R. N. Smirnov

1958

SovietRxiv

Abstract

Full Text

R. N. Smirnov

On the Mercuration of Polystyrene

(Presented by Academician A. V. Topchiev on 27 XI 1957)

Until recently, chemists working in the field of high-molecular-weight substances were mainly limited to the synthesis of new monomeric compounds. The polymeric substances obtained as a result of synthesis were rarely considered as raw material for further synthesis. Recently, however, the view of this question has changed, and a large number of works have appeared devoted to so-called "grafted polymers."

The present work is devoted to the synthesis of new derivatives of polystyrene obtained by means of organomercury compounds. The mercuration method has long been used for the analysis of polymers; however, the study of mercury derivatives has received no attention, and they have not been used for synthetic purposes.

Mercuration of polystyrene, naturally, proceeds under conditions different from those of the reaction with the monomer according to Nesmeyanov and Freidlina ([1,2]), or from the reaction with fatty-aromatic compounds according to Makarova and Nesmeyanov ([3]).

For the work a preparation of polystyrene from the Kuskovo Chemical Plant with $n_{\text{cp}} \simeq 1000$ (passport data) was taken. The preparation was purified by double reprecipitation from benzene solution, washed with a mixture of methyl alcohol and benzene $(3:1)$, ground, and dried at 105°. Mercuration of polystyrene with mercury acetate in water, methyl alcohol, and ethyl alcohol proceeds very weakly. A degree of substitution of 17-18% can be achieved in reaction in a boiling solvent over 25 hours.

The mercuration reaction in acetic acid proceeds in a distinctive way. At temperatures up to 50°, sorption of mercury acetate mainly occurs; in boiling acid, the polystyrene is partially carbonized; in addition, a brown, light amorphous product and metallic mercury are formed. Preliminary swelling of polystyrene in a solution of mercury acetate in acetic acid occurs best when the following proportions are observed: 10 g of polystyrene, 200 ml of glacial acetic acid, and 30 g of mercury acetate. After 4-5 days the reacting mixture is transferred to a three-necked flask equipped with a stirrer, reflux condenser, and thermometer, and the reaction is carried out for 10 hours, gradually raising the temperature from 50 to 100° until dissolution of the product begins. After this, the speed of the stirrer is increased to 100–120 rpm and the mixture is brought to boiling.

After the dissolution stage comes the stage of precipitation; usually soon after this it is necessary to stop the reaction, since the product begins to burn onto the bottom of the flask. The hot solution is poured, with stirring, into cold water, and the precipitate is washed by decantation with hot water. The brittle precipitate is ground in a mortar and again washed with hot water. In this product, by means of a color reaction with KI, the Hg ion can readily be detected. To remove the Hg ion, the mercury derivative was kept for swelling in acetic acid for 20–30 hours, and then 10–15 ml of perhydrol was added to it; after 30 min of oxidation the solution was decanted and treated with water, as described above.

The mercury derivative of polystyrene is a white brittle product, insoluble in ordinary organic solvents, but strongly swelling in glacial acetic acid and its mixtures with benzene and acetaldehyde, as well as in pyridine and quinoline.

Table 1

Results of elemental analysis of polystyrene and its derivatives

	C, %	H, %	N, %	S, %	Hg, %	O, % (by difference)	Substitution in benzene rings, % relative to polystyrene	Substitution in benzene rings, % relative to its mercurate II
Polystyrene	92,30	7,70						
Polystyrene mercurate I					34,17		62,12	
Polystyrene mercurate II					28,34		51,71	
Copolymer of styrene with *p*-vinyldiphenyl sulfone	81,72	7,85	—	4,56	—	5,87	34,8	67,1

	C, %	H, %	N, %	S, %	Hg, %	O, % (by difference)	Substitution in benzene rings, % relative to polystyrene	Substitution in benzene rings, % relative to its mercurate II
Copolymer of styrene with 4,4′-vinylnitrodiphenyl ketone	80,10	6,14	2,17	—	—	11,59	28,5	55,1
Copolymer of styrene with *p*-vinylacetophenone	88,56	7,55	—	—	—	3,89	31,1	59,9
Copolymer of styrene with *p*-vinylphenylacetic acid	82,36	7,00	—	—	—	10,64	45,4	87,8

Table 1 gives the analytical data for the original polystyrene and two samples of its mercurates. From mercurate II, swollen in glacial acetic acid, the corresponding copolymers were synthesized with benzenesulfochloride, *p*-nitrobenzoyl chloride, bromoacetic acid, and acetyl chloride. The synthesis was carried out in the apparatus described earlier, at a component ratio of 1 : 1.5, first for 10 h on a water bath, then for 4—6 h in boiling acetic acid. After completion of the reaction, 5—10 ml of perhydrol was added to oxidize the Hg ion; then the contents were diluted with water, and the precipitate was washed on a filter with water, 5% HCl, and again with water.

The reaction products were dissolved in organic solvents, filtered off from metallic mercury, washed with aqueous $NaHCO_3$ solutions and with water. The copolymers were isolated by precipitation with additives. It should be noted that, when small amounts of polystyrene mercurate taken into the reaction are used, low yields of copolymers are obtained owing to their inhomogeneity and large losses during purification of the samples.

Analysis of the samples obtained, conventionally called copolymers, shows a substantial difference from the theoretical calculations.

Thus, the substitution reaction of the mercurate group in polystyrene with the aid of various RH l in acetic acid proceeds in a peculiar manner, leading to the formation both of reduction products and of substitution products. The absence of stoichiometric ratios between N and O, S and O for the two copolymers shows that acetic acid, evidently, also participates in the reaction. In pyridine medium, analogous results

Fig. 1. Thermal decomposition of polystyrene mercurate I (by the method of N. S. Kurnakov)

are obtained more rapidly (15–25 min), but pyridine does not enter into the reaction, as is evident from the analytical results. A comparison of the reaction results for the polymer and for the styrene monomer shows that the reactions proceed in a more complex manner for the polymer. The explanation of this fact should probably be sought in the little-studied stereochemistry of macromolecules.

Figure 1 presents the thermogram of decomposition of polystyrene mercuriacetate (sample 1) according to N. S. Kurnakov, which shows the comparatively low thermal stability of the substance. From the thermogram it may be concluded that polystyrene mercuriacetates are unlikely to find application as plastics; however, considerable possibilities exist for the synthesis of new high-molecular-weight substances based on mercury derivatives.

Polystyrene itself (Fig. 2) and its copolymers, according to X-ray structural analysis, are amorphous substances, whereas its mercuriacetates (Fig. 3) are crystalline. Thus, the mercuration reaction may also be used for structural analysis of certain high-molecular-weight compounds.

The X-ray structural analysis was carried out by B. V. Lukin, and the elemental analysis by A. A. Zakharova. The author expresses gratitude to them for their assistance in the work.

Institute of Fossil Fuels
Academy of Sciences of the USSR

Received
26 XI 1957

REFERENCES

1. A. N. Nesmeyanov, R. Kh. Freidlina, ZhOKh, **7**, 2748 (1937).

2. J. Chatt, *Chem. Rev.*, **48**, 7 (1951).
3. L. G. Makarova, A. N. Nesmeyanov, *Synthetic Methods in the Field of Organomercury Compounds*, Publishing House of the Academy of Sciences of the USSR, 1945.

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

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