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Vinyl Polymerization. CLXXXV. Polymerization of Methyl Methacrylate Initiated with Benzoic Anhydride and Dimethylaniline N-Oxide. Effects of Solvent and the Substituent of the Initiator

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Summary

Studies on the rate of the reaction of substituted dimethylaniline N-oxide (DMAO) with substituted benzoic anhydride (Bz_2O) and the rate of polymerization of methyl methacrylate (MMA) with their systems were made. The solvent effects on the rate of the reaction of DMAO with Bz_2O and on the polymerization of MMA with the system were also studied.

In previous papers [1], we have shown that the benzoic anhydride (Bz_2O)-dimethyl aniline N-oxide (DMAO) system could initiate the polymerization of several vinyl monomers, such as methyl methacrylate, acrylonitrile, or styrene, through a radical mechanism, and the polymerization was accelerated by the presence of alcohol, which seemed to affect the initiator efficiency [2].

The present paper deals with a study on the effects of the substituents introduced in DMAO and Bz_2O and of the solvents on the rates of the reaction between substituted DMAO and substituted Bz_2O and on the rate of the polymerization of MMA initiated with substituted DMAO and Bz_2O .

EXPERIMENTAL

Materials

Benzoic anhydride was purified by repeated recrystallization from ethanol, m.p. 43°C. p-Substituted benzoic anhydrides were

prepared by the reaction of corresponding benzoic acid and acetic anhydride, according to the method of Berliner and Alstchul [3]. *p*-Chloro-benzoic anhydride was recrystallized from benzene, m.p. 192–193°C (lit. [3] 192.9–193.4°C). *p*-Bromobenzoic anhydride was recrystallized from benzene, m.p. 217–218°C (lit. [4] 218°C). *p*-Methoxybenzoic anhydride was recrystallized from benzene-petroleum benzine, m.p. 98–99°C (lit. [3] 98.5–98.8°C). *p*-Toluic anhydride was recrystallized from petroleum benzine, m.p. 94–95°C (lit. [3] 94.3–94.8°C). *p*-Cyanobenzoic anhydride was purified by passing its benzene solution through a column packed with silica gel and recrystallized from benzene, m.p. 208–209°C.

Anal.: Calcd. for $C_{16}H_8O_3N_2$: C, 69.56; H, 2.92. Found: C, 69.53; H, 3.04.

Dimethylaniline N-oxide (DMAO) was prepared in the same manner as described in the preceding paper [1]. *p*-Substituted DMAO's were also prepared in the same way and recrystallized from acetone. *p*-Chloro-DMAO hydrochlorate was prepared from *p*-chlorodimethylaniline (DMA), which was prepared by methylation of *p*-chloroaniline with dimethyl sulfate, according to the method by Hünig [5], and recrystallized from methanol-acetone, m.p. 144–145°C (lit. [6] 142–143°C). *p*-Bromo DMAO hydrochlorate was prepared from *p*-bromo-DMA obtained by the reaction of DMA with bromine according to the method of Fries [7] and recrystallized from methanol-acetone, m.p. 168–169°C.

Anal.: Calcd. for $C_8H_{11}NOClBr$: C, 38.04; H, 4.39. Found: C, 38.02; H, 4.55.

p-Methyl-DMAO hydrochlorate was prepared from *p*-methyl-DMA obtained by the methylation of *p*-toluidine with methyl iodide, according to the method by Fukui et al. [8] and recrystallized from acetone, m.p. 140–141°C (lit. [6] 138°C). *p*-Methoxy-DMAO hydrochlorate was prepared from *p*-methoxy-DMA obtained by the methylation of *p*-anisidine with methyl iodide and recrystallized from acetone, m.p. 156°C.

Anal.: Calcd. for $C_9H_{14}O_2NCl$: C, 53.07; H, 6.92. Found: C, 53.18; H, 7.19.

Solvents and MMA were purified in the usual manner.

Determinations of the Rate of the Reaction of DMAO with Bz_2O and of the Rate of the Polymerization of MMA

The reaction of Bz_2O with DMAO was carried out at 40°C in benzene under stirring in a four-necked flask, which was flushed continuously with nitrogen. A small amount of ethanol was added to the reaction system to dissolve the DMAO. The concentrations of reagents can be seen in the figures. The rate of the reaction of DMAO with Bz_2O was determined by measuring the concentration of remaining DMAO iodometrically as described in the previous

paper [2] and the rate constant k was calculated according to

$$-d[\text{DMAO}]/dt = k[\text{DMAO}][\text{Bz}_2\text{O}]$$

Polymerization of MMA with the DMAO-Bz₂O system was carried out at 40°C in a tube which was flushed several times with oxygen-free nitrogen and sealed under vacuum, as in the previous paper [1].

The initiator efficiency f was calculated using the data given by Bevington [9], $k_p/k_t^{1/2} = 95 \exp(-4500/RT)$, and the rate equation previously obtained by us: $R_p = k[\text{Bz}_2\text{O}]^{1/2} [\text{DMAO}]^{1/2} [\text{C}_2\text{H}_5\text{OH}]$.

RESULTS AND DISCUSSION

Reaction Rate of Bz₂O with DMAO

Effects of Substituents on the Rate of the Reaction of Bz₂O with DMAO. First, the effect of the substituent of Bz₂O on the reaction rate was studied in benzene solution. Figure 1 shows second-order

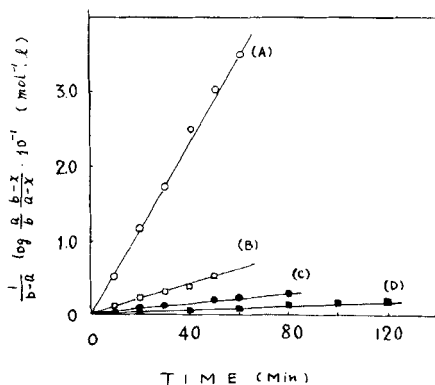


FIG. 1. Substituent effect on the reaction rate of DMAO with Bz₂O (1) in benzene at 40°C. (A) p-Cl-Bz₂O, (B) p-H-Bz₂O, (C) p-CH₃-Bz₂O, (D) p-CH₃O-Bz₂O. $[\text{DMAO}] = a = 1.33 \times 10^{-3}$ mole/liter, $[\text{x-Bz}_2\text{O}] = b = 8.75 \times 10^{-3}$ mole/liter in (A). $[\text{DMAO}] = a = 2.66 \times 10^{-2}$ mole/liter, $[\text{x-Bz}_2\text{O}] = b = 3.50 \times 10^{-2}$ mole/liter in (B), (C), and (D). $[\text{C}_2\text{H}_5\text{OH}] = 0.856$ mole/liter.

plots of the reaction rate vs. time. As can be seen from the figure, the reaction was accelerated by the electron-withdrawing substituent of Bz₂O. Second, the effect of the substituent of DMAO on the

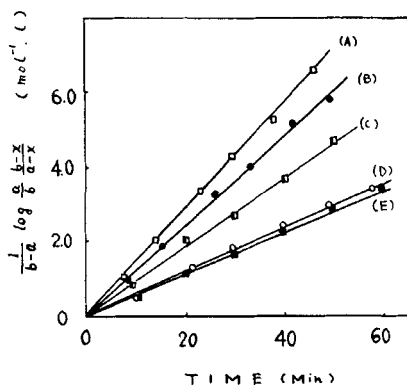
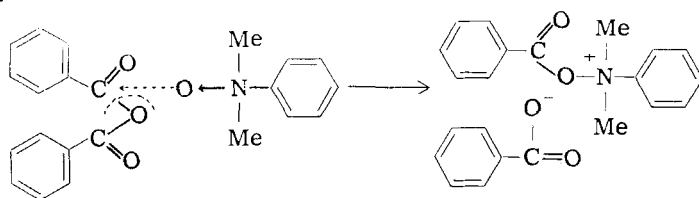


FIG. 2. Substituent effect on the reaction rate of DMAO with Bz_2O (2) in benzene at $40^\circ C$. (A) $p-CH_3O$ -DMAO, (B) $p-CH_3$ -DMAO, (C) $p-H$ -DMAO, (D) $p-Br$ -DMAO, (E) $p-Cl$ -DMAO. $[x-DMAO] = a = 2.66 \times 10^{-2}$ mole/liter, $[Bz_2O] = b = 3.50 \times 10^{-2}$ mole/liter. $[C_2H_5OH] = 0.856$ mole.

reaction rate was studied. The second-order dependence was also observed, as can be seen from Fig. 2. In contrast with the case of Bz_2O , introduction of an electron-releasing group in DMAO was found to increase the reaction rate. Both results obeyed Hammett's relationship, as shown in Fig. 3; the reaction constant ρ was obtained as 3.0 in the former case and -0.8 in the latter case.

These results suggest that the rate-determining step is the attacking reaction of the lone pair of oxygen of $N \rightarrow O$ group on the positive carbonyl carbon of Bz_2O , as shown in the following mechanism:



Considering the small value of ρ , -0.8 , the effect of the substituent of DMAO seems to be small, which was due partly to the presence of ammonium nitrogen between the benzene ring and the oxygen of reaction site, and partly to the formal negative charge on oxygen.

Solvent Effect on the Reaction of DMAO with Bz_2O . The reaction of DMAO with Bz_2O was carried out at $40^\circ C$ in various solvents in the presence of 0.856 mole/liter of ethanol, where the initial concentrations of DMAO and Bz_2O were kept constant at 2.66×10^{-2}

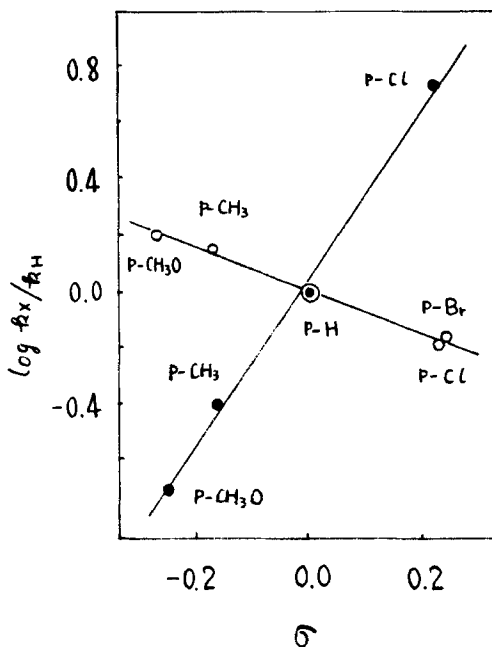
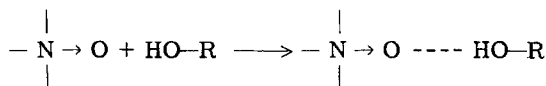


FIG. 3. Hammett's relationship for the reaction of DMAO with Bz_2O : \circ —, for the reaction of subst.—DMAO with Bz_2O , $\rho = -0.8$; \bullet —, for the reaction of DMAO with subst.— Bz_2O , $\rho = 3.0$.

mole/liter and 3.50×10^{-2} mole/liter, respectively. Time-conversion curves were shown in Fig. 6. Solvents used were acetonitrile, chloroform, dioxane, dimethylformamide (DMF), ethanol, and benzene. As can be seen from Fig. 4, aprotic polar solvents, such as acetonitrile or DMF, accelerated the reaction, while protic solvent, such as ethanol, retarded the reaction. This result seems to coincide with the conclusion that the attack of the oxygen of DMAO on the carbonyl carbon of Bz_2O is the rate-determining step, because the proton may cover the reactivity of the negative oxygen of the N-oxide, by the following mechanism:



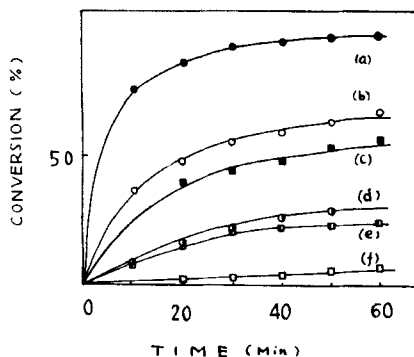


FIG. 4. Solvent effect on the reaction rate of DMAO with Bz_2O at $40^\circ C$. $[DMAO] = 2.66 \times 10^{-2}$ mole/liter, $[Bz_2O] = 3.50 \times 10^{-2}$ mole/liter, $[C_2H_5OH] = 0.856$ mole/liter. (a) DMF, (b) dioxane, (c) acetonitrile, (d) benzene, (e) chloroform, (f) ethanol.

Polymerization of MMA with the DMAO- Bz_2O System

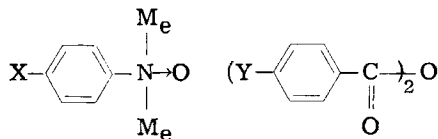
Effect of the Substituents on the Rate of the Polymerization Carried Out in Benzene. The effect of the substituents introduced in Bz_2O or DMAO on the rate of the polymerization of MMA with the Bz_2O -DMAO system was studied under about the same conditions as in the reaction of DMAO with Bz_2O .

The initial rates of polymerization are summarized in Table 1, together with the values of initiator efficiency f , and relative rates. As seen from this table, electron releasing and electron attracting of DMAO could accelerate the polymerization, although the effect was larger in the former case than that in the latter.

Initiator efficiencies, f , were markedly small. The rate of polymerization seems to be controlled predominantly by the magnitude of this efficiency. As stated repeatedly, the reaction of DMAO with Bz_2O proceeds in a solvent cage, especially in the case of nonpolar solvent. Only when the benzoate radical escapes out from the cage, it can initiate a polymerization. By this idea the above conclusion, that the introduction of the substituent increased the value of f and accordingly the rate of polymerization, may be interpreted.

Polymerization of MMA in Acetonitrile by Unsubstituted DMAO and Bz_2O . As described earlier [2], the polymerization of MMA in acetonitrile proceeded at a much higher rate, even in the absence of alcohol, than in benzene and in the presence of alcohol. In the present paper, the polymerization was further carried out kinetically at $40^\circ C$ in the absence of alcohol. The concentrations of DMAO and Bz_2O varied in the range between 3.92×10^{-3} and 5.36×10^{-2} mole/liter, keeping the molar ratio of the reagents

TABLE 1. Substituent Effect on Polymerization Rate of MMA in Benzene with the DMAO-Bz₂O System at 40°C ([MMA] = 4.46 moles/liter; [X-DMAO] = [Y-Bz₂O] = 4.77 × 10⁻² mole/liter; [EtOH] = 0.816 mole/liter)



| Substituent | | $R_p \times 10^5$, mole/liter sec | Relative rate | Initiator efficiency, f |
|-----------------|-------------------|---------------------------------------|------------------|------------------------------|
| X | Y | | | |
| CH ₃ | H | 11.3 | 3.6 | 6.3×10^{-3} |
| H | H | 3.1 | 1.0 | 0.8×10^{-3} |
| Cl | H | 4.2 | 1.3 | 2.1×10^{-3} |
| Br | H | 4.5 | 1.4 | 2.3×10^{-3} |
| H | CH ₃ O | 4.5 | 1.4 | 8.0×10^{-3} |
| H | CH ₃ | 3.3 | 1.1 | 2.3×10^{-3} |

constant at 1:1. At Fig. 5 shows, the rate equation was obtained as follows:

$$R_p = k([\text{DMAO}][\text{Bz}_2\text{O}])^{0.31}$$

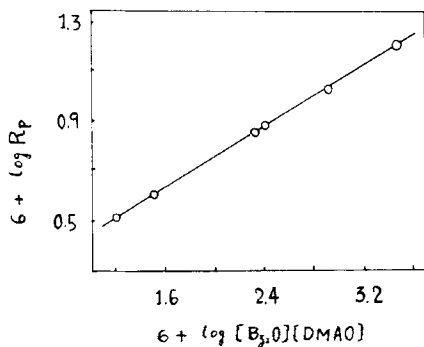
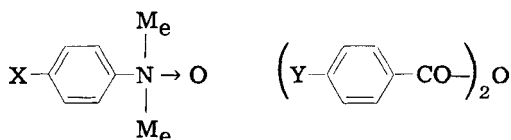


FIG. 5. Relationship between R_p and concentration of initiator in acetonitrile at 40°C. [MMA] = 4.46 moles/liter, in the absence of ethanol.

As the polymerization proceeded homogeneously through a radical mechanism, the exponential of 0.31 was abnormal. The reason is obscure. As already reported [1], the rate equation in benzene was expressed as $R_p = k[\text{DMAO}]^{1/2} [\text{Bz}_2\text{O}]^{1/2}$.

Polymerization of MMA in Acetonitrile by Substituted DMAO and Bz₂O. The polymerization was carried out in the same conditions as described above in the absence of alcohol. The initial rate of the polymerization and their relative values are listed in Table 2.

TABLE 2. Substituent Effect on Polymerization of MMA in Acetonitrile with the DMAO-Bz₂O System at 40°C ([MMA] = 4.46 moles/liter)



| Substituent | | Concentration of catalyst 10 ² , moles/liter | | moles/liter sec | Relative rate |
|-----------------|-------------------|--|---------------------|-----------------|---------------|
| X | Y | X-DMAO | Y-Bz ₂ O | | |
| H | CH ₃ O | 1.59 | 1.59 | 0.43 | 0.58 |
| H | CH ₃ | 1.59 | 1.59 | 0.51 | 0.68 |
| H | H | 1.59 | 1.59 | 0.75 | 1.00 |
| H | Cl | 0.795 | 0.795 | 1.14 | 2.34 |
| H | Br | 0.398 | 0.398 | 0.69 | 2.26 |
| H | CN | 0.398 | 0.398 | 1.83 | 6.0 |
| CH ₃ | H | 1.59 | 1.59 | 1.03 | 1.4 |
| Br | H | 1.59 | 1.59 | 0.60 | 1.08 |
| Cl | H | 1.59 | 1.59 | 0.64 | 0.85 |

As can be seen from the table, the polymerization in acetonitrile was accelerated by an electron-withdrawing group of Bz₂O or an electron-releasing group of DMAO. This trend is quite similar to that observed in the reaction of DMAO with Bz₂O in benzene. Hammett's plots of these results gave $\rho = 1.1$ for substituents of Bz₂O and $\rho = -0.6$ for those of DMAO, as shown in Fig. 6.

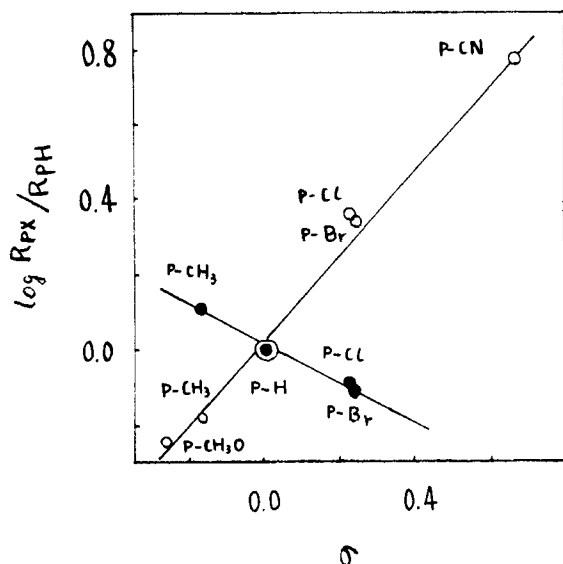
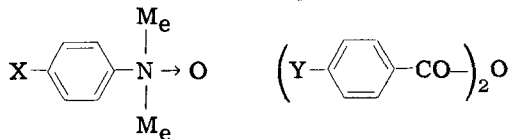


FIG. 6. Hammett's relationship for the polymerization of MMA with the Bz_2O -DMAO system in the absence of ethanol in acetonitrile at 40°C . —●—, for polymerization with the subst. —DMAO- Bz_2O system, $\rho = -0.6$; —○—, for polymerization with the DMAO-subst. — Bz_2O system, $\rho = 1.1$.

The substituent effect on the rate of polymerization carried out in the presence of ethanol was studied, where the concentrations of MMA, ethanol, substituted DMAO, and substituted Bz_2O were kept constant at 4.46, 0.816, 3.98×10^{-3} , and 3.98×10^{-3} mole/liter, respectively. The results obtained are tabulated in Table 3. As can be seen from the table, an electron-withdrawing group of Bz_2O accelerated, and electron-releasing groups retarded, the polymerization, as was observed in the absence of ethanol, but their effects were smaller than in the presence of alcohol. On the other hand, the substituents of DMAO have little effect on the polymerization. Hammett's plots of these results gave $\rho = 0.6$ for substituents of Bz_2O and $\rho \sim 0$ for those of DMAO, as shown in Fig. 7.

Effect of the Solvent on the Polymerization Rate of MMA with Substituted DMAO and Bz_2O . The polymerization of MMA with the DMAO- Bz_2O system was also carried out at 40°C in various solvents, where the concentrations of MMA, ethanol, Bz_2O , and DMAO were kept constant at 4.46, 0.816, 4.77×10^{-2} , and 4.77×10^{-2}

TABLE 3. Substituent Effect on Polymerization of MMA in Acetonitrile in the Presence of Ethanol at 40°C
 ([MMA] = 4.46 moles/liter, [Y-Bz₂O] = [X-DMAO] = 3.98 × 10⁻³ mole/liter [EtOH] = 0.816 mole/liter)



| Substituent | | $R_p \times 10^4$ moles/liter sec | Relative rate | R_p (in the pres- ence of EtOH) |
|-----------------|-------------------|--------------------------------------|------------------|--------------------------------------|
| X | Y | | | R_p (in the absence of EtOH) |
| H | CH ₃ O | 0.85 | 0.60 | 4.8 |
| H | CH ₃ | 1.16 | 0.81 | 5.6 |
| H | H | 1.43 | 1.00 | 4.7 |
| H | Cl | 2.12 | 1.48 | 3.0 |
| H | Br | 2.02 | 1.41 | 2.9 |
| CH ₃ | H | 1.35 | 0.95 | 3.2 |
| Cl | H | 1.59 | 1.11 | 6.1 |
| Br | H | 1.45 | 1.02 | 6.0 |

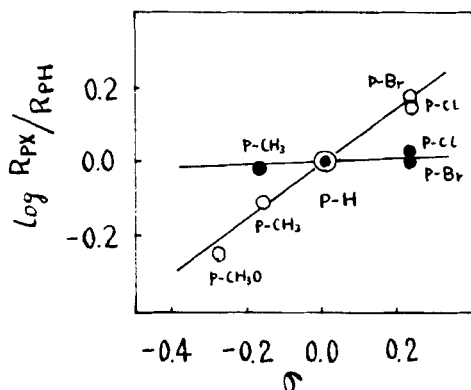


FIG. 7. Hammett's relationship for the polymerization with the Bz₂O-DMAO system in the presence of ethanol in acetonitrile, at 40°C. —○—, for polymerization with the DMAO-subst.-Bz₂O system, $\rho = 0.6$; —●—, for polymerization with the subst.-DMAO-Bz₂O system, $\rho \sim 0$.

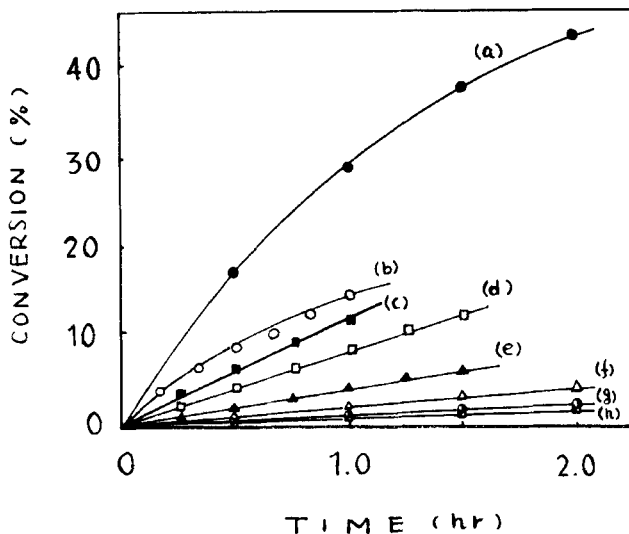


FIG. 8. Solvent effect on polymerization rate of MMA with DMAO-Bz₂O system at 40°C. [MMA] = 4.46 moles/liter, [DMAO] = [Bz₂O] = 4.77 × 10⁻² mole/liter, [C₂H₅OH] = 0.816 mole/liter. (a) ethanol, (b) acetonitrile, (c) benzonitrile, (d) DMF, (e) acetone, (f) benzene, (g) dioxane, (h) THF.

mole/liter, respectively. Time conversion curves are shown in Fig. 8. In contrast with the case of the reaction between Bz₂O and DMAO, the polymerization was accelerated in ethanol and retarded in dioxane or tetrahydrofuran. Such nonparallelism between the rate of polymerization and that of the reaction may be due to the difference of the ratio of the radical process to the ionic one.

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Zusammenfassung

Es wird über Untersuchungen der Reaktionsgeschwindigkeit von substituiertem Dimethylanilin-N-oxid (DMAO) mit substituiertem Benzoesäureanhydrid (Bz_2O) und der Polymerisationsgeschwindigkeit mit Methylmethacrylat (MMA) berichtet. Ebenfalls untersucht wurden Lösungsmittelleffekte auf die Reaktionsgeschwindigkeit von DMAO mit Bz_2O und die Polymerisationsgeschwindigkeit dieses Systems mit MMA.

Résumé

On a fait des études sur la vitesse de la réaction du N-oxyde de la diméthylaniline (DMAO) substituée avec l'anhydride benzoïque (Bz_2O) substitué et sur la vitesse de polymérisation du méthacrylate de méthyl avec le système de ces réactifs. L'effet de solvant sur la vitesse de ces deux réactions a également été étudié.