Reactivity Ratios in the Redox Copolymerization of Acrylamide and n-Butyl Acrylate in Dimethylformamide

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ABSTRACT

Copolymerization of acrylamide and n-butyl acrylate in DMF initiated by the redox system $CNCH_2 COOH/Mn(OAc)_3$ has been investigated in the temperature range 20 to 35°C. The data on reactivity ratios are compared with those of other monomer pairs involving acrylamide, and the values obtained using benzoyl peroxide as the initiator are presented.

INTRODUCTION

Although reports on the redox polymerization of vinyl monomers in aqueous and nonaqueous media are extensive, only a few reports have appeared on redox copolymerizations in nonaqueous media. The redox system $CNCH_2 COOH/Mn(OAc)_3$ has been investigated by us for homopolymerization [1] in nonaqueous media. In this paper we report the use of this system for copolymerization in DMF medium.

EXPERIMENTAL

All reagents used were of AnalaR grade. The solvents DMF, ether, ethanol, hexane, and acetic acid were purified by standard methods. $Mn(OAc)_3.2H_2O$ was prepared according to Andrulis et al. [2]. Cyanoacetic acid (CAA) was purified by recrystallization from ether/hexane. Acrylamide (AA) was recrystallized from chloroform (mp 85°). n-Butyl acrylate (nBuA) was freed from inhibitor by wash-ing with 5% sodium hydroxide and water, and dried over calcium chloride. It was distilled twice under reduced pressure. Stock solu-tions of CAA and $Mn(OAc)_3.2H_2O$ were prepared in DMF and assayed by titration with standard alkali and by cerimetry, respectively.

Preliminary experiments showed that polyacrylamide is insoluble in DMF as well as in DMF/ethanol mixture while poly-n-butyl acrylate is soluble in both. The copolymer was found to be insoluble in DMF/ethanol mixtures while being freely soluble in DMF. A typical polym-erization procedure consisted of deaerating a mixture of the appropri-ate amounts of AA, n-BuA, and CAA in DMF which was thermostated at the required temperature. After deaeration, addition of the requi-site amount of a degassed solution of $Mn(OAc)_3$ initiated the reaction. After the time required for 10-15% conversion, the reaction was ar-rested by the addition of a solution of hydroxylamine hydrochloride in DMF. Total monomer concentration was maintained at 1.5 mol/L while the ratio [AA]/[n-BuA] was varied. If the monomer feed ratio $F = M_1/M_2$ was very high (> 6), it was found that a precipitate of polyacrylamide formed. Generally, the reaction mixture remained homogeneous. The copolymer was precipitated from solution by the addition of an equal volume of absolute ethanol, washed thoroughly with ether and hexane to remove DMF, and dried to constant weight. With benzoyl peroxide as initiator, the required amounts of the two monomers and peroxide in DMF were deaerated and the reaction tube sealed. The tube was placed in a thermostat maintained at 70°C for 120-150 min, ensuring 15% conversion. The copolymer was isolated and purified as before.

The acrylamide content of the copolymer samples were determined by a micro-Kjeldhal method to obtain data on the copolymer composi-tion $f = m_1/m_2 = [AA]/[n-BuA]$. Data were obtained for various mono-mer feed ratios F as well as for $[CAA]/[Mn(OAc)_3]$ ratios.

RESULTS AND DISCUSSION

Tables 1-3 contain some of the data. The data were treated accord-ing to Fineman and Ross [3], and plots of $(f - 1)/F = (r_1 - r_2 f)/F^2$, where r_1 and r_2 refer to the reactivity ratios, appear in Figs. 1 and 2. The slopes and intercepts of these plots were estimated by the method of least squares. Similar linear plots were obtained for the copolymers

TABLE 1. Monomer Feed Ratios and Copolymer Composition: 34°C, [CAA]/[Mn(OAc)$_3$] = 0.0699 $\underline{M}$/0.0091 $\underline{M}$

F = M$_1$/M$_2$	% N	% AA	% n-BuA	f = m$_1$/m$_2$
3.0	10.95	55.53	44.47	1.25
3.29	11.37	57.70	42.29	1.36
3.62	11.72	59.42	40.58	1.46
4.41	12.47	63.27	36.73	1.72
5.00	12.82	60.07	34.93	1.86

TABLE 2. Monomer Feed Ratios and Copolymer Composition: 20°C, [CAA]/[Mn(OAc)$_3$] = 0.0996 $\underline{M}$/0.0086 $\underline{M}$

F = M$_1$/M$_2$	% N	% AA	% n-BuA	f = m$_1$/m$_2$
3.00	10.36	52.56	47.44	1.11
3.29	10.62	53.87	46.13	1.17
3.62	10.99	55.77	44.23	1.26
4.00	11.41	57.89	42.11	1.37
4.41	11.79	59.83	40.17	1.49
5.00	12.12	61.48	38.52	1.60

TABLE 3. Monomer Feed Ratios and Copolymer Composition: 70°C, benzoyl peroxide = 0.028 $\underline{M}$

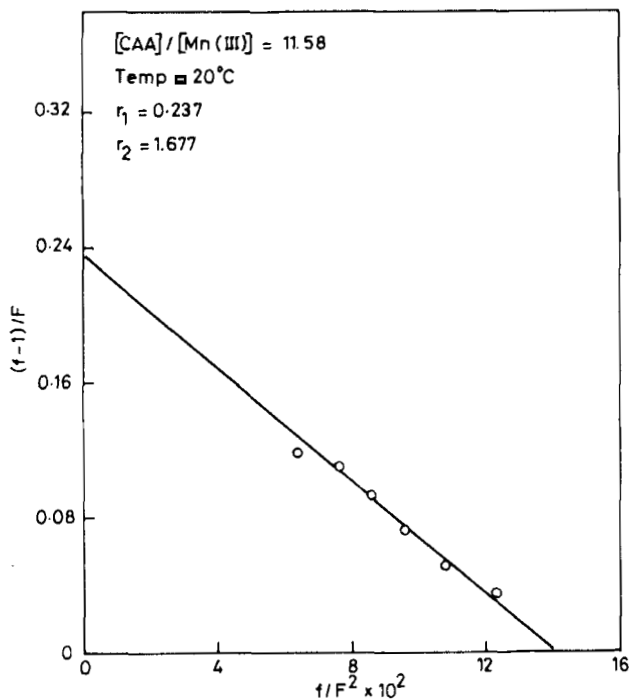| F	% N	% AA	% n-BuA	f
2.00	9.74	49.41	50.59	0.98
2.01	9.80	49.74	50.26	0.99
2.33	10.25	52.00	48.00	1.08
2.79	10.96	55.60	44.40	1.25
3.29	11.73	59.52	40.48	1.47

FIG. 1.   Plot of $(f - 1)/F$ vs f/F^2.

prepared using peroxide as initiator.   The collected data appear
in Table 4.   In the same table are given some literature values
of reactivity ratios for a few other monomer pairs involving
acrylamide.   It can be seen that n-butyl acrylate closely re-
sembles methyl methacrylate and acrylic acid in its copolymeri-
zation behavior with acryamide.   Also, the data obtained using
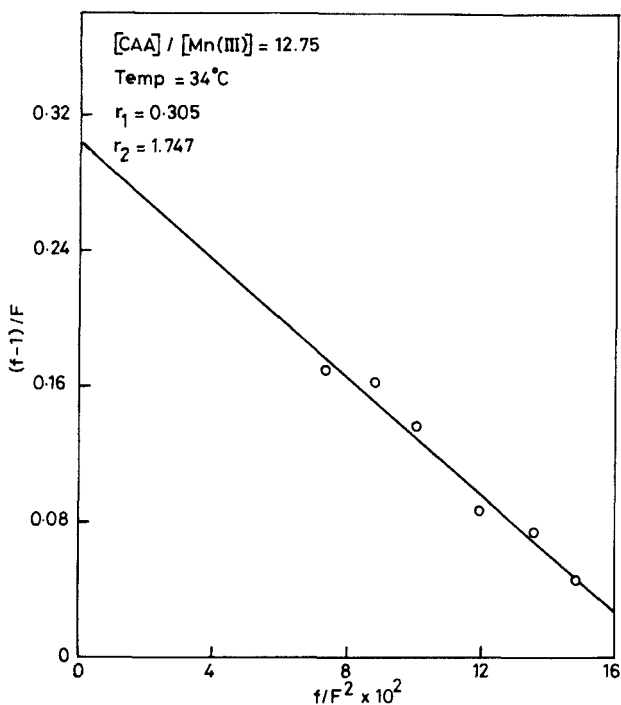peroxide as initiator are of the same order of magnitude as

FIG. 2. Plot of $(f - 1)/F$ vs f/F^2.

those for redox initiation. The ratio of the redox components does not influence the reactivity very much. Not much can be inferred about the temperature dependence of the values. In conclusion, we can state that redox initiation of copolymerization by the $CNCH_2COOH/Mn(OAc)_3$ system is a convenient procedure for preparing random copolymer in good yields at ambient conditions.

TABLE 4. Data on Reactivity Ratios

No.	M_1	M_2	r_1	r_2	Temperature (°C)	Refs.
1	Acrylamide	Methyl methacrylate	0.25	2.5	50	4
2	"	Methyl acrylate	1.3 ± 0.05	0.05 ± 0.05	60	5
3	"	Acrylic acid	0.6 ± 0.02	1.43 ± 0.03	25	5
4	"	Acrylonitrile	1.357	0.875	30	5
5	"	n-Butyl acrylate	0.29 ± 0.04	1.75 ± 0.25	34	Redox initiation
6	"	"	0.24 ± 0.01	1.40 ± 0.27	20	"
7	"	"	0.32	1.357	70	Peroxide initiation

ACKNOWLEDGMENT

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