

# Radical Copolymerization of 2-Ethylacrylic Acid and Methacrylic Acid

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## Synopsis

Copolymers of 2-ethylacrylic acid (EAA) and methacrylic acid (MAA) were prepared in bulk and in *N,N*-dimethylformamide (DMF). Although precipitation of the copolymers was observed in bulk, the reaction mixtures remained apparently homogeneous in DMF. Best-fit terminal-model reactivity ratios were determined by a nonlinear least squares technique to be  $r_{\text{MAA}} = 1.14$  and  $r_{\text{EAA}} = 0.23$  in bulk, and  $r_{\text{MAA}} = 1.91$  and  $r_{\text{EAA}} = 0.09$  in 50% DMF solution. Examination of  $^{13}\text{C}$ -NMR spectra provided convincing evidence for the formation of statistical copolymers. Copolymerizations richer in MAA provided copolymers of higher molecular weights.

## INTRODUCTION

Poly(2-ethylacrylic acid) (PEAA) undergoes a conformational transition to a globular structure upon acidification of its aqueous solutions.<sup>1-3</sup> The globular polymer associates strongly with bilayer vesicles prepared from phosphatidylcholines and phosphatidylglycerols, and causes profound disruption of bilayer organization.<sup>4,5</sup> We have exploited these phenomena to prepare phospholipid vesicles that release their contents rapidly and quantitatively in response to small changes in pH,<sup>5</sup> temperature,<sup>5</sup> glucose concentration,<sup>6</sup> or light intensity.<sup>7</sup> Although similar experiments with poly(methacrylic acid) (PMAA) are complicated by vesicular aggregation, it appeared likely that the copolymerization of EAA with MAA would provide a new set of poly(carboxylic acid)s with useful conformational and solution properties. The present paper describes this copolymerization.

Copolymerizations of monomers containing polar or ionizable groups, or groups capable of hydrogen-bonding interactions, are influenced strongly by the nature of the reaction medium. Plochocka<sup>8</sup> has reviewed these effects, which may be attributed to: (i) electrostatic repulsion of charged monomers and radicals, (ii) changes in monomer polarity (e.g., upon ionization), (iii) participation of monomer complexes, or (iv) hydrogen-bonding of monomers with one another, with the polymer chain, or with solvent. The copolymerizations of acrylic acid (AA) or methacrylic acid (MAA) with various vinyl monomers have been widely studied,<sup>8-13</sup> and the reactivity ratios found in such systems for AA or MAA are higher in nonpolar solvents (e.g.,  $\text{C}_6\text{H}_6$  or  $\text{CCl}_4$ ) than in polar solvents (e.g., *N,N*-dimethylformamide (DMF)).<sup>11-16</sup> Harwood and Plochocka have suggested that differential partitioning of polar and nonpolar monomers between

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free solvent and the domains of propagating radicals constitutes the principal reason for the large differences in reactivity ratios determined from such copolymerizations in different solvents.<sup>12,17-19</sup>

Although many copolymerizations of carboxylic acid monomers have been reported, we are aware of only two papers<sup>20,21</sup> that discuss copolymerization between two different carboxylic acids. Chapiro and co-workers examined the copolymerization of AA and MAA in bulk and in organic solvents, and reported important medium effects. We describe herein the analogous copolymerization of EAA and MAA.

## EXPERIMENTAL

### Materials

Diethyl ethylmalonate, formaldehyde solution (37% w/w in water) and diethylamine were purchased from Aldrich Chemical Co. and used without further purification. 2-Ethylacrylic acid (EAA) was prepared from diethyl ethylmalonate by the method described previously,<sup>22</sup> and fractionally distilled (bp 46°C/2.8 torr). Methacrylic acid (MAA, Aldrich) was distilled (bp 46°C/4.0 torr). Cycloheptanone (Aldrich) was distilled twice (bp 42°C/3.5 torr). Thin-layer chromatography and gas chromatography revealed no impurities in either of the monomers or in the cycloheptanone. 2,2'-Azobis(isobutyronitrile) (AIBN, Aldrich) was recrystallized twice from methanol and dried at room temperature under reduced pressure for 48 h. *N,N*-Dimethylformamide (DMF, Aldrich) was stirred with molecular sieves (Fisher) type 3A for 24 h, dried over powdered BaO for 12 h, and decanted before distillation (bp 25°C/3.8 torr). Reagent grade diethyl ether and methanol (Fisher) were used without further purification.

### Radical Copolymerization of EAA and MAA in Bulk

In a typical experiment, a glass ampule was charged with 0.0034 g (0.5 mol % of monomers) of AIBN, 0.3305 g (3.305 mmol) of EAA, 0.3110 g (3.616 mmol) of MAA, and 0.0620 g (0.5 mmol) of cycloheptanone as an internal standard. A small portion of this mixture was removed and diluted with ca. 9 volumes of methanol for subsequent chromatographic analysis. The ampule was then attached to a vacuum line, subjected to four to five freeze-degas-thaw cycles, and finally sealed under vacuum. The copolymerization was carried out by heating the ampule in a bath maintained at  $60 \pm 1^\circ\text{C}$ ; agitation was provided by a magnetic stirring bar. The polymer began to precipitate immediately on warming. Copolymerizations were run for various time intervals (to conversions of less than 5%) for the different monomer feeds, and the ampules were removed from the bath and quickly quenched in liquid nitrogen. Reaction mixtures were poured into 10 volumes of ether with vigorous stirring to precipitate the polymer. The ether solution was stirred for 5 min and the precipitated polymer was separated by filtration and rinsed again with ether. The ether solutions were then combined and analyzed by gas chromatography. Ethereal monomer solutions were analyzed on a Varian 1400 gas chromatograph (6 ft,  $\frac{1}{4}$  in. glass column; 10% SP-1000 on 80/100 mesh Supelcoport; flame ionization detection;

TABLE I  
 Bulk Copolymerization of EAA and MAA<sup>a</sup>

Monomer feed		Mole fraction MAA		Conversion (%)	Monomer feed		Mole fraction MAA		Conversion (%)
MAA (g)	EAA (g)	Feed	Copolymer <sup>b</sup>		MAA (g)	EAA (g)	Feed	Copolymer <sup>c</sup>	
0.0	1.0	0.0	0.0	—	0.0	1.0	0.0	0.0	—
0.0630	0.6159	0.108	0.266	3.3	1.8421	19.2776	0.100	0.246	4.2
0.1188	0.5166	0.211	0.417	4.0	3.7025	17.1568	0.201	0.351	3.1
0.1681	0.4648	0.296	0.505	5.5	11.0562	29.9838	0.300	0.507	2.7
0.2190	0.3909	0.394	0.602	2.5	7.3685	12.8520	0.400	0.603	5.2
0.3110	0.3305	0.522	0.670	4.3	0.8515	1.0100	0.500	0.664	3.9
0.3414	0.2554	0.609	0.683	3.9	—	—	—	—	—
0.3611	0.1922	0.686	0.768	5.3	12.902	6.4772	0.698	0.809	4.7
0.4322	0.1437	0.778	0.816	1.5	—	—	—	—	—
0.5001	0.0678	0.896	0.913	2.3	—	—	—	—	—
1.0	0.0	1.0	1.0	—	1.0	0.0	1.0	1.0	—

<sup>a</sup> 60°C, AIBN.

<sup>b</sup> Determined by gas chromatography.

<sup>c</sup> Determined by <sup>13</sup>C-NMR spectrometry.

column 170°C; injector 200°C; detector 190°C). The errors in determination of relative amounts of residual monomers were found to be  $\leq 2.6\%$ .

### Radical Copolymerization of EAA and MAA in DMF

In a typical experiment, a glass ampule was charged with 0.0079 g (0.5 mol % of monomers) of AIBN, 0.3832 g (3.83 mmol) of EAA, and 0.5036 g (6.23 mmol) of MAA. Sufficient DMF was then added to the mixture to afford a solution containing either 50% or 75% DMF. After degassing, copolymerizations were run at  $60 \pm 1^\circ\text{C}$  for various time intervals (to conversions of less than 5%) for the various monomer feeds, and the ampules were removed from the bath and quickly quenched in liquid nitrogen. The reaction mixture was dissolved in methanol and the copolymer was precipitated by dropwise addition of the solution into a large excess of ether with vigorous stirring. After separation of the polymer on a fritted glass filter, the precipitation was repeated, and finally the copolymer was rinsed with ether. The copolymer was dried at room temperature, ground to a fine powder, and dried in a drying pistol at  $56^\circ\text{C}$  (refluxing acetone) under reduced pressure. After 48 h the copolymer was weighed to determine conversion.

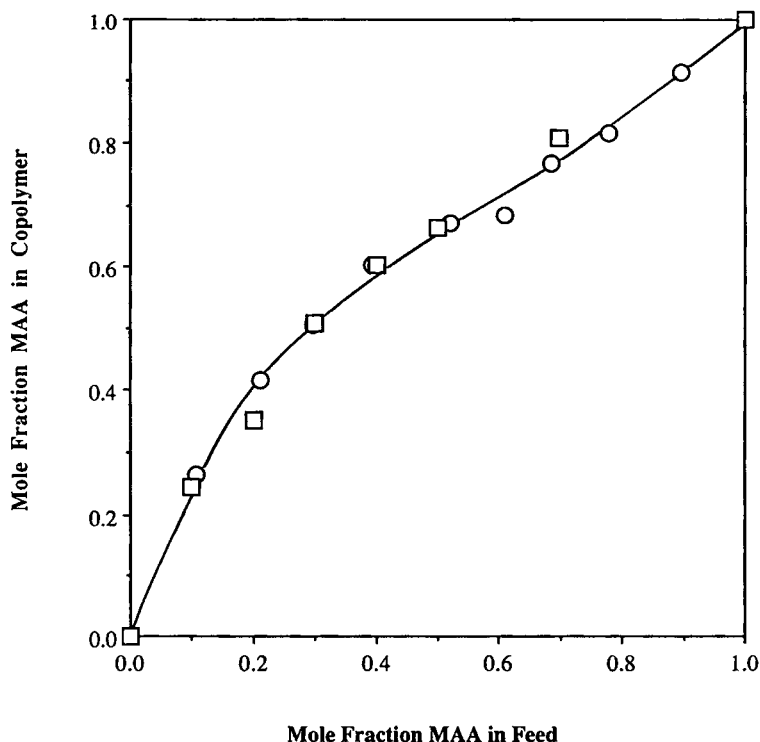


Fig. 1. Mole fraction MAA in copolymer versus mole fraction MAA in feed for bulk copolymerization of EAA and MAA. The curve was calculated from the terminal-model composition equation with reactivity ratios determined as  $r_{\text{MAA}} = 1.14$  and  $r_{\text{EAA}} = 0.23$ : (○) experimental compositions from gas chromatography, (□) experimental compositions from  $^{13}\text{C}$ -NMR spectrometry.

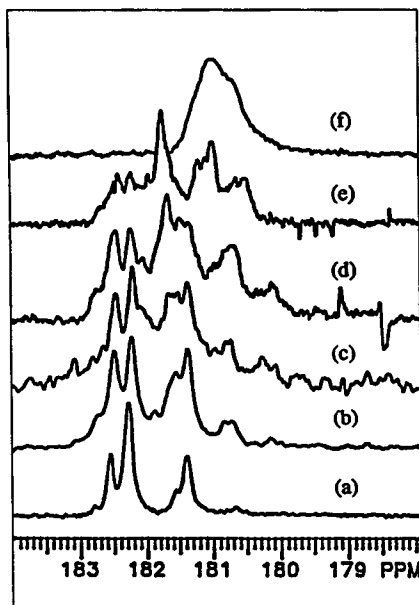


Fig. 2.  $^{13}\text{C}$ -NMR spectra of carbonyl regions of a series of copolymers in methanol- $d_4$  at  $50^\circ\text{C}$ . MAA in monomer feed: (a) 100% (PMAA), (b) 80%, (c) 70%, (d) 50%, (e) 30%, (f) 0% (PEAA).

### Measurements

$^{13}\text{C}$ -NMR spectra were recorded on a Varian XL-200 NMR spectrometer using a standard single pulse sequence and broad-band  $^1\text{H}$  decoupling at various temperatures in the following solvents: dimethyl sulfoxide- $d_6$  (DMSO- $d_6$ ),  $100^\circ\text{C}$ ;  $\text{D}_2\text{O}$ -NaOH,  $50^\circ\text{C}$ ; methanol- $d_4$ ,  $50^\circ\text{C}$ .  $^1\text{H}$ -NMR spectra of copolymers were recorded on a Varian XL-300 NMR spectrometer in DMF- $d_7$  at  $75^\circ\text{C}$ . Spin-lattice relaxation times ( $T_1$ ) for the methyl carbons of the EAA and MAA units in the copolymers were obtained at  $50^\circ\text{C}$  in methanol- $d_4$  on a Varian XL-300 NMR spectrometer by using an inversion-recovery technique. The measured  $T_1$  for the methyl carbon of the EAA units was  $0.75 \pm 0.03$  s; that of the methyl carbon of the MAA units 0.09 s with negligible error. Quantitative  $^{13}\text{C}$ -NMR spectra of the copolymers were recorded on a Varian XL-300 NMR spectrometer with gated decoupling to suppress nuclear Overhauser effects and a pulse delay of 12 s (longer than 5 times the longest methyl group  $T_1$ ).

Molecular weights of the copolymers were determined relative to poly(ethylene oxide) (PEO) by gel permeation chromatography (GPC) with a set of three columns (TSK 3000 PW, TSK 5000 PW, TSK 6000 PW) and a differential refractometer. Calibration was done using five PEO samples of narrow molecular weight distribution (Toyo Soda Mfg. Co.) with average molecular weights in the range from 18,000 to 996,000. The polymer concentration was about 0.1 wt % in a phosphate buffer solution (0.036 M, pH 9.5) that contained 0.33 M NaCl. Inherent viscosities were measured in a Ubbelohde capillary viscometer (Cannon, 75/E468) at a concentration of 0.2 wt % polymer in DMF at  $35^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Copolymerization in Bulk

Table I summarizes the results of the copolymerization of EAA and MAA in bulk. These reactions were analyzed by gas chromatography and by  $^{13}\text{C}$ -NMR spectroscopy, and the two methods are in general in excellent agreement with regard to determination of copolymer composition as a function of monomer feed composition. Figure 1 shows a plot of the mole fraction of MAA in the copolymer versus the MAA mole fraction in the feed, and reveals no systematic differences between compositions determined by the two methods.

The data in Table I were fit to the composition equation derived for the terminal copolymerization scheme, which relates the instantaneous copolymer composition to monomer feed as follows:

$$m_1/m_2 = (M_1/M_2)(r_1M_1 + M_2)/(M_1 + r_2M_2)$$

where  $r_1$  and  $r_2$  are the reactivity ratios of the monomers,  $m_1/m_2$  the mole ratio of monomers in the copolymer, and  $M_1/M_2$  the mole ratio of monomers in the feed. The best-fit reactivity ratios were estimated by a nonlinear least squares technique. The solid line in Figure 1 is a plot of the terminal model composition equation with  $r_{\text{MAA}} = 1.14$  and  $r_{\text{EAA}} = 0.23$ . The line reproduces the experimentally observed compositions in satisfactory fashion.

Although we have not interpreted the  $^{13}\text{C}$ -NMR spectra of these EAA-MAA copolymers in terms of detailed sequence distributions, preliminary examination of such spectra provides convincing evidence for the formation of statistical copolymers. Figure 2 shows the carbonyl regions of the spectra of the homopolymers of EAA and MAA, and of a series of copolymers of varying composition. The complexity of these signals, and their variation with composition, argue against the presence of long blocks of either EAA or MAA in any of these copolymer samples.

A final note on the bulk copolymerization concerns the heterogeneity of these copolymerization reaction mixtures. Because the EAA-MAA copolymers are insoluble in the monomer mixtures from which they are prepared, precipitation was observed in every case, even at low conversion. The copolymerization thus occurs in a two-phase system, and one might then expect differential partitioning of the monomers between the two phases. Harwood<sup>19</sup> has coined the term "bootstrap" copolymerization to describe this phenomenon, in order to emphasize the role played by the growing copolymer chain in determining its own composition. And while precipitation is not a prerequisite for such an effect, differential monomer partitioning would be expected to be most significant in mixtures subject to phase separation. Thus we regard our estimated values of  $r_1$  and  $r_2$  as apparent reactivity ratios which are complex functions of the intrinsic reactivity ratios and the partition coefficients that govern the concentrations of EAA and MAA at the growing chain end.

### Copolymerization in Solution

Table II summarizes the results of the EAA-MAA copolymerization in DMF. No precipitation was observed in these reactions, and the compositions of the

TABLE II  
 Copolymerization of EAA and MAA in DMF<sup>a</sup>

Monomer feed		Mole fraction MAA		Conversion (%)
MAA (g)	EAA (g)	Feed	Copolymer	
0.0	1.0	0.0	0.0	—
0.1272	1.2647	0.105	0.417	3.4
0.1589	0.7339	0.200	0.484	0.7
0.5293	1.4353	0.300	0.610	1.1
0.1705 <sup>b</sup>	0.4623	0.300	0.668	3.0
0.3020	0.5416	0.393	0.671	2.0
0.2955 <sup>b</sup>	0.5301	0.393	0.734	1.7
0.5900	0.6950	0.497	0.748	4.3
0.5036	0.3832	0.604	0.801	2.1
0.9182	0.4571	0.700	0.849	3.4
1.0346	0.2970	0.802	0.902	3.1
1.0385 <sup>b</sup>	0.2925	0.805	0.937	2.7
1.2412	0.1568	0.902	0.947	1.2
1.0	0.0	1.0	1.0	—

<sup>a</sup> 60°C, AIBN, DMF : monomer 1 : 1 (w : w).<sup>b</sup> DMF : monomer 3 : 1 (w : w).

resulting copolymers were analyzed by <sup>1</sup>H-NMR spectrometry. Best-fit reactivity ratios for the copolymerization in 50% DMF solution were estimated by a nonlinear least-squares technique. Figure 3 shows a plot of the mole fraction of MAA in the copolymer versus the MAA mole fraction in the monomer feed, as well as a plot of the terminal model composition equation with  $r_{\text{MAA}} = 1.91$  and  $r_{\text{EAA}} = 0.09$ . The line again reproduces the experimentally observed compositions in satisfactory fashion.

The MAA contents of the copolymers produced in DMF were higher than those of copolymers prepared in bulk at the same monomer feed ratios. Furthermore, an increase in the DMF content of the reaction mixture from 50 to 75% was accompanied by additional enrichment in MAA (Fig. 3). While none of these mixtures was visibly heterogeneous, we regard these results as further evidence for preferential monomer partitioning. We suggest that in bulk and in mixtures relatively poor in DMF, EAA associates strongly with the poorly solvated polymer chain. Addition of DMF solvates the chain more effectively and reduces its selective association with EAA. The reactivity ratios determined for copolymerizations in DMF then reflect more accurately the higher intrinsic reactivity of MAA. Chapiro and co-workers have reported analogous results for the copolymerization of AA and MAA.<sup>21</sup> The reactivity ratios of MAA and AA were found to be 2.3 and 0.3, respectively, for copolymerization in bulk, in which the precipitation of polymers was observed (precipitation was also observed in hexane and in 25–50% methanol solutions where reactivity ratios were found to be similar to those determined in bulk). On the other hand,  $r_{\text{MAA}}$  and  $r_{\text{AA}}$  were determined to be 6.0 and 0.02, respectively, in 75% methanol solution, in which the reaction medium was homogeneous. Thus the hetero-

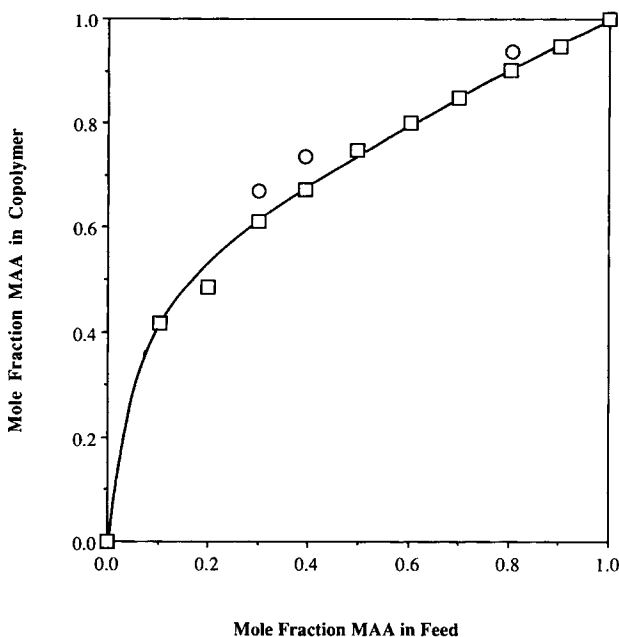


Fig. 3. Mole fraction MAA in copolymer versus mole fraction MAA in feed for copolymerizations in DMF. The curve was calculated from the terminal-model composition equation with reactivity ratios determined as  $r_{\text{MAA}} = 1.91$  and  $r_{\text{EAA}} = 0.09$  for copolymerization in a 1 : 1 (w : w) mixture of DMF and monomer. Experimental compositions from  $^1\text{H}$ -NMR spectrometry for copolymerizations in 1 : 1 ( $\square$ ) and 3 : 1 ( $\circ$ ) (w : w) mixtures of DMF and monomer.

geneity of the reaction mixture serves to obscure differences in the intrinsic reactivities of the two monomers.

Table III summarizes the molecular weights and inherent viscosities of the EAA-MAA copolymers prepared in the course of this work. In general, copo-

TABLE III  
Molecular Weights and Inherent Viscosities of EAA-MAA Copolymers

Mole fraction EAA in feed	$\bar{M}_w \times 10^{-4}$ <sup>a</sup>		Inherent viscosities <sup>b</sup> (dL/g)	
	Bulk	DMF <sup>c</sup>	Bulk	DMF <sup>c</sup>
0.9	25.7	—	0.84	0.16
0.8	—	—	1.17	—
0.7	46.7	4.8	1.30	0.27
0.6	—	—	1.65	0.27
0.5	—	—	—	0.33
0.3	58.1	19.7	—	—
0.1	—	25.0	—	—

<sup>a</sup> Relative to poly(ethylene oxide) in aqueous phosphate buffer.

<sup>b</sup> 0.2 g/dL in DMF, 35°C.

<sup>c</sup> Copolymerization in 1 : 1 (w : w) mixture of DMF and monomer.



lymerizations richer in MAA resulted in copolymers of higher molecular weight, and bulk copolymerization was superior to solution copolymerization in this regard. We have not determined the nature of the reactions responsible for limiting the chain length in these systems.

## CONCLUSIONS

Copolymers of 2-ethylacrylic acid and methacrylic acid were prepared in bulk and in DMF. The reactivity ratios of monomers were estimated by fitting copolymerization data to the composition equation derived for the terminal copolymerization scheme. With increasing amounts of DMF in the copolymerization mixtures (from bulk to 75% DMF solution), copolymers richer in MAA were produced from the same monomer feeds. Partitioning of monomers between the domains of copolymer radicals and the solvent was suggested the origin of this result.  $^{13}\text{C}$ -NMR spectra provided convincing evidence for the formation of statistical copolymers. Increases in the EAA content of the reaction mixture were accompanied by reduction in the apparent molecular weights of the copolymers.

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