Polymer Bulletin 41, 1–5 (1998)

Polymer Bulletin

Synthesis and characterization of poly(2-furyl)methylene sulfide

R. Lago[1], P. Ortiz[1], J. Rieumont[2,*], R. Sanchez[2]

[1] Faculty of Chemistry, University of Havana, Havana 10400, Cuba
[2] State University of the North Fluminense, Center of Science and Technology,
Ave. Alberto Lamego 2000, Campos dos Goytacazes, RJ, Brazil, CEP 28015-620

Received: 7 December 1997/Revised version: 13 May 1998/Accepted: 14 May 1998

Summary

Linear, low molecular weight poly(2-furyl)methylene sulfide was obtained bubbling hydrogen sulfide by through aqueous furfuraldehyde solutions. The product was soluble in chloroform and acetone. Characterization was carried out by elemental analysis, IR, NMR ^{1}H and ^{13}C (DEPT) techniques. Evidence for the presence of OH and SH terminal groups was found. This fact points to a plausible mechanism through the initial formation of unstable α-hydroxythiols. A scheme for the polymerization mechanism is offered.

Introduction

Polymers containing sulphur in the backbone have interesting properties and uses. Polyalkylenesulfides or Thiokol exhibit very low swelling in organic solvents. These materials have been used as sealants in the aircraft industry for fuel tanks and in the rubber industry in rings and hoses to improve the solvent resistance of butadiene-styrene rubbers (1,2). Polyphenylenesulfide (3) is another commercial polymer that has received special attention as flame retarder due to its degradation resistance.

Thioaldehydes or trials are very unstable and do not usually exist in monomeric form due to their great ability to polymerize yielding both linear polymer and cyclic trimers (2).

The reaction of 2-furfuraldehyde with hydrogen sulfide produces a thioaldehyde, the thiofurfural, which may exists as a mixture of the α and ß forms of a cyclic trimer or as a linear polymer depending on the conditions of the reaction (4,5,6).

In our view the structure and properties of poly(2-furyl)methylene sulfide have received little attention and hence its structure has not been determined in detail. Furthermore the possibility of its functionalization encouraged us to explore this material.

The aim of the present paper is to carry out a full characterization of this material in order to improve their properties and uses.

Experimental

Materials

Furfuraldehyde (from Merck) was purified by distillation under pressure (10^{-1} mm Hg). Hydrogen sulfide was generated from reaction between concentrated hydrochloric acid (BDH) and ferrous sulfide (BDH).

---

* Corresponding author

Procedures

An aqueous solution of furfuraldehyde (3%) was saturated by bubbling hydrogen sulfide through a porous glass frit during 6 hours at room temperature. A milky suspension was obtained and then coagulated at pH = 4, under stirring, by adding a dropwise fashion hydrochloric acid. The reaction product was thoroughly washed to neutral and dried at 40°C under vacuum.

NMR spectra were recorded by a Bruker AC-250P NMR spectrometer at 250 MHz (^{1}H) and 62.9 MHz (^{13}C). Samples were dissolved in deuterated chloroform. ^{13}C spectra were recorded using a distortion enhancement by polarization transfer (DEPT) pulse sequence technique.

Number-average molecular weights were determined by vapour-pressure osmometry with Knauer instrument using chloroform as solvent.

Elemental analysis was performed using a Carlo Erba Analyzer.

Infrared spectra (IR) were recorded in potassium bromide using an UNICAM SP-200 spectrometer.

Results and discussion

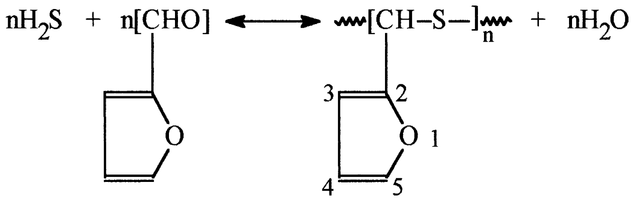
Poly(2-furyl) methylene sulfide was obtained as a white powder with a rather unpleasant odor in spite of thoroughly washing (yield < 45%). The product was soluble in acetone and chloroform and its molecular weight (Mn) was 2560, indicating a degree of polymerization of 22, assuming linear chains. The elemental analysis (Table 1) confirmed this assertion:

TABLE 1. Elemental Analysis of Poly(2-furyl) methylene sulfide.

	C	H	S
Theoretical	53,57	3,57	28,56
Experimental	53,06	3,32	29,72

For polymer bearing a furan side group $[-CH(C_4 H_3 O)-S-]$ the sulphur content was a little above theorical, indicating that at least one thiol end group is present.

Thus the material obtained under our experimental conditions was not a cyclic trimer as it has been reported (4) when the reaction is conducted in ethanol. The resulting low molecular weight and yield indicated that an equilibrium stopped the linear chain growing probably due to the fact that water remained in the reaction medium:



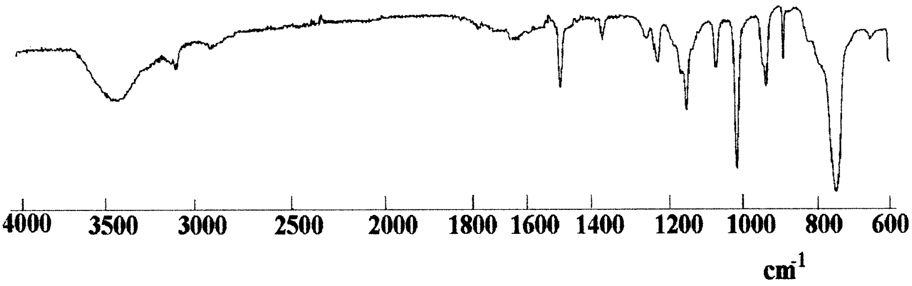


Figure 1. Infrared spectrum of poly(2-furyl)methylene sulfide in BrK.

The furan moiety was characterized by IR spectroscopy as a monosubstituted ring (7, 8) (Figure 1): 3110; 1500; 1010; 1150; 930; 740, all signals in cm^{-1}. However, this technique did not succed in identifying the thiol end group ν(S-H) around 2550-2600 cm^{-1} possibly due to its small quantity, nor the weak ν(C-S) signal at 670-705 cm^{-1} for similar compounds (1, 9).

The NMR ^{1}H spectrum is shown in Figure 2. Furan ring protons are observed at 7.25 ppm (H-5) and 6.14 ppm (H-4/(H-3) and for the methynic (C-H) at 5.00 ppm according to the integration values. Two weak signals appear at 2.65 ppm and 1.75 ppm. These signals disappeared by adding deuterated water (Figure 3) hence they were assigned to the protons on the end groups OH and SH respectively. In order to confirm this assignment the NMR ^{1}H spectrum signals were used for the furfuryl mercaptan at 1.9 ppm (8), liquid thiokol (1) and furfuryl alcohol at 3.2 ppm (10). The integration for these signals in comparison with the four protons of the 22 monomeric units of the polymer gave a ratio of 1:88 indicating that each chain has an OH and SH groups at each end.

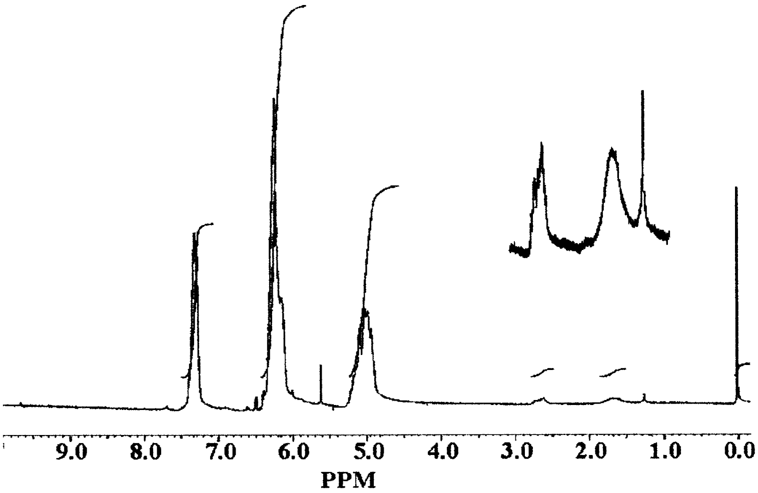


Figure 2. NMR ^{1}H spectrum of poly(2-furyl)methylene sulfide in deuterated chloroform.

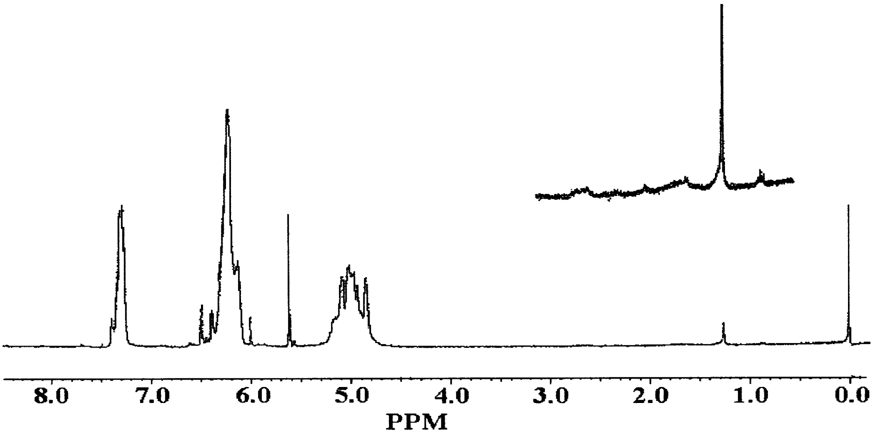


Figure 3. NMR ^{1}H spectrum of poly(2-furyl)methylene sulfide in deuterated chloroform adding deuterated water.

The presence of the SH group was confirmed by using the well known reaction for thiol end groups of liquid thiokol with lead dioxide giving higher molecular weights. The polymer was dissolved in a small volume of butyl phthalate, and under the action of lead dioxide at room temperature became a hard material (11).

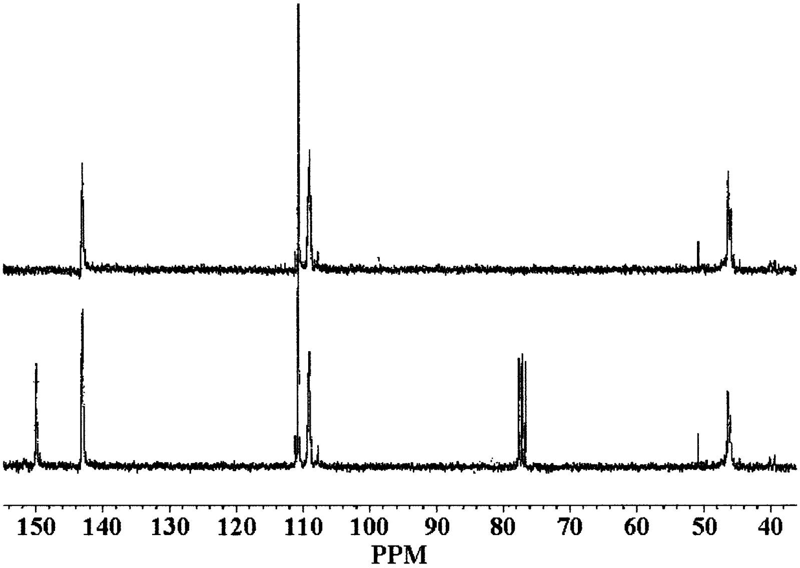
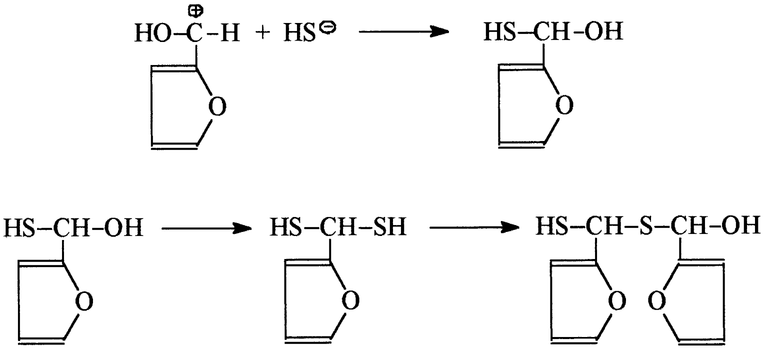


Figure 4. NMR 13C spectra of poly(2-furyl)methylene sulfide in deuterated chloroform (bottom) and using DEPT-90 (top).

^{13}C spectra recorded with the DEPT technique (12) helped in assigning the chemical shifts: 149.79 ppm. (C-2); 142.84 ppm (C-5); 110.54 ppm (C4); 109.02 ppm (C-3) and 46.25 ppm (CH). Signals missing (Figure 4) from the sub-spectrum are those of the C-2 quaternary carbon nuclei.

The terminal groups detected suggest that the mechanism could occur through initiation by addition of HS$^-$ species to protonated furfuraldehyde giving unstable α-hydroxythiols (13), followed by the formation of gem-dithiols and finally hemimercaptals:



This forms the end groups of the polymer.

References

1. Ennis BC, Hanhela PJ, Huang RHE, Long GJ, Paul DB (1990) J. Appl. Polym. Sc. 41: 2837.
2. Gaylord NG (1962) High polymers Vol. XIII Part.III - Polyalkylene Sulfides: 28. Interscience Publish, U.S.A.
3. Cowie JMG (1991) Polymers: Chemistry and Physics of Modern Materials. 2nd Ed. Blackie & Sons, London.
4. Meints RE, Wilkinson JA (1929) J.Am.Chem.Soc. 51:803.
5. Dunlop AP, Peters FN (1953) The Furans. Reinhold Publish.Corp., New York.
6. Bruins DF (1929) J.Am.Chem.Soc. 51: 1270.
7. Fetizon M (1958) J. Guy. Compt. Rend. France. 247: 1182.
8. Choura M, Belgacen NM, Gandini A (1996) Macromolecules 29: 3839.
9. Silverstein RM, Bassler GC, Morrill TC (1994) Spectroscopic Identification of Organic Compounds. Ed. Guanabara Koogan, Rio de Janeiro.
10. Simons WW, Zanger M (1973) NMR Spectra of Polymers. Sadtler Research Lab., Philadelphia.
11. Kennedy JP, Tomqvist EGM (1969) Polymer Chemistry of Synthetic Elastomers. Vol.XXIII, Part II, Ch. 8. High Polymers. Ed. H. Mark, Interscience Publish, New York.
12. Friebolin H (1993) Basic One and Two-dimensional Nuclear Magnetic Resonance Spectroscopy. 2nd Ed. VCH Publish, New York.
13. March J (1992) Advanced Organic Chemistry. 4th Ed. Ch. 16. John Wiley. New York.