to make a homogeneous mixture, was heated under a reflux condenser for thirty minutes. The new salt which separated was precipitated from a water solution by acetic acid; yield 1.4 g. It crystallized from hot water as small needles which partially melted at 256–258° with foaming. It has been assumed that methylation occurs in position one.

Anal. Calcd. for $C_7H_9N_3O_3$: C, 45.9; H, 4.9. Found: C, 45.7; H, 5.0.

1,2,3,6-Tetrahydro-2-imino-5-amino-6-ketopyrimidine-4-acetic Acid.—Five grams of II dissolved in cold nitric acid quickly reprecipitated as the corresponding salt which charred if separated and heated to 100°. Sufficient water was added to the pasty mixture to clear it, after which it was evaporated to dryness in a porcelain dish on a water-bath. A vigorous reaction followed, in which oxides of nitrogen were released; yield 2–3 g. Two grams of the nitro compound suspended in hydrochloric acid containing tin slowly dissolved, following digestion on a steam-bath. The needle-like crystals that separated on standing were dissolved in water containing ammonia and reprecipitated by dilute acetic acid; yield 0.5 g. of microscopic plates; m. p. indefinite with decomp.

Anal. Calcd. for $C_6H_8N_4O_3$: H, 4.3; C, 39.1. Found: C, 38.7; H, 4.5.

1,2,3,6-Tetrahydro-2-imino-5-bromo-6-ketopyrimidine-4-acetic Acid.—Three grams of II suspended in a small volume of glacial acetic acid quickly reacted with the molar equivalent of bromine. No fumes of hydrogen bromide were noticed although, if the mixture was heated, bubbles of carbon dioxide escaped. A rather poor yield of product (3 g.) resulted on dilution with ice water and proved to be the hydrogen bromide salt of the expected product. Unless repeatedly recrystallized, the bromine content of the plate-like crystals ran high. The free base obtained by neutralization with ammonia followed by precipitation with acetic acid, crystallized from hot water or alcohol as small straw colored needles. Both substances melt indefinitely with blackening.

Anal. Calcd. for $C_6H_6BrN_3O_3$: Br, 32.3. Found: Br, 32.3. HBr salt. Calcd. for $C_6H_7Br_2N_3O_3$: Br, 48.6. Found: Br, 48.5.

Summary

The properties of 2-iminopyrimidine-4-acetic acid have been investigated. Certain nitric, amino and halogen derivatives have been prepared as well as an ester, a chlorinated ester and the acid amide.

MEDFORD, MASSACHUSETTS RECEIVED JULY 27, 1943

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Copolymers of *p*-Chlorostyrene and Methyl Methacrylate[1]

BY C. S. MARVEL AND G. L. SCHERTZ[2]

It has been found that the polymerization of mixtures of vinyl chloride and vinyl acetate[3] gives heterogeneous copolymers because of the unequal tendency of the two monomers to enter the growing polymer chain. The high volatility of vinyl chloride made it difficult to measure accurately the α-value of Wall[4] which is the ratio of the rates at which the monomers enter the chain. It seemed worth while, therefore, to select a pair of monomers which were more readily handled and study the effect of the polymerization conditions on the α-value in order to see if changes in these conditions might lead to an α-value of one and thus permit the formation of more homogeneous products.

Some indication that the ratio of the rates at which vinyl chloride and vinyl acetate enter the growing copolymer chain approaches a value of one at 150° was noted by Jones[5] but the reliability of the results was questioned because of the practical difficulty in handling vinyl chloride. Lawson[6] has reported that polymerization of a mixture of vinyl chloride and vinyl acetate in ethyl acetate solution at 120° gives a copolymer in which the ratio of vinyl chloride to vinyl acetate is less than it was in the monomer mixture from which the copolymer is formed, thus indicating an α-value of less than one. These pieces of work indicate that the α-value for a given pair of monomers entering a copolymer can be changed by conditions of the reaction.

By selecting *p*-chlorostyrene and methyl methacrylate for this study it was possible to obtain pure, fairly high boiling monomers which could be weighed accurately to determine the composition of the monomer mixtures. The copolymers produced were readily isolated as solids which were easy to handle. The composition of the copolymers could be obtained by analysis for chlorine.

When bulk polymerizations of these two mono-

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[1] This is the seventeenth communication on the structure of vinyl polymers. For the sixteenth see THIS JOURNAL, **65**, 1710 (1943).

[2] Monsanto Fellow in Chemistry, University of Illinois, 1942–43.

[3] Marvel, Jones, Mastin and Schertz, THIS JOURNAL, **64**, 2356 (1942).

[4] Wall, *ibid.*, **63**, 1862 (1941).

[5] Jones, Ph.D. Thesis, University of Illinois, 1942.

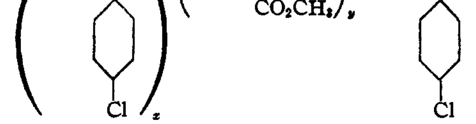
[6] Lawson, U. S. Patent 1,867,014 (1932).

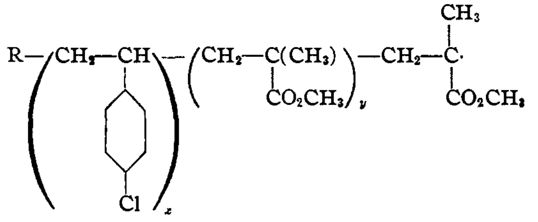
mers catalyzed by benzoyl peroxide were carried out at room temperature for various times it was found that the ratio of the rate of entry of *p*-chlorostyrene into the polymer to that of methyl methacrylate was 1.46 ± 0.20. Changes in temperature of polymerization over the range of 40 to 120° did not change this value. Polymerizations carried out under ultraviolet irradiation, and in the solvents dioxane, acetone and methyl alcohol gave the same value for α.

When these two monomers were polymerized alone in bulk under comparable conditions, methyl methacrylate alone polymerized to give 85.6% yield of polymer in forty-five hours whereas *p*-chlorostyrene gave only a 23.8% yield in forty-five hours and a 40.2% yield in sixty-six hours. The copolymer forms at about the same rate as the *p*-chlorostyrene polymer, since a 45.2% yield was obtained in sixty-six hours. Thus apparently the *p*-chlorostyrene polymerizes more slowly alone than does methyl methacrylate whereas in the copolymerization it enters the growing polymer chain faster. Norrish and Brookman[7] have measured the rates of polymerization of styrene, methyl methacrylate and various mixtures of the two. They have found that methyl methacrylate polymerizes three to four times as fast as styrene and that the rate of copolymerization is governed by the styrene content.

For the purpose of determining whether or not the chlorine atom accelerated the rate of polymerization of the styrene, mixtures of *p*-chlorostyrene and styrene were polymerized in bulk with benzoyl peroxide. The substituted styrene polymerized more rapidly than styrene under these conditions; α had the value 1.34 ± 0.20. Since nearly the same ratio, 1.28 ± 0.20, was obtained when *m*-chlorostyrene was polymerized with styrene, it is apparent that this activation by chlorine substitution is not dependent upon a particular position in the ring. A second comparison of the *meta* and *para* isomers was made by polymerizing each with methyl methacrylate. The values obtained for α, 1.46 ± 0.20 for *p*-chlorostyrene with methyl methacrylate and 1.42 ± 0.20 for the *meta* isomer, are essentially the same. *m*-Chlorostyrene was used in the last seven experiments described in Table I.

Growing *p*-chlorostyrene–methyl methacrylate copolymer chains can have either of the monomeric units as terminal groups as is represented by formulas I and II.

I 

II 

Experiments show that the chlorostyrene monomer adds more readily than the ester monomer to either type of chain (I or II). The analyses of polymers 13 and 16 (Table I) when expressed as mole fraction *p*-chlorostyrene are 0.59 and 0.20, respectively. During the formation of polymer 13, 59% of the end groups on active chains on the average must have been chlorostyrene units whereas on the average only 20% of the active chains ended with this unit during the formation of polymer 16. Despite these differences α remained the same.

The molecular weights of these copolymers as measured by viscosity were not affected by the time of polymerization. The results in Table IV show that polymers prepared from three portions of the same solution but isolated in yields of 9, 19 and 37% had nearly the same ratio of specific viscosity to concentration. In the second experiment polymers were isolated in yields of 22, 44 and 62% without major differences in molecular weights. It appears that once the chain is started it rapidly grows to the average molecular weight attained in the particular polymerization.

When mixtures of *p*-chlorostyrene and vinyl acetate were polymerized polymers were obtained in low yields. Chlorine analyses indicated these polymers contained more than 91% chlorostyrene. It therefore seems unlikely that a copolymer formed. The results are summarized in Table V.

Certain symmetrically disubstituted ethylenes, as the maleate and fumarate esters, have not been made to undergo the usual self-addition polymerization but they can be made to polymerize with a second more active monomer. The work of Wagner-Jauregg[8] indicates that only those interpolymers which contain these symmetrically disubstituted ethylenes in a 1:1 or smaller molecular ratio to the second monomer can be prepared. We polymerized mixtures containing more than two moles of dimethyl fumarate or diethyl maleate per mole of chlorostyrene. The polymers obtained all contained forty-nine mole per cent. or less of the ester units. These results are summarized in Table VI.

Experimental

Methyl Methacrylate.—A commercial grade of methyl methacrylate was used. It was distilled through a 10-in. Fenske type column and boiled at 61° (200 mm.); n^{20}_D 1.4162.

***p*-Chlorophenylmethylcarbinol.**—This carbinol has been described previously but the methods of preparation are

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[7] Norrish and Brookman, *Proc. Roy. Soc.* (London), **171A**, 147 (1939).

[8] Wagner-Jauregg, *Ber.*, **63**, 3213 (1930).

not convenient to use.[9] Accordingly we are describing our method of preparation.[10] *p*-Chloroacetophenone was reduced by the method of Meerwein and Schmidt.[11] Six hundred and twenty cubic centimeters of dry isopropyl alcohol and 90 g. of *p*-chloroacetophenone were added to a solution of aluminum isopropoxide prepared from 13.5 g. of aluminum and 500 cc. of dry isopropyl alcohol. The mixture was heated on the steam cone in a 2-liter flask fitted with a 12-inch carborundum column which had a cold finger. The column was jacketed with a glass tube and connected to a downward condenser. Acetone began to distil as soon as the solution was heated on the steam cone. The solution was heated for six hours. During this time from 125 to 600 cc. of acetone and alcohol was collected as distillate. (Comparable yields were obtained when either quantity was permitted to distil during the reduction.) The carborundum column was then replaced by a still head and most of the isopropyl alcohol distilled off. The remaining solution was cooled in an ice-bath and acidified with 400 cc. of 10% hydrochloric acid. The organic layer was then removed and the aqueous layer extracted twice with 150-cc. portions of benzene which were added to the carbinol. The benzene was removed at reduced pressure and the carbinol distilled in a modified Claisen flask. The carbinol boiled at 81–86° (1 mm.); n^{20}_{D} 1.5420. The yield was 74 g. (81% of the theoretical amount).

***p*-Chlorostyrene.**—The carbinol has been dehydrated by Staudinger and Suter,[9b] who give no details of their procedure. Since the temperatures and pressures are fairly critical if a good yield is to be obtained, we are reporting the details on our method. A mixture of 20 g. of fused potassium bisulfate and 2.5 g. of hydroquinone was fused in a 100-ml. modified Claisen flask and then maintained between 208 and 215° by means of a metal bath. Nitrogen was introduced beneath the surface of the fused mixture by means of a capillary. While the pressure was maintained between 90 and 110 mm., 52 g. of *p*-chlorophenylmethylcarbinol was added by means of a dropping funnel at the rate of about 1 drop per second. The combined distillates from six runs were dissolved in ether, washed with 5% sodium hydroxide, then with a saturated calcium chloride solution, and finally dried over calcium chloride. A small amount of hydroquinone was added and the ether removed by distillation. The styrene was distilled through a 10-inch column packed with glass helices. It distilled at 38–39° (2 mm.); n^{20}_{D} 1.5648. The yield was 166 g. or 60% of the theoretical amount. Thirty-four grams of the carbinol was recovered.

***m*-Chlorophenylmethylcarbinol.**—A solution of 229 g. (1.2 moles) of *m*-chlorobromobenzene in 900 cc. of dry ether was slowly added with stirring to 29.2 g. (1.2 moles) of magnesium turnings in a 3-liter three-necked flask fitted with a reflux condenser, dropping funnel, and mechanical stirrer. Two and one-half hours were required for the addition. A solution of 60 g. (1.32 moles) of freshly distilled acetaldehyde in 600 cc. of dry ether was then added dropwise with continued stirring.

The organomagnesium compound was decomposed by the addition of 190 cc. of a 25% solution of ammonium chloride in water. The ether was decanted and after the solution was dried with magnesium sulfate the ether was removed by distillation. The carbinol was distilled through a 10-inch Fenske type column and boiled at 93–94° (3 mm.); n^{20}_{D} 1.5434; d_4^{20} 1.185. The yield was 147.5 g. or 78.5% of the theoretical amount.

Anal. Calcd. for C_8H_9OCl: C, 61.35; H, 5.79. Found: C, 63.39; H, 6.23.

The high values for carbon and hydrogen indicate that the carbinol has dehydrated to some considerable degree. Since excellent analytical values were obtained for the styrene prepared from this carbinol no further work on it was done.

Lock and Böck[12] have prepared this carbinol from *m*-chlorobenzaldehyde and methylmagnesium iodide. The only physical constant reported is the b. p. 240–246° (749 mm.).

***m*-Chlorostyrene.**—*m*-Chlorophenylmethylcarbinol was dehydrated with potassium bisulfate under the same conditions used for the *para* isomer. From 164.4 g. of carbinol 33.7 g. (23% of the theoretical amount) of the styrene was obtained. Forty-nine grams of the carbinol was recovered. The *m*-chlorostyrene boiled at 41–43° (3 mm.); n^{20}_{D} 1.5620; d_4^{20} 1.100.

Anal. Calcd. for C_8H_7Cl: C, 69.31; H, 5.09. Found: C, 69.32; H, 5.33.

Polymerization of *p*-Chlorostyrene and Methyl Methacrylate.—The quantities of monomers, catalyst, solvents conditions, yield, and composition of polymers are reported in Table I. Polymerizations in bulk were carried out in sealed Pyrex tubes. Elevated temperatures were obtained with an oven. Those polymerizations in solvents were carried out in Erlenmeyer flasks.

Isolation and Purification of Copolymers.—Chlorostyrene–methyl methacrylate copolymers were purified by dissolving the polymer and unreacted monomer in dioxane or acetone. Concentrations of 1 to 4% were used. The polymer was then precipitated by slowly dropping the solution into methyl alcohol that was stirred mechanically. For 50 cc. of polymer solution approximately 300 cc. of methyl alcohol was used. The polymer was isolated by suction filtration through a Buchner filter. In a few cases where yields of less than 1 g. were obtained the polymers were collected in tared sintered glass crucibles. This method of isolating the polymer was checked by dissolving 2.12 g. of copolymer in 50 cc. of acetone, precipitating in 225 cc. of methyl alcohol, and collecting the polymer on a Buchner filter. Ninety-seven per cent. of the polymer was recovered. The method has been used for isolating methacrylate resins in 99% yields.[13] The yields of the polymers were based upon the weight of powder obtained after drying to constant weight over phosphorus pentoxide in a vacuum desiccator. The composition was determined by fusing samples in the Parr bomb and determining the chlorine by the Volhard method. A sample was redissolved in dioxane and precipitated a second time. The analysis was not changed.

Calculation of α.—The method of calculating the ratio of the rate constants for the two monomers is illustrated here with the data for polymer 21 in Table I. The polymer was isolated in a yield of 3.50 g.

$$\begin{aligned} W_{x_0} &= 4.11 \\ W_{y_0} &= 2.34 \\ W_x &= 4.11 - 0.683\,(3.50) = 1.72 \\ W_y &= 2.34 - 0.317\,(3.50) = 1.23 \\ \alpha &= \frac{\log \frac{4.11}{1.72}}{\log \frac{2.34}{1.23}} = 1.36 \end{aligned}$$

Comparative Rates of Polymerization.—To compare the rates of polymerization of *p*-chlorostyrene, methyl methacrylate, and the mixed monomers two dioxane solutions of the same concentration of each monomer were prepared. Benzoyl peroxide was added in the amount of 1% of the weight of the monomers. The monomers were polymerized under an ultraviolet light at 40°. Experiments 37 and 38 show that methyl methacrylate polymerizes more than three times as fast as *p*-chlorostyrene. Experiments 39 and 40 afford a comparison of the rates of polymerization of the mixed monomers and *p*-chlorostyrene.

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(9) (a) Gastaldi and Cherchi, *Gazz. chim. ital.*, **45**, II, 251 (1915); (b) Staudinger and Suter, *Ber.*, **53**, 1099 (1920); (c) Zal'kind, Anusin and Berkovich, Russian Patent 38,630; *C. A.*, **30**, 3445 (1936).

(10) This method was first worked out by Dr. Joseph Dec: see Dec., Ph.D. Thesis, University of Illinois, 1940.

(11) Meerwein and Schmidt, *Ann.*, **444**, 221 (1925); Ponndorf, *Z. angew. Chem.*, **39**, 138 (1926).

(12) Lock and Böck, *Ber.*, **70**, 916 (1937).

(13) E. I. du Pont de Nemours and Co., *Ind. Eng. Chem.*, **28**, 1160 (1936).

TABLE I

COPOLYMERS OF METHYL METHACRYLATE WITH *p*- AND *m*-CHLOROSTYRENE

Polymer no.	*p*-Chlorostyrene, g.	Methyl methacrylate, g.	Conditions used Solvent Cpd.	Cc.	Light	Temp., °C.	Time	Benzoyl peroxide,[c] g.	Yield, %	% by weight of *p*-chlorostyrene in polymer	α
1	3.809	3.687	Me_2CO	35	U. v.[a]		h 111	0.2	30.8	56.2	1.29
3	3.32	4.68	MeOH	20	U. v.		h 69	.2	67.2	44.7	1.28
4	3.32	4.64	MeOH	20	U. v.		h 69	.2	67.2	47.5	1.55
5	3.03	3.05	Dioxane	20	U. v.		h 66	.09	45.2	56.0	1.40
6	2.846	3.167	Dioxane	50		101	h 1.25	.05	30.8	54.6	1.44
7	2.846	3.167	Dioxane	25		101	m 50	.05	30.3	55.6	1.45
8	2.277	2.534	Dioxane	25		101	m 30	.04	15.2	55.6	1.41
9	2.277	2.534	Dioxane	25		101	m 20	.04	17.1	54.6	1.37
10	4.054	5.060	Dioxane	50	U. v.		h 22.5	.11	9.2	56.6	1.44
11	4.054	5.060	Dioxane	50	U. v.		h 47	.11	19.4	54.1	1.36
12	8.65	9.60	Dioxane	100	U. v.		h 88	.22	36.9	55.4	1.51
13	3.23	2.13	Dioxane	18	U. v.		h 99.5	.08	29.7	66.9	1.39
14	2.66	2.78	Dioxane	18	U. v.		h 92.5	.08	25.9	57.7	1.50
16	1.44	5.58	Dioxane	23	U. v.		h 92.5	.08	52.6	25.7	1.57
17	1.85	4.56	Dioxane	20	U. v.		h 116	.06	59.0	38.6	1.6
18	9.774	13.05	Dioxane	230	U. v.		h 96	.22	1.3	54.0	1.5
19	4.50	4.24	None		Oven	115	m 55	.09	54.5	56.4	1.27
20	4.54	3.79	None		Oven	121	m 30	.08	52.0	61.1	1.48
21	4.11	2.34	None		Oven	120	m 24	.06	54.3	68.3	1.36
22	4.11	3.75	None		Oven	120	m 23	.08	52.9	57.7	1.38
23	3.09	2.67	None		Oven	100	m 25	.06	54.3	59.3	1.42
24	2.70	2.85	None		Oven	100	h Several	None	28.1	57.9	1.64
25	3.35	2.96	None		Oven	80	m 42	.06	66.6	58.9	1.41
26	3.11	2.92	None		Oven	80	m 42	.06	65.3	58.2	1.60
27	2.66	2.92	None		U. v.		h 30	.07	29.1	49.5	1.59
28	3.82	2.88	None		U. v.		h 36	.07	32.6	61.6	1.28
29	4.44	3.61	None		U. v.		h 37	.08	28.7	62.3	1.42
										Ave.	1.46
30	2.18[b]	1.92	Dioxane	50	U. v.		h 48	.04	22.2	61.5	1.49
31	1.09[b]	0.96	Dioxane	25	U. v.		h 84	.02	4.39	56.4	1.22
32	1.09[b]	0.96	Dioxane	25	U. v.		h 204	.02	61.9	57.0	1.27
33	2.51[b]	2.91	None		U. v.		h 40	.05	26.8	56.0	1.58
34	2.71[b]	1.95	None		U. v.		h 51	.05	29.0	66.0	1.48
35	2.53[b]	2.17	None		Oil-bath	100	m 7	.05	59.0	71.0	1.50
36	2.60[b]	2.57	None			75-90	h 2	.05	54.2	56.0	1.42

[a] The temperature under the light was from 30-40°. [b] *m*-Chlorostyrene was used instead of the para isomer in polymers 30 to 36. [c] The benzoyl peroxide used was that sold under the trade name "Lucidol."

TABLE II

AMOUNTS OF POLYMER PRODUCED IN STANDARD TIME

Expt.	*p*-Chlorostyrene, g.	Methyl methacrylate, g.	Dioxane solution, cc.	Time, hr.	Yield, %
37		4.570	15	45	85.6
38	6.054		20	45	23.8
39	6.054		20	66	40.2
40	3.027	3.046	20	66	45.2

Polymerization of *p*-Chlorostyrene in the Presence of Styrene.—These two monomers were polymerized in bulk in sealed tubes with benzoyl peroxide as catalyst. The peroxide was added in the amount of 1% of the weight of the monomers. The styrene was of commercial grade. It was washed with 2% sodium hydroxide, alkaline mercuric iodide, dried over anhydrous magnesium sulfate, and distilled through an 18-inch Fenske type column. It boiled at 49.5-50°; n^{20}_D 1.5465.

This work is summerized in Table III. These polymers were prepared in sealed Pyrex tubes in a water-bath at 50°.

TABLE III

COPOLYMER OF *p*-CHLOROSTYRENE AND STYRENE

p-Chlorostyrene, g.	Styrene, g.	Yield, %	% by weight of *p*-chlorostyrene in the polymer	α
4.73	4.45	13	58.7	1.35
4.23	4.50	14	56.3	1.38
4.37	3.35	20.8	61.9	1.29
4.50[a]	3.79	34.8	59.2	1.28

[a] In this polymer *m*-chlorostyrene was used.

Comparison of Molecular Weights with Polymerization Time.—Table IV gives the data to show how polymers were prepared in various yields from the same solutions. The ratio of η_{sp}/C is used as a measure of comparison for the molecular weights. This is based on the Staudinger[14] viscosity method.

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(14) Staudinger, "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932.

TABLE IV

VISCOSITY MOLECULAR WEIGHTS OF COPOLYMERS PRODUCED AT DIFFERENT TIMES

Solution	Expt.	Time, hr.[a]	Yield, %	η_{sp}/C	Grams of polymer per cc. of dioxane solution
1[b]	37	$22\frac{1}{2}$	9.2	4.11	0.0246
	38	47	19.4	3.99	.0246
	39	88	36.9	3.71	.0244
2[c]	40	48	22.2	2.23	.0311
	41	84	43.9	1.47	.0315
	42	204	61.9	1.40	.0314

[a] These solutions were placed under an ultraviolet lamp at 40°. [b] Solution 1 contained the following: 18.22 g. of *p*-chlorostyrene, 20.24 g. of methyl methacrylate, 0.38 g. of benzoyl peroxide ("Lucidol"); diluted to 200 cc. with dioxane; samples were withdrawn for experiments 37, 38 and 39. [c] Solution 2 contained the following: 4.37 g. of *m*-chlorostyrene, 3.84 g. of methyl methacrylate, 0.08 g. of benzoyl peroxide ("Lucidol"); diluted to 100 cc. with dioxane; samples were withdrawn for experiments 40, 41 and 42.

Polymerization of Mixtures of *p*-Chlorostyrene and Vinyl Acetate.—The polymerization of *p*-chlorostyrene in the presence of vinyl acetate was inhibited. Polymers were obtained in very low yields containing very little vinyl acetate. These results are summarized in Table V. The amount of benzoyl peroxide used was 1% of the weight of the monomers.

TABLE V

ATTEMPTS TO PREPARE COPOLYMERS OF *p*-CHLOROSTYRENE AND VINYL ACETATE

Polymer no.	*p*-Chlorostyrene, g.	Vinyl acetate, g.	Solvent	Conditions	Yield, %	*Anal.* as % by wt. of *p*-chlorostyrene
41	3.32	7.49	Methanol	65°, 5.5 hr.	4.7	92.6
42	3.32	4.67	Methanol	u. v. light, 112 hr.	15.7	95.1
43	2.04	4.43	40 cc. Dioxane	u. v. light, 48 hr.	10.4	91.4
44	2.53	0.93	None	u. v. light, 380 hr.	59.5	97.3
45	3.54	3.31	Acetone	u. v. light, 100 hr.	10.7	93.5

Polymerization of *p*-Chlorostyrene with Dimethyl Fumarate and Diethyl Maleate.—A large excess of the symmetrically disubstituted ethylene was used in an attempt to produce polymers containing more than 50 mole % of this unit. Only with dimethyl fumarate was a polymer obtained which contained approximately a 1.1 ratio of the two monomers. These results are summarized in Table VI. Dimethyl fumarate was used for experiment 46. For experiments 47 and 48 diethyl maleate was used.

TABLE VI

COPOLYMERS OF *p*-CHLOROSTYRENE AND DIMETHYL FUMARATE OR DIMETHYL MALEATE

Polymer no.	Initial ratio: moles of ester to moles of *p*-chlorostyrene	Conditions	Yield, %	Ratio: moles of ester to *p*-chlorostyrene in polymer
46	2.98/1	Methanol solvent, 65°, 42 hr.	12	49/51
47	2.45/1	No solvent, u. v. light, 39°, 383 hr.	29	25/75
48	2.41/1	Acetone solvent, u. v. light, 383 hr.		19/81

Summary

The method of interrupted copolymerization of mixed monomers has been used to determine the relative rates at which *p*-chlorostyrene and methyl methacrylate enter a growing copolymer chain. This ratio was 1.46 and remained constant when the temperature, solvents, and relative concentrations of the monomers were varied. The same ratio was obtained when *m*-chlorostyrene was substituted for its *para* isomer. Both *m*- and *p*-chlorostyrenes polymerize more rapidly in bulk than styrene when mixtures of the chlorostyrene and styrene were copolymerized.

The molecular weights of chlorostyrene–methyl methacrylate copolymers obtained when the reaction was 9% complete were in the same range as were those when the reaction gave higher conversions.

Polymers prepared from mixtures containing more than one mole of dimethyl fumarate or diethyl maleate per mole of *p*-chlorostyrene contained less than 50 mole % of the symmetrically disubstituted ethylenes.

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