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.

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[17] Unpublished results by Drs.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

[CONTRIBUTION NO. 71 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

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

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[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).

hours with a trace of iodine and apparently obtained an equilibrium mixture containing 76% fumaronitrile as determined from the melting point phase diagram.

Other materials have been described in previous papers.

Procedure.—Except as indicated, experiments were put up and polymers isolated as described previously. When a polymer was of low molecular weight, the solution above the precipitate was concentrated and examined for polymer, which was combined with the main lot when found in appreciable quantities. This procedure permitted distillation of the monomer from a small fraction of the polymer instead of from the whole product.

Results are summarized in Tables I and II.

TABLE I

RATES OF COPOLYMERIZATION OF EQUIMOLECULAR MIXTURES OF MALEIC ANHYDRIDE AND STILBENE AT 60°

Moles of each monomer	Stilbene isomer	Chloroform, cc.	Reaction time, hr.	Yield, wt. %
0.0250	*trans*	7.00	15.3	61.0[a]
.0250	*cis*	7.00	15.3	35.6[b]
.0100	*trans*	2.80	3	21.9[c]
.0100	*cis*	2.80	3	13.3[c]

[a] Stiff polymer cut into thin slices, extracted twice with boiling methyl ethyl ketone, washed with petroleum ether, dried, ground, and heated to 100° at 1 mm. pressure for two to three hours. [b] Soft polymer broken up and soaked in methyl ethyl ketone for three days, washed on filter with petroleum ether and dried as in *a*. [c] Reaction products heated slowly at 3 mm. pressure up to 175°. Residue taken as polymer.

TABLE II

COPOLYMERIZATION OF REFERENCE MONOMERS (M_1) WITH *cis* AND *trans* ISOMERS (M_2) WITH 0.2 MOLE % BENZOYL PEROXIDE AT 60°

$[M_1]_0$[a]	$[M_2]_0$[a]	$[M_1]$[a]	$[M_2]$[a]	Reaction time, hr.	Polymer analyses	
	Styrene–Dimethyl Fumarate				% C	
64.00	16.68	47.38	8.46	32.0	75.28	75.06
40.40	39.53	25.46	26.80	35.1	70.02	79.86
16.10	62.60	3.16	49.25	30.2	67.33	67.31
	Styrene–Dimethyl Maleate				% C	
63.90	17.42	28.50	15.85	42.7	88.91	89.72
40.00	42.18	22.40	39.76	21.1	85.75	85.45
16.07	67.80	79.15	63.45	11.4	77.54	77.39
	Styrene–Monoethyl Fumarate				% C	
69.80	21.75	60.10	16.08	5.0	73.24	73.34
39.50	32.60	29.40	32.30	3.2	67.34	67.58
20.05	44.30	11.45	32.80	2.2	64.78	64.93
	Styrene–Monoethyl Maleate				% C	
72.70	61.85	23.35	16.04	2.1	71.85	71.87
40.00	34.91	48.68	43.90	3.0	68.03	
16.05	35.78	78.00	62.85	2.1	65.77	65.74
	Styrene–Fumaronitrile				% N	
80.10	21.55	54.45	7.42	8.5[c]	10.06	
79.10	20.00	50.60	6.09	8.5[c]	9.63	
19.95	79.20	5.01	65.70	3[c]	14.50	
19.80	79.82	4.20	66.85	3[c]	14.31	
78.70	19.86	73.229	16.997	2[d]	10.00	10.23
	Styrene–Maleonitrile				% N	
19.89	4.62	16.30	2.818	8.5[d]	9.81	
6.795	28.10	3.507	25.30	32.5[e]	13.90	
78.60	19.43	74.324	17.083	2[c]	10.48	10.45
	Styrene–*trans*-Dichloroethylene				% Cl	
78.89	19.18	54.29	19.00	24	0.43	0.55
79.06	19.57	54.96	19.38		0.54	0.54
	Styrene–*cis*-Dichloroethylene				% Cl	
77.83	20.47	59.12	20.44	24	0.09	0.12
78.18	20.35	51.48	20.31		0.07	0.12
	Vinyl Chloride–Diethyl Fumarate				% Cl	
16.48	78.65	11.02	59.07	26	5.13	5.31
17.40	79.32	11.96	62.82	25	6.05 5.51	6.41 5.90
95.19	21.65	78.94	11.03	5.6	20.26	20.27
100.50	21.75	86.69	12.68	5.6	20.17	20.20
	Vinyl Chloride–Diethyl Maleate				% Cl	
28.85	64.96	12.56	51.78	53	17.56	17.60
32.48	64.40	12.99	49.06	51	17.84	17.99
87.74	10.32	63.63	7.096	15.25[b]	41.52	41.44
84.89	10.13	60.01	6.925	15.25[b]	41.77	42.01
	Vinyl Acetate–Diethyl Fumarate				% AcOH[f]	
15.90	62.90	11.75	51.13	8	10.45	
15.82	63.34	11.95	52.38	8	10.48	
58.30	11.79	51.56	5.03	1.25	23.20	
59.07	12.14	51.68	4.75	1.25	23.24	
	Vinyl Acetate–Diethyl Maleate				% AcOH[f]	
15.63	66.55	9.56	59.50	9	21.00	
16.07	64.33	9.82	56.98	9	20.80	
57.72	13.47	49.33	8.73	2.5	32.76	
58.68	13.69	50.29	9.11	2.5	33.37	
	Vinyl Acetate–*trans*-Dichloroethylene				% Cl	
78.15	18.86	33.97	9.81	7.5	13.74	13.70
78.40	20.26	34.88	10.65	7.5	14.51	14.59
19.46	79.25	1.09	49.50	121	47.19	47.33
18.91	76.95	0.41	46.44	136	47.59	47.53
	Vinyl Acetate–*cis*-Dichloroethylene				% Cl	
78.30	20.51	17.15	16.37	7.5	5.22	5.11
78.40	20.46	15.71	16.22	7.5	5.18	5.13
19.00	81.25	0.35	65.87	121	35.07	35.22
19.61	79.75	.19	64.57	121	34.12	34.15

[a] Millimoles of unreacted monomers; zero subscripts indicate initial concentrations. [b] Contained 5.00 cc. chlorobenzene. [c,d,e] Contained 10,[c] 2.5,[d] or 3.75[e] cc. of chloroform, respectively. [f] The % acetic acid was determined by the method described by Mayo, Walling, Lewis and Hulse, THIS JOURNAL, 70, 1523 (1948), corrected empirically from the error in the nearest known sample: copolymers of diethyl fumarate and vinyl acetate, known to contain 10.97, 21.06 and 28.24% acetic acid, analyzed for 11.45, 20.90 and 27.95% acetic acid.

Vinyl acetate runs containing a high proportion of dichloroethylene were not precipitated at all but were heated slowly at 1 mm. pressure to remove monomer, finally for a minute or two at 150–175°. These residues were then analyzed directly.

The high vinyl chloride runs with diethyl maleate gave a precipitate of polymer and chlorobenzene was therefore added to some to keep them homogeneous. In low vinyl chloride runs, monomer reactivity ratios for the maleate radical varied with the isolation procedure although checks were obtained with each procedure: (a) simply distilling off the monomer from the soft liquid polymer at 150–200° and 2 mm. pressure gave 0.10; (b) precipitating the polymer three times, concentrating the liquors at reduced pressure and combining this residue with the polymer gave 0.05; (c) distilling off the bulk of the unreacted diethyl maleate first, then treating as in (b) with repeated washings of precipitated polymer with petroleum ether gave 0.009, the recorded results. The high vinyl chloride runs showed little difference between procedures (b) and (c), the polymers being harder and less readily soluble.

Chloroform was used as a solvent for all the dinitrile runs because fumaronitrile was immiscible with styrene. The polymers precipitated from solution as highly swollen gels; they were precipitated three times from methyl ethyl ketone with methanol and were then swollen in benzene

TABLE III

COMPARISON OF *Cis* AND *Trans* ISOMERS IN COPOLYMERIZATION

Reference monomer (M_1)	r_1	*cis–trans* isomer (M_2)	r_2	More reactive isomer	Less stable isomer	Planar *cis* form hindered
Styrene	0.30 ± 0.02[a]	Diethyl fumarate	0.070 ± 0.007[a]	*trans*	*cis*	+
	6.52 ± .50[a]	Diethyl maleate	< .01[a]	(21)[f]		
Styrene	0.21 ± .02	Dimethyl fumarate	.025 ± .015	*trans*	*cis*	+
	8.5 ± .2	Dimethyl maleate	.03 ± .01	(40)		
Styrene	0.18 ± .10	Monoethyl fumarate	.25 ± .10	no significant difference		
	.13 ± .01	Monoethyl maleate	.035 ± .01		*cis*	−
Styrene	.19 ± .03	Fumaronitrile	.0		*cis*	−
	.19 ± .01	Maleonitrile	.0			
Styrene	37 ± 3	*trans*-Dichloroethylene	.0	*trans*	*trans*	−
	210 ± 15	*cis*-Dichloroethylene	.0	(6)		
Vinyl chloride	.12 ± .01	Diethyl fumarate	.47 ± .05	*trans*	*cis*	+
	.77 ± .03	Diethyl maleate	.009 ± .003	(6.5)		
Vinyl acetate	.011 ± .001	Diethyl fumarate	.444 ± .003	*trans*	*cis*	+
	.17 ± .01	Diethyl maleate	.043 ± .005	(15)		
Vinyl acetate	.99 ± .02	*trans*-Dichloroethylene	.086 ± .01	*trans*	*trans*	−
	6.3 ± .2	*cis*-Dichloroethylene	.018 ± .003	(6.5)		
Maleic anhydride	0.03 ± .03	Stilbene	.03 ± .03	*trans*	*cis*	+
	.08 ± .08	Isostilbene	.07 ± .07	(1.5–2.0)[b]		
Diethyl maleate or fumarate		Diethyl fumarate		*trans*	*cis*	+
		Diethyl maleate		(52,[c] 10[d], >7[e])		
Dichloroethylene		*trans*-Dichloroethylene		*trans*	*trans*	−
		cis-Dichloroethylene		(4.8)[d]		

[a] Experimental errors for ethyl esters are based on a possible 0.1 or 0.2% error in carbon analyses.[10] Experimental errors in other instances represent the areas of the intersections obtained in graphical solutions of the copolymerization equation. [b] From rates of polymerization, Table I. [c,d,e] From copolymerizations with vinyl chloride, vinyl acetate, and styrene, respectively. [f] Ratio of reactivities of two isomers toward reference radical.

and subjected to the freezing procedure, or dried in powder form when obtainable.

The copolymers formed from all maleic anhydride-stilbene feeds were 1:1 copolymers within experimental error. The *rates* of copolymerization of the two isomers were therefore compared. Even in chloroform the polymers formed a gel, including all the reaction mixture and becoming stiffer as the reaction progressed. Data are summarized in Table I.

Discussion

Results of comparisons of *cis* and *trans* isomers are summarized in Table III. The experimental errors given were, in general, obtained from the standard deviation of individual experiments.[10] In the cases of some of the maleic and fumaric esters, however, the low volatility of these monomers and their high solubility in the polymer made their complete removal difficult and actual errors may be larger. This is especially likely for the vinyl acetate–maleate and fumarate and styrene–methyl maleate and fumarate systems with which special precautions[10] (see Experimental part, also ref. 10) were not taken.

The addition of a free radical to either a *cis* or *trans* isomer presumably results in the formation of the same free radical with the three attached substituents in the same plane[11] or with a pyramidal configuration which is easily reversible. Accordingly, addition to the isomer which is less stable thermodynamically might be expected to require less activation energy, so that this isomer should be the more reactive. However, the data show that dialkyl fumarates are 6–20 times as reactive as the maleates toward the styrene, vinyl chloride, and vinyl acetate radicals. Our previous conclusion that the possibilities of resonance in the activated complex[1] is a major factor governing the reactivity of double bonds toward free radicals suggests a probable explanation for such results. When a radical adds to these monomers, the activated complex can be stabilized by resonance between forms I–III only if the oxygen of the carbonyl group involved lies in the same plane as the other atoms attached to the doubly-bound carbon atoms.

Consideration of models shows that the two ester groups in maleic esters cannot be coplanar simultaneously and interference between them is such that a coplanar configuration for either is not very probable. On the other hand, in the fumaric esters either or both ester groups may be coplanar. Such an interpretation also suggests a reason for the high reactivity of the double bond of maleic anhydride[1] in which both carbonyl groups are constrained to a coplanar configuration by the five-membered ring. Price[12] has proposed that purely steric effects can account for the observed differences without considering resonance.

Similarly, in *cis*-stilbene, both rings cannot be

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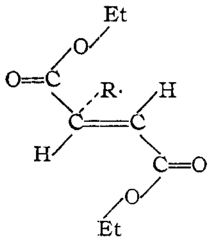
(10) Lewis, Walling, Cummings, Briggs and Mayo, THIS JOURNAL, **70**, 1519 (1948).

(11) An unsuccessful search for differences in the free radicals from the *sym*-dichloroethylenes was made by K. E. Wilzbach in this Laboratory.

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



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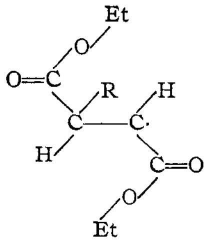

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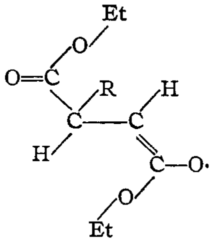

III

simultaneously coplanar and the possibilities of activation of the double bond by the phenyl groups are less favorable than in *trans*-stilbene. The rate data show that the *trans* form is 1.5–2 times as reactive as the *cis* form toward the maleic anhydride radical.[13] The half esters of maleic and fumaric esters did not differ significantly. Here the smaller size of the substituent and the possibilities (at least) of hydrogen bonding and ring formation in the *cis* form reduce the difference found between the normal esters.

In the cases of the dichloroethylenes and the dinitriles, no steric inhibition of resonance can be involved. Although the ratio of *cis* to *trans* forms in the equilibrium mixture of the dichloroethylenes is about 3.5, the *trans* form reacts 6–7 times as fast with both the styrene and vinyl acetate radicals. Thus the difference in free energy of activation is greater than the free energy difference in the monomers. The equilibrium *trans*:*cis* ratio in the dinitriles is about 3.0, but there is no difference in reactivity. Here the difference in rate of reaction is less than would be anticipated. These results show that the isomer pairs do not yield the same activated complex (whether or not they are eventually converted to the same radical) and that there is no consistent relation between the free energies of the isolated monomers and their free energies of activation. The results further suggest that the dipole and resonance effects and energy levels which determine the relative stabilities of the pure monomers lead to larger differences in the stabilities of the activated complexes.

Our data show that coplanarity of conjugated groups is an important factor determining the relative reactivities of *cis–trans* isomers in copolymerization. The general principle that the less stable isomer should be more reactive is only a qualitative guide in other cases, showing that other factors must be considered. Factors such as general availability of electrons in the double bonds[14] or dipole moment have not led to useful correlations in these compounds. The present work suggests also that the steric inhibition of resonance should be important in the copolymerization of 1,1-disubstituted ethylenes: vinylidene chloride is considerably more reactive than vinyl chloride and 1,1-dicyanoethylene should be much more reactive than acrylonitrile, but because of interference between the 1-substituents, considerably less difference should be expected between 1,1-diphenylethylene and styrene, or between methylenemalonic esters and acrylic esters.

Summary

The relative reactivities of the *cis* and *trans* forms of six pairs of isomers have been compared with radicals from a total of four monomers. The order of decreasing activity, maleic anhydride, fumaric esters, maleic esters, parallels the decreasing ability of these monomers to assume a planar configuration and thus to stabilize the activated complex by resonance with the carbonyl groups. Similarly, the inability of both phenyl groups in isostilbene to resonate with the double bond accounts for the higher reactivity of stilbene.

Of the 1,2-dichloroethylenes, the less stable *trans* form is more reactive, while maleonitrile and fumaronitrile are equally reactive. Thus, steric inhibition of resonance, when it occurs, seems to determine the relative reactivities of geometrical isomers, and the relative stabilities of the isomers has only a qualitative relation to reactivity in other cases.

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(13) This comparison of rates assumes that the rate of chain initiation is the same in both monomer mixtures, and that both isomers yield the same free radical, so that the rates of reaction of this radical with maleic anhydride and the rates of chain termination are the same in both experiments.

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