Photoinitiated Radical Copolymerization of Vinyl Ether and Maleate System

LIPING ZHANG, LAN LIU, YONGLIE CHEN

Institute of Polymer Science, Zhongshan University, Guangzhou 510275, People's Republic of China

ABSTRACT: The photoinitiated radical copolymerization of difunctional vinyl ether/unsaturated polyester containing maleate has been studied by differential photocalorimetry. The copolymerization kinetics were found to be affected by various factors, such as the composition, the photoinitiator concentration, the light intensity and the presence of oxygen. No temperature effect on the copolymerization was found. The mixture of vinyl ether and unsaturated polyester containing maleate was studied by fluorospectrophotmetry and the existence of a complex of electron donor-acceptor was detected. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 3541–3547, 1999

Key words: copolymerization; vinyl ether; unsaturated polyester; UV-curing; DPC

INTRODUCTION

Nonacrylate ultraviolet (UV) curable coatings have received considerable attention in recent years.[1] Major classes of nonacrylate materials are: epoxies and vinyl ether that cure by a cationic mechanism, as well as maleate/vinyl ether which cures by a free radical mechanism. Unsaturated polyester (UPE) resins have good mechanical properties, convenient curing cycles, and lower cost as compared with other thermoset resins available on the market[2]; for this reason, oligomers based on these system have been studied. The vinyl ether electron-rich double bond associates with highly electron-deficient maleate (contained in UPE) to form charge transfer complexes, which, on polymerization, give alternating copolymers.[3] As a reactive diluent, vinyl ethers are well known for their low viscosity, low odor, and efficient diluency. They are available in various molecular structures that are capable of imparting a wide variety of chemical and physical properties to the formulation. Li et al.[4] reviewed the mechanism of photoinduced charge transfer copolymerization of some vinyl ether monomers, but they didn't mention vinyl ether/maleate system and the existence of a donor-acceptor complex.

The objective of the present work was to study the kinetics of the copolymerization of vinyl ether and UPE containing maleate functional group, and attempt to find evidence of the existence of a donor-acceptor complex to shed some light on the polymerization mechanism. Differential scanning photocalorimetry (DPC) was used to record exotherm rate vs reaction time. DPC has the advantage that the rate of the reaction can be measured directly, assuming that the heat produced by the polymerization is proportional to the number of monomer units reacted.[5] Because only a small amount of sample is required, good temperature control can be maintained. Additionally, the output of the DPC can be digitized. Therefore data can be treated easily by computer to yield reaction rate as a function of monomer conversion.

EXPERIMENTAL

Materials

The photocurable formulation mainly used in this work contained three components: 1. the divinyl

Table I   The Formulation of the Unsaturated Polyester

Component	mol
Maleic anhydride	3
Triethylene glycol	0.5
Ethylene glycol	4.5
Trimethylol propane	0.5
Phthalic anhydride	2

ether of triethyleneglycol (Rapi Cure DVE-3 from International Speciality Products, Inc., USA); 2. the unsaturated polyester containing maleate; and 3. a hydroxyphenyl ketone photoinitiator (Darocur 1173 from CIBA). The formulation of UPE is given in Table I. All chemicals used in Table I were analytically pure.

Synthesis of the UPE

The components mentioned in Table I were put into a 250-mL three-necked flask with mechanical stirrer, rectifying column, and purging system. The mixture was heated to 160°C in oil bath and refluxed for 2 to 5 h with mechanical stirring (stirring speed was approximately 200 rpm). Then the temperature of oil bath was raised to 205°C, and kept at this temperature for 4 h. The temperature of the oil bath was then lowered to 160°C and the system was subjected to a vacuum of 40 mmHg for an hour to remove water in the system. The reaction was performed under N_2 protection. The acid value of obtained UPE was determined by titration with 0.1 mol/L KOH/ethanol solution. The conversion of UPE used in the present study was over 90% and its molecular weight was 864 g/mol as determined by a vapor pressure osmometer.

Irradiation

The mixture of UPE and triethyleneglycol divinyl ether (DVE-3) was charged into a sample cell of a DPC instrument. The cell was specially shaped (shown in Fig. 1) to maintain uniform sample thickness with the sample sizes (~ 6 mg) used. The mixture was exposed for a few minutes to the UV radiation from a medium-pressure mercury lamp (250 W). The light intensity at the sample position could be changed by some filters. A blank cell was used as the reference. The digitized data were analyzed by using a Microcal Origin 4.1 software (Microcal Software, Inc., USA) and the integration was performed numerically.

A few experiments were performed on a UV-curing line equipped with a 2400 W medium-pressure mercury lamp. The light intensity was measured to be 19.8 mW/cm^2 (the detector was sensitive in the wavelength range of 320–400 nm) at the sample position. The mixture film was polymerized in the presence of air, by a single pass under the lamp at a speed of 50 m/min.

Analysis

The existence of a donor-acceptor complex was determined by a Shimadzu RF5000 fluorospectrophotometer using methylene chloride as the solvent. The excitation and emission slits were both set at 5 nm.

RESULTS AND DISCUSSION

Fluorescence Spectra of DVE-3 and UPE Mixture

Figure 2 shows the fluorescence emission spectra of the DVE-3/UPE mixture. There is only one band (I) for UPE at 335 nm. DVE-3 has no emission band under the same experimental condition. A new band (II) was found at 385 nm for the mixture of DVE-3 and UPE (double bond ratio VE/MA = 1). The fluorescence intensity of band (II) increases with the increasing of concentration of the mixture. There is a shift for band (II) when the concentration of the mixture is above 2.68×10^{-5} mol/L [band (II) is at 365 nm when the concentration is 2.68×10^{-6} mol/L and it shifts to 385 nm when the concentration is 2.68×10^{-5} mol/L or 6.7×10^{-4} mol/L]. This may be a result of the influence of band (I) on band (II) when the concentration is low enough (2.68×10^{-6} mol/L) and the influence decreased while the concentration was increased. It is well known that the vinyl ether electron-rich double bond associates with
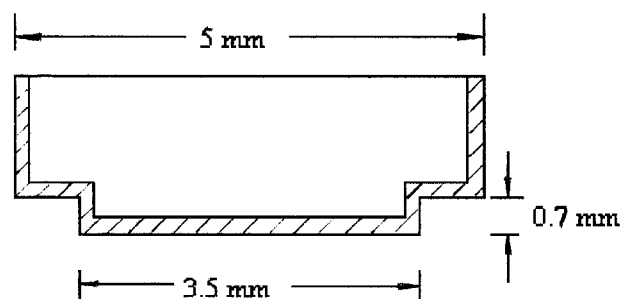
Figure 1   The specially shaped aluminum sample cell used for photopolymerization studies.
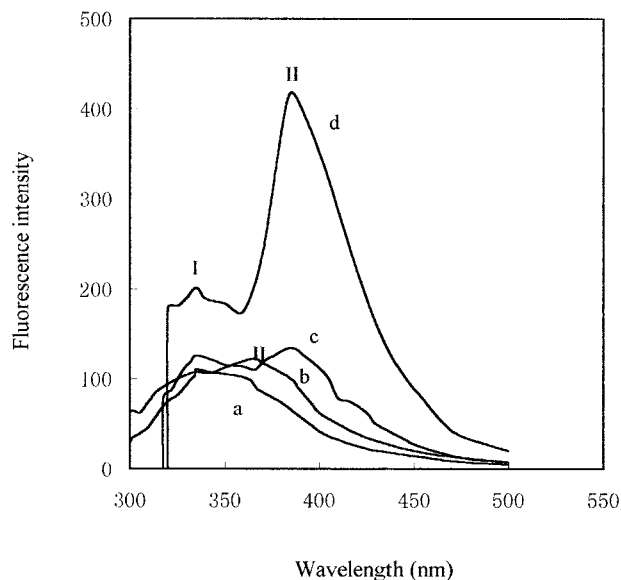
Figure 2 Fluorescence emission spectra of UPE and a 1 : 1 (mol ratio) mixture of DVE-3 and UPE. The excitation wavelength is 290 nm. (a) UPE, (b) DVE-3/UPE (2.68×10^{-6} mol/L), (c) DVE-3/UPE (2.68×10^{-5} mol/L), and (d) DVE-3/UPE (6.7×10^{-4} mol/L).

electron-deficient maleate forming donor-acceptor complex.[6] Thus it can be concluded that band (II) is attributed to the donor-acceptor complex and that the complex does exist in the mixture of DVE-3/UPE.

DPC Data Analysis and Total Heat of Copolymerization

Figure 3 shows a sample DPC trace obtained for the photoinitiated copolymerization of DVE-3 and UPE. From a simple kinetic treatment of free radical polymerization, the maximum rate is expected to occur soon after the light is turned on, when the free radical concentration has reached the steady-state value and the concentration of unconsumed monomers is the highest. This is the case for copolymerization of DVE-3 and UPE when photoinitiator concentration is 2% (wt %); the maximum rate occurs within approximately 30 s after the shutter is opened. This delay is due to the oxygen inhibition since the monomers mixture is weighted out in the air.

The conversion of monomers is calculated from the following equation:

$$\alpha = \frac{\Delta H_t}{\Delta H_T} \qquad (1)$$

Here ΔH_t is the heat of copolymerization when reaction time is t and ΔH_T is the overall heat of copolymerization (i.e., conversion of monomers is 100%).

Total heat evolved from the thermal copolymerization of model molecule hydroxybutyl vinyl ether (HBVE) and dimethyl maleate (DMA) (double bond ratio, HBVE/DMA = 1 : 1) using azo-bis-isobutyronitrile as initiator in N_2 atmosphere at a heating rate of 10°C/min was taken as ΔH_T. The overall heat of copolymerization was not simply the addition of the heat of homopolymerization of the two monomers, it should be related to the heat of the modes of monomer connection, the reactivity ratios, and the polymer composition.

Sawada[7] reported that, for random copolymerization, the molar heat of copolymerization is

$$H = H_{AA} + H_{BB} + \psi \Omega X_A X_B \qquad (2)$$

Here H_{AA}, H_{BB} are the heat of homopolymerization of the two monomers, respectively, X_A, X_B are the mol ratio of the two monomer units in copolymer, and Ω is a constant independent of composition. The randomness parameter ψ is defined as

$$\psi = \frac{1 - [1 - 4X_A X_B (1 - r_1 r_2)]^{1/2}}{2(1 - r_1 r_2)X_A X_B} \qquad (3)$$
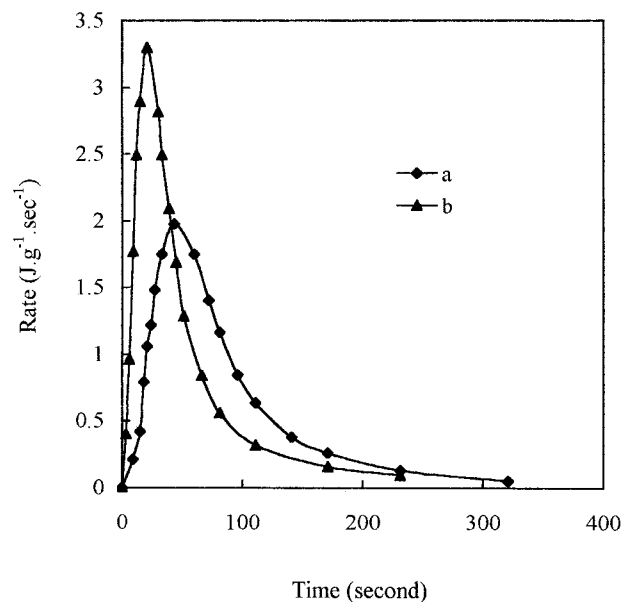
Figure 3 DPC trace for copolymerization of a mixture of DVE-3 and UPE (VE/MA = 1) using Darocur 1173 as photoinitiator in air, light intensity: 0.52 mW/cm². (a) [PI] = 0.5 wt %, (b) [PI] = 2 wt %.

Table II   Total Heat of Copolymerization for DVE-3 and Unsaturated Polyester at Various Compositions

Sample	Double Bond Density (for UPE) (mmol/g Mixture)	Double Bond Density (for DVE-3) (mmol/g Mixture)	Calculated Heat for 100% Reaction (J/g Mixture)
UPE + DVE-3 (10 wt %)	2.93	0.99	131.9
UPE + DVE-3 (20 wt %)	2.60	1.98	263.9
UPE + DVE-3 (23 wt %)	2.51	2.25	300.0
UPE + DVE-3 (30 wt %)	2.28	2.97	303.2
UPE + DVE-3 (40 wt %)	1.95	3.96	259.9

Because the two monomers studied copolymerized alternatingly, according to Sawada's[7] theory, $\psi = 2$. The overall heat of copolymerization in this study was determined to be 133.3 kJ/mol, whereas the heat of homopolymerization of vinyl ether is 59 kJ/mol, and that of maleate is 60 kJ/mol.[8]

Table II shows the overall heat of copolymerization for DVE-3 and unsaturated polyester at various compositions. The last column of Table II indicates the heat of copolymerization expected for a complete reaction. These heats are calculated by assuming a heat of reaction of 133.3 kJ/mol for 1 : 1 complex (composed of monofunctional monomer: HBVE/DMA) when all double bonds have reacted, as determined by DSC for a thermally initiated copolymerization and the copolymerization of the mixture of DVE-3 and UPE proceeds through a donor-acceptor complex mechanism.
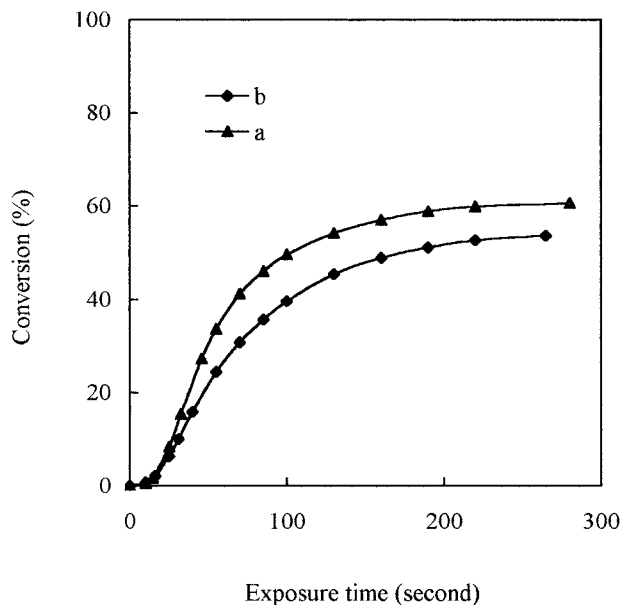
Kinetics of Copolymerization

When DVE-3 or UPE containing maleate was separately exposed to UV radiation in the presence of a radical photoinitiator [(Darocur 1173) = 2 wt %], no significant homopolymerization could be detected on the DPC trace. In contrast, a fast copolymerization was found to proceed when the mixture of DVE-3 and UPE was irradiated under the same conditions, forming an insoluble polymer. Figure 4 shows some typical conversions of monomers vs time recorded by DPC for three formulations with the concentration of the 1 : 1 complex of 1.98 mmol/g mixture (a), 2.28 mmol/g mixture (b), and 1.95 mmol/g mixture (c), respectively. As can be seen from Figure 4, the copolymerization rate of sample b is much higher than those of samples a and c, whereas the copolymerization rate of sample a is a little higher than that of sample c. This is in agreement with the con-

centration of the 1 : 1 complex. The copolymerization rate increases with the increasing of concentration of the complex and is not related directly to monomer feed ratios.

The "S" shape of the kinetics curve is attributed to two major factors: 1. the slight induction period observed initially is because of the inhibition effect of the oxygen dissolved in the mixture on radical-induced copolymerization. Once the oxygen has been consumed by the initiator radicals, the copolymerization develops very rapidly. 2. the slowing of the reaction for conversion above 45% is because of the gel effect.
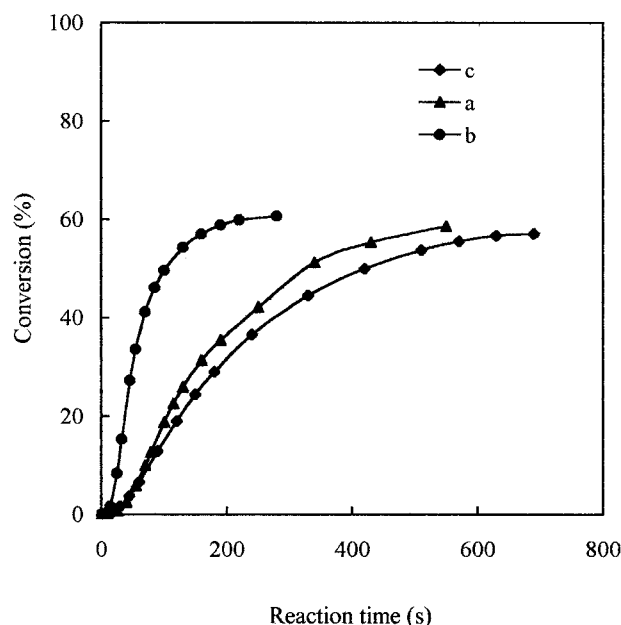
Figure 4   Conversion vs reaction time for copolymerization of a mixture of DVE-3 and UPE, under N_2 using Darocur 1173 (2 wt %) as photoinitiator, light intensity: 0.765 mW/cm^2, (a) DVE-3: 20 wt %, (b) DVE-3: 30 wt %, and (c) DVE-3: 40 wt %.

Figure 5 Influence of oxygen on the copolymerization of a mixture of DVE-3 and UPE (VE/MA = 1.3) using Darocur 1173 (2 wt %) as photoinitiator, light intensity: 0.763 mW/cm^2. (a) in N$_2$, (b) in air.

Influence of Oxygen

Atmosphere oxygen inhibits this type of copolymerization by reacting with both the initiating radicals and propagating polymer radicals, but this effect is more profound than for epoxy acrylate resins (CN104) irradiated in the presence of the same photoinitiator. The propagating species must be more easily exposed to the oxygen molecule because of lower viscosity of the system.

Figure 5 shows the copolymerization profile recorded for DVE-3/UPE film irradiated at a light intensity of 0.763 mW/cm^2, either in the presence of air or in the presence of an N$_2$ atmosphere. The copolymerization with N$_2$ protection proceeds about 25% faster than the film in contact with air. On the other hand, DVE-3/CN104 (VE/acrylate system) copolymerization was found to develop almost at the same rate (especially when conversion was below 50%) whether in air or in N$_2$ (Fig. 6). Because the viscosity of the DVE-3/CN104 mixture is much higher than that of DVE-3/UPE, the oxygen molecule can easily diffuse into the DVE-3/UPE system. The experiment performance on UV curing equipment operating at a much higher light intensity can further close the gap between the two curves, as it shortens the reaction time during which air can diffuse into the liquid sample.

Influence of Light Intensity

In a systematic study, the DVE-3/UPE mixture (VE/MA = 1.3) was exposed to UV radiation of intensity ranging from 0.15 to 0.755 mW/cm^2; the photoinitiator concentration was 2 wt %. The plot of copolymerization rate vs square root of light intensity was found to yield a straight line (Fig. 7).

The rate of polymerization for bimolecular termination mechanism is determined by the following equation[5]:

$$R_p = [k_p/(k_t)^{1/2}](\phi \cdot I_0 \cdot \varepsilon \cdot l \cdot [PI])^{0.5}[M] \quad (4)$$

Where ϕ is the initiation quantum yield, I_0 is the light intensity, ε is the extinction coefficient of the photoinitiator (PI), l is the thickness of the sample, and $[M]$ is the monomer concentration.

From Figure 7, it can be seen that the oxygen inhibition does exist and the maximum of rate of polymerization will be reached at about 30 s after the light is turned on.

Influence of Photoinitiator Concentration

The concentration of photoinitiator plays an important role on the copolymerization kinetics because it controls the rate of initiation. Figure 8 shows the experimentally observed rate with var-
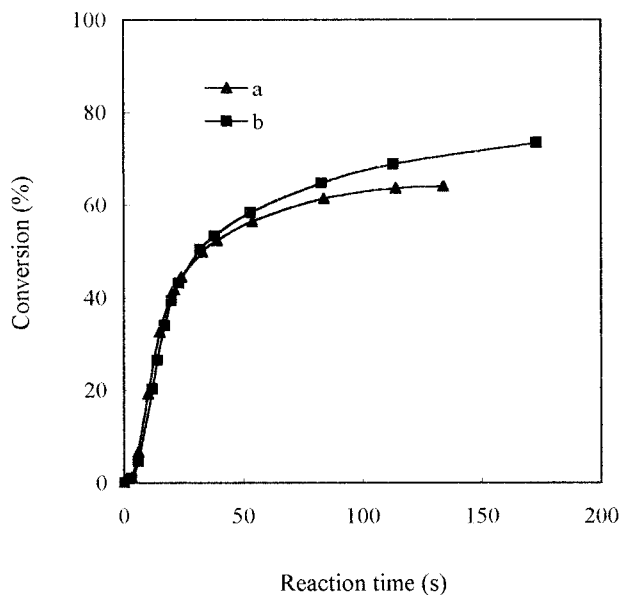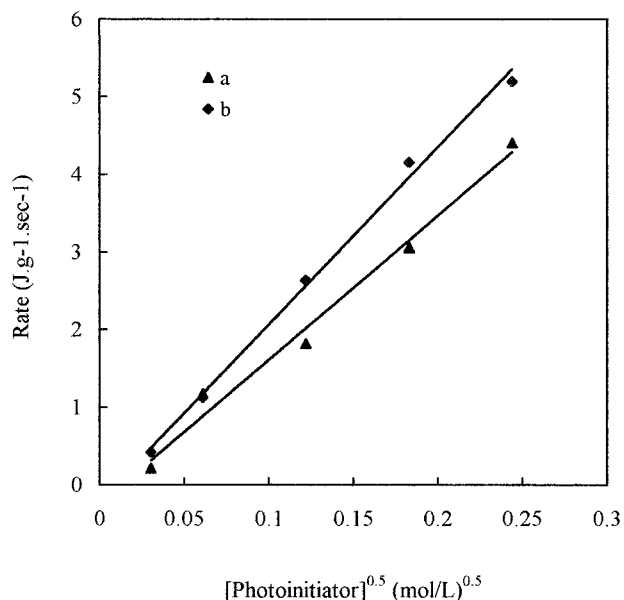

Figure 6 Influence of oxygen on the copolymerization of a mixture of DVE-3 and CN104 (DVE-3/CN104 = 2.83) using Darocur 1173 (2 wt %) as photoinitiator, light intensity: 0.603 mW/cm^2. (a) in air, (b) in N$_2$.
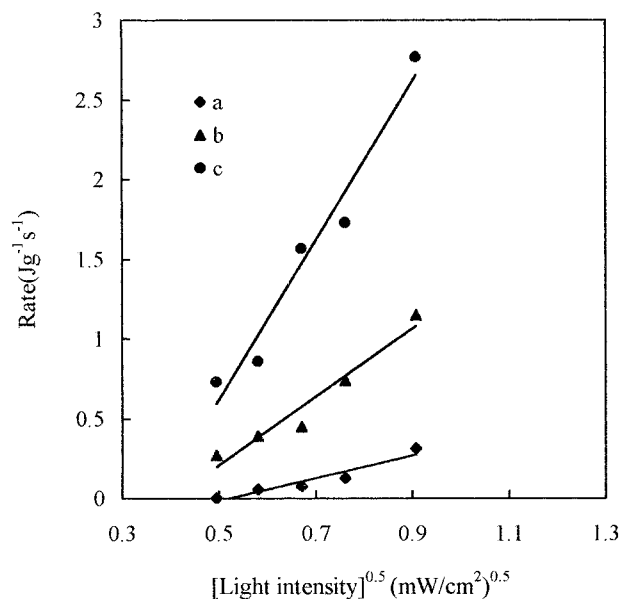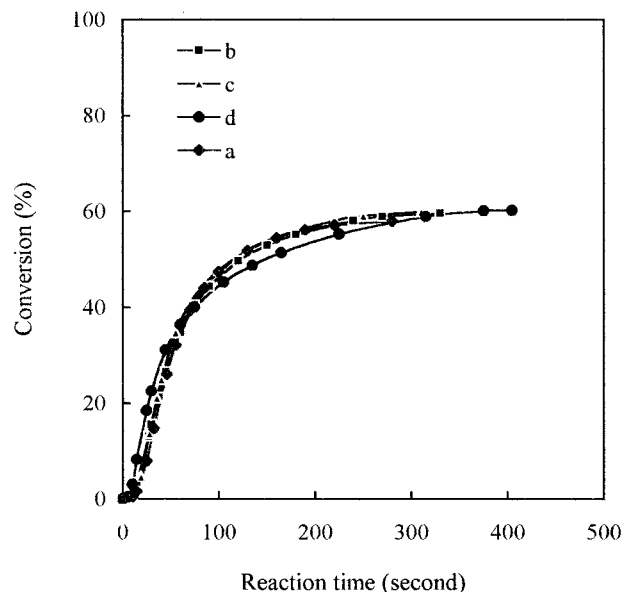
Figure 7 Influence of light intensity on the copolymerization rate of a mixture of DVE-3 and UPE (VE/MA = 1.3) using Darocur 1173 as photoinitiator (2 wt %) in air. (a) 10 s, (b) 15 s, and (c) 30 s.
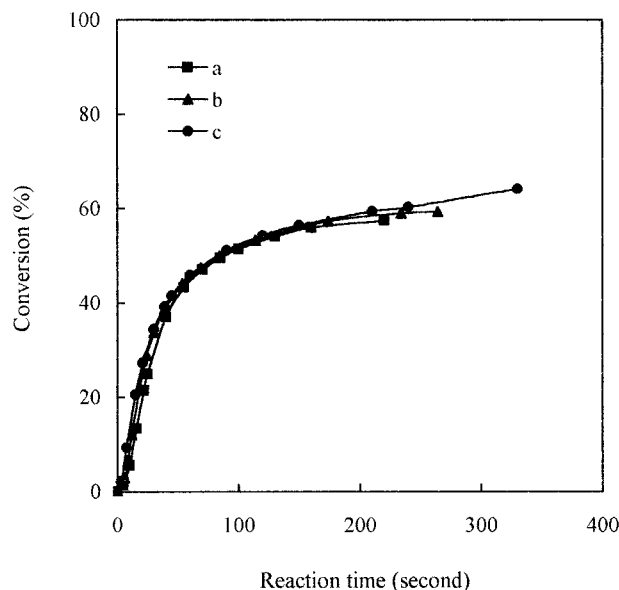

Figure 9 Influence of temperature on copolymerization of a mixture of DVE-3 and UPE (VE/MA = 1.3), using Darcour 1173 (2 wt %) as photoinitiator in air, light intensity: 0.765 mW/cm². Temperature: (a) 30°C, (b) 50°C, (c) 75°C, and (d) 100°C.

ious initiator concentrations in air or in N_2 vs the square root of the photoinitiator concentration. A linear relationship was found to exist for a pho-

Figure 8 Influence of the photoinitiator concentration on the rate of the copolymerization of a mixture of DVE-3 and UPE (VE/MA = 1) using Darocur 1173 as photoinitiator, light intensity: 0.520 mW/cm². (a) in air, (b) N_2.

toinitiator concentration within the experimental range. From this analysis we conclude that the rate of copolymerization depends on the square root of the initiator concentration and this agrees with eq. (4) for photoinitiated polymerization of low absorbing media.

As can be seen from Figure 8, the rate of copolymerization can be raised by increasing initiator concentration, but the gap between the two lines broadened with increased photoinitiator concentration. To achieve a fast polymerization rate and decreased the influence of oxygen, one should therefore use a photoinitiator concentration high enough to provide a large initiation rate.

Influence of Reaction Temperature

Figures 9 and 10 show a kinetics curve at various reaction temperatures for two samples with different monomer feed ratios. It is surprising to note that temperature has no effect on the copolymerization rate and this is true regardless of the monomer feed ratio. It is well known that reaction rate usually increases with increasing temperature, so there must be some factors that retard the copolymerization when the temperature is raised. As mentioned above, copolymerization occurs through a donor-acceptor complex mechanism; the copolymerization rate is propor-

Figure 10 Influence of temperature on the copolymerization of a mixture of DVE-3 and UPE (VE/MA = 0.76) using Darocur 1173 (2 wt %) as photoinitiator in air, light intensity: 0.765 mW/cm^2. Temperature: (a) 50°C, (b) 75°C, and (c) 100°C.

systems that are widely used in UV curing applications. Under intense radiation, the photoinitiated curing of a DVE-3/UPE mixture proceeds within seconds. The reaction kinetics can be finely controlled by changing the light intensity, photoinitiator concentration, and by using different atmospheres. The fluorescence spectra of the DVE-3/UPE mixture reveals the existence of a donor-acceptor complex in the system. The rate of copolymerization is affected by oxygen and depends on the square root of the initiator concentration and the light intensity. It is surprising to note that temperature has no effect on the rate of copolymerization and this is tentatively interpreted by the inverse effect of temperature on the stability of the complex; however, further study is needed to disclose the mechanism.

tional to the concentration of the complex. When the temperature is raised, the stability of the complex may be decreased, which results in decreasing the concentration of the complex, thereby decreasing the copolymerization rate. We assume that this is the main offsetting factor that decreases the copolymerization rate when raising the copolymerization temperature; however, direct evidence supporting this mechanism is yet lacking.

CONCLUSION

The vinyl ether/UPE containing the maleate system seems to be a good alternative to the acrylate

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