Dimerization of α-Methylstyrene *via* a Photoexcited Charge Transfer Complex

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The yields of α-methylstyrene dimers and polymer produced upon photoexcitation under rigorously dry conditions of the charge transfer complex formed from the monomer and an electron acceptor, pyromellitic dianhydride, in dichloromethane solution have been determined. The processes of formation are discussed in terms of the different kinds of reactive species, the excited charge transfer complex, the ion pair, and the free ion, which contribute to product formation depending on the polarity of the solution. The dimers were found to be produced from the excited charge transfer complex and the ion pair but not from the free ion, which exclusively produced polymer. On the other hand, polymerization is initiated both by the ion pair and the free ion.

THERE has been much interest recently in the chemical and physical behaviour of charge transfer complexes, especially in their ionic dissociation in polar solvents.[1] In polymer chemistry attention has been paid to photoinduced ionic polymerization where the monomer is an electron donor or acceptor.[2] Another attractive chemical reaction occurring *via* ionic dissociation is photoinduced dimerization of aromatic vinyl compounds in the presence of electron acceptors resulting in the formation of cyclic dimers, *viz.* cyclobutanes and/or tetrahydronaphthalenes.[1b,3] The major photochemical product is tetrahydronaphthalene in the case of styrene, α-methylstyrene, *p*-methylstyrene, and 1,1-diphenylethylene in the presence of electron acceptors.[3d,g] The radical cation of the monomer produced through ionic dissociation of the excited charge transfer complex has been proposed as the intermediate in dimerization.

On the other hand, during the course of our investigation of the photoinduced cationic polymerization of α-methylstyrene, it was shown that both ion pair and free ion contribute to polymerization.[2c,4] This was shown by physicochemical studies on the polymerization system and by determination of the molecular weight distribution of the polymers produced. Polymerization is always accompanied by the formation of α-methylstyrene dimers.[3c] In this paper the mechanism of dimerization is discussed and compared with that of polymerization in order to clarify the reactivities of the ion pair and free ion derived from the photoexcited charge transfer complex.

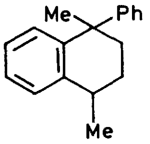
EXPERIMENTAL

Materials.—α-Methylstyrene obtained from Wako Pure Chemical Industrial Co. was washed three times with an aqueous solution of sodium hydroxide and with water, and then distilled over calcium hydride. The middle fraction was distilled into barium oxide, which had been baked for *ca.* 72 h at *ca.* 400 °C, under high vacuum (*ca.* 10^{-6} mmHg). Methylene chloride was purified and dried by the same method as α-methylstyrene. Pyromellitic dianhydride was purified by sublimation before use.

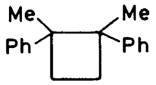
Procedure.—Reaction mixtures were prepared *in vacuo* as follows. A weighed amount of pyromellitic dianhydride was sublimed into a Pyrex tube, which had been evacuated at a pressure of 10^{-6} mmHg for *ca.* 24 h with periodic heating and then known amounts of the monomer and the solvent were introduced into the tube by trap-to-trap distillation. In these operations breakable seals were used instead of cocks in order to avoid contamination by impurities from grease. The illumination of the samples was carried out with a super-high-pressure mercury lamp, and excitation was limited to the charge transfer band situated around 360 nm by the use of a colour filter (Toshiba UV 35) transmitting at longer than 350 nm. The radiation-induced polymerization was carried out by irradiation with ^{60}Co γ-rays at a dose rate of 5.9×10^5 rad h^{-1}. The dimers were analysed by gas chromatography using an Apiezon L column at 180 °C. Polymer was precipitated by an excess of methanol, filtered, dried in a vacuum oven, and then weighed.

RESULTS

Three dimers were produced simultaneously with polymer when the charge transfer complex of α-methylstyrene and pyromellitic dianhydride (PMDA) was photoexcited in dichloromethane solution under rigorously dry conditions. These dimers are 1,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (I) and *cis*- (II) and *trans*-1,2-dimethyl-1,2-diphenylcyclobutane (III).† Dimer (I) was the major product under all conditions studied.



(I)



(II) *cis*

(III) *trans*

Figure 1 shows the dependence of the yields of the dimers and polymer on the monomer concentration at 4 °C.‡ As reported in a previous paper,[2c] polymerization at 4 °C predominantly occurs *via* the ion pair; polymerization by the free ion becomes important below −50 °C at a monomer

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† Several other kinds of dimers were produced in some experiments; their formation was less reproducible. These dimers were not taken into consideration in the present study.

‡ Although the samples were immersed in ice–water during illumination, the temperature was maintained at 4 °C by the heat due to illumination. Similarly, the temperature of the samples in dry ice–methanol was maintained at −74 °C. The yield of dimers and polymer are calculated from the conversion of monomer into products corrected for illumination time and for absorbance at the charge transfer band (λ 360 nm) by the samples and should be regarded as relative yields proportional to the quantum yields of the monomer consumption divided by the monomer concentration. The dimer yield is the sum of the yields of the three dimers.

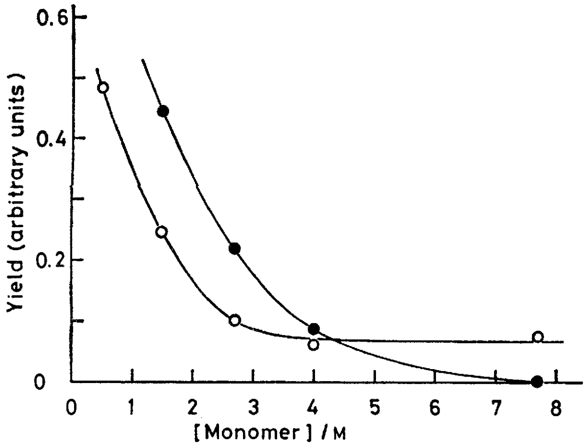

FIGURE 1 Dependence of the yields of dimers and polymer on monomer concentration at 4 °C: ○, sum of the dimers; ●, polymer

concentration of 0.57M. The polymer yield is negligible in bulk, 7.72M, though it increases with decreasing monomer concentration. On the other hand, the dimers are formed to a certain extent even in bulk. The yield is almost constant up to a monomer concentration of 4M. Figure 2 shows the ratios of the three dimers at 4 °C. The ratio of dimer (I) increases with decreasing monomer concentration. These concentration dependences clearly indicate that dimer formation, especially that of dimer (I), is enhanced by the dissociation of the excited charge transfer complex into an ion pair, since the increase of polarity of the solution with decreasing monomer concentration favours dissociation. The formation of the dimers in bulk, where ionic dissociation hardly occurs, suggests that the dimers are also produced from the excited charge transfer complex, whereas polymerization is not initiated by excited charge transfer complex in bulk.

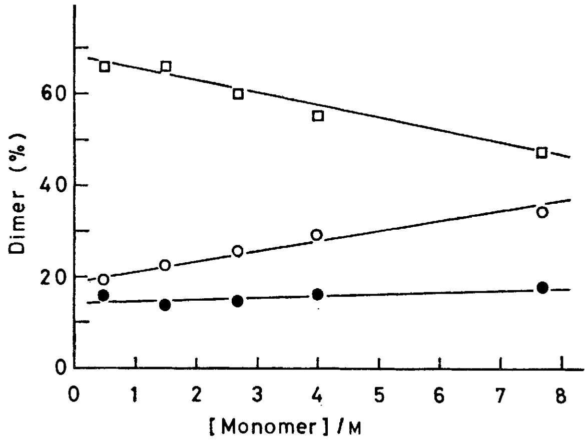

FIGURE 2 Percentages of the three dimers at 4 °C: □, 1,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene; ●, *cis*-1,2-dimethyl-1,2-diphenylcyclobutane; ○, *trans*-1,2-dimethyl-1,2-diphenylcyclobutane

Figure 3 shows the dependence of the yields of the dimers and polymer on the monomer concentration at −74 °C. Below 1M the dimer yield decreases drastically, while the polymer yield increases. As reported previously,^{2c} polymerization by the free ion becomes important below 1M at −74 °C, that is, under conditions where the ion pair is appreciably dissociated into free ions. On this basis, it is considered that the free dimer radical cation produced from free α-methylstyrene radical cation reacts with monomer intermolecularly to initiate polymerization more effectively than the dimer radical cation ion pair and does not form dimeric products. The dimer radical cation ion pair, on the other hand, effectively produces the dimeric product by intramolecular reaction. Figure 4 shows the ratios of the three dimers at −74 °C. The ratio of dimer (I) increases with decreasing monomer concentration at this temperature as well as at 4 °C.

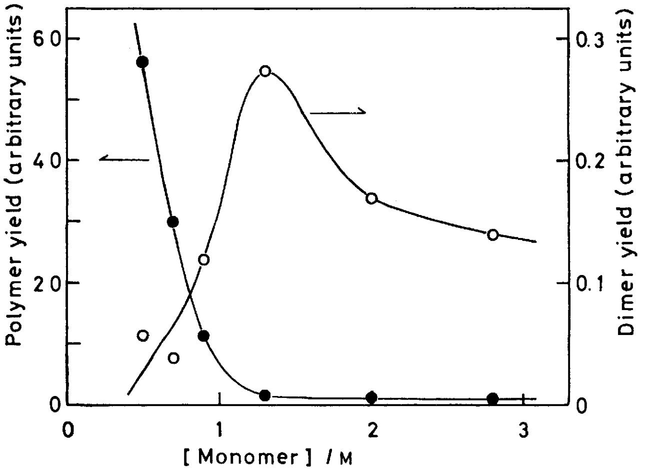

FIGURE 3 Dependence of the yields of the dimers and polymer on monomer concentration at −74 °C: ○, sum of the dimers; ●, polymer

Figure 5 shows the temperature dependence of the yield of the dimers and polymer at a monomer concentration of 0.57M. Upon decreasing the temperature, the polymer yield increases as expected from the fact that the contribution of free ionic polymerization becomes important below −50 °C.^{2c} The dimer yield, on the other hand, decreases drastically at the lower temperature. This temperature dependence also substantiates the reactivity of free radical cation, *i.e.* that it does not form the dimeric products.

In order further to confirm that the free ion produces exclusively polymer but not the dimers, the radiation-

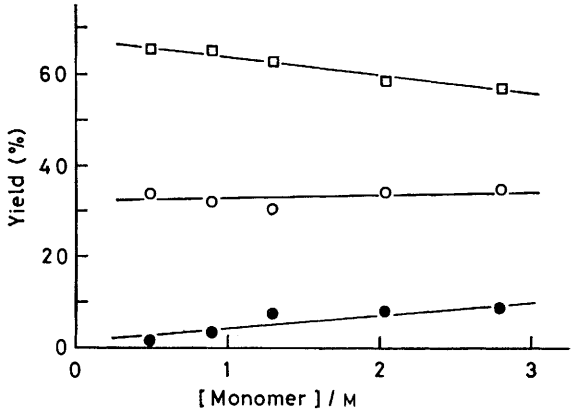

FIGURE 4 Percentages of the three dimers at −74 °C: □, 1,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene; ●, *cis*-1,2-dimethyl-1,2-diphenylcylobutane; ○, *trans*-1,2-dimethyl-1,2-diphenylcyclobutane

induced polymerization, where the free radical ion is directly produced by irradiation, was examined in bulk at 4 °C. It is well established that free cationic polymerization is initiated by γ-ray-irradiation of α-methylstyrene when the sample is rigorously dried in the same manner as that used in photoinduced polymerization.[5] Upon an irradiation dose of 1.2×10^6 rad polymer was produced in 33% yield; the G value of monomer consumption by polymerization was 2 300. However, no dimer was detected, and the G value of dimer formation, if there is any, must be < 0.005. Since the G value for the initiation of polymerization is estimated to be 0.1 [6] it is reasonable to consider that the contribution of the free ion to dimerization is much less than that of polymerization.

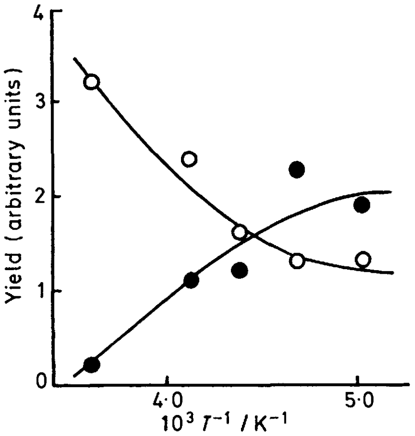

FIGURE 5 Temperature dependence of the yields of dimers and polymer at a monomer concentration of 0.57M: ○, sum of the dimers; ●, polymer

DISCUSSION

On the basis of the results obtained in the present study, the processes of the photoinduced dimerization and polymerization can be represented by reactions (1)—(9) where D and A denote the electron donor, α-methylstyrene, and acceptor, respectively, which together form the excited charge transfer complex (D·A), and $D_s^{+\cdot}$, $A_s^{-\cdot}$, and $(D_s^{+\cdot} \cdots A_s^{-\cdot})$ denote the solvated donor and acceptor radical ions and their ion pair, respectively.

$$D + A \rightleftharpoons (D{\cdot}A) \quad (1)$$

$$(D{\cdot}A) \xrightarrow{h\nu} (D{\cdot}A)^* \quad (2)$$

$$(D{\cdot}A)^* + D \longrightarrow D_2 + A \quad (3)$$

$$(D{\cdot}A)^* \longrightarrow (D_s^{+\cdot} \cdots A_s^{-\cdot}) \rightleftharpoons D_s^{+\cdot} + A_s^{-\cdot} \quad (4)$$

$$(D_s^{+\cdot} \cdots A_s^{-\cdot}) + D \longrightarrow (D_2^{+\cdot} \cdots A_s^{-\cdot}) \quad (5)$$

$$(D_2^{+} \cdots A_s^{-\cdot}) \longrightarrow D_2 + A \quad (6)$$

$$(D_2^{+\cdot} \cdots A_s^{-\cdot}) \xrightarrow{D} \text{polymer} \quad (7)$$

$$D_s^{+} + D \longrightarrow D_2^{+} \quad (8)$$

$$D_2^{+} \xrightarrow{D} \text{polymer} \quad (9)$$

Ionic dissociation of the excited charge transfer complex occurs in dichloromethane solution resulting in the formation of the ion pair. The ion pair is further dissociated into free ions [reaction (4)] when the polarity of the solution is increased by lowering the temperature as well as the monomer concentration. The dimers, D_2, are produced from the excited charge transfer complex [reaction (3)] and from the ion pair [reaction (6)] but not from the free ion. On the other hand, polymerization is initiated both by the ion pair [reaction (7)] and the free ion [reaction (8)], the latter propagating rapidly without giving neutral dimeric products.

The proportion of dimer (I) increases with decreasing monomer concentration (Figures 2 and 4). This result suggests that dimer (I) is produced to a larger extent by the ion pair than by the excited charge transfer complex since the ionic dissociation of the excited charge transfer complex is enhanced by lowering the monomer concentration. The result that the dimers are hardly produced from the free ion indicates that the counterion, *i.e.* the PMDA radical anion, plays an important role in the dimer formation process, and the processes of dimer formation from the ion pair are considered to be as shown in the Scheme. Intramolecular electrophilic substitution of the aromatic ring [path (A)] leading to the formation of dimer (I) is favoured over the cyclobutane ring formation [path (B)]. Polymerization is also initiated by the dimer cation.

Cyclodimerization of *N*-vinylcarbazole *via* radical cation chain reaction is reported to be enhanced in the presence of a counteranion, such as O_2^-, while in the absence of the anion polymerization is induced instead of cyclodimerization.[3b] Clear evidence of the necessity of oxygen for the cycloaddition reaction is observed in the radiation-induced dimerization of *N*-vinylcarbazole.[7] Linear dimer formation is reported in the reaction of the radical cation of styrene or α-methylstyrene produced by an electrochemical method.[8]

These results, as well as ours, indicate that the radical cations of olefins have a tendency to produce polymers or linear dimers by reaction with the neutral olefin, while the formation of cyclodimers results given the assistance of a counteranion or when polar substituents are present. This conclusion is further substantiated by a theoretical study.[9] The selection rules for radical reactions predict that the associated dimer radical cations of olefins can be formed thermally but they cannot be converted into the corresponding radical cations of cyclobutanes.

Upon photoexcitation of the monomer in the absence of the electron acceptor the three kinds of dimers were also produced, but in this case dimer (I) was the minor product.† The yield of dimer (I) increases upon photoexcitation at the charge transfer band in the presence of an electron acceptor. An increasing cationic nature of the system seems to facilitate the formation of dimer (I); in the excited charge transfer complex, charge separation occurs to a certain extent. The excited charge transfer complex is considered to react with the monomer

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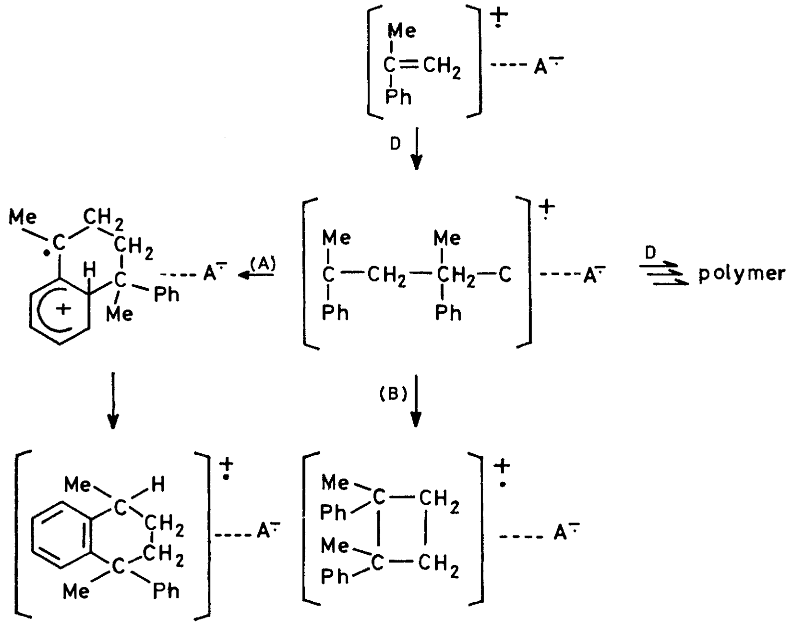
† The ratio of the three dimers (I)—(III) was 1 : 0.71 : 1.52 in bulk at 4 °C; illumination was carried out using a colour filter (Toshiba UV 27) transmitting above 270 nm in the absence of PMDA.



SCHEME

molecule prior to dissociation into the components. It seems reasonable to assume that the dimerization proceeds *via* the triple excited charge transfer complex (DDA)* [reactions (10) and (11)].† The formation of a

$$(D\cdot A)^* + D \longrightarrow (D\cdot D\cdot A)^* \qquad (10)$$

$$(D\cdot D\cdot A)^* \longrightarrow D_2 + A \qquad (11)$$

triple excited complex, a triplex, has been reported for several systems.[10] We have observed, tentatively, the formation of the triple excited complex in the present system.

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† An alternative interpretation of the formation of the dimers, especially the cyclobutane dimers, in the higher concentration region is that a local triplet state of α-methylstyrene is formed *via* geminate recombination of the ion pair. This mechanism, however, cannot account for the formation of the *cis*-dimer and dimer (I).

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