Photopolymerization of N,N-Dimethylaminoethylmethacrylate Studied by Photocalorimetry

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ABSTRACT: Photopolymerization of dimethylaminoethylmethacrylate (DMAEMA) is studied in bulk and in solutions in the presence of different photoinitiators using differential photocalorimetry (DPC). The rate of DMAEMA photopolymerization is slow compared to that of alkylmethacrylates. Bimodal DPC curves of DMAEMA photopolymerization in bulk are obtained. The type I photoinitiators (IRGACURE® 651 and IRGACURE® 1700), which produce free radicals by homolytic fragmentation of photoexcited molecules, are more effective in promoting photopolymerization of DMAEMA. The type II photoinitiators (benzophenone and IRGACURE® 500), which initiate DMAEMA photopolymerization through an H-abstraction mechanism involving an amino group from the monomer (polymer), are less efficient and favor the formation of partly crosslinked products. The effects of the photoinitiator concentration, temperature, and solvent on the kinetic data are evaluated and discussed. A scheme of photopolymerization of DMAEMA, including the formation of intermediate DMAEMA based macromonomers, is proposed. The main point of the suggested scheme is a high chain transfer to the DMAEMA monomer. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 579–588, 2002

Key words: photopolymerization; photoinitiators; dimethylaminoethylmethacrylate; differential, photocalorimetry

INTRODUCTION

The importance of water-soluble polymers is growing equally for technical applications, biological and medical purposes, and environmental aspects. Much of the interest recently shown in the polymerization and copolymerization of aminoalkylmethacrylates and their salts is related to the valuable properties of the resulting polymers. Such polymers gain their utility from their large macromolecular size, ionic substitution, and expanded configuration in aqueous solution. Homopolymers of dimethylaminoethylmethacrylate (DMAEMA) or diethylaminoethylmethacrylate and their copolymers with acrylamide are applied for fines retention in paper making, as flocculants and biocides in water treatment, as stabilizers in emulsion polymerization, and in cosmetics and pharmaceuticals.[1,2] Aminoalkylmethacrylates are used to modify the properties of bulk plastic materials (such as polyethylene, polyacrylonitrile, and polymethylmethacrylate) by means of grafting or copolymerization.[3] DMAEMA or its (co)polymers combined with camphorquinone or various benzophenone derivatives (monomeric and polymeric) were used as initiating agents for photocuring formulations.[4–7]

Amines are known to participate in redox initiation and chain transfer reactions of radical polymerization. Tertiary amines are good synergists in photoinitiation with benzophenone, and amines are also used as oxygen captors in photocuring formulations.[8] The photopolymerization of DMAEMA in bulk using 2,2′-azodiisobutyronitrile,[3] (diacetoxyiodo)benzene, and [bis(trifluoroacetoxy)iodo]-benzene[9] as photoinitiators (PIs) was studied earlier.

Compensated power differential photocalorimetry (DPC) is a relatively new technique for studying photopolymerization or photocrosslinking processes in thin layers. The DPC technique is particularly valuable for optimizing UV curable formulations, the coatings industry, UV printing inks, and dental resins, as well as studying photochemical reactions and obtaining kinetic data.[10,11] Polymerization reactions are usually strongly exothermic. Moore was the first to apply a differential scanning calorimeter with a surmounted UV lamp for the investigation of photocuring kinetic. DPC measures heat flow that is related to the rate of reaction, as well as the total amount of heat that is related to the ultimate degree of conversion.

A photocalorimetric study of DMAEMA photopolymerization in bulk and solutions in thin layers as initiated by different PIs is reported in this work. The amine group if DMAEMA can interact with radicals or photo-

excited molecules of PI, thus changing the ordinary pathway of polymerization. The kinetic data of DMAEMA photopolymerization could be useful to predict the behavior of this monomer in photocuring formulations.

EXPERIMENTAL

Materials

Monomeric DMAEMA (Aldrich) and the PI (Ciba–Geigy) were used as received. The IRGACURE® 651 (2,2-dimethoxy-2-phenylacetophenone) PI is a white powder with a melting range of 63–66°C. Its structure is the following:
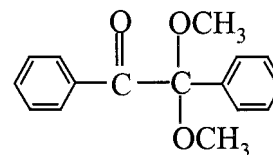
IRGACURE®. 1700 is a yellow liquid mixture of 25% bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide (**I**) and 75% 2-hydroxy-2-methyl-1-phenyl-propan-1-one (DAROCUR® 1173, **II**):

I   **II**
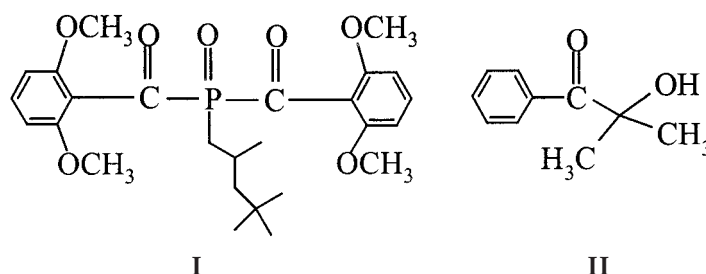
Benzophenone is a white powder with a melting point of 48–49°C.
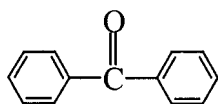
IRGACURE® 500 is a liquid mixture of benzophenone (50%) and DAROCUR 1173 (50%).

The solvent *N,N*-dimethylformamide (DMF) was used as received from Aldrich. Water was distilled twice before use.

Photocalorimetry technique

The photocalorimeter (DPC 930, TA Instruments from DuPont) was composed of a differential calorimeter scanning device and a UV light source mounted on the top. The light source was a standard 200-W super high-pressure mercury arc lamp. The intensity of the light in the sample compartment was approximately 5 mW/cm^2. Typically 1–3 mg of the monomer mixture with the PI were placed in an aluminum DPC pan. In order to prevent evaporation of the monomer the pan was covered with a thin Mylar film. Polymerizations were carried out in an air atmosphere. The sample and reference (completely polymerized sample) were placed with DPC head, covered by a quartz window, and equilibrated at the given temperature. Then they were irradiated through a second quartz window for a chosen period of time. The evolution of the heat re-

sulting from polymerization was measured as a function of time (dH/dt) and produced a thermogram curve. The standard heat of DMAEMA polymerization (ΔH_0) was calculated as follows:

$$\Delta H_o = 13.6 \times 1000 \times 4.184/157.22 = 361.9 \ (J/g),$$

where 13.6 is the theoretical enthalpy of methacrylate-type monomer polymerization (kcal/mol), 4.184 is the coefficient from the calories to joules, and 157.22 is the molecular weight of DMAEMA.

The area under the recorded thermogram curve was assumed to be the enthalpy of the reaction ΔH, and the ratio $\Delta H/\Delta H$ was assumed to be the conversion of the monomer. The induction time of the reaction (τ_{ind}) was considered for 1% conversion of the monomer.

TABLE I
Data of DMAEMA Photopolymerization in Bulk at 40°C Using Different Photoinitiators

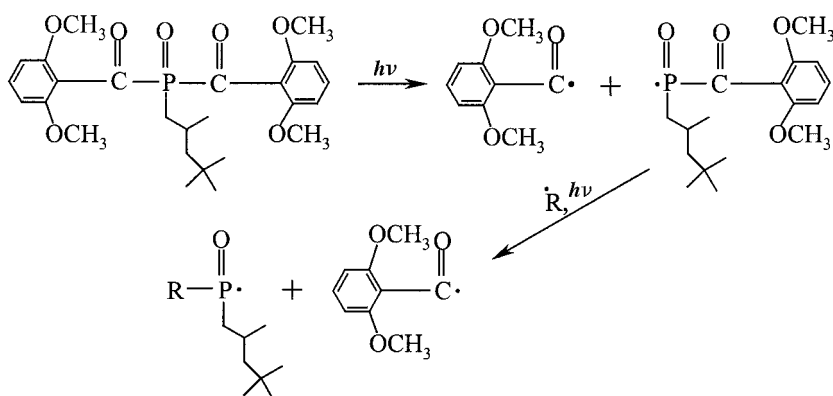| Photoinitiator	Final conversion (%)	k_i (min^{-1})	τ_{ind} (s)	Reacted at peak max. (%)
IRGACURE 651	99.0	1.16	5.7	11.8
IRGACURE 1700	91.8	2.70	4.4	2.9
Benzophenone	88.9	0.38	14.9	47.1
IRGACURE 500	80.4	0.36	15.3	63.3

τ_{ind}, induction time.

It is known[10] that photopolymerization is an auto-catalytic-type reaction and the rate of it can be expressed by the following equation:

$$R = d\alpha/dt = k\alpha^m(1 - \alpha)^n$$

where R is the polymerization rate; α is the degree of conversion; k is the rate constant; and m,n are the orders of the reactions, where m is the initiation and n is the propagation.

The order of the propagation reaction was chosen to be constant at $n = 1.5$.[13] The values of R and k for the initial period of polymerization (until the first peak maximum of the DPC curve) were calculated using the DPC V4.1A DuPont 2100 program.

The rate maximum of polymerization (R_{max}) was calculated as the ratio of DMAEMA conversion at the first peak maximum and the peak maximum time. The data presented in Tables I–III and Figures 1 and 2 were

calculated as averages from two runs.

RESULTS AND DISCUSSION

Effect of PI type

Photogeneration of free radicals can be achieved by at least two different methods[14] Method I is the homolytic fragmentation of a photoexcited PI molecule, giving a radical pair; method II is an intermolecular hydrogen abstraction from a hydrogen donor by a triplet excited photosensitizer. According to the above, the PIs are called type I PI and type II PI.

The PIs that generate free radicals by inechanism I are various acetophenone derivatives, acylphosphine, and bisacylphosphine oxides.[11] Photogeneration of free radicals by mechanism I usually occurs from the $n-\pi$ triplet state. For example, the component from IRGACURE 1700 decomposes as follows:

As a result, one molecule yields at least four initiating radicals; hence, IRGACURE 1700 is a very efficient type I PI.[15,16]

It is known that the photopolymerization of alkyl-methacrylates (AMAs) in thin layers using a type I PI is very fast, lasting no more than 1 min.[10] The heat flow curves of AMA photopolymerization have a sharp peak in the initial stage of polymerization. Our results show that photopolymerization of DMAEMA lasts about 10–15 min (Fig. 3) at a light intensity of 5 mW/cm^2 and a temperature of 40°C, and the shape of the heat flow curves in some cases is bimodal. One can observe a shoulder of the peak [Fig. 3(a)] or a second maximum [Fig, 3(b–d)] on the DPC curves in all cases. The final conversion of the monomer is 80–99% (Table I, Fig. 4).

Photogeneration of free radicals by mechanism II employs derivatives of aromatic ketones and quinones (benzophenone, substituted benzophenones, fluorenone, xanthone, thioxanthone, camphorquinone, some dyes, heterocyclic compounds, water-soluble benzophenone, and thioxanthone derivatives, etc.)[11,12,14] as photosensitizers in combination with tertiary

amines as hydrogen donors or synergists that enhance the effectiveness of the PIs A well-known system of this type is benzophenone/tertiary amine.[17,18]

The DPC curves of DMAEMA photopolymerization using type II PIs benzophenone and IRGACURE 500

TABLE II
Data of DMAEMA Photopolymerization in Bulk at Different Temperatures

Temperature (°C)	τ_{ind} (s)	τ_{max} (s)	Reacted at first peak max. (%)	k (min^{-1})	Final conversion (%)
			IRGACURE 651 (3.2 wt %)		
30	8.5	18.2	4.2	0.93	34.6
35	6.2	16.0	5.2	1.17	81.7
40	5.4	16.4	7.1	1.29	99.2
45	5.6	15.2	6.2	1.89	98.7
			IRGACURE 1700 (3.78 wt %)		
30	4.5	8.8	3.4	3.11	69.6
35	4.1	7.6	3.1	3.32	71.9
40	4.3	9.4	4.3	4.06	99.1
45	3.9	8.4	4.3	4.48	97.7

τ_{ind}, induction time; τ_{max}, time of the first peak maximum.

TABLE III
Data of DMAEMA Photopolymerization in Solutions at 40°C with IRGACURE 1700

Solvent	PI (wt %)	[DMAEMA] (wt %)	τ_{ind} (s)	k (min^{-1})	Final conversion (%)
In bulk	3.08	96.92	5.4	2.70	98.3
DMF	2.69	46.93	6.05	1.60	42.7
1:1 DMF:H$_2$O	3.08	30.04	4.75	2.38	41.9
H$_2$O	2.76	47.4	3.5	3.90	72.4

τ_{ind}, induction time.

are presented in Figure 3(c,d). According to the shape of the heat flow curves, the rate of the polymerization reaction is almost constant, until 50–60% conversion of the monomer is reached. Moreover, the thermogram of photopolymerization initiated by IRGACURE 500 has a well-expressed bimodality (autoacceleration) as in the IRGACURE 1700 initiation. One should suggest that strong autoacceleration depends on the component that is present in both initiators (DARO-CUR 1173). The comparison of the DPC profiles using DAROCUR 1173 and IRGACURE 1700 PIs is given in Figure 5.

According to the R_{max} and τ_{ind} (Table I), the type I, PIs (IRGACURE 651 and IRGACURE 1700) are much more effective PIs of DMAEMA than the type II PI. On the other hand, photopolymerization of DMAEMA is slow using all PIs tested. This phenomenon could be related to the polymerization retardation effect of the tertiary amine group present in the monomer.

The experimental data show (Table I) that with respect to the type of initiation that, despite a high final conversion, the other kinetic parameters of DMAEMA photopolymerization are different. The R_{max} of photopolymerization initiated by the type II PI is 2–3 times lower and the τ_{ind} of corresponding runs is about 3 times longer. This means that type I PIs are less effective in promoting the photopolymerization of DMAEMA. This phenomenon could be explained by a relatively low activity of α-amino radicals because only they initiate polymerization when a type II PI is used.

The bimodal character of the DPC curves is related to acceleration of photopolymerization at certain conversions that could be caused by the following:

1. the gel (Tromsdorf) effect[19];
2. specific features of radical-generation, chain growth, and termination processes of the monomer containing an amine group; and
3. participation of oxygen dissolved in the sample in radical reactions.

The gel effect could be eliminated because of the absence of autoacceleration in the DPC curves of AMA and the particularly slow process of DMAEMA photopolymerization.[10,11]

The effect of simple amines on the process of photopolymerization initiated by type I PIs was studied earlier.[8,11,12] Amines interact with radicals produced by PI cleavage, thus generating α-amino radicals that initiate the growth of new polymer chains. However, the scheme is different if the α-amino radical belongs to a monomer or polymer. The reactions of such α-amino radicals could lead to branching or crosslinking of a polymer. Branching or crosslinking reactions usually have only a small influence on the kinetics of polymerization. Moreover, the amine group in the close vicinity of an unpaired electron could reduce the activity of the radical. This means that we should expect a slower rate of polymerization of amine-containing monomer but not autoacceleration at a certain conversion of the monomer.

Interesting results were reported concerning the influence of oxygen on polymerization in the presence of simple amine.[8] An amine, depending on its concentration, can either accelerate or reduce the rate of polymerization of acrylic monomers. The decelerating effect was obtained for a deoxygenated sample cured in an N$_2$ atmosphere. While the amine concentration increased the polymerization rate decreased, reflecting the increasing role of chain transfer to amine.[8] On the contrary, the rate of acrylic photopolymerization in an air atmosphere in the presence of amines, like etha-
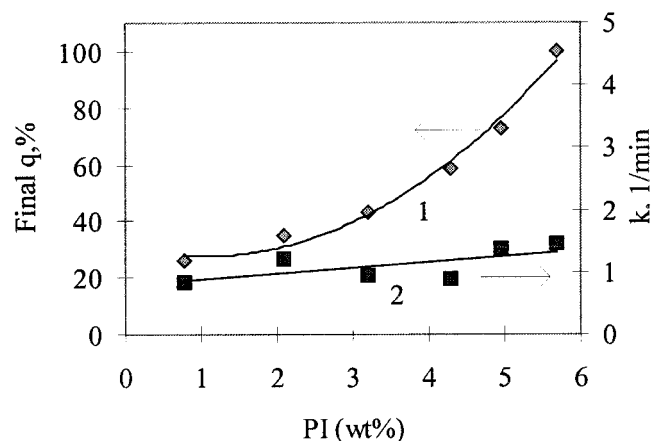

Figure 1 The IRGACURE 651 concentration effect on final conversion (curve 1) and initial rate maximum R_{max} (curve 2) at photopolymerization of DMAEMA in bulk at 30°C.
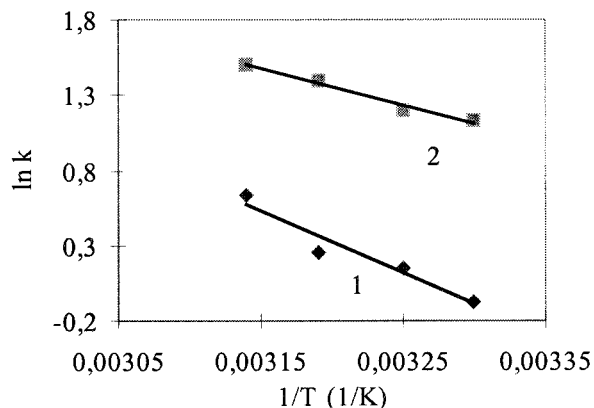
Figure 2 The log of the initial rate constant *k* at photopolymerization of DMAEMA versus the inverse temperature. The photoinitiators are IRGACURE 651 (3.2 wt %, curve 1) and IRGACURE 1700 (3.78 wt %, curve 2).

nolamine, dimethylaminoethanol, or triethylamine, increases up to a certain concentration of amine but decreases at high concentrations of the latter. An accelerating effect of small quantities of amines is explained by the reaction between α-amino radicals and oxygen, leading to formation of R'—CH$_2$—O' and 'OH radicals, which are very active and promote further polymerization processes.

We suppose that autoacceleration of DMAEMA photopolymerization is related to chain transfer to monomer (polymer) and could be accounted for by at least two reasons:

1. the reaction between growing a radical and an amine group depends on where the amine group is, on the monomer or polymer. The reaction of the radical with polymeric amine is much more complicated (and less expected) because of conformational and steric factors, meaning that the role of chain-transfer reactions decreases with conversion and the overall rate of polymerization reflects it;
2. the reaction of growing radicals with amine groups, as well as the reactions presented above, are relatively slow: the accumulation of active radicals (like R'—CH$_2$—O' and 'OH) reaches its maximum after some minutes from the beginning of photopolymerization and then autoacceleration starts.

Some data prove the explanation presented above. First, poly-DMAEMA synthesized using a type I PI is acetone soluble (i.e., the polymer is not crosslinked). It means that reactions involving α-amino radicals lead mainly to branching but not to crosslinking, which is in accordance with little chain transfer to the polymer. Second, the intensity of autoacceleration depends on the nature of the PI (Fig. 4). The reaction rate decreases slowly in the IRGACURE 651 initiation and autoacceleration is not well expressed. On the contrary, the rate of IRGACURE 1700 initiated photopolymerization drops quickly but rises again when 40–50% conversion of the monomers is reached.
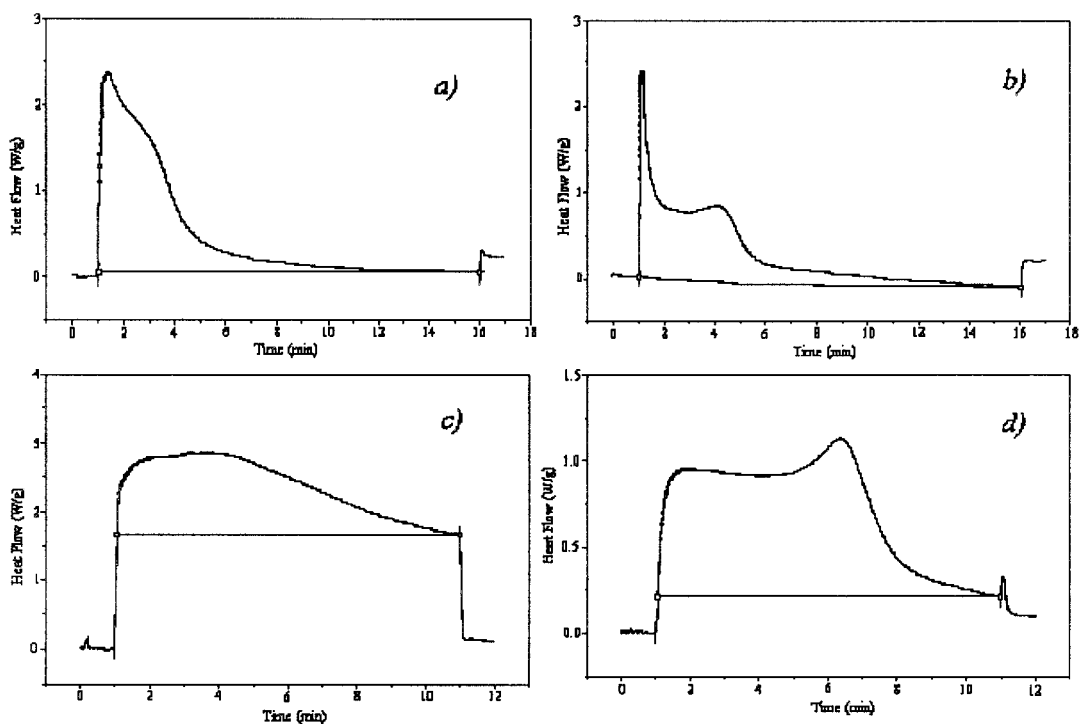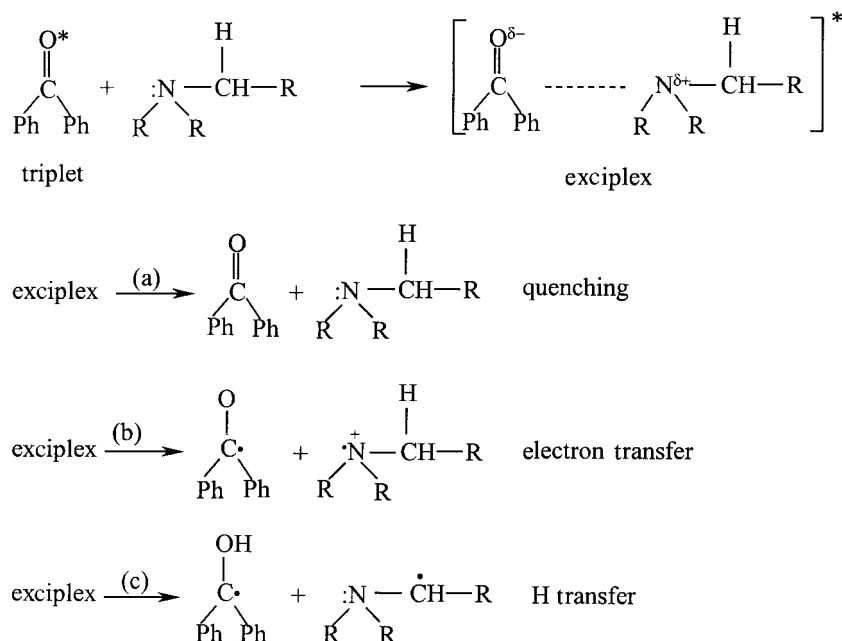

Figure 3 The DPC curves of DMAEMA photopolymerization in bulk at 40°C. The photoinitiators are (a) IRGACURE 651 (5.35 wt.%), (b) IRGACURE 1700 (3.08 wt %), (c) benzophenone (3.83 wt %), and (d) IRGACURE 500 (3.11 wt %).

Using amines along with a type II PI, H transfer may proceed through rapid formation of an excited state complex (exciplex) between the amine and triplet ketone.[12]

The facility of complex formation between triplet ketone and amine may be attributed to charge-transfer stabilization, which is due to the relatively low ionization potential of amines. The rate of complex formation increases with decreasing ionization (oxidation) potential of the amine, as well as increasing electron affinity (reduction potential) of the triplet ketone. The efficiency of H abstraction depends upon the nature of both the triplet ketone and the H donor.[8]

Poly-DMAEMA, synthesized by photopolymerization in the presence of type II PIs, is partly crosslinked and forms a gellike material in acetone. This is expected because of initiation through α-amino radicals that belong to the monomer or polymer. On the other hand, crosslinking is not difficult. Possibly some other more active radicals like R'—CH_2—$O^{\cdot}$; leading to linear macromoleculars, were formed as a result of the reaction between the α-amino radicals and oxygen presented above.
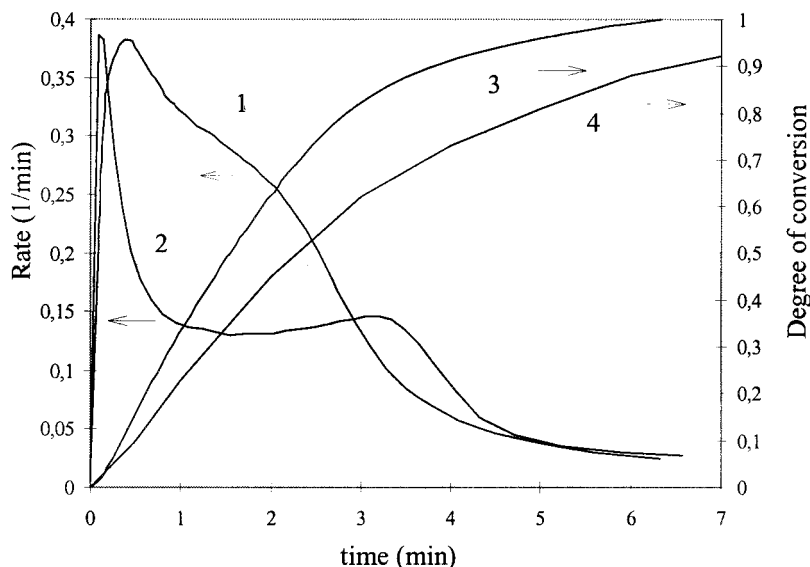

Figure 4 The rate of DMAEMA photopolymerization (curves 1 and 2) and degree of conversion (curves 3 and 4) versus the reaction time at 40°C. The photoinitiators are IRGACURE 651 (5.35 wt %, curves 1 and 3) and IRGACURE 1700 (3.08 wt %, curves 2 and 4).
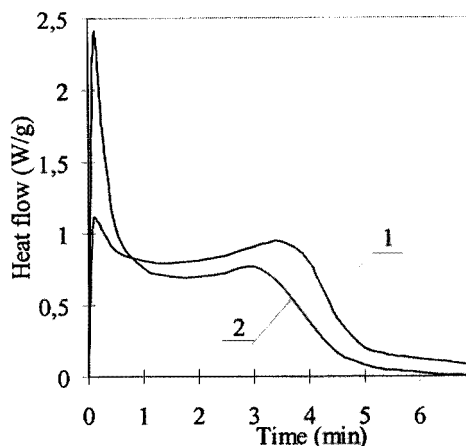
Figure 5 The DPC curves of DMAEMA photopolymerization at 40°C using DAROCUR 1173 (3.76 wt %, curve 1) and IRGACURE 1700 (3.08 wt %, curve 2).

Figure 7 The DPC curves of DMAEMA photopolymerization in bulk at 30°C (curve 1), 36°C (curve 2), and 45°C (curve 3). The photoinitiator is IRGACURE 651 (3.2 wt %).

Effect of PI concentration

The DPC of DMAEMA photopolymerization in bulk reflecting the effect of the IRGACURE 651 PI concentration are presented in Figure 6. At a relatively low PI concentration the heat flow curves have a sharp peak at the beginning followed by a slow decrease. The heat flow curves become bimodal at a higher PI concentration (more than 4 wt%) because of autoacceleration of the photopolymerization at a certain conversion.

The final conversion of the monomer also depends on the concentration of the PI (Fig. 1, curve 1). At PI concentrations of less than 3 wt% the final conversion does not reach 40%. One hundred percent monomer conversion at 30°C is achieved if the PI concentration exceeds 5 wt%. The effect of the PI concentration on the final conversion of DMAEMA could be related to consumption of free radicals in chain-transfer and oxygen-elimination reactions.[8] At a relatively low PI

concentration a significant number of free radicals are captured by oxygen or amine groups, leading to termination or production of less active radicals (like α-amino radicals). However, if the concentration of the PI is over a critical value, the part of the active carbochain radicals remains in the system and polymerization proceeds until full consumption of the monomer is achieved. Moreover, almost 100% conversion of the monomer (of double bonds) and autoacceleration indicate that some products of the chain transfer to the monomer accumulated in the system take part in polymerization.

A complex relationship between the concentration of IRGACURE 651 and the kinetics of photopolymerization also reflects the small increase in the R_{max} value with the concentration (Fig. 1, curve 2). About a seven fold increase of the number of initiating radicals produced results in only a two fold increase of the maximum rate of polymerization.

Temperature effect

The temperature effect on photopolymerization of DMAEMA is found to be somewhat different when using IRGACURE 651 (Fig. 7) or IRGACURE 1700 PIs (Fig. 8) PIs Photopolymerization in the presence of IRGACURE 1700 is characterized by bimodal DPC curves: autoacceleration is well expressed at every temperature used. It is evident (Fig. 8) that the time until the second peak maximum decreases with the temperature. It is notable that the DPC curves when using IRGACURE 651 become bimodal at higher temperature only and the dependence of the second peak maximum on the temperature is opposite to that when using IRGACURE 1700 as the PI.

The overall rate constants k of DMAEMA photopolymerization using IRGACURE 1700 as a PI were 2.5–3 times higher than those when using IRGACURE 651
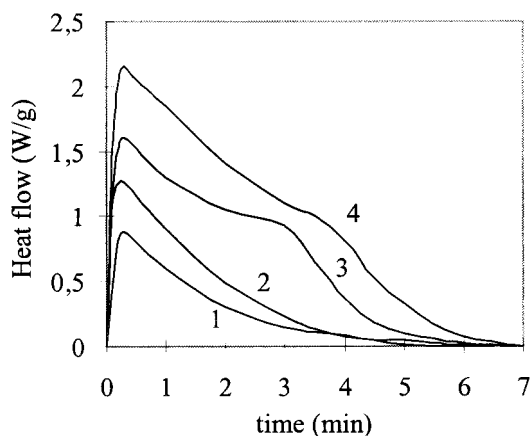

Figure 6 The DPC curves of DMAEMA photopolymerization in bulk at 30°C. The concentrations (wt %) of IRGACURE 651 0.78 (curve 1); 3.2 (curve 2); 4.96 (curve 3) and 5.68 (curve 4).
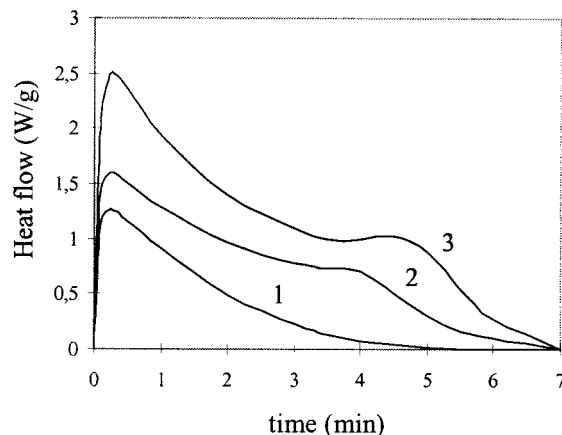
(Table II). The dependence of in k on the inverse temperature gave linear plots for both PIs (Fig. 2). The energies of activation (E_a) calculated from the slope of these plots were 34.1 and 20.1 kJ/mol for IRGACURE 651 and IRGACURE 1700, respectively. The lower value of E_a for IRGACURE 1700 indicates the higher efficiency of this PI. The high efficiency of IRGACURE 1700 is confirmed by other data presented in Table II: a higher k value, shorter τ_{ind}, and shorter time until the first peak maximum (τ_{max}) Thus, IRGACURE 1700 is preferable to initiate photopolymerization of DMAEMA in bulk.

Solvent effect

There was a certain interest in studying solvent effects on the rate of photopolymerization of DMAEMA in thin layers and especially on the course of DPC curves during the reaction. Data of photopolymerization of DMAEMA in semidiluted solutions of DMF, water, and a mixture of DMF with water are presented in Figure 9 and Table III. The lowest initial rate is characteristic for photopolymerization of DMAEMA in DMF and the highest is for photopolymerization in water, which is in accordance with data published earlier.[2,20] The DPC curve of the photopolymerization carried out in water has a characteristic hump on the "tail," indicating weakly expressed autoacceleration. It is evident that autoacceleration of photopolymerization in water starts much earlier than that in bulk (Fig. 9, curves 2 and 3). No acceleration could be observed during slow photopolymerization in DMF and the DMF–water mixture, but the long-lasting tail of the DPC curves instead of it is possibly defined by a low rate of accumulation of α-amino radicals and similar compounds in the reaction mixture. The low conversion of the monomer (about 40%) could be reached only under photopolymerization in DMF and DMF–
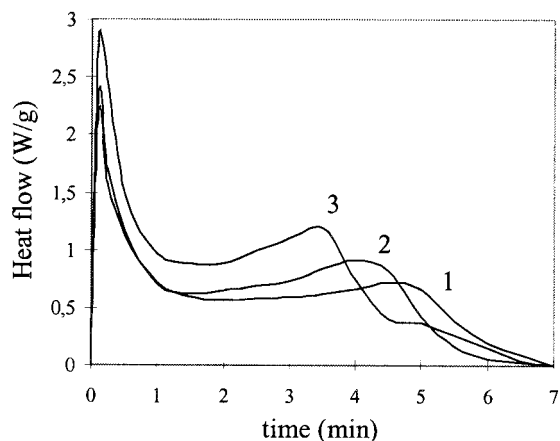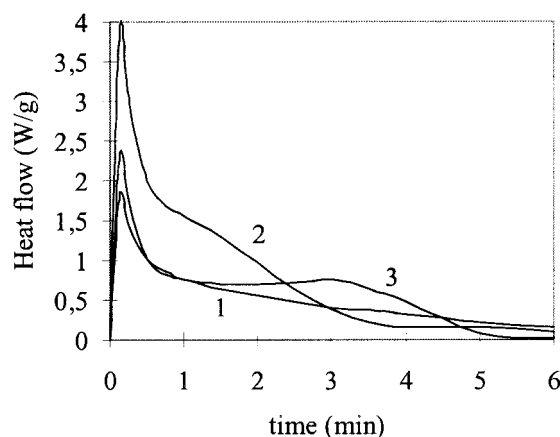

Figure 9 The DPC curves of DMAEMA photopolymerization at 40°C in DMF (curve 1), water (curve 2), and bulk (curve 3). The photoinitiator is IRGACURE 1700 at concentrations (wt %) of 2.69 (curve 1), 2.76 (curve 2), and 3.08 (curve 3).

water solutions. It is surprising that the final conversion of DMAEMA under photopolymerization in water is not high (about 70%). Thus, it is possible to conclude that the consumption of the monomer is related to the well-expressed autoacceleration rather than to the high initial rate of photopolymerization.

An analysis of DMAEMA photopolymerization kinetics in different solvents revealed that autoacceleration of the reaction at a certain conversion depends on the initial rate of photopolymerization and/or on the concentration of PI rather than on nature of the solvent used. Once again it confirms that autoacceleration of DMAEMA photopolymerization is not related to complexation and protonation of monomer molecules or to the conformation of growing macroradicals; it is caused by the internal characteristics of the monomer. A high chain-transfer constant to monomer DMAEMA could be the most important of these characteristics. The DMAEMA chain-transfer constant was evaluated earlier and found to be 0.093.[7]

Mechanism of DMAEMA photopolymerization

Comparing the PI type, concentration, and temperature effects on the second peak maximum in photopolymerization of DMAEMA allows some important conclusions to be drawn:

1. Radicals produced by homolytic fragmentation of photoexcited molecules of PI directly influence the course of photopolymerization, even at relatively high conversion (40–60%). Primary radicals possibly interact with compounds accumulated in the reaction mixture as a result of chain transfer to DMAEMA. The rate of interaction, as well as products of that interaction, depend on

Figure 8 The DPC curves of DMAEMA photopolymerization in bulk at (curve 2), and 40°C (curve 3). The photoinitiator is IRGACURE 1700 (3.78 wt %).

the type of PI. It is usual to expect a higher rate of reaction and shorter time until the second peak maximum at higher temperatures as is found in IRGACURE 1700 initiated photopolymerization (Fig. 8). The different results seen in Figure 7 could be explained by a lesser reactivity of IRGACURE 651 radicals. The reaction rate increases with the temperature in this case, too, but the position of the second peak maximum has an opposite trend. No acceleration was observed at 30°C using IRGACURE 651, and final conversion of DMAEMA was only about 35% (see Table II). High conversion of the monomer in DMAEMA photopolymerization is only achieved in those cases when the autoacceleration effect takes place. This possibly means that some products of chain transfer to DMAEMA are unsaturated compounds that are relatively inactive but polymerizable.
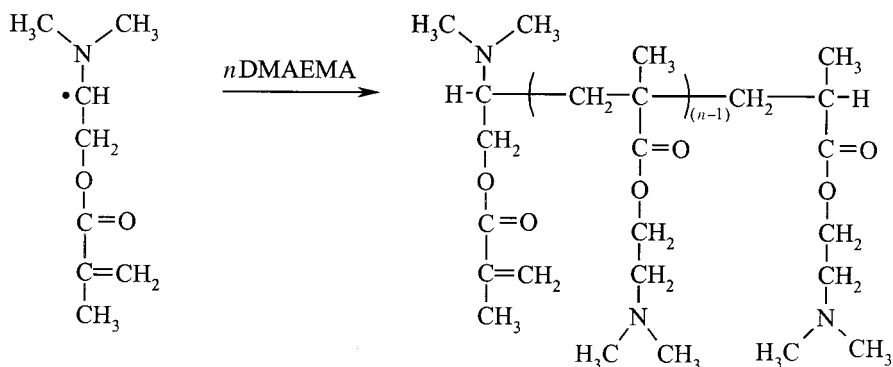
2. DMAEMA as a tertiary amine is an effective chain-transfer agent,[7] and chain-transfer reactions are competing with chain growth reactions in this system. As a result of chain transfer to monomer, DMAEMA based α-amino radicals should be produced.

Taking these considerations into account, we propose the following scheme of DMAEMA photopolymerization in the presence of type I PIs. Type I PIs produce free radicals by homolytic fragmentation of the photoexcited molecules. Some of these primary radicals initiate DMAEMA polymerization. The growth of macrochains is terminated in many cases as a result of chain transfer to the monomer:

$$\text{\textasciitilde CH}_2\text{-C}^{\bullet}(\text{CH}_3)(\text{C=O-O-CH}_2\text{CH}_2\text{N(CH}_3)_2) \;+\; \text{(CH}_3)_2\text{N-CH}_2\text{CH}_2\text{-O-C(=O)-C(=CH}_2)\text{CH}_3 \xrightarrow{\text{transfer}} \text{\textasciitilde CH}_2\text{-C-H}(\text{CH}_3)(\text{C=O-O-CH}_2\text{CH}_2\text{N(CH}_3)_2) \;+\; (\text{CH}_3)_2\text{N-}^{\bullet}\text{CH-CH}_2\text{-O-C(=O)-C(=CH}_2)\text{CH}_3$$
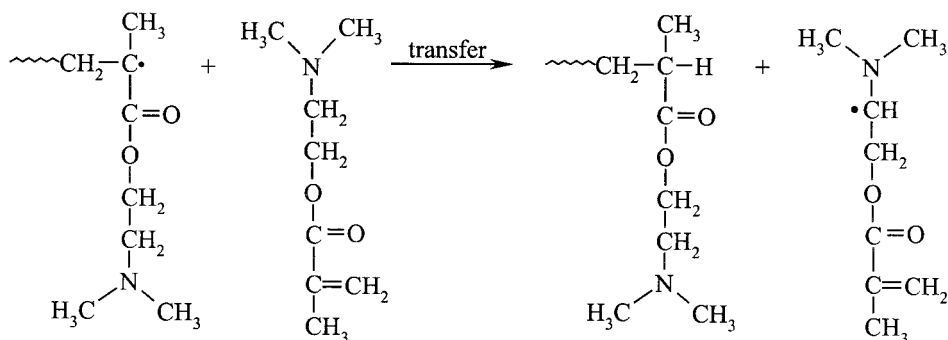
The α-amino radicals produced by this way have lower reactivity than carbochain radicals; nevertheless, they can initiate polymerization of DMAEMA, resulting in macromonomers:

$$(\text{CH}_3)_2\text{N-}^{\bullet}\text{CH-CH}_2\text{-O-C(=O)-C(=CH}_2)\text{CH}_3 \xrightarrow{n\text{DMAEMA}} (\text{CH}_3)_2\text{N-CH(CH}_2\text{-O-C(=O)-C(=CH}_2)\text{CH}_3)\text{-H} \cdots (\text{CH}_2\text{-C(CH}_3))_{(n-1)} \cdots \text{CH}_2\text{-C-H}$$

Termination can occur either by chain transfer to the monomer or polymer or by recombination reactions with any radicals present in the system. The formed macromonomers have double bonds at the end of the chain and are possibly characterized by reduced activity in polymerization because of steric and conformation factors, but primary or carbochain radicals could polymerize with them. The influence of the PI type on the course of photopolymerization at high conversion proves this hypothesis. The possibility of copolymerization of macromonomers gives the chance to produce high molecular weight products, even in the case of significant chain transfer to the monomer. The products of DMAEMA polymerization using type I PIs can be branched but not crosslinked or with a low degree of crosslinks.

The main difference of polymerization of DMAEMA in the presence of type II PIs is the high concentration

of α-amino radicals from the beginning of the process. Initiation of polymerization proceeds exclusively through α-amino radicals, which are produced by the scheme presented earlier in this article. Because of reduced activity and the high concentration of such radicals, the growth of macromonomer chains could terminate by chain transfer to DMAEMA, as well as recombination with any other radicals. It means that part of the formed macromonomers has two double bonds and can participate in crosslinking reactions. Moreover, some α-amino radicals could be produced on the polymer (or macromonomer) chain as a result of exciplex formation between the amino group of the macromolecule and the triplet ketone that is also a potential source of crosslinking. Reduced activity of α-amino radicals is responsible for the lower rate of DMAEMA photopolymerization in the presence of type II PI.

CONCLUSIONS

The rate of DMAEMA photopolymerization is slow as compared to that of AMAs. The PIs IRGACURE 651 and IRGACURE 1700, which produce free radicals by homolytic fragmentation of photoexcited molecules, are effective in promoting photopolymerization of DMAEMA. The benzophenone and IRGACURE 500 PIs, which initiate DMAEMA photopolymerization through an H-abstraction mechanism, involving the amino group from the monomer or polymer, are less efficient and favor the formation of partly crosslinked products. The scheme of DMAEMA photopolymerization includes high chain transfer to the monomer, the formation of intermediate DMAEMA based macromonomers, and branching or crosslinking of macromolecules.

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