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STRUCTURE OF POLYMERS ON THE BASIS OF CHLORINATED STYRENE AND SODIUM DISULPHIDE

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ABSTRACT

A polycondensation of a mixture of halogen derivatives of styrene obtained at direct chlorination of styrene and cantaining ~80% α,βdichlorethylbenzene and sodium disulphide was studied.Polysulphide liquid low molecular polymers were obtained.By means of molecular spectroscopy,fractionation and the elemental analysis the structure of the synthesized products was studied.It was proved,that the essential unit is the styrenedisulphide one.The role of monofunctional monomer and of nonchlorinated styrene in reaction conditions was indicated.

INTRODUCTION

Due to their high chemical resistance and the ability to vulcanize at room temperature,the liquid polysulphide polymers are in great demand among the polymers for special purpose(ref.I.). In this paper the results from structure investigation of liquid polysulphide polymer of chlorinated styrene and sodium disulphide are given.Direct chlorination of styrene,product of SC"Neftochim"-Bourgas was carried out at 273-283K temperature with chlorine.The obtained products are introduced in a process of polycondensation with sodium disulphide using a knoun method(ref.2). Polysulphide polymers with liquid viscous consistence were obtained.

RESULTS AND DISCUSSION

By comparison of IR spectra of chlorinated product with ethalone one of α,βdichlorethilbenzene it was established that together with the bands of the corresponding compounds there are such at:8I5 and 730 cm^{-I}(Ar-Cl),related to chlorine in the benzole nucleous;2976(νCH$_3$) and I380(δCH$_3$) which show that a process of chlorination has occurred and a αchlorethylbenzene is obtained; 990,9I0,760 cm^{-I},which show that there is unchanged styrene in the investigated substance.

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Data from IR spectroscopy are confirmed by those of UV spectro scopy.Together with the absorbtion at 232 nm,corresponding to α,βdichlorethylbenzene there is absorbtion in the range of 250-270 nm with a maximum at 254 and 264 nm,corresponding to the αchlorethylbenzene,chlorination in the benzene nucleous products and unchanged styrene.The existence of the mixture of these products is proved by comparing the spectrum correlation and the thermostability with those of a model mixture.It was found that the content of α,βdichlorethylbenzene,αchlorethylbenzene and styrene in the mixture is respectively 75-80%,5-8% and 8-9%.

In order to study the ingredients of the mixtures in the polymer products,precipitation of the latter with methyl alcohol out of chloroform solution was carried out.On comparison of IR spectra of the feed and precipitation product it was established that after precipitation the bands at 990, 9I0 and 780 cm^{-I} dissappear (Fig.I),which shows that there is styrene in the polymer product when it is in the form of a mixture.

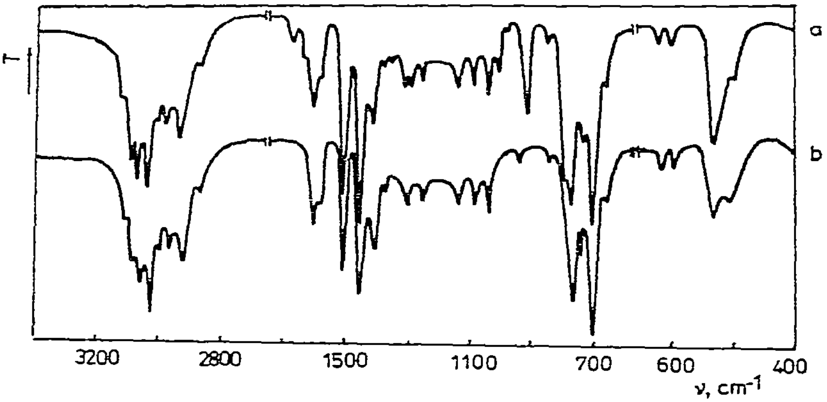


Fig.I. IR spectra of polysulphide polymer,obtained from chlorinated styrene and sodium disulphide before (a) and after (b) purifying.

Its quanfity (2-3%) was determined by differential IR spectroscopy method using a variable thickness cell.

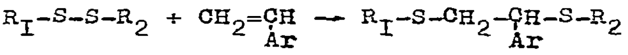
Since the main process is polycondensation of α,βdichlorethylbenzene and sodium disulphide the main structure unit in polymer is expected to be styrenedisulphide one.The results from IR and NMR spectra presented in Table I confirm the above.

TABLE I

Spectrum data for polymer on the basis of chlorinated styrene and sodium disulphide

Group	Data from		
	IR, cm^{-I}	^{I}H NMR, ppm	^{I3}C NMR, ppm
	3I00-3000 I600-I400	7,9	I44-I38 I30-I27
CH_2-S	I405-I250	2,8-3,0	44
CH–S	I320,I240	3,2	5I
CH_3	2870,I380	I,2	2I

More thorough investigation of the composition and structure of polysulphide polymer is done after fractionation. Spectrum relations and molecular weight, viscosity and sulphur content were studied. It was established that with a decrease of molecular weight from 4300 to 970 viscosity decreases from 4,3 to 3,4 and sulphur content from 35 to 30%. At similar molecular weight changes in other polysulphide polymers the change in sulphur content is lower than 2,2% (ref.3). Taking into consideration the conditions of synthesis which are suitable for disulphide-disulphide exchange and styrene disposition towards polymerisation, it can be suppossed that these changes are due to the unchanged styrene, which is present in the feed monomer mixture. In order to prove that, polycondensation was carried out after preliminary purification of the feed monomer from the unchanged styrene by distillation. In the fractions obtained at analogical molecular weights the sulphur content is by 2,0% higher than that of the products obtained without preliminary purification of styrene. This shows that together with polycondensation a process of incorporation of the styrene units into disulphide bonds takes place according to the scheme:



$$R_I-S-S-R_2 + CH_2=\underset{Ar}{CH} \rightarrow R_I-S-CH_2-\underset{Ar}{CH}-S-R_2 \qquad (I)$$

This process explaines the decrease of sulphur content in these products and it is an indication for a dicrease of the class of sulphidity of the polymers.

As an admixture in the feed monomer mixture there is a chlorinated product in the benzene nucleous too. The presence of I,2% chlorine in the polymers after precipitation is an indication that it takes part in the polycondensation with sodium disulphide at the expense of chlorine in the aliphatic part of the compound. Since R-Cl bond is much lower than Ar-Cl the latter remains unchanged during the reaction.

The study of the end groups of polymer molecules was an object of our investigation too.The content of end -OHgroups in the polymers was I,I%.By thorough investigation of all fractions using differential IR spectroscopy method it was established that with a decrease of the molecular weight of the products,the content of methyl groups increases-Fig.2.The methyl groups mainly result from the participation of αchlorethylbenzene in polycondensation. In our previous work it was proved that styrene is also a regulator of molecular weight producing methyl end groups though to a smaller degree than αchlorethylbenzene.Regardles of the presence of the latter groups,under certain conditions the tested liquid polysulphide polymer can be cured,which makes it possible to be used as a hermetizing material.

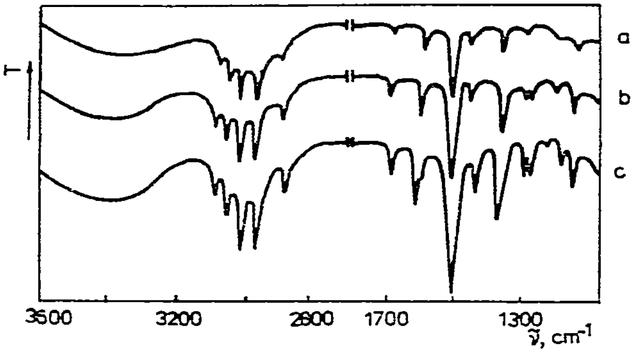


Fig.2.Differential IR spectra,obtained by equilibrate frequencies of $-S-CH_2-CH(Ar)-S-$ units in a fraction with molecular weight of 4300 with some in fractionss with molecular weight of I890(a), I350(b),970(c).

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