

Activity of Divinylsulphonyl- and Divinylsulphanyl-Tetrafluorobenzenes in Polymerizations

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Abstract

Quantitative and comparative analysis of the activity of 3,6-bis(vinylsulphonyl)-1,2,4,5-tetrafluorobenzene and 3,6-bis(vinylsulphonyl)-1,2,4,5-tetrafluorobenzene in radical copolymerizations with styrene has been carried out. 3,6-Bis(vinylsulphonyl)-1,2,4,5-tetrafluorobenzene possesses high reactivity in radical reactions due to the effect of the tetrafluoro-substituted benzene ring as an acceptor substituent on the vinyl groups of the monomer.

INTRODUCTION

Polyfluoroarenes are an important and promising class of fluoroorganic compounds, particularly essential to the creation of polymer materials [1]. Due to their high stability, nontoxicity, and unique service characteristics, fluorine-containing polymers have found wide application. Prior to our research [2, 3], no data had been published on polyfluorobenzenes with vinylsulphanyl and vinylsulphonyl groups. At the same time, these compounds are of interest from both theoretical and practical viewpoints and are useful as monomers and cross-linking agents.

When 3,6-bis(vinylsulphonyl)-1,2,4,5-tetrafluorobenzene (VS) was synthesized for the first time, investigation of its chemical properties revealed increased activity of vinyl groups in radical reactions. Thus under mild conditions (20–55 °C) VS reacted with tetrahydrofuran at both vinylsulfonyl groups, forming a homolytic addition product [4]. In further studies of the unusual reactivity of vinylsulfonyl groups of VS in radical addition reactions we investigated the interaction of VS with dialkylphosphites, giving 3,6-bis(dialkoxyphosphonoethylsulphonyl)-1,2,4,5-tetrafluorobenzenes with up

to 60 % yields. An EPR study indicated that a thermally initiated reaction of VS with diethylphosphite (70 °C) gave diethoxyphosphonyl radicals, which actively added at both vinylsulphonyl groups [5].

The unusual activity of vinylsulphonyl groups of VS in radical reactions is an unexpected result because the double bond of vinylsulphones does not typically undergo radical addition reactions, although these compounds readily undergo nucleophilic addition reactions [6, 7]. The lower activity of the double bond of vinylsulphones in radical reactions is explained by the loss of conjugation with the vinyl group (vinyl sulphides, however, typically exhibit high activity in radical reactions) [8].

To evaluate the reactivity of vinylsulphonyl groups of VS we performed copolymerization of this compound with styrene. For the sake of comparison, we estimated the reactivity of vinylsulphones; for this purpose, we employed 3,6-bis(vinylsulphanyl)-1,2,4,5-tetrafluorobenzene (VSB) as a structural analog of VS.

EXPERIMENTAL

3,6-Bis(vinylsulphanyl)-1,2,4,5-tetrafluorobenzene was synthesized from hexafluoroben-

TABLE 1

Copolymerization of 3,6-bis(vinylsulphonyl)-1,2,4,5-tetrafluorobenzene (M_1) with styrene.
Content of DAC 0.1 mass %, 60 °C, mass ratio ($M_1 + M_2$) : chloroform = 0.5 : 0.5 %

Content of M_1 in starting mixture, mol. %	Yield, %	Mass fraction of elements, %				Content of M_1 in copolymer, mol. %
		C	H	S	F	
10	3.2	74.69	6.21	5.11	6.06	22.32
20	4.0	71.25	5.54	6.63	9.24	27.77
50	4.4	43.42	2.55	16.92	17.67	54.50
70	4.8	39.34	2.47	18.71	19.47	58.09

zene and divinyl sulphide; when treated with sodium in liquid ammonia, the latter easily generates ethenethiolate anions with up to 80 % yields. The reaction occurred in dimethylformamide for 4–5 h at 20–30 °C [2].

3,6-Bis(vinylsulphonyl)-1,2,4,5-tetrafluorobenzene was obtained with 65 % yield by oxidation of 3,6-bis(vinylsulphanyl)-1,2,4,5-tetrafluorobenzene with excess hydrogen peroxide (30–33 °C) in acetic anhydride for 2 or 3 days at 20–25 °C. The compounds were identified by IR, ^1H , ^{13}C , and ^{19}F NMR spectroscopy [2, 3].

Radical-initiated [azo-bis-isbutyric acid dinitrile (DAC), 60 °C] copolymerization was performed in chloroform at different initial ratios of monomers up to 5 % conversion. The ampules with the reaction mixture were degassed in a high-vacuum apparatus (pressure 10^{-3} Torr); then they were unsealed and placed in a thermostat. The copolymers were placed in a mixture of ethyl ether and hexane, washed with chloroform, and dried in vacuum until they ceased to lose weight. The compositions of the copolymers were derived from element analysis data [9]; the copolymerization constants were calculated by the nonlinear “curve selection” method reported in elaborate form in [10], using the two-parameter model and the nonlinear regression procedure [11]; the activity factors of the monomers were obtained by the procedure of [12]. The calculations employed the Mayo – Lewis differential equation, which suggests that the reaction should be performed to moderate (~5 %) conversion.

IR spectra of the copolymers were recorded on an IFS-25 spectrometer using KBr pellets.

RESULTS AND DISCUSSION

Copolymerization of VS with styrene (Table 1) occurs selectively at the double bonds of the vinyl groups of the comonomers. The composition of the copolymer depends on the initial proportion of monomers in the mixture.

The IR spectra of the copolymer show characteristic vibration bands of the following groups: C_6H_5 (537, 697, 757, 1451, 1584, 1601 cm^{-1}), SO_2 (117, 1344 cm^{-1}), and $\text{C}_{\text{Ar}}\text{--F}$ (1490 cm^{-1}). The stretching vibration bands of the vinyl group of styrene vanished, while the absorption bands of the vinylsulfonyl ($\text{CH}=\text{CH}\text{--SO}_2$) groups are weak in both monomer and copolymer. Copolymers are white powders well soluble in acetone and toluene.

Data about the dependence of the composition of the copolymer on the initial monomer ratio (see Table 1) were employed for calculating the copolymerization constants of VS with styrene. The copolymerization constants of VSB with styrene were calculated using the data of [13].

The copolymerization constant was evaluated as the ratio of the rate constant of the reaction of the radical with its “own” monomer to the rate constant of the reaction with another radical’s monomer: $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$. This makes it possible to evaluate the relative reactivity in order to compare the activities of a number of vinylsulphones and vinyl sulphides (Table 2) relative to the standard reaction of styrene (M_2) with its radical k_{22} (from the value of $1/r_2$).

The copolymerization constants of VS and styrene ($r_1 = 0.34$, $r_2 = 0.32$) indicate that the

TABLE 2

Copolymerization constants (r_1 , r_2) of sulphur-containing monomers (M_1) in copolymerizations with styrene and activity factors of these monomers (e , Q)

Monomer	r_1	r_2	$r_1 r_2$	$1/r_2$	e_1	Q_1
Divinyl sulphide [14]	0.47	1.90	0.48	0.53	-1.11	0.58
3,6-Bis(vinylsulphanyl)-1,2,4,5-tetrafluorobenzene	0.90	1.02	0.92	0.98	0.51	4.90
Divinylsulphone [15]	0.01	1.30	0.01	0.77	1.33	0.01
3,6-Bis(vinylsulphonyl)-1,2,4,5-tetrafluorobenzene	0.34	0.32	0.11	3.13	0.69	0.95
Methylvinylsulphone [15]	0.01	3.30	0.03	0.30	1.29	0.11
Phenylvinylsulphone [15]	0.01	3.30	0.03	0.30	1.29	0.11

monomers show an aptitude toward alternation of units in a polymer (see Table 2). The azeotropic point is calculated from the copolymerization constants for the initial molar ratio VS : styrene = 49 : 51 % and is comparable to the experimental value. All monomer pairs have a tendency toward alternation in the copolymer ($r_1 r_2 < 0$). In the series of monomers being compared, VS possesses the highest reactivity with styrene radicals ($1/r_2 = 3.13$); this confirms that VS has increased reactivity in radical reactions.

The quantity e_1 is the polarity factor, while Q_1 is the conjugation criterion for the vinylsulphonyl and vinylsulphanyl groups. The positive value of e_1 corresponds to an electron-acceptor substituent at the vinyl group, and the negative value implies that the substituent is an electron donor.

To assess the effect of the tetrafluorobenzene ring on the reactivity of vinylsulphonyl and vinylsulphanyl groups in VSB and VS (for comparison) we chose structural analogs with related electronic structures of the reaction center. These were divinyl sulphide for VSB and divinylsulphone for VS.

For divinyl sulphide, the polarity factor is negative ($e_1 = -1.11$); consequently, sulphide sulphur is electron donor, which is liable to copolymerization with electron-accepting monomers (see Table 2). When the tetrafluorobenzene ring, possessing electron-accepting properties, is introduced in the compound [16], the sign of the polarity factor of the vinylsulphanyl groups of VSB is not reversed, but the electron-donor effect of S^{-2} decreases ($e_1 = -0.51$). In copolymerization with styrene,

VSB is a more active monomer than divinyl sulphide, is conformity with the polarity factors of these compounds.

Vinylsulphones (see Table 2) have positive values of the polarity factor, indicating that the sulphonyl groups are electron acceptors. Divinylsulphone has the largest polarity factor in the series. When phenyl is substituted for the alkyl substituent in methylvinylsulphone, the polarity of the vinyl group does not change ($e_1 = 1.29$). Introduction of the tetrafluorobenzene ring decreases the positive polarity of the vinylsulphonyl groups of VS. This tendency must be responsible for the decreased activity of monomers in radical polymerizations where the radical acts as a donor and the monomer is an acceptor. In the vinylsulfone series, the polarity factor changes oppositely to the reactivity of these compounds.

When the tetrafluorobenzene ring is introduced in molecules containing vinylsulphanyl and vinylsulphonyl groups (VSB and VS), the polarity of the vinyl group decreases, while the activity of the compound in copolymerization with styrene increases ($1/r_2$).

For the monomer pairs being compared (divinyl sulphide – VSB and divinyl sulphone – VS), the reactivity factor Q_1 and the activity in reactions with the styrene radical ($1/r_2$) for VSB and VS increased after the tetrafluorobenzene ring had been introduced in the compounds.

For VS, the reactivity factor was the largest (0.95) in the series of vinylsulfones in agreement with the higher reactivity of this compound (see Table 2, $1/r_2$), but much smaller than that of the VSB structural analog (4.9).

TABLE 3

¹H and ¹³C chemical shifts of divinylsulphanyl and divinylsulphonyl groups, ppm

X	δH_A	δH_B	δH_C	δC_α	δC_β	$\Delta\delta_{\alpha\beta}$	$\delta C_\beta - \delta C_{CH_2=CH_2}$
S [14]	6.39	5.26	5.26	129.88	114.34	15.54	-8.96
SC ₆ F ₄ S	6.39	5.32	5.41	128.39	116.81	11.58	-6.49
SO ₂ [14]	6.73	6.13	6.29	136.94	129.63	7.31	6.33
SO ₂ C ₆ F ₄ SO ₂	7.04	6.42	6.61	135.64	131.58	4.06	8.28

Quantitative relationship between the monomer reactivity in copolymerizations and the structural parameters may be revealed by comparing the reactivity ($1/r_2$) and activity (e , Q) of the monomers with their various physicochemical characteristics.

As is known, the NMR chemical shifts (CS) of the monomers define the electron density on the corresponding atoms and directly reflect the structural characteristics of the compounds. Therefore, one can determine the electronic structure characteristics of the monomers, which can presumably correlate with their reactivity and hence can serve as reactivity indices in copolymerizations.

Table 3 lists the CS of the vinyl group as a reaction center in copolymerizations.

According to [17, 18], the conjugation effects between the vinyl group and the substituents are reflected by the CS of C_β and H_C , and the polarity e of the vinyl group correlates with the difference between the CS of C_α and C_β of the vinyl group ($\Delta\delta_{\alpha\beta}$). If evaluated from $\Delta\delta_{\alpha\beta}$ (see Table 3), the polarity of the vinyl group is lower for VS than for divinylsulphone. Comparative evaluation of the polarities of the vinyl groups of the monomers from the NMR spectral parameters agrees with conclusions about changes in polarity drawn from the calculated polarity factors (e_1).

When the degree of oxidation of sulphur changes from S^{-2} to S^{+6} in the series of compounds presented in Table 3, the vinyl group changes its polarity from negative in sulphides

to positive in sulphones (according to the value of e_1 from Table 2). This indicates that polarization of the double bond of the vinyl group is reversed. To evaluate this change, we introduced the CS of the ethylene carbon atoms ($\delta C_{CH_2=CH_2} = 123.3$ ppm [19]) as a "zero reference". The reversal of polarization was estimated from NMR spectral data using the difference between δC_β of the sulphur-containing monomers and $\delta C_{CH_2=CH_2}$. For divinyl sulfide and VSB, this difference equals -8.96 and -6.49, respectively (see Table 3), indicating that polarization of the vinyl group decreases in VSB, while overall conjugation in the molecule increases because the π system of the tetrafluoro-substituted ring is involved in conjugation. For divinylsulphone and VS, the corresponding values are 6.33 and 8.28, respectively. This suggests that conjugation between the vinyl groups and the substituents in VS increases, while double bond polarization of the vinyl groups is not reversed. In the series of monomers under discussion, the largest values of conjugation (see Table 3, chemical shifts of C_β and H_C) are observed for VS and correspond to the highest reactivity in copolymerization with styrene.

CONCLUSIONS

Thus comparative evaluation of the activities of 3,6-bis(vinylsulphonyl)-1,2,4,5-tetrafluorobenzene and 3,6-bis(vinylsulphanyl)-1,2,4,5-

tetrafluorobenzene from the series of divinyl sulphide and vinyl- and divinylsulphones revealed that introduction of fluorine atoms in the benzene ring enhances conjugation between the vinyl group and the substituent. The vinyl group may be defined as “conjugated” in 3,6-bis(vinylsulphonyl)-1,2,4,5-tetrafluorobenzene, but nonconjugated in vinylsulphones. The substantial degree of conjugation between the vinyl group and the tetrafluorobenzene ring is responsible for the increased reactivity in radical addition reactions.

Acknowledgement

This work was supported by RFBR grant No. 02-03-32844.

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