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LETTER TO THE EDITORS

COPOLYMERIZATION OF SOME FURTHER MONOMER PAIRS

Continuing the studies of copolymerization previously reported (1-5), we have investigated the copolymerization behavior of the following monomer pairs: (a) styrene/vinyl carbazole, (b) methyl methacrylate/vinyl carbazole, (c) styrene/1,2-dichloro-2-propene, (d) methyl methacrylate/1,2—dichloro—2—propene. The reactivity ratios obtained for these systems are reported in Table I.

TABLE I. Reactivity Ratios*

System No.	M_1	M_2	r_1	r_2
I	Styrene	Vinyl carbazole	5.5	0.012
II	Methyl methacrylate	Vinyl carbazole	2.0	0.20
III	Styrene	1,2-Dichloro-2-propene	5.0	0.06
IV	Methyl methacrylate	1,2-Dichloro-2-propene	5.5	0.17

*Estimated probable errors in r_1 and r_2 values: $\pm$15% of reported values.

Experimental

Styrene was purified by several washings with dilute sodium hydroxide, followed by several washings with distilled water. It was later dried over calcium chloride and distilled under vacuum. Methyl methacrylate and 1,2-dichloro-2-propene (supplied by Halogen Chemicals) were purified by simple vacuum distillation. Vinyl carbazole was purified by crystallization from petroleum ether.

Pairs of monomer mixtures were prepared over the entire range of composition, sealed in glass tubes and placed in a constant-temperature water bath maintained at 70°C. All mixtures contained 0.1% by weight of benzoyl peroxide as the catalyst. Polymerization was allowed to proceed until a conversion of about 5% had taken place.

The copolymers were purified by precipitating in methanol and redissolving in methyl ethyl ketone, and reprecipitating several times, followed by "benzene freezing" (6) and vacuum drying at 45°C. The copolymers containing 1,2-dichloro-2-propene were analyzed for chlorine whereas those containing vinyl carbazole were analyzed for nitrogen by the micro-Dumas method.

The following tables, Systems I through IV, indicate the composition of the initial monomer mixture, the chlorine or nitrogen analysis and the molar composition of the copolymer.

System I. Styrene (M_1) - Vinyl Carbazole (M_2)

M_2*	Per cent nitrogen in polymer	m_2**
0.0445	0.16	0.012
0.1160	0.28	0.021
0.3226	0.87	0.068
0.8256	2.70	0.242
0.9280	4.20	0.426
1.0000	7.15	0.975

System II. Methyl Methacrylate (M_1) - Vinyl Carbazole (M_2)

M_2*	Per cent nitrogen in polymer	m_2**
0.1150	0.94	0.072
0.3230	2.40	0.204
0.5056	2.98	0.266
0.8950	5.63	0.643
0.9210	6.00	0.713

System III. Styrene (M_1) - 1,2-dichloro-2-propene (M_2)

M_2*	Per cent chlorine in polymer	m_2**
0.0752	1.47	0.022
0.1940	3.34	0.049
0.5850	16.17	0.241
0.7961	25.20	0.379
0.9131	35.00	0.532
0.9350	37.60	0.573

System IV. Methyl Methacrylate (M_1) - 1,2-Dichloro-2-propene (M_2)

M_2*	Per cent chlorine in polymer	m_2**
0.0730	0.99	0.014
0.1841	2.39	0.034
0.3740	6.81	0.097
0.7821	27.28	0.402
0.9140	41.40	0.624

*Mole fraction (M_2) in monomer mixture.
**Mole fraction (m_2) in copolymer.

Discussion of Results

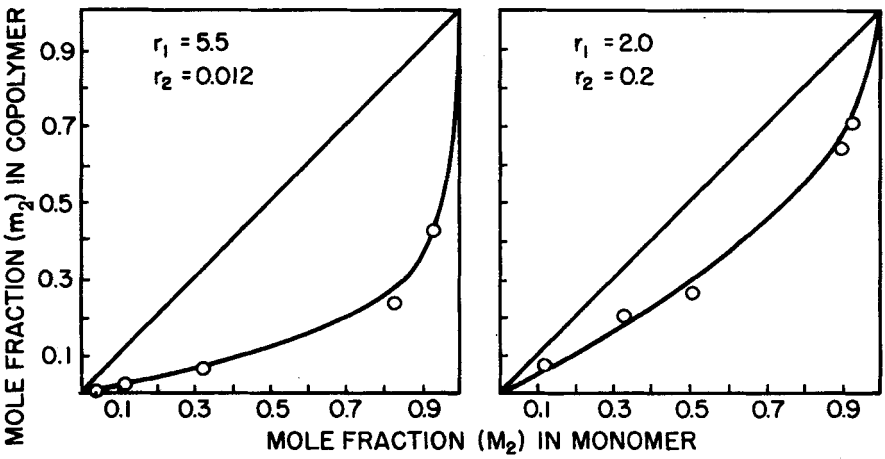

Fig. 1. Copolymer composition curve for the system styrene (M_1)-vinyl carbazole (M_2).

Fig. 2. Copolymer composition curve for the system methyl methacrylate (M_1)-vinyl carbazole (M_2).

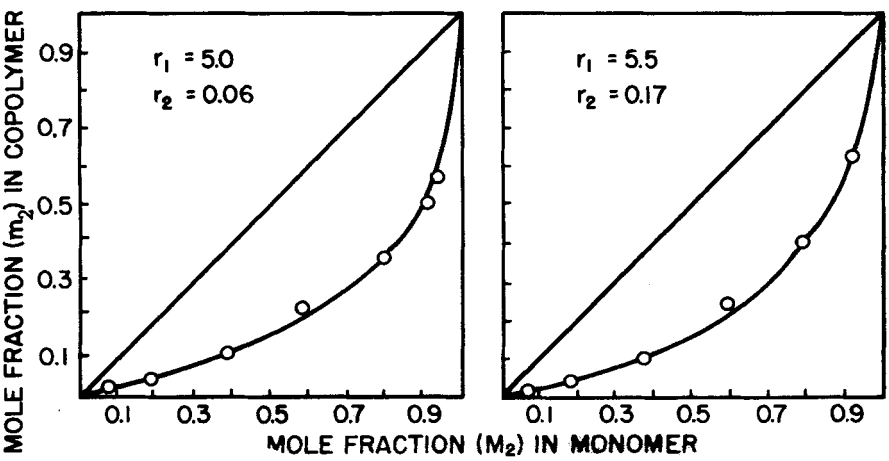

Fig. 3. Copolymer composition curve for the system styrene (M_1)-1,2-dichloro-2-propene (M_2).

Fig. 4. Copolymer composition curve for the system methyl methacrylate (M_1)-1,2-dichloro-2-propene (M_2).

The experimental results of the above four systems are in Figures 1-4, respectively. From these studies we can make the following observations.

(a) Styrene monomer adds both to its own radical and to a vinyl carbazole radical (or 1,2-dichloro-2-propene radical) at a considerably faster rate than does vinyl carbazole monomer (or 1,2-dichloro-2-propene monomer). Vinyl carbazole and 1,2-dichloro-2-propene monomers have approximately equal tendencies to add to a styrene radical.

(b) Methyl methacrylate, in its copolymerization with vinyl carbazole or 1,2-dichloro-2-propene, follows the general pattern of styrene. However, vinyl carbazole monomer adds to a methyl methacrylate radical nearly two and a half times as fast as does a 1,2-dichloro-2-propene monomer.

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Turner Alfrey, Jr.
Sham Lal Kapur

Polymer Research Institute
Polytechnic Institute of Brooklyn
Brooklyn, New York

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