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High Temperature Bulk Copolymerization of Methyl Methacrylate and Acrylonitrile: II. Full Conversion Range Experiments

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Full conversion range copolymerization of methyl methacrylate and acrylonitrile has been studied in the bulk phase. Experiments were conducted at 60, 100, and 140°C. The rates of reaction, copolymer composition, \bar{M}_n , \bar{M}_w , PDI, and Tg of samples were measured. Also, the WATPOLY model and Meyer-Lowry equation were employed to model the copolymerization and to calculate some copolymerization variables. The results show that higher levels of acrylonitrile in the feed composition significantly decrease the gel effect, number, and weight average molecular weights. Also, the gel effect at higher temperatures decreases. In addition, the reactivity ratios estimated for this copolymer system over the entire temperature range were confirmed from trends in cumulative copolymer composition.

Keywords copolymerization, full conversion, high temperature, methyl methacrylate, acrylonitrile

Introduction

Kinetic studies for methyl methacrylate (MMA) and acrylonitrile (AN) copolymerization are very limited, even in the conventional temperature range (40°C–80°C). Most studies described in the literature are low conversion range studies carried out to estimate reactivity ratios of this copolymer system in the conventional temperature range. It is difficult to find any study in the literature on the full conversion range of MMA/AN copolymerization. This kinetic study of copolymerization of MMA/AN is part of a larger project to study the terpolymerization of styrene (STY)/MMA and AN for optical applications.

The addition of AN as a termonomer to the STY/MMA copolymer system can improve some desired chemical and mechanical properties, such as solvent resistance and toughness of the product (1). Also, bulk polymerization under thermal conditions can improve the clarity of the terpolymer (2). Therefore, thermal terpolymerization or terpolymerization at higher temperatures may improve the optical properties of STY/MMA copolymer.

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In order to study the thermally initiated terpolymerization, the three copolymer pairs of STY/MMA, STY/AN and MMA/AN should be investigated at elevated temperatures (100–140°C) (3). The STY/MMA system has been very well studied at the conventional temperature range (40–80°C) (4); however, studies at elevated temperatures are scarce. STY/AN copolymerization has also been well studied at conventional temperatures and there is some work reported in the literature for higher temperatures (4).

Copolymerization of MMA/AN at a low conversion level has been studied by Khesareh et al. (5) over a wide temperature range (60–140°C) and the reactivity ratios were estimated. Brar et al. (6) characterized the stereo-chemistry of MMA/AN copolymer produced from low conversion polymerizations, using different spectroscopic techniques and also estimated reactivity ratios. Micro-emulsion copolymerization of MMA/AN was studied by Reddy et al. (7, 8) at 70°C for low conversions and the reactivity ratios were evaluated by different methods. Steinfatt and Schmidt-Naake (9) studied micro-emulsion terpolymerization of MMA/AN/STY at 60°C. Terpolymer composition data from elemental analysis, infrared and Raman spectroscopy were used to estimate reactivity ratios for all three copolymerizations. Also, a full conversion range experiment was carried out with 7 data points and rheological investigations were performed to show that higher molecular weight terpolymer was produced by micro-emulsion compared to samples produced with emulsion polymerization. Hatada et al. (10) reported an assessment of MMA/AN copolymers using ^1H and ^{13}C -NMR spectroscopic analysis. The copolymerizations were performed in DMSO solution at 40, 50, and 60°C at the low conversion range. The penultimate model was employed to determine reactivity ratios. It was suggested that even the existence of a pre-penultimate effect is possible, however in drawing this conclusion, the statistical analysis of uncertainty used was not reliable enough to show the effect of experimental error. Finally, Simionescu et al. (11) performed low conversion range experiments and estimated the reactivity ratios at 70°C.

In the present work, the MMA/AN copolymerization system has been studied in bulk at 60°C and elevated temperatures (100–140°C) over the full conversion range. Conversion vs. time, the gel effect, limiting conversion levels, number and weight average molecular weights (\bar{M}_n and \bar{M}_w), polydispersity indices (PDI), composition drift, and the glass transition temperatures were studied over the full conversion range for this poorly studied copolymer system.

Experimental

Purification of Reagents

Methyl methacrylate (Aldrich) was washed three times with a solution of 10% by weight sodium hydroxide (NaOH) in water, three times with de-ionized water and then dried over CaCl_2 for 24 h. The washed monomer was distilled under reduced pressure and the middle fraction of the distillate was collected for polymerization (12).

Acrylonitrile (Aldrich) was purified by being passed over an inhibitor removal resin (Aldrich) and then purged by nitrogen gas. Throughout this work, monomer 1 refers to MMA and monomer 2 to AN. 2,2'-Azobisisobutyronitrile (AIBN) (Polysciences) was recrystallized three times from cold absolute methanol, dried in a vacuum oven at room temperature, and stored in a freezer at -10°C . This initiator was used for experiments at 60°C. Tert-butylperoxy 2-ethylhexyl carbonate (TBEC) (Aldrich) was used without purification in experiments at 100°C. The purity of TBEC used in these experiments

was 95%. Di-tert-butyl peroxide (Trigonox B (TgB), AKZO Chemicals) was used without purification for copolymerizations at 140°C.

All solvents (dichloromethane, acetonitrile, ethanol, N,N-dimethyl-formamide) were used without further purification.

Methods

Experiments were carried out in borosilicate glass ampoules. The monomers and initiators were weighed and then approximately 2 ml of solution pipetted into the ampoules. AIBN, TBEC and TgB were used as initiators for experiments at different temperatures. A standard degassing procedure (13) was used to remove any traces of oxygen. All ampoules were sealed and then stored in liquid nitrogen until use.

Polymerizations were carried out in a temperature controlled oil bath, at 60°C, 100°C, and 140°C. The ampoules were placed in the oil bath at desired temperatures and removed at appropriate intervals over time to cover full conversion of monomers. Ampoules were subsequently submerged in liquid nitrogen, thawed, cleaned, dried, and weighed. Then, ampoules were scored and broken and the contents poured into a 10-fold excess of methanol; the empty ampoules were then reweighed. The precipitated copolymer was dried in a vacuum oven at 75°C for seven days to reach a constant weight. The conversion was measured based on total polymer by gravimetry. The resulting polymers were isolated as described above and analyzed for cumulative polymer composition by elemental analysis of nitrogen (Guelph Chemical Laboratories Ltd).

The GPC used in this work was a combination of a Waters 515HPLC pump, Waters 717 Plus Autosampler and Viscotek TDA 302 triple detector array with three Styragel HR5E columns and its specific software OmniSEC3Data to analyze the interpretation of chromatograms and the precision of the results. The detectors employed were low-angle laser light scattering (LALLS), right-angle laser light scattering (RALLS), a differential refractive index (DRI) detector and a viscometer. The glass transition temperature (T_g) of samples was measured with a differential scanning calorimeter (DSC). The TA Instruments DSC 2920 with standard a DSC cell determines the temperature and heat flow associated with material transitions as a function of time and temperature. The experiments were done at the temperature range of 40–200°C with a heating rate of 10°C/min. The samples sizes were between 2 to 7 mg and Indium was used as the standard.

Results and Discussion

Experimental conditions are summarized in Table 1. The full conversion experiments at 60°C were done in five individual segments in order to reach maximum conversion. The monomer conversion vs. time results, plotted in Figure 1, show that all data points obtained in the five segments follow the same trend. This means these data points are highly reproducible.

Also, Figure 1 shows that the conversion vs. time is apparently linear up to 30% conversion. This means the copolymerization up to this level is predominantly chemically controlled. The curve shows that slight auto acceleration started after 30% and increased at higher conversions. Although the mole-fraction of MMA in the feed is larger than the mole-fraction of AN, the magnitude of the gel effect shown in Figure 1 is fairly small and close to that seen for homo-polymerization of AN (14).

In addition, this figure shows a limiting conversion of 93%, which can be explained based on polymerization theory. The reaction temperature is 60°C, which is lower than the

Table 1
Summary of full conversion range experiments for MMA/AN
copolymerization

Run	Temperature (°C)	Initiator		f_1 (MMA)
		Type	Conc. (mol/l)	
1	60	AIBN	0.01	0.58
2	100	TBEC	0.0033	0.58
3	100	TBEC	0.0033	0.8
4	140	TgB	0.001	0.58

glass transition temperature (T_g) for MMA/AN copolymer ($\sim 100^\circ\text{C}$). Therefore, the conversion should not reach 100%. The conversion reached a maximum level in 550 min, and after that, the conversion was essentially constant as indicated by the last data point for 1380 min, which was still at the limiting conversion (93%).

It was also observed that the last sample was different from the other samples. All other samples did not have any color, but the last sample had a yellowish color and the polymer produced was not soluble in dichloromethane. A mixture of acetonitrile and dichloromethane was used to dissolve this polymer sample. The experiments showed that the yellowish color did not appear until reaching this limiting conversion. If the samples remained in the oil bath for extended times, the yellowish color appeared and the color became stronger at the later stages. The solubility of the sample seemed to be related to the color of the sample. To explain this change in polymer property, the copolymer composition had to be investigated.

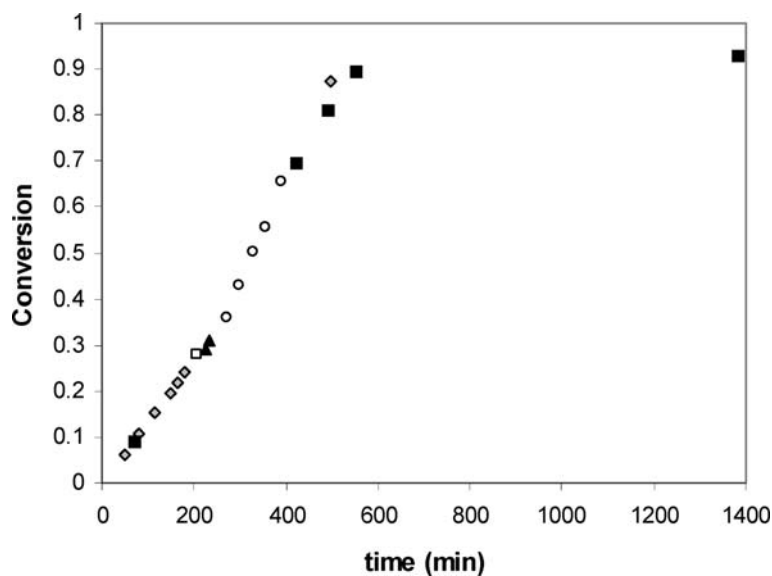


Figure 1. Conversion vs. time for MMA/AN with 58 mol% MMA at 60°C with 0.01 mole/l AIBN obtained from five different segments—each symbol represents an individual segment.

The cumulative copolymer composition vs. conversion for the reaction at 60°C is plotted in Figure 2. As shown in the figure, the copolymer composition did not have significant drift over the entire conversion range, and at lower conversions, it was almost constant. The data points from all five different segments followed the same trend, which confirmed the good reproducibility of the data.

The cumulative copolymer composition calculated using the Meyer-Lowry model (15) and that using our simulation package (WATPOLY) first described by Gao and Penlidis (4) are also plotted in Figure 2. Reactivity ratios used to calculate the model composition trends are those estimated by Khesareh et al. (5) for 60°C which are r_1 (MMA) = 1.04 and r_2 (AN) = 0.15. As shown in Figure 2, the Meyer-Lowry model fits the data points very well at low and medium conversions, whereas the WATPOLY model fits the data points over the entire conversion range. The WATPOLY employs the overall free volume of the copolymer system to take into account the diffusion-controlled kinetics (4).

As shown in Figure 2, copolymer composition does not show a significant drift until very high conversion. At this point, most of MMA in the feed has been consumed and the remaining monomer mixture is rich in AN. Calculating the mole-fraction of monomers in the remaining monomer mixture showed that 75 mol% of residual monomers (at 90% conversion of total monomers) was AN. This may explain the insolubility and the yellowish color of the last sample, which was discussed earlier. Given the mole fraction of residual AN (at 90% conversion) is 0.75, prolonging the polymerization time may cause grafting polymerization of AN or extended sequences of AN in the copolymer chains, which would significantly decrease the solubility of the polymer. The grafted or extended sequences of AN in the polymer grow and the AN may start cyclization reactions (16), which in turn would produce the yellowish color. The amount of grafted and cyclized AN in the polymer should increase with extension of the polymerization time.

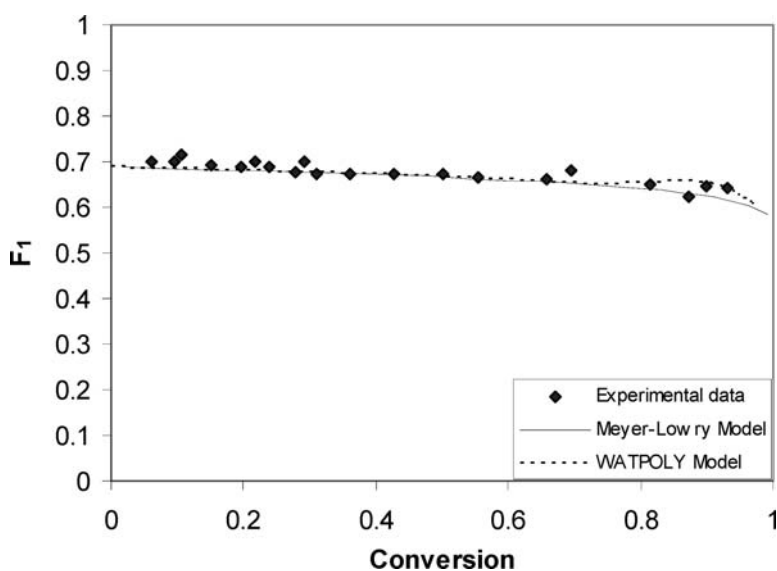


Figure 2. Cumulative copolymer composition for MMA vs. conversion for MMA/AN with 58 mol% MMA at 60°C, showing experimental data and model fits.

The number and weight average molecular weights of samples are plotted in Figure 3. As shown in the figure, both \overline{M}_n and \overline{M}_w of samples are almost constant up to 30% of conversion, which is dominated by chemical control. The molecular weights increased after 30% conversion, which is the diffusion controlled region. It was observed that for samples with conversion greater than 80%, the filtration of polymer solution in THF (for GPC) was not as easy as the samples from lower conversion. This means some larger molecules in these samples were trapped in the filter, therefore the values of \overline{M}_n , \overline{M}_w are not precise. The filtration of the last reaction sample (time = 1380 min) was much more difficult than other samples and this specific sample was not totally soluble. The polydispersity (PDI) of the samples is plotted in Figure 4. The PDI of samples is almost 2 as expected for a standard Flory-Schultz distribution (17) up to 30% of conversion (chemically controlled region) and after this point it increases.

The glass transition temperatures of selected samples are presented in Table 2. As shown, the Tg of samples over the entire conversion range is 94.3–97.5°C, which is almost constant, considering the typical error for DSC measurements.

As shown in Table 1, runs 2–4 were conducted at 100°C and 140°C. The experiments at 100°C were done at two feed compositions. The initiator type and level at 100°C and 140°C were different because it is almost impossible to work with the same type and level of initiator over the whole temperature range (100–140°C), since the rate of initiation for most initiators at 140°C is almost 100 times faster than the rate of initiation at 100°C.

The conversion versus time profiles for full conversion range experiments for 100°C at both feed compositions (runs 2 and 3 in Table 1) are plotted in Figure 5. As shown in this figure, the rate of polymerization up to 25% of conversion is similar for both curves and almost linear. This means that in the conversion region dominated by chemically controlled polymerization, changing the feed composition from 58 to 80 mol% MMA did not make a significant difference in the rate of polymerization. However, the auto

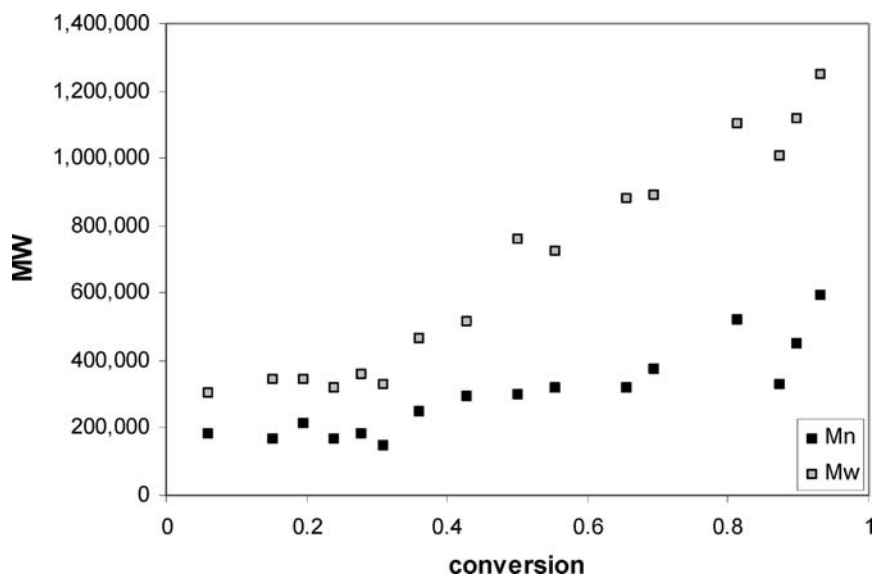


Figure 3. Cumulative number and weight average molecular weights of MMA/AN produced at 60°C with 58 mol% MMA and 0.01 mol/l AIBN.

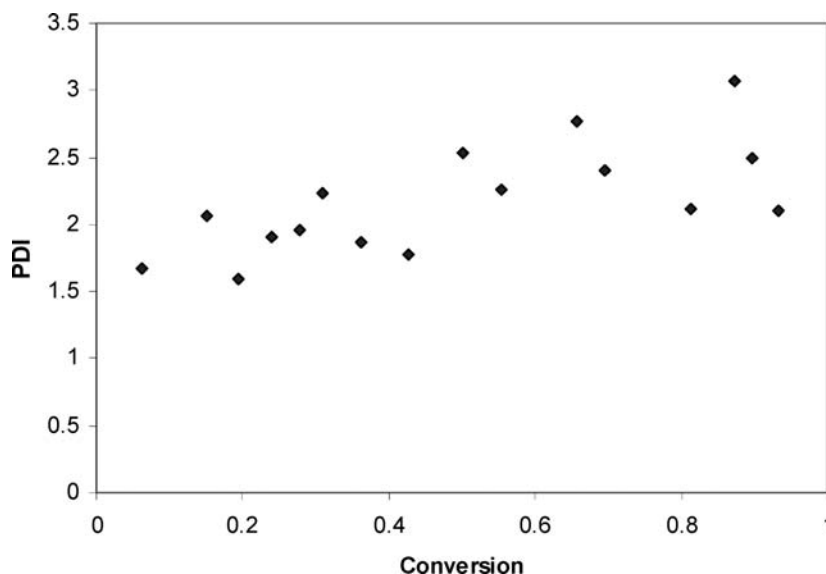


Figure 4. PDI (M_w/M_n) for MMA/AN copolymer produced at 60°C with 58 mol% MMA and 0.01 mole/l AIBN.

acceleration in the curve with 80% MMA started before the curve with 58% MMA. Also, the auto acceleration for 80% MMA was much more pronounced than the feed with 58% MMA. This was expected because it is known that MMA has a strong gel effect and increasing MMA in the feed composition increases the magnitude of the gel effect (14).

There are some replicate data for both curves in Figure 5. The replicate data points for both curves are very close to the original ones and the additional data points generated in the replicate runs fit perfectly within the trend of the conversion profile. Therefore, both experiments are well reproducible.

As for the study at 60°C, a final sample was maintained for an extended period in each feed. These are not shown in the figure. The time for the last point for the experiment with 58 mol% MMA was 1328 min, and the sample reached 99.79% conversion. This shows that there is almost no limiting conversion; hence, the glass transition temperature of this copolymer should be around 100°C. The time for the last data point for the experiment with 80 mol% MMA was 1155 min, and the sample reached 99.97% conversion.

The final samples for both reactions showed a yellowish color, but the color in the sample with 58 mol% MMA was stronger and similar to the last point for experiments

Table 2
Glass transition temperatures for MMA/
AN copolymer produced at 60°C

Conversion	Mw	Tg (°C)
0.0617	302429	97.5
0.5011	755789	96
0.898	1120000	94

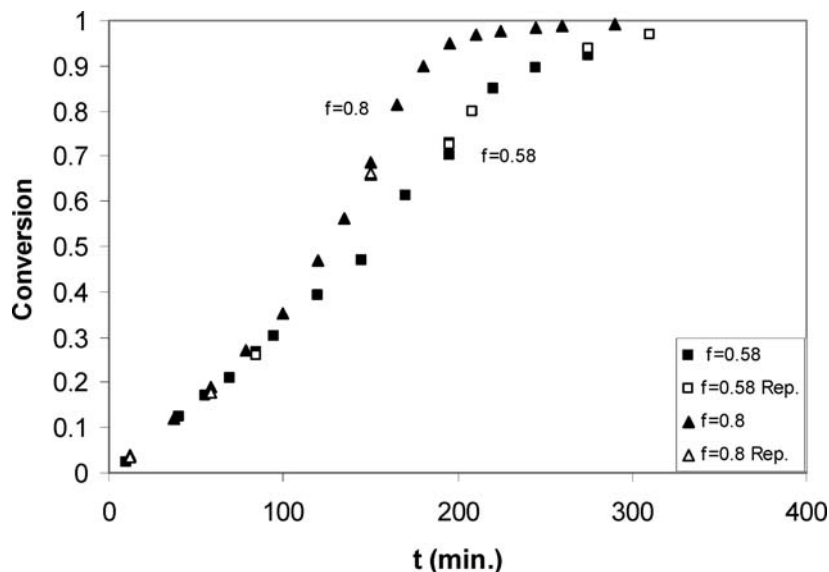


Figure 5. Conversion vs. time profiles for MMA/AN at 100°C at two initial feed compositions; 58 and 80 mol% MMA with 0.0033 mole/l TBEC.

at 60°C. The last point for the set with 80 mol% MMA was only slightly yellow, which supports further the role of AN in producing this color.

The cumulative copolymer composition vs. conversion for the reactions at 100°C is plotted in Figure 6. As shown in this figure, the copolymer composition does not show significant drift over the entire conversion range for both data sets. The copolymer composition drift for the data set with 80 mol% MMA is almost negligible, which was predicted well by model calculations and as shown in Figure 6. The data points from experiments and replicates followed the same trend, which again confirms the reproducibility of the data. The reactivity ratios used to plot model predictions were the reactivity ratios estimated at elevated temperatures (100–140°C) by Khesareh et al. (5), which are r_1 (MMA) = 1.04 and r_2 (AN) = 0.25.

The number and weight average molecular weights of samples from the 100°C runs are plotted in Figure 7. As shown in the figure, both number and weight average molecular weights of both samples are almost constant up to 20% of conversion, which is the chemically controlled region. The molecular weights for the experiment using 80 mol% MMA increased at a lower conversion level than those from the experiment with 58 mol% MMA, which confirms the stronger gel effect in the experiments with higher MMA. This is confirmed by the fact that molecular weights increased after 20–25% conversion.

The number and weight average molecular weights for the experimental data set using 80 mol% MMA are significantly higher than those from the experiment using 58 mol% MMA. The replicates for the data set with 58 mol% MMA showed higher values for \bar{M}_n at 73% conversion possibly because of experimental error. Most replicates are reasonably close to the original experimental data points.

As shown in Figure 7, the \bar{M}_n and \bar{M}_w of samples with 80 mol% MMA decreased at very high conversion. The reason is, like the samples at 60°C, that the larger (insoluble in THF) molecules were separated during filtration. It was observed that the samples at high

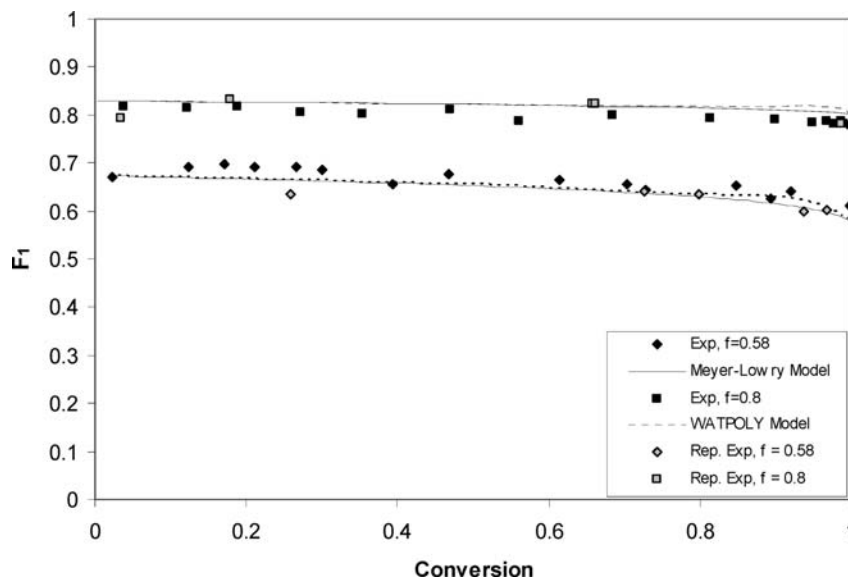


Figure 6. Cumulative copolymer composition for MMA vs. conversion for MMA/AN at 100°C with 58 and 80 mol% MMA in the feed.

conversion (more than 80%) had more resistance to filtration and the resistance of samples with 80 mol% MMA was more than the resistance of similar samples with 58 mol% of MMA. Therefore, the M_w values for samples above 80% of conversion are not that reliable.

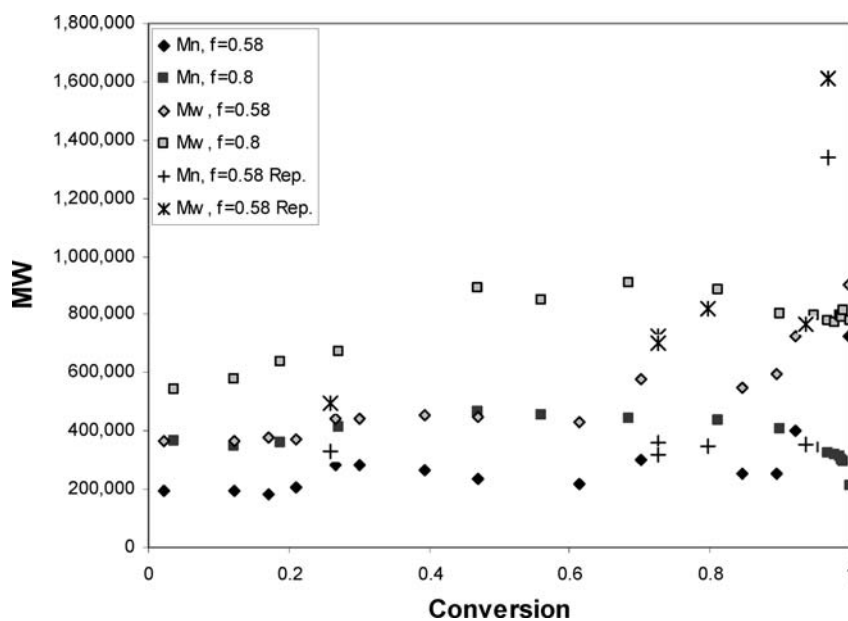


Figure 7. Cumulative number and weight average molecular weights of MMA/AN produced at 100°C with TBEC using 58 and 80 mol% MMA.

The glass transition temperatures of selected samples from both experiments are plotted in Figure 8. As shown in the figure, the glass transition temperature with 80 mol% MMA is about 102–104°C and is higher than the average T_g for samples from the other experiment (94–96°C). This means there should be no limiting conversion for the experiment at 100°C using 80 mol% MMA, whereas the limiting conversion for the other data set is close to 100% as discussed before.

The copolymerization of MMA/AN at 140°C with 0.001 mole/l TgB and initial feed composition of 58 mol% MMA (run 4- in Table 1) can be nominally compared with analogous experiments at 100°C with 0.0033 mole/l TBEC and the same feed composition (run 2 in Table 1). The conversion vs. time curves of these experiments are plotted in Figure 9. The conversion curve for 140°C compared that for 100°C does not show significant auto acceleration. The molecular weights of samples produced at 140°C are expected to be smaller and the viscosities of the reaction mixture lower at the same level of initiation, therefore the diffusion mechanism should not dominate the polymerization rate.

The replicate data for experiment at 140°C had a general shift towards slightly lower conversion values. This could mean a systematic error. The initiator level in this experiment is fairly low (0.001 mole/l), which may increase the relative error in weighing initiator.

No limiting conversion is expected for this experiment because the reaction temperature is much higher than the glass transition temperature of the copolymer. The last sample, which is not shown in Figure 10, was maintained at 140°C for 1055 min, and reached 100% conversion.

The yellowish color was noticeable above 65% conversion and the color became more distinct at higher conversions. The AN content in the residual monomer at 65% conversion is about 50%, which means a low possibility of grafting polymerization of AN. The cyclization of AN possibly happened in polymer chains with longer sequences of AN. The last data point had a strong yellow color. The solubility of this polymer was good

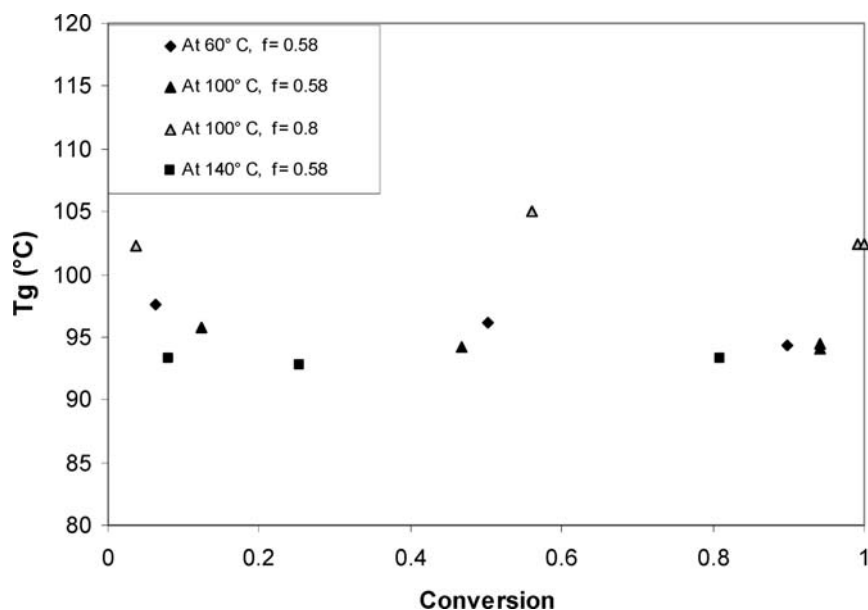


Figure 8. Glass transition temperatures vs. conversion for selected samples from all experiments.

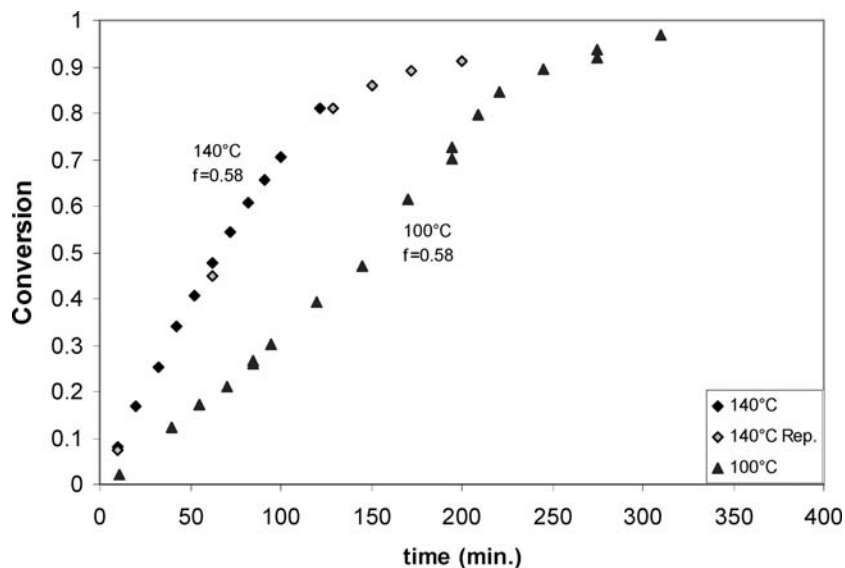


Figure 9. Conversion vs. time profiles for MMA/AN at 100 and 140°C with 58 mol% MMA as the initial feed composition.

(in THF and dichloromethane) which showed the effect of lower molecular weight on solubility (as opposed to earlier observations). The sample, which was considerably yellow, was not as soluble as other samples and it took more time to dissolve, than colorless samples.

Yellowish polymer was of lower solubility. This color is enhanced by higher temperatures and higher AN levels. Therefore, there are limits for both reaction temperature and

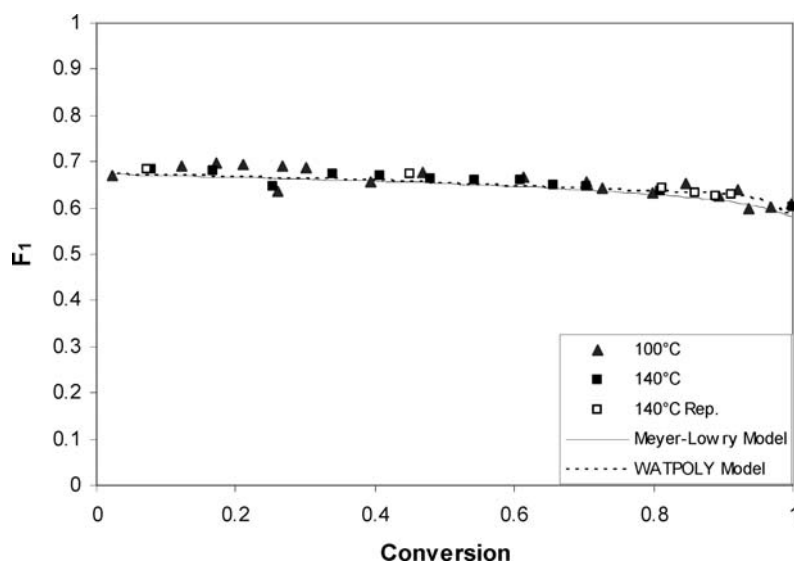


Figure 10. Cumulative copolymer composition for MMA vs. conversion for MMA/AN at 140°C and 100°C for 58 mol% MMA in the feed.

the level of AN in the feed composition to avoid discoloration in the polymer. Experiments at 140°C showed that the discoloration occurred at lower conversions. This means that temperature and feed composition of AN are above a certain critical limit. Adding AN into the copolymer decreases the solubility of the product in conventional solvents, but on the other hand it also decreases the molecular weight of polymer, which in turn should increase the solubility of the polymer. The results from GPC for experiments at 100°C showed that the amount of trapped polymer during filtration of samples (dissolved in THF which is slightly polar) for experiments with 20 mol% AN was higher than the ones with 42 mol% AN. But the solubility of samples with 20 mol% AN in dichloromethane was slightly better. Therefore, adding more AN in the feed composition (at least for the range of 20 to 42 mol% AN), yields lower molecular weight polymer with little change in solubility.

The cumulative copolymer composition vs. conversion is plotted for different experiments in Figure 10. As shown in this figure, the copolymer composition for MMA at 140°C is very similar to the copolymer composition at 100°C. This confirms that the reactivity ratios for this temperature range are essentially constant. The replicates at 140°C show a good reproducibility of the data points. The Meyer-Lowry and WATPOLY models predict the copolymer composition well.

The cumulative number and weight average molecular weights are plotted in Figure 11. As shown in this figure, both \overline{M}_n and \overline{M}_w , for samples obtained at 140°C, are significantly lower than those from 100°C. The data for 140°C show that there is no increase in either \overline{M}_n or \overline{M}_w . This confirms that there was no significant gel effect at 140°C. The glass transition temperatures and PDI values for experiments at 100°C and 140°C are similar.

The experiments at three temperatures were performed with three different types and levels of initiators (see Tables 1 and 3), therefore, the rates of polymerization can not be

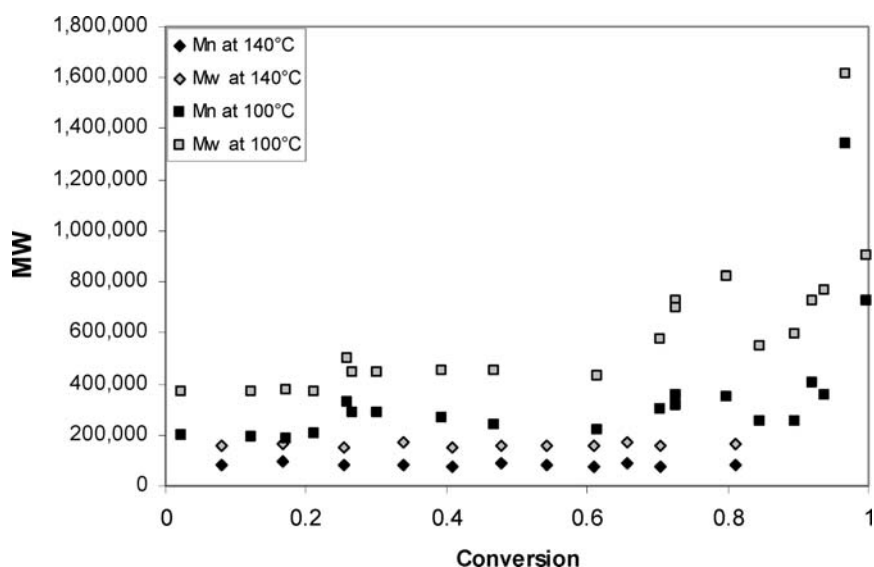


Figure 11. Cumulative number and weight average molecular weights of MMA/AN produced at 140°C (0.001 mol/l TgB) and 100°C (0.0033 mol/l TBEC) with feed composition of 58 mol% MMA.

Table 3
The initial rate of copolymerization calculated from experimental data and from the WATPOLY model with k_p and k_t for MMA/AN at 60°C, 100°C and 140°C

Experiment temperature f (MMA)	$(dx/dt)_0$ Experimental (min^{-1})	$(dx/dt)_0$ Model (min^{-1})	R_{po} Model ($\text{mol}/\text{l} \cdot \text{min}$)	k_{po} Model ($\text{l}/\text{mol} \cdot \text{min}$)	k_{to} Model ($\text{l}/\text{mol} \cdot \text{min}$)
60°C, f = 0.58	1.33×10^{-3}	1.07×10^{-3}	0.011	5.7×10^4	7.38×10^9
100°C, f = 0.58	3.03×10^{-3}	3.02×10^{-3}	0.0322	1.18×10^5	7.36×10^9
100°C, f = 0.8	3.25×10^{-3}	4.28×10^{-3}	0.0418	4.84×10^4	2.62×10^9
140°C, f = 0.58	8.04×10^{-3}	7.92×10^{-3}	0.0727	2.1×10^5	7.42×10^9

compared directly for different temperatures. Normalization of the conversion vs. time curves based on the rate of initiation can be employed to omit the effect of different initiators at different levels and temperatures. The rate of initiation in free radical polymerization is defined by:

$$R_i = 2fk_d[I] \quad (1)$$

k_d (rate constant for initiator dissociation) values for three initiators at three temperatures were calculated (14), the initiator levels $[I]$ are known and the initiator efficiencies (f) at three temperatures are almost similar and about 0.5 to 0.65. (14). Thus, the rates of initiation for all experiments were calculated and normalized to the rate of initiation of 0.01 mol/l AIBN at 60°C by multiplying the time by the square root of the rate of initiation at the temperature over the square root of the rate of initiation for 0.01 mol/l AIBN at 60°C (Eq. (2)). The normalized conversion vs. time curves for all experiments are plotted in Figure 12.

$$\text{Normalized time of polymerization} = t_i \times \left(\frac{k_{di}[I_i]}{k_{do}[I_o]} \right)^{1/2} \quad (2)$$

where the index 'i' stands for any temperature with any temperatures and the index 'o' stands for the initiation rate for 0.01 mol/l AIBN at 60°C.

As shown in the figure, the gel effect at lower temperatures is more significant. Also, higher MMA in the feed composition enhances the gel effect. The rate at 140°C slows down at higher conversions. The reason is that the initiator is consumed very fast at this temperature. The half-life time of TgB at 140°C is 1.15 h so that, after 100 min, 65% of initial TgB is consumed and most of the MMA impurities causing thermal initiation are exhausted. Therefore, the rate of reaction slows down. The normalized

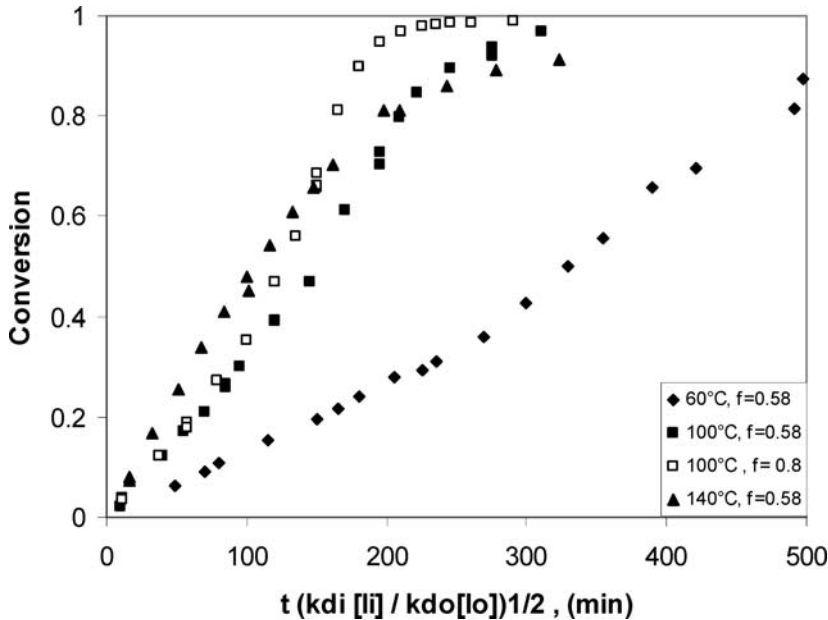


Figure 12. Normalized initiator type and concentration effects on rate at 60°C, 100°C, and 140°C.

conversion curves with 58 mol% MMA, reveal a significant increase in the initial rate of polymerization from 60°C to 100°C. However, the increase in the initial rate of polymerization from 100°C to 140°C is small.

Conclusions

The magnitude of the gel effect in MMA/AN copolymerization is rather small at 58 mol% feed composition and decreases at higher temperatures. Adding MMA into the feed composition considerably increases the gel effect. Glass transition temperatures of copolymers were in good agreement with the limiting conversions observed in the conversion-time curves. The cumulative copolymer compositions at different temperatures confirm the reactivity ratios obtained in an earlier report (5), which were used for modeling the elevated temperature range (100–140°C). Adding more AN in the feed composition significantly decreases the \bar{M}_n and \bar{M}_w , however increasing the reaction temperature while maintaining a similar rate of initiation does not have a significant effect on \bar{M}_n and \bar{M}_w .

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