3160 *Macromolecules* **2003,** *36,* 3160−3165

Vibrational Overtone Activated Photo-Cross-Linking of Ethylene Glycol Dimethacrylate Using Benzoyl Peroxide and 2,2′-(Azobis)isobutyronitrile as Initiators

Hua Gu and D. L. Snavely*

Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403

Received September 12, 2002; Revised Manuscript Received February 5, 2003

ABSTRACT: Laser vibrational overtone initiated polymerization of ethylene glycol dimethacrylate (EGDMA) has been demonstrated using two initiators, benzoyl peroxide (BP) and 2,2′-(azobis)-isobutyronitrile (AIBN). Excitation of the initiator occurs through absorption of a single photon by the fifth CH stretching vibrational overtone transition at 604 nm (16 556 cm^{-1}) for BP and 628 nm (15 924 cm^{-1}) for AIBN. This vibrational excitation creates radicals that initiate radical chain polymerization. Monomer conversion was followed quantitatively by monitoring the intensity change of the vinyl combination band at 6169 cm^{-1} in the first overtone spectrum of EGDMA. Considering the concentration, the molar extinction coefficient, and laser power, AIBN was a factor of 3.2 more efficient than BP for vibrational overtone polymerization. In both cases, the rate of polymerization depends on the excitation wavelength. The influence of the initiator concentration and the photolysis duration is also presented.

Introduction

Vibrational overtone polymerization is a radical chain photopolymerization that uses the absorption of visible light by vibrational overtone states to initiate polymerization reactions.[1−3] Typically, vibrational overtone absorptions of the fifth CH stretching vibrations are used to activate a radical precursor capable of initiating polymerization. This photopolymerization process does not use typical excited electronic state photochemistry that governs most photopolymerization processes. Vibrational overtone photochemistry is initiated through excited vibrational states of the ground electronic state, so initiators employed in thermal polymerization processes may be used. This distinction between excited electronic state and excited vibrational state means that the photon energies needed for initiation can be lower than those needed in electronic state photopolymerization. Furthermore, as shown in this work, it is possible to vary the rate of the polymerization reaction by tuning the excitation laser wavelength to different vibrational overtone absorption features or wavelengths where no absorption occurs. Vibrational overtone excitation offers the possibility of long wavelength photoinitiation, laser selective photodegradation, and wavelength selectivity.

Vibrational overtone polymerization is based on a technique for gaseous reactions wherein laser light initiates chemical reactions by creating vibrationally excited states in the ground electronic state of a reactive species.[4] In general, vibrational overtone activation of liquid-state reactions has been unsuccessful; however, the proton transfer from nitromethane was performed by exciting the CH stretch ($\Delta\nu = 3$) band at 1144 nm.[5] Vibrational overtone polymerization is possible since the propagation step of the radical chain mechanism competes with fast collisional deactivation.

Vibrational overtone polymerization has been demonstrated using methyl methacrylate (MMA)/BP and ethyl acrylate (EA)/BP mixtures.[1,2] A mixture of MMA/BP was irradiated with light corresponding to the fifth CH stretch overtone transition of BP at 604 nm during an intracavity laser photolysis. The sample polymerized at an initial rate of 1% per hour until autoacceleration began at the 20% conversion point. When the laser was tuned off the BP absorption (to the blue at 598 nm or the red at 611 nm), the samples polymerized at a slow rate similar to the control (dark) experiment. Similarly, a mixture of EA/BP was irradiated at 604 nm in an extracavity photolysis. In the EA/BP polymerization the percent conversion increased linearly with time at 42% per hour; however, this polymerization did not exhibit the wavelength selectivity observed for MMA/BP. The molecular weights of both MMA/BP and EA/BP were 9 and 7 times larger, respectively, than the molecular weights obtained in a 60 °C thermal polymerization with the same initiator concentration. When AIBN was used as the initiator with MMA, the reaction exhibited the autoacceleration typical of MMA polymerization with a maximum conversion of 86% after 24 h.[3] The polymerization rate varied with excitation wavelength. At 628 nm, the peak maximum for the fifth CH stretch of AIBN, the sample reacted 4 times faster than when 602 nm light, the maximum of the fifth CH stretch of MMA, was used.

In the previous work, the vibrational overtone polymerization of methyl methacrylate (MMA) with AIBN, three different quantum yields were considered:[3] the quantum yield for initiation, the overall quantum yield for polymerization at 628 nm (the initiator peak absorption), and the overall quantum yield for the polymerization at 602 nm (the monomer peak absorption). Attempts to measure the initiation quantum yield failed due to the inability to measure any changes in the initiator concentration by UV absorption. The molar extinction coefficient of 6.2×10^{-5} L mol^{-1} cm^{-1} for vibrational overtone absorption of AIBN leads to a very small concentration of radicals even if one assumes that every photon absorbed creates a radical. The overall quantum yields for polymerization for the irradiations at 628 and 602 nm were 9937 and 1810, respectively.[3]

Since the polymerizations of methyl methacrylate and ethyl acrylate occur with vibrational overtone activation,

---

* Corresponding author: Fax +1 419 372 9809; e-mail snavely@bgnet.bgsu.edu.

10.1021/ma0214714 CCC: $25.00

radical-initiated polymerizations should be possible with other monomers. This work presents the vibrational overtone polymerization of a cross-linking monomer, ethylene glycol dimethacrylate with both BP and AIBN initiators. AIBN and BP are commonly used commercial initiators with thermal decomposition barriers of 121 and 125 kJ/mol, respectively.[6] The progress of polymerization was monitored by NIR spectroscopy comparing the intensities of olefinic combination CH first overtone absorptions. This work demonstrates the photopolymerization of EGDMA with BP and AIBN by vibrational overtone activation and the wavelength selectivity of this process.

Experimental Section

The EGDMA/BP and EGDMA/AIBN samples were prepared and deaerated by bubbling Ar gas through the monomer/initiator mixture for 20 min. Irradiations were carried out in a 1 mm sealed glass cell outside the cavity of a continuous wave dye laser (operating with Rhodamin 6G dye) pumped by a Spectra Physics 2050 Ar ion laser. The samples were irradiated for a timed period from 0.5 to 8 h at a selected wavelength. After irradiation, the sample cell was placed in the dark. The first overtone spectra of these samples were recorded after 22, 28, 51, 72, and 96 total hours (including the irradiation time).

The diameter of the laser beam is 0.54 mm. The irradiation laser was tuned to the desired wavelength by an intracavity birefringent filter. The wavelength of the dye laser was determined by a 0.35 m monochromator. The dye laser output power ranged from 0.07 to 0.4 W over the tunable range from 585 to 630 nm measured with a calibrated Newport 815 digital power meter. Although the laser power within the cavity is larger than the extracavity power, it was easier to control the laser power for the extracavity photolyses. The wavelength selectivity experiments were carried out extracavity since it is essential to maintain the same power at all wavelengths.

The vibrational overtone spectrum of AIBN and the first overtone NIR spectrum of EGDMA were recorded on a Mattson FT-IR spectrometer with a tungsten lamp and a quartz beam splitter. The spectrum of AIBN in the range 4500−7000 cm^{-1} was recorded in a 1 mm quartz cell with 100 scans and a PbSe detector. The spectrum of AIBN in the range 7000−10 000 cm^{-1} was recorded in a 1 cm quartz cell with 300 scans and a PbSe detector. The 10 000−12 500 cm^{-1} region was recorded in a 2 cm quartz cell with 800 scans and a Si detector, and the portion of the spectrum from 12 500 to 15 000 cm^{-1} was recorded in a 10 cm quartz cell with 1300 scans and a Si detector. The first overtone spectrum of EGDMA was recorded in a 1 mm glass cell with 100 scans and a PbSe detector.

The vibrational overtone spectrum of AIBN was recorded in EGDMA solution. The spectrum of EGDMA was used as the background. Even after ratioing the spectrum of AIBN in EGDMA to the spectrum of neat EGDMA, there were still weak absorptions of EGDMA remaining in the spectrum of AIBN. The subtraction function in the FTIR software was used to subtract these weak absorptions of EGDMA.

The NIR spectra were deconvoluted with Peaksolve software (Galactic Industries Corp.). The first overtone spectra of monomer and polymer EGDMA were deconvoluted assuming six peaks at 6167, 5996, 5936, 5894, 5783, and 5669 cm^{-1} using the standard routine in the Peaksolve software. The integrated areas of these separated peaks were used in monitoring the polymerization progress.

Results and Discussion

Vibrational overtone absorption spectra are characterized by simple progressions corresponding to light atom−heavy atom stretches (called local modes) with peak widths around 200 cm^{-1} (about 5 nm wide at 600 nm).[7,8] Only those vibrations with large anharmonicities absorb near-infrared (NIR) and visible light, so the deformations, torsions, and CC stretches are not observed. In addition, olefinic, methylenic, and methyl CH stretches can often be distinguished.[9−14] The vibrational overtone absorptions in the region from 4500 to 15 000 cm^{-1} of both the monomer and polymer EGDMA have been recorded.[15] Features corresponding to the vinyl, methylenic, and methyl type CH stretches were identified for the first through the fourth CH stretching vibrations. The peak at 5997 cm^{-1} in the first overtone spectrum corresponds to the vinyl CH stretch, and the second, third, and fourth transition wavenumbers of this progression are 8764, 11 472, and 14 115 cm^{-1}.[15] The anharmonicities and the mechanical frequencies for the monomer and the polymer, determined from these vibrational progressions in a Birge−Sponer plot, were also reported. The fifth overtone absorption is expected to occur at 16 502 cm^{-1} (606 nm) which is also extrapolated from the Birge−Sponer plot. Using the transition wavenumbers for the two methyl CH stretch progressions,[15] the fifth overtone absorptions for the methyl stretches are expected to occur at 15 674 cm^{-1} (638 nm) and 15 924 cm^{-1} (628 nm).

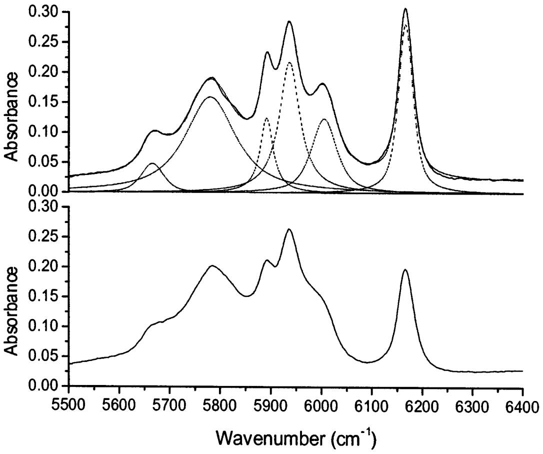

Figure 1. Vibrational overtone polymerization progress of EGDMA monitored by the first overtone spectrum of EGDMA with deconvolution of the first overtone spectrum of EGDMA using Peaksolve software. The top spectrum is the first overtone spectrum of the sample recorded at 0 h, and the bottom spectrum is the first overtone spectrum of the sample recorded at 72 h.

The photopolymerization progress monitored by the first overtone spectra of the photolysis mixture is shown in Figure 1. Because the peak at 6167 cm^{-1}, assigned as the olefinic combination band, is a single strong peak, and the decrease in this peak indicates the increase in the polymer component, this peak was selected to monitor the monomer conversion. The first overtone spectrum, taken at various times after photolysis, was deconvoluted by Peaksolve software, and the areas of the 6167 cm^{-1} peak were calculated. By comparing the integrated areas to the area of this peak for the monomer, the monomer conversion at any time throughout the polymerization process was obtained.

For the EGDMA/BP mixture the irradiation wavelength was selected to correspond to the absorption for the fifth CH stretch of benzoyl peroxide at 16 556 cm^{-1} (604 nm). The vibrational overtone spectrum of benzoyl peroxide has been recorded and discussed in our previous work.[1,2] The spectrum is simple since there are only benzyl CH stretches in BP. The mechanical frequency and anharmonicity for the benzyl CH stretch were reported as 3055 and 59 cm^{-1}, respectively. The fifth

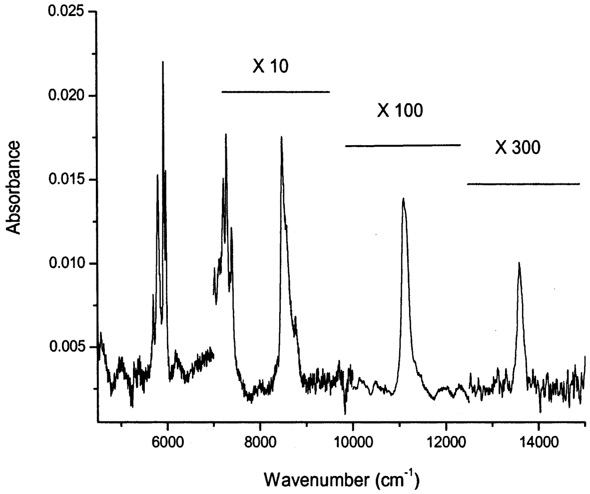

Figure 2. Vibrational overtone spectrum of 2,2′-(azobis)-isobutyronitrile, first through fourth vibrational overtone measured at room temperature.

overtone (16 556 cm^{-1}) was extrapolated from a Birge–Sponer plot using the transition wavenumbers for the first (5991 cm^{-1}), second (8808 cm^{-1}), third (11518 cm^{-1}), and fourth (14 100 cm^{-1}) overtones. The energy of the irradiation wavelength selected (604 nm) is above the activation barrier to the formation of radicals from benzoyl peroxide. According to the extrapolated Birge–Sponer plot discussed in the previous paragraph, the 604 nm light is also absorbed by ethylene glycol dimethacrylate. A control experiment with only ethylene glycol dimethacrylate confirmed that absorption of monomer at 604 nm does not initiate the polymerization.

The vibrational overtone spectrum of AIBN in EGDMA is shown in Figure 2. The peak at 5803 cm^{-1} in the first overtone spectrum corresponds to the methyl CH stretch, and the second, third, and fourth transition wavenumbers of this progression are 8485, 11 098, and 13 590 cm^{-1}. Using these wavenumbers in a Birge–Sponer plot, the fifth overtone absorption is expected to occur at 15 920 cm^{-1} (628 nm). This wavenumber is used in the vibrational overtone polymerization of EGDMA/AIBN. The energy of this wavenumber is above the activation barrier to the formation of radicals from AIBN. Since the 628 nm light is also absorbed by EGDMA, a control photolysis experiment containing only monomer confirmed that absorption of monomer at 628 nm does not initiate the reaction.

A mixture of 5 wt % (0.22 M) BP in EDGMA was irradiated at 604 nm for 4 h with 140 mW of extracavity laser power. Figure 3 shows the percent polymerization with increasing time as determined from changes in the first overtone spectrum of EGDMA. As can be seen, the polymerization process proceeds slowly at about 0.4% per hour, and no autoacceleration behavior (the “gel effect”) is observed for this process. It is known that the polymerization of a neat monomer exhibits prominent rate autoacceleration due to the increased viscosity and the hindered mobility of reactive chain ends.[16] Autoacceleration may be reduced or eliminated due to low radical concentration and slow polymerization rate.[17,18] In the overtone polymerization of EGDMA, the low laser power and the small irradiation area result in a low radical concentration which leads to a small polymerization rate decreasing autoacceleration. The cross-linked structure of the monomer leads to diffusional resistance impeding the vinyl groups so that the polymerization rate slows and the final conversion is limited.[19] After the 72 h duration, a plateau in the monomer conversion appears in Figure 3.

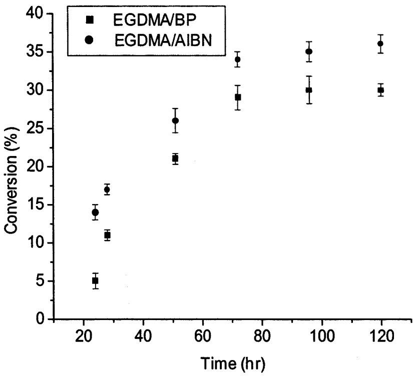

Figure 3. Monomer conversion (%) vs time (h) for vibrational overtone polymerization of EGDMA/BP (604 nm, 4 h, 140 mW, 5 wt % BP) and EGDMA/AIBN (628 nm, 4 h, 70 mW, 4 wt % AIBN).

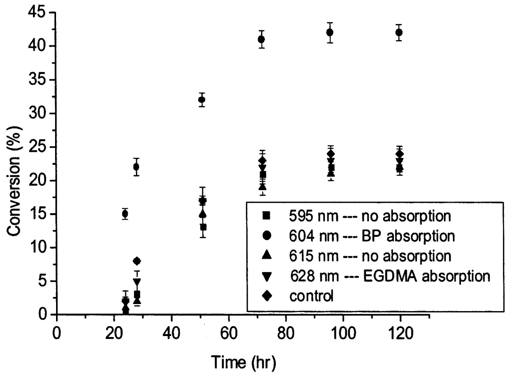

Figure 4. Monomer conversion (%) vs time (h) for EGDMA/BP (5 wt %) at different photolysis (250 mW, 4 h) wavelengths.

It is known that ethylene glycol dimethacrylate is less reactive than ethyl acrylate (EA) or methyl methacrylate (MMA),[16,20] so a slower polymerization rate should be possible with an EGDMA/BP mixture. In the overtone polymerization of EA/BP, the reaction proceeds at 42% per hour.[2] For the overtone polymerizations of MMA/BP and MMA/AIBN, both reactions proceed at 4% per hour.[1,3] The overtone polymerization rate of EGDMA/BP (0.4% per hour) is 10 times less than the polymerization rate of MMA and 100 time less than the polymerization rate of EA.

Wavelength selectivity experiments for EGDMA/BP were carried out at four selected wavelengths. The data in Figure 4 are the result of three trials at each wavelength. The error bars in the plot are the standard deviations for these three trials. After 72 h, the monomer conversions are a factor of 1.9 larger for irradiation at 604 nm, the BP absorption, than for irradiations at 595, 615, and 628 nm. The wavelength of 628 nm falls on the methylenic absorption band of EGDMA, and 595 and 615 nm are wavenumbers where neither the monomer nor the initiator absorbs light. In Figure 4, the ◆ marks indicate the results of the control experiment without photolysis. The results for the 595, 615, and 628 nm irradiations are similar to those of the control experiment, indicating that polymerization at these wavenumbers is essentially from the thermal background reaction.

A mixture of 4 wt % (0.22 M) AIBN in EGDMA was photolyzed at 628 nm for 4 h with 70 mW of extracavity laser power. The maximum conversion after a 72 h time period is 37%. Figure 3 compares the EGDMA/BP and the EGDMA/AIBN results. The polymerization rate for the two cases is about the same; however, because of the additional power in the BP case, the laser delivers about twice the number of photons to the sample. The molar extinction coefficients for the initiator and the monomer should also be considered.

To estimate the molar extinction coefficients for the initiator and the monomer at the excitation wavelengths (in the fifth overtone region), the molar extinction coefficients for the absorptions corresponding to the excitation wavelengths in each overtone region (from first to fourth overtone) were calculated using the following equation:

$$A = \epsilon c l \qquad (1)$$

For each spectral region the molar concentration, c, and the path length, l, were known. The experimental details concerning the recording of these spectra are presented in the Experimental Section. From the experimental absorbance, the molar extinction coefficient, ϵ, was determined. To determine the molar extinction coefficient for the fifth vibrational overtone, a graph was constructed of the experimental ϵ values plotted against the vibrational quantum number. This plot was extrapolated to the fifth vibrational overtone level.

For the polymerization of EGDMA/AIBN, both initiator and monomer can absorb light at 628 nm. AIBN has an absorption peak maximum at this wavelength with molar extinction coefficient (estimated) of $(8.53 \pm 0.49) \times 10^{-5}$ L mol^{-1} cm^{-1}; the molar extinction coefficient for EGDMA is $(5.54 \pm 0.58) \times 10^{-5}$ L mol^{-1} cm^{-1}. Therefore, considering the molar concentration of AIBN and EGDMA in the solution, 7% of the absorbed light is absorbed by AIBN while 93% is absorbed by the monomer. For the polymerization of EGDMA/BP, both monomer and initiator can absorb light at 604 nm. BP has an absorption peak maximum at this wavelength with molar extinction coefficient (estimated) of $(6.54 \pm 0.77) \times 10^{-5}$ L mol^{-1} cm^{-1}; the molar extinction coefficient for EGDMA at this wavelength is $(1.93 \pm 0.36) \times 10^{-5}$ L mol^{-1} cm^{-1}. Considering the molar extinction coefficients and the molar concentrations of BP and EGDMA, 10% of the absorbed light is absorbed by BP. The more light absorbed by the initiator, the more radicals formed. Considering the concentration, the molar extinction coefficients, and the laser power, AIBN is a more efficient initiator than BP for the vibrational overtone polymerization of EGDMA by a factor of 3.2.

Wavelength selectivity experiments were carried out for EGDMA/AIBN at four different wavelengths: 628, 615, 606, and 595 nm. The result shown in Figure 5 is the average of three trials at each wavelength. The error bars are the standard deviations for these three trials. These experiments were performed with the same conditions: 4 wt % initiator concentration, 70 mW laser power, and 4 h photolysis duration. The light at 628 nm corresponds to the methyl CH stretch absorption for AIBN, 606 nm is the vinyl CH stretch absorption band of EGDMA, and 595 and 615 nm are the wavelengths where both monomer and initiator do not absorb light. Figure 5 shows that monomer conversion for 628 nm (the absorption maximum for the initiator) is a factor of 1.4 larger than for 606 nm (the monomer absorption peak) and is a factor of 1.7 larger than for 595 and 615 nm (no monomer or initiator absorption). The ◆ marks in Figure 5 present the result of the control experiment without photolysis. The monomer conversions for the control experiment are almost the same as those for the 595 and 615 nm irradiations, which means that these polymerizations proceed according to the thermal background reaction. The monomer conversions for irradiation of the monomer absorption peak (606 nm) are a little larger than for irradiations where no absorption occurs and the control experiment.

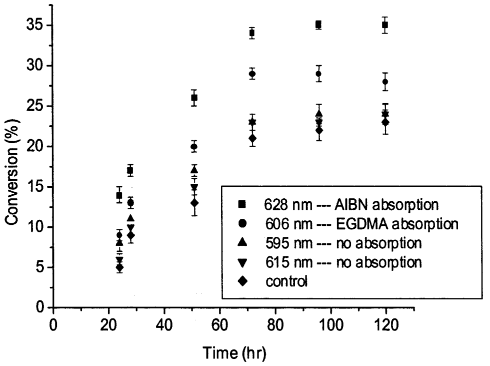

Figure 5. Monomer conversion (%) vs time (h) for EGDMA/AIBN (4 wt %) at different photolysis (70 mW, 4 h) wavelengths.

The formation of radicals in vibrational overtone polymerization can occur by two different processes: direct light absorption by the initiator creating initiator radicals and collisional energy transfer between highly vibrationally excited molecules of monomer and molecules of initiator leading to initiator radicals. Both processes are possible for the irradiations at the two initiator absorption peaks (604 and 628 nm) because both initiator and monomer can absorb light at these two wavelengths. The second process should be inefficient in creating radicals because it is unlikely that six quanta of CH stretch are transferred in one collision.

Collisional energy transfer for large polyatomic molecules in the gas phase has been extensively studied for several decades.[21−25] The amount of energy transferred per collision (ΔE) can be positive (activating collision) and negative (deactivating collision).[21] ΔE is usually represented by a function of energy transfer probability vs amount of energy transferred.[21] The activation and deactivation of a polyatomic molecule are accomplished through many collisions. The average amount of energy transferred depends on the bath molecule.[22] Typically, a collision between a large polyatomic molecule and another large molecule (average from different experimental data)[21−25] transfers about 1500 cm^{-1}. In the irradiation of the monomer absorption peak (628 nm) for the EGDMA/BP case, no significant polymerization occurred. However, for the irradiation of EGDMA/AIBN at the monomer absorption peak (606 nm), the monomer conversions are larger than the control experiment. In this case the conversions result not only from thermal background reaction but also from the creation of radicals through collisional energy transfer after a vibrational overtone absorption event. At least seven collisions are needed to transfer enough energy for the initiator to attain its decomposition barrier ($E_a = 10\,101$ cm^{-1}). If it is assumed that half of these collisions are deactivating processes, then at least 14 collisions are needed to reach the decomposition barrier. Since the initiator concentration in the EGDMA/

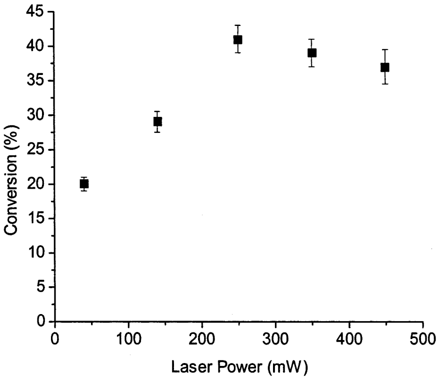

Figure 6. Monomer conversion (%) for EGDMA/BP (5 wt %) using different laser powers (604 nm, 4 h, monomer conversion at 72 h).

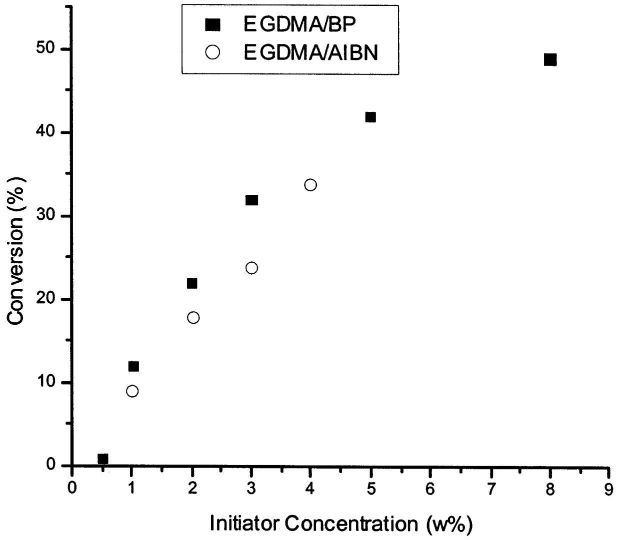

Figure 7. Monomer conversion (%) for EGDMA/BP (604 nm, 250 mW, 4 h) and EGDMA/AIBN (628 nm, 70 mW, 4 h) with different initiator concentrations at 72 h.

AIBN mixture is 4 wt %, the ratio of monomer molecules to initiator molecules is about 20:1. Given these considerations, it is possible that enough collisions occur so that a small fraction of the initiator molecules accumulate enough energy to react.

The effect of laser power on monomer conversion for the EGDMA/BP mixtures is shown in Figure 6. The data are the average of three trials for each laser power. The error bars are the standard deviations for these three trials. Five different powers 40, 150, 250, 350, and 450 mW were used. The monomer conversion was quantitatively determined as a function of laser power. After 250 mW, monomer conversion does not continue to increase. To understand this effect, the number of photons absorbed by the initiator and the number of initiator molecules were calculated to be 6.2×10^{17} and 5.2×10^{17} (at 250 mW), respectively. As the power increased, the initiator molecules were depleted.

To study the influence of the initiator concentration on the vibrational overtone polymerization of EGDMA, the initiator was varied from 1 to 4 wt % for BP and 0.5 to 8 wt % for AIBN. The data in Figure 7, which is the average of two trials at each initiator concentration, show that the monomer conversions increase with increased concentration of initiator.

Figure 8 presents results from an investigation into the effect of the duration of the irradiation. The experiments were carried out by irradiating the samples for the different timed periods (such as 1, 3, or 4 h) which are the irradiation time. Then the sample cell was placed in the dark. The monomer conversions were monitored by recording the first overtone spectra of the samples after 72 h (including the irradiation time). Figure 8 is a plot of the monomer conversion obtained at 72 h vs the irradiation time. The data in Figure 8 are the average of three trials for each irradiation duration. For BP the polymerization rate increases when the photolysis duration increases from 0.5 to 4 h, but the monomer conversion does not continue to increase when photolysis duration increases from 4 to 8 h. For AIBN the monomer conversions increase when the photolysis duration increases from 1 to 3 h, but it does not continue to increase when the photolysis duration is above 3 h. In the laser power dependence shown in Figure 6, a similar plateau was observed. As the irradiation duration increased, the initiator molecules were depleted; this depletion results in a plateau for the polymerization rate.

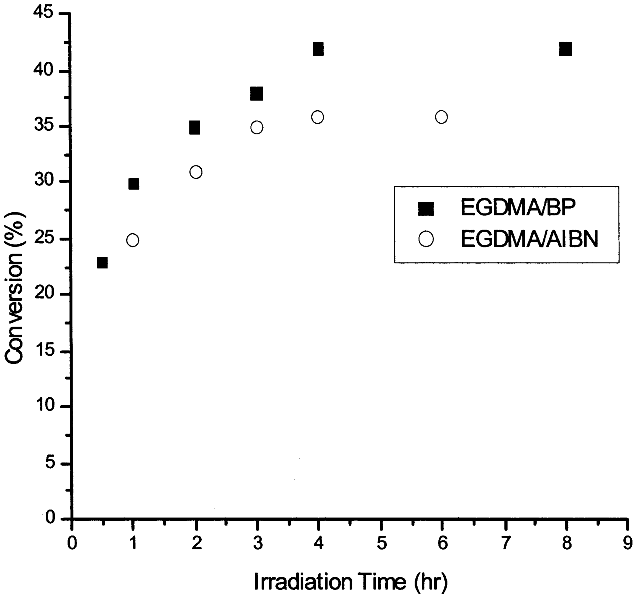

Figure 8. Monomer conversion (%) for EGDMA/BP (604 nm, 250 mW, 5 wt %) and EGDMA/AIBN (628 nm, 70 mW, 4 wt %) with different photolysis durations at 72 h.

The overall quantum yields (Φ) of overtone polymerization of EGDMA/BP and EGDMA/AIBN were calculated using the following equations:

$$\Phi = \frac{\text{number of monomer molecules converted}}{\text{number of photons absorbed}} \quad (2)$$

$$N_a = N_0 - (N_0/10^A) \quad (3)$$

where A is absorbance of the sample and N_0 and N_a are numbers of incident and absorbed photons, respectively. The quantum yield of polymerization of EGDMA/BP for the initiator absorption peak at 604 nm and the quantum yield of polymerization of EGDMA/BP at the monomer absorption peak 628 nm after 72 h were calculated to be 215 and 2, respectively. The quantum yields of polymerization of EGDMA/AIBN at the initiator absorption peak at 628 nm and at the monomer absorption peak at 606 nm after 72 h were calculated to be 516 and 223, respectively. These results confirm that AIBN is a more efficient initiator than BP for the vibrational overtone polymerization of EGDMA. The ratio of the quantum yields of polymerization of EGDMA/BP at the initiator absorption peak and at the monomer absorption peak is larger than that for the polymerization of EGDMA/AIBN. Therefore, there is a larger wavelength effect for the vibrational overtone polymerization of EGDMA/BP compared to EGDMA/AIBN.

Conclusions

Photo-cross-linking of EGDMA using vibrational overtone polymerization has been demonstrated with two initiators, BP and AIBN. The monomer conversion was monitored by NIR spectroscopy. Excitation into the fifth vibrational overtone of the CH stretch of BP and AIBN initiates polymerization of the liquid mixture. The polymerization rate of EGDMA/AIBN is a factor of 3.2 faster than that of EGDMA/BP at the same initiator concentration. For both initiators the polymerization rate is specific to the irradiation wavelength. When BP was irradiated at 604 nm (the initiator absorption wavenumber) and 628 nm (the monomer absorption peak), the quantum yield for polymerization after 72 h was 215 and 2, respectively. For AIBN irradiation at 628 nm (the initiator absorption wavenumber) and 606 nm (the monomer absorption peak), the quantum yield for polymerization was 516 and 223, respectively. The monomer conversion depends on the initiator concentration and photolysis duration.

References and Notes

(1) Grinivich, O.; Snavely, D. L. *Chem. Phys. Lett.* **1997**, *267*, 313.
(2) Grinivich, O.; Snavely, D. L. *Chem. Phys. Lett.* **1999**, *304*, 202.
(3) Gerasimov, T. G.; Snavely, D. L. *Macromolecules* **2002**, *35*, 5796.
(4) Crim, F. F. *Annu. Rev. Phys. Chem.* **1984**, *35*, 657.
(5) Goodall, D. M.; Chetwood, I. *Chem. Phys. Lett.* **1986**, *129*, 291.
(6) Pryor, W. A. *Introduction to Free Radical Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1966.
(7) Henry, B. R. *Vibr. Spectra Struct.* **1981**, *10*, 269.
(8) Child, M. S. *Acc. Chem. Res.* **1985**, *18*, 45.
(9) Henry, B. *Acc. Chem. Res.* **1987**, *29*, 430.
(10) Wong, J. S.; MacPhail, R. A.; Moore, C. B.; Strauss, H. L. *J. Chem. Phys.* **1982**, *86*, 1478.
(11) Moore, C. B.; Wong, J. S. *J. Chem. Phys.* **1982**, *77*, 603.
(12) Snavely, D.; Dubsky, J. *J. Polym. Sci., Part A* **1996**, *34*, 2575.
(13) Snavely, D.; Angevine, C. *J. Polym. Sci., Part A* **1996**, *34*, 1669.
(14) Rasheed, T.; Shamsudeen, S.; Jayaraj, M. *Indian J. Pure Appl. Phys.* **1996**, *34*, 534.
(15) Gerasimov, T.; Snavely, D. L. *Appl. Spectrosc.* **2002**, *56*, 2.
(16) Odian, G. In *Principles of Polymerization*, 3rd ed.; Wiley-Interscience: New York, 1991.
(17) Yu, Q.; Zeng, F.; Zhu, S. *Macromolecules* **2001**, *34*, 1612.
(18) Cioffi, M.; Hoffmann, A. C.; Janssen, L. P. B. M. *Chem. Eng. Sci.* **2001**, *56*, 911.
(19) Huang, C. W.; Sun, Y. M.; Huang, W. F. *J. Polym. Sci., Part A* **1997**, *35*, 1873.
(20) Stevens, M. *Polymer Chemitry*, 2nd ed.; Oxford University Press: New York, 1990.
(21) Oref, I.; Tardy, D. C. *Chem. Rev.* **1990**, *90*, 1407.
(22) Heymann, M.; Hippler, H.; Troe, J. *J. Chem. Phys.* **1984**, *80*, 1853.
(23) Barker, J. R. *Chem. Phys.* **1983**, *77*, 301.
(24) Miller, L. A.; Barker, J. R. *J. Chem. Phys.* **1996**, *105*, 1383.
(25) Flynn, G. W. *Acc. Chem. Res.* **1981**, *14*, 334.

MA0214714