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Abstract

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CHEMISTRY

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POLYMERIZATION OF VINYL ETHYL SULFONE UNDER THE ACTION OF FREE-RADICAL INITIATORS

Vinyl ethyl sulfones possess a very active double bond; however, their polymerization has been studied very little. At the same time, according to available patent data, polymers obtained on the basis of vinyl sulfones may be of unquestionable practical interest. Introduction of a sulfone group into a polymer helps to increase its heat resistance and benzene resistance ([1,2]). There are indications ([3]) that, during polymerization in an aqueous-emulsion medium and copolymerization of alkyl vinyl sulfones in the presence of persulfate salts, substances useful in the textile industry, as well as benzene-resistant rubbers, are formed. In the study of Prince ([4]), it was shown that, during copolymerization with styrene and vinyl acetate in the presence of dinitrile of azoisobutyric acid (DINA), vinyl methyl sulfone exhibits comparatively low reactivity. There are no published works devoted to the polymerization of vinyl sulfones.

The present investigation was begun with the aim of filling this gap. Vinyl ethyl sulfone was chosen as the object of study, as the most readily accessible from the standpoint of its preparation ([5]). For polymerization, vinyl ethyl sulfone was used that had been purified by the freezing-out method ([6]) and that differed by a higher degree of purity from the sulfone used for synthetic purposes. The results obtained showed that, in bulk polymerization under the action of DINA (catalyst concentration 1 mole %, temperature 60°, polymerization time 10 h), the yield of polymer from vinyl ethyl sulfone purified by freezing out is considerably higher than from that purified by simple distillation, and amounts to 82.6 and 62.0%, respectively. The influence of catalyst concentration, polymerization time, and the use of various initiators and solvents on the yield and molecular weight of the polymer was studied (Tables 1, 2). A sufficiently high yield of polymer is already achieved in 6 h; with a further increase in polymerization time, the polymer yield is quantitative. Judging from the rate of polymerization, vinyl ethyl sulfone is a sufficiently reactive monomer. However, under the action of organoboron compounds, which have been successfully used (7–11) for the polymerization of acrylonitrile, methyl methacrylate, and other polar monomers, it was not possible to obtain positive results in the polymerization of vinyl ethyl sulfone. As catalysts, $(iso\text{-}C_4H_9)_3B$ and $(n\text{-}C_3H_7)_2BOB(n\text{-}C_3H_7)_2$ were used (at concentrations of 1-2 mole %), applied both individually and with additives (HYPERIZ and boron trifluoride etherate), with heating times up to 100 h at 60–80° in bulk and in solution. The negative results are evidently connected with the specific nature of vinyl ethyl sulfone and are unlikely to be due to the possible presence of traces of moisture, since it was purified by us no less carefully than other monomers whose polymerization under the action of organoboron compounds has been studied in the literature.

Table 1

Polymerization of vinylethyl sulfone in bulk

Experiment No.	Catalyst conc., mol. %	Duration, h	Polymer yield, %	$[\eta]$	Mol. wt.** cryoscopy in dioxane	Mol. wt.** light scattering
Catalyst — DINIIZ	**Catalyst — DINIIZ**	**Catalyst — DINIIZ**	**Catalyst — DINIIZ**	**Catalyst — DINIIZ**	**Catalyst — DINIIZ**	**Catalyst — DINIIZ**
1	1	2	32.0	–	1,100	
2	1	4	47.8	–		
3	1	6	65.4	0.0410	1,700	4,600
4	1	8	72.4	–		
5	1	10	82.6	0.0425		4,950
6	0.2	12	74.0	0.0470		
7*	1	10	62.0	–		
Catalyst — benzoyl peroxide	**Catalyst — benzoyl peroxide**	**Catalyst — benzoyl peroxide**	**Catalyst — benzoyl peroxide**	**Catalyst — benzoyl peroxide**	**Catalyst — benzoyl peroxide**	**Catalyst — benzoyl peroxide**
8	1	2	25.0	–		
9	1	6	57.0	0.0450		
10	1	10	67.0			
11	0.2	10	30.0	0.0410		

* Vinylethyl sulfone purified by simple distillation.

** Because of the polarity of the polymer, it appeared possible to measure its molecular weight by the light-scattering method. The discrepancy in the molecular weight of the polymer measured by light scattering and by cryoscopy indicates the polydispersity of the polymer.

In addition to bulk polymerization, the polymerization of vinylethyl sulfone under the action of DINIIZ in solution was studied (Table 2). Toluene, benzene, dioxane, acetone, and dimethylformamide were used as solvents.

Table 2

Polymerization of vinylethyl sulfone in solution (monomer conc. 5 mol/l, temperature 60°)

Solvent	Polymer yield, %	η	Precipitant
Dimethylformamide	17.4	–	Methanol
Toluene	28.0	0.0205	*n*-Butanol
Acetone	29.4	–	Methanol
Dioxane	30.0	0.0190	*n*-Butanol
Benzene	54.5	0.0260	Methanol

The yield of polymer and its molecular weight (see $[\eta]$) are considerably lower than in bulk. This fact is evidently explained by chain transfer through the solvents, with formation of a less reactive radical, which leads to destruction of the active polymerization centers and thereby lowers the yield and molecular weight of the polymer. The polymers obtained are white powders, readily soluble in acetone, dioxane, and methyl ethyl ketone, and insoluble in methanol, benzene, toluene, and *n*-heptane. On evaporation of the solvents they do not form stable films. The melting point lies in the range 125–200°.

Thus, under conditions of radical polymerization both in bulk and in solution, it was not possible to obtain a polymer of high molecular weight.

In conclusion, we give preliminary data on the copolymerization of vinylethyl sulfone with methacrylic acid and methyl methacrylate (Table 3). From the data in Table 3 it is evident that the incorporation of vinylethyl sulfone into copolymerization is small, which indicates its lower reactivity in comparison with the comonomers used.

Experimental part

Purification of vinylethyl sulfone. Vinylethyl sulfone was obtained by dehydration of 2-hydroxyethyl sulfone over H_3PO_4, then purified by freezing out followed by distillation. Freezing out was carried out—

Table 3

Copolymerization

Comonomer	Molar ratio vinyl ethyl sulfone : comonomer	Polymer yield, %	S content in polymer, %	Sulfur-containing component, mol. %
Methyl methacrylate	1 : 3	75.0	2.02	6.4
Methyl methacrylate	1 : 1	52.5	4.28	13.73
Methyl methacrylate	3 : 1	28.3	7.78	25.6
Methacrylic acid	1 : 3	73.4	1.73	4.74
Methacrylic acid	1 : 1	56.8	4.20	11.81
Methacrylic acid	3 : 1	27.8	8.21	24.15

was carried out as follows: to each gram of vinyl ethyl sulfone, 0.7 ml of absolute ether was added; the mixture was cooled with dry ice and acetone, with constant stirring, until freezing began, and was rapidly pressed out under continuous suction with a filter rod fitted with a No. 3 glass filter. The dry crystals were again stirred with a small portion of ether, and the suction operation was repeated. After drying over Na_2SO_4, the frozen-out vinyl ethyl sulfone was distilled in the vacuum of an oil pump. B.p. 95°/4 mm Hg, n_D^{20}1.4622. Vinyl ethyl sulfone purified in this way was stored in sealed ampoules purged with nitrogen. The constants of vinyl ethyl sulfone did not change with time.

Polymerization of vinyl ethyl sulfone under the action of DINITZ and benzoyl peroxide was carried out in ampoules purged with nitrogen, at 60°. Solution and bulk polymerization were investigated at catalyst concentrations of 1 and 0.2 mol. % relative to the amount of vinyl ethyl sulfone. In the case of solution polymerization, the monomer concentration was 5 mol/l. The polymers obtained were purified by repeated reprecipitation from solution in acetone, benzene, methanol, and *n*-butanol. The polymers were dried in vacuum at 2–3 mm to constant weight. The intrinsic viscosity was measured in a suspended-level viscometer in acetone at 25°. The molecular weight was determined by the cryoscopic method in dioxane.

Copolymerization of vinyl ethyl sulfone with methyl methacrylate and methacrylic acid*. Ampoules containing weighed portions of DINITZ (0.1 mol. %) are purged with nitrogen, cooled with ice, and the corresponding amounts of vinyl ethyl sulfone and methyl methacrylate (methacrylic acid) are introduced. The ampoules are then sealed and placed in a thermostat for 60 hours at 60°. The contents of the ampoules are dissolved, in the case of the copolymer of vinyl ethyl sulfone with methyl methacrylate, in benzene and precipitated with methanol; in the case of the copolymer with methacrylic acid, in ethyl alcohol, followed by precipitation with benzene. The copolymers are dried in vacuum at 60°.

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* The work was carried out by N. G. Starova.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.