

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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

T. R. Balasubramaniam<sup>a</sup>; V. Mahadevan<sup>a</sup>

<sup>a</sup> Department of Chemistry, Indian Institute of Technology, Madras, India

**To cite this Article** Balasubramaniam, T. R. and Mahadevan, V.(1984) 'Reactivity Ratios in the Redox Copolymerization of Acrylamide and n-Butyl Acrylate in Dimethylformamide', *Journal of Macromolecular Science, Part A*, 21: 2, 245 – 251

**To link to this Article:** DOI: 10.1080/00222338408056553

**URL:** <http://dx.doi.org/10.1080/00222338408056553>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

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

T. R. BALASUBRAMANIAM and V. MAHADEVAN

Department of Chemistry  
Indian Institute of Technology  
Madras 600036, India

### ABSTRACT

Copolymerization of acrylamide and n-butyl acrylate in DMF initiated by the redox system  $\text{CNCH}_2\text{COOH}/\text{Mn}(\text{OAc})_3$  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  $\text{CNCH}_2\text{COOH}/\text{Mn}(\text{OAc})_3$  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.  $Mn(OAc)_3 \cdot 2H_2O$  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  $85^\circ$ ). n-Butyl acrylate (nBuA) was freed from inhibitor by washing with 5% sodium hydroxide and water, and dried over calcium chloride. It was distilled twice under reduced pressure. Stock solutions of CAA and  $Mn(OAc)_3 \cdot 2H_2O$  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 polymerization procedure consisted of deaerating a mixture of the appropriate amounts of AA, n-BuA, and CAA in DMF which was thermostated at the required temperature. After deaeration, addition of the requisite amount of a degassed solution of  $Mn(OAc)_3$  initiated the reaction. After the time required for 10-15% conversion, the reaction was arrested 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  $70^\circ C$  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 composition  $f = m_1/m_2 = [AA]/[n-BuA]$ . Data were obtained for various monomer 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 according 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 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

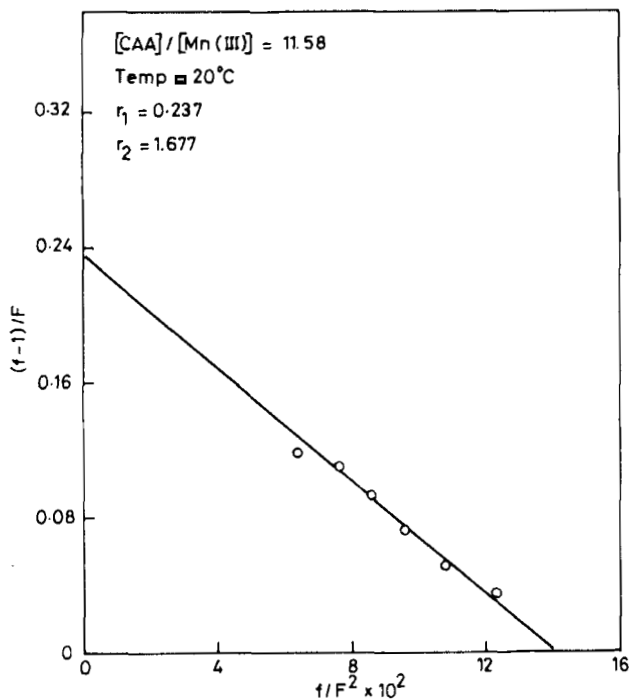


FIG. 1. Plot of  $(f - 1)/F$  vs  $f/F^2$ .

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 resembles methyl methacrylate and acrylic acid in its copolymerization behavior with acrylamide. Also, the data obtained using peroxide as initiator are of the same order of magnitude as

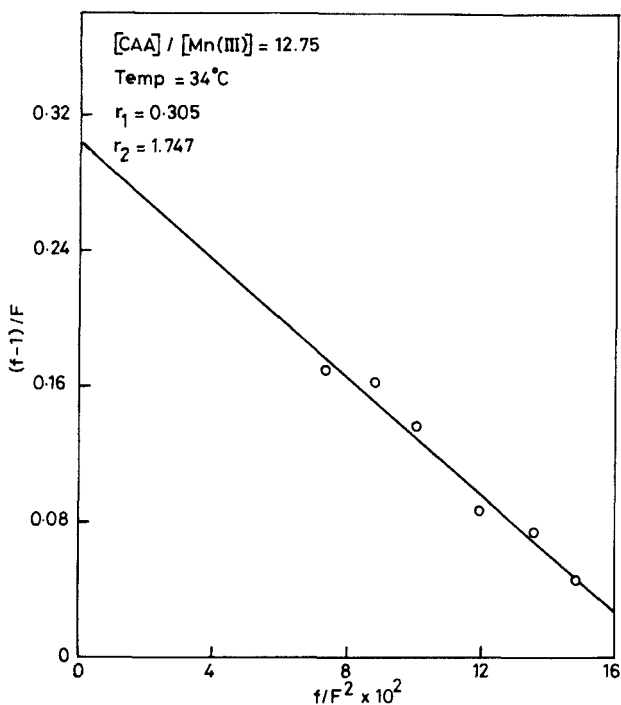


FIG. 2. Plot of  $(f - 1)/F$  vs  $f/F^2$ .

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 <sub>1</sub>	M <sub>2</sub>	r <sub>1</sub>	r <sub>2</sub>	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

Financial assistance by the CSIR, New Delhi, is gratefully acknowledged.

## REFERENCES

- [1] M. Haragopal and V. Mahadevan, Makromol. Chem., **181**, 1189 (1980).
- [2] P. J. Andrusis et al., J. Am. Chem. Soc., **88**, 5473 (1966).
- [3] M. Fineman and S. D. Ross, J. Polym. Sci., **5**, 259 (1950).
- [4] S. Bhadani et al., J. Polym. Sci., Polym. Chem. Ed., **18**, 1459 (1980).
- [5] J. Brandrup and E. H. Immergut (eds.), Polymer Handbook, Wiley-Interscience, New York, 1966.

Accepted by editor July 14, 1983

Received for publication August 11, 1983