

Stepwise Photopolymerization of Bichromophoric Chains by Cycloaddition of Dibenz[*b,f*]azepine Groups

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ABSTRACT: Triplet-sensitized stepwise photopolymerization was carried out with a bichromophoric polymethylene compound. There is a critical chain length in this polymerization system, beyond which the linear oligomer becomes photopolymerized. The critical chain length P_n (the degree of polymerization) was 3. The propagation rate of this polymerization decreased rapidly at a high conversion (>99.5%). The data obtained on this polymerization by laser photolysis was analyzed kinetically. The decrease of the concentration of the terminal photoactive reactant, dibenz[*b,f*]azepine (DBA) group, decreases both triplet-triplet (T-T) energy transfer efficiency and intermolecular reaction efficiency. As the chain length becomes longer, the intrinsic rate of deactivation of the terminal reactant exceeds the propagation rate. Then polymerization proceeds very little.

KEY WORDS Dibenz[*b,f*]azepine / Laser Photolysis / Inter- and Intramolecular Cycloaddition / Sensitized Photopropagating Polymerization / T-T Energy Transfer / Bichromophoric Compound / Cyclomer /

A number of "photopolymerization" systems, most of which consist of polymerization of vinyl compounds, has been reported.^{1,2} The light absorption process participates only in the initiation step of these polymerizations systems. Active species, which are radical species in most cases, are generated by photoexcitation, and initiate the polymerization of vinyl compounds. The polymerization of these active species usually continues even in the dark. In other words, the process of light absorption does not participate in the propagation of the "photopolymerization" of vinyl compounds.

On the other hand, bichromophoric compounds, *e.g.*, a polymethylene chain having a pair of photodimerizable compounds as the terminal reactant, are able to undergo the intermolecular cycloaddition reaction. The

consecutive intermolecular photochemical reaction is regarded as "photopolymerization." In this type of photopolymerization, the absorption of light is indispensable for the propagation step. This point is very different from the "photopolymerization" of vinyl compounds mentioned above.

De Schryver and his co-workers pointed out that photopolymerization is divided into two types.³ One is a polymerization in which an excited state, singlet and/or triplet, is induced in each propagation step,⁴⁻⁹ and the other is a polymerization in which each propagation reaction occurs by the reaction of a ground state species generated in a prior photochemical reaction. The former type of polymerization is a "photopropagating polymerization," and the latter is a "photoinitiated polymerization." In this sense, we have distin-

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guished between "sensitized photopropagating polymerization" and "sensitized photo-initiated polymerization." The former is the polymerization in which the end group chromophore is excited by energy transfer at each reaction step, and the latter is used for radical or the ionic chain reaction initiated by a photosensitive compound.

In the present work, benzophenone-sensitized photopolymerization was investigated from a synthetic viewpoint by using a bichromophoric compound, DC-10 (see Figure 1), which has a pair of terminal dibenz[b,f]azepine (DBA) groups as photo-active reactants at the ends of the *n*-decane chain. Triplet sensitized DBA gives rise to the cycloaddition reaction and forms a dimeric product¹⁰ which has *anti*-configuration.¹¹ In general, a bichromophoric compound like DC-10 can give two kinds reaction products: an intermolecular cycloadduct and an intramolecular cyclomer. In the present reaction system, however, the monomer of DC-10 never gives the intramolecular cyclomer, since a pair of terminal DBA cannot take *anti*-configuration intramolecularly in this chain length. Therefore, the monomer of DC-10 causes only the intermolecular cycloaddition reaction. In this system, every chain-

propagation step involves the excitation of the terminal DBA by T-T energy transfer from benzophenone, and the triplet excited DBA gives rise to a cycloaddition reaction. Therefore, this stepwise intermolecular cycloaddition reaction is named "triplet-sensitized photopropagating polymerization." Furthermore, kinetic analysis by laser photolysis clarified the feature of "photopropagating polymerization" in this bichromophoric system.

EXPERIMENTAL

Materials

The bichromophoric compound, DC-10, was synthesized by the acylation reaction of decanedicarboxylic acid chloride with 5*H*-DBA. Decanedicarboxylic acid chloride was prepared from decanedicarboxylic acid by the reaction with thionyl chloride. Decanedicarboxylic acid chloride dissolved in dry benzene was added dropwise to a stirred solution of 5*H*-DBA in benzene at room temperature. The reaction mixture was refluxed for 5 h, then cooled and washed with water. The 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 a mixture of dichloromethane and methanol (500:3). The product was recrystallized from ligroin.

Benzophenone was purified by recrystallization from ligroin several times and dried *in vacuo*.

Dichloromethane was used as a solvent and purified in the usual way.

Photoirradiation

Photoirradiation of all sample solutions was carried out at room temperature. A Toshiba 300 W high-pressure mercury lamp was used as the excitation light source. A mercury line 365 nm was selected through a combination of filters: a Toshiba UVD-2 and a Corning C.S.

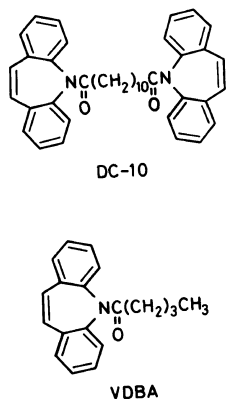


Figure 1. Structure of the bichromophoric compound, DC-10 and the monofunctional compound, 5-valeryl DBA (VDBA).

0-52 filter.

Sample solutions were prepared in glass tubes, 1 cm in diameter and deaerated by several freeze-pump-thaw cycles at *ca.* 10^{-6} Torr.

The concentrations of the chromophore unit and benzophenone were $1.0 \times 10^{-1} \text{ mol l}^{-1}$ and $2.5 \times 10^{-3} \text{ mol l}^{-1}$, respectively. For quantitative analysis, the concentration of benzophenone was $2.0 \times 10^{-2} \text{ mol l}^{-1}$ to increase the efficiency of light absorption at 365 nm.

Product Analysis

Polymers obtained were analyzed by a Toyo Soda HLC 802 UR gel permeation chromatograph with double GMH6 columns and/or double G2000HS eluted by THF. UV, IR, and NMR spectra of the polymers were measured by a Shimadzu UV-200S double beam spectrophotometer, by a JASCO IR-G infrared spectrophotometer, and by a JOEL FX-90Q NMR spectrometer (TMS as the internal standard), respectively. The spectroscopic data for the obtained polymer are as follows: IR (KBr), 1660 cm^{-1} (s, C=O), 1450 cm^{-1} (m, CH); NMR (CDCl_3), $\delta = 1.1\text{--}2.1$ ppm (m, CH_2), $\delta = 2.2\text{--}2.9$ ppm (m, COCH_2), $\delta = 4.0$ ppm (s, CH), $\delta = 6.7\text{--}7.4$ ppm (m, ArH).

Laser Photolysis

An NEC SLG 2009 ruby laser was used for laser photolysis.¹² 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 optical density of $T_n \leftarrow T_1$ absorption was not larger than 0.2. Under such conditions, the T-T annihilation processes became negligible.

RESULTS AND DISCUSSION

Stepwise Photopolymerization

Photopolymerization of DC-10 proceeded in a homogeneous condition and precipitation

did not occur in any sample solutions during irradiation. Polymers produced by repetition of the intermolecular dimerization of terminal DBA groups are colorless and soluble in dichloromethane. This shows that the side reaction, *e.g.*, photo-Fries rearrangement reaction or cross-linking reaction, hardly occurred under the present irradiation conditions.

The IR spectra of these polymers showed the absence of olefinic absorption of DBA groups at 800 cm^{-1} . The ^1H NMR spectra of the polymers show methine protons of the cyclobutane ring at 4.0 ppm, which is formed by a cycloaddition reaction of terminal DBA groups. Not only from the NMR spectra but also from the IR spectra, the repeating cyclobutane rings in the polymers were found to take only an *anti*-configuration.¹¹

Figure 2 shows the GPC diagrams of the crude products with GMH6 columns after different irradiation times. The molecular weight of the product increases with increasing irradiation time. The dependence of molecular weight on the irradiation time indicates

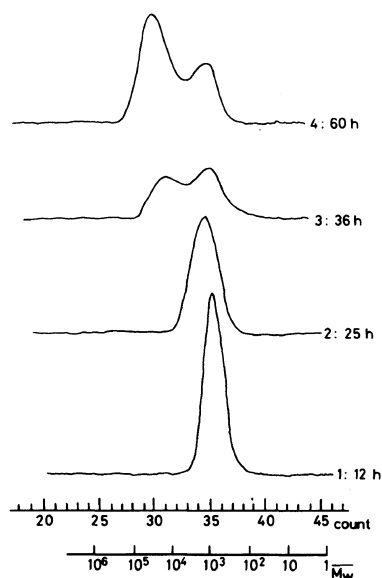


Figure 2. GPC diagrams of crude products after different irradiation times: (1), 12 h; (2), 25 h; (3), 36 h; (4), 60 h.

that this polymerization proceeds by a stepwise addition mechanism. However, elution curves after a long irradiation, *e.g.*, 36 h, show two peaks. The high molecular weight fraction is undoubtedly due to a linear polymer of DC-10, because the GPC elution count number at its peak decreases with increasing irradiation time. In contrast with the high molecular weight fraction, the count number of low molecular weight fraction was unchanged with irradiation time. Further analysis on the low molecular weight fraction by GPC with G2000HS columns (Figure 3) shows that the signals at the 19.3 count and the 17.9 count correspond to the linear dimer and the linear trimer, respectively, with that for the residual monomer at the 21.9 count. At the irradiation time of 25 h, signal intensities for the linear trimer and higher oligomers increased and further, a weak but new signal appeared at the 20.6 count. At the irradiation time of 36 h, the signal for monomer and linear dimers disappeared completely, and the intensity of the

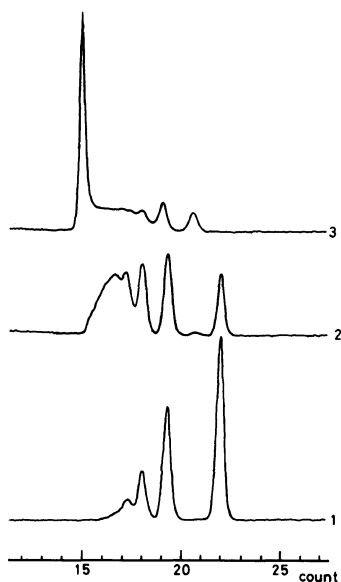


Figure 3. GPC diagrams for the low molecular weight fraction obtained after different irradiation times: (1), 12 h; (2), 25 h; (3), 36 h.

linear trimer decreased remarkably. In contrast to this behavior, the signal at the 20.6 count increased in intensity and another new signal appeared at the 19.0 count. The compounds which gave the new signals on the GPC diagram were fractionated, and were analyzed by IR and NMR spectroscopies. The IR spectra of these compounds showed the disappearance of olefinic absorption at 800 cm^{-1} , and in the NMR spectra, the signal of methine protons of cyclobutane ring at 4.0 ppm appeared instead of ethylenic protons at 6.9 ppm. Furthermore, the numbers of elution count of GPC agreed perfectly with those of the cyclomers of linear dimers and trimers obtained by the excitation of the dilute solution of DC-10 ($[\text{DBA}] = 2.0 \times 10^{-3}\text{ M}$). On the basis of these data, these new signals were assigned to the cyclomers of a linear dimer and a trimer. The intensities of these signals were not affected by the irradiation time beyond 36 h. These cyclomers are excluded from the photocycloaddition reaction.

Yields of monomer, dimers, and trimers after different irradiation times were determined by GPC (Figure 4). This figure shows that the monomer completely disappeared by 36-h irradiation. As shown in Figure 2, the chromatogram at the irradiation time of 60 h

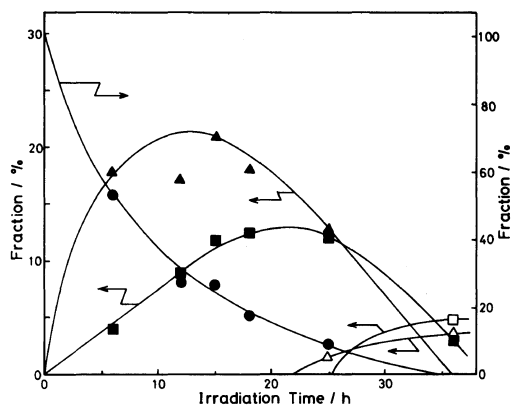


Figure 4. Yields of monomer, dimer, and trimer: (●), monomer; (▲), linear dimer; (■), linear trimer; (△), cyclic dimer; (□), cyclic trimer.

indicates that the molecular weight of the polymer increases compared with that at the irradiation time of 36 h. This means that after the monomer is consumed completely, the propagation reaction is still proceeding. On the other hand, Figure 4 shows that the linear dimer and trimer are formed by consumption of the monomer. After the linear dimer and trimer are produced, cyclodimers start to form.

For the intramolecular cycloaddition reaction in a series of bichromophoric polymethylene systems, the following experimental results have already been obtained¹³: the maximum yield of the reaction is given by the compound having a hexacosane chain (26 methylene unit), and the monomer of DC-10 never gives an intramolecular reaction product, since a pair of terminal DBA cannot take an *anti*-configuration intramolecularly in this chain length. If a linear dimer or trimer gives rise to intramolecular cyclization preferentially, the photopolymerization does not proceed. The intramolecular reaction in polymethylene systems¹³ suggests that intramolecular cyclization occurs most easily for the linear trimer and that the linear trimer which has escaped from the intramolecular cycli-

zation undergoes photopolymerization progressively. Therefore, the oligomers longer than the linear trimer preferentially undergo photopolymerization.

Figure 5 shows the dependence of the degree of conversion, p , and the P_n value, calculated by eq 3, on irradiation time. In this figure, p in the initial time region of irradiation increases rapidly. After long-time irradiation, the increment of p levels off. On the other hand, the P_n value increases very slowly at the initial stage of irradiation. After more than 6 h, P_n begins to increase linearly with increasing irradiation time; that is to say, the degree of polymerization is proportional to irradiation time after a long irradiation. However, at a very high conversion (>99.5%), the linearity between the degree of polymerization and irradiation time does not hold.

This photopolymerization is regarded as a kind of polyaddition reaction of polymerization process. The photopolymerization of a bichromophoric compound was examined quantitatively. In this system, the degree of conversion, p , is represented as:

$$p = (N_0 - N) / N_0 \quad (1)$$

where N_0 is the number of bifunctional DC-10 molecules at the initial time, and N , that after irradiation time t . The total number of cyclobutane rings formed during irradiation time t , is $N_0 - N$. Since two terminal DBA groups are consumed for each intermolecular cycloaddition reaction, the total number of consumed DBA groups is represented as $2(N_0 - N)$. In this bichromophoric compound, the number of terminal DBA groups is $2N_0$ at the initial state. Therefore, the degree of conversion is represented by eq 1.

Furthermore, the number-average degree of polymerization of polymer, P_n , is expressed as:

$$P_n = N_0 / N \quad (2)$$

From eq 1 and eq 2, the following equation is obtained:

$$P_n = 1 / (1 - p) \quad (3)$$

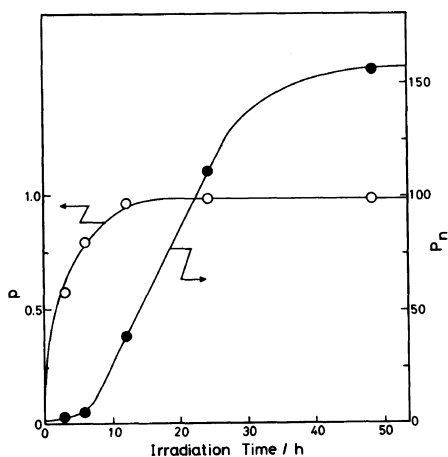


Figure 5. Dependence of the degree of conversion, p , and the number-average degree of polymerization, P_n on irradiation time.

The number of bifunctional DC-10 molecules at irradiation time t , was determined by the UV absorption spectra of terminal DBA group. For this determination, the products were precipitated with *n*-hexane in which benzophenone is soluble, but the monomer and the polymer are almost insoluble. Table I shows the results of the photopolymerization.

Figure 6 shows the plot of the degree of polymerization of the polymer against the degree of conversion. The degree of polymerization of the polymer increases remarkably

Table I. Results of the Photopolymerization of a bichromophoric system, DC-10^a

Irr. time/h	p	\bar{M}_n	P_n
3.0	0.677	1.8×10^3	3.1
6.0	0.801	2.9×10^3	5.0
12.0	0.974	2.2×10^4	38.5
24.0	0.991	6.4×10^4	111.1
48.0	0.994	9.1×10^4	156.3
96.0	0.994	1.0×10^5	172.4

^a \bar{M}_n was estimated by end group analysis from UV absorption spectra of the polymers.

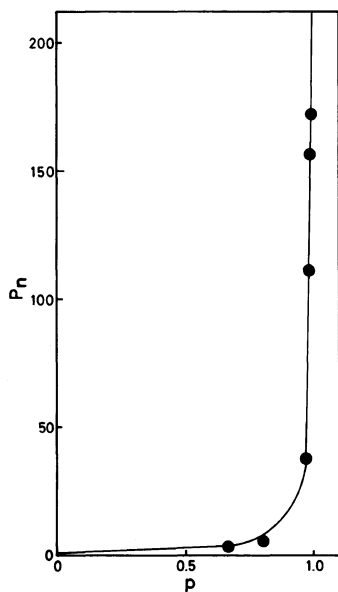


Figure 6. Plot of the degree of polymerization of the polymer, P_n , against the degree of conversion, p .

with conversion, particularly when the degree of conversion comes close to unity. This feature of photopolymerization of DC-10 is well explained by eq 3.

Kinetic Treatment by Laser Photolysis

Figure 7 shows the time course of benzophenone sensitized $T_n \leftarrow T_1$ absorption spectra of DC-10 in dichloromethane at room temperature, with the $T_n \leftarrow T_1$ absorption spectrum of benzophenone in the absence of DC-10 as

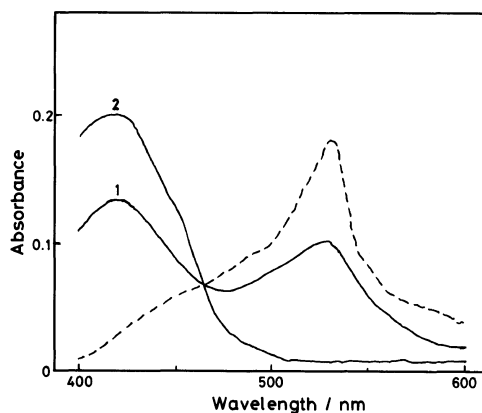


Figure 7. Benzophenone (BP) sensitized $T_n \leftarrow T_1$ absorption spectra of DC-10 in dichloromethane at room temperature: (1) 100 ns after excitation; and (2) 500 ns after excitation [BP] $=2.5 \times 10^{-3}$ mol l⁻¹; [DBA] $=2.0 \times 10^{-3}$ mol l⁻¹. $T_n \leftarrow T_1$ absorption spectrum of benzophenone is also shown as the reference (----).

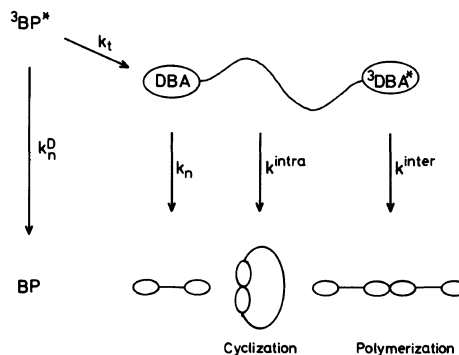


Figure 8. Reaction scheme of the triplet sensitized photopropagating polymerization. BP represents the triplet sensitizer, benzophenone.

the reference. In this figure, it is found that $T_n \leftarrow T_1$ absorption of DC-10 at 420 nm increases with the decreasing $T_n \leftarrow T_1$ absorption of benzophenone at 520 nm by T-T energy transfer, and that the benzophenone triplet is completely quenched by DC-10 at 500 ns after excitation. In these spectra, there is little absorption of the DBA triplet at 520 nm and of the benzophenone triplet at 400 nm. Therefore, the analysis of the decay curves of $T_n \leftarrow T_1$ absorption at 400 nm and 520 nm gives kinetic information about the excited triplet states of DC-10 and benzophenone, respectively.

Figure 8 shows the kinetic scheme of benzophenone sensitized propagation reaction in this polymerization system. According to this scheme, the T-T energy transfer efficiency, ϕ_t , from benzophenone to terminal DBA groups is:

$$\phi_t = k_t[\text{DBA}]/(k_n^D + k_t[\text{DBA}]) \quad (4)$$

where k_t is the rate constant of T-T energy transfer from benzophenone to DBA, k_n^D the sum of the rate constants for all unimolecular decay processes of benzophenone, and $[\text{DBA}]$ the concentration of the DBA group at the polymer ends. The rate parameters in eq 4 can be determined by laser photolysis in dichloromethane at room temperature, where we can directly observe the deactivation of the transient species of the cycloaddition reaction. The lifetime of the benzophenone triplet (τ_0^D) in dichloromethane in the absence of DC-10 is: $\tau_0^D = 1/k_n^D = 3.6 \times 10^{-6}$ s. The lifetime of benzophenone was measured in the presence of the several concentrations of DC-10 which is the triplet energy acceptor. Stern-Volmer plot for the lifetime of benzophenone triplet was found to be linear and from the slope of the straight line, k_t was obtained: $k_t = 3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.¹⁴ From eq 4, it is understandable that the T-T energy transfer efficiency depends on the concentration of the terminal DBA group. On the other hand, the intermolecular reaction efficiency, ϕ^{inter} , of this system is obtained according to the deactivation scheme (Figure

8) as follows,

$$\phi^{\text{inter}} = k^{\text{inter}}[\text{DBA}]/(k_n + k^{\text{intra}} + k^{\text{inter}}[\text{DBA}]) \quad (5)$$

where k_n is the sum of the rate constants for all unimolecular decay processes of DBA groups, k^{inter} the rate constant for the intermolecular interaction, and k^{intra} the rate constant for the intramolecular interaction, which is a function of the degree of polymerization (chain length), P_n . For a high molecular weight polymer, k^{intra} can be ignored, because it is proportional to the -1.5 th power of P_n ,¹⁵ and becomes very small compared with $k^{\text{inter}}[\text{DBA}]$. Therefore, eq 5 can be rewritten as,

$$\phi^{\text{inter}} = k^{\text{inter}}[\text{DBA}]/(k_n + k^{\text{inter}}[\text{DBA}]) \quad (6)$$

The rate parameters, k_n and k^{inter} , were obtained by the decay curve analysis of the terminal DBA triplet at 400 nm. From the deactivation scheme (Figure 8), the lifetime of the DC-10 triplet, τ^A , is represented by the following equation,

$$1/\tau^A = k_n + k^{\text{intra}} + k^{\text{inter}}[\text{DBA}] \quad (7)$$

The plot of $1/\tau^A$ against several concentrations of terminal DBA group was found to be linear. From the slope of the straight line, the rate parameter, k^{inter} , was determined:¹⁴ $k^{\text{inter}} = 1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, which is almost independent of the degree of polymerization.¹⁶ The

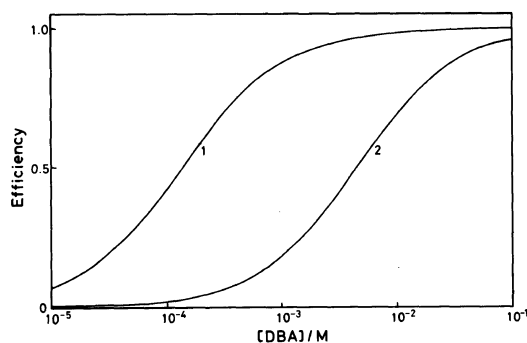


Figure 9. Plot of T-T energy transfer efficiency (1) and intermolecular reaction efficiency (2) against DBA concentrations.

k_n value is considered to be inherent to the DBA chromophore; that is to say, the value is presumably equal to the reciprocal of the lifetime for the monofunctional compound, 5-valeryl DBA (VDBA), shown in Figure 1 ($k_n = 5.9 \times 10^4 \text{ s}^{-1}$). On the basis of the rate parameters obtained by laser photolysis, the T-T energy transfer efficiency from benzophenone to DBA and intermolecular reaction efficiency of DBA can be calculated for different concentrations of the terminal DBA group as shown in Figure 9. The T-T energy transfer efficiency decreases rapidly when the concentration of the DBA group is less than $10^{-3} \text{ mol l}^{-1}$. On the other hand, the reaction efficiency also decreases rapidly when the concentration is less than $10^{-2} \text{ mol l}^{-1}$. Owing to the decrease in efficiency, the propagation rate decreases rapidly with increase in the conversion of the DBA group, which leads to deviation from the linearity between the degree of polymerization and irradiation time. This

makes it difficult to obtain polymers with a higher degree of polymerization than several hundreds in this photopolymerization system. As compared with other polyaddition systems, the most remarkable feature of this system is that the terminal reactants have limited lifetimes.

Figure 10 shows the relation between the rate of various reactions and the degree of polymerization. In this figure, the polymerization rate was simulated on the basis of the rate constants, k^{inter} and k_n , obtained by laser photolysis and the concentration of the terminal DBA group at the corresponding degree of polymerization of polymers. The reaction rates were simulated assuming an initial concentration of DBA of 0.1 mol l^{-1} . From the kinetic point of view, this photopolymerization is characterized as follows. The possibility of polymerization is determined by the inter- and intramolecular reactions of dimer or trimer molecules at an early stage of reaction. If a cyclomer is formed, a further cycloaddition reaction does not occur. From the results obtained in a bichromophoric polymethylene system,¹³ the rate constant, k^{intra} , does not go beyond $3.7 \times 10^4 \text{ s}^{-1}$, which is independent of the concentration of the DBA group. As the polymerization proceeds, the rate of the intramolecular reaction decreases in proportion to the -1.5 th power of P_n of the polymer.¹⁵ Therefore, most of the oligomers higher than a trimer undergo the propagation reaction. On the other hand, the polymerization rate depends on the concentration of the terminal DBA group. As P_n reaches *ca.* 20, the rate of polymerization (1, in Figure 10) becomes comparable to the decay rate of the DBA triplet, k_n (2, in Figure 10). As the polymerization proceeds further, the deactivation rate of the terminal reactant exceeds the polymerization rate. Therefore, the rate of polymerization starts decreasing when P_n exceeds 20.

In this paper, the polyaddition reaction of the bichromophoric compound, DC-10, was

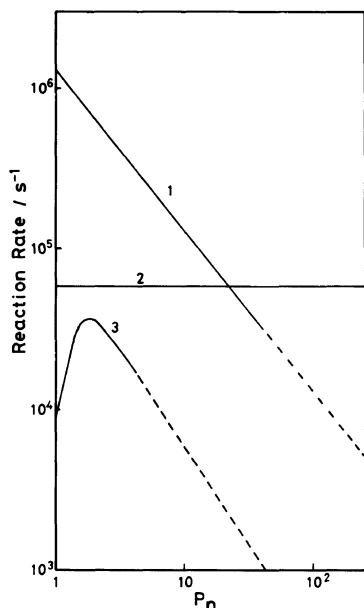


Figure 10. Plot of rate of various reactions against the degree of polymerization: (1) intermolecular reaction; (2) unimolecular deactivation of DBA triplet; (3) intramolecular reaction.

carried out by photoirradiation. In this polymerization, a polymer having cyclobutane ring units in the main chain was obtained. Furthermore, this polymerization can easily be controlled by irradiation conditions, which has been verified by kinetic investigations using laser photolysis. This fact is a remarkable feature of this polymerization which is not seen in other polyaddition reactions.

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