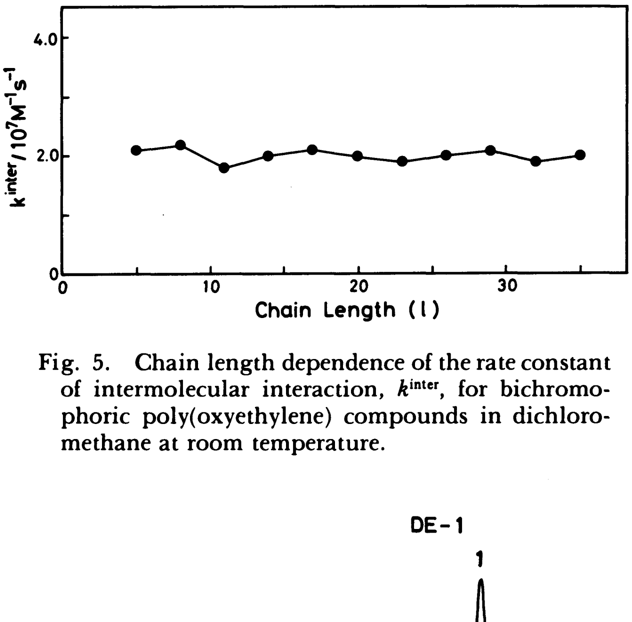


Fig. 5. Chain length dependence of the rate constant of intermolecular interaction, k^{inter}, for bichromophoric poly(oxyethylene) compounds in dichloromethane at room temperature.

The rate constant, k^{inter}, was determined from the slope of the straight line obtained by the plot of $1/\tau^A$ against the DBA concentration. Figure 5 shows a plot of the k^{inter} value against the chain length of the DE compounds. It is apparent that the rate constant for the deactivation by intermolecular interaction k^{inter}, is independent of the chain length of the poly(oxyethylene) chain. The k^{inter} values in this system are nearly equal to those in polymethylene system reported previously ((1—2)$\times 10^7$ M^{-1} s^{-1}).[1] The absence of the influence of chain length on the rate constant k^{inter} is partly due to an activation-controlled process[26] and partly due to the rather small molecular weights of the bichromophoric compounds.

In this section, the ring-closure probability of a poly(oxyethylene) chain was examined through an analysis of the intramolecular deactivation rate constant, k^{intra}; the experimental results indicate that the flexibility of a moleculr chain exerts a great influence upon the ring-closure probability.

Intra- and Intermolecular End-to-End Cycloaddition Reactions. A series of bichromophoric compounds, DE-*n* (*n*=0—10), which are excited by a T-T energy transfer from BP, have two kinds of reaction paths (Fig. 2): intramolecular ring-closure reaction and intermolecular dimer formation reaction.

Figure 6 shows typical GPC diagrams of the reaction products obtained after 0.5 h irradiation. For DE-1, only one intermolecular reaction product **2** was

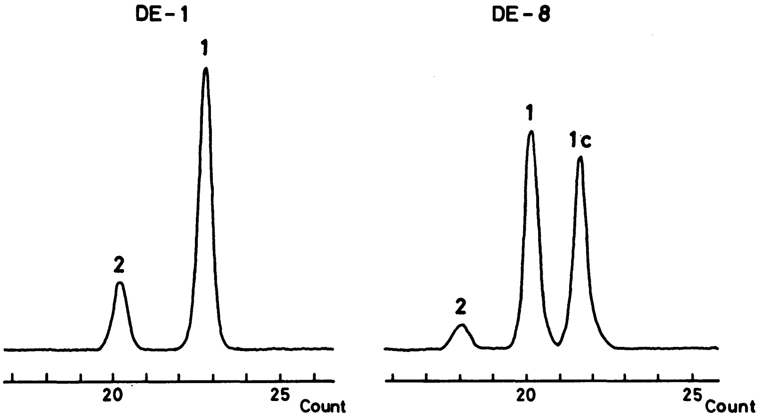


Fig. 6. Typical GPC diagrams of photoreaction products obtained by 0.5 h irradiation of bichromophoric compounds, DE-1 and DE-8. Unreacted monomer **1**, intramolecular ring-closure product **1c**, and intermolecular dimer **2**.

detected at 20.2 counts, together with the residual unreacted monomer **1** at 22.7 counts. This situation is the same as that for the shorter-chain compounds. The intramolecular reaction does not occur, since the oxyethylene chain is too short for a pair of terminal DBA group to form intramolecularly. On the other hand, with longer-chain compounds, such as DE-8, not only the intermolecular reaction product **2** at 18.0 counts but also the intramolecular ring-closure product **1c** at 21.6 counts was detected together with the unreacted monomer **1** at 20.0 counts. A GPC analysis showed that an intramolecular ring-closure product is produced for samples of $l \geqq 14$, but not for samples of $l \leqq 11$. These experimental facts can be explained in terms of the configuration of the terminal groups; DBA group forms only anti-cyclobutane ring[4] and for the compounds having an oxyethylene chain shorter than $l=14$, a pair of terminal DBA groups cannot take a favorable orientation to form an anti-cyclobutane ring intramolecularly. Such a chain-length dependence of the intramolecular ring-closure reaction for this system is almost the same as that for the polymethylene system; in the polymethylene system, the intramolecular ring-closure product cannot be detected for the compounds having a chain shorter than $l=14$.[1]

The quantum yields of both the intra-and intermolecular cycloaddition reactions in each bichromophoric compound were determined by the quantitative analyses of the reaction products with GPC. In these BP-sensitized systems, the quantum yields for the intramolecular ring-closure product (ϕ_d^{intra}) and for the intermolecular dimer (ϕ_d^{inter}) are defined as follows:

ϕ_d^{intra} = the number of intramolecular ring-closure products/the number of photons absorbed by BP,

ϕ_d^{inter} = the number of intramolecular dimers/the number of photons absorbed by BP.

As described in the previous section, the rate constant of a T–T energy transfer, k_t, is almost independent of the chain length, and the efficiency of a triplet energy transfer from BP to the terminal DBA group is close to unity. Therefore, the values, ϕ_d^{intra} and ϕ_d^{inter}, are nearly equal to the quantum yields defined by the ratio of the number of the product molecules to the number of initial molecules in the excited triplet state.

The effect of the chain-length dependence of the intramolecular ring-closure reaction was examined. Figure 7 shows a plot of the quantum yield for intramolecular ring-closure reaction against the chain length, l ($l=3n+5$) for the poly(oxyethylene) system, together with the values obtained for the polymethylene system. The quantum yield increases sharply for a chain length $l=20$ and the maximum quantum yield of the intramolecular ring-closure reaction appears at $l=26$ (DE-7). The chain length that gives the maximum quantum yield of the intramolecular ring-closure reaction is different from that of the intramolecular end-to-end interaction: in other words, the chain length for the maximum quantum yield of intramolecular ring-closure reaction shifts to chains longer than that for the maximum intramolecular deactivation rate constant. The NMR examination shows that a pair of terminal DBA groups of intramolecular ring-closure products forms an anti-cyclobutane ring. This suggests that a pair of terminal DBA groups take the most favorable orientation for the anti-cyclobutane formation at the chain length $l=26$, i.e., the ring-closure probability for a pair of terminal bonds to be put in an opposite direction becomes maximum at $l=26$. The chain length which gives the maximum quantum yield ϕ_d^{intra} for the poly(oxyethylene) system is in fair agreement with that for the polymethylene system.

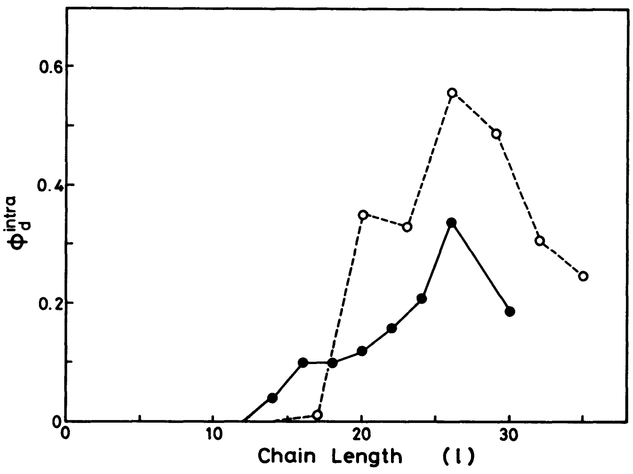


Fig. 7. Chain length dependence of the quantum yield of intramolecular ring-closure reaction, ϕ_d^{intra}, for bichromophoric compounds, poly(oxyethylene) system (○), and polymethylene system (●), in dichloromethane at 25 °C.

Figure 8 shows a plot of the quantum yield of the intermolecular dimerization against the chain length. In this figure, the ϕ_d^{inter} values show a marked dependence on the chain length. This is in contrast to the independence of the k^{inter} value on the chain length in the previous section (Fig. 5). This chain-length dependence of the ϕ_d^{inter} value is probably due to the influence of the triplet lifetime of the terminal DBA group. The lifetime is mainly determined by the k^{intra} value. Compounds $l \geqq 14$ have large k^{intra} values compared with compounds $l \leqq 11$. This therefore reduces the intermolecular reaction rate for the longer-chain compounds. That is, because of the short lifetime for $l \geqq 14$, these compounds have little chance to react with other DBA groups intermolecularly. Hence, ϕ_d^{inter} values are low in this region of chain length. In addition, the ϕ_d^{inter} values in the poly(oxyethylene) system are nearly the same as those of the previous polymethylene system in the range of

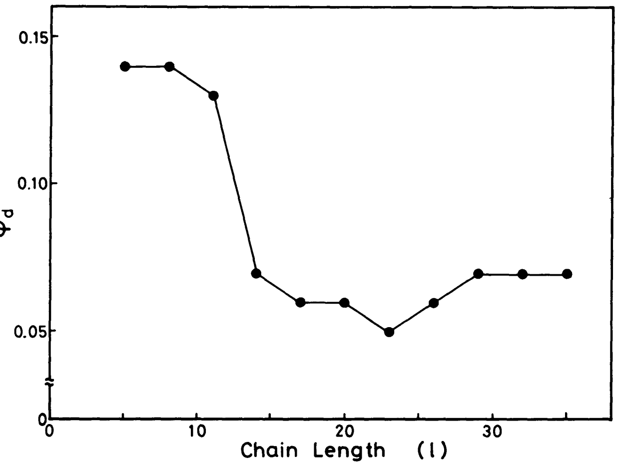


Fig. 8. Chain length dependence of the quantum yield of intermolecular dimerization, ϕ_d^{inter}, for bichromophoric poly(oxyethylene) compounds in dichloromethane at 25 °C.

the short chain length ($\phi_d^{inter} \simeq 0.14$). This trend implies that intermolecular dimerization is not affected by the nature of a molecular chain: it is controlled by the lifetime of the terminal reactants.

In the present work, the chain length which gives the highest ring-closure probability of a poly(oxyethylene) chain was found to be $l=20$ ($n=5$) by laser photolysis. On the other hand, the maximum quantum yield for the ring-closure reaction appears at a longer chain length, $l=26$ ($n=7$): that is, a longer chain length is needed for the intramolecular ring-closure reaction. In this case, the terminal bonds must point to opposite directions to take anti-configuration, that is, the chain length which yields the maximum quantum yield for the ring-closure reaction shifts to a longer chain length. In the present system, the steric factor of a pair of terminal groups must be considered in an examination of the intramolecular reaction probability. It is concluded that the reaction yield of the intramolecular ring-closure reaction is determined by the equilibrium ring-closure probability of a molecular chain with a certain direction of terminal bonds. Furthermore, the ϕ_d^{intra} values for the poly(oxyethylene) system are larger than those for the polymethylene system. This means that the effective concentration of a terminal group of poly(oxyethylene) in the vicinity of the other terminal group is higher than that in a polymethylene system, i.e., the ring-closure probability of a poly(oxyethylene) chain in equilibrium is higher than that of a polymethylene chain. The flexibility of a molecular chain is said to be one of the most important factors in determining intrachain reactivity.

This work was supported by a Grant-in-Aid for Special Project Research, No. 61123006, from the Ministry of Education, Science and Culture.

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