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COPOLYMERS OF α-METHYLSTYRENE WITH *N*-CYCLOHEXYLACRYLAMIDE: SYNTHESIS, MONOMER REACTIVITY RATIOS, AND MEAN SEQUENCE LENGTH

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ABSTRACT

Copolymerization of α-methylstyrene and *N*-cyclohexylacrylamide was carried out in toluene at 60 ± 1°C using azobisisobutyronitrile as the free-radical initiator. The total concentration of the comonomers was 1.5 $\text{mol}\cdot\text{L}^{-1}$ in the solvent. The copolymers were characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopy, and the copolymer compositions were determined primarily from the ^{1}H-NMR spectra. The reactivity ratios were found to be $r_1 = 0.08 \pm 0.01$ and $r_2 = 2.45 \pm 0.03$ by the Fineman–Ross method, and $r_1 = 0.06 \pm 0.01$ and $r_2 = 2.43 \pm 0.08$ by the Kelen–Tüdös method. Mean sequence lengths in the copolymer were estimated from r_1 and r_2 values.

INTRODUCTION

The copolymerization of α-methylstyrene with various electron acceptors was described in earlier studies [1, 2] and it was shown that free-radical-initiated polymerization leads to alternating copolymers, under normal conditions. Moreover, the copolymerization of α-methylstyrene with vinyl monomers, like methyl methacrylate and methacrylonitrile, was studied [3, 4]. In the case of α-methylstyrene–

methyl methacrylate copolymers, sequence lengths and stereochemical configurations were reported. Literature indicates that no studies have been made on the copolymerization of α-methylstyrene with *N*-cyclohexylacrylamide.

Spectroscopic methods have been found to be simple, rapid, and accurate for the determination of copolymer composition [5–9]. The present paper deals with a study of copolymerization of α-methylstyrene (AMS) and *N*-cyclohexylacrylamide (NCHA) in solution, characterization of copolymers using ^{1}H-NMR and ^{13}C-NMR spectroscopy, and subsequent determination of monomer reactivity ratios and mean sequence length ($\bar{l}$).

EXPERIMENTAL

The monomer α-methylstyrene was freed from inhibitor by washing with 10% NaOH followed by distilled water, dried over CaH_2, and then distilled thrice. Azobisisobutyronitrile (AIBN) was recrystallized from chloroform. The solvents were purified by distillation. The comonomer *N*-cyclohexylacrylamide (NCHA) was prepared by the procedure described in the literature [10].

Copolymerization

The copolymerization was carried out in glass reaction tubes (80 mL), provided with a gas inlet and outlet, at 60 ± 1°C using AIBN as the free-radical initiator. The reaction tube containing the required amount of monomers and initiator dissolved in toluene was deaerated by flushing with pure, dry nitrogen gas, sealed, and placed in a thermostated water bath. The total concentration of the comonomers was 1.5 $mol \cdot L^{-1}$ in toluene, and the initiator concentration was 0.2 wt%. After the polymerization, the copolymers were filtered off and washed with cold toluene. The copolymers obtained were purified twice by dissolving in a $CHCl_3$ and DMSO mixture and reprecipitating with methanol. The polymers were dried in vacuum at 60°C for 24 hours.

Instrumentation

The ^{1}H-NMR spectra of the copolymers were recorded on a Jeol GSX-400 spectrometer operating at 400 MHz with $CDCl_3$ and DMSO(d_6) mixed solvent at 23°C. ^{1}H-NMR spectra were obtained using a spectral width of 5000 Hz, an acquisition time of 2 seconds and a pulse delay of 3.3 seconds. Spectra were generally obtained after accumulating 32 scans.

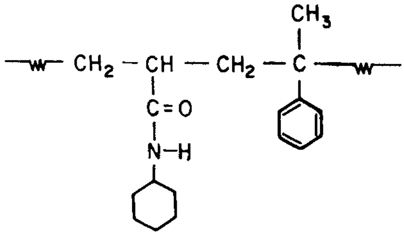
The proton noise decoupled ^{13}C-NMR spectra of polymers were recorded using a Jeol GSX-400 spectrometer operating at 100 MHz. The details of operation conditions are given in Table 1. These experimental conditions ensure the optimum parameters required for quantitative estimation of ^{13}C resonance [11].

TABLE 1. Operation Conditions

Sample	15-20% (w/v) solution in $CDCl_3$-DMSO(d_6)
Temperature of the probe	23 °C
Reference	$CDCl_3$ at 78 ppm and DMSO at 39.0 ppm
Pulse width	4 μs (45° flip angle)
Pulse delay	1.7 seconds
Spectral width	25,000 Hz
Completely decoupled	Proton noise decoupled
Off-resonance	Off-resonance irradiated

RESULTS AND DISCUSSION

Seven copolymers of AMS and NCHA with different feed compositions were prepared by free-radical polymerization in toluene using AIBN as initiator. Copolymerization was restricted to give less than 10% conversion. A schematic representation of the copolymer structure is given below:



Characterization

The copolymers were sparingly soluble in chloroform and DMSO taken separately, but soluble in their mixture.

The ^1H-NMR spectrum of the copolymer is shown in Fig. 1. The peak assignments for the copolymer are based on the spectra of monomers NCHA and AMS. The following peaks appear in the copolymer spectrum: at 0.9–1.8 ppm for cyclohexyl methylenes, at 2.1 ppm for α-CH_3, at 3.4 ppm due to water and its shoulder, at 3.7 ppm due to backbone methyne $(-\overset{|}{C}H-)$ and methylene $(-CH_2-)$, at 6.6–7.4 ppm for —CH— of phenyl ring, and at 8.2 ppm for N—H.

In the ^{13}C-NMR spectrum (Fig. 2) of the copolymer the following peaks appear: at 22.8 ppm for α-methyl carbon; at 24.5, 25.2, 32.3, and 47.4 for cyclohexyl carbons (C_4, C_3, C_2, and C_1 respectively); at 38.8–42.1 ppm for —C—H and $-CH_2-$ carbons; at 124.6–143.7 ppm for phenyl carbon resonances; and at 164.2 ppm for $-\overset{|}{C}=O$ carbon. The backbone quaternary carbon resonance of α-methylstyrene is overlapped by the DMSO(d_6) solvent peak.

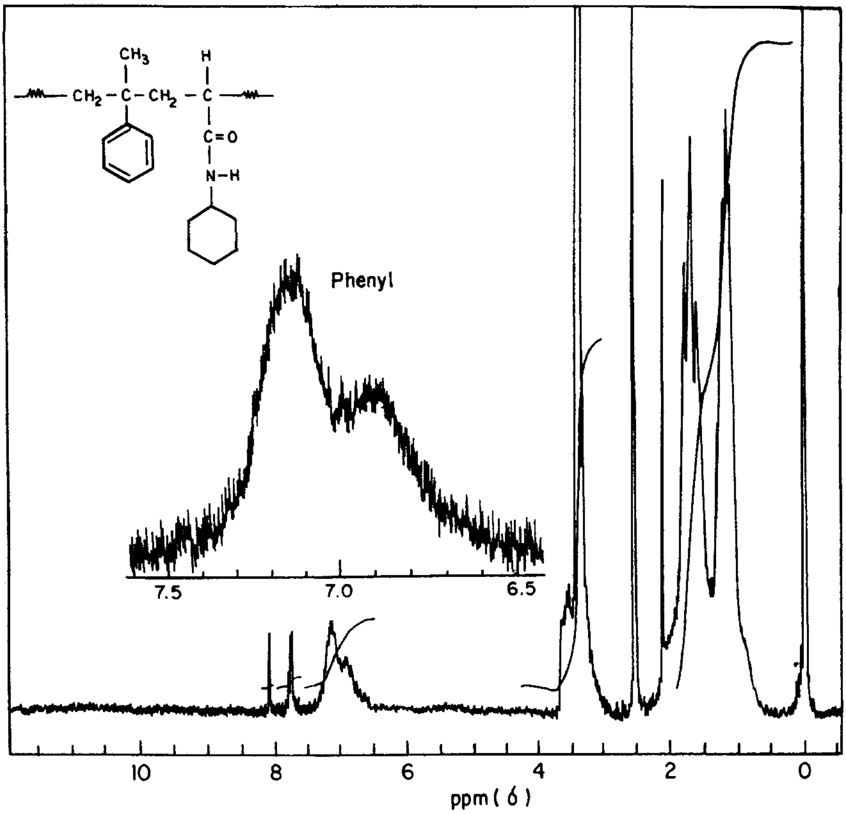


FIG. 1. ^{1}H-NMR spectrum of AMS-NCHA copolymer (X_{AMS} = 0.43).

^{1}H-NMR Spectra: Determination of Copolymer Composition

In this work the copolymer compositions were obtained primarily on the basis of ^{1}H-NMR data.

The phenyl peak area is used to determine the copolymer composition [12-15]. Resonance signals at 6.6-7.4 ppm correspond to aromatic protons, and their integrated intensity was compared to the total integrated intensities of all proton signals. The copolymer compositions can be readily obtained from

$$X_{AMS} = \frac{3A(\text{phenyl})}{A(\text{total}) + A(\text{phenyl})} \tag{1}$$

where X = mole fraction and A = peak area.

Table 2 gives the values of the corresponding mole fractions in the copolymers.

Reactivity Ratios

From the monomer feed ratios and the resultant copolymer compositions, the reactivity ratios of monomer 1 (AMS) and monomer 2 (NCHA) were evaluated by the methods of Fineman-Ross [16] and Kelen-Tüdös [17]. According to Fineman-Ross (F-R), the reactivity ratios of a monomer pair can be found by using

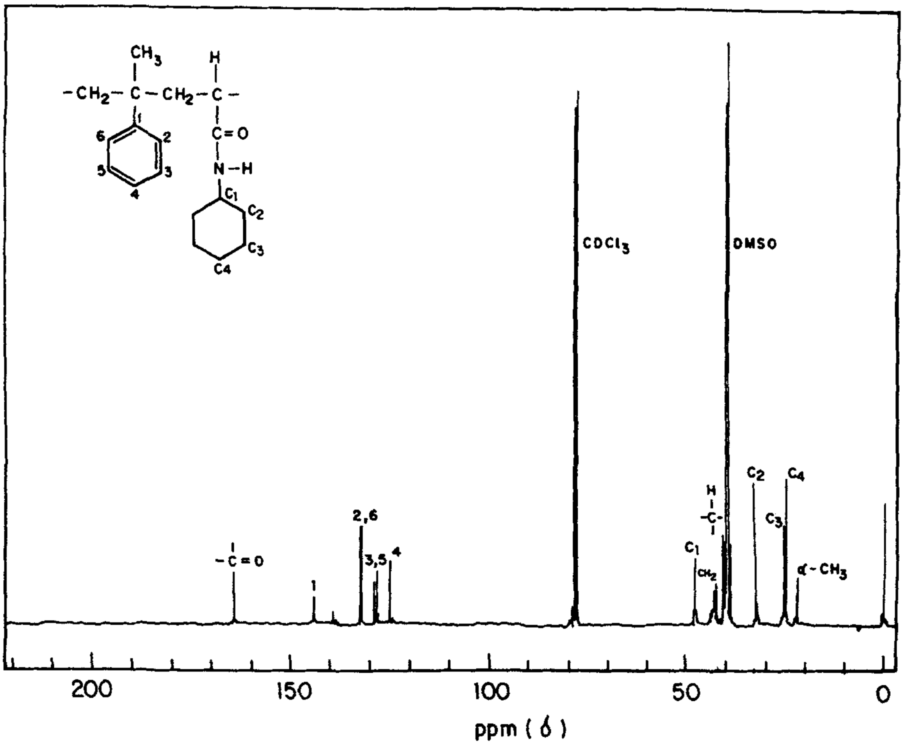


FIG. 2. ^{13}C-NMR spectrum of AMS-NCHA copolymer (X_{AMS} = 0.41).

TABLE 2. Copolymerization of α-Methylstyrene and *N*-Cyclohexylacrylamide in Toluene at 60 ± 1°C[a]

Mole fraction of AMS in feed, M_1	Time of reaction, minutes	Percentage of conversion	Mole fraction of AMS in copolymer, m_1	$F = M_1/M_2$	$f = m_1/m_2$
0.84	180	6.4	0.43	5.25	0.75
0.75	180	6.8	0.39	3.00	0.64
0.66	180	7.4	0.34	1.94	0.52
0.57	180	7.0	0.29	1.33	0.41
0.47	180	5.8	0.21	0.89	0.27
0.28	180	6.0	0.13	0.39	0.15
0.25	180	4.0	0.11	0.33	0.12

[a] The total concentration of comonomers in the feed was 1.5 mol·L^{-1}; the initiator concentration was 0.2 wt%; α = 5.78.

$$\frac{(f-1)}{F} = -r_2 \frac{f}{F^2} + r_1 \tag{2}$$

A plot of $(f - 1)/F$ as the ordinate and f/F^2 as the abscissa is shown in Fig. 3. A straight line is obtained whose slope is $-r_2$ and intercept r_1.

In the Kelen-Tüdös (K-T) method, the reactivity ratios of monomer pair can be found by using

$$\eta = \left[r_1 + \frac{r_2}{\alpha}\right]\varepsilon - \frac{r_2}{\alpha} \tag{3}$$

where $\eta = G/(\alpha + H)$; $\varepsilon = H/(\alpha + H)$; $\alpha = (H_{\min}\cdot H_{\max})^{1/2}$; $G = F(f - 1)/f$; $H = F^2/f$. By plotting η against ϵ, a straight line is obtained (Fig. 4) whose intercepts at $\varepsilon = 0$ and $\epsilon = 1$ give $-r_2/\alpha$ and r_1, respectively.

The reactivity ratios obtained from F-R and and K-T plots are

F-R method: $r_1 = 0.08 \pm 0.01$ and $r_2 = 2.45 \pm 0.03$

K-T method: $r_1 = 0.06 \pm 0.01$ and $r_2 = 2.43 \pm 0.08$

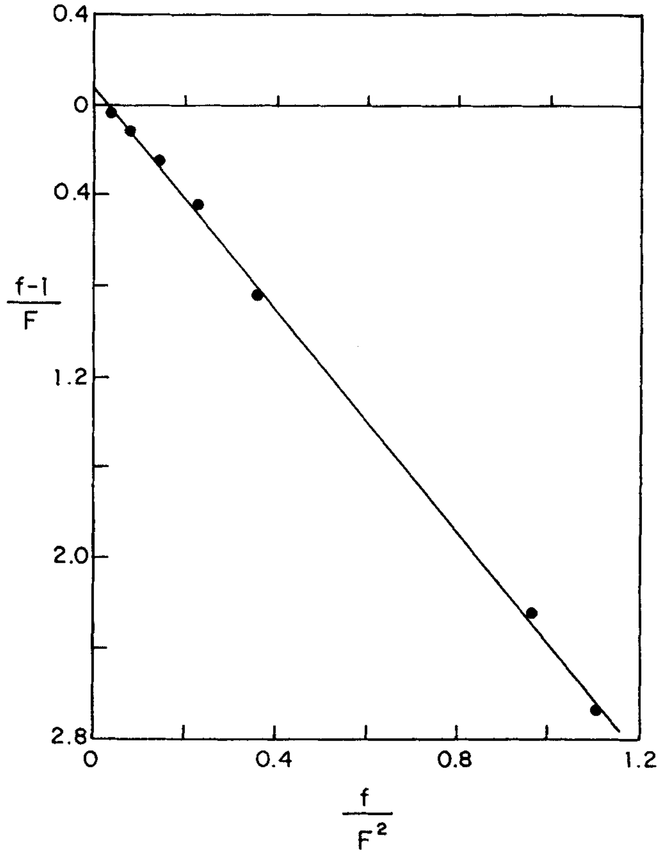


FIG. 3. F-R plot for the determination of reactivity ratios of AMS-NCHA copolymer system in toluene at 60 ± 1°C.

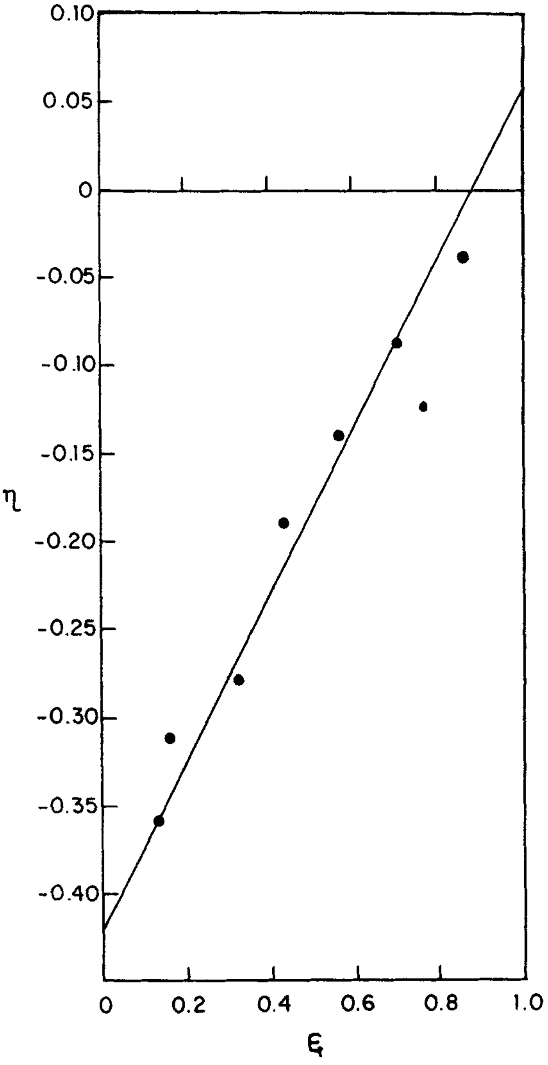


FIG. 4. K-T plot for the determination of reactivity ratios of AMS-NCHA copolymer system in toluene at 60 ± 1°C.

The observed r_1 and r_2 values are in accordance with the values reported for other AMS systems [1-4].

In the present work $r_1 < 1$ and $r_2 > 1$. r_1 shows that α-methylstyrene favors cross-propagation as opposed to homopropagation, and r_2 shows that NCHA favors homopropagation over cross-propagation. r_1 and r_2 together show that NCHA is generally more reactive than α-methylstyrene, hence the copolymers contain a higher proportion of NCHA units.

Although the product of r_1 and r_2 is less than unity, this can only be truly said to indicate a random distribution of the monomeric units where the values of r_1 and r_2 are close to unity themselves. The more these values diverge from unity, the less random the distribution will be. Table 3 shows that the mean sequence length of

TABLE 3. Mean Sequence Lengths in AMS and NCHA Copolymerization in Toluene at 60 ± 1 °C[a]

Mole percentage of NCHA in feed, M_2	$\bar{l}_1$	$\bar{l}_2$	$\bar{l}_1:\bar{l}_2$	Distribution[b]
16	1.42	1.47	1:1	
25	1.24	1.81	1:2	
34	1.16	2.26	1:2	—ANNA—
43	1.10	2.88	1:3	—ANNNA—
53	1.09	3.83	1:4	—ANNNNA—
72	1.03	7.35	1:7	
75	1.03	8.52	1:9	

[a] $r_1 = 0.08, r_2 = 2.45$.

[b] Only a few cases are illustrated (A = AMS; N = NCHA).

NCHA increases as the concentration of NCHA in the feed increases. This suggests that the copolymers are becoming more ordered and therefore less random in nature, containing longer blocks of NCHA, as its concentration in the feed increases.

A plot of copolymer composition against the composition of the feed is shown by a solid line in Fig. 5. The dashed line represents the ideally random copolymerization conditions. It can be seen from the plot that even when the feed contains only 20% NCHA, the copolymer formed contains around 60% NCHA. This indicates that there is less random distribution of the monomeric units even though $r_1 r_2 < 1$ (0.196).

^{13}C-NMR Spectra: Determination of Copolymer Composition

A typical ^{13}C-NMR spectrum of AMS-NCHA copolymer ($X_{\mathrm{AMS}} = 0.41$) is shown in Fig. 2. The copolymer composition can be obtained from the ratio of area of the carbonyl carbon peak to that of the aromatic carbons [7]. The results for the two typical copolymers are $X_{\mathrm{AMS}} = 0.41$ and 0.28, respectively, in favorable agreement with the results determined via ^{1}H-NMR: $X_{\mathrm{AMS}} = 0.43$ and 0.29, respectively.

Mean Sequence Length

The mean sequence length [18, 19] can be determined using the pertinent equations.

$$\bar{l}_1 = r_1 \frac{[M_1]}{[M_2]} + 1 \tag{4}$$

$$\bar{l}_2 = r_2 \frac{[M_2]}{[M_1]} + 1 \tag{5}$$

where r_1 and r_2 are the reactivity ratios and $[M_1]$ and $[M_2]$ represent the concentrations of AMS and NCHA, respectively, in the monomer feed. The mean sequence lengths of copolymers are given in Table 3.

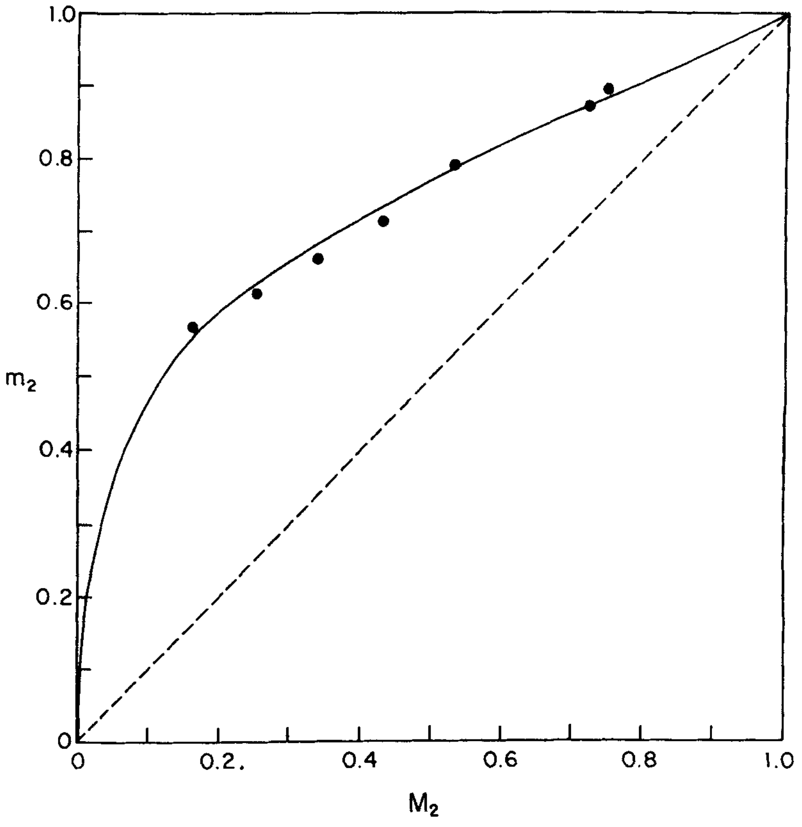


FIG. 5. Composition diagram of AMS-NCHA copolymer system in toluene at 60 ± 1°C; total comonomer concentration = 1.5 mol·L^{-1}. M_2 and m_2 are mole fractions of NCHA in the comonomer feed and in the copolymers, respectively.

It is significant to note from Table 3 that the number of NCHA units increases in a linear fashion in the polymer chain as the concentration of NCHA increases in the monomer feed.

CONCLUSION

Copolymers of AMS and NCHA were prepared by free-radical polymerization at 60 ± 1°C. The total conomomer concentration was 1.5 mol·L^{-1} in toluene. Characterization and evaluation of copolymer compositions were done by both ^{1}H- and ^{13}C-NMR spectroscopy. The reactivity ratios were found to be r_1 = 0.08 ± 0.01 and r_2 = 2.45 ± 0.03 by the Fineman-Ross method and r_1 = 0.06 ± 0.01 and r_2 = 2.43 ± 0.08 by the Kelen-Tüdös method. The values are in good agreement. $r_2 > 1$ indicates that NCHA is more reactive than AMS. The values of r_1 and r_2 diverge from unity even though $r_1r_2 < 1$ (0.196) shows less random distribution. r_2 shows that NCHA favors homopropagation over cross-propagation. Even when the feed contains only 20% NCHA, the copolymer formed contains around

60% NCHA, thereby favoring the formation of longer blocks of NCHA as its concentration in the feed increases. The mean sequence length determination shows that the number of NCHA units increases in a linear fashion in the polymer chain as the concentration of NCHA increases in the monomer feed.

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