Offline Monitoring of Hydroxyethyl Methacrylate and 3-Dimethylaminopropyl Methacrylamide Copolymerization: Correlation Between FTIR and GC Quantifications

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Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy is classically used to monitor homopolymerizations. In this article, this analytical technique was extended to monitor the synthesis of VIVIPRINT 300, which is a copolymer of 2-hydroxyethyl methacrylate (HEMA) and N-[3-dimethylaminopropyl]methacrylamide (DMAPMA). The calibration curves devised for this study were based on the two homopolymers P(HEMA) and P(DMAPMA). A good correlation was realized between the FTIR absorbance intensities observed respectively at 1300 cm⁻¹ (polymerized C-O ester bond) and 1230 cm⁻¹ (polymerized C-N amide bond) and the level of residual HEMA and DMAPMA monomers determined by GC. Application of these calibration curves to the copolymerization also exhibited a good correlation of data relating to residual monomer determination by FTIR and GC, validating the success of this spectroscopic in situ technique.

Keywords: ATR-FTIR, copolymerization, DMAPMA, HEMA, quantification, VIVIPRINT 300

Introduction

Traditionally, polymer characterizations involve different methodologies in order both to obtain an accurate view of their microstructure and to follow the kinetic of the monomer polymerization. Thus, gas chromatography (GC)¹ and gravimetry² are used to measure monomer conversion. Nuclear magnetic resonance (NMR) spectroscopy can be utilized to get cumulative composition, sequence length, and other structural information. In parallel, gel permeation chromatography (GPC)³ with various detectors provides additional molecular weight information. Additionally, a wide range of vibrational spectroscopic techniques such as near-infrared (NIR), mid-infrared (MIR), and Raman spectroscopies have been used to monitor polymerization.⁴

Given the competitiveness of the polymer industry, the real-time monitoring of monomer polymerization has become crucial to the manufacturing processes. In this respect, Fourier transform infrared (FTIR) spectroscopy can be a good alternative due to its fast and less expensive setup. This technique is usually developed for characterizing the degree of conversion (DC).⁵,⁶

More particularly, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy has also been used to monitor radical polymerization kinetics.

Nevertheless, this methodology has mainly been applied to radical homopolymerization, particularly for vinyl and acrylic monomer quantifications based on the unsaturated C=C band centered at around 1635 cm⁻¹. While GC analysis allows only the quantification of the residual monomer levels, FTIR can also be used to calculate the percentage of monomer conversion during the polymerization. Moreover, these analyses are usually realized without sample pretreatment, avoiding any quantification distortions. Thus, Bunel⁷ explained the kinetics of photoinitiated crosslinking with a thiol-methacrylate by FTIR. The absorbance of these bands is proportional to their concentration based on the Lambert-Beer Law⁸ (Eq. (1)):

\[ A = e c l, \] (1)

where \( e \) is the molar absorptivity (extinction coefficient) of the absorber (L mol⁻¹ cm⁻¹), \( c \) is the molar concentration of absorbing species in the material (mol L⁻¹), and \( l \) is the path length of the sample (cm).
Fourier Transform Infrared Spectroscopy

ATR-FTIR spectra were acquired on a Perkin Elmer Spectrum 100 spectrometer equipped with an ATR crystal over a total range of 7800–370 cm\(^{-1}\) as the sum of 25 accumulations with 0.5-cm\(^{-1}\) resolution using an LiTaO\(_3\) (lithium tantalate) detector. The velocity of the moving mirror was 0.6329 cm/s. The ambient temperature and the relative humidity for the spectrometer were respectively set between 18°C and 25°C and less than 30%. A background of the blank ATR crystal was obtained and performed and all of the in-process aliquots were analyzed without further polymer precipitation.

Gas Chromatography

**Apparatus and Conditions**

A GC-7890A gas chromatography (GC) equipped with a split/splitless injector, a 7693 auto-sampler, and a flame ionization detector (FID) from Agilent Technology Inc. was used in this study. The separation was carried out on a DB-624 capillary column (30 m × 0.53 mm i.d., 3.00-μm film thickness) from J and W Scientific. A volume of 2-μL sample was injected in the split mode at a split ratio of 5:1 and with an injector temperature of 250°C. GC oven temperature was initially set at 80°C, then programmed to 130°C at a rate of 5°C/min and maintained for 40 min, and finally to 250°C at 5°C/min and maintained for 15 min. Ultra-high-purity helium was used as the carrier gas with a head pressure of 4.4 psi and a constant flow rate of 33 mL/min measured into the detector at room temperature and uncorrected. The detector temperature was set at 250°C.

**Sample Preparation**

All the samples were analyzed using N-methylpyrrolidone (NMP) as an internal standard.

A 1-g sample and 1 g of 0.5 g/L NMP were mixed in 10 mL butanol and centrifuged in a sealed centrifuge tube at 4200 rpm for 10 min at room temperature. The supernatant was then recovered for the analysis.

**Calibration Curve**

One gram of various concentrations of monomers (2, 1.2, 0.4 g/L) and 1 g of 0.5 g/L NMP were spiked in 10 mL butanol, respectively. The samples were prepared as described above and the calibration curve was constructed by plotting the peak area ratio of monomers to NMP versus the ratio of their corresponding concentrations (2)\(^{[14]}\):

\[
\frac{e_i}{k_i} = \frac{C_{ei} A_i}{C_i A_{ei}}
\]

where Cei and Ci are the mass concentrations of the internal standard (ei) and the solute (i) in solution, respectively; \(k_i/e_i\) is the coefficient of the solute i relative to the internal standard ei; and Aei and Ai are the peak areas of internal standard (Aei) and the solute (Ai).

Using the internal standard and the correlation factor, the residual level of each monomer is calculated according to Eq. (3):

\[
C_i = k_i/e_i \times \frac{C_{ei} A_i}{A_{ei}}
\]

**Experimental**

**Reagents**

2-Hydroxyethyl methacrylate (HEMA) (Aldrich, Milwaukee, WI), N-[3-dimethylaminopropyl] methacrylamide (DMAPMA) (Aldrich, WI) were used without any further purification. The radical initiator was 2,2’-Azobis(2-methylbutyronitrile) (Vazo 67) (Aldrich, Milwaukee, WI). Solvents were isopropanol (IPA) (Acros Organics) and Butanol (BuOH) (Aldrich, Milwaukee, WI). N-Methyl-2-pyrrolidone (NMP) (Aldrich, Milwaukee, WI) has been used as the internal standard for GC analysis.

If this methodology is well defined for homopolymer characterization, the literature is much less abundant for copolymer monitoring. In this case, only a few examples described copolymerization\(^{[9]}\) of two monomers with distinct functionalities.\(^{[10]}\)

In our case, we focused our attention on VIVIPRINT 300. It is a copolymer of 2-hydroxyethyl methacrylate (HEMA) and N-[3-dimethylaminopropyl] methacrylamide (DMAPMA) (Fig. 1).

This polymer has been specifically designed by our company to provide faster dry times, gloss, and crosslinking in inkjet media formulations.\(^{[11]}\)

To overcome the difficulties in obtaining the expected reproducibility of the copolymer properties using standard conditions, a specific protocol has been developed consisting of the sequential addition of a radical initiator and monomers all throughout the reaction time. As a consequence, it would be advantageous for such a process to identify a fast and nonexpensive in situ characterization methodology.

The originality of the work described in this article consists of the in situ monitoring of the statistical copolymerization reaction using ATR-FTIR methodology. The aim is to demonstrate the influence of the specific radical initiation and the monomer introduction process described in the cited patent. To validate this complete methodology, a concomitant GC characterization was performed.

Finally, if an ATR-FTIR probe can be directly added in the reactor,\(^{[12]}\) we could possibly establish real-time in situ monitoring strategies for more complex heterogeneous systems such as emulsion or mini-emulsion polymerizations.
Polymer Syntheses and IR Characterization

All the reactions were performed under nitrogen at atmospheric pressure.

Synthesis of P(HEMA)

Sixty grams (0.461 mol) of HEMA with 162 g of IPA and 172 g of water were introduced in the reactor at room temperature. The solution was then heated to 75°C and VAZO 67 radical initiator (1 g, 5.2 mmol) was added by eight equal fractions (0.125 g, 0.65 mmol) over the first 7 hr. At the end of this period the reaction mixture continued to be stirred at 75°C for one further hour. At this point, the residual level of HEMA was reported by GC analysis to be 3000 mg/kg.

The P(HEMA) FTIR spectrum exhibits various bands centered at 3400 cm⁻¹ [ν(OH)], 2990 cm⁻¹ [ν(CH₃)as], ν(CH₂)as, 2973 cm⁻¹ [ν(CH₃)s, ν(CH₃)as], 2882 cm⁻¹ [δ(CH₂)s, δ(CH₂)as], 1726 cm⁻¹ [ν (C=O)], 1484 cm⁻¹ [δ(CH₂)], 1453 cm⁻¹ [δ(CH₃)], 1389 cm⁻¹ [δ(CH₃)s], 1365 cm⁻¹ [δ(CH₂)], 1275 cm⁻¹ [δ(CH₂), δ(CH)], 1260 cm⁻¹ [ν(C-O)], 1162 cm⁻¹ [ν(CH₃), τ(OH)], 1074 cm⁻¹ [ν(O-C), alkene, δ(CH₂), δ(CH₃), γ(CH₂), γ(CH₃), and 749 cm⁻¹ [δ(CH)=O] cm⁻¹⁻¹.

In order to monitor residual HEMA by FTIR during the polymerization, a resolvable absorbance characteristic of the monomer must be recognized. In the 1100–1800-cm⁻¹ region of the IR spectrum of the HEMA monomer, four characteristic absorbance bands were identified: 1726 cm⁻¹ [ν (C=O)], alkene C=C at 1637 cm⁻¹, and 1368 cm⁻¹ [ν(C=O), ester], 965–805 cm⁻¹ [ν(C-C), (CH₃)s], and 749 cm⁻¹ [δ(CH)=O] cm⁻¹⁻¹.

Again, as in the HEMA polymerization, to monitor residual DMAPMA monomer during the polymerization by FTIR, an absorbance characteristic of the monomer must be identified. In the 1100–1800-cm⁻¹ region of the IR spectrum of DMAPMA monomer, five characteristic absorbance bands were identified: 1661 cm⁻¹ (alkene, C=C), 1630 cm⁻¹ and 1540 cm⁻¹ (amide I and II), and 1308 cm⁻¹ and 1230 cm⁻¹ (C=N). Of these absorbances, only the 1230-cm⁻¹ band is well resolvable from that of the P(DMAPMA) and therefore was selected to follow the DMAPMA monomer consumption during the polymerizations.

As with the HEMA, a correlation between the intensity of the FTIR absorbance observed at 1230 cm⁻¹ and the residual DMAPMA level obtained by GC can be realized. Consequently, a method to evaluate the residual monomer level by FTIR can be developed using the intensity of the FTIR absorbance band and the GC results to establish the calibration curves.

Synthesis of VIVIPRINT 300

Ninety grams (0.528 mol) of DMAPMA with 162 g of IPA and 172 g of water were charged in the reactor. The reaction mixture was then flushed with nitrogen for 30 min. Then the mixture was heated at 75°C and a HEMA precharge (3 g, 0.023 mol) was rapidly added to the solution. The remaining HEMA monomer (57 g, 0.438 mol) was then gradually added with a syringe pump over the first 4 hr (flow at 13.3 mL/h). Concomitantly, the VAZO 67 radical initiator (1 g, 5.2 mmol) was added by eight equal fractions (0.125 g, 0.65 mmol) over the first 7 hr. At the end of this period the reaction mixture was allowed to be stirred at 75°C for one additional hour. Finally, the reaction mixture was cooled down, producing the expected copolymer with the following characteristics: percentage of solid (around 30%), pH = 9.5, specific gravity (25°C) = 0.9801, refractive index (25°C) = 1.4098, Mw = 288000 g/mol, Tg = 102°C. The residual levels of HEMA and DMAPMA determined by GC are below 3000 mg/kg.

An analysis of the decrease of the residual monomer level during the polymerization by GC provides a good insight into the kinetics of this copolymerization.

The FTIR spectrum of VIVIPRINT 300 presents the following characteristic absorbances: 327 cm⁻¹ [ν(OH)], 2973 cm⁻¹ [ν(CH₂), ν(CH₃)], 1726 cm⁻¹ [ν(C=O)], 1706 cm⁻¹ [ν(C=O), carbonyl ester], 1651 cm⁻¹ [ν(C=ONH)], 1533 cm⁻¹ [ν(CON-H)], 1482 cm⁻¹ [δ(CH₂)], 1463 cm⁻¹ [δ(CH₂)], 1381 cm⁻¹ [δ(CH₃)s], 1365 cm⁻¹ [δ(CH₂)], 1303 cm⁻¹ [ν(C-O), ester], 1275 cm⁻¹ [δ(CH₂), δ(CH)], 1260 cm⁻¹ [ν(C-O)], 1162 cm⁻¹ [ν(CH₃), τ(OH)], 1025 cm⁻¹ and 1225 cm⁻¹ [ν(N-H)], 1074 cm⁻¹ [ν(O-C), alcohol], and 1021 cm⁻¹ [ν(C-O), ester].

Results and Discussion

In order to follow the evolution of both HEMA and DMAPMA monomers over the 6-h reaction time, we have to find specific FTIR regions that are sufficiently discriminating. Indeed, the selection of inappropriate bands presenting partial overlap could lead to an inaccurate in situ FTIR determination of residual monomer concentration.
In the MIR region, each FTIR spectrum of HEMA and DMAPMA monomers during the homopolymerizations present several patterns of vibration that lead to numerous absorption bands. Furthermore, VIVIPRINT 300 is a copolymer based on the two previous monomers. As a consequence, the potential for polymerization characterization appears to be uncertain both for residual monomer evaluation and for the copolymer monitoring since many FTIR band overlaps are observed.

The first FTIR region of interest was centered at 1630–1650 cm\(^{-1}\), corresponding to the C=\(\text{C}\) monomers’ vibration band. Nevertheless, a strong overlap between the two vibration bands are observed that forbids any precise monitoring of the copolymerization as already mentioned in the literature.\[^19,20\] In order to overcome this difficulty, we concentrated our interest on the ester and amide functional group and more particularly on the carbonyl C=O stretching FTIR region (1600–1750 cm\(^{-1}\)).

Indeed, a discrimination between the HEMA and DMAPMA monomers appears as two distinct absorbances are observed; the ester absorbance centered at 1735 cm\(^{-1}\) (\(\nu_{\text{C=O}}\) HEMA) and the amide absorbance (\(\nu_{\text{C=O}}\) DMAPMA). However, as the homopolymerizations (and copolymerization) proceed, similar absorbance bands from the HEMA and DMAPMA in the polymerizations overlap with the monomer absorbance bands, and therefore measuring residual monomers from this region would be challenging.

Finally, inspection of the fingerprint region around 1200–1300 cm\(^{-1}\) gave rise to two distinct bands for the monomers centered at 1300 cm\(^{-1}\) (\(\nu_{\text{C=O}}\) HEMA) and 1230 cm\(^{-1}\) (\(\nu_{\text{C=N}}\) DMAPMA), respectively. Since no overlap is noticed during the polymerization, these two bands were selected to follow the polymerization in both the homopolymerizations and copolymerization.

In order to quantify the conversion level of each monomer during the copolymerization by FTIR, GC calibration curves were devised based on the homopolymerizations. Thus, it will be possible to correlate FTIR results and GC values and consequently obtain, for further experiments, a precise value from direct FTIR analysis.

These calibration curves were generated from the homopolymerization of each monomer (HEMA and DMAPMA) using a radical polymerization process. A kinetic analysis of each reaction was performed by GC, measuring the residual values of monomers over the reaction time. As expected, a standard monomer concentration decrease was observed as described in Figs. 2 and 3 and total monomer consumption was noticed after 8 hr.

Concomitantly, the FTIR analysis of the in-process homopolymerization samples taken for GC study was conducted. Based on the previously selected bands (1300 cm\(^{-1}\) for HEMA and 1230 cm\(^{-1}\) for DMAPMA), it was possible to observe a decrease in intensity of these two bands and the evolution of a new band centered at 1200 cm\(^{-1}\) corresponding to the polymerized C-O and C-N ester and amide bond (Figs. 4 and 5).

From this data, a correlation between IR absorbance intensity and monomer consumption by GC is obtained and a calibration curve devised. From these curves for residual HEMA and DMAPMA, a linear correlation is observed to 30,000 mg/kg with R\(^2\) = 0.9971 and 0.9908, respectively. These curves were applied to a subsequent HEMA and DMAPMA homopolymerization and a good correlation between GC and FTIR was then realized, leading to Figs. 6 and 7. Moreover, when the same experiment is repeated five times, we did not notice strong variations. The good correlation observed in these curves allowed us to extend this FTIR evaluation on the copolymerization.

Utilizing the previous calibration curves for HEMA and DMAPMA monomers, the synthesis of VIVIPRINT 300...
was directly followed by FTIR. The aliquots taken for FTIR analysis were also analyzed by GC for comparison. As with the homopolymerizations, the limit of the detection of the FTIR calibration for both HEMA and DMAPMA is around \(3000 \text{ mg/kg} \) (<1.6%). As mentioned in the Introduction, monitoring of copolymerizations has not been extensively studied by FTIR despite its interest as demonstrated by Bakhshi and coworkers on poly(butyl acrylate-co-glycidyl methacrylate).

Figure 8 illustrates the correlation between the FTIR and GC results for residual HEMA and DMAPMA monomers during the copolymerization.

As the data from Figs. 9 and 10 illustrates, the analytical model supports the residual monomer levels obtained by ATR-IR spectroscopy, but with limitations. In the case of the residual HEMA monomer (Fig. 10), the IR data provides a good correlation to that of the GC, which is evidenced by the correlation of determination value \(R^2 = 0.9977\) for that line. However, in the case of DMAPMA, we can see that...
the experimental IR data doesn’t agree with the GC data throughout the range, which is why we achieve a lower correlation of determination value ($R^2 = 0.9757$). Our model for DMAPMA works well at higher residual monomer levels, but at lower levels the experimental data deviates from the model, which demonstrates the poorer sensitivity of the IR technique and explains the lower $R^2$ value.

As a possible extension to this study, it would be interesting to determine if the calibration curves devised for this analysis of the polymerization of VIVIPRINT 300 could be extended to other polymers with varying amounts of DMAPMA and HEMA.

**Conclusions**

Based only on ATR-FTIR spectroscopy, this study demonstrated that copolymerization reactions using two monomers possessing different reactivities can be successfully monitored in situ. Thus, the prediction of HEMA and DMAPMA copolymerization has been performed, allowing the fast optimization of reaction conditions (initiator and monomer introduction in the reactor). Moreover, it has been possible to predict the experimental conditions to be applied. This methodology is currently under investigation for the monitoring of new radical copolymerizations starting from other monomers.

**References**


