

Preparation of acrylamide/2-ethylhexyl acrylate copolymer and calculation of monomer reactivity ratios

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Recently, available petroleum resources on the earth are being exhausted gradually while its consumption is increasing. To improve oil recovery yield, a new profile control agent has been developed and reported here for scientific and application concerns. Acrylamide (AM)/2-Ethylhexyl acrylate (2-EHA) copolymer is an inexpensive profile control agent, but it is not facile to regulate the controllable factors during the preparation of AM/2-EHA copolymer. Hence, it is necessary to clarify the copolymerization mechanism which are related to the monomer reactivity ratio. The copolymerization of AM and 2-EHA by free radical copolymerization method was studied. Based on the copolymer composition obtained by FT-IR method reactivity ratio was determined by Yezrielev-Brokhina-Roskin method. The result indicates that the reactivity ratios of AM and 2-EHA are 0.913 and 0.477 respectively. The effect of temperature on the reactivity ratios was also discussed. It can be a significant quantitative reference for industrial production.

Keywords: Reactivity Ratio, FT-IR, Acrylamide, Copolymer

INTRODUCTION

Recently, available petroleum resources on the earth are being exhausted gradually while its consumption is increasing. The necessity for enhancing oil recovery becomes imperative [1, 2]. Acrylamide (AM)/2-Ethylhexyl acrylate (2-EHA) copolymer is an inexpensive profile control agent with properties of thermal stability, alkali tolerance and salt resistance [3, 4], but it is not facile to regulate the controllable factors during the preparation of AM/2-EHA copolymer. In this paper, a new profile control agent fabricated by AM and 2-EHA was synthesized by free radical copolymerization. Reactivity ratio[5-7], which is an important parameter for free radical copolymerization, was also optimized. The monomer reactivity ratio can be calculated by Q-e scheme[8, 9] from some handbooks but it is not universal constants decided by the species of radical and monomer. The monomer reactivity ratio is also affected by the environment such as polymerization temperature, solvent, polarity, calculation method and so on. Hence, the results will be quite different. In this paper, AM/2-EHA copolymer was synthesized with varied AM-2-EHA feeding molar ratios and the monomer conversion is less than 10 wt %. Copolymer composition was determined by FT-IR method. The reactivity ratios of AM and 2-EHA were calculated using Yezrielev-Brokhina-Roskin (YBR) calculative method [10, 11]. The

effect of temperature on the monomer reactivity ratios was also discussed. Due to the calculations of reactivity ratios at different temperature, the relations between the monomer reactivity ratios and temperature were also obtained respectively. This was beneficial to industrial production in mass.

MATERIAL AND METHOD

Materials

Monomer. Acrylamide (AM) and 2-Ethylhexyl acrylate (2-EHA) ; Initiator. Benzoyl Peroxide (BPO); Solvent. Ethyl Alcohol and Ethyl Acetate. AM (99.9%) and 2-EHA (99.9%) were used for the copolymerization without any purification. All the solvents were freshly distilled before use. Benzoyl peroxide (BPO, 99%) was recrystallized from the chloroform solution.

Preparation of AM/2-EHA copolymer

AM/2-EHA copolymer was prepared using a solution polymerization technique as follows: AM and 2-EHA, 20g; BPO, 0.4 mol% of total monomers; and solvents ethyl alcohol and ethyl acetate, 50 ml respectively, were mixed in a four-necked flask under a nitrogen atmosphere. The reaction mixture was stirred at 60°C. The four-necked flask was equipped with a centigrade thermometer and a water condenser and placed in a thermostat which was maintained at the desired temperature. Termination of free radical chain took place in a constant temperature bath (0°C). The monomer conversion is less than 10 wt % in weight. The reaction mixtures, after polymerization, were poured into an excess of

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ethyl alcohol to precipitate out the product. The product was Soxhlet-extracted with water to remove polyacrylamide. The copolymer was dried in vacuo overnight at room temperature to a constant weight and used for characterization and monolayer studies.

Characterization of AM/2-EHA copolymer

Fourier transforms infrared spectroscopy (FT-IR) Fourier transform infrared spectra recorded on a Perkin-Elmer infrared spectrometer using KBr pellets. The spectra were collected over a range of 400-4000 cm^{-1} and each sample was measured for thrice.

$^{13}\text{C-NMR}$ $^{13}\text{C-NMR}$ spectra were run on a Bruker 400 MHz spectrometer using benzene and CDCl_3 as solvents. It allows the identification of carbon atoms in an organic molecule.

The calculation of monomer reactivity ratios

The standard samples were prepared by AM and 2-EHA homopolymers at different molar ratio of two monomers. The reaction conditions of AM homopolymer and 2-EHA homopolymer are the same as that of copolymer. The blend samples were prepared to 20 wt % toluene solution. The solution samples were tested in coating method by FT-IR at the same spectral slit width. FT-IR spectra of blend samples synthesized at 60°C was shown in Fig.1(b). The absorption of C-N and C-O-C were the characteristic peaks of AM and 2-EHA respectively and the relative peak areas were obtained. The standard curve was plotted between the blend ratio and the peak area ratio of the characteristic absorption crests, see Fig.2. The copolymer samples were prepared to 20 wt% toluene solution in the same way. The solution samples were tested in coating method by FT-IR at the same spectral slit width and the peak area ratio of the characteristic absorption crests was obtained respectively. The molar ratio of two monomers in the copolymer was ascertained by the standard curve.

RESULTS AND DISCUSSION

FT-IR analysis

The FT-IR spectrum of copolymer was shown in Fig.1(a). The absorption band at 2872 cm^{-1} and 2962 cm^{-1} were due to symmetrical and antisymmetrical stretching vibration of C-H in primary alkyl.

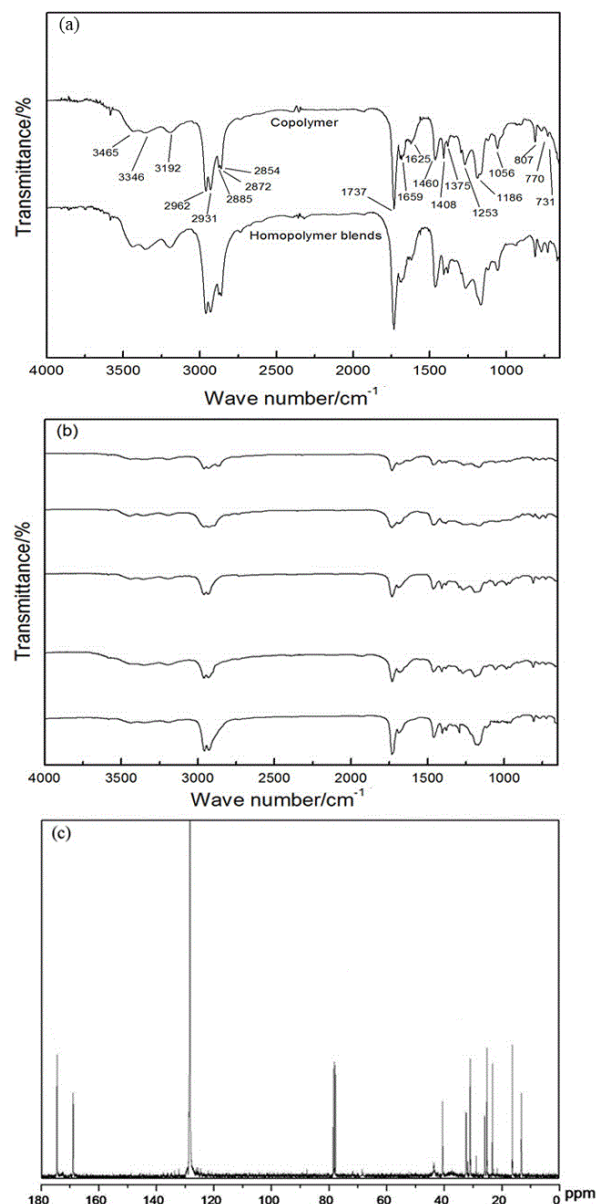


Fig.1. Characterization of Copolymer and Homopolymer blends.(a) FT-IR spectra of Copolymer and Homopolymer blends;(b) FT-IR spectra of Copolymer and Homopolymer blends; (c) The ^{13}C NMR of Copolymer.

The absorption band at 2854 cm^{-1} and 2931 cm^{-1} were due to symmetrical and antisymmetrical stretching vibration of C-H in secondary alkyl. The absorption band at 2885 cm^{-1} was assigned to symmetrical stretching vibration of C-H in tertiary alkyl. The absorption band at 1375 cm^{-1} and 1460 cm^{-1} were due to symmetrical and antisymmetrical bending vibration of C-H in primary alkyl. The absorption band at 1253 cm^{-1} was assigned to bending vibration of C-C in alkyl. The absorption band at 3192 cm^{-1} and 3346 cm^{-1} were due to symmetrical and antisymmetrical stretching vibration of N-H in $-(\text{CO})\text{NH}_2$. The absorption band at 1659 cm^{-1} was assigned to stretching vibration of

C=O in-(CO)NH₂. The absorption band at 1625 cm⁻¹ was assigned to bending vibration of C-N in-(CO)NH₂. The absorption band at 1408 cm⁻¹ was assigned to stretching vibration of C-N in-(CO)NH₂. The absorption band at 807 cm⁻¹ was assigned to bending vibration of N-H in-(CO)NH₂. The absorption band at 1737 cm⁻¹ was assigned to stretching vibration of C=O inR₁(CO)OR₂. The absorption band at 1056 cm⁻¹ and 1186 cm⁻¹ were due to symmetrical and antisymmetrical stretching vibration of C-O-C in R₁(CO)OR₂. The absorption band at 3465 cm⁻¹ was assigned to stretching vibration of C=O overtones absorption peak inR₁(CO)OR₂. There is no absorption peak at 3100 cm⁻¹~3000 cm⁻¹ of C-H in double bonds. Consequently, AM and 2-EHA had reacted completely and AM/2-EHA copolymer had been prepared.

¹³C-NMR analysis

The ¹³C-NMR spectrum of copolymer was shown in Fig.1 (c). Signals due to the carbons of long alkyl side chains were observed in the region 10-40 ppm. The signal at 175 ppm is due to ester carbonyl carbon. The signal at 169 ppm is due to Amide Groups. There was only one signal (at δ=129) when δ was between 100 and 150 and we could infer that double bonds had reacted completely. The results of ¹³C-NMR showed that AM and 2-EHA were in copolymerization.

The calculation of monomer reactivity ratios

The standard samples and the copolymer samples were prepared at 60°C respectively.

The standard samples were prepared by AM homopolymer and 2-EHA homopolymer at different molar ratio. The blend samples were prepared to 20

wt% toluene solution. The solution samples were tested in coating method by FT-IR (see Fig.1 (c)). The absorption of C-N (1408cm⁻¹) and C-O-C (1056 cm⁻¹) were the characteristic peaks of AM and 2-EHA respectively, and the relative peak areas A₁/A₂ were obtained (see Fig. 2). To minimize deviation the data in Table 1 were treated by least square method. The standard curve can be obtained, see Fig. 2.

The copolymer samples were prepared to 20 wt % toluene solution. The solution samples were tested in coating method by FT-IR and the peak area ratio of the characteristic absorption crests was obtained respectively. The molar ratio of two monomers in the copolymer were ascertained by the standard curve, see Table 1. The monomer reactivity ratios of AM and 2-EHA were calculated by YBR calculative method. R stands the mole fraction of AM to 2-EHA in feed, ρ stands the mole fraction of AM to 2-EHA in copolymer, r₁ and r₂ are the reactivity ratio of two monomers.

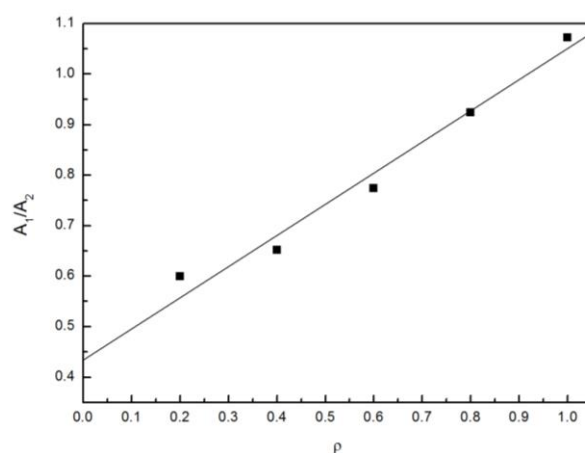


Fig.2. The Standard Curve.

Table 1. The copolymer compositions at different temperatures*

R	323.15K		333.15K		343.15K		353.15K		363.15K	
	ρ	Y	ρ	Y	ρ	Y	ρ	Y	ρ	Y
0.1	0.1896	7.6	0.1841	4.7	0.1823	5.2	0.181	3.7	0.1758	5.1
0.2	0.3942	1.2	0.3657	6.1	0.3458	3.6	0.3349	4.1	0.3145	2.6
0.4	0.6258	3.5	0.6148	3.3	0.5985	6.1	0.5842	5.0	0.5433	9.1
0.6	0.9287	6.8	0.9247	8.4	0.9245	4.2	0.9241	7.3	0.9103	4.8
0.8	1.0215	2.5	1.0246	7.5	1.0387	7.6	1.0458	6.4	1.0549	5.7

*Y is 'Yeild' and the unit is '%'

Table 2. The relative data for the calculation of r_1 and r_2 . **

T/K	T'/K	r_1	r_1'	r_1^*	$r_1'^*$	E_a	A	r_2	r_2'	r_2^*	$r_2'^*$	E_b	B
323.15	333.15	0.863	0.913	0.872	0.901	2931.70	2.60	0.446	0.477	0.450	0.470	3871.29	1.90
323.15	343.15	0.863	0.926	0.872	0.929	2926.00	2.59	0.446	0.488	0.450	0.490	3901.18	1.92
323.15	353.15	0.863	0.967	0.872	0.956	2924.10	2.59	0.446	0.507	0.450	0.509	3911.14	1.93
323.15	363.15	0.863	0.973	0.872	0.983	2923.14	2.59	0.446	0.529	0.450	0.528	3916.13	1.93
333.15	343.15	0.913	0.926	0.901	0.929	2919.94	2.59	0.477	0.488	0.470	0.490	3932.92	1.94
333.15	353.15	0.913	0.967	0.901	0.956	2919.94	2.59	0.477	0.507	0.470	0.509	3932.92	1.94
333.15	363.15	0.913	0.973	0.901	0.983	2919.94	2.59	0.477	0.529	0.470	0.528	3932.92	1.94
343.15	353.15	0.926	0.967	0.929	0.956	2919.94	2.59	0.488	0.507	0.490	0.509	3932.92	1.94
343.15	363.15	0.926	0.973	0.929	0.983	2919.94	2.59	0.488	0.529	0.490	0.528	3932.92	1.94
353.15	363.15	0.967	0.973	0.956	0.983	2919.94	2.59	0.507	0.529	0.509	0.528	3932.92	1.94
AVG						2922.46	2.59					3919.73	1.93

** r_1, r_1', r_2 and r_2' are the monomer reactivity ratios of AM and 2-EHA calculated by YBR method while $r_1^*, r_1'^*, r_2^*$ and $r_2'^*$ are the monomer reactivity ratios of AM and 2-EHA by regression treatment.

The FR method can be expressed by the following:

$$\rho = R(r_1 R + 1) / (r_2 + R), \quad (1)$$

YBR method is the combination of FR equation and least square method. For instance, eq (1) is multiplied by $R^{-1}\rho^{-1/2}$ to give the following [12]:

$$(R/\rho^{1/2}) r_1 - (\rho^{1/2}/R) r_2 + (1/\rho^{1/2} - \rho^{1/2}) = 0, \quad (2)$$

Taking into account least square method, eq (3) is given by:

$$r_1 A_1 - r_2 n = B_1, \quad (3)$$

And

$$-r_1 n + r_2 A_2 = B_2, \quad (4)$$

$$\text{Where, } A_1 = \sum_{i=1}^n \frac{R_i^2}{\rho_i}, \quad B_1 = \sum_{i=1}^n R_i \left(1 - \frac{1}{\rho_i}\right),$$

$A_2 = \sum_{i=1}^n \frac{\rho_i}{R_i^2}, \quad B_2 = \sum_{i=1}^n \frac{\rho_i}{R_i} \left(\frac{1}{\rho_i} - 1\right)$; n: the number of experimental data.

Consequently,

$$r_1 = (A_2 B_1 + n B_2) / (A_1 A_2 - n^2), \quad (5)$$

$$r_2 = (A_1 B_2 + n B_1) / (A_1 A_2 - n^2), \quad (6)$$

Eq (5) and eq (6) are the YBR method. Accordingly, reactivity ratios of AM and 2-EHA are 0.913 and 0.477 respectively.

The effect of temperature on the monomer reactivity ratios

The reactivity ratio is defined as :

$$r_1 = k_{11}/k_{12}, \quad (7)$$

and with Arrhenius equation defined as:

$$k_{11} = A_{11} \times e^{-E_{11}/(8.314 \times T)}, \quad (8)$$

$$k_{12} = A_{12} \times e^{-E_{12}/(8.314 \times T)}, \quad (9)$$

Another form of equation (7) is:

$$r_1 = k_{11}/k_{12} = (A_{11}/A_{12}) \times e^{-(E_{11}-E_{12})/(8.314 \times T)} = A \times e^{-E_a/(8.314 \times T)}, \quad (10)$$

Where, $A = A_{11}/A_{12}$, $E_a = E_{11} - E_{12}$, A_{11} 、 A_{12} are collision factor, E_{11} is the activation energy of chain propagation reaction in self-polymerization while E_{12} is the activation energy of chain propagation reaction in copolymerization. When r_1 is less than 1, k_{11} is less than k_{12} and E_{11} is more than E_{12} . When r_1 is more than 1, k_{11} is more than k_{12} and E_{11} is less than E_{12} .

r_2 can also be obtained as:

$$r_2 = k_{21}/k_{22} = (A_{21}/A_{22}) \times e^{-(E_{21}-E_{22})/(8.314 \times T)} = B \times e^{-E_b/(8.314 \times T)}, \quad (11)$$

Where, $B = B_{21}/B_{22}$, $E_b = E_{21} - E_{22}$

The monomer reactivity ratios were calculated by YBR method at 50, 60, 70, 80, 90°C respectively, and the composition in feed was shown Table 1. As the results shown in Table 2, the monomer reactivity ratios increase as temperature goes up, but only a little. Each two sets of data treated by least square method was used to calculate the equations of r_1 and r_2 by Eq (10) and Eq (11). The relative data for the calculation of r_1 and r_2 was shown in Table 2. r_1 and r_2 can be obtained as:

$$r_1 = (2.59 \pm 0.01) \times e^{-2922.46 \pm 9.24/(8.314 \times T)} = (2.59 \pm 0.01) \times e^{-351.51 \pm 1.11/T}$$

$$r_2 = (1.93 \pm 0.03) \times e^{-3919.73 \pm 48.44/(8.314 \times T)} = (1.93 \pm 0.03) \times e^{-471.46 \pm 5.83/T}$$

DISCUSSION

There is not much difference between FT-IR spectra of AM/2-EHA copolymer and that of the blend composed of homopolymers of AM and 2-EHA (see Fig.1(a)). The wave numbers of absorption peaks did not change but absorption intensity changed. The characteristic peaks in homopolymer blends behaved the same absorption effect as that in copolymer(see Fig.1(b)). As a result the standard curve obtained by homopolymer blends can be used to calculate the molar ratio of two monomers in the copolymer.

The monomer reactivity ratios of AM and 2-EHA are 0.913 and 0.477 respectively. It is noted that both of the monomer reactivity ratios r_1 and r_2 , even r_1r_2 , are <1 , which implies that: (1)The copolymerization of AM and 2-EHA is non-ideal and has azeotropic copolymerization point. Namely, the concentration of monomer in solution equals that in copolymer at the azeotropic copolymerization point. (2) AM and 2-EHA are prone to alternating copolymerization because terminal groups of the copolymer tend to polymerize heterogeneous monomer, i.e. alternating copolymerization.

CONCLUSION

AM/2-EHA copolymers were synthesized by free radical copolymerization using benzoyl peroxide (BPO) under nitrogen atmosphere at different temperatures and characterized by FT-IR and ^{13}C -NMR method. The results showed that AM and 2-EHA were in copolymerization. The monomer reactivity ratios of AM and 2-EHA were calculated by YBR calculative method. The copolymer compositions were obtained by FT-IR.

The standard curve was obtained by homopolymer blends and the molar ratios of two monomers in the copolymer were ascertained by the standard curve. The absorption of C-N (1408cm^{-1}) and C-O-C (1056cm^{-1}) were the characteristic peaks of AM and 2-EHA respectively. Peak area ratio of two characteristic peaks was used in the calculation of the molar ratio of two monomers in the copolymer and homopolymer blends. The reactivity ratios of

AM and 2-EHA were calculated, by YBR method, to be 0.913 and 0.477 respectively. It can be inferred that Random copolymerization occurred in the copolymerization of AM and 2-EHA and there are many alternating units in the copolymer chain. The effect of temperature on the monomer reactivity ratios for AM and 2-EHA was also discussed. As temperature goes up, the monomer reactivity ratios increase, but only a little. The relations between r_1 , r_2 and T were also obtained respectively. It is simple and reliable to calculate the monomer reactivity ratios for AM and 2-EHA in free radical copolymerization by FT-IR spectroscopy. The method can be used to calculate the monomer reactivity ratios which have the separate characteristic peaks in the copolymer. The monomer reactivity ratios can be a significant quantitative reference for industrial production.

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