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HOMOPOLYMERIZATION AND COPOLYMERIZATION BEHAVIOR OF α -CHLOROSTYRENE

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ABSTRACT

Homopolymerization of α -chlorostyrene using AIBN as an initiator at 50–53°C yields a polymer having a molecular weight of 2,000 in less than 1 percent yield. The structure of the polymer obtained was studied by ¹H- and ¹³C-NMR, IR, and UV spectroscopies. The spectra were similar to that of trans-cisoidal poly(phenylacetylene), which suggests that substantial dehydrochlorination accompanies the polymerization.

Copolymerizations involving α -chlorostyrene with monomers such as styrene and methyl methacrylate were conducted. A small amount of α -chlorostyrene was found to decrease substantially both the yields and molecular weights of the copolymers produced.

The possibility that enchainment of α -chlorostyrene units in polymers leads to structures that inhibit vinyl polymerization was investigated by conducting studies on the capability of cumyl chloride to inhibit the polymerization of vinyl monomers. The influence on vinyl monomer polymerizations of products obtained from α -

chlorostyrene/styrene copolymerizations was also investigated. It was found that these materials were inhibitors for vinyl polymerization.

INTRODUCTION

This paper concerns the polymerization behavior of α -chlorostyrene. In contrast to many halogen-substituted olefins, α -chlorostyrene [1, 2, 3] and α -bromostyrene [4] have been reported to be incapable of polymerization by free radical methods. There is only a small amount of fundamental information available concerning the behavior of these monomers in the presence of free radicals. Since α -fluorostyrene [5] and α,β,β -trifluorostyrene [6] polymerize without difficulty, as do a variety of other α -halogenated monomers, including α -haloacrylates [7, 8, 9, 10] and N-(4-substituted-phenyl)- α -chloromaleimide [11], it was of interest to learn more about the chemical behavior of α -chlorostyrene in the presence of free radicals. Furthermore, since polymers containing α -chlorostyrene residues are of potential interest for graft copolymer synthesis, etc., it was hoped that a way to polymerize this monomer would be uncovered.

This paper discusses the results of polymerization and copolymerization experiments conducted using α -chlorostyrene as monomer and as chain-transfer agent. The influence of products obtained from such polymerizations as inhibitors for styrene polymerization will also be described.

EXPERIMENTAL

Materials

Styrene (Fisher Scientific Company) was washed three times with 10 percent sodium hydroxide solution to remove inhibitor, then six times with distilled water, dried with anhydrous magnesium sulfate and distilled in the presence of calcium hydride under reduced pressure prior to use. Azo-bis(isobutyronitrile) (AIBN) (Alfa Products) was recrystallized from methanol and dried under vacuum prior to use.

α -Chlorostyrene was prepared by a modification of the procedure used by Newman, *et al.* [12] to obtain a mixture of α -chlorostyrene and unreacted acetophenone. The unreacted acetophenone was removed by conversion to its oxime and filtration. α -Chlorostyrene, boiling at 64°C/9 mm Hg, was obtained by vacuum distillation. Figure 1 shows the 200 MHz $^1\text{H-NMR}$ spectrum of α -chlorostyrene. It

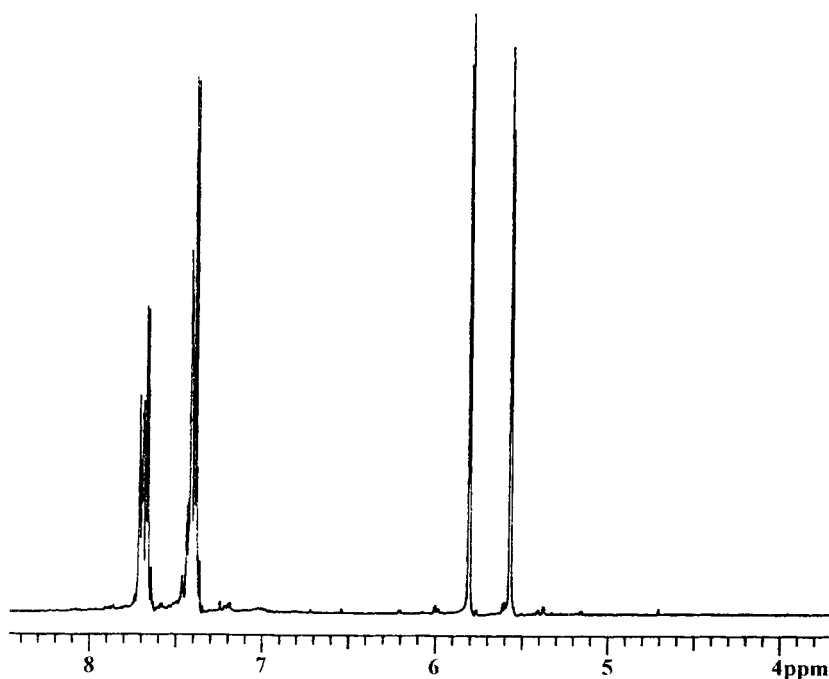


Figure 1. 200 MHz ^1H -NMR spectrum of α -chlorostyrene.

contains aromatic ($\delta = 7.3$ - 7.8 ppm) and olefinic ($\delta = 5.5$ - 5.9 ppm) proton resonances having relative intensities of 5:2.

Cumyl chloride was obtained by adding hydrogen chloride to a solution of freshly distilled α -methylstyrene in dry CH_2Cl_2 with stirring. The solution was concentrated by using a rotary evaporator. The complete conversion to cumyl chloride and the absence of CH_2Cl_2 were confirmed by the ^1H -NMR spectrum of the product. This cumyl chloride was used without further purification.

Polymerization Techniques

Homopolymerization of α -Chlorostyrene and Copolymerization of α -Chlorostyrene with Styrene

The α -chlorostyrene was homopolymerized and copolymerized with styrene in glass tubes sealed under nitrogen. The polymerizations were conducted in bulk at 50 - 53°C for 50 hours using 0.2 mole percent AIBN as initiator. After polymerization, the mixtures were poured into excess methanol or hexane to precipitate the polymers. These were reprecipitated from benzene solution into

TABLE 1. Yields and Molecular Weights of Products Obtained from Attempts to Copolymerize α -Chlorostyrene and Styrene as a Function of the Amount of α -Chlorostyrene

Sample	Mole % α -chlorostyrene	Yield (wt%)	Mn($\times 10^{-4}$) (g/mol)	Mw($\times 10^{-4}$) (g/mol)	MWD*
Polystyrene	0	87.6	9.87	18.75	1.9
S05CIS	0.5	79.0	8.54	16.63	2.0
S2CIS	2	60.1	5.06	9.62	1.9
S5CIS	5	29.6	1.98	3.28	1.7
S10CIS	10	9.4	0.54	0.87	1.6
S20CIS	20	4.8	0.48	0.69	1.4
S33CIS	33	1.4	0.39	0.53	1.4
S43CIS	43	1.2	0.38	0.52	1.4
S50CIS	50	1.3	0.32	0.43	1.3
S75CIS	75	1.0	0.22	0.29	1.3
S100CIS	100	0.8	0.21	0.26	1.3

*MWD = Mw/Mn

TABLE 2. Effect of Cumyl Chloride on the Polymerization Styrene^a

$\frac{[\text{Cumyl Chloride}]}{[\text{Styrene}]}$	Yield(wt%)	Mn($\times 10^{-4}$)	Mw($\times 10^{-4}$)	MWD
0	60.2	2.75	5.23	1.9
0.02	52.6	2.21	4.65	2.1
0.05	42.3	1.47	2.93	2.0
0.11	38.2	0.88	1.55	1.8
0.33	20.2	0.33	0.58	1.8
1	1.4	0.21	0.27	1.3
3	0.5	0.16	0.18	1.1

^aReaction Conditions

Initiator: AIBN (0.2 mole%); Temperature: 50°C; Reaction Time: 68 Hrs

methanol or hexane and were dried under vacuum at room temperature. The amounts of α -chlorostyrene and styrene used are shown in Table 1, along with yields and molecular weights obtained in these experiments.

Polymerization of Styrene in the Presence of Cumyl Chloride

Solutions containing various amounts of cumyl chloride in styrene were introduced into glass tubes along with 0.2 mole percent AIBN. The mixtures were flushed with dry nitrogen and the polymerizations were conducted for 68 hours at 50°C. The amounts of cumyl chloride and styrene used are shown in Table 2, along with yields and molecular weights obtained in these experiments.

Polymerization of Styrene in the Presence of Copolymers of α -Chlorostyrene and Styrene

Effect of copolymer compositions

A solution of an α -chlorostyrene-styrene copolymer (0.05 g) and AIBN (0.016 g) in styrene (5 ml) was flushed with nitrogen and sealed in a glass ampoule. The mixture was heated at 50-53°C for 40 hours and then poured into excess methanol to precipitate the polymer. The compositions of the copolymers used, and the conversions and molecular weights obtained in the experiments are shown in Table 3.

Effect of copolymer concentration

Various amounts of a copolymer (S05CIS) derived from an α -chlorostyrene-styrene mixture containing 5 mole percent α -chlorostyrene were dissolved in styrene (3 ml) and AIBN (0.0095 g) was added. Each mixture was flushed with dry nitrogen and sealed in a glass ampoule. Polymerization was conducted at 50-53°C for 19 hours. The polymers were isolated as described above. The amounts of the copolymer used, and the conversions and molecular weights obtained in the experiments are listed in Table 4.

Characterization Methods

Molecular Weight Determination

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (Waters Associates, Model 150C High Temperature GPC, refractive index detector, α -styrigel column set: 10⁶, 10⁵, 10⁴, 10³, 500 and 100 Å). Calibration curves were made by using well-fractionated polystyrene and poly(methyl methacrylate) samples with narrow molecular weight distributions ($M_w/M_n = 1.1$).

TABLE 3. Effect of α -Chlorostyrene-Styrene Copolymers on the Polymerization of Styrene^a

Copolymer	Yield of Poly-styrene (wt%)	Mn(x10 ⁻⁴)	Mw(x10 ⁻⁴)	MWD
Polystyrene	34.7	12.3	20.9	1.7
S05CIS	35.0	10.2	15.5	1.5
S5CIS	33.9	7.0	14.9	2.1
S10CIS	25.9	6.6	13.0	2.0
S20CIS	10.1	7.2	11.9	1.7
S50CIS	8.4	6.4	10.7	1.7
S2FS*	31.9	8.3	15.9	1.9

*2/98: α -Fluorostyrene/Styrene Copolymer***Reaction Conditions**

Initiator: AIBN (0.2 mole%); Polymer Concentration: 1 wt percent

Temperature: 50°C; Reaction Time: 50 Hrs

TABLE 4. Effect of 5/95- α -Chlorostyrene/Styrene Copolymer Concentration on the Polymerization of Styrene^a

Concentration of Copolymer (wt %)	Yield of Poly-styrene (wt%)	Mn(x10 ⁻⁴)	Mw(x10 ⁻⁴)	MWD
0.0	34.7	12.32	20.94	1.7
0.9	33.9	7.02	14.89	2.1
1.2	20.1	7.34	15.30	2.1
2.0	15.3	5.35	12.71	2.4
5.0	3.4	1.61	3.47	2.2

***Reaction Conditions**

Initiator: AIBN (0.095g); Styrene (3 ml); Temperature: 50°C

Reaction Time: 19 Hrs

NMR Spectra

^1H -NMR spectra were recorded using a Varian Associates, Gemini-200 NMR spectrometer. ^{13}C -NMR spectra were recorded using Varian Associates Gemini-200 and XL-400 NMR spectrometers. In all cases, the samples were dissolved in CDCl_3 and measurements were made at ambient temperature.

Infrared Absorption Spectra

Infrared spectra of polymers dispersed in KBr pellets were recorded using a Nicolet Model 5SXC FT-IR spectrometer.

U.V. Absorption Spectra

U.V. spectra were recorded on a Hewlett Packard Model HP 8452 Diode Array spectrophotometer.

Elemental Analysis

Carbon, hydrogen and chlorine analyses were done by Galbraith Laboratories, Inc., Knoxville, TN.

RESULTS AND DISCUSSION

Homopolymerization of α -Chlorostyrene

When α -chlorostyrene containing 0.2 mole percent AIBN was heated at 50-53°C under nitrogen, the reaction mixture began to turn brown after 3-4 hours and this color deepened with increasing reaction time. However, there was no visible evidence of polymerization or of substantial chemical change of α -chlorostyrene. It seems that monomer decomposition did not occur during the polymerization attempt. However, the acidity of the monomer mixture sharply increased during the course of the reaction. The pH of aqueous extracts of the polymerization mixture was initially 7 but it fell to 2 during the reaction.

A small amount of polymer was isolated by adding the polymerization mixture to hexane, in which it is insoluble. It was purified by reprecipitation from benzene solution into hexane. The yield and molecular weight of the polymer were very low; in the case of a 40 hour reaction, the yield was less than 1 percent and the number average molecular weight was 2,000 g/mol.

As another observation, when the polymerization was conducted for more than 40 hours, a crystalline substance was formed in addition to a polymeric product, but it was hard to purify for characterization. The NMR spectrum of the

unpurified crystalline substance contains resonances in the 7-8 ppm region. This suggests that it is a naphthalene compound.

Infrared and NMR spectra of polymer isolated from the reaction mixture indicate that it has a very low content of aliphatic hydrogens. In fact, the spectrum of the polymer is very similar to that of *trans*-cisoidal poly(phenylacetylene) [13].

IR Spectrum

Figure 2 shows the IR spectrum of the polymer prepared from α -chlorostyrene, along with the IR spectra of polymers prepared from styrene and styrene- α -chlorostyrene mixtures. If this spectrum is compared with the IR spectrum of polystyrene, significant differences can be noted. The strong absorbance at 2900 cm^{-1} in the spectrum of polystyrene, which is due to CH_2 stretching vibrations, is absent from the spectrum of the product derived from α -chlorostyrene although aromatic C-H stretching absorption between 3100 cm^{-1} and 3000 cm^{-1} is evident in both spectra.

The absence of aliphatic C-H absorption in the spectrum of the polymer derived from α -chlorostyrene, the absence of a broad band of medium intensity in the $600\text{-}850\text{ cm}^{-1}$ range due to carbon-chlorine bond stretching modes and the detection of acidity in the polymerization mixture suggest that dehydrochlorination reactions occur in addition to, or instead of, polymerization when α -chlorostyrene is heated with AIBN.

NMR Spectra

Figure 3 shows typical ^1H -NMR spectra of polymers obtained from α -chlorostyrene, styrene and α -chlorostyrene-styrene mixtures. The spectrum of the polymer derived from α -chlorostyrene homopolymerization consists of aromatic proton resonance at $\delta = 6\text{-}8\text{ ppm}$ with only weak resonance in the aliphatic region ($\delta = 1\text{-}4\text{ ppm}$). The ^1H -NMR spectrum of the polymer is similar to the spectrum of poly(phenylacetylene) [12]. Also, it does not show a signal at $\delta = 7.75\text{ ppm}$, which occurs in the NMR spectrum of 1,3,5-triphenylbenzene.

The ^{13}C -NMR spectrum of the polymer derived from α -chlorostyrene is shown in Figure 4. It exhibits strong aromatic carbon resonance at $\delta = 124\text{-}130\text{ ppm}$ but only weak aliphatic carbon resonance.

UV Spectra

Figure 5 shows the UV spectra of polymers derived from α -chlorostyrene, styrene and their mixtures. The spectrum of the homopolymer derived from α -

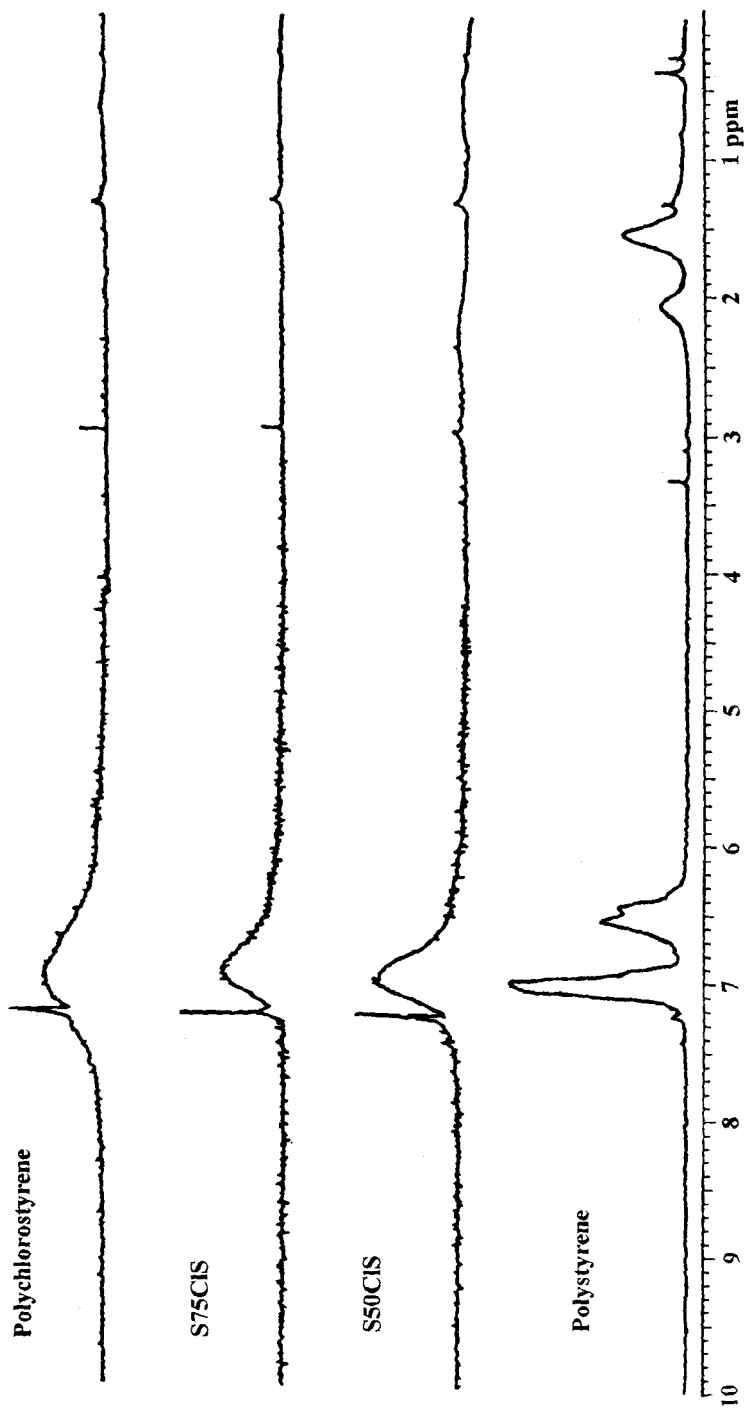


Figure 3. 200 MHz $^1\text{H-NMR}$ spectra of products obtained from copolymerizations of α -chlorostyrene with styrene.

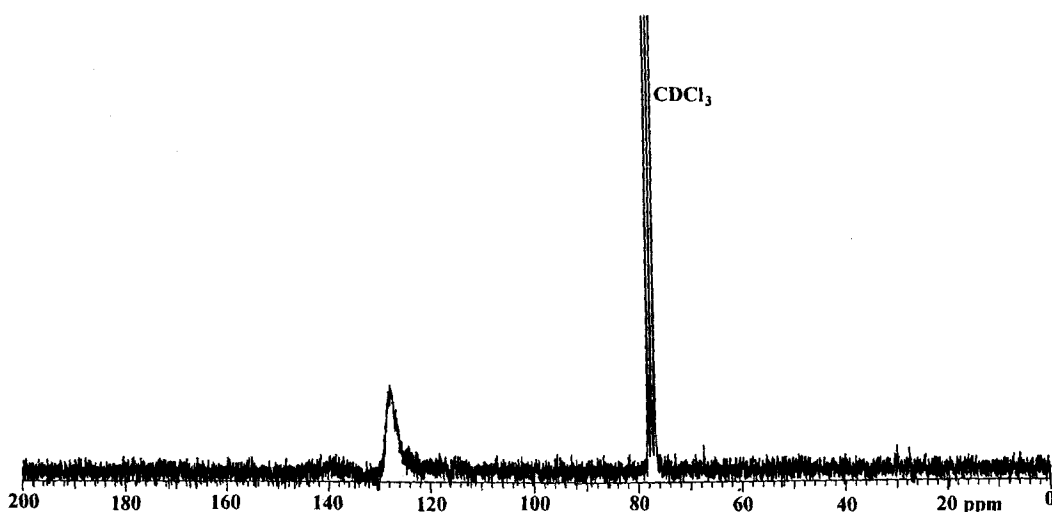


Figure 4. 50 MHz ¹³C-NMR spectrum of polymer obtained from α -chlorostyrene (SIOOCIS).

chlorostyrene contains, in addition to the absorption at 250 nm that is evident in the spectrum of polystyrene, longer wavelength absorption which extends out to above 460 nm. This long wavelength absorption is probably due to the presence of polyene segments in the polymer backbone.

The studies conducted on the homopolymerization of α -chlorostyrene indicate that low molecular weight polymer is formed in very low conversion and that dehydrochlorination processes accompany the reaction. Several possibilities may be considered as explanations for the low conversions and low molecular weights obtained in these polymerization experiments. One is that, by some means, α -chlorostyrene can act as an inhibitor for free radical polymerizations. Another is that α -chlorostyrene units, when incorporated into polymers, can in some way become capable of inhibiting free radical polymerization.

To evaluate these possibilities, copolymerization experiments involving α -chlorostyrene were conducted. Also, products derived from the copolymerization experiments were investigated as components of those polymerization reactions to determine if they could inhibit other polymerizations.

Copolymerization of α -Chlorostyrene with Styrene

The yields and molecular weights of the products obtained during studies on the copolymerization of α -chlorostyrene with styrene are shown in Table 1.

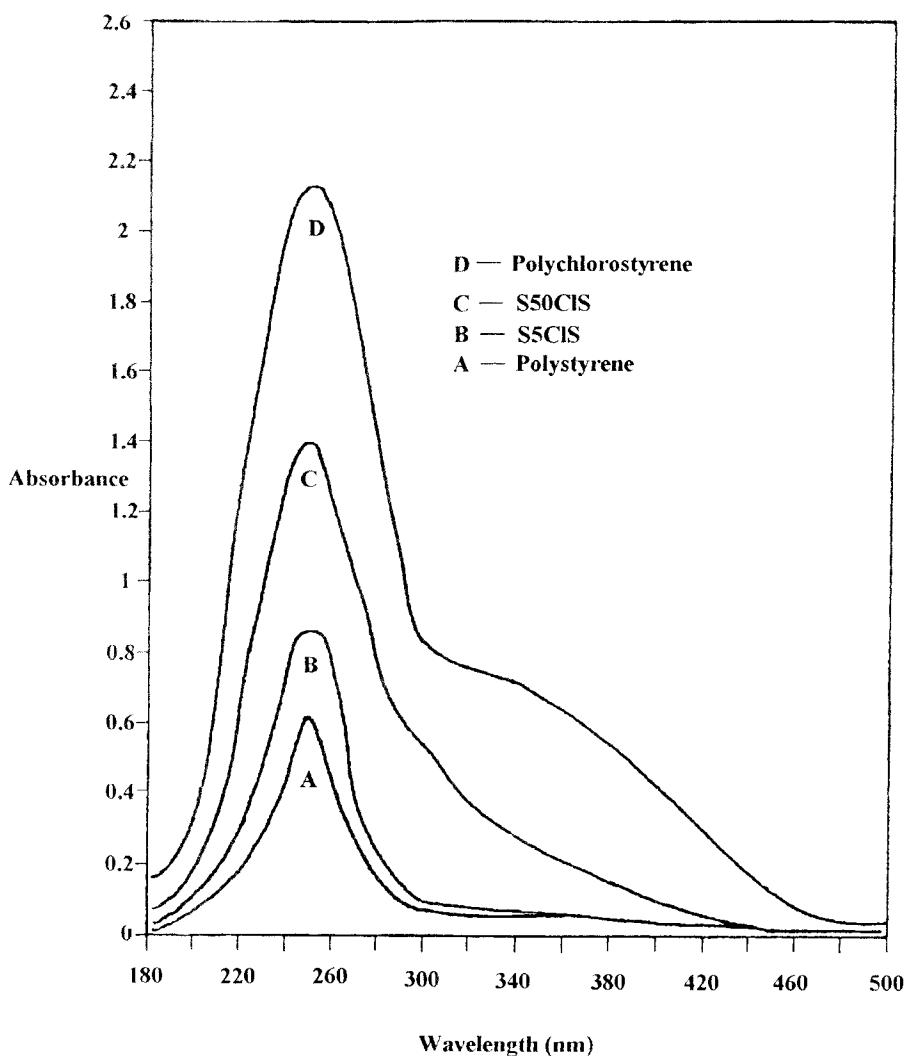


Figure 5. UV spectra of products obtained from polymerizations and copolymerizations of α -chlorostyrene and styrene.

These results indicate that the overall rate of polymerization decreases with increasing α -chlorostyrene content of the copolymerization mixture. Furthermore, the molecular weights of the copolymers decrease regularly with increasing α -chlorostyrene content. These results suggest that α -chlorostyrene markedly inhibits the polymerization of styrene.

IR Spectra

Figure 2 shows the infrared spectra of products obtained from copolymerizations of α -chlorostyrene-styrene mixtures. The characteristic decrease of aliphatic C-H absorption ($2800\text{--}2900\text{ cm}^{-1}$) compared to aromatic and olefinic C-H absorption ($3000\text{--}3200\text{ cm}^{-1}$) and the absence of broad bands of medium intensity due to C-Cl stretching ($600\text{--}850\text{ cm}^{-1}$) indicate that evolution of HCl occurs during the copolymerization reactions, causing unsaturation to become incorporated in the backbone of the polymers.

$^1\text{H-NMR Spectra}$

$^1\text{H-NMR}$ spectra of several products obtained from the copolymerization of α -chlorostyrene with styrene are shown in Figure 3. The proportion of aliphatic proton resonance ($\delta = 1\text{--}2\text{ ppm}$) decreases as the mole percent of α -chlorostyrene used in the copolymerization experiments increases. The weak signals due to aliphatic protons in the spectra of the copolymerization products are consistent with the IR data and with the suggestion that dehydrochlorination processes accompany the copolymerization process.

UV Spectra

Figure 5 shows the UV spectra of several products obtained from the copolymerization experiments. From these data it is seen that intensities of absorption at 250 and 340 nm increase as the amount of α -chlorostyrene in the copolymerization mixtures increases. The higher values of products obtained from polymerization mixtures containing 50 and 100 mole percent α -chlorostyrene indicate that there is conjugation between phenyl rings and unsaturated double bonds in the backbone.

Thermal Analysis

Figure 6 shows TGA curves of several products obtained from the polymerization and copolymerization experiments. It can be seen that the product obtained when 50 mole percent α -chlorostyrene was present in the copolymerization mixture shows weight loss at 150°C , presumably due to dehydrochlorination of α -chlorostyrene units in the polymer. However, the product obtained from pure α -chlorostyrene is somewhat more stable than that obtained from an equimolar styrene- α -chlorostyrene mixture. This means that the dehydrochlorination reaction occurred already during the homopolymerization because there was no significant weight loss at 150°C due to dehydrochlorination. All of the copolymers obtained from α -chlorostyrene and styrene were less thermally stable than polystyrene.

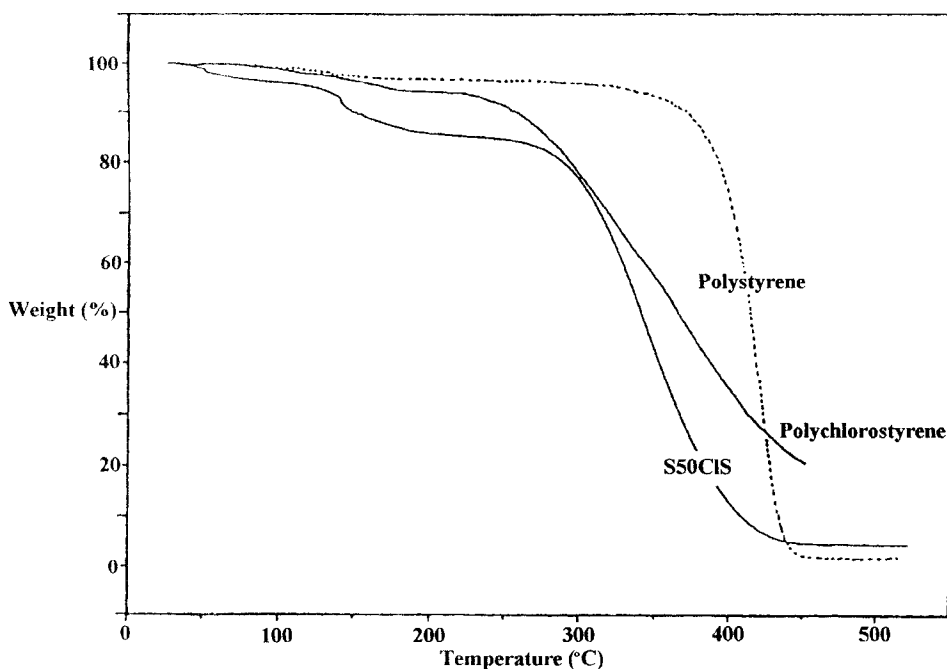


Figure 6. TGA curves of products obtained from polymerizations and copolymerizations of α -chlorostyrene and styrene.

Elemental Analysis

Analysis of the products obtained from the copolymerization experiments indicated that the products formed from reaction mixtures employing less than 40 mole percent α -chlorostyrene contained substantial amounts of chlorine, as much as four times as much as would be expected if styrene (S) and α -chlorostyrene (CIS) copolymerized homogeneously ($r_S = r_{CIS} = 1$). This suggests that α -chlorostyrene is more reactive than styrene in this copolymerization system.

On the other hand, products formed from reaction mixtures employing more than 40 mole percent α -chlorostyrene contained less chlorine than would be expected, assuming homogeneous copolymerization. These results are summarized in Table 5. They suggest that the dehydrochlorination reactions that occur during the copolymerization attempts involve several contiguous α -chlorostyrene units. Perhaps dehydrochlorination of an α -chlorostyrene- α -chlorostyrene dyad in the copolymer is more favorable than dehydrochlorination of an α -chlorostyrene unit that has styrene neighbors, due to the relief in steric crowding that would be present at a pair of α -chlorostyrene units.

TABLE 5. Elemental Analysis on Copolymers of a α -Chlorostyrene and Styrene

Sample	Mole %	Cl%	C%	H%
	α -Chlorostyrene	T*/E	T*/E	T*/E
S05CIS	0.5	0.17/ 0.91	92.16/91.52	7.67/7.77
S2CIS	2	0.67/ 1.49	91.71/90.16	7.62/7.56
S5CIS	5	1.66/ 3.64	90.82/88.84	7.52/7.26
S10CIS	10	3.26/ 4.93	89.39/88.12	7.35/7.07
S25CIS	25	7.78/10.54	85.33/82.80	6.89/6.50
S50CIS	50	14.46/11.41	79.18/82.91	6.36/6.22
S75CIS	75	20.27/11.30	74.13/82.87	5.60/6.10
S100CIS	100	25.36/ 5.19	69.57/89.03	5.07/5.78

T*: Theoretical values (assuming homogeneous copolymerization)

E: Experimental values

TABLE 6. Yields and Molecular Weights of Copolymers Obtained by Copolymerizing α -Chlorostyrene with Methyl Methacrylate^a

Mole % α -Chlorostyrene	Yield (%)	Mn($\times 10^{-4}$) (g/mol)
2	4.11	0.70
5	1.59	0.41

*Reaction Conditions

Initiator: AIBN (0.2 mole%); Temperature: 50°C; Reaction Time: 50 Hrs

Copolymerization of α -Chlorostyrene with Methyl Methacrylate

Table 6 shows the yields and molecular weights of products obtained when attempts were made to copolymerize α -chlorostyrene with methyl methacrylate. The yields and molecular weights of products obtained from copolymerizations involving α -chlorostyrene and methyl methacrylate are lower than those of products obtained from analogous copolymerizations involving styrene and α -chlorostyrene.

The stronger effect of α -chlorostyrene as an inhibitor for the polymerization of methyl methacrylate compared to that of styrene may be due to a polar effect.

Effect of Cumyl Chloride on the Polymerization of Styrene

The previous discussion makes it clear that α -chlorostyrene is an inhibitor for polymerization. Several possibilities can be proposed to explain this characteristic, including inhibition by polymers that are derived from α -chlorostyrene and by dehydrohalogenated structures that are derived from α -chlorostyrene units that become enchainned in polymers.

To evaluate the first of these possibilities, studies on the effect of cumyl chloride on the polymerization of styrene and methyl methacrylate were undertaken. Since the structure of cumyl chloride is very similar to that of an α -chlorostyrene unit that is incorporated into a polymer, it was believed that the behavior of cumyl chloride would provide an indication of how α -chlorostyrene units in polymers would behave toward radicals.

Table 2 summarizes the effect of cumyl chloride on polymerizations of styrene. It can be seen that cumyl chloride is also an inhibitor for these polymerizations.

Calculation of Inhibitor Constants

The studies described above show that α -chlorostyrene and cumyl chloride inhibit polymerizations of styrene and methyl methacrylate. They should be regarded as inhibitors rather than as chain-transfer agents because the products derived from their reactions with free radicals do not appear to be capable of reinitiating the polymerization of these monomers. This is shown by the dramatic reductions in polymer yields that occur when very small amounts of α -chlorostyrene or cumyl chloride are present in polymerization mixtures.

To obtain some idea of the reactivity of these compounds toward free radicals, the molecular weights of the products obtained from the various copolymerization attempts were used with the Mayo equation to determine inhibitor constants for these materials. The Mayo equation is usually used for determining chain transfer constants, but it can be used in the present instance to evaluate inhibitor constants or "apparent chain transfer constants". The form of the Mayo equation used in this work is given below:

$$\frac{1}{DP} = \frac{1}{DP_0} + I_s \frac{(S)}{(M)}$$

TABLE 7. Inhibitor Constants Evaluated for α -Chlorostyrene and Cumyl Chloride

Inhibitor	Monomer	Inhibitor Constant ($\times 10^4$)
α -Chlorostyrene	Styrene	2,200
Cumyl chloride	Styrene	714
Cumyl chloride	MMA	390

In this equation, I_s is the inhibitor constant for a substance, S, this being equal to k_s/k_p , where k_s , and k_p are the rate constants for the inhibition and propagation reactions, respectively.

Other terms in this equation include DP and DP₀, the degrees of polymerization obtained in the presence and absence of inhibitor. The results obtained are given in Table 7. The values of the inhibitor constants are very high. They are in the range between the chain transfer constants for carbon tetrachloride (110×10^{-4}) and carbon tetrabromide ($22,000 \times 10^{-4}$), which are very effective chain transfer agents for styrene polymerization. The higher inhibitor constant of α -chlorostyrene compared to cumyl chloride may indicate that inhibition in the case of α -chlorostyrene involves addition of radicals to this substance.

Three possible factors may affect the inhibitor constant of α -chlorostyrene: first, a low reactivity of the α -chlorostyrene radical; second, the resonance stabilization of the tertiary radical produced after abstraction of chlorine from the backbone of the polymer; and third, the effect of conjugated double bonds in the resulting polymer backbone are dehydrochlorination.

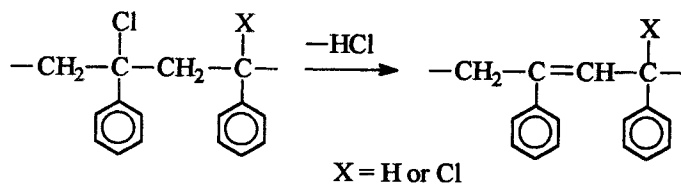
In the next discussion, the effect of conjugated double bonds in the polymer backbone will be discussed in more detail by studying the effect of polymers derived from efforts to copolymerize α -chlorostyrene and styrene on the polymerization of styrene.

Effect of Polymers Derived from Efforts to Copolymerize α -Chlorostyrene and Styrene on the Polymerization of Styrene

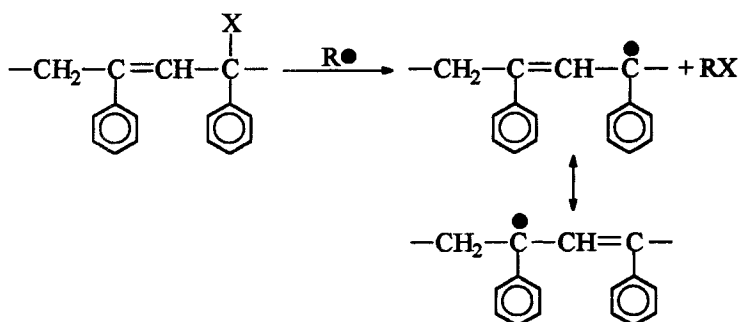
Table 3 summarizes the results of experiments in which small amounts (1 wt. percent) of products derived from α -chlorostyrene-styrene copolymerizations were present in styrene polymerization mixtures. It can be seen that the yields and molecular weights of the polystyrenes produced were reduced when any of the products of the α -chlorostyrene-styrene copolymerizations were present.

In another series of experiments, the product obtained from attempts to copolymerize 5 mol% α -chlorostyrene and 95 mol% styrene was added to styrene polymerization mixtures and its effect on the polymerization was observed. Table 4 shows the effect of the concentration of the copolymerization product on the polymerization of styrene. It shows that the copolymer caused a large decrease in molecular weight and yield of the polystyrene produced and that its effect increased as its concentration in the polymerization mixture increased. Based on these results, it seems very likely that enchainment of α -chlorostyrene in a copolymer generates a structure that is an effective inhibitor for free radical polymerization. From the structural point of view, the high activity of the copolymerization product as an inhibitor is probably due to the weak strength of the benzylic carbon-chlorine bonds present, and to the allylic hydrogen or chlorine atoms, such as $-\text{C}\phi = \text{CH} - \text{CH}\phi-$ or $-\text{C}\phi = \text{CH} - \text{C} - \text{Cl}\phi$ which are produced by dehydrochlorination of α -chlorostyrene units that are incorporated into the polymer.

The results obtained in this study suggest that polymers derived from α -chlorostyrene are able to inhibit the polymerization of vinyl monomers. This may be due to propagating radicals reacting directly with tertiary chlorine atoms present on α -chlorostyrene units present on α -chlorostyrene units, but it is also likely that α -chlorostyrene units become converted to unsaturated structures by dehydrochlorination processes, *viz.*,



Dechlorination might be caused by either radical or ionic processes, but the unsaturated structures that are formed are capable of being very effective inhibitors, since they can be converted to very stable radicals when another radical abstracts an allylic hydrogen or chlorine atom.



CONCLUSIONS

Polymerization of α -chlorostyrene by free radical initiated processes yields a highly unsaturated low molecular weight polymer in very low yield. Copolymerization of α -chlorostyrene with styrene also affords low molecular weight, unsaturated polymers in low yield when the molar percentage of α -chlorostyrene is greater than about one percent. α -Chlorostyrene and polymers derived from it inhibit polymerizations of styrene and methyl methacrylate, apparently because dehydrochlorination of α -chlorostyrene units in the polymers leads to unsaturated structures that are very effective polymerization inhibitors.

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