

Chemical Transformations of Polymers. XI.

Mercuration of Polystyrene*

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Synopsis

The mercuration of soluble polystyrene was investigated, and it was found that an addition of perchloric acid to the reaction mixture significantly accelerated the polymer transformation. The mercuration proceeds as a polymer analogous reaction, i.e., without any change in the degree of the polymerization. The mercurated product could be converted back to the original polystyrene by hydrolysis or to the corresponding bromopolystyrene by bromination. Ultracentrifuge measurements show that even at low conversion rates all macromolecules were mercurated and unreacted polystyrene could not be identified in the product. Calorimetry indicated the presence of styrene-mercuric acetate blocks in copolymers with high mercury contents.

INTRODUCTION

The mercuration of aromatic hydrocarbons was first described in the last century and studied in greater detail lately by Brown et al. as reviewed by Whitmore¹ and Kitching.² Polystyrene was mercurized with mercuric acetate.^{3,4} As reported by Okawara, Tanaka, and Imoto,⁵ a catalytic effect of perchloric acid is observed when the acid is introduced into the reaction mixture. The catalytic effect of the acid in the low molecular weight reaction system has yet to be proved.²

Since polymers containing mercuric groups are of importance as selective sorbents or reactive carriers,⁶⁻⁹ we investigated the polymer analog, namely, the mercuration of polystyrene, in more detail.

EXPERIMENTAL

Materials. Polystyrene, BX Plastics Limited, twice reprecipitated from benzene solution (5%) into methanol (1:10), MW 2.9×10^5 (viscometrically); perchloric acid 70% (analytical purity grade); mercuric acetate (reagent grade); nitrobenzene (reagent grade). The other chemicals used were analytical purity grade.

Mercuration. Polystyrene (1 g; 9.6 mmole structural units) was dissolved in 20.5 ml [60 ml] nitrobenzene and 0.5 ml glacial acetic acid. The mercurizing solution containing variable amounts of mercuric acetate and perchloric acid in 20 ml [50 ml] glacial acetic acid was added with stirring at a reaction temperature T during 10 min (1 min in experiments according to Fig. 3). (Values given

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in square brackets hold for experiments in Fig. 4.) After a reaction time τ_r , the mixture was poured into an excess of methanol, the product was filtered off, washed with methanol to a negative reaction toward mercury with diphenylcarbazine, and dried in air, and the mercury content was determined. The molar conversion of the polymer, K , was calculated with respect to styrenemercuric acetate: $K = \% \text{ Hg} \times 10,414 / [20,061 - (\% \text{ Hg} \times 258.66)]$.

Protolysis of Mercurized Polystyrene. A sample (0.3 g, 0.65 mmole structural units) of poly(styrenemercuric acetate) (43.47% Hg; $K = 51.33\%$) was mixed with 4.5 g dioxan, 0.24 g glacial acetic acid, and 1.45 g (3.6 meq/ml) of strongly acid styrene cation exchanger in the H^+ form after centrifugation swollen in aqueous dioxan (1:1). The mixture was then heated in an ampoule to 90°C with occasional shaking. The mercurized polystyrene dissolved after 24 hr, the cation exchanger was filtered off and washed with dioxan, and the combined filtrates were evaporated to dryness (0.22 g). One part of the dry residue was used in measurements in the ultracentrifuge; the rest (0.1 g) was dissolved in benzene (3 ml) and precipitated into methanol (300 ml). The polymer thus obtained was analyzed after drying, and some traces of mercury were detected ($<0.1\%$).

Bromination of Mercurized Polystyrene. A sample (1.83 g, 3.99 mmole structural units) of pulverized poly(styrenemercuric acetate) ($K = 52\%$), finely ground, was stirred (1 hr) with a KBr solution (1.2 g) in methanol (50 ml) and washed with methanol on the filter to give a negative reaction toward Br^- . Poly(styrenemercuric bromide) dried in air was mixed with bromine (0.52 ml, 10 mmole) in chloroform (50 ml) at room temperature, mercuric bromide was filtered off on the following day, and the dissolved polymeric product was precipitated into methanol (250 ml). The dried product contained 32.6% Br (calculated for theoretical conversion, 31.2% Br).

Analytical Procedure. The mercury content in the polymer was detected by burning on Pt-asbestos in a stream of oxygen, trapping Hg on an Au film, and weighing. Infrared spectra were measured with a UR-10 (Carl Zeiss, Jena) apparatus by the KBr disc technique.

Ultracentrifuge. The samples were characterized by measuring sedimentation velocities in an analytical ultracentrifuge SPINCO E-HT (rotor An-D, 50 740 rpm, 12-mm cell, temperature measurement and control by using the RTIC system). The photographic recording of the course of sedimentation by means of the Philpot-Svenson optical system was evaluated on a two-dimensional Zeiss Jena reading microscope. The sedimentation coefficients (at a given concentration) were determined from the positions of the maxima on the gradient curves; a semiquantitative evaluation or the gradient curves enabled the molecular weight distribution to be estimated.

The mercurated polystyrene ($K = 6.58\%$) was measured in tetrahydrofuran at 25°C ($c_0 = 0.66\%$); the protolyzed poly(styrenemercuric acetate) (with the original $K = 51.33\%$) was measured in cyclohexane at 40°C ($c_0 = 0.56\%$). Both samples were compared with the original polystyrene, each time under the same experimental conditions.

DSC Calorimetry. A Perkin-Elmer DSC-1 apparatus was used, with the samples placed in a hermetically sealed aluminum vessel under N_2 . The course of the heat capacity as a function of temperature was followed within a temperature range from 300° to 500°K ; the rate of the temperature increase was $8^\circ/\text{min}$. Samples containing 11% and 20.5% Hg were chosen to evaluate the thermal

stability of poly(styrenemercuric acetate). At 510°K the samples did not show any sign of decomposition accompanied by heat evolution or consumption.

RESULTS AND DISCUSSION

In accordance with Traylor,⁴ linear polystyrene can be mercurated in nitrobenzene solution with mercuric acetate only at an elevated temperature. Unlike Okawara, Tanaka, and Imoto,⁵ it was observed, however, that after the addition of perchloric acid to the mercuration mixture, the mercuric group added to polystyrene even at room temperature and much more rapidly than in a noncatalyzed system (Table I).

We were interested to find out to what extent the mercuration proceeded by a polymer analogous route, according to Staudinger's definition, i.e., without any change in the degree of polymerization. For this purpose the starting polystyrene was compared with a sample obtained by protolytic cleavage of the mercurated product. Owing to the highly insoluble character of poly(styrenemercuric) salts, the protolysis of C—Hg proceeded only with difficulty. In the first experiment we used hydrogen chloride, the anions of which form undissociated ion pairs with mercury, and a medium which proved useful in the mercuration, namely, nitrobenzene–glacial acetic acid. Since the mineral acid reduced the dissolving power of the reaction medium, we succeeded (after 6.5 hr at 70°) only in lowering the mercury content from the initial 42.88% to 2.22%. In further experiments, the hydrochloric acid was excluded from the protolytic mixture, so that the reaction mixture dissolved the formed polystyrene. In order to support the protolytic effect of the weak acetic acid, a sulfonic acid styrene cation exchanger was added to the reaction mixture; this exchanger is known for its high affinity for mercuric cations. Under these conditions (see experimental section) the unfavorable protolytic equilibrium was shifted by removing mercuric cations via ion exchange, so that the mercury attached to polystyrene was removed almost completely. As can be seen from Table II, traces of mercury lower the solubility of polystyrene in cyclohexane (cyclohexane is a θ -solvent of

TABLE I
Noncatalyzed and Catalyzed Mercuration of Polystyrene

	0 ^a	1 ^a
<i>T</i> , °C	100	25
τ_r , h	4.5	1
<i>K</i> , %	49.8	53.1

^a HClO₄/(CH₃COO)₂Hg molar ratio.

TABLE II
Solution Behavior of Original Polystyrene Sample and of Samples After Protolysis

Sample	<i>s</i> ^a	Solubility in cyclohexane
Original polystyrene (A)	6.0	above 30° clear solution
Protolyzed sample (B)	6.4	at 30° polymer precipitates, at 30–38°C opalescence of solution
Reprecipitated protolyzed sample (C)	6.9	above 38°C clear solutions

^a Sedimentation coefficient in Svedberg's units, cyclohexane, 40°C, *c*₀ = 0.56%.

polystyrene at 35°C). Differences in the sedimentation coefficients sensitively illustrate the incomplete removal of the traces of mercury in the protolytic cleavage (samples B and C) and the partial change of the molecular weight distribution due to the loss of low molecular weight fractions by reprecipitation (sample C). The course of the gradient curves (Fig. 1) shows that the molecular weight distribution of all samples is practically identical (in the case of sample C, the low molecular weight fraction is lowered). It can be surmised that the mercuration of polystyrene catalyzed with perchloric acid proceeds by an analogous polymeric mechanism.

Mercuration is known not to be oriented into the aromatic ring like other electrophilic substitutions, e.g., sulfonation.² Brown and McGary¹⁰ found that toluene is first mercurated in the para and ortho positions; but if the reaction time is extended, all positions become operative to the same degree, including the meta position. If the methyl group in toluene is replaced with a bulkier alkyl group, such as a *tert*-butyl group, the ortho positions are eliminated from substitution.¹¹ A similar steric hindrance must also be expected for polystyrene, where sulfonation does not even occur in the ortho position.¹² Okawara, Tanaka, and Imoto⁵ attempted to establish the position of the acetatomercury(II) groups in polystyrene by means of IR spectral analysis, after exchange with iodide. From the presence of the out-of-plane CH deformation band 812–815 cm^{-1} , they inferred that para substitution was operative in this case. In our experiments the acetatomercury(II) groups were exchanged by bromide in a sample with an average molar conversion $K = 52\%$ (see experimental section). Characteristic bands at 825 and 783 cm^{-1} corresponding to disubstitution in positions 1,4 and 1,3 were found in the IR spectra. The spectral proof of the role played by the meta positions of polystyrene in the mercuration reaction contributes to the

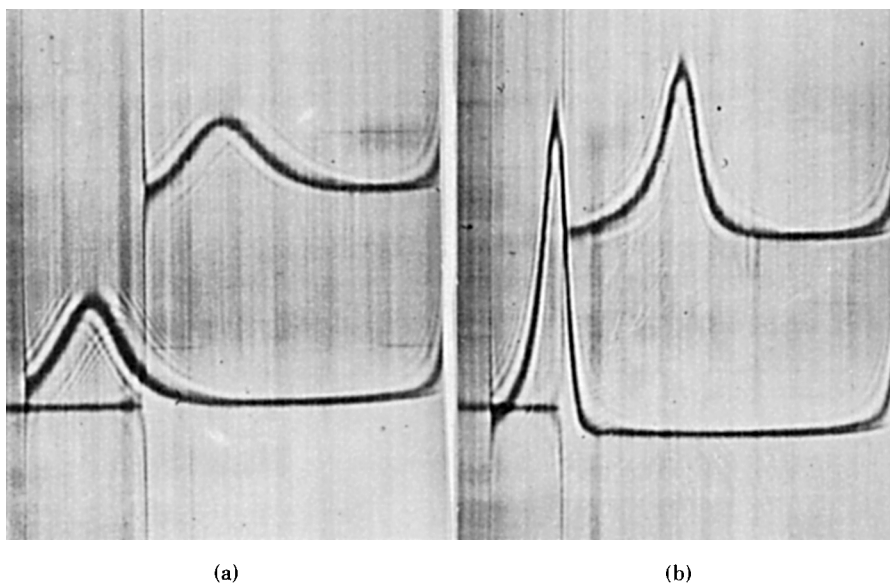


Fig. 1. Sedimentation diagrams of mercurated polystyrene of the sample after protolysis and of the original sample: (a) cyclohexane, 40°C, $c_0 = 0.56\%$, 35 min at 50, 740 rpm; lower gradient curve, original polystyrene (A); upper gradient curve, reprecipitated protolyzed sample (C); (b) tetrahydrofuran, 25°C, $c_0 = 0.66\%$, 59 min at 50, 740 rpm; lower gradient curve, original polystyrene; upper gradient curve, mercurated polystyrene ($K = 6.68\%$).

interpretation of results (Fig. 5). The observed fact that by increasing the mercury content in the reaction mixture polystyrene can be not only monosubstituted but polysubstituted, thus approaching the molar conversion $K = 150\%$, can be explained by both the para and meta positions being identically operative in the mercuration.

Unlike the mercuration of low molecular weight aromatic hydrocarbons,² a number of polymeric effects were observed in the transformation of polystyrene by following the sol/gel phase transition during the polymer analog reaction. In Figure 2, which shows the time dependence of catalyzed mercuration, one can see an initially rapid phase, followed by a sudden slowing down connected with gel formation. In spite of this, however, the reaction proceeded also in the gel phase until mercury was consumed almost completely. The dependence of the molar conversion on temperature (Fig. 3) at a constant reaction time exhibited a maximum in the polymer analog mercuration, while in the same temperature range the rate constants of mercuration of low molecular aromatic hydrocarbons showed a continuously rising trend. The different behavior of the polymer reaction system is attributed to the shorter gel time at higher reaction temperatures. An indication of a maximum was also observed in Figure 4, which shows the effect of addition of perchloric acid to the mercuration mixture. The reactive complex $\text{CH}_3\text{COOHg}(\text{II})\text{ClO}_4$, which is formed in the reaction mixture by adding perchloric acid, considerably accelerated mercuration, as with low molecular weight aromatic hydrocarbons.¹³ It should be pointed out, however, that while in low molecular weight systems the optimal composition was an equimolar

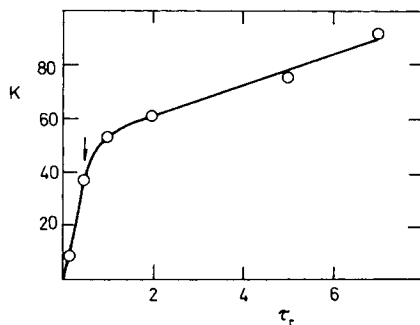


Fig. 2. Time course of mercuration. K , molar conversion (%), τ_r , reaction time (hr). Reaction conditions: molar ratio of mercury to styrene repeat unit, $\text{Hg}/\text{St} = 1$; reaction temperature, $T = 25^\circ\text{C}$. Arrow indicates time of formation of the first fractions of insoluble polymer, τ_g .

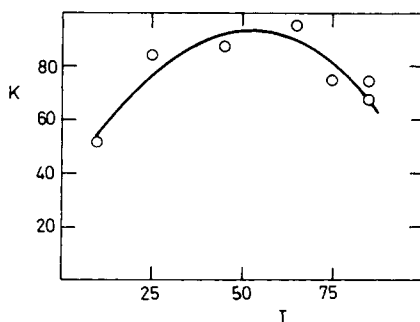


Fig. 3. Dependence of mercuration on temperature. Reaction conditions: $\text{Hg}/\text{St} = 1$; $\text{HClO}_4/\text{Hg} = 1$; $\tau_r = 5$ hr (see Fig. 2).

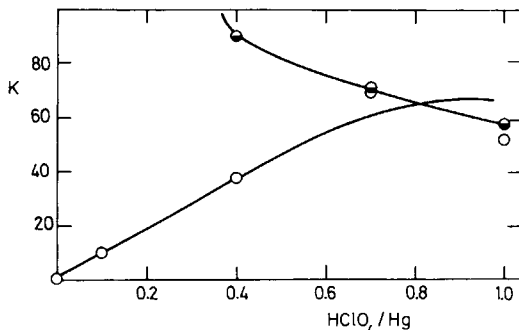


Fig. 4. Effect of perchloric acid on the course of mercuration: (○) K (%), (●) τ_g (min). Reaction conditions: Hg/St = 1; $T = 25^\circ\text{C}$; $\tau_r = 5$ hr (see Fig. 2).

mixture of perchloric acid and mercuric acetate, the optimal results in the case of the polymer analog route were obtained at a lower content of HClO_4 , as shown by Figure 4. The catalyzing acid impairs the dissolving power of the reaction medium in the polymer transformation, thus also reducing the time needed for gel formation.

The phase transition in the mercuration mixture obviously plays an important role in the polymer transformation, and it is therefore described in greater detail. As illustrated by Figure 5, the phase transition does not have only a single corresponding value of molar conversion; quite the contrary, K for τ_g varies within a broad range, depending not only on the composition of the reaction mixture but also on other experimental conditions (temperature, rate of mixing, etc.). Smirnov³ related the phase transition in a polymer analog mercuration mixture with the formation of the crystalline structure. We showed, however,¹⁴ that under our conditions the crystalline phase is not formed and that the cause of the phase transition should rather be sought in the attainment of the insolubility which generally characterizes organic compounds containing mercuric groups. We attempted also to answer the question about the structure of the polymer or of the polymer mixture formed in the polymer analogous mercuration. Measurements performed with an ultracentrifuge showed that also low-mercured polystyrene exhibits a high sedimentation coefficient. The sedimen-

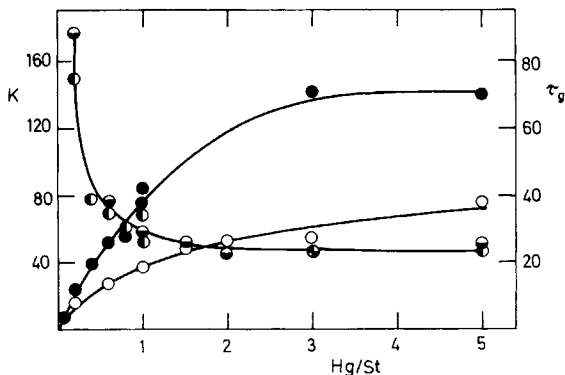


Fig. 5. Effect of concentration of the mercuration agent on the course of mercuration: (●) K for $\tau_r = 5$ hr; (○) K for $\tau_r = \tau_g$; (●)(○) corresponding τ_g (for ● and ○, respectively). Reaction conditions: $\text{HClO}_4/\text{Hg} = 1$; $T = 25^\circ\text{C}$ (see Fig. 2).

tation coefficient for the initial polystyrene in tetrahydrofuran solution was found to be 3.4, while that for mercurated polystyrene with molar conversion $K = 6.68\%$ under the same conditions was 5.9. One could expect, therefore, that in the gravitational field of the ultracentrifuge it will be possible to separate also the low-mercurated product from the starting polystyrene. In spite of this, however, the gradient curve of mercurated polystyrene (Fig. 1) has only one peak, and its shape suggests the presence of a single polymeric species, i.e., of a derivative of polystyrene containing mercuric groups. Calorimetric measurements of dry mercurated polystyrenes showed that the introduction of mercury into the structure led to a marked change in the mobility of polymer chains. T_g increases with increasing molar conversion for highly mercurated samples (prepared in excess of mercuration species) by up to 60°C compared to polystyrene. Generally, the glass transitions on the curves are not pronounced; particularly for samples with 25–40% Hg they cannot be reliably identified. For samples with a high mercury content there also was an indication of another T_g at temperatures of about 370°K , i.e., in the glass transition region of the initial polystyrene.

It may be inferred from measurements performed with the ultracentrifuge and from calorimetric measurements that in the initial stage of mercuration occurring in homogeneous solution, all macromolecules undergo random partial transformation. After gel formation in the reaction mixture, the process of further transformation is greatly limited, which may lead even to polystyrene blocks in the highly substituted final copolymer.

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