Reactivity Ratio Determination of Newly Synthesized Copolymers from Glycidyl Methacrylate and Tetrahydrofurfuryl Acrylate

Penentuan Nisbah Kereaktifan Kopolimer Baru yang Disintesis daripada Glisidil Metakrilat dan Tetrahidrofurfuril Akrilat

AHMAD DANIAL AZZAHARI, ROSIYAH YAHYA* & AZIZ HASSAN

ABSTRACT

Copolymers from different feed compositions of glycidyl methacrylate (GMA) and tetrahydrofurfuryl acrylate (THFA) were synthesized using free radical polymerization in toluene solution at 70±1°C using benzoyl peroxide (BPO) as initiator. The polymers were characterized by 1H NMR, 13C NMR and DEPT spectroscopic techniques. The copolymer compositions were determined using 1H NMR analysis. Reactivity ratios for GMA and THFA were determined by the Kelen-Tudos, Tidwell-Mortimer and error-in-variables model methods. The results showed that all these copolymerizations were strictly linear systems describable by the Mayo-Lewis equation based on the terminal model and that accurate reactivity ratio data can be obtained.

Keywords: Copolymerization; glycidyl methacrylate; reactivity ratios; tetrahydrofurfuryl acrylate

ABSTRAK

Kopolimer daripada komposisi glisidil metakrilat (GMA) dan tetrahidrofurfuril akrilat (THFA) telah disintesis dengan menggunakan pempolimeran radikal bebas dalam larutan toluena pada 70±1°C menggunakan benzoyl peroksida (BPO) sebagai pemula. Kopolimer ini dicirikan oleh teknik spektroskopi 1H NMR, 13C NMR dan DEPT. Nisbah kereaktifan untuk GMA dan THFA telah ditentukan oleh kaedah Kelen-Tudos, Tidwell-Mortimer dan model ralat-dalam-pemboleh ubah. Keputusan menunjukkan bahawa semua kopolimerisasi ini merupakan sistem linear yang boleh diterangkan oleh persamaan Mayo-Lewis berdasarkan model terminal dan data nisbah kereaktifan yang tepat boleh diperoleh.

Kata kunci: Glisidil metakrilat; kopolimerisasi; nisbah kereaktifan; tetrahidrofurfuril akrilat

INTRODUCTION

Acrylic copolymers have achieved prime importance in various avenues of industrial application (Adhikari & Majumdar 2004; Arica et al. 2004; Bayramoglu et al. 2003; Hall et al. 1996; Malmsten & Larsson 2000; Nino et al. 2004; Pérez et al. 2006; Yang et al. 1999). GMA, which is of interest to us, is used to provide epoxy functionalization to our acrylate resin. However, due to the similarity in the constituent units of copolymers containing acrylate and methacrylate monomers, it is difficult to determine their compositions by normal analytical techniques (Bakhshi et al. 2009; Grassie et al. 1965). UV and IR spectroscopic methods are not very helpful and other methods such as gas-liquid chromatography, radiometric and isotopic analysis are time consuming. The determination of copolymer composition by NMR techniques would then be a better option since this technique has many advantages not only for the calculation of composition and sequence distribution of copolymers but also for the estimation of tacticity (Espinosa et al. 2001; Ghi et al. 1999; Schaefer 1969).

The precise determination of monomer reactivity ratios (MRR) would serve as a useful tool towards the accurate estimation of copolymer composition, understanding their properties and utility for tailoring copolymers with desired physicomechanical properties. Typically, reactivity ratios are estimated using the instantaneous copolymer composition equation, based on low conversion yield copolymer composition data, otherwise known as the Mayo-Lewis model. It has been suggested that, for a given pair of monomers 1 and 2 (in this case corresponding to GMA and THFA, respectively), the instantaneous copolymer composition is a function of instantaneous feed only (Mayo & Lewis 1944). The estimation method used to determine the reactivity ratios from the Mayo-Lewis model however varies from linear least squares techniques (LLS) to nonlinear (NLLS). In this paper, both methods are compared and considered for any potential improvement gained in MRR estimation. The present paper reports the synthesis, NMR spectroscopic characterization and determination of reactivity ratios \( r_1 \) and \( r_2 \) for copolymers of glycidyl methacrylate (GMA) with tetrahydrofurfuryl acrylate (THFA), respectively.

EXPERIMENTAL DETAILS

GMA (Merck) and THFA (Aldrich) were purified by distillation under reduced pressure. BPO (Merck) was recrystallized from ethanol and dried under vacuum at...
40°C. All the other solvents were purified by distillation prior to their use.

Each of the copolymerization reactions was carried out with predetermined ratios of GMA and THFA monomers in toluene at 70±1°C under N₂ atmosphere for a period sufficient to keep conversion yields low. The total concentration of monomers and initiator was kept at 1.39 M and 34.33 mM, respectively. Polymeric material was precipitated twice in excess of n-hexane and dried in vacuum at ambient temperature. Conversion yields were calculated gravimetrically.

¹H NMR and ¹³C NMR measurements were performed with a JEOL-Lambda 400 MHz spectrometer using CDCl₃ as solvent. The nature of each carbon atom was determined using the DEPT spectral editing technique, with proton pulses at θ = 135°.

RESULTS AND DISCUSSION

The copolymers of GMA with THFA in toluene were synthesized with composition of mole fractions ranging from 0.10 to 0.85 as shown in Table 1. The copolymers obtained were colourless solids with intermediate properties of polyGMA (hard solid) and polyTHFA (soft adhesive). The synthesis of the copolymer is outlined in Figure 1.

The typical ¹H NMR spectra of the copolymer are presented in Figure 2. The proton assignments are based on their corresponding monomers as well as comparison with spectra of analogous chemical groups taken from the literature (Bakhshi et al. 2009; Espinosa et al. 2001; Ghi et al. 1999; Rajendrakumar & Dhamodharan 2009). Due to the tacticity of the α-CH₃ from the GMA unit, a series of the corresponding resonance signals appear at 0.93, 1.02 and 1.09 ppm which have been assigned to syndiotactic (rr), heterotactic (mr+rm) and isotactic (mm), respectively. Three very well-defined peaks, belonging to the epoxy groups, appear between 2.5 and 3.4 ppm. The proton of the chiral carbon on the oxirane ring resonates at 3.22 ppm whereas protons on the –OCH₂– of the oxirane ring resonates at 2.63 ppm and 2.83 ppm. These peaks were used as references to follow the GMA modification. The GMA unit’s protons on the –OCH₂– of the ester group resonates at about 3.8 ppm and 4.3 ppm which overlaps with five other protons of the THFA unit in the range of 3.68 to 4.44 ppm. The peaks in the range of about 1.4 to 2.5 ppm consists of the methylene protons of the polymer chain backbone of both the GMA and THFA units, as well as the methine proton of the polymer chain backbone of the THFA unit along with four of the –CH₂– protons on the THF ring.

The proton decoupled ¹³C NMR and the DEPT 135 spectrum of poly(GMA-co-THFA) are presented in Figure 3. The DEPT experiment differentiates between primary, secondary and tertiary carbon groups by variation of the

<table>
<thead>
<tr>
<th>f₁</th>
<th>yield (wt%)</th>
<th>I_U</th>
<th>F₁</th>
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<td>0.849</td>
<td>3.8</td>
<td>3.440</td>
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</tr>
</tbody>
</table>

FIGURE 1. Synthesis of copolymer of GMA and THFA
The distinctive absorption of the lone proton of the chiral carbon on the oxirane ring of the GMA unit is compared against the overlapping protons of the GMA unit (2 protons) and THFA unit (5 protons) located downfield from the lone proton of the chiral carbon signal on the GMA unit. The integral of the lone proton signal is normalized to a value of 1, hence the equation to determine the copolymer composition becomes: 

\[ F_i = \frac{5(I_{GMA} + 3)}{F_i} = 1 - F_i, \]

where \( I_{GMA} \) is the integrated area of the ester protons in the GMA unit. Other methylene carbons belonging to the polymer backbone of the THFA unit show a signal at 44.68 ppm (C\(_5\)) whereas the methine carbon shows a signal at 48.69 and 48.88 ppm (C\(_3\)). A series of resonance signals between 65.54 and 66.63 ppm corresponds to the methylethoxy group on both the GMA and THFA units (C\(_4\) and C\(_6\)). The carbonyl carbon of the THFA unit resonates between 174.14 and 174.23 ppm (C\(_7\)) whereas the GMA unit resonates between 175.04 and 177.20 ppm (C\(_8\)).

The experimental results presented in Table 1 have been treated with several methods to calculate the MRR for the GMA-THFA system. All these methods are based on the terminal model, viz. the Mayo-Lewis equation (Mayo & Lewis 1944). The straight line in Figure 4 is an ideal case where \( f_i = F_i \). However, due to the different MRR, there is a drift in observed \( F_i \) from \( f_i \). Both reactivity ratios are less than unity as shown by an azeotropic composition at approximately 55% GMA feed. As such, a tendency towards alternation and no long homopolymeric blocks is expected (Odian 2004).

The KT method overcomes this by introducing a selection angle parameter: \( \theta = 135^\circ \) gives all CH and CH\(_3\) in a phase opposite to CH\(_2\). The carbons assignments are based on their corresponding monomers as well as comparison with spectra of analogous chemical groups taken from literature (Espinosa et al. 2001; Rajendrakumar & Dhamodharan 2009). The \( \alpha\)-CH\(_3\) from the GMA unit resonates at 16.65, 16.80 and 17.83 ppm due to tacticity (C\(_1\)). Carbons on the THF ring show resonance signals at 25.52, 28.16, 68.08 and 76.06 ppm (C\(_9\), C\(_2\), C\(_11\) and C\(_10\)); respectively. The peak at 76.06 ppm which is almost hidden by the nearby CDCl\(_3\) signals in the DEPT spectra since signals from the quaternary carbons and other carbons with no attached protons are always absent in the DEPT spectra.

The methine carbon on the polymer backbone of the THFA unit shows a signal at 41.14 ppm (C\(_8\)) whereas the methylene carbon shows a signal at 44.56 ppm (C\(_9\)). The distinctive absorption of the lone proton on the terminal model, viz. the Mayo-Lewis equation (Mayo & Lewis 1944), defined as 

\[ \eta = r \xi - r (1 - \xi) \alpha \text{ where } \eta = (G/F - 1)/F \text{ and } H = f^2 F, \]

where \( f = f_i / f \) and \( F = F_i / F \). The Fineman-Ross method however, has an unfortunate consequence of having certain experimental points with inappropriate weights in the plot. One of the well-known LLS methods to determine \( \alpha \) is given by the Kelen-Tudos (KT) method (Kelen et al. 1974, 1975): 

\[ \eta = r \xi - r (1 - \xi) \alpha \text{ where } \eta = (G/F - 1)/F \text{ and } H = f^2 F, \]

where \( f = f_i / f \) and \( F = F_i / F \). The Fineman-Ross method however, has an unfortunate consequence of having certain experimental points with inappropriate weights in the plot. The KT method overcomes this by introducing a symmetry parameter defined as 

\[ \alpha = H_{min} \times H_{max} ^{0.5} \]

A plot of \( \eta \times \xi \) gives a straight line, with an intercept equaling to \( -r_i \times \alpha \) and the slope as \( r_i + r_i / \alpha \). The \( \eta \times \xi \) plot is shown in Figure 5.
The 95% individual confidence intervals method (Box et al. 1978), of the \( r_1 \) and \( r_2 \) can be calculated by:

\[
\Delta r = \pm t_{n-2,0.025} \frac{S_y}{n-2} \left( \sum (1-\xi_i)^2 \right)^{1/2} D^{-1} 
\]

and

\[
\Delta r = \pm t_{n-2,0.025} \frac{S_y}{n-2} \left( \sum (1-\xi_i)^2 \right)^{1/2} D^{-1},
\]

where \( t_{n-2,0.025} \) is the student’s \( t \) distribution with \( n-2 \) degrees of freedom and with each tail area probability equaling 0.025. \( n \) is the number of experimental points. The quantities \( S_y \) and \( D \) are as follows:

\[
S_y = \sum (n_i - \bar{r}_i) \left( \sum (1-\xi_i)^2 \right)^{1/2}
\]

\[
D = \sum (1-\xi_i)^{-2} \left( \sum (1-\xi_i)^2 \right)^{-1}
\]

The results of this method, using the data from Table 1 are: \( r_1 = 0.388 \pm 0.092 \) and \( r_2 = 0.282 \pm 0.061 \). Since \( r_1 \) and \( r_2 \) are not independent of one another, it would be more appropriate to use the 95% joint confidence region (JCR), according to the following equation:

\[
(n_i - \bar{r}_i)^2 \sum (1-\xi_i)^2 + \frac{2}{\alpha} \left( (r_i - \bar{r}_i) \sum (1-\xi_i)^2 \right) \sum (1-\xi_i)^2 = 2 \frac{S_y}{n-2} F_{(n-2,0.025)}
\]

where \( F_{(n-2,0.025)} \) is the \( F \) distribution having 2 and \( n-2 \) degrees of freedom and \( \bar{r}_i \) and \( \bar{r}_j \) are the least-squares estimation of \( r_1 \) and \( r_2 \) respectively. The JCR for this method as well as the other methods are shown in Figure 6.

The Tidwell-Mortimer (TM) method (Tidwell & Mortimer 1965) is one of the commonly used techniques for solving NLLS problems. The method consists of the following: given initial estimates of the parameters \( r_1 \) and \( r_2 \) obtained by some other method, the mathematical model \( g_i \) is calculated by:

\[
g_i = \frac{r_1 f_{1i}^2 + r_2 f_{2i}}{2f_{1i}^2 + r_1 f_{1i}^2}
\]

The differences between the observed and computed polymer compositions would then be

\[
d_i = \frac{F_{1i}}{F_{1i} + F_{2i}} - g_i.
\]

The objective is to minimize the sum of the squares of the differences by iteration. The computation procedure is basically a Gauss-Newton NLLS method with a modification (Box 1958) to assure rapid convergence to a pair of values. Values of \( S_k = [\sum d_i^2]_k \) for \( r_1 = r_1 + [(k-1)/2]b_1 \) and \( r_2 = r_2 + [(k-1)/2]b_2 \) are determined for values of \( k = 1, 2, \text{ and } 3 \) where:

\[
b_1 = \frac{1}{C} \left[ \frac{\alpha}{\gamma} \sum \left( \frac{\partial g}{\partial \xi} \right)^2 \frac{\partial g}{\partial \xi} \right] + \frac{d_i^2}{\sum \left( \frac{\partial g}{\partial \xi} \right)^2}
\]

\[
b_2 = \frac{1}{C} \left[ \frac{\alpha}{\gamma} \sum \left( \frac{\partial g}{\partial \xi} \right)^2 \frac{\partial g}{\partial \xi} \right] + \frac{d_i^2}{\sum \left( \frac{\partial g}{\partial \xi} \right)^2}
\]

\[
C = \frac{\alpha}{\gamma} \left[ \frac{\alpha}{\gamma} \sum \left( \frac{\partial g}{\partial \xi} \right)^2 \frac{\partial g}{\partial \xi} \right] + \frac{d_i^2}{\sum \left( \frac{\partial g}{\partial \xi} \right)^2}
\]

and \( S_k = [\sum d_i^2]_k \) for \( r_1 = r_1 + V b_1 \) and \( r_2 = r_2 + V b_2 \) where \( V = 0.5 + (S_1 - S_3)/(4S_1 - 2S_2 + S_3) \). \( S_1 \) and \( S_3 \) are evaluated by repeating this process with the new estimates of \( r_1 \) and \( r_2 \) being the \( r \) values calculated at \( S_4 \). If \( S_4 > S_1 \), then \( V \) is reevaluated by first halving \( b_1 \) and \( b_2 \). This process is repeated until the sum of the squares of the differences is minimized. For most systems with a good initial estimate of reactivity ratios, less than ten iterations are required to
obtain the minimum difference. However, different initial guesses may lead to different local optima, depending on the $S_i$ surface as shown in Table 2. The number of iterations shown is when the local optima are consistent up to three decimal places.

The 95% JCR as shown in Figure 6, which is enclosed by the ellipse for $r_i^*$ and $r_j^*$, the natural log of the least-squares estimates of $r_i^*$ and $r_j^*$, is defined by $a_{1i}(t_i^*-t_i^*)^2 + a_{2i}(t_i^*-t_i^*) + a_{3i}(t_i^*-t_i^*)^2 = 2 F_{(a, n-2)}[\Sigma(d)^2]/(n-2)$ where $a_{1i} = (r_i^*)/\Sigma(\partial g/\partial r_i)^T$, $a_{2i} = (r_i^*)/\Sigma(\partial g/\partial r_i)^T$, and $a_{3i} = (r_i^*)/\Sigma(\partial g/\partial r_i)^T$.

The algorithm starts by using the initial parameter true (yet unknown) values of the parameters, $\theta$. It consists of two statements, the first being the vector of true values, $\theta_0$, of the vector of measurements, $g_j$, and the second relates the natural log of the least-squares estimates, $\theta$, to the local optima, $\theta_0$, via the mathematical model represented by $\begin{align*}
\xi = (\theta_0 - f_2)^T \Sigma^{-1}(\theta_0 - f_2) + \frac{1}{2} \Sigma^{-1} f_2^T f_2 + \ln f_2 + \frac{1}{2} \ln(2\pi)\end{align*}$.

where $\theta_0$ is the chosen initial parameter value, $f_2$ is the set of input data, and $\xi$ is the error covariance matrix for the measurements, $a_i = (\partial g_i/\partial r_i)^T$.

The error-in-variables-model (EVM) approach used in this experiment is another NLLS technique based on the algorithm by (Reilly & Patino-Leal 1981; Reilly et al. 1993). It consists of two statements, the first being the vector of measurements $x_i$, which is equated to the vector of true values $\xi$, plus an error term, $e_i$, where $i$ is the trial number. The second statement relates the true (yet unknown) values of the parameters, $\theta$, and variables, $\xi$, via the mathematical model represented by $g(\xi, \theta) = f_1 - [r_i f_1 - f_2 (1-f_2)]/f_1 2 f_1 (1-f_2) + r_i (1-f_2) = 0.05$.

The algorithm starts by using the initial parameter estimates, $\theta_{00}$, where $\begin{align*}
\xi = (\theta - \theta_0)^T \Sigma^{-1}(\theta - \theta_0) + \frac{1}{2} \Sigma^{-1} \theta + \ln f_2 + \frac{1}{2} \ln(2\pi)\end{align*}$, of the function, $g(\xi, \theta)$, which is the vector of partial derivatives with respect to the parameters given by $\begin{align*}
Z = [\partial g(\xi, \theta)/\partial \ln f_2, \partial g(\xi, \theta)/\partial \ln f_2] \end{align*}$.

and $B$ is the vector of partial derivatives of the function, $g(\xi, \theta)$, with respect to the logarithm of the variables, $\begin{align*}
B_i = [\partial g(\xi, \theta)/\partial \ln f_2, \partial g(\xi, \theta)/\partial \ln f_2] \end{align*}$.

The 95% JCR is given by $\begin{align*}
\chi^2 = (\theta - \theta_0)^T G(\theta - \theta_0) + \frac{1}{2} \chi^2_{(a, n-1)}\end{align*}$, where $\chi^2$ represents the value of the chi-squared distribution, $p$ is the number of parameters, $\theta$, $1-\alpha$ is the chosen confidence level and **"** indicates estimates of the parameters. The assumptions required for the EVM are that the model is correct and that successive measurement vectors are independent of one another. The JCR overlay of all the three methods used, as shown in Figure 6, reveals that the calculated results from the EVM method is the better choice since it has the smallest region of uncertainty which also encompasses the MRR point estimates determined from the KT and TM methods.

![Figure 6. 95% JCR for the evaluated values of $r_i$ and $r_j$ by KT, TM and EVM method](image)

**TABLE 2. Results of the Tidwell Mortimer method**

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<tr>
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<th>$r_{2\text{ input}}$</th>
<th>$r_{1\text{ output}}$</th>
<th>$r_{2\text{ output}}$</th>
<th>Iterations required</th>
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**TABLE 3. Results of the EVM method**

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<th>$r_{2\text{ output}}$</th>
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CONCLUSION
A series of copolymers of poly(GMA-co-THFA) were prepared using BPO as initiator in toluene at 70±1°C. H- and 13C-NMR spectroscopies reveal the presence of both monomeric constituents in the copolymer. The copolymer compositions were determined by the 1H-NMR method. The MRR were obtained by the KT, TM and EVM methods. Of the three, the EVM method provides the most accurate MRR estimates because it has the smallest JCR area (which leads to a higher confidence in the point estimates). The values of \( r_1 \) and \( r_2 \) are less than unity indicating that the system gives rise to an azotropic polymerization and a strong tendency to alternation.

ACKNOWLEDGEMENT
We gratefully recognize the financial support for this project from the University of Malaya under the grant number PS371-2010B.

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Received: 23 June 2011
Accepted: 23 March 2012