Polymorphism in Syndiotactic Polystyrene: A ^1H NMR Relaxation Study

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Received June 8, 1991; Revised Manuscript Received October 26, 1991

ABSTRACT: A marked shortening of T_1 relaxations in solid aromatic polymers can be attributed to O_2 adsorbed on the aromatic rings. This effect, observed as a function of temperature, is modulated by the amount of adsorbed O_2, which, in turn, varies according to the molecular packing and crystalline/amorphous ratio. Within the temperature range 77–400 K, semicrystalline syndiotactic polystyrenes (s-PS) in the α, β, and γ polymorph modifications were studied by pulse ^1H NMR at 30 MHz. Due to the presence of many relaxation components, 1,2,2-trideuterio-s-PS was synthesized, crystallized, and characterized by X-ray powder diffraction. At low temperature, when both the O_2 diffusion and the spin-diffusion processes are slow enough, the backbone-deuteriated polymers exhibit multiple T_1 relaxations: three for α and β s-PS and two for γ s-PS. These T_1 components are attributed to crystalline and amorphous phases. From the study of these components as a function of temperature and from direct comparison of T_1 values in the different phases, the following conclusions were drawn: (i) Clear differentiation was possible between different s-PS polymorphs. (ii) Determination of the crystalline vs amorphous ratio fully consistent with X-ray diffraction data was achieved. (iii) The amorphous component of different semicrystalline s-PS polymorphs could be distinguished.

Introduction

It has been previously shown[1] that pulsed ^1H NMR relaxation is a technique able to discriminate between syndiotactic polystyrenes (s-PS) differing only in their molecular packing. The absorption of paramagnetic O_2 on aromatic rings is able to modulate T_1 values. Thus polymorphism in aromatic polymers can be studied not only with diffractometric techniques[2] or, eventually, infrared spectroscopy[3] and thermogravimetric analysis[4] but also through the measure of spin–lattice relaxation times. In fact, spin–lattice relaxations are strongly affected by the presence of adsorbed paramagnetic O_2 molecules, whose amount is modulated by the molecular packing. Another factor which may affect O_2 adsorption in aromatic polymers is the amount of amorphous material; this can be conformationally regular but irregularly packed or it may be present in an irregular conformation; moreover, boundary surfaces between amorphous and crystalline domains may also be thought to affect the content of adsorbed O_2. Consequently, a ^1H NMR relaxation study was performed on three crystalline modifications of s-PS. These are the α, β, and γ forms, which were studied over a very large temperature range not only on fully protonated polymers but also on purposely made polymers deuteriated on the backbone.

The δ polymorph modification,[2,5] which has solvent molecules present as guest in the host polymeric matrix, will be discussed in a separate paper.[6]

Experimental Section

Materials. Syndiotactic polystyrenes, fully protonated or deuteriated on the backbone, were synthesized according to known procedures.[7] Styrene-α,β,β-d_3 (isotopic purity 98%) was purchased from Merck Sharp and Dohme, Isotopes Division, and used without further purification.

The α, β, and γ polymorphic forms of s-PS were prepared according to methods already described.[2] The powder precipitated from *o*-dichlorobenzene solutions is originally in the clathrate structure (δ form). Powders in the γ and α forms have been obtained respectively by drying the δ form at 130 °C under vacuum (γ form) or by annealing the δ form at 200 °C (α form). Samples in the β form were obtained by rapid heating of the δ form at high temperature (≈200 °C); in this way a direct transformation of the δ form into the β form occurs.

Wide-angle X-ray diffraction patterns were obtained with nickel-filtered Cu Kα radiation with an automatic Philips powder diffractometer.

The X-ray diffraction spectra of the α, β, and γ forms are reported in Figure 1. According to the previously proposed nomenclature,[2] spectra A and B of Figure 1 correspond respectively to the disordered α' and ordered β'' modifications.

Experimental NMR Procedure. On fully protonated polymers only, ^{13}C CP MAS NMR spectra were recorded at 75.5 MHz on a Bruker AC300 instrument according to already published methods.[8] All pulse low-resolution ^1H NMR spectra were measured at 30 MHz on a commercial Spinmaster spectrometer (Stelar, Mede, Pavia, Italy). The dead time of this instrument is 6 μs. Within the full temperature range, 77–400 K, a continuously variable attenuator was introduced between the transmitter output and the receiver input to minimize experimental errors; in this way, it was possible to obtain fixed 90° and 180° pulses, corresponding respectively to 4.7 ± 0.1 and 9.4 ± 0.1 μs for each sample. The samples were contained in standard 5-mm-diameter NMR tubes with a height well within the coil. A variable-temperature unit (Stelar VTC87) equipped with a standard Bruker N_2 evaporator system or with a N_2 flux from a pressurized line was used between 130 and 400 K. Temperature control (±0.2 °C) was ensured with a chromel–alumel thermocouple placed in the probe head at a distance less than 1 mm from the coil. Measurements at 77 K were performed on a purpose-made Stelar probe head with both ends open. This has a 10-mm diameter, which can accommodate a glass Dewar having a long cold finger with an internal diameter ≈6 mm (Varian, ESR standard kit, insert Dewar for liquid N_2 temperature). The Dewar is manually refilled. In this way, the same sample can be used and constant 90° and 180° pulses maintained over the full temperature range.

Spin–lattice relaxation times were measured by the standard inversion–recovery method with phase detection and relaxation

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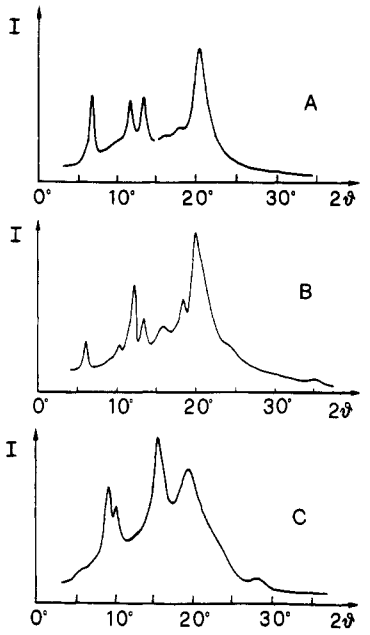

Figure 1. X-ray diffraction patterns of semicrystalline s-PS polymorphs: (A) α form (α' modification); (B) β form (β'' modification); (C) γ form.

delay always greater than 5 times the longest T_1. Data were accumulated with a multiblock, multiscan procedure, repeated a specified 2^n number of times; this procedure ensures that the full selected phase cycle[9,10] is executed on the complete set of acquisition blocks. Thus any slow drift in experimental conditions affects all data in the same way; this procedure is very convenient for experiments lasting many hours and/or with relaxation delays which can be of the order of 60 s. At each temperature, due to the Boltzmann dependence of spin populations, a different number of scans is required to get a satisfactory signal to noise ratio; this number was kept the same for each s-PS sample, while the number of blocks, corresponding to the number of different τ intervals, was never less than 64 for single-exponential decays and at least 128 or 256 in the case of multiexponential decays.

The magnetization obtained in each inversion–recovery experiment is the result of a fixed number of digitized points covering the appropriately chosen size (64 words); due to the fast T_2 value, the chosen time difference between each digitized point was always equal to 1 μs.[9]

To minimize experimental errors of the instrument, the first 12 points of the magnetization following the dead time were always taken; their mean value is the one used for the calculation of relaxation values.

Data Analysis. Inversion–recovery experiments lead to an equation of the type $M = \sum_i A_i \exp(-t/T_i) + A_0$ ($i = 1, ..., N$), where N is the number of different T_i relaxations having relative weight A_i, while A_0 is the M_∞ value, i.e., the value of the magnetization M after a single 90° pulse. This equation was fitted with the commercial computer program FIT,[11] which uses a Simplex algorithm.[12] To evaluate the goodness of the fit, experimental points were compared with the calculated ones; their compatibility was tested to a 95% confidence level according to an F distribution. The presence of a comparable number of negative and positive deviations was also checked. The number of sign changes of the ordered experimental points was tested with respect to the calculated function. The deviations of the number of sign changes were also evaluated and compared with a binomial distribution (degree of asymmetry of the distribution[12]); distributions within a 95% confidence level were accepted.

To verify this statistical approach for multiexponential functions and evaluate the goodness of the results obtained, two other computer programs were also used for both the A_i and T_i values. One of these,[13] MRQ, uses a nonlinear least-squares fitting method based on the Marquart algorithm.[14] The second program, GraFit,[15] also based on the Marquart algorithm, gives T_i^{-1} values, with standard deviations for the inverse value; for this reason this program was only used in ambiguous cases as a further test.

All values reported in Table I and the figures are within the following limits: single exponential, error within 3%; multiple exponentials, error on the longest T_i value within 3%; error on other T_i values within 6%; error on A_i values less than 10% for each component. All best-fit values of T_1 and relative uncertainties are reported in Table I.

Results and Discussion

Figure 2 shows the result of an inversion–recovery experiment on the γ form of s-PS at $T = 200$ K (curve a). As already observed by Froix et al.,[16] the presence of at least two components can be clearly observed, having respectively T_1 less than 100 ms and T_1 about 1 s, with relative intensities near a 5/3 ratio. This observation clearly supports our previous observation that paramagnetic O_2 is selectively adsorbed on the aromatic rings. Thus, at low temperature, when the diffusion of O_2 is no longer able to average the ring and the backbone spin–lattice relaxations, these give different T_1 values. The shorter component is due to phenyl protons which are nearer to the paramagnetic center. For a further confirmation of this interpretation, syndiotactic polystyrene was prepared normally protonated on the phenyl ring but fully deuteriated on the backbone. This polymer was crystallized according to known procedures[2,17] obtaining the α, β, and γ crystal forms and characterized by powder X-ray diffraction. These s-PS polymorphs were investigated by pulsed ^{1}H NMR. Curve b in Figure 2 represents the result of an inversion–recovery experiment on the γ form of the deuteriated polymer; here only the fast component previously observed is still present while the slow component is missing. Thus the slow component is effectively due to backbone protons only. The fast component, due to the aromatic ring of γ s-PS, will be discussed later. Analogous observations at 200 K can be made for the α and β forms fully hydrogenated or partially deuteriated. Since the deconvolution of multiple exponential decays is rather difficult and we were mostly interested in a complete study of relaxations as a function of temperature, the full study was actually performed mostly on the deuteriated polymers. In this way T_1 relaxation studies correlate the polymer behavior to the presence of O_2, a paramagnetic center, adsorbed on the aromatic rings. Note that other properties, such as chain motions, can be better studied by a completely different approach, for instance, through ^{2}H NMR studies.[18,19]

d_3-s-PS α. In Figure 3 a plot of T_1 as a function of temperature is shown for the backbone-deuteriated α form of s-PS. At temperatures above 180 K, only one T_1 value, due to ^{1}H of the phenyl rings, can be observed. Below 180 K, the single-exponential decay splits into two components whose intensity progressively reaches a steady ratio (Figure 3 and Table I). These two components can be attributed respectively to the crystalline and amorphous fractions. In fact, the crystalline vs amorphous ratio ($\approx$2/3), determined by X-ray diffraction on the same powder sample (Figure 1A), compares well with NMR data, provided that the faster relaxing component is attributed to the amorphous phase and the slower component to the crystalline phase. It thus appears that O_2 is more easily adsorbed in the amorphous phase than in the crystalline phase. Since CP MAS ^{13}C NMR spectra clearly show that the α form is almost completely in a planar zigzag conformation,[8,21] this means that the amorphous fraction, compared to its crystalline counterpart, should have larger holes, capable of accommodating O_2 molecules. Note that a few conformational defects can be accompanied by a much larger number of holes and vacancies, exactly as a few configurational defects can be accompanied by a much larger

Table I
T_1 Best-Fit Values and Relative Uncertainties for the Backbone-Deuteriated α, β, and γ Polymorphs of s-PS as a Function of Temperature[a]

	backbone-deuteriated s-PS α				backbone-deuteriated s-PS β				backbone-deuteriated s-PS γ		
temp (K)	T_1(av) (ms)	T_1(lc) (ms)	T_1(mc) (ms)	T_1(sc) (ms)	T_1(av) (ms)	T_1(lc) (ms)	T_1(mc) (ms)	T_1(sc) (ms)	T_1(av) (ms)	T_1(lc) (ms)	T_1(sc) (ms)
400	700 ± 10				920 ± 18				735 ± 15		
390	880 ± 15				1060 ± 20				843 ± 18		
380	1130 ± 22				1272 ± 26				910 ± 22		
370	1280 ± 40				1288 ± 32				960 ± 28		
360	1370 ± 40				1390 ± 35				1010 ± 20		
350	1480 ± 32				1654 ± 43				1035 ± 22		
340	1700 ± 36				1619 ± 30				1020 ± 20		
330	1710 ± 30				1595 ± 42				1018 ± 20		
320	1744 ± 30				1385 ± 30				1017 ± 20		
310	1364 ± 20				1410 ± 33				895 ± 15		
300	1360 ± 22				1280 ± 25				850 ± 20		
293	1225 ± 20				1225 ± 22				826 ± 17		
280	1070 ± 20				992 ± 20				701 ± 14		
260	695 ± 15				680 ± 13				635 ± 13		
240	393 ± 10					540 ± 11	185 ± 6		417 ± 10		
220	205 ± 5					340 ± 10	96 ± 5		252 ± 5		
200	152 ± 4					299 ± 11	106 ± 3			172 ± 4	79 ± 3
180		95 ± 3	34 ± 2			449 ± 8	61 ± 2			89 ± 2	40 ± 2
170		78 ± 2	30 ± 2			583 ± 14	67 ± 2	33 ± 1		68 ± 2	31 ± 1
160		167 ± 4	27 ± 1			813 ± 21	69 ± 2	23 ± 1		42 ± 1	16 ± 1
150		264 ± 7	31 ± 2	16 ± 1		921 ± 20	92 ± 3	20 ± 2		35 ± 2	13 ± 1
140		312 ± 8	26 ± 1	10.0 ± 0.6		1100 ± 32	129 ± 5	22 ± 1		45 ± 1	10.5 ± 0.5
135										43 ± 2	7.4 ± 0.4
130		452 ± 9	31 ± 2	9.0 ± 0.5		1110 ± 50	130 ± 7	26 ± 1		35 ± 1	8.2 ± 0.5
77		1245 ± 25	107 ± 4	39 ± 2		1187 ± 60	261 ± 16	45 ± 2		239 ± 12	40 ± 2

[a] T_1(av) = single T_1 value (spin and O_2 diffusion processes average different T_1's, giving a single value). T_1(lc) = long T_1 component. T_1(mc) = middle T_1 component. T_1(sc) = short T_1 component.

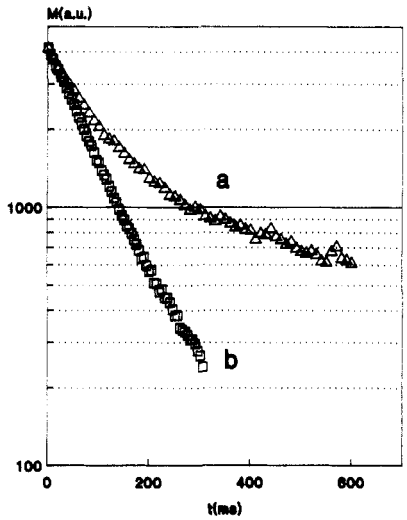

Figure 2. Semilogarithmic plot of experimental points obtained from an inversion–recovery experiment at T = 200 K on the γ form of s-PS: (a) fully protonated; (b) deuteriated on the backbone.

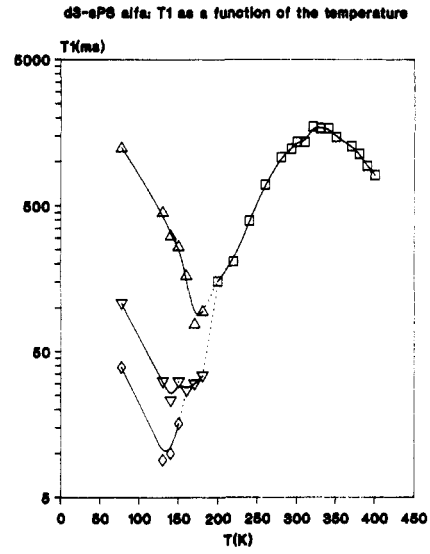

Figure 3. Plot of T_1 relaxation time as a function of temperature for the backbone-deuteriated s-PS α form. Different symbols refer to the best fitted different T_1 relaxations.

number of conformational defects.[22] It is worth noticing that the above explanation implies that spin diffusion between phenyl rings in the amorphous and crystalline domains is negligible, which is reasonable at the low temperatures where a biexponential decay is observed in the T_1 relaxation.

From 150 K to lower temperatures, in the inversion–recovery experiment of the α form, a third exponential decay can be observed; its T_1 value is difficult to evaluate since it is rather short, $T_1 \approx 5$–10 ms, and of low intensity; however, at 77 K, the presence of this third component not only can be observed but can be accurately determined. In Figure 4a, for the sake of clarity, a logarithmic plot of the inversion–recovery experiment is shown; the nonlinearized experimental data and its best fit are shown in Figure 4b. Experimental data are also reported in Table I. At 77 K the longest relaxation component ($T_1 \approx 1.2$ s) corresponds to ≈35% of the total intensity, the intermediate one ($T_1 \approx 110$ ms) corresponds to ≈60% of the signal, while the shortest component ($T_1 \approx 40$ ms) accounts for an amount lower than ≈10%.

To rationalize these data, two completely different experiments must be employed, namely, CP MAS ^{13}C NMR spectra on samples in the α form[8] and X-ray powder diffraction spectra. The latter (see also Figure 1A) indicate that the α form has a crystalline content of the order of 30–40%; thus the longest T_1 component, whose amount is ≈35%, can be assigned to the crystalline α phase.

CP MAS ^{13}C NMR spectra show that the α and β forms are both in a planar zigzag conformation. However, the

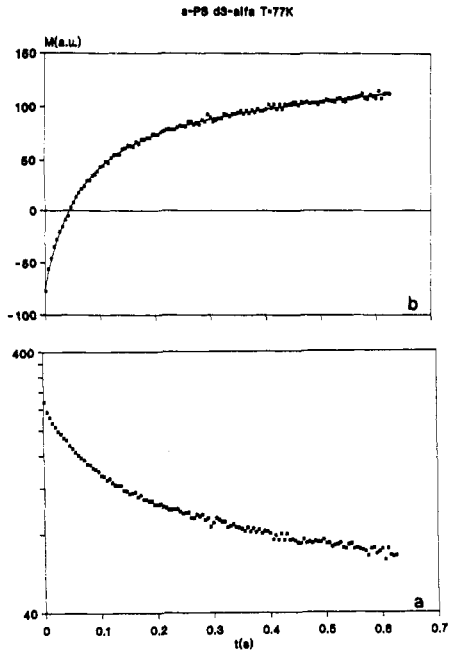

Figure 4. ^{1}H NMR signal intensity as a function of $n\tau$ in an inversion–recovery experiment: τ is the delay between the 180° and 90° pulses, and n is the number of different delays (n = 128); the sample is the backbone-deuteriated s-PS α form; T = 77 K. (a) Semilogarithmic plot of the inversion–recovery experiment. (b) Inversion–recovery experiment: the line through the experimental points represents the best fit of three exponentials, T_1 values are as follows: T_1' = 1245 ± 25 ms (≈35%), T_1' = 107 ± 4 ms (≈56%), and T_1' = 39 ± 2 ms (≈9%).

presence of some weak signal accounting for an intensity less than 10% can be also observed.[8,20] Since chemically shifted signals in ^{13}C spectra mostly originate through conformational effects,[21] it seems reasonable to hypothesize that a small amount of material is present in highly irregular nonplanar conformations. Thus, two different types of material seem to be present in the amorphous component of the α polymorph of s-PS. One type, conformationally regular, i.e., in a planar zigzag conformation, accounts for ≈60% of the total polymer and is irregularly packed; between 180 and 130 K, its T_1 relaxation is very short, of the order of 30 ms. At 77 K, however, when O_2 mobility is strongly reduced, this value becomes longer, ≈100 ms. Thus, at 77 K, the presence of a small amount of another very fast component can be well determined (Table I). The fastest relaxing component, accounting for less than 10%, may be due to conformationally irregular macromolecules which are also irregularly packed. A large number of holes, capable of accommodating O_2 molecules, may be present, giving rise to a very short spin–lattice relaxation time. This component might also be due to a few configurational irregularities which can induce a larger number of conformational defects.[22] In either case, the fast-relaxing components seem to be related to "gross" defects, while the component with the intermediate T_1 value may be reasonably attributed to "conformationally regular chains, irregularly packed".

It is worth noting that at liquid N_2 temperature, where the intrinsic mobility of free O_2 molecules is strongly reduced (since the boiling point of liquid air is higher than 77 K), the relaxation time of the aromatic protons of the α crystalline form strongly increases, reaching a value greater than 1.2 s. This high value may be due to an average value between a very slow value ($T_1 > 10$ s) and a very fast value ($T_1 < 10^{-5}$ s) due to a few O_2 molecules trapped into holes and dislocations, which can be related to steric defects such as meso diads,[23,24] while the bulk of the polymer

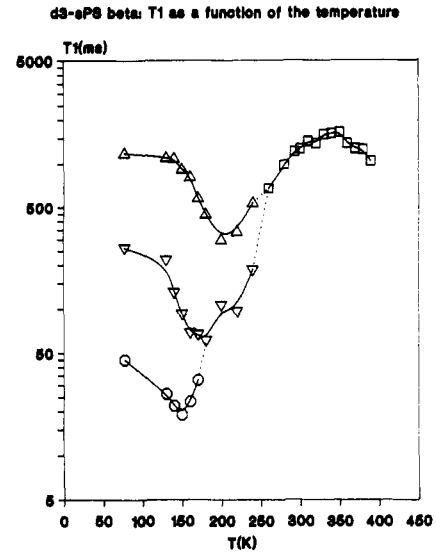

Figure 5. Plot of T_1 relaxation time as a function of temperature for the backbone-deuteriated s-PS β form. Different symbols refer to the best fitted different T_1 relaxations.

should have a rather long T_1 relaxation, as in well-degassed polymers.[1] This means that, at 77 K, for the crystalline component of the α phase the adsorption of O_2 molecules on aromatic rings is minimal.

In the amorphous phase, the number of defects capable of including O_2 is high enough so that, even at 77 K, a shortening of the T_1 relaxation is still observable. However, the T_1 value is about 3 times longer than that observed at 130 K.

Within the low-temperature range, between 77 and 200 K, fully protonated s-PS in the α crystalline form shows only one slow component, due to the backbone protons. The fast component, due to the aromatic ring protons, shows a multiple exponential decay with T_1 values which compare well with the analogous values of the partially deuteriated polymer; the quantitative analysis of these fast components shows larger uncertainties, confirming the complexity of evaluating multiple exponential functions.

Since the T_1 values of the aromatic rings in both polymers (deuteriated and nondeuteriated) are very similar and rather short, it appears evident that the dominating mechanism of relaxation is through the paramagnetic O_2.[25]

d_3-s-PS β. In Figure 5, a plot of T_1 as a function of temperature is shown for the β polymorph of s-PS deuteriated on the backbone. Only one relaxation is present at temperatures higher than 240 K, two components can be observed between 180 and 240 K, while three components can be clearly observed and evaluated at temperatures lower than 180 K. Experimental data are reported in Table I.

The intensity of the three components reaches a steady value at rather low temperatures (T < 130 K); consequently, as in the case of the α form, the relative intensities that will be discussed are those evaluated at liquid nitrogen temperature.

The longest relaxation component corresponds to ≈60% of the signal, the intermediates one to ≈30% of the signal, while the shortest component accounts for less than ≈10%. Again comparing CP MAS ^{13}C NMR and X-ray data, it is clear that the longest T_1 component, whose amount is ≈60%, can be safely assigned to the crystalline β phase.

Again, it is argued that a small amount of material is present in highly irregular nonplanar conformations which account for the shortest T_1 component. This interpretation is a tentative one but seems to agree with all

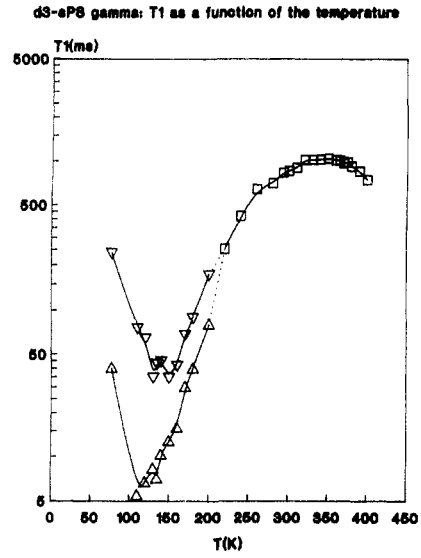

Figure 6. Plot of T_1 relaxation time as a function of temperature for the backbone-deuteriated s-PS γ form. Different symbols refer to the best fitted different T_1 relaxations.

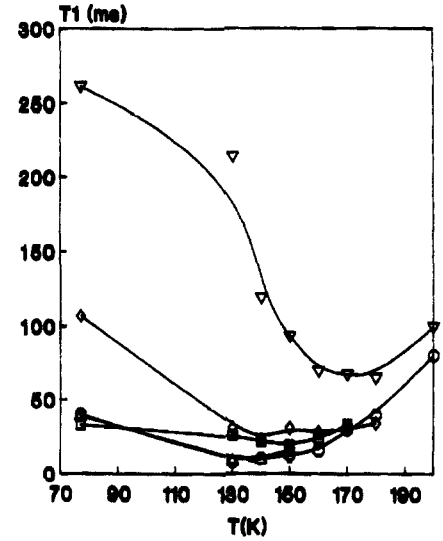

Figure 7. Backbone-deuteriated s-PS fast components of ^1H spin–lattice relaxations due to the amorphous fractions: (◇) α_1, amorphous phase with planar zigzag chains; (△) α_2, amorphous phase with nonplanar chains; (▽) β_1, amorphous phase with planar zigzag chains; (□) β_2, amorphous phase with nonplanar chains; (○) γ, amorphous phase.

experimental data presently available for the α and β polymorphs. The total amount of adsorbed O_2 molecules in the β crystalline form is very low over the whole temperature range, as shown by the rather long relaxation values; probably intra-ring distances are too short to allow the entrance of O_2 molecules, which must be confined in vacancies and dislocations,[26] possibly related to steric defects such as meso diads. This observation is consistent with the low permeability of the β form to organic solvents.[27] In the fully protonated polymer, so many different relaxations in the β form make the analysis of the multiple exponential decay extremely difficult. In fact, the presence of relaxation times differing at least 3 order of magnitudes over a large temperature range makes not only the mathematical analysis of the experiment difficult but also the proper setup of the experiment itself. However, at liquid N_2 temperature, a very slow component with a T_1 value $\approx$ 2 s was observed. This component, which was absent in the deuteriated polymer, is certainly due to backbone protons; however, its intensity does not conform to a 3/5 ratio. Since many long, medium, or fast relaxing components are present in the multiple exponential decay, no analysis of these data was attempted.

d_3-s-PS γ. The dependence of T_1 on the temperature is shown in Figure 6 for the γ polymorph of s-PS deuteriated on the backbone. Experimental values are given in Table I. In the inversion–recovery experiments at temperatures higher than 200 K, only a single-exponential decay is observed, corresponding to a single T_1 value. The inversion–recovery experiments at temperatures lower than 200 K clearly show a biexponential decay, with both relaxations rather short (T_1 values less than 100 ms). At temperatures lower than 140 K the relative amount of the longer decay to the shorter one becomes temperature independent. The intensity ratio of these components is $\approx$35/65, which compares well with a crystalline/amorphous ratio $\approx$40/60 obtained from an analysis of X-ray powder spectra.[28] It follows that, as in the case of the s-PS α and β polymorphs, the shorter component is due to the amorphous phase.

The fully hydrogenated polymer at temperatures lower than 200 K clearly shows three T_1 components, the longest of which is absent in the deuteriated polymer and is again assigned to backbone protons; the other two components, both fast relaxing, give T_1 values very near the corresponding values of the deuteriated polymer. While this agreement holds well for T_1 values, the relative intensities do not correlate well. Thus in the γ form, either in the crystalline state or in the amorphous state, the aromatic protons relax almost completely owing to paramagnetic O_2.[25]

Semicrystalline Polymorphous s-PS: The Amorphous Components. The observation that in all cases the amount of adsorbed O_2 is larger in the amorphous phase than in the crystalline phase and also is different in the different amorphous phases (Figure 7) requires a clear definition of the nature of the amorphous phase in a semicrystalline polymer. In this regard some information may be obtained by comparing T_1 relaxations from the amorphous phases of polymers differing in their crystalline component.

Two main causes can be thought to contribute to the amount of O_2 which can be adsorbed on the aromatic rings. One is the conformation of the single macromolecule; this defines molecular distances among aromatic rings belonging to the same macromolecule and can be thought of as a fully *intramolecular* effect. This information, i.e., the conformation of the single macromolecule in the amorphous phase, can be obtained by CP MAS ^{13}C NMR.

Other causes which can increase O_2 adsorption in the amorphous fraction are the total amount of holes and vacancies, folding conformations, and any other cause capable of changing interatomic distances among aromatic rings such as the type, the number, and the distribution of steric defects.[21]

Both the α and β polymorphs of s-PS are essentially in a planar zigzag conformation. However, their T_1 relaxations relative to the aromatic ring of their amorphous component are very different; as a consequence the amount of adsorbed O_2 is measurably different in two amorphous phases having the same chain conformation. This observation can be rationalized by evoking some kind of short distance order, which can also be regarded as a residual memory of the crystalline phase;[29] this means that, at least for α and β s-PS, the amorphous phase is rather similar to its crystalline counterpart and not at all random.[30]

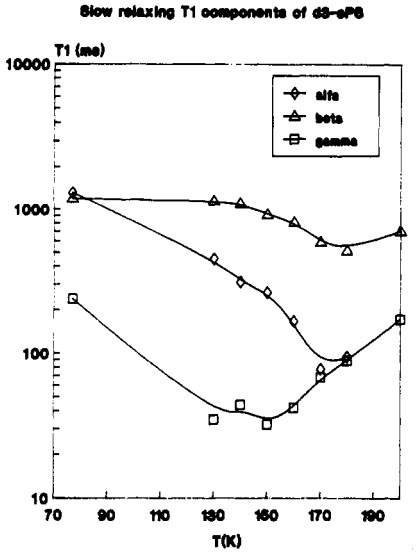

Figure 8. Backbone-deuteriated s-PS slow components of ^1H relaxations due to the α (◇), β (△), and γ (□) crystalline fractions of the polymorphous forms.

As previously reported[5] the γ crystalline form is completely different from α and β s-PS, since it mostly comprises helices; as shown by CP MAS ^{13}C NMR spectra this conformation is characteristic of both the amorphous and the crystalline phases.[8] In the amorphous phase of the γ form, T_1 is short, which points to a rather large amount of adsorbed O_2; even at 77 K, when the O_2 mobility is drastically reduced, the T_1 value is shorter than 50 ms. Thus at 77 K, a temperature at which "normal" O_2 molecules are in a liquid state, a rather large amount of O_2 molecules adsorbed on the aromatic rings must have a high mobility, giving rise to a shortening of T_1 of the amorphous phase in the γ form, to a degree which is comparable to the effects exerted by O_2 molecules in the gaseous state.

The faster relaxing components, relative to the weak component of the amorphous fractions of the α and β forms, at low temperatures show irregular behavior similar to that of the amorphous phase of the γ form, supporting the interpretation that it is not due to planar chains, but more likely to irregular fragments, perhaps with a helical conformation. By considering together all the amorphous fractions of the different polymorphs of s-PS, this highly irregular amorphous component, with a very short T_1, is probably the only one corresponding to a definition of real conformational randomness, i.e. comparable to the conformation in the melt. Note that for this component the amount of sorbed-O_2 is about the same at 77 K as at higher temperatures (130–170 K), i.e. when O_2 is in the gaseous state.

Polymorphous s-PS: The Crystalline Components. In Figure 8 the behavior of the crystalline component of the α, β, and γ polymorphs are shown together. While the β crystalline form is almost completely incapable of adsorbing O_2 molecules, the α and γ forms show a noticeable decrease in T_1 between 180 and 130 K. Thus, within this range of temperature, the amount of O_2 adsorbed allows a clear distinction between the three polymorphs. However, at 77 K, when the mobility of O_2 is strongly reduced, the crystalline α form gives a T_1 value equal, within experimental error, to that of the β form, while T_1 of the γ form is an order of magnitude shorter. Since in the γ form there are empty channels which can act as hosts for O_2 guest molecules,[5] residual O_2 can be trapped not only in irregular vacancies and dislocations but also in these channels, thus facilitating adsorption onto aromatic rings. Thus, even at 77 K, the short T_1 value for the γ form, both in the crystalline state and in the amorphous state, can be justified. This observation seems completely analogous to the way in which the nature of water affects its melting point, whether it is free or bound;[31] bound water can be highly mobile down to temperatures ≈30 °C below water's normal melting point.

Conclusion

By comparing all previous experimental observations some conclusions can be drawn.

For aromatic polymers, spin–lattice relaxation values, modulated by O_2 adsorption, can give information on polymorphism. Moreover, since O_2 is adsorbed differently by amorphous and crystalline domains, by measuring the various components of T_1 in suitably tailored inversion–recovery experiments, it is possible to obtain a quantitative measure of the amorphous/crystalline ratio. At different temperatures a clearer distinction occurs between different polymorphous forms and/or between the crystalline and the amorphous fractions. These temperatures must be experimentally found since they depend on many factors such as the polymer itself, O_2 diffusion coefficients, spin diffusion, crystalline vs amorphous content, rotational barriers, and so on. Thus it is always necessary to perform a full study of the temperature dependence of the spin–lattice relaxation. Moreover, since the mathematical resolution of functions due to many different exponential functions is difficult,[32] when many different relaxation values are present, the use of partially deuteriated polymers seems unavoidable.

Very long relaxation times, rather common for backbone protons at low temperatures, define relaxation delays longer than 5 times the longest T_1; this fact can be very inconvenient when it is necessary to measure a weak component, which requires a large number of scans. The whole measurement can be difficult when many very short and very long T_1's are present.

Finally, for the amorphous phases of different semicrystalline polymorphous s-PS, by the combined use of X-ray diffraction analysis, CP MAS ^{13}C NMR, and pulse low-resolution NMR, a clear experimental differentiation of contributions can be made and a tentative model proposed. This model suggests the presence of partial or short-range order in the amorphous phase of crystallizable polymers; it is worth noting that similar results have been recently proposed on poly(ethylene terephthalate) on the basis of a careful deconvolution of X-ray diffraction profiles.[33] The present paper presents only experimental data and their simplest tentative interpretation; theoretical calculations are in progress[34] on the selective adsorption of O_2 on aromatic rings, a physicochemical phenomenon on which very few calculations have been made up to now.[35] Other experiments are in progress to increase the temperature range as much as possible and to perform measurements at different partial pressures of O_2 for this and other aromatic polymers.

Acknowledgment. This research was partly supported by the CNR special ad hoc program "Chimica Fine II".

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