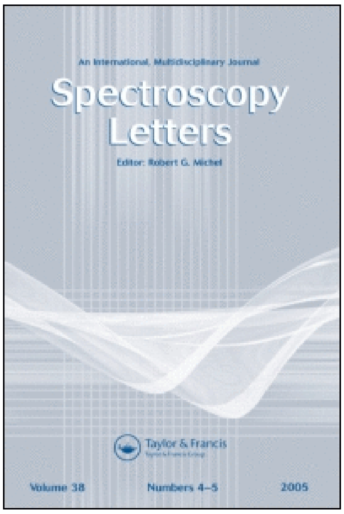


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Composition and Structure of Liquid Polysulfide Oligomers Based on Sulfur, Styrene and Methacrylic Acid

D. Todorova[a]; St. Todorov[a]
[a] University "Prof. Dr. As. Zlatarov", Bourgas, Bulgaria

To cite this Article Todorova, D. and Todorov, St.(1999) 'Composition and Structure of Liquid Polysulfide Oligomers Based on Sulfur, Styrene and Methacrylic Acid', Spectroscopy Letters, 32: 2, 321 — 331

To link to this Article: DOI: 10.1080/00387019909349987

URL: http://dx.doi.org/10.1080/00387019909349987

SPECTROSCOPY LETTERS, 32(2), 321-331 (1999)

COMPOSITION AND STRUCTURE OF LIQUID POLYSULFIDE OLIGOMERS BASED ON SULFUR, STYRENE AND METHACRYLIC ACID

Key words: Polysulfide oligomers, composition, structure, spectroscopy.

D. Todorova and St. Todorov
University "Prof. Dr. As. Zlatarov", 8010 Bourgas, Bulgaria

ABSTRACT

Liquid polysulfide oligomers have been prepared in bulk as well as under the conditions of known methods. Styrene, methacrylic acid and sulfur were used as starting materials. The composition of the oligomer products was determined by using IR spectroscopy as the principal method. The absorption bands at 1600 and 700 cm^{-1} for styrene and 1697 cm^{-1} for methacrylic acid were employed as an analytical tool. Both the kind of chemical bonds between the monomer fragments and length of polysulfide bonds were studied by the combined application of IR and ^1H NMR spectroscopy. Methacrylic acid was found to be bound chemically to the sulfur atoms *via* its vinylidene group and the class of polysulfidity decreased from 2.8 to 2.5.

The oligomers synthesized were introduced into elastomer compositions utilized for the packing of high-voltage cable sleeves. An improvement of the adhesive properties towards metal surfaces by 43 % was observed as oligomer containing 10.3 mol % of methacrylic acid fragments was employed.

INTRODUCTION

The viscous-liquid thiokol poly(styrene polysulfide) indicated further as PStPS synthesized by us[1] and other authors[2] is known to be utilized in the construction work and other technical fields. A number of valuable properties such as easy preparation, flowability, solidification at room temperature, oil and thermal stability range this material close to the commercially available liquid thiokols. The structure of PStPS oligomer has been studied by IR spectroscopy[3] as well as NMR and mass-spectrometry[4]. To improve the unsatisfactory adhesion towards metal surfaces, modification with methacrylic acid (MAA) was conducted in two modes. According to the first one, the PStPS oligomer synthesized preliminarily was modified by MAA under the conditions of active interchain exchange[5]. The second method involved the simultaneous introduction of MAA and styrene as the starting comonomer feed under the conditions of synthesis of PStPS. These products are further indicated as copolymers. Fourteen oligomer products were obtained by using the two methods under the conditions of varying MAA content with respect to styrene (St) from 0.1 to 0.7 mol/mol St. The products synthesized were yellow oligomers of viscous-liquid consistency. Poly (methacrylic acid polysulfide) (PMAAPS) synthesized, according to method[1] was employed as a model compound.

The aim of the present work was to study both the structure and composition of the polysulfide oligomers, as well as some properties of the latter which are of a significant importance for the thiokols. Threefold preliminary precipitation of the products was conducted for their purification and the following analyses. Chloroform was used as a solvent whereas n-hexane was the precipitant selected.

METHODS

IR spectroscopy was employed mainly in order to study both the structure and composition of oligomers. The spectra were recorded on

Specord IR 75 instrument and the samples were prepared as thin layers placed between KBr windows. For the samples of MAA content below 10 mol %, spectroscopy cells with sample layer of 0.0017 and 0.0019 cm were respectively used. For the samples of the higher MAA content, the thickness of the layer was determined by using the equation $b = P/S\rho$, where b was the sample thickness, [cm]; P represented the weight of the sample for analysis, [g]; ρ was the corresponding density, [g/cm^3]; and S was the area of sample placed between the two KBr windows and kept under the conditions of beam irradiation for one hour at constant temperature, [cm^2].

Spectral method was designated in order to determine the sample composition. The absorption bands at 1697 cm^{-1} and 1600 (or 700 cm^{-1}) were selected for quantitative determination of MAA and styrene segments respectively. The *Harwood* method [6] was adopted to verify the applicability of these bands for the quantitative spectral analysis. To this purpose, the IR spectra of samples of a certain thickness derived from five modified oligomers of various composition were recorded in the 1850 - 1550 and 800 - 650 cm^{-1} regions. The corresponding dependencies, as expressed by the functions:

$$A_{1697}/b = f(A_{1600}/b) \tag{1}$$

and

$$A_{1697}/b = f(A_{700}/b) \tag{2}$$

were studied, where A_{1697}, A_{1600} and A_{700} are the light absorbencies corresponding to the bands at 1697, 1600 and 700 cm^{-1} respectively. The above dependencies (1) and (2) were found to represent straight lines which, according to Harwood, indicated that the bands were non-sensitive towards change of the wave length. Therefore, these parameters could be used for the purpose of quantitative analysis.

The calibration was conducted by using model compositions. The latter were prepared by blending PStPS and PMAAPS synthesized preliminarily which were taken in a predetermined quantitative ratio. Seven blends were thus prepared. After the "activation" of an interchain exchange in the blends, compounds with known composition, having the structure of the modified products synthesized were obtained. For the compositions studied, the functions:

$$A_{1697}/A_{1600} = f\,(m_{MAA}/m_{St}) \qquad (3)$$

and

$$A_{1697}/A_{700} = f\,(m_{MAA}/m_{St}) \qquad (4)$$

where m_{MAA} and m_{St} represent the molar parts of methacrylic acid and styrene fragments in the oligomer chain respectively, were studied. The calibration curve (3) was employed successfully under the conditions of PStPS content in the blends exceeding 90 %. The calibration curve (4) was found to be more convenient at PStPS content below this value because of the stronger absorbency at 700 cm^{-1}. The standard deviation evaluated for the straight-line sections of the curves and calculated from ten measurements was $\sigma = 0.004$ for 95 % confidence interval. The composition of the oligomers synthesized was determined according to the following expressions:

$$A_{1697}/A_{1600} = k_1\, m_{MAA}/m_{St} \qquad (5)$$

and

$$A_{1697}/A_{1600} = k_2\, m_{MAA}/m_{St} \qquad (6)$$

where $k_1 = 24.3$ and $k_2 = 2.9$ were determined from the calibration curves

The integral intensity B within the 450 - 530 cm^{-1} region was determined by using a compensatory self-recorder K-201.

1H NMR spectra were recorded by the *Bruker* instrument at 80 MHz.

To study the adhesive properties, a basic elastomer composition applied for the packing of high-voltage cable sleeves was prepared. Various quantities of oligomers synthesized on the basis of styrene, MAA and sulfur were subsequently introduced into this composition. Then the adhesive properties of the system consisting of rubber and metal were determined by employing the so called *H-methods*, according to the Bulgarian State Standard BSS 17078-85.

RESULTS AND DISCUSSION

Some basic characteristics of PStPS oligomer used as the starting material for the modification procedure are shown in Table 1.

The composition of the copolymers and the modified products was determined, according to the method of the calibration curve (Table 2).

The increase of MAA content in the initial blend for the modification procedure up to 0.6 mol led to the corresponding increase of MAA fragments bound chemically. At higher initial MAA content, however, the modification process occurred more slowly. The increase of MAA content in the comonomer feed for the copolymerization procedure from 0.1 to 0.7 mol resulted in the gradual and continuous increase of the content of MAA fragments bound chemically. The products of the higher content of MAA, however, were considered to be impractical because of their increased solubility.

Another principal goal of the present work was to study the structure of the oligomer products prepared. This study comprised the estimation of the chemical bonds involved and the class of polysulfidity.

To determine the kind of chemical bonds, IR spectra of PStPS as shown in Fig. 1a and of the modified oligomer containing 9.8 mol % MAA (Fig. 1b) were compared. All of the characteristic IR bands for PStPS were observed in the spectrum indicated in Fig. 1b, however the band at 1697 cm^{-1} (ν(C=O)) was also present. No band at 1630 cm^{-1} (ν(C=C) in MAA) was observed. Therefore, the attachment of the MAA fragments occurred *via* the double bonds of the vinyl groups. The rest of the absorption bands were superimposed with those of PStPS. Therefore, the record of a differential spectrum was preferred (Fig. 2a). The latter was obtained through the full compensation of the bands for the PStPS fragments. As a result, the absorption bands of MAA fragments chemically attached to the oligomer chain were only indicated. This spectrum was compared to that

TABLE 1
Basic Characteristics of Poly(Styrene Polysulfide) Oligomers Used as Starting Materials for the Chemical Modification

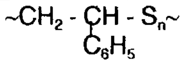
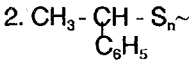
Characteristics	Parameters
Basic structural unit	 $\sim CH_2-CH(C_6H_5)-S_n\sim$
End groups	1. - SH 2.  $CH_3-CH(C_6H_5)-S_n\sim$
Thiol (- SH) groups content, %	0.75
Class of polysulfidity	2.8
Average molecular mass	2814
Viscosity at 25°C , Pa.s	230

TABLE 2
Composition of the Synthesized Products Obtained Under the Conditions of Various MAA Content in the Initial Blend

No.	Initial PStPS/MAA Ratio in the Initial Blend, mol	Content of MAA Fragments in the Modified Oligomers, mol %	St/MAA Ratio in the Initial Comonomer Feed, mol	Content of MAA Fragments in the Copolymer, mol %
1	1.0 : 0.1	3.1	1.0 : 0.1	2.2
2	1.0 : 0.2	4.0	1.0 : 0.2	3.5
3	1.0 : 0.3	6.3	1.0 : 0.3	5.9
4	1.0 : 0.4	9.8	1.0 : 0.4	8.1
5	1.0 : 0.5	11.5	1.0 : 0.5	9.2
6	1.0 : 0.6	12.4	1.0 : 0.6	10.3
7	1.0 : 0.7	12.5	1.0 : 0.7	11.6

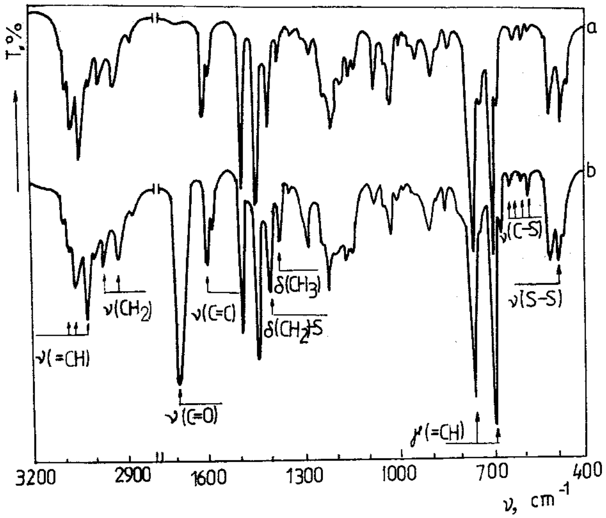


FIG.1. IR spectra of PStPS oligomer (a) and PStPS oligomer modified with MAA (b).

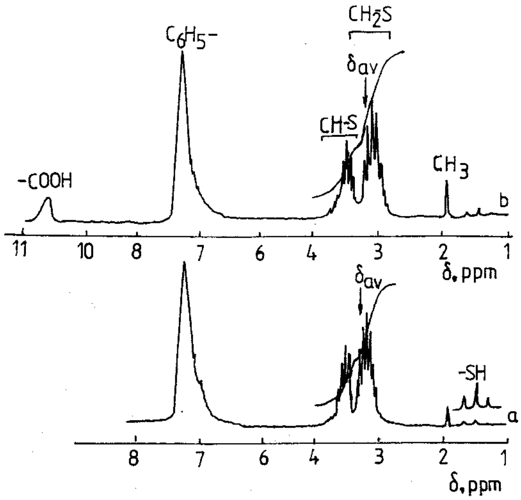
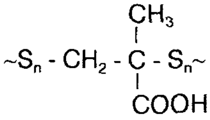


FIG.2 Differential IR spectrum of PStPS oligomer modified with MAA. The spectrum was recorded by compensating the absorption of PStPS fragments (a); IR spectrum of poly(methacrylic acid) (b).

of poly(methacrylic acid), PMAA alone (Fig. 2b). The difference between the two spectra was significant because all of the bands were changed in terms of parameters such as intensity and half-width. The band at 1490 cm^{-1} derived from MAA block fragments disappeared completely. Besides, the band at 1460 cm^{-1} ($\delta(CH_2)$) was shifted towards 1403 cm^{-1} ($\delta(CH_2)$ in the CH_2 - S fragment). The observed bands at 1270 and 1110 cm^{-1} ($\delta(CH_2)$-S) were clearly pronounced. Two new absorption bands were observed in the 700 - 550 cm^{-1} region, i.e., the bands at 675 cm^{-1} ($\nu(CH_2$ - S) and 580 cm^{-1} (ν(C - S)) whose intensity was characteristic for thiokols.

On the basis of the data obtained, it might be suggested that MAA fragments are chemically attached to the sulfur atoms *via* the vinyliden double bonds and methacrylic acid polysulfide (MAAPS):



$$\sim S_n - CH_2 - \underset{\displaystyle COOH}{\overset{\displaystyle CH_3}{C}} - S_n \sim$$

where n = 1 - 4 is formed.

The bond of the vinylidene group of MAA with the sulfur atoms probably caused the shift in the absorption bands and the change of both the relative intensity and half-width of the latter for the modified products (Fig. 2b). The C - S_n bonds are believed to contribute to less hindered free rotation of the monomer fragments which is expected to result in the reduction of the number of stable conformers. The steric hindrance caused by PStPS fragments in the oligomers is likely to render the association of the carboxylic functional groups *via* hydrogen bonds more difficult. Thus, with the same intensity of the band at 1697 cm^{-1} (ν(C=O)), much weaker absorption at 940 cm^{-1} ($\nu(COOH)_{dimers}$)) and at the 3600 - 2400 cm^{-1} region ($\nu(OH)_{assoc.}$) was observed.

The differential spectrum in Fig. 2a was compared with the identical one obtained for the copolymer based on styrene, MAA and sulfur. Both spectra were identical within the 3600 - 500 cm^{-1} region. The only

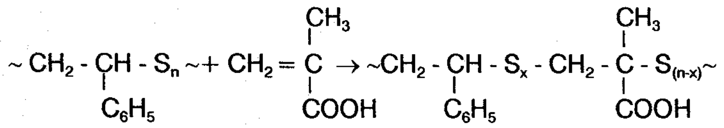
TABLE 3
Integral IR Absorption Intensities B, Calculated Within the 510 - 450 cm^{-1} Range for PStPS Oligomers Modified by MAA and the Copolymers Prepared on the Basis of Styrene, Methacrylic Acid and Sulfur

MAA Content in the Modified Products, mol %	$B_{510-450}$, cm^2	MAA Content in the Copolymers, mol %	$B_{510-450}$, cm^2
0.0	28.9	0.0	28.9
3.1	26.9	2.2	28.5
4.0	25.2	3.5	28.0
6.3	23.9	5.9	27.7
9.8	21.8	8.1	27.3
11.5	20.3	9.2	26.9
12.4	19.5	10.3	26.6
12.5	19.4	11.6	26.3

difference observed was the intensity of the band at 490 cm^{-1} (ν(S-S)) which was positive, unlike that shown in Fig. 2a. Therefore, with the exception of the class of polysulfidity, all chemical bonds in the copolymers were identical to those of the modified products.

To estimate the changes occurring with the polysulfide bonds, the integral intensity of the absorbency within the 510 - 450 cm^{-1} region was determined, as shown in Table 3.

The increased MAA content in the modified products was accompanied by strong decrease of the integral intensity in the 510 - 450 cm^{-1} region. Therefore, the chemical modification took place at these sites of the oligomer chain predominantly, where polysulfide S_x (x = 3 and/or 4) bonds were located.



$$\sim CH_2-\underset{C_6H_5}{CH}-S_n\sim + CH_2=\overset{CH_3}{\underset{COOH}{C}} \rightarrow \sim CH_2-\underset{C_6H_5}{CH}-S_x-CH_2-\overset{CH_3}{\underset{COOH}{C}}-S_{(n-x)}\sim$$

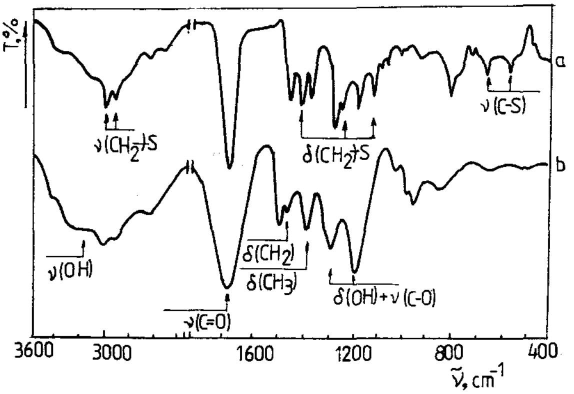


FIG.3 ^{1}H NMR spectrum of PStPS oligomer (a) and PStPS oligomer modified with MAA (b).

In the case of the copolymers, part of the fragments were only bound in this mode. Most of these fragments actually took part in the chain propagation process thus keeping the trisulfide bonds intact.

The above structure was also confirmed by the ^{1}H NMR analysis. The starting PStPS oligomer indicated a peak at 7.35 ppm for benzene protons and multiplets which corresponded to the presence of CH - S and CH_2 - S fragments within the 3.8 - 3.0 ppm interval (Fig. 3a). The calculation of the half-height of the integral curve led to the "average" chemical shift $\delta_{av} = 3.28$ ppm which, in turn, corresponded to n = 2.8 [7]. The ^{1}H NMR spectrum of the copolymer of 11.6 mol % MAA content (Fig. 3b) indicated peak at 10.75 ppm for the carboxylic group protons, whereas the multiplets for the CH-S and CH_2-S fragments remained almost unchanged. For the modified oligomer containing 12.5 mol % MAA, the signals for CH_2 - S and CH - S bonds were shifted upfield towards δ_{av} = 3.23. According to literature data [7], such chemical shifts occur as the length of the polysulfide bonds decreases. The class of polysulfidity for the copolymers was found to decrease insignificantly from 2.8 to 2.7 whereas for the modified products the corresponding value was 2.5.

The oligomers based on styrene, methacrylic acid and sulfur were introduced as additives into a basic elastomer composition utilized for the packing of high-voltage cable sleeves. The adhesion to the metal surface was found to become stronger as MAA content in the oligomer products increased, however, some mechanical properties such as relative elongation were deteriorated. Optimum results were obtained with the copolymer of 10.3 mol % MAA content which was introduced as 20 mass parts into the basic elastomer composition. In this case, an improvement of the adhesion by, approximately, 43 % was achieved and the corresponding value of adhesive force determined experimentally reached 100.1 N.

REFERENCES

1. Bulg. Pat. No. 404411, 1985

2. Yamalieva L. N., Nigmatulina F. G., Averko-Antonovitch L. A., Volfson S. I., *Proceedings of III USSR Conference on Chemistry and Physical Chemistry of Oligomers*, Chernogolov (USSR), 1986, 229 *(Russ.).*

3. Todorov St.,Todorova D., Koinov V., *Rubber International Conference IRC*, France, 1990, 62 - 63.

4. Efremov Yu. Y., et al., *Visokomolekuliarnie Soedinenija*, 1991, **A33**, No. 2, 298 *(Russ.).*

5. Owen G. P., Macknight M. I., Tobolski A. V., *J. Am. Chem. Soc.*, 1964, **68**, No. 4, 784.

6. Harwood H. J., Ritchey W. M., *J. Polymer Sci*, 1964, **B2**, 601.

7. Aliev A. D., Zhumavaev Zh., Koshevnik A. Yu., *Azerbaidzhanskij Khimicheskij Journal*, 1980, **33**, No. 3, 77 *(Russ.).*

Date Received: November 23, 1998
Date Accepted: December 17, 1998