Study of the copolymerization parameters of *N*-antipyryl acrylamide with different alkyl acrylates and styrene monomer

S. H. El-Hamouly*
Laboratory of Polymer Chemistry, Faculty of Science, El Menoufeia University, Shebin El Kom, Egypt

and M. M. Azab
Department of Chemistry, Faculty of Science, Benha University, Benha, Egypt

and O. A. Mansour
Microanalytical Centre, Faculty of Science, Cairo University, Egypt
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N-Antipyryl acrylamide monomer [2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-ylacryloylamine) was synthesized by the reaction of 4-aminoantipyrine with either acryloyl chloride or acrylic acid in the presence of *N*,*N*′-dicyclohexyl carbodiimide as the dehydrating agent. Binary copolymerizations of this new monomer with methyl acrylate, ethyl acrylate, butyl acrylate and styrene were performed in dimethylformamide at 65°C using 1 mol% azobisisobutyronitrile as the initiator. The copolymer compositions were determined from the nitrogen analyses. Copolymerization parameters for each system were calculated by the Fineman–Ross and Kelen–Tüdös methods.

(Keywords: copolymerization parameters; binary copolymerization; *N*-antipyryl acrylamide)

INTRODUCTION

4-Aminoantipyrine and its derivatives are being used in many drugs as antipyretics and analgesics[1] and are found to have considerable antischistosomiatic activity[2–4], in addition to other biomedical and biological effects[5].

In our previous work, we described the binary copolymerizations of *N*-antipyryl acrylamide (NAA) with methyl methacrylate (MAA), n-butyl methacrylate (BuMA), acrylonitrile (AN) and vinyl acetate (VA)[6].

The aim of this investigation was to study the copolymerization parameters of *N*-antipyryl acrylamide with methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BuA) and styrene (ST).

EXPERIMENTAL

Materials

4-Aminoantipyrine was provided by Fluka, acryloyl chloride, MA, EA, BuA, acrylic acid and ST were supplied by Aldrich and *N*,*N*′-dicyclohexylcarbodiimide (DCCI) was purchased from Merck. All the monomers were purified by distillation at reduced pressure and the middle fractions were retained. Azobisisobutyronitrile (AIBN), purchased from Merck, was recrystallized from ethanol.

Synthesis of the monomer

NAA monomer was synthesized by two different methods: (1) the acid chloride method, according to our previous work[6]; and (2) the *N*,*N*′-dicyclohexylcarbodiimide method, according to a literature procedure[7]. The yields were 65% and 39%, respectively. NAA prepared from the acid chloride method was used for the following copolymerization.

Copolymerization procedure

NAA copolymers with each of MA, EA, BuA and ST were obtained by solution polymerization in dimethylformamide (DMF) ($2\,\mathrm{mol\,l^{-1}}$) under N_2 at 65°C and in the presence of 1 mol% AIBN. The total monomer concentration was $2\,\mathrm{mol\,l^{-1}}$. The overall conversions were $< 10\%$ in every case. The copolymers obtained were soluble in the reaction medium and were recovered by precipitation in water. They were redissolved, reprecipitated, washed with water, dried and weighed.

Spectral measurements

I.r. spectra were recorded as KBr discs using a Perkin–Elmer 598 (4000–$200\,\mathrm{cm^{-1}}$) spectrophotometer. The copolymer compositions of NAA and the different alkyl acrylates and styrene were calculated based on the nitrogen content in each copolymer, determined using a Perkin–Elmer 2400 CHN elemental analyser. The analyses were carried out at the Microanalytical Centre, University of Cairo.

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* To whom correspondence should be addressed

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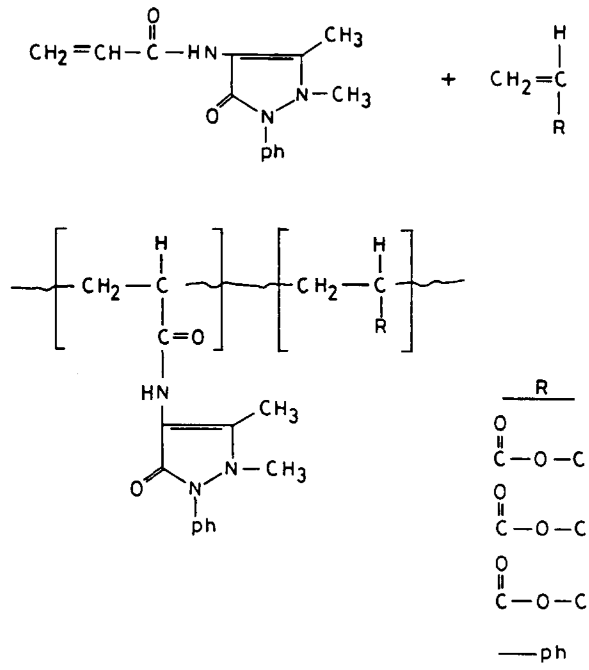
RESULTS AND DISCUSSION

NAA was synthesized and the spectral data were studied[6]. The copolymerizations of NAA with MA, EA, BuA and ST can be represented as in the following scheme



The copolymers NAA–MA, NAA–EA and NAA–BuA were obtained as white powders which were soluble in most organic solvents, whereas NAA–ST was a yellowish solid which was soluble in DMF and dimethyl sulfoxide.

The structures of the copolymers were investigated by i.r. spectroscopy. As an example, the i.r. spectrum of NAA–EA is shown in *Figure 1*. It shows bands for ν(N-H) (3500 cm^{-1}), aromatic and aliphatic ν(C–H) (3200 and 2970–2920 cm^{-1}), ν(C=O) of the acrylate ester (1730 cm^{-1}), ν(C=O) of the pyrazoline ring (1660 cm^{-1})[8], ν(C=O) of the acryloyl moiety (amide I) (1620 cm^{-1}), δ(N-H) bending vibrations (amide II) (1590 cm^{-1}) and ν(C=C) of the aromatic ring (1530–1480 cm^{-1}).

The nitrogen contents of the copolymers were determined by the Kjeldahl method. The results for NAA–BuA for equimolar monomer feeds in each system are illustrated in *Table 1* as an example. The monomer

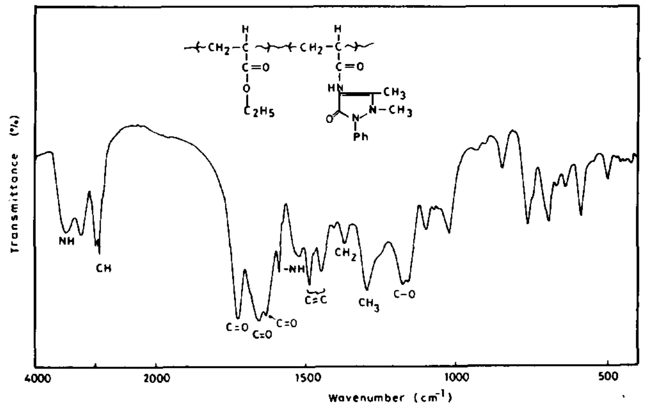


Figure 1 I.r. spectrum of NAA–EA

Table 1 Analytical data for copolymerizations of NAA with BuA

Feed composition		Conversion	N content	Copolymer composition	
a^a	$f_1{}^b$	(%)	(%)	b^a	$F_1{}^b$
0.1111	0.1001	7.42	6.84	0.373	0.2717
0.3330	0.2499	8.42	9.45	0.810	0.4475
0.4285	0.3000	5.64	9.86	0.928	0.4813
0.6666	0.3999	6.28	10.41	1.129	0.5303
0.9999	0.5000	7.84	10.93	1.387	0.5811
2.3360	0.7000	6.82	12.06	2.417	0.7073

[a] Molar ratio of M_1 (NAA) to M_2 (BuA)
[b] Molar fraction of M_1 (NAA)

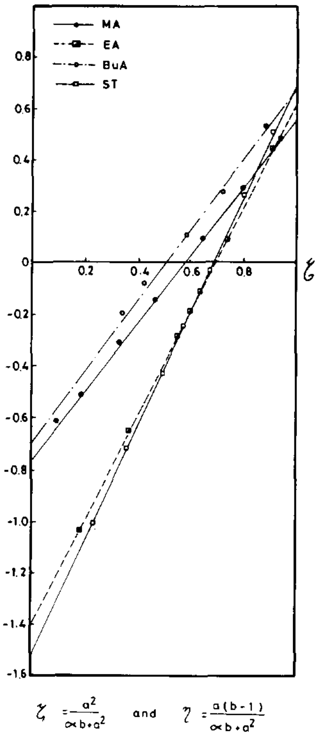


Figure 2 Kelen–Tüdös plots for copolymerizations of NAA monomer with MA, EA, BuA and ST, where a and b are the molar ratios (M_1/M_2) of the comonomer in the feed and copolymer, respectively, and $\alpha = (a_{min} a_{max})/(b_{min} b_{max})^{1/2}$

Table 2 Monomer reactivity ratios for copolymerizations of NAA with MA, EA, BuA and ST

Copolymer system	Fineman–Ross		Kelen–Tüdös			
M_1–M_2	r_1	r_2	r_1	r_2	r_1r_2	α^a
NAA–MA	0.582 ± 0.023	0.304 ± 0.009	0.567 ± 0.021	0.318 ± 0.032	0.180	0.413
NAA–EA	0.618 ± 0.038	0.197 ± 0.010	0.636 ± 0.035	0.176 ± 0.018	0.112	0.127
NAA–BuA	0.689 ± 0.013	0.192 ± 0.007	0.697 ± 0.042	0.194 ± 0.011	0.135	0.273
NAA–ST	0.706 ± 0.042	0.226 ± 0.013	0.713 ± 0.046	0.219 ± 0.014	0.156	0.137

[a] See *Figure 2*

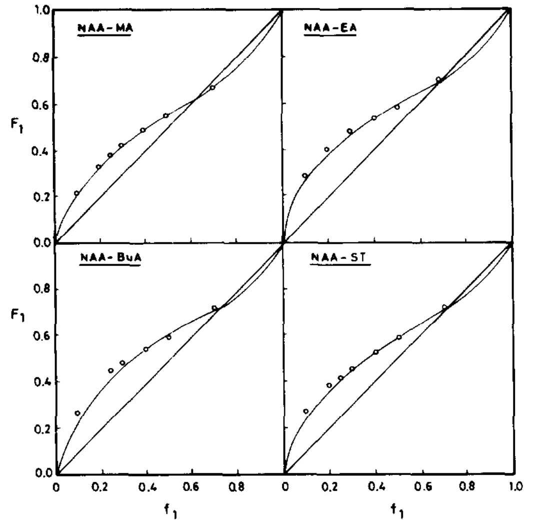


Figure 3 Composition curves for copolymerizations of NAA with MA, EA, BuA and ST (f_1 = molar fraction of M_1 in the feed and F_1 = molar fraction of M_1 in the copolymer). The solid lines represent the calculated values and the points correspond to the experimental values

reactivity ratios r_1 and r_2 for the four systems were deduced (*Table 2*) using the Fineman–Ross[9] and Kelen–Tüdös[10] methods. These results reveal a good agreement between the reactivity ratios found by the two methods. *Figure 2* shows the Kelen–Tüdös plots for the four systems. The copolymerization parameters and r_1r_2 values, given in *Table 2*, as well as the composition curves in *Figure 3*, were interpreted according to the structures and reactivities of the monomers and radicals incorporated in the copolymers.

For the copolymer system NAA–ST the pyrazoline ring of NAA is stabilized by resonance[11], but the carbonyl group of the pyrazolone tends to decrease the resonance stabilization of the $(n-\pi)$ electrons of the nucleus. In contrast to the former effect, styrene monomer is more effective in stabilizing its own radicals because of the loosely held π electrons[12], i.e. –ST$^{\bullet}$ is more stable than –NAA$^{\bullet}$. It is known that the more stable radicals are less reactive. Consequently, –ST$^{\bullet}$ is less reactive than –NAA$^{\bullet}$ towards copolymerization. The r_1r_2 value indicates a relative tendency towards alternation.

The growing chain radicals of the acrylate esters –AE$^{\bullet}$ also show a resonance stability which is in principle lower than that of –ST$^{\bullet}$, i.e. –AE$^{\bullet}$ is less stable than –ST$^{\bullet}$; consequently, –AE$^{\bullet}$ is more reactive than –ST$^{\bullet}$ towards copolymerization. Here also, the r_1r_2 value indicates a tendency towards alternation.

The results also show that the four copolymer systems have azeotropic compositions at $f_1 = 0.612$, 0.694, 0.727 and 0.731, calculated from the Kelen–Tüdös results.

The Q and e values for NAA were calculated from the monomer reactivity ratios, and the Q and e values of the vinyl monomers were calculated using the Alfrey–Price equation[13]. The average values for NAA were found to be $Q = 0.48$ and $e = 0.28$.

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