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FREE-RADICAL-INITIATED COPOLYMERIZATION OF 2-CHLOROSTYRENE, 4-CHLOROSTYRENE, AND 2,6-DICHLOROSTYRENE WITH MALEIC ANHYDRIDE

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ABSTRACT

The title copolymers have been prepared by the free-radical-initiated copolymerization of 2-chlorostyrene (2-ClSt), 4-chlorostyrene (4-ClSt) and 2,6-dichlorostyrene (2,6-DCISt) with maleic anhydride (MAn) in toluene at 65°C. Copolymers of chlorinated styrenes with MAn prepared under different monomer-to-monomer ratios in the feed have alternating composition. In all cases, the mixture of comonomers forms charge-transfer complex monomers (CTC). The initial rate of copolymerization increases with the increase of electron donors in the comonomer feed, and the highest rates were at the equimolar ratios of comonomers in the feed. The thermal stability of the polymers was measured by thermogravimetric analysis in nitrogen. Homopolymers decompose by a one-step mechanism, while copolymers are more thermostable and decompose by a two-step mechanism. Glass transition temperatures (T_g s) of homopolymers are lower than T_g s of copolymers. The number and weight average molecular weights of chlorinated copolymers are higher than those of the corresponding homopolymers.

Key Words: Mechanism of copolymerization; Charge-transfer-complex monomers; Poly(2-chlorostyrene-co-maleic anhydride); Poly(4-chlorostyrene-co-maleic anhydride); Poly(2,6-dichlorostyrene-co-maleic anhydride); Thermal properties; Rate of copolymerization.

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INTRODUCTION

The studies of the preparation and properties of polymers and copolymers of chlorinated styrenes are of interest because they have higher thermal stability, lower flammability, and often have significant influence on the miscibility behavior of blends in which polystyrene is substituted with halogenated styrene polymers and copolymers (1–3). In a recently published article (4), we have shown that in the free-radical-initiated copolymerization of 2,6-dichlorostyrene with maleimide, *N*-methylmaleimide and *N*-phenylmaleimide, respectively, the copolymers with random arrangement of monomers were obtained.

In continuation of our studies on the mechanism of copolymerization of chlorinated styrene derivatives, we wish to describe in this article the copolymerization of 2-ClSt, 4-ClSt and 2,6-DClSt with powerful electron accepting maleic anhydride monomer. It is well known that maleic anhydride (MAN) is not easily homopolymerized, but that it readily copolymerizes with a great variety of other monomers. It is further known that copolymers of MAN improve the physicochemical properties of copolymers by increasing polarity, glass transition temperature, and functionality (5).

EXPERIMENTAL

Chemicals

All chlorostyrene monomers are commercial products (Aldrich Chemical Company) and were purified by vacuum distillation before used. MAN (Aldrich Chemical Company) was purified by sublimation before used.

Polymerization Procedure

Polymerization was performed in vacuum-sealed 10-mL glass vials thoroughly degassed, filled with nitrogen, and placed into an oil bath thermostated at 65°C. Homopolymerization of chlorinated styrene derivatives and copolymerization with MAN were initiated with 0.5 wt% of AIBN in toluene. The solution of polymers was diluted with butanone and precipitated by a drop-wise addition of methanol. The polymer was filtered off and dried in vacuum at 80°C overnight. Composition of copolymers was determined from the chlorine content (Tabs. 1–3).

Physicochemical Measurements

Proton nuclear magnetic resonance (¹H-NMR) spectra, differential scanning calorimetry, thermogravimetric analysis, and molecular weights were determined in the same manner as previously described (4,6). Charge-transfer-complex

Table 1. Polymerization Conditions and Properties of Poly(2-ClSt-co-MAN) in Toluene at a Total Comonomer Concentration of 2 mol L⁻¹ at 65°C with 0.5 wt% of AIBN

Molar fraction of 2-ClSt in feed		in copolymer		Polymer. time (min)	Polymer yield (g)	Conversion (%)	Cl (%)	T _g (°C)	Molecular weight M _w ·10 ⁻³ M _n ·10 ⁻³ (g mol ⁻¹)	
0.2	0.49	30	0.06990	16.3	14.86	204	-	-		
0.3	0.50	30	0.06870	15.6	15.07	204	481.8	284.3		
0.4	0.51	30	0.07500	16.4	15.18	202	478.4	284.4		
0.5	0.51	30	0.07885	16.7	15.32	199	393.7	206.0		
0.6	0.53	30	0.07805	16.0	15.63	196	-	-		
0.7	0.53	45	0.08695	17.2	15.80	192	-	-		
0.8	0.52	75	0.06375	17.0	15.48	180	289.6	118.7		
1.0	-	1042	0.36690	66.2	25.28	130	67.6	37.6		

monomers (CTC-monomers) were determined by transformed Benesi-Hildebrand ¹H NMR method in CDCl₃ at 25°C (7,8). The concentration of MAN was constant, 0.01 mol L⁻¹, whereas the concentration of chlorinated monomers varied from 0.4 to 2.6 mol L⁻¹. The chemical shifts of the olefinic protons of MAN appear at 7.03 ppm. The equilibrium constant is obtained as intercept of the plot (Fig. 1) of the reciprocal of the molar concentration of chlorinated styrene derivatives

Table 2. Polymerization Conditions and Properties of Poly(4-ClSt-co-MAN) in Toluene at a Total Comonomer Concentration of 2 mol L⁻¹ at 65°C with 0.5 wt% of AIBN

Molar fraction of 4-ClSt in feed		in copolymer		Polymer. time (min)	Polymer yield (g)	Conversion (%)	Cl (%)	T _g (°C)	Molecular weight M _w ·10 ⁻³ M _n ·10 ⁻³ (g mol ⁻¹)	
0.2	0.49	30	0.10935	25.8	14.79	226	-	-		
0.3	0.50	30	0.11415	25.9	15.03	226	187.2	47.5		
0.4	0.51	30	0.11600	25.1	15.35	226	196.2	66.5		
0.5	0.51	30	0.11770	24.9	15.20	225	254.7	101.7		
0.6	0.49	30	0.10085	20.6	14.84	223	-	-		
0.7	0.50	30	0.08000	15.8	14.87	223	-	-		
0.8	0.55	30	0.05151	9.9	16.12	215	209.7	68.9		
1.0	-	1042	0.20000	36.2	25.45	130	46.6	28.2		

Table 3. Polymerization Conditions and Properties of Poly(2,6-DClSt-co-MAn) in Toluene at a Total Comonomer Concentration of 2 mol L⁻¹ at 65°C with 0.5 wt% of AIBN

Molar fraction of 2,6-DClSt in feed	Molar fraction of in copolymer	Polymer. time (min)	Polymer yield (g)	Conversion (%)	Cl (%)	T _g (°C)	Molecular weight	
							M _w ·10 ⁻³	M _n ·10 ⁻³ (g mol ⁻¹)
0.2	0.49	300	0.08365	18.47	25.65	241	-	-
0.3	0.49	300	0.13950	29.25	25.72	241	49.5	29.2
0.4	0.48	300	0.18460	37.26	25.46	241	58.9	31.1
0.5	0.49	300	0.18540	34.52	25.82	240	75.7	35.0
0.6	0.50	300	0.18330	31.87	25.98	240	-	-
0.7	0.50	300	0.18250	30.34	25.98	240	-	-
0.8	0.50	300	0.12520	19.69	26.13	233	72.3	35.3
1.0	-	300	0.06885	9.95	41.43	163	23.5	13.7

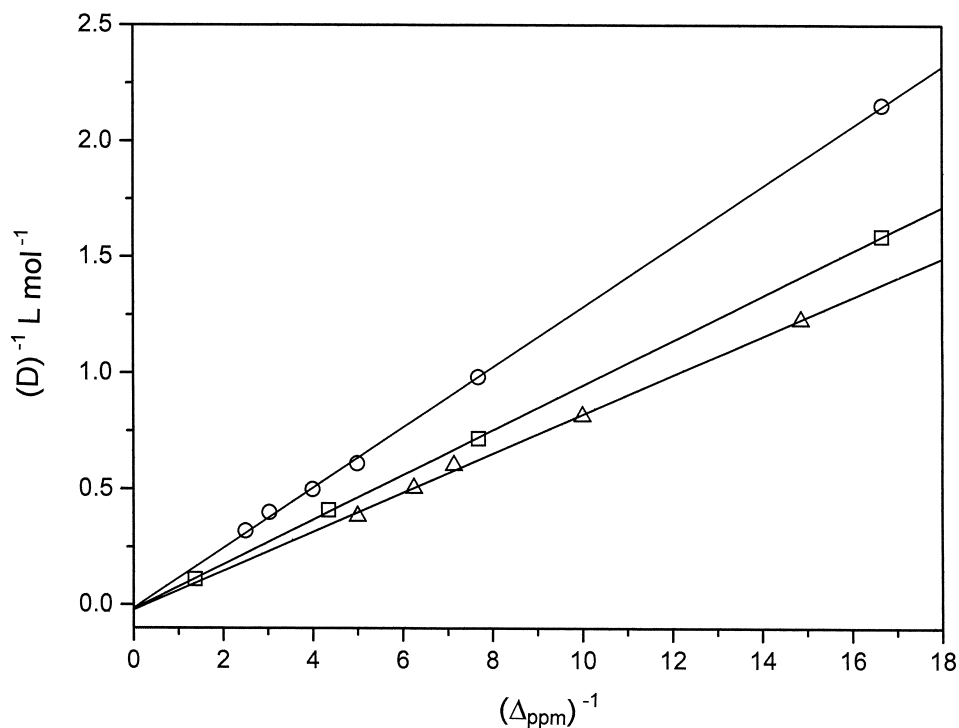


Figure 1. Determination of equilibrium constants of CTC-monomers of 2-ClSt/MAN (o); 4-ClSt/MAN (□); 2,6-DClSt/MAN (Δ); $(\Delta_{\text{ppm}})^{-1}$ is reciprocal of the difference between chemical shifts of complex and uncomplex MAn; (D^{-1}) is reciprocal of molar fraction of chlorinated monomers in copolymers.

against the reciprocal of the chemical shifts of the difference between complexed and uncomplexed MAn molecule, $(\Delta_{\text{ppm}})^{-1}$ (9).

RESULTS AND DISCUSSION

Free-Radical-Initiated Polymerization of 2-ClSt, 4-ClSt, and 2,6-DClSt with MAn

On admixture of the studied chlorinated styrene monomers with MAn in CDCl_3 , no change of color was observed, but by applying the transformed Benesi-Hildebrand $^1\text{H-NMR}$ procedure (7, 8), it was found that all three systems show the presence of CTC-monomers. Although the equilibrium constants have very low numerical values, they were determined with high precision and reproducibility (Fig. 1). The numerical values of equilibrium constants are: $K_{2\text{-ClSt/MAn}} = 0.01 \text{ mol L}^{-1}$, $K_{4\text{-ClSt/MAn}} = 0.02 \text{ mol L}^{-1}$, and $K_{2,6\text{-DClSt/MAn}} = 0.02 \text{ mol L}^{-1}$.

Polymerization conditions and properties of title compounds are presented in Tables 1–3.

It is evident that although equilibrium constants have low numerical values, the copolymerization of 2-ClSt, 4-ClSt, and 2,6-DClSt with MAn results in the formation of alternating copolymers regardless of the ratio of comonomers in the feed. In our previous article, it was shown that in the copolymerization of α -methylstyrene with *N*-phenylmaleimide, alternating copolymers were formed through the participation of CT-complex monomers, although the complexation constant has a low value of 0.02 mol L^{-1} (10). It is of interest to note that copolymerization of studied chlorinated monomers with MAn proceeds by alternating mechanism, while the copolymerization of 2,6-DClSt with maleimide results in the formation of copolymers with random arrangement in polymer chains (Fig. 2).

The dependence of the initial rate of copolymerization, R_p , on the monomer composition at different monomer-to-monomer ratios in the feed, at constant total monomer concentration of 2 M, are plotted in Figure 3. The data in Figure 3 indicate that $R_p(4\text{-ClSt/MAn}) > R_p(2\text{-ClSt/MAn}) > R_p(2,6\text{-DClSt/MAn})$, but in all cases, the maximal initial rate of copolymerization is highest at the equimolar concentration of comonomers in the feed. The difference in initial rates of copolymerization can be attributed to the steric hindrance due to position of halogen atom in the styrene monomer.

The data in Tables 1–3 indicate that molecular weights of copolymers are much higher than the weights of the corresponding homopolymers and the molecular weight of copolymers increase in following order: $M_w(2\text{-ClSt/MAn}) > M_w(4\text{-ClSt/MAn}) > M_w(2,6\text{-DClSt/MAn})$. It is of interest to mention that in gel permeation chromatography (GPC) measurements of molecular weights of poly(chlorinated St-co-MAn), when tetra hydrofuran (THF) was used as mobile phase, the chromatograms are skewed with significant tailing. The same was previously described in case of molecular weight determination of poly(St-co-MAn) (11).

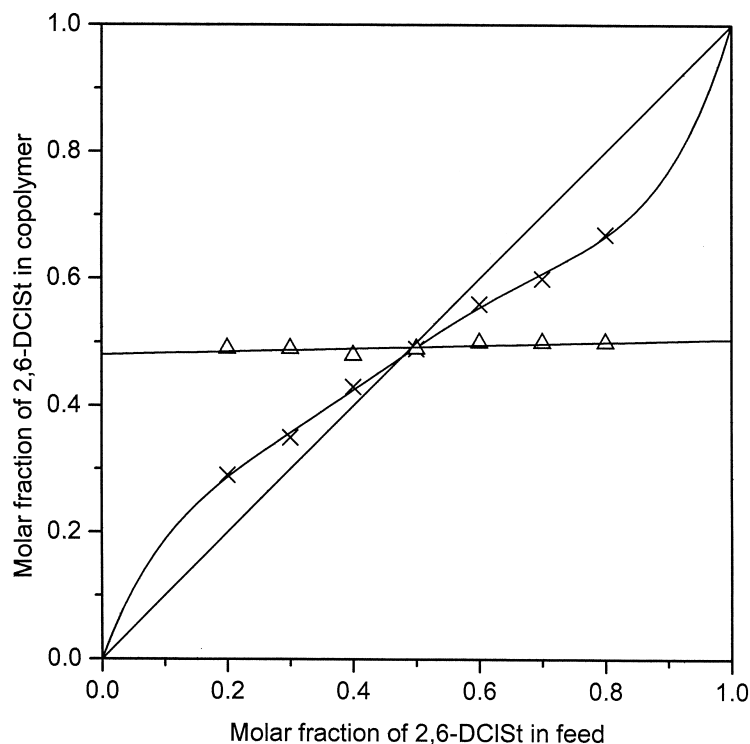


Figure 2. Ratio of molar fraction of 2,6-DCISt in feed and in copolymers with MAn (Δ) and maleimide (x).

Thermal Stability and Mechanism of Decomposition of Poly(2-ClSt), Poly(4-ClSt), Poly(2,6-DCISt) and Copolymers with MAn

Homopolymers of 2-ClSt 4-ClSt and 2,6-DCISt decomposes by a one-step mechanism as shown in Figure 4. As seen, the poly(2,6-DCISt) is the most stable homopolymer that decomposes in a relatively narrow range between 400°C and 450°C.

Figure 5 plots the thermograms of copolymers with MAn, which decompose by a two-step mechanism. In the first step, copolymers decompose similarly to homopolymers, but at a certain transition temperature, they form a stable residue, which decomposes at a temperature over 600°C.

Numerical values of glass transition temperatures of the studied homopolymers and copolymers are listed in Tables 1–3. All T_g s are within the thermostable region of thermograms in Figures 4 and 5. T_g s of homopolymers are lower than that of copolymers and have the following values: T_g (2-ClSt/MAn) and T_g (4-ClSt/MAn) = 130°C, T_g (2,6-DCISt/MAn) = 163°C. T_g s of copolymers are: T_g [poly(2-ClSt-co-MAn)] \approx 200°C, T_g [poly(4-ClSt-co-MAn)] \approx 226°C, T_g [poly(2,6-DCISt-co-MAn)] \approx 240°C.

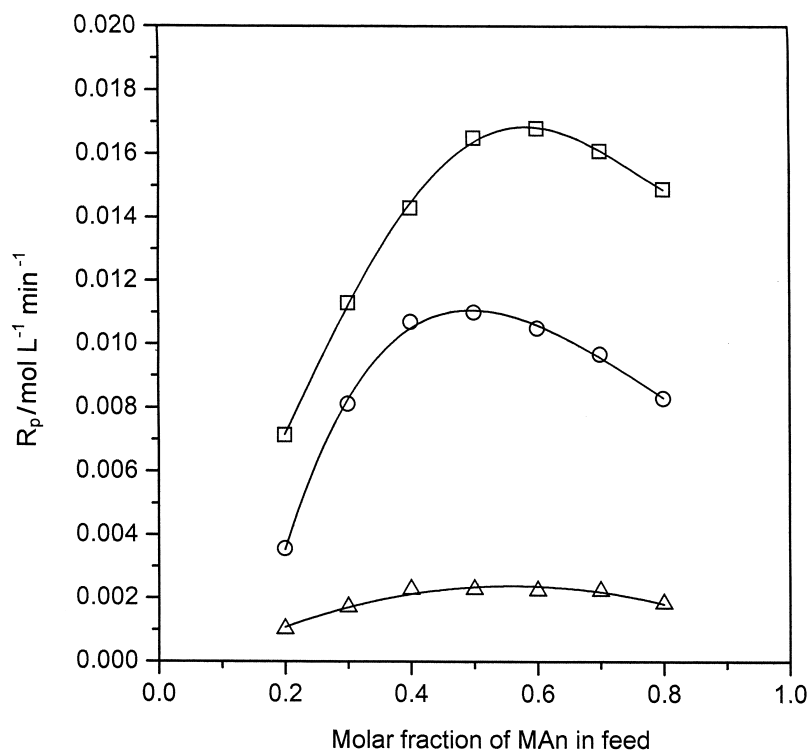


Figure 3. Initial copolymerization rates versus feed molar ratios in the copolymerization with MAn of 2-ClSt/MAn (o); 4-ClSt/MAn (\square); 2,6-DClSt/MAn (Δ); 0.5 wt.% of AIBN in toluene at 65°C; total monomer concentration 2 mol L⁻¹.

CONCLUSION

Under the free-radical-initiated copolymerization of 2-ClSt, 4-ClSt, and 2,6-DClSt with MAn in toluene, alternating copolymers were obtained regardless of the ratio of comonomers in the feed.

The initial rates of copolymerization of equimolar ratio of comonomers in the feed increase in the following order: $R_p(4\text{-ClSt/MAn}) > R_p(2\text{-ClSt/MAn}) > R_p(2,6\text{-DClSt/MAn})$.

Molecular weights (M_w) of copolymers are higher than M_w of homopolymers. The M_w of copolymers increases in the following order: $M_w(2\text{-ClSt/MAn}) > M_w(4\text{-ClSt/MAn}) > M_w(2,6\text{-DClSt/MAn})$.

In thermogravimetric analysis, homopolymers of 2-ClSt, 4-ClSt, and 2,6-DClSt decompose by a one-step mechanism, while copolymers decompose by a two-step mechanism under the formation of residue stable at temperatures higher than 600°C.

T_g s of homopolymers and copolymers are within the thermally stable region in thermogravimetric analysis. T_g s of copolymers are higher than T_g s of

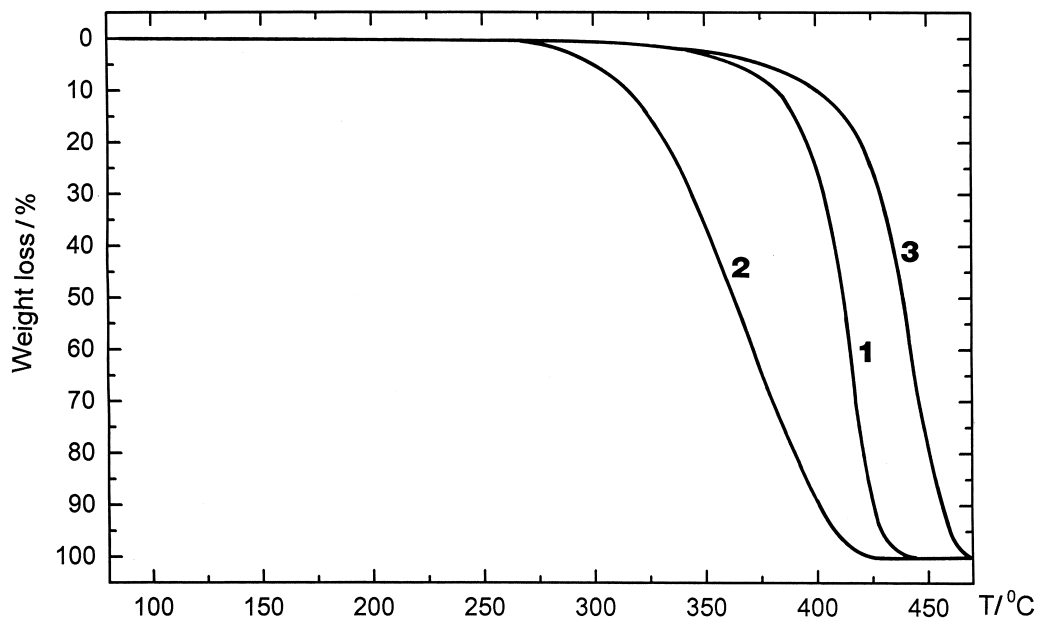


Figure 4. Thermograms of poly(2-ClSt) (1); poly(4-ClSt) (2); poly(2,6-DClSt) (3); heating rate $10^{\circ}\text{C min}^{-1}$ in nitrogen.

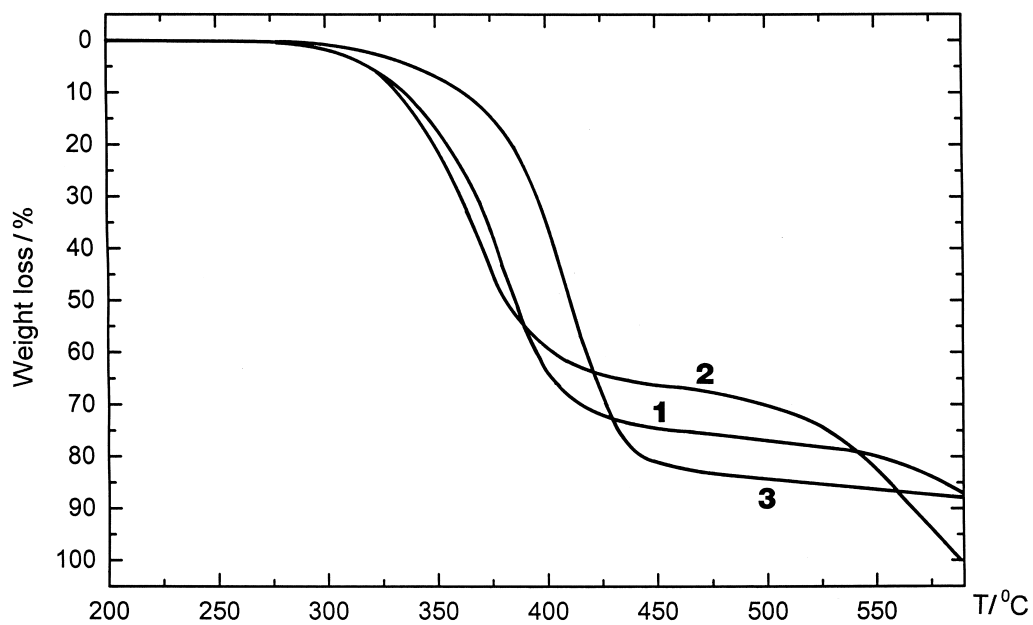


Figure 5. Thermograms of poly(2-ClSt-co-MAN) (1); poly(4-ClSt-co-MAN) (2); poly(2,6-DClSt-co-MAN) (3); heating rate $10^{\circ}\text{C min}^{-1}$ in nitrogen.

homopolymers, and increase in the following order: $T_g[\text{poly}(2\text{-ClSt-co-MAn})] < T_g[\text{poly}(4\text{-ClSt-co-MAn})] < T_g[\text{poly}(2,6\text{-DClSt-co-MAn})]$.

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