Vibrational Overtone Initiated Photopolymerization of Acrylonitrile

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ABSTRACT: Vibrational overtone activated polymerization of acrylonitrile (AN) has been demonstrated using two initiators, benzoyl peroxide (BP), and 2,2'-(azobis)isobutyronitrile (AIBN). Excitation of the fifth vibrational overtone of the CH stretch of AIBN at 627 nm and BP at 604 nm initiates the reaction. Monomer conversions were monitored by a gravimetric method. In both cases, the wavelength selectivity was investigated by irradiating the monomer/initiator mixtures at the absorption maximum of the initiator, the absorption maximum of the monomer, and at a wavelength (580 nm for AN/AIBN and 625 nm for AN/BP) where neither the initiator nor the monomer absorbs light. For the AN/AIBN mixture, after 48 h the monomer conversion for the irradiation on the peak absorption of AIBN (627 nm) is about twice as large as the irradiation at 580 nm. For the AN/BP mixture, after 48 h the monomer conversion for the irradiation on the peak absorption of BP (604 nm) is about a factor of 2.2 larger than for the irradiation at 625 nm. The overall quantum yields of both polymerizations were estimated. After 48 h the overall quantum yield for the AN/AIBN mixture irradiated at the initiator absorption ($\Phi_{627} = 21083$) is about 10 times larger than for the sample irradiated at the pure monomer absorption ($\Phi_{595} = 1942$). For the AN/BP mixture, the 604 nm quantum yield ($\Phi_{604} = 1096$) is about 2.4 times larger than the 595 nm quantum yield ($\Phi_{595} = 448$). The influence of the initiator concentration is also presented. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 565–571, 2003

Key words: photopolymerization; infrared spectroscopy; irradiation

INTRODUCTION

Vibrational overtone polymerization is a newly achieved photopolymerization process. This new method does not use excited electronic state photochemistry which is typically used in photopolymerization processes. The vibrational photochemistry is initiated through excited vibrational overtone transitions of the ground electronic state.[1] Single photons are absorbed by the initiator to polymerize a liquid monomer via a radical chain reaction. Although many reactions in the gas phase have been demonstrated with this vibrational overtone activation technique,[2–6] liquid phase reactions initiated by vibrational excitation are few due to the fast collisional deactivation. However, in vibrational overtone polymerization the free radical propagation step amplifies the product yield in order to overcome the fast collisional deactivation.

In preliminary work, the polymerization systems, methyl methacrylate/benzoyl peroxide (MMA/BP) and ethyl acrylate/benzoyl peroxide (EA/BP) have been photopolymerized using excitation of the fifth vibrational CH stretch overtone absorption (604 nm) of BP.[7,8] In the intracavity photolysis of MMA/BP, the polymer yield was enhanced when the photolysis wavelength corresponded to the absorption peak of BP (604 nm) as opposed to the photolyses at two other wavelengths. The average number molecular weight of the vibrational overtone polymer was 3×10^6 as compared with 4×10^5 for a similar polymer produced by thermal methods (@60°C).[7] The vibrational overtone polymerization of EA/BP was a factor of 40 times faster than the MMA/BP polymerization, so it was performed by an extracavity photolysis. The reaction of EA/BP was not wavelength selective. No significant difference in the polymer yield was observed when irradiation occurred at the absorption peak of BP (604 nm) versus four other wavelengths. The polymer produced with the vibrational overtone activation had an average molecular weight of 8×10^5 whereas the polymer produced with thermal initiation at 60°C possessed an average molecular weight of 8×10^4.[8]

In further work, 2,2'-(azobis)isobutyronitrile (AIBN) was used as the initiator for MMA. When the mixture was irradiated at a wavelength where neither the initiator nor the monomer absorb light, the polymerization rate equaled that of the dark reaction. The peak absorption for AIBN falls at 628 nm where the molar extinction coefficient, ϵ, is estimated to be 6.2×10^{-5} L

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mol^{-1} cm^{-1}. At this same wavelength the monomer also absorbs light ($\epsilon = 0.8 \times 10^{-5}$ L mol^{-1} cm^{-1}) so that given the molar concentration, 13% of the absorbed light is absorbed by the initiator with the remaining 87% absorbed by the monomer. Irradiation at 628 nm resulted in a monomer conversion of 86% after 24 h. Polymerization also occurs when the monomer peak absorption is irradiated at 602 nm. After 24 h, the monomer conversion was four times less than for the 628 nm experiment. The overall quantum yield for monomer conversion after 24 h was estimated to be 9937 for the 628 nm (initiator absorption) and 1810 for the 602 nm (monomer absorption) experiments. Thus the overall quantum efficiency for the 628 nm irradiation is 5.5 times larger than for the irradiation at 602 nm.

Another acrylate monomer, ethylene glycol dimethacrylate (EGDMA), which is known to be capable of crosslinking, was shown to react using an extracavity vibrational overtone irradiation.[9] There were two polymerization systems used in these experiments. A mixture of EGDMA/BP was polymerized using benzoyl peroxide as the initiator with 604 nm light. In addition, AIBN was used as the initiator and the fifth CH stretch overtone transition of AIBN (628 nm) was used as the irradiation wavelength.[9] Wavelength selectivity was observed in the polymerizations of these two mixtures. In the reaction of EGDMA/BP, the polymer yield was a factor of 1.9 larger in a 24 h time period for the irradiation on the absorption peak of BP (604 nm) than for the other three wavelengths and the control experiment (with no irradiation). In the reaction of EGDMA/AIBN, the polymer yield was a factor of 1.7 larger during a given time period for the photolysis on the absorption peak of AIBN (628 nm) than for the other two wavelengths. Taking into account the initiator concentration, the molar extinction coefficients at the irradiation wavelengths and the laser power, AIBN was a more efficient initiator than BP for the vibrational overtone polymerization of EGDMA.[9]

The work reported in this article demonstrates the possibility of vibrational overtone polymerization of another acrylate, namely acrylonitrile (AN), CH$_2$=CHCN. The photopolymerizations of AN/BP and AN/AIBN mixtures were investigated. The polymer yield was measured by a gravimetric method. The wavelength dependence was observed.

EXPERIMENTAL

AN monomer was purchased from Aldrich Chemical Company and the inhibitor was removed using the Aldrich disposable remover column. Benzoyl peroxide, 2,2′–(azobis)isobutyronitrile, acrylonitrile, and polyacrylonitrile were purchased from Aldrich Chemical Company (Milwaukee, WI) and used without further purification.

The AN/AIBN and AN/BP samples were prepared and deaerated by bubbling Ar gas through the monomer/initiator mixture for 20 min. Photolyses were carried out in a 2 mL sealed glass vial outside the cavity of a continuous wave Rhodamin 6G dye laser pumped by an Ar ion laser. The photolysis 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.

The vibrational overtone spectrum of neat AN was measured with a Mattson Galaxy Series 5000 NIR spectrometer with a tungsten lamp and a quartz beamsplitter and either a PbSe (4500–10000 cm^{-1}) or Si (10000–15000 cm^{-1}) detector. The spectrum of AN in the range of 4500–7000 cm^{-1} and the range of 7000–10000 cm^{-1} was recorded in a 1 mm quartz cell with 100 scans and in a 1 cm quartz cell with 200 scans, respectively. The portion of the spectrum from 10000 to 12500 cm^{-1} was recorded in a 1 cm cell with 500 scans, and the range of 12500–15000 cm^{-1} was recorded in a 2 cm cell with 500 scans.

The FTIR spectra of monomer AN, commercial poly(acrylonitrile) purchased from Aldrich, and the poly(acrylonitrile) produced from vibrational overtone activation were recorded on a Mattson Galaxy Series 6020 FTIR spectrometer. The spectrum of liquid monomer was measured in a cell made of two KBr plates. The samples of solid polymers were prepared by combining with KBr powder and making the thin films.

The polymer yield was obtained by a gravimetric method. After polymerization, the sample vial was open and allowed to dry in an oven. The final weight of the polymer produced from overtone irradiation was used to calculate the polymer yield. This simple method was checked by dissolving the polymer in methanol to remove the residual monomer. The final weight of the dissolved polymer was then used to calculate the polymer yield. The two procedures varied by 2.5%. All of the data presented in this work were corrected by subtracting this difference from the data obtained from the gravimetric method.

RESULTS AND DISCUSSION

Vibrational overtone spectrum of AN

The vibrational overtone spectrum of AN is shown in Figure 1. The peaks at 6187, 9197, and 11980 cm^{-1} form a progression belonging to the olefinic combination band seen in other acrylate spectra.[7,8] The peak at 5966 cm^{-1} in the first overtone spectrum corresponds to the olefinic CH stretch, and the second, third, and fourth transition wavenumbers of this progression are 8813, 11559, and 14160 cm^{-1}. Using these wavenumbers in a
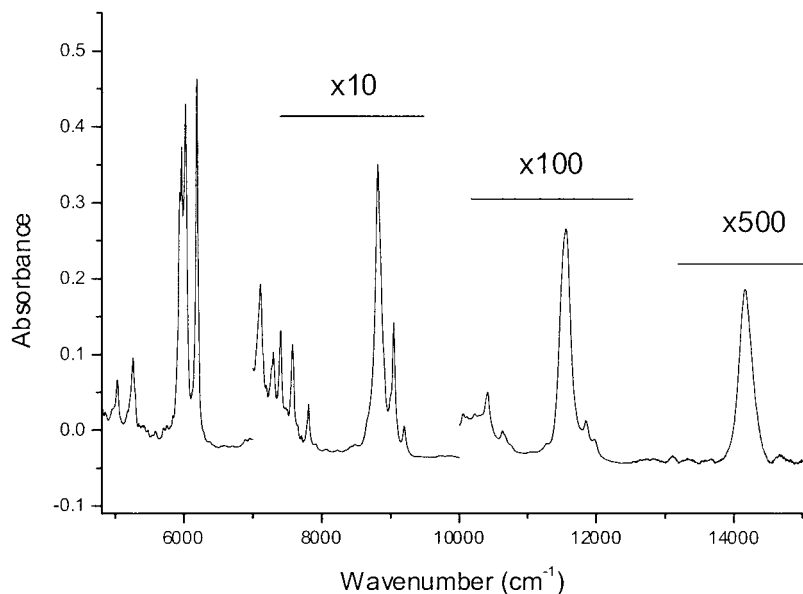
Figure 1 Vibrational overtone spectrum of acrylonitrile, first through fourth vibrational overtone transitions measured at room temperature.

Birge-Sponer plot, the fifth overtone absorption is expected to occur at 16790 cm^{-1} (595 nm). This transition wavenumber can be compared to the fifth stretch transition of the benzyl CH of BP[7] at 16556 cm^{-1} (604 nm) and the fifth CH stretch of the methyl group of AIBN at 15920 cm^{-1} (628 nm). For AIBN dissolved in AN, its fifth CH stretch overtone absorption shifts from 15920 cm^{-1} (628 nm) (dissolved in EGDMA) to 15962 cm^{-1} (627 nm), which lies far below the absorption peak of AN (16790 cm^{-1}, 595 nm). This fact suggests that no significant amount of light will be absorbed by the monomer during the irradiation of the initiator at 604 and 627 nm.

Vibrational overtone polymerization of AN/AIBN mixture

A mixture of 5% (wt) AIBN in AN was irradiated at 627 nm for 4 h with 80 mW of extracavity laser power. The polymer produced from irradiation was characterized by FTIR spectroscopy. Figure 2 presents the spectrum of the photo-polymer (c), compared with the spectra of commercial polyacrylonitrile (b) and the monomer (a). In Figure 2a, absorptions typical of AN are observed: 3040 cm^{-1} for the CH stretch, 1420 cm^{-1} for the scissors vibrations, 976 cm^{-1} for the CH deformation in alkenes and 2260 cm^{-1} for the CN stretch.[10] For the commercial polymer (Figure 2b), the peaks at 3040, 1420, and 976 cm^{-1} do not appear, and peaks at 2941 and 1465 cm^{-1} appear, corresponding to the CH stretch and scissors vibrations, respectively, of the CH$_3$ and CH$_2$ groups.[10] The spectrum of the photo-product, Figure 2c, is identical to that of the commercial polyacrylonitrile.

The monomer conversion of the irradiated sample after a 48 h duration is 92%. The polymerization rate reaches 1.9% per hour. Similar experiments were per-
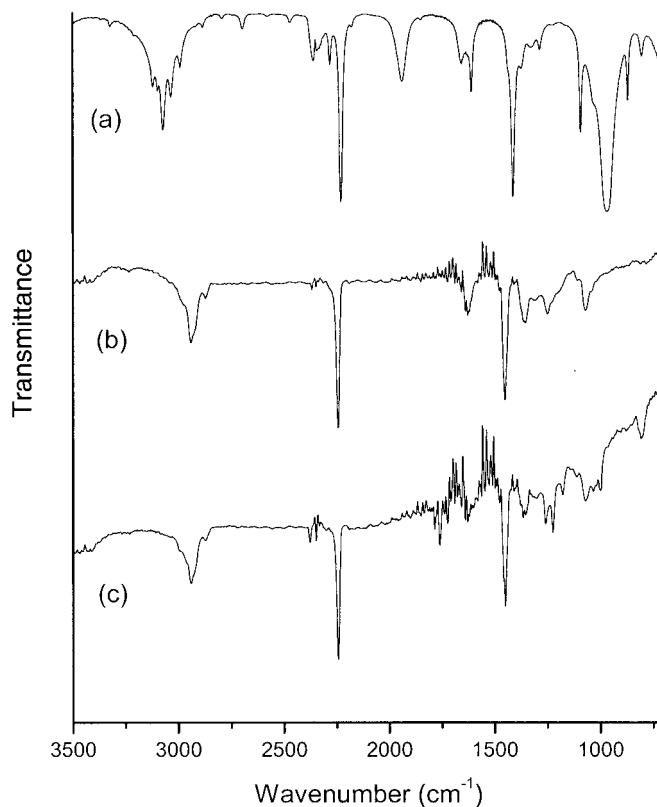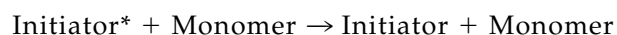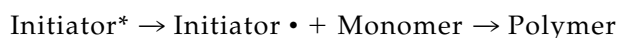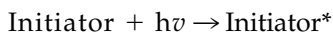

Figure 2 FTIR spectra of acrylonitrile and polyacrylonitrile. (a) FTIR spectrum of the monomer acrylonitrile; (b) FTIR spectum of commercial polyacrylonitrile; (c) FTIR spectrum of the photo-polyacrylonitrile.
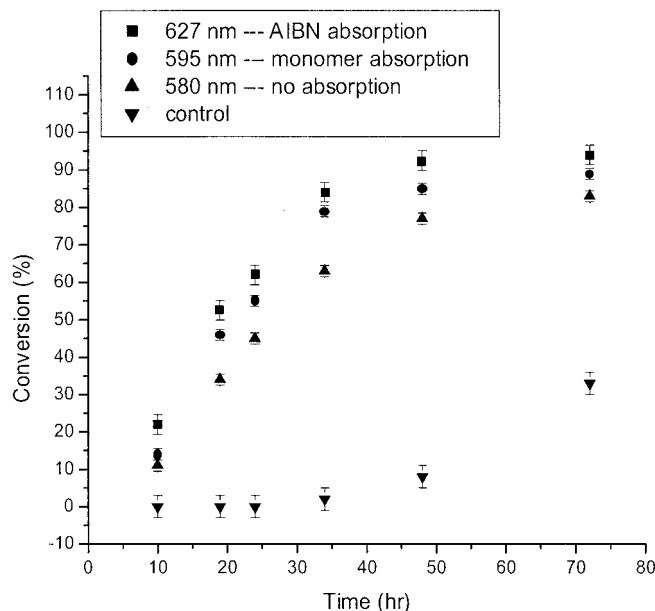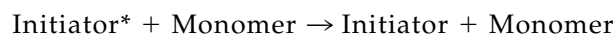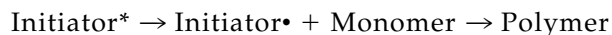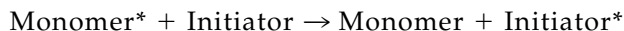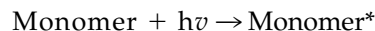
Figure 3 Monomer conversion (%) versus time (h) for AN/ AIBN 5% (wt) at different irradiation (80 mW, 4 h) wavelengths.

formed at three different wavelengths: 627 nm (absorption peak of AIBN), 595 nm (absorption peak of AN), and 580 nm (no absorption). The data points shown in Figure 3 are the average of three trials at each wavelength. The experiments were carried out under the same conditions: 5% (wt) initiator concentration, 80 mW laser power, and 4 h photolysis duration. At 48 h it appears that the monomer conversion for the 627 nm irradiation is about 2 times larger than that for the 580 nm irradiation and about a factor of 1.3 larger than for irradiations on the monomer absorption peak (595 nm).

There are two initiation mechanisms involved, as mentioned in the vibrational overtone polymerization of methyl methacrylate/AIBN[11]: direct light absorption by initiator followed by the creation of radicals, and collisional energy transfer between highly vibrationally excited monomer and initiator resulting in decomposition of the initiator. For the irradiation at 627 nm, only the first mechanism occurs. Single photons are used to excite highly excited vibrational states in the ground electronic state of the initiator molecules, which undergo subsequent chemical reaction leading to polymerization. The following set of reactions describes this process.

$$\text{Initiator} + h\nu \rightarrow \text{Initiator*}$$

$$\text{Initiator*} \rightarrow \text{Initiator} \cdot + \text{Monomer} \rightarrow \text{Polymer}$$

$$\text{Initiator*} + \text{Monomer} \rightarrow \text{Initiator} + \text{Monomer}$$

Initiator* is highly vibrationally excited initiator, and Initiator• is the initiator radical. For the irradiation at 595 nm, only the collisional energy transfer mechanism is responsible for the polymerization. The process involved here is presented in the following set of reactions.
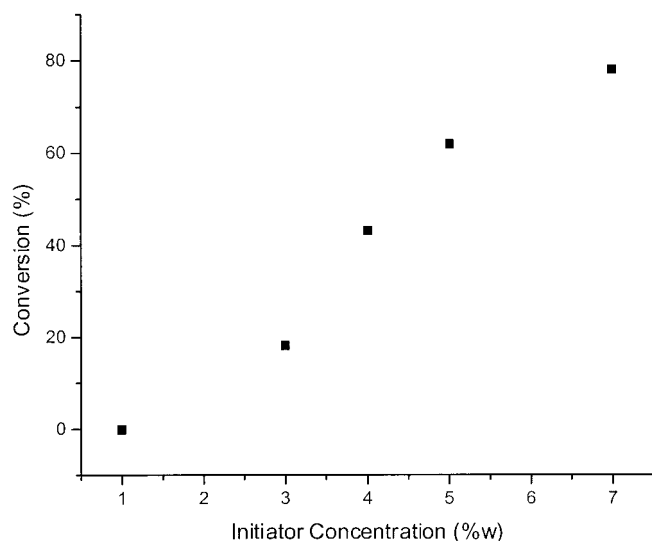
$$\text{Monomer} + h\nu \rightarrow \text{Monomer*}$$

$$\text{Monomer*} + \text{Monomer} \rightarrow 2 \text{ Monomer}$$

$$\text{Monomer*} + \text{Initiator} \rightarrow \text{Monomer} + \text{Initiator*}$$

$$\text{Initiator*} \rightarrow \text{Initiator} \cdot + \text{Monomer} \rightarrow \text{Polymer}$$

$$\text{Initiator*} + \text{Monomer} \rightarrow \text{Initiator} + \text{Monomer}$$

Monomer* is highly vibrationally excited monomer. The second mechanism should be inefficient in creating radicals because it is unlikely that six quanta of CH stretch are transferred in one collision. The amount of energy transferred per collision (ΔE) can be positive (activating collision) or negative (deactivating collision).[12] Many collisions are required to activate a polyatomic bath molecule or deactivate a highly excited polyatomic molecule. The average amount of energy transferred depends on the bath molecule.[13] The typical amount of energy transferred per collision for a large polyatomic molecule with another large molecule as a bath molecule (average from different experimental data)[12–16] is about 1500 cm^{-1}. Therefore, at least seven collisions are needed to transfer enough energy to reach the decomposition barrier ($E_a = 10101$ cm^{-1}) of the initiator in the case of AN/AIBN. If we assume that half of these collisions are deactivating processes, then at least fourteen collisions are needed to activate an initiator molecule. The ratio of monomer molecules to initiator molecules is about 20:1. Therefore through multiple collisions involving monomer-monomer and monomer-initiator encounters, a small fraction of initiator molecules acquire enough energy to react.

The influence of the initiator concentration on the vibrational overtone polymerization of AN/AIBN was also investigated. The experiments were carried out by varying the amount of initiator from 1 to 7%. Figure 4 presents the results. After a 24 h duration, no polymerization was observed at the 1% concentration. The reaction increases with increased concentration over the 1–7% range.

The overall quantum yield (Φ) of overtone polymerization of AN/AIBN was calculated using the following equations:

$$\phi = \frac{\text{number of monomer molecules converted}}{\text{number of photons absorbed}}$$

$$(1)$$

Figure 4 Monomer conversion (%) versus time (h) for AN/AIBN (627 nm, 80 mW, 4 h) with different initiator concentrations.

$$N_a = N_0 - (N_0/10^A) \qquad (2)$$

where A is absorbance of the sample and N_0 and N_a are numbers of incident and absorbed photons, respectively. During a 4 h irradiation at 627 nm with a laser power of 80 m the number of incident photons, N_0, was calculated to be 3.63×10^{21}. The absorbance, from AIBN only, is 3×10^{-1} (see Fig. 5). Figure 5 represents a simulation of the fifth vibrational overtone of the CH stretch for the monomer AN as well as the initiators AIBN and BP. This simulation is based on the concentration, the transition wavenumbers, the FWHM and molar absorbance parameters for the first through fourth vibrational overtone progressions of the CH stretch absorptions of AN, AIBN and BP. Using the values of N_0 and A calculated above, the number of absorbed photons, N_a, was calculated to be 2.50×10^{17}. The initial number of monomer molecules in the sample was 9.03×10^{21}. Monomer conversion after 48 h was 92%, and the conversion from the control experiment was 8%. So the photo-product of the polymerization was estimated as 84% by subtracting the conversion of the control experiment from the total conversion. Thus, the number of molecules converted during the 48 h time period was 7.59×10^{21}. Using eq. (1), the quantum yield (Φ_{627}) of polymerization of AN/AIBN at 627 nm after 48 h was calculated as 21083. During a 4 h irradiation at 595 nm with a laser power of 80 mW, N_0 was 3.44×10^{21}. The absorbance, A, only from the monomer, is 5.03×10^{-4} (see Fig. 5). So N_a was calculated as 3.44×10^{18} using eq. (2). The photo-product for the monomer conversion after 48 h was 74% so the number of monomer molecules converted was 6.68×10^{21}. Therefore, the quan-

tum yield (Φ_{595}) of polymerization of AN/AIBN after 48 h is 1942.

The estimated quantum yield Φ_{627} is about 10 times larger than Φ_{595}. Considering the molar ratios of the initiator and monomer, the creation of radicals by vibrational overtone activation of the initiator is about 100 times more efficient than the creation of radicals via collisional energy transfer between vibrationally excited molecules of monomer and initiator.
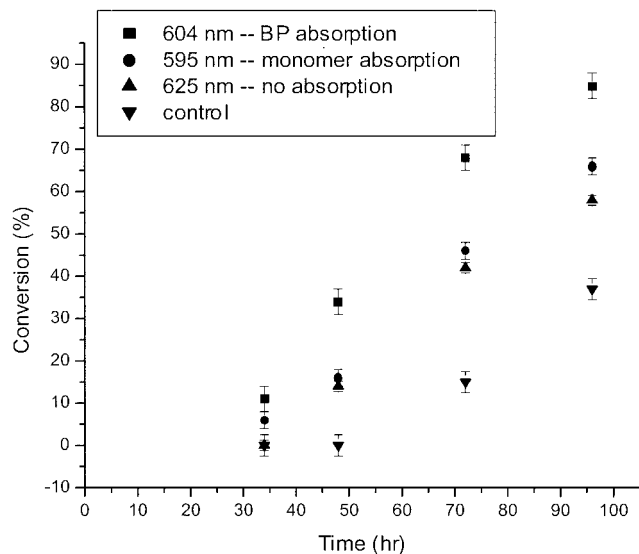
Vibrational overtone polymerization of AN/BP mixture

A mixture of 5% (wt) BP in AN was irradiated at 604 nm for 4 h with 80 mW of extracavity laser power. The monomer conversion detected after a 48 h duration was 33%. The overall rate of polymerization is 0.8% per hour. The investigation of wavelength selectivity was performed at three selected wavelengths: 604, 595, and 625 nm. The 604 nm corresponds to the fifth CH stretch absorption peak, 595 nm is the absorption peak of the monomer, and 625 nm is the wavelength where neither monomer nor initiator absorbs light. Figure 6 shows the data obtained from the experiments. At 48 h the monomer conversion for 604 nm (the initiator absorption peak) irradiation is about a factor of 2.2 larger than for 625 nm (no monomer or initiator absorption), and is about a factor of 1.8 larger than for 595 nm (monomer absorption peak).

To study the effect of the initiator concentration on the overtone polymerization of AN/BP, the amount of initiator varied from 1 to 7%. The similar result to that of AN/AIBN was obtained. As seen in Figure 7, the monomer conversion increases with the increased initiator concentration from 1 to 7%.
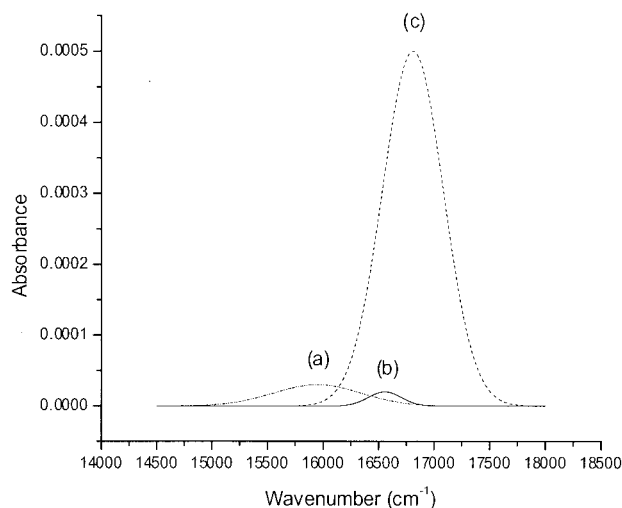

Figure 5 Simulation of the fifth vibrational overtone of the CH stretch for (a) initiator AIBN; (b) initiator BP; (c) monomer AN.

Figure 6 Monomer conversion (%) versus time (h) for AN/BP 5% (wt) at different irradiation (80 mW, 4 h) wavelengths.

The overall quantum yield of overtone polymerization of AN/BP was estimated using the same equations described above. During a 4 h irradiation period at 604 nm with a laser power of 80 mW, N_0 was 3.50 $\times 10^{21}$. The total absorbance, A, from both AN and BP is 3.60 $\times 10^{-4}$ (see Fig. 5). The number of absorbed photons, N_a, was calculated to be 2.80 $\times 10^{18}$. The photo-product of polymerization after 48 h was 33%; the number of monomer molecules converted was 3.07 $\times 10^{21}$. This leads to a quantum yield (Φ_{604}) of polymerization of AN/BP after 48 h as 1096. During a 4 h irradiation at 595 nm with a laser power of 80 mW, N_0 was 3.44 $\times 10^{21}$. The absorbance, A, from the mono-
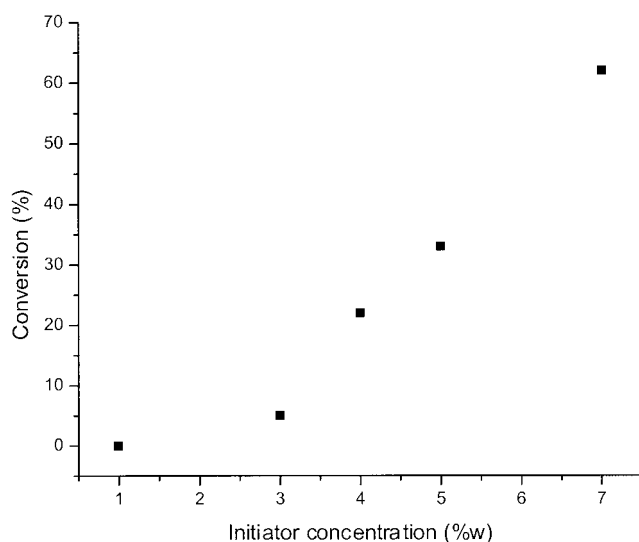
Figure 7 Monomer conversion (%) versus time (h) for AN/BP (604 nm, 80 mW, 4 h) with different initiator concentrations.
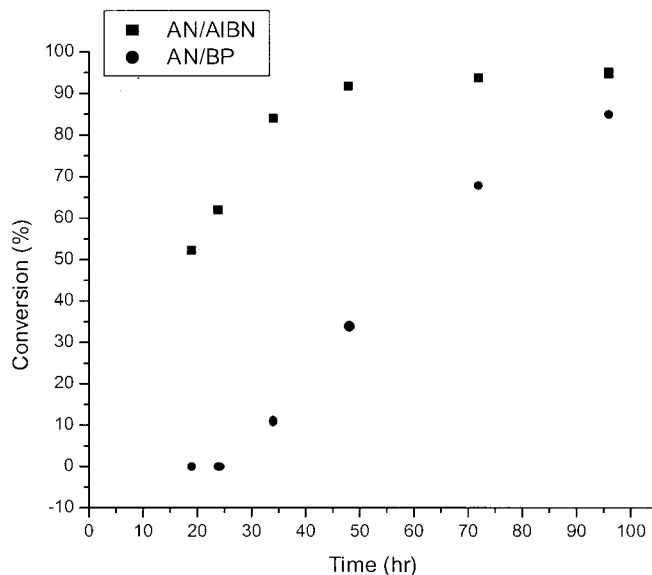
Figure 8 Difference between the vibrational overtone polymerizations of AN/AIBN (627 nm, 5%, 8 mW, 4 h) and AN/BP (64 nm, 5%, 8 mW, 4 h).

mer only, is 5.03 $\times 10^{-4}$ (see Fig. 5). N_a was then calculated as 3.44 $\times 10^{18}$ using eq. (2). The photoproduct for the monomer conversion after 48 h was 17% so that the number of monomer molecules converted was 1.54 $\times 10^{21}$. Therefore, the quantum yield (Φ'_{595}) of polymerization of AN/AIBN after 48 h is 448.

The estimated quantum yield Φ_{604} is about 2.4 larger than Φ_{595}. Therefore, in the vibrational overtone polymerization of mixture AN/BP, considering the molar ratios of the initiator and monomer, the creation of radicals by vibrational overtone activation of the initiator is about 20 times more efficient than the creation of radicals via collisional energy transfer between vibrationally excited molecules of monomer and initiator.

Comparison of the wavelength selectivity of AN/AIBN and AN/BP mixtures

Given the estimated quantum yields, Φ_{627} and Φ_{595} for AIBN and Φ_{604} and Φ_{595} for BP, the creation of radicals that initiate polymerization is more efficient for AIBN. This increased efficiency leads to a higher polymer yield for the AIBN case. For example, after 24 h the monomer conversion for the AIBN case is over 60% whereas for BP at 24 h the monomer conversion is only around 8%. However, it is interesting to note that there is a larger difference between irradiation at the initiator peak absorption and the monomer peak absorption for BP, the case with the least efficient polymerization. For both the AIBN and BP cases when the monomer conversion reached 65% for the initiator irradiation, the samples where the monomer was irra-

diated were at 60 and 42% for AIBN and BP, respectively. Using this 65% monomer conversion as a reference point, the BP initiated experiment displayed one third more monomer conversion for the initiator irradiation compared to the monomer irradiation. The least efficient initiator proved to yield the best wavelength selectivity.

In comparison to the case of EGDMA in previous work, a similar trend is observed. Once again BP acts as a less efficient initiator for the crosslinking of EGDMA, but displays a stronger wavelength selectivity between initiator versus monomer irradiation. In this case the overall reaction is slow and the final conversion is low because of the crosslinked structure of the polymer. Combining the less efficient initiator, BP, with the unreactive monomer, results in the dark reaction and the monomer irradiation experiment reacting at essentially the same rate. Using a more active initiator, AIBN, makes it possible to see a small amount of reaction when the monomer is irradiated. For the vibrational overtone polymerization of ethyl acrylate, no wavelength dependence was observed due to the high reactivity of the monomer.

CONCLUSION

The vibrational overtone polymerization of AN has been demonstrated using AIBN and BP as initiators. The fifth CH stretch overtone absorptions of AIBN (627 nm) and BP (604 nm) were used as irradiation wavelengths. The photopolymerizations of AN/AIBN and AN/BP are both wavelength selective. The monomer conversion was enhanced when the photolysis wavelengths corresponded to the absorption peak of BP (604 nm) and AIBN (627) as opposed to the photolyses on two other wavelengths. The overall quantum efficiencies for both overtone polymerizations after 48 h were estimated to be $\Phi_{627} = 21083$ and $\Phi_{595} = 1942$ for AN/AIBN mixture and $\Phi_{604} = 1096$ and $\Phi_{595} = 448$ for AN/BP mixture. Holding all other parameters constant, the overtone polymerization rate of AN/AIBN (1.9% per hour) is faster than that of AN/BP (0.8% per hour). The influence of initiator concentration on the overtone polymerizations of AN/AIBN and AN/BP mixtures was also investigated. The results show that the monomer conversion increases when the initiator concentration increases from 1 to 7%.

References

1. Crim, F. F. Ann Rev Phys Chem 1984, 35, 657.
2. Goodall, D. M.; Chetwood, I. Chem Phys Lett 1986, 129, 291.
3. Fleming, P. R.; Rizzo, T. R. J Phys Chem 1991, 95, 149.
4. Schwebel, A.; Brestel, M.; Yogev, A. Chem Phys Lett 1984, 107, 579.
5. Snavely, D. L.; Zare, R. N.; Miller, J. A.; Chandler, D. W. J Phys Chem 1986, 90, 3544.
6. Jasinski, J. M.; Frisoli, J. K.; Moore, C. B. J Phys Chem 1983, 79, 1312.
7. Grinevich, O.; Snavely, D. L. Chem Phys Lett 1997, 267, 313.
8. Grinevich, O.; Snavely, D. L. Chem Phys Lett 1999, 304, 202.
9. Gu, H.; Snavely, D. L. Macromolecules 2003, 36, 3160.
10. Alpert, N. L.; Keiser, W. E.; Szymanski, H. A. IR theory and practice of infrared spectroscopy; Plenum Press: NJ, 1970.
11. Gerasimov, T. G.; Snavely, D. L. Macromolecules 2002, 35, 5796.
12. Oref, I.; Tardy, D. C. Chem Rev 1990, 90, 1407.
13. Heymann, M.; Hippler, H.; Troe, J. J Chem Phys 1984, 80, 1853.
14. Barker, J. R. Chem Phys 1983, 77, 301.
15. Miller, L. A.; Barker, J. R. J Chem Phys 1996, 105, 1383.
16. Flynn, G. W. Acc. Chem Res 1981, 14, 334.