The Effect of Aromatic Amines on the Photopolymerization of 1,6-Hexanediol Diacrylate

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Synopsis

The ability of aromatic amines to accelerate the photoinitiated polymerization of multifunctional acrylates in the presence of oxygen is shown to be dependent on the structure of the amine. For N,N-dimethylaniline, a rapid oxygen-scavenging process which proceeds by a radical-chain mechanism accounts for the large polymerization rate increase. Conversely, aniline cannot sustain an oxygen-scavenging process and inhibits the polymerization of air-saturated monomers. In general, the degree of rate enhancement and/or inhibition of the aromatic amines investigated is subject to the amine concentration.
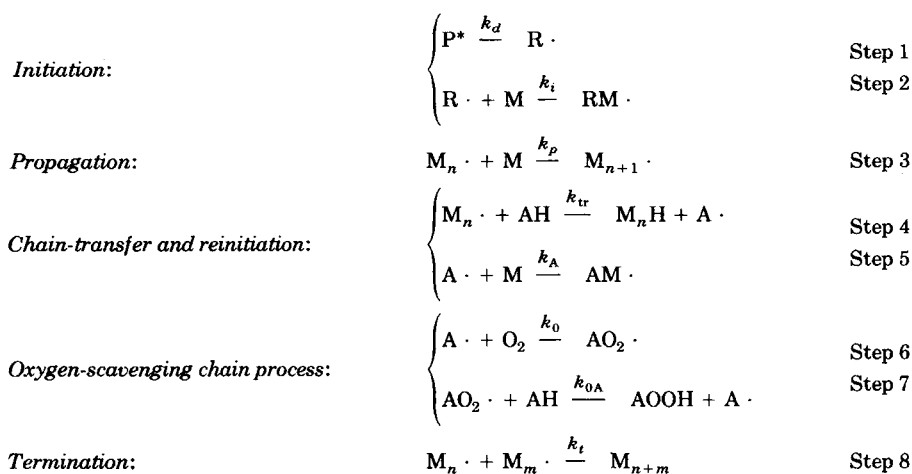
INTRODUCTION

While it has long been recognized that amines are effective synergists when used with benzophenone-type photoinitiators, it has recently been shown that the photopolymerization of air-saturated acrylates initiated by cleavage-type photoinitiators are enhanced in the presence of tertiary aliphatic amines.[1] Using exotherm units based on either a modified differential scanning calorimeter (DSC) or a thin-foil heat flow gauge, it was shown that while aliphatic amines inhibit the photoinitiated polymerization of nitrogen-saturated 1,6-hexanediol diacrylate (HDODA), they accelerate the polymerization of air-saturated HDODA. The polymerization rate enhancement is manifested in the maximum rate of polymerization obtained (H_{max}) and the time (T_{max}) required to reach H_{max}.

Preliminary results indicate that the aliphatic amines act both as chain-transfer agents as well as effective oxygen scavengers (Scheme I). The oxygen scavenging mechanism has·been postulated to proceed by a radical chain process[2] where up to 15 oxygen molecules are consumed per aminyl radical produced.

Steps 1–3 and 8 are standard initiation, propagation, and termination steps for photoinitiated free radical polymerizations. Steps 4 and 5 are chain-transfer and reinitiation steps, and steps 6 and 7 represent a radical-chain oxygen scavenging process which may occur in the polymerization of oxygen-saturated monomers.

In contrast to the results for aliphatic amines which participate in the oxygen-scavenging process depicted in steps 6 and 7, alcohols, ethers, and acrylamides do not effect the polymerization of either oxygen or nitrogen-saturated HDODA. Thus, it is not a sufficient condition simply to have

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Initiation:

$$\begin{cases} P^* \xrightarrow{k_d} R\cdot & \text{Step 1} \\ R\cdot + M \xrightarrow{k_i} RM\cdot & \text{Step 2} \end{cases}$$

Propagation:

$$M_n\cdot + M \xrightarrow{k_p} M_{n+1}\cdot \qquad\qquad \text{Step 3}$$

Chain-transfer and reinitiation:

$$\begin{cases} M_n\cdot + AH \xrightarrow{k_{tr}} M_nH + A\cdot & \text{Step 4} \\ A\cdot + M \xrightarrow{k_A} AM\cdot & \text{Step 5} \end{cases}$$

Oxygen-scavenging chain process:

$$\begin{cases} A\cdot + O_2 \xrightarrow{k_0} AO_2\cdot & \text{Step 6} \\ AO_2\cdot + AH \xrightarrow{k_{0A}} AOOH + A\cdot & \text{Step 7} \end{cases}$$

Termination:

$$M_n\cdot + M_m\cdot \xrightarrow{k_t} M_{n+m} \qquad\qquad \text{Step 8}$$

Scheme I. P^* = excited photoinitiator, $R\cdot$ = free radical initiator, M = monomer, $M_n\cdot$, $M_m\cdot$ = polymer chain with n and m monomer units, AH = amine, $A\cdot$ = aminyl radical, $AO_2\cdot$ = peroxy radical, and M_{n+m} = polymer with $n + m$ monomer units.

abstractable hydrogen species available, but if a synergist is to function as an accelerator in the presence of oxygen it must be capable of sustaining a radical chain process for oxygen scavenging as in steps 6 and 7. Apparently, amines, and in particular tertiary aliphatic amines with α-hydrogens, are well suited for this purpose.

In this paper, we extend our previous investigation to consider the effect of aromatic amine synergists on the homopolymerization of air-saturated HDODA. The effect of the amine structure on the photopolymerization rate parameters (H_{max} and T_{max}^{-1}) is reported. The results clearly demonstrate that the overall ability of the amine synergist to accelerate (or inhibit) the polymerization is directly related to the type of substitution (methyl, ethyl, etc.) on the central nitrogen atom of the aromatic amine.

EXPERIMENTAL

1,6-Hexanediol diacrylate (HDODA, Celanese) and benzoin isopropyl ether (BIPE, Polysciences) were used as received. 2,2'-Azobisisobutyronitrile (AIBN, Kodak) was recrystallized from methanol. All aromatic amines were obtained from Aldrich and distilled before use.

A thin-foil exotherm unit was employed to record the polymerization exotherm in the presence of oxygen. It consists of a basic thin-foil heat flow gauge mounted on an aluminum heat sink as described in earlier papers.[3, 4] The exotherm unit was connected to a Keithly Model 1155 microvoltmeter whose output was recorded on strip chart recorder. The sample was placed between two glass cover slides (22 × 22 × 0.15 mm) with a glass-fiber scrim between in order to give a constant film thickness of ~ 100 μm. For the photopolymerization in the absence of oxygen and the thermal polymerizations, a modified Perkin-Elmer 1B differential scanning calorimeter (DSC) was used to record the polymerization exotherms. An open aluminum pan was placed in the sample cell and 6 μL of sample was loaded by a GC syringe
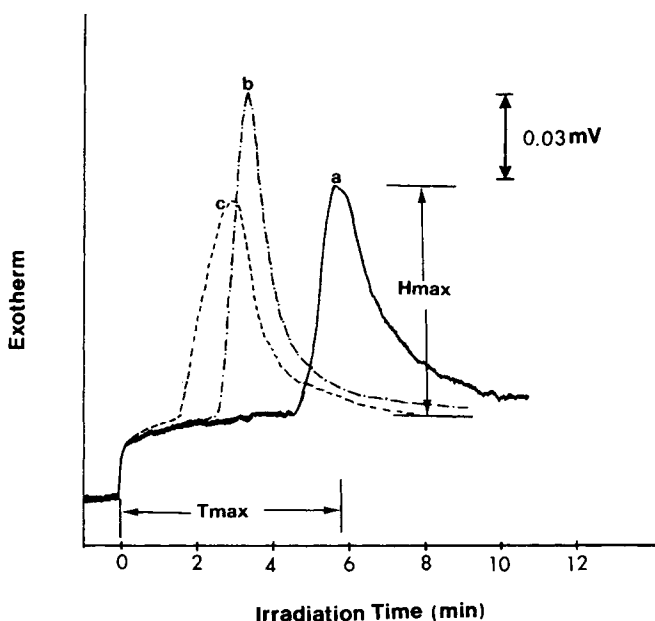
Fig. 1. Thin-foil exotherm curves for the photoinitiated polymerization of air-saturated HDODA: (a) no amine; (b) 0.25 wt % N,N-DMA; (c) 3.0 wt % N,N-DMA.

(Hamilton, 10 μL). An empty pan was placed in the reference cell. A Corning 7-37 filter (transmitting wavelengths 320–380 nm) was mounted on the top of the cell. Heat generated during the polymerization was recorded isothermally at 310 K with a continuous nitrogen purge. The nitrogen purge was used to deoxygenate the sample for 3 min before the polymerization was initiated. Isothermal measurements of the exotherms generated by the thermal polymerization at 333 K were carried out with continuous nitrogen flowing through the DSC chamber. However, no prenitrogen purging was employed for the thermal polymerization. A Strobex Model 271-B pulsed UV lamp from Chadwick-Helmuth was mounted on the top of the exotherm unit at a distance of 40 cm. The pulse rate of the UV lamp (50 Hz) was controlled by a Wavetek Model 142 HF VCG generator.

RESULTS AND DISCUSSION

Figure 1 shows exotherms for the photoinitiated polymerization of HDODA [0.035 wt % benzoin isopropyl ether (BIPE) photoinitiator] in the presence of an increasing concentration of N,N-dimethylaniline (N,N-DMA). The exotherms were recorded using the thin-foil exotherm unit, and, due to the system configuration, the HDODA sample is air-saturated before the onset of polymerization. The rate parameters H_{max} and T_{max} are shown for curve a (no synergist). It is noteworthy that relatively low levels of N,N-DMA result in a dramatic increase in the maximum rate of polymerization (H_{max}) accompanied by a reduction in the time (T_{max}) required to obtain H_{max}. In practice, T_{max}^{-1} is used in the present study since it has been shown to be a measure, just as H_{max} is, of the photopolymerization rate.[5] In order to illustrate the effect
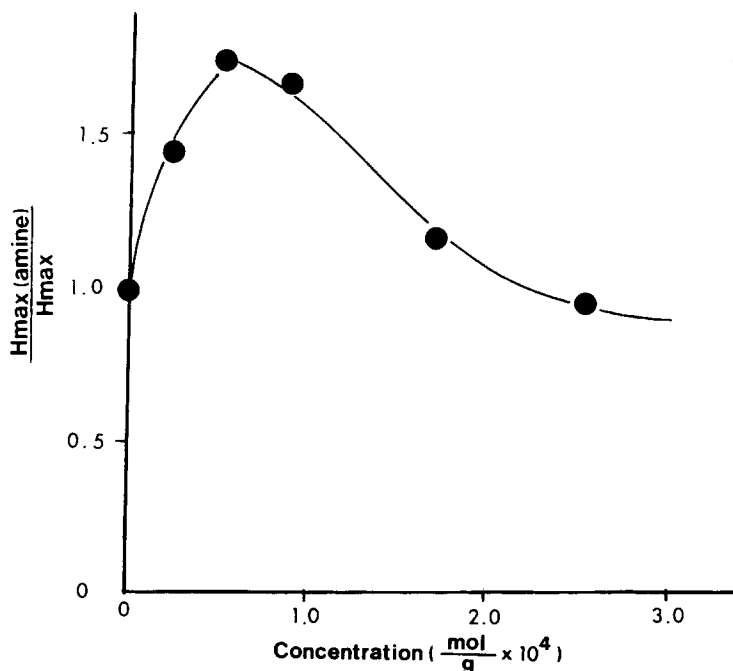
Fig. 2. Plot of H_{max} (amine)/H_{max} vs. N,N-DMA concentration for the photoinitiated polymerization of air-saturated HDODA (thin-foil unit).

of amine concentration on both H_{max} and T_{max}^{-1}, plots of the ratio H_{max} (amine)/H_{max} and T_{max}^{-1} (amine)/T_{max}^{-1} are used in place of the simple parameters H_{max} and T_{max}^{-1}. In accordance with this reasoning, plots in Figures 2 and 3 of H_{max} (amine)/H_{max} vs. N,N-DMA concentration (given in moles of amine per gram of HDODA) and T_{max}^{-1} (amine)/T_{max}^{-1} vs. N,N-DMA concentration show that the polymerization rate increases to a maximum level. In the case of H_{max}, a further increase in N,N-DMA concentration beyond a certain critical value results in a drop of H_{max}. This critical amine concentration occurs at about 9×10^{-5} mol/g. These results are identical to those reported for the photopolymerization of HDODA with triethylamine and dimethylethanol amine as the cosynergists.[1]

Further consideration of the results in Figures 2 and 3 leads to the question of how the exotherm curves for the photopolymerization of HDODA in an oxygen free (nitrogen-saturated) atmosphere would differ from those obtained using the thin-foil unit. In Figure 4, results for H_{max} are shown for the photopolymerization of HDODA (0.035 wt % BIPE photoinitiator) in a DSC with a nitrogen-saturated atmosphere as a function of N,N-DMA concentration. In contrast to the results in Figure 2 where oxygen was initially present, H_{max} (amine)/H_{max} decreases. Evidently, N,N-DMA retards or inhibits (steps 4 and 5 in Scheme I) the photopolymerization of nitrogen-saturated HDODA whereas it increases the polymerization rate of air-saturated HDODA. Corroborative evidence for the N,N-DMA effect in the photopolymerization of HDODA is provided by exotherms for the thermal polymerization (60°C; 0.2% AIBN initiator) of HDODA (nitrogen-saturated) in the absence and presence
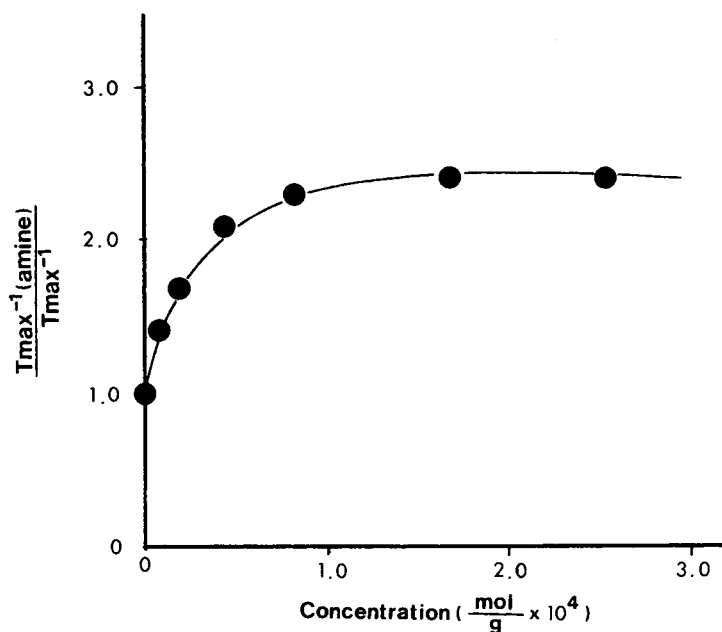
Fig. 3. Plot of T_{max}^{-1} (amine)$/T_{max}^{-1}$ vs. N,N-DMA concentration for the photoinitiated polymerization of air-saturated HDODA (thin-foil unit).
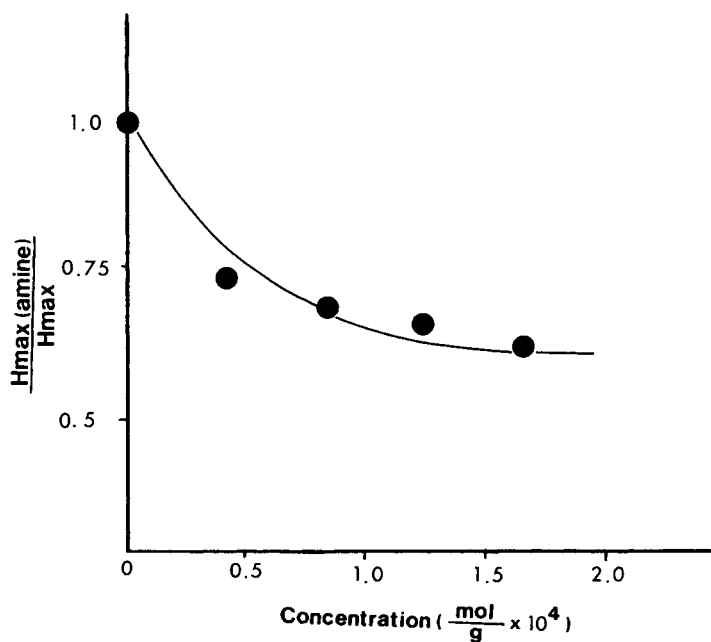

Fig. 4. Plot of H_{max} (amine)$/H_{max}$ vs. N,N-DMA concentration for the photoinitiated polymerization of nitrogen-saturated HDODA (DSC unit).
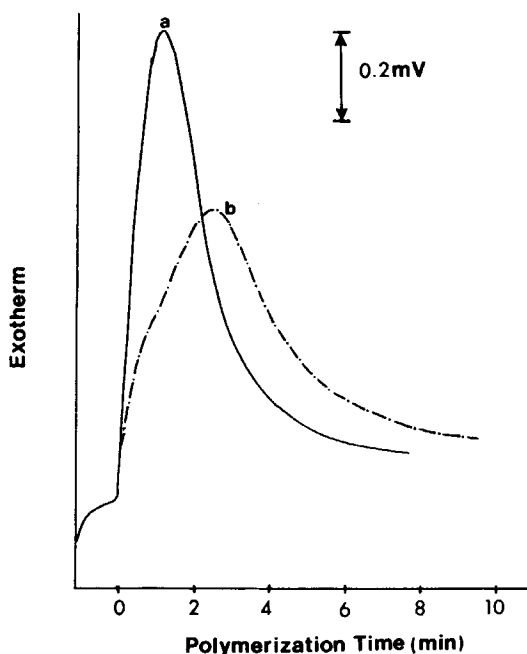
Fig. 5.   DSC exotherm curves for the thermally initiated polymerization (0.2 wt % AIBN) of nitrogen-saturated HDODA: (a) no amine; (b) 1.0 wt % N,N-DMA.

of N,N-DMA. Comparison of the two exotherms in Figure 5 reveals that N,N-DMA also inhibits the thermal polymerization of HDODA. Values of H_{max} for the thermal polymerization in Figure 5 are listed in Table I along with other entries to be discussed later in the paper.

The results for the photopolymerization of HDODA in the presence of N,N-DMA can be explained by invoking the chain-transfer and oxygen-scavenging processes shown in Scheme I. The initial hydrogen abstraction from N,N-DMA (step 4) results in the radical shown below.
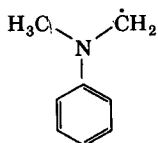
TABLE I
Thermal Polymerization[a, b] of HDODA[c]

Additive[d]	H_{max} (mV)
None	1.18
N,N-DMA	0.76
N,N-DEA	0.65
Aniline	0.64

[a] DSC, nitrogen atmosphere.
[b] 0.2 wt % AIBN.
[c] Polymerization temperature 60°C.
[d] 1 wt %.

This nitrogen-substituted methyl radical is unstable and readily reacts with molecular oxygen (step 6) to initiate the oxygen-scavenging chain process shown in steps 6 and 7. This accounts for the large values of H_{max} (amine)/H_{max} and T_{max}^{-1} (amine)/T_{max} obtained at low N,N-DMA concentrations. The subsequent decrease in H_{max} (amine)/H_{max} at higher amine concentrations (Fig. 2) is due to a somewhat lowered propensity for the substituted methyl radical to reinitiate the polymerization process. In other words, step 5 is slow compared to step 3. This is vividly demonstrated for the photopolymerization of HDODA in nitrogen atmosphere (DSC) in Figure 4 and the thermal polymerization in nitrogen atmosphere in Figure 5.

In summarizing the results, while N,N-DMA acts as a moderate inhibitor to free radical polymerization of acrylated monomers, due to its ability to initiate and sustain an oxygen scavenging process, low concentrations of N,N-DMA actually increase the polymerization rate of air-saturated acrylated monomers. At higher concentrations as the inhibitor process begins to dominate, H_{max} (amine)/H_{max} decreases.

At this point, it is worth pointing out a crucial, and somewhat limiting, factor which requires the use of both the thin-foil exotherm unit and the DSC apparatus to record the polymerization exotherms reported in Figures 1–5. While it would be advantageous to measure the polymerization exotherms generated in air- and nitrogen-saturated samples of HDODA under identical experimental conditions on the same unit, i.e., the DSC, it is simply not feasible to do so. Repeated attempts to record the polymerization of air-saturated HDODA in the DSC resulted in no measurable exotherms. This is not at all surprising since our lamp system was chosen in these experiments not for its high-intensity, but for its consistency in spectral output and its low intensity. Use of a high-intensity lamp source would, of course, provide the photon flux necessary to induce polymerization of air-saturated HDODA, but it generates so much heat in the sample cell that the resultant exotherm is small in comparison to the background heat absorbed by the sample. In addition, this results in a large rise in the sample temperature, thus rendering isothermal measurements impossible. It is for these reasons that the two exotherm units were required to demonstrate the effect of aromatic amines on the photopolymerization of HDODA. The thin-foil unit employs samples sandwiched between two cover slips, thereby providing a constant initial concentration of oxygen which is not replenished by oxygen diffusion from the atmosphere as the polymerization proceeds. This allows measurements to be made using the rather low intensity pulsed xenon light source and provides the unique opportunity to observe the chain oxidation process directly. It should be noted that the experimental conditions employed to measure the oxygen scavenging process attributed to N,N-DMA are not identical to the conditions employed in real UV curing operations which use very high-intensity medium-pressure lamp sources to cure acrylic monomers in which oxygen in the sample is continually replenished during the photopolymerization process by diffusion from the atmosphere. Nonetheless, our experimental apparatus is highly useful in measuring the effect of aromatic amines on the photopolymerization of HDODA.

In order to extend our results, polymerization studies were conducted for N,N-diethylaniline (N,N-DEA) and aniline (AN). The results for N,N-DEA are presented first. Figures 6 and 7 show plots of H_{max} (amine)/H_{max} and
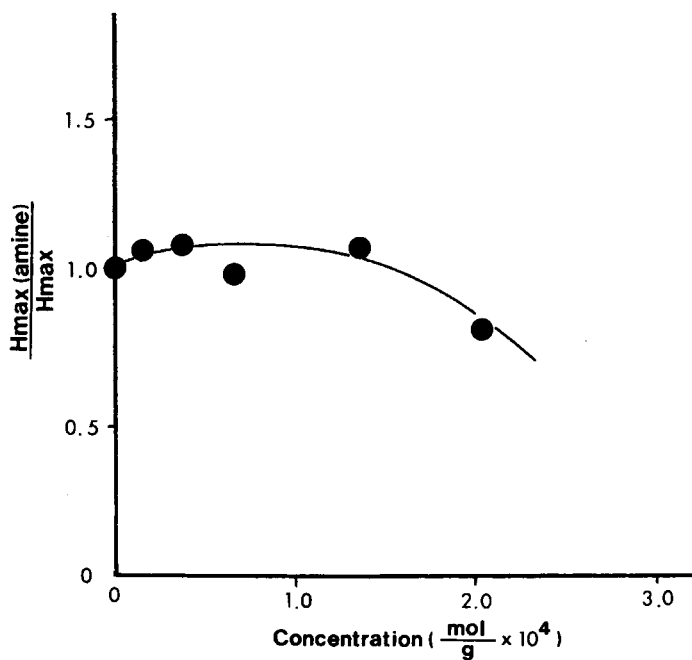
Fig. 6. Plot of H_{max} (amine)/H_{max} vs. N,N-DEA concentration for the photoinitiated polymerization of air-saturated HDODA (thin-foil unit).
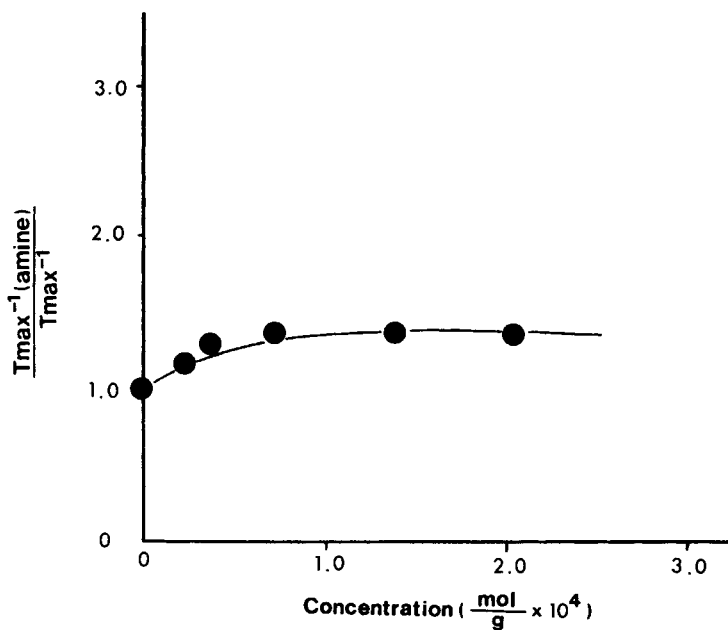

Fig. 7. Plot of T_{max} (amine)$^{-1}/T_{max}^{-1}$ vs. N,N-DEA concentration for the photoinitiated polymerization of air-saturated HDODA (thin-foil unit).

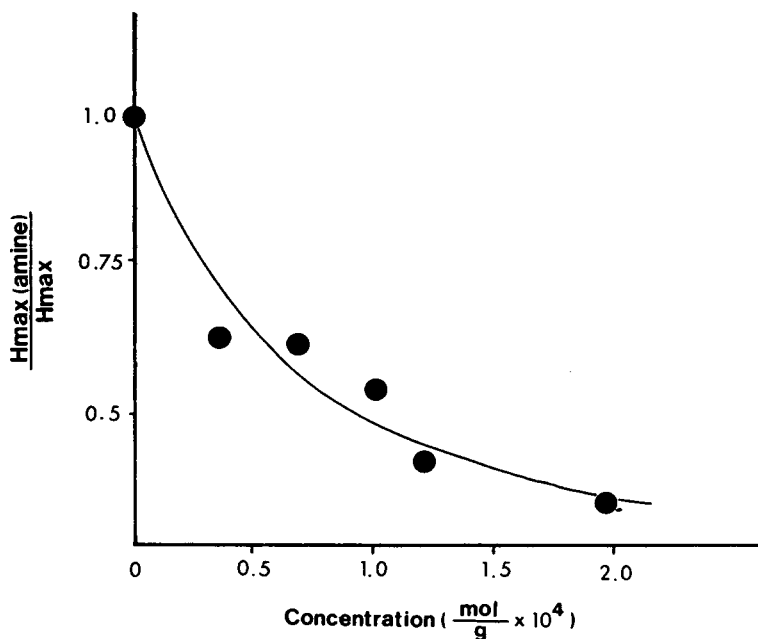Fig. 8. Plot of H_{max} (amine)/H_{max} vs. N,N-DEA concentration for the photoinitiated polymerization of nitrogen-saturated HDODA (DSC unit).

T_{max}^{-1} (amine)/T_{max}^{-1} vs. N,N-DEA concentration for the photopolymerization (0.035 wt % BIPE photoinitiator) of HDODA in the thin-foil exotherm unit. There is little, if any, increase in either ratio at low concentrations of N,N-DEA, and in fact at higher concentrations of N,N-DEA, H_{max} (amine)/H_{max} is less than 1.0.

The results for photopolymerization of nitrogen-saturated HDODA in the DSC are given in Figure 8. Obviously, N,N-DEA is a radical inhibitor (step 5 is slower than step 3) for HDODA polymerization. Although the results in Figure 8 for N,N-DEA and Figure 4 for N,N-DMA indicate that both are effective inhibitors, the results for N,N-DEA with oxygen present (Figs. 6 and 7) are in marked contrast to the results for N,N-DMA in Figures 2 and 3, which show a rapid rise in H_{max} (amine)/H_{max} and T_{max}^{-1} (amine)/T_{max}^{-1} at low amine concentrations. Apparently, the radical formed by hydrogen abstraction from N,N-DEA (shown below) is relatively ineffective in generating and sustaining the oxygen scavenging process in steps 6 and 7:
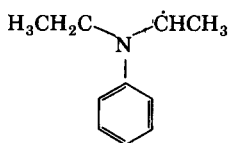
As in the case of N,N-DMA, the thermal polymerization (60°C; 0.2% AIBN initiator) of HDODA in a nitrogen atmosphere (DSC) with N,N-DEA present (1 wt %) results in a decrease in H_{max} (Table I). The reinitiation step 5 must be slow compared to the chain propagation reaction in step 3. This fact,
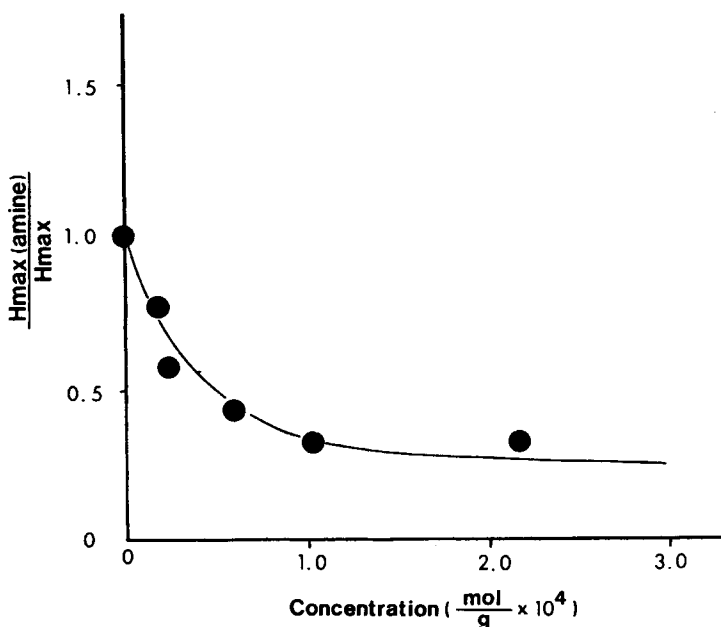
Fig. 9.   Plot of H_{max} (amine)/H_{max} vs. AN concentration for the photoinitiated polymerization of air-saturated HDODA (thin-foil unit).

combined with the inability of the radical to initiate and maintain an oxygen scavenging process, accounts for the ineffectiveness of N,N-DEA in enhancing the photopolymerization of air-saturated HDODA.

Figures 9 and 10 show that, for the photopolymerization of air-saturated HDODA (thin-foil unit) with aniline present, the polymerization is inhibited even at low amine concentrations. One might be tempted to attribute this to a low reinitiation rate (step 5) by the anilinyl radical (shown below):
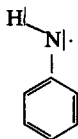
However, the results in Figure 11 for the photopolymerization (0.035 wt % BIPE photoinitiator) of HDODA in a nitrogen atmosphere (DSC) clearly indicate that the anilinyl radical inhibits the reaction to about the same extent as the radicals derived from N,N-DMA and N,N-DEA (see Figs. 4 and 8). As a consequence, it must be concluded that the oxygen-scavenging chain process in steps 6 and 7 is totally prohibited for the anilinyl radical. This is intuitively obvious since one would certainly not expect an anilinyl radical to add to oxygen to form a peroxy radical.

Finally, as with N,N-DMA and N,N-DEA, the rate of the thermal polymerization (60°C; 0.2% AIBN initiator) of HDODA in the DSC (nitrogen-atmosphere) is lowered in the presence of aniline (Table I), confirming the results for the photopolymerization in the DSC. It can be concluded, then,
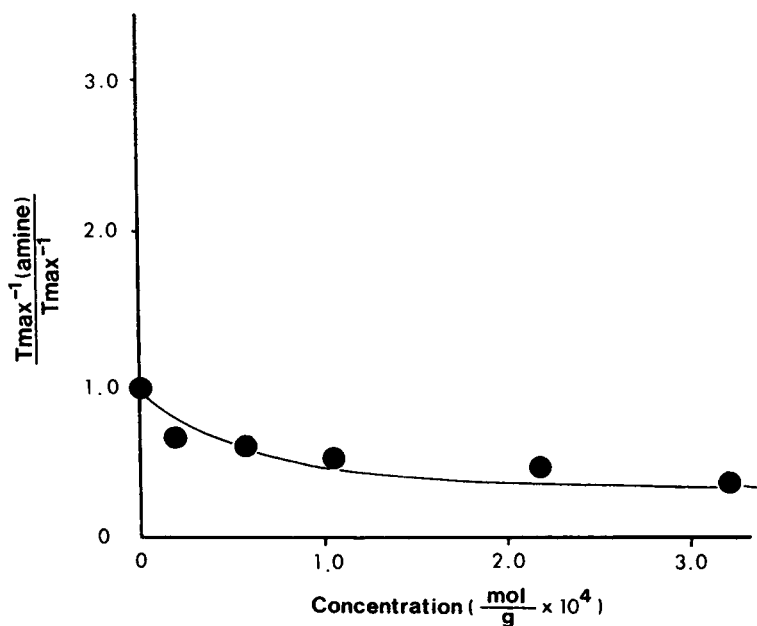
Fig. 10.   Plot of T_{max} (amine)$^{-1}/T_{max}^{-1}$ vs. AN concentration for the photoinitiated polymerization of air-saturated HDODA (thin-foil unit).
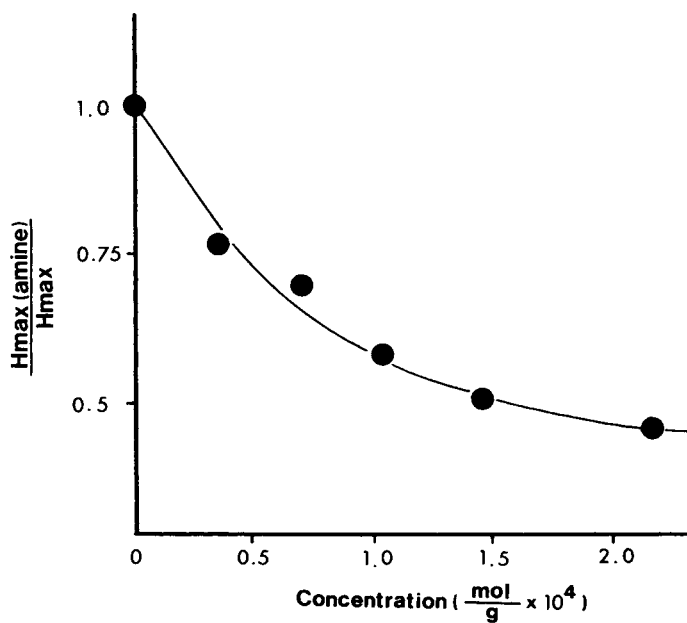

Fig. 11.   Plot of H_{max} (amine)$/H_{max}$ vs. AN concentration for the photoinitiated polymerization of nitrogen-saturated HDODA (DSC unit).

that aniline acts solely as an inhibitor to the free radical polymerization of HDODA in the absence and presence of oxygen both for the photo and thermal initiated polymerization.

SUMMARY

The results in this paper confirm the ability of substituted amines to enhance the photopolymerization rates of multifunctional acrylates as demonstrated for 1,6-hexanediol diacrylate. Specific conclusions to be drawn from this investigation are:

1. N,N-dimethylaniline is more effective than N,N-diethylaniline in enhancing the photopolymerization rate of oxygen saturated 1,6-hexanediol diacrylate.

2. The relatively large rate enhancement afforded by N,N-dimethylaniline can be attributed to an efficient oxygen scavenging mechanism.

3. At all concentrations, aniline inhibits the photopolymerization of oxygen saturated 1,6-hexanediol diacrylate since it is not able to initiate and/or sustain an efficient oxygen scavenging process.

In conclusion, it can be stated that, depending on their structure, substituted aromatic amines may either accelerate or inhibit the photopolymerization of oxygen-saturated acrylated monomers. In cases where rate enhancement is desired, care must be exercised in choosing the correct aniline derivative and optimum concentration.

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