

Off-Line Monitoring of Butyl Acrylate and Vinyl Acetate Homopolymerization and Copolymerization in Toluene

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ABSTRACT: A study of butyl acrylate (BA) and vinyl acetate (VAc) solution homopolymerization and copolymerization in toluene was carried out. The conversion and copolymer composition were monitored using traditional techniques (gravimetry and $^1\text{H-NMR}$ spectroscopy) and attenuated total reflectance-Fourier transform IR (ATR-FTIR) spectroscopy with a diamond-composite probe and light conduit technology. The peak height of the characteristic absorbances of the monomer(s) during the course of the reaction was used to calculate the conversion and copolymer composition for the ATR-FTIR monitoring. The data obtained using a ReactIR™ 1000 reaction analysis system in the off-line mode showed very good agreement with data obtained using traditional techniques. The solvent effects on BA and VAc solution homopolymerizations and copolymerizations in toluene were also investigated. Improvement to model predictions was obtained by allowing the lumped constant ($k_p/k_t^{0.5}$) to vary with the solvent concentration. Experimental data and model predictions of the number- and weight-average molecular weights for the investigated systems are also presented. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2958–2977, 2001

Key words: butyl acrylate; vinyl acetate; solution polymerization; attenuated total reflectance-Fourier transform IR spectroscopy; copolymerization kinetics; modeling

INTRODUCTION

Vinyl acetate (VAc) is a widely used monomer for the production of architectural coatings, adhesives, sealants, and a variety of other products. Some applications require the modification of some of the final product properties. In these applications the VAc monomer is copolymerized with another monomer such as butyl acrylate (BA). The polymer product properties are affected by the copolymer composition, molecular weight, and molecular weight distribution; these are in turn affected by the reactivities of the individual

monomers. Monomer reactivities are described by monomer reactivity ratios, which are parameters in the Mayo–Lewis equation (the terminal model). Because the reactivity ratios for BA (r_{BA}) and VAc (r_{VAc}) are quite different ($r_{\text{BA}} = 5.93$ and $r_{\text{VAc}} = 0.026$), the copolymer composition drift is inevitable during batch polymerizations.¹ One way to deal with composition drift is to predict it with a model and/or monitor the polymerization reaction in real time and take appropriate steps when composition drift is observed (e.g., using semi-batch control policies²).

There are several models proposed for the simulation of free-radical polymerizations. Extensive overviews of the models developed in the last two decades were given by Gao and Penlidis^{3,4} and Dubé et al.⁵ These overviews present models de-

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veloped for the simulation of free-radical homopolymerizations and copolymerizations in bulk and solution under a variety of conditions, reactor configurations, and operating modes. These models were the basis for a model developed by Badeen.⁶ This JAVA™-based model for the simulation of free-radical polymerizations in bulk and solution is used in this work. The model employs terminal model kinetics and the pseudokinetic rate constant method.² The free-volume approach was used for the modeling of diffusion-controlled rate constants.⁷

Techniques for monitoring polymer composition drift are rather limited to date. Despite their accuracy, traditional techniques (e.g., gravimetry and ¹H-NMR spectroscopy) are not very useful when the real-time monitoring of polymerization reactions is required because they result in significant time lags. In recent years several attempts were made to utilize various dielectric, acoustic, and spectroscopic techniques to monitor polymerization reactions.^{8,9} Kammona et al.¹⁰ summarized the recent developments in hardware sensors for on-line conversion and copolymer composition monitoring. Techniques such as near-IR (NIR) and mid-IR (MIR) spectroscopy are attractive to utilize for real-time reaction monitoring because they offer much information about the reaction system at the molecular level. Most of the early work reported the utilization of NIR spectroscopy^{11–13} or MIR spectroscopy^{14,15} through instruments developed in-house.

The ReactIR™ 1000 (ASI Applied Systems Inc.) commercial instrument was recently developed for monitoring chemical reactions. Attenuated total reflectance—Fourier transform IR spectroscopy (ATR-FTIR) was combined with new technological achievements (i.e., light conduit technology and a diamond-composite insertion probe) to form a powerful tool for real-time, *in situ*, and off-line chemical process monitoring. The reaction pathway and kinetic information can be obtained without complicated reactor modifications and sample handling. Some of the results on the use of this state of the art instrument in polymer reaction engineering were already reported: Storey et al.^{16,17} used the ReactIR 1000 to monitor carbocationic polymerizations of isobutylene and Pasquale and Long¹⁸ used it to monitor stable free-radical polymerizations of styrene. The excellent performance of the instrument was outlined therein.

The BA and VAc solution homo- and copolymerizations in toluene have been investigated

only sparingly. Aside from the work by McKenna et al.,¹⁹ McKenna and Villanueva,²⁰ and Othman et al.,²¹ recent literature studies on solution homo- and copolymerizations of BA and VAc are scarce. Copolymerization of these two monomers in aromatic solvents such as toluene can be challenging for process modeling because very significant radical–solvent effects take place. Even though there are several mechanisms by which a solvent can affect the propagation kinetics of free-radical polymerization reactions, it is commonly believed that in vinyl monomers the formation of complexes of the propagating radicals and an aromatic solvent is taking place.^{22,23} Coote et al.²³ stated that radical–solvent complexes are favored in systems containing unstable radical intermediates (such as VAc) in which complexation may lead to the stabilization of these radicals and therefore to the reduction of the propagation rate constant. On the other hand, the termination rate constant might be chain-length dependent.^{19–21,24} In case of extremely high rates of transfer to the solvent, this would lead to an increase in the termination rate constant with the solvent concentration.^{19–21} Gaining insight into the influence of solvents on the propagation and termination rate constants is further complicated by the fact that, even when the pulsed laser polymerization technique is employed, it is difficult to determine absolute values of these constants for BA and VAc.²⁵ In light of these challenges, the most suitable approach at this time is to estimate the value of the “lumped” kinetic constant (the ratio of the propagation rate constant to the square root of the termination rate constant, $k_p/k_t^{0.5}$). This approach was recently used by McKenna et al.¹⁹ and McKenna and Villanueva²⁰ for the solution homopolymerizations of BA and VAc in toluene and ethyl acetate and the copolymerization of BA/VAc in ethyl acetate.

The primary focus of the work reported herein was to monitor the homo- and copolymerizations of BA and VAc in toluene solution using an ATR-FTIR probe. The first steps involved the use of the probe in an off-line mode to determine the conversion and copolymer composition and to compare these results to those using conventional off-line measurement techniques. This procedure involved the identification of characteristic IR absorbance peaks for each monomer and the use of these peaks to follow the reaction profile. A secondary goal was to continue ongoing polymerization model development. The data collected in this study were used to evaluate our JAVA-based

model and direct further experimentation. An investigation of suspected solvent effects was also undertaken.

EXPERIMENTAL

Reagent Purification

The BA and VAc (Sigma–Aldrich) were received inhibited by 0.05 ppm hydroquinone. To remove the inhibitor the VAc was distilled under a vacuum and the BA was washed 3 times with a 10% (v/v) sodium hydroxide solution, washed 3 times with distilled deionized water, dried over calcium chloride, and vacuum distilled. Distillations were completed a maximum of 24 h prior to polymerization, and the monomers were stored at -10°C . The initiator 2,2'-azobisisobutyronitrile (Sigma–Aldrich) was recrystallized 3 times in absolute methanol. The toluene solvent (ACP Chemicals), *n*-dodecyl mercaptan chain transfer agent (CTA, Sigma–Aldrich), and all other solvents used for sample characterization were used without further purification.

Procedures

The monomer feed was prepared by weighing the monomer(s), solvent, CTA, and initiator into a flask. The feed was pipetted into a series of 5-mL glass ampoules (17-cm length, 0.8-cm outer diameter). The ampoules were degassed by several freeze–thaw cycles under high vacuum. After sealing, the ampoules were weighed and subsequently submerged in a constant temperature water bath. At the appropriate time interval, two ampoules were removed from the bath simultaneously and placed in an ice bath to quench the reaction.

One ampoule was used for the determination of conversion by the traditional gravimetric tech-

Table I Experimental Conditions

Experiment	BA (wt %)	VAc (wt %)	Toluene (wt %)	AIBN (mol/L)	CTA (mol/L)
BT55	50	—	50	0.002	0.02
BT28	20	—	80	0.002	0.02
VT55	—	50	50	0.105	0.02
VT28	—	20	80	0.105	0.02
BVT55	25	25	50	0.002	0.02
BVT28	20	40	50	0.002	0.02

Table II Mark–Houwink Parameters

Polymer	$K (\times 10^3 \text{ mL/g})$	α	Reference
Poly(butyl acrylate)	11	0.708	19
Poly(vinyl acetate)	15.6	0.708	29
Polystyrene	16	0.700	30

nique. The ampoule was broken, the contents poured into a preweighed crystallizing dish, and a 10-fold excess of ethanol was added. After evaporation of the solvents, the precipitated polymers were dried in a vacuum oven at 30°C until a constant weight was reached. After being dried the polymers were weighed and analyzed for conversion. For the copolymerization the dry polymers were analyzed for cumulative copolymer composition using $^1\text{H-NMR}$ spectrometry.

The second ampoule was used for the ATR-FTIR measurements. When the ampoule was broken, part of its contents were weighed and toluene was added to the vial to ensure that enough sample was present to fully immerse the probe. After the collection of spectra of the air as a background, the ATR-FTIR probe was immersed in the vial and spectra were recorded at a resolution of 8 cm^{-1} . There were 64 scans, and less than 1 min was required to collect a spectrum.

The cumulative number- and weight-average molecular weights were determined using gel permeation chromatography.

The solution polymerization experimental conditions are summarized in Table I. All reactions were carried out at 60°C .

Product Characterization

ATR-FTIR

Polymerization reactions were monitored off-line using an ATR-FTIR spectrometer-ReactIR™ 1000. The instrument is primarily designed for in-line monitoring of chemical reactions in the MIR spectral region ($4000\text{--}650 \text{ cm}^{-1}$), but our intention was to employ it off-line to test its capabilities and limitations before its in-line utilization in our pilot-scale reactor. In this reaction monitoring system the traditionally used fiber optic probe technology has been replaced by light conduit technology, which consists of six mirrors and three tubes that provide a purged path through which the IR beam travels to a remote sampling device and back to a detector. The sampling device is a dia-

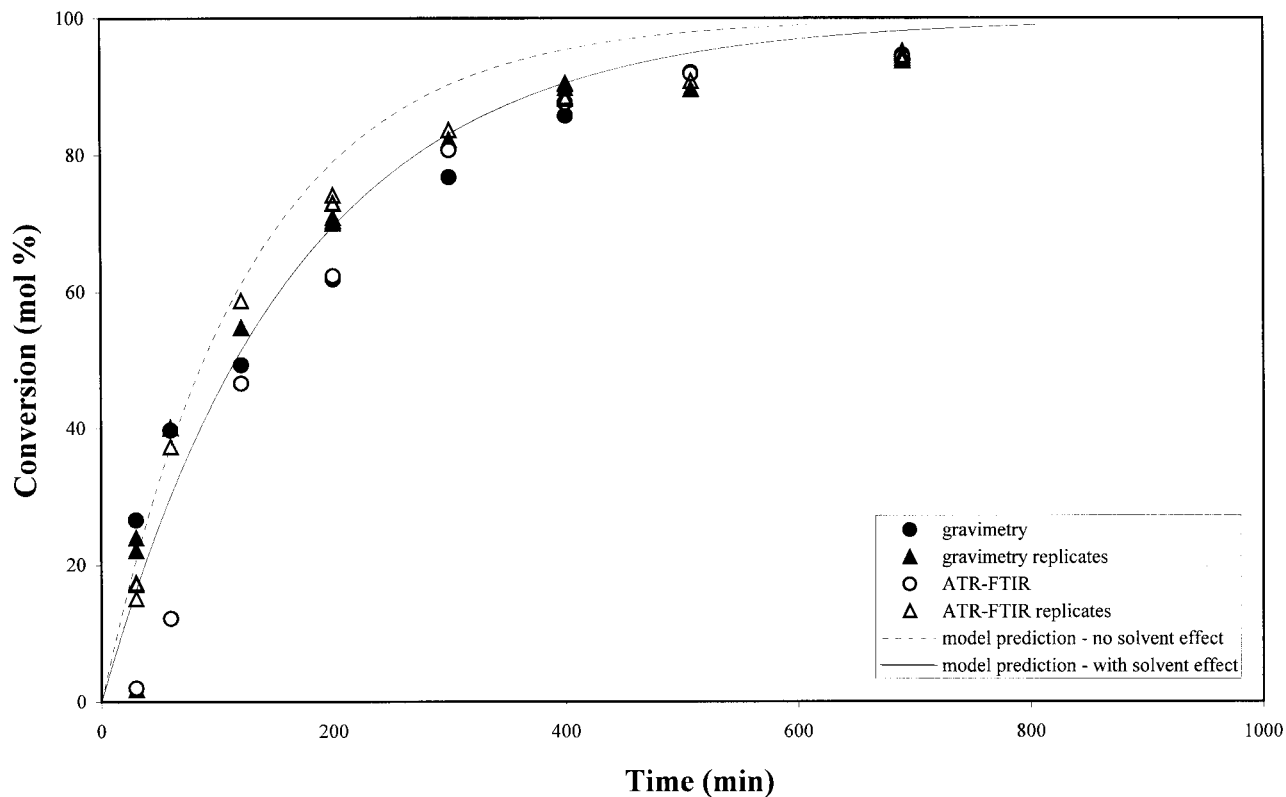


Figure 1 Conversion versus time for BA solution homopolymerization in toluene (50/50 wt %).

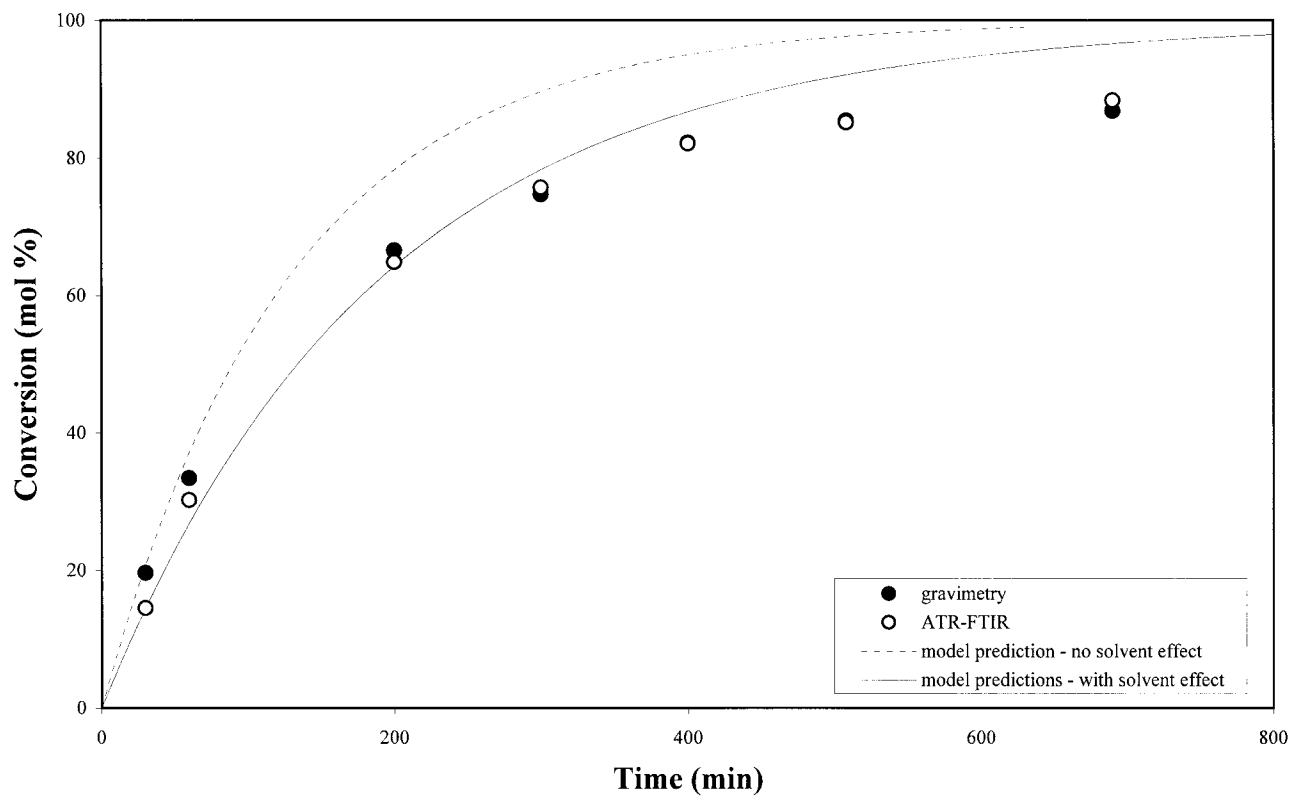


Figure 2 Conversion versus time for BA solution homopolymerization in toluene (20/80 wt %).

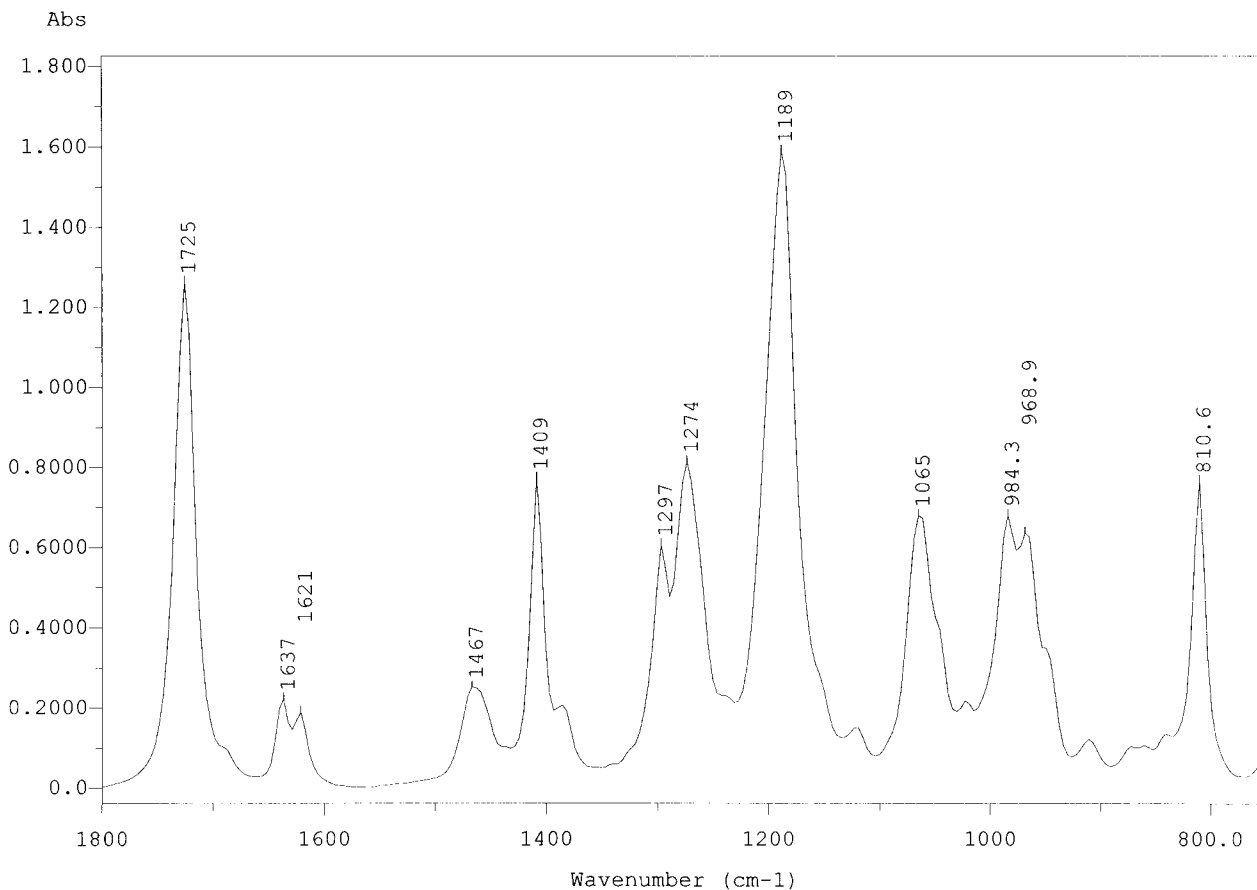


Figure 3 ATR-FTIR spectra of the BA monomer.

mond-composite (DiComp) insertion probe with a stainless steel body (18.42-cm. length, 1.59-cm. diameter) and a six reflection bilayer ATR element with a diamond surface element (6-mm diameter, 0.25-mm thickness) at the top. Interfacing with the diamond and acting as a focusing

element is an IR transmitting optic (a focusing crystal made of composite material). The design enables IR radiation to enter the focusing crystal and then, in a controlled manner, the side of the diamond disk. Once inside the disk, it forms a standing wave of radiation called an evanescent wave that penetrates a finite distance into a sample. The distance is called the depth of penetration (DP), and it is analogous to the path length in transmission sampling techniques. The DP is given by the following equation²⁶:

Table III Vibrational Assignments for Butyl Acrylate

Wavenumber (cm ⁻¹)	Peak Assignment
1725	C=O stretching
1640	C=C stretching
1409	=CH ² deformation
1274	=CH rock
1189	C—O asymmetric stretching
1065	=CH ₂ rock
984.3	trans CH wag
968.9	=CH ₂ wag
810.6	=CH ₂ twist

$$DP = \frac{1}{2\pi W N_c (\sin^2 \Theta - N_{sc}^2)^{1/2}} \quad (1)$$

where W is the wavenumber, N_c and N_{sc} are the crystal refractive index and ratio between the sample and crystal refractive indices, respectively, and Θ is the angle of incidence. It can be seen that the absorption intensity at a certain frequency is proportional to the wavenumber for constant N_c , N_{sc} , and Θ values. As a consequence,

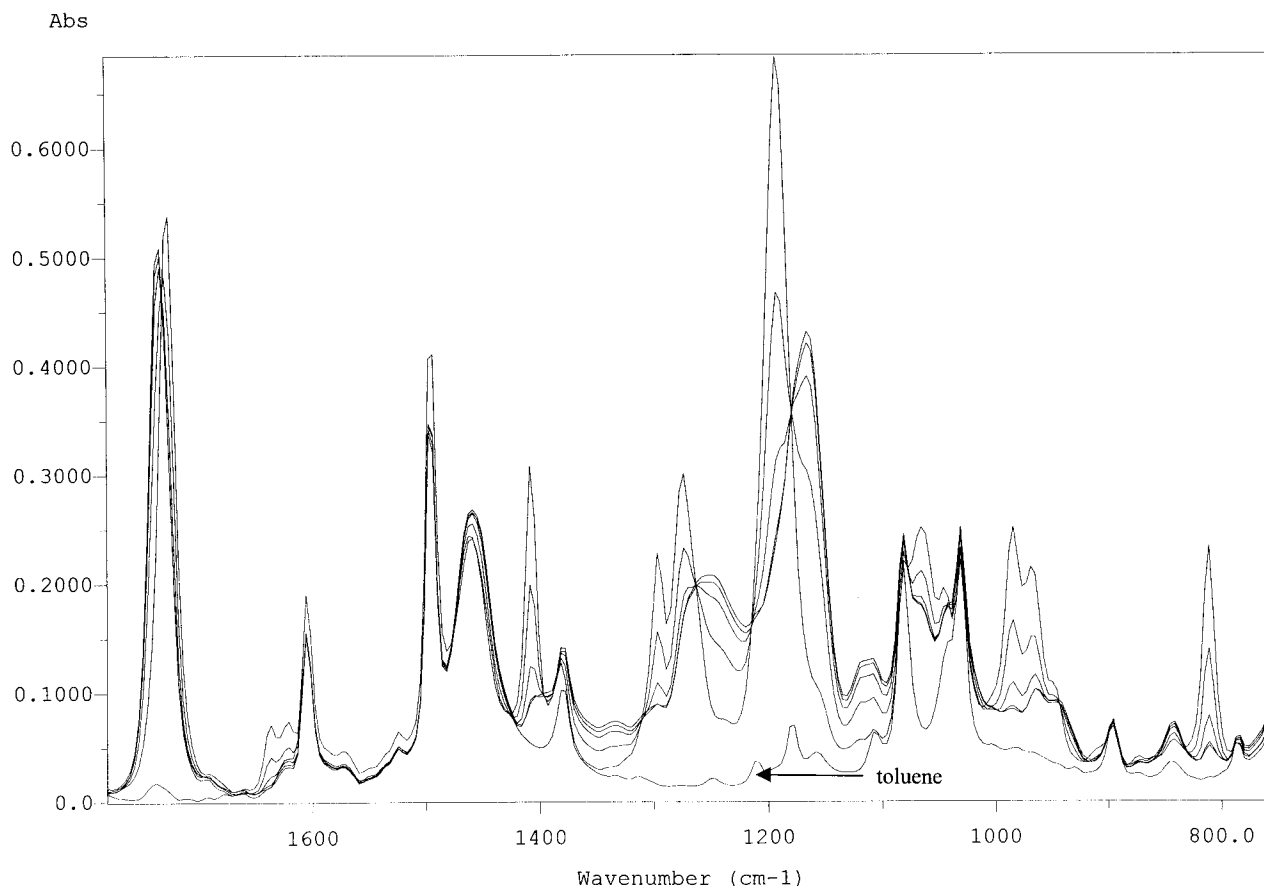


Figure 4 ATR-FTIR spectra of BA solution homopolymerization in toluene (50/50 wt %).

the peaks are more intense at a low wavenumber than at a high wavenumber because the low wavenumber radiation penetrates further into the sample.

The basis for monitoring polymerization reactions is the determination of the characteristic peaks that represent functional groups inside a monomer or polymer and tracking their absorbances throughout the course of the reaction. The determination of characteristic peaks is straightforward because the MIR spectra consist of well-defined fundamental vibrational frequencies that correspond to specific functional groups and interactions between them. According to Beer's law, the concentration of a component is proportional to the absorbance, which can be measured as the peak height, peak height ratio, peak area, or peak area ratio. In our case, the peak height was found to give the best results. The peak heights were determined after a baseline correction. Following the general rule that the less manipulation of the original spectra, the less error induced in the quantitative analysis,²⁶ the subtraction of the sol-

vent spectra was omitted because the solvent was not absorbing at the same wavelength as the chosen characteristic peaks. The following equations were used for determination of the conversion (x) of individual monomers,

$$x \text{ (mol \%)} = 1 - \frac{\text{peak height at } t}{\text{peak height at } t = 0} \times 100 \quad (2)$$

where t is the time, and the overall conversion (X) for the copolymerization,

$$X \text{ (mol \%)} = \frac{n_1}{n_1 + n_2} x_1 \text{ (mol \%)} + \frac{n_2}{n_1 + n_2} x_2 \text{ (mol \%)} \quad (3)$$

where $n_i/(n_i + n_j)$ denotes the mole fraction of monomer i in the reaction mixture. This method was previously reported by Chatzi et al.¹⁵

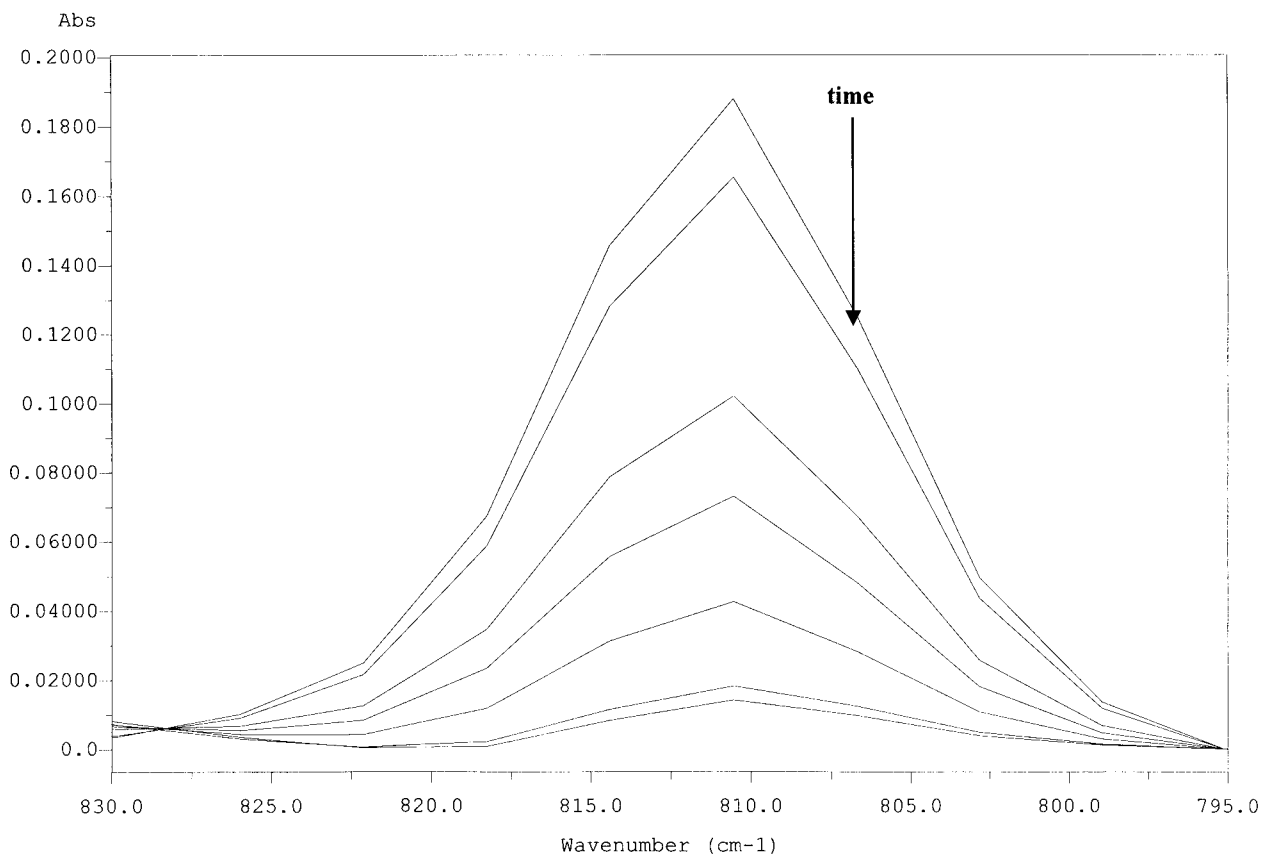


Figure 5 Changes in the absorbance of BA monomer during the course of the reaction.

ReactIR™ software was used for the postprocess data analysis.

Gravimetry

Gravimetry was used for the determination of X (mass %) and was based on the total polymer. The following equation was used:

$$X = \frac{\text{wt. of dish with dry polymer} - \text{wt. of empty dish}}{[(\text{wt. of ampoule and reaction mixture} - \text{wt. of empty ampoule}) \times (\text{wt. fraction of total monomer(s) in reaction mixture})]} \times 100 \quad (4)$$

For the copolymerization the mass percentage of conversion was transformed into the mole percentage of conversion using the cumulative copolymer composition data in order to compare the gravimetric and ATR-FTIR data.

$^1\text{H-NMR}$ Spectroscopy

Cumulative copolymer compositions were determined using a Bruker AMX-500 Fourier trans-

form $^1\text{H-NMR}$ spectrometer. The analyses were carried out in deuterated chloroform [chloroform- d , approximate 2% (w/v) solution] at room temperature. A standard one-pulse experiment was employed using 45° pulses. Sixteen transients, each 4.6 s in duration with no additional relaxation delay, were signal averaged and Fourier transformed. The relative amounts of monomer bound into the polymer were estimated using the areas under the appropriate absorption peaks. A good separation of the spectral peaks of the $-\text{OCH}_2$ group in BA ($\delta \approx 4.0$ ppm) and the α -hydrogen in VAc ($\delta \approx 4.9$ ppm) was achieved, thus allowing the unambiguous interpretation of the results. The following expressions were used to calculate the mole fractions of BA (\bar{F}_{BA}) and VAc (\bar{F}_{VAc}) monomer bound into the polymer:

$$\bar{F}_{\text{BA}} = \frac{\frac{A_{\text{BA}}}{2}}{A_{\text{VAc}} + \frac{A_{\text{BA}}}{2}} \quad (5)$$

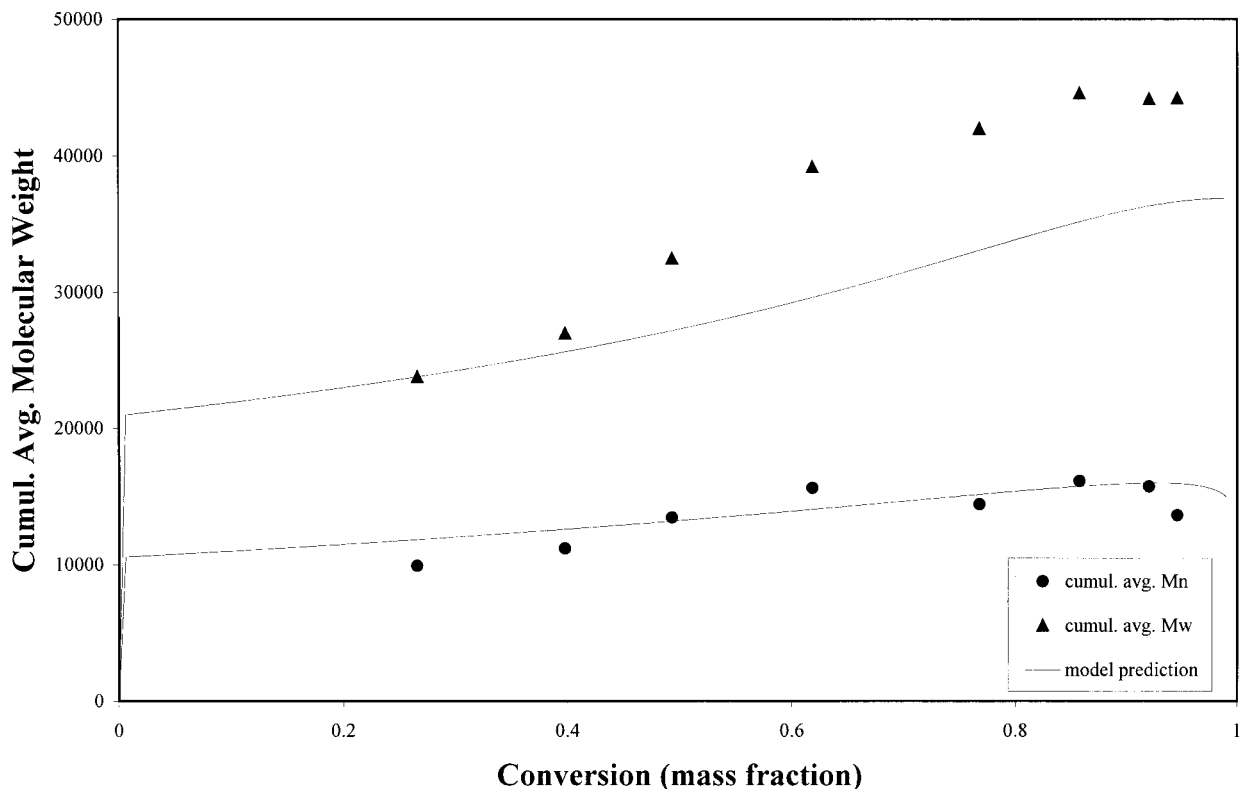


Figure 6 Cumulative average molecular weight versus conversion for BA solution homopolymerization in toluene (50/50 wt %).

$$\bar{F}_{\text{VAc}} = \frac{A_{\text{VAc}}}{A_{\text{VAc}} + \frac{A_{\text{BA}}}{2}} \quad (6)$$

where A_{BA} and A_{VAc} represent the areas under the VAc and BA spectral peaks, respectively. The use of these spectral peaks for the determination of the cumulative copolymer composition was reported previously.^{27,28}

Gel Permeation Chromatography

The cumulative number- and weight-average molecular weights were determined using gel permeation chromatography. A Waters Associates gel permeation chromatograph equipped with a Waters model 410 refractive index detector was employed. Three Waters Ultrastyrigel packed columns (10^3 , 10^4 , and 10^6 Å) were installed in series. Tetrahydrofuran (THF, HPLC grade, EM Science) was filtered and used as the eluent at a flow rate of 0.3 mL/min at 38°C. Calibration of the instrument was performed with 10 standard sam-

ples of polystyrene (Shodex) with peak molecular weights between 1.3×10^3 and 3.15×10^6 g/mol. Standards and samples were prepared in THF [0.2% (w/v) solutions] and filtered prior to injection through 0.45- μm filters to remove high molecular weight gel, if present. Millennium 32™ software (Waters) was used for data acquisition and manipulation.

The absolute cumulative number- and weight-average molecular weights were determined using a universal calibration curve. The Mark-Houwink K and α parameters determined in THF as a solvent are given in Table II.^{29,30}

For the copolymers the weighted averages of the K and α values were calculated using the cumulative copolymer composition data obtained earlier using $^1\text{H-NMR}$ spectrometry. The observed difference between the relative and absolute values of the number- and weight-average molecular weights for most of the samples was minimal because the K and α values for the polymers and polystyrene standards were close.

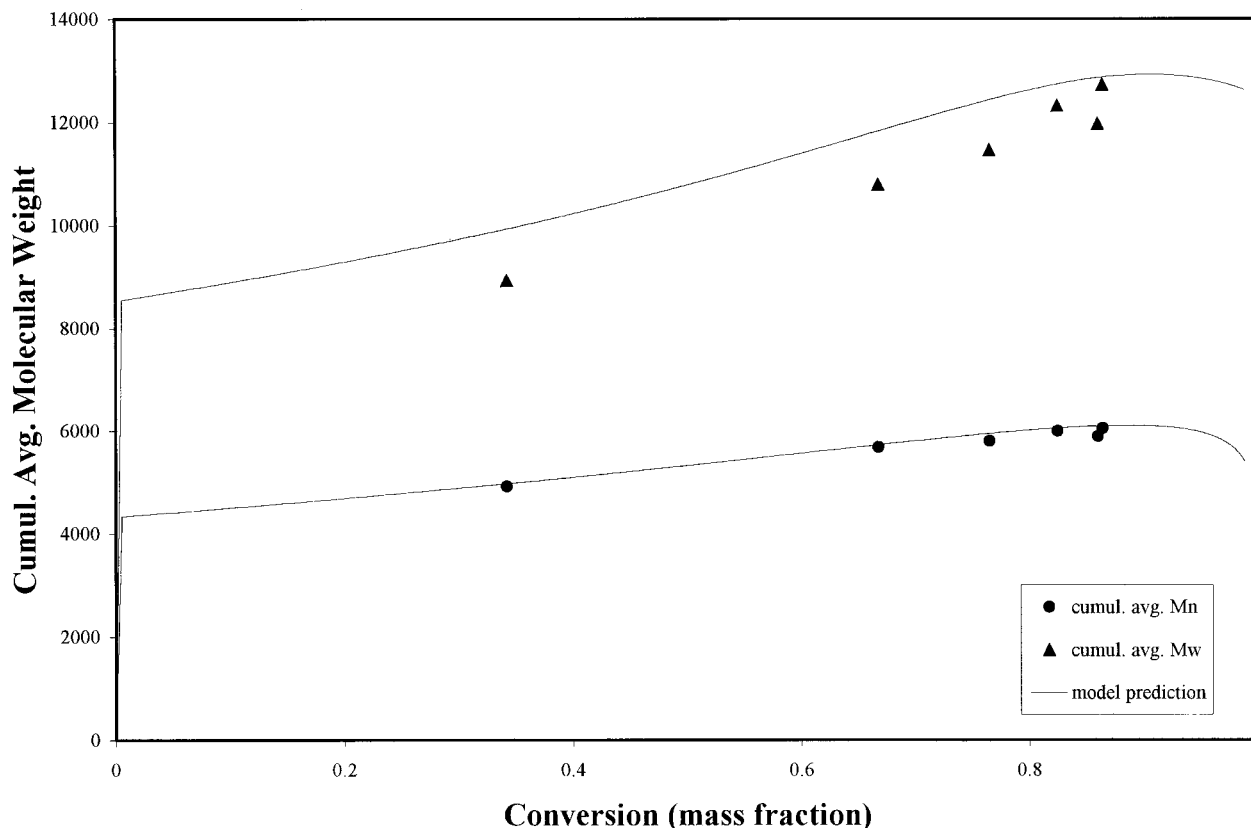


Figure 7 Cumulative average molecular weight versus conversion for BA solution homopolymerization in toluene (20/80 wt %).

RESULTS AND DISCUSSION

BA Homopolymerizations

Two BA homopolymerizations in toluene were carried out with different monomer concentrations (see Table I). The experimental data for BA/toluene ratios of 50/50 and 20/80 wt %, which were obtained using the ReactIR™ 1000, are compared to gravimetric data in Figures 1 and 2, respectively.

The first step after the spectra were collected was to make peak assignments and determine which of the peaks could be used to calculate the conversion. For the purposes of peak assignments, the spectra of the BA monomer shown in Figure 3 were collected under conditions similar to the reaction spectra. The assignments for the major peaks are given in Table III.^{31,32}

After careful examination of the spectra collected during the BA polymerization in toluene (Fig. 4), several peaks (1409, 1193, 984.3, 968.9, and 810.6 cm^{-1}) were identified as appropriate for use in the quantitative estimation of the con-

version of the BA monomer. Because the subtraction of the solvent was intentionally omitted, the number of peaks that could have possibly been used for monitoring the monomer conversion was reduced. After baseline correction the calculation using the peak height referenced to a two-point baseline for the absorbance band at 810.6 cm^{-1} ($=\text{CH}_2$ twist) was found to give the best predictions of monomer conversion compared to the gravimetric data. The conversion was calculated using eq. (2). The absorbance (peak height) at time zero was the absorbance (peak height) of the reaction mixture collected prior to polymerization. The change of the absorbance (peak height) during the course of the reaction is given in Figure 5.

The same 810.6 cm^{-1} peak was used to obtain the conversion versus time data for both polymerization reactions (50/50 and 20/80 wt % BA/toluene). There was no need to subtract the solvent spectra from the overall spectra because toluene does not absorb in the range (i.e., 830–790 cm^{-1}) where the absorbance of BA was observed. Good

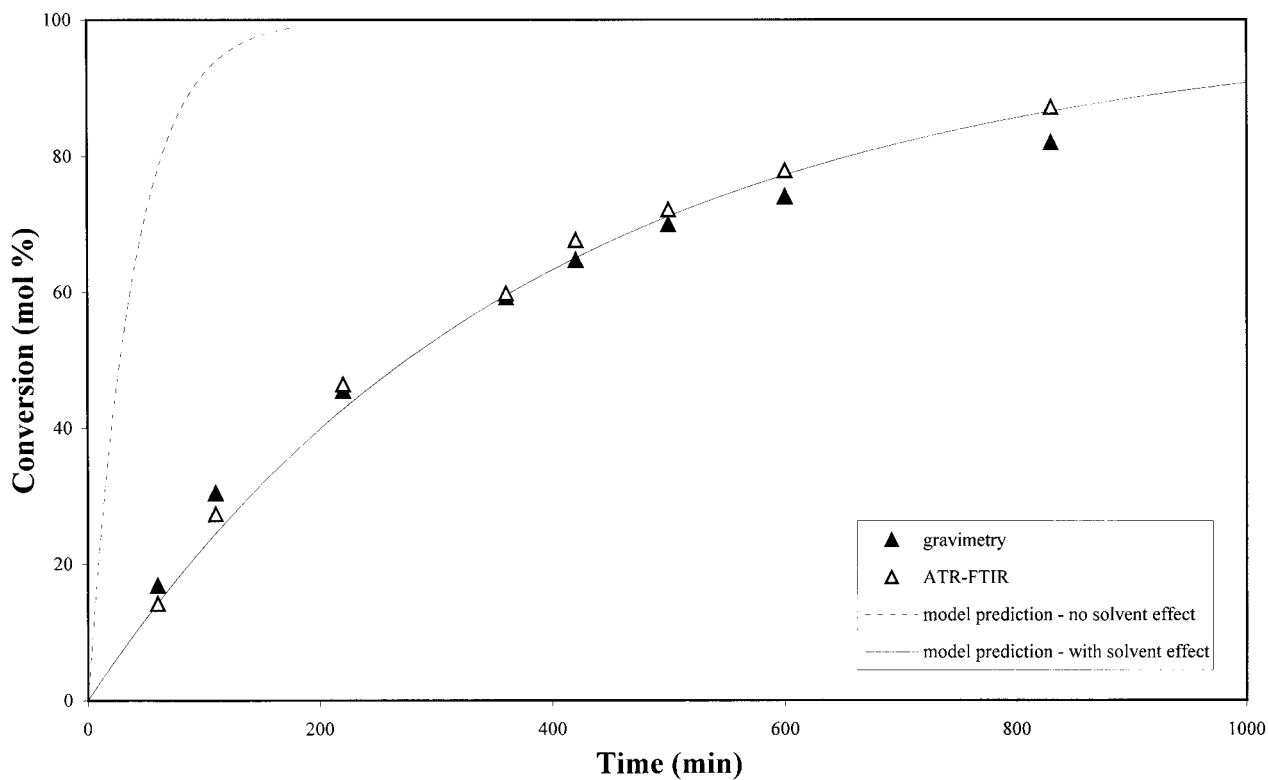


Figure 8 Conversion versus time for VAc solution homopolymerization in toluene (50/50 wt %).

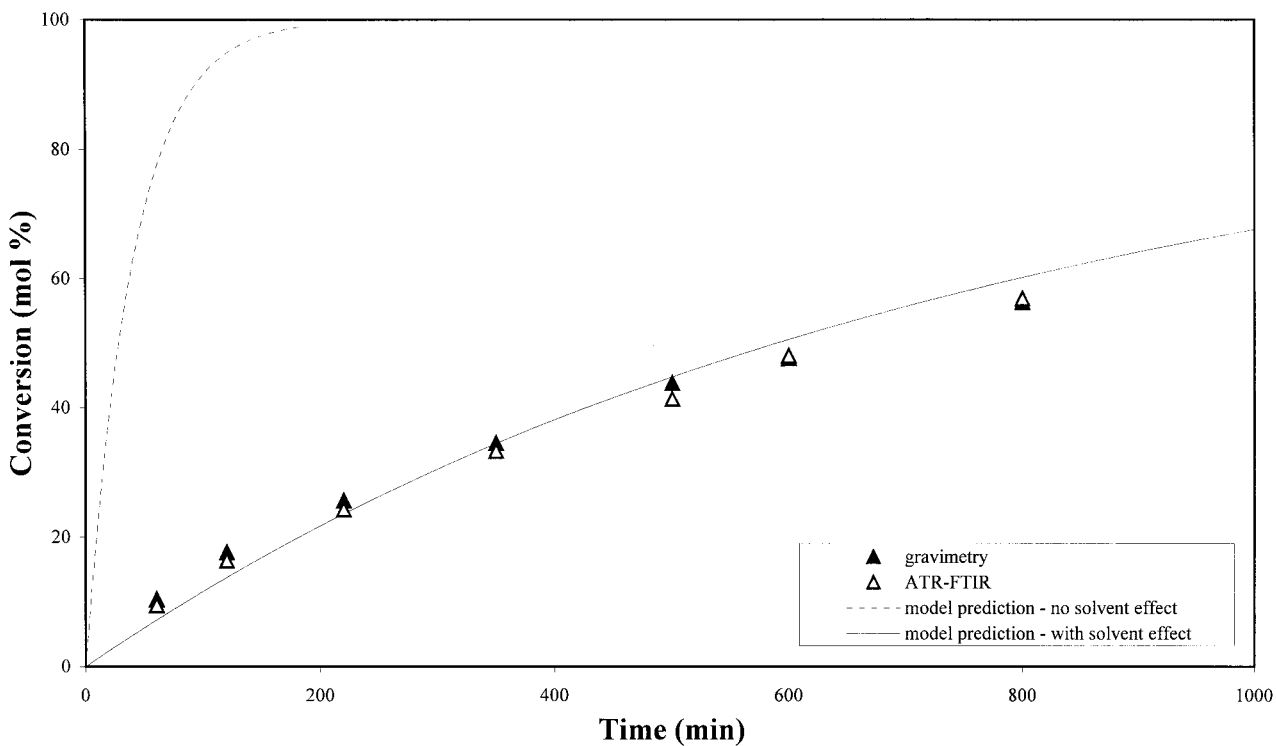


Figure 9 Conversion versus time for VAc solution homopolymerization in toluene (20/80 wt %).

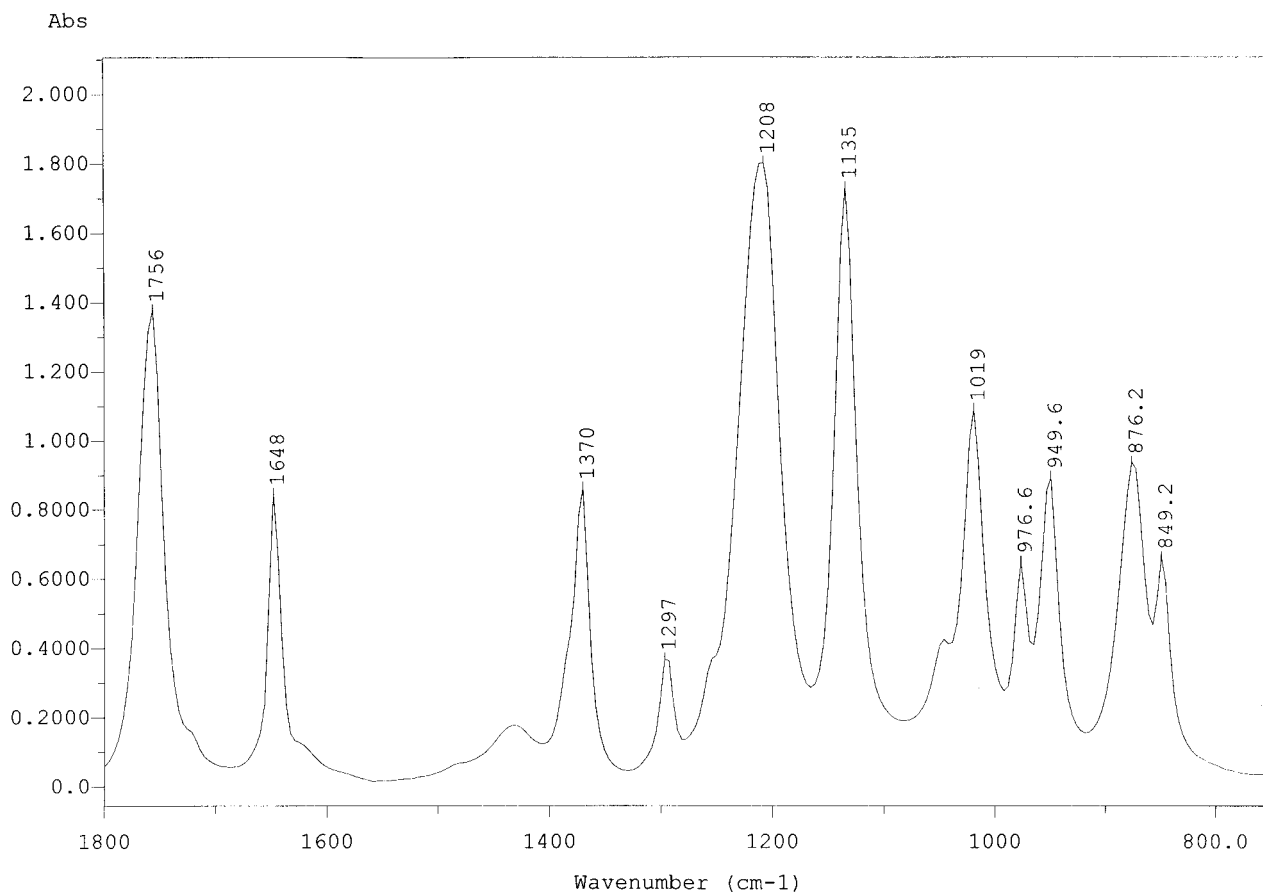


Figure 10 ATR-FTIR spectra of the VAc monomer.

agreement between the data obtained by gravimetry and the ATR-FTIR probe was observed as shown in Figures 1 and 2. One should recall that separate ampoules were used for each measurement and two ampoules were quenched simultaneously: one was analyzed by gravimetry and the

other was analyzed using ATR-FTIR. For certain ampoules inadequate degassing resulted in an induction time and lower than expected conversions (see the low conversion samples in Fig. 1). To verify these results, several repeated runs were performed and they revealed that the results were within experimental error. The obtained results confirmed that the monitoring of BA homopolymerizations in solution using an ATR-FTIR probe in an off-line mode is not only possible but also sufficiently accurate.

In our attempt to model BA solution homopolymerizations, we were faced with the fact that BA rate constants are affected by the presence of solvent in the reaction mixture.²³ The value of the ratio of the propagation rate constant (k_p) and the square root of the termination rate constant (k_t), henceforth referred to as the lumped constant ($k_p/k_t^{0.5}$), depends on the concentration of BA in a reaction mixture. Its value increases with the concentration of BA. This effect was observed for methyl methacrylate homopolymerization in ben-

Table IV Vibrational Assignments for Vinyl Acetate

Wavenumber (cm^{-1})	Peak Assignment
1725	C=O symmetric stretching
1648	C=C stretching
1370	CH ₃ symmetric deformation
1290	C—O stretching
1208	C—C—O symmetric stretching
1135	C—O stretching
1019	C—O—C symmetric stretching
949.6	trans CH wag
876.2	—CH ₂ wag

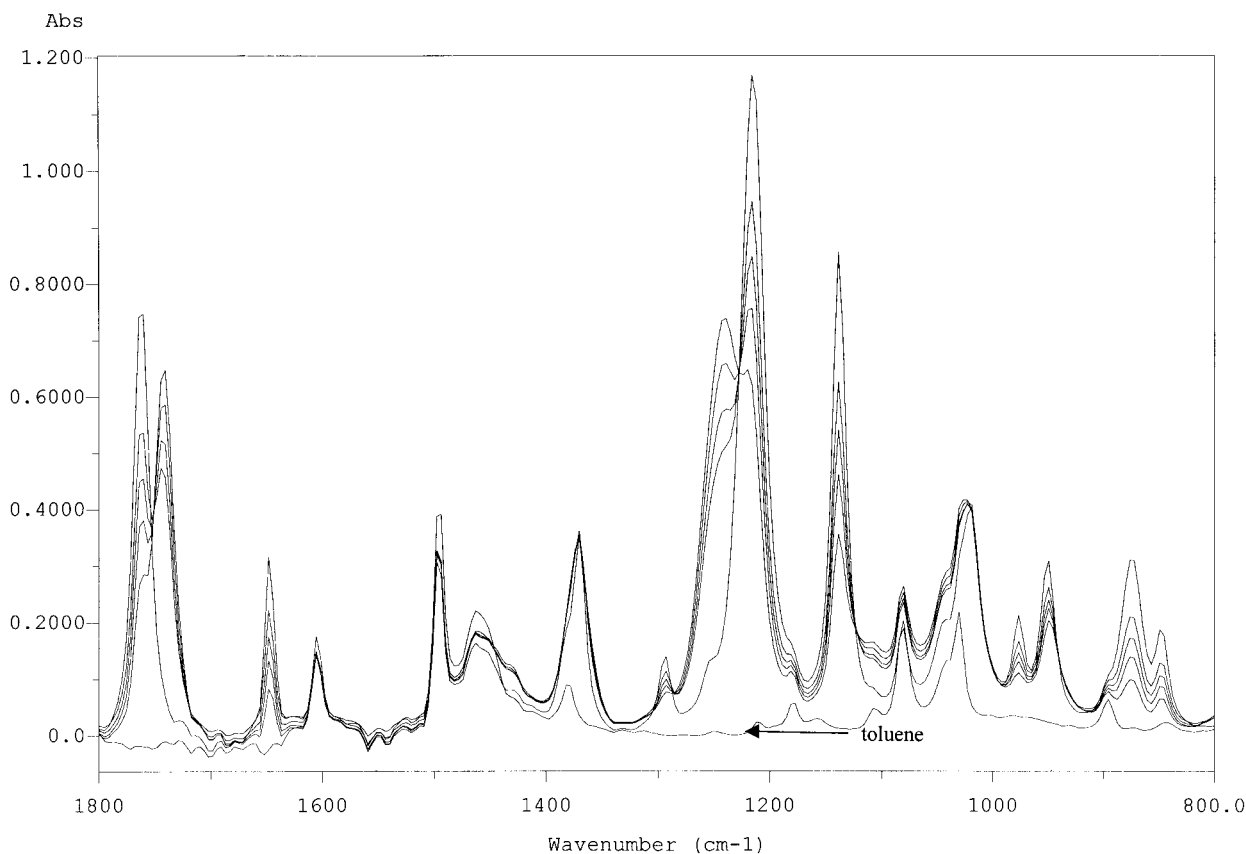


Figure 11 ATR-FTIR spectra of VAc solution homopolymerization in toluene (50/50 wt %).

zene³³ and for BA and VAc homopolymerizations in toluene and benzene.^{19,20} Both groups suggested that it was unlikely that the k_p was significantly affected by the solvent concentration.^{19,20,33} The variation of the lumped constant with the solvent concentration might instead be explained by the chain-length dependence of k_t .²⁴ Thus, short chain radicals would have higher values of k_t compared to longer ones and therefore lower $k_p/k_t^{0.5}$ values. McKenna et al.¹⁹ and Othman et al.²¹ used this concept to explain variations in the lumped constant values for BA and VAc polymerizations in different solvents. The high number of chain transfer to solvent reactions that take place in these systems leads to the formation of a considerable fraction of short chain radicals. Because short radicals move and terminate more quickly, the value of the termination rate constant will increase and the value of the lumped constant will decrease with an increase in the solvent concentration. In light of the experimental difficulties involving the determination of the absolute rate constants for these systems,²⁵ it

is impossible to say with certainty that changes in k_t exclusively cause the variation of the lumped constant with the solvent concentration.

In Figures 1 and 2 two model predictions are shown for each run. Use of our JAVATM-based model⁶ with bulk polymerization rate constants resulted in reasonable but not sufficiently accurate predictions (Figs. 1, 2). In light of the previous discussion, the value of the lumped constant was then changed with the solvent (or monomer) concentration. The values for k_t at 60°C that showed the best fit to experimental data were $(2.67$ and $2.13) \times 10^8$ L/mol/s for 20 and 50 wt % of BA in the reaction mixture, respectively. The value of the lumped constant was increased from 4.89 to 5.47 as the concentration of BA increased. The chain transfer to monomer constant (the ratio of the propagation rate constant over the chain transfer to the monomer rate constant, C_{fm}) was 1.44×10^{-4} . McKenna et al.¹⁹ reported a C_{fm} of 1×10^{-4} while a C_{fm} of 6.6×10^{-5} was obtained using Maeder and Gilbert's³⁴ parameters in an Arrhe-

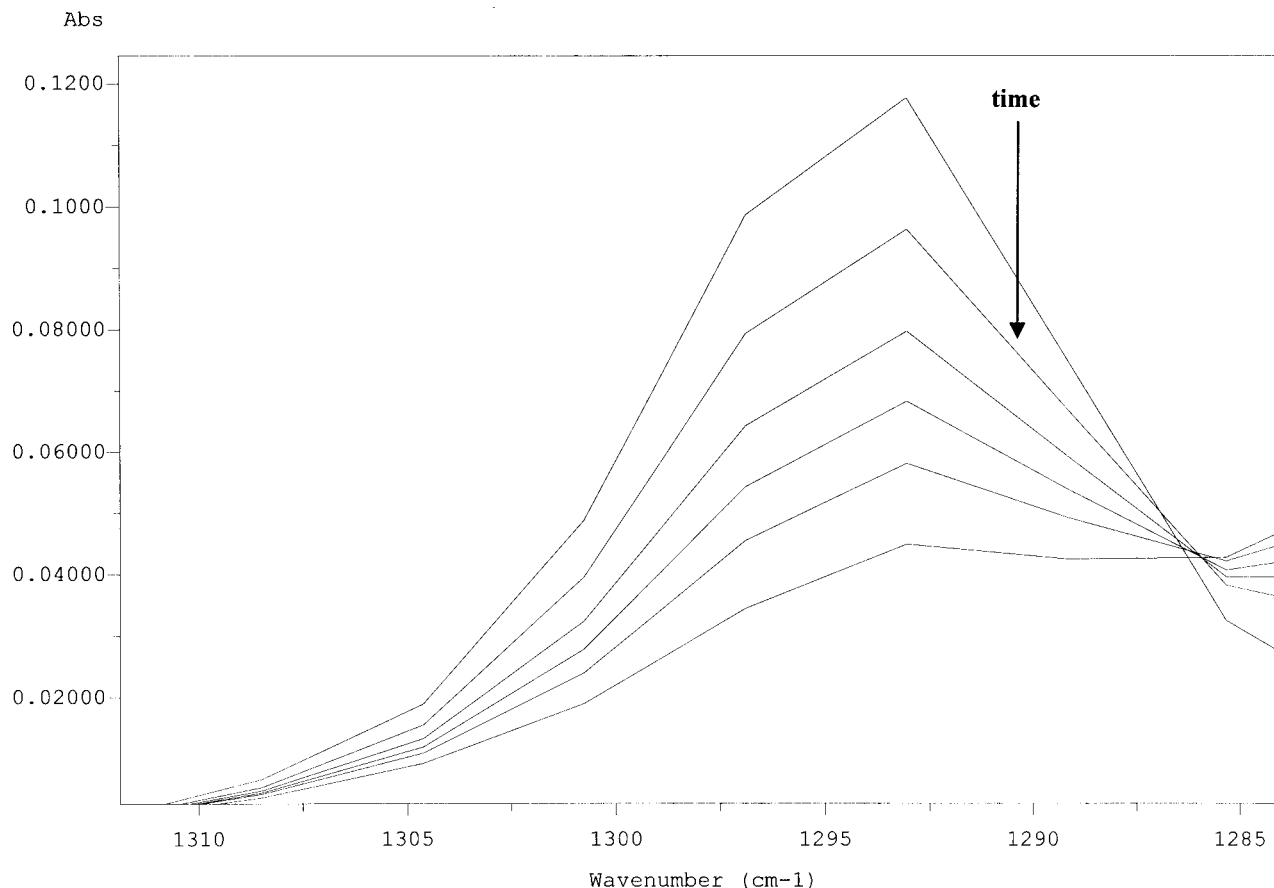


Figure 12 Changes in the absorbance of the VAc monomer during the course of the reaction.

nius expression for C_{fm} at 60°C. The value used for the chain transfer to solvent constant (the ratio of the propagation rate constant over the chain transfer to solvent rate constant, C_{fs}) was 3.25×10^{-4} , which is close to a C_{fs} value of 1.8×10^{-4} reported by McKenna et al.¹⁹ The chain transfer to CTA constant (the ratio of the propagation rate constant over the chain transfer to CTA rate constant, C_{fCTA}) was 1.9. De la Fuente and Madruga³⁵ reported C_{fCTA} values of 0.455–1.056 for *n*-dodecyl mercaptan in the copolymerization of BA with methyl methacrylate at 60°C, which depended on the feed composition and the method used for determination of the chain transfer constant. Use of the above parameters resulted in improved model predictions (Figs. 1, 2).

Changes in the cumulative number- and weight-average molecular weights with conversion for 50/50 and 20/80 wt % BA/toluene are presented in Figures 6 and 7, respectively. In comparing these two figures it is evident that the cumulative num-

ber- and weight-average molecular weights increased with the monomer concentration. The model predictions were obtained by accounting for the solvent effect. The molecular weight predictions were very sensitive to changes in the lumped rate constant: model predictions without the solvent effect were an order of magnitude higher than the experimentally observed values.

The individual influence of the chain transfer reactions on the molecular weight development was also investigated. Using the instantaneous molecular weight distribution method (for demonstration purposes only, because branching reactions are present for these polymerization systems), the instantaneous number- (M_n) and weight-average molecular weights (M_w) can be expressed as

$$M_n = \frac{(MW)_m}{\tau + \beta} \quad (7)$$

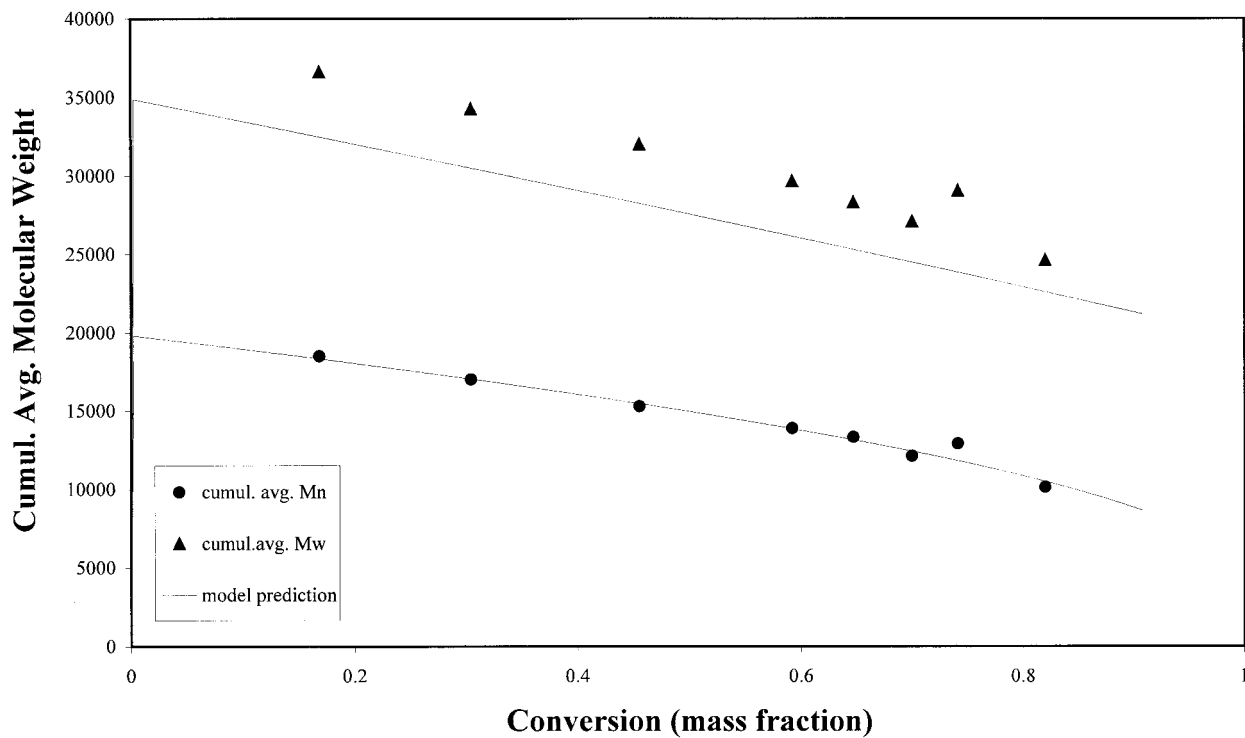


Figure 13 Cumulative average molecular weight versus conversion for VAc solution homopolymerization in toluene (50/50 wt %).

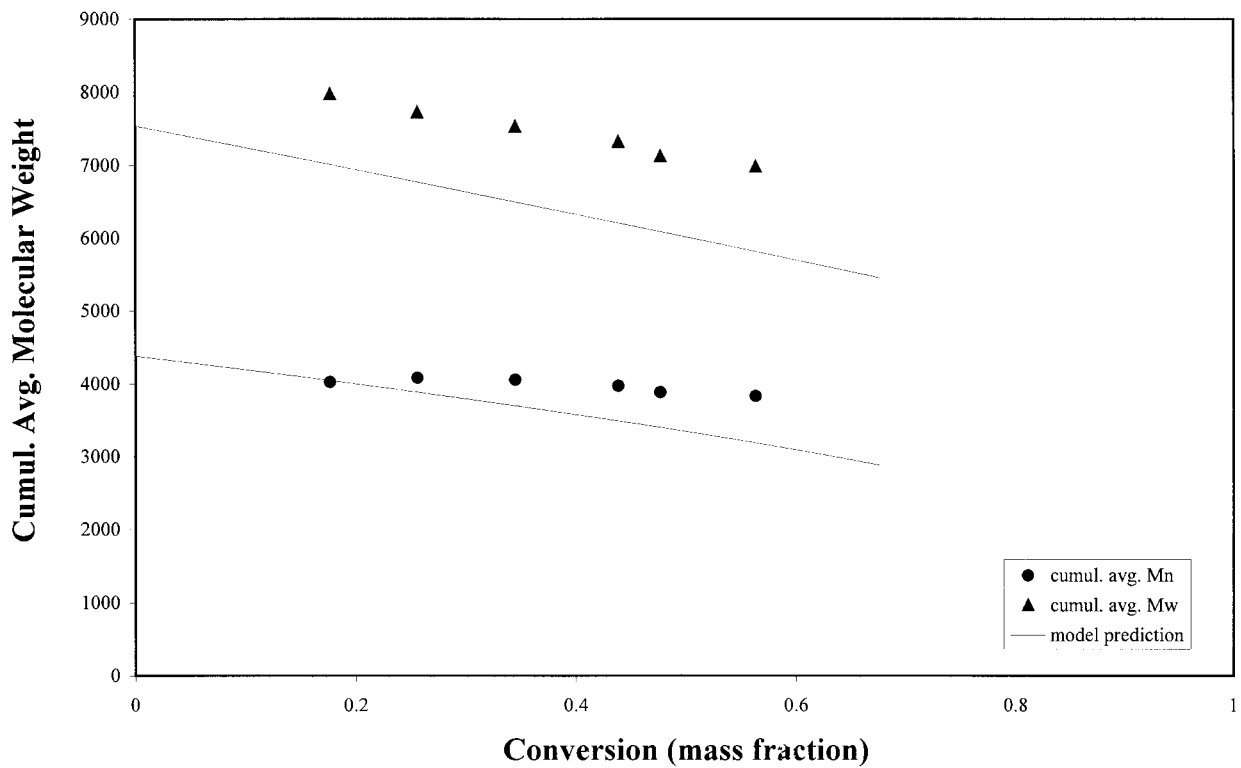


Figure 14 Cumulative average molecular weight versus conversion for VAc solution homopolymerization in toluene (20/80 wt %).

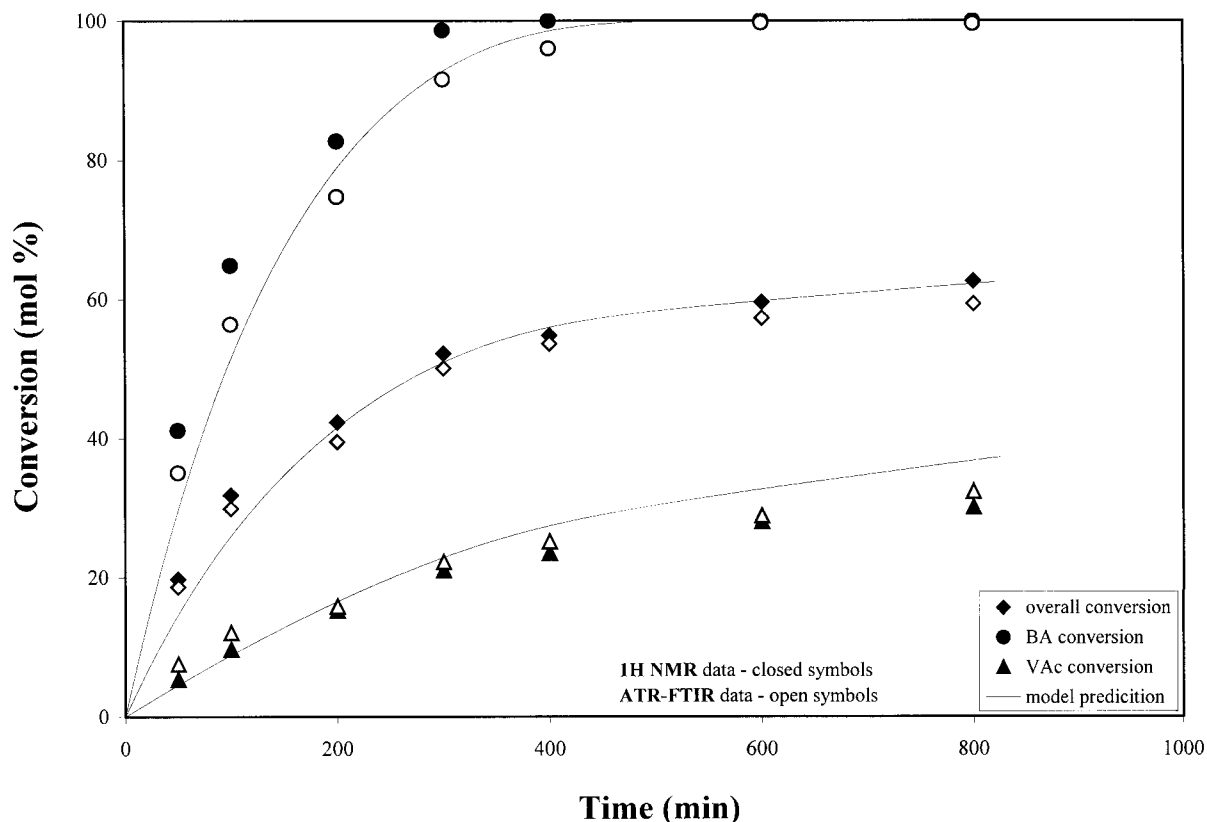


Figure 15 Conversion versus time for BA/VAc (50/50 wt %) solution copolymerization in toluene (50 wt %).

$$M_w = \frac{(MW_m)(2\tau + 3\beta)}{(\tau + \beta)^2} \quad (8)$$

where MW_m represents the molecular weight of the repeat unit, τ is the molecular weight contribution due to termination by disproportionation and transfer to small molecules, and β is the molecular weight contribution due to termination by combination. These are given as

$$\tau = \frac{k_{td}R_p}{(k_p[M])^2} + C_{fm} + C_{fs} \frac{[S]}{[M]} + C_{fcta} \frac{[CTA]}{[M]} \quad (9)$$

$$\beta = \frac{k_{tc}R_p}{(k_p[M])^2} \quad (10)$$

The individual terms in eq. (9) were calculated in order to assess their change during the course of the reaction. In both systems the $C_{fs}([S]/[M])$ was the dominant term throughout the course of the reaction and it showed an increase of 2 orders of magnitude toward the end of the reaction.

VAc Homopolymerizations

As for the case of BA, two homopolymerizations of VAc in toluene were carried out (Table I). The ATR-FTIR off-line monitoring of the VAc homopolymerizations was accomplished using the same method as the BA homopolymerizations. The obtained results are shown in Figures 8 and 9 for VAc/toluene ratios of 50/50 and 20/80 wt %, respectively.

The ATR-FTIR spectra ($1800\text{--}800\text{ cm}^{-1}$) of the VAc monomer shown in Figure 10 were used for the peak assignments. The assignments of the characteristic peaks are given in Table IV.^{31,36}

The characteristic change of the absorbances during the course of the reaction, which represented the changing concentration of monomer or polymer in the reaction mixture, was observed with several peaks that are represented in Figure 11.

For the sake of clarity, some of the collected spectra are not shown. After careful examination of the spectra, the absorbance bands for which

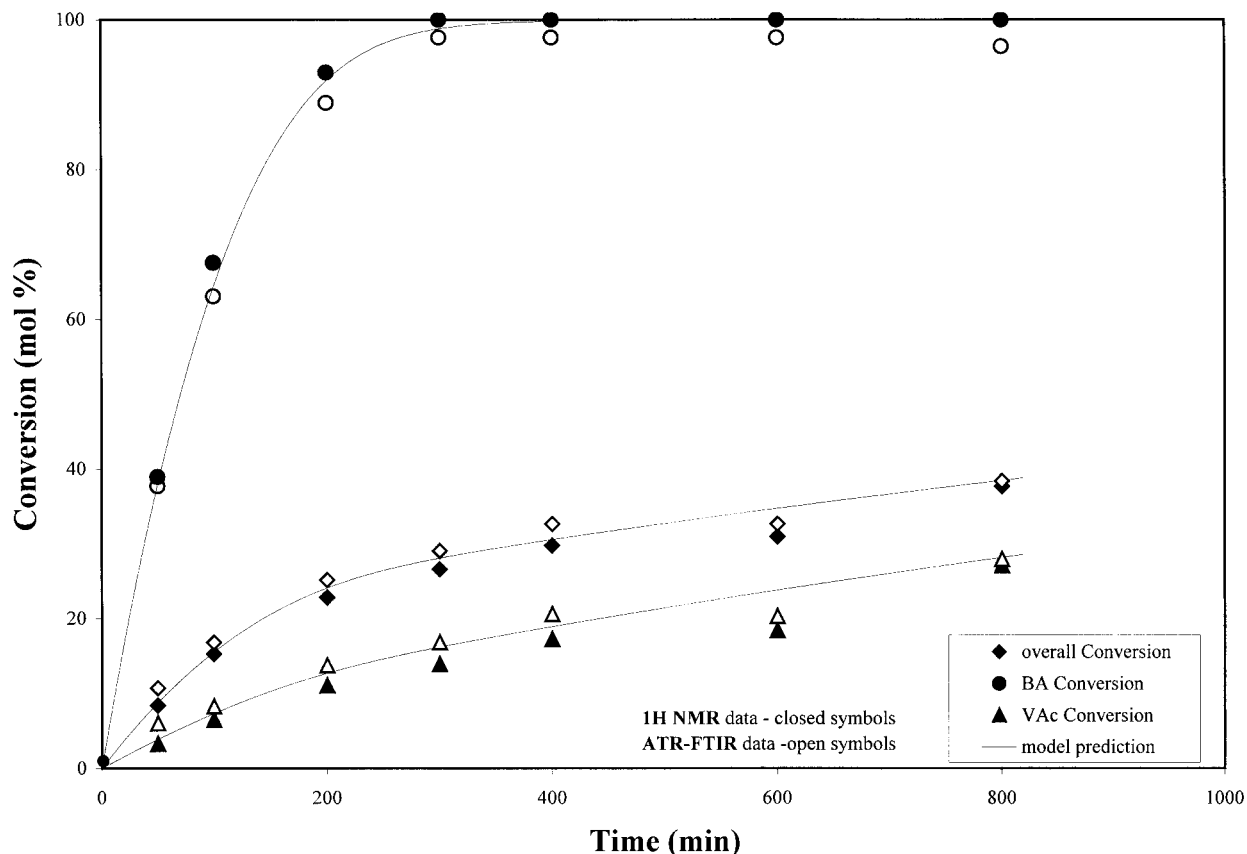


Figure 16 Conversion versus time for BA/VAc (20/80 wt %) solution copolymerization in toluene (50 wt %).

there was no absorption of toluene were used for calculating the conversion. Calculations performed using the peak height referenced to a two-point baseline for the absorbance band at 1293 cm^{-1} showed the highest degree of agreement between the gravimetric data and the ATR-FTIR data. Changes in the absorbance of the VAc monomer at 1293 cm^{-1} during the course of the reaction are shown in Figure 12. Equation (2) was used to calculate the monomer conversion. As in the case for BA, good agreement between gravimetry and ATR-FTIR was observed. Therefore, conversion of monomer in VAc solution homopolymerizations can be successfully monitored off-line using ATR-FTIR.

It is well known that toluene, like other aromatic solvents, acts as a strong retardant for VAc homopolymerization.²³ The solvent effect is more pronounced for VAc than for BA. Changes in the lumped constant with the solvent concentration were observed in toluene and in benzene.^{20,21} As with BA, a chain-length dependence for k_t is suspected.

Figures 8 and 9 present two models: one that incorporates parameters for VAc bulk homopolymerization and another in which the solvent effect was taken into account. As previously mentioned, our approach was to adjust the termination rate constant to fit the model to the experimental data. For 20/80 wt % VAc/toluene the value of the termination rate constant was $2.17 \times 10^{12}\text{ L/mol/s}$ and that for the lumped rate constant was 0.1624; these gave the best fit to the experimental data. The value of the lumped rate constant depends on the ratio of monomer to solvent at a constant initiator concentration. Therefore, when the concentration of the monomer was increased to 50 wt %, the value of the lumped rate constant was 0.3349 for the best estimate of k_t ($5.1 \times 10^{11}\text{ L/mol/s}$). The values of chain transfer constants used in the model for solution polymerizations were a C_{fm} of 1.75×10^{-4} , which falls near the end of the range of values reported in the Polymer Handbook²⁹; a C_{fs} of 20×10^{-4} , which is slightly lower than the $(21\text{--}34) \times 10^{-4}$ range of

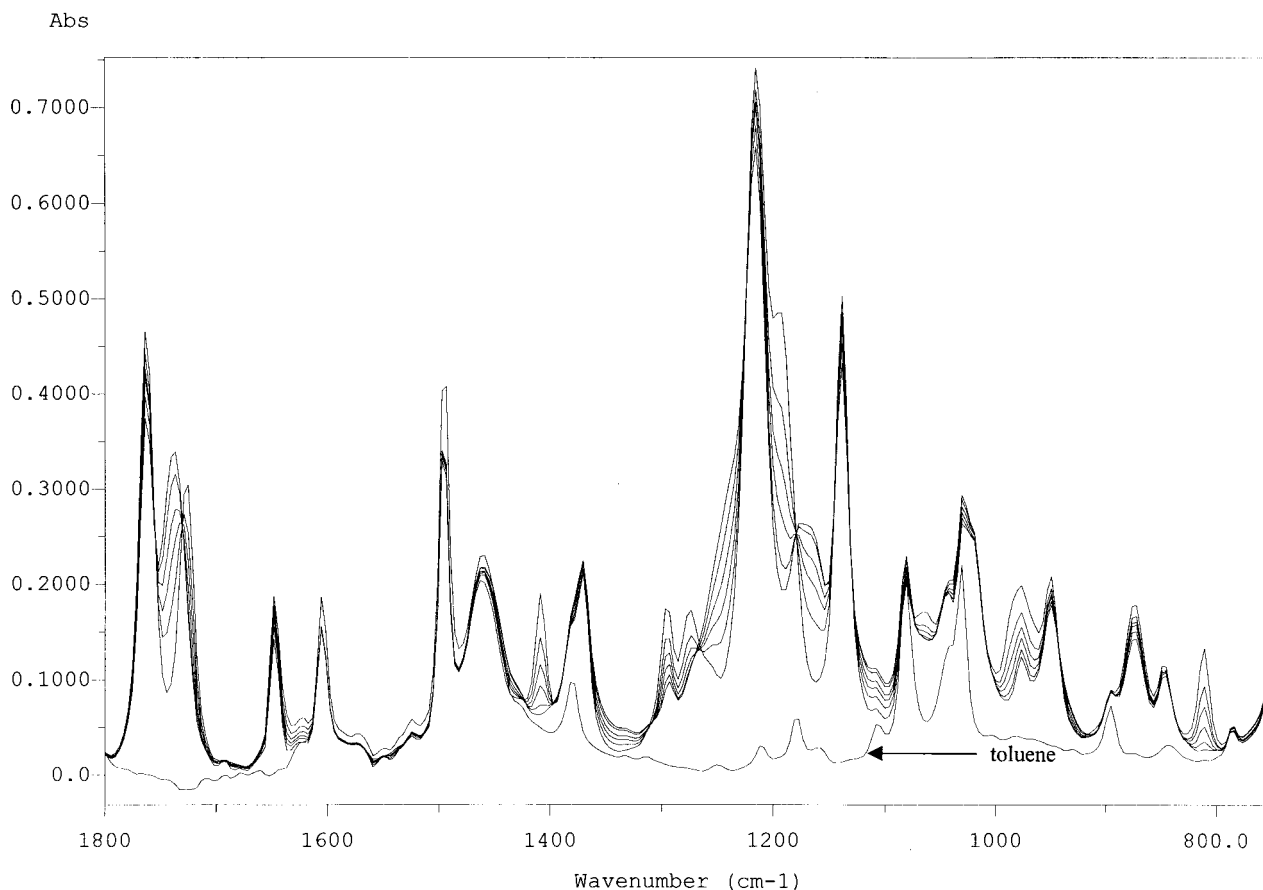


Figure 17 ATR-FITR spectra of BA/VAc (50/50 wt %) solution copolymerization in toluene (50 wt %).

values reported by Ham³⁷; and a C_{FCTA} of 3.48×10^{-4} .

Changes in the cumulative number- and weight-average molecular weights with conversion are shown in Figures 13 and 14. The cumulative number- and weight-average molecular weights for the 50/50 wt % VAc/toluene run were much higher than for the 20/80 wt % VAc/toluene run because there was more solvent present in the former case.

In light of the changes introduced in the model used for the prediction of the bulk polymerization, the molecular weights were greatly affected by changes in the k_t . As with the BA solution homopolymerizations, neglecting the solvent effect yielded model predictions for cumulative number- and weight-average molecular weights that were an order of magnitude higher than the experimental data.

The influence of the individual chain transfer reactions on the molecular weight development was also investigated. The individual terms in

eqs. (9) and (10) were calculated in order to assess their change during the course of the reaction. It was found that the term $k_{tc}R_p/(k_p[M])^2$ was dominant followed by C_{fs} during the course of the reaction. This is unlike the bulk polymerization where the C_{fm} term dominates throughout the reaction.

BA/VAc Copolymerizations

Two BA/VAc copolymerizations in toluene were carried out under the conditions described in Table I. In Figures 15 and 16 the experimental data obtained by traditional techniques (gravimetry and ¹H-NMR) and ATR-FTIR are presented along with model predictions.

For ATR-FTIR monitoring, the determination of characteristic peaks to represent the changing monomer concentrations was complicated by the presence of both monomers and the solvent in the collected spectra. The same approach was used as in the homopolymerizations. The spectra of pure

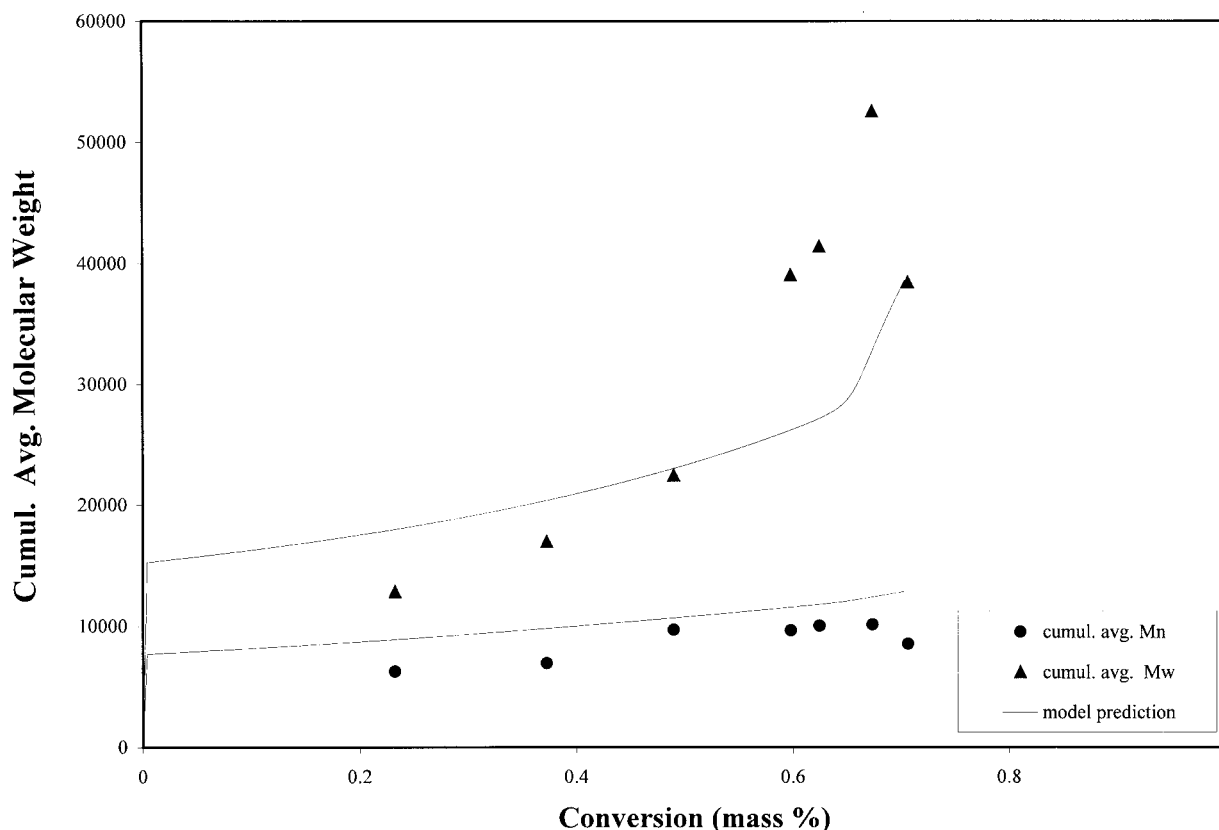


Figure 18 Cumulative average molecular weight versus conversion for BA/VAc (50/50 wt %) solution copolymerization in toluene (50 wt %).

monomers collected under the same conditions as the reaction spectra were compared to the spectra collected during the reaction. As a result, the peaks observed during the reactions could be easily assigned to each of the monomers. The absorbance peak previously used for the VAc homopolymerization to determine conversion overlapped with an absorbance peak for BA, and it was necessary to use another absorbance peak. As described previously, there was no need to subtract the solvent because toluene was not absorbing at the same wavelengths as the selected BA and VAc peaks. Figure 17 shows characteristic spectra for a BA/VAc copolymerization.

The absorbances of BA at 810.6 cm^{-1} and VAc at 872.4 cm^{-1} were used to obtain the conversion versus time data for both copolymerizations (25/25/50 and 10/40/50 wt % BA/VAc/toluene). Conversion of the individual monomers and the overall conversion were calculated using eqs. (2) and (3) after baseline correction. The peak height used in the calculation was referenced to a single-point baseline and the peak height at time zero was the peak height determined for the reaction mixture

prior to polymerization. Good agreement between the data obtained by the traditional approach (gravimetry and $^1\text{H-NMR}$ spectroscopy techniques) and ATR-FTIR spectroscopy was observed. As Chatzi et al.¹⁵ suggested, ATR-FTIR can be a very powerful technique for the determination of not only the overall conversion but also the copolymer composition. Monitoring is not only possible but is also sufficiently accurate.

As shown earlier, solution homopolymerizations of BA and VAc are affected by the type and concentration of the solvent. Therefore, it is expected that the solution copolymerization of these two monomers would show similar behavior. Recent work on BA/VAc copolymerization in solution is scarce, apart from that of McKenna and Heredia³⁸ where ethyl acetate was used as a solvent. They concluded that, similar to the homopolymerization reactions of VAc and BA, the lumped constant was dependent on the solvent concentration. Our approach in modeling the BA/VAc solution copolymerization in toluene was as follows: the previously determined rate constants for the solution homopolymerizations of BA and VAc in

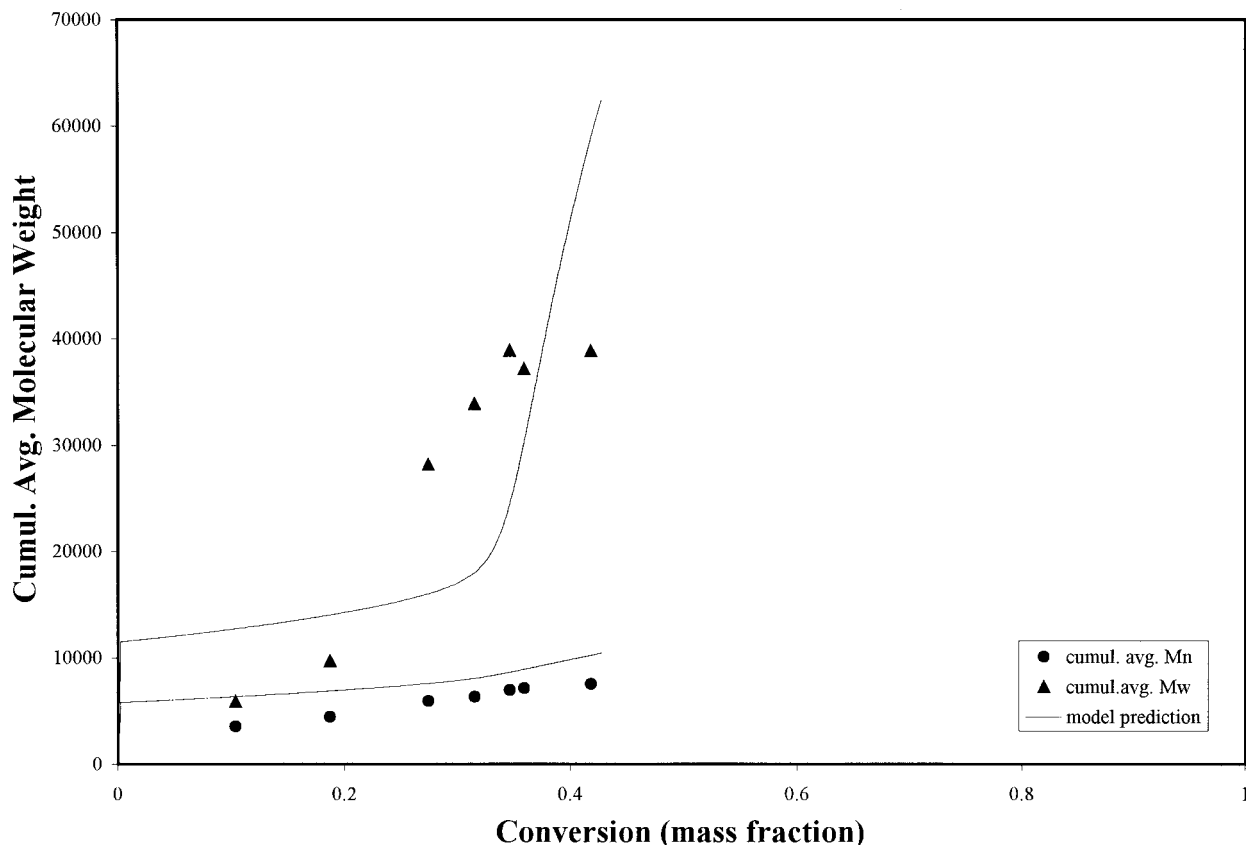


Figure 19 Cumulative average molecular weight versus conversion for BA/VAc (20/80 wt %) solution copolymerization in toluene (50 wt %).

toluene were left unchanged for the particular toluene concentration (50 wt %) and, as such, were used for the prediction of the BA/VAc solution copolymerizations. As seen in Figures 15 and 16, very good agreement between the experimental data and the model predictions was obtained for both BA/VAc ratios in the reaction mixture.

The cumulative number- and weight-average molecular weights for the obtained copolymers are shown in Figures 18 and 19. As for the homopolymerizations, a considerable improvement in the molecular weight predictions was observed when the lumped constant was changed to incorporate the solvent effect.

CONCLUSIONS

The results presented herein confirm that the monitoring of BA and VAc solution homo- and copolymerizations using an ATR-FTIR probe in an off-line mode is not only possible but also sufficiently accurate compared to traditional tech-

niques (gravimetry and $^1\text{H-NMR}$ spectroscopy). These findings are especially important for systems such as BA/VAc copolymerization where there is a possibility of composition drift due to the differences in the reactivity ratios of the monomers. Even though measurements were made off-line, reliable composition data were obtained without a significant time lag. Only a few minutes were enough to analyze a sample and obtain the results compared to gravimetry and $^1\text{H-NMR}$ where significant time lags (measured in days) were present. In addition to the short analysis time, the ability to monitor individual monomer conversions is another advantage of ATR-FTIR spectroscopy. Systems where compositional drift is expected are common in polymer reaction engineering. Knowing that the compositional drift affects the final polymer properties, the ability to monitor copolymer composition during the polymerization reaction is of the utmost importance. ATR-FTIR spectroscopy provides opportunities for appropriate steps to be taken, if necessary, when composition drift is observed.

Our preliminary results for in-line monitoring of BA/VAc emulsion copolymerizations confirm that the approach developed for the off-line measurements is applicable to in-line measurements as well. These findings are useful for industrial-scale polymerization monitoring and process control.

Previously reported solvent effects on BA and VAc homo- and copolymerizations in solution were observed in this study. Using previously reported knowledge on these and similar systems, we were able to significantly improve the predictions of our model. This was done by incorporating the change of the lumped constant with the solvent concentration through the change of the termination rate constant. Despite the fact that the lumped constant with the solvent concentration is evident, there is no real physical evidence that only the termination rate constant changes with the concentration of solvent in these systems. This is especially true for VAc where suspected monomer-solvent interactions that influence k_p are quite likely.²³ Thus, until more accurate measurements of the individual rate constants for BA and VAc are obtained, this uncertainty will continue.

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