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Polymerization of methylmetacrylate in the presence of quaternary ammonium salts

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SUMMARY

At 50°C, trioctyl methyl ammonium salts influence the rate of bulk polymerization of methylmetacrylate initiated by dibenzoyl peroxide. Acetate increases it, chloride, chlorate, and bromate increase it only on start, hydroxide, bromide, tetrachlorozincate, trifluoroacetate and trifluoromethanesulfonate decrease it, iodide and dichromate inhibit the polymerization, whereas fluoride, perchlorate, some (substituted) benzoates as well as sulfonates do not change the reaction rate. The influence on kinetic parameters of polymerization and the formation of intermediates and products suggest that the exchange of anions between the quaternary ammonium salt and dibenzoyl peroxide is the primary mechanism of action of these salts and other effects accompany it.

INTRODUCTION

It has been reported, that quaternary ammonium salts took part in initiation of vinyl polymerization in the presence of peroxides in emulsion systems (1) as well as in solution systems (2,3). Their use in bulk systems was prevented by the limited solubility of the salts used in pure monomers. The good enough solubility of trioctyl methyl ammonium salts (**TOMAX**) in monomers enabled the study of the bulk systems too. It has been observed that counterions, i.e., anions, exerted definite influences on the onset and kinetics of the polymerization of methylmetacrylate (**MMA**) initiated by the dibenzoyl peroxide (**DBPO**) - TOMAX systems (4). The study of the reaction at molar ratio 1:1 with help of a radical trapping agent has shown that with acetate or benzoate (**PhCOO⁻**) as counterions, the spin trap products absorbing at 254 nm were the same as in the absence of quaternary ammonium salts whereas with chloride as counterion those usual products represented only minor components (5,6). The volatile products of reaction were different too (7). The kinetics was reexamined including a greater number of anions and the products of reaction between the TOMA salts, DBPO and solvents or MMA were examined.

EXPERIMENTAL

TOMACl (Merck No. 818079) was purified on a silica column by applying excess of its solution in diethylether (Et_2O), washing with Et_2O-MeOH 95:5, elution with MeOH and vacuum drying the eluate. TOMAOH was prepared by mixing ethanolic solutions of TOMACl and KOH, other salts by neutralizing TOMAOH with corresponding acid or equilibrating with a salt solution.

MMA was freed from hydroquinone by extraction with 4% NaOH, washing, drying and distillation. If needed, 10 mg of 2-tert-butyl-4,6-dimethylphenol per kg of MMA was added. Polymerization was carried out in dilatometers at 50+/-0.05°C with 6 g DBPO/kg MMA. Conversion range was <10%. Residual initiator was determined iodometrically or checked by thin layer chromatography (TLC). Polymer was precipitated in Et_2O, the solution purified on a silica column and analysed by TLC and/or GC and/or GC/MS. Polymer was redissolved in CH_2Cl_2, precipitated once again with Et_2O, later several times with MeOH, followed by exhaustive extraction with MeOH. Dying was performed with an Orange II solution in phosphate buffer, pH 2 to 10. Molar mass distribution was measured by GPC, Waters Mod. 510, column u Styragel, against polystyrene standards. FTIR spectra were recorded on a Bio-Rad FTS 15/80 spectrometer in transmission or reflexion mode. NMR spectra were obtained with a Varian VXR 300 spectrometer. TLC was performed on silica sheets (Merck No. 5554). Eluents: Et_2O-MeOH 95:5 for TOMAX and amines, hexane-Et_2O 9:1 and (8) for peroxides, (9) for fluorescein derivatives. GC : Varian 3700 Gas Chromatograph, 3% OV-101 on Varaport 30, FID or 30 m SPB-5, ECD. GC/MS: HP 5840-A/HP 5985, 30 m SPB-5, I.D. 0.2 mm.

RESULTS AND DISCUSSION

Polymerization kinetic data

The dilatometer readings were found to obey the **Eq. 1**

$$v=a(t-t_1)^n \tag{1}$$

v - dilatometer reading, t_1 - lag time

to within the experimental error with exceptions discussed separately. The coefficients of **Eq. 1** are summerised in **Tab. 1**. According to the value of the exponent **n**, the anions in TOMAX could be divided into two groups; on one hand those giving rise to **n**=1 like DBPO alone, e.g., OH^-, F^-, ClO_4^-, HSO_4^-, $ZnCl_4^{2-}$, acetate, benzoate, substituted benzoates, sulfonates, and on the other hand those exhibiting **n**<1: Cl^-, Br^-, ClO_3^-, BrO_3^-. The dependence of exponent **n** on molar ratio of TOMAX : DBPO for TOMACl and TOMABr is presented in **Fig. 1**. With anions giving rise to **n**=1 the value of **n** did not depend on the ratio of [TOMAX] : [DBPO].

The relative initial rate of polymerization expressed as **$a_x n/a_0$** did not differ from that without TOMAX in most cases. At high concentrations, only Cl^-, ClO_3^-, BrO_3^- (**n**<1) and acetate (**n**=1) increased the initial rate of polymerization, whereas OH^-, Br^-, $ZnCl_4^{2-}$, CF_3COO^-, $CF_3SO_3^-$, and especially iodide and dichromate decreased it. Azide reacted immediately with gas evolution and slow residual polymerization. From **Fig. 2** follows that the initial rate of polymerization increased but the rate observed after 2 hours decreased with increasing TOMACl concentration. **Fig. 3** on the other hand shows that only a decrease of the rate of polymerization was observed with increasing TOMABr concentration. Diffuse daylight had a pronounced accelerating effect when bromine was the only initiator, whereas this effect was less expressed with $TOMABr_3$ as initiator. The results obtained with TOMABr + DBPO as

Table 1. Kinetic parameters as constants of Eq.1 in presence of different TOMA salts. [TOMAX] : [DBPO] = 3:1; 00 and 10: inhibitor,mg/kg; t_I, min; a_x: with TOMAX, a_0: no TOMAX.

TOMAX	t_I		n	$a_x n/a_0$	TOMAX	t_I		n	$a_x n/a_0$
	00	10				00	10		
none(0)	22	56	1.0	1.0	CH_3COO	15	15	1.0	1.5
OH	35	**	1.0	0.9	CF_3COO	42	75	1.0	0.9
F	15	22	1.0	1.0	PhCOO	37	47	1.0	1.0
Cl	<5	<5	0.6	1.5	$4CH_3PhCOO$	67	**	1.0	1.0
Br	10	12	0.7	0.1	$2OCH_3PhCOO$	22	33	1.0	1.0
I, I_3				0.01	2,4diClPhCOO	17		1.0	1.0
ClO_3	15	22	0.9	1.4	2,5diClPhCOO	30	40	1.0	1.0
BrO_3	7	5	0.8	1.6	$3,5diNO_2PhCOO$	20	45	1.0	0.9
ClO_4	20	52	1.0	1.0					
HSO_4	21	37	1.0	1.0	$4CH_3PhSO_3$	20	40	1.0	1.0
Cr_2O_7	35	50		0.03	CH_3SO_3	30	**	1.0	1.0
$ZnCl_4$	27	65	1.0	0.3	CF_3SO_3	22	50	1.0	0.8

** more than 120 min

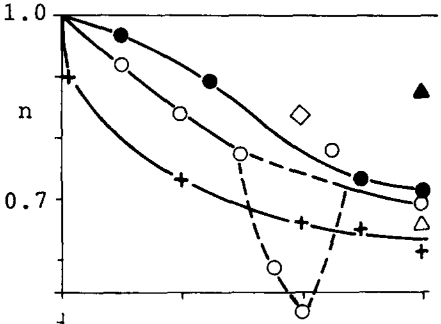

Fig. 1. The dependence of exponent **n** of Eq. 1 on the ratio [TOMAX] : [DBPO]. +: X=Cl; ○: X=Br, light; ●: X=Br, dark; ◇: Br_2, light; △, ▲: $TOMABr_3$, light and dark, respectively.

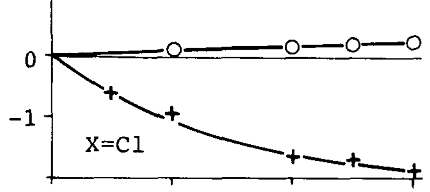

Fig. 2. The dependence of the relative rate of polymerization on the ratio [TOMACl] : [DBPO]. ×: initial rate; +: rate after 2h.

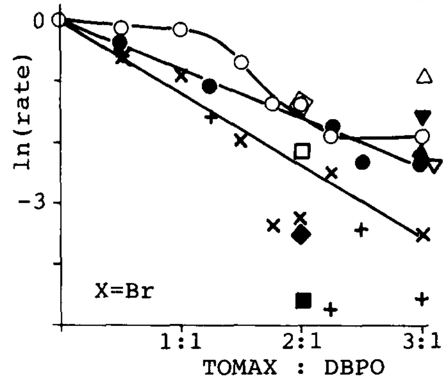

Fig. 3. The dependence of the relative rate of polymerization on the ratio [TOMABr] : [DBPO]. ○, ●: initial rate; ×, +: rate after 2h. Other initiators: ◇, ◆: Br_2, initial rate; □, ■: Br_2 after 2h; △, ▲: Br_3^-, initial rate; ▽, ▼: Br_3^-, after 2h. All in diffuse daylight and in dark, respectively.

initiator system indicate the gradual transition of characteristics from DBPO over Br_2 to $TOMABr_3$ as initiator with a higher loss of initiator at higher [TOMABr] : [DBPO] ratios. The sigmoid curve suggests a 2:1 molar reaction.

Regarding the lag time of polymerization most TOMAX tended to shorten it even in the presence of a phenolic inhibitor, **Tab. 1**. Especially active in this respect were those salts exhibiting $n<1$. On the other hand, OH^-, $ZnCl_4^{2-}$, $CH_3SO_3^-$, $4\text{-}CH_3PhCOO^-$ and CF_3COO^- increased the lag time. In the presence of inhibitor lag time decreased linearly with increasing TOMACl concentration and leveled off at its approx. eightfold molar excess, **Fig. 4**.

The correlation factor r was mostly >>0.99. It showed a deterioration of the fit of **Eq. 1** to below 0.98 when [TOMAX]:[DBPO], X= Br or Cl, increased over 2:1. In such cases, careful observation of dilatometric curves suggested that the course of polymerization could be divided into three parts: at the beginning fast polymerization lasting approx. 30 or 10 min, respectively, followed by an intermediate region and after one hour slow polymerization as if there were little initiation but slow termination of polymerization.

Kinetics of DBPO decay

The last mentioned observation suggested the question about the fate of dibenzoyl peroxide in the presence of TOMAX. This could be studied only with TOMACl since in benzene as solvent a strong greenish yellow color and smell of chlorine developed that could be quenched within a few seconds by MMA, whereas with TOMABr the orange color developed during the reaction persisted for more than 10 min after addition of MMA. The results of measurements in benzene and MMA as solvents, **Fig 5**, suggested a virtually first order decay of total oxidant in both solvents. In MMA, the half time for the reaction was approx. 3 min at $50^{\circ}C$ and the reaction was over within 10 min,

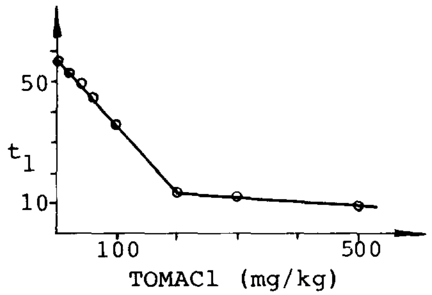

Fig. 4. Lag time vs. concentration of TOMACl in MMA + 10 ppm inhibitor.

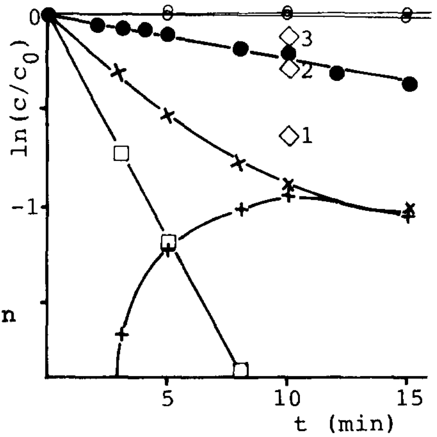

Fig. 5. Decay of DBPO in benzene and MMA. ○ - no TOMACl; [TOMACl] : [DBPO] 2:1 : ●, +, × - in benzene, total oxidant, Cl_2, and DBPO, resp.; □, ◇1, ◇2, ◇3 - in MMA, [PhCOOH] : [TOMACl] : [DBPO] = 0:2:1, 1:2:1, 2:2:1, and 3:2:1, respectively.

cf. dilatometric results. In benzene, the decay of total oxidant was much slower. The residual oxidant seemed to be composed of chlorine that could be quenched by MMA, and the nonquenched part was found to be DBPO by TLC. In some trials traces of another UV absorbing compound could be observed. The maximum chlorine concentration seemed to be reached within 1o min too and during this time the equilibrium seemed to be approached. Addition of benzoic acid decreased the rate of reaction of DBPO towards that without TOMACl in a manner suggesting strong competition between PhCOO$^-$ and Cl$^-$. HCl and (TOMA)$_2$ZnCl$_4$ did not react with DBPO under these conditions.

Reaction products

When reacting TOMAX and DBPO in benzene, fluorescein and 2,7-dichlorofluorescein got chlorinated if exposed to the gas phase over benzene solution in the case of TOMACl and brominated in case of TOMABr. With DBPO alone as well as on addition of TOMA benzoate, the usual products, i.e., benzene, benzoic acid, diphenyl, traces of phenylbenzoate and some unidentified higher boiling products were obtained in all solvents tested. With excess DBPO over TOMACl, the usual degradation products of DBPO could be detected only after the reaction with TOMACl ceased. In the presence of an excess of TOMACl only benzoic acid and some chlorinated derivatives of solvents were obtained, but no higher boiling products. In MMA, methyl-2,3-dichloroisobutirate was detected as the main chlorinated derivative together with some minute traces of other chlorinated compounds, **Fig. 6**. In anisole, o- and p-chloroanisole, the former prevailing, could be detected (t_R=12.1 and 12.7, resp.; M^+=142, one-Cl pattern). In the presence of phenol, 2-chlorophenol and a dichlorophenol but no 4-chlorophenol could be detected (t_R=10.8, 8.9, 13.3 on Carbowax 20M; M^+= 94, 128, 162; Cl pattern: 0, 1, and 2; respectively). When substituted benzoates were taken as counterions in TOMAX, their reaction products could be obtained too. TOMA 2-metoxybenzoate reacted slowly with DBPO giving two

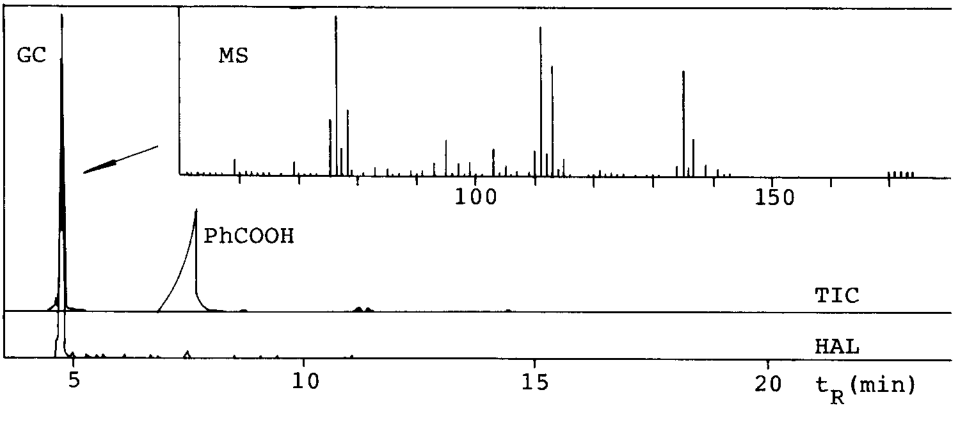

Fig. 6. GC/MS of volatile products in system MMA-DBPO-TOMACl. TIC: total ionic current; HAL: halogen containing compounds.

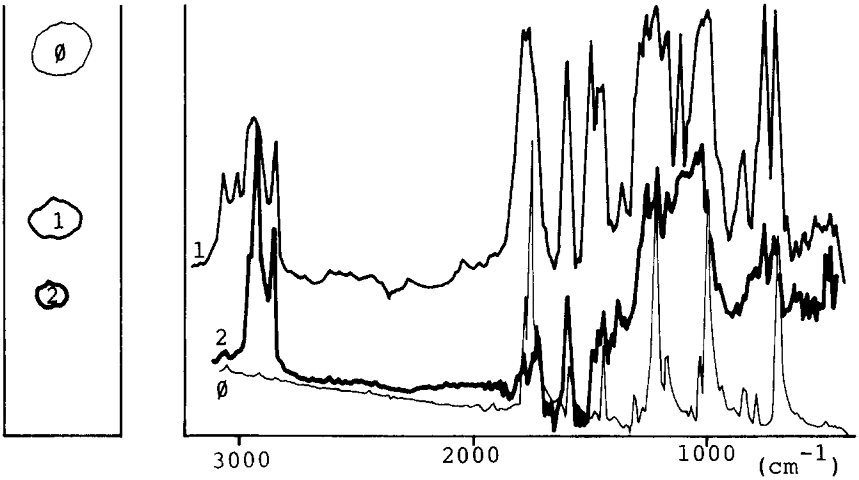

Fig. 7. Peroxidic products in the system benzene, DBPO, TOMA-2-metoxybenzoate. Left: TLC, 0 - DBPO, 1 - 2-OMeDBPO, 2 - 2,2'-diOMeDBPO. Right: FTIR spectra of 0, 1 and 2.

peroxidic products that decayed fast in diffuse daylight giving reddish brown products. Initially one identified as 2-metoxy-DBPO was observed and later also that identified as 2,2'-dimethoxy-DBPO, **Fig.** 7. TOMA 2,4-dichlorobenzoate and 2,5-dichlorobenzoate gave rise to a number of halogenated compounds. Until now, some di- and polychlorobenzenes, di- and polychlorodiphenyls, e.g., 2,5-dichlorodiphenyl, as well as di- and tetrachlorophenylbenzoates were tentatively identified by GC/MS and further work is in progress. With acetate and trifluoroacetate as counterions, no aromatic compounds besides benzoic acid could be detected nor any octyl or decyl esters.

Polymer formed

The molar mass distribution of polymer formed during the reaction of MMA, DBPO, and excess of TOMACl is presented in **Fig.** 8 compared to polymer obtained in the absence of TOMACl. At the beginning, PMMA with MW of approx. $30*10^3$ according to the polystyrene standard was formed, whereas in later stages MMA with MW over 10^6 was formed. The latter compared to the situation in the absence of TOMACl. This two-stage situation corresponded to the dilatometric results as well as to the formation of intermediate products. It could be understood as follows: at the beginning of reaction the initiation and termination occured as the addition of chlorine to MMA and as formation of low molar mass polymer exhausting most of the initiator present. In later stages, the residual activity lead to the formation of high MW polymer.

The tacticity of polymer as calculated from the ^{13}C NMR spectrum (2,1% iso-, 34,0% hetero-, and 63,9% sindiotactic) compared to that of PMMA obtained without TOMACl; only the isotactic part was somewhat lower.

Ghosh et al. (2) reported their ability to dye the PMMA formed suggesting that amino groups derived from the quaternary ammonium cation were incorporated into polymer. We were neither able to detect chlorine in our polymer with help of the Beilstein reaction, nor could our polymer be dyed with Orange II. When some of these reactions seemed positive, they became negative after reprecipitation and reextraction of polymer with methanol. The trials to destroy TOMA⁺ with DBPO in toluene below 100°C proved negative since TLC of the reaction mixture revealed no tertiary amines and the coloration with Orange II in alkaline media, where tertiary and lower amines do not contribute, was essentially unchanged.

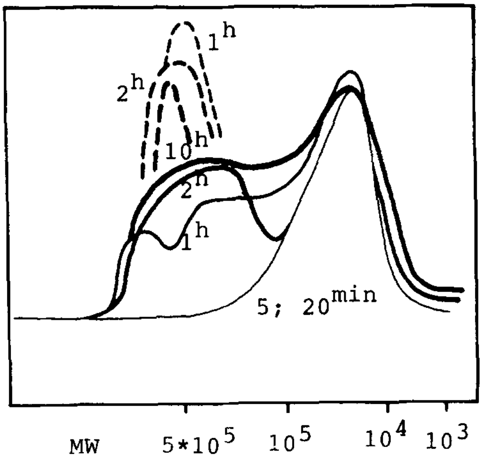

Fig. 8. Molar mass distribution of PMMA at different times [h]. ——— [TOMACl] : [DBPO] 3:1, ------ DBPO.

The mechanism of reaction

Ghosh et al. (2) discussed two parallel mechanisms of reaction of hexadecyl trimethyl ammonium bromide with DBPO at low molar ratios. Our results obtained at high [TOMAX] : [DBPO] ratios indicating the formation of chlorine, lack of formation of chloroalkanes and of tertiary amines from TOMACl, analogous situation in case of TOMABr, formation of substituted dibenzoyl peroxides as well as of polychloroarylcompounds when **X** is appropriatly substituted benzoate, lack of formation of aromatic compounds other than benzoic acid from TOMA acetate and trifluoroacetate suggest that in our case the mechanism of exchange of anions between the TOMA salts and dibenzoyl peroxide prevailed by far as the first step of reaction. Thus the mechanism can be formulated in general as follows, **Eq.** 2, Ct^+ = cation, in our case $TOMA^+$:

$$\begin{array}{ccccc} [Y\text{-}Y\text{—}Y\cdot + Y\cdot\,] & \underset{Ct^+Y^-}{\overset{Ct^+X^-}{\rightleftharpoons}} & [X\text{-}Y\text{—}X\cdot + Y\cdot\,] & \underset{Ct^+Y^-}{\overset{Ct^+X^-}{\rightleftharpoons}} & [X\text{-}X\text{—}X\cdot + X\cdot\,] \\ \downarrow & & \downarrow & & \downarrow \\ \text{initiation,} & & \text{initiation,} & & \text{initiation,} \\ \text{products} & & \text{products} & & \text{products} \end{array} \qquad (2)$$

Eq. 2 seems to be a general scheme including our case as well as some other reactions, e.g. the Hunsdiecker one, where $Ct^+ = Ag^+$, $X^- = RCOO^-$, $Y_2 = Br_2$, and the product is RBr.

The lack of influence of different anions on the initiation of polymerization of MMA by DBPO at 50°C could be explained by thermodynamic or kinetic reasons. The former ones could apply for F^-, ClO_4^- and possibly also for $ZnCl_4^{2-}$ that can not be oxidized by DBPO, whereas sulfonates have higher affinities for $TOMA^+$ than benzoate, so these anions do not enter into the first step of reaction to a measurable extent. The kinetic reason seems to apply for substituted benzoates, where the affinities for $TOMA^+$ do not seem to be too different and the rate of exchange of anions is much slower than the initiation reaction caused by DBPO. Acetate, on the other hand, has lower affinity for $TOMA^+$ than benzoate and exchanges more readily giving rise to less stable products that cause a virtually higher rate of polymerization. The preferential ortho chlorination of phenol and anisole suggests at least some orientational influence of the quaternary cation, whereas the influence on the lag time could suggest some activating effect of the TOMA cation and the desactivating effect of some anions or some TOMA salts as a whole.

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