A Kinetic Investigation on High Conversion Copolymerization of Lauryl Methacrylate-Isobutyl Methacrylate in Solution

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Received 15 May 2002; accepted 6 August 2002

\textbf{ABSTRACT}

Copolymers of isobutylmethacrylate (i-BMA), and laurylmethacrylate (LMA), were prepared by solution free radical copolymerizations at 70°C using 2,2'-azobisobutyronitrile, as initiator. The synthesis of these copolymers were investigated over a wide composition and conversion range. Copolymer compositions were determined as a function of conversion from the %C, %H, and %O contents of copolymer by elemental analysis. In order to avoid the complications of copolymerization kinetics, the “pseduokinetic rate constant method” (PKRC) was applied to constant and variable volume polymerization system. Theoretical values of coupled parameter $k_p/k_1^{0.5}$ calculated from the “implicit penultimate unit effect” model (IPUE) based on instantaneous monomer feed composition, were determined from Meyer-Lowery integrated copolymer composition equation. The results have been compared with experimentally determined kinetic parameters.

\textit{Iranian Polymer Journal, 12 (3), 2003, 191-199}

\textbf{INTRODUCTION}

One of the main prerequisites for design and optimum operation of a polymerization reactor is the knowledge of the reaction kinetics. Experimental studies on high conversion polymerization are quite rare, therefore, considering that the copolymers of technical importance are normally produced at high conversions, it is necessary to obtain information on the high conversion kinetics of polymerization systems.

It is well known that products of a typical free radical copolymeriza-
ation show a gradual drift in copolymer composition over the course of copolymerization. In a gradient copolymer, the chemical composition gradually changes along the polymeric chain. During chain growth, the ratio of monomers incorporated changes as well. This phenomenon is called intramolecular composition drift, i.e. the process in which a shift occurs in the build-in ratio of the two monomers during the time of growth of the copolymer, leading to the formation of chemically heterogeneous polymeric chains. It is necessary to understand and control the process of intramolecular composition drift. When this is achieved, the knowledge may be used to produce copolymers with pre-defined intramolecular sequence distributions.

Most of the experimental studies of copolymerization taken to high conversion have focused on the variation of composition with conversion and have ignored the absolute rate behaviour at high conversion [1]. It is generally found that the copolymer composition and sequence distribution unlike the copolymerization rate are well described by the terminal model [2-6]. Rate abnormalities have been attributed to termination reactions and represented by introducing physically unrealistic cross-termination rate constants [7]. A growing body of evidence, however, convincingly shows that rate deviations cannot be attributed to the diffusion-controlled termination reactions but result from the failure of the terminal model to explain the propagation kinetics [8]. The failure of Mao-Lewis model to describe propagation rate constants in free radical copolymerization was originally reported by Fukuda et al. [9]. These investigators reconciled this apparent contradiction suggesting what has come to be called the implicit penultimate unit effect (IPUE) which means that the penultimate unit influences only the value of the copolymerization rate propagation constant but not the values of reactivity ratio.

Recent studies [10] show that isobutyl methacrylate-lauryl methacrylate (i-BMA/LMA) copolymerization system is an important base for oil additives with several functions such as viscosity-index improver, pour point depressant and sludge dispersant. These copolymers give a good shear and thermal stability to the oil. The system (i-BMA/LMA) is interesting, as both monomers resemble each other closely. A behaviour near to ideal can be expected. This copolymer exhibits interesting properties on account of its comb-like structures and surprisingly has not been studied, at least to the author’s knowledge.

In a previous work a simulator program was developed which upon coupling of experimental data, nonlinear least square (NLLS) approaches and D-optimal criteria calculates the best optimized values of reactivity ratios and monomer feed compositions in a sequential and iterative order for terminal and penultimate models [11,12]. This system seems to follow well the IPUE model, given values of $r_1 = 1.633$ and $r_2 = 0.927$ for reactivity ratios and $S_1 = 1.659$ and $S_2 = 0.571$ for the chain end reactivity ratios. Efficiency factor of initiator; $f$, which has been determined from mean kinetic chain length approach by in-situ measurements is nearly 0.62, in the range of values reported by other investigators and shrinkage factor [11], calculated from eqn (8) is nearly 9%.

The data collected and presented in this article have elucidated the kinetics pertaining to the high conversion solution copolymerization of i-BMA/LMA. The data will be used in future works for the development of detailed polymerization database that should be an integral part of any effort towards the mathematical modelling and computer simulation of polymerization processes.

THEORITICAL BACKGROUND

Terminal Unit Model (TUM)

In order to describe the copolymerization and to explain copolymer compositions, sequence distributions and average propagation rate coefficients, several models have been proposed. The simplest one is the terminal unit model [13,14] that disregards any physical interactions between constituents in the reaction media and, beside the two monomer species, only takes into account two growing radicals with different monomer units at their chain ends. The most commonly used method to determine the polymerization rate or polymer productivity, copolymerization parameters, copolymer composition and polymer molecular weight averages, is to utilize the Mayo-Lewis equation:

$$\frac{F_1}{F_2} = \frac{r_1 f_1}{r_2 f_2} = \frac{1 + f_1}{1 + f_2}$$

where:

1. $f$ represents the efficiency factor of the initiator.
2. $S$ is the shrinkage factor.
3. $r$ is the reactivity ratio.
4. $F$ is the propagation rate at a given conversion.
5. $S_1$ and $S_2$ are the chain end reactivity ratios.
6. $S_{11}$ and $S_{12}$ are the reactivity ratios of the terminal monomers.
7. $S_{21}$ and $S_{22}$ are the reactivity ratios of the penultimate monomers.

In addition, the Mayo-Lewis equation is a simplification of the terminal model, which assumes that the monomer units at the chain ends do not affect the propagation rate constants. This approximation is often valid for systems that have similar monomer units or when the monomer units at the chain ends are significantly more reactive than the interior units. However, in systems where the monomer units at the chain ends have significantly different reactivity ratios, the terminal model may not be an accurate representation of the copolymerization process.
Table 1. The results of overall conversion and cumulative copolymer composition for i- BMA/LMA.

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<th>Time (min)</th>
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M1 and M2 are the bulk-phase monomer concentrations and f1 and f2 are the bulk-phase mole fraction of M1 and M2 in the feed, respectively. Copolymerization kinetics can also be investigated by using the Meyer-Lowry [15] integrated form of the copolymerization equation:

\[
\frac{F_1}{F_2} = \frac{d[M_1]}{d[M_2]}, \quad \frac{f_1}{f_2} = \frac{[M_1]}{[M_2]}
\]

Eqn (1b)

\[X = 1 - \left(\frac{f_1}{f_{10}}\right)^\alpha \left(\frac{I - f_{10}}{I - f_1}\right)^\beta \left(\frac{f_{10} - \delta}{f_1 - \delta}\right)^\gamma\]

where:

\[\alpha = \frac{r_2}{I - r_2}; \quad \beta = \frac{r_1}{I - r_1}; \quad \delta = \frac{I - r_1 r_2}{(I - r_1)(I - r_2)}; \quad \gamma = \frac{I - r_2}{2 - r_1 - r_2}\]

Eqn (2a)

\[\frac{F_1}{f_1} = \frac{f_{10} - f_1(I - X)}{X}\]

Eqn (3)

**Figure 1.** Variation of cumulative copolymer composition with conversion. Solid lines calculated are based on Meyer-Lowery equation.

\[k_p = \frac{1}{\rho} \left(\frac{2f[I]}{K_p K_d}\right)^{\alpha \beta} (I - e^{-\frac{K_d}{d} t/2})\]

Due to the difference in densities between polymer and monomer, the reaction volume shrinks, as polymerization proceeds. The knowledge of the density of terminal copolymerization model. The use of this equation for estimating kinetic parameters has the advantage that one is no longer restricted to low conversions to determine copolymerization parameters [16], conversion effects can be studied [17] and also one single copolymerization reaction can provide numerous data.

**Copolymerization Rate**

Modelling conversion against time is difficult because of the uncertainty of the rate parameter values, which usually are both composition and conversion dependent. Pseudokinetic rate constant method (PKRC) is a useful tool to analyze the kinetics of copolymerization [18-19]. In this method of treatment, kinetics of a multicomponent polymerization reduces to that of homopolymerization. This method applies to chain statistics based on terminal model, as well as higher order Markov chain statistics such as penultimate model. The average values of propagation and termination rate constants, which are functions of conversion because of compositional drift, are expressed as $K_p$ and $K_t$, respectively. Using average composition dependent values based on PKRC method for kinetic parameters, the overall rate expressions for copolymerization reduce to those of homopolymerization [20-21].
the polymer-monomer mixture as a function of copolymer composition and conversion is required in order to estimate the contraction factor. The rate of polymerization in shrinkage mode [22] is given by:

\[
\frac{dX}{dt} = (2/tk) \frac{k}{d} [1]^{0.5} \frac{1-X}{(1+\varepsilon X)^{0.5}} \exp(-t_0/2)
\]

Integration of the above equation with respect to time yield:

\[
\left\{ \frac{1}{1+\varepsilon X} - \frac{1}{1+\varepsilon} \right\} = \int \frac{\tanh^{-1}\left( \frac{1}{1+\varepsilon} \right)}{1+\varepsilon} dt
\]

where:

\[
\overline{K} = \frac{r}{k_0} [1]^{0.5}
\]

and

\[
\varepsilon = \frac{V_{x=1}}{V_{x=0}} - \frac{\rho_{x=1}}{\rho_{x=0}} - 1
\]

Following the treatment of Fukuda and coworkers [2], assuming that termination in copolymerization can be expressed by the Walling chemical factor \( \Phi = 1 \), the IPUE model gives:

\[
\overline{W} = \frac{r_f f_1^2 + 2 f_f f_2^2 + r_s f_2^2}{\left( \frac{r_f f_1}{W_1} \right) + \left( \frac{r_s f_2}{W_2} \right)}
\]

where, \( r_i = k_{ii} / k_j (i \neq j) \) are the terminal model reactivity ratios. Following the nomenclature of Fukuda et al., \( k / k_0 \) is expressed by \( W_1 \), and \( W_1 \) and \( W_2 \) are given by:

\[
W_i = \frac{w_f (r_f + f^2)}{r_f + f S^{1}} (i \neq j)
\]

where, \( w_i = k_{ii}/k_{0} \) and the chain end reactivity ratios are given by \( S_1 = k_{pj}/k_{ii} \). This model assumes that the ordinary reactivity ratios, \( r_1 \) and \( r_2 \) are not affected by penultimate units, but that the ratios \( S_1 \) and \( S_2 \) differ from unity because of penultimate effects.

**EXPERIMENTAL**

**Monomer Purification**

AIBN (Fluka, Chemica, >98%) as an initiator was crystallized three times from mixture of chloroform and methanol below 40 C in subdued light. Dried under vacuum at room temperature over \( P_2 O_5 \) and stored in dark place below -10 C until used. The melting point was measured by Perkin-Elmer DSC at a heating rate of 5 C/min, and was noted 104.2 C. The monomers, isobutyl methacrylate (Aldrich 99%) and lauryl methacrylate (Fluka 98%), with 15 ppm methyl-ethyl hydroquinone (MEHQ) were washed three times with a 10% NaOH, and then three times with freshly distilled water, dried over CaCl_2 and distilled under vacuum [23]. Copper stearate was used for peroxide breaking in distillation chamber and middle fraction of distillate was collected and dried under vacuum at room temperature over \( CaCl_2 \) and stored at -10 C.
10 C. All other solvents and other reagents used over the course of experiments and characterization were employed as packaged without further purification.

**Polymerization**

Borosilicate glass ampoules of length 10 cm and outer diameter 1.7 cm were prepared. All solution polymerizations were performed in benzene and the initiator concentrations were 0.1 molar. In all solution copolymerizations, the volume ratio of monomers to solvent was 50%. The initial feed mixture was prepared by weighing the monomers, initiator and benzene into a flask and pipetting the contents into several numbered ampoules. Then the ampoules were flushed with oxygen-free nitrogen for 10 min in order to remove the dissolved gases prior to sealing.

The reaction mixture was then subdued to three freeze-pump-thaw cycles to remove residual oxygen. The sealed ampoules were vigorously shaken on the vortex mixer and immersed into a water bath regulated at the polymerization temperature. All copolymerization reactions were carried out at 70 C. After a certain period of time, the reaction mixture was quenched and precipitated in 10-20 fold excess by volume of isopropyl alcohol (IPA) in a flask. The precipitate was allowed to stand for about 10 min, followed by swirling the contents of the flasks to coagulate the polymers and collecting the solids. The polymer was redissolved in THF and again precipitated in IPA. The copolymer was dried in a vacuum oven at 40 C for several days to reach constant weight. Conversions were calculated by gravimetry.

**Polymer Characterization**

**Elemental Analysis**

A Heraeus apparatus model CHN-O-Rapid was uti-
lized for elemental analysis. The apparatus was first calibrated and then checked for gas leaking. Approximately 2 mg sample was accurately weighed and sealed in a tin or silver capsule. The analyzer was swept with the gas that has been treated to remove traces of O₂, H₂O and CO₂. At the start of the run, a measured excess volume of O₂ was added to the stream. Then, the sample capsule was dropped into a preheated ceramic crucible, where the capsule melts and the sample was rapidly oxidized to give predominantly CO₂, H₂O and N₂. A hot oxidation catalyst completed the process, and hot Cu scavenged excess oxygen analysis was carried out by pyrolysis in the absence of oxygen, a process that ultimately converted oxygen from the compound to CO. The product was separated by chromatography and measured by their thermal conductivity.

**Densitometry**

The density of monomer mixture was calculated by a simple mixing rule without considering the interaction between constituents. Density of polymerization samples was determined by Anton Par digital densitometer. A small volume of sample (about 0.7 mL) was introduced into an oscillating sample tube and the change in the oscillating frequency caused by the change in the mass of the tube was used in conjunction with calibration data to determine the density of the sample. The samples were homogeneous and free of even the smallest bubbles. After the instrument displayed a steady reading to four significant figures, it indicated that temperature equilibrium is being reached, and the reading for density change was recorded. Shrinkage factor was determined by linear assumption according to eqn (8).

**RESULTS AND DISCUSSION**

At least ten replicate polymerization runs at each monomer feed composition were performed at different conversion levels. The CHO content of copolymer, overall mass conversion and global copolymer composition at different reaction times for this system were determined. The copolymer composition was calculated by solving the following set of linear algebraic equations through a constrained optimization program:

\[
\begin{align*}
\text{Obj. fun.:} & \quad 96F_1 + 192F_2 - C\% (142F_1 + 254F_2) = 0 \\
\text{Subj. to.:} & \quad 14F_1 + 30F_2 - H\% (142F_1 + 254F_2) = 0 \\
& \quad 32F_1 + 32F_2 - O\% (142F_1 + 254F_2) = 0 \\
& \quad F_1 + F_2 = 1.0
\end{align*}
\]

The results are collectively shown in Table 1. The cumulative copolymer compositions as a function of conversion for different initial feed compositions are shown in Figure 1. The solid lines, calculated according to the TUM, indicate that the terminal unit model predictions of the compositional data are quite good and support the validity of the reactivity ratios were estimated in the previous work [12].

Because of small differences between reactivity ratios, the compositional drift for the condition used for this system was low.

It is interesting to note in Figure 2, where the results of the kinetic measurements are represented, that not only a higher copolymerization rate but also an increase of the sigmoidal character of the curves are obtained when the LMA mole fraction in the feed increases. The solid lines drawn in Figure 2 are empirically fitted to fifth-order polynomials.

The high conversion kinetics of i-BMA/LMA copolymerization is determined by the appearance of gel effect, which is illustrated in Figure 3. The overall copolymerization rate \( R_{\text{cop}} \), which was standardized on the actual initial value, is plotted as a function of polymerization time for different monomer feed compositions. For high LMA mole fractions the polymerization rate increases by a factor of 2.33 of its initial value; even at lower LMA content in the feed, it increases nearly by a factor of 1.76 of its initial value. In addition, the loci of maximum polymerization time for dif-
ferent monomer feed compositions are shown by a dashed line in Figure 4. The data in Figure 3 is similar to those in Figure 4, but from Figure 4 it is clear that the position of gel point would be delayed in polymerization system by increasing the amount of i-BMA in the feed.

The individual conversion of each monomer as a function of polymerization time can be obtained from the overall conversion and its corresponding cumulative copolymer composition.

Experimental results are presented in Figure 5. From this figure it is clear that, in accordance with the previous reported reactivity ratios [12], i-BMA is more rapidly consumed than LMA for all values of i-BMA mole fraction used in the feed.

Taking into account the homopolymerization kinetic parameters \( r_p/r_t^{0.5} = 1.573 \) and \( 2.847 \text{ (L/mol.min)}^{0.5} \) for i-BMA and LMA, respectively) previously reported [11], along with the chain end reactivity ratios given above and assuming that the aforementioned values do not change with monomer conversion, the variation of \( W = r_p/r_t^{0.5} \) with conversion has been calculated from eqn (9) by considering the instantaneous monomer feed composition throughout the course of polymerization. From empirically fitted fifth-order polynomials of Figure 2 and using eqns (4) and (6), it is possible to determine the \( k_p/k_t^{0.5} \) ratio as a function of monomer conversion. In this analysis, it is assumed that the average values of previously determined initiator efficiency, initiator decomposition rate constant and shrinkage factor do not change appreciably with conversion. Comparative views between the values obtained from experimental curves and those calculated by the penultimate effect model are given in Figure 6. Dotted lines are penultimate effect model predictions, and solid lines are experimental data. The simulation seems to adequately predict \( k_p/k_t^{0.5} \) up to conversions, which is a function of the LMA mole fraction in the feed. Beyond these conversions, experimental values increase more markedly than the corresponding IPUE predictions. Considering the above mentioned results and taking into account that the termination rate constant in copolymerization depends on the homopolymerization rate constants of monomers and the copolymer composition, it is reasonable to assume that not only the copolymer composition but also the homotermination rate constants of monomers will change as the reaction proceeds. Then the deviations between the theoretical calculation and the experimental values start with the onset of the gel effect.

**CONCLUSION**

Because of small differences between reactivity ratios, the compositional drift for the condition used for this system is low. An increase in the sigmoidal character of the kinetic curves is obtained when the LMA mole fraction in the feed increases. Also a close examination of the individual comonomer conversion-time data included in Figure 5 indicates an increase of the rate of the polymerization, which usually happens in cases where autoacceleration has a role. The locus of maximum polymerization rate (i.e., gel point) is shifted to higher conversions by increasing the amount of i-BMA in the feed.

The simulation adequately predicts \( k_p/k_t^{0.5} \) up to conversions, which are a function of the LMA mole fraction in the feed. Beyond these conversions, experimental values increase more markedly than the corresponding IPUE predictions. Considering the above mentioned results and taking into account that the termination rate constant in copolymerization depends on the homopolymerization rate constants of monomers and the copolymer composition, it is reasonable to assume that not only the copolymer composition but also the homotermination rate constants of monomers will change as the reaction proceeds. Then the deviations between the theoretical calculation and the experimental values start with the onset of the gel effect.

**REFERENCES**
