Effect of Dielectric Solvent Medium on Copolymerization*

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Alfrey and Price[1] have presented an interpretation of "copolymerization ratios"[2] in terms of two constants characteristic of each monomer, one related to resonance stabilization factors and one to electrical interaction of charges or dipoles in the transition state involving addition of monomer to the intermediate free radical. Evans, Gergely, and Seaman[3] have presented an interpretation of the process in terms of modern transition state theory which lends validity to the Alfrey-Price treatment. Recently, however, Walling and Mayo[4] suggested that the lack of dependence of copolymer ratios on the dielectric constant of the polymerization medium is to be interpreted as evidence against the Alfrey-Price treatment, since the latter incorporates a classical electrical interaction which should be influenced by the effective dielectric constant between the charges.

It was the purpose of the work reported herein to confirm the independence of the copolymerization ratios on dielectric constant and to propose a satisfactory explanation for this fact. The monomer pairs chosen for such a study should be a pair with a maximum difference in electrical factors. The two pairs chosen were: methyl methacrylate and styrene, previously investigated by Lewis, Mayo, and Walling,[5] with values for the electrical factor, e, of 0.4 and -0.8, respectively[6]; and maleic anhydride and alpha-methylstyrene, with e values of approximately 1.5 and -1.2.[6] The high and low dielectric solvents chosen were acetonitrile and benzene.

EXPERIMENTAL

Purification of Monomers. The three liquid monomers were distilled freshly before using through a 70-cm. glass helices-packed column, with total condensation, partial take-off distilling head, and only the middle fractions were taken. The companies of their origin and their final physical constants were as follows: styrene (Dow), b.p. 39.4–39.5°C. at 9 mm., $n_D^{25} = 1.5405$; alpha-methylstyrene (Dow), b.p. 55°C. at 14 mm., $n_D^{25} = 1.5354$; methyl methacrylate (Rohm and Haas), b.p. 100°C., $n_D^{25} = 1.4100$. The maleic anhydride used was Eastman Kodak white-label grade, and was purified by sublimation. This purification was found to

be necessary since the commercial product contained a small amount of white solid which was insoluble in benzene, even at 60°C., above the melting point of maleic anhydride. The product of the sublimation was readily soluble in benzene, and melted sharply at 57°C. All monomers were stored under refrigeration until used.

Purification of Solvents. The benzene (Baker and Adamson, thiophene-free grade) was dried over anhydrous magnesium sulfate and distilled through the same column; b.p. 82.0°C., $n_D^{25} = 1.3436$.

Copolymerization Procedures. Pairs of monomer mixtures containing a total of approximately 0.08 mole of monomers and 0.00008 mole of benzoyl peroxide (0.1 mole per cent) were made up over the entire range of composition. The monomers were weighed on an analytical balance; 50 ml. of solvent and the peroxide were added. The vessels were flushed thoroughly with dry nitrogen and finally sealed. The reaction mixtures were then placed in a constant temperature water bath which was held at 60.0 ± 0.1°C. Polymerizations were continued until it was estimated that about 10% of the monomer in lesser concentration had reacted. The copolymers of styrene and methyl methacrylate were precipitated in 500 ml. of methanol, filtered, redissolved in about 30 ml. of benzene, and reprecipitated from 300 ml. of methanol; after filtration, the samples were thoroughly dried and analyzed. The copolymers of alpha-methylstyrene and maleic anhydride were precipitated from 500 ml. of anhydrous ether, filtered, washed with more ether, dried, and analyzed. In both cases, all the polymers were analyzed for carbon and hydrogen, and the oxygen content calculated. Since in all cases one monomer contained oxygen and the other did not, the oxygen content was used to calculate the polymer composition because this would be the most accurate method. The results are listed in Tables I and II.

TABLE I		TABLE II	
COPOLYMERIZATION OF STYRENE (M₁) WITH METHYL METHACRYLATE (M₂)		COPOLYMERIZATION OF ALPHA-METHYLSTYRENE (M₁) AND MALEIC ANHYDRIDE (M₂)	
In benzene	In acetonitrile	In benzene	In acetonitrile
r_1....... 0.54 ± 0.04	0.44 ± 0.08	r_1.... 0.005 ± 0.005	0.038 ± 0.003
r_2....... 0.42 ± 0.1	0.50 ± 0.04	r_2.... 0.27 ± 0.03	0.08 ± 0.03
$r_1 r_2$...... 0.23	0.22	$r_1 r_2$.. 0.015 ± 0.015	0.030 ± 0.015

DISCUSSION

Since the Alfrey-Price equations for the copolymerization ratios, r_1 and r_2:

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

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

give an expression for the product dependent only on e_1 and e_2:

$$r_1 r_2 = \exp\left\{-(e_1 - e_2)^2\right\}$$

this product should be a measure of the constancy of the electrical factors, e_1 and e_2, in solvents of different dielectric constant.

From Table I, it can be seen that the values for r_1 and r_2 for the styrene–methyl methacrylate system agree within experimental error. Furthermore the values for the product $r_1 r_2$, are in close agreement, 0.23 and 0.22, and agree well with the value of 0.24 for benzene, acetonitrile, and methanol as solvent from the data of Lewis, Mayo, and Walling.[5]

From Table II, it can be seen that the values for r_1 and r_2 for the alpha-methylstyrene–maleic anhydride system do *not* agree within the experimental error. The major source of disagreement is, however, not to be ascribed to the electrical factor since the product of r_1 and r_2 for the two solvents does agree within experimental error.

These experiments thus lend support to the conclusion expressed by Walling and Mayo[4] that, whatever the electrical factor may be in copolymerization, it is not susceptible to detectable influence by the dielectric of the solvent medium. However, we do not agree with their conclusion, based on an impossible hypothetical model, that there should be such an effect on classical coulombic interaction and that therefore the interaction cannot be such a direct coulombic interaction.

In the model proposed by Walling and Mayo, one of the interacting charges is placed exactly on the border between polymer dielectric and solvent dielectric. A far more accurate model would be the type utilized by Kirkwood and Westheimer.[7] For the case in point, we would suggest a model in which the interacting charges in monomer unit and polymer radical are perhaps no further separated than 2 A. from each other and at least 3 A. separated from charges on neighboring solvent molecules.
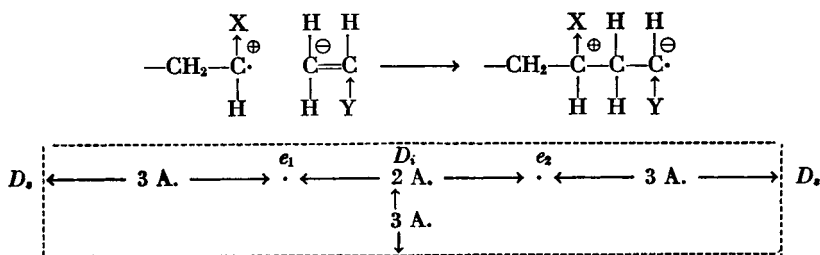
The calculations of Kirkwood and Westheimer show that, for such a model, the effective dielectric constant is almost exactly the internal dielectric of the reactant molecules, D_i, and that the solvent dielectric, D_s, has virtually no effect. It is only when the distance between the charges is large compared to the distance separating the solvent dielectric from the "internal" dielectric that the solvent dielectric makes an important contribution to the effective dielectric constant, and then only when the charges are poles rather than dipoles.

References

1. Alfrey and Price, *J. Polymer Sci.*, **2,** 101 (1949).
2. Alfrey and Goldfinger, *J. Chem. Phys.*, **12,** 205 (1944).   Mayo and Lewis, *J. Am. Chem. Soc.*, **66,** 1594 (1944).   Wall, *ibid.*, **66,** 2050 (1944).   Alfrey, Mayo, and Wall, *J. Polymer Sci.*, **1,** 581 (1946).
3. Evans, Gergely, and Seaman, *J. Polymer Sci.*, **3,** 866 (1948).
4. Walling and Mayo, *J. Polymer Sci.*, **3,** 895 (1948).
5. Lewis, Mayo, and Walling, *J. Am. Chem. Soc.*, **70,** 1519 (1948).
6. Price, *J. Polymer Sci.*, **3,** 772 (1948).
7. Kirkwood and Westheimer, *J. Chem. Phys.*, **6,** 506 (1938).

Résumé

L'absence d'influence de la constante diélectrique du solvant dans le facteur électrique d'Alfrey-Price dans la copolymérisation a été confirmée pour les systèmes styrène–méthacrylate de méthyle et le système alpha-méthylstyrène–anhydride maléique. L'examen de la structure de l'état de transition à la lumière de l'influence du solvant diélectrique sur les interactions des charges au sein d'une molécule indique qu'une influence minime ou nulle peut seulement être prévue dans le complexe radical actif-monomère de la part du pouvoir dielectrique du solvant sur les interactions coulombiennes ordinaires.

Zusammenfassung

Das Fehlen des Einflusses der dielektrischen Konstante des Lösungsmittel-Mediums auf den elektrischen Faktor von Alfrey-Price in der Copolymerisation wurde für die Systeme Styrol–Methylmethacrylat und alpha-Methylstyrol–Maleinsäureanhydrid bestätigt.   Die Untersuchung der Struktur des Transitionsstadiums im Lichte des Einflusses des Lösungsmittel-Dielektrikums auf Ladungseinwirkungen innerhalb eines Moleküls zeigt, dass wenig oder kein Einfluss des Lösungsmittel-Dielektrikums auf einfache Coulombische Einwirkungen im aktiven radikal–monomeren Transitionen-Komplex erwartet werden kann.