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Tsuneyuki Sato[a]; Kunio Hibino[a]; Takayuki Otsu[a]
[a] Department of Applied Chemistry Faculty of Engineering, Osaka City University Sugimoto-cho, Sumiyoshi-ku, Osaka, Japan

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Vinyl Polymerization Initiated with Phenylglyoxal and Dimethylaniline-N-oxide

TSUNEYUKI SATO, KUNIO HIBINO, and TAKAYUKI OTSU

Department of Applied Chemistry
Faculty of Engineering
Osaka City University
Sugimoto-cho, Sumiyoshi-ku, Osaka 558, Japan

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ABSTRACT

The combination of dimethylaniline-N-oxide (DMAO) and phenylglyoxal (PhG) was found to serve as an effective initiator for the polymerizations of methyl methacrylate (MMA) and methyl acrylate. The results of copolymerization of MMA with styrene, the effect of benzoquinone, and a spin trapping technique study indicated that the polymerization initiated with the DMAO/PhG system proceeds via a radical mechanism. The polymerization with the DMAL/PhG system was investigated kinetically in acetonitrile, where PhG was used as monohydrate ($PhG \cdot H_2O$). The overall activation energy of this polymerization was calculated to be 11.3 kcal/mol. The polymerization rate was found to show a maximum at a molar ratio of ~0.6 of DMAO to $PhG \cdot H_2O$ when the concentration of one initiator component was varied while keeping that of the other constant. From these observations and the result of an electronic spectroscopic study of this system, an initiation mechanism involving an electron-transfer reaction from DMAO to PhG has been proposed.

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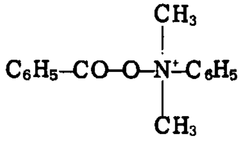
INTRODUCTION

In earlier works [1-7] we investigated vinyl polymerizations initiated with dimethylaniline-N-oxide (DMAO) and some electrophilic compounds such as benzoic anhydride (Bz_2O) [1-4], tosyl chloride [5], tetracyanoquinodimethane (TCNQ) [6], and cobaltous nitrate [7]. It has been concluded that the reaction of DMAO with Bz_2O proceeds via the N-benzoyloxyammonium intermediate (I) which decomposes homolytically at the $N^+{-}O$ bond, while the system of DMAO and TCNQ involves an electron-transfer process from DMAO to TCNQ where the TCNQ anion radical is detected by ESR spectroscopy.



$$C_6H_5{-}CO{-}O{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}{-}C_6H_5$$

I

Recently, the hypothesis of Szent-Györgyi [8] has received some attention. It states that a radical process involving an electron transfer from a protein to a certain α-dicarbonyl compound is responsible for the cause of cancer. Meanwhile, N-oxides of tert-amines have been observed both in animals and in plants, and their behaviors in biochemistry have become of interest. Therefore, it is quite interesting to note that the system of DMAO and phenylglyoxal (PhG) induces a radical polymerization.

This paper deals with the vinyl polymerization initiated with the combination of DMAO and PhG, an effective electrophile. PhG was used as monohydrate ($PhG{\cdot}H_2O$).

EXPERIMENTAL

Phenylglyoxal monohydrate ($PhG{\cdot}H_2O$) was prepared by oxidation of acetophenone with selenium dioxide [9] and recrystallized from chloroform (mp 81°C). Dimethylaniline-N-oxide (DMAO) was prepared by oxidation of dimethylaniline with hydrogen peroxide as described previously [1] and recrystallized from acetone. The spin trapping reagents N-phenyl-tert-butylnitrone and 2-methyl-2-nitrosopropane were prepared by the methods of Emmonds [10] and Perkins [11], respectively.

Polymerizations were carried out in sealed tubes under shaking and light-intercepted conditions. The resulting polymers were isolated by pouring the polymerization mixtures into a large amount of methanol.

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TABLE 1. Polymerizations of Some Vinyl Monomers with the DMAO/PhG·H_2O System at 60°C for 6h[a]

Monomer	Solvent	Polymer yield (%)
AN	CH_3CN	0.7
VAc	CH_3CN	3.9
St	CH_3CN	5.3
MA	CH_3CN	81.1
MMA	CH_3CN	25.2
MMA	EtOH	10.6
MMA	$CHCl_3$	6.8
MMA	CH_3CO_2Et	14.0
MMA	C_6H_6	26.0
MMA	CH_3COCH_3	15.9
MMA[b]	CH_3CN	0

[a] Polymerization conditions: monomer, 5 mL; solvent, 5 mL; [DMAO] = 3.0×10^{-2}, [PhG·H_2O] = 5.0×10^{-2}.

[b] In the presence of p-benzoquinone (5.0×10^{-2} mol/L).

The reaction of DMAO with PhG·H_2O was performed in the presence of a spin trapping reagent in an ESR tube which was degassed and sealed under vacuum. The ESR spectrum of the reaction mixture was recorded by a JES-ME-3X spectrometer equipped with 100 kc/s modulation.

The electronic spectrum of the DMAO/PhG·H_2O system in acetonitrile was measured by using a Hitachi-EPS spectrometer.

RESULTS AND DISCUSSION

Polymerization of Some Vinyl Monomers with DMAO and PhG·H_2O

Table 1 lists the results obtained when some vinyl monomers were polymerized at 60°C in acetonitrile by using the DMAO/PhG·H_2O system as initiator. This initiator system was found to be quite effective for the polymerizations of methyl methacrylate (MMA) and methyl acrylate (MA), while styrene (St), vinyl acetate (VAc), and acrylonitrile

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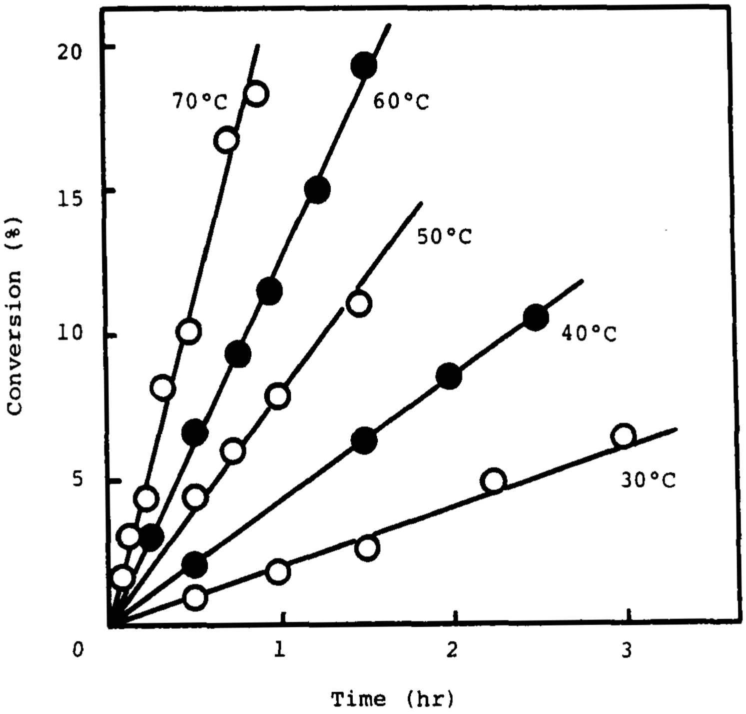

FIG. 1. Time-conversion curves of the polymerization of MMA with the DMAO/PhG·H_2O system in acetonitrile: [DMAO] = 3.0 × 10^{-2}, [PhG·H_2O] = 5.0 × 10^{-2}, [MMA] = 4.68 mol/L.

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(AN) were polymerized in relatively low yields. The polymerization of MMA was also carried out in various solvents. The result obtained is also shown in Table 1. A considerable solvent effect was observed.

The presence of a small amount of benzoquinone completely inhibited the polymerization of MMA. Furthermore, when copolymerization of St with MMA (equimolar monomer mixture) was carried out at 60°C by using the DMAO/PhG·H_2O system, the resulting copolymer was found to contain nearly equimolar monomer units (MMA:St = 46:54). These results strongly indicate that the vinyl polymerization initiated with the combination of DMAO and PhG·H_2O proceeds via a radical mechanism.

Kinetic Study of the Polymerization of MMA with the DMAO/PhG·H_2O system

The polymerization of MMA with DMAO and PhG·H_2O was investigated kinetically in detail in acetonitrile.

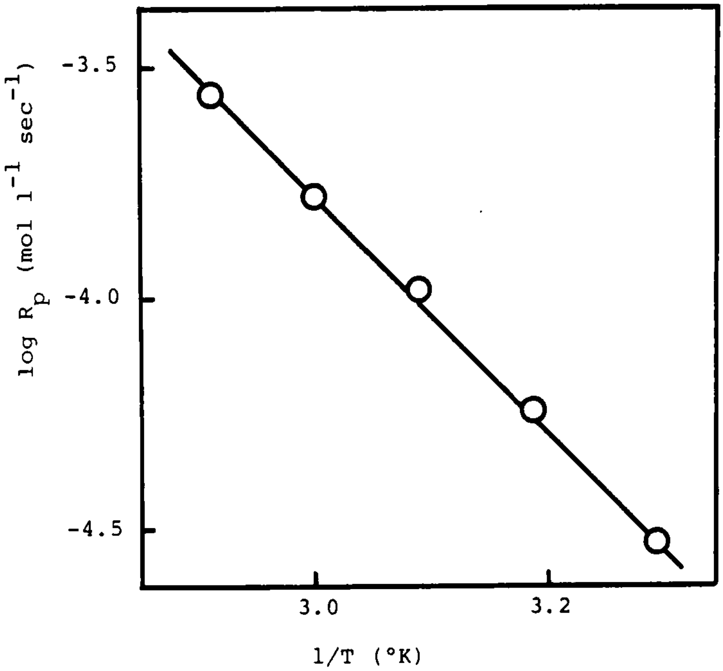

FIG. 2. Arrhenius plot of the polymerization of MMA with the DMAO/PhG·H_2O system in acetonitrile.

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Figure 1 shows the time-conversion curves obtained in the temperature range from 30 to 70°C. Figure 2 shows an Arrhenius plot for the polymerization rate (R_p) observed, from which the overall activation energy of this polymerization was calculated to be 11.3 kcal/mol, a rather low value.

Figure 3 shows the relationship between R_p and the monomer concentration. An unexpected result was observed: R_p depends only slightly on the monomer concentration in the low ($<$ 2.8 mol/L) and in the high ($>$ 5.6 mol/L) ranges of monomer concentration. A high dependence of R_p on monomer concentration was, however, observed in the range of 2.8-5.6 mol/L.

The effect of the initiator concentration on R_p was also examined at 60°C. The results obtained are shown in Fig. 4. Curve (a) in Fig. 4 shows the relationship between R_p and DMAO concentration observed when the concentrations of PhG·H_2O and MMA were kept constant. Curve (b) shows the effect of PhG·H_2O concentration on

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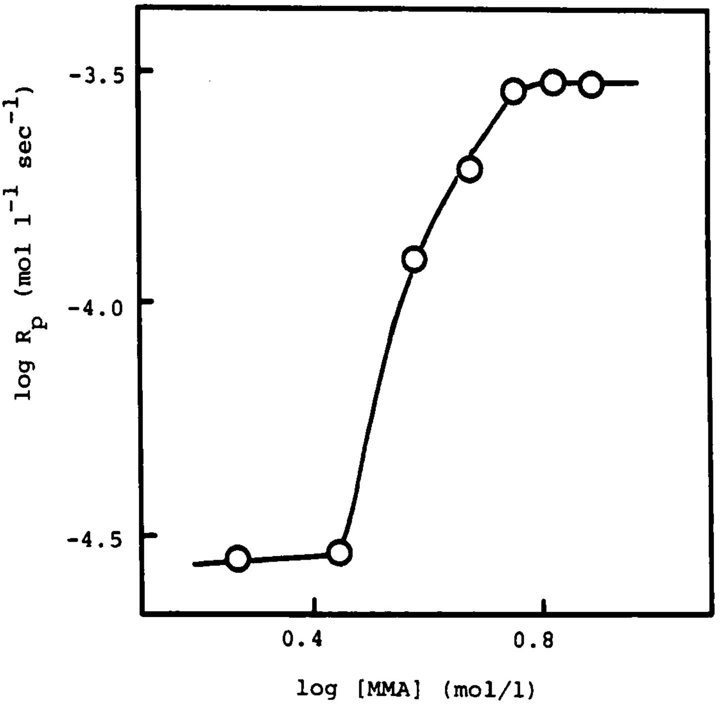

FIG. 3. Effect of the monomer concentration on the polymerization rate (R_p) at 60°C in acetonitrile: [DMAO] = 3.0 × 10^{-2}, [PhG·H_2O] = 5.0 × 10^{-2} mol/L.

R_p observed when the concentrations of DMAO and MMA were kept constant. In both cases a maximum or R_p was observed at a molar ratio of [DMAO]/[PhG·H_2O] ≃ 0.6. No polymerization was found to proceed at a higher DMAO concentration than 0.1 mol/L.

Electronic Spectrum of the DMAO/PhG·H_2O System

As shown in Fig. 5, an acetonitrile solution of PhG·H_2O was found to show an absorption (λ_{max} = 420 nm) in the visible region caused by anhydrous PhG. The absorption due to free PhG increases with increasing concentration of MMA in the solution.

Figure 6 shows the effect of DMAO on the spectrum of free PhG. The addition of DMAO causes another broad absorption, which is so intensified with increasing concentration of DMAO that the absorption

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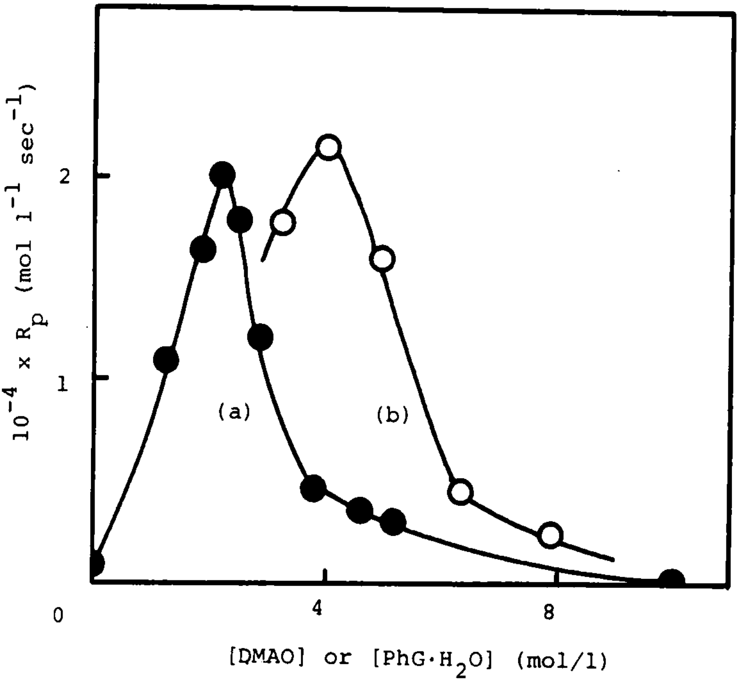

FIG. 4. Effect of the initiator concentration on R_p at 60°C in acetonitrile: [MMA] = 4.68. (a) [PhG·H_2O] = 5.0×10^{-2}; (b) [DMAO] = 3.0×10^{-2} mol/L.

due to free PhG is covered at high DMAO concentration. This finding suggests that a complex is formed between DMAO and PhG in this system. As shown in Fig. 7, the absorption due to the complex was found to decrease by the addition of MMA, suggesting that the formation of the complex is suppressed by the presence of MMA.

Reaction of DMAO with PhG·H_2O in the Presence of a Spin Trapping Reagent

In order to clarify the initiation mechanism, a spin trapping technique was applied to the DMAO/PhG·H_2O system.

Figure 8 shows the ESR spectrum of the reaction mixture obtained when the reaction of DMAO with PhG·H_2O was carried out at 60°C in acetonitrile in the presence of phenyl-tert-butylnitrone (PBN).

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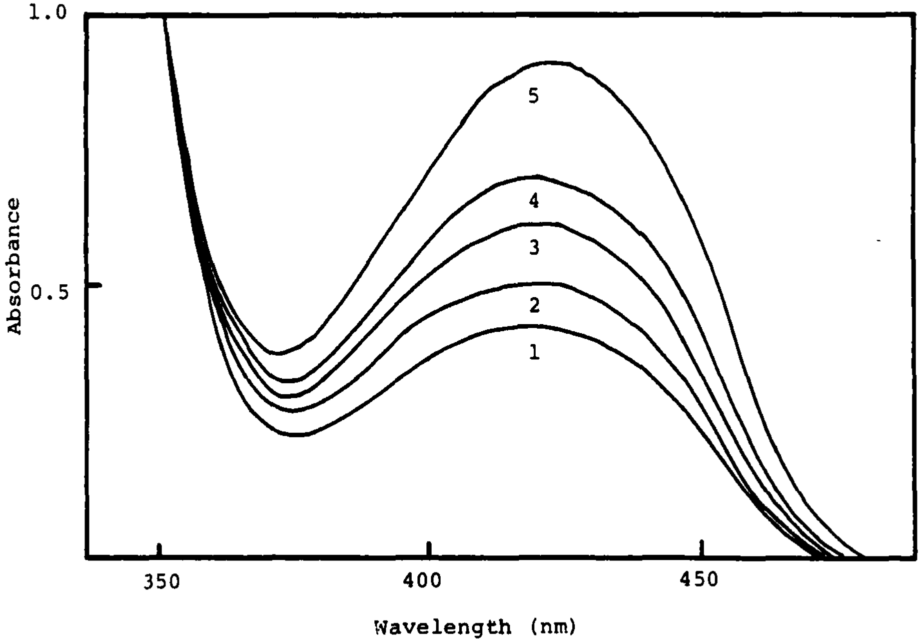
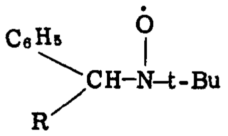


FIG. 5. Effect of MMA on the visible spectrum of PhG·H_2O at room temperature in acetonitrile: [PhG·H_2O] = 5.0×10^{-2}, [MMA] (1) 0.0, (2) 2.34, (3) 4.68, (4) 7.02, (5) 9.36 mol/L.

This spectrum shows the formation of nitroxide II (A_N = 13.9 G, $A_{\beta\text{-H}}$ = 4.5 G) which is generated by the addition to PBN of a radical (R·) produced in this system.



II

The spectrum shown in Fig. 9 was observed when the reaction was performed in a MMA-acetonitrile mixture in the presence of 2-methyl-2-nitrosopropane (BNO). This spectrum is assigned to nitroxide IV (A_N = 14.5 G, $A_{\beta\text{-H}}$ = 10.3 G) which is derived from hydrogen-abstraction from the α-methyl group of MMA (Eqs. 1 and 2).

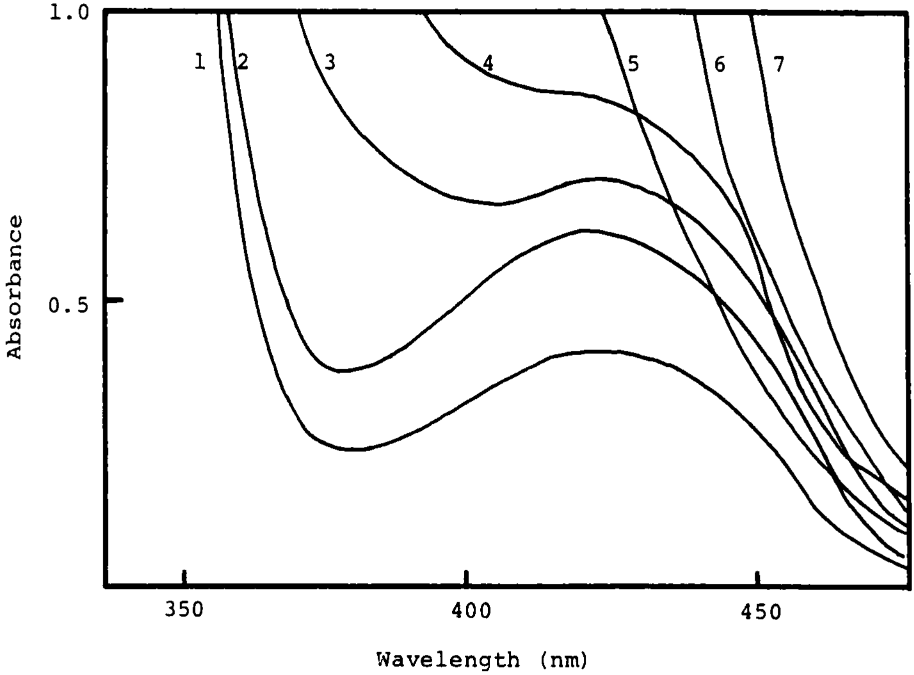
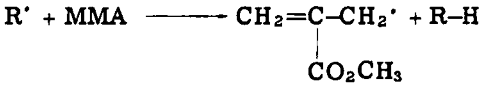
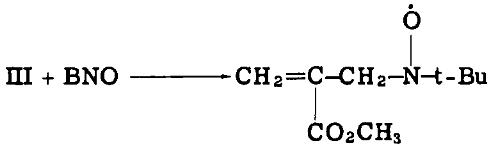


FIG. 6. Effect of DMAO on the visible spectrum of PhG·H$_2$O at room temperature in a 1:1 (v/v) MMA-acetonitrile mixture: [PhG·H$_2$O] = 1.0 × 10^{-2}, [DMAO] (1) 0.0, (2) 2.5 × 10^{-3}, (3) 5.0 × 10^{-3}, (4) 1.0 × 10^{-2}, (5) 5.0 × 10^{-2}, (6) 1.0 × 10^{-1}, (7) 2.0 × 10^{-1} mol/L.



$$R^{\bullet} + MMA \longrightarrow \underset{CO_2CH_3}{CH_2{=}\underset{|}{C}}{-}CH_2^{\bullet} + R{-}H \qquad (1)$$

III



$$III + BNO \longrightarrow \underset{CO_2CH_3}{CH_2{=}\underset{|}{C}}{-}CH_2{-}\overset{\overset{\bullet}{O}}{\overset{|}{N}}{-}t\text{-}Bu \qquad (2)$$

IV

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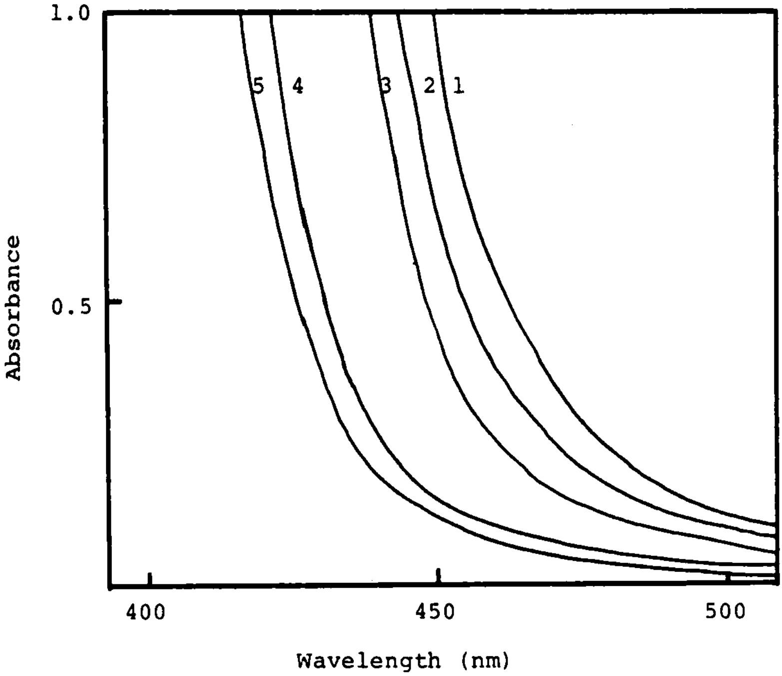

FIG. 7. Effect of MMA on the visible spectrum of the DMAO/ $PhG{\cdot}H_2O$ system at room temperature in acetonitrile: [DMAO] = [$PhG{\cdot}H_2O$] = 5.0×10^{-2}, [MMA] (1) 0.94, (2) 2.81, (3) 4.68, (4) 6.55, 8.42 mol/L.

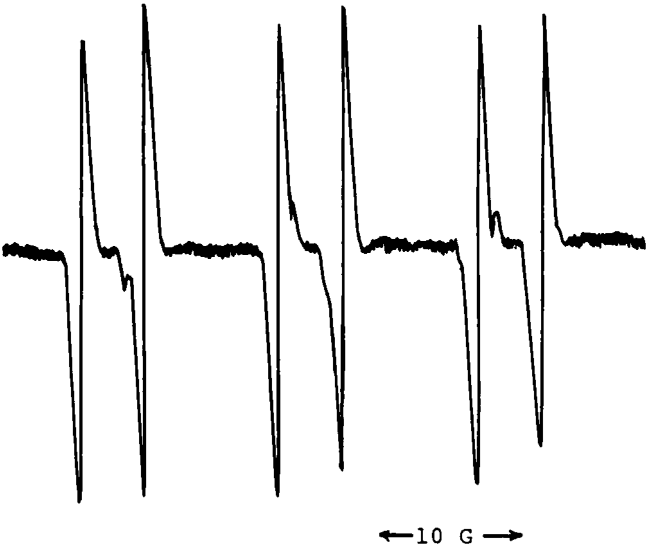

FIG. 8. ESR spectrum of the DMAO/$PhG{\cdot}H_2O$/PBN system after reacting at 60°C for 45 min in acetonitrile: [DMAO] = 3.0×10^{-2}, [$PhG{\cdot}H_2O$] = 5.0×10^{-2}, [PBN] = 1.0×10^{-1} mol/L.

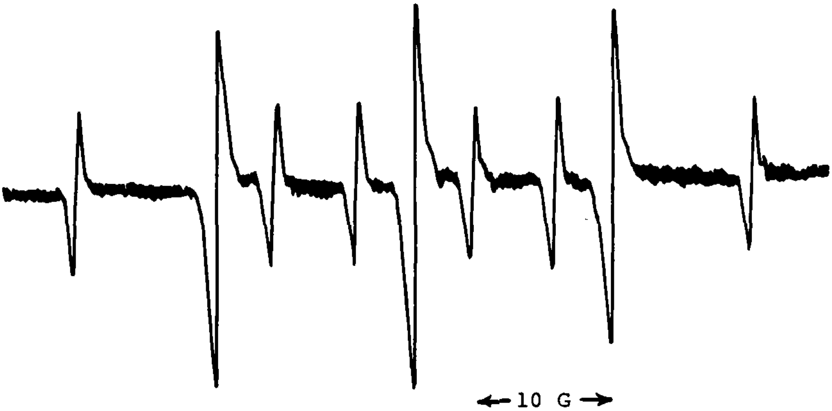

FIG. 9. ESR spectrum of the DMAO/PhG·H$_2$O/BNO system after reacting at room temperature for 21 h in a 1:1 (v/v) MMA-acetonitrile mixture: [DMAO] = 1.5×10^{-2}, [PhG·H$_2$O] = 5.0×10^{-2}, [BNO] = 5.0×10^{-3} mol/L.

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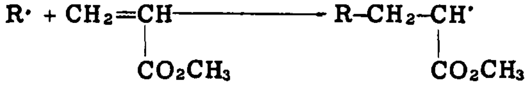
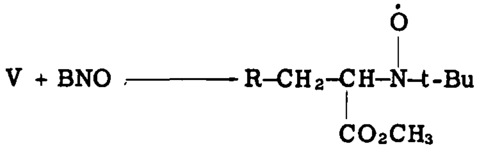
From the DMAO/PhG·H$_2$O/MA/BNO system, nitroxide VI (A_N = 15.2 G, $A_{\beta\text{-}H}$ = 2.7 G) was observed. It is formed by the reaction of MA with a radical (R·) in the presence of BNO (Eqs. 3 and 4).



$$R\cdot + CH_2{=}\underset{\displaystyle CO_2CH_3}{\underset{|}{CH}} \longrightarrow R{-}CH_2{-}\underset{\displaystyle CO_2CH_3}{\underset{|}{CH^{\cdot}}} \qquad (3)$$

V



$$V + BNO \longrightarrow R{-}CH_2{-}\underset{\displaystyle CO_2CH_3}{\underset{|}{CH}}{-}\overset{\overset{\cdot}{O}}{\overset{|}{N}}{-}t\text{-}Bu \qquad (4)$$

VI

These observations conform to the conclusion obtained from the results of the copolymerization of MMA with St and of the effect of inhibitor: this polymerization propagates via radical mechanism.

Initiation Mechanism

From the results obtained, the following initiation mechanism is proposed for the DMAO/PhG·H$_2$O system. The electron-transfer

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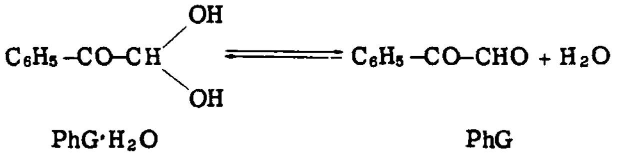
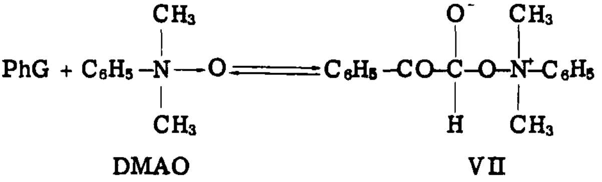
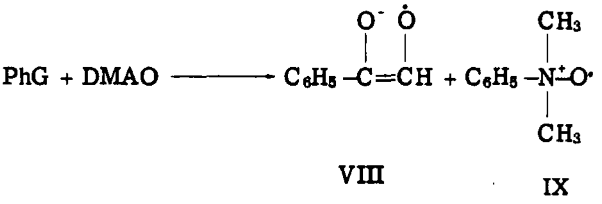
reaction from DMAO to free PhG (Eq. 7) seems to be responsible for initiation of polymerization.



$$\underset{\text{PhG}\cdot\text{H}_2\text{O}}{C_6H_5\text{-CO-CH}(OH)_2} \rightleftharpoons \underset{\text{PhG}}{C_6H_5\text{-CO-CHO}} + H_2O \qquad (5)$$

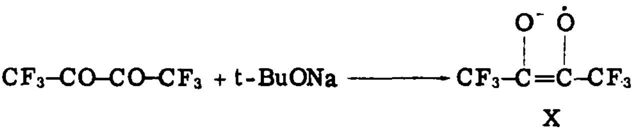


$$\text{PhG} + \underset{\text{DMAO}}{C_6H_5\text{-}\overset{CH_3}{\underset{CH_3}{N}}\text{—O}} \rightleftharpoons \underset{\text{VII}}{C_6H_5\text{-CO-}\overset{O^-}{\underset{H}{C}}\text{-O-}\overset{CH_3}{\underset{CH_3}{N^+}}\text{-}C_6H_5} \qquad (6)$$



$$\text{PhG} + \text{DMAO} \longrightarrow \underset{\text{VIII}}{C_6H_5\text{-}\overset{O^-}{C}\text{=}\overset{\dot{O}}{CH}} + \underset{\text{IX}}{C_6H_5\text{-}\overset{CH_3}{\underset{CH_3}{N^+}}\text{-}O^\bullet} \qquad (7)$$

Many semidiones involving anion radical VIII has been known to be generated by reduction of the corresponding diketones by alkali metal or iodide salt. Recently, perfluorodiacetyl was reported to be easily reduced by tert-butoxide or iodide ion to form the corresponding semidione (X) [12].



$$CF_3\text{-CO-CO-}CF_3 + \text{t-BuONa} \longrightarrow \underset{\text{X}}{CF_3\text{-}\overset{O^-}{C}\text{=}\overset{\dot{O}}{C}\text{-}CF_3} \qquad (8)$$

The complex of DMAO and PhG shown in Fig. 6 might correspond to Adduct VII, and consequently its formation reduces the concentrations of DMAO and free PhG. Therefore, when the concentration of DMAO (or PhG·H_2O) is much higher than that of PhG·H_2O (or DMAO), R_p is reduced since the concentration of free PhG (or DMAO) becomes quite low. This trend is apparently observed in Fig. 4.

Further, the addition of MMA accelerates dissociation of PhG·H_2O (as observed in Fig. 5) and suppresses formation of complex VII (in Fig. 7). Accordingly, the presence of MMA results in an increase of the concentrations of free DMAO and free PhG. In fact, the high dependence of R_p on MMA concentration is observed in the concentration range 3.8-5.6 mol/L (in Fig. 3).

Radicals VIII and IX produced by Reaction (7) might abstract hydrogen from the α-methyl group of MMA, which results in formation of nitroxide IV. A similar result was also observed in our previous study on the initiation system of DMAO and TCNQ in which the electron transfer from DMAO to TCNQ is considered to occur in the initiation step [6]. Recently, tert-butoxy radical, an oxy radical, was found to have a high reactivity for hydrogen-abstraction from the α-methyl groups of MMA and methacrylonitrile [13].

REFERENCES

[1] M. Imoto, T. Sato, and K. Takemoto, Makromol. Chem., 95, 117 (1966).
[2] T. Sato, K. Takemoto, and M. Imoto, Ibid., 104, 297 (1967).
[3] T. Sato and T. Otsu, Ibid., 137, 43 (1970).
[4] T. Sato, S. Kita, and T. Otsu, Ibid., 180, 1911 (1979).
[5] T. Sato, M. Yoshioka, and T. Otsu, Ibid., 153, 47 (1972).
[6] T. Sato, M. Yoshioka, and T. Otsu, Ibid., 177, 2009 (1976).
[7] T. Sato and T. Otsu, Ibid., 125, 1 (1969).
[8] A. Szent-Györgyi, Chem. Eng. News, p. 16 (July 25, 1975).
[9] H. A. Riley and A. R. Gray, Organic Syntheses, Collective Vol. II, 1943, p. 509.
[10] W. D. Emmons, J. Am. Chem. Soc., 79, 5739 (1957).
[11] R. J. Holman and M. J. Perkins, J. Chem. Soc., C, p. 2195 (1970).
[12] G. A. Russell and J. L. Gerlock, J. Am. Chem. Soc., 96, 5838 (1974).
[13] T. Sato and T. Otsu, Makromol. Chem., 178, 1941 (1977).

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