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S. Todorov [a], V. Koinov [a], D. Todorova [a] & Sh. Marinova [a]
[a] Department of Polymers, Bourgas University of Technology, Bourgas, 8010, Bulgaria
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PREPARATION AND PROPERTIES OF COMPOSITIONS BASED ON EPOXY RESINS AND POLYSULFIDE OLIGOMERS CONTAINING HYDROSULFIDE END GROUP

S. TODOROV, V. KOINOV, D. TODOROVA, SH. MARINOVA
Department of Polymers, Bourgas University of Technology, Bourgas 8010, Bulgaria

Abstract Liquid disulfide oligomers with high content of thiol groups has been obtained. Modification of this product with chloracetic acid was done. Viscous-liquid polysulfide oligomers with controled content of thiol groups were obtained on their base. Compositions on the base of this oligomers and epoxy resin (16-18% content of epoxy groups) are obtained.

ITRODUCTION

Obtaining of polysulfide oligomers from glycols is a prospective method for synthesis.[1] There are reports for their preparation as a result of esterification of glycols.[2,3] Thiokols with high molecular weight can be obtained if measures are under- taken for exchange of the hydroxyl end groups with halogen atoms[4] during the esterification process and after it. As a result the polycondensation with alkaline halides becomes possible and oligomers with high molecular weight are synthesized. The process of their depolymerization is carried out.[5]

EXPERIMENTAL

Method for synthesis of liquid polysulfide oligomers on the base of 2,2'-diethanol disulfide is proposed in the present work. The last one is introduced in the process of etherification in the presence of catalyst p-toluene sulfuric acid. The obtained oligomer is modified with chloracetic acid. The products obtained are introduced in the process of poly-

condensation with Na_2S_2 in which thiokol with high molecular weight is obtained. Liquid polysulfide oligomers with controlled content of thiol groups are obtained by depolymerization with NaSH - Na_2SO_3 or NaOH - $Na_2S_3O_4$.

RESULTS AND DISCISSION

The interaction between sodium hydrosulfide and 2-chlorethanol is realized according to the technique described in reference № 7. In order to find the optimum proportion, the ratio NaSH: $Cl-CH_2-CH_2-OH$ is varied from 1.0:1.0 to 3.0:1.0. It is determined that yield of the synthesized product (about 93% of theoretic yield) is obtained at ratio 1.0:1.0. The compound,obtained is purified through precipitation in aqueous solution of ethyl alcohol .Some of its basic characteristics are shown in Table 1.

The content of carbon, hydrogen and sulfur is determined by elemental analysis (Karlo Erba). The content of hydroxyl groups is determined by the acetylation method and the molecular weight-by the ocmometric method. The structure of the prepared compound is studied by IR spectroscopy (Fig.1a).

TABLE I Some basic characteristics of obtained oligomers.

Characteristics	Product,obtained from sodium hydrosulfide and 2-chlorethanol	Oligomer based on 2,2'-diethanol disulfide	Polysulfide polymer on the base of $Na_2S_{2,2}$
Content of C,%	31.20	34.90	33.70
Content of H,%	6.50	5.80	5.40
Content of S,%	41.30	46.50	47.00
Content of O,%	21.00	12.80	13.90
Content of OH,%	21.90	2.30	0.27
Content of SH,%	-	-	0.84
Molecular weight	154.00	1400.00	6200.00

An absorbance is observed in the spectrum at 1050 cm^{-1}- ν(C-O) for primary hydroxyl groups, a strip at 1450 cm^{-1}- $\delta(CH_2)$ in the groups CH_2-O, at 1410 cm^{-1}-$\nu(CH_2)$ in CH_2-S,

800 cm^{-1}-ν(C-S) and 490 cm^{-1}-ν(S-S).

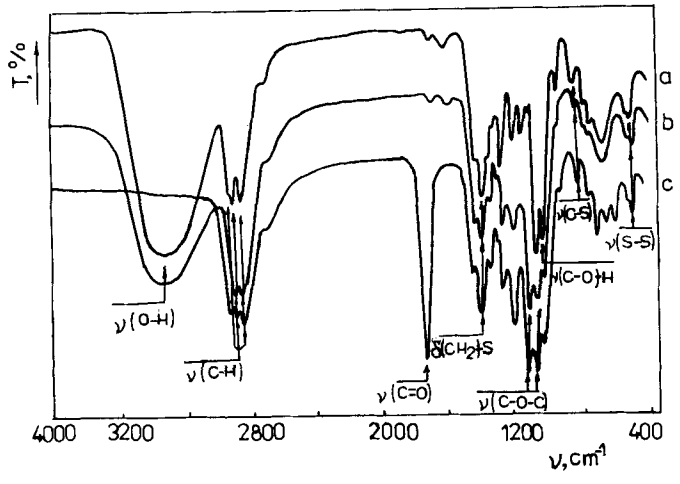

FIGURE 1 IR spectra of a product obtained from sodium hydrosulfide and 2-chlorethanol (a), oligomer on the base of 2,2'-diethanol disulfide before (b) and after modification with chloracetic acid (c).

The study of these results show that the compound obtained is 2,2'-DEDS.After the esterification of 2,2'-DEDS liquid product is obtained whose main characteristics are shown in Table 1. The empirical formula $C_4H_9S_2O$ and the molecular weight show that polysulfide oligomer is obtained.

The following changes are observed in the IR spectrum (Fig. 1b). The intensity of absorbance strongly decreases at 1050 cm^{-1}, a band at 1210 cm^{-1}-ν(C-O) in ethers appears. In the ^1H NMR spectra (Fig.2a) a multiplet at 3.75 ppm for CH_2-O and weak impulses at 2.7 ppm for protons in the hydroxyl group.

The results confirm that the main unit in the obtained oligomer is the chlorex unit:

$$K\text{-}\left[\text{-}S\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}S\text{-}\right]_n\text{-}K$$

where n varied from 8 to 12 and K is CH_2-CH_2-OH. The modification with chloracetic acid is carried out by

varying the molar ratio of the modification agent: polysulfide oligomer from 0.1:1.0 to 0.3:1.0.

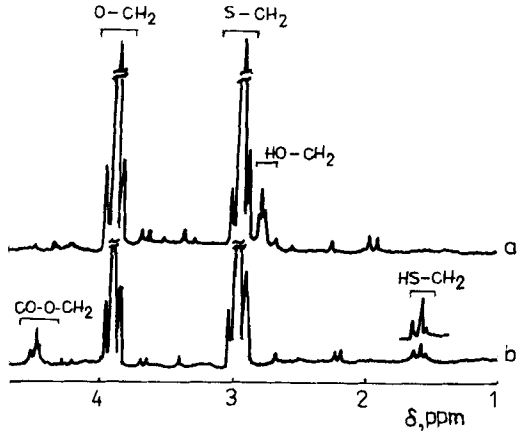

FIGURE 2 ^{1}H NMR spectra of oligomer based on 2,2'-diethanol disulfide (a) and depolymerized polysulfide oligomer with content of hydrosulfide groups 5.09% (b).

The structure of the synthesized products is studied after purification by precipitation through solution of chloroform with methyl alcohol. An absorbance appears in the IR spectra (Fig.1c) at 1740 cm^{-1}-ν(C=O) which is characteristic for ester groups and bands at 680 and 570 cm^{-1} valency oscillation for the bound C-Cl.The intensity increases at 1410 cm^{-1} - $\nu(CH_2)$ in CH_2-S and CH_2-Cl groups. The results confirm that modification is a condensation process between hydroxyl groups of the polysulfide oligomers and carboxy groups of the chloracetic acid. An investigation was carried out to determine the optimum quantity modifying agent for one moll of polysulfide oligomer (Table 2).

The contents of chlorine atoms (Karlo Erba equpment),and the ester groups are determined by the intensity of absorption at 1740 cm^{-1} using preliminary developed IR spectral method. It is seen on Table 2, that when the quantity of chloracetic acid increases to 0.25 moll per 1 moll oligomer, the content of the hydroxyl groups decreases and the content of chlorine atoms and acrylate groups icreases.

Further increase of the quantity of the modifying agent does not lead to change of the contant of the end groups.

Table II Variation, change, alteration of the content of hydroxyl and ester groups and chlorine atom in the modification of one moll polysulfide oligomer with varying quantities chloracetic acid

Quantity of chloracetic acid, moll	Content of hydroxyl groups, %	Content of chlorine atoms, %	Content of ester groups, %
0.00	2.30	0.00	0.00
0.10	1.50	1.60	2.02
0.15	1.00	2.86	3.32
0.20	0.45	3.70	4.70
0.25	0.27	4.05	5.11
0.30	0.27	4.05	5.11

Therefore for 1 moll polysulfide oligomer with molecular weight 1400,the optimum quality chloracetic acid is 0.25 moll. After polycondensation of the modified products with $Na_2S_{2,2}$, a polymer with high molecular weight is obtained. Its main characteristics are given in Table 3.

Table III Influence of the quantity of depolymerizing agents NaSH-$NaSO_3$and $Na_2S_2O_4$- NaOH (used for one moll polysulfide) on the content hydrosulfide groups and the molecular weight of the obtained oligomers.

Quantity of NaSH moll	$NaSO_3$	Content of -SH groups,%	Molec. weigh	Quantity of $Na_2S_2O_4$ moll	NaOH	Content of -SH groups,%	Molec. weight
0.35	0.65	0.84	6200	0.20	2.60	0.84	5700
0.47	0.90	1.03	5100	0.25	2.60	0.94	5500
0.59	1.12	2.31	2300	0.31	2.60	1.20	4300
0.72	1.35	3.59	1500	0.35	2.60	1.28	4000
0.83	1.58	4.34	1200	0.40	2.60	1.34	3800
0.95	1.80	5.09	1600	0.45	2.60	1.44	3600

For the purpose of hermetic sealing this product is not suitable. That is why it is depolymerized. Two ways for depolymerization are studied, first one with NaSH-$Na_2SO_3$and the second with NaOH-$Na_2S_2O_4$. It is seen on Table 3, that the first one gives better results.In the ^1H NMR spectrum impulses for the protons in the hydrosulfide groups are observed (Fig. 2b). Oligomers with controlled content of

thiol end groups and molecular weight are obtained. The products are viscous-liquid, easy to mix with other components and improve flow ability.

Compositions on the base of this oligomers and epoxy resin (16-18% content of epoxy groups) are obtained. They are cross linked in the presence of polyamines and isocyanates. The physicomechanical and electrical properties of the prepared compositions are studied (Table 4).

TABLE IV Physicomechanical and electrical properties of epoxythiokol compositions containing different quantities epoxy resin with 18% epoxy groups content and 2-ethylen 3-amin (10 w.p. per 100 w.p. of compound).

Characteristics	Epoxy resin content, w.p./100 w.p. thiokol						
	0	5	10	20	30	40	50
-utmost strenght,MPa	0.8	1.2	1.6	2.0	2.9	2.3	4.0
-relatively elongation,%	800	650	570	500	420	300	180
-residual elongation,%	45	35	30	29	25	20	14
-strenght of current,KV/mm	8.0	9.0	9.5	13.0	13.5	12.0	11.0
-specific volumetric resistance,om.m.10^8	1.5	5.0	8.0	19.5	108.0	90.0	70.0

The values of the strength increase with the increase of the content of epoxy resins, relative deformation decreases and elastic properties of the compounds bacome better.An improvement of dielectric properties is observed at resin content from 20 to 40 weight parts. It is caused by the existence of threedimensional network.

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