Copolymers of N-cyclohexylacrylamide and n-butyl acrylate: synthesis, characterization, monomer reactivity ratios and mean sequence length

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Abstract. Copolymerization of N-cyclohexylacrylamide (NCHA) and n-butyl acrylate (BA) was carried out in dimethylformamide at $55 \pm 1^\circ\text{C}$ using azobisisobutyronitrile as a free radical initiator. The copolymers were characterized by $^1\text{H-NMR}$ spectroscopy and the copolymer compositions were determined by $^1\text{H-NMR}$ analysis. The reactivity ratios of the monomers were determined by both linear and non-linear methods. The reactivity ratios of monomers determined using linear methods like Fineman-Ross ($r_1 = 0.37$ and $r_2 = 1.77$), Kelen-Tudos ($r_1 = 0.38$ and $r_2 = 1.77$), ext. Kelen-Tudos ($r_1 = 0.37$ and $r_2 = 1.75$) Yezrieler-Brokhina-Roskin ($r_1 = 0.37$ and $r_2 = 1.77$) and non-linear methods like Tidwell-Mortimer ($r_1 = 0.37$ and $r_2 = 1.76$), ProCop ($r_1 = 0.36$ and $r_2 = 1.82$). The Q and e values for NCHA are 0.67 and 0.68 respectively. Mean sequence lengths of copolymers are estimated from r_1 and r_2 values. It shows that the BA units increases in a linear fashion in the polymer chain as the concentration of BA increases in the monomer feed.

Keywords: polymer synthesis, molecular engineering, reactivity ratios, mean sequence length

1. Introduction

Functional polymers are now being synthesized and used not only for their macromolecular properties but also for the properties of the functional groups [1]. Acrylic polymers have acquired prime importance in various avenues of application in leather, textile and building materials.

Moreover, the N-substituted acrylamides are used to prepare thermosensitive materials like poly(N-isopropylacrylamide) and copolymers of N-ethylacrylamide and styrene [2]. The thermosensitive polymers present also great potential in application as drug delivery system [3], human gene vectors [4] and biocatalysts [5].

The determination of copolymer composition and reactivity ratios of the monomers is important in

evaluating the specific application of the copolymer [6]. The monomer reactivity ratios determined by conventional linearization methods are not always accurate and several non-linear methods have been attempted to determine their value [7–9]. $^1\text{H-NMR}$ spectroscopic analysis has been established as a powerful tool for the estimation of copolymer composition [10, 11].

The present article reports the synthesis and characterization of copolymers of N-cyclohexylacrylamide with n-butyl acrylate. The determination of monomer reactivity ratios of the monomers and mean sequence lengths of copolymers are also reported.

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2. Experimental

2.1. Materials

The monomer N-cyclohexylacrylamide (NCHA) was prepared by the procedure described in the literature [12]. The comonomer n-butyl acrylate (BA) was freed from inhibitor by washing with 5% NaOH followed by distilled water, dried over CaH₂ and then distilled twice under reduced pressure. Azobisisobutyronitrile (AIBN) was recrystallized from chloroform. All the solvents were purified by distillation prior to their use.

2.2. Copolymerization

The copolymerization was carried out in glass reaction tubes (80 ml), provided with a gas inlet and outlet, at 55±1°C using AIBN as the free-radical initiator. The reaction tubes containing the required amount of monomers and initiator dissolved in DMF was deaerated by flushing with pure, dry nitrogen gas and then sealed. The conversions of the polymerization were controlled to be less than 10%. After the polymerization, the copolymers were precipitated by adding ice cold water. The precipitated polymers were filtered off and washed repeatedly with fresh methanol. The copolymers obtained were purified twice by dissolving in DMF and reprecipitating with methanol. The polymers were dried in vacuum at 60°C for 24 hours.

2.3. ¹H-NMR spectroscopy

The ¹H-NMR spectra of monomers and copolymers were recorded on the EM-390 NMR Spectrometer operating 90 MHz with CDCl₃ as solvent. The following peaks appear in NCHA spectrum; at 1.2–2.02 ppm for cyclohexyl CH₂ at 3.72 ppm for cyclohexyl methyne, at 5.38–6.28 ppm for vinyl protons and at 7.3 ppm for N–H proton. The fol-

lowing peaks appear in BA spectrum; at 0.9 ppm for CH₃, at 1.1–1.7 ppm for (CH₂)_{b,c} at 4.1 ppm for OCH₂ and at 5.5–6.2 ppm for vinyl proton.

3. Results and discussion

Copolymers of NCHA and BA with different feed compositions were prepared by free-radical polymerization in DMF using AIBN initiator. Copolymerization was restricted to give less than 10% conversion. The monomer units in the copolymer are shown in Figure 1. The copolymer composition data of the monomers in the feed and copolymers is presented in Table 1.

3.1. Characterization

The ¹H-NMR spectrum of copolymer, poly(NCHA-co-BA) (0.5:0.5) is shown in Figure 2. The peak assignments for the copolymers were based on the spectra of monomers NCHA and BA. The following peaks appear in the copolymer spectrum: at 0.8 ppm for CH₃, at 1.1–2.1 ppm for cyclohexyl-methylenes and (CH₂)_{b,c} of BA, at 2.1–2.3 ppm for backbone CH₂, at 2.5 ppm due to backbone

Figure 1. Synthesis of poly (NCHA-co-BA)

Table 1. Copolymerization of NCHA and BA in DMF at 55±1°C

Copoly- mers	Mole fraction of NCHA, M ₁	Mole fraction of BA, M ₂	% of conversion	Mole fraction of BA in copolymer m ₂	F = M ₁ /M ₂	f = m ₁ /m ₂	H	G	η	E
1	0.2	0.8	7.08	0.88	0.250	0.136	0.460	-1.588	-0.6257	0.1813
2	0.3	0.7	8.10	0.82	0.429	0.220	0.836	-1.521	-0.5220	0.2869
3	0.4	0.6	8.40	0.74	0.667	0.351	1.267	-1.233	-0.3686	0.3788
4	0.5	0.5	7.60	0.67	1.000	0.493	2.028	-1.029	-0.2506	0.4939
5	0.6	0.4	8.04	0.58	1.500	0.724	3.108	-0.572	-0.1103	0.5993
6	0.7	0.3	8.52	0.48	2.333	1.083	5.026	0.179	0.0252	0.7075
7	0.8	0.2	7.84	0.37	4.000	1.703	9.395	1.651	0.1439	0.8187

$$\alpha = (H_{\min} \cdot H_{\max})^{1/2} = 2.078$$

Figure 2. ^1H -NMR spectrum of copolymer, poly(NCHA-co-BA) (0.5:0.5)

methyne C–H, at 3.3 ppm for cyclohexyl methyne proton, at 3.9–4.2 ppm for OCH_2 and at 7.9 ppm for N–H.

3.2. Copolymer compositions

The copolymer composition was determined from ^1H -NMR spectral analysis of the copolymer. The assignment of the resonance peaks in the ^1H -NMR spectrum allows the accurate evaluation of the content of each kind of monomer incorporated into the copolymer chain.

The oxymethylene (OCH_2) peak area is used to determine the copolymer composition. The integrated intensity of this peak is compared to the total intensities of all the peaks in the copolymer spectrum, which is a measure of their relative areas [6]. The copolymer compositions can be obtained using Equation (1):

$$X_{\text{BA}} = \frac{15A(\text{OCH}_2)}{2A_{\text{total}} + 3A(\text{OCH}_2)} \quad (1)$$

where X – mole fraction and A – peak area. Table 1. gives the values of the corresponding mole fractions in the copolymers. The kinetic behavior was determined by plotting the mole fraction of BA in the feed against that in the copolymer (Figure 3).

Figure 3. Copolymer composition diagram of poly(NCHA-co-BA) system

3.3. Reactivity ratios

From the monomer feed ratios and the resultant copolymer compositions, the reactivity ratios of monomer 1 (NCHA) and monomer 2 (BA) were evaluated by the methods of Fineman-Ross [13] (FR), Kelen-Tudos [14] (KT) and extended Kelen-Tudos [15] (EKT).

Table 2. Extended KT parameters for NCHA and BA copolymer system

Parameters	Copolymer system						
	1	2	3	4	5	6	7
ξ_2	0.0791	0.1018	0.1064	0.1050	0.1204	0.1411	0.1493
ξ_1	0.0430	0.0522	0.0560	0.0517	0.0581	0.0656	0.0636
Z	0.5334	0.4994	0.5123	0.4785	0.4666	0.4460	0.4064
F	0.2550	0.4405	0.6852	1.0303	1.5517	2.4282	4.1905
H	0.4780	0.8821	1.3371	2.1528	3.3257	5.4450	10.3087
G	-1.6198	-1.5619	-1.2668	-1.0601	-0.5915	0.1861	1.7298
H	-1.0715	-0.8153	-0.5343	-0.3327	-0.1355	0.0287	0.1525
E	0.3162	0.4604	0.5640	0.6756	0.7616	0.8405	0.9089

$\alpha = (F_{min} \cdot F_{max})^{1/2} = 1.0337$ $r_1 = 0.38$ and $r_2 = 1.77$ – KT
 $r_1 = 0.37$ and $r_2 = 1.75$ – EKT

Figure 4. F-R Plot for (NCHA-co-BA) system

Figure 5. K-T (O) and EK-T (▲) plot for poly(NCHA-co-BA) system

Table 3. Copolymerization parameter, for the NCHA and BA copolymer system

Methods	r_1^a	r_2^a	$r_1 r_2$
Fineman-Ross (F-R)	0.37	1.77	0.65
Kelen-Tudos (K-T)	0.38	1.77	0.67
Ext. Kelen-Tudos (EK-T)	0.37	1.75	0.65
Yezrielev-Brokhina-Roskin (YBR)	0.37	1.77	0.65
Tidwell-Mortimer (TM)	0.37	1.76	0.65
Procop Opt Pex2	0.36	1.82	0.65

^a r_1 and r_2 are the reactivity ratios for NCHA and BA respectively

The significant parameters of FR, KT and EKT equation are presented in Table 2. The reactivity ratios for NCHA (r_1) and BA (r_2) from the FR plot (Figure 4), KT and EKT plot (Figure 5) are given in Table 3.

The monomer reactivity ratios determined by conventional linearization methods are not always accurate and several non-linear methods have been attempted to determine their values [8]. The reactivity ratios were also determined by non-linear method (TM and Opt-Pex2) by using the ProCop computer program [16].

Tidwell-Mortimer (TM) method is the best non-linear method when the differential Mayo-Lewis equation is applied. The reactivity ratios estimated by TM are $r_1 = 0.37$ and $r_2 = 1.76$. The 95% joint confidence region for the determined r_1 and r_2 values using ProCop computer program is shown in Figure 6. The other differential methods used to estimate reactivity ratios provide very similar results and all reactivity ratios are located inside confidence domain.

The value(s) of r_1 is less than 1 and r_2 is greater than 1. r_1 shows that NCHA favors cross-propagation as opposed to homopropagation and r_2 shows that BA favors homopropagation over cross-propa-

Figure 6. 95% joint confidence region of r_1 and r_2 values by Procop computer program

gation. r_1 and r_2 together show that BA is generally more reactive than NCHA, hence the copolymers contain a higher proportion of BA units. The product of r_1 and r_2 is less than the unity (0.65), which indicates random distribution. The more these values diverge from unity, less random the distribution will be. A plot of copolymer composition against the composition of the feed is shown by a solid line in Figure 3. The dashed line represents the ideal random copolymerization.

3.4. Effect of conversion value

The ProCop computer program uses a non-linear calculation method (OPT-Pex2) which is able to minimize $F(2)$ value taking into account the conversion values as well (Equation (2)):

$$F = \sqrt{\frac{\sum_{i=1}^n (m_i^{exp} - m_i^{cal})^2}{n - 2}}$$
 (2)

where m_i^{exp} is the copolymer composition experimentally determined for the i point, m_i^{cal} is the copolymer composition calculated at the conversion mentioned in Table 1 for the i experiment and n is the overall number of experiments. The conversion effect may be a function of the feed composition and of the comonomer pair to undergo polymerization. If r_i and $r_j < 1.0$ the effect of conversion is relatively unimportant. Conversion values are more important to estimate the reactivity ratios when $r_i > 1.0$ and $r_j < 1.0$ [17]. In our copolymerization system the $r_1 < 1.0$ and $r_2 > 1.0$. Hence, the conversion values (7.1%–8.5%) play an important role in the estimation of reactivity ratios. The reactivity ratios of NCHA and BA estimated via the ProCop method are $r_1 = 0.36$ and $r_2 = 1.82$ respectively. The reactivity ratio determined by

Figure 7. r_1 and r_2 values by (—) Procop, (□) Procop, (Δ) TM, (×) KT, (*) FR, (●)EKT

various differential methods are shown in Figure 7 along with the result determined via a non-linear, method (ProCop) involving conversion. Regardless of the low conversion values, the reactivity ratios estimated by differential methods (linear or non-linear) are located outside of the confidence region because of the conversion effect. EKT, which also takes into account conversion values within a linear method, provides better reactivity ratios, located at the limit of the confidence domain. When conversion is taken into consideration the superiority of the non-linear integral method becomes obvious.

3.5. Mean sequence length

The mean sequence length [10] can be determined using the pertinent equations ((3) and (4)):

$$\bar{l}_1 = r_1 \frac{M_1}{M_2} + 1$$
 (3)

$$\bar{l}_2 = r_2 \frac{M_2}{M_1} + 1$$
 (4)

where r_1 and r_2 are the reactivity ratios and M_1 and M_2 represent the concentration of NCHA and BA respectively, in the monomer feed. The mean

Table 4. Mean sequence lengths in NCHA and BA copolymerization^a

BA in feed, M ₂ [Mole%]	l ₁	l ₂	l ₁ :l ₂	Distribution ^b
0.80	1.09	8.26	1:8	N BBBBBBBBN
0.70	1.15	5.26	1:5	NBBBBBN
0.60	1.24	3.72	1:3	NBBBN
0.50	1.36	2.82	1:2	NBBN
0.40	1.54	2.21	2:2	
0.30	1.84	1.78	1:1	
0.20	2.44	1.45	2:1	

^a $r_1 = 0.36, r_2 = 1.82$
^bOnly a few cases are illustrated (N = NCHA; B = BA)

sequence lengths of copolymers are given Table 4. It is significant to note from Table 4 that the BA units increases in a linear fashion in the polymer chain as the concentration of BA increases in the monomer feed.

4. Conclusions

Copolymers of NCHA and BA having different composition were synthesized in DMF by free radical polymerization. The structure of the copolymers was confirmed by $^1\text{H-NMR}$ Spectroscopy. The copolymer compositions were determined from $^1\text{H-NMR}$ analysis data. The reactivity ratios of monomers were determined by linear methods like Fineman-Ross ($r_1 = 0.37$ and $r_2 = 1.77$), Kelen-Tudos ($r_1 = 0.38$ and $r_2 = 1.77$), Ext. Kelen Tudos ($r_1 = 0.37$ and $r_2 = 1.75$) Yezrieler-Brokhina-Roskin ($r_1 = 0.37$ and $r_2 = 1.77$) and non-linear methods like Tidwell-Mortimer ($r_1 = 0.37$ and $r_2 = 1.76$), Procop ($r_1 = 0.36$ and $r_2 = 1.82$). The values are in good agreement. $r_2 > 1$ indicates BA is more reactive than NCHA thereby favouring the formation of longer blocks of BA as its concentration in the feed increases. The values of r_1 and r_2 diverge from unity, $r_1, r_2 < 1$ (0.65) shows random distribution. r_2 shows that BA favours homopropagation over cross-propagation. The mean sequence length determination shows that BA units increases in a linear fashion in the polymer chain as the concentration increases in the monomer feed.

References

- [1] Akelah A., Moet A.: Functionalized polymers and their applications. Chapman and Hall, London, 1990.
- [2] Nichifor M., Zhu X. X.: Copolymers of N-alkylacrylamide and styrene as new thermosensitive materials. *Polymer*, **44**, 3053–3060 (2003).
- [3] Leroux J., Roux E., Le Garrec D., Hong K., Drummond D. C.: N-isopropylacrylamide copolymers for the preparation of pH-sensitive liposomes and polymeric micelles. *Journal of Controlled Release*, **72**, 71–84 (2001).
- [4] Kurisawa M., Yokayama M., Okano T.: Gene expression control by temperature with thermo-responsive polymeric gene carriers. *Journal of Controlled Release*, **69**, 127–137 (2000).
- [5] Kokufuta E.: Novel application for stimulus-sensitive polymer gels in the preparation of functional immobilized biocatalysts. *Advances in Polymer Science*, **110**, 157–177 (1993).
- [6] Pitchumani S., Rami Reddy C., Rajadurai S.: Reactivity ratios of ethyl acrylate, n-butyl methacrylate copolymer system by $^1\text{H-NMR}$ analysis. *Journal of Polymer Science: Polymer Chemistry Edition*, **20**, 277–282 (1982).
- [7] Dube M., Sanayei R. A., Penlidis A., O' Driscoll K. F., Reilly P. M.: A microcomputer program for estimation of copolymerization reactivity ratios. *Journal of Polymer Science*, **29**, 703–708 (1991).
- [8] Polic A. L., Duever T. A., Penlidis A.: Case studies and literature review on the estimation of copolymerization reactivity ratios. *Journal of Polymer Science Part A: Polymer Chemistry*, **36**, 813–822 (1998).
- [9] Hagiopol C., Frangu O., Dumitru L.: A nonlinear method for estimation of reactivity ratios in copolymerization processes. *Journal of Macromolecular Science Chemistry Edition*, **26**, 1363–1379 (1989).
- [10] Pazhanisamy P., Ariff M., Anwaruddin Q.: Copolymers of α -methylstyrene with N-cyclohexylacrylamide: Synthesis, monomer reactivity ratios and mean sequence length. *Journal of Macromolecular Science: Pure and Applied Chemistry*, **34**, 1045–1054 (1997).
- [11] Pazhanisamy P., Sulochana P., Anwaruddin Q., Ariff M.: Reactivity ratios of N-cyclohexylacrylamide-styrene copolymers by ^1H and $^{13}\text{C-NMR}$ spectroscopy. *Journal of Polymer Science Part A: Polymer Chemistry*, **35**, 193–195 (1997).
- [12] Plaut H., Ritter J. J.: A new reactions of nitriles IV. Unsaturated amides. *Journal of American Chemical Society*, **73**, 4076–4077 (1951).
- [13] Fineman M., Ross S. P.: Linear method for determining monomer reactivity ratios in copolymerization. *Journal of Polymer Science*, **5**, 259–262 (1950).
- [14] Kelen T., Tüdös F.: Analysis of the linear methods for determining copolymerization reactivity ratios I. A new improved linear graphical method. *Journal of Macromolecular Science: Pure and Applied Chemistry*, **9**, 1–27 (1975).
- [15] Kelen T., Tüdös F., Turcsányi B., Kennedy J. P.: Analysis of the linear method for determining copolymerization reactivity ratios. IV. A comprehensive and critical re-examination of carbocationic copolymerization data. *Journal of Polymer Science*, **15**, 3047–3074 (1977).
- [16] Hagiopol C.: Copolymerization- towards a systematic approach. Kluwer-Academic/Plenum Publisher, New York (1999).
- [17] Hagiopol C., Frangu O.: Strategies in improving the accuracy of reactivity ratios estimation. *Journal of Macromolecular Science: Pure and Applied Chemistry*, **40**, 571–584 (2003).