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Photopolymerization of acrylates using N-aliphaticmaleimides as photoinitiators

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Abstract

The photopolymerization of a diacrylate monomer with an N-aliphaticmaleimide as the photoinitiator has been investigated by photo-differential scanning calorimetry (photo-DSC), real-time infrared (RTIR) spectroscopy, and real-time UV (RTUV) spectroscopy. Photo-DSC exotherm results for relatively thick films (~150 μm) showed an increase in the polymerization reactivity (*R*) up to a concentration of only about 2 mol% N-aliphaticmaleimide. RTIR analysis was used to determine that the reactivity of a diacrylate thin film (~10 μm) increased continually as the concentration of AcOEMI increased from 0.1 to 30 mol%. Both RTIR and RTUV spectroscopy indicated that essentially AcOEMI was completely consumed in the polymerization process, and colorless crosslinked acrylate films with little absorbance above 300 nm were produced. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Photopolymerization; Maleimides; Acrylates

1. Introduction

Photoinitiated polymerization, a method for the rapid production of highly crosslinked, durable films, is detailed in numerous papers and reviews [1–7]. A critical component in all photopolymerizations is the photoinitiator, which absorbs light efficiently and generates radicals or cations capable of initiating chain growth polymerization. Unfortunately, most currently used photoinitiators are not consumed during the polymerization process and/or produce colored byproducts.

In contrast to traditional photoinitiators, maleimides have enjoyed increasing interest in the UV curing field for their ability to function both as a photoinitiator and a polymerizable monomer with vinyl ethers, acrylates and styrene oxides [8–12]. Since the basic UV absorbing chromophore, i.e. the maleimide group, is consumed during the polymerization process, the films produced upon photopolymerization are colorless and absorb little light at wavelengths greater than 300 nm. In preliminary mechanistic investigations, it has been shown that excited state maleimides readily abstract hydrogens, presumably yielding two initiating radicals [11].

Herein, we report the photopolymerization rate and reactivity results for mixtures comprised of N-aliphaticmaleimides and diacrylates using photo-differential scanning calorimetry (photo-DSC) and real-time infrared (RTIR) spectroscopy, where the concentration of the N-aliphatic-maleimide was systematically increased. Real-time UV (RTUV) spectroscopy was used to monitor the conversion of the maleimide during the photopolymerization and to assess the film absorbance after exposure to UV radiation.

2. Experimental

2.1. Characterization

Characterization was performed on a Bruker 200 MHz NMR.

2.2. Monomer

Polyethylene glycol 400 diacrylate (PEG400DA) from Sartomer was used without additional purification.

2.3. Reagents

Ethyl chloroformate and maleimide from Aldrich Chemical Co. were used without additional purification.

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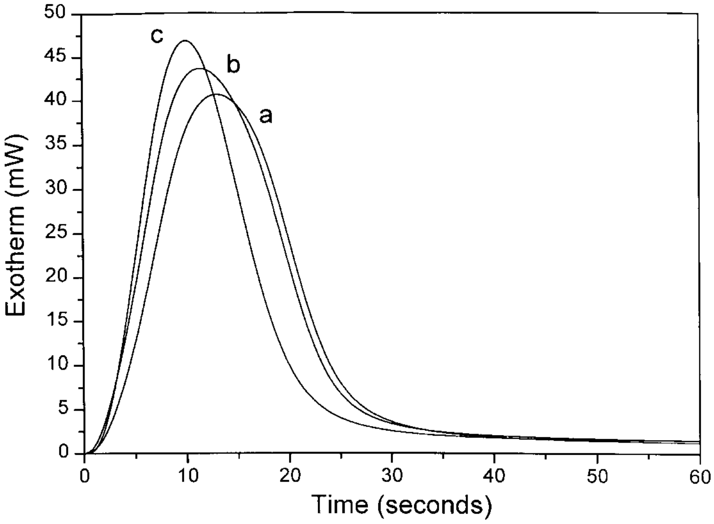


Fig. 1. Photo-DSC exotherms for the photopolymerization of a mixture of PEG400DA and (a) 10 mol% AcOEMI, (b) 10 mol% ECEMI, (c) 10 mol% HMMI. Sample weight 2.24 mg and light intensity 31.02 mW/cm^2.

2.4. 2-Hydroxy-N-ethylmaleimide (HEMI)

The synthesis of HEMI was based upon a known procedure [13].

2.5. N-hydroxy methylmaleimide (HMMI)

The synthesis of HMMI was based upon a known procedure [14].

2.6. 2-Acetoxy-N-ethylmaleimide (AcOEMI)

The synthesis of AcOEMI was based upon a known procedure [15].

2.7. 2-Ethylcarbonate ethylmaleimide (ECEMI)

HEMI (29.87 g, 0.212 mol) and pyridine (16.7 g, 0.212 mol) were dissolved in THF (170 ml), and the solution was stirred at room temperature. Ethyl chloroformate (22.97 g, 0.212 mol) was added dropwise and stirred for 90 min. The pyridine salt was filtered off, and the solution was combined with 200 ml of a 1 N HCl solution. The product was extracted with methylene chloride and washed with a 1 N HCl solution followed by water and then dried over magnesium sulfate. The red solution was concentrated and the red crystals purified by sublimation, yielding white crystals, m.p. 52°C (34.76 g, 77.04%).

^{1}H NMR ($CDCl_3$), (δ, ppm): 1.26–1.34 (3H, $-CH_3$, t), 3.81–3.87 (2H, $-NCH_2-$, t), 4.14–4.25 (2H, δ-$CH_2OC{=}O$, q), 4.25–4.30 (2H, β-CH_2O-, t), 6.74 (2H, $-CH{=}CH-$, s).

^{13}C NMR ($CDCl_3$, δ, ppm): 14.2 (1C, $-CH_3$), 36.8 (1C, $-NCH_2-$), 64.3 (1C, δ-CH_2O), 64.5 (1C, β-CH_2-), 134.4 (2C, $-CH{=}CH-$), 154.9 (1C, $O(C{=}O)O$), 170.4 (2C, $-C{=}O$).

2.8. Photo-DSC

A modified Perkin-Elmer DSC 7 differential scanning calorimeter was used for photo-DSC measurements. A known mass (~ 2.24 mg) of a mixture of an N-aliphatic-maleimide/PEG400DA was applied to a crimped aluminum sample pan, yielding a film thickness of ~ 150 μm. The samples were exposed to the unfiltered output of a 450 W medium pressure mercury bulb mounted above the photo-DSC head. The UV radiation was delivered to the sample and reference chamber by using a cover head that had been bored out and resealed with quartz windows. The closed chamber was purged with dry nitrogen prior to exposure. The light intensity was 31.02 mW/cm^2 as calculated using carbon discs.

The exotherm area was calculated using an instrumental software package from Perkin-Elmer. The polymerization enthalpy values for the heats of fusion for the maleimide and acrylate were 88.5 and 78 kJ/mol, respectively [16]. The sample mass fraction of the maleimide and acrylate monomers was used to calculate an average value for the heat of fusion for the copolymerization process. [There is some error in this assumption, but it should not alter the basic conclusions drawn.] The total exotherm area and average heat of fusion were used to obtain the final conversion. The original maleimide content in the mixture is expressed as a mole percentage based on the number of diacrylate molecules. For the concentration calculation, the solution volume used was taken as the sum of the volume of the diacrylate

Table 1
Exotherm results for the photopolymerization of PEG400DA using 10 mol% N-aliphaticmaleimide as the photoinitiator. Conditions described in Fig. 1

Photoinitiator	R (s^{-1})	Conversion (%)
AcOEMI	0.059	90
ECEMI	0.063	92
HMMI	0.064	80

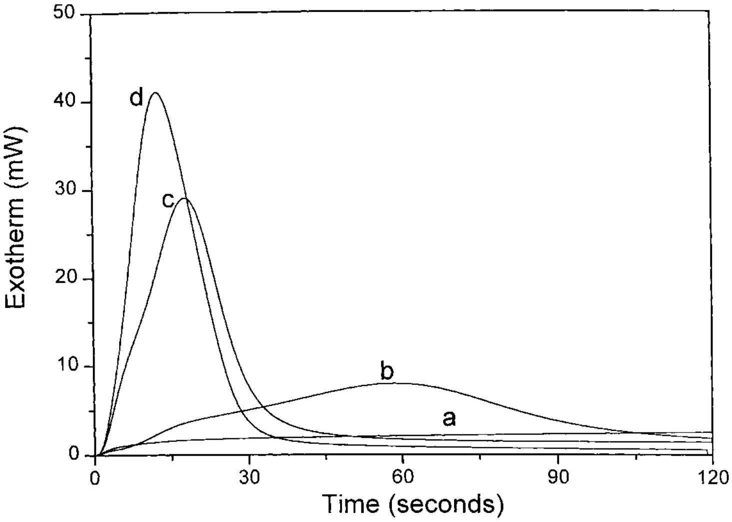


Fig. 2. Photo-DSC exotherms for the photopolymerization of a mixture of PEG400DA and (a) 0 mol% AcOEMI, (b) 0.1 mol% AcOEMI, (c) 1 mol% AcOEMI, (d) 5 mol% AcOEMI. Sample weight 2.24 mg and light intensity 31.02 mW/cm^2.

(1.120 g/ml) and the volume of AcOEMI, assuming a density of AcOEMI equal to that for N-tert-butylmaleimide (1.059 g/ml). Ultimately, the percentage conversion at any exposure time could be calculated.

2.9. RTIR spectroscopy

The photopolymerizable system, comprised of a mixture of an N-aliphaticmaleimide and diacrylate, was coated onto a polypropylene film at a thickness of ~10 μm. To simulate the polymerization under nitrogen atmosphere, a second polypropylene film was laminated on top of the liquid resin to prevent the diffusion of atmospheric oxygen. The sample was placed in the compartment of a Perkin-Elmer 781 infrared spectrophotometer where it was exposed for a few seconds to the UV radiation of a medium pressure mercury lamp (HOYA-SCHOTT-UV-200 S) via a fiber optic light pipe. The light intensity at the sample position was measured by a radiometer (International Light IL-390) and found to be either 37 or 57 mW/cm^2. The polymerization was followed in situ using RTIR spectroscopy. The disappearance of each monomer in a mixture was monitored continuously at the wavelength where the double bond characteristic to the individual monomer is infrared active: 829 cm^{-1} or 697 cm^{-1} for the maleimide and 1640 cm^{-1} or 812 cm^{-1} for the acrylate. Conversion versus time curves were measured directly by setting the spectrophotometer in the absorbance mode. The induction period (I_p) is the intercept for the time axis and is obtained using the regression information from the slope determination.

Table 2
Results for the photopolymerization of PEG400DA with increasing AcOEMI content. Values are taken as the average of two exotherms. Conditions described in Fig. 2

AcOEMI (mol%)	R (s^{-1})	Conversion (%)
0.1	0.012	68
1	0.042	81
2	0.054	85
3	0.056	87
4	0.058	89
5	0.059	92
8	0.062	91
10	0.059	93
20	0.056	87

2.10. Polymerization reactivities

As indicated in the discussion of the photo-DSC and RTIR analysis, the conversion can be determined at any exposure time. From the slope obtained just after the early part of the photo-DSC and RTIR conversion versus time plots, the polymerization reactivity R (s^{-1}), which is equal to the fractional conversion per unit time [4], is readily obtained. Reproducibility errors in the data are generally less than 5%.

2.11. RTUV spectroscopy

Using a Beckman DU 7400 spectrophotometer, the entire UV spectrum of the maleimide mixture was monitored from 200 to 400 nm before and after the films were photopolymerized. In kinetic studies, one wavelength (305 nm) attributed to the absorption of the maleimide chromophore was monitored continuously during the polymerization. This technique yields an absorbance versus time curve, which is readily transformed into a conversion versus time plot.

3. Results and discussion

3.1. Photo-DSC

In previous work, we have shown that the efficiencies of

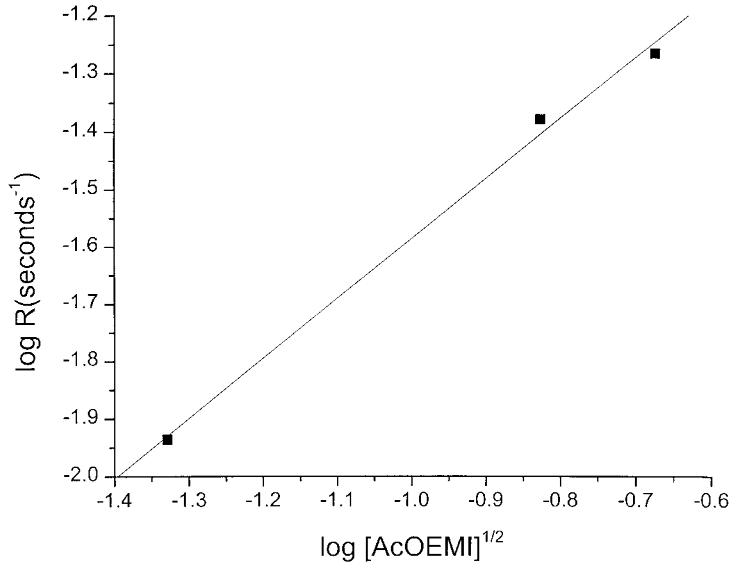
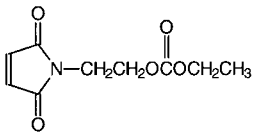


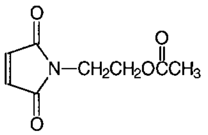
Fig. 3. Linear squares analysis of the photopolymerization of PEG400DA using the results obtained from photo-DSC to generate the log–log plot of *R* versus [AcOEMI].

N-substituted maleimides [9] for initiation of acrylate polymerization are greater for N-aliphaticmaleimides than N-alkylmaleimides. Fig. 1 shows photo-DSC exotherm curves for photopolymerization of polyethylene glycol 400 diacrylate (PEG400DA) using the following maleimides as photoinitiators:

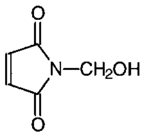
ECEMI



AcOEMI



HMMI



The ultimate percentage conversions and the polymerization reactivities, *R*, extracted from the exotherms in Fig. 1 are collected in Table 1. In the present case, *R* is defined as the rate of polymerization derived from the slope of the portion of the percentage conversion versus time plot (not shown) just after the early part of the curve; the early part of the plot is non-linear and impossible to analyze since it is influenced by such factors as oxygen and instrument response time. The results in Table 1 indicate that all three N-aliphaticmaleimides are capable of initiating a rapid polymerization rate with ultimate conversions well above 80%.

It has been shown in past work [8–12] that it is necessary for species present in the polymerization medium to have abstractable hydrogens in order for maleimides to initiate free-radical polymerization. Accordingly, if maleimides with no readily abstractable hydrogens are used, such as N-methylmaleimide or t-butylmaleimide, much slower rates are obtained for PEG400DA under similar conditions to those employed for the polymerizations depicted in Fig. 1 (previously illustrated in Ref. [9]) and Table 1. There is no doubt that the presence of labile hydrogens on the N-aliphatic group plays a distinctive role in the ability of N-aliphatic maleimides to initiate free-radical polymerization of acrylates. Further investigation into the effect of the N-aliphatic functional group on the hydrogen abstraction/initiation process is currently under extensive investigation and will be the subject of a separate paper. Certainly, there is a contribution to the initiation process by hydrogen abstraction from PEG400DA.

Herein, we concentrate on establishing a correlation between polymerization rates and operational parameters such as light intensity and initial maleimide concentration. In order to illustrate the effect of the maleimide concentration on the recorded polymerization exotherm rate, one of the N-aliphatic maleimides, AcOEMI, was selected for further study.

Photo-DSC exotherms for photopolymerization of polyethylene glycol 400 diacrylate (PEG400DA) using AcOEMI as the photoinitiator, where the AcOEMI content was systematically increased, are presented in Fig. 2. The diacrylate monomer in the absence of photoinitiator has no appreciable exotherm (curve a), while the addition of only 0.1 mol% AcOEMI (curve b) yielded an *R* value of 0.012 s^{-1} and conversion of 68%. A further increase in the AcOEMI content to 1 mol% (curve c) and 5 mol% (curve d) resulted in an increase in *R* to 0.042 s^{-1} and 0.059 s^{-1}, respectively. Results for exotherms of PEG400DA samples with AcOEMI concentrations ranging up to 20 mol% are listed in Table 2. For samples having compositions greater than approximately 2 mol% AcOEMI, *R* does not increase significantly within the error limits of our measurements. Additionally, a terminal conversion of approximately 90% is attained for mixtures with higher AcOEMI compositions. The failure of *R* to continue to increase with increasing AcOEMI content is typical for photo-DSC results of thick films of multifunctional monomers, and can be attributed to an inner filter effect [5].

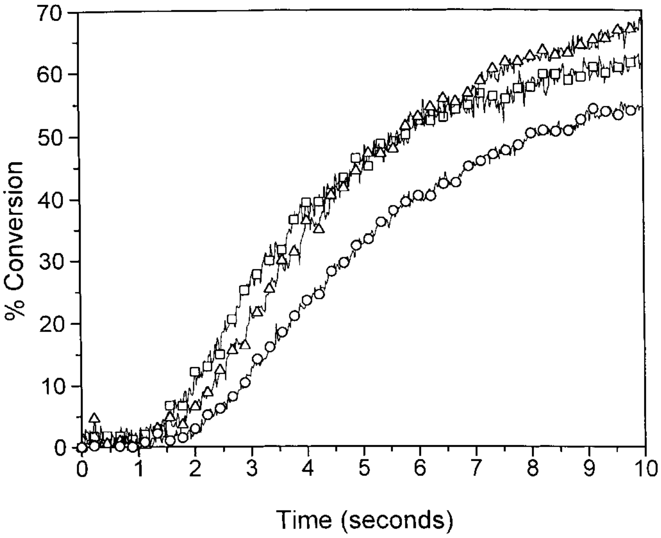


Fig. 4. Acrylate conversion profiles from RTIR for the photopolymerization of PEG400DA containing: (△) 10 mol% ECEMI, (?) 10 mol% HMMI, (○) 10 mol% AcOEMI. Sample thickness ~ 10 μm and light intensity 37 mW/cm^2.

For free-radical polymerization with termination involving two radicals, the expected dependence of R on initiator concentration is 1/2 as shown in Eq. (1), where R_p is the rate of polymerization, k_p is the rate constant for propagation, ϕ is the quantum yield for formation of initiating radicals, ε is the extinction coefficient of the initiator, I_0 is the light intensity, [I] is the initiator concentration, b is the path length, and k_t is the rate constant for termination [17]:

$$R = \frac{R_p}{[M]} = k_p\left(\frac{\phi\varepsilon[I]b}{k_t}\right)^{1/2} \tag{1}$$

In Eq. (1), [I] is given by [AcOEMI] which is the AcOEMI concentration in mol/l calculated from the mole fraction of AcOEMI in the mixture. Accordingly, a log–log plot of R versus [AcOEMI]$^{1/2}$ is essentially linear up to a concentration corresponding to about 2 mol% AcOEMI (Fig. 3). While photo-DSC analysis is useful for the characterization of maleimide initiated polymerization of PEG400DA, it is not suitable for evaluation of systems with high AcOEMI concentration. This limitation of photo-DSC is attributed to the fact that the photopolymerization is carried out on relatively thick films (~150 μm) resulting in an inner filter effect. Additionally, assumptions about the heat of addition of radical chain ends to double bonds were made that cause some error in the calculation of rates and percentage conversions. Also, analysis of the exotherm curve does not allow for separate evaluation of the acrylate and maleimide rate loss. RTIR spectroscopy, on the other hand, is a fast and sensitive technique for the investigation of the efficiency of maleimides as a photoinitiator in thin PEG400DA films. This allows for correlation of polymerization rates for systems with much higher AcOEMI concentrations, as well as direct measurement of both maleimide and acrylate functionality as the polymerization proceeds.

Table 3
Results for the photopolymerization of PEG400DA with 10 mol% N-aliphaticmaleimide. Values are taken as the average of two runs. Conditions described in Fig. 4

Photoinitiator	R (s^{-1})	I_p (s)	Conversion (%)
ECEMI	0.15	1.1	67
HMMI	0.14	1.3	61
AcOEMI	0.12	2.0	55

3.2. RTIR spectroscopy

The acrylate conversion profiles derived from RTIR for the photopolymerization of ~10 μm thick films of PEG400DA with 10 mol% of the three maleimides considered previously are shown in Fig. 4. R (reactivity) values for the rate of acrylate polymerization can be obtained from the slopes of the portion of the percentage conversion versus time plots just after the early parts of the curves [4]. (Note that the reactivity values obtained from the RTIR results are defined for acrylate polymerization, whereas the reactivities obtained from photo-DSC represent overall polymerization reactivities since the rate of acrylate loss cannot be determined explicitly from photo-DSC results). Likewise, the ultimate percentage conversion and the induction period (I_p), which is related to molecular oxygen or inhibitor interference with the polymerization process, can also be obtained. Polymerization results including R, I_p, and the percentage acrylate conversion attained after the 10 s UV exposure (derived from the RTIR data in Fig. 4) are listed in Table 3.

In agreement with the photo-DSC, the RTIR results for PEG400DA containing all three N-aliphaticmaleimides result in reasonably rapid polymerizations. Next, we take

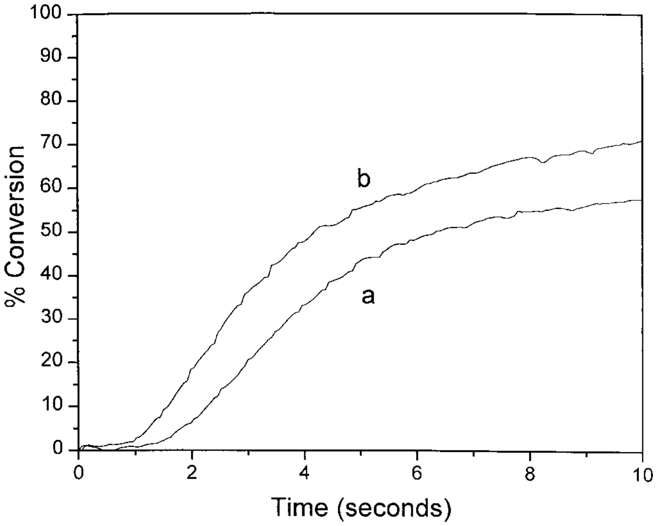


Fig. 5. Acrylate conversion profiles from RTIR for the photopolymerization of PEG400DA containing 10 mol% AcOEMI at the following light intensity: (a) 37 mW/cm^2, (b) 57 mW/cm^2. Sample thickness ~ 10 μm.

Table 4
Results illustrating the effect of light intensity on the photopolymerization of PEG400DA with 10 mol% AcOEMI. Values are taken as the average of two experiments. Conditions described in Fig. 5

Intensity (mW/cm^2)	R (s^{-1})	I_p (s)	Conversion (%)
37	0.13	1.50	54
57	0.17	0.95	80

advantage of the thin films used for the RTIR evaluation to observe rates for higher maleimide content.

As for the photo-DSC work, we have chosen to evaluate PEG400DA/AcOEMI systems to illustrate the effects of light intensity and maleimide concentration on the polymerization rate, this time observing the acrylate conversion directly. It is expected from Eq. (1) that the rate of

Table 5
Acrylate group conversion versus time profiles for photopolymerization of AcOEMI/PEG400DA. Values are taken as the average of two plots. Conditions described in Fig. 6

AcOEMI (mol%)	R (s^{-1}) (%)	I_p (s)	Conversion (%)
0.1	0.006	19.8	23
1	0.053	4.6	61
2	0.070	2.7	67
3	0.098	2.4	68
4	0.107	1.3	77
5	0.116	1.4	72
8	0.158	1.1	76
10	0.172	0.94	80
15	0.242	0.75	80
20	0.318	0.74	83
30	0.386	0.57	81

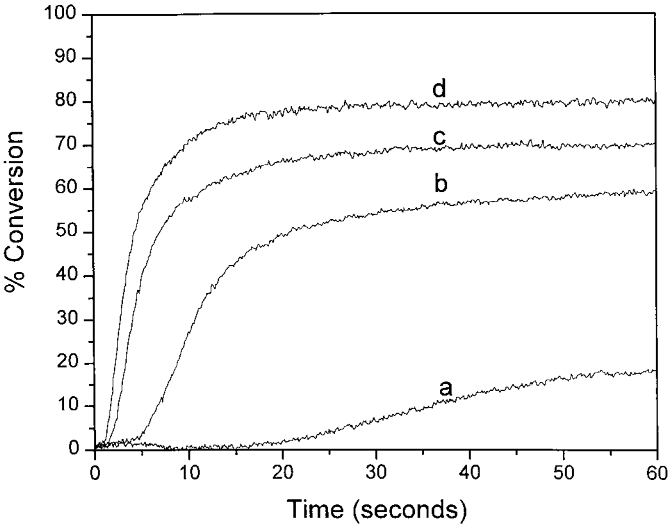


Fig. 6. Acrylate conversion profiles from RTIR for the photopolymerization of PEG400DA containing: (a) 0.1 mol% AcOEMI, (b) 1 mol% AcOEMI, (c) 5 mol% AcOEMI, (d) 10 mol% AcOEMI. Sample thickness ~ 10 μm and light intensity 57 mW/cm^2.

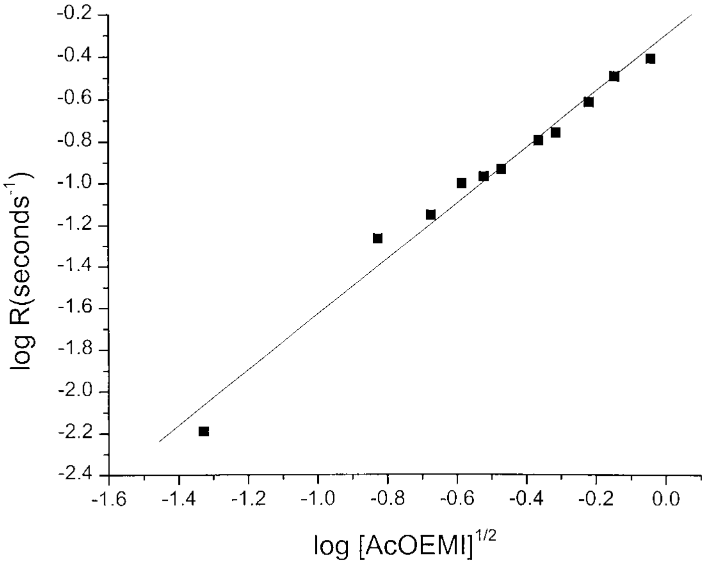


Fig. 7. Linear least squares analysis of the log–log plot of R versus [AcOEMI] for the photopolymerization of PEG400DA using the results obtained from RTIR spectroscopy.

conversion of acrylate functional groups in PEG400DA systems containing maleimide photoinitiator should increase with the square root of the light intensity. Veritably, as shown in Fig. 5 and Table 4, an increase in light intensity from 37 mW/cm^2 to 57 mW/cm^2 for a 10 mol% AcOEMI mixture yields a marked increase in R for acrylate conversion from 0.13 to 0.17, an increase in conversion from 54% to 80%, and a decrease in the induction period from 1.50 to 0.95 s. This represents a root dependence of the rate of acrylate conversion on the light intensity of 0.62, close to that expected from Eq. (1).

Next, the effect of the AcOEMI content on the acrylate rate of polymerization for AcOEMI/PEG400DA mixtures was determined using a light intensity of 57 mW/cm^2. The mixture containing 0.1 mol% AcOEMI required almost 20 s of exposure to overcome oxygen inhibition. As the AcOEMI increased from 0.1 mol% to 10 mol%, R, the overall conversion of acrylate groups increased (Fig. 6). Table 5 lists R, I_p, and conversion data from RTIR profiles for systems with maleimide compositions from 0.1 mol% to 30 mol% AcOEMI. Although a continual increase in R and concomitant decrease in I_p were observed for AcOEMI compositions up to 30 mol%, little difference in the overall conversion was observed for systems with AcOEMI compositions greater than about 4 mol%. A linear log–log plot of R versus [AcOEMI]$^{1/2}$ (Fig. 7) was obtained for AcOEMI

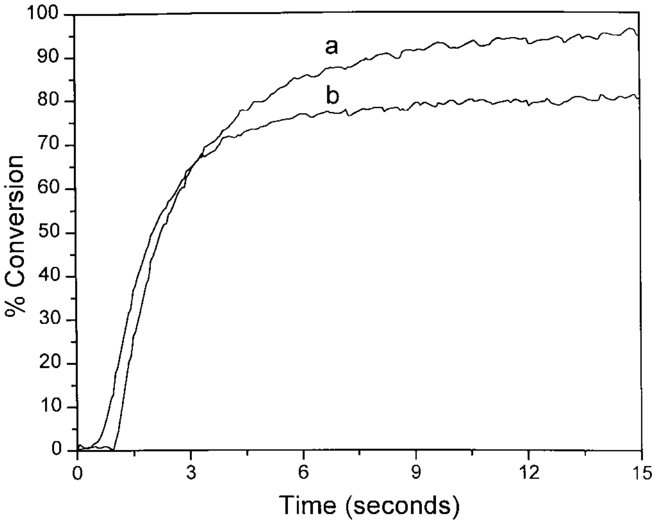


Fig. 8. Conversion profiles from RTIR for the photopolymerization of PEG400DA containing 30 mol% AcOEMI: (a) maleimide conversion, (b) acrylate conversion. Sample thickness ~ 10 μm and light intensity 57 mW/cm^2.

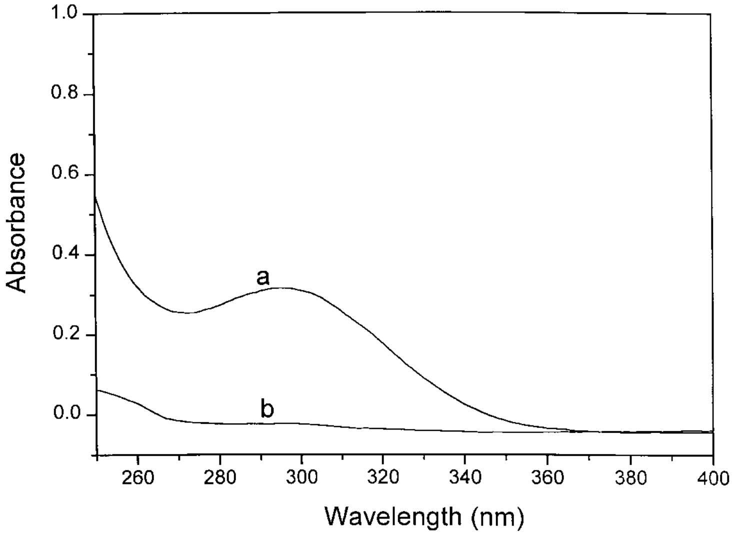


Fig. 9. UV of PEG400DA film containing 30 mol% AcOEMI: (a) before exposure, (b) after 15 s exposure to UV radiation. Sample thickness ~ 10 μm and light intensity 57 mW/cm^2.

concentrations up to 30 mol%. It is notable that the R for acrylate conversion continues to increase even at large AcOEMI concentrations, probably because much thinner films (~10 μm) were used in the RTIR study than in photo-DSC experiments.

The copolymerization of maleimides with acrylates was demonstrated by monitoring both the acrylate and maleimide functionality for the 30 mol% mixture. Conversion profiles (Fig. 8) indicate that both the maleimide and acrylate groups react rapidly to give ultimate conversions of approximately 95% and 80%, respectively. We have not yet determined the exact contributions of homopolymerization (both acrylate and maleimide) and copolymerization (between acrylate and maleimide).

3.3. RTUV spectroscopy

The photo-bleaching ability of the 30 mol% mixture of AcOEMI and PEG400DA can be vividly demonstrated by UV spectroscopy under the identical conditions employed for the RTIR analysis at a light intensity of 57 mW/cm^2. Steady-state UV shows that the maleimide chromophore absorption with a peak maximum near 300 nm (Fig. 9, curve a) dramatically decreases upon a 15 s exposure to the mercury lamp (curve b). Examination of the UV spectrum after polymerization (curve b) shows that little or no photo-byproducts that absorb light at wavelengths of 300 nm or greater were created. RTUV was next used to monitor in real-time the time-dependent decrease in the

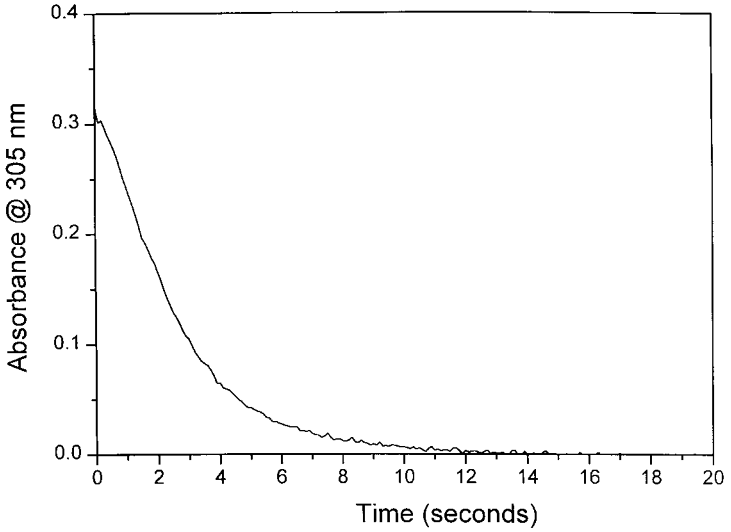


Fig. 10. RTUV at 305 nm for the photopolymerization of PEG400DA containing 30 mol% AcOEMI. Sample thickness ~ 10 μm and light intensity 57 mW/cm^2.

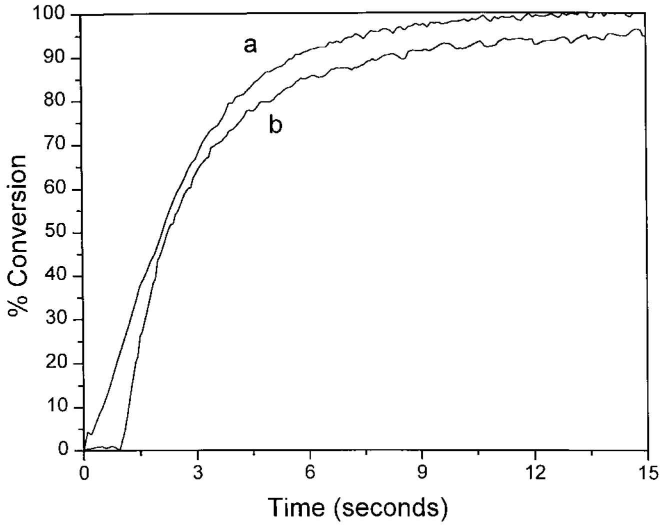


Fig. 11. Conversion profiles for the photopolymerization of PEG400DA containing 30 mol% AcOEMI: (a) RTUV, (b) RTIR. Sample thickness ~ 10 μm and light intensity 57 mW/cm^2.

absorbance of the maleimide chromophore at 305 nm (Fig. 10). After approximately 15 s, no absorbance of the maleimide chromophore could be detected. As a result of this fast photo-bleaching, the incident UV radiation will penetrate deep into the N-aliphaticmaleimide/PEG400DA samples. We note that this should allow for curing of thick specimens: indeed a 7 cm thick sample of a 10 mol% ECEMI/PEG400DA mixture was readily polymerized using a light intensity of 30 mW/cm^2.

The RTUV decay curve in Fig. 10 was transformed into a conversion profile (Fig. 11, curve a) and compared to the profile obtained using RTIR spectroscopy (curve b). The percentage conversion versus time plots in Fig. 11 for the RTUV and RTIR data are essentially identical. The RTUV data thus graphically represent the time-dependent photo-bleaching of N-aliphaticmaleimides due to loss of maleimide chromophore, and support the conclusions obtained by the RTIR analysis.

4. Conclusions

The initiation of N-substituted maleimides was shown to be efficient for several N-aliphaticmaleimides. Photo-DSC was successfully used to determine the photopolymerization rate dependence of AcOEMI/acrylate mixtures on the maleimide concentration. A linear dependence of the polymerization rate on the square root of the AcOEMI concentration for systems with low AcOEMI content (≤ 2 mol%) was obtained.

Real-time infrared spectroscopy extended the photo-DSC results to evaluation of mixtures with higher AcOEMI content. The rate of acrylate loss and ultimate conversion for the photopolymerization of an AcOEMI/PEG400DA system was shown to increase with an increase in light intensity from 37 mW/cm^2 to 57 mW/cm^2: the root dependence of the reactivity, *R*, on light intensity was found to be 0.62. RTIR showed that for thin films of AcOEMI/PEG400DA, the acrylate functionality reactivity increased approximately linearly with the square root of the AcOEMI concentration even for samples with high AcOEMI content. The acrylate and maleimide groups were both found to react rapidly, indicating that the maleimide was consumed by the polymerization process. AcOEMI attained a maximum conversion of approximately 100%, according to both RTIR and RTUV techniques, while the acrylate conversion plateaued at about 80%. UV spectroscopy analysis has shown that the use of maleimides as photoinitiators for diacrylates did not result in the formation of colored photo-byproducts, and that photo-bleaching for mixtures containing the maleimide chromophore was essentially complete (100% conversion of maleimide groups). Maleimides have thus been shown to be both photoinitiators and polymerizable monomers when mixed with diacrylates.

Finally, it must be noted that for direct excitation of N-aliphaticmaleimides, which is the subject of this paper, the polymerization rates obtained for a given light source are much lower than can be achieved with conventional cleavage type photoinitiators. While the slower rates achievable when N-aliphaticmaleimides are used is a disadvantage, the ability of maleimides to participate both as an initiator as well as a comonomer may afford unique opportunities with respect to extractables and residual chromophores absorbing light at wavelengths greater than 300 nm in the final cross-linked film.

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