Copolymerization of Phenylacetylene with Vinylpyridine*

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The recent work by Doak[1] on the copolymerization of phenylacetylene with methyl acrylate and acrylonitrile prompts us to report results of some experiments on the copolymerization properties of phenylacetylene. Since preliminary investigation indicated that copolymerization occurred most readily with 2-vinylpyridine, our quantitative data are confined to that monomer.

As reported by Doak,[1] we have found phenylacetylene to be an effective retarder of free-radical polymerization, as indicated by low yields, slow conversion, and low molecular weights, a factor which greatly limits its study and application in copolymer systems.

EXPERIMENTAL

Preparation of Styrene Dibromide.[2] Into a 2-l. three-necked flask equipped with a mineral oil-sealed stirrer, reflux condenser, and dropping funnel was weighed 326 g. of ethylbenzene (3 moles) (Eastman Kodak White Label). The ethylbenzene was heated to reflux by an oil bath kept at 145–155° while 930 g. of bromine (6 moles) was added dropwise over a period of about two hours. The hydrogen bromide evolved was led down the drain. The flask was illuminated with a 1000-watt bulb during the reaction to facilitate side-chain bromination. After all the bromine had been added the heating was continued for another fifteen minutes, and then the product was poured into a 3-l. beaker and crystallized from 1.5 parts of Skellysolve L. The crystals were washed with Skellysolve F and dried. The yield was 544 g. of styrene dibromide (69%).

Preparation of Phenylacetylene.[2] Sodamide was prepared by dropping 115 g. (5 moles) of sodium metal which had been cut into about quarter-inch cubes into about 2 l. of liquid ammonia to which had been added a few tenths of a gram of ferric nitrate nonahydrate. The liquid ammonia was contained in a 5-l. three-necked flask equipped with a stirrer. The addition of the sodium required about two hours. The styrene dibromide was

slowly sifted into the stirred suspension of sodamide in liquid ammonia. The reaction was quite vigorous and often caused the ammonia to boil. After all the styrene dibromide had been added the solution was allowed to stand until most of the ammonia had evaporated. Then about 2 l. of water was poured into the flask, and the crude phenylacetylene was steam distilled out of the flask. A small amount of ether was added to the distillate to facilitate the separation of the organic layer. The organic layer was then washed three times with about 100 cc. of water, dried with magnesium sulfate, and fractionated under reduced pressure to yield 97 g. (46%) of phenylacetylene (b.p. 37° at 13 mm.) within the acceptable refractive index range of 1.5465 to 1.5484 at 20°.

Preliminary Tests on the Copolymerization of Phenylacetylene. A set of test tubes was made up in which approximately equal parts of phenylacetylene and another monomer (undistilled) were placed in each tube along with a generous portion (about 2%) of benzoyl peroxide. The tubes were stoppered and placed in a water bath at 60° for several hours. The contents of the tube were then poured into methanol, and the extent of the polymerization was judged by the quantity of precipitate. The results are given in Table I.

TABLE I

PRELIMINARY PHENYLACETYLENE COPOLYMERIZATION TESTS AT 60°C.

Monomer	Time, hours	Results
Styrene.....................	14	Slightly polymerized
Acrylonitrile...............	34	" "
Vinyl acetate...............	34	" "
Methyl acrylate............	34	" "
2-Vinylpyridine.............	14	Much polymerized

Copolymerization of Phenylacetylene and 2-Vinylpyridine. The phenylacetylene used in these experiments had a refractive index of 1.5478 at 20°. The 2-vinylpyridine used was freshly distilled material from Reilly Tar & Chemical Corp. Each tube was made up as follows: A specified amount of each of the two monomers was weighed into a test tube, correct to the nearest milligram, so that each tube contained a total of 0.08 mole. Then 20 mg. (0.1%) of benzoyl peroxide was weighed into the tube. The tube was then flushed with dry nitrogen for one minute and sealed. The tubes were placed in a water bath at 60° until the increase in viscosity indicated that polymerization to the extent of a few per cent had taken place. The tubes were opened and poured into about 300 cc. of dry either at −20°. The precipitated polymer was filtered, washed, and dried. Samples were sent to Micro-Tech Laboratories at Skokie, Illinois, for analysis. The results of these experiments are summarized in Table II.

Since analysis of a sample of purified 2-vinylpyridine polymer indicated 12.70% nitrogen, the copolymer composition calculated on this basis is presumed to be the more reliable. Using these data in the copolymerization

TABLE II

COPOLYMERIZATION OF 2-VINYLPYRIDINE (M_1) WITH PHENYLACETYLENE
AT 60°C.

$M_1{}^a$	Time, hours	% conversion	% N	$m_1{}^b$	$m_1{}^c$
0.050	92	0			
.100	92	0			
.200	92	0			
.282	220	0.5	8.25	0.619	0.650
.350	38	0.8	8.76	.658	.690
.503	3.25	2.5	10.25	.770	.807
.655	2.0	5.0	11.44	.859	.901
.800	0.25	2.2	11.97	.899	.942
.900	0.33	2.2	12.30	.923	.968
.951^d	0.50	1.2	12.31	.924	.969

^{a} Mole fraction M_1 in monomer mixture.
^{b} Mole fraction M_1 in copolymer calcd. on basis: 13.33% N = 100% 2-vinylpyridine.
^{c} Mole fraction M_1 in copolymer calcd. on basis: 12.70% N = 100% 2-vinylpyridine.
^{d} Contained only 5 mg. of benzoyl peroxide.

equation, graphic solution indicated the values for the copolymerization ratios to be $r_1 = 4.0 \pm 0.7$ and $r_2 = 0.2 \pm 0.05$.

Copolymerization of Phenylacetylene with Other Monomers at 60°C. The experimental procedure was the same as with the 2-vinylpyridine copolymerizations. The results are given in Table III.

TABLE III

COPOLYMERIZATION OF PHENYLACETYLENE WITH OTHER MONOMERS AT
60°C.

Monomer (M_1)	% M_1	Time, hours	% conversion
Methyl acrylate...............	80.0	145	3.2
	60.0	215	0.5
	40.0	237	0
	22.2	237	0
α-Methylstyrene...............	47.5	135	0
Methyl vinyl sulfide...........	80.4	135	0
Styrene......................	74.0	70	10.6

Properties of the Phenylacetylene-2-Vinylpyridine Copolymer. A mixture of 20% phenylacetylene and 80% 2-vinylpyridine was polymerized at 60° for 2.5 hours. The copolymer was precipitated from cold ether, filtered, washed, and dried. About 11% of the mixture was converted into polymer. This polymer was quite soluble in benzene, methanol, and chloroform, and slightly soluble in acetone. The melting range of the polymer in a capillary tube was 129° to 143°. A viscometric molecular weight determination was made, using benzene as the solvent. The value of K_m was chosen arbitrarily to be 3×10^{-4}. A sample of the polymer weighing 0.1407 g. was dissolved in 5.83 g. (6.63 cc.) of benzene, The efflux time for this solution through a Fenske viscometer was 60.7 seconds as compared to 40.0 seconds

for pure benzene. This indicates the molecular weight to be 8500. The infrared absorption spectrum of a solution of 0.158 g. of the polymer in 0.819 g. of methanol was run between 2.9 and 5.5 microns, the region of carbon-carbon triple bond absorption (4.8 microns). It showed no absorption whatever in this region except for the solvent.

Properties of 2-Vinylpyridine Polymer. A sample of pure 2-vinylpyridine polymer was obtained by heating 7 g. of the monomer and 20 mg. of benzoyl peroxide for 30 minutes at 60° and then precipitating the polymer from cold ether. The yield was 10%. The polymer had the same solubility characteristics as the phenylacetylene-2-vinylpyridine copolymer. Its melting range was 125° to 148°. The molecular weight, determined by the viscosity method, was 12,500. A solution of 0.0729 g. of the polymer in 10 cc. of benzene required 50.5 seconds efflux time through a Fenske viscometer as compared to 40.0 seconds efflux time for pure benzene. The value of the constant, K_m, was arbitrarily chosen to be 3×10^{-4}.

A sample of the pure 2-vinylpyridine polymer was sent to Micro-Tech Laboratories for analysis with the following results:

Calcd. for $(C_6H_7N)_{100}$: C, 80.00; H, 6.67; N, 13.33; mol. wt., 10,500.
Calcd. for $(C_6H_7N)_{100}O_{19}$: C, 77.75; H, 6.48; N, 12.95; mol. wt., 10,800.
Found: C, 77.85; H, 6.40; N, 12.70; mol. wt., *ca.* 12,500.

DISCUSSION

From the values of r_1 and r_2 estimated for copolymerization of phenylacetylene, it is possible to calculate values for the resonance factor, Q, and the polar factor, e, for this monomer from the Alfrey-Price equations:[3]

$$r_1 = Q_1 e^{-e_1(e_1 - e_2)}/Q_2$$

$$r_2 = Q_2 e^{-e_2(e_2 - e_2)}/Q_1$$

Using values for Q_1 and e_1 of 1.1 and -0.1 for vinylpyridine, 0.4 and 0.6 for methyl acrylate, and 0.4 and 1.0 for acrylonitrile,[4] values for Q and e for phenylacetylene were calculated and are summarized in Table IV.

TABLE IV
COPOLYMERIZATION CONSTANTS FOR PHENYLACETYLENE (M_2)

M_1	r_1	r_2	Q_2	e_2
2-Vinylpyridine....	4.0 (± 0.7)	0.2 (± 0.05)	0.30 (± 0.05)	-0.5 (± 0.2)
Methyl acrylate[1]...	0.62	0.27	0.25	-0.7
Acrylonitrile[1]......	0.26	0.33	0.34	-0.6

The agreement in values for Q and e from the three pairs of copolymers is quite satisfactory. A comparison with the values for styrene ($Q = 1.0$, $e = -0.8$) indicates nearly the same electrical factor but an appreciably smaller degree of resonance stabilization of the intermediate radical adduct:

$$\text{\textasciitilde\textasciitilde}M\cdot + C_6H_5C{\equiv}CH \longrightarrow \text{\textasciitilde\textasciitilde}M-CH{=}\overset{\displaystyle C_6H_5}{C}\cdot$$
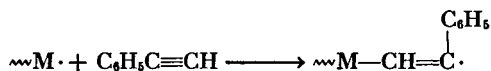
References

1. Doak, 116th Meeting of the American Chemical Society, Atlantic City, September 20, 1949.

2. Directions for the preparation of styrene dibromide and phenylacetylene by a private communication from Dr. K. N. Campbell.

3. Alfrey and Price, *J. Polymer Sci.*, **2**, 101 (1947).

4. Price, *J. Polymer Sci.*, **3**, 772 (1948).

English Synopsis, see Summaries, page S18, Vol. V, 1950.

Résumé

Les expériences de copolymérisation du phénylacétylène avec la 2-vinylpyridine donnent des rapports de copolymérisation $r_1 = 4.0 \pm 0.7$ et $r_2 = 0.20 \pm 0.05$. Les constantes de la copolymérisation s'évaluent à $Q = 0.3$ et $e = 0.6$, au départ de ces résultats; ils sont en accord avec les valeurs des constantes de copolymérisation, récemment rapportées par Doak dans ses études de copolymérisation du phénylacétylène avec l'acrylate de méthyle et l'acrylonitrile. Les expériences, ici rapportées, confirment l'assertion de Doak, suivant laquelle le phénylacétylène agit comme un retardateur net, tout aussi bien que comme co-monomère.

Zusammenfassung

Copolymerisationsexperimente von Phenylacetylen mit 2-Vinylpyridin ergaben Werte für die Copolymerisationsverhältnisse $r_1 = 4.0 \pm 0.7$ und $r_2 = 0.20 \pm 0.05$. Die aus diesen Experimenten abgeschätzten Copolymerisationskonstanten $Q = 0.3$ und $e = 0.6$ stimmen mit denen überein, die aus Werten der Copolymerisationskonstanten erhalten werden, welche kürzlich von Doak durch Studien der Copolymerisation von Phenylacetylen mit Methylacrylat und Acrylnitril berichtet wurden. Die hier dargestellten Resultate unterstützen den Bericht von Doak, dass Phenylacetylen eine deutlich verzögernde Wirkung hat, sowie auch eine verschlechternde.