[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Ionic Polymerization. Copolymerization of Nuclear and Side-chain Alkyl-substituted Styrene Monomers[1]

BY C. G. OVERBERGER, D. TANNER[2] AND ELI M. PEARCE[2]

RECEIVED FEBRUARY 17, 1958

Copolymerization of nuclear and side-chain alkyl-substituted styrene monomers has been used as a method for determining the relative steric effect for the addition of an ion pair to an olefinic double bond. Monomer reactivity ratios are reported for the copolymerization of α-, β- and *p*-alkyl-styrenes with a reference monomer (*p*-chlorostyrene) and show the following order of reactivity: α-methyl > *p*-methyl > *p*-ethyl > styrene > *trans*-β-methyl > *cis*-β-methyl > β-ethyl. An interpretation of results in terms of steric factors, hyperconjugation and proximity to the reaction site is given.

Most 1,1[3a]- and 1,2[3b]-disubstituted ethylenes show a reluctance to add to themselves during attempted free radical polymerizations. This is generally attributed to steric effects which are clearly demonstrated in copolymerization studies. In contrast to free radical polymerization, steric effects have not received any extensive study in cationic polymerization. Recent kinetic studies on the cationic polymerization of α-methylstyrene showed an abnormally low propagation rate due to steric factors.[4] β-Methylstyrene polymerized less rapidly than α-methylstyrene under the influence of acids and this may be attributed to enhanced steric effects.[5] The successful cationic polymerization of these methylstyrenes probably is due to the ability of the methyl group to sufficiently activate the double bond toward reaction with an electrophilic carbonium ion so that steric effects play a small role.

The purpose of this research has been to correlate the size and location of the alkyl groups on the styrenes with the extent of steric domination of their reactivities during cationic polymerization. To investigate these steric effects quantitatively, *cis*- and *trans*-β-methylstyrene, β-ethylstyrene (predominantly the *trans* isomer), β-*n*-propylstyrene and *p*-ethylstyrene were copolymerized with *p*-chlorostyrene as the reference monomer and stannic chloride as the cationic catalyst.

A convenient synthesis of isomer-free α- and β-alkylstyrenes from the acetates of appropriate carbinols has been reported in a separate paper.[6]

Experimental

Solvents and Catalyst.—Carbon tetrachloride, nitrobenzene and stannic chloride were purified and ampules of the latter prepared according to procedures described previously.[7]

Monomers.—β-Methyl-, β-ethyl- and β-*n*-propylstyrenes were prepared by pyrolysis of the acetates of the appropriate carbinols.[6] *cis*- and *trans*-β-methylstyrene were separated by distillation through a spinning band column of over 50 theoretical plates; *cis*-β-methylstyrene, b.p. 55° (15 mm.), $n^{22}\text{D}$ 1.5430, 15% yield of olefin mixture obtained, $\lambda_{\max}$ 242 mμ, log ε 4.12, $\lambda_{\max}$ 280 mμ, log ε 2.51 (57% yield, b.p. 52.1° (12 mm.), $n^{20}\text{D}$ 1.5430, $d^{20}{}_4$ 0.902, by decarboxylation of *trans*-2-methyl-3-phenylpropenic acid)[8]; *trans*-β-methylstyrene, b.p. 71° (25 mm.), $n^{25}\text{D}$ 1.5480, 85% of olefin mixture obtained, $\lambda_{\max}$ 249 mμ, log ε 4.22; $\lambda_{\max}$ 283 mμ, log ε 3.01 (77% yield, b.p. 53° (8 mm.), $n^{20}\text{D}$ 1.5507, $d^{20}{}_4$ 0.902, by dehydration of 1-phenyl-1-propanol).[8]

p-Ethylstyrene was prepared from *p*-ethylbenzene using the Perrier modification of the Friedel and Crafts reaction to obtain the ketone,[9] reducing the latter with lithium aluminum hydride and dehydrating the resulting carbinol with potassium bisulfate.[10] From 80 g. of *p*-ethylphenylmethylcarbinol was obtained 45 g. (64%) of *p*-ethylstyrene, b.p.40° (1 mm.), $n^{25.5}\text{D}$ 1.5349 (yield 85%, b.p. 68° (16 mm.), $n^{25}\text{D}$ 1.5350, prepared by vapor phase dehydration over activated alumina).[9]

p-Chlorostyrene was purified as previously described.[7]

Polymerization Technique.—The polymerization technique throughout was identical to that described by Overberger, Ehrig and Tanner.[11]

Conversions were calculated from the weight of polymer obtained. The following formula was used to correct M_2 for conversions above 6%

$$M_2 = M_2' + \frac{M_2' - m_2}{2} \times \text{conversion}$$

where M_2 and M_2' are the corrected and uncorrected values, respectively, for the mole fraction of monomer 2 in the monomer mixture and m_2 is the mole fraction of monomer 2 in the polymer.

Results and Discussion

The data for the copolymerization of *p*-chlorostyrene with *cis*- and *trans*-β-methyl-, β-ethyl-, β-*n*-propyl- and *p*-ethylstyrenes are summarized in Table I. The data for the copolymerization of *p*-chlorostyrene with α-methyl-[12] α-ethyl-[13] and *p*-methylstyrenes,[12] and styrene[11] have been previously reported. The copolymer composition curves and monomer reactivity ratios are given in Fig. 1 and Table II, respectively.

The data may be interpreted in terms of two opposing reactivity factors in operation, the polar and resonance effects as contrasted with steric effects. Experimental monomer reactivity ratios indicate the order of reactivity of methyl-

---

(1) This is the 11th in a series of papers concerned with ionic polymerization. For the 10th paper in this series, see C. G. Overberger, F. Ang and H. Mark, *J. Polymer Sci.*, in press (1958).

(2) A portion of theses of D. Tanner and E. M. Pearce submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(3) T. Alfrey, Jr., J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., 1952; (a) p. 76. (b) p. 49.

(4) D. J. Worsfold and S. Bywater, THIS JOURNAL, **79**, 4917 (1957).

(5) J. M. Van der Zanden and T. R. Rix, *Rec. trav. chim.*, **75**, 1166 (1956).

(6) C. G. Overberger and D. Tanner, THIS JOURNAL, **77**, 369 (1955).

(7) C. G. Overberger, L. H. Arond and J. J. Taylor, *ibid.*, **73**, 5541 (1951).

(8) W. R. R. Park and G. F Wright, *J. Org. Chem.*, **19**, 1435 (1954).

(9) D. T. Mowry, M. Renoll and W. F. Huber, THIS JOURNAL, **68**, 1105 (1946).

(10) C. G. Overberger and J. H. Saunders, in "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 204.

(11) C. G. Overberger, R. J. Ehrig and D. Tanner, THIS JOURNAL, **76**, 772 (1954).

(12) C. G. Overberger, L. H. Arond, D. Tanner, J. J. Taylor and T. Alfrey, Jr., *ibid.*, **74**, 4848 (1952).

(13) C. G. Overberger, E. M. Pearce and D. Tanner, *ibid.*, **80**, 1761 (1958).

TABLE I

COPOLYMERIZATION OF α-, β- AND *p*-ALKYL-SUBSTITUTED STYRENES (M_2) WITH *p*-CHLOROSTYRENE (M_1)[a]

M_2 in monomer mixture[b]	Reaction time, hr.	Conversion, %	Cl, %[c]	m_2 in copolymer
trans-β-Methylstyrene (M_2) and *p*-chlorostyrene (M_1)				
0.215	2.5	1	20.19	0.239
.321	3.5	2	18.46	.312
.485	18.5	7	15.53	.432
.600	20.0	5	14.09	.489
.699	21.0	3	12.39	.555
.227	3.0	5	20.04	.245
.315	4.0	2	18.63	.305
.509	20.0	1	15.19	.445
.608	24.0	3	13.86	.498
.714	48.0	9	11.98	.571
cis-β-Methylstyrene (M_2) and *p*-chlorostyrene (M_1)				
0.210	1.3	5	21.64	0.176
.315	2.3	2	19.52	.267
.486	18.0	4	16.68	.385
.609	60.0	5	13.92	.496
.708	64.0	1	12.10	.567
β-Ethylstyrene (M_2) and *p*-chlorostyrene (M_1)				
0.196	24.8	6	21.91	0.145
.302	24.8	6	19.85	.230
.392	24.8	6	18.20	.295
.496	25.8	5	17.18	.338
.595	40.8	5	15.81	.394
.740	93.5	5	14.08	.460
β-*n*-Propylstyrene (M_2) and *p*-chlorostyrene (M_1)				
0.164	0.5	9	22.60	0.110
.399	0.8	8	19.12	.245
.625	48.0	6	18.62	.262
p-Ethylstyrene (M_2) and *p*-chlorostyrene (M_1)				
0.190	0.05	8	12.67	0.517
.294	.04	6	10.44	.604
.399	.01	5	6.08	.702
.483	.01	6	5.45	.795
.594	.01	8	4.16	.844
.697	.03	44	2.20	.918
.741	.01	20	1.94	.927

[a] All copolymerizations were carried out at 0° in 20 mole % solution (based on solvent) with a 1 mole % concentration of stannic chloride catalyst (based on monomers). A 1:1 mole ratio of nitrobenzene and carbon tetrachloride mixture was used as solvent. [b] Corrected for conversions above 6% using the equation given in the Experimental section. [c] Analyses by Dr. K. Ritter, Zurich, Switzerland, and Dr. H. A. Clark, Urbana, Ill.

substituted styrenes toward their respective carbonium ions as α-methyl >> *p*-methyl > styrene > *cis*- and *trans*- β-methyl (r_2 = 15.0, 4.5, 2.0, 0.32, respectively). Thus, for alkyl groups of similar size, substitution in the side chain α-position or in the nuclear *p*-position increases the reactivity of the monomer toward a carbonium ion, the former case being much more pronounced since the electron-donating group is attached directly to the double bond. When the alkyl group is substituted in the side-chain β-position, steric factors become increasingly important and although the polar factors are present, the monomer reactivity is such that the β-methylstyrene carbonium ion preferentially reacts with *p*-chlorostyrene rather than with the *cis*- or *trans*- β-methylstyrene. It is also of interest to note that these results can be correlated with the decrease in stability of the resultant methyl-substituted carbonium ion due to hyperconjugation effects.

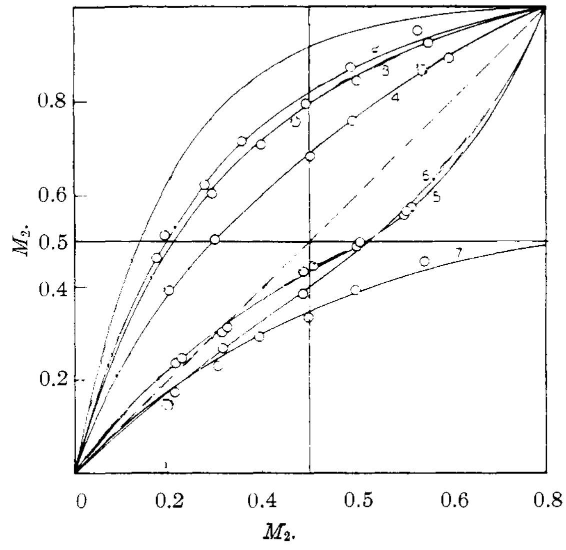


Fig. 1.—Copolymerization of alkyl substituted styrenes (M_2) with *p*-chlorostyrene (M_1): 1, α-methyl; 2, *p*-methyl; 3, *p*-ethyl; 4, styrene; 5, *trans*-β-methyl; 6, *cis*-β-methyl; 7, β-ethyl.

The reactivity of methyl-substituted styrenes toward a *p*-chlorostyrene carbonium ion gave similar but yet different results. The order of reactivity is *p*-methyl > styrene ~α-methyl > *trans*- β-methyl > *cis*- β-methyl (r_1 = 0.22, 0.34, 0.35, 0.74, 1.0, respectively).

TABLE II

MONOMER REACTIVITY RATIOS FOR ALKYL-SUBSTITUTED STYRENES (r_2) AND *p*-CHLOROSTYRENE (r_1)

M_2	r_1	r_2
α-CH_3[a]	0.35 ± 0.05	15.0 ± 1.5
p-CH_3[a]	.22 ± .05	4.5 ± 0.7
p-C_2H_5	.29 ± .04	4.1 ± .5
Styrene[b]	.34 ± .05	2.0 ± .2
trans-β-CH_3	.74 ± .06	0.32 ± .04
cis-β-CH_3	1.0 ± .1	0.32 ± .02
β-C_2H_5	0.88 ± .30	0

[a] Reference 12. . [b] Aluminum bromide used as catalyst, reference 11.

The higher reactivity of *trans*-β-methylstyrene when compared with the *cis* isomer on the basis of the r_1 values can be explained by the difference in steric requirements for the reaction of a carbonium ion with the *cis* and *trans* isomers. A suggested explanation is that the reaction between the carbonium ion and the double bond may be considered to occur in a direction approximately perpendicular to the nodal plane of the C=C double bond, as the extreme mode of reaction.[14] When the methyl group and the benzene ring are on the

(14) This point of view is particularly useful if one considers the formation of a π-complex the first part of the reaction followed by [J. B. Levy, R. W. Taft, Jr., and L. P. Hammett, THIS JOURNAL, **75**, 1253 (1953)] rearrangement to the carbonium ion. The formation of the initial π-complex easily can be understood in terms of a perpendicular attack to the nodal plane.

same side of the double bond, rotation of the benzene ring through the position corresponding to coplanarity with the double bond is resisted by interference between the hydrogen at the *o*-position of the benzene ring and the methyl group[15] and thus the perpendicular interaction with a carbonium ion is hindered for *cis*-β-methylstyrene. This interference phenomenon also is shown by a comparison of the ultraviolet absorption spectra of *cis*- and *trans*-β-methylstyrene (see Experimental). Alternately, a more likely explanation is that the transition state configuration resembles the initial state and thus more resonance stabilization is obtained with the *trans* isomer, the actual differences between the *cis* and *trans* isomers being small in the ground state. The fact that the r_2 values are the same may be justified on the basis that additional steric interactions between the β-methylstyrene carbonium ion and *cis*- and *trans*-β-methylstyrene are large enough to overshadow the previously discussed small interference or transition state stabilization factors. Large differences in the reactivity of *cis*- and *trans*- olefins in free radical initiated copolymerizations have been frequently observed.[16] These large differences as compared with the relatively small difference observed by us in the cationic copolymerization of *cis*- and *trans*-β-methylstyrene may be explained by the recent suggestion of Bader, Buckley, Leavitt and Szwarc that the most probable approach of a radical is along the C═C axis[17] as compared to the more perpendicular approach of the carbonium ion and the C═C double bond.

When the methyl group in the β-position is lengthened by one or more methylene units, steric effects become completely dominant over polar influences and the reactivity of the monomer is changed. The shape of the copolymerization composition curves (Fig. 1) show that although *cis*- and *trans*-β-methylstyrene are able to add to themselves in the growing chain this is not possible for β-ethylstyrene where $r_2 = 0$.

When the alkyl group is situated in the nuclear *p*-position, the steric interference is small (if at all) and the reactivity of *p*-ethylstyrene is only slightly less than that of *p*-methylstyrene (r_2 = 4.1 and 4.5; r_1 = 0.29 and 0.22, respectively). This small difference in reactivity may be explained on the basis of a small additional hyperconjugative stabilization of the carbonium ion formed from *p*-methylstyrene.

Acknowledgment.—We are grateful for the support of the work of D. Tanner by the Office of Naval Research, Contract No. NR-356-262, and of Eli M. Pearce of a fellowship from E. I. du Pont de Nemours and Co., Inc., and a "Grant in Aid" from the Research Corporation.

---

[15] D. J. Cram, THIS JOURNAL, **71**, 3883 (1949). This interference was previously discussed by this author for *cis*- and *trans*-α,β-dimethylstyrene.

[16] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 127–129.

[17] A. R. Bader, R. P. Buckley, F. Leavitt and M. Szwarc, THIS JOURNAL, **79**, 5621 (1957).

BROOKLYN 1, N. Y.

[CONTRIBUTION NO. 1398 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

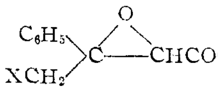
Epoxy Ketones Derived from the Reactions of 1,4-Dihalo-1,4-dibenzoylbutanes with Base[1a,1b]

BY HARRY H. WASSERMAN AND MARINA J. GORBUNOFF

RECEIVED MARCH 20, 1958

As in the reactions of phenacyl halides with alkoxides, epoxy ketones are formed when α-halo- and α,α'-dihalo-1,4-dibenzoylbutanes are treated with bases. Whereas 1-chloro- or 1-bromo-1,4-dibenzoylbutane is converted to a β,γ-epoxy ketone, 1,4-dihalo-1,4-dibenzoylbutanes form γ-halo-α,β-epoxy ketones. The proof of structure of these products is based on ultraviolet absorption spectral measurements of model phenacyl type bromides and chlorides, and on reduction studies using zinc in polar solvents.

In previous articles[2–4] it has been shown that phenacyl halides undergo condensation in base to form *cis*- and *trans*-γ-halo-α,β-epoxy ketones corresponding to structure I.[5]



I, X = Br, Cl

Although the reaction leading to I is analogous in many respects to the Darzens glycidic ester condensation,[6,7] it is unusual in that the reaction involves two molecules of an α-halo ketone instead of the usual combination of aldehyde (or ketone) and α-halo ester. A related example of the use of α-halo ketones in this type of condensation was reported some years ago[8–10] during the course of

---

[1] (a) Taken from a dissertation submitted by M. J. Gorbunoff in partial fulfillment of the requirements for the Ph.D. degree, Yale University, 1956. (b) Presented at the Meeting of the American Chemical Society in Dallas, Texas, April, 1956.

[2] H. H. Wasserman, N. E. Aubrey and H. E. Zimmerman, THIS JOURNAL, **75**, 96 (1953).

[3] J. Berson, *ibid.*, **74**, 5175 (1952).

[4] C. L. Stevens, R. J. Church and V. J. Traynelis, *J. Org. Chem.*, **19**, 522 (1954).

[5] For discussions of the stereochemistry of epoxy ketones related to dypnone oxide, see (a) H. H. Wasserman and J. B. Brous, *ibid.*, **19**, 515 (1954); (b) H. H. Wasserman and J. B. Brous, THIS JOURNAL, **76**, 5811 (1954); (c) H. H. Wasserman and N. E. Aubrey, *ibid.*, **77**, 590 (1955); (d) H. H. Wasserman and N. E. Aubrey, *ibid.*, **78**, 1726 (1956); (e) C. L. Stevens and V. J. Traynelis, *J. Org. Chem.*, **19**, 533 (1954); (f) N. H. Cromwell and R. A. Setterquist, THIS JOURNAL, **76**, 5752 (1954).

[6] G. Darzens, *Compt. rend.*, **139**, 1214 (1904).

[7] For a review of the Darzens reaction, see M. S. Newman and B. J. Magerlein, "Organic Reactions," Vol. V, 1949, p. 413.

[8] T. Y. Kao and R. C. Fuson, THIS JOURNAL, **54**, 313 (1932).

[9] T. Y. Kao, *ibid.*, **62**, 356 (1940).

[10] R. C. Fuson, H. H. Hully, J. F. McPherson and F. W. Spangler, *J. Org. Chem.*, **7**, 462 (1942).