Preparation of styrene oligomers
I. Synthesis and fundamental characteristics

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Dedicated to Professor Dr. Ing. A. Tkáč, DrSc., in honour of his 60th birthday

The polymerization of styrene by the effect of phosphoric acid and potassium bichromate in heterogeneous experimental arrangement was studied. Silica gel was used as a carrier of catalyst. The synthesis was carried out in the medium of nonpolar solvent (decalin) at 186°C. The reaction resulted almost in 100% conversion of monomer and a mixture of oligomers came into existence. The dimer (50 mass %) and trimer (33 mass %) component prevailed in this mixture. The fractionation and analysis of oligomer mixture was performed by rectification and gas chromatography. The obtained reaction products were characterized by means of mass spectroscopy, index of refraction, temperature increment of the index of refraction, average numerical molecular mass, and viscosity measurements in the temperature interval 20—50°C.

Изучена полимеризация стирола, приводящая к гетерогенной экспериментальной упорядоченности, под действием фосфорной кислоты и бихромата калия. В качестве носителя катализатора использовался силикагель. Синтез проводился в неполярном растворителе (декалин) при 186 °C. Реакция проходила с почти 100%-ной конверсией мономера на смесь олигомеров. В этой смеси преобладали димерные (50% по массе) и тримерные (33%) фрагменты. Деление и анализ смеси олигомеров проводились методами ректификации и газовой хроматографии. Полученные продукты реакции далее характеризовались с помощью масс-спектрометрии, показателя преломления, температурного инкремента показателя преломления, среднечисловой молярной массы, а также измерения вязкости в интервале температур 20—50 °C.

The importance of oligomers for physical chemistry and physics of polymers was disclosed as early as in papers published by *Staudinger* [1] who was one of the pioneers of polymer science. The systematic investigation of oligomers, especially as regards polyamides, started after the Second World War [2, 3].

The first coherent paper dealing with the properties of oligostyrenes was published by *Braun* and *Meier* [4]. These authors have found that linear oligostyrenes up to pentamer can be isolated from a solid polymer sample by extraction of polystyrene with methanol. The amount of isolated oligomers depends on chemical structure of the polymer, preceding thermal stress, and extraction conditions.

The common feature of almost all syntheses used up to the present is a successive stepwise mechanism of the preparation of individual *i*-mers [5, 6] or a radical mechanism of polymerization giving rise to a mixture of oligomers [7—9].

The cationic polymerization affording a product in particular level of *n*-mer is structurally more variable than the process of radical polymerization involving the population of free radicals and, for this reason, it appears to be very important from the view-point of the preparation of oligomers [10, 11]. The resulting composition is significantly affected by character of the active particle (ion) which starts the reaction. This fact results in the characteristic specifity of individual ionic catalysts and procedures of their application. The general feature of these reactions is a heterogeneous character of reaction. The composition of products of this reaction is sensitive to the composition of the starting mixture monomer—initiator——medium [9—13]. The process of reaction termination itself is usually less influencial in reactions of this type.

Though polystyrene belongs among the most investigated and very important plastic substances, the knowledge concerning its oligomers, except for some dimers, is poor for the time being. Some relatively precise methods of gas chromatography [4, 14—17] have been developed for the determination of low-molecular fractions arising in the polymerization of styrene. The gas chromatographic separation of dimeric styrenes has been investigated in more detail [5], but the behaviour of higher oligomers is little known. It is due to the fact that the oligomers of styrene are hardly to be obtained by any preparation method. For this reason, the mixtures of oligomers obtained by cationic polymerization [6, 18] were primarily used for gas chromatographic separation. Besides the chemical methods (addition of iodine to double bonds) [19], the method of ultraviolet spectroscopy [20] can be also used for determining the monomer of styrene. However, this method is not specific enough because the unsaturated oligomers absorb in the same region as styrene.

The aim of this study was to develop a new method of the synthesis of the mixtures of styrene oligomers with high yield of dimer with respect to original monomer, fractionate, and analytically evaluate the reaction mixture. This aim has been motivated by the knowledge that the oligomers of styrene are able to catch oxygen by the effect of ultraviolet irradiation and provided they are heated, they can then initiate polymerization reactions or cross-link the diene systems, which suggests the possibility of preparing a negative offset plate.

Experimental

Chemicals

Decalin (Lachema, Brno) — before use distilled in a rectification column (20 TP), ϱ (20°C) = (893.5 ± 0.5) kgm⁻³.

Styrene, purity 99.74 mass %, ϱ (20°C) = (919.5 ± 0.5) kgm⁻³.

Phosphoric acid, 85%, anal. grade chemical (Lachema, Brno).

Potassium bichromate, anal. grade chemical (Lachema, Brno).

Silica gel (Lachema, Brno), grain diameter 2 mm. It was washed with distilled water, subjected to sieve analysis and used as a carrier of catalyst.

Altogether, seven mixtures of catalyst and silica gel were used. They contained the following amounts of phosphoric acid expressed in mass %: *I* — 5%, *II* — 10%, *III* — 15%, *IV* — 20%, *V* — 25%, *VI* — 30%, and *VII* — 35%. The content of potassium bichromate was 0.01 mass % in each mixture.

The mixtures thus prepared were exposed to thermal activation (140°C, 10 h) and used to charging of the reactor with a fixed bed. The internal diameter of the reactor was 3.5 cm and the catalyst fixed on the carrier was freely shed to the height of 44.0 cm.

The scheme of the apparatus used for synthesis is represented in Fig. 1. Styrene of the volume of 200 ml was dosed with continuous rate (2 ml in 18—20 s) into the evaporation part filled with 700 ml of decalin. The temperature of boiling was held constant (186 ± 2°C). Each packing of catalyst was used twice. The first synthesis is denoted by symbol *a*, the second one by *b*. Sample *Ia, b* served for orientation and, for this reason, it has not been described.

The synthesis was carried out in the atmosphere of electric bulb nitrogen which was continuously introduced into the boiling flask from a pressure vessel. Its pressure was held constant (101.3 kPa). The synthesized mixture was bubbled through with nitrogen and subjected to vacuum rectification (20 TP, 800 Pa).
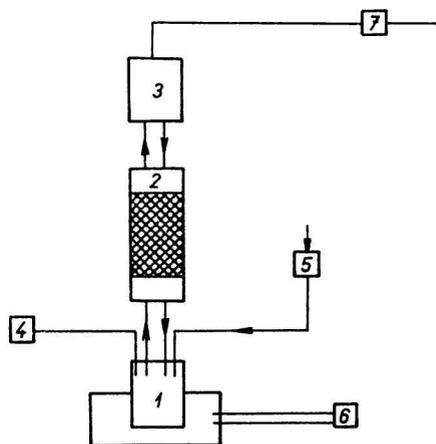

Fig. 1. Block diagram of the apparatus for synthesis.
1. Evaporation part; 2. reactor with fixed bed; 3. dephlegmator; 4. manostat of protective atmosphere; 5. dosage of monomer; 6. thermostat; 7. decalin liquid diaphragm.

It was assumed that the decrease in pressure should result in separation of major part of decalin while oligomers should remain as distillation residue. The vacuum rectification of the synthesized mixture was finished when the state p, T=const was reached, *i.e.* when no further fraction could be obtained from the distillation flask.

The masses of the products of synthesis (distillation residues) are given in Table 1.

Table 1

Masses of the obtained products of synthesis

Sample	Mass of sample g	
	a	*b*
II	174.8	165.9
III	188.3	185.6
IV	185.6	171.8
V	198.2	183.6
VI	178.9	197.8
VII	195.8	175.3

The product thus obtained was washed with a 1% solution of calcium hydroxide. After separation in a separatory funnel, it was washed with water till the alkaline reaction disappeared. The rests of water were removed from the sample by adding methyl alcohol and drying to constant weight in a vacuum drier for 10 h at 50°C. Partial dissolution of the product in methanol was negligible because the contact time of both phases was very short.

The mixture of styrene oligomers was analyzed by gas chromatography (CHROM IV) according to *Braun* and *Meier* [4]. The conditions of separation were as follows: temperature of column — 100—270°C, rate of heating — 1/6°C s^{-1}, carrier gas — nitrogen, detector — FID — dual, electrolytic hydrogen flow — 5×10^{-7} m^{3}s^{-1}, air flow — 83.3×10^{-7} m^{3}s^{-1}, amount of analyzed sample — 0.2×10^{-9} m^3, column length — 1.2 m, column diameter — 4 mm, packing — 5% of SE-30 on Chromaton N AW-HMDS, grain diameter — 0.16—0.20 mm.

By the use of gel chromatography *Braun* and *Meier* [4] isolated di-, tri-, tetra-, and pentastyrenes, determined their molecular mass and retention by gas chromatography. They have found that the oligomers of styrene with the degrees of polymerization 2—5 can be well separated and give multiple chromatographic waves, which means that particular oligomers are not homogeneous substances but mixtures of isomers.

The quantitative estimation of the proportion of individual oligomers (Table 2) is based on the assumption of a linear relation between the value of signal and the amount of substance. As the analyzed samples contained the solvent (decalin), they were analyzed without preceding dilution. Then the percentage of individual components in the whole analyzed sample was directly calculated for quantitative evaluation. For illustration, the chromatogram of sample *IIa* is represented in Fig. 2.

Table 2

Composition of styrene oligomers determined by gas chromatography

Sample		Composition of sample %				$\bar{M}_n$ of sample calculated
		R	II	III	IV	
IIa	1	40.9	26.9	24.2	7.7	215.3
	2	—	45.7	41.1	13.1	275.6
IIb	1	7.6	55.7	25.0	11.7	247.4
	2	—	60.2	27.0	12.6	258.9
IIIa	1	18.7	38.5	28.1	14.4	249.4
	2	—	47.4	34.7	17.8	274.5
IIIb	1	40.3	31.3	18.5	9.7	213.2
	2	—	52.2	31.0	16.4	271.4
IVa	1	20.7	39.3	27.8	12.0	242.8
	2	—	49.6	35.1	15.1	275.6
IVb	1	47.8	24.9	16.9	10.2	211.5
	2	—	47.9	32.4	19.6	278.7
Va	1	48.9	25.7	16.6	8.7	191.4
	2	—	50.3	32.4	17.1	274.5
Vb	1	69.5	15.1	10.3	4.9	178.4
	2	—	49.7	34.1	16.1	274.5
VIa	1	46.6	26.3	18.9	8.2	210.1
	2	—	49.3	35.3	15.2	273.5
VIb	1	60.7	19.1	12.9	7.3	188.8
	2	—	48.6	32.7	18.6	274.1
VIIa	1	74.8	12.0	7.7	5.6	169.7
	2	—	47.5	30.3	22.0	282.8
VIIb	1	67.4	16.3	11.7	4.4	176.7
	2	—	50.2	36.0	13.6	270.4

R — Solvent (decalin); *II* — dimer of styrene; *III* — trimer of styrene; *IV* — tetramer of styrene; $\bar{M}_n$ — average numerical relative molecular mass.
1. Composition of sample with solvent; *2.* composition of sample without solvent.

The viscosimetric measurements were carried out with an Ubbelohde viscosimeter according to CSN 656216.
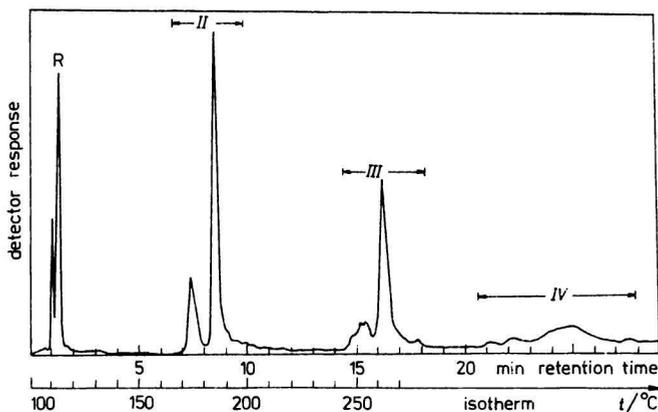
Fig. 2. Chromatogram of sample *IIa*.
R — decalin; *II* — dimers; *III* — trimers; *IV* — tetramers.

Results and discussion

The relatively high values of the indices of refraction of products *II—VII* (1.5116—1.5856) ± 0.0001 are not surprising because a high content of cyclanaromates may be expected in the reaction mixture [7—9, 12], which is also evidenced by high values of the temperature increments of the index of refraction. These
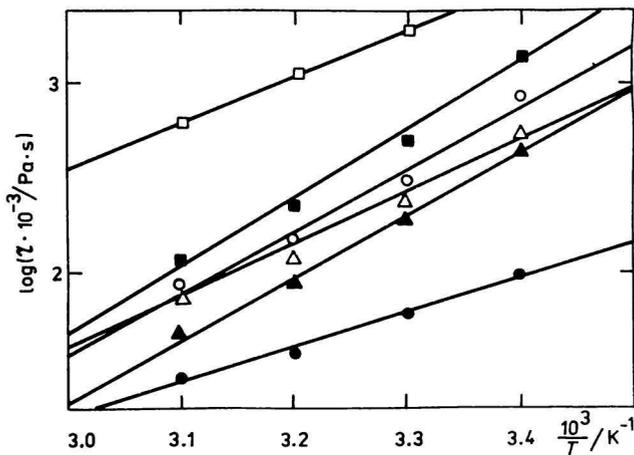

Fig. 3. Variation of dynamic viscosity with temperature.
● *IIa*; ▲ *IIIa*; ■ *IVa*.
○ *IIb*; △ *IIIb*; □ *IVb*.

increments are defined as follows

$$an_D = \frac{n_D^{20} - n_D^{50}}{30} \quad [K^{-1}]$$

and their numerical values varied in the interval $(3.5—4.2) \times 10^{-4} \, K^{-1}$. The temperature dependence of viscosity represented in Figs. 3 and 4 is also interesting.
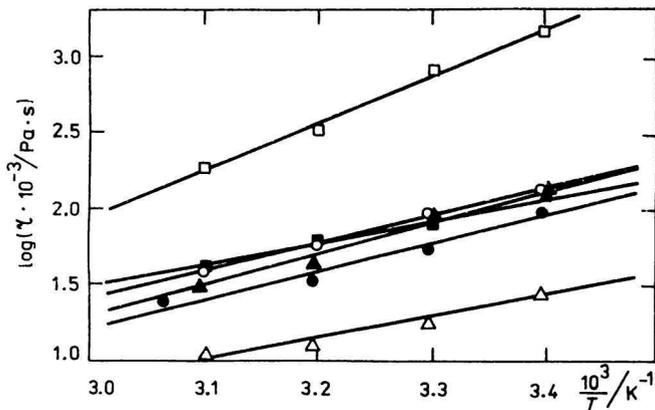
Fig. 4. Variation of dynamic viscosity with temperature.
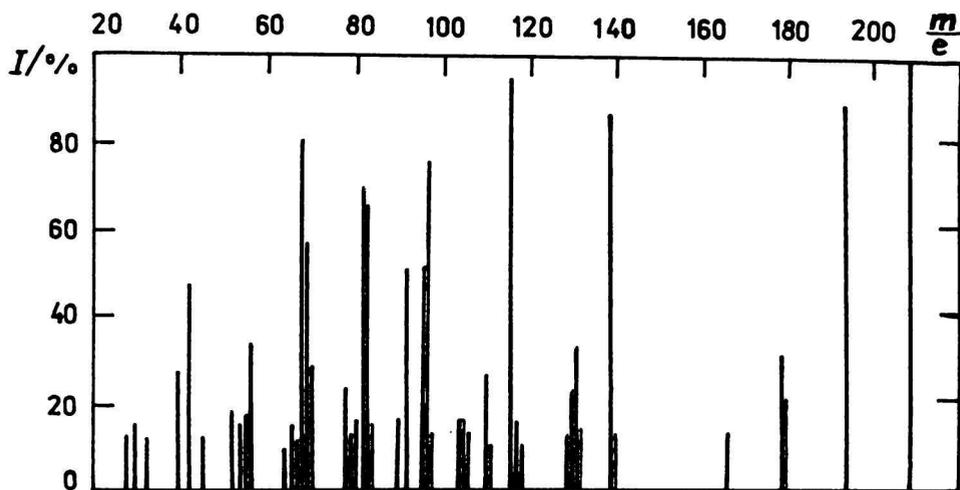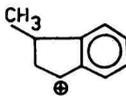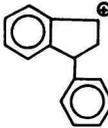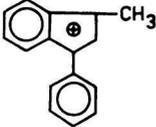● Va; ▲ VIa; ■ VIIa.
○ Vb; △ VIb; □ VIIb.

Fig. 5. Mass spectrum of the selected mixture of oligomers (after removal of decalin).

The course of the plot viscosity against temperature is very dependent on the type composition of the investigated sample since the measured values of viscosity of the investigated systems are related to the composition of particular fractions. A wide series of styrene oligomers and cyclanaromates was also evidenced on the basis of mass spectra of the investigated samples. A typical spectrum of the selected mixture of oligomers is represented in Fig. 5 and the following ion fragments were ascertained [21]

The viscosity of hydrocarbon mixtures with major content of alkanes changes relatively little with temperature and the curve $\log \eta = f(\log T)$ is flat. The curve viscosity against temperature gets steeper with increasing content of cyclanes. The most abrupt rise appears with the mixtures with prevailing content of aromates, which also occurs in our case. The absolute viscosity of polymer solutions usually

decreases with increasing temperature according to the equation put forward by Frenkeľ [22]

$$\eta = A \, \exp[\Delta Q/RT] \qquad (1)$$

where A is the preexponential factor expressing the viscosity at hypothetical temperature limiting to infinity and ΔQ is the qualitative structural parameter of the liquid. The values of the factor A varied in the interval 8×10^3—4×10^5 Pa·s.

As evident from the preceding text, the reaction product of styrene oligomerization is in good agreement with the Frenkeľ equation.

The average values of molecular masses (or average numerical molecular masses — relative error 3—5%) given in Table 3 which were determined by the ebullioscopic method on the assumption of validity of the Raoult law indicate that the dimer component prevails in the mixture. This fact has been also confirmed by the results of gas chromatographic analysis of the fractional products. The content of dimer in the "pure" mixture of oligomers is about 50 mass % (Table 2).

The differences in the values of average numerical molecular masses may be explained by the following facts:

a) High content of decalin which has the highest relative volatility. (It manifests itself by lower value of molecular mass which was determined ebullioscopically and compared with the value found chromatographically.)

b) Small sensitivity of chromatographic procedure to higher n-mers ($n > 4$). The relative error for the concentration of tetramers of styrene was $\pm 10\%$.

It may be assumed that the real value of molecular mass is somewhat higher than the value found ebullioscopically and occurs in the interval between both values and is nearer to the value determined ebullioscopically.

Table 3

Molecular masses of samples of oligomer styrene determined ebullioscopically in benzene solutions

Sample	$\bar{M}_n \cdot 10^3$	
	a	b
	kgmol^{-1}	
II	255	281
III	273	265
IV	330	279
V	226	210
VI	232	178
VII	223	243

The critical concentration of catalyst is smaller than 5 mass % of phosphoric acid because the wear of catalytic component in one working cycle is negligible.

As further intention was to process mixtures of the oligomers of styrene by polymerization in thin layer of decalin solutions, a full separation of decalin from the reaction mixture was not regarded as necessary.

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