

Copolymerization Characteristics of Fumaronitrile

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INTRODUCTION

In view of the fact that interpretation of copolymerization data for fumarates and maleates is complicated by the bulk of the functional groups,¹ it seemed of some interest to compare these esters with fumaronitrile, which would have similar chemical but very much smaller steric effects. We have therefore checked the copolymerization of fumaronitrile with styrene^{1,2} and have added data on its copolymerization with methyl methacrylate.

EXPERIMENTAL

Fumaronitrile, m.p. 95.6–96.6°, was prepared in 78% yield by dehydration of fumaramide with phosphorus pentoxide according to the directions of Mowry and Butler.³ It was recrystallized three times from a mixture of benzene (2 parts) and hexane (1 part), m.p. 96.0–96.9°, corr.

Styrene (Dow) was redistilled through a 40-cm., helix-packed column before use, b.p. 29.7–29.87° (7 mm.), as was **methyl methacrylate** (Rohm and Haas), b.p. 99.2–99.6°

Copolymerization was carried out as previously reported by Price and Zomlefer⁴ except that fumaronitrile was not soluble in styrene and methyl methacrylate. Addition of 10 ml. of chloroform to each 0.08 mole copolymerization mixture gave a clear solution, which remained clear until about 5–10% of polymerization had occurred.

To check the possibility of chain transfer with the solvent, several samples were analyzed for chlorine, all showing less than 0.1% chlorine.

A 50–50 styrene–fumaronitrile copolymerization was run with 10% of benzene added. Polymer began to precipitate almost immediately at 60°. The fact that the polymerization proceeded more rapidly in a nonsolvent for the polymer (Table I) and gave material of higher molecular weight (Table III) is in agreement with other reports in the literature.⁵

The copolymers were precipitated by pouring the contents of the tube, with stirring, into 200 ml. of filtered absolute methanol. The ampules were flushed with a stream of methanol to remove any polymer which stuck to the walls. After allowing the copolymer to settle several hours, as much

* From a Ph.D. thesis submitted to the Graduate School of the University of Notre Dame by Richard D. Gilbert, American Cyanamid Fellow, 1948–1950.

methanol as possible was decanted and the polymer was filtered through a Hirsch funnel onto hardened filter paper. The polymer was then redissolved, in the case of the fumaronitrile-styrene copolymers, in 10 ml. of acetone; and the fumaronitrile-methyl methacrylate polymers in 10 ml. of benzene. The solutions were filtered through fritted-glass filter funnels and then poured with stirring into 200 ml. of filtered, absolute methanol. The polymer was allowed to settle and again the methanol decanted. The polymer was recovered on tared, fritted-glass Gooch filter funnels, and dried at room temperature overnight at 0.2 mm. Before submitting for analysis the polymers were dried again at 44° and 2 mm. pressure. The data are summarized in Tables I and II.

TABLE I
COPOLYMERIZATION OF STYRENE (M_1) WITH FUMARONITRILE (M_2)

M_1^a	Time, min.	Conversion, %	Percentages			dM_2^b (N)	dM_2^c (C)
			N	C	H		
0.125 ^d	120	4.76	9.57	83.97	6.22	0.326	0.330
0.250	55	0.86	10.67	81.67	6.11	0.359	0.413
0.375	25	0.97	11.25	81.00	5.98	0.378	0.436
0.500 ^d	35	1.57	12.31	80.00	5.73	0.411	0.469
0.625 ^d	20	0.71	13.30	80.07	5.68	0.439	0.467
0.750	30	1.38	13.31	80.37	5.84	0.439	0.458
0.875	25	0.25	14.55	77.81	5.71	0.476	0.542
0.500 ^e	35	4.81	14.32	78.75	5.77	0.467	0.538

^a Mole fraction of fumaronitrile in original monomer mixtures; 10 ml. of chloroform was added to each monomer pair as fumaronitrile was immiscible with styrene, except in case of last pair to which 10 ml. of benzene was added.

^b Mole fraction of fumaronitrile in copolymer, calculated from nitrogen analysis.

^c Mole fraction of fumaronitrile in copolymer, calculated from carbon analysis.

^d Analysis corrected for ash content.

^e In benzene.

TABLE II
COPOLYMERIZATION OF METHYL METHACRYLATE (M_1) WITH FUMARONITRILE (M_2)

M_1^a	Time, hr.	Conversion, %	Percentages			dM_2^b
			N	C	H	
0.125 ^c	1.75	6.20	1.31	60.09	7.96	0.046
0.250 ^c	1.25	2.77	1.62	59.93	7.84	0.057
0.375 ^c	3.00	1.10	2.58	59.84	7.72	0.090
0.500 ^c	7.00	8.02	3.42	59.74	7.53	0.119
0.625	12.00	8.17	4.47	59.13	7.20	0.154
0.750	24.00	8.63	5.60	59.28	7.14	0.192
0.875	24.00	2.46	8.37	59.28	6.85	0.234

^a Mole fraction of fumaronitrile in original monomer mixture; 10 ml. of chloroform added to each monomer pair as fumaronitrile was immiscible with methyl methacrylate.

^b Mole fraction of fumaronitrile in copolymer, calculated from nitrogen analysis.

^c Analysis corrected for ash content.

Determination of Molecular Weights. The molecular weights were estimated from viscosity data obtained at $25.0 \pm 0.1^\circ$, using an Ostwald-type viscometer and pure acetone as the solvent. The weight-average molecular weight of the copolymer was approximated by use of the Staudinger relation:

$$\eta_{sp}/c = KM$$

The value of K was arbitrarily chosen as 3×10^{-4} for the purpose of these calculations. The concentration was approximated by the calculation of the molecular weight of a copolymer unit from the values of known copolymer composition which in turn was based on microanalysis. The results are shown in Table III.

TABLE III
VISCOMETRIC MOLECULAR WEIGHTS

M_1	Concn. ^a	η_{sp}	Molecular weight
A. Fumaronitrile (M_2)-Styrene Copolymers			
0.125	0.026	0.24	30,800
0.500	0.011	0.06	18,500
0.750	0.013	0.11	22,400
0.500 ^b	0.016	0.50	106,000
B. Fumaronitrile (M_2)-Methyl Methacrylate			
0.125	0.029	0.13	14,500
0.500	0.016	0.04	9,240
0.750	0.021	0.05	8,020

^a Moles of monomeric unit per liter.

^b Styrene-fumaronitrile pair polymerized in benzene solution.

DISCUSSION

Copolymerization ratios, r_1 and r_2 , were estimated from the data in Tables I and II by plotting the straight lines of the following equation:

$$r_2 = \frac{M_1}{M_2} \left[\frac{dM_2}{dM_1} \left(1 + \frac{M_1}{M_2} r_1 \right) - 1 \right]$$

The results are summarized in Table IV, the limits of r_1 and r_2 being estimated from the area of intersection of the lines. Our values for r_1 and r_2 for the styrene-fumaronitrile pair are in agreement with those of Lewis and Mayo¹ ($r_1 = 0.19 \pm 0.03$, $r_2 = 0.0$) but not with those of Fordyce and Ham² ($r_1 = 0.09 \pm 0.005$, $r_2 = 0.0$), although the divergence of the latter may be due to the fact that their experiments were run at $79 \pm 1^\circ$ whereas our copolymerization and those of Lewis and Mayo were carried out at 60° .

From the values of r_1 and r_2 , values of the resonance stabilization factor, Q , and the electrical factor, e , were calculated according to the Alfrey-Price equations:⁶

$$r_1 = (Q_1/Q_2) \exp \{e_1(e_1 - e_2)\}$$

$$r_2 = (Q_2/Q_1) \exp \{e_2(e_2 - e_1)\}$$

using the following values⁷ for Q_1 and e_1 : styrene, $Q = 1.0$ and $e = -0.8$; methyl methacrylate, $Q = 0.74$ and $e = 0.4$. These results are also included in Table IV. The values for Q and e for fumaronitrile, $Q = 0.5$

TABLE IV
COPOLYMERIZATION CHARACTERISTICS

M_1	M_2	r_1	r_2	Q_2	e_2
Styrene	Fumaronitrile	0.23 ± 0.1	0.01 ± 0.01	0.6	1.6
Methyl methacrylate	Fumaronitrile	3.5 ± 0.5	0.01 ± 0.01	0.4	2.0

and $e = 1.8$, are very much as expected.

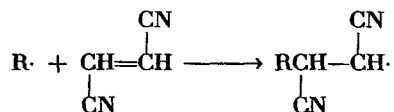
The values for Q and e for fumaronitrile may also be calculated from the r_1 values for the two different copolymerizations by solving the following simultaneous equations:

$$0.23 = (1.0/Q_2) \exp \{0.8 (-0.8 - e_2)\}$$

$$3.5 = (0.74/Q_2) \exp \{-0.4 (0.4 - e_2)\}$$

The values so obtained, $Q_2 = 0.4$, $e_2 = 2.1$, are in agreement with those reported in Table IV but do not have the uncertainty arising from the large error in the values for r_2 . The authors are indebted to Dr. Turner Alfrey, Jr., for suggesting this alternative procedure for calculating Q and e .

Since only one nitrile group can resonate with the free radical in the intermediate in chain growth:



the resonance factor should be, and is, very close to that for acrylonitrile ($Q = 0.5-0.7$).⁷

The two nitrile groups give an electrical factor very close to twice that for acrylonitrile ($e = 0.9-1.3$).

The general similarity of the Q and e values for fumaronitrile and those reported⁷ for diethyl fumarate ($Q = 0.3-0.8$; $e = 1.2-1.9$) indicates that there was not a serious steric hindrance factor in the copolymer pairs involved in calculating Q and e for the latter.

References

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- (5) See, e.g., W. I. Bengough and R. G. W. Norrish, *Nature*, **163**, 325 (1949).
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Summary

Copolymerization of fumaronitrile (M_2) with styrene (M_1) gave the following values for characteristic copolymerization constants: $r_1 = 0.23 \pm 0.1$; $r_2 = 0.01 \pm 0.01$; $Q_2 = 0.6$; $e_2 = 1.6$. With methyl methacrylate (M_1) the values were $r_1 = 3.5 \pm 0.5$; $r_2 = 0.01 \pm 0.01$; $Q_2 = 0.4$; $e_2 = 2.0$.

Résumé

La copolymérisation du fumaronitrile (M_2) avec le styrène (M_1) fournit les valeurs suivantes pour les constantes caractéristiques de la copolymérisation: $r_1 = 0.23 \pm 0.1$; $r_2 = 0.01 \pm 0.01$; $Q_2 = 0.6$; $e_2 = 1.6$. Avec le méthacrylate de méthyle (M_1) les valeurs obtenues étaient $r_1 = 3.5 \pm 0.5$; $r_2 = 0.01 \pm 0.01$; $Q_2 = 0.4$; $e_2 = 2.0$.

Zusammenfassung

Copolymerisation von Fumarsäurenitril (M_2) mit Styrol (M_1) ergab die folgenden Werte für die charakteristischen Copolymerisationskonstanten: $r_1 = 0,23 \pm 0,1$; $r_2 = 0,01 \pm 0,01$; $Q_2 = 0,6$; $e_2 = 1,6$. Mit Methylmethacrylat (M_1) waren die Werte $r_1 = 3,5 \pm 0,5$; $r_2 = 0,01 \pm 0,01$; $Q_2 = 0,4$; $e_2 = 2,0$.

Received July 12, 1951

Revised November 28, 1951