Vibrational Photopolymerization of Methyl Methacrylate and Quantitative Analysis of Polymerization Results

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ABSTRACT: Radical photopolymerization of methyl methacrylate (MMA) with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator was carried out by visible light excitation. Excitation of the fifth vibrational overtone of the CH stretch of AIBN at 628 nm initiates the reaction with subsequent monomer conversion of up to 86% after 24 h. The quantitative analysis of monomer conversion was accomplished by a partial least-squares (PLS) analysis of the second vibrational overtone spectra of methyl, methylenic, and vinyl CH stretch absorptions. The wavelength selectivity of the process was studied by irradiating samples at the fifth vibrational overtone of the methyl CH stretch of AIBN (628 nm), the fifth vibrational overtone of vinyl CH stretch of MMA (602 nm), and a wavelength where both monomer and initiator do not absorb light (595 nm). The mixtures irradiated at the monomer absorption peak exhibited about 4 times less polymer formation than mixtures irradiated at the initiator absorption peak after 24 h. The overall quantum yields (φ) for 24 h of polymerization were estimated to be $\phi_{628} = 9937$ and $\phi_{602} = 1810$ for the mixtures irradiated at 628 and 602 nm, respectively.

Introduction

Chemical reactions can be initiated by creating vibrationally excited states in the ground electronic state using laser light absorption. Many reactions in the gas phase have been carried out with this technique, known as vibrational photochemistry, using excitation of the fourth, fifth, and sixth CH stretch overtone transitions. These include ring openings, isomerizations, and dissociations.[1−5] Vibrational photochemistry in the liquid phase is prohibited by fast collisional deactivation; however, the chain nature of free radical polymerization amplifies the product yield for overtone-initiated reactions.[6−8]

Work in our laboratory introduced a novel method of polymerization using overtone excitation to form radicals which subsequently polymerize a monomer in the liquid phase. Vibrational overtone photopolymerization of methyl methacrylate with benzoyl peroxide as a radical precursor was performed.[7,8] The irradiation was carried out inside a quartz cuvette aligned within a dye laser cavity. Excitation into the fifth vibrational overtone of the CH stretch of benzoyl peroxide at 604 nm initiated polymerization. Near-IR spectra in the region of the first vibrational overtone were used to monitor polymerization progress. The overtone spectrum of poly-MMA showed the reduced intensity of the vinyl CH stretch and a concomitant increase in the overall intensity of the methylenic CH stretches. The estimation of the percent polymerization by overtone spectroscopy was confirmed by NMR spectroscopy.[7,8] The rate of reaction was found to be specific to the absorption wavenumber of the vibrational overtone transition used in the irradiation. No significant polymer formation was detected when samples were irradiated at 598 nm (to the blue of the initiator absorption peak) or at 611 nm (to the red of the initiator absorption peak).[7,8]

The vibrational overtone spectra of the monomer, polymer, and initiator were also reported in this previous work. The features in vibrational overtone spectroscopy arise from the specific absorptions belonging to the OH, NH, and different types of CH stretching motions,[9,10] called local modes.[11] Local mode theory has been applied to interpret the vibrational overtone spectra of polymeric systems[8,9,12,13] as well as a variety of gaseous and liquid samples.[10,14−16] The vibrational overtone spectra of ethyl acrylate (EA), methyl methacrylate (MMA), benzoyl peroxide (BP), and 2,2′-azobis(isobutyronitrile) (AIBN) have been recorded and analyzed in terms of local mode theory and were published elsewhere.[6−8]

In the current work a study of the vibrationally initiated polymerization of methyl methacrylate monomer with 2,2′-azobis(isobutyronitrile) initiator is presented. AIBN was chosen as the initiator for several reasons. First, the thermal decomposition barrier is lower than that of benzoyl peroxide, making lower irradiation energies possible. Second, the solubility of AIBN in MMA is higher than that of BP. Finally, the absorption features of AIBN do not overlap with the vinyl absorption of MMA. In the previous work the absorption peak of BP overlapped the vinyl absorption of methyl methacrylate, so that light used to irradiate BP also irradiated MMA. In this case, two mechanisms for the initiation step were possible. The first mechanism involves direct light absorption and decomposition of BP while the second involves collisional energy transfer from excited monomer to BP with subsequent decomposition of initiator. The methyl CH stretch absorption of AIBN at 15 922 cm^{-1} (628 nm) only partially overlaps with the methyl absorption of MMA at 16 142 cm^{-1} (619 nm) and does not overlap at all with the vinyl absorption of MMA at 16 599 cm^{-1} (602 nm), allowing the opportunity to irradiate samples at both wavelengths. The absorption wavelengths, noted above, refer to the absorption spectra of pure MMA and a saturated solution of AIBN in CCl$_4$. It is known that the vibrational overtone frequencies of any given molecule depend on its environment. The red shift between the gaseous and liquid-phase spectra has been documented, as well as shifts that occur between free and hydrogen-bonded forms of OH and NH groups.[10,17] However, for the MMA/AIBN system the absorption frequency shifts are not significant, as discussed below.

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The following work will demonstrate the possibility of photopolymerization of MMA with AIBN initiator by vibrational overtone excitation. Wavelength selectivity will be evaluated by irradiating the monomer/initiator mixtures at 15 922 cm^{-1} (628 nm), 16 599 cm^{-1} (602 nm), and 16 800 cm^{-1} (595 nm) followed by the comparison of the polymerization results. The polymerization progress will be monitored by NIR spectroscopy of the second vibrational overtone spectra. From these spectra the degrees of polymerization will be determined using a nonlinear curve-fitting method and a partial least-squares (PLS) method.

Experimental Section

Methyl methacrylate monomer was purchased from Aldrich Chemical Co., and the inhibitor was removed using the Aldrich disposable inhibitor remover column. AIBN and $CDCl_3$ were purchased from Aldrich Chemical Co. and used without further purification. Poly(methyl methacrylate) (average $M_w = 15\,000$) was purchased from Aldrich Chemical Co. and reprecipitated from methanol.

Mixtures of monomer and initiator were prepared by dissolving 3 wt % of AIBN in MMA and deaerated by bubbling dry argon for 20 min through the sample. The purging was performed at room temperature, 23 °C. The evaporation of MMA was kept to a minimum by fitting the cells with septa and controlling the argon flow. The small increase in AIBN concentration was consistent for all samples.

The samples were placed inside the glass cells with 5 mm spectroscopic path length. The cells were placed extracavity of a Spectra Physics model 375B continuous wave tunable dye laser pumped by Spectra Physics Series 2000 Ar ion laser and irradiated at a desired wavelength (602, 628, or 595 nm) with 70 mW of laser power for 2 h. An intracavity birefringent filter was used to tune the dye laser to a desired wavelength. A 0.35 m monochromator and a Newport 815 digital power meter were used to measure the dye laser wavelength and power.

The progress of polymerization was monitored by NIR spectroscopy. A Mattson Galaxy series 5000 NIR spectrometer with a tungsten lamp, a quartz beam splitter, and PbSe (3000–10 000 cm^{-1}) detector. The region from 6500 to 9500 cm^{-1} (second vibrational overtone) was used for monitoring. The resolution for all spectra was 4 cm^{-1}.

A set of 11 standards with known polymeric content was used as a reference database. Standards 1 to 5 were 90–10, 80–20, 70–30, and 60–40 wt % mixtures of MMA and poly-MMA, respectively. Because of solubility constraints, solutions of poly-MMA in MMA with polymeric content 50% and higher could not be prepared. For these more concentrated solutions the monomer/polymer mixture was dissolved in deuterated chloroform. The chloroform-*d* was a solvent of choice because it offers good solubility for both components and possesses a very weak absorption of the CD bond at 6560 cm^{-1}, which does not overlap the CH absorptions of MMA or poly-MMA in the region of interest. Standards 6 to10 were 25% (molar) solutions in $CDCl_3$ of 50–50, 40–60, 30–70, 20–80, and 10–90 wt % mixtures of MMA and poly-MMA, respectively. Standard 11 is pure poly-MMA. Spectra of these standards were recorded using a 5 mm glass cell identical to the photolysis cell for standards 1–5 and 11 and a 20 mm quartz cell for the standards 6–10.

UV–vis absorption spectra were recorded on a Hewlett-Packard 8452A diode array UV–vis spectrometer. Spectra of 1.85% (molar) solutions of AIBN in $CDCl_3$ were taken. The absorption peak for the azo group at 343 nm was monitored.

Peaksolve by Galactic Industries Corp. software was used for the nonlinear curve fitting. The spectra were deconvoluted using Gaussian type line shapes with fixed peak centers.

PLS Quant by Analytical Technology Inc. was used as a multivariate statistical tool. The software utilizes a partial least-squares method, which was used to develop a calibration model to determine a monomer conversion.

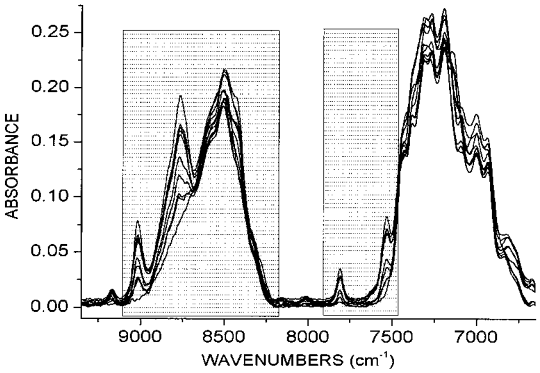

Figure 1. Changes in the second vibrational overtone spectra of MMA/AIBN mixture as polymerization takes place.

Results and Discussion

Mixtures of AIBN and MMA were irradiated at three different wavelengths within the fifth vibrational overtone transition, and the polymerization was monitored for a 24 h interval. For each wavelength used a set of five samples was prepared. Thus, the polymerization results for the irradiation at each wavelength are average values. The low activation barrier of AIBN means that the third vibrational overtone of the CH stretch at 11 091 cm^{-1} (901 nm) is the lowest overtone required to form radicals from AIBN. However, the fifth vibrational overtone of the CH stretch at 15 931 cm^{-1} (628 nm) was used for irradiation, allowing the creation of more vibrationally excited species using a wavelength which falls near the maximum of the Rhodamine-6G laser dye gain curve.

Vibrational overtone spectroscopy is an important analytical tool used to determine monomer and initiator absorptions as well as to monitor polymerization progress. In previous work, the vibrational overtone spectra of methyl methacrylate and 2,2′-azobis(isobutyronitrile) have been recorded and analyzed. The first vibrational overtone spectrum was used to monitor polymerization progress. Since the vinyl CH stretch peak at 5945 cm^{-1} overlapped the methyl CH stretch absorption at 5790 cm^{-1}, the peak at 6163 cm^{-1} corresponding to the combination of vinyl CH stretch, where one quantum of vibrational energy is allocated in each carbon–hydrogen bond of the vinyl group,[18] was used as a measure of the polymerization yield.[7,8]

In this work, the second overtone spectrum was used to determine the progress of polymerization. Figure 1 shows the changes in the spectrum of MMA after irradiation. The decrease in the peak areas for the vinyl absorption of MMA at 8768 cm^{-1} and for the vinyl combination band at 9017 cm^{-1} indicates the conversion of double bonds. The increase in the peak area for the methyl/methylenic absorption of MMA at 8502 cm^{-1}, though not as obvious, corresponds to the formation of polymer in the mixture. The intensity of the vinyl combination band drops sharply as the vibrational quantum number increases. In addition, because of the peak broadening, it is partially overlapped with the vinyl CH stretch and is no longer a good tool for quantitative analysis. Therefore, for the second vibrational overtone, the decrease in the vinyl CH stretch peak is a quantitative measure of double-bond conversion.

Unfortunately, because of the harmonic character of the C=O bond, it does not absorb light in the region of interest and cannot be used as an internal standard.

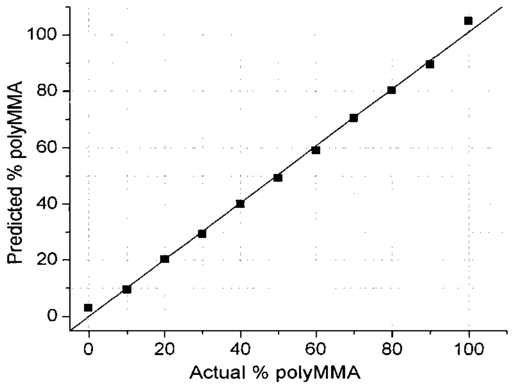

Figure 2. Calibration plot for the monomer conversion calculated by a PLS method.

However, it is known that for high vibrational overtone transitions the absorption cross section per CH bond is independent of type, although bandwidth and peak height may vary.[19] It was assumed that the difference in absorption cross sections of the methyl, methylenic, and vinyl CH stretches is small enough to be neglected. In addition, for each MMA molecule, there are six methyl CH bonds that remain throughout the reaction for every two vinyl bonds that convert to methylenic. Therefore, we can assume that the total area under both peaks does not change during the polymerization. Hence, the comparison of the area under an individual peak to the total area serves as an indicator of polymer formation.

The vinyl and methyl absorption peaks of MMA for the second stretching overtone are partially overlapped, making a direct integration method not possible. To overcome these difficulties, a deconvolution technique was investigated. For the purpose of calibration, a set of standards with known polymeric content (see Experimental Section) was prepared. Spectra of these standards were recorded and deconvoluted using the PeakSolve software. The polymerization yields calculated by this deconvolution technique correspond well to the standards with low polymeric content. However, there is a considerable error for the standards with high (>50%) polymeric content. In addition, the spectrum for each data point should be deconvoluted separately, which, considering a large number of data points, makes the procedure very time-consuming.

An alternative procedure that does not require peak deconvolution and area integration was developed by applying a partial least-squares method[20] using the PLS Quant software. In this method *X* variables (standards) and *Y* variables (concentrations) are used to build a calibration model. The method focused on the spectral regions from 7470 to 7900 cm^{-1} and 8200 to 9100 cm^{-1} where the largest changes were observed as the component concentration varied (Figure 1). An internal validation of the method was performed where standards were reused as unknowns. A calibration plot for poly-MMA was created and shown in Figure 2. A PRESS (predicted residual sum of squares) plot for the calibration is shown in Figure 3. A small number of dimensions introduces error by excluding important information from the calibration model; however, a large number of dimensions adds noise and makes the procedure more time-consuming. Figure 3 indicates that the best choice of dimension is 4. This value was used in this analysis.

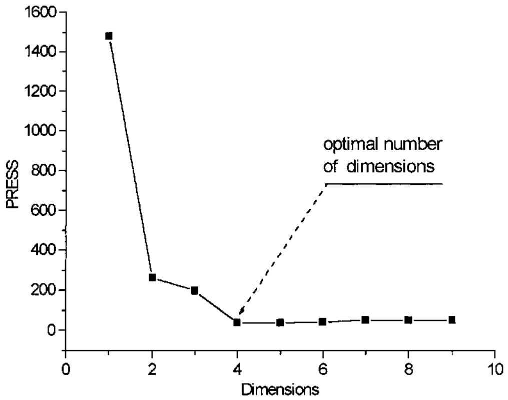

Figure 3. Predicted residual sum of squares plot for PLS method.

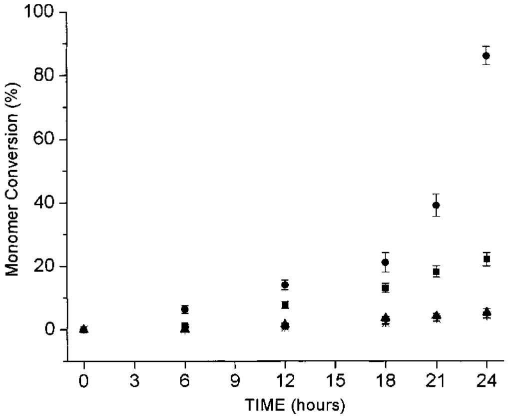

Figure 4. Monomer conversion for MMA/AIBN mixture irradiated at (●) 628 nm, (■) 602 nm, (▲) 595 nm, and (*) no irradiation.

Table 1. External Validation of PLS Method

actual monomer conversion (%)	15	20	25	30	35	40
predicted monomer conversion (%)	14	20	26	29	37	40

An external validation was performed on a separate set of six samples with known polymer percentage. The results are shown in Table 1. Once a reference database is created, the PLS method provides a faster and more convenient determination of the yield. Therefore, the PLS method was used for the quantitative analysis of the photopolymerization results.

For AIBN, the change of solvent from CCl_4 (used to determine an irradiation wavelength) to MMA results in a blue shift of 20 cm^{-1}. The FWHM for the fifth vibrational overtone of the CH stretch of AIBN is about 200 cm^{-1}. Thus, the irradiation wavelength of 628 nm was still at the absorption maximum. A mixture of 3 wt % AIBN in MMA was irradiated at 628 nm (fifth overtone absorption of AIBN) for 2 h with an extracavity power of 70 mW. The maximum conversion of monomer detected after a 24 h time period was 86%. The percent conversion for vibrational overtone initiated polymerization of MMA during the entire 24 h interval after irradiation is shown in Figure 4.

To investigate the wavelength dependence, the samples with concentrations of monomer and initiator identical to the first set were irradiated at 602 nm for 2 h at 70 mW extracavity laser power. The vibrational overtone spectrum of MMA is not affected by 3 wt % AIBN. The irradiation wavelength at 602 nm falls at the absorption maximum of the fifth overtone of the vinyl CH stretch. The maximum conversion of monomer detected after a 24 h period was 22%. In the bulk polymerization of MMA, it is known that autoacceleration (gel effect)

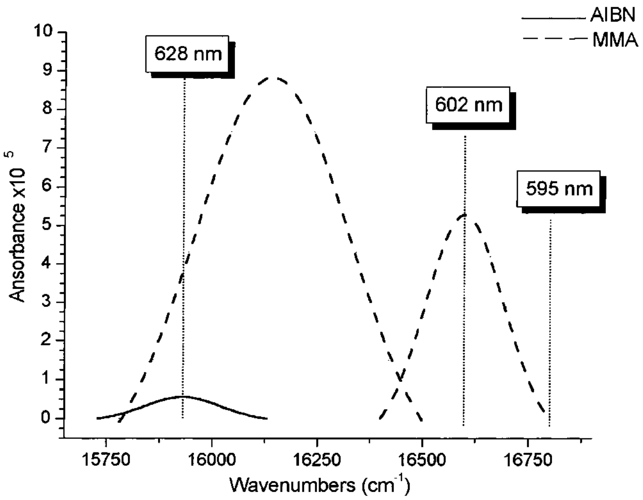

Figure 5. Reconstructed absorption peaks for the fifth vibrational overtones of the methyl CH stretch of AIBN (solid line) and the methyl and vinyl CH stretches of MMA (dashed line). The absorbances are scaled to the molar concentrations of the components and to the path length.

occurs. The autoacceleration begins after about 20% of the monomer is converted to polymer. The conversions shown in Figure 4 indicate that the time to the onset of autoacceleration is dependent on the irradiation wavelength. The autoacceleration occurs at earlier times for irradiation on the peak of the initiator (628 nm).

To understand the wavelength dependence, the concentration factor should be considered. Both initiator and monomer are able to absorb light at 628 nm wavelength. AIBN has an absorption peak maximum at this wavelength with molar extinction coefficient (estimated) of 6.2×10^{-5} L mol^{-1} cm^{-1}; the molar extinction coefficient for methyl methacrylate absorption at this wavelength is approximately 0.8×10^{-5} L mol^{-1} cm^{-1}. Figure 5 represents a reconstructed view of the fifth vibrational overtone of the CH stretch for the MMA/AIBN mixture. This reconstruction is based on the FWHM and molar absorbance parameters for the first through fourth vibrational overtone progressions of the CH stretch absorptions of AIBN and MMA. The absorptions are scaled according to the molar concentration of each component in the mixture and to the path length. Gaussian line shapes were used to simulate the shapes of the absorption peaks.

Thus, with 628 nm irradiation, 13% of the absorbed light excites the initiator while 87% of the light is absorbed by monomer. However, only monomer absorbs the 602 nm light. The absorption of 13% of the light by the initiator increases the polymer yield by a factor of 4. There are two initiation mechanisms involved: direct light absorption by AIBN followed by the formation of radicals and collisional energy transfer between highly vibrationally excited molecules of monomer and molecules of initiator leading to decomposition of the initiator. For the irradiation at 628 nm both mechanisms are possible. For the irradiation at 602 nm, only the collisional energy transfer mechanism occurs.

Another set of samples was irradiated at 595 nm for 2 h at 70 mW extracavity laser power. This is a region where both monomer and initiator do not absorb light. No significant polymerization (~6%) was detected within a 24 h period of time after irradiation.

For each set of samples, one of the prepared samples was not irradiated. These control samples did not show any significant polymerization (~5%) within the 24 h period. A sample of pure MMA (no initiator) was also irradiated at 602 nm, and no polymerization was detected.

The attempt was made to evaluate the quantum efficiency of the overtone initiation process. A solution of AIBN in $CDCl_3$ was irradiated at 628 nm for 2 h at 70 mW laser power, and the change in the initiator concentration was monitored by UV−vis spectroscopy. No changes were observed when monitoring the 343 nm absorption of the azo group of AIBN after 2 h of irradiation. Given this result, it was impossible to measure the quantum efficiency for the initiation process.

However, it is possible to estimate the overall quantum efficiency for monomer conversion. The overall quantum yield (φ) of polymerization can be calculated from the following equations:

$$\phi = \frac{\text{no. of converted monomer molecules}}{\text{no. of photons absorbed}} \qquad (1)$$

$$N_{\rm ab} = N_0 - (N_0/10^A) \qquad (2)$$

where A is absorbance and N_0 and $N_{\rm ab}$ are the numbers of incident and absorbed photons, respectively.

Irradiation at 628 nm. N_0 during a 2 h irradiation period at 628 nm with a laser power of 70 mW was calculated to be 1.59×10^{21}. The absorbance of the AIBN/MMA mixture at 628 nm does not change within the 2 h irradiation period. The total absorbance, A, from both AIBN and MMA is 4.36×10^{-5} (see Figure 5). From this, the number of the absorbed photons, $N_{\rm ab}$, can be calculated as 1.60×10^{17}. The initial number of monomer molecules in the sample was 1.97×10^{21}. Monomer conversion after 24 h was 86%. The dark component from the control experiment was 5%, so the photocomponent of the polymerization was assumed to be 81%. Therefore, the number of molecules converted during the 24 h time period was 1.59×10^{21}, leading to a quantum yield of polymerization after 24 h, φ_{628}, of 9937.

Irradiation at 602 nm. N_0 during a 2 h irradiation period at 602 nm with a laser power of 70 was 1.53×10^{21}. From Figure 5, the absorbance of the vinyl peak of MMA is 5.25×10^{-5}. Thus, the number of the absorbed photons can be calculated as 1.85×10^{17}. After 24 h the photocomponent for the monomer conversion was 17% so that the number of monomer molecules converted was 3.35×10^{20}. This leads to a quantum yield of polymerization after 24 h, φ_{602}, of 1810.

The estimated overall quantum efficiency φ_{628} is about 5.5 times larger than φ_{602}. Considering the molar ratios of the initiator and monomer, the formation of radicals by vibrational overtone excitation of the initiator is about 50 times more efficient than the formation of radicals through collisional energy transfer between vibrationally excited molecules of monomer and initiator.

Conclusions

Excitation at the fifth vibrational overtone transition of the CH stretch of AIBN initiates polymerization in a mixture of AIBN and MMA. The reaction is wavelength specific since there is no polymerization detected when the sample is irradiated at a wavelength where both monomer and initiator have no absorption. However, polymerization proceeds when irradiated on the monomer absorption peak due to vibrational energy transfer between vibrationally excited molecules of monomer and molecules of initiator. The mixtures irradiated at the monomer absorption peak exhibited about 4 times less polymer formation than mixtures irradiated at the initiator absorption peak. The polymerization was monitored by overtone spectroscopy, and the conversion of monomer was determined using a PLS method. The overall quantum efficiencies for polymerization after 24 h were estimated. After 24 h the overall quantum yield for the mixtures irradiated at initiator/monomer absorptions ($\varphi_{628} = 9937$) is more than 5 times larger than for the mixtures irradiated at pure monomer absorption ($\varphi_{602} = 1810$).

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