



N-TERT-AMYLACRYLAMIDE BASED COPOLYMERS –II : SYNTHESIS, CHARACTERIZATION, REACTIVITY RATIOS AND MEAN SEQUENCE LENGTHS OF POLY(NTA-co-BA)

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ABSTRACT

Copolymers of N-tert-amylacrylamide (NTA) and n-butyl acrylate (BA) were prepared by free radical polymerization in DMF at 60 °C using BPO as initiator. The copolymer compositions were determined by ¹H-NMR analysis. The reactivity ratios of monomers were determined by Fineman-Ross ($r_1 = 2.79$ and $r_2 = 0.78$), Kelen-Tudos ($r_1 = 2.72$ and $r_2 = 0.77$). The $r_1.r_2=2.18$ indicated the formation of random copolymers. The mean sequence lengths of copolymers indicated that the NTA units increases in a linear fashion in the polymer chain as the concentration of NTA increases in the monomer feed.

Keywords: N-tert-amylacrylamide, reactivity ratios, copolymer composition, Mean Sequence lengths.

INTRODUCTION

The determination of copolymer composition and reactivity ratios of the monomers is important in evaluating the specific application of the copolymer¹. The monomer reactivity ratios determined by conventional linearization methods are not always accurate and several non-linear methods have been attempted to determine their value²⁻⁴. ¹H-NMR spectroscopic analysis has been established as a powerful tool for the estimation of copolymer composition^{5,6}.

Knowledge of the copolymer composition is an important step in the evaluation of its utility. Copolymer composition and monomer distribution in the copolymer are dependent on the reactivity ratios. The most common mathematical model of copolymerization is based on finding the relationship between the composition of copolymers and the composition of the monomer feed in which the monomer reactivity ratios are the parameters to be determined⁷. The accurate estimation of copolymer composition and determination of monomer reactivity ratios are significant for tailor-made copolymers with required physical and chemical properties and in evaluating the specific end application of the copolymers.

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

EXPERIMENTAL

Benzoyl peroxide(BPO) was recrystallized from chloroform. All the solvents were purified by distillation prior to their use. N,N'-dimethylformamide(DMF) was dried in Magnesium Sulphate. Acrylonitrile was first washed with 5% NaOH solution in water to remove the inhibitor and then with 3% Orthophosphoric acid solution in water to remove basic impurities. Then the acrylonitrile was washed with double distilled water and dried over anhydrous CaCl₂. The acrylonitrile was then distilled at reduced pressure in atmosphere of Nitrogen. It was then collected in a clean dry amber colored bottle and kept in the refrigerator at 5 °C. 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.

The monomer N-tert-amylacrylamide was prepared by the reaction of acrylonitrile and t-amyl alcohol⁸. N-tert-amylacrylamide wrecrystallized in warm dry benzene. The white crystals have mp.91 °C (Lit.91-92 °C) and the yield was -87%.

A total feed of 5 gm of monomers N-tert-amylacrylamide, n-butyl acrylate and 50mg of BPO initiator were dissolved in 25ml of DMF placed in a standard reaction tube to obtain a homogenous solution. The mixture was flushed with oxygen free dry nitrogen gas. The inlet and outlet of the reaction tube were closed by means of rubber tubes and pinch cock. The reaction vessel is then immersed in a thermostatic water bath maintained at 60 °C. The copolymerization reaction was allowed to proceed for an appropriate duration that would give a conversion below 10%. After the reaction vessel was removed from the thermostat and cooled under the tap. The solution poured in ice cold water to precipitate the copolymer and the copolymer washed with methanol. It was then dried in vacuum oven for 24 hours

RESULTS AND DISCUSSION

Copolymers of N-tert-amylacrylamide (NTA) and n-butyl acrylate (BA) were prepared by free-radical polymerization at 60 °C using BPO as the free-radical initiator. The conversions of the polymerization were controlled to be less than 10%. A schematic representation of the copolymer structure is given in Schem-1.

¹H-NMR spectral values of N-tert-amylacrylamide : at 0.78ppm for-CH₃, at 1.2ppm for-(CH₃)₂, at 1.7 ppm for-CH₂, at 5.49 ppm for =CH vinylic proton and at 6.1ppm for vinylic =CH₂ proton. ¹H-NMR spectral values of n-butyl acrylate(data from standard spectrum) :at 0.9 ppm for CH₃, at 1.1-1.7 ppm for (CH₂)₂ at 4.1 ppm for OCH₂ and at 5.5- 6.2 ppm for vinyl proton.

The ¹H-NMR spectrum of copolymer, poly (NTA-co- BA) (0.2 : 0.8) is shown in Figure-1. The following peaks appear in the copolymer spectrum : at 0.85-.89 ppm for CH₃ (NTA & BA), at 0.91 - 1.1 ppm for tert -methyl group of NTA and (CH₂)₂ BA, 2.08-2.3 ppm backbone CH₂, at 2.5 ppm due to backbone methyne C-H, 4.01 ppm for OCH₂ and at 7.9 ppm for N-H.

The copolymer composition was determined 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 (OCH₂) peak area⁹ 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. The copolymer compositions can be obtained using-

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

Where X= mole fraction and A= peak area. Table 2. gives the values of the corresponding mole fractions in the copolymers.

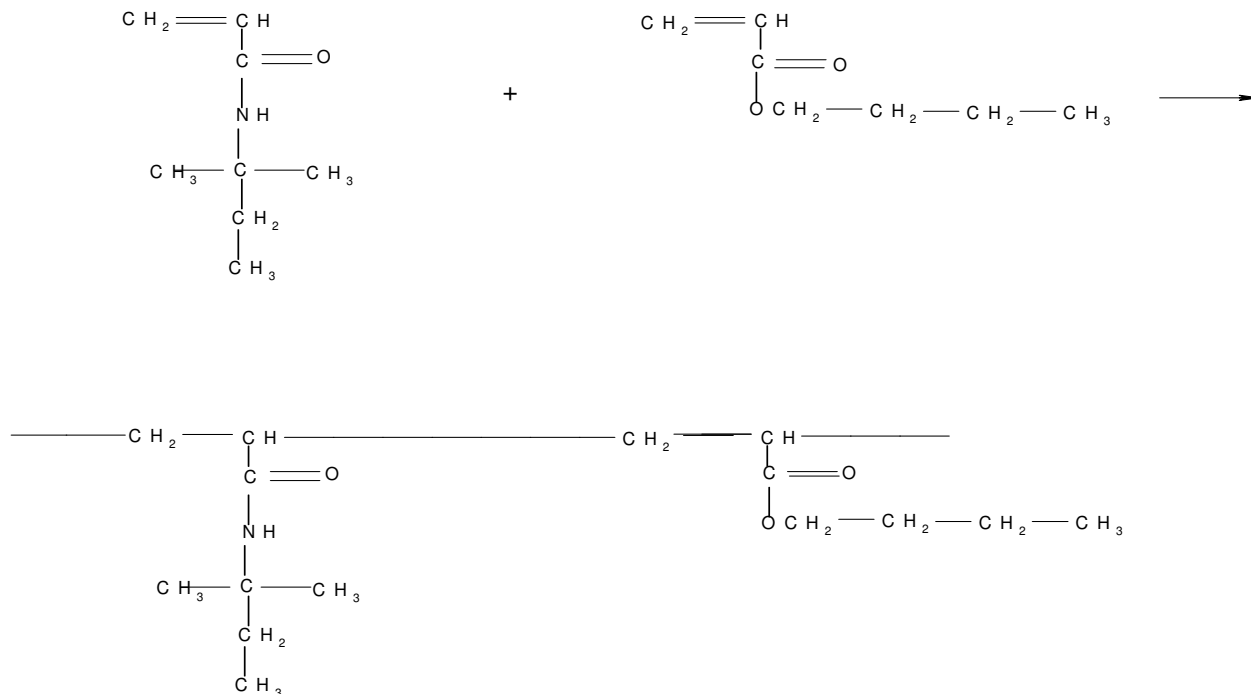
From the monomer feed ratios and the resultant copolymer compositions, the reactivity ratios of monomer 1 (NTA) and monomer 2 (BA) were evaluated by the methods of Fineman-Ross (FR) and Kelen-Tudos (KT). The significant parameters of F-R and K-T and equation are presented in Table1 and Table 2 respectively. The reactivity ratios of NTA (r₁) and BA (r₂) from the F-R plot (Figure 2) and K-T plot are given in Table 3. The values of r₁ is greater than 1 and r₂ is less than 1. The r₁ shows that NTA favours homopropagation over cross-propagation and r₂ shows that BA favours cross-propagation as opposed to homopropagation. The r₁ and r₂ together shows that NTA is generally more reactive than BA. The mean sequence lengths⁷ can be determined using the pertinent equations:

$$l_1 = r_1 (M_1/M_2) + 1 \quad (2)$$

$$l_2 = r_2 (M_2/M_1) + 1 \quad (3)$$

Where r_1 and r_2 are the reactivity ratios and $[M_1]$ and $[M_2]$ represent the mole fractions of NTA and BA.

The mean sequence lengths of copolymers are given Table 4. From Table 4, it may be noted that the NTA units increases in a linear fashion in the polymer chain as the concentration of NTA increases in the monomer feed¹⁰.



Scheme-1: Copolymerization of NTA and BA

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Table -1: Fineman-Ross parameters for the Copolymerization of N-tert-amylacrylamide and n-butyl acrylate

$G = F(f-1) / f$	$H = F^2 / f$	$\eta = G / (\alpha + H)$	$\epsilon = H / (\alpha + H)$
- 0.428	0.169	-0.624	0.246
-0.242	0.288	-0.301	0.358
-0.121	0.364	-0.137	0.413
0. 507	0.493	0.502	0.488
1.077	0.635	0.935	0.551
1.921	0.960	1.301	0.650
3.644	1.582	1.736	0.754

Table- 2: Kelen-Tudos parameters for the Copolymerization of N-tert-amylacrylamide and n-butyl acrylate

Mole fraction of NTA in feed, M_1	Mole fraction of BA in feed, M_2	Mole fraction of NTA in copolymer, m_1	Mole fraction of BA in copolymer, m_2	$F = M_1 / M_2$	$f = m_1 / m_2$	$(f - 1) / F$	f / F^2
0.2	0.8	0.27	0.73	0.250	0.369	-2.524	5.904
0.3	0.7	0.39	0.61	0.429	0.639	-0.841	3.473
0.4	0.6	0.55	0.45	0.667	1.222	0.333	2.746
0.5	0.5	0.67	0.33	1.000	2.030	1.030	2.030
0.6	0.4	0.78	0.22	1.500	3.545	1.697	1.576
0.7	0.3	0.85	0.15	2.333	5.667	2.001	1.041
0.8	0.2	0.91	0.09	4.000	10.11	2.278	0.632

$\alpha = 0.51$

Table-3: Copolymerization parameter, for the NTA and BA copolymer system

Methods	r_1	r_2	$r_1 \cdot r_2$
Fineman-Ross (FR)	2.79	0.78	2.18
Kelen-Tudos (KT)	2.72	0.77	2.09

Table -4: Mean Sequence Lengths in NTA and BA copolymers ^a

Mole fraction of NTA in feed, M_1	l_1	l_2	$l_1 : l_2$	Distribution ^b
0.20	1.69	4.12	2:4	
0.30	2.19	2.82	2:3	
0.40	2.86	2.17	3:2	NNNBNNN
0.50	3.79	1.78	4:2	NNNN BB NNNNN
0.60	5.19	1.52	5:2	NNNNNBBNNNNN
0.70	7.50	1.33	8:1	(N) ₈ B (N) ₈
0.80	12.16	1.19	12:1	(N) ₁₂ B (N) ₁₂

^a $r_1 = 2.79$, $r_2 = 0.78$; ^b Only a few cases are illustrated (N = NTA ; B= BA)

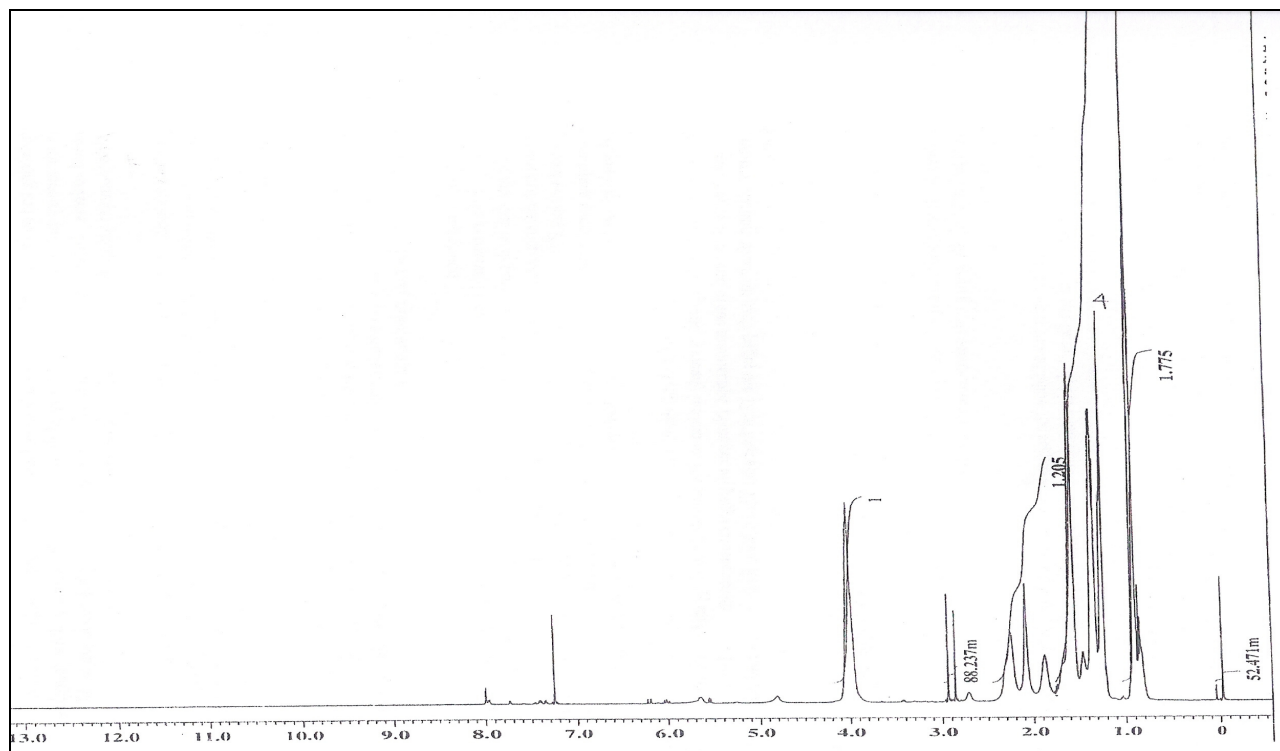


Fig.-1 : $^1\text{H-NMR}$ spectrum of Poly (NTA-co- BA) (0.2 : 0.8)

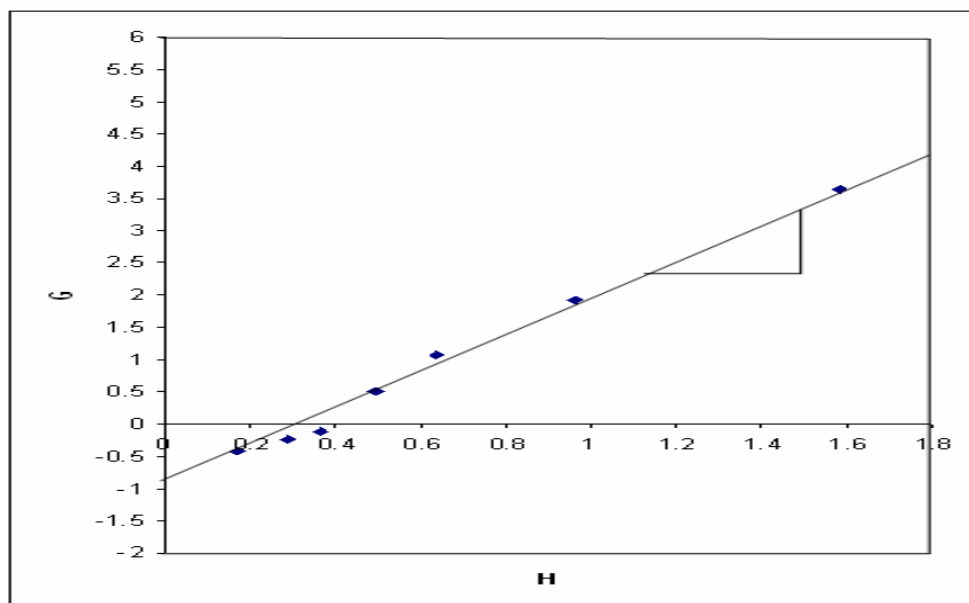


Fig.-2: Fineman-Ross (FR) Plot for Poly (NTA-co- BA)

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