INTRODUCTION

Helical polymers have a current interest due to application in diverse fields as molecular recognition, controlled drug delivery systems, chiral separation mediums or nonlinear optical materials [1].

Cholesteric liquid crystals polymers present a special mesophase with nanometric planes stacked in a helical superstructure with a prevalent screw direction [2]. The structure chemical of cholesteric polymers is usually formed by a main unit composed by aromatic rings called mesogen, a flexible hydrocarbonated chain and side chain linking the other parts, as Fig. 1 shows.

Liquid crystal polymer PTOBME [3,4,13,16,18] poly[4-terphenyl-3,5-di-oxybenzoyl-3-[4-(4-oxybenzoyl)] chloride and BS-1,2-2,2-bis-norincenyl] both mesogenic materials [3]. The polymer is obtained in two fractions, with different kinetic rates. It presents optical activity even in the second portion. The material is easily derivatized with different functionalities. The two mesogens present an extended helical structure which is close and incomplete. The differences and similarity of 1H NMR of PTSME with different screw sense; c) Bis (S) MPA of (R) MPA of (R) and (S) MPA can be observed in the special distribution of the substituent groups, as Fig. 3 c, d). The orientation of phenyl groups are different with respect to the protons H1, H2, H3, and H2. The two diastereomers produce different shielding and unshielding effects and the chemical shift of the proton changes one respect to other (9).

In the case of PTOBME, its helical nature that it was determined by conformational analysis and molecular modeling based on XRD, Raman and thermal analysis (TGA), can be the cause of the presence of the double of expected signals. The combination of the different cross-seconds (M and F) due to the helical and the configuration of R or S of the asymmetric carbon attached to Hc generates four diastereomers, or two enantiomers, as Fig. 3 a, b).

The mesogen unit can produce different shielding and unshielding effect in the two parts of enantiomers and it would make the presence of the double of signals in the 1H-NMR spectra. The conformational analysis in Fig. 4 performed with [7] according to experimental results of vicinal coupling constant J between Hc and Hb and Hc and Hg, indicates us that in the (nat) system, which it has at experimental JHc-Hb=3.9 Hz and JHc-Hg=6.3 Hz, the principal conformer is c). The analysis of (1) system is more complex due to the overlapping of Hb, but the experimental JHc-Hb is very low (2 Hz) and it would correspond with conformer b).

The comparison with the dials derivatized with MPA permits us to identify the protons Hc at HgRk and Hb at HgSs. They present the same conformer (g) and the same differences of chemical shift. In the case of Hb and Hc, they do not present the same principal conformer but the structure of the signals of the spectrum as vicinal coupling at chemical shift are similar and it is very reasonable that they are also HgRk and HgSs respectively.

RESULTS AND DISCUSSION

In the 1H-NMR spectra, in Fig. 2 the double of signal expected for the structure are obtained a) PTOBME, b) STOBDME and PTOBME of 6 hours of reaction, and therefore the obtained PTOBME is the same polymer and the signal observed of 6 hours of reaction, with different relative integration. The signals are divided in two independent systems how it is showed in the TOCSY 2D experiment in Fig. 5. The two independent structures are designated by NMR although only one was expected.

In order to understand better the cases of these phenomena, it has been studied in the bibliography an easier system as the one used by Figures a) and b) for the determination of the absolute stereochemistry of (S) propionic acid derivatized with the (S) enantiomer of a-methoxyphenylacetic acid (MPA) in Fig. 6. They show an exact agreement with our experimental data.

CONCLUSIONS

The conformational analysis of PTOBME presents the double of expected signals.

The pattern is very similar to the dials derivatized by Bis (R) and S MPA of PTOBME. The combination of helical structure and asymmetric carbon in the polymer can generate a similar espacial distribution to the presented in the diastereomers formed by dials derivatized by Bis (R) and S MPA of PTOBME.

By comparison with the dials we can indicate that Hc is HgRk and Hb is HgSs.

REFERENCES:

Bibliography