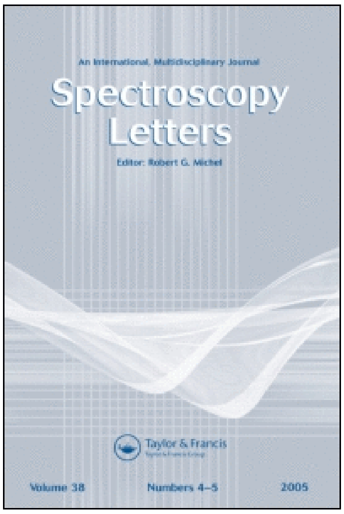

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The Average Molecular Weight Determination of Polysulfide Polymers by Using IR Spectroscopy

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ABSTRACT

IR spectroscopy method has been designed in order to determine the average molecular weight of polysulfide polymers of the general formula:

$$\textbf{End} - [- S_x - CH_2 - CH(C_6H_5)]_m - [S_x - CH_2 - CH_2 -]_n - \textbf{End}$$

where: the symbol **End** denotes the fragment $H_3C - CH(C_6H_5)$ or SH functionality; $\mathbf{x} = 1 - 4$, $m = 1 - 40$ and $\mathbf{n} = 1 - 40$.

The average molecular weight was determined, according to the formula:

$$M = 2\,\frac{L_1.M_1 + L_2.x.M_2 + L_3.M_3 + L_4.M_4 + L_5.M_5}{L_1 + L_5}$$

where L_1 represented the number of $H_3C - CH(C_6H_5)$ fragments; L_2 corresponded to the number of polysulfide bonds; the parameter x was the number of sulfur atoms per one polysulfide bond; L_3 was the number of $CH_2 - CH(C_6H_5)$ fragments bound along the polymer chain; L_4 represented the number of the ethylene fragments involved; L_5 denoted the number of - SH end groups and M_1, M_2, M_3, M_4, M_5 corresponded to the molecular masses of the various structural fragments indicated above.

To determine the content of ethylene fragments in the copolymers, the characteristic absorption band at 1104 cm^{-1} was selected, whereas the band at 1600 cm^{-1} was used for the evaluation of the fragments containing benzene rings. The content of the end methyl groups was, in turn, calculated by employing the band at 1380 cm^{-1}. The class of polysulfidity **x** was determined by using both the

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elemental analysis method and IR spectroscopy, particularly, the absorption band at 492 cm^{-1}. The results obtained from the spectroscopic determination of the average molecular weight were compared to those obtained by using the cryoscopic method. The relative analytical error for the determination of the average molecular weight did not exceed 5.9 %.

INTRODUCTION

Polysulfide polymers of the general formula:

$$\mathbf{End} - [- S_x - CH_2 - CH(C_6H_5)]_m - [S_x - CH_2 - CH_2 -]_n - \mathbf{End} \qquad (I)$$

where: the symbol **End** denotes the fragment $H_3C - CH(C_6H_5)$ or SH functionality; **x** = 1 - 4, m = 1 - 40 and **n** = 1 - 40, have been synthesized by the reaction of 1,2-dichloroethane (DCE), styrene (St) and sodium tetrasulfide (STS) [1]. The application of these polymers in industry and everyday life is associated with various technical fields such as construction work, electronics, cable insulation, *etc.* Therefore, both the analytical determination and control of the various structural and other characteristics such as average molecular weight, thermal stability, functional groups content, *etc.* are considered to be important and, frequently, urgent tasks necessary to evaluate the polymer applicability. Linear macromolecules were found to form the polymer structure and a random distribution of the styrene-polysulfide and ethylene-polysulfide fragments along the macromolecular chains without any formation of styrene block-segments was proved [2, 3]. One of the basic properties of thiokoles represents their insolubility in both the mineral oils and common solvents which renders the average molecular mass determination by employing 'traditional' methods somewhat difficult task [4].

Thirty polymers were synthesized forthe purpose of the present study by varying the reaction conditions such as temperature, reaction time and the molar ratio of the starting materials employed. Two kinds of model compounds were prepared. The first one, denoted further as MC1, MC2, MC3, MC4 and MC5 included copolymers of known composition which were prepared by blending polyethylene tetrasulfide and polystyrene polysulfide [6] of a pre-determined quantitative ratio under the conditions of active interchain exchange. The second kind of model compounds denoted as MC6, MC7, MC8, MC9 and MC10 were products which contained structural fragments consisting of both the benzene rings and methyl groups. These compounds were synthesized by polycondensation reaction between STS, DCE and 1-chloro-1-phenylethane, according to known methods [1].

For the analytical purposes of the present study, the products obtained were purified by re-precipitation. IR spectra were recorded by using *Bruker IFS 66 FTIR* spectrophotometer.

METHODS

For **P** molecules of a given polymer of the structure (I) the number-average molecular mass can be determined according to the formula:

$$M = 2\,\frac{L_1.M_1 + L_2.x.M_2 + L_3.M_3 + L_4.M_4 + L_5.M_5}{L_1 + L_5} \qquad \text{(II)}$$

where L_1 represents the number of CH_3 - $CH(C_6H_5)$ fragments L_2 corresponds to the number of polysulfide bonds; the parameter x is the number of sulfur atoms per one polysulfide bond; L_3 is the number of CH_2 - $CH(C_6H_5)$ fragments bound along the polymer chain; L_4 represents the number of the ethylene fragments involved; L_5 denotes the number of - SH end groups, and M_1, M_2, M_3, M_4, M_5 corresponds to the molecular masses of the various structural fragments indicated above.

Each fragment of the sum $N = L_1 + L_2$ contains one benzene ring, to which an absorption band at 1600 cm^{-1} ($\nu^{(C=C)}$) could be assigned. On the other hand,an absorption band at 1107 cm^{-1} corresponds to the ethylene groups included in the ethylene polysulfide fragments. Each of the parameters L_4 and N can be determined by solving the following set of equations:

$$\frac{A_{1107}}{A_{1600}} = \frac{\varepsilon_{1107}.L_4.b}{\varepsilon_{1600}.(L_1 + L_3).b} = k_1\frac{L_4}{N} \qquad \text{(III)}$$

$$L_4 + N = R$$

where A is the light absorbency; ε is the molar absorptivity at the corresponding wave number [$l.mol^{-1}.cm^{-1}$]; **b** represents the thickness of the layer [cm]; $\mathbf{k_1}$ = 0.69 is a constant which has been determined by employing the copolymers of known composition (MC1 - MC5) mentioned above; and **R** represents each randomly selected number (preferably, 10, 100, *etc.*) which depends on the number of macromolecules **P** selected.

To determine the number-average molecular mass, each of the parameters L_1 and L_3 needs to be evaluated. The fragments L_1 only contained methyl groups which corresponded to the characteristic band at 1380 cm^{-1} (δ^{CH_3}). Thus L_1 can be determined in accordance with the following equation:

$$\frac{A_{1380}}{A_{1600}} = \frac{\varepsilon_{1380}.L_1.b}{\varepsilon_{1600}.(L_1 + L_3).b} = k_2\frac{L_1}{N} \qquad \text{(IV)}$$

where $k_2 = 1.48$ is a constant which was determined by employing the model compounds MC6 - MC10 which contained structural fragments consisting of both the benzene rings and methyl groups.

The parameter L_2 was determined, bearing in mind that polysulfide bonds do not take part in the formation of the macromolecular end groups [7]. The number of the polysulfide bonds in each macromolecule is, in any case, less by an unity than the number of the organic co-monomer fragments. Thus if **P** macromolecules contained $R = L_1 + L_3 + L_4$ of such fragments, the number of polysulfide bonds L_2 can be calculated, according to the following equation:

$$L_2 = (L_1 + L_3 + L_4) - (L_1 + L_5)/2 \qquad \text{(V)}$$

where the parameter L_5 can be determined iodometrically.

The parameter **x** was, in turn, determined by using both the elemental analysis and IR spectroscopy. The elemental analysis method included the use of the following equation:

$$C = \frac{L_2.32.x}{L_1.105 + L_3.104 + L_2.32.x + L_4.28 + L_5.33} \qquad \text{(VI)}$$

where **C** was the sulfur content [wt. %]. The elemental analysis of sulfur, according to the *Schoeniger* method, included a special removal of the sulfur which was not bound chemically by the treatment with mercury under an agitation or with an aqueous solution of sodium sulfide. Some desulfurization of the products was, however, expected and the method was only considered as subsidiary.

The determination of the parameter **x** by IR spectroscopy was conducted by the graphical presentation of the following dependence:

$$\frac{A'_{492}}{A_{1107}} = f(x) \qquad \text{(VII)}$$

where A'_{492} was the so-called „reduced" light absorbency at 492 cm^{-1} ($\nu^{(S-S)}$); This value was calculated for $L_2 = L_4$, i.e., assuming that each polysulfide bond corresponded to one ethylene fragment in accordance with the following expression:

$$A'_{492} = \frac{A_{492}.L_4}{L_2} \qquad \text{(VIII)}$$

and corresponded to the light absorbency related to the ethylene fragments in the polymer only.

RESULTS AND DISCUSSION

IR spectra of the copolymer based on STS, DCE and St of the average molecular weight of 2294 recorded within the corresponding intervals of 1640 - 1560, 1400 - 1360, 1120 - 1060 and 520 - 450 cm^{-1} (Fig. 1) indicated that the absorption bands at 1600.3, 1379.6, 1107.1 and 492.5 cm^{-1} were clearly pronounced and their intensities were commensurable. The corresponding light absorbencies A for the bands were determined by using the baseline method. The suitability of these absorption bands for the quantitative IR spectral analysis was estimated. The function of the kind:

$$A_\nu = f(\mathbf{m}.\mathbf{b}) \qquad \text{(IX)}$$

was estimated, where ν corresponded to the wavenumbers 1600,1380, 1107 and 492 cm^{-1}; **m** were the molar parts of the structural fragments in the polymer containing benzene rings, methyl groups, ethylene segments and polysulfide bonds respectively [mol %] and **b** represented the thickness of the sample layer. This function was found to be linear for the bands at 1600, 1380 and 1104 cm^{-1} respectively. Consequently, these bands were considered to be convenient for the evaluation of parameters L_1, L_3 and L_4. The absorptivity for the band at 492 cm^{-1}, however, increased as the class of polysulfidity became higher, which

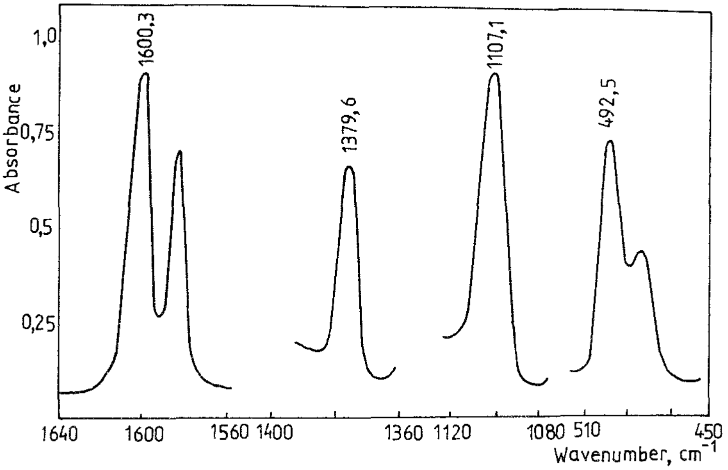

Fig. 1. FTIR spectrum of polysulfide polymer based on STS, DCE and St within the wavenumber intervals 1640-1560, 1400-1360, 1120-1060 and 520-450 cm^{-1}.

hampered the utilization of this band for the determination of the parameter **x** in accordance with equation (II). Therefore, the calibration necessary to employ the quantitative spectral method for analysis required the determination of the class of polysulfidity by elemental analysis. To this purpose, polymers of various composition and viscosity were employed. The corresponding calculations were made, assuming that R = 100 (Table 1).

Apparently, the composition of the copolymers had a pronounced influence on the number-average molecular mass by changing the parameters such as $\frac{A_{1107}}{A_{1600}}$, $\frac{A_{1380}}{A_{1600}}$ and the class of polysulfidity **x**. The content of the terminal - SH groups remained within 1.5 to 1.6 mol %, whereas the value of the parameter **x** varied from 2.05 to 3.41.

For all of the copolymers studied, the value of the ratio $\frac{A'_{492}}{A_{1107}}$ was also determined. The corresponding graphic dependence $\frac{A'_{492}}{A_{1107}} = f(x)$ was drawn,

Table 1

Number-Average Molecular Weight of Copolymers of Various Composition Based on Sodium Tetrasulfide, 1,2-Dichloroethane and Styrene

Run No.	$\frac{A_{1107}}{A_{1600}}$	$\frac{A_{1380}}{A_{1600}}$	C Elemental Analysis	x	- SH Groups Content, %	Number-Average Molecular Mass	$\frac{A'_{492}}{A_{1107}}$
1	1.51	0.42	66.59	3.41	1.61	3728	1.12
2	1.39	0.44	64.11	3.20	1.60	3293	0.95
3	1.32	0.45	63.91	3.15	1.59	3084	0.92
4	1.23	0.48	62.56	3.08	1.58	2877	0.88
5	1.18	0.54	61.89	3.05	1.56	2595	0.81
6	1.03	0.59	60.33	3.01	1.55	2294	0.82
7	0.95	0.66	58.92	2.93	1.54	2025	0.76
8	0.73	0.78	55.02	2.76	1.50	1595	0.70
9	0.50	1.03	48.74	2.46	1.50	1119	0.57
10	0.45	1.11	44.68	2.20	1.50	952	0.49
11	0.41	1.15	42.31	2.05	1.50	914	0.45

which turned out to represent a curve (Fig. 2). An attempt was made to evaluate the average molecular mass of the products by employing the above-mentioned analytical curve. The study was conducted for the fractions of the copolymers which were soluble in chloroform. The results were compared to those obtained by using the cryoscopic method (Table 2).

In all cases, the content of the terminal - SH functional groups was within 1.5 to 1.6 % and the relative analytical error for the average molecular mass determination did not exceed 5.9 %. These experimental facts allowed the utilization of the method, also, to insoluble samples of copolymers, for which the „conventional" methods for molecular mass determination proved to be non-applicable. The corresponding results are shown in Table 3.

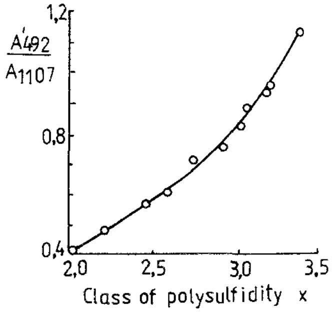

Fig. 2. Dependence of the $\frac{A'_{492}}{A_{1107}}$ absorbency ratio and the class of polysulfidity in the polysulfide polymers based on STS, DCE and St as starting materials.

Table 2

Number-Average Molecular Mass for Soluble in Chloroform Fractions of Polysulfide Polymers of Various Composition, Based on ST, DCE and St

Run No.	$\frac{A_{1107}}{A_{1600}}$	$\frac{A_{1380}}{A_{1600}}$	Value of x according to Fig.2	- SH Groups Content (%)	Number- Average Molecular Mass Determined By		Relative Error $(\Delta M/M).10^2$
					Formula (II)	Cryoscopic Method	
1	0.65	0.81	2.95	1.55	1646	1680	2.02
2	0.65	0.88	2.92	1.56	1464	1400	4.57
3	0.60	0.95	2.86	1.53	1343	1390	3.58
4	0.58	1.00	2.81	1.56	1272	1300	2.15
5	0.53	1.11	2.76	1.56	1157	1100	5.18
6	0.50	1.23	2.67	1.52	1052	1050	0.19
7	0.46	1.36	2.51	1.51	941	1000	5.90

Table 3

Number-Average Molecular of Insoluble Polysulfide Polymers Prepared on the Basis of ST, DCE and St and Determined by Using the IR Spectroscopy

Run No.	$\frac{A_{1107}}{A_{1600}}$	$\frac{A_{1380}}{A_{1600}}$	Value of x, according to Fig. 2	L_1	L_2	L_3	L_4	Ave. Molecular Mass
1	1.61	0.40	3.30	6.38	96.03	23.62	70.00	3889
2	1.46	0.42	3.21	7.09	95.68	25.00	67.90	3496
3	1.35	0.45	3.21	7.89	95.28	25.94	66.17	3037
4	1.20	0.55	3.11	9.89	95.28	26.62	63.49	2611
5	1.06	0.59	3.02	11.24	93.61	28.19	60.57	2332
6	0.97	0.64	2.95	12.55	92.95	29.02	58.43	2098
7	0.74	0.60	2.81	13.54	92.46	34.71	51.75	1960

The determination of the number-average molecular mass by using IR spectroscopy is easy and can be conducted promptly. The method does not require any preliminary purification for the removal of the free (unbound) sulfur which is inactive with respect to any registration in the spectra. The exact determination of the thickness of the sample layer is not necessary, since the use of the corresponding absorbency ratios is actually involved. The value of parameter L_5 is within 1.2 to 1.3 and, therefore, its determination by elemental analysis is not always needed. The calculation of the value of the number-average molecular mass requires only a few minutes.

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