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Reactivity Ratios in the Redox Copolymerization of Methacrylamide and Methyl Methacrylate in Dimethylformamide

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Copolymerization of methacrylamide and methyl methacrylate in dimethylformamide initiated by the redox system $CNCH_2COOH/Mn(OAC)_3$ and AIBN has been investigated at the temperatures 35 and 60° respectively. The data on reactivity ratios are compared with those of other monomer pairs involving methacrylyamide and the values obtained using AIBN as the initiator are presented. The mean sequence lengths ($\bar{n}$) in the formation of various structural units were estimated for these copolymers.

ALTHOUGH reports on the redox polymerization of vinyl monomers in aqueous and non-aqueous media are extensive, only a few reports have appeared on redox copolymerization in non-aqueous media. Reactivity ratios in the copolymerization of acrylamide and n-butyl acrylate in DMF has been studied by Balasubramanian and Mahadevan[1] using $CNCH_2COOH/Mn(OAC)_3$ redox system. Saini *et al*[2]. studied the free radical copolymerization of methacrylamide and methyl methacrylate in dioxane and ethanol and concluded that the nature of solvent influences the reactivity ratios. Reactivity ratios of methacrylamide (MAM) with methyl acrylate and methacrylic acid[3] were also determined by various workers. In our earlier paper[4] we derermined the reactivity ratios of MAM with ethyl methacrylate. We report herein the use of this redox system for evaluating the reactivity ratios and sequence length distribution of these copolymers.

Experimental

All reagents used were of AnalaR grade. The solvents DMF, ether and hexane were purified[5]. $Mn(OAC)_3.2H_2O$ was prepared according to reported method[6]. Cyanoacetic acid (CAA) was purified by recrystallisation from ether/hexane and methacrylamide (MAM) from chloroform. Methyl methacrylate (MMA) was freed from inhibitor by washing with 5% sodium hydroxide and water, dried over calcium chloride and distilled twice under reduced pressure. Stock solutions of CAA and $Mn(OAC)_3.2H_2O$ were prepared in DMF and assayed by titration with standard alkali and by cerimetry, respectively.

A typical polymerization procedure consisted of deaerating a mixture of the appropriate amounts of MAM, MMA 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 (75 min for AIBN and 150 min for redox systems) the reaction was arrested by adding a solution of hydroxylamine hydrochloride in DMF. Total monomer concentration was maintained at 1.4 mol dm^{-3} while the ratio of [MAM]/[MMA] was varied. Generally, the reaction mixture remained homogeneous. The copolymer was precipitated from solution by adding excess distilled water, washed thoroughly with ether and hexane to remove DMF and dried to constant weight. With AIBN as the initiator, the required amounts of the two monomers and initiator in DMF were deaerated and the reaction tube was sealed. The tube was placed in a thermostat maintained at 60°. The copolymer was isolated and purified as stated before.

The MAM content of the copolymer samples were determined by a Carlo Erbac elemental analyser to obtain data on the copolymer composition, $f=m_1/m_2=[MAM]/[MMA]$.

Results and Discussion

The copolymer composition was ascertained from the MAM content in the copolymers. The copolymerization results are listed in Table 1. The *r*-values for the MAM – MMA system in DMF were estimated by Fineman-Ross[7] and Kelen-Tudos[8] methods. The values of reactivity ratios so determined were r_1 (MAM) $=0.43 \pm 0.01$, $r_2=1.94 \pm 0.03$ (MMA) by K-T and $r_1=0.43 \pm 0.02$, $r_2=1.90 \pm 0.02$ by F-R methods for redox initiation. For AIBN initiation, the reactivity ratio values were $r_1=0.28 \pm 0.01$, $r_2=2.48 \pm 0.03$ and $r_1=0.26 \pm 0.02$, $r_2=2.40 \pm 0.02$ according to K-T and F-R methods

TABLE 1—MONOMER FEEDS AND COPOLYMER COMPOSITION* FOR METHACRYLAMIDE—METHYL METHACRYLATE COPOLYMER SYSTEM

Sl. no.	Redox initiation temperature=35°					AIBN Initiation temperature=60°		
	Feed composition		N%	Copolymer composition		N%	Copolymer composition	
	MAM(M_1)	MMA(M_2)		MAM(m_1)	MMA(m_2)		MAM(m_1)	MMA(m_2)
1.	0.408	0.591	3.51	0.246	0.754	2.72	0.190	0.810
2.	0.472	0.527	4.23	0.290	0.710	3.42	0.236	0.764
3.	0.538	0.461	5.67	0.383	0.617	4.52	0.308	0.692
4.	0.606	0.393	6.34	0.425	0.575	5.22	0.354	0.646
5.	0.667	0.332	7.25	0.482	0.518	6.12	0.411	0.589

*In mole fraction.

TABLE 2—REACTIVITY RATIOS FOR DIFFERENT MONOMERS (M_2) WITH METHACRYLAMIDE (M_1)

Sl. no.	M_2	r_1	r_2	Tem. (°C)	Ref.
1.	Styrene	1.29±0 08	1.46±0 09	70	*a*
2.	Methylmethacrylate	1.27±0 19	1.55±0.22	70	*a*
3.	Methylacrylate	0.22	2.0	65	*b*
4.	Methacrylic acid	0.22	2.0	50	*b*
5.	Methylmethacrylate	KT 0.43±0.01 FR 0.43±0.02	1 94±0.03 1.90±0.02	35	Redox initiation
6.	Methylmethacrylate	KT 0.28±0.01 FR 0.26±0.02	2.48±0.03 2.40±0.02	60	AIBN

[a]Ref. 2. [b]Ref. 3.

respectively. In the Table 2 some literature values of reactivity ratios are given for a few other monomer pairs involving MAM copolymers prepared using AIBN as initiator. It can be seen that MMA closely resembles to methyl acrylate and methacrylic acid in its copolymerization behaviour with MAM. Also the data obtained using thermal initiators are of the same order of magnitude as those for redox initiation. The ratio of the redox component does not influence the reactivity very much. The r_1 and r_2 values are not much affected by changing the temperature.

Sequence length distribution : Table 3 shows that the mean sequence-lengths $\bar{n}_1$ and $\bar{n}_2$ for the formation of M_1 and M_2 units calculated using the equations suggested by Ekpenyong[9]. For example, at 59% M_2(MMA) [40.8%M_1 (MAM)] in the monomer mixture, each copolymer segment with M_1 units in the redox initiation was approximately four times longer than its adjoining segment with M_2 units. The sequence may be expressed as −122221−. For the same monomer feed ratio in AIBN initiation, on the other hand, each segment with M_1 units is approximately five times longer than its adjoining segment with M_2 units. This difference between the $\bar{n}_1$ and $\bar{n}_2$ values is reduced considerably in the range of 46−33% M_2 in monomer mixtures for redox and in the range of 39−33% for AIBN initiation. The ratio of the mean sequence lengths $\bar{n}_1/\bar{n}_2$, theoretically corresponds to the ratio dm_1/dm_2 ; dm_1 and dm_2 are the corresponding compositions of M_1 and M_2 in the copolymer for each monomer mixture.

TABLE 3—MEAN SEQUENCE-LENGTH DISTRIBUTION OF METHACRYLAMIDE AND METHYLMETHACRYLATE COPOLYMERIZATION : REDOX INITIATION, AIBN

M_2 (mol%)	$\bar{n}_1$	$\bar{n}_2$	$\bar{n}_1 : \bar{n}_2$	Distribution[a]	$\bar{n}_1/\bar{n}_2$
			Redox initiation		
59.1	1 1286	3.922	1 : 4	−122221−	0.327
52.7	1.353	3.370	1 : 3		0.401
46.1	1.501	2 668	2 : 3	−11222−	0.562
39 3	1.657	2.273	2 : 2		0.728
33 2	1 864	1.968	2 : 2	−1122−	0.947
			AIBN initiation		
59.1	1.186	4.726	1 : 5	−122222−	0.251
52 7	1.229	4.023	1 : 4		0.305
46.1	1.326	3 127	1 : 3	−1222−	0 424
39 3	1.427	2.623	1 : 3		0.544
33 2	1.563	2.234	2 : 2	−1122−	0 699

[a]Only a few cases are illustrated.

The microstructure of a copolymer is defined by the distributions of the various lengths of the M_1 and M_2 sequences, that is, the sequence-length distribution. The probabilities or mole fractions $(N_1)_x$ and $(N_2)_x$ of forming M_1 and M_2 sequence of length x are given by[10],

$$(N_1)_x = P_{11}^{\,x-1}\ P_{12} \tag{1}$$

$$(N_2)_x = P_{22}^{\,x-2}\ P_{21} \tag{2}$$

$$\text{where, } P_{11} = \frac{r_2[M_1]}{r_1[M_1]+[M_2]}\ , \quad P_{12} = \frac{[M_2]}{r_1[M_1]+[M_2]}$$

$$P_{22} = \frac{r_2[M_2]}{r_2[M_2]+[M_1]}\ , \quad P_{21} = \frac{[M_1]}{r_2[M_2]+[M_1]}$$

Equations (1) and (2) allow one to calculate the mole fractions of different lengths of M_1 and M_2 sequences. Figs. 1a and 1b show the sequence-length distribution for redox system with $r_1 = 0.43 \pm 0.01$, $r_2 = 1.94 \pm 0.03$ for 0.595/0.867 and 0.975/0.485 feed compositions respectively, and Figs. 2a and 2b show the sequence-length distribution for AIBN system with

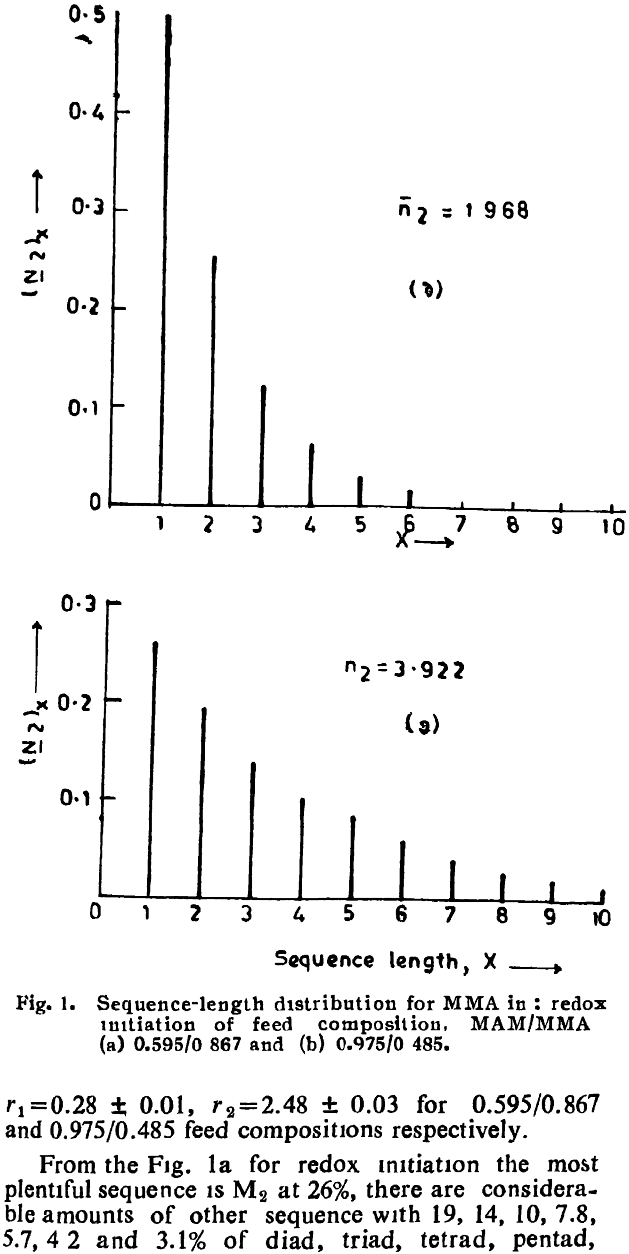

Fig. 1. Sequence-length distribution for MMA in : redox initiation of feed composition, MAM/MMA (a) 0.595/0 867 and (b) 0.975/0 485.

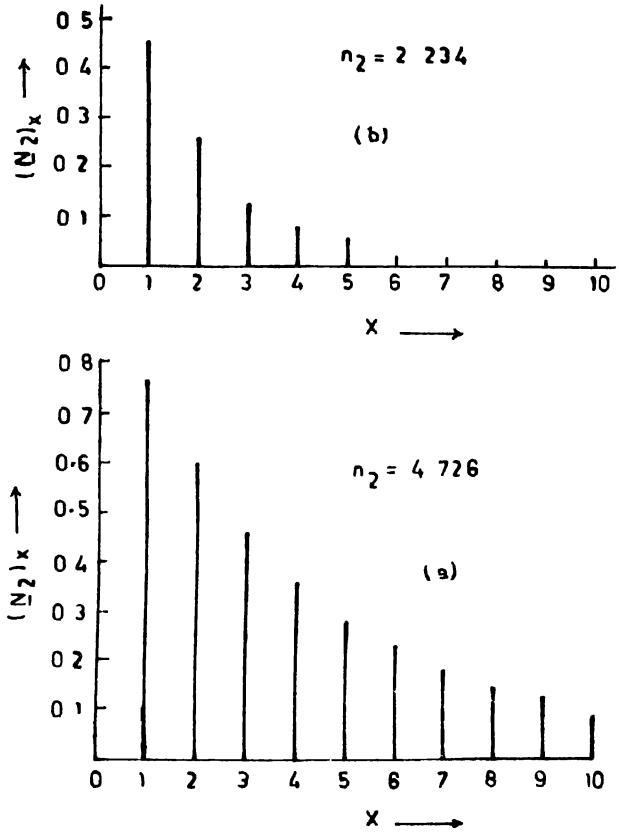

Fig. 2 Sequence-length distributions for MMA in AIBN initiation of feed composition, MAM/MMA : (a) 0 595/0.867 and (b) 0.975/0.485.

$r_1 = 0.28 \pm 0.01$, $r_2 = 2.48 \pm 0.03$ for 0.595/0.867 and 0.975/0.485 feed compositions respectively.

From the Fig. 1a for redox initiation the most plentiful sequence is M_2 at 26%, there are considerable amounts of other sequence with 19, 14, 10, 7.8, 5.7, 4 2 and 3.1% of diad, triad, tetrad, pentad, hexad, heptad and octad M_2 sequences. There are smaller amounts of longer sequences 2.3 and 1.7% of nonad and decad M_2 sequences. For other feed composition (Fig. 1b) the most plentiful sequence is M_2 at 50% with 25, 12.3 and 6% respectively of diad, triad and tetrad M_2 sequences. There are smaller amounts of longer sequences 3% and 1.4% of pentad and hexad M_2 sequences.

From the Fig. 2a for AIBN initiation the most plentiful sequence is M_2 at 76%, there are considerable amounts of other sequence with 60, 46.6, 36.5, 28.6, 22.4, 17.5, 13.7, 11 and 8% of diad, triad, tetrad, pentad, hexad, heptad, octad, nonad and decad M_2 sequences. For other feed composition (Fig. 2b) the most plentiful sequence is M_2 at 45% with 25, 13.6, 7.5 and 4.1% respectively of diad, triad, tetrad and pentad M_2 sequences. There are smaller amounts of longer sequences 2.3 and 1.3% of hexad and heptad M_2 sequences.

In conclusion, we can state that redox initiation of copolymerization by the $(NCH_2COOH/MnOAC)_2$ system is a convenient procedure for preparing random copolymers in good yields at ambient conditions.

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