factors being constant, the index of refraction of the copolymers is a linear function of composition,[7] the same relation has been assumed here for oil-phase copolymers, using for the pure polymers of styrene and butadiene, made under the same conditions as the copolymers, $n^{20}D$ 1.5935 and 1.5160, respectively. The high-styrene polymer was quite hard and an optical surface was generated by pressing the polymer against a hot glass plate and allowing it to cool in contact. Optical contact of the resulting surface with the prism of an Abbe refractometer was made with a saturated aqueous solution of cadmium borotungstate and the refractive index was measured by reflected light. The intermediate-styrene polymer was soft enough to make optical contact with the prism directly under pressure, allowing measurement by reflected light. The low-styrene polymer was soft enough to squeeze between the two prisms of the refractometer for measurement by transmitted light. All readings were reproducible to ±0.0002.

(7) "Analyses by Refractive Index," Lundstedt and Hampton, Akron Copolymer Research Group Meeting, June 12–13, 1944.

## Summary

1. Copolymerization data and monomer reactivity ratios at 60° are given for eight new monomer pairs.

2. Monomer reactivity ratios of lower precision are given for six additional pairs.

PASSAIC, NEW JERSEY RECEIVED JULY 17, 1947

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[CONTRIBUTION NO. 70 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

# Copolymerization. VIII. The Relation Between Structure and Reactivity of Monomers in Copolymerization[1]

BY FRANK R. MAYO, FREDERICK M. LEWIS AND CHEVES WALLING

The first papers in this series[2] showed that series of copolymerizations make possible the determination of the relative reactivities of monomers toward certain radicals, and that such relative reactivities are independent of the feed composition, conversion, solvents, regulators, sources of free radicals used and rates of polymerization. On the other hand, such relative reactivities do appear to depend upon the particular attacking radical, and the results indicate a general order of monomer reactivity toward radicals on which is superimposed a tendency of certain monomers to alternate in copolymerization. In some monomer pairs this alternating effect appears to be negligible; relative reactivities of the monomers are the same toward both types of radicals and the monomer reactivity ratio product, $r_1r_2$, $\cong$ 1. Such systems, of which styrene–butadiene is an example ($r_1r_2$ = 1.08) have been termed "ideal" by Wall.[3] In other systems the "alternating effect" appears dominant, $r_1r_2 \cong 0$, and the initial copolymer from any feed consists of regularly alternating units of the two monomers (*e. g.*, styrene–maleic anhydride $r_1r_2 \leq 0.001$).[4] In the great majority of copolymerizations, however, both effects appear of importance and monomer reactivity ratios have intermediate values: styrene–methyl methacrylate, $r_1r_2 = 0.26$; acrylonitrile–methyl methacrylate, $r_1r_2 = 0.24$.

The purpose of the present paper is to discuss these phenomena in more detail using the extensive experimental data recently presented from this Laboratory,[5] and also making reference to additional material to appear in subsequent papers in this series.[6]

**The Alternation Tendency in Copolymerization.**—An earlier paper[2b] stated that the alternating effect "seems sometimes to be due to steric effects, at other times to dipole effects or specific interactions (compound formation) between monomers." This section will amplify this statement in the light of the work cited above.[5,6] Price[7] has proposed that substitutents in a radical or monomer may withdraw or supply electrons from the site of reaction, resulting in effective charges on the trivalent or doubly bound carbon atoms. The alternating effect then arises from an attraction between a negative double bond and a positive radical, or *vice versa*. Alfrey and Price[8] have since attempted to place this suggestion on a general and quantitative basis, describing the reactivity of each monomer in terms of two parameters, referring to the "general monomer reactivity" ($Q$) and "polarity factor" ($e$). Bartlett and Nozaki[9] have mentioned the possibility that electron transfer from a donor radical to an acceptor monomer, or *vice versa*, in the activated complex may account for alternation tendencies, and we have developed and discussed this concept further in later papers in this series.[10]

(1) This paper is based on papers presented at the Atlantic City Meeting of the American Chemical Society, April 9, 1946 (Symposium on the Physical Chemistry of Copolymers and Copolymerization) and at the Gibson Island Conference on High Polymers, July 1, 1946.

(2) (a) Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944); (b) Lewis, Mayo and Hulse, *ibid.*, **67**, 1701 (1945).

(3) Wall, *ibid.*, **66**, 2050 (1944). This theoretical paper shows clearly how copolymer compositions depend on feed for representative monomer reactivity ratios. Some special cases were considered earlier by Jenckel, *Z. physik. Chem.*, **190A**, 24 (1942).

(4) Alfrey and Lavin, *ibid.*, **67**, 2044 (1945).

(5) (a) Lewis, Walling, Cummings, Briggs and Mayo, *ibid.*, **70**, 1519 (1947); (b) Mayo, Walling, Lewis and Hulse, *ibid.*, **70**, 1523 (1948); (c) Doak, *ibid.*, **70**, 1525 (1948); (d) Lewis, Walling, Cummings, Briggs and Wenisch, *ibid.*, **70**, 1527 (1948).

(6) (a) Lewis and Mayo, *ibid.*, **70**, 1533 (1948); (b) Walling, Briggs and Wolfstirn, *ibid.*, **70**, 1543 (1948).

(7) Price, *J. Polymer Sci.*, **1**, 83 (1946).

(8) Alfrey and Price, *ibid.*, **2**, 101 (1947); Alfrey, paper presented at Atlantic City Meeting, April, 1946.[1]

(9) Bartlett and Nozaki, THIS JOURNAL, **68**, 1495 (1946).

(10) (a) Walling, Briggs, Wolfstirn and Mayo, *ibid.*, **70**, 1537 (1948); (b) Walling, Seymour and Wolfstirn, *ibid.*, **70**, 1544 (1948).

TABLE I

PRODUCTS OF MONOMER REACTIVITY RATIOS IN COPOLYMERIZATIONS AT 60°

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Vinyl acetate | | | | | | | |
| | Butadiene | | | | | | |
| | 1.08 | Styrene | | | | | |
| 0.3 | | | Allyl acetate | | | | |
| .39 | | 0.34 | | Vinyl chloride | | | |
| <.3 | 0.19 | .26 | | | Methyl methacrylate | | |
| <.1 | | .16 | | | 0.61 | Vinylidene chloride | |
| | | .14 | | | | | Methyl acrylate |
| | | .10 | | | | | Methyl vinyl ketone |
| | | .054 | <.3 | | | .8 | β-Chloroethyl acrylate |
| | | .05 | | | .43 | | Methacrylonitrile |
| .25 | | .02 | | .07 | .24 | .34 | 1.1 Acrylonitrile |
| .004 | | .02 | | .06 | | .56 | Diethyl fumarate |

Both of these schemes lead to the prediction that the larger the *difference* in polarity or donor-acceptor properties between two monomers, the greater will be the alternation tendency, a conclusion which is given qualitative support by Table I. In this table, monomers have been arranged approximately in order of their increasing tendency to alternate with styrene, as measured by the decreasing products of monomer reactivity ratios. The monomers are then seen to be arranged approximately in order of the tendency of the substituents to accept electrons from the double bonds (*i. e.*, decrease the rate of substitution in the benzene ring). The acetoxy, vinyl and phenyl groups seem to be the best donors and poorest acceptors, followed by substituted alkyl, chlorine, carbalkoxy, carbonyl and nitrile groups. The effects of substituents are roughly additive. Considering the rather large experimental errors in some of the products, Table I is surprisingly consistent and gives strong support to the qualitative notion: in each horizontal row, the monomer reactivity ratio products tend to increase from a minimum value at the left margin to unity at the right end, and the products in each column tend to decrease from unity at the top to a minimum value at the bottom.

On the other hand, there are enough inconsistencies in Table II to suggest that such a scheme will not work quantitatively. For example, using the $Q$ and $e$ values of Alfrey and Price[8] for styrene, methyl methacrylate and acrylonitrile, $Q$ and $e$ values for methyl vinyl ketone and methacrylonitrile[5d] were each calculated from two independent sets of data. Styrene data give for methyl vinyl ketone, $Q = 0.75$ and $e = 0.51$, while the acrylonitrile data give $Q = 0.59$, $e = 1.00$. For methacrylonitrile, our styrene data give $Q = 0.59$, $e = 0.74$ while our methacrylate data give $Q = 0.95$, $e = 0.914$. Clearly some other factors must be considered. One of these is the existence of specific resonance interactions between certain radicals and monomers, often large, and perhaps involving actual electron transfer.[9,10] Another is the effect of differences in entropies of activation, or steric effects, most striking in the case of copolymerization of a 1- or 1,1-substituted ethylene with a 1,2-substituted derivative (as with styrene–diethyl fumarate[5a]), where alternation results (in half the steps) in more crowding of substituents. Such an effect may account for the abnormally low alternation tendency (large $r_1r_2$) in the diethyl fumarate-vinylidene chloride system (Table I) and for the high alternation tendency in the vinyl acetate–trichloroethylene system.[5b] In the latter case, polyvinyl acetate and the copolymer may be constructed from Fisher–Hirschfelder models while polytrichloroethylene cannot: an alternation tendency should be expected in general when a radical from a small monomer prefers to react with a more highly substituted monomer which cannot polymerize with itself. Further, comparison of *cis* and *trans* isomers in copolymerizations shows that even configurations of substituents in the activated complex are important in determining reactivity.[6a] While the above examples are all concerned with 1,2-substituted ethylenes, where steric effects were anticipated by Alfrey and Price,[8] there is good evidence of steric hindrance in the polymerization of 1,1-disubstituted ethylenes where these workers neglect steric effects: heats of polymerization of 1,1-substituted ethylenes (methyl methacrylate, 11.6 kcal./mole, isobutylene, 12.8 kcal./mole)[11] are significantly lower than for 1-substituted ethylenes (styrene, 16.1 kcal./mole,[12] acrylic acid, 18.3 kcal./mole[11]).

**Average Activities of Monomers in Copolymerization.**—The reciprocals of a series of monomer reactivity ratios for a reference radical with a number of monomers are the relative reactivities of the monomers toward the reference radical.[2] Table II summarizes data on monomers which have been tested in enough combinations to be of interest. The first column of figures gives the relative reactivity of monomers toward the vinyl acetate-type radical, taking the relative reactivity of vinyl acetate as one. Similarly, the second column gives the relative reactivity of monomers toward the styrene-type radical, taking the relative reactivity of styrene as one, *etc.* Since

(11) Evans and Polanyi, *Nature*, **152**, 738 (1943).

(12) Tong and Kenyon, THIS JOURNAL, **69**, 1402 (1947).

TABLE II

RELATIVE REACTIVITIES OF MONOMERS WITH VARIOUS RADICALS AT 60°[a]

| Radical Monomer | Vinyl acetate | Styrene | Allyl acetate | Vinyl chloride | Methyl methacrylate | Vinylidene chloride | Methyl acrylate | β-Chloroethyl acrylate | Acrylonitrile | Diethyl fumarate |
|---|---|---|---|---|---|---|---|---|---|---|
| α-Vinylpyridine | | 1.82 | | | 2.54 | | | | | |
| o-Chlorostyrene | | 1.78 | | | 2.0 | | | | | |
| Styrene | >50 | 1.00 | >50 | 50 | 2.2 | 12 | 5.5 | 10 | 25 | 14 |
| Methyl methacrylate | 70 | 1.9 | >50 | | 1.00 | 4.0 | | | 5.5 | |
| Methyl vinyl ketone | | 3.5 | | | | | | | 1.6 | |
| Methacrylonitrile | | 3.3 | | | 1.5 | | | | | |
| Acrylonitrile | 16 | 2.5 | | 50 | 0.75 | 2.7 | | | 1.00 | |
| β-Chloroethyl acrylate | | 1.9 | >50 | | | | 1.1 | 1.00 | | |
| Methyl acrylate | 10 | 1.34 | | | | *1.0** | 1.00 | 1.1 | | |
| Vinylidene chloride | >30 | 0.54 | | *3.2** | .40 | 1.00 | *1.0** | | 1.1 | 22 |
| Methallyl chloride | 8[c] | *.05* | | 3.2[d] | *.13* | 0.9 | | | | |
| Methallyl acetate | | .014[g] | | | *.1* | *.42* | | 0.25 | | |
| Vinyl chloride | 4.3 | .06 | | 1.00 | *.08* | *.31* | *0.2* | | 0.30 | 2.1 |
| Vinyl acetate | 1.00 | .02 | 2.2 | 0.60 | .05 | .28 | .11 | | .25 | 2.3 |
| Isobutylene | | | | .49 | | *.65* | | | | *0.3** |
| Vinyl ethyl ether | 0.33 | .01 | | | | *.31* | *.3* | | *.2* | |
| Allyl chloride | | .03[b] | | | *.02* | *.22* | | | *.18* | |
| Allyl acetate | 1.7 | .011[g] | 1.00 | .86[e] | .043[g] | *.15* | *.2* | .18 | | |
| Maleic anhydride | >50 | | >130[f] | | | .11 | *.4** | | *.17* | |
| Diethyl fumarate | 90 | 3.3 | | 8.3 | | .08 | | | *.12* | 1.00 |
| Diethyl maleate | 6 | .15 | | 1.3 | *.05** | *.08* | | | *.08* | |
| Trichloroethylene | 1.5 | .06 | | | *.01* | | *.03** | | *.015* | |
| *trans*-Dichloroethylene | 1.0 | .03 | | | | | | | | |
| *cis*-Dichloroethylene | .16 | .005 | | | | | | | | |
| Tetrachloroethylene | .15 | .005 | | | | | .005 | | .007 | |

[a] Italic values have been calculated from α-values obtained from single experiments in a preliminary survey carried out largely by Mr. W. F. Hulse. The results have not been reported elsewhere, but, except when starred, are probably accurate within a factor of two. [b] Alfrey and Harrison, THIS JOURNAL, **68**, 299 (1946) (70°). [c,d,e] Calculated from Moffett and Smith, U. S. Patent 2,356,871. Reactions at 80°, 45°, 40°, respectively. [f] Ref. (9), 35°, [g] Doak and Walling, unpublished work.

the reactivities in various columns are related by the ratios of the rate constants for chain growth of the standard monomers, relations between columns must await determinations of these constants.

The radicals at the top of Table II are arranged in order of decreasing electron-donor tendencies, increasing electron-acceptor tendencies, as listed in Table I. Except that 1,2-disubstituted ethylenes have been arbitrarily grouped at the bottom for later discussion, the order of the monomers in the first column is a compromise arranged so that the reactivities decrease in each column. The decrease in each column is sufficiently uniform, within the often considerable experimental error, that the order approximates the average activities of the monomers. The lack of uniformity can be correlated qualitatively with the alternating tendency. For example, the monomers immediately below styrene are more reactive toward the styrene-type radical for this reason. Similarly, the relative reactivities of vinyl chloride and vinyl acetate change as the electron-accepting properties of the attacking radical increase. Quantitative changes in relative reactivities, without change in order, in other addition reactions of double bonds suggest that the order of stability of radicals is tertiary > secondary > primary.[13] Thus, those addition reactions to double bonds are preferred where the new radical formed is the most stabilized by resonance. However, the conjugation and hyperconjugation which stabilize the radicals should also stabilize the double bonds (but to a lesser extent since there will be a greater energy difference between the main and resonating structures), making the double bonds less reactive. Since the conjugated double bonds are actually more reactive, the conjugation must stabilize the activated complex more than the monomer, a conclusion consistent with the expectation that the resonance stabilization in the activated complex should be intermediate between the initial and final states. In other words, direct attachment of a vinyl, phenyl, carbonyl, carboxyl, nitrile or alkyl group to a double bond reduces the activation energy required for formation of the activated complex when any radical approaches. This conclusion is consistent with the proposal to be developed later[10] relating alternation effects to resonance contributions to the activated complex.

It follows from the above conclusions about

(13) Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 238; Mayo and Walling, *Chem. Rev.*, **27**, 373 (1940).

resonance stabilization in monomers and radicals that, in general, the most reactive monomers are converted, in polymerization, to the least reactive radicals and the least reactive monomers yield the most reactive radicals.

**Effects of Substituents.**—The conclusions of the last two sections on the copolymerization of the 1- and 1,1-substituted ethylenes are summarized in Table III. The "average activity series," based on Table III, shows the effects of substituents on the ease with which an ethylene derivative reacts with an average radical and on stabilizing the radical which will be formed. The electron "donor-acceptor series," based on Table I, is a measure of the abilities of the substituents to serve as donors or acceptors in radical monomer interactions. The effects of a second $\alpha$-substituent are roughly additive in both series.[14]

TABLE III

THE EFFECTS OF SUBSTITUENTS ON THE COPOLYMERIZATION OF MONOSUBSTITUTED ETHYLENES, R'—CH=CH$_2$

| Average activity series (Increasing activity ↑) | Donor-acceptor series (Increasing acceptor ability ↓ / Decreasing donor ability ↑) |
|---|---|
| $C_6H_5$— | R—O— |
| $H_2C$=CH—[a] | $H_2C$=CH— |
| R—CO— | $C_6H_5$— |
| N≡C— | R—$CH_2$— |
| R—O—CO— | H—(?) |
| Cl— | Cl |
| R—O— } | R—CO— } |
| R—$CH_2$— } | R—O—CO— } |
| H—(?) | N≡C— |

[a] As pointed out to us by Dr. T. Alfrey, although butadiene is about four-thirds as reactive as styrene, it contains two vinyl groups, each of which must be two-thirds as reactive as the vinyl group in styrene.

When two monomers lie close together in the donor–acceptor series then the copolymer will be the "ideal" or random type. If the monomers are also close together in the average activity series (example, styrene–butadiene),[5d] the composition of the copolymer will approximate the composition of the feed. The greater the separation of the monomers in the average activity series, the greater will be the tendency of the more reactive monomer to predominate in the copolymer; the less reactive monomer may be practically excluded (example, styrene–vinyl acetate[5b]).

When two monomers are well-separated in the donor-acceptor series, then they will have a marked tendency to alternate in copolymerization. If neither monomer polymerizes easily by itself (*e. g.*, stilbene–maleic anhydride),[6a] or if they lie close together in the average activity series (*e.g.*, styrene–acrylonitrile)[2b] then the products will approximate a 1:1 copolymer as long as the feed permits. These are the conditions under which a system is most likely to form an azeotropic copolymer, the only requirement being that both monomer reactivity ratios be less than unity.[8] On the other hand, if the monomers are well separated in both series, then the more reactive monomer will predominate to an extent such that the alternating effect will be apparent only from the monomer reactivity ratios or their product (example, acrylonitrile–vinyl acetate).[5b]

**Copolymerization of 1,2-Disubstituted Ethylenes.**—Toward the styrene-type radical, diethyl fumarate is 2.5 times as reactive as methyl acrylate[5a] and fumaronitrile[6a] is twice as reactive as acrylonitrile, but these bifunctional monomers have two equally probable sites of reaction. The fumaric ester is about ten times as reactive as the acrylic ester toward the vinyl acetate-type radical. Toward the radicals which are poorer donors, however, the acrylate seems more reactive than the fumarate. These results show that a 2-carbethoxy group enhances the reactivity of ethyl acrylate toward donor monomers but decreases activity toward acceptor monomers. However, results in the polychlorinated ethylenes[5c] reveal only a retarding effect of 2-substituents.

**Rates of Polymerization and Copolymerization.**—Comparison of some over-all rates of polymerization of single monomers has yielded the following order of decreasing rates with 0.1 mole % of benzoyl peroxide at 60°: methyl acrylate, acrylonitrile, vinyl acetate, methyl methacrylate, vinyl chloride, vinylidene chloride, styrene, $\alpha$-methacrylonitrile, allyl chloride, allyl acetate, isobutylene, vinyl ethyl ether.[15] This order has no relation to the order of activity of these monomers in copolymerization, or to conjugation, since over-all rates are determined primarily by the competition between chain growth and chain termination reactions and since they involve the rate of reaction of a different radical with each monomer, not the relative reactivities of monomers toward a common radical. Over-all rates in copolymerization are even more complex, and can be discussed quantitatively only if absolute rate constants are known.[16] Although such a discussion will be presented shortly from this Laboratory, some qualitative generalizations are worth mention here. First, copolymerization of two monomers far apart on the polarity series will frequently lead to much higher rates than are obtained for either monomer alone. This effect is observed in most copolymerizations of maleic anhydride with donor monomers[9] and arises because the rate of the chief growth step for each radical is greatly increased. Second, addition of a small amount of a reactive monomer may markedly inhibit the polymerization of an unreactive monomer close to it in the polarity series, as in the inhibition by styrene of the polymerization of vinyl acetate. A series

(14) An interesting observation is that even rather remote substitution may change monomer reactivity ratios appreciably. Thus values for styrene–methyl acrylate, 0.75 and 0.18,[5a] are changed to 0.54 and 0.10, respectively, for styrene-$\beta$-chloroethylacrylate.[5d]

(15) Experiments in this Laboratory by R. Van Meter and D. M. Alderman.

(16) Melville, Noble and Watson, *J. Polymer Sci.*, **2**, 229 (1947).

of experiments[17] showed that the inhibition depended on the catalyst concentration. Below about 0.4 mole % of styrene, one molecule of catalyst per molecule of styrene would permit the formation of a hard polymer in twenty-four hours at 70° while less catalyst (although ample to polymerize vinyl acetate alone) gave little polymer. At higher styrene concentrations, a higher ratio of catalyst to styrene was required unless much longer reaction times and addition of fresh catalyst were allowed. The result was then a mixed polymer. Copolymerization data show that styrene is at least fifty times as reactive as vinyl acetate toward both radicals. Hence with about 0.1% styrene in vinyl acetate, although the vinyl acetate radicals can add rapidly to vinyl acetate, they have a strong preference for styrene and are rapidly converted to styrene-type radicals. While these styrene radicals can add readily enough to styrene, this monomer is present only in very low concentration and the vinyl acetate is unreactive, acting like a rather inert diluent. As a result, relatively little chain growths occurs before two radicals meet and destroy each other, but if enough catalyst is supplied to sweep out the last traces of styrene, then the vinyl acetate can polymerize normally.

(17) Unpublished results by Drs. R. T. Armstrong and D. W. Sherwood, obtained in these laboratories in 1942.

## Summary

Survey of the extensive new data from this laboratory is shown to support the conclusion that the reactivities of monomers in copolymerization are determined by an order of average monomer activity on which is superimposed a tendency toward alternation. The average activity of monomers depends largely on conjugation, *i. e.*, on the possibilities of resonance stabilization of the activated complex and resulting radical. The alternation tendency seems to result from several factors which are roughly summarized as the ability of one monomer (or radical) of a pair to donate electrons to the other radical (or monomer) of the pair. Tables show the effects of substituents on both the average activity and electron-donating ability of monomers.

Limited data on symmetrically substituted ethylenes show that the behavior of these monomers is more complicated than that of the 1- and 1,1-substituted monomers.

The qualitative relations between reactivity in copolymerization and over-all polymerization rates are discussed.

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# Copolymerization. IX. A Comparison of Some *cis* and *trans* Isomers[1,2]

BY FREDERICK M. LEWIS AND FRANK R. MAYO

As a study of the principles governing copolymerization was getting under way in this Laboratory, the paper by Marvel and Schertz[3] called our attention to the fact that dimethyl fumarate had a greater tendency than dimethyl maleate to enter a copolymer with *p*-chlorostyrene. Since any general scheme of copolymerization must account for such differences, we have compared the behavior of six pairs of geometrical isomers with a total of four other monomers. The results support our previous conclusion[1] that the possibilities of resonance stabilization of the activated complex is a critical factor determining the activity of a monomer toward a free radical.

## Experimental

**Materials.**—Stilbene, maleic anhydride and methyl fumarate and maleate esters were Eastman Kodak Co. materials used without purification. The half esters were prepared according to the directions of Shields.[4] Eastman Kodak Co. mixed dichloroethylenes were separated by fractional distillation through a packed column: *trans*, b. p. 48.0 at 752 mm., $n^{20}D$ 1.4454; *cis*, b. p. 60.6 at 772 mm., $n^{20}D$ 1.4486. Wood and Dickinson[5] give: *trans*, b. p. 47.2° at 745 mm.; *cis*, b. p. 59.6 at 745 mm. Isostilbene was prepared by Mr. R. W. Strassburg by the partial hydrogenation of tolane. It distilled at 82.5° at 0.5 mm. and melted at −28 to −26°, although the melt was slightly cloudy up to 0°. This clearing point indicates that the product contains less than 3% *trans*-stilbene.[6]

Fumaronitrile was prepared from fumaramide and phosphorus pentoxide.[7] The nitrile was then partially isomerized to maleonitrile with hydrogen chloride in ether.[8] From 24 g. of crude product were obtained, by fractional distillation and crystallization, 12.6 g. fumaronitrile (m. p. 96–97°), 3.1 g. maleonitrile (m. p. 23–27°) and 2.10 g. chlorosuccinonitriles. These yields are in fair agreement with determinations of equilibrium mixtures. Mommaerts[9] isomerized the *cis* isomer thermally to a 50% *cis-trans* mixture in 1180 hours at 105–110° but apparently did not reach equilibrium. We have heated the *trans* isomer in a sealed, evacuated tube at 140° for seventy

(1) For the preceding paper in this series, see Mayo, Lewis and Walling, THIS JOURNAL, **70**, 1529 (1948).

(2) The conclusions of this paper were presented at the Symposium on the Physical Chemistry of Copolymers and Copolymerization at the Atlantic City Meeting of the American Chemical Society, April 9, 1946, and at the Gibson Island Conference on High Polymers, July 1, 1946.

(3) Marvel and Schertz, THIS JOURNAL, **65**, 2054 (1943).

(4) Shields, *J. Chem. Soc.*, **59**, 736 (1891).

(5) Wood and Dickinson, THIS JOURNAL, **61**, 3259 (1939). Extrapolation of their data indicates that the equilibrium mixture of the isomers contains 22% *trans* at 60°. Equilibria in the vapor phase are not greatly different: *cf.*, Olson and Maroney, *ibid.*, **56**, 1320 (1934).

(6) Taylor and Murray, *J. Chem. Soc.*, 2078 (1938).

(7) de Wolfe and van de Straete, *Bull. soc. chim. Belg.*, **44**, 288 (1935).

(8) Mommaerts, *Bull. Acad. Roy. Belg.*, **27**, 579 (1941).

(9) Mommaerts, *Bull. soc. chim. Belg.*, **52**, 79 (1943).