

## AGGREGATE STATE OF MERCURATED POLYSTYRENE

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The mercuration of polymers is a suitable method for the preparation of selective adsorbents<sup>1-4</sup>. For polystyrene, this reaction was described by Smirnov<sup>5</sup> and improved by Traylor<sup>6</sup>. According to Smirnov<sup>5</sup>, during the process of mercuration a transition from the amorphous to the crystalline state occurs. The interest taken by us in the mercuration reaction is motivated by an attempt to find an appropriate system which would allow to study the polymer-analogous reactions during the transition from the liquid into the solid phase. For this reason, we also investigated the structure of mercurated polystyrene in various stages of the mercuration reaction.

If in the case of the mercuration of polystyrene the reaction system contains perchloric acid as catalyst<sup>7</sup>, the reaction proceeds much easier than an uncatalyzed reaction<sup>6</sup>. By using the described procedure<sup>7</sup>, the reaction components first form a homogeneous mixture, but in the course of reaction a copolymer is formed which then separates from the solution. This behaviour could

TABLE I

## Mercuration of Polystyrene

*T* Reaction temperature,  $\tau_r$  reaction time,  $\tau_g$  time of gelation,  $c_{\text{Hg}}$  mercury content in the product, *K* molar conversion, *I* integral intensity of reflexion at  $2\theta = 6.2^\circ$  (in a relative scale).

Sample	Hg(OAc) <sub>2</sub>	HClO <sub>4</sub> <sup>b</sup>	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	AcOH	<i>T</i> °C	$\tau_r$ h	$\tau_g$ h	$c_{\text{Hg}}$ %	<i>K</i> <sup>c</sup> %	<i>I</i>
	mol/mol <sup>a</sup>									
A	0.1	0.1	20.9	37.3	25	5.0	5.000	14.61	9.34	0.5
B	0.2	0.2	20.9	37.3	25	5.0	1.253	29.43	23.94	1
C	1.0	0.4	61.2	91.0	25	5.0	1.125	37.41	37.52	2
D	1.0	1.0	20.9	37.3	25	0.5	0.488	37.53	37.74	2
E	1.5	1.5	20.9	37.3	25	0.4	0.431	42.69	49.28	4
X <sup>d</sup>	1.05	0.0	7.6	0.9	100	4.5	—	42.88	49.80	—
F	0.6	0.6	20.9	37.3	25	5.0	0.578	43.84	52.34	4
G	1.0	1.0	20.9	37.3	65	5.0	0.014	54.56	95.36	4
H	5.0	5.0	20.9	37.3	25	5.0	0.393	60.16	139.25	10
I	3.0	3.0	20.9	37.3	25	5.0	0.389	60.39	141.66	14
J	5.0	5.0	20.9	37.3	25	24.0	0.378	62.82	171.59	11

<sup>a</sup> Molar ratio related to a structural unit of polystyrene (corresponds to the total reaction mixture). <sup>b</sup> 70% aqueous solution. <sup>c</sup> Calculated for poly[styrene-co-(vinyl)phenylmercury acetate], %:  $K = 10.414c_{\text{Hg}} / (20.061 - 258.66c_{\text{Hg}})$ . <sup>d</sup> Prepared according to Traylor<sup>6</sup>.

apparently be interpreted in terms of the transition from the amorphous into the crystalline state, mentioned by Smirnov<sup>5</sup>.

A sample of the initial polystyrene gives two amorphous maxima on the intensity curve (Fig. 1), as has been described, *e.g.*, by Krimm and Tobolski<sup>8,9</sup>. The maxima of these two broad diffractions correspond to distances of 8.84 and 4.67 Å (if Bragg's law is applied to the angular position of these maxima). The samples A and B, whose mercury content is very low (Table I), also have these two reflexions in their intensity curves; the reflexions are characteristic of amorphous polystyrene, but are very weak here. The two maxima do not exist in the other samples with a higher content of mercury. All samples of mercurated polystyrene with different contents of mercury, prepared by a catalyzed reaction, exhibit two broad diffusion maxima on the intensity curves; their positions differs from that of the initial polymer. Fig. 1 (curve 2) shows an intensity curve of the sample H as an example. The position of the first reflexion is  $2\theta = 6.2^\circ$  (corresponding to a distance 14.2 Å), and is the same for all samples. The intensity of this reflexion increases with the increasing degree of mercuration, as follows from the last column of Table I, where the integral intensities of this reflexion are given in relative units. The second maximum has a position around  $2\theta = 28^\circ$  (corresponds to a distance 3.2 Å). The intensity of this reflexion does not virtually vary in dependence on the mercury content. In contrast with the other samples, the intensity curve of sample X (prepared according to Traylor<sup>6</sup>) exhibits only one broad and diffuse maximum at a position  $2\theta = 27^\circ$  (corresponding to a distance of 3.3 Å). The sample has no maxima at lower angles.

The mercurated polystyrene has a structure different from that of the initial polystyrene. This is due to the fact that polystyrene is bonded with mercury atoms carrying acetate anions. Only samples A and B, owing to a very low content of mercury, have partly the same structure as the other samples of the mercurated polystyrene and partly that of the initial polystyrene. Assuming monosubstitution, these samples have mercury bonded to only 9% or 24% of the benzene rings (Table I).

It follows from the results of the X-ray diffraction analysis that samples of polystyrene mercurated over a broad range of contents of the mercury atoms are not crystalline. The intensity curve of sample X, prepared in a different way from samples A to J (and similarly to Smirnov<sup>5</sup>), exhi-

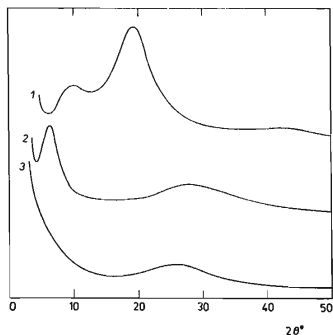


FIG. 1

X-Ray Intensity Curves of Polystyrene and Mercurated Polystyrene

1 Initial polystyrene, 2 sample H, 3 sample X.

bits only one very broad maximum, indicating the amorphous structure. In comparison with sample X, the other samples have besides the maximum situated in the same angular region another maximum corresponding to  $14.2 \text{ \AA}$ . The maximum at  $14.2 \text{ \AA}$  may be due to interferences between atoms of the adjacent chains. On this assumption, smectic structure<sup>10</sup> with the chain molecules arranged parallel to each other might arise in these samples besides the amorphous phase. Their distances have a broader distribution due to the fact that the reflexion indicating the smectic order is fairly broad. On this assumption, the portion of the smectic structure would increase with increasing degree of mercuration, since the integral intensity of the reflexion in question grows proportionately to the mercury content (Table I).

It follows from the above that our results differ from those published by Smirnov<sup>5</sup>: at a certain degree of mercuration the gel formation cannot be related with the transition from the amorphous into the crystalline phases. Neither is it due to the chemical crosslinking, since the just formed gel may again be dissolved in a mixture containing more acetic acid than the original reaction mixture. The gel formation is therefore due to a decreasing solubility of the gradually mercurated polystyrene.

#### EXPERIMENTAL

**Mercuration.** Polystyrene, mol. weight 290 000, dissolved in a mixture of nitrobenzene and glacial acetic acid, was subjected to the action of a mixture of mercury acetate, glacial acetic acid and perchloric acid. Samples of mercurated polystyrene containing various amounts of mercury were taken in various stages of the mercuration reaction: sample A was taken before the formation of the gel, samples D and E were taken in the course of its formation, and the other samples were taken after the formation of the gel (Table I). On drying, the mercurated polymer became powderlike<sup>7</sup>.

**X-Ray diffraction.** Powderlike samples were pressed under a considerable pressure to form thin plates. The measurements were carried out with a Hilger and Watts diffractometer, adapted for measurements with a bent crystal quartz monochromator. The  $\text{CuK}\alpha$  radiation (40 kV and 20 mA) was used in the measurements. The diffracted radiation was recorded by a scintillation counter with an amplitude analyzer. With respect to the low diffracted intensities, the measurements were made point after point at a constant value of the reference channel.

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