

EFFECT OF TEMPERATURE ON COPOLYMERIZATION PARAMETERS OF HYDROXYETHYL ACRYLATE AND METHYL METHACRYLATE

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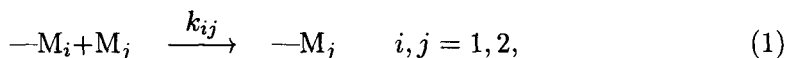
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Abstract The copolymerization of 2-hydroxyethyl acrylate (HEA, M_1) and methyl methacrylate (MMA, M_2) in cyclohexanone was studied. The multiple experiments of solution copolymerization with low conversion were carried out at two sensitive composition feed points at 60, 80, 100, 120 and 140°C, respectively. The composition of the copolymers was analyzed by $^1\text{H-NMR}$. The reactivity ratios which were estimated by the Error-in-Variable Method (EVM) of Mayo-Lewis equation were found to be $r_1 = 0.328$, $r_2 = 1.781$ for 60°C; 0.375, 1.709 for 80°C; 0.406, 1.654 for 100°C; 0.439, 1.540 for 120°C and 0.455, 1.400 for 140°C, and the 95% joint confidence intervals of the reactivity ratios were also determined. According to r_1 and r_2 , Arrhenius relations and the activity energy difference between the homo- and cross-propagation were calculated.

Keywords Reactivity ratio; 2-Hydroxyethyl acrylate; Methyl methacrylate; Copolymerization; Copolymer composition

INTRODUCTION

In the copolymerization of vinyl monomers, propagation is usually described by the following reactions:



where $-M_i$ and $-M_j$ are chain radicals ending in monomer units i or j , and monomer reactivity ratios (MRRs) are defined as:

$$r_1 = k_{11}/k_{12} \quad r_2 = k_{22}/k_{21} \quad (2)$$

As one of the most basic parameters of polymer chemistry, relative reactivity ratio is an important data of copolymerization. From reliable reactivity ratios, one is able to measure the composition and chain distribution of copolymer and to study the reaction mechanism readily. The determination of reactivity ratios with small confidence intervals requires sensitive analytical techniques, careful planning of experiments and use of statistically valid methods of estimation.

Though there are a lot of MRRs data available in the literatures, it is well known that uncertainties in the values of reactivity ratios are large when the values of r_1 and r_2 are quite different^[1]. Most of the MRRs published to date have not been calculated using statistically valid methods, and the confidence intervals were not usually given. Furthermore, most of the literature data have been obtained at temperature well below 100°C, while the effect of temperature on MRRs has been neglected. On the other hand, the rapid production of polymer materials in industry usually proceeds at a higher temperature. So it is essential to obtain reliable reactivity ratios at a wide temperature range.

2-Hydroxyethyl acrylate (HEA) is a functional vinyl monomer and the polymers based on it were important in applications^[1]. There were few literatures about the reactivity ratios of HEA with other vinyl monomers^[2,3,4]. In fact, the reactivity ratios of HEA (M_1)-MMA (methyl methacrylate, M_2) system has not been reported yet.

In order to estimate the reactivity ratios, the feed monomer compositions were designed at the upper and lower sensitive composition points and can be calculated as the following^[5]:

When

$$r_2 \geq r_1, \quad f_1 = r_1/(2 + r_1), \quad f'_1 = 2/(2 + r_2) \quad (3)$$

For this system, there is lack of value of the reactivity ratios reported. So the values of r_1 and r_2 calculated by Q - e values are as follows^[6]:

$$r_1 = Q_1 \exp[-e_1(e_1 - e_2)]/Q_2 \quad r_2 = Q_2 \exp[-e_2(e_2 - e_1)]/Q_1 \quad (4)$$

The Q - e values of HEA and MMA were found to be $Q_1 = 0.75$, $e_1 = +0.65$ ^[7] and $Q_2 = 0.74$, $e_2 = +0.40$ ^[8] respectively. Then the reactivity ratios calculated from the Q - e values were $r_1 = 0.86$, $r_2 = 1.10$ for this pair of monomers. So the two sensitive points were calculated to be $f_1 = 0.65$, the upper feed composition and $f'_1 = 0.35$, the lower feed composition point.

At the present study, copolymerizations were carried out at five different temperatures, which were 60, 80, 100, 120 and 140°C. The compositions of copolymers were analyzed by ¹H-NMR, the reactivity ratios and the 95% Joint Confidence Intervals were estimated by Error-in-Variable Method (EVM). From the values of r_1 and r_2

obtained at various temperatures, the Arrhenius relation and the activity energy difference between the homo- and cross-propagation were calculated.

EXPERIMENTAL

Purification of reagents

AIBN (azobisisobutyronitrile) was chosen as the initiator, which was recrystallized twice from 95% ethanol, dried under reduced pressure at room temperature, and stored in a sealed brown reagent bottle and placed in a refrigerator before using.

Methyl methacrylate (MMA) was washed three times with 5—10% NaOH aqueous solution to remove inhibitor, the organic phase was washed by deionized water to neutral, decanted, and then dried in a conical flask to dry overnight with anhydrous magnesium sulfate. The monomer was distilled under reduced pressure.

2-Hydroxyethyl acrylate (HEA) usually contains varying amount of a multifunctional monomer, ethylene glycol diacrylate (EGDA), which offers the possibility of introducing crosslinkage. It is very difficult to prepare a monoester of ethylene glycol without any diester, the latter being formed by reesterification even from pure monoester, for example during distillation. A better method was tried to refine HEA by passing it through a neutral Al_2O_3 column.

Cyclohexanone was dried with anhydrous sodium sulfate overnight, then distilled under reduced pressure.

Preparation of copolymers

Refined monomers HEA, MMA and solvent cyclohexanone were weighed and mixed in glass ampoules. Freeze-degas-thaw cycle was made for at least three times to every ampoule (the vacuum is about 10^{-3} torr). Then the ampoules were sealed under vacuum. The copolymerization were carried out in an oil bath at designed temperature. To terminate the copolymerization, the ampoule were taken out rapidly and plunged into liquid nitrogen.

Composition analysis of copolymer

The composition of copolymers was analyzed in CDCl_3 solvent with NMR DMX-500 at 300 K.

RESULTS AND DISCUSSION

Analysis of copolymer composition

The compositions of copolymer were analyzed with NMR technique. Two typical high resolution proton NMR spectra of the copolymers are shown in Fig.1.

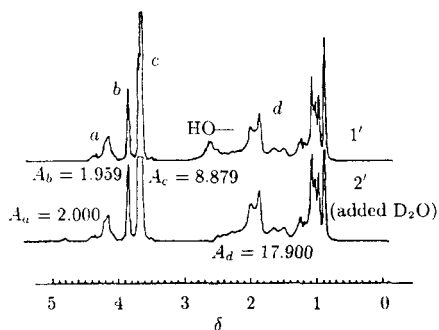
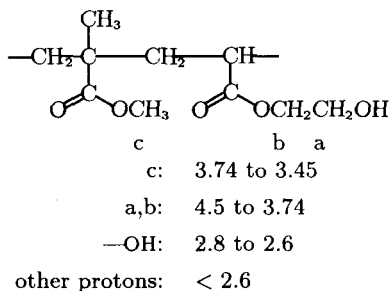


Fig.1 ^1H NMR spectra of the copolymer of HEA and MMA

The chemical shift (ppm in CDCl_3) for HEA-MMA copolymer is given as follows:



The assignment of hydrogen in $-\text{OH}$ group could be testified by the following two methods. As shown in Fig.1, the peak of $\delta = 2.8 - 2.6$ ppm disappeared by adding D_2O into NMR sample solution. Or alternatively, by studying the spectra and calculating the number of protons in the copolymers (No.2 spectrum as an example), we could get the following equations:

$$A_{d(\text{exp.})} = A_{-\text{CH}_2--\text{CH}_3} + A_{-\text{CH}_2--\text{CH}=} = 17.900 \quad (5)$$

$$A_{d(\text{theo.})} = 5A_{-\text{OCH}_3}/3 + 3A_{-\text{OCH}_2\text{CH}_2-}/4 = 5A_c/3 + 3A_{ab}/4 = 17.768 \quad (6)$$

It is apparent that the theoretical $A_{d(\text{theo.})} = 17.768$, calculating sum proton peak area of $-\text{CH}_2-\text{C}(\text{CH}_3)-$ group of MMA unit and $-\text{CH}_2-\text{CH}=$ of HEA unit, is very close to actually measured area $A_{d(\text{exp.})} = 17.900$. We could then confirm that the peak $\delta = 2.8 - 2.6$ ppm to be assigned to $-\text{OH}$ group. According to the relation between the formula of 2-hydroxyethyl acrylate unit (M_1) and methyl methacrylate unit (M_2) and the peak areas, the compositions of the copolymers F_1 were calculated by the following equation:

$$4F_1/3(1 - F_1) = A_{-\text{OCH}_2\text{CH}_2\text{O-}}/A_{-\text{OCH}_3} = A_{ab}/A_c \quad (7)$$

$$\begin{aligned}
 F_1 &= [A_{-\text{OCH}_2\text{CH}_2\text{O-}}/4]/[A_{-\text{CH}_2\text{CH}_2\text{O-}}/4 + A_{-\text{OCH}_3}/3] \\
 &= (A_{ab}/4)/(A_{ab}/4 + A_c/3)
 \end{aligned} \quad (8)$$

where: $A_{-\text{OCH}_3}$ is the peak area of $-\text{OCH}_3$ of MMA unit in copolymer.

$A_{-\text{OCH}_2\text{CH}_2\text{O-}}$ is the peak area of $-\text{OCH}_2\text{CH}_2\text{O-}$ of HEA unit

F_1 is the mole fraction of HEA unit in copolymer

The results of copolymerization, including the feed compositions (f_1) and the calculated compositions (F_1) of the copolymers are summarized in Table 1.

Calculation of monomer reactivity ratios

Since Fineman and Ross^[9] developed the first equation in 1950s for determining the monomer reactivity ratios (MRRs) using a linear form of Mayo-Lewis copolymerization equation^[10], there has been great progress in the field of determining MRRs. Among them, (EVM) was one of the most reasonable methods. It is a weighted least-squares method, and takes into account not only the analytical error of copolymer composition but also the measuring error from monomer composition. In fact, this method assumes that all observations are derived from true values plus measuring errors. The errors are assumed to be normally distributed. On the other hand, the r_1 and r_2 values are correlated. The approximate 95% confidence limit^[11] or intervals^[12] which clearly conveys the degree of uncertainty associated with the point estimates MRRs.

Table 1 Results of copolymerization of HEA and MMA at various temperatures

Sample	60°C		80°C		100°C		120°C		140°C	
	f_1	F_1	f_1	F_1	f_1	F_1	f_1	F_1	f_1	F_1
1	0.3555	0.2217	0.3559	0.2380	0.3505	0.2356	0.3621	0.2506	0.3563	0.2620
2	0.3555	0.2176	0.3559	0.2212	0.3505	0.2274	0.3621	0.2518	0.3563	0.2611
3	0.3555	0.2252	0.3559	0.2215	0.3642	0.2390	0.3621	0.2529	0.3563	0.2640
4	0.3570	0.2129	0.3559	0.2306	0.6382	0.4709	0.6430	0.4888	0.3563	0.2600
5	0.6456	0.4718	0.6453	0.4651	0.6382	0.4584	0.6430	0.4889	0.6397	0.4992
6	0.4656	0.4652	0.6453	0.4657	0.6382	0.4584	0.6430	0.4887	0.6397	0.5120
7	0.6456	0.4537	0.6453	0.4631	0.6382	0.4705	0.6430	0.4986	0.6397	0.5072
8	0.6724	0.4998							0.6397	0.4920

The reactivity ratios (r_1, r_2) and the 95% Joint Confidence Intervals at different temperatures (T) were estimated by RREVM (reactivity ratio by error-in-variable method) program, and the results were shown in Table 2 and Fig.2, respectively.

Table 2 Reactivity ratios of HEA/MMA system at different temperatures

Temp.(°C)	60	80	100	120	140
r_1	0.328	0.375	0.406	0.439	0.455
r_2	1.781	1.709	1.654	1.540	1.400

From Table 2, it could be found that the reactivity ratios of HEA increase with the increase of temperature, while the reactivity ratios of MMA decrease with the increase of temperature. Both of them show a tendency towards unity.

Effect of temperature on MRRs

It would be instructive to visualize how temperature increase from 60 to 140°C

affects MRRs. The temperature dependence of rate constants may be written as an Arrhenius equation (9).

$$k = A \exp(-E/RT) \quad (9)$$

then:

$$r_i = A_{ii}/A_{ij} \exp[-(E_{ii} - E_{ij})/RT], \quad (i, j = 1, 2, i \neq j) \quad (10)$$

$$\ln r_i = \ln(A_{ii}/A_{ij}) - (E_{ii} - E_{ij})/RT, \quad (i, j = 1, 2, i \neq j) \quad (11)$$

$\ln(r_1)$ and $\ln(r_2)$ were calculated and plotted versus $1000/T$ as shown in Fig.3. From the slopes of the lines of $\ln(r_1)$ versus $1000/T$ and $\ln(r_2)$ versus $1000/T$, the activation energy differences between homo- and cross-propagation, $\Delta E_1 = E_{11} - E_{12}$ and $\Delta E_2 = E_{22} - E_{21}$, were calculated. The relationship between MRRs and temperature can be described as the following expressions:

$$\ln r_1 = -566/T + 0.595 \quad (\text{correlation coefficient } 0.98)$$

$$\ln r_2 = 396/T - 0.592 \quad (\text{correlation coefficient } 0.92)$$

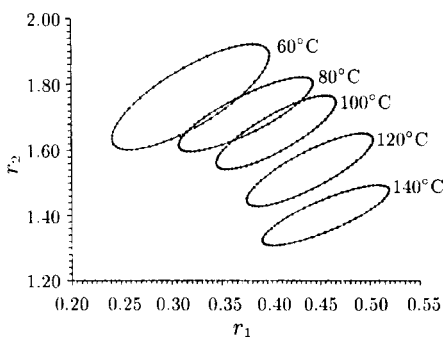


Fig.2 95% Joint confidence intervals of reactivity ratios of HEA/MMA at various temperatures

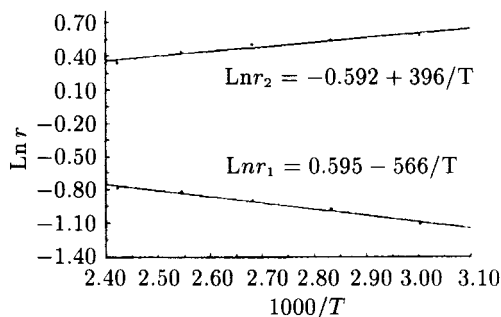


Fig.3 Effect of temperature on r_1 and r_2

From the two expressions, we could predict MRR of HEA-MMA system for a broad range of temperatures and estimate the activation energy differences, $\Delta E_1 = E_{11} - E_{12}$ and $\Delta E_2 = E_{22} - E_{21}$ to be 4.71 KJ/mol and -3.29 KJ/mol, respectively.

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