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Abstract

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COPOLYMERIZATION OF α, β, β-HALOGEN-SUBSTITUTED PARADIVINYLBENZENES WITH STYRENE

It is known that replacement of hydrogen atoms in the vinyl group of styrene by fluorine and chlorine atoms leads to a sharp decrease in the reactivity of the monomer in polymerization [1–3]. However, α, β-substituted styrenes copolymerize with vinyl monomers. Molecules of α, β, β-halogen-substituted paradivinylbenzenes contain two vinyl groups with different activity. It therefore seemed of interest to investigate the ability of these monomers to undergo polymerization and copolymerization.

We investigated four previously unstudied divinylbenzenes: *n*-vinyl-α, β-difluoro-β-chlorostyrene (I), *n*-isopropenyl-α, β-difluoro-β-chlorostyrene (II), *n*-bis-(α, β-difluoro-β-chlorovinyl)-benzene (III), and *n*-bis-(α, β-difluoro-β-chlorostyryl) (IV). Monomers III and IV, containing only difluorochloro-substituted vinyl groups, like the previously studied α, β-difluoro-β-chlorostyrene, did not polymerize. This is evidently explained by steric hindrance created by the halogen atoms and by delocalization of the electron-cloud density of the π-bond of the substituted vinyl group [2]. Monomers I and II contain, respectively, vinyl and isopropenyl groups. Double bonds in such groups are opened during the polymerization of other monomers, for example styrene and α-methylstyrene. Comparison of the infrared (IR) spectra of styrene and monomer (I) showed that introduction of the difluorochlorovinyl group does not weaken the interaction of the π-electrons of the benzene ring and the vinyl group. Thus, the polarization of the double bond of the vinyl group is not diminished thereby, and because of this bond monomer I should be no less active in polymerization than styrene. However, polymers of monomers I and II could not be obtained. Upon prolonged heating of these monomers only viscous yellow liquids are formed. Their IR spectra differ from the spectra of the pure monomers by a lower intensity of the absorption bands due to stretching vibrations of double bonds (1629 and 1685 cm^{-1}), and by changes in the position and intensity of the absorption bands due to deformation vibrations of the C–F and C–H bonds of the difluorochlorovinyl and vinyl

groups, respectively (regions 900–1400 cm^{-1} and 1820–1830 cm^{-1}). This made it possible to conclude that monomers I and II dimerize. Formation of dimers was also observed for α,β-halogen-substituted styrenes [1,2]. Apparently, the molecules of monomers I and II cannot form polymer chains because of steric hindrance created by the bulky difluorochlorovinyl groups, which do not lie in the plane of the benzene ring [4].

Thus, none of the monomers I–IV studied is active in the radical polymerization reaction. However, monomers I, II, and III copolymerize with styrene.

By methods of radical copolymerization in emulsion (according to the procedure described earlier [1,5]), in bulk, and in solution (initiator—azo-bis-isobutyric acid dinitrile in an amount of 0.5% of the mass of the monomers), copolymers of monomers I–III with styrene were obtained (Table 1). In comparison with the previously studied α,β-halogen-substituted styrenes [1,2], these monomers proved to be···

Table 1

Comonomers	Method of carrying out the copolymerization reactions	Composition of the initial monomer mixture, mol. % M_1^0	Composition of the initial monomer mixture, mol. % M_2^0	Copolymerization time, h	Copolymer yield, %	Copolymer composition, mol. % M_1	Copolymer composition, mol. % M_2
p-Vinyl-α,β-difluoro-β-chlorostyrene (M_1) and styrene (M_2)	In bulk: 12 h—60°, 5 h—80°, 8 h—100°	9.06	90.94	25	70	6.9	93.1

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p-Vinyl-α,β-difluoro-β-chlorostyrene (M_1) and styrene (M_2)	In bulk: 20 h—60°, 5 h—100°	8.53	91.47	25		8.4	91.6
p-Vinyl-α,β-difluoro-β-chlorostyrene (M_1) and styrene (M_2)	In emulsion	50.0	50.0	10	57	47.6	52.4
p-Vinyl-α,β-difluoro-β-chlorostyrene (M_1) and styrene (M_2)	In emulsion	33.33	66.67	10	52	32.0	68.0

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p-Vinyl-α,β-difluoro-β-chlorostyrene (M_1) and styrene (M_2)	In emulsion	29.0	71.0	18	90	27.6	72.4
p-Vinyl-α,β-difluoro-β-chlorostyrene (M_1) and styrene (M_2)	In solution in toluene	10.30	89.70	35	52	17.1	82.9
p-Vinyl-α,β-difluoro-β-chlorostyrene (M_1) and styrene (M_2)	In solution in CCl_4	31.64	68.36	20	31	50.0	50.0

Comonomers	Method of carrying out the copolymerization reaction	Composition of the initial monomer mixture, mol. % M_1^0	Composition of the initial monomer mixture, mol. % M_2^0	Copolymerization time, h	Copolymer yield, %	Copolymer composition, mol. % M_1	Copolymer composition, mol. % M_2
p-Isopropenyl-α,β-difluoro-β-chlorostyrene (M_1) and styrene (M_2)	In bulk: 20 h—60°, 2 h—80°, 4 h—100°	5.88	94.12	26	90	6.4	93.6
p-Isopropenyl-α,β-difluoro-β-chlorostyrene (M_1) and styrene (M_2)	In bulk: 20 h—60°, 2 h—80°	3.34	96.66	22	90	3.4	96.6
p-Isopropenyl-α,β-difluoro-β-chlorostyrene (M_1) and styrene (M_2)	In bulk: 20 h—60°, 2 h—80°, 22 h—100°, 30 h—130°	30.72	69.28	74	30	22.5	77.5

Comonomers	Method of carrying out the copolymerization reaction	Composition of the initial monomer mixture, mol. % M_1^0	Composition of the initial monomer mixture, mol. % M_2^0	Copolymerization time, h	Copolymer yield, %	Copolymer composition, mol. % M_1	Copolymer composition, mol. % M_2
p-Isopropenyl-α,β-difluoro-β-chlorostyrene (M_1) and styrene (M_2)	In solution	5.38	94.62	17		9.3	90.7
p-Isopropenyl-α,β-difluoro-β-chlorostyrene (M_1) and styrene (M_2)	In toluene	29.79	70.21	75		32.0	68.0
p-Isopropenyl-α,β-difluoro-β-chlorostyrene (M_1) and styrene (M_2)	In solution in CCl_4	30.62	69.38	25	20	35.2	64.8

Comonomers	Method of carrying out the copolymerization reaction	Composition of the initial monomer mixture, mol. % M_1^0	Composition of the initial monomer mixture, mol. % M_2^0	Copolymerization time, h	Copolymer yield, %	Copolymer composition, mol. % M_1	Copolymer composition, mol. % M_2
p-Bis-(α,β-difluoro-β-chlorovinyl)benzene (M_1) and styrene (M_2)	In bulk: 12 h—60°, 11 h—100°	25.31	74.69	23	30	30.7	69.3
p-Bis-(α,β-difluoro-β-chlorovinyl)benzene (M_1) and styrene (M_2)	50°	1.81	98.19	40	90	1.4	98.6
p-Bis-(α,β-difluoro-β-chlorovinyl)benzene (M_1) and styrene (M_2)	100°	1.81	98.19	15	90	2.5	97.5

Comonomers	Method of carrying out the copolymerization reaction	Composition of the initial monomer mixture, mol. % M_1^0	Composition of the initial monomer mixture, mol. % M_2^0	Copolymerization time, h	Copolymer yield, %	Copolymer composition, mol. % M_1	Copolymer composition, mol. % M_2
p-Bis-(α,β-difluoro-β-chlorovinyl)benzene (M_1) and styrene (M_2)	50°	3.78	96.22	40	90	3.6	96.4
p-Bis-(α,β-difluoro-β-chlorovinyl)benzene (M_1) and styrene (M_2)	100°	3.78	96.22	15	90	2.7	97.3

proved to be more reactive. The composition of all the copolymers obtained is close to the composition of the initial reaction mixture (Table 1).

By the methods listed above it was not possible to initiate the copolymerization reaction of monomer IV with styrene. Such a copolymer could be obtained only by simultaneously using initiation with azo-bis-isobutyric acid dinitrile and ultraviolet (UV) irradiation.

To determine in which of the vinyl groups the double bond opens during copolymerization, the kinetics of copolymerization of monomers I with styrene and II with styrene in solution were studied by IR spectroscopy. Carbon tetrachloride was used as the solvent, as the most transparent of all the solvents available in the laboratory, although it is known that polymerization in CCl_4 gives low-molecular-weight products because of the high rate of the chain-transfer process. The number of monomer molecules that had entered the reaction was calculated

from the decrease in absorption of the reaction mixture in the region of the stretching vibrations of the double bonds of the vinyl and difluorochlorovinyl groups. Simultaneously, the copolymer yield by weight was determined. The frequencies of the stretching vibrations of the double bonds in the vinyl groups of styrene and monomer I and in the isopropenyl group of monomer II in the spectra of the comonomer solutions are indistinguishable. The decrease in absorption in this region is due to a decrease in the concentration of both monomers. The kinetic curves of copolymerization are given in Fig. 1. For comparison, the kinetic curves of homopolymerization of styrene in toluene and in CCl_4 are shown there as well. The rate of copolymerization is 5-6 times lower than the rate of homopolymerization of styrene. The relative decrease in the number of difluorochlorovinyl groups with double bonds during the copolymerization of monomer II with styrene did not exceed 3-4%, i.e., it is of the order of the measurement error. In the copolymerization of monomer I with styrene, this decrease is more noticeable. By the time the reaction ceased, the double bonds had opened in approximately 10% of the difluorochlorovinyl groups and in 30% of the vinyl groups. Chemical analysis of the finished copolymer showed that the copolymer contained

50 mole % of the divinyl component. In all copolymers no unsaturated bonds of the type

$$> C = CH_2$$

were detected. This is indicated by the negative results of bromination reactions and by the absence of absorption bands due to valence vibrations of double bonds and deformation vibrations of C–H in $= CH_2$ groups. If, in the course of copolymerization, all double bonds were opened, then in a copolymer of composition $1 : 1$ there would be two $-CH-CH_2-$groups per one $-CF-CFCl-$ group. According to the IR spectrum of the reaction mixture, for every 9 vinyl groups that entered the copolymerization reaction there is one $-FC-CFCl-$ group in which the double bond has opened. Thus, in the copolymer, double bonds should be opened in approximately 0.2 of all difluorochlorovinyl groups.

Fig. 1. Kinetics of copolymerization of n-vinyl-α,β-difluoro-β-chlorostyrene (1, 2, 3) and n-isopropenyl-α,β-difluoro-β-chlorostyrene (4) with styrene in CCl_4. Relative decrease in the number of $-CH=CH_2$ groups (1), $-CF=CFCl$ (2), yield of copolymers by weight (3) ($C_0 = 8.1$ mol/l; $M_1^0 : M_2^0 = 31.64 : 68.36$); relative decrease in the number of $-CH=CH_2$ and $-(CH_3)C=CH_2$ groups (4) ($C_0 = 3.26$ mol/l, $M_1^0 : M_2^0 = 30 : 70$). Kinetics of polymerization of styrene in CCl_4, $C_0 = 3.26$ mol/l (5); in toluene, $C_0 = 3.30$ mol/l (6) (black points–yield of polymers by weight).

But according to the IR spectra and nuclear magnetic resonance spectra of solutions of the copolymers, double bonds are opened in 0.1 of all difluorochlorovinyl groups. The difference in the IR spectra of the reaction mixture at the moment the reaction is stopped and of the copolymer solution is evidently explained by

Fig. 1. Kinetics of copolymerization of n-vinyl-α,β-difluoro-β-chlorostyrene (1, 2, 3) and n-isopropenyl-α,β-difluoro-β-chlorostyrene (4) with styrene in CCl_4. Relative decrease in the number of $-CH{=}CH_2$ groups (1), $-CF{=}CFCl$ (2), yield of copolymers by weight (3) ($C_0 = 8.1$ mol/l; $M_1^0 : M_2^0 = 31.64 : 68.36$); relative decrease in the number of $-CH{=}CH_2$ and $-(CH_3)C{=}CH_2$ groups (4) ($C_0 = 3.26$ mol/l, $M_1^0 : M_2^0 = 30 : 70$). Kinetics of polymerization of styrene in CCl_4, $C_0 = 3.26$ mol/l (5); in toluene, $C_0 = 3.30$ mol/l (6) (black points—yield of polymers by weight).

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the presence in the reaction mixture of dimers, which are removed during reprecipitation of the copolymer. Groups with unsaturated difluorochlorovinyl bonds are present not only in soluble but also in insoluble copolymers. Proof of this is the formation of graft copolymers of styrene onto copolymers of paradivinylbenzenes with styrene (the copolymers were allowed to swell at room temperature in styrene, in which an initiator had first been dissolved; after this the ampoules were evacuated and placed in a thermostat). Monomeric styrene units can add to copolymer molecules at those sites where $-CF{=}CFCl$ groups are present.

Thus it has been shown that, by the radical mechanism, the monomers studied do not polymerize, but copolymerize with styrene; moreover, the copolymers contain unsaturated bonds in $-CF{=}CFCl$ groups.

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Note: Figure translations are in progress. See original paper for figures.