Photocuring Systems Composed of Vinyl Ether Terminated Polyurethane and Maleate

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ABSTRACT: Vinyl ether terminated polyurethane (VE–PU) was synthesized in this investigation. The copolymerization behavior of VE–PU and dimethyl maleate (DMA) was investigated by ^{13}C-NMR. It was found that the copolymerization of VE–PU and DMA is of alternating composition, and no homopolymer structure was found in the polymerization products. Differential photocalorimetry results show that, when the monomer feed molar ratio was close to 1 : 1, the total conversion increased, whereas the effective conversion decreased. The rate of copolymerization was affected by oxygen and reaction temperature and depended on the square root of both the initiator concentration and the light intensity. The rheological properties of VE–PU/DMA system were also studied. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1930–1935, 2005

Key words: copolymerization; polyurethanes; differential scanning calorimetry (DSC); FTIR; rheology

INTRODUCTION

Vinyl ethers, with electron-rich double bonds, can undergo radical copolymerization with electron-deficient olefins.[1,2] Vinyl ethers are currently used in many demanding UV/EB-curable applications because of their fast cure speed, low toxicity, and outstanding physical properties. They are available in various molecular structures that are capable of imparting a wide variety of chemical and physical properties to the formulation. The curable systems of unsaturated polyester containing a maleate functional group and vinyl ether functionalized polyurethane (VE–PU) were used in the formulations of UV-curable powder coatings.[3–5] Noren[6] studied the UV-curable system with VE–PU in place of triethylene divinyl ether (DVE-3), and found that the toughness and flexibility of the coating were both improved. It was also found by Sitzmann and coworkers,[7,8] when they studied the copolymerization of a VE–PU/epoxy system, that the curing system had excellent adhesion to glass and metal, the abrasion resistance was also improved. The cured film had a wide service-temperature range: low-temperature flexibility and high-temperature stability. Oligomers containing vinyl ether functional groups were used as a resin base instead of a reactive diluent in the UV-curable system because of its excellent properties.

The primary aims of the work described in this article were to introduce new VE-terminated polyurethane oligomers, which can provide the formulator with a wide range of end-use properties, to study the kinetics of the copolymerization of VE–PU and dimaleate, and to demonstrate the polymerization mechanism of this UV-curable system.

EXPERIMENTAL

Materials

All chemicals used in the synthesis and formulation were analytically pure.

Synthesis of the VE–PU

Polyethyleneglycol 200 (20 g) was charged to a 250-mL three-neck flask with mechanical stirrer, dripping funnel, and purging system. Acetone (10 mL) was added to decrease the viscosity of the system. Hydroxybutyl vinyl ether (HBVE, 23.2 g) was placed into two separated dripping funnels. The mixture was heated to 40–50°C in an oil bath with mechanical stirring (stirring speed was around 200 rpm). Toluene-2,4-diisocyanate (TDI) was slowly dripped into the reaction system. This step lasted for about 1 h, and then the reaction lasted for another 2 h, after which HBVE was dripped into the reaction system at the same speed as that of TDI. The system was stirred at the above temperature for another 3 h, carried out under N_2 protection. The system was then cooled to room temperature and was subjected to a vacuum at 68°C for 1 h to remove acetone in the system. The VE–PU obtained was a colorless, transparent, viscous liquid. The yield
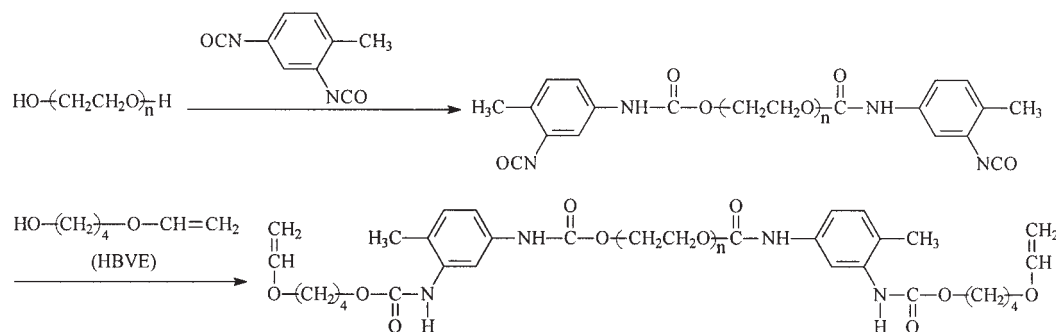
Scheme 1 Reaction process for the synthesis of VE–PU.

used in the present study was >90% and its molecular weight was 772 g/mol, as determined by a vapor pressure osmometer. Scheme 1 shows the above reaction process.

Irradiation

The mixture of VE–PU, DMA, and radical photoinitiator (Darocur 1173) was charged into a sample cell of a DPC instrument. The content of photoinitiator was 2 wt % unless specified otherwise. The cell was specially shaped to maintain uniform sample thickness with the sample sizes ($\sim$ 6 mg) used, which was illustrated in a previous article.[9] The mixture was exposed to the UV radiation from a medium-pressure mercury lamp (250 W) and, at the same time, the DPC instrument continuously recorded the heat flow versus time. The light intensity at the sample position was adjusted by using some metallic networks as filters. A blank cell was used as the reference. The digitized data were analyzed by use of Origin 6.0 software (Microcal Software, Inc., Northampton, MA) and the integration was performed numerically.

The polymerization of the vinyl ether formulation was monitored by following the decrease of the IR absorption peak area at 1635 cm^{-1} of the vinyl ether double bond (C=C stretching) upon UV exposure.

A few experiments were performed on an 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

^{13}C-solution nuclear magnetic resonance (NMR) spectra were obtained using a Varian Unity Inova 500 spectrometer (Varian Associates, Palo Alto, CA) in a complete proton decoupling mode. Samples with lower degrees of crosslinking were prepared by limited UV curing, and then swollen in acetone-d_6. The

measurements were carried out at room temperature with tetramethylsilane as the internal standard.

VE–PU/DMA mixtures containing 2 wt % of Darocur 1173 were coated onto tin plates and then cured under a 2400 W medium-pressure mercury lamp for seconds to form cured films. Some physical properties of the cured films were measured according to Chinese National Standard Test procedures (GB 1743-79 for gloss, GB 1720-79 for adhesion, GB/T1732-93 for impact strength, and GB/T1731-93 for flexibility).

RESULTS AND DISCUSSION

Copolymerization behavior of VE–PU and DMA

The copolymerization tendency of the two types of carbon double bonds in the VE–PU/DMA system was investigated by ^{13}C-NMR spectroscopy. A sample spectrum is shown in Figure 1. The ^{13}C-NMR chemical shift data of the above system are shown in Table I. The typical chemical shift at 86.6 and 152.6 ppm of the vinyl ether double bond did not disappear, which indicated that there was some vinyl ether monomer in the system resulting from the lower conversion of the sample with a low degree of crosslinking. Similarly, the typical shift at 133.7 ppm of maleate indicated that some maleate monomer also remained in the system. It was noticed that if there were any homopolymer of vinyl ether in the system, the chemical shift of methylene carbon should be at 39–42 ppm.[10] No such
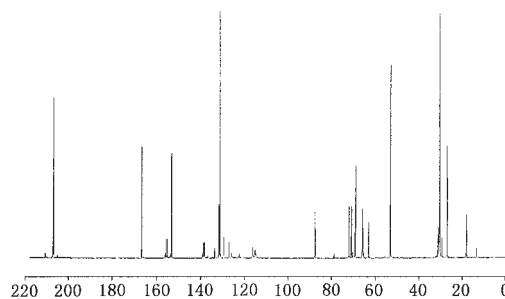

Figure 1 ^{13}C-NMR spectrum for VE–PU/DMA system at low degree of crosslinking.

TABLE I
^{13}C-NMR Chemical Shift Values of VE–PU/DMA System at Low Degree of Crosslinking[10]

	a	b	c	d	e	f	g	h	i	j
Chemical shift, ppm	17.3	126.3	128.7–138.3	71.0	65.0	69.9	166.2	62.0	64.5	30.1

chemical shift was found in the spectra, suggesting that there was no homopolymer of vinyl ether in the crosslinked system. Similarly, the absence of the chemical shift of homopolymer of maleate at 41 ppm indicates that there is no homopolymer of maleate in the crosslinked system. On the other hand, the chemical shift at 30.1 ppm attributed to the methylene carbon in vinyl ether–maleate (VE–MA) copolymer structure was found in the spectra. Consequently, it can be concluded that the copolymer must be completely alternating and no VE–VE or MA–MA linkages are identifiable. This is reasonable for the copolymerization between the electron-rich vinyl ether and the highly electron deficient maleate.

Kinetics of copolymerization

The conversion of monomers is calculated from the following equation:

$$\alpha = \frac{\Delta H_t}{\Delta H_\infty} \tag{1}$$

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

The total heat evolved from the thermal copolymerization of the model molecule hydroxybutyl vinyl ether (HBVE) and dimethyl maleate (DMA) with VE/MA double-bond molar ratio of 1 : 1, using azobisisobutyronitrile (AIBN) as an initiator in N_2 atmosphere at a heating rate of 10°C/min up to 200°C, was taken as ΔH_∞. The overall heat of copolymerization in this study was determined to be 133.3 kJ/mol.

For the systems with VE/MA molar ratio other than 1 : 1, the reaction heat should consist of the heat of alternating copolymerization of VE/MA and that of homopolymerization of the surplus double bonds (VE or MA), if the homopolymerization of VE or MA could take place. The heats of polymerization of VE and MA are 60 and 59 kJ/mol, respectively, which were taken from the published data.[11] Samples of the VE–PU/DMA system with various VE/MA molar ratios were

prepared, and the overall heat of copolymerization (ΔH_∞) for these samples is listed in Table II. Curves of conversion of monomers versus reaction time recorded by DPC for these samples are shown in Figure 2(A). It is found that the conversion of monomers is up to 85% for the sample with a molar ratio of 1 : 1, whereas it is obviously lower for other samples. As mentioned above, the copolymerization of vinyl ether and maleate is an alternating one. No VE–VE unit or MA–MA unit was found from ^{13}C-NMR spectroscopy. In fact, When VE–PU or DMA 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. Thus, the overall conversion of monomers for VE–PU/DMA systems with a VE/MA ratio other than 1 : 1 will be relatively low because the two kinds of carbon double bonds copolymerize in the molar ratio of 1 : 1 by alternating copolymerization, whereas the surplus carbon double bands cannot be converted by homopolymerization. It is reasonable that the effective conversion of monomers for VE–PU/DMA systems should be calculated from the overall heat of alternating copolymerization ($\Delta H'_\infty$), ignoring the existence of surplus double bonds. The values of $\Delta H'_\infty$ were calculated from the molar heat of alternating copolymerization (133.3 kJ/mol as mentioned earlier) and the amount of 1 : 1 monomers in the samples. The results are listed in Table II. Effective conversions (α_e) based on $\Delta H'_\infty$ were then obtained. The results are shown in Figure 2(B). The rather high effective conversion for

TABLE II
H_∞ and H_∞' for VE–PU/DMA Systems with Various VE/MA Ratios

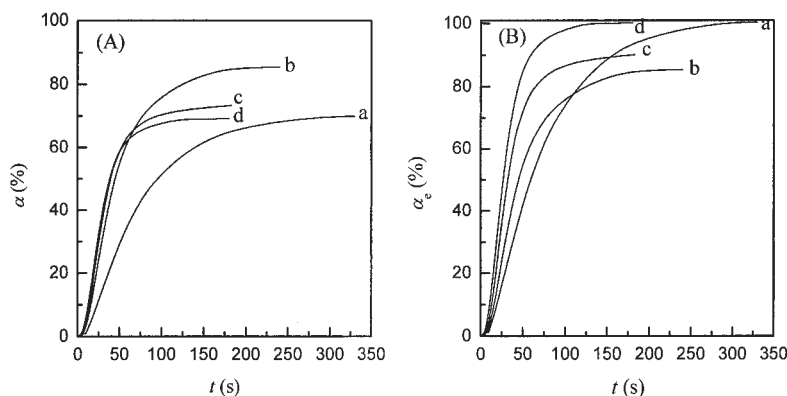| Sample	VE/MA (molar ratio)	Concentration of 1:1 monomers in mix (10^{-3} mol/g)	H_∞ (J/g)	H_∞' (J/g)
a	0.5	1.47	282.7	195.9
b	1.0	1.89	251.9	251.9
c	1.5	1.36	222.0	181.2
d	2.0	1.08	208.7	143.9

Figure 2 Curves of (A) total conversion (α) and (B) effective conversion (α_e) versus reaction time (t) for photoinduced polymerization of VE–PU/DMA system with VE/MA ratios of (a) 0.5 : 1, (b) 1 : 1, (c) 1.5 : 1, and (d) 2 : 1. The samples in N_2 atmosphere were exposed to a UV source with light intensity of 0.601 mW/cm^2, using Darocur 1173 as photoinitiator (2 wt %).

samples **a** and **d** was attributed to the large excess of one kind of monomer over another. The effective conversion for sample **b**, with a molar ratio of 1 : 1, is the lowest. Obviously, the chance of one kind of monomer to contact and copolymerize with another will increase when another kind of monomer is in excess, resulting in a higher effective conversion.

The polymerization rate increased with increasing content of VE–PU in VE–PU/DMA systems, as shown in Figure 3. Notice that VE–PU is an oligomer with high viscosity, and DMA is a monomer with low viscosity. Thus the viscosity of VE–PU/DMA systems increases with increasing content of VE–PU in monomer feed ratio. Higher viscosity can decrease the termination of free radicals at the end of propagating chains and thus result in a higher polymerization rate. On the other hand, the viscosity of the samples is not high enough to substantially reduce monomer diffusion, which decreases the polymerization rate.
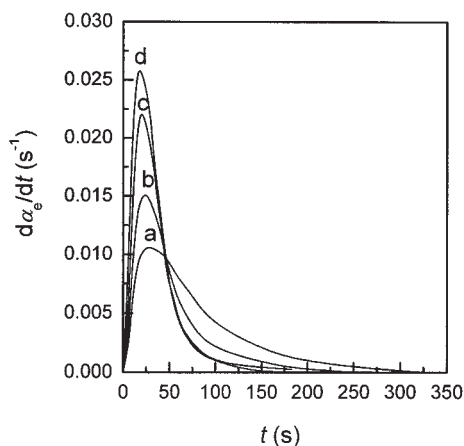
Influence of oxygen

It is well known that oxygen inhibits photoinitiated free-radical polymerization by reacting with both the initiating radicals and propagating polymer radicals, but this effect is not obvious for VE–PU/DMA alternating copolymerization systems, compared to traditional photoinitiated free-radical polymerization such as an acrylate system. As demonstrated in Figure 4, VE–PU/DMA copolymerization developed almost at the same rate, especially when the conversion is <60%, whether in air or in N_2. The conversion of the system is about 6% higher with N_2 protection than that of the system in contact with air. One possible reason is that the higher viscosity of the VE–PU/DMA mixture limited the diffusion of oxygen molecule into the matrix because VE–PU is a high-viscosity oligomer, whereas DMA works just as crosslinker instead of an efficient diluent.
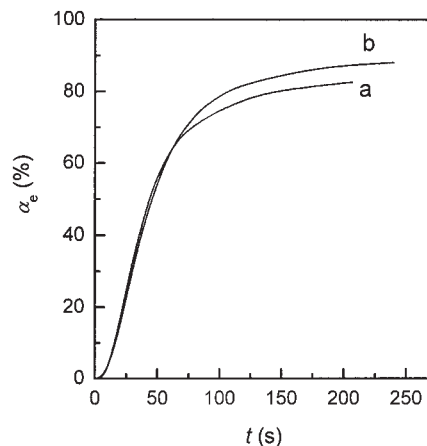

Figure 3 Curves of polymerization rates ($d\alpha_e/dt$) versus reaction time (t) for photoinduced polymerization of VE–PU/DMA system with VE/MA ratios of (a) 0.5 : 1; (b) 1 : 1; (c) 1.5 : 1, and (d) 2 : 1. The curing conditions were the same as those in Figure 2.

Figure 4 Curves of effective conversion (α_e) versus reaction time (t) for photoinduced polymerization of VE–PU/DMA system with VE/MA ratios of 1 : 1 in (a) N_2 atmosphere and (b) air, using a UV source with light intensity of 0.644 mW/cm^2 and Darocur 1173 as photoinitiator (2 wt %).
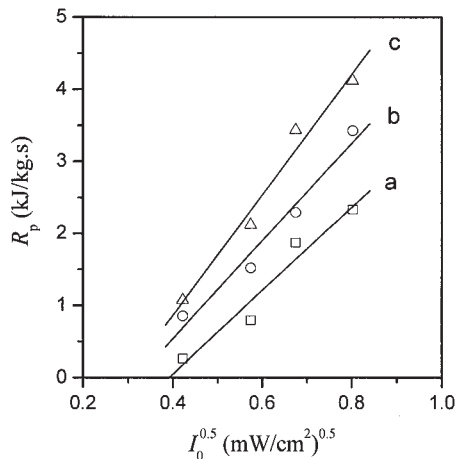
Figure 5 Influence of light intensity on the rate of photocuring of VE–PU/DMA system (VE/MA = 1 : 1) at reaction time of (a) 9, (b) 12, and (c) 15 s, respectively, using 2 wt % of Darocur 1173 as photoinitiator.

Influence of light intensity

The rate of polymerization for bimolecular termination mechanism is determined by the following equation[12]:

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

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.

The VE–PU/DMA mixture (VE/MA = 1 : 1) containing 2 wt % of photoinitiator was exposed to UV radiation of intensity ranging from 0.18 to 0.64 mW/cm^2. The plot of polymerization rate versus square root of light intensity was found to yield a straight line (Fig. 5), corresponding to the above equation.
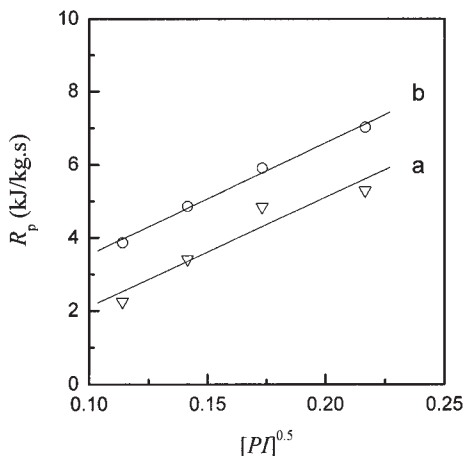

Figure 6 Influence of photoinitiator concentration on the rate of photocuring of VE–PU/DMA system (VE/MA = 1 : 1). The samples were exposed to a UV source with light intensity of 0.601 mW/cm^2 in (a) air and (b) N$_2$ atmosphere.
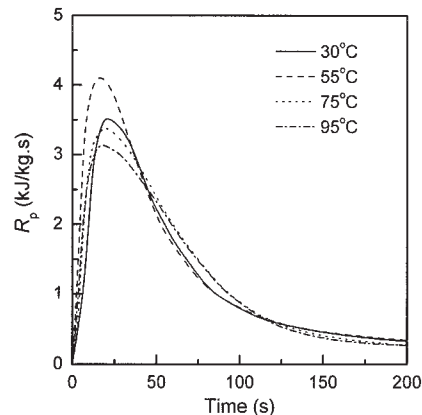

Figure 7 DSC traces for photocuring of VE–PU/DMA system, using Darocur 1173 as photoinitiator. The samples were exposed to a UV source with light intensity of 0.601 mW/cm^2 in N$_2$ atmosphere at various temperatures as labeled in the figure.

Influence of photoinitiator concentration

The VE–PU/DMA mixture (VE/MA = 1 : 1) containing various amounts of photoinitiator was exposed to UV radiation. It is found from Figure 6 that the plot of polymerization rate versus square root of photoinitiator concentration yields a straight line, corresponding to eq. (2). It is suggested from the above results that the alternating copolymerization of VE–PU and DMA was in accordance with a bimolecular termination mechanism. Higher light intensity, as well as higher photoinitiator concentration, increases the curing rate.

Influence of temperature

VE–PU/DMA mixture (VE/MA = 1 : 1) containing Darocur 1173 as photoinitiator was exposed to UV radiation at different temperatures. The DPC results are shown in Figure 7. The curing rate increased as the
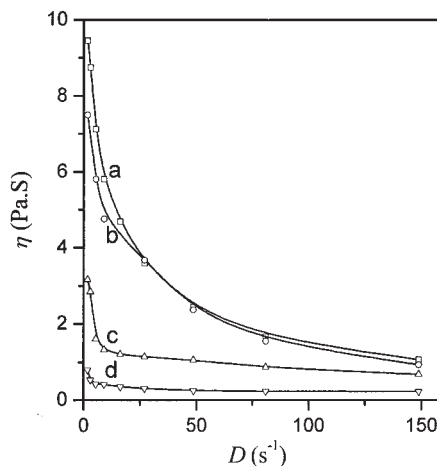

Figure 8 Relationship between viscosity and shear rate for VE–PU/DMA systems with DMA content (in wt %) of (a) 0, (b) 10, (c) 20, and (d) 40.

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TABLE III
Properties of Cured Films from VE–PU/DMA Coatings with Various
VE/MA Molar Ratios

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Sample (mol ratio) VE/MA	DMA (wt %)	Gloss (60°)	Impact strength (kg/cm)	Shore hardness	Adhesion (grade)	Flexibility (mm axis)
0.5	44.4	133	50	75	2	1
1.0	28.4	144	50	80	1	1
1.5	21.4	144	50	80	1	1
2.0	16.6	130	50	70	1	1

temperature rose from 30 to 55°C, which may be attributed to the higher collision frequency of reaction groups at higher temperature. However, the inverse sequence was found at temperatures > 55°C. One possible reason is that as VE–PU and DMA copolymerize, the vinyl ether electron-rich double bond associates with the electron-deficient maleate to form a charge-transfer complex (CTC), after which the alternating copolymer forms by the polymerization of CTC. At higher temperature, the CTC should partially decompose, and the polymerization rate should decrease as a consequence of decreasing concentration of CTC. The evaporation of Darocur 1173 at 95°C may also account for the decrease of the polymerization rate.[13]

Rheological properties

DMA acts as a reactive diluent in VE–PU/DMA systems. Because the electron-deficient maleate in DMA may interact with the vinyl ether electron-rich double bond in VE–PU to form CTC, as mentioned above, the effect of DMA should be somewhat different from that of traditional diluents. As we can find from Figure 8, the viscosity of VE–PU oligomer changed only slightly when 10 wt % of DMA was used. The content of DMA was so low in this composition (VE/MA molar ratio was about 3 : 1), that almost all the DMA molecules attached to the end of VE–PU molecular chains by CTC, thus minimally affecting the state of the VE–PU oligomer chains. Thus, DMA at such low levels showed poor diluent effect.

For compositions containing higher levels of DMA (20 and 40%), the solvation of DMA to the oligomer was strong enough to cause an obvious decrease of viscosity, as shown in Figure 8 (curves c and d). On the other hand, the viscosity was highly shear sensitive at the lower shear-rate region. This property is very useful in many printing and coating applications.

Properties of cured films

Table III shows that the VE–PU/DMA systems can confer good physical properties to cured films. It was also found that formulations with a VE/MA molar ratio of 1 : 1 are preferable for obtaining cured films with better properties.

CONCLUSIONS

The free-radical alternating copolymerization behavior of VE–PU and DMA was confirmed by ^{13}C-NMR. When the monomer feed molar ratio was close to 1 : 1, the total conversion increased, whereas the effective conversion decreased. The rate of copolymerization was affected by oxygen and reaction temperature, and depended on the square root of both the initiator concentration and the light intensity. The diluent effect of DMA at a level of 10% is poor, but obviously improved when the content of DMA was increased to 20%.

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