Photopolymerization of 1,6-hexanediol diacrylate: the effect of functionalized amines

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It is clearly demonstrated that amine-functionalized methacrylates are quite effective in accelerating the photopolymerization of air-saturated 1,6-hexanediol diacrylate (HDODA). For each amine investigated, the extent of rate enhancement is dependent both on the type and degree of alkyl substitution as well as the amine concentration. Dimethyl substituted amines are more effective than diethyl substituted amines in sustaining the rapid oxygen-scavenging process responsible for the polymerization rate increase. At higher amine concentrations, an inhibition process dominates the polymerization and the oxygen-scavenging process is rendered relatively ineffective. The general effect of the functionalized methacrylates is confirmed by investigation of alkyl substituted diaminoethylene compounds.

(Keywords: photopolymerization; functionalized amines; chain-transfer; oxygen scavenger; exotherm; molecular weight)

INTRODUCTION

It has recently been demonstrated[1-5] that both aliphatic and aromatic amines can be utilized in photopolymerization of air-saturated multifunctional acrylates to accelerate the polymerization process. The degree of rate enhancement is directly dependent on the structure of the amine as well as its concentration. Since the amines act both as oxygen scavengers and chain-transfer agents, the concentration of the amine required to maximize the polymerization rate is critical and depends on the amount of oxygen dissolved in the polymerization medium and the intensity of the photolysing lamp source.

One of the problems encountered in employing simple aromatic and aliphatic amines for the oxygen scavenging process is the chain transfer and/or inhibition step involving transfer of the polymer radical to the amine by a standard hydrogen-abstraction mechanism. If the amine concentration is large, the hydrogen abstraction process dominates and the kinetic chain length of the average growing polymer chain is decreased. If, in addition, the reinitiation process is slower than the chain propagation process, the polymerization rate decreases. The first problem can be minimized by selection of an amine with rapid reinitiation rate constant. This course of action (concentration adjustment, amine selection) cannot alter the detrimental effects resulting from a decrease in the average kinetic chain length of polymerization. One way of minimizing the detrimental effect of chain transfer to amines is to incorporate the amine functional groups into monomers which themselves are capable of participation in the polymerization process[6]. By inclusion of both the amine functionality and the reactive monomer group into a single reactive molecule, the pernicious effect in decreasing molecular weight and crosslink density caused by chain transfer is lost since the amine would be 'locked into' the final matrix by virtue of polymerization through the reactive monomer group.

In this paper, we report kinetic results for the photopolymerization of a typical difunctional acrylate monomer (1,6-hexanediol diacrylate; HDODA) utilizing a photoinitiator package comprising benzoin isopropyl ether (BIPE) and amine functionalized methacrylates. The BIPE acts as a typical cleavage type photoinitiator for free radical polymerization. The amine functionalized methacrylates meet the criteria set forth in the preceding discussion. The type of alkyl substitution (methyl or ethyl) on the amine is found to significantly alter the polymerization kinetics both in air and nitrogen saturated atmospheres. The *n*-alkyl substitution effect is confirmed by an investigation of the influence of model substituted *N*-alkyl diaminoethylenes on the polymerization kinetics of HDODA and ethyl acrylate.

EXPERIMENTAL

1,6-Hexanediol diacrylate (HDODA, Celanese) and benzoin isopropyl ether (BIPE, Polysciences) were used as received. *N,N*-Dimethylaminoethyl methacrylate and *N,N*-diethylaminoethyl methacrylate were obtained from Polysciences and purified by vacuum distillation. *N,N'*-Dimethylethanol amine (Union Carbide) was distilled before use. Ethylenediamine, triethylamine, *N,N,N',N'*-tetramethylethylenediamine, and *N,N,N',N'*- tetraethylethylenediamine were purchased from Aldrich and used without further purification.

For measurement of the photopolymerization of HDODA in the presence of oxygen a thin-foil exotherm unit was used to record the polymerization exotherm generated by the pulsed Xenon lamp source. It consists of a basic thin-foil heat flow gauge mounted on an aluminium heat sink as described in an earlier paper[8]. The exotherm unit was connected to a Keithley Model 1155 microvoltmeter whose output was recorded on a strip chart recorder. A Strobex Model 271-B pulsed u.v. lamp from Chadwick–Helmuth was mounted on the top of the exotherm unit at a distance of about 40 cm. The pulse rate for the u.v. light (50 Hz) was controlled by a Wavetek

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Table 1 Photopolymerization of air-saturated ethyl acrylate[a,b]

Amine[c]	M_v[d] ($\times 10^{-6}$)
None	2.21
Isopropyl alcohol	1.50
N,*N*-Dimethylethanol amine (1)	1.08
N,*N*-Dimethylaminoethyl methacrylate (1)	2.26
Triethyl amine	0.38

[a] 0.1 wt% BIPE, 300 nm in Rayonet Reactor, 30 min
[b] Neat
[c] 0.5 wt%
[d] Apparent viscometric molecular weight calculated from relationship in experimental section

Model 142-HF VCG generator. The sample was placed between 2 glass cover slides with a glass fibre scrim between in order to give a reproducible thickness of about 100 microns.

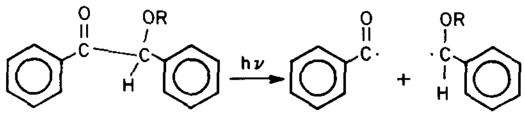
For measurement of the photopolymerization of HDODA in the absence of oxygen a modified Perkin–Elmer Model 1B differential scanning calorimeter was employed to record the polymerization exotherms. An open aluminium pan was placed in the reference cell and 6 microlitres of sample was loaded by a g.c. syringe into the sample pan. A Corning 7–37 filter was mounted on the top of the cell to restrict the wavelength range of the u.v. light source (320 nm–400 nm). Heat generated during the polymerization was recorded isothermally at 310 K. A continuous nitrogen purge was initiated 3 min prior to and continued throughout the polymerization process.

In the bulk polymerization of ethyl acrylate in the presence of various amines, ethyl acrylate (2 g) containing benzoin isopropyl ether was weighed into a Pyrex tube (10 mm x 75 mm) capped with a rubber stopper. The sample was irradiated in a Rayonet Reactor with 300 nm lamps for 30 min (for the results in *Table 1*) or with 350 nm lamps for 35 min (under nitrogen atmosphere for the results in *Figure 9*). Following polymerization, each test tube was broken and the contents were dissolved in warm acetone. The polymers were isolated by precipitating the solutions in water. The precipitated polymers were collected and dried in a vacuum oven at about 60°C for 12 h. Molecular weights were measured from dilute solution viscosities in acetone at 25°C with a Cannon–Fenske viscometer. From intrinsic viscosities and the following Mark–Houwink equation[9], viscosity-average molecular weights were calculated.

$$[\eta] = 51 \times 10^{-3} M_v^{0.59} \text{ (ml/g)}$$

RESULTS AND DISCUSSION

The basic free radical polymerization of HDODA can be initiated by the photochemical α-cleavage of excited benzoin ethers (see below for a typical example):



The free radical species formed from the α-cleavage process and/or subsequently generated radicals have been shown to be effective in initiating free radical polymerization of acrylate monomers[7]. It has recently been postulated that the photopolymerization of 1,6-hexanediol diacrylate proceeds by *Scheme 1* in the presence of aliphatic[1] or aromatic amines[5].

Scheme 1

$$\mathrm{I} \xrightarrow{h\nu} \mathrm{I}^* \qquad \text{Step 1}$$

$$\mathrm{I}^* \xrightarrow{k_d} \mathrm{R}\cdot \qquad \text{Step 2}$$

$$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_i} \mathrm{RM}\cdot \qquad \text{Step 3}$$

$$\mathrm{P}_n\cdot + \mathrm{M} \xrightarrow{k_p} \mathrm{P}_{n+1}^{\cdot} \qquad \text{Step 4}$$

$$\mathrm{P}_n\cdot + \mathrm{P}_m\cdot \xrightarrow{k_t} \mathrm{P}_{n+m} \qquad \text{Step 5}$$

$$\mathrm{P}_n\cdot + \mathrm{P}_m\cdot \xrightarrow{k_{td}} \mathrm{P}_n + \mathrm{P}_m \qquad \text{Step 6}$$

$$\mathrm{P}_n\cdot + \mathrm{AH} \xrightarrow{k_{tr}} \mathrm{P}_n\mathrm{H} + \mathrm{A}\cdot \qquad \text{Step 7}$$

$$\mathrm{A}\cdot + \mathrm{M} \xrightarrow{k_a} \mathrm{AM}\cdot \qquad \text{Step 8}$$

$$\mathrm{A}\cdot + \mathrm{O}_2 \xrightarrow{k_{O_2}} \mathrm{AO}_2\cdot \qquad \text{Step 9}$$

$$\mathrm{AO}_2\cdot + \mathrm{AH} \xrightarrow{k_{OOH}} \mathrm{AOOH} + \mathrm{A}\cdot \qquad \text{Step 10}$$

where I = photoinitiator; R· = radical initiator; M = monomer; $P_n\cdot$, $P_m\cdot$ = polymer radicals; P_{n+m}, P_nHP_n, P_m = polymers; A· = aminyl radical; AH = aliphatic or aromatic amine.

Steps 1–6 involve the standard initiation, propagation and termination process of free radical polymerization. Steps 7, 9 and 10 depict the radical chain process for oxygen scavenging wherein a radical A·, produced by hydrogen abstraction of a labile amine hydrogen (A–H) by a polymer radical $P_n\cdot$, reacts with oxygen to generate a peroxy radical ($AO_2\cdot$). Once formed the reactive peroxy radical readily abstracts a hydrogen from a second amine to give a hydrogen peroxide plus an aminyl radical. The sequence represented in steps 9 and 10 is then repeated until approximately 15 oxygen molecules[5] are consumed for each aminyl radical originally produced in step 7. Of course, as shown in Step 8, the aminyl radical may add to monomer M and reinitiate the polymerization process. In interpreting the results for the photopolymerization of HDODA in the presence of functionalized amines, *Scheme 1* will be continually referred to.

The data will be divided into three sections. The first section will describe exotherm data for the photopolymerization of HDODA with two amine functionalized methacrylates present. The second section presents similar results for three diamines which have no methacrylate groups attached. The final results section deals with the effect of the amine functionalized methacrylates on the molecular weights of polymers generated from a typical monofunctional acrylate monomer.

Exotherm measurements for the photopolymerization of HDODA with amine-functionalized monomer present

Figure 1 shows exotherm curves for the photopolymerization of HDODA in the thin-foil exotherm unit (air-saturated sample, 0.035 wt% BIPE

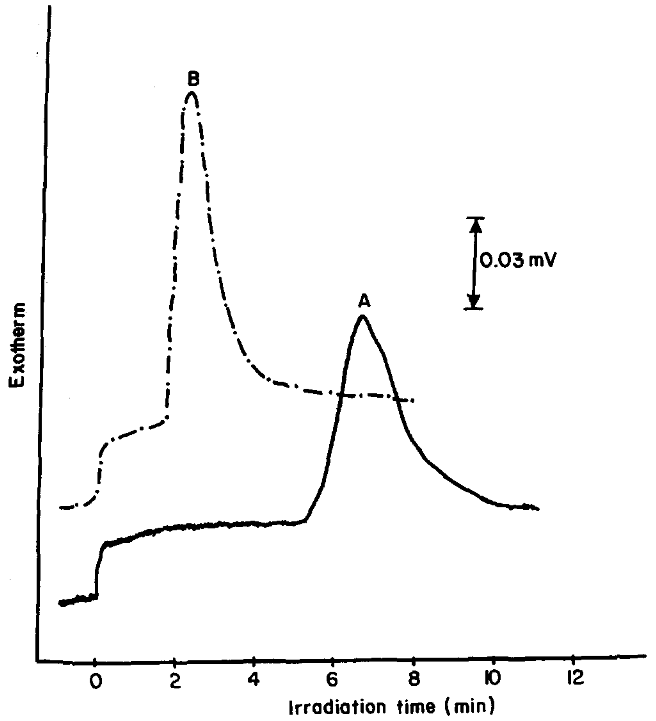
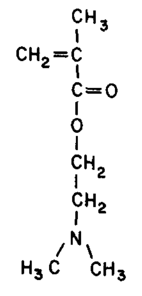


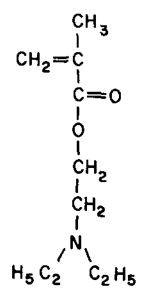
Figure 1 Thin-foil exotherm curves for the photoinitiated polymerization of air-saturated HDODA. (A) No amine. (B) 1 wt% *N*,*N*-dimethylaminoethyl methacrylate

photoinitiator) in the absence and presence of *N*,*N*-dimethylaminoethyl methacrylate (**1**, 1 wt%). Similar results are shown in *Figure 2* for *N*,*N*-diethylaminoethyl methacrylate (**2**).



$CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH_2{-}N(CH_3)_2$

1



$CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH_2{-}N(C_2H_5)_2$

2

In each case, as functionalized amine **1** or **2** is added, the resultant exotherm maximum (H_{max}) increases and the time to reach the exotherm maximum (T_{max}) decreases. Both are indicative of an increased rate of polymerization. In order to extend these results, exotherm curves were recorded for the photopolymerization of HDODA as a function of added concentration of **1** and **2** (given in moles of amine per gram of HDODA). The results from analysing the peak maxima (H_{max}) and T_{max}^{-1} values are given in *Figures 3* and *4*. Plots of H_{max}(amine)/H_{max} and T_{max}^{-1}(amine)/T_{max}^{-1} *versus* concentration of **1** and **2** are utilized to illustrate the data obtained in our studies since both factors (H_{max}(amine)/H_{max} and T_{max}^{-1}(amine)/T_{max}^{-1}) are indicative of the relative increase (or decrease) in the polymerization rate. H_{max}(amine) and T_{max}^{-1}(amine) are simply values for H_{max} and T_{max}^{-1} with the amine added. (Incidentally, it has previously been shown[1,5] that T_{max}^{-1}, as well as H_{max}, is an excellent representation of the overall polymerization rate.)

Figures 3 and *4* show that both H_{max} and T_{max}^{-1} experience a rapid rise at relatively low amine concentrations. At higher amine concentrations H_{max} (*Figure 3*) begins to decline, the decrease occurring at lower amine concentrations for the *N*,*N*-diethyl substituted compound **2** than for the *N*,*N*-dimethyl substituted compound **1**. The exotherm data in *Figures 3* and *4* were obtained for air-saturated (at least initially) HDODA samples using the thin-foil exotherm unit.

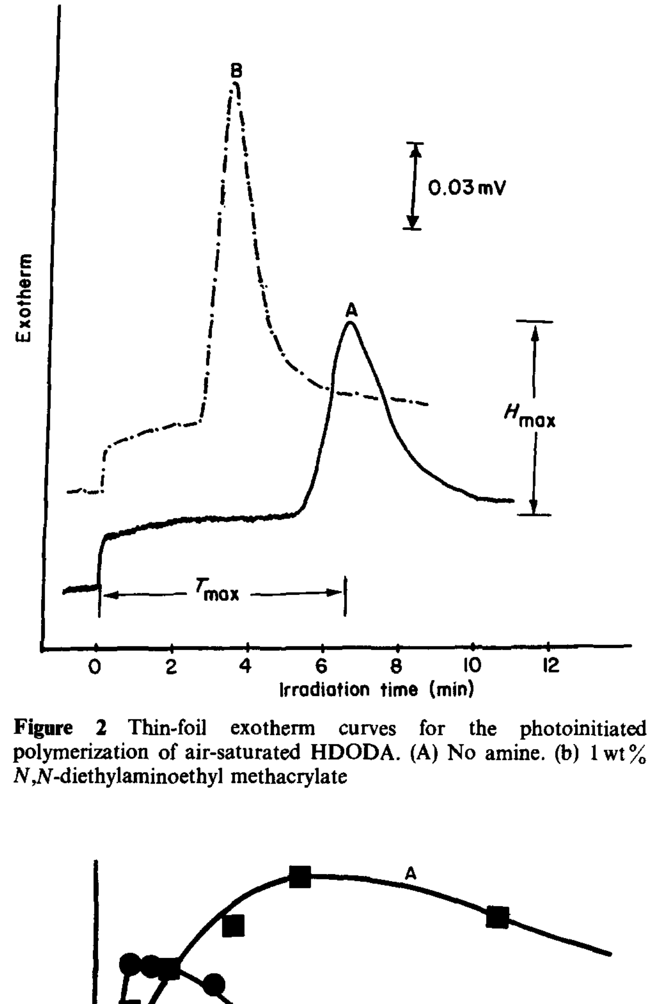


Figure 2 Thin-foil exotherm curves for the photoinitiated polymerization of air-saturated HDODA. (A) No amine. (b) 1 wt% *N*,*N*-diethylaminoethyl methacrylate

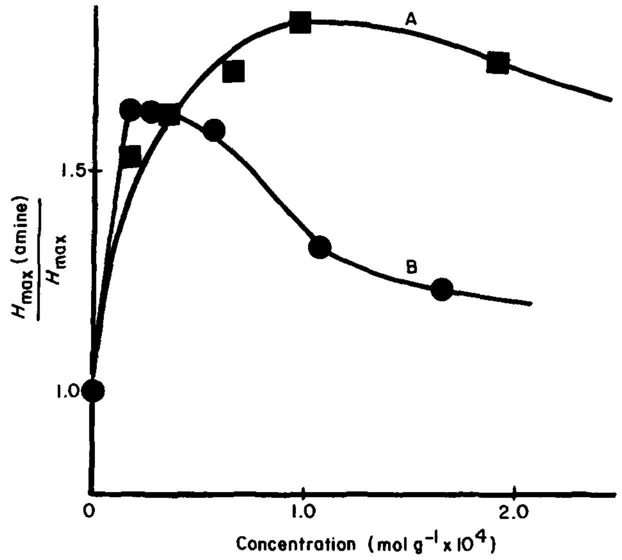


Figure 3 Plot of H_{max}(amine)/H_{max} *versus* amine concentration for the photoinitiated polymerization of air-saturated HDODA (thin-foil unit). (A) *N*,*N*-dimethylaminoethyl methacrylate (■). (B) *N*,*N*-diethylaminoethyl methacrylate (●)

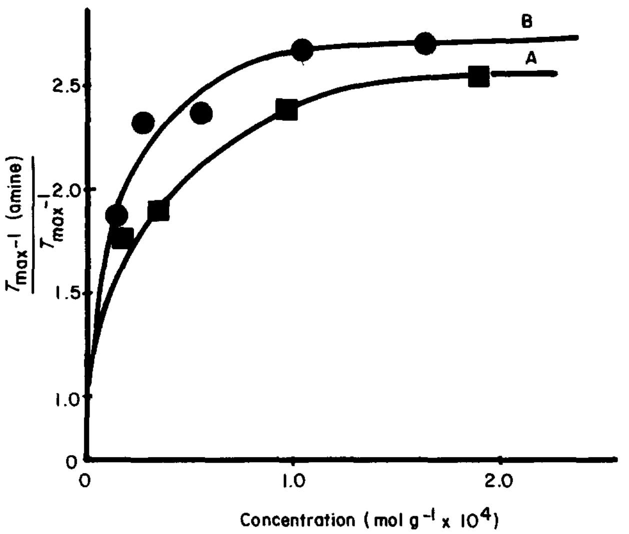


Figure 4 Plot of T_{max}^{-1}(amine)/T_{max}^{-1} *versus* amine concentration for the photoinitiated polymerization of air-saturated HDODA (thin-foil unit). (A) *N*,*N*-dimethylaminoethyl methacrylate (■). (B) *N*,*N*-diethylaminoethyl methacrylate (●)

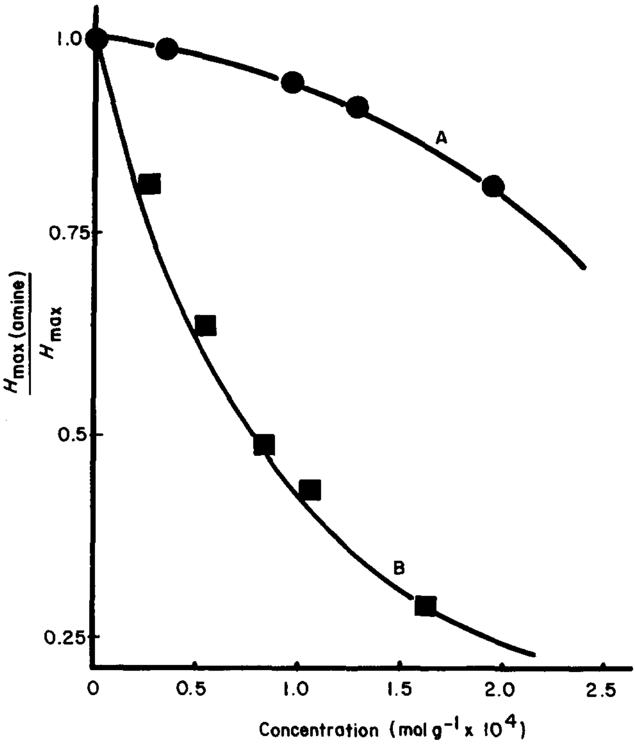


Figure 5 Plot of H_{max}(amine)/H_{max} *versus* amine concentration for the photoinitiated polymerization of nitrogen-saturated HDODA (d.s.c. unit). (A) *N*,*N*-dimethylaminoethyl methacrylate (●). (B) *N*,*N*-diethylaminoethyl methacrylate (■)

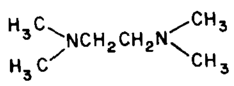
Figure 5 shows a plot of H_{max}(amine)/H_{max} *versus* amine concentration (compounds **1** and **2**) for d.s.c. data with a continual nitrogen purge of the HDODA sample. It is quite clear that the *N*,*N*-diethyl substituted amine (*Figure 5*, curve B) results in a very rapid decrease in H_{max} at relatively low concentrations. Apparently the chain transfer/reinitiation sequence (steps 7 and 8 in *Scheme 1*) becomes quite prominent at rather modest concentrations of **2**. This most assuredly results from the availability of secondary hydrogen atoms on the carbon alpha to the nitrogen atom of compound **2**. Abstraction of such hydrogen atoms (*Scheme 2*, part a) is an efficient process which yields a relatively stable radical that is slow to reinitiate polymerization compared with the methylene radical formed by hydrogen abstraction of one of the methyl protons of compound **1** (*Scheme 2*, part b). Thus, higher concentrations of **2** reduce the polymerization rate much more than higher concentrations of **1**. The impact of the results in *Figure 5* on the polymerization of HDODA in the air-saturated samples (*Figure 3*) suggests that while **2** is effective in elimination of oxygen at relatively low concentrations, at higher levels it actually results in a reduction in H_{max}. Consequently, the reinitiation Step 8 (*Scheme 1*) becomes the dominant factor in determining the overall polymerization rate. This occurs as a result of depletion of the oxygen content at rather low concentrations of amine, thereby decreasing the overall rate of the bimolecular process depicted in Step 9 of *Scheme 1*.

Exotherm measurements for the photopolymerization of HDODA with diamines present

To provide additional insight into the effect of compounds **1** and **2** on the photopolymerization of HDODA, compounds **3–5** were investigated on both the thin-foil (air-saturated HDODA) and the d.s.c. (nitrogen purged (HDODA) exotherm units. Plots shown in *Figures 6–8* for compounds 3–5 show identical trends to those in *Figures 3–5* and provide corroborative evidence for the conclusions drawn previously for compounds **1** and **2**. Specifically, the *N*,*N*,*N*′,*N*′-tetraethyl substituted diamine (compound **5**) causes the greatest reduction in

$H_2NCH_2CH_2NH_2$

3



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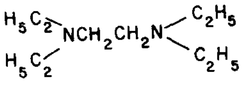
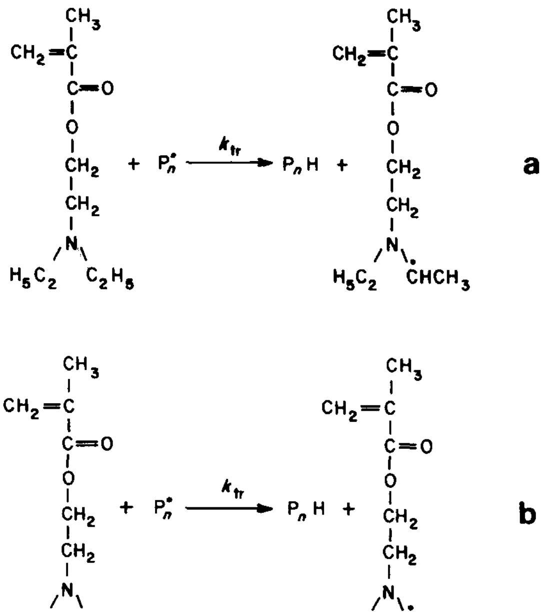


5

Scheme 2



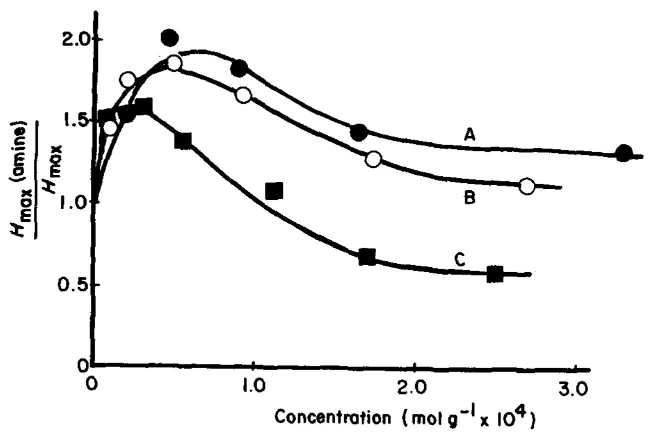


Figure 6 Plot of H_{max}(amine)/H_{max} *versus* amine concentration for the photoinitiated polymerization of air-saturated HDODA (thin-foil unit). (A) Ethylenediamine (●). (B) *N,N,N′,N′*-tetramethylethylenediamine (○). (C) *N,N,N′,N′*-tetraethylethylenediamine (■)

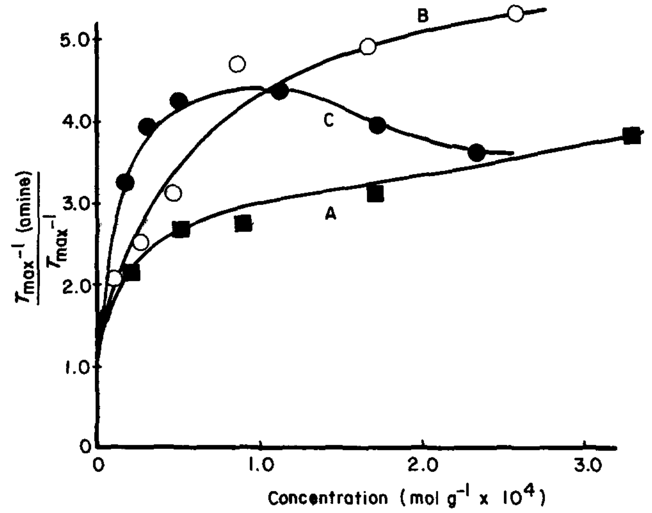


Figure 7 Plot of T_{max}^{-1}(amine)/T_{max}^{-1} *versus* amine concentration for the photoinitiated polymerization of air-saturated HDODA (thin-foil unit). (A) Ethylenediamine (■). (B) *N,N,N′,N′*-tetramethylethylenediamine (○). (C) *N,N,N′,N′*-tetraethylethylenediamine (●)

H_{max} (curve C in *Figures 6–8*). In fact, compound **5** even results in a decrease in T_{max}^{-1} at concentration levels above 1.0×10^{-4} mol g^{-1}. This is the first example we have found where T_{max}^{-1} actually decreases at higher amine concentrations and is probably due to the particularly large number of readily abstractable secondary hydrogen atoms (12 for compound **5** as opposed to 4 for compounds **3** and **4**) on carbons alpha to the nitrogen atoms.

At this point one is justified in asking how the chain transfer rate constants (Step 7) differ for compounds **3**–**5**. This can best be answered by consideration of the plot in *Figure 9* for the photopolymerization of an appropriate model ethyl acrylate compound which shows a linear relationship between DP_v^{-1} and the [amine]/[ethyl acrylate] concentration ratio. (DP_v is the viscosity-average degree of polymerization.) Unfortunately, exact chain transfer constants cannot be extracted from the plots in *Figure 9* for two reasons; first, DP_v is not a number-average degree of polymerization; second, the polymerization rate itself is dependent on the concentration of both amine and monomer present. The relative slopes are, however, indicative of the overall efficiency of the amines in retarding the polymerization process. Thus, it is safe to say that **5** is more effective than **4** or **3** in lowering the polymerization rate of ethyl acrylate. This can best be explained by consideration of the radicals formed upon hydrogen abstraction from

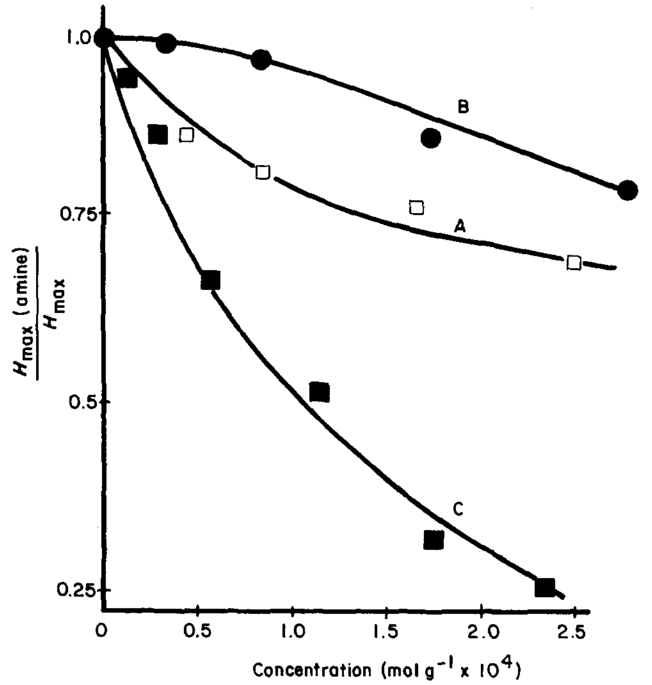


Figure 8 Plot of H_{max}(amine)/H_{max} *versus* amine concentration for the photoinitiated polymerization of nitrogen-saturated HDODA (d.s.c. unit). (A) Ethylenediamine (□). (B) *N,N,N′,N′*-tetramethylethylenediamine (●). (C) *N,N,N′,N′*-tetraethylethylenediamine (■)

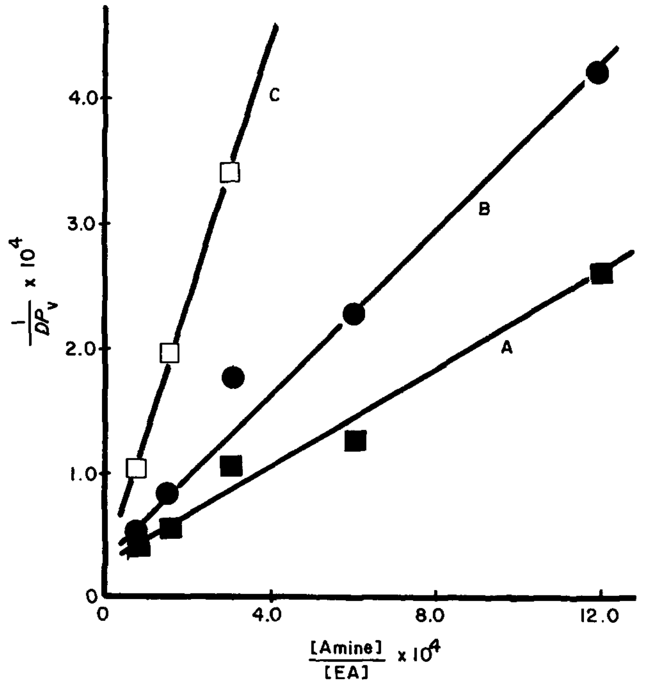
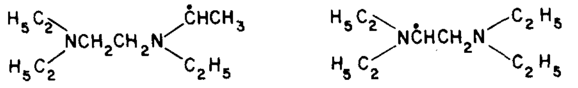
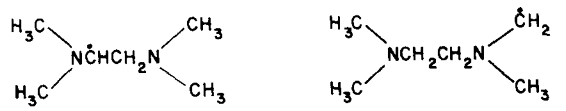


Figure 9 Plot of DP_v^{-1} *versus* the [amine]/[ethyl acrylate] concentration ratio. (A) Ethylenediamine (■). (B) *N,N,N′,N′*-tetramethylethylenediamine (●). (C) *N,N,N′,N′*-tetraethylethylenediamine (□)

compounds **4** and **5** (see structures below). In both cases hydrogen abstraction from the bridging ethyl group yields radicals of similar stability/reactivity. However, abstraction of the primary hydrogens of compound **4** (see structure below) results in highly reactive radicals capable



Radicals from 5



Radicals from 4

of rapid reinitiation of polymerization (Step 8, *Scheme 1*). The radicals formed from abstraction of the relatively labile secondary hydrogens on the *N*-ethyl groups of compound **5** are expected to be somewhat stabilized and thus effective in increasing the chain transfer rate (*Scheme 1*, step 7) and/or reducing the reinitiation rate (*Scheme 1*, step 8). Compound **3**, which has a bridging ethyl group with four hydrogens as well as four hydrogens attached directly to the two nitrogens, has a low overall efficiency for the inhibition process. Apparently, for **3** the overall rate of radical generation is slow and/or the subsequent rate of reinitiation of the polymerization process is very rapid. Incidentally, only the radicals formed by abstraction of the ethyl hydrogens of **3** (not the aminyl radicals) would be capable of initiating the oxygen scavenging process directly.

The effect of functionalized amines on the molecular weight of poly(ethyl acrylate)

Since one of the salient features of amine functionalized monomers discussed in the introduction section is their potential use as oxygen scavengers which do not induce loss in molecular weight or crosslink density, it is important to consider the effect of compounds **1** and **2** on polymer molecular weight. Clearly HDODA which forms a crosslinked polymer does not readily lend itself to molecular weight measurements. We have previously shown[1] that photopolymerization of ethyl acrylate monomer, which yields a linear polymer upon polymerization, serves as an excellent model system for the HDODA polymerization. Molecular weight studies show that addition of simple aliphatic amines, e.g. triethyl amine, lowers the apparent molecular weight (viscosity-average) significantly[1]. Molecular weights (viscosity-average) for photopolymerization of (0.1 wt% BIPE) ethyl acrylate in the presence of triethyl amine, *N,N*-dimethylethanol amine, and *N,N*-dimethylaminoethyl methacrylate are given in *Table 1*. Both of the non-functionalized amines cause significant reduction in the viscosity average molecular weights; however, the functionalized amine (*N,N*-dimethylaminoethyl methacrylate) which is closely related in structure to *N,N*-dimethylethanol amine, shows no decrease in the apparent viscosity-average molecular weight of poly(ethyl acrylate). Apparently the functionalized amine, when incorporated into the polymer, causes crosslinking. This results in poly(ethyl acrylate) having an apparent viscosity-average molecular weight equivalent to the polymer obtained when no amine is present (entry 1 in *Table 1*). It should be noted that caution must be exercised in interpreting the apparent viscosity-average molecular weights for poly(ethyl acrylate) generated in the presence of the amine functionalized monomers since the polymer formed is crosslinked. With this in mind a general comparison between the values calculated in *Table 1* illustrates that the functionalized amine is indeed incorporated into the polymer resulting in a substantially higher viscosity average molecular weight than obtained when polymerization is conducted in the presence of triethyl amine or *N,N*-dimethylethanol amine.

CONCLUSION

In this paper, the photopolymerization of an air-saturated 1,6-hexanediol diacrylate (HDODA) bifunctional acrylate monomer has been studied in the presence and absence of two amine functionalized methacrylates. Both amine synergists are effective in increasing the maximum rate of polymerization ($H_{\max}$) and decreasing the time ($T_{\max}^{-1}$) required to obtain $H_{\max}$. Apparently, these amines act as radical-chain oxygen scavengers with the added advantage that they become 'locked into' the polymer network by virtue of their methacrylate functionality.

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