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Pulsed ^{1}H NMR Relaxation in Crystalline Syndiotactic Polystyrene

Syndiotactic polystyrene can crystallize in four major crystalline modifications.[1] This complex polymorphism arises for two different reasons. The first derives from the conformation of the single macromolecule. In the α and β forms[2] of syndiotactic polystyrene, the TT chain gives rise to macromolecules in a planar zigzag conformation, with a 5.1-Å identity period,[1] while, in the γ and δ forms, a TTGG conformation was proposed on the basis of energy calculations.[3] These last two forms[3,4] have $s(2/1)2$ symmetry and an identity period close to 7.7 Å.

The second cause of polymorphism is molecular packing; this is the origin of the structural difference between the α and β forms.[5-7]

Due to varying γ-gauche contributions,[8] ^{13}C CP-MAS NMR distinguishes clearly between polymers differing in the backbone conformation, but distinguishing polymorphs that have their origin only in molecular packing is rather ambiguous[9] and sometimes unsuccessful.[10]

Here we report a study of the four crystalline modifications of syndiotactic polystyrene by pulsed ^{1}H NMR, the measured parameters being the spin-lattice relaxation times, T_1 and $T_{1\rho}$, vs the temperature. The dependence of the spin-lattice relaxation time T_1 on temperature for two polystyrene samples, one highly isotactic and the other highly syndiotactic (γ-form), is reported in Figure 1. Both samples were carefully degassed.

The usual progressive decay of T_1 vs temperature can be seen; note that, on this basis, a distinction between the two polymers is not clear. In the temperature range 240–480 K the FID shows only one component, either lorentzian or gaussian or any combination of the two, depending on the temperature.[11,12] In the same range of temperature, the spin response to an inversion-recovery pulse sequence is a single exponential. Experiments at lower temperature are in progress. The dependence of T_1 on temperature for the four polymorphous modifications of syndiotactic polystyrene is reported in Figure 2. All samples were undegassed. Since the four curves are well separated, a clear distinction between all four polymorphous forms can be observed. Note that the same measurements in well-degassed samples do not show any appreciable difference.

A large variation between degassed and undegassed aromatic polymers was previously observed by Froix et al.[13-15] This effect was attributed to the presence of O_2 molecules adsorbed on the aromatic rings. In the case of syndiotactic polystyrenes, the O_2 molecules act as a relaxation reagent that greatly affects the T_1 relaxation values, while the absorption of O_2 is modulated by the molecular packing. Thus, sorbed O_2 allows NMR relaxation to distinguish between syndiotactic polystyrenes having polymorphism as a unique difference.

The behavior of $T_{1\rho}$, the relaxation in the rotating frame, vs the temperature is reported in Figure 3. The strong difference observed in the T_1 plots is lacking, owing to the fact that $T_{1\rho}$ is mostly sensitive to low-frequency motions. However, the α form seems to relax faster than the other forms, probably because of some cooperative motion. All plots, in T_1 and $T_{1\rho}$, collapse into a single plot at temperatures higher than the T_g ($T_g \sim 90$ °C).[16] Their scattering can be regarded as a measure of the experimental error.

From all these data taken together, several conclusions may be drawn:

(i) The pulsed ^{1}H NMR technique is capable of discriminating between polymorphous polystyrenes.

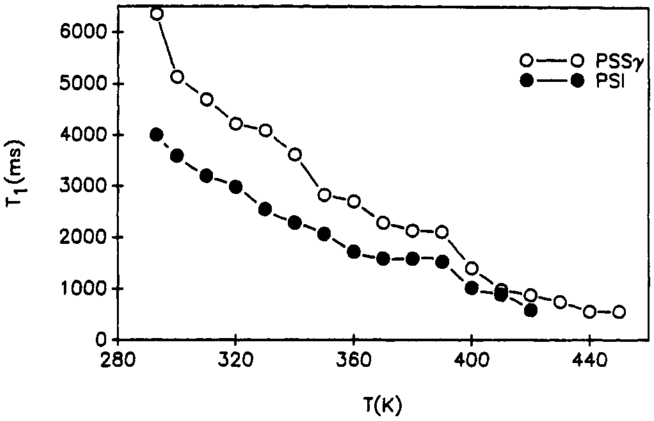

Figure 1. T_1 as a function of the temperature for syndiotactic and isotactic polystyrene.

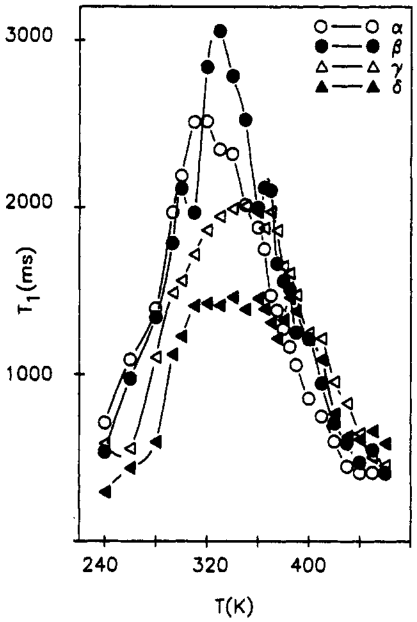

Figure 2. T_1 as a function of the temperature for four crystalline modifications of syndiotactic polystyrene.

(ii) T_1 relaxations give a clear warning on the intensities used in CP-MAS techniques regardless of contact times. Spectral intensity differences might be due to differences in proton relaxation times.

(iii) An optimal temperature can be found, where the difference between T_1 relaxations is the highest; at this temperature (by means of properly tailored 2D experiments) ^{13}C CP-MAS might be carried out to give the best results.

(iv) The value of the maxima (see Figure 2) defines a scale

$$T_{1\delta} < T_{1\gamma} < T_{1\alpha} < T_{1\beta}$$

The order of this scale strictly matches the solubility scale and solvent permeability of the four mesomorphous forms.[17] Since O_2 adsorption shortens T_1 relaxations, it seems possible to correlate these values to the amount of sorbed O_2.

Work is in progress to extend this study to the low-temperature range and to partially deuteriated polymers.

Experimental Section. Syndiotactic polystyrene was prepared according to the literature;[18] α, β, γ, and δ polymorphs were crystallized and characterized by X-ray by Guerra and Corradini.[2]

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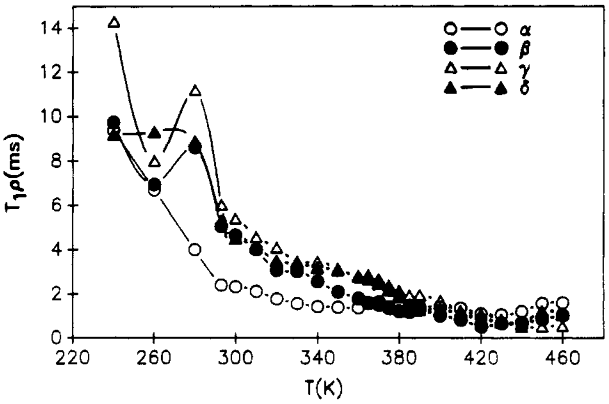

Figure 3. $T_{1\rho}$ as a function of the temperature for four crystalline modifications of syndiotactic polystyrene.

Since the δ form converts into other polymorphs,[2] NMR measures were carried out only at increasing temperatures.

Spin-lattice relaxation times, T_1, were measured at 30 MHz by a conventional inversion-recovery sequence with relaxation delays larger than 5 T_1. Spin-lattice relaxation times in the rotating frame, $T_{1\rho}$, were measured at 40 kHz by a standard spin-locking sequence. The signal to noise ratio was improved by multiple scans (at least 32). The reported T_1 values are the result of a three-parameter best fit procedure over at least 64 experimental points. In all measurements, experimental error is well within 10% of the reported value.

All low-resolution ^{1}H NMR spectra were taken on a commercial spectrometer (Spinmaster, 4, 7-μs 90° pulse, 7-μs dead time), equipped with a variable-temperature unit controller, from Stelar, Mede (PV), Italy.

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