Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Tadao Nakaya[a]; Hiroshi Wada[a]; Mamoru Tanaka[a]; Minoru Imoto[a]
[a] Osaka City University Faculty of Engineering Sugimoto-cho, Osaka, Japan

To cite this Article Nakaya, Tadao , Wada, Hiroshi , Tanaka, Mamoru and Imoto, Minoru(1971) 'Vinyl Polymerization. 269. Polymerization of Methyl Methacrylate Initiated by p,p'-Dimethoxydiphenyldiazomethane', Journal of Macromolecular Science, Part A, 5: 6, 1043 — 1055

To link to this Article: DOI: 10.1080/00222337108061088

URL: http://dx.doi.org/10.1080/00222337108061088

J. MACROMOL. SCI.–CHEM., A5(6), pp. 1043-1055, October, 1971

Vinyl Polymerization. 269. Polymerization of Methyl Methacrylate Initiated by p,p'-Dimethoxydiphenyldiazomethane

TADAO NAKAYA, HIROSHI WADA, MAMORU TANAKA,
and MINORU IMOTO

Osaka City University
Faculty of Engineering
Sugimoto-cho, Sumiyoshi-ku
Osaka, Japan

SUMMARY

Using p,p'-dimethoxydiphenyldiazomethane (DMDM) as initiator, the polymerization of methyl methacrylate (MMA) in benzene or in bulk was carried out. The initial rate of polymerization, R_p, was found to be expressed by the following equation:

$$R_p = k[\text{DMDM}]^{0 \cdot 53}\ [\text{MMA}]^{0 \cdot 84}$$

The polymerization was confirmed to proceed by a radical mechanism. The over-all activation energy for the polymerization in benzene was calculated as 19.3 kcal/mole. The rate of thermal decomposition of DMDM was also measured in benzene and the rate equation was obtained as follows:

$$k_d\ (\text{sec}^{-1}) = 1.0 \times 10^{15} \exp\ (-29.1\ \text{kcal/RT})\ (\text{for } 50\text{-}80°\text{C})$$

Explanations of these observations are discussed in connection with those of the preceding papers.

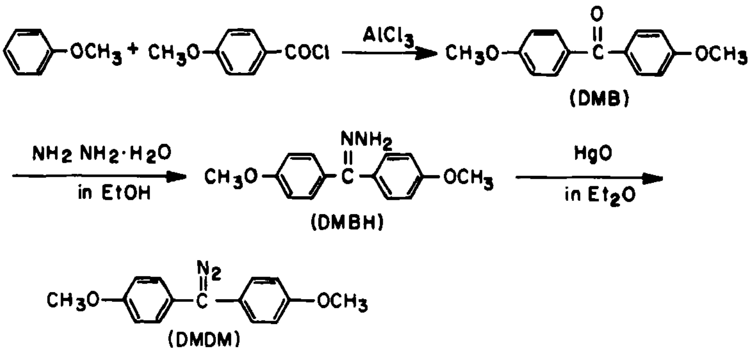
INTRODUCTION

In the first paper [1] of this series it was shown that diphenyldiazomethane (DDM) can initiate the radical polymerization of methyl methacrylate (MMA). Furthermore, we reported the mechanistic study of the polymerization of MMA by an unsymmetrically substituted DDM, that is, p-methoxy-p′-cyanodiphenyldiazomethane [2]. The present paper is concerned with the kinetic and mechanistic studies of the polymerization of MMA by p,p′-dimethoxydiphenyldiazomethane (DMDM), having two electron-donating groups at both para positions of DDM. The role of the substituents on the reactivity as initiator caused by both para substitution is discussed.

EXPERIMENTAL

Preparation of p,p′-Dimethoxydiphenyldiazomethane (DMDM)

The following sequence of reactions was applied for the synthesis of DMDM:



p,p′-Dimethoxybenzophenone (DMB)

In a 300-ml three-necked flask equipped with a mechanical stirrer and a reflux condenser were placed 10 g of p-methoxybenzoyl chloride and 50 g of anisole. To the ice-cold and stirred mixture was added, over a period of 10 min, 12 g of anhydrous aluminum chloride. After the addition, the mixture was heated under stirring at about 60°C for 2 hr. The resulting deep red solution was cooled to 5°C, and 100 g of crushed ice was added. The mixture was then extracted with two 100-ml portions of benzene. The benzene extracts were washed with two 50-ml portions of water and dried over 45 g of anhydrous sodium sulfate. After the drying agent was removed, the benzene and unchanged anisole were evaporated under reduced pressure. The residue was crystallized from ethanol to give 8.5 g (50%) of DMF as colorless needles, melting at 141-142°C. The nuclear magnetic resonance spectrum, recorded in deuterochloroform solution with tetramethylsilane as internal standard, gave the signals as 3.90-3.95 ppm (six protons) for methoxy groups, 6.95-7.25 ppm (four protons) for meta protons of phenyl groups to carbonyl group, and 7.80-8.00 ppm (four protons) for ortho protons of phenyl groups to carbonyl group.

Analysis calculated for $C_{15}H_{14}O_3$: C, 74.35; H, 5.82. Found: C, 74.18; H, 5.85.

p,p′-Dimethoxybenzophenone Hydrazone (DMBH)

A mixture of 12 g of DMB and 12 g of 100% hydrazine hydrate in 200 ml of absolute ethanol was heated at about 75°C for 4 hr. The mixture was allowed to cool to room temperature and then filtered and the precipitate discarded. After removal of the solvents from the filtrate, the residue was recrystallized from ethanol to give 2.8 g (22%) of DMBH, melting at 83-84°C. The NMR spectrum showed a doublet at 3.75-3.90 ppm (6H) for methoxy protons, a singlet at 4.75-4.80 ppm (2H) for amine protons, and a multiplet at 6.70-7.90 ppm (8H) for phenyl protons.

Analysis calculated for $C_{15}H_{16}O_2N_2$: C, 70.28; H, 6.29. Found: C, 70.54; H, 6.26.

p,p′-Dimethoxydiphenyldiazomethane (DMDM)

A mixture of 5 g of DMBH, 7.5 g of anhydrous sodium sulfate, 100 ml of ethyl ether, 2.5 ml of ethanol saturated with potassium hydroxide, and 18 g of yellow mercuric oxide was stirred under nitrogen at room temperature for 5 hr. A reaction mixture was filtered and the solvent removed from the filtrate under reduced pressure at room temperature. The purple solid thus obtained was dissolved in petroleum ether and again filtered. The removal of the solvent from the filtrate under reduced pressure gave DMDM as purple crystals, melting at 98-99°C, in a 70% yield.

Reaction of DMDM with Methyl Methacrylate (MMA)

A mixture of 1 g of DMDM and 8 g of MMA in 100 ml of ethyl ether was allowed to stand overnight at room temperature. The solvent and the MMA remaining unchanged were removed by distillation under reduced pressure and the residue was dissolved in 100 ml of methanol. The solution was filtered off to exclude the small amount of the polymeric materials. The filtrate was evaporated under reduced pressure to separate the white crystals. Recrystallization from methanol gave methyl-l-methyl-2,2-(p,p′-dimethoxydiphenyl) cyclopropylcarboxylate, mp 91-92°C, in 0.3 g yield. The NMR spectrum showed the absorptions at 1.15-1.40 ppm (three protons) for methyl protons, 2.00-2.25 ppm (two protons) for methylene protons, 3.35-3.40 ppm (three protons) for methoxycarbonyl protons, 3.60-3.70 ppm (six protons) for methoxy protons, and 6.60-7.40 ppm (eight protons) for phenyl protons.

Analysis calculated for $C_{20}H_{22}O_4$: C, 73.57; H, 6.81. Found: C, 73.49; H, 6.85.

Measurement of the Rate of Decomposition

The decomposition rate of DMDM in benzene was followed, as described previously [2], by observing the fall in absorbance at 552 mμ (ϵ = 92) due to diazo group of DMDM, using a Hitachi Model EPS-2U recording spectrophotometer.

Polymerization

MMA and styrene were purified by the usual method and distilled under reduced pressure three times in a stream of nitrogen before use. Benzene was purified by the usual method.

The polymerization procedure was the same as that described previously [1, 2].

Calculation of the Rate of Polymerization

The rate of polymerization, R_p, was calculated by the following equation [3, 4]:

$$R_p^2 = R_p^2(\text{total}) - R_p^2(\text{thermal}) \qquad (1)$$

where R_p(total) and R_p(thermal) are the observed rates of polymerization of MMA in the presence and absence of DMDM, respectively.

Degree of Polymerization

Intrinsic viscosity, [η], of the resulting poly(methyl methacrylate) was determined by viscosity measurement of its dilute benzene solution at

30°C with an Ubbelohde viscometer. The number-average degree of polymerization was calculated from $[\eta]$ by applying the following equation [5]:

$$P_n = 2.22 \times 10^3 \ [\eta]^{1/0.76} \tag{2}$$

Analysis of Copolymer Composition

The copolymerization product from MMA and styrene was analyzed by elementary analysis.

RESULTS

The Decomposition Rate of DMDM

The decomposition rate of DMDM in benzene was followed by the disappearance of the characteristic peak of DMDM as determined by UV absorption at 552 mμ, depending on the concentration of DMDM. The first-order rate constants (k_d) at 50, 60, 70, and 80°C are summarized in Table 1.

Table 1. The Rate of Decomposition of DMDM

Temperature (°C)	50	60	70	80
$k_d \times 10^4$ (sec^{-1})	0.16	0.39	2.62	10.00

The plot of log k_d against 1/T gave a straight line as shown in Fig. 1, from which the following equation was obtained:

$$k_d(\text{sec}^{-1}) = 1.0 \times 10^{15} \exp(-29.1 \text{ kcal/RT}) \tag{3}$$

As for the rate constants of decomposition for diphenyldiazomethane (DDM) and p-methoxy-p′-cyanodiphenyldiazomethane (MCD), the following results were described previously [2].

$$\text{For DDM:} \quad k_d(\text{sec}^{-1}) = 1.32 \times 10^{13} \exp(-27.5 \text{ kcal/RT}) \tag{4}$$

$$\text{For MCD:} \quad k_d(\text{sec}^{-1}) = 0.74 \times 10^{13} \exp(-25.7 \text{ kcal/RT}) \tag{5}$$

As can be seen from these equations, the values of the activation energy

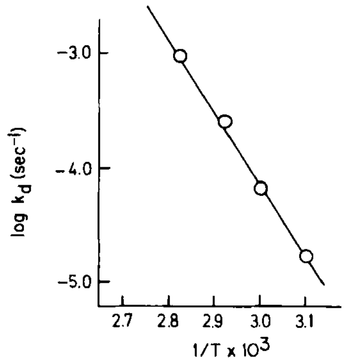


Fig. 1. Arrhenius plot for decomposition of DMDM.

and frequency factor of DMDM were larger than those of DDM and MCD.

Dependence of the Rate of the Polymerization on Temperature

The polymerization of MMA initiated by DMDM was carried out in benzene by varying the temperature between 60 and 90°C. The results are shown in Fig. 2.

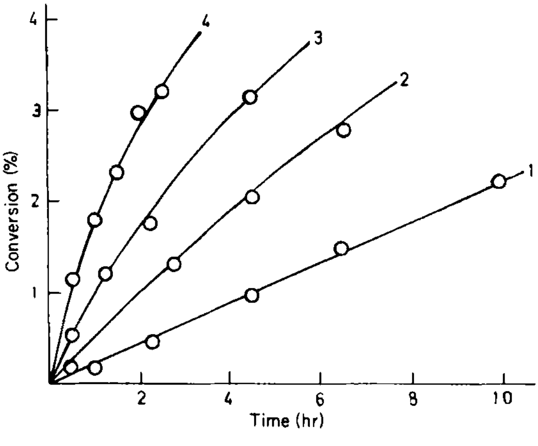


Fig. 2. Conversion vs. time plot for the polymerization of MMA initiated by DMDM. [MMA] = 4.68 moles/liter, [DMDM] = 3.00 X 10^{-2} mole/liter. Curve 1: 60°C; 2: 70°C; 3: 80°C; 4: 90°C.

The plot of the rate of polymerization, R_p, against 1/T gave a linear relationship (Fig. 3). From the slope, the over-all activation energy of the polymerization was calculated as 19.3 kcal/mole, using an Arrhenius equation. This value is smaller than those obtained by DDM and MCD, as seen in Table 2.

Table 2. The Comparison of the Over-All Activation Energies of the Polymerization of MMA Initiated by DDM, MCD, and DMDM

Initiator	DDM[a]	MCD[a]	DMDM[a]
E (kcal/mole)	13.1	18.8	19.3

[a] DDM, MCD, and DMDM denote diphenyldiazomethane, p-methoxy-p′-cyanodiphenyldiazomethane, and p,p′-dimethoxydiphenyldiazomethane, respectively.

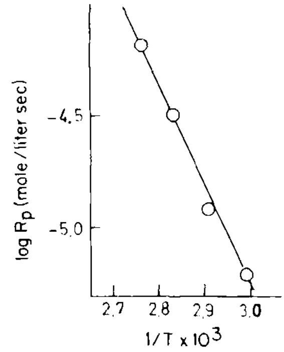


Fig. 3. Relationship between R_p and polymerization temperature.

Confirmation of a Radical Mechanism of the Polymerization Initiated by DMDM

In order to check that the polymerization proceeds through a radical mechanism, a copolymerization of MMA with styrene was carried out in benzene at 70°C. Figure 4 shows the coposition curve of the copolymers obtained, which is characteristic of a radical copolymerization. Furthermore, hydroquinone was found to act as inhibitor for the polymerization of MMA by DMDM. These observation suggested that DMDM can serve as radical initiator for the polymerization of MMA.

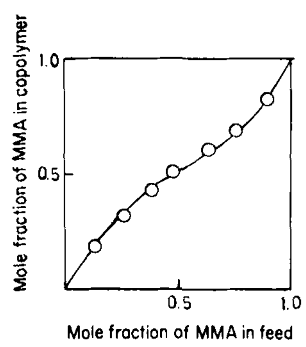


Fig. 4. Monomer-copolymer composition curve for radical copolymerization of MMA (M_2) with styrene (M_1) in benzene at 70°C. [DMDM] = 3.0×10^{-2} mole/liter.

Dependence of the Rate of Polymerization on the Concentration of DMDM

The polymerization of MMA initiated by DMDM was carried out in benzene at 70°C, varying [DMDM], while [MMA] was kept constant. The results were shown in Fig. 5. From the figure, the rate of polymerization, R_p, was found to be proportional to the 0.53 power of [DMDM].

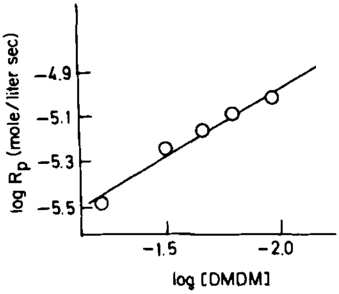


Fig. 5. Relationship between R_p and the concentration of DMDM (in benzene at 70°C).

Dependence of the Rate of Polymerization on the Concentration of MMA

The polymerization was also carried out at 70°C in which [DMDM] was kept constant and [MMA] was varied. As can be seen from Fig. 6, the rate of polymerization was proportional to the 0.84 power of [MMA]. Therefore,

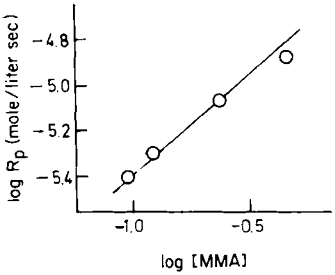


Fig. 6. Relationship between R_p and the concentration of MMA (in benzene at 70°C).

the rate of polymerization, R_p, was given by

$$R_p = k[\mathrm{DMDM}]^{0.53}\ [\mathrm{MMA}]^{0.84} \qquad (6)$$

Determination of the Chain Transfer Constants to Monomer and Initiator

In order to estimate the chain transfer constants of monomer, C_m, and of initiator, C_i, the bulk polymerization of MMA was carried out by using different values of [DMDM] at 70°C for 3 hr. The results are summarized in Table 3. From the data, a linear relationship between the reciprocals of

Table 3. Dependences of [DMDM] on Rp and the Degree of Polymerization of the Polymer, P_n, at 70°C for 3 hr. [MMA] = 4.68 moles/liter

[DMDM] × 10^2 (moles/liter)	R_p × 10^5 (moles/liter sec)	P_n × 10^{-4}
0.5	1.33	2.89
2.0	1.77	2.88
3.0	1.94	2.86
4.0	2.09	2.84
5.0	2.48	2.80

P_n and R_p was obtained, as shown in Fig. 7. The slope of the straight line was equal to the term A in the following equation:

$$1/P_n = A \cdot R_p + C_m + C_i[\mathrm{DMDM}]/[\mathrm{MMA}] \tag{7}$$

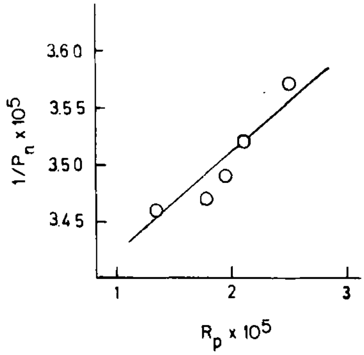


Fig. 7. Relationship between the reciprocals of P_n and R_p.

From Fig. 7, the value of A was estimated as 0.8 liter sec/mole. Using the value of A, the plot of $[1/P_n - A \cdot R_p]$ against [DMDM]/[MMA] gave a straight line, as shown in Fig. 8. From the figure, C_m and C_i were estimated as follows:

$$C_m = 3.3 \times 10^{-5} \quad C_i = 0.0 \quad (70°\mathrm{C}) \tag{8}$$

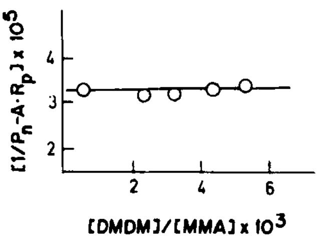


Fig. 8. Relationship between $[1/P_n - A \cdot R_p]$ and [DMDM]/[MMA].

These values of C_m and C_i are close to those ($C_m = 2.0 \times 10^{-5}$, $C_i = 0.0$) obtained by the polymerization of MMA with DDM.

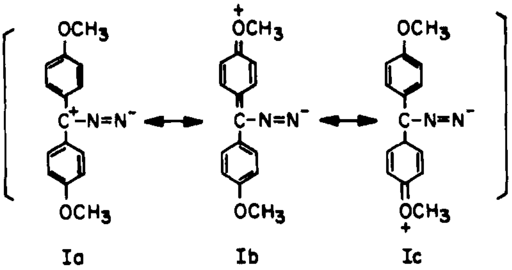
An Attempt to Polymerize MMA with Methyl-1-methyl-2,2-(p,p′-dimethoxydiphenyl)cyclopropylcarboxylate

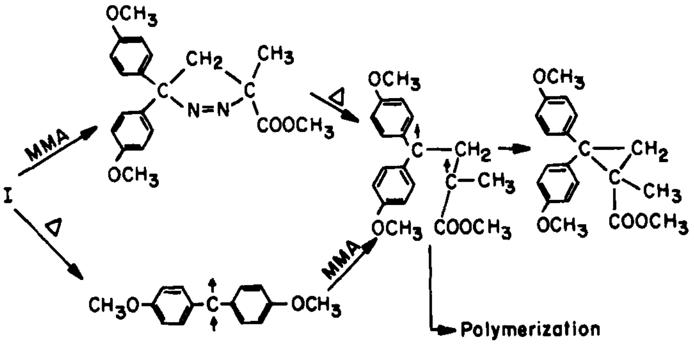
In order to check whether methyl-1-methyl-2,2-(p,p′-dimethoxydiphenyl) cyclopropylcarboxylate can initiate the polymerization of MMA, the bulk polymerization with this compound was carried out in vacuum at 75°C. However, the conversion of the monomer was negligible even after 4 hr.

DISCUSSION

From the kinetics of the polymerization obtained above, the rate of polymerization was proportional to the 0.53 power of [DMDM] and the 0.84 power of [MMA]. And it was found that methyl-1-methyl-2,2-p,p′-dimethoxydiphenyl)cyclopropylcarboxylate could not initiate the polymerization of MMA. The activation energy of initiation, E_i, was estimated as 29.6 ± 2 kcal/mole from the over-all activation energy for the polymerization, by the same method described previously [2]. The E_i value is in good agreement with that of the activation energy of decomposition for DMDM (29.1 kcal/mole). These findings suggest that the formation of p,p′-dimethoxydiphenylcarbene by thermal decomposition of the corresponding diazomethane is an important step in the initiation of the polymerization, as shown below. For the radical polymerization of MMA initiated by unsubstituted diphenyldiazomethane, we previously proposed the initiation mechanism involving the carbene intermediate resulting from thermal decomposition of diphenyldiazomethane. On the other hand, it is well known that the carbenes containing α-oxygen are unstable and reactive species due to the resonance interaction between the electron-deficient carbene carbons and electron-rich oxygen atoms [6]. When two p-anisyl groups are bonded to divalent carbene carbon, the resonance interaction between the carbene carbon and the electron-rich methoxy groups through the benzene ring makes the carbene possess nucleophilic character. Accordingly, it is very interesting to see whether p,p′-dimethoxydiphenyl carbene can serve as a common radical initiator for the polymerization of MMA despite the introduction of electron-donating groups. Comparison of Eqs. (3) and (4) shows that the thermal stability of DMDM is increased by two methoxy groups. On the other hand, the reactivity of DMDM in cycloaddition is expected to increase by the two methoxy group because of the resonance interaction involved from Structures Ib and Ic [7]. Therefore, the minor part of DMDM, which acts as an initiator, becomes smaller than that of diphenyldiazomethane.

Thus from the present and previous data [8-11], the following initiation mechanism may be proposed.





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Accepted by editor February 27, 1971
Received for publication April 12, 1971