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MACROMOLECULAR CHEMISTRY
AND POLYMERIC MATERIALS

Copolymerization of 2-Chloro-Substituted *p*-Cyclopropylstyrenes with Styrene and Properties of the Resulting Copolymers

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Abstract—2,2-Dichloro- and 2-chloro-1-(*p*-vinylphenyl)cyclopropanes were prepared and brought into copolymerization with styrene. The effect of substituents on the reactivity of the monomers was examined. The physicomechanical properties of the copolymers were studied.

One of the ways to improve the physicomechanical, thermal, and optical properties and enhance the flame resistance of polystyrene plastics is copolymerization of styrene with other monomers. In so doing, it is possible to vary the properties of the copolymers in a wide range.

The copolymerization of styrene with substituted styrenes has been studied extensively [1–7].

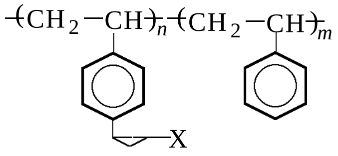
In this study, we prepared 2,2-dichloro- and 2-chloro-1-(*p*-vinylphenyl)cyclopropanes (**I**, **II**, respectively) and performed their copolymerization with styrene in the bulk and in solution; we also examined the effect of the chlorinated substituents on the reactivity of the monomers and on the properties of the resulting copolymers. We found that styrene smoothly copolymerizes with the monomers synthesized, without opening of the cyclopropane ring; the resulting copolymers are soluble.

The copolymerization under the conditions of our experiments occurred through opening of the double bond, yielding macromolecules with pendant phenyl groups (unsubstituted and those bearing chlorinated cyclopropane fragments). This is suggested by the spectra of the copolymers. The ratio of the monomeric units (**I** or **II** to styrene) in the copolymer was estimated from the chlorine content determined by elemental analysis.

The IR spectra of both the starting monomers and copolymers thereof contain characteristic bands belonging to vibrations of the C–Cl bond (675 cm^{-1}) and cyclopropane ring (1030–1040 cm^{-1}). The spectra of the copolymers also contain well-defined bands at 1450, 1500, 1585, and 1605 cm^{-1} belonging to vibrations of the benzene ring. Strong bands at 1213 and 1170 cm^{-1} and bands at 1110 and 1013 cm^{-1} are characteristic of 1,4-disubstituted benzenes and belong to the in-plane bending modes of the four hydrogen atoms of the benzene ring.

Changes in the intensities of the bands belonging to the main functional groups of **I** and **II** suggest changes in the composition of the monomeric units.

The IR data allow us to ascribe the following structure to the copolymers:



where X = 2Cl (**I**), Cl (**II**).

For this pair of monomers, we calculated the copolymerization constants and the Alfrey–Price parameeters *Q* and *e* [8]. To evaluate the distribution of units in the macromolecular chain, we calculated the microstructural parameters L_{M_1}, L_{M_2}, and R [9]. The results are listed in Table 1.

Table 1 shows that, at any ratio of the starting monomers, the copolymer is always enriched in units of mono- or gem-dichloro-substituted cyclopropylstyrenes, which is due to the higher reactivity of these monomers, caused by the presence of the substituted cyclopropane ring.

The chlorine atoms, which are present in **I** and **II** as substituents in the cyclopropane ring and are separated from the reaction center by the phenyl ring and a cy-

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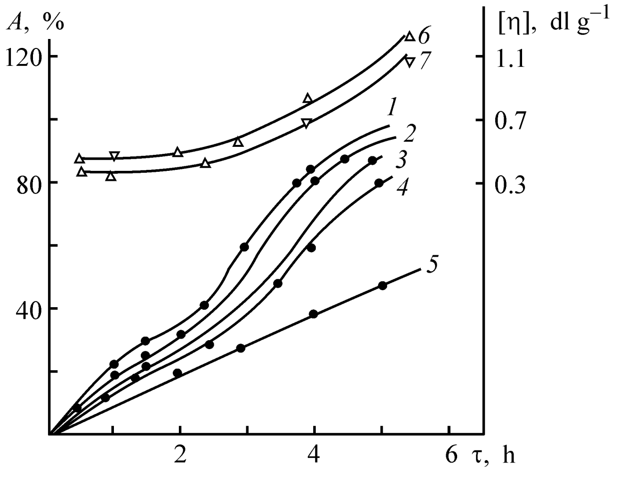
Table 1. Copolymerization of 2,2-dichloro- and 2-chlorocyclopropylstyrenes **I** and **II** (M_1) with styrene (M_2)

Starting mixture, mol %		Copolymer composition, mol %		Microstructure*			Parameters of copolymerization of **I** and **II** (M_1) with styrene (M_2)					
M_1	M_2	M_1	M_2	L_{M1}	L_{M2}	R	r_1	r_2	r_1r_2	Q_1	e_1	Cl, %
Cyclopropylstyrene (**I**)												
10	90	17.10	82.90	1.134	5.500	30.15	1.21 ± 0.06	0.50 ± 0.03	0.605	3.523	–1.508	5.70
25	75	35.95	64.05	1.403	2.500	51.24						11.98
50	50	59.75	40.43	2.210	1.500	53.91						19.86
75	25	79.87	20.19	4.630	1.167	34.50						26.62
90	10	91.85	8.15	11.890	1.056	15.45						30.62
Cyclopropylstyrene (**II**)												
10	90	16.66	83.34	1.13	5.68	29.37	1.20 ± 0.04	0.52 ± 0.02	0.624	2.77	–1.486	3.31
25	75	35.07	64.93	1.4	2.56	50.5						6.98
50	50	59.13	40.87	2.2	1.52	53.76						11.76
75	25	79.68	20.32	4.6	1.17	34.66						15.85
90	10	91.77	7.96	10.72	1.06	16.98						18.25

* (L_{M_1}, L_{M_2}) Mean lengths of blocks of the corresponding monomeric units; (R) harwood parameter of block structure.

clopropane fragment in the *p*-position relative to the styrene double bond, decrease the copolymerization constants relative to unsubstituted styrene. This is due to increased conjugation in the monomer molecule as a result of the effect of the substituents additionally stabilizing the forming radical. The copolymerization constants of **I** and **II** differ insignificantly.

The influence exerted by the chlorine atoms on the vinyl group through the three-membered carbon ring and phenyl ring leads to an increase in the extent of conjugation in the monomer molecule, but only slightly depends on the number of chlorine atoms. This is confirmed by the UV spectra of **I** and **II**, in which the absorption maxima are located at 295 and 292 nm, respectively.



Variation with time τ of the (*1*–*5*) yield *A* and (*6*, *7*) intrinsic viscosity [η] of 2,2-dichloro-1-(*p*-vinylphenyl)cyclopropane (**I**)–styrene copolymer. 70°C. Content of **I** in the starting mixture, %: (*1*, *7*) 100, (*2*) 90, (*3*) 80, (*4*, *6*) 70, and (*5*) 0.

To reveal regular trends in the polymerization and study the properties of the copolymers, we performed copolymerization of **I** and **II** with styrene in a wide range of ratios of the starting monomers.

The kinetic curves of initiated copolymerization of **I** with styrene at 70°C (see figure) show that, after 37–46% conversion of the monomers is reached, the copolymerization occurs with autoacceleration. The effect becomes more pronounced as the content of **I** in the mixture is increased. The molecular weight of the forming polymers appreciably increases at high conversions.

Experiments on thermal copolymerization at high temperatures (110–150°C) revealed no appreciable self-acceleration, and the intrinsic viscosity of the copolymers remained virtually constant at all the conversions. Some properties of the copolymers are given in Table 2.

Table 2 shows that introduction of chloro-substituted cyclopropylstyrene units into the polystyrene chain increases the Vicat softening point and enhances the optical and physicomechanical properties, compared to styrene homopolymer. Some of the copolymers obtained show self-extinguishing behavior. This property becomes more pronounced with an increase in the content of **I** in the copolymer.

Table 2. Physicomechanical characteristics of the copolymers prepared

Parameter	Polystyrene	Copolymers with indicated content of **I** or **II**, %			
		40		60	
		I	**II**	**I**	**II**
Intrinsic viscosity [η], dl g^{-1}	1.15	1.17	–	–	
Refractive index	1.5895	1.6010	1.5905	1.6040	1.6010
Vicat softening point, °C	103	119	116	128	126
Brinell hardness, kgf cm^{-2}	14	16	15	–	–
Ultimate tensile strength, MPa	39.0	34.8	35.0	35.0	
Relative elongation at break, %	1.7	1.5	–	1.5	–

Parameter	Polystyrene	Copolymers with indicated content of **I** or **II**, %					
		70		80		90	
		I	**II**	**I**	**II**	**I**	**II**
Intrinsic viscosity [η], dl g^{-1}	1.15	1.13	–	1.15	–	–	–
Refractive index	1.5895	1.6053	1.6038	1.610	1.6080	1.6115	1.6105
Vicat softening point, °C	103	132	130	139	–	148	136
Brinell hardness, kgf cm^{-2}	14	24	16	–	–	27	19
Ultimate tensile strength, MPa	39.0	–	–	45.0	47.0	46.8	48.7
Relative elongation at break, %	1.7	–	–	1.9	–	1.9	–

Thus, the properties of the copolymers derived from chloro-substituted cyclopropylstyrenes are governed by the substituent in the monomers, and the activity of the monomers in the copolymerization depends on the extent of conjugation of the vinyl π electrons with the substituent *p* electrons.

EXPERIMENTAL

The starting monomer, 2,2-dichloro-1-(*p*-vinylphenyl)cyclopropane **I**, was prepared as described in [6]. 2-Chloro-1-(*p*-vinylphenyl)cyclopropane **II** was prepared as follows. Sodium metal (0.1 mol, 2.3 g) was added in small pieces to a solution of **I** (0.2 mol, 42.6 g) in benzene, after which methanol was added dropwise with stirring and cooling on an ice bath. After the reaction was complete, distilled water was added, the organic layer was separated, and the aqueous layer was extracted with ether. The combined organic phases were evaporated, and the product was vacuum-distilled; bp 78–80°C/1 mm Hg. Yield 36% (12.85 g); n_D^{20} = 1.5630, d_4^{20} = 1.12, $MR_{D\text{calc}}/MR_{D\text{exp}}$ = 52.388/51.76. Analytical data:

Found, %: C 73.95, H 6.16, Cl 19.88.
Calculated, %: C 73.58, H 6.05, Cl 19.75.

The purity of the monomers was checked chromatographically; it was 99.9% in all the cases. The kinetics of the copolymerization of **I** and **II** with styrene was studied in ampules in a nitrogen atmosphere at various ratios of the starting monomers. To determine the copolymerization parameters, the reaction was stopped at ≤10% conversion. The compositions of the copolymers were determined by elemental analysis for chlorine, and their molecular weights were estimated from the intrinsic viscosity, determined with an Ubbelohde viscometer at 25°C in benzene. All the copolymers were reprecipitated from a benzene solution with methanol. The softening points of the copolymers were determined by the Vicat method. The physicomechanical parameters of the copolymers were determined with film samples prepared by casting from a benzene solution. The IR spectra were measured with a Specord M-80 spectrophotometer.

After appropriate purification and drying, all the copolymers were white powders soluble in aromatic and chlorinated hydrocarbons.

CONCLUSIONS

(1) New monomers, 2,2-dichloro- and 2-chloro-1-(*p*-vinylphenyl)cyclopropanes, were prepared, and

their copolymerization with styrene was performed. These monomers are more reactive than styrene in polymerization, owing to the presence of a substituted cyclopropane ring.

(2) The copolymerization constants and Alfrey–Price parameters of the cyclopropylstyrenes were calculated. The chlorine substituents in the cyclopropane ring make higher the relative reactivity constants and the specific activity of the monomers.

(3) The physicomechanical properties of the copolymers were determined. Introduction of chlorosubstituted cyclopropylstyrene units into the polystyrene chain increases the softening point, refractive index, and hardness of the copolymers.

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