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SEPARATION OF THIODIGLYCOL POLYETHERS AND RELATED COMPOUNDS BY REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

Low-molecular-weight (MW < 3000) thiodiglycolpolyether polymers were separated by reversed-phase high-performance liquid chromatography into as many as twenty oligomeric species. This separation was accomplished by using gradient elution with water and methanol on a semi-microbore ODS reversed-phase column. Detection was by the use of a diode-array UV detector. The method was also used in the separation of sulfur-containing cyclic compounds, polysulfur thiodiglycol compounds and polythiodiglycol formal oligomers. The separation of these compounds provides data that indicate that the separation mechanism for the thiodiglycolpolyether polymers is a combination of precipitation dissolution and sorption mechanisms. Structural proof of the polysulfur thiodiglycol compounds was obtained by NMR.

INTRODUCTION

At Morton Thiokol research is being conducted on the synthesis of low-molecular-weight (MW < 3000) thiodiglycolpolyether polymers. The object of the present investigation was to obtain both qualitative and quantitative information about the content of the oligomeric species in the polymer. These data were used to develop material with the desired end-use properties.

In the last several years there has been considerable interest in separating synthetic organic polymers into their oligomeric species by high-performance liquid chromatography (HPLC). Chromatographic separations of this type provide better insight into the composition of a polymer than data obtained from gel permeation chromatography. Work by Barka and Hoffmann [1] showed that polyethylene glycols (PEG) could be separated into as many as 110 oligomeric species by reversed-phase HPLC. In work cited by Kuo *et al.*[2], HPLC played a key role in characterizing the oligomeric species of resins used in coatings. Munteanu[3] used reversed-phase HPLC to separate the oligomers of bisphenol A glycidyl methacrylate.

Several researchers have speculated as to the type of mechanisms that are involved in these separations. Barka and Hoffman[1] theorized that the separation mech-

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anism for PEG included both sorption effects and molecular-size effects. Jinno and Sato[4] stated that both hydrophobic interaction effects and molecular size and shape played a role in the separation of polystyrene oligomers.

Work by Armstrong and Bul[5] demonstrated that various narrow-range molecular-weight polystyrene standards could be separated by a selective precipitation dissolution mechanism. Van den Berg and Clockner[6,7] found that copolymers of styrene–acrylonitrile and styrene–methyl methacrylate were separated into their various components by the combination of precipitation dissolution and sorption mechanisms. Mourey and Smith [8] and Mourey[9] also found that polystyrene oligomers were separated by a precipitation dissolution–sorption mechanism.

The reversed-phase HPLC separation of sulfur-containing compounds has been extensively studied by Mockel[10]. This work showed that *n*-aliphatic polysulfides R_2S_n (where $n = 2$–10) could be easily separated by reversed-phase HPLC. These species were separated according to the number of sulfur atoms in the molecule and to the length of the alkyl chains. Mockel also found that for non-cyclic and cyclic sulfur compounds the number and substitution pattern of the sulfur atoms were a major factor determining the separation of these compounds.

EXPERIMENTAL

The HPLC system consisted of a Hewlett-Packard (Avondale, PA, U.S.A.) 1090A chromatograph, equipped with a ternary solvent-delivery system, temperature-controlled column compartment, autosampler, diode-array detector, and HP (Hewlett-Packard) workstation. The column used for this work measured 150 mm × 2.0 mm I.D. and was packed with Phenomenex (Rancho Palos Verdes, CA, U.S.A.) Spherex (ODS) with a mean particle size of 3 μm.

The NMR was determined with a Varian VXR 300 (Varian Instrument Group 205 W. Touhy Avenue Park Ridge, IL, U.S.A.). The ^{13}C spectrum was run at 75 MHz with complete decoupling. Deuterated dimethylsulphoxide (DMSO) was used as the solvent and tetramethylsilane (TMS) as the reference.

Methanol, dichloromethane and water were purchased from EM Science (Cherry Hill, NJ, U.S.A), Omni Solv grade. The solvents were degassed with helium. The gradient elution programs used for the various separations are listed in Table I.

Samples

The thiodiglycolpolyether polymers $H[OCH_2CH_2SCH_2CH_2]_nOH$, polysulfur thiodiglycol compounds $[HOCH_2CH_2]_2S_n$, and the polythiodiglycolformal $H[OCH_2CH_2SCH_2CH_2OCH_2]_nOCH_2CH_2SCH_2CH_2OH$ were synthesized by the Morton Thiokol Woodstock Technical Center organic synthesis group. 2-Hydroxyethyl sulfide (thiodiglycol) (>99%), 2-hydroxyethyl disulfide (dithiodiglycol) (95%), 1,4-thioxane (98%), 1,4-dithiane (97%), and 1,3-dithiane (97%) were purchased from Aldrich (Milwaukee, WI, U.S.A.).

Sample preparation

The thiodiglycolpolyether samples were dissolved in dichloromethane unless otherwise indicated. All other samples were dissolved in methanol. The concentrations used for each sample are listed in the figures. A 3-μl amount of the diluted sample was injected into the column.

TABLE I

GRADIENT ELUTION PROGRAMS

Program	*Flow-rate (μl/min)*	*Time (min)*	*Water (%)*	*Methanol (%)*	*Dichloromethane (%)*
A	300	0	100	0	0
		1	100	0	0
		30	0	100	0
		35	0	100	0
		45	0	0	100
		50	0	0	100
		60	0	100	0
		65	0	100	0
		75	100	0	0
		85	100	0	0
B	350	0	70	30	0
		10	70	30	0
C	350	0	80	20	0
		30	0	100	0
		40	0	100	0
		45	80	20	0
		5	80	20	0
D	300	0	100	0	0
		1	100	0	0
		25	0	100	0
		40	0	100	0
		50	100	0	0
		60	100	0	0
E	350	0	80	20	0
		20	0	100	0
		30	0	100	0
		35	80	20	0
		45	80	20	0

Chromatograms

All of the chromatograms shown in this work, except for the polysulfur thiodiglycol, were obtained by setting the diode-array detector to 210 nm. At this wavelength, the solvent programs used showed a considerable increase in absorption as analysis time increased. The chromatograms presented here were obtained by recording a blank solvent run and then using the HP workstation to subtract the solvent absorption from the sample run.

RESULTS AND DISCUSSION

Figs. 1 and 2 illustrate the separation of two different thiodiglycolpolyether polymers (TDPEP) by means of gradient elution program A (Table I). The chromatograms show the separation of at least twenty oligomeric species. The peak at 5 min corresponds to the retention time of thiodiglycol. The other peaks correspond to an increase in length of the polymeric chain. The relative differences in the intensity of

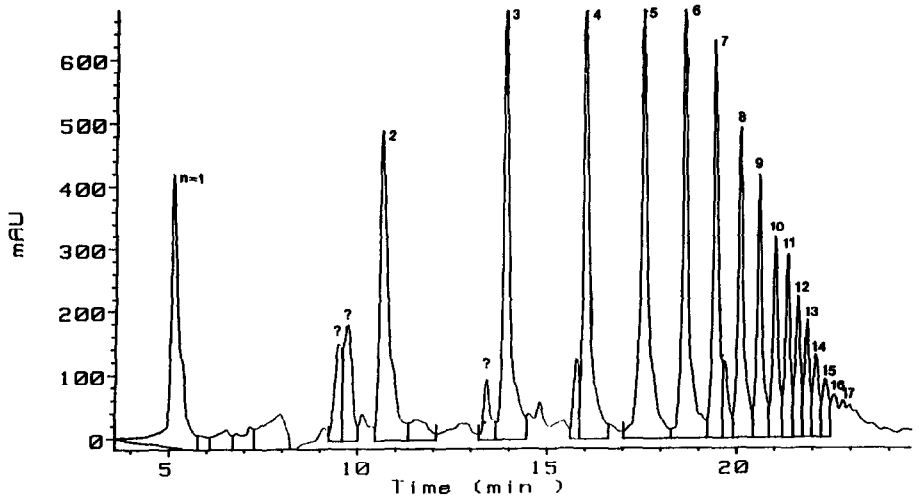

Fig. 1. Chromatogram of thiodiglycolpolyether polymer sample 1, 0.5 g in 10 ml dichloromethane. Gradient elution program A. The numbers (n) indicate the polymer chain length, $H(OCH_2CH_2SCH_2CH_2)_nOH$ for each peak.

higher-molecular-weight species peaks between these two samples are related to changes in the synthetic scheme.

Increase in system pressure are observed upon injection of these samples. Dichloromethane and long equilibration times are required to permit multiple injections without increase in back-pressure after a few injections. No further oligomeric species were eluted from the column when the eluent was at 100% dichloromethane. The

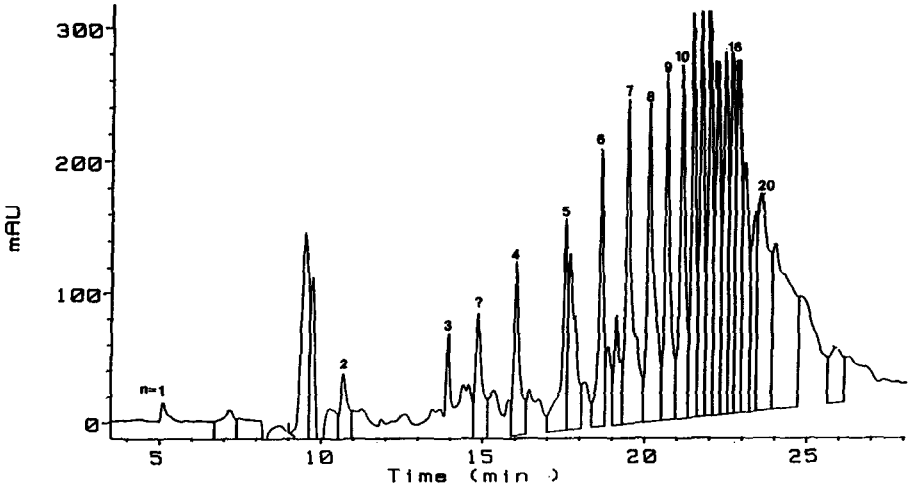

Fig. 2. Chromatogram of thiodiglycolpolyether polymer sample 2, 0.5 g in 10 ml dichloromethane. Gradient elution program A. The numbers (n) indicate the polymer chain length, $H(OCH_2CH_2SCH_2CH_2)_nOH$ for each peak.

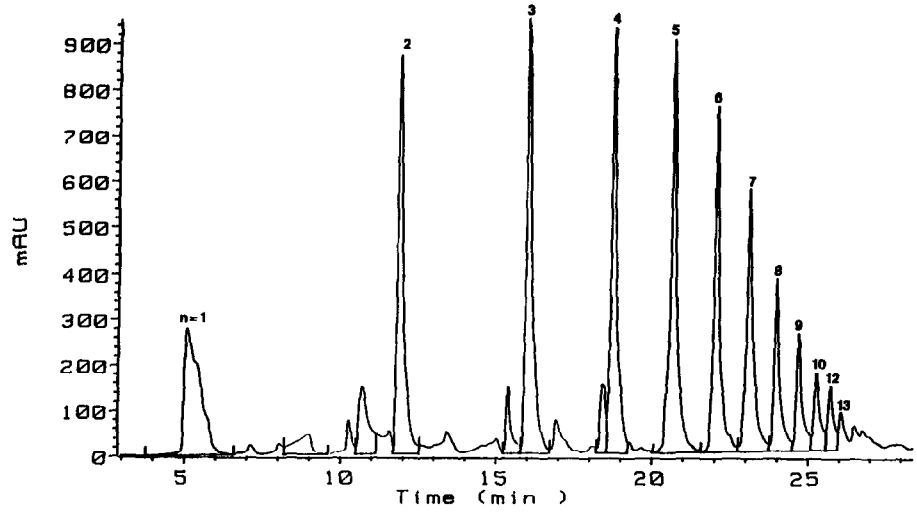

Fig. 3. Chromatogram of thiodiglycolpolyether polymer sample 1, 0.5 g in 10 ml methanol. Gradient elution program A. The numbers (n) indicate the polymer chain length, $H(OCH_2CH_2SCH_2CH_2)_nOH$ for each peak.

TDPEP samples are only partly soluble in methanol. Figs. 3 and 4 illustrate the separation observed when methanol extracts are chromatographed with gradient elution program A. The major change observed is the lower relative amount of the higher-molecular-weight species, which is due to their low solubility in methanol.

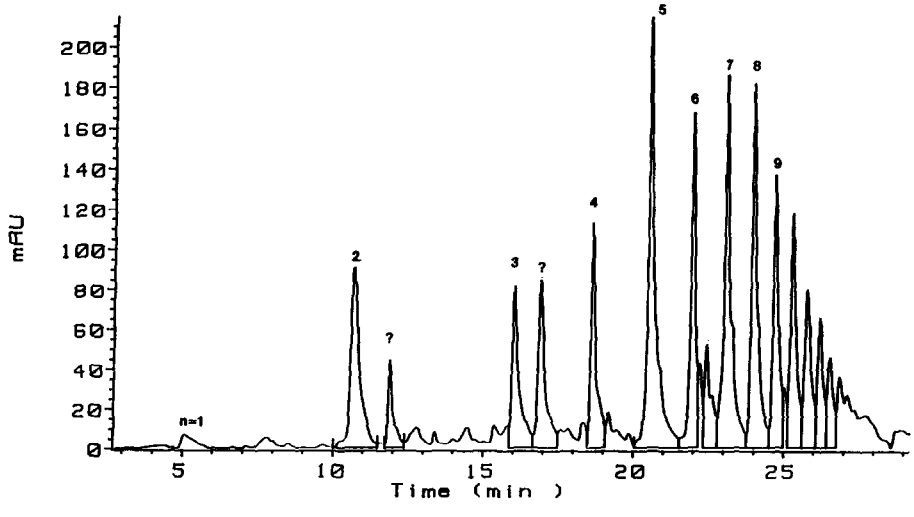

Fig. 4. Chromatogram of thiodiglycolpolyether polymer sample 2, 0.5 g in 10 ml methanol. Gradient elution program A. The numbers (n) indicate the polymer chain length, $H(OCH_2CH_2SCH_2CH_2)_nOH$ for each peak.

When samples dissolved in dichloromethane or methanol were diluted with water, precipitation occured. When samples are chromatographed with gradient elution program A, initially precipitation occured, resulting in a pressure increase. When the samples were chromatographed using 100% methanol, very little separation of the oligomers was observed. If the observed elution pattern of the oligomers is due solely to a precipitation dissolution mechanism, oligomeric species should be eluted with dichloromethane. However, all of the oligomeric species observed are eluted before the elution program reaches 100% methanol, indicating that the species are undergoing some type of hydrophobic interaction. Further evidence for this is provided by the narrow peak shape observed. This would not be expected if only precipitation dissolution occurred. Thus the data would seem to support both a precipitation dissolution mechanism and a sorption mechanism cooperating in the separation of these sulfur-containg species.

Further evidence that a sorption mechanism plays a role in separating these types of sulfur-containing compounds is the separation of a mixture of thiodiglycol (TDG), dithiodiglycol (DTDG), 1,4-thioxane, 1,3-dithiane, and 1,4-dithiane. Fig. 5 shows the separation of these compounds by means of elution program B. The separation of TDG and DTDG is consistent with the separation of polysulfides observed by Mockel[10] in that the retention time increases with the number of sulfur atoms. The separation of thioxane, 1,3-dithiane and 1,4-dithiane also agrees with the observations of Mockel[10].

Further evidence that increasing the number of sulfur atoms in these glycol compounds increases, the retention time is found in Fig. 6. Using elution program C, polysulfur thiodiglycol was resolved into nine species with 2–10 sulfur atoms. This chromatogram also shows that the retention time increases with the number of sulfur atoms. It is interesting that sulfur (S_8) was eluted after the other sulfur-containing species. This probably occured because sulfur is insoluble in water and precipitated

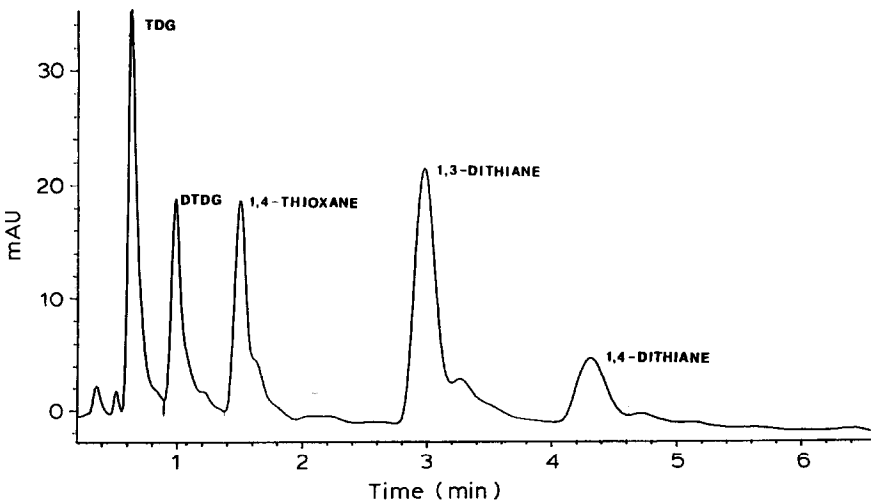

Fig. 5. Chromatogram of TDG, DTDG, 1,4-thioxane, 1,3-dithiane and 1,4-dithiane samples, *ca.* 400 ppm each in methanol. Gradient elution program B.

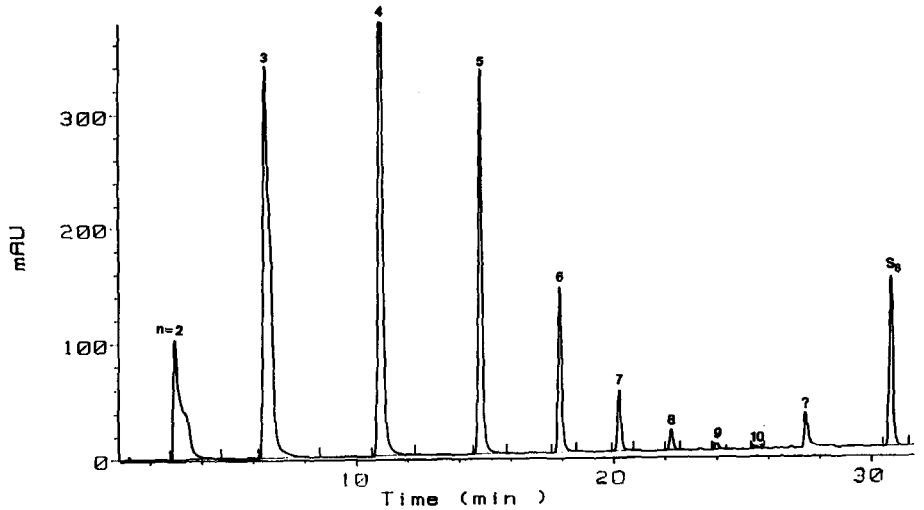

Fig. 6. Chromatogram of polysulfur thiodiglycol sample, 0.5 g in 10 ml methanol. Gradient elution program C. The numbers (n) indicate the sulfur chain length, $(HOCH_2CH_2)_2S_n$ for each peak.

initially on the column and then underwent a separation by a mechanism similar to that for TDPEP.

Supporting evidence for polysulfur species in the sample of polysulfur thiodiglycol was obtained by NMR. Fig. 7 shows the ^{13}C NMR spectrum of DTDG. It contains two peaks: the methylenes attached to sulfur atoms at 41.3 ppm and the hydroxyl-terminated methylenes at 59.6 ppm. Fig. 8 shows the ^{13}C NMR spectrum of the polysulfur thiodiglycol. It contains five peaks in the region of 41.1–42.1 ppm, instead of the single peak at 41.3. The extra peaks correspond to the higher rankings of sulfur linkages (S_3, S_4, S_5, etc.). Based on the relative intensities of the HPLC peaks and the NMR signals the following assignments have been made:

$-CH_2S_2$ 41.3 ppm
$-CH_2S_3$ 41.1 ppm
$-CH_2S_4$ 41.8 ppm
$-CH_2S_5$ 42.1 ppm
$-CH_2S_6$ 42.0 ppm

A four-peak separation was also visible for the hydroxyl-terminated methylenes in the 59.4–59.6 ppm region. A peak corresponding to sulfur S_6 species was not observed, possibly due to the number of bonds separating the methylenes in the 59.4–59.6 ppm region which cause overlap with the other peaks.

An interesting phenomenon was observed in the ^{13}C NMR spectrum of the polysulfur thiodiglycol sample (Fig. 8). The S_2 methylene was seen at 41.3 ppm and the S_3 methylene at 41.1 ppm, while the S_4 and S_5 methylenes were at 41.8 and 42.1 ppm, respectively. Some type of sulfur shielding effect may be producing the upfield

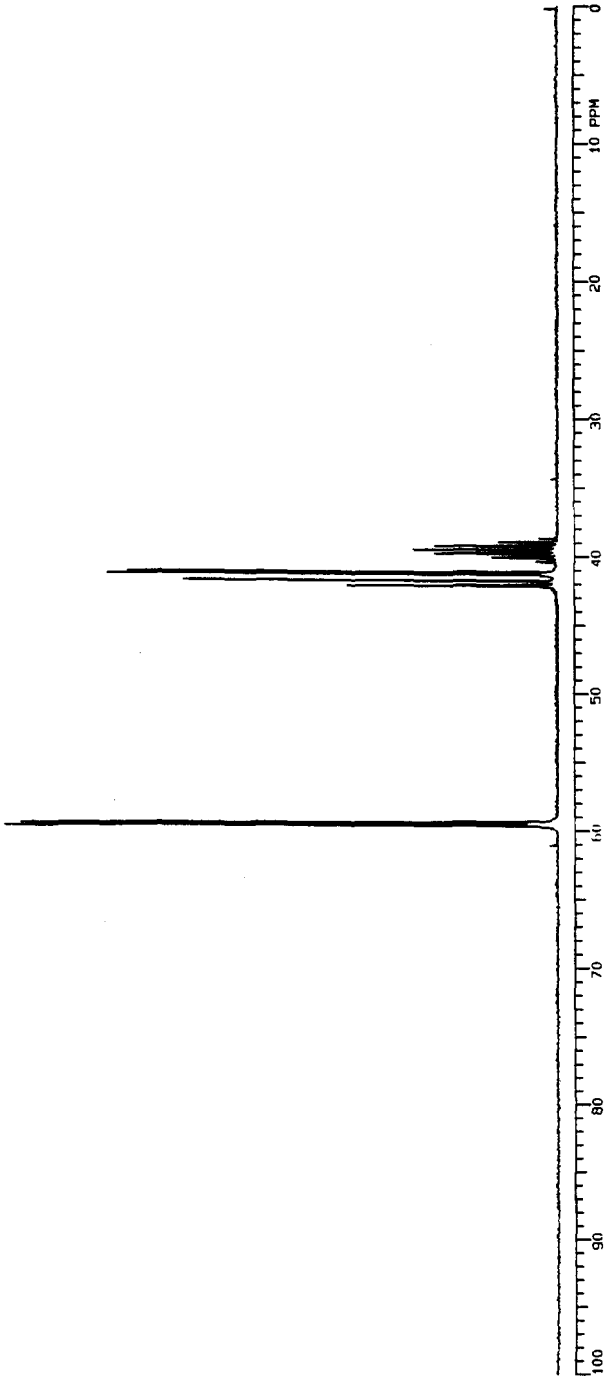

Fig. 7. ^{13}C NMR Spectrum of dithiodiglycol, $(HOCH_2CH_2)_2S_2$.

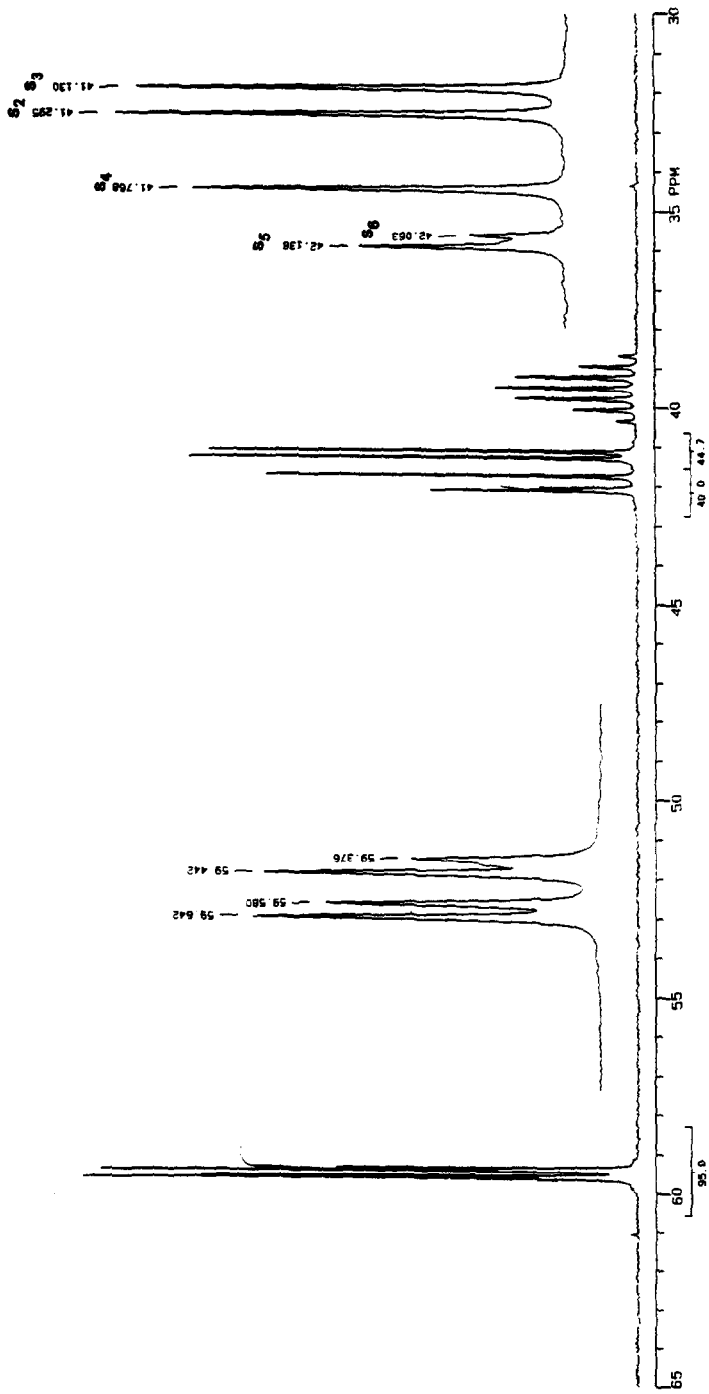

Fig. 8. ^{13}C NMR spectrum of polysulfur thiodiglycol ($HOCH_2CH_2)_2S_n$.

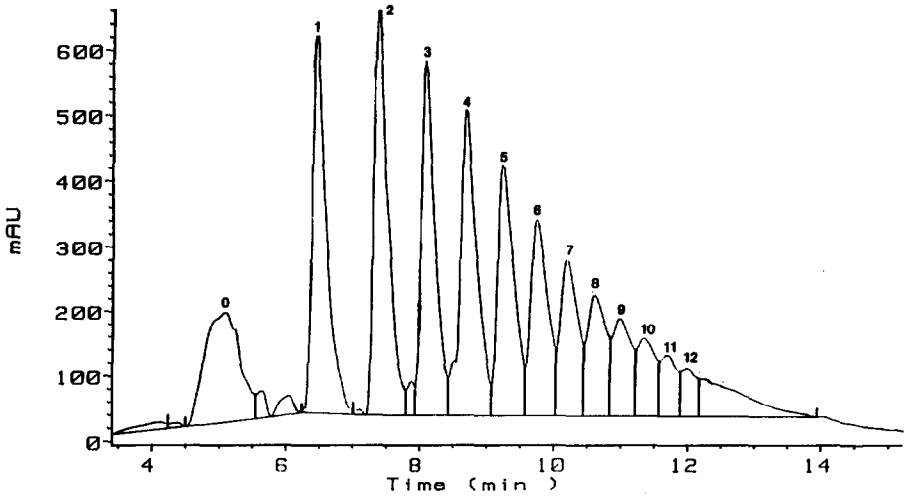

Fig. 9. Chromatogram of oxidized thiodiglycolpolyether polymer sample, 0.5 g in 10 ml methanol. Gradient elution program D. The numbers (n) indicate the polymer chain length, $H(OCH_2CH_2SOCH_2CH_2)_n$-OH for each peak.

shift of the $-CH_2S_3-$ while the higher rankings of sulfur (S_4, S_5, etc.) were shifted downfield, as expected.

A sample of polythiodiglycol polyethers was oxidized to the structure represented by $H(OCH_2CH_2SOCH_2CH_2)OH$. Fig. 9 shows the separation of this material by means of elution program D. The corresponding oxidized *vs.* unoxidized TDPEP

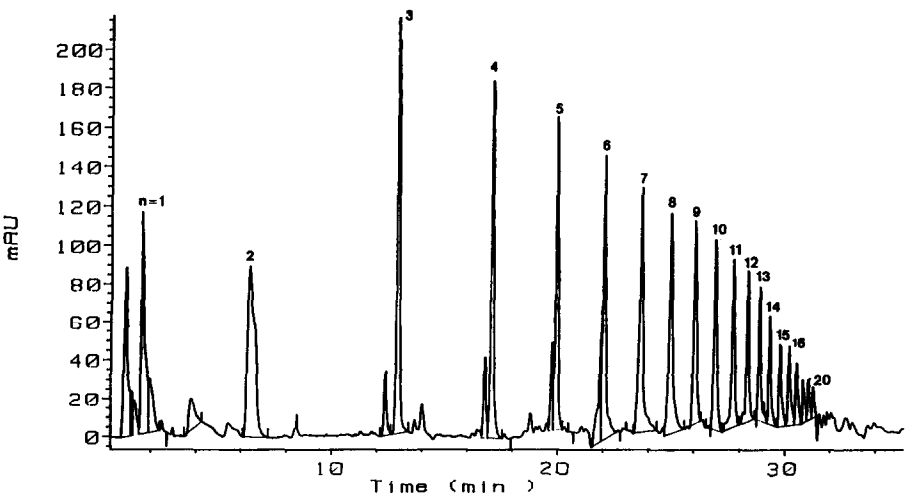

Fig. 10. Chromatogram of polythiodiglycol formal polymer sample, 0.5 g in 10 ml methanol. Gradient elution program E. The numbers (n) indicate the polymer chain length, $H(OCH_2CH_2SCH_2CH_2)_n$-$OCH_2CH_2SCH_2CH_2OH$ for each peak.

oligomeric species decrease in retention time dramatically. Since this material is soluble in water and methanol in all proportions, it does not precipitate on the column under these conditions. Thus, these oligomeric species were separated exclusively by a sorption mechanism. The large decrease in retention time may also be partly a result of the increase in oxygen content. This may be similar to the decrease in retention time observed by Mockel[10] when comparing alkyl ethers to the corresponding alkylthio ethers. Mockel speculated that this effect was due to the increase in hydrogen bonding with the eluent, due to the increase oxygen content.

Fig. 10 illustrates the separation of at least twenty polythiodiglycol formal oligomeric species by means of elution program E. A pressure increase was observed when this sample was injected. This was due to the material being only partly soluble in water and totally soluble in methanol, which resulted in precipitation on the column. If the resulting resolution of this material was due only to a sorption mechanism, the increase in oxygen content in these species should have decreased the retention time relative to corresponding TDPEP species. But the gradient program for this separation had to reach 100% methanol 10 min sooner than the solvent program for the corresponding TDPEP to obtain similar retention times. Thus, the corresponding formal oligomers were retained on the column more strongly than the TDPEP species. It can be argued that the increase in retention time could be a result of the increase in the alkyl chain length. Mockel[10] observed that the retention time of polysulfides increased as the alkyl chain length increased. Most likely, these compounds were separated by a combination of all of these mechanisms.

CONCLUSIONS

Semi-micro-bore reversed-phase HPLC has been shown to resolve effectively thiodiglycolpolyether polymers into at least twenty oligomeric species. It is apparent that these oligomeric species are separated by a sorption mechanism as well as a precipitation dissolution mechanism. Our separation scheme was applied to other compounds with similar structures.

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REFERENCES

1 G. Barka and P. Hoffmann, *J. Chromatogr.*, 389 (1987) 273.
2 C. Kuo, T. Provder and A. F. Kah, *Paint & Resin*, March/April (1983) 26.
3 D. Munteanu, A. Isfan and D. Bratu, *Crhomatographia*, 23 (1987) 412.
4 K. Jinno and T. Sato, *J. Liq. Chromatogr.*, 6 (1983) 1631.
5 D. W. Armstrong and K. H. Bul, *Anal. Chem.*, 54 (1982) 706.
6 G. Glockner, J. H. M. van den Berg, N. L. J. Meijerink, T. G. Scholte and R. Koningsveld, *Macromolecules*, 17 (1984) 962.
7 G. Glöckner and J. H. M. van den Berg, *J. Chromatogr.*, 352 (1986) 511.
8 T. H. Mourey and G. A. Smith, *Anal. Chem.*, 56 (1984) 1773.
9 T. H. Mourey, *Anal. Chem.*, 56 (1984) 1777.
10 H. J. Möckel, *J. Chromatogr.*, 317 (1984) 589.