

Polymerization Rates of Monochlorostyrenes

L. C. RUBENS, *Physical Research Laboratory, The Dow Chemical Company, Midland, Michigan*

Synopsis

The polymerization rates of *o*- and *p*-chlorostyrenes have been determined under a variety of reaction conditions. These monomers polymerize much more rapidly than styrene thermally with peroxide, or high energy radiation. With no initiator the polymerization of chlorostyrene follows a behavior similar to styrene, i.e., the reaction exhibits a maximum rate during the initial stage of the reaction. With initiator, the form of the rate curve changes and acceleration is observed in the midconversion range. The ratio of the accelerated rate to the initial rate increases with initiator concentration. Mixtures of chlorostyrene with small amounts of certain difunctional monomers (e.g., divinylbenzene, ethylene dimethacrylate, and biacrylophenone) copolymerize much more rapidly than the chlorostyrene polymerizes alone. Polyester resins containing maleic or fumaric unsaturation copolymerize much more rapidly with chlorostyrene than with styrene under identical reaction conditions.

Introduction

Ring-chlorinated styrenes are known to polymerize more rapidly than styrene.^{1-3a} There is some disagreement, however, on the actual polymerization rates of the isomeric monochlorostyrenes, and little has been published on the effects of initiator type and concentration, temperature, and cross-linking comonomers upon the overall conversion rates.

The present study is concerned with the polymerization rates of *o*- and *p*-chlorostyrenes under a variety of reaction conditions. The data have been obtained via the flexible film bag dilatometric technique described in a previous paper.⁴ The conversion of monomer to polymer was calculated on the basis of a linear density increase with the weight per cent polymer produced. The precision of this interpretation is not absolutely certain at this time, but there is sufficient experimental evidence to assure only minor errors.

Monochlorostyrene Monomers

The *o*- and *p*-chlorostyrenes were prepared by the catalytic dehydrogenation process.^{5,6} The physical properties of these monomers have been described in detail.⁷ The freshly distilled monomers were analyzed by infrared spectroscopy,⁸ vapor-phase chromatography,⁹ and coulometric bromination.¹⁰ The bromination indicated a purity of >99.8% as chlorostyrenes. Infrared analysis showed the *o*-chlorostyrene to contain 1.4% *para*

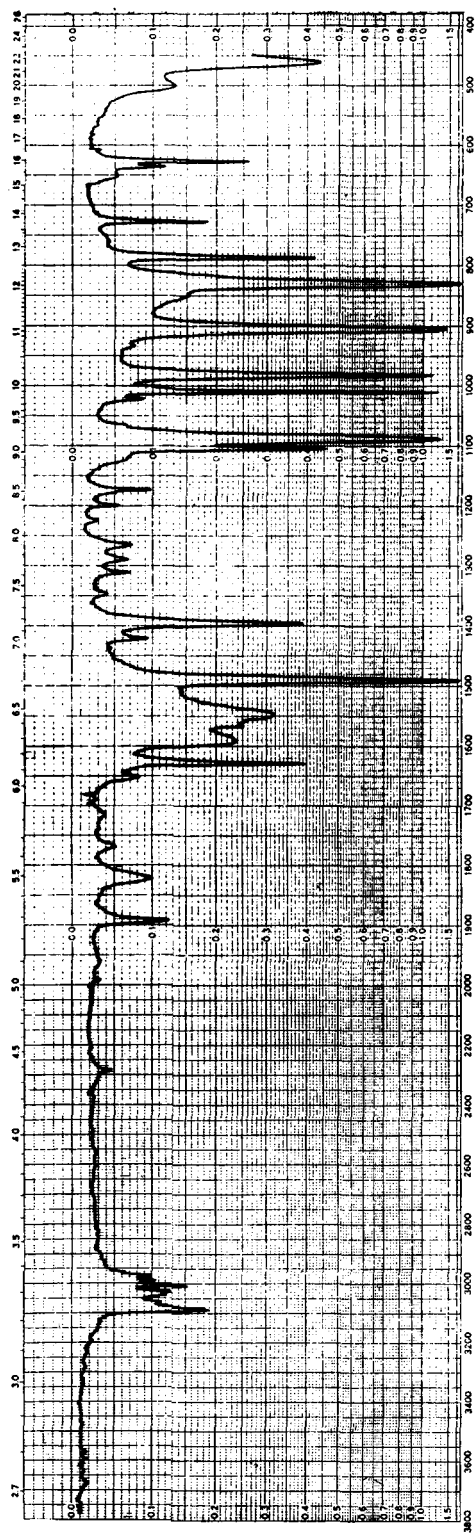


Fig. 1. Infrared spectrum of *o*-chlorostyrene.

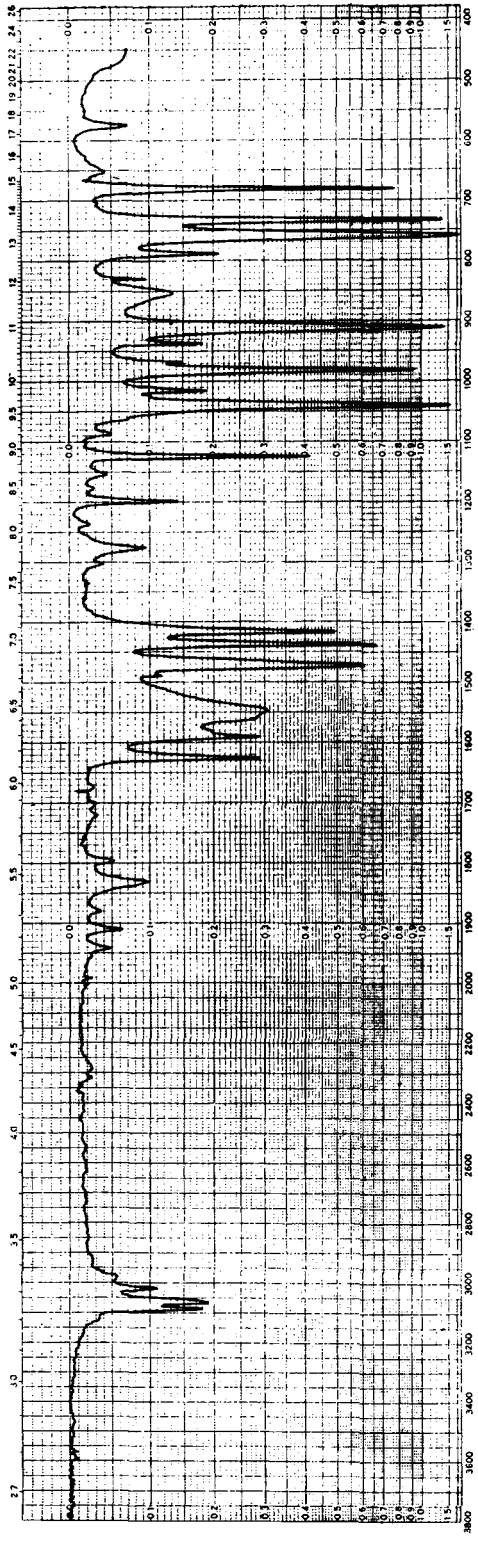


Fig. 2. Infrared spectrum of *p*-chlorostyrene.

isomer. Trace impurities were mainly ethylchlorobenzenes (*ortho-para* mixture). The infrared spectra of these monomers appear in Figures 1 and 2.

Densities of Chlorostyrene Monomer and Polymer

Density data for *o*-chlorostyrene monomer and polymer are presented in Table I.¹¹ The values for the polymer were obtained on a cast bubble-free specimen which had been polymerized for three days at 80°C., followed by two days at 100°C. and one day at 125°C. The second-order transition temperature of poly-*o*-chlorostyrene appears to be about 100°C. from these data. The coefficient of cubical expansion of the polymer is $2.085 \times 10^{-4} \text{ } ^\circ\text{C.}^{-1}$ below 100°C. and $4.73 \times 10^{-4} \text{ } ^\circ\text{C.}^{-1}$ between 100 and 130°C.

TABLE I
Densities of *o*-Chlorostyrene Monomer and Polymer

Temperature, °C.	Density, g./cc.	
	Monomer	Polymer
25	1.0950	1.2478
39	1.0815	1.2443
55	1.0668	1.2404
69	1.0537	1.2370
86	1.0379	1.2323
101	1.0235	1.2287
115	1.0105	1.2197
125	1.001	1.2140

The shrinkage which occurs during polymerization at different temperatures has been calculated from these data (Fig. 3). The shrinkage of styrene during polymerization has been included for comparison.¹²

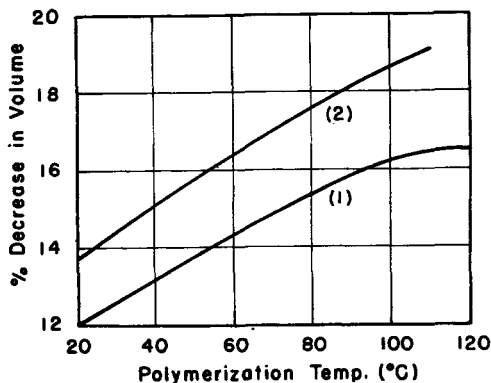


Fig. 3. Volume changes during polymerization: (1) *o*-chlorostyrene; (2) styrene.

Thermal Polymerization of Monochlorostyrenes

The *o*- and *p*-chlorostyrenes were polymerized in poly(vinyl fluoride) film bags supported in thin sheet form in the recording dilatometer. At polymerization temperatures of 70–90°C. the reaction was slow enough to per-

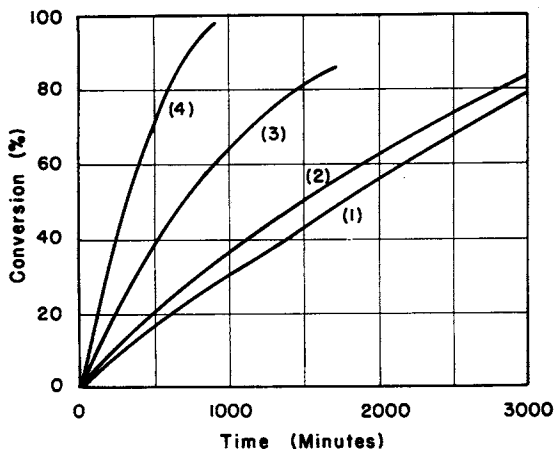


Fig. 4. Thermal polymerization of monochlorostyrenes: (1) *p*-chlorostyrene at 80°C.; (2) *o*-chlorostyrene at 69.8°C.; (3) *o*-chlorostyrene at 80°C.; (4) *o*-chlorostyrene at 90.3°C.

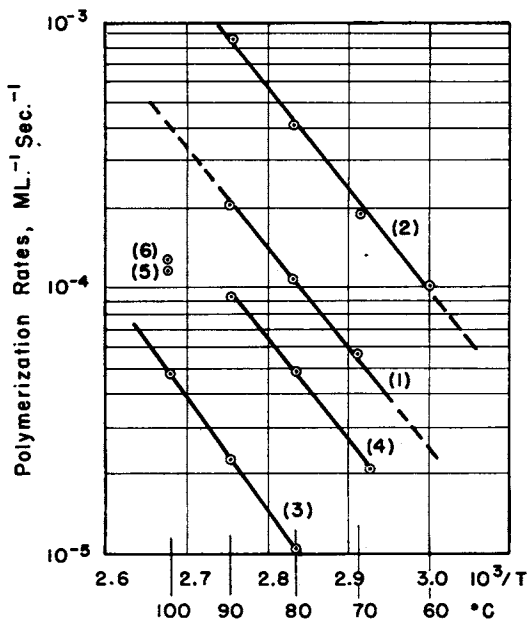


Fig. 5. Initial polymerization rates: (1) *o*-chlorostyrene; (2) *o*-chlorostyrene + 4.3×10^{-3} mole/l. Bz_2O_2 ; (3) styrene;¹⁴ (4) *p*-chlorostyrene; (5) *p*-chlorostyrene;² (6) *o*-chlorostyrene.²

mit the surrounding mercury to conduct evolved heat away to maintain isothermal conditions.

The polymerization of chlorostyrenes without added initiator follows a course similar to that shown for styrene.^{13,14} In general, the thermal polymerization rate is at a maximum during the initial phase of the reaction and it decreases progressively with conversion. The overall reaction appears to be between zero and first order, according to data in Figure 4.

The activation energy for the initial phase of the thermal polymerization of *o*-chlorostyrene is about 17.5 kcal./mole. The data show that the initial rates of thermal polymerization for styrene, *p*-chlorostyrene, and *o*-chlorostyrene are in the ratio 1:4:10.7 (Fig. 5).

The data also show that *o*-chlorostyrene polymerizes at a much faster rate than found by Ushakov and Matuzov.²

Benzoyl Peroxide-Initiated Polymerization of *o*-Chlorostyrene

With the addition of as little as 0.01% benzoyl peroxide (4.3×10^{-4} mole/l. at 80°C.) to *o*-chlorostyrene the form of the conversion versus time curve changes. The initial part of the curve is linear and there is acceleration in the mid-conversion range. The ratio of the rate in the accelerated portion of the curve to the initial rate increases with initiator concentration.

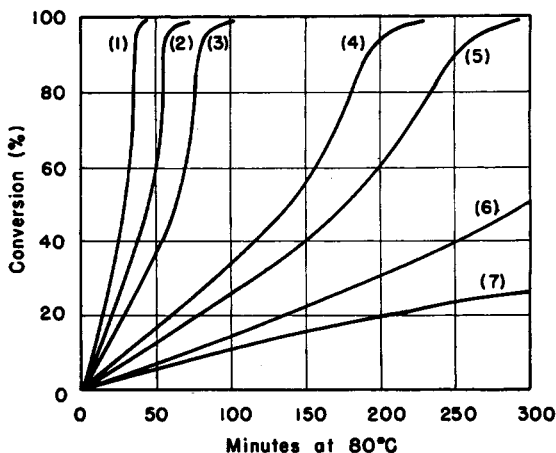


Fig. 6. Polymerization of *o*-chlorostyrene with various concentrations of benzoyl peroxide: (1) 1.33×10^{-1} mole/l.; (2) 4.3×10^{-2} mole/l.; (3) 2.15×10^{-2} mole/l.; (4) 4.3×10^{-3} mole/l.; (5) 2.15×10^{-3} mole/l.; (6) 4.3×10^{-4} mole/l.; (7) 0.00.

With 0.05% peroxide the accelerated rate is 2.3 times the initial rate at 80°C.; with 0.5% peroxide the ratio increases to 4 (Fig. 6).

The rates of polymerization of *o*-chlorostyrene with 0.1% benzoyl peroxide at 60–90°C. are shown in Figure 7. Midconversion acceleration is observed over the entire temperature range. The initial rate data from this experiment are plotted versus reciprocal temperature in Figure 5.

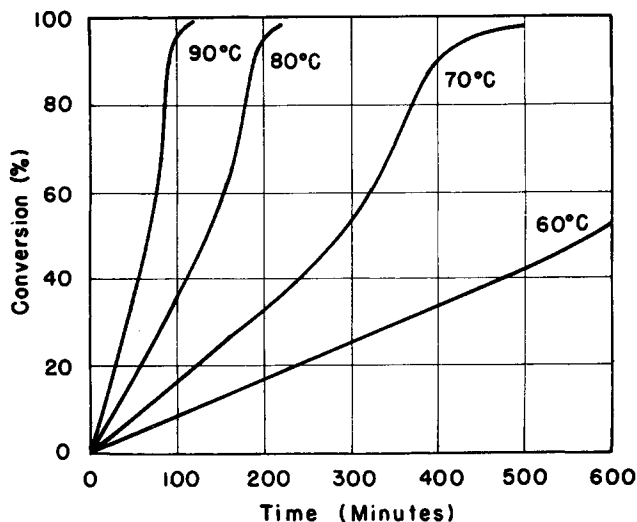


Fig. 7. Polymerization of *o*-chlorostyrene with 4.3×10^{-3} mole/l. benzoyl peroxide (0.1% by wt.).

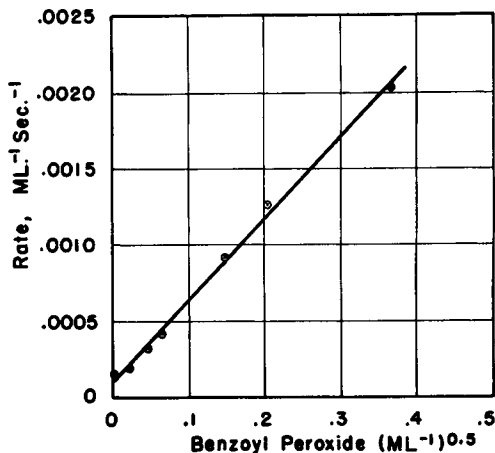


Fig. 8. Initial polymerization rate of *o*-chlorostyrene at 80°C.

The initial rate data for *o*-chlorostyrene initiated with benzoyl peroxide follow the classical behavior of other vinyl monomers, i.e., the rate is proportional to the square root of the initiator concentration (Fig. 8).

The molecular weights of the polymers prepared in these rate studies were determined according to a relationship shown by Fuhrman and Mesrobian.¹⁵ The values appear in Table II.¹⁶

At a polymerization temperature of 80°C. the molecular weight of poly-*o*-chlorostyrene is seen to increase with up to 0.1% benzoyl peroxide, and then to decrease with higher initiator concentrations. The classical explanation for acceleration of polymerization in the gel phase^{17,18} could ac-

TABLE II
Degree of Polymerization of Polychlorostyrenes

Polymerization temp., Monomer °C.	Number-average DP of polymer						
	0% Bz ₂ O ₂	0.01% Bz ₂ O ₂	0.05% Bz ₂ O ₂	0.1% Bz ₂ O ₂	0.5% Bz ₂ O ₂	1.0% Bz ₂ O ₂	3.0% Bz ₂ O ₂
<i>o</i> -Chloro- styrene	60				2790	1236	892
	70	3255			1825	1190	
	80	2056	2357	2372	2582	1100	526
	90	1322			1782	825	340
<i>p</i> -Chloro- styrene	80			1001	450	221	

count for the observed results with low peroxide concentrations. Since the ratio of the accelerated rate to initial rate continues to increase with peroxide concentration, however, factors other than a reduced termination rate must be considered to provide a consistent explanation of the results.

γ -Radiation Initiation of Polymerization of Chlorostyrenes

The dilatometric cell containing monochlorostyrenes was exposed to γ -radiation from cobalt-60. The cobalt emits γ -radiation in both the 1.17 and 1.33 M.e.v. range. After passage through the metal face of the cell, about 84.6% of the original radiation entered the monomer. The dose rate was varied by changing the distance of the dilatometer from the radiation source. The temperature was maintained at 31°C. Conversion rates of *o*-chlorostyrene exposed to γ -radiation doses of 1600, 30,000 and 60,000 rads/hr.

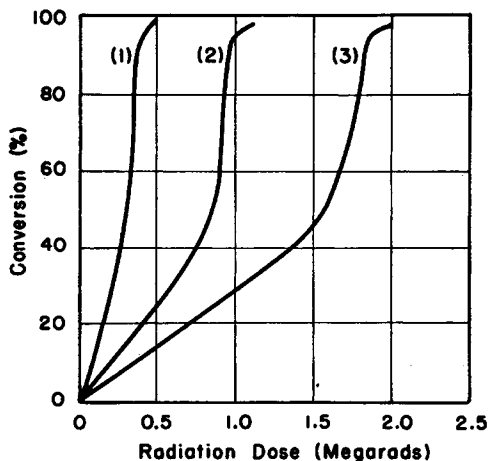


Fig. 9. Co⁶⁰ γ -radiation-initiated polymerization of *o*-chlorostyrene at 31°C. at various dose rates: (1) 1600 rad/hr.; (2) 30,000 rad/hr.; (3) 60,000 rad/hr.

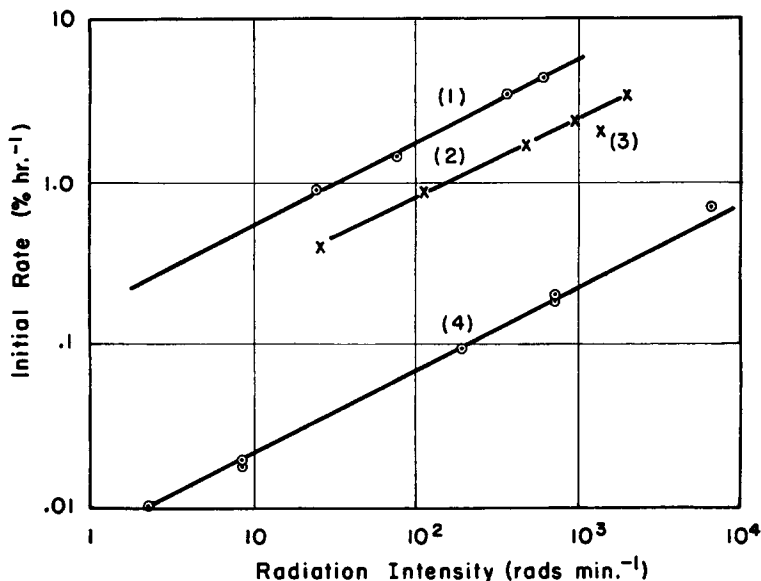


Fig. 10. γ -Radiation polymerization of vinyl monomers: (1) methyl methacrylate;¹⁹ (2) *o*-chlorostyrene; (3) *p*-chlorostyrene; (4) styrene.¹⁹

are shown in Figure 9. Acceleration of polymerization in the midconversion range was observed for all intensities studied.

The initial polymerization rate of *o*-chlorostyrene is plotted versus the square root of the radiation intensity in Figure 10. The line has the same slope as shown by Charlesby¹⁹ for styrene and methyl methacrylate and is in accord with classical theory for radiation initiation of polymerization.

The number-average molecular weights of poly-*o*-chlorostyrenes prepared at several γ -radiation intensities are listed in Table III. These values should be accepted with reservation, since slight over-irradiation may crosslink or degrade the polymer with consequent alteration of molecular weight values.

TABLE III
Degree of Polymerization of Radiation-Polymerized *o*-Chlorostyrenes

Polymerization temp., °C.	Radiation intensity, rads/hr.	Radiation time, hr.	Number-avg. DP
31	1,600	93	5963
31	30,000	35	4135
31	60,000	26	3337

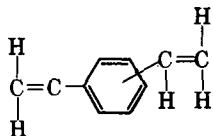
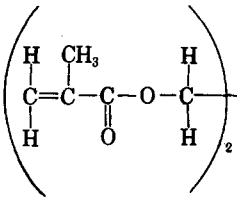
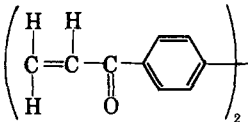
Copolymerization Rates of Chlorostyrene with Monomers Containing Two Reactive Vinyl Groups

The copolymerization of mixtures of reactive mono- and divinyl monomers usually results in the formation of crosslinked insoluble polymers.

Styrene and divinylbenzene,^{3b,20} for example, form firm gels when only a few per cent of the monomer mixture is converted to polymer. Polymerization rate curves for such mixtures frequently show acceleration with increasing conversion, and this behavior is responsible for the descriptive expression "gel-phase polymerization."

There are relatively few available data on the overall polymerization rates of mixtures of mono- and divinyl monomers. Older techniques have been laborious for obtaining conversion data on gelled systems. These data can now be obtained very readily by use of the recording film bag dilatometer.

TABLE IV
Difunctional Monomers

Name	Structure	Mol. wt.	Melt- ing point, °C.	Source
Divinyl- benzene (DVB)		130.08	—	Dow Chemical Co. ^a
Ethylene dimeth- acrylate (EDMA)		198.21	—	Sartomer Resins, Inc.
Biacrylo- phenone (BAP)		262.3	118	Dow Chemical Co. ^b

^a Commercial mixture of 56.1% divinylbenzene and 43.9% ethylvinylbenzene.

^b Experimental monomer prepared by F. Leavitt, The Dow Chemical Co.

Extensive studies have been made on the copolymerization rates of both styrene and chlorostyrenes with many monomers containing multiple vinyl groups. A full description of this work will be published in the future. The monomers listed in Table IV are representative of the types copolymerized with chlorostyrenes.

Polymerization inhibitors were removed from the divinylbenzene and ethylene dimethacrylate by the usual caustic wash method.

Shrinkage versus time curves were obtained by the dilatometric method for compositions listed in Table V.

TABLE V
o-Chlorostyrene-Difunctional Monomer Mixtures for Polymerization Rate Studies

No.	Composition ^a				
	<i>o</i> -Chloro- styrene, mole	BAP, mole	EDMA, mole	DVB, mole	Benzoyl peroxide, mole
1	0.9943	0	0	0	5.72×10^{-3b}
2	0.9553	0.039	0	0	"
3	0.9553	0	0.039	0	"
4	0.9253	0	0	0.039	"

^a For identification of abbreviations see Table IV.

^b This is equivalent to about 1% by weight of benzoyl peroxide.

The conversion rates of these mixtures to polymers at 80°C. are shown in Figure 11. All of the difunctional monomers cause autoacceleration to occur at a much lower conversion than for the pure *o*-chlorostyrene. Biacrylophenone causes a much greater rate increase than the other monomers studied. Other tests have shown that the mixture of *o*-chlorostyrene and biacrylophenone produces a very firm gel structure at only 2-3% conversion to polymer. It should be noted that at the rate which the sample containing the biacrylophenone polymerized, it is doubtful that the temperature of the sample remained constant despite its thin sheet form in contact with mercury.

Copolymerization Rates of Chlorostyrene with Unsaturated Polyesters

Monochlorostyrenes copolymerize readily with polyesters containing maleic or fumaric unsaturation. When these polyesters contain more than one unsaturated group per polymer chain, copolymerization proceeds in a manner similar to that described for divinyl monomers in the previous section. The formation of a gel structure is observed at a low conversion. Despite the extremely rapid copolymerization of these mixtures, it is possible to produce high strength, void and bubble free, clear castings.

A typical unsaturated polyester resin was prepared from the following reactants by the method of Carlston et al.:²¹ 0.57 mole maleic anhydride; 0.43 mole isophthalic acid; 1.02 mole glycol (mixture of 0.7 mole diethylene glycol and 0.3 mole ethylene glycol). The acid number of the final polyester was 16.8.

The polyester was mixed with both styrene and *o*-chlorostyrene in the weight ratio of 6 parts of polyester to 4 parts vinyl monomer. To each mixture 0.5% benzoyl peroxide was added and the shrinkage rate measured at 80°C. in the recording film bag dilatometer. After polymerization was completed, the samples of both compositions were hard, colorless, void- and bubble-free, tough solids.

The polymerization rate data for these compositions (Fig. 12) show that the composition with *o*-chlorostyrene polymerizes several times faster than

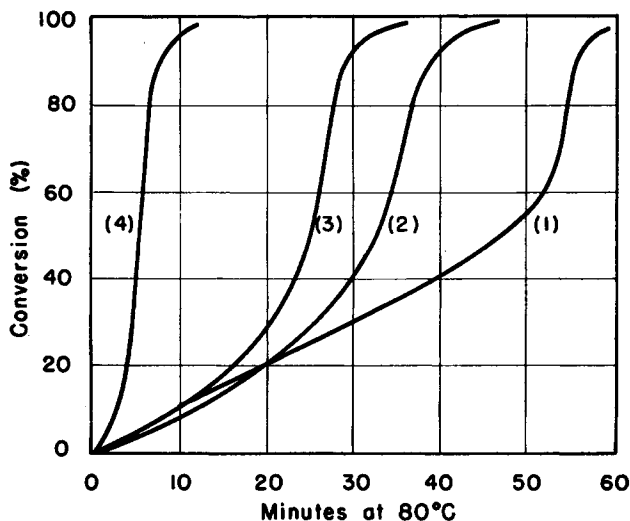


Fig. 11. Copolymerization of *o*-chlorostyrene (OCS) with difunctional monomers and 1% Bz_2O_2 : (1) pure *o*-chlorostyrene; (2) 0.931 mole OCS + 0.039 mole divinylbenzene; (3) 0.961 mole OCS + 0.039 mole ethylene dimethacrylate; (4) 0.961 mole OCS + 0.039 mole biacrylophenone.

the styrene composition. It should be noted that here again the reaction is too fast to dissipate the exotherm completely, and it is quite probable that the divergence of the curves at high conversion is partially a consequence

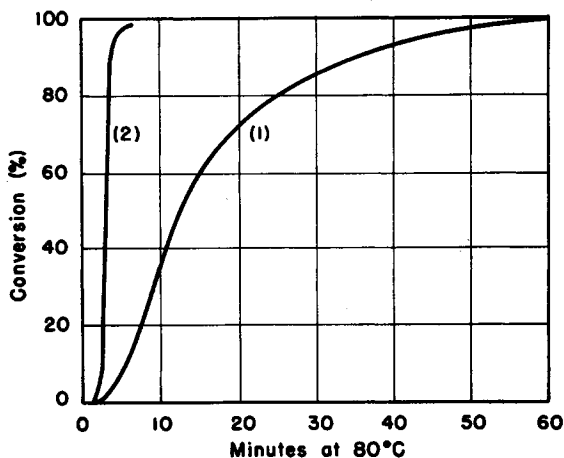


Fig. 12. Copolymerization of isophthalic-maleic polyester with styrene and *o*-chlorostyrene with 0.5% Bz_2O_2 : (1) 40% styrene; (2) 40% *o*-chlorostyrene.

of a thermal runaway in the chlorostyrene sample. It is clear, however, that unsaturated polyesters do copolymerize with *o*-chlorostyrene at a very high rate compared to that observed for styrene.

Conclusions

The polymerization rates of *o*- and *p*-chlorostyrenes have been determined under a variety of reaction conditions. These monomers polymerize much more rapidly than styrene thermally with peroxide, or high energy radiation.

With no initiator the polymerization of chlorostyrene follows a behavior similar to styrene, i.e., the reaction exhibits a maximum rate during the initial stage of the reaction. With initiator, the form of the rate curve change and acceleration is observed in the midconversion range. The ratio of the accelerated rate to the initial rate increases with initiator concentration.

Mixtures of chlorostyrene with small amounts of certain difunctional monomers (e.g., divinylbenzene, ethylene dimethacrylate, and biacrylphenone) copolymerize much more rapidly than the chlorostyrene polymerizes alone.

Polyester resins containing maleic or fumaric unsaturation copolymerize much more rapidly with chlorostyrene than with styrene under identical reaction conditions.

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Résumé

On a déterminé les vitesses de polymérisation de l'*o*- et *p*-chlorostyrène dans différentes conditions. Ces monomères polymérisent beaucoup plus rapidement que le styrène, aussi bien thermiquement que par les peroxydes ou par radiation de haute énergie. En absence d'initiateur, la polymérisation du chlorostyrène se comporte de façon identique à celle du styrène, c'est à dire que la réaction se caractérise par une vitesse maximum durant l'étape d'initiation. En présence d'initiateur, la forme de la courbe de vitesse changes et on observe une accélération dans le domaine de demi-conversion. Le rapport entre la vitesse accélérée et la vitesse initiale augmente avec la concentration en initiateur. Des mélanges de chlorostyrène avec des petites quantités de certains monomères bifonctionnels (par ex. le divinylbenzène, le diméthacrylate d'éthylène, et la bi-acrylophénone) copolymérisent beaucoup plus rapidement que le chlorostyrène seul. Des résines de polyester contenant des insaturations maléiques ou fumariques copolymérisent plus rapidement avec le chlorostyrène qu'avec le styrène, dans des conditions identiques de réaction.

Zusammenfassung

Die Polymerisationsgeschwindigkeit von *o*- und *p*-Chlorstyrol wurde unter verschiedenen Reaktionsbedingungen bestimmt. Diese Monomeren polymerisieren thermisch, mit Peroxyd oder unter hochenergetischer Strahlung viel rascher als Styrol. Ohne Starter zeigt die Polymerisation von Chlorstyrol ein ähnliches Verhalten wie diejenige von Styrol, d.h. die Reaktion besitzt ihre maximale Geschwindigkeit während des Anfangstadiums. Bei Anwesenheit eines Starters ändert sich die Form der Geschwindigkeitskurve und im mittleren Umsatzbereich tritt eine Beschleunigung auf. Das Verhältnis der beschleunigten Geschwindigkeit zur Anfangsgeschwindigkeit nimmt mit der Starterkonzentration zu. Mischungen von Chlorstyrol mit kleinen Mengen gewisser difunktionaler Monomere (z.B. Divinylbenzol, Äthylendimethacrylat und Biacrylophenon) copolymerisieren viel rascher als Chlorstyrol allein polymerisiert. Polyesterharze mit Malein- oder Fumarsäure-Doppelbindungen copolymerisieren mit Chlorstyrol viel rascher als mit Styrol unter identischen Reaktionsbedingungen.

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