

Copolymerization of 1-Acrylamido-1-deoxy-D-glucitol and of 1-Deoxy-1-methacrylamido-D-glucitol with Various Vinyl Monomers*

ROY L. WHISTLER and JAMES L. GOATLEY,

Department of Biochemistry, Purdue University, Lafayette, Indiana

Recently,¹ there has been described the preparation and characteristics of homopolymers of 1-acrylamido-1-deoxy-D-glucitol (I) and of 1-deoxy-1-methacrylamido-D-glucitol (II). Further work is now undertaken to investigate the copolymerization of these compounds.

In a suitable solvent system these compounds are found to copolymerize with various vinyl monomers under free radical initiators. Copolymerizations of I and II with vinyl acetate are performed in water, while copolymerizations with methyl methacrylate and styrene are done in aqueous methanol solvent.

Reactivity ratios r_1 and r_2 , as defined by the equation

$$\frac{dM_1}{dM_2} = \frac{M_1(r_1M_1 + M_2)}{M_2(r_2M_2 + M_1)}$$

are calculated, where M_1/M_2 is the molar ratio of monomers in the starting mixture. Use is made of the approximation: $m_1/m_2 = dM_1/dM_2$ for low conversion, where m_1/m_2 is the molar ratio of monomers in the polymer. Reactivity ratios are determined from reactions with less than 15% conversions, and in application of the equation average monomer compositions are used rather than initial compositions. Since I and II contain nitrogen, the composition of the polymers is readily determined by the micro-Kjeldahl method. Data are plotted and ratios determined according to the method of Fineman and Ross.² Q and e values are calculated according to the scheme of Alfrey and Price³ on the basis of values for styrene of $Q = 1.0$ and $e = -0.8$.

EXPERIMENTAL

Monomers. Amide monomers I and II were prepared as described in the previous paper.¹ Styrene, methyl methacrylate, and vinyl acetate were distilled under reduced pressure and stored under nitrogen at 3°C. until used (never more than 24 hr.).

* Journal Paper No. 1645 of the Purdue University Agricultural Experiment Station.

Low-Conversion Polymerization. Copolymerizations for determining reactivity ratios were made in 2 oz. screw cap vials. The amide monomer and initiator, 0.015 g. benzoyl peroxide or ammonium persulfate, were weighed into the vial, solvent added, and the vial weighed. The comonomer was added, the vial flushed with nitrogen, sealed, and reweighed. The vial was then placed in an oven maintained at 50°C. Polymerization was stopped when it was estimated that 5–10% conversion had taken place. Vinyl acetate copolymers were precipitated with five volumes of cold methanol. Other copolymers were precipitated with ten volumes of cold acetone. All of the polymer products were redissolved and reprecipitated twice from suitable solvents, filtered, washed with precipitating solvent and ether, dried under vacuum at 30°C., and then weighed. In the usual run 0.2–0.8 g. of amide monomer was used and 0.01–0.6 g. of the second monomer. Ordinarily these were dissolved in 15 ml. of solvent. However, where a larger amount of material was required for accurate analysis due to low nitrogen content of the polymer, these quantities were doubled.

High-Conversion Polymerization. Scaled reactions like those described for low-conversion polymerization were used. However, the reactions were allowed to proceed for 48–96 hr. before the polymers were isolated.

Solvents. For copolymerizations with vinyl acetate, water was used as a solvent. For copolymerizations with styrene and methyl methacrylate the solvent was made by diluting 100 ml. of water to 500 ml. with methanol. All solvents were flushed with nitrogen before use.

Analysis of Polymers. Molar ratios of monomers in the polymer were determined by nitrogen analysis by the micro-Kjeldahl method.⁴

Measurement of Viscosity. Viscosities were measured in an Ostwald-Cannon-Fenske viscometer. Aqueous solutions were used for the vinyl acetate copolymers and for the styrene copolymer with I. Dimethylformamide solutions were used for the other polymers. Limiting viscosity numbers,⁵ $[\eta] = \lim_{c \rightarrow 0} (\eta - \eta_0)/\eta_0 c$ were calculated without application of density or kinetic data.

Initiators. Benzoyl peroxide was recrystallized twice from chloroform by addition of methanol. Ammonium persulfate was recrystallized twice from saturated aqueous solutions by chilling.

Molecular Weight Determinations. Osmotic molecular weights were determined using the Stabin and Immergut⁶ modification of the Zimm and Myerson⁷ osmometer. Four concentrations were used for each polymer and the molecular weights calculated from $\lim_{c \rightarrow 0} \pi/c$ and $M_n = RT/(\pi/c)_0$.

Copolymerization of I and II with vinyl acetate and with methyl methacrylate went nearly to completion in 10–30 hr. Copolymerization with styrene, however, gave yields only of the order of 10–15%, even after several days. In the polymerizations in aqueous methanol solvent, part of the polymer precipitated out in some cases.

The molar ratios of the various monomers and polymers in the various reaction mixtures are given in Table I. Plots of these data are given

in Figure 1 where $([M_1]/[M_2])^2/(m_1/m_2)$ is plotted as the abscissa and $([M_1]/[M_2]) \times (m_1/m_2)/[(m_1/m_2) - 1]$ as the ordinate. Since r_2 is the negative of the ordinate intercept and r_1 is the slope of the line, these reactivity ratios can be calculated from the graphs. These are shown in Table II.

The Q and e values were calculated for I and II from the reactivity ratios by means of the Alfrey-Price equations:

$$\begin{aligned} r_1 &= (Q_1/Q_2) \exp \left\{ -e_1(e_1 - e_2) \right\} \\ r_2 &= (Q_2/Q_1) \exp \left\{ -e_2(e_2 - e_1) \right\} \end{aligned}$$

TABLE I
Molar Ratios in Monomer Mixture (M_1/M_2) and Polymer (m_1/m_2)

M_1	M_2	Initiator	M_1/M_2	m_1/m_2
I	Vinyl acetate	Ammonium persulfate	0.331	0.923
			2.24	6.04
			0.517	1.78
			2.01	5.16
I	Styrene	Benzoyl peroxide	0.62	0.192
			1.54	0.395
			2.29	0.519
			3.08	0.642
I	Methyl methacrylate	Benzoyl peroxide	3.80	0.694
			0.47	0.110
			0.82	0.192
			1.66	0.372
II	Vinyl acetate	Ammonium persulfate	2.08	0.480
			0.645	1.13
			1.41	1.70
			1.55	1.62
II	Styrene	Benzoyl peroxide	1.09	1.35
			0.86	0.296
			2.32	0.539
			2.97	0.588
II	Methyl methacrylate	Benzoyl peroxide	4.36	0.693
			1.12	0.216
			2.08	0.354
			2.69	0.425

TABLE II
Reactivity Ratios for Copolymerizations

M_1	M_2	r_1	r_2
I	Vinyl acetate	2.41	0.18
I	Styrene	0.056	2.72
I	Methyl methacrylate	0.206	4.22
II	Vinyl acetate	0.56	0.16
II	Styrene	0.005	2.09
II	Methyl methacrylate	0.036	4.20

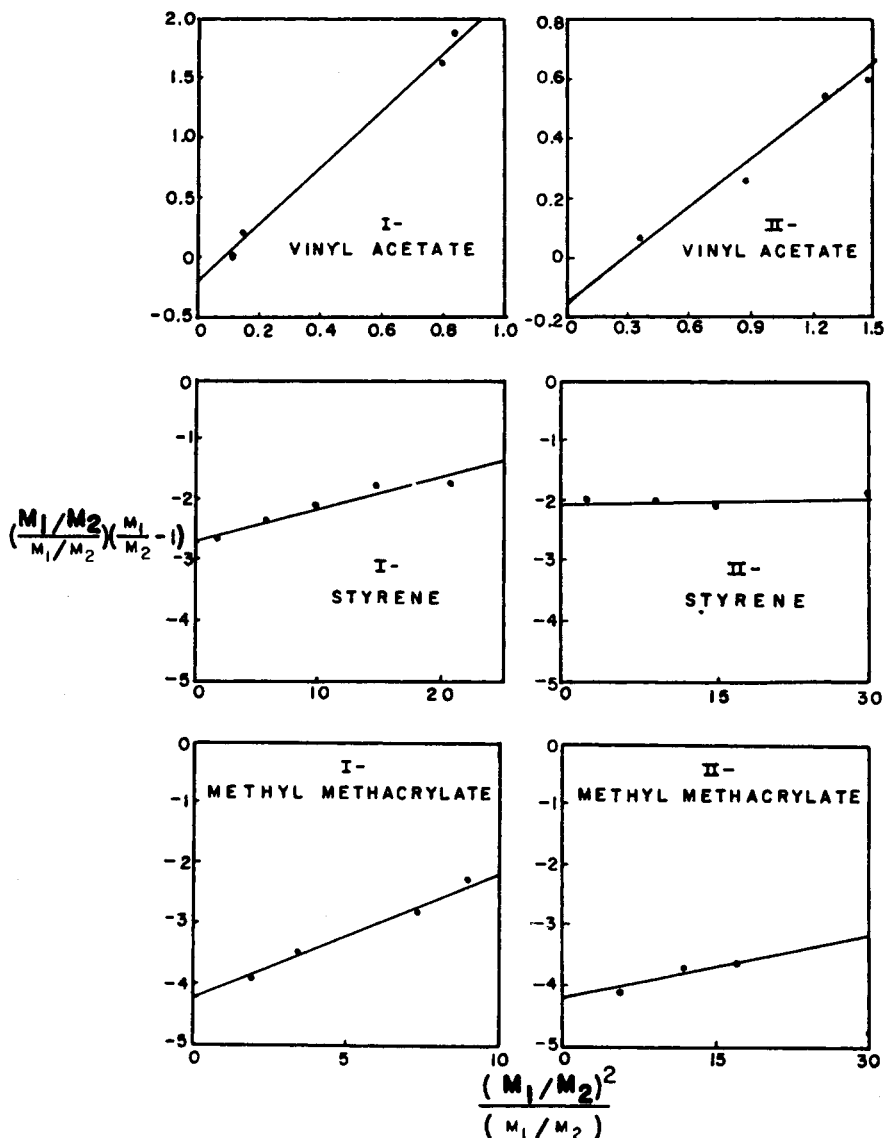


Fig. 1. Plots for determining reactivity ratios.

Using reactivity ratios from the styrene copolymerizations wherein $Q = 1.0$ and $e = -0.8$, the values for I were found to be $Q = 0.12$ and $e = 0.6$ and for II $Q = 0.089$ and $e = 1.3$. Employing these values and the reactivity ratios of I and II with vinyl acetate and methyl methacrylate, Q and e values for the latter two compounds were calculated and found to be in general agreement with published figures.⁸

Some physical characteristics of representative copolymers are shown in Table III. In general, solubilities of the polymers are rather limited.

TABLE III
Physical Properties of Representative Copolymers

Number	M_1	M_2	m_1 , mole fraction M_1 in polymer	$[\eta]$	Osmotic molecular wt.
1	I	Vinyl acetate	0.36	109.4	117,000
2	I	Styrene	0.85	46.2	240,000
3	I	Methyl methacrylate	0.45	44.7	78,000
4	II	Vinyl acetate	0.80	55.2	48,000
5	II	Styrene	0.54	42.3	63,000
6	II	Methyl methacrylate	0.48	29.3	34,000

Vinyl acetate copolymers and other copolymers with a very high molar ratio of amide are water soluble. All are soluble in ethylenediamine, and all but 2 and 4 in dimethylformamide. All are soluble or slightly soluble in *N*-methyl-2-pyrrolidone. None are soluble in ethanol, benzene, carbon tetrachloride, acetone, or chloroform, although some swelling may take place in the latter. Compounds 1 and 3 swell in pyridine. The opposite solubility properties of the very water soluble amides and the other monomers greatly limit the choice of solvents for the polymers as well as the choice of solvent for the polymerization.

The authors wish to thank the National Science Foundation for a grant in support of this work, and the Corn Products Corporation for a gift of *D*-glucamine oxalate.

References

1. Whistler, R. L., H. Panzer, and H. J. Roberts, *J. Org. Chem.*, in press.
2. Fineman, M., and S. D. Ross, *J. Polymer Sci.*, **5**, 259 (1950).
3. Alfrey, T., J. J. Bohrer, and H. Mark, Eds., *Copolymerization*, Interscience, New York, 1952, Chaps. 3 and 4.
4. *Official Methods of Analysis*, 8th ed., Association of Official Agricultural Chemists, 1955, p. 805.
5. International Union of Pure and Applied Chemistry, *J. Polymer Sci.*, **8**, 257 (1952).
6. Stabin, W., and E. H. Immergut, *J. Polymer Sci.*, **14**, 209 (1954).
7. Zimm, B. H., and I. Meyerson, *J. Am. Chem. Soc.*, **68**, 911 (1946).
8. Price, C. C., *J. Polymer Sci.*, **3**, 772 (1948).

Synopsis

Copolymerization characteristics for 1-acrylamido-1-deoxy-*D*-glucitol and of 1-deoxy-1-methacrylamido-*D*-glucitol with various vinyl monomers is given. For the former compounds *Q* and *e* values are found to be 0.12 and 0.6 respectively and, for the latter, 0.08 and 1.3. In addition, viscosity, osmotic molecular weights, and solubilities for representative compounds are given.

Résumé

Les caractéristiques de la copolymérisation du 1-acrylamido-1-désoxy-*D*-glucitol et du 1-désoxy-1-méthacrylamido-*D*-glucitol avec divers monomères vinyliques ont été déterminées. Pour le premier composé les valeurs de *Q* et de *e* sont respectivement égales à 0.12 et 0.6, tandis que pour le second elles sont de 0.08 et 1.3. Les poids

moléculaires viscosimétriques et osmotiques ainsi que les solubilités pour des composés typiques sont signalés.

Zusammenfassung

Copolymerisationsparameter für 1-Acrylamido-1-desoxy-D-glucitol und 1-Desoxy-1-methacrylamido-D-glucitol mit verschiedenen Vinylmonomeren werden angegeben. Die Q - und e -Werte der erstgenannten Verbindung sind 0,12 bzw. 0,6, die der zweitgenannten 0,08 bzw. 1,3. Zusätzlich werden Viskosität, osmotische Molekulargewichte und Löslichkeit für typische Verbindungen angegeben.

Received July 28, 1960

Revised November 10, 1960