

NOTE

Synthesis and Study of Polysulfide Polymers Based on Sulfur and Epithioglycidyl Ester of Acetic Acid

D. TODOROVA, G. KOSTOV, A. POPOV, ST. TODOROV

University "Prof. Dr. As. Zlatarov," Bourgas, Bulgaria

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INTRODUCTION

The application of episulfides and their derivatives as monomer precursors for the synthesis of polysulfide polymers has opened new horizons in extending the complex of valuable technological and end-use properties of thiokols.^{1–9} Yet, there have been relatively few studies devoted to the synthesis and structure of this particular class of products, and most of these publications are, to some extent, contradictory.^{5–9} Some authors have recommended synthesis at relatively high temperature,⁵ whereas others have set 50°C as the upper temperature limit.⁶ According to the first group of authors,⁵ the "length" of polysulfide bonds could reach the value of 12, but their opponents have claimed that it rarely exceeded 2.⁷ There have also been differences concerning the solubility in organic solvents and stability of polymers on storage. Therefore, the present study was intended to throw additional light on these and other contradictory reports in the literature regarding this interesting class of organosulfur compounds.

In this work, epithioglycidyl ester of acetic acid (ETGEAA) was prepared from glycidyl ester of acetic acid (GEAA) as the starting material. The copolymerization of ETGEAA with sulfur was carried out at various temperatures of 50, 75, and 100°C. The aim of the present study was to examine both the structure and

properties of the copolymers obtained on the basis of these starting materials.

EXPERIMENTAL

Fifty milliliters of GEAA were stirred with 34 g ammonium thiocyanate at 0°C according to the methods described previously.¹⁰ The product (ETGEAA) was then subjected to selective extraction with chloroform.

Toluene (140 mL), 7 g sulfur, and 0.30 g crystalline CdCO₃ were added to 50 mL ETGEAA under continuous agitation. The reaction mixture was heated to 75°C, and the stirring was carried out for 12 h. As a result, yellowish rubber-like polymer was obtained.

¹H-NMR spectra were obtained by using a Bruker instrument (80 MHz), samples having been dissolved in CDCl₃. IR spectra were recorded by employing Bruker IFS 66 FTIR spectrophotometer with samples prepared as capillary layers (for the liquid substances) or films (for the polymers).

RESULTS AND DISCUSSION

Synthesis of ETGEAA/Sulfur Copolymers and Their Properties

IR spectra of GEAA before [Fig. 1(a)] and after the reaction with ammonium thiocyanate [Fig. 1(b)] were compared. The characteristic absorption bands for the

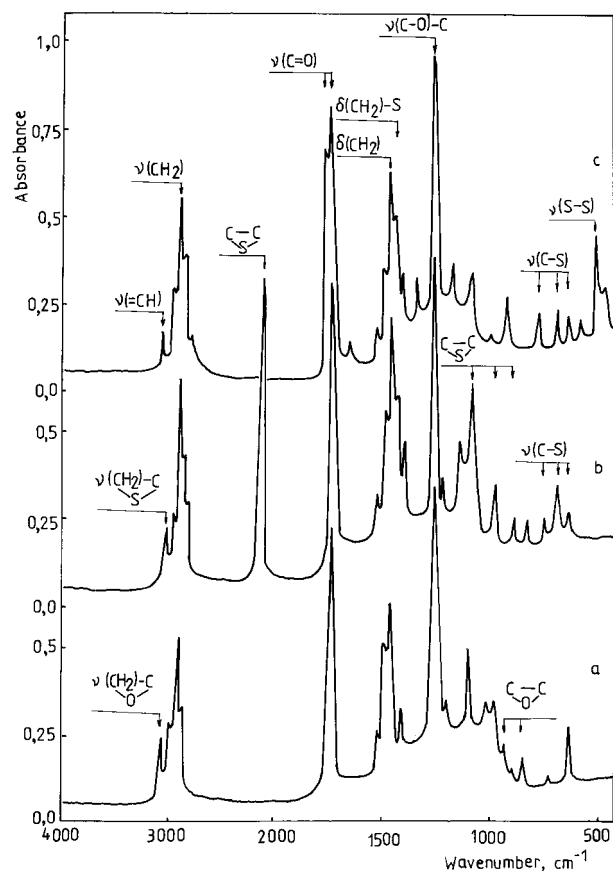
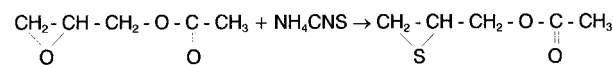


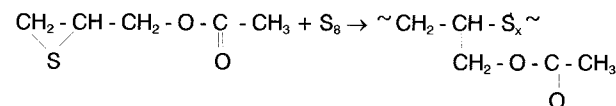
Figure 1 FTIR spectra of glycidyl ester of acetic acid (GEAA) (a), epythioglycidyle ester of acetic acid (ETGEAA), (b) and the copolymer based on ETGEAA and sulfur (c).

epoxide ring at 3008, 917, and 840 cm⁻¹ [Fig. 1(a)] disappeared, and new bands at 3003 [$\nu(\text{CH}_2)$], 1409 $\delta(\text{CH}_2)$, and 2063, 1056, 943, and 871 cm⁻¹ typical for alkene sulfide three-membered ring^{10,11} were observed in the final product [Fig. 1(b)]. Some new bands at 735, 663, and 603 cm⁻¹ [$\nu(\text{C}-\text{S})$] also appeared. The rest of the bands at 1709 [$\nu(\text{C}=\text{O})$], 2926 [$\nu(\text{CH}_2)$], 1460 [$\delta(\text{CH}_2)$], 1380 [$\delta(\text{CH}_3)$], and 1253 cm⁻¹ [$\nu(\text{C}-\text{O})$] did not change. Therefore, GEAA was converted into ETGEAA, because the results from the IR spectroscopy were in accordance with the literature data for thioepoxide ring.¹² The corresponding reaction occurred, according to the following scheme:



The elemental analysis data confirmed the successful preparation of ETGEAA.

The comparison of IR spectra of ETGEAA before [Fig. 1(b)] and after the anionic copolymerization with sulfur [Fig. 1(c)] indicated disappearance of the characteristic bands for the three-membered thioepoxide ring. The bands corresponding to the -CH₂-S and >CH-S fragments were slightly shifted towards the lower or higher wavenumbers, for example, to 1411 [$\delta(\text{CH}_2)$] and to 740, 671, and 610 cm⁻¹ [$\nu(\text{C}-\text{S})$], respectively. Simultaneously, the relative intensities of these bands were also changed. Moreover, the observed splitting of the band for the carbonyl group [$\nu(\text{C}=\text{O})$] into two absorption maximums corresponding to 1740 and 1705 cm⁻¹ indicated certain conformation changes due to the formation of copolymer structure. All changes mentioned above confirmed the occurrence of the copolymerization process accompanied by the ring opening, which resulted in the preparation of the copolymer, according to the following scheme:



where $x = 1-4$.

The more precise determination of the average sulfur rank x was associated with the use of ¹H-NMR spectroscopy. To this purpose, the homopolymer of ETGEAA was employed as a model substance and reference sample. The corresponding ¹H-NMR spectrum [Fig. 2(a)] indicated several groups of signals within the interval of 2.25–2.00 (CH₃-COO); 3.23–2.60 (CH-S and CH₂-S protons); and 3.95–3.75 ppm (CH₂-O). Two modes of changes were observed in the corresponding spectrum of the copolymer pre-

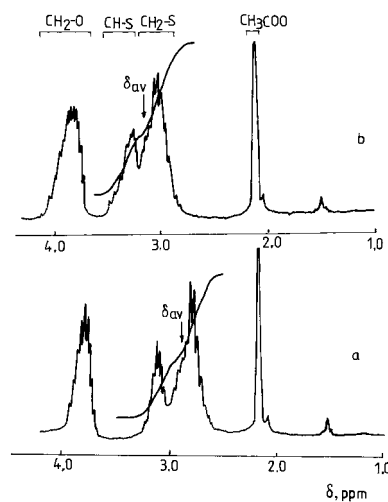


Figure 2 Figures 2 ¹H-NMR spectra of the ETGEAA homopolymer (a) and the copolymer based on ETGEAA and sulfur (b).

Table I Basic Characteristics of Epythioglycidyle Ester of Acetic Acid (ETGEAA), the Homopolymer Prepared Therefrom and Its Copolymers with Sulfur Synthesized at Various Temperatures

Characteristics	ETGEAA	ETGEAA Homopolymer	Copolymers of ETGEAA with Sulfur Synthesized at Different Temperatures (°C)		
			50	75	100
Elemental analysis:					
C, %	45.35	45.25			
H, %	6.09	6.11			
S, %	24.13	24.11	44.35	42.41	40.25
Content of —SH groups, %		1.13	1.31	1.18	1.08
Average sulfur rank:					
by elemental analysis			2.5	2.3	2.1
by ¹ H-NMR		1.0	2.4	2.2	2.0
Starting temperature of Decomposition, °C			180	185	185
Average molecular mass		3950	4230	4150	4080
Solubility:					
Methanol, %	100	0	0	0	0
1,4-Dioxane, %	100	49	38	42	45
Chloroform, %	100	98	88	91	92

pared at 50°C [Fig. 2(b)]. The first one was the widening of multiplets, which could be attributed to an increased structural heterogeneity. The second change was the shift of the signals downfield, which could be explained by the increase in the average sulfur rank. For the multiplet corresponding to the (CH—S) and (CH₂—S) protons, the parameter δ_{av} (average value of the chemical shift) was determined from the half-height of the corresponding integral curve. The value of δ_{av} changed from 2.85 for the homopolymer (monosulfide, $x = 1$) to 3.19 for the copolymer, which corresponded to the average sulfur

rank $x = 2.4$, according to the literature.¹³ For the copolymers synthesized at 75 and 100°C, values of δ_{av} amounting to 3.16 and 3.12 were found, which in turn, referred to the average sulfur rank $x = 2.2$ and $x = 2.0$, respectively.

These results were compared with the data for the average sulfur rank obtained from the elemental analysis (Table I). The latter gave somewhat higher results for all of the copolymers prepared. Therefore, the copolymer products are likely to contain unreacted sulfur, which was included mechanically in the macromolecules.

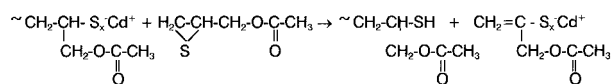
Table II Properties of the Vulcanized Basic Compositions with Various Content of Modifying Additive Based on Copolymer of ETGEAA with Sulfur

Characteristics	Basic Composition	Content of the Modifying Additive (Mass Parts per 100 Mass Parts of Elastomer)			
		3	6	9	12
Prevulcanization time, min	14.1	11.6	9.5	9.3	9.3
Optimum vulcanization time at 143°C, min	90	68	59	63	75
Tensile strength, MPa	7.78	12.13	12.61	12.68	12.70
Elongation at break, %	700	668	550	550	570
Module at 300% elongation, MPa	0.08	1.38	1.76	1.70	1.65

Table III Adhesion of the Basic Elastomer Composition and Elastomer Compositions of Various Content of the Modifying Additive Introduced

Run No.	Content of the Modifying Additive (Copolymer of ETGEAA with Sulfur), Mass Parts per 100 Mass Parts of Elastomer	Adhesion Determined by the H-Method Towards Different Materials, N	
		Polyamide Cord PA 187/1	Brass-Electroplated Steel Cord
1	0.0	110	71.2
2	2.0	130	92.3
3	4.0	140	103.5
4	6.0	150	111.2
5	8.0	145	108.3
6	10.0	140	105.1

The end-group analysis was also conducted. Weak signals in the $^1\text{H-NMR}$ spectrum were observed at 1.5 ppm for the protons of the $-\text{SH}$ groups typical for thiokols (Fig. 2). The content of the latter determined iodometrically was found to be within 1.10 to 1.35%. IR spectra indicated bands at 1636 [$\nu(\text{C}=\text{C})$] and 906 cm^{-1} [$\gamma(\text{=CH})$], which corresponded to the double bond in vinylidene groups. This could be explained by a chain transfer involving the monomer precursor in accordance with the following scheme:



The copolymerization process that took place did not result in the preparation of polymers with high average molecular mass. The value of the latter ranged between 3950 and 4230, depending on the temperature of synthesis (Table I). The products obtained had good solubility in strong polar solvents, which resulted from both the relatively low average molecular mass and presence of polar functional groups in the copolymers.

ETGEAA/Sulfur Copolymers as an Additive for Rubber Compositions

The copolymer that was synthesized at 50°C was introduced as a modifying additive into the basic rubber composition containing butadiene–styrene elastomer Bulex 1500. The changes of the vulcanization characteristics and some physicomechanical properties (Table II) as well as the adhesion (Table III) were studied for several compositions of various additive content.

The decrease of the initial vulcanization temperature (Table II) could be explained by the formation

of intermediate structures, a process that would, possibly, require small activation energy. Thus, the induction period preceding the “true” vulcanization process was reduced. The physicomechanical properties were also changed. For example, the tensile strength and the modulus of elongation increased, whereas the relative elongation was reduced, compared to the corresponding characteristics of the basic elastomer composition. The “crosslinking” effect of the additive and the formation of $(\text{C}-\text{S}_x-\text{C})$ bonds are believed to cause the improvement of the physicomechanical characteristics and the optimum content of the additive was found to be 6.0 mass parts (Table II).

Some improvement of the adhesive properties towards both the polyamide and brass-electroplated steel cords on introducing the modifying additive was also observed. The adhesion increased by ca. 80% with respect to the basic elastomer composition as the content of the polysulfide copolymer introduced as modifying additive reached 6 mass parts.

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