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# TACTICITY MEASUREMENTS ON POLYPROPYLENE SULPHIDE BY $^{13}$C-NMR SPECTROSCOPY

P. GUERIN, S. BOILEAU, F. SUBIRA and P. SIGWALT
Laboratoire de Chimie Macromoléculaire, associé au C.N.R.S., Université de Paris VI, Tour 44,
4, Place Jussieu, 75230 Paris Cédex 05, France

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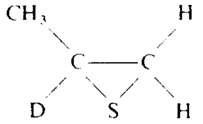
**Abstract**—Determination of tacticity of polypropylene sulphide is studied by NMR. The measurements made by $^{13}$C-NMR are compared with those obtained by $^1$H 100 MHz NMR on corresponding selectively deuterated polymers. The good correlation between the two sets of results shows that stereoregularity of polypropylene sulphide can be easily found with 5 per cent precision.

## INTRODUCTION

Initiation of propylene sulphide polymerization by soluble cadmium thiolates can give crystalline polymers [1]. We have shown that these systems are of the "living polymer" type and we have examined the conditions leading to crystalline products [2, 3]. In order to study the effects of various factors on the stereoselection process, it was necessary to measure the polymer stereoregularity. This has already been done by $^1$H-NMR at 100 MHz on polymers obtained from selectively deuterated monomer [4–6]. Configuration of crystalline and amorphous samples of polypropylene sulphide has recently been studied by $^{13}$C-NMR [7–10]. The spectra are very simple and monomer deuteration is thereby avoided. In the present paper, we make a comparison of the $^{13}$C and $^1$H spectra of undeuterated and deuterated polypropylene sulphides prepared in the same way and we discuss the precision of measurements of polymer stereoregularity.

## EXPERIMENTAL

All the experiments were made in glass apparatus sealed under high vacuum as usual. Catalysts were obtained by reaction of several thiols with cadmium acetate in stoichiometric proportions, in refluxing methanol. For each polymerization, "seeds" ($\overline{DP}n \sim 150$) were prepared in solution, at room temperature, in order to initiate the polymerization with soluble species. Selectively deuterated propylene sulphide:



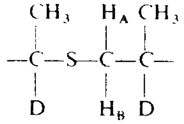
was synthesized as previously described [4].

$^1$H spectra were obtained at 60°, with Varian HA 100 and Jeol PFT 100 spectrometers, on solutions of polymers in carbon tetrachloride with TMS as internal standard. $^{13}$C spectra were taken at 160° on a Jeol PFT 100 and on a Varian XL 100 15 Fourier transform spectrometer operating at 25 MHz, with solutions of about 250–300 mg of polymer in 4 ml of $CCl_4$–$C_6D_6$ (90:10). The computer was working on 8 K data points in every case.

## RESULTS AND DISCUSSION

Preliminary studies have shown the influence of factors such as temperature, solvent, monomer and catalyst concentrations on polymer stereoregularity. According to the experimental conditions, polymers were opaque and hard, or tacky and transparent. The former show a melting point around 52° by differential thermal analysis. However, it is impossible to compare the crystallinity of different samples in this way because the method is only qualitative. Furthermore, "crystallinity" is dependent not only on the degree of stereoregularity of the polymer.

The $^1$H 100 MHz spectrum of polypropylene sulphide is rather complex since it is an ABC $X_3$ system. Use of monomer deuterated at the tertiary position affords some simplification. One of the two methylene protons is found to have a chemical shift which is sensitive to diad structure.



$$—\overset{CH_3}{\underset{D}{C}}—S—\overset{H_A}{\underset{H_B}{C}}—\overset{CH_3}{\underset{D}{C}}—$$

The spectra consist of at least two overlapping AB quartets giving rise to two lines in the upfield and four lines in the down field part of the spectrum (Fig. 1). In the downfield part, two lines were assigned to "meso" diads and the two others to "racemic" diads. The relative peak heights or areas vary with the conditions of polymer preparation as shown on Fig. 1. Thus the $\sigma$ ratio of meso diads over the total diads can be evaluated by measuring peak heights or areas.

Samples of different stereoregularity were prepared using deuterated monomer and $\sigma$ was found to vary between 0·5 and 1·0. The results are collected in Table 1.

We have recently shown that the chemical shift of the tertiary carbon in the $^{13}$C spectrum of polypropylene sulphide is also sensitive to diad structure [7–10]. Such spectra are quite simple and eliminate the need for deuteration of the monomer. The methine peak is split into two (41·3 and 41·1 × $10^{-6}$), the relative peak heights varying with the conditions of polymer preparation (Fig. 2). Use of several models of diads and examination of their $^{13}$C spectra allowed us to assign the 41·3 peak to rr + mr triads and the 41·1 peak to mm +

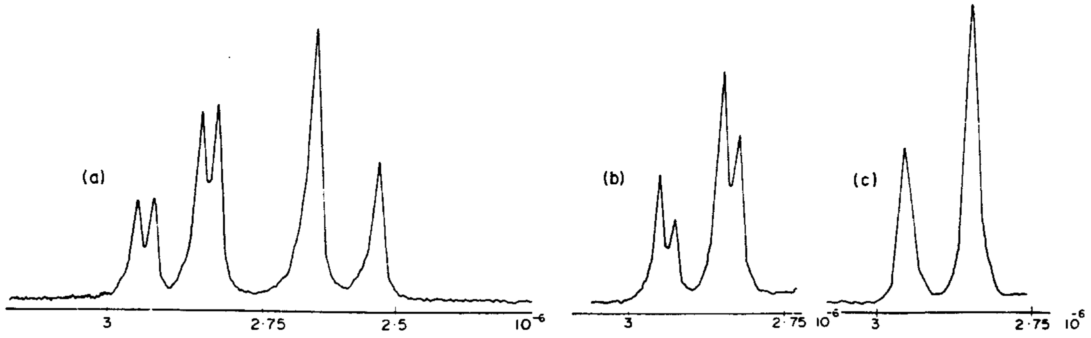


Fig. 1. NMR spectra (100 MHz) of deuterated polypropylene sulphide. (a) Polymer prepared at room temperature in toluene solution with $(Bu—S—CH_2—CH_2—S)_2Cd$: experiment VII. (b) Polymer prepared at 0° in toluene solution with $(Bu—S—CH_2—CH_2—S)_2Cd$: experiment V. (c) Polymer prepared at −20° from pure monomer with $(CH_2{=}CH—CH_2—S)_2Cd$: experiment I.

Table 1. Tacticity measurements on polypropylene sulphide by $^1$H- and $^{13}$C-NMR*

| Exp. | Catalyst | [C] × $10^3$ (mole/l) | [M] (mole/l) | Polymerization temperature | $^1$H NMR $\sigma_h$† | $^1$H NMR $\sigma_a$‡ | $^{13}$C NMR $\sigma_h$ |
|---|---|---|---|---|---|---|---|
| I | $Cd(S—CH_2—CH{=}CH_2)_2$ | 13·0 | 12·8 | −20 | >0·8 | >0·8 | 1·00 |
| II | $Cd(S—CH_2—CH{=}CH_2)_2$ | 3·4 | 3·0 | 0 | 0·72 | 0·80–0·64 | $\mathrm{II_A}$ 0·75§<br>$\mathrm{II_B}$ 0·76$_5$ |
| III | $Cd(S—CH_2—CH_2—S—Bu)_2$ | 2·5 | 5·5 | 0 | 0·73$_5$–0·66 | 0·72–0·80 | $\mathrm{III_A}$ 0·70–0·74§<br>$\mathrm{III_B}$ 0·70 |
| IV | $Cd(S—CH_2—CH_2—S—Bu)_2$ | 3·0 | 4·0 | 0 | 0·67 | 0·77 | 0·67$_5$ |
| V | $Cd(S—CH_2—CH_2—S—Bu)_2$ | 2·0 | 2·7 | 0 | 0·56–0·61 | 0·62 | 0·61 |
| VI | $Zn(S—CH_2—CH{=}CH_2)_2$ | 3·2 | 4·5 | 0 | 0·55 | — | 0·55$_5$ |
| VII | $Cd(S—CH_2—CH_2—S—Bu)_2$ | 2·4 | 2·5 | 20 | 0·50 | 0·58–0·63 | 0·47$_5$–0·50 |

* Polymers prepared in toluene solution except for I prepared without solvent.

† $\sigma_h$ Determined by measuring peak heights.

‡ $\sigma_a$ Determined by measuring peak areas.

§ Two distinct polymerizations were made for the same conditions.

rm triads [10]. Thus measurements of peak heights give $\sigma = (h_{41\cdot1})/(h_{41\cdot1} + h_{41\cdot3})$.

There is a good correlation between the two sets of results, viz. those obtained by $^{13}$C-NMR and those determined by measuring the relative peak heights on $^1$H-NMR spectra. It is thus possible to study polypropylene sulphide stereoregularity without using deuteration of the monomer. Another advantage of this method is that values of $\sigma$ included between 0·8 and 1·0 can be easily determined in this way, whereas this is rather difficult with $^1$H spectra.

We tried to see if the measurement of areas would be more accurate than the peak heights measurement. Assuming that the peak shape corresponds to a Lorentz curve, areas were measured by deconvolution. However, the results are not convincing. For example,

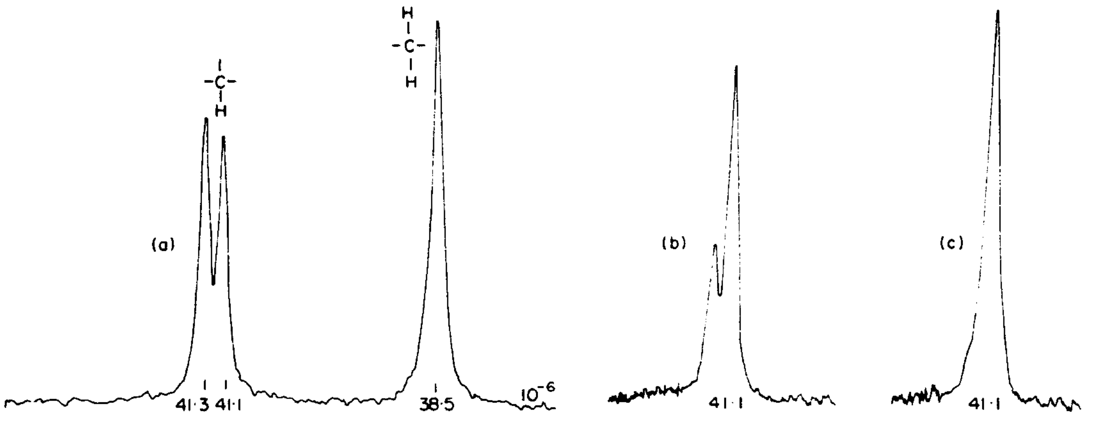


Fig. 2. $^{13}$C NMR spectra (25 MHz) of polypropylene sulphide. (a) Polymer prepared at room temperature in toluene solution with $(Bu—S—CH_2—CH_2—S)_2Cd$: experiment VII. (b) Polymer prepared in toluene solution with $(Bu—S—CH_2—CH_2—S)_2Cd$ at 0°: experiment IV. (c) Polymer prepared from pure monomer at −20° with $(CH_2{=}CH—CH_2—S)_2Cd$: experiment I.

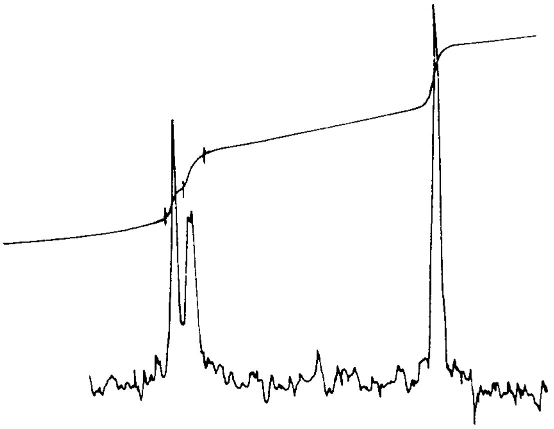


Fig. 3. High resolution 25 MHz NMR spectra of amorphous polypropylene sulphide: experiment VII.

repeated determinations give $\sigma_u$ values between 0·80 and 0·64 for experiment II. In the same way, $\sigma_u$ values are scattered between 0·80 and 0·72 for experiment III. In the case of a polymerization at 20 in toluene solution (VII), peak heights are exactly the same, though $\sigma_u = 0{\cdot}58$–$0{\cdot}63$ by measuring the areas. Even taking as reference a curve the equation of which is a combination of Gauss and Lorentz curves [11], this does not afford any improvement.

The amorphous polymer sample has been studied by $^{13}C$-NMR with a high resolution spectrometer (Fig. 3). The peak at $41{\cdot}1 \times 10^{-6}$ is slightly split and thus larger than the 41·3 one. The integration shows that relative areas are equal. Conformational analysis of polypropylene sulphide is being studied with a 68 MHz $^{13}C$-NMR spectrometer; results will be published elsewhere.

In order to determine the reproducibility of the measurements, spectra were taken starting with several solutions of a given polymer. $\sigma_H$ determined on $^1H$ spectra varies from $0{\cdot}73_5$ to 0·66 while $\sigma_c$ varies between 0·74 and 0·70 (Exp. III, Table 1). For this last sample, two spectra were made at different times on the same solution and the values of $\sigma_c$ were 0·71 and $0{\cdot}73_5$. All these results show good reproducibility.

On the other hand, some experiments were repeated in exactly the same conditions. That is the case for $II_A$, $II_B$ and $III_A$, $III_B$ and the agreement between the two sets of results is satisfactory.

In conclusion, we have shown that stereoregularity of polypropylene sulphide can be measured by $^{13}C$ NMR with 5 per cent precision. The results are in good agreement with those obtained from $^1H$ NMR spectra on corresponding deuterated polymers. This analytical method avoids the need for selective deuteration of the monomer and allows examination of the influence of various factors on stereoselection processes during the homogeneous polymerization of propylene sulphide. The results of this study will be published elsewhere [12].

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