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### Purification of hydrogenated styrene–isoprene copolymer from residual nickel acetylacetonate by chromatography on dextran gels

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Hydrogenated styrene–isoprene block copolymers are applied in a number of fields, and this fact has promoted great interest in their synthesis<sup>1–4</sup>. A serious problem in the synthesis is the removal of the residual hydrogenation catalyst from the final product. This is usually achieved by adding other substances to the catalyst complex or by a special treatment of the reaction product after hydrogenation<sup>1–4</sup>. It is particularly difficult to remove metal chelates. Having in mind the large difference between the molecular size of the hydrogenated copolymer and that of the metal chelate, it was felt that gel chromatography would enable their complete separation and thus the purification of the polymer.

The present work concerns the possibility of achieving such a purification by chromatography on dextran gels, namely Sephadex LH-20 and Sephasorb HP. The chromatographic behaviour of the impure polymer sample and the pure substances nickel acetylacetonate and acetylacetone was studied with *n*-hexane–tetrahydrofuran (THF) (1:1) as eluent.

#### EXPERIMENTAL

The polymer sample was synthesized<sup>3,4</sup> by “living” anionic copolymerization of isoprene and styrene, initiated by *tert.*-butyllithium, and subsequent hydrogenation with the catalytic system tris(isobutyl)aluminium–nickel acetylacetonate. The molecular weight of the polymer as determined by light scattering, was  $\bar{M}_w = 150\,000$ . The content of nickel in the impure polymer sample was 0.13%.

Nickel acetylacetonate, Ni(AA)<sub>2</sub>, acetylacetone, *n*-hexane and THF were obtained from Fluka.

After swelling in the eluent hexane–THF (1:1), Sephadex LH-20 and Sephasorb HP yielded gel beds of about 2.3 and 1.6 cm<sup>3</sup>/g dry gel, correspondingly. The chromatographic experiments were made with a simple apparatus<sup>5</sup> comprising a glass column, a Mariotte flask and a fraction collector. The total volume of the gel bed maintained in the chromatographic columns was 106–125 cm<sup>3</sup> for Sephadex LH-20 and 30–35 cm<sup>3</sup> for Sephasorb HP. The void volumes of the columns were determined

periodically by using polystyrene standard with  $\bar{M}_w = 390\,000$  (Waters Assoc.). The volumes of the samples fed into the columns of Sephadex LH-20 and Sephasorb HP were 0.6 and 0.2 cm<sup>3</sup>, respectively.

The compositions of the fractions were analyzed by recording their UV spectra on a Specord UV-VIS spectrophotometer (Karl Zeiss, Jena, G.D.R.). The elution volumes,  $V_e$ , of hydrogenated copolymer and acetylacetone were determined by measuring the absorbances of the fractions at 263 and 273 nm, respectively (Fig. 1). The chromatographic behaviour of Ni(AA)<sub>2</sub> is discussed below.

## RESULTS AND DISCUSSION

The hydrogenated styrene-isoprene copolymer from the impure polymer sample was eluted with the void volume of the gel bed on both Sephadex LH-20 and Sephasorb HP. After elution of the sample with several column volumes of eluent, no other substance except the copolymer was found in the eluate by spectral analysis. The initial solution of the polymer sample and samples of both gels taken from the tops of the columns showed the presence of Ni<sup>2+</sup> upon reaction with dimethylglyoxime, but none of the eluate fractions did so, even after concentration.

These observations indicated that it was necessary to study the chromatographic behaviour of Ni(AA)<sub>2</sub> and of acetylacetone. Saitoh and Suzuki<sup>6</sup> studied the behaviour of acetylacetone and its metal chelates on Merckogel OR-2000 with THF as eluent. They established that Ni(AA)<sub>2</sub> gives a particularly distorted peak and the UV absorption profile of the eluate is different from that of the original solution of Ni(AA)<sub>2</sub>. It was assumed that the complex decomposed in the column, but the fate of the decomposition products was not discussed. Our results also showed that the UV spectra of the fractions obtained upon elution of Ni(AA)<sub>2</sub> on both Sephadex LH-20 and Sephasorb HP did not coincide with the spectrum of the original solution

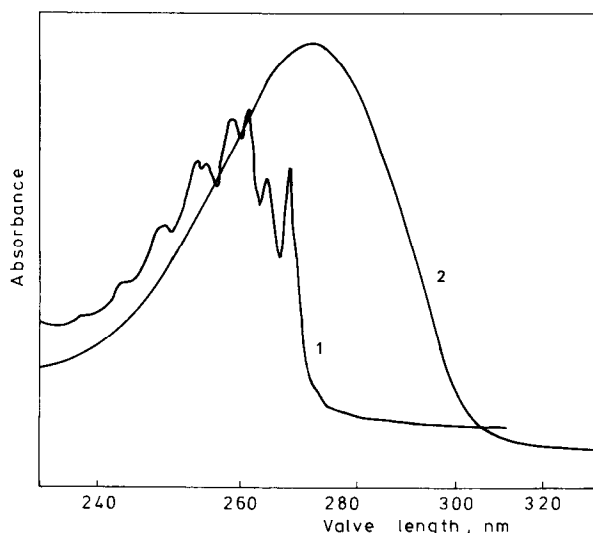


Fig. 1. UV spectra of hydrogenated styrene-isoprene copolymer (1) and of acetylacetone (2).

of the complex. The maximum at 294 nm in the spectrum of  $\text{Ni}(\text{AA})_2$  was hypsochromically shifted to 273 nm in the spectra of the eluate (Fig. 2), thus resembling the spectrum of acetylacetonate (Fig. 1). In addition, the value of the distribution coefficient,  $K_{av}$ , for the substance passing into the eluate after elution of  $\text{Ni}(\text{AA})_2$  was very similar to that for acetylacetonate at large concentrations (Table I). Finally, samples from both gel beds gave a positive reaction for  $\text{Ni}^{2+}$  after elution of  $\text{Ni}(\text{AA})_2$ .

Therefore, our results confirm that, as on Merckogel OR-2000 with THF as eluent<sup>6</sup>, during elution of  $\text{Ni}(\text{AA})_2$  on both Sephadex LH-20 and Sephasorb HP with hexane-THF (1:1) the chelate complex decomposes. Also that  $\text{Ni}^{2+}$  is adsorbed on the gels and acetylacetonate appears in the eluate. However, unlike the peak of  $\text{Ni}(\text{AA})_2$  on Merckogel OR-2000, the peaks of acetylacetonate released from  $\text{Ni}(\text{AA})_2$  after its elution on both Sephadex LH-20 and Sephasorb HP were symmetrical (Fig. 3), demonstrating the complete decomposition of the complex. The same process of decomposition of  $\text{Ni}(\text{AA})_2$  certainly took place also during elution of the impure polymer sample, but because of the low concentration of acetylacetonate in the eluate it could not be detected.

The results presented above allow us to suggest a method for removing the residual hydrogenation catalyst, namely  $\text{Ni}(\text{AA})_2$ , from the hydrogenated styrene-isoprene copolymer, which includes frontal chromatography on Sephadex LH-20 or Sephasorb HP with hexane-THF (1:1) as eluent and subsequent separation of the polymer from the eluate by one of the traditional techniques, e.g., evaporation *in vacuo*. The use of such a method yielded a high purity polymer, the content of  $\text{Ni}^{2+}$  as determined by atomic absorption spectroscopy with a Diffraction Spectrograph PGS-2 (Carl Zeiss, Jena) being below 1 ppm.

In order to determine the amount of sample which can be purified by a gel bed of a definite volume, the dynamic adsorption capacity of both gels towards  $\text{Ni}^{2+}$  was determined by frontal chromatography of a solution of  $\text{Ni}(\text{AA})_2$  of known concen-

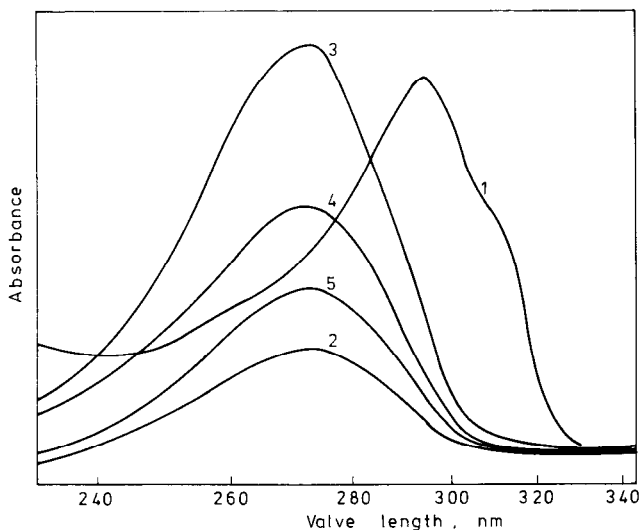


Fig. 2. UV spectra of nickel acetylacetonate (1) and of the fractions (2-5) obtained after its elution on Sephadex LH-20 with hexane-THF (1:1) as eluent.

TABLE I

$K_{av}$  VALUES OF PURE ACETYLACETONE AND ACETYLACETONE RELEASED UPON ELUTION OF  $Ni(AA)_2$  FROM SEPHADEX LH-20 AND SEPHASORB HP WITH HEXANE-THF (1:1) AS ELUENT

<i>Sephadex LH-20</i>				<i>Sephasorb HP</i>			
<i>Acetylacetone</i>		<i>Acetylacetone from Ni (Acac)<sub>2</sub></i>		<i>Acetylacetone</i>		<i>Acetylacetone from Ni (Acac)<sub>2</sub></i>	
<i>Amount of sample (μl)</i>	$K_{av}$	<i>Amount of sample (mg)</i>	$K_{av}$	<i>Amount of sample (μl)</i>	$K_{av}$	<i>Amount of sample (mg)</i>	$K_{av}$
0.10	0.57	0.10	0.53	0.10	0.38	0.10	0.32
0.20	0.55	0.20	0.56	0.13	0.36	0.20	0.35
0.30	0.55	0.30	0.55	0.25	0.37	0.33	0.38
0.40	0.56	0.40	0.56	0.40	0.35	0.40	0.36
—	—	0.50	0.57	—	—	0.50	0.37

tration. The saturation threshold of the gels was determined by the drop reaction with dimethylglyoxime. Thus it was established that the capacities of Sephadex LH-20 and of Sephasorb HP were 2.2 and 1.4 meq.  $Ni^{2+}$  per 100  $cm^3$  gel bed respectively. Hence, a 100- $cm^3$  bed of each gel could purify in one experiment 49 and 33 g, respectively, of impure polymer sample with a nickel content as mentioned above.

Regardless of the relatively low capacity of Sephadex LH-20 and Sephasorb HP for the purified copolymer, the purification process is highly effective and could

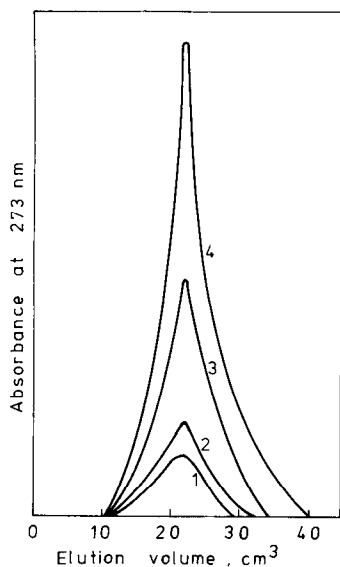


Fig. 3. Gel chromatograms of acetylacetone released from  $Ni(AA)_2$  after its elution from Sephasorb HP with hexane-THF (1:1) as eluent.

be used as a laboratory method for purification of impure copolymer samples needed for analysis. When the column becomes saturated with  $\text{Ni}^{2+}$ , it may be regenerated as follows: washing with a 5% solution of acetic acid in methanol to a negative reaction for  $\text{Ni}^{2+}$  (the gel increases its volume) following by washing with pure methanol to neutrality and finally with the eluent to yield an equilibrium shrinking of the gel bed. If, in the course of regeneration, the integrity of the gel bed is broken, the column must be emptied, the gel washed in a separate vessel and then the column refilled. It should be noted that the bed of Sephasorb HP is more stable than that of Sephadex LH-20 during regeneration.

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