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Use of Some Organic Acids and Amines as Photoinitiators of Vinyl Polymerization in the Absence and in the Presence of Benzophenone Photosensitizer

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ABSTRACT

Preliminary studies on the suitability of some organic acids and amines, separately and in combination with each other, as photoinitiators for the polymerization of methyl methacrylate were made. Combinations of maleic acid or phthalic acid with any of the tertiary amines–triethyl amine, demethyl aniline, and diethylaniline–proved to be interesting photoinitiator systems in view of the fact that the initiator components in each combination were ineffective as initiators when used separately. The rate of photopolymerization in each of the above acid-amine combination system was much enhanced and the respective inhibition period largely reduced when benzophenone was used as the photoinitiator. Aliphatic diamine or polyamines such as ethylene diamine, diethylene triamine, and triethylene tetramine, were ineffective as photoinitiators when used alone or in combination with maleic acid, but became effective

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photoinitiators in the presence of a benzophenone photosensitizer. The failure of these amines to become effective in combination with acids, such as maleic acid, is attributed to salt formation and consequent precipitation from the monomer medium.

INTRODUCTION

It was shown by Ghosh et al. [1] that certain organic acids (dicarboxylic acids and polyfunctional acids) readily induced photopolymerization of methyl methacrylate (MMA) by radical mechanisms. Yokota et al. [2] studied the photopolymerization of MMA using certain amines as initiators or sensitizers. Amines are also reported to produce inhibition or retardation effects in vinyl polymerization [3, 4]. However, amines produce very effective initiator systems, particularly under photoactivation, in the presence of such suitable additives as halomethanes ($CHCl_3$, CCl_4, etc.) [5-8] and aromatic ketones [9-14] (benzophenone and the like). In each case initiation is reported to take place radically via complexation between the amine and the additive used under thermal or photoexcited condition. Combinations of amines and acids, acid anhydrides, or acid chlorides are also known to initiate the radical polymerization of vinyl or diene compounds through the intermediary of C.T. complexes formed between the initiating components [15-19]. Studies made so far on the use of acid/amine systems or combinations thereof as initiators of polymerization are disjointed in nature. We recently made further studies of the polymerization of MMA using initiators based on a number of acid-amine combinations under photoactivation. Results of preliminary rate studies mostly done dilatometrically and those showing the effect of benzophenone (BP)-sensitization on the photopolymerization of MMA using a limited number of acids and amines separately and in combinations as initiators are reported in this paper.

EXPERIMENTAL

The monoamines dimethyl aniline (DMA), diethylaniline (DEA), and triethyl amine (TEA), obtained from E. Merck, were kept on NaOH pellets. They were finally purified by distillation following standard procedures. The diamine and polyamines (ethylene diamine (EDA), diethylene triamine (DETA) and triethylene tetramine (TETA)) were purified by distillation under reduced pressure. All acids used, except acrylic acid, were of A.R. grade from E. Merck. They were recrystallized following standard procedures. Acrylic acid (BDH) was purified by distillation before use. Benzophenone (E. Merck) was purified by recrystallization. Monomer MMA was obtained through the kind courtesy of National Organic Chemical Industries Ltd., Calcutta.

Polymerization of MMA, purified by standard procedures, was studied dilatometrically under nitrogen atmosphere in the presence of light (visible and near-UV) at 40°C using different acids and amines and combinations thereof with or without BP according to procedures given before [14].

RESULTS

Tertiary (mono) Amine Systems

Results of preliminary investigations at 40°C without benzophenone sensitizer are given in Table 1. Oxalic acid, succinic acid, citric acid, tartaric acid, salicylic acid, or acrylic acid, when used alone, could initiate the photopolymerization of MMA, but each of the remaining

TABLE 1.[a] Photopolymerization of MMA Using Combinations of Some Organic Acids and Tertiary Amines as Photoinitiators at 40°C: [acid] = 3.76×10^{-2} mol/L, [amine] = 3.76×10^{-2} mol/L, [MMA] = 8.27 mol/L

	Amine used			
Acid used	None	TEA	DMA	DEA
Oxalic	4.55; 140	5.24; 100	7.65; 55	8.14; 50
Succinic	13.36; 25	15.68; 25	20.87; 25	22.20; 21
Citric	14.61; 21	14.82; 21	16.70; 19	16.91; 18
Tartaric	15.03; 20	15.54; 15	16.70; 7	17.29; 7
Maleic	-	7.21; 60	12.53; 38	16.70; 26
Fumaric	-	-	-	-
Itaconic	-	-	-	-
Phthalic	-	5.64; 130	10.50; 117	12.35; 110
Salicylic	14.61; 17	15.31; 15	17.89; 7	19.26; 5
Acrylic	6.78; 115	-	-	-

[a] A requisite volume (0.5 mL) of a dilute solution of each acid and amine in acetone solution was used. In each column under "Amine used," the two values given indicate the rate of polymerization ($R_p \times 10^5$) in mol/L· s and the inhibition period (arising due to adventitious impurities such as traces of oxygen) in minutes, respectively. - indicates no polymer formation in 200 min.

acids (maleic acid, fumaric acid, itaconic acid, and phthalic acid) as well as the tertiary amines (DMA, DEA, and TEA) when used as a lone initiator in comparable concentrations failed to induce photopolymerization of MMA within 150 min. In combination with a tertiary (mono) amine (DMA, DEA, and TEA), however, maleic acid and phthalic acid readily initiated photopolymerization of MMA, but fumaric acid and itaconic acid failed to do so under similar conditions. Generally, inhibition periods of the photopolymerizations induced by the above acid-amine combinations are lower than the corresponding inhibition periods observed in the presence of the respective acids only. For acid-amine combinations using a particular acid, the inhibition periods followed a decreasing order and the corresponding rates of polymerization followed an increasing order as the amine was changed from TEA to DMA to DEA. The rates of photopolymerization induced by acid-amine combinations as initiators are higher by marginal to significant extents than those induced by the corresponding acids as lone initiators, Table 1.

For preliminary studies of the sensitization effect of benzophenone (BP), the following three acid-amine initiator systems were selected: maleic acid (MA)-triethyl amine (TEA), maleic acid (MA)-dimethyl aniline (DMA), and phthalic acid (PA)-dimethylaniline (DMA). The limited choice was largely because none of the MA, PA, and the tertiary amines selected could induce photopolymerization when used as a lone initiator, and as a result, in such acid-amine combinations the polymerizations would be free from complications due to coinitiation effects of individual initiator components.

Results of preliminary studies of the sensitizing role of BP in the photopolymerization of MMA at 40°C using the three binary catalyst systems, viz., MA-TEA, MA-DMA, and PA-DMA combinations, are presented in Table 2. In each case the rate of photopolymerization increased and the inhibition period decreased appreciably when a low concentration of BP was used as the photosensitizer.

Diamine and Polyamine Systems

Ethylene diamine (EDA), diethylene triamine (DETA), and triethylene tetramine (TETA) were then examined as initiators of polymerization. None of them could initiate polymerization of MMA when used alone in the dark or in the presence of light at 40-50°C, but, in the presence of benzophenone (BP) as photosensitizer, polymerization took place readily and the rate of polymerization was very high in the diamine and polyamine systems, the rate following an increasing trend and the inhibition period a decreasing trend from EDA to DETA to TETA, Table 3. However, in the presence of maleic acid (MA), the above diamine and polyamines also produced polymer at much lower rates only when BP was used as the photosensitizer, Table 4. MA and other acids readily formed crystalline precipitates with the diamine and polyamines in MMA or other organic mediums, presumably due to salt formation. A lower rate or percent conversion for a given

TABLE 2.[a] Effect of Benzophenone (BP) Photosensitizer on the Photopolymerization of MMA Using Selected Acid-Amine Combinations as Photoinitiators: [acid] = 3.76×10^{-2} mol/L, [amine] = 3.76×10^{-2} mol/L, [BP] = 1×10^{-2} mol/L, [MMA] = 8.27 mol/L (as in Table 1)

	Photosensitizer used	
Acid-amine combination used	None	BP
Maleic acid-triethylamine (MA-TEA)	7.21; 60	13.75; 30
Maleic acid-dimethylaniline (MA-DMA)	12.53; 38	30.16; 0
Phthalic acid-dimethylaniline (PA-DMA)	10.50; 117	38.60; 2

[a] In each column under "Photosensitizer used," the two values given indicate the rate of polymerization ($R_p \times 10^5$) in mol/L•s and the inhibition period in minutes, respectively.

TABLE 3.[a] Photopolymerization of MMA in Bulk Using EDA, DETA, and TETA as the Initiator With and Without Benzophenone as Photosensitizer at 40°C: [amine] = 4×10^{-2} mol/L, [BP] = 4×10^{-2} mol/L, [MMA] = 9.2 mol/L

	Photosensitizer	
Amine used	None	BP
Ethylene diamine (EDA)	-	11.87; 120
Diethylene triamine (DETA)	-	15.58; 54
Triethylene tetramine (TETA)	-	19.52; 39

[a] In each column under "Photosensitizer," the two values given indicate the rate of polymerization ($R_p \times 10^5$) in mol/L•s and the inhibition period in minutes, respectively. - indicates no polymer formation in 300 min.

TABLE 4.[a] Effect of Benzophenone (BP) Photosensitizer on the Photopolymerization of MMA Using EDA, DETA, and TETA as Initiator in the Presence and the Absence of Maleic Acid (MA) at 40°C: [amine] = 1×10^{-2} mol/L, [BP] = 1×10^{-2} mol/L, [MMA] = 8.69 mol/L, time of polymerization = 3 h.

		% Conversion, photosensitizer used	
Amine used	Maleic acid (mol/L)	None	BP
EDA	Nil	Nil	6.52
EDA	1×10^{-2}	Nil	1.68
DETA	Nil	Nil	21.0
DETA	1×10^{-2}	Nil	3.18
TETA	Nil	Nil	23.0
TETA	1×10^{-2}	Nil	6.32

[a] Requisite volumes (0.3 mL) of acetone solutions of amine and maleic acid were used.

time in the presence of MA, Table 4, can be understood on the basis of fast depletion of the diamine or polyamine molecules from solution due to their interaction with MA. In contrast, a similar kind of salt formation and precipitation was absent in the acid-amine systems involving MA, PA, DMA, DEA, and TEA, Tables 1 and 2. These binary acid-amine systems proved to be very efficient photoinitiators of vinyl polymerization, presumably due to formation of photoactive complexes between the initiator components in-situ. Studies on such complexation reactions and on the kinetics and mechanics of photopolymerization employing these complex systems as initiators are in progress.

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