Oxygen-Doped Polymers: An ^1H NMR Spin−Lattice Relaxation Study

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ABSTRACT: Selective adsorption of oxygen on aromatic rings acts as a strong relaxation contrast agent. The effect is maximal at rather low temperatures, in the 80−160 K range, where a well-defined minimum is observed. The positions of the minima and the relative value of the spin−lattice relaxation times are modulated by the chemical nature of the polymer, by its packing (polymorphism), by the crystalline vs amorphous ratio, and by the maximal amount of adsorbed oxygen. A full theoretical treatment of relaxation parameters has been carried out, leading to a best fit treatment of relaxation data. The proton−proton dipolar term at high temperatures and the proton−oxygen scalar term at lower temperatures provide the major contribution to spin−lattice relaxation. From the full theoretical treatment, the best fit of experimental data on polymorphous polystyrenes permits the evaluation of a number of physico-chemical parameters. The activation energy for the phenyl ring libration is obtained, which is different for each polymorphous form. Moreover, for each aromatic polymer, the maximal number of adsorbable oxygen molecules is obtained, giving a scale of polymers suitable to act as oxygen scavengers.

Introduction

The adsorption of paramagnetic oxygen on aromatic polymers causes a major shortening of spin−lattice (T_1) relaxation times.[1,2] The amount of adsorbed oxygen is modulated by the chemical nature of the aromatic polymer, by the molecular packing (polymorphism),[2] by the crystalline vs amorphous ratio, and also by molecular motions.[3] Two important remarks can be made concerning the temperature dependence of T_1 relaxations. The first is that, among different chemical groups relaxing through different relaxation mechanisms within the polymer, at a temperature adequately low, the spin diffusion process does not operate.[2-4] In the present case, in fact, aliphatic protons relax through the usual dipole−dipole spin-like interaction while, due to the presence of the unpaired electrons in the oxygen molecule, aromatic protons, at low temperature, mostly relax on the oxygen through the spin-unlike interaction. Note that the spin diffusion process is fully operative between groups relaxing with the same mechanism; in fact, in the whole temperature range, in well-degassed polymers both the backbone and the phenyl rings relax with the usual dipolar spin-like mechanism, and T_1 experiments show the usual exponential decay. In the case of undegassed aromatic polymers, the spin diffusion process operates within phenyl groups belonging to the same domain but is not active in transferring the magnetization between the backbone and aromatic protons.

Moreover it must be noted that this observation is by no means limited to polymers since it has been reported on nonpolymeric solids such as benzoic acid.[5]

The second remark deals with the overall shape of the curve representing T_1 as a function of the temperature. In fact, in all aromatic polymers studied up to now[2,3,6,7] in the presence of oxygen, by lowering the temperature, the value of T_1 shortens and after a deep minimum its value increases again, reaching a flat plateau. The position and depth of the minimum and the flatness of the plateau as a function of the temperature are different in different polymers, in different polymorphs, or even in the different phases of the same semicrystalline polymer. This paper deals with the full relaxation theory necessary to describe the experimental results and with the physico-chemical parameters whose value can be derived from the best fit of the relaxation data.

Experimental Section

Materials. Syndiotactic polystyrenes, fully protonated or deuteriated on the backbone, were synthesized according to known procedures.[8] The α, β, and γ polymorphous forms of backbone-deuteriated polystyrenes have been extensively described elsewhere.[2]

Experimental NMR Procedure. All pulse low-resolution NMR measurements were performed at 30 and 57 MHz on a commercial spectrometer "Spinmaster" (Stelar, Mede, Pavia, Italy). Experimental procedure and data analysis have been fully described elsewhere.[2,3] Spin−lattice relaxation times were measured by the aperiodic saturation recovery method.[9] This sequence, much faster than the standard inversion-recovery (IR) method previously used, was checked carefully by direct comparison with IR results. Multiscan procedures (at least 128 scans) were performed in order to obtain a very good signal/noise ratio. Moreover 256 different delays were used in order to measure T_1 values at each temperature. Therefore the obtained T_1 values are carefully determined and are affected only by small experimental errors (<3% on the longer T_1 component and <6% on the shorter one).

Most experimental data at 30 MHz have been reported elsewhere.[1,2] The value of relaxation times at 57 MHz, never reported before, are only given in the figures; tables with T_1 values at 30 and 57 MHz are available on request.

Experimental Results

As previously reported,[2] in the absence of oxygen, T_1 relaxation times of aromatic polymers are similar to the corresponding values observed in any other polymeric system (see Figure 1). Here the behavior of T_1 relaxation is shown as a function of $1000/T$ for a well-degassed backbone-deuteriated syndiotactic polystyrene in the γ polymorphous form (upper trace); in the same

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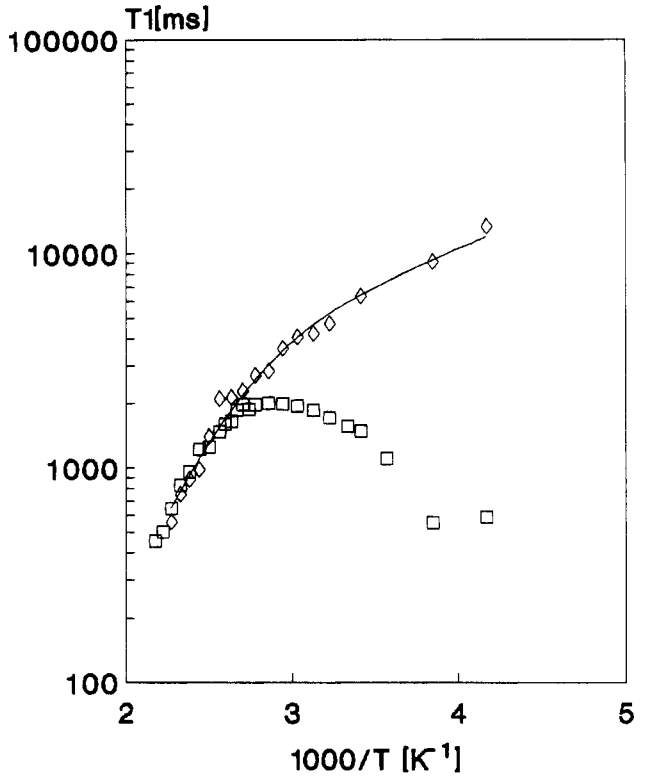

Figure 1. Semilogarithmic plot of T_1 relaxation times (in milliseconds), measured at 30 MHz, as a function of $1000/T$ (K^{-1}) for a well-degassed sample of syndiotactic polystyrene in γ polymorphous form (upper trace) and for the same undegassed sample. The solid line through the experimental points results from the best fit procedure.

figure T_1 relaxation values are reported for the same sample undegassed (lower trace). Note that the effect is so large that in order to present the data, a semilogarithmic representation is necessary. It must also be noted that in other polymers, such as poly(phenylene oxide)[3] (PPO) or the poly(1-oxy-2-phenyltrimethylene)[10] (i.e. the alternate copolymer CO–styrene), the T_1 shortening can be extremely large, up to 4 orders of magnitude.

Spin–lattice relaxation values vs $1000/T$ at 30 MHz for backbone-deuteriated α, β, and γ semicrystalline syndiotactic polystyrenes, are shown in Figure 2a–c. In each figure the upper trace has been attributed to relaxation values due to protons belonging to crystalline domains while the lower trace is due to protons in the amorphous domains (a very small amount of another highly irregular amorphous form present in the α and β polymorphs has been previously discussed[2] and it is not shown). The corresponding data at 57.0 MHz are shown in Figure 3a–c. It is worth noting that any theory on NMR relaxations requires the use of at least two different frequencies in order to discriminate among possible relaxation mechanisms.[4]

Theory of Relaxation

Consider a system of N_I nuclear resonant spins I_i ($I_i = I = 1/2$) and N_S nonresonant spins S_k ($S_k = S$) with Larmor precession frequencies ω_I and ω_S, respectively, in a strong external magnetic field $\mathbf{B}_0$. In the presence of molecular motions the spin Hamiltonian for such a system can be expressed as a sum of a strong Zeeman interaction $\mathcal{H}_Z$ and time-dependent spin interactions $\mathcal{H}_L(t)$ with local fields, namely (1) dipolar interaction $\mathcal{H}_d^{II}(t)$ between like spins[11] $\mathbf{I} - \mathbf{I}$, (2) dipolar (or pseudo-dipolar) interactions $\mathcal{H}_d^{IS}(t)$ between unlike spins[12] $\mathbf{I} -$

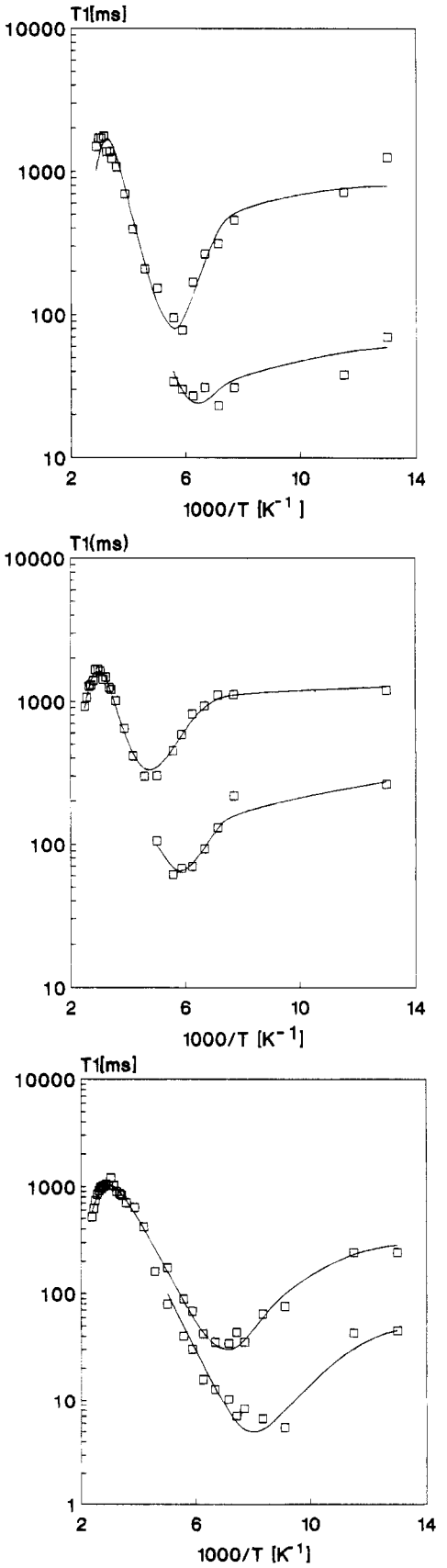

Figure 2. Semilogarithmic plot of T_1 relaxations (in milliseconds) as a function of $1000/T$ (K^{-1}) respectively for (a) backbone-deuteriated syndiotactic polystyrene in α polymorphous form, (b) backbone-deuteriated syndiotactic polystyrene in β polymorphous form, (c) backbone-deuteriated syndiotactic polystyrene in γ polymorphous form. Relaxations were measured at 30 MHz within the temperature range 77–400 K; the solid line through the experimental points results from the best fit procedure.

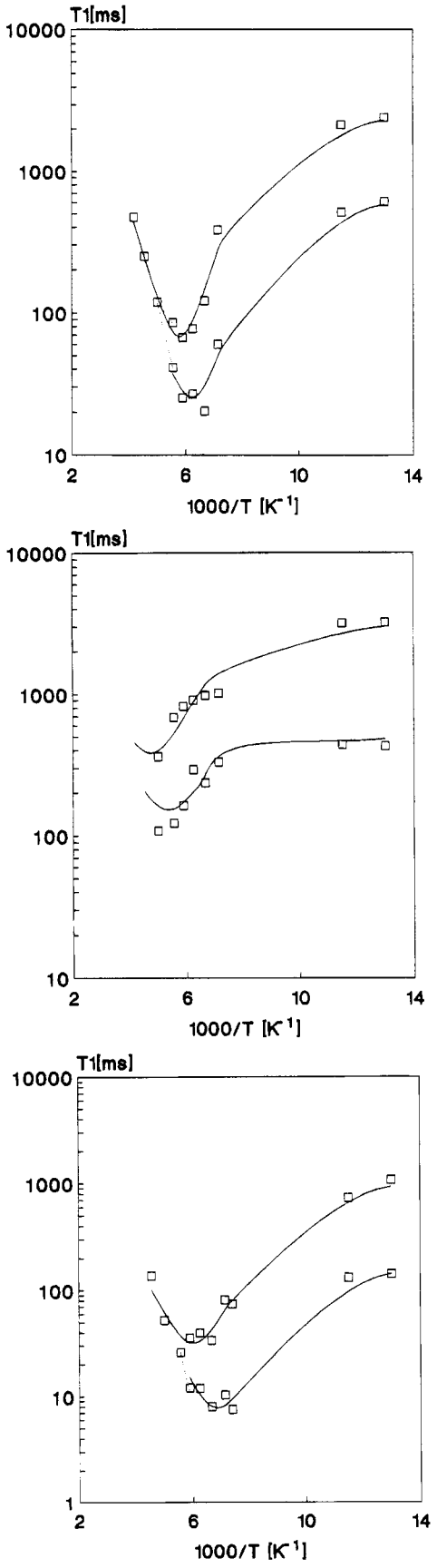

Figure 3. Semilogarithmic plot of T_1 relaxations (in milliseconds) as a function of $1000/T$ (K^{-1}) respectively for (a) backbone-deuteriated syndiotactic polystyrene in α polymorphous form, (b) backbone-deuteriated syndiotactic polystyrene in β polymorphous form, (c) backbone-deuteriated syndiotactic polystyrene in γ polymorphous form. Relaxations were measured at 57 MHz within the temperature range 77–298 K; the solid line through the experimental points results from the best fit procedure.

S, and (3) scalar spin–spin interactions $\mathcal{H}_J^{IS}(t)$, which consist of a dominant static part $\mathcal{H}_0$ and a fluctuating traceless perturbation $\mathcal{H}(t)$ in the following form:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_L(t) = \mathcal{H}_0 + \mathcal{H}(t) \quad (1)$$

$$\mathcal{H}_0 = \mathcal{H}_Z + \langle \mathcal{H}_L \rangle \quad (2)$$

$$\mathcal{H}(t) = \mathcal{H}_L(t) - \langle \mathcal{H}_L \rangle \quad (3)$$

$$\mathcal{H}_Z = -\omega_I I_Z - \omega_S S_Z \quad (4)$$

$$\mathcal{H}_L(t) = \mathcal{H}_d^H(t) + \mathcal{H}_d^{IS}(t) + \mathcal{H}_J^{IS}(t) \quad (5)$$

$$\mathcal{H}_d^H(t) = \sum_{i<j} \sum_{m=-2}^{2} A_{2m}(I_i,I_j) F_m^{ij*}(t) \quad (6)$$

$$\mathcal{H}_d^{IS}(t) = \sum_{i \neq s} \sum_{m=-2}^{2} A_{2m}(I_i,S_s) F_m^{is*}(t) \quad (7)$$

$$\mathcal{H}_J^{IS}(t) = \sum_{i \neq s} J_{is}(t) I_i \cdot S_s(t) \quad (8)$$

$$F_m^{ik}(t) = -\frac{\mu_0}{4\pi} \gamma_i \gamma_k r_{ik}^{-3}(t) C_{2m}(\theta_{ik}(t),\Phi_{ik}(t)) \quad (9)$$

$$A_{2m}(I,K) = (I \cdot \nabla)(K \cdot \nabla)(r^2 C_{2m}(\theta,\Phi)) \quad (10)$$

$$C_{2m}(q,F) = \left(\frac{4\pi}{5}\right)^{1/2} Y_{2m}(\theta,\Phi) \quad (11)$$

where $A_{2m}(I,K)$, $C_{2m}(\theta,\Phi)$, and $Y_{2m}(\theta,\Phi)$ are second rank spherical tensors, Racah functions, and spherical functions, respectively, $\gamma_i = \gamma_j = \gamma_I$ and $\gamma_s = \gamma_S$ are gyromagnetic ratios of the spins, r_{ik} are distances between the interacting spins i and k, and $\theta_{ik}(t)$ and $\Phi_{ik}(t)$ are time-dependent angles defining the orientation of the interspin vectors r_{ik} in the laboratory frame with the z axis parallel to the $\mathbf{B}_0$ field.

$J_{is}(t) = (J_{is},0)$ is a step function in the presence of the exchange process and J_{is} is the spin–spin coupling constant for nearest neighbors.

In the weak collision case[4,11,13] and high-field approximation ($\mathcal{H}_0 \approx \mathcal{H}_Z$) the spin–lattice relaxation time T_1 for spin **I** may be calculated from the following equation:

$$\frac{1}{T_1} = \frac{1}{2Tr(I_z^2)} \int_{-\infty}^{\infty} Tr\{[\tilde{\mathcal{H}}(t),I_z][\tilde{\mathcal{H}}(t+\tau),I_z]^+\}\, d\tau \quad (12)$$

where

$$\tilde{\mathcal{H}}(t) = e^{i\mathcal{H}_Z t} \mathcal{H}(t) e^{-i\mathcal{H}_Z t} \quad (13)$$

Using eqs 1–13 and transformation and commutation relations for spherical tensors,[14,15] one can obtain the following expressions for the relaxation time T_1 in the presence of fast spin diffusion:

$$\frac{1}{T_1} = I(I+1) N_I^{-1} \sum_{i \neq j} [J_1^{ij}(\omega_I) + 4J_2^{ij}(2\omega_i)] + N_I^{-1} \sum_{i,s} [J_0^{is1}(\omega_s - \omega_I) + 3J_1^{is0}(\omega_i) + 6J_2^{is1}(\omega_s + \omega_I) + J^{is1}(\omega_s - \omega_I)] \quad (14)$$

where $i = 1, \ldots, N_I$ and $s = 1, \ldots, N_S$ and $J_v(\omega) =$

$(J_m^{ij}(\omega),J_n^{isq}(\omega),J^{is}(\omega))$ are spectral densities (Fourier transforms) of the correlation functions $K_v(t)$:

$$J_v(\omega) = \int_{-\infty}^{\infty} K_v(t) e^{i\omega\tau}\, d\tau \tag{15}$$

for $K_v(\tau) = (K_m^{ij}(\tau),K_n^{isq}(\tau),K^{isq}(\tau))$ in the respective forms

$$K_m^{ik}(\tau) = \langle X_m^{ik}(\tau) X_m^{ik*}(t+\tau)\rangle = \langle |X_m^{ik}|^2\rangle k^{ik}(\tau) \qquad (k = j, s) \tag{16}$$

$$K_n^{isq}(\tau) = K_n^{is}(\tau) K_s^q(\tau) \tag{17}$$

$$K^{isq}(\tau) = K^{is}(\tau) K_s^q(\tau) \tag{18}$$

$$K_s^q(\tau) = \langle S_s^q(t) S_s^{q*}(t+\tau)\rangle = \frac{1}{3} S(S+1) k_s^q(\tau) \tag{19}$$

$$K^{is}(\tau) = \langle J_{is}'(t) J_{is}'(t+\tau)\rangle = \langle J_{is}'\rangle^2 k^{is}(\tau) \tag{20}$$

$$X_m^{ik}(t) = F_m^{ik}(t) - \langle F_m^{ik}\rangle \qquad (k = j, s) \tag{21}$$

$$J_{is}'(t) = J_{is}(t) - \langle J_{is}\rangle \tag{22}$$

$$S_s^q = (S_s^0, S_s^{\pm 1}) \equiv \left(S_s^z, \pm\frac{1}{2^{1/2}}(S_s^x \pm i S_s^y)\right) \tag{23}$$

It is useful to introduce the reduced correlation functions

$$k_v(\tau) = K_v(\tau)/K_v(0)$$

and their reduced spectral densities (Fourier transform), $j_v(\omega)$, expressed by an equation analogous to eq 15. In most cases one obtains an exponential form[11] of the type

$$k_v(\tau) = \exp(|\tau|/\tau_{cv})$$

with effective correlation times τ_{cv} for molecular motions.

Hence the following equation is obtained:

$$j_v(\omega) = j(\omega,\tau_{cv}) = \frac{2\tau_{cv}}{1 + \omega^2 \tau_{cv}^2} \tag{24}$$

This equation may be applied not only in the case of molecular reorientations, librations, and exchange but also in the presence of fast relaxation of nonresonant spins and in the case of translational diffusion with long mean flight path.[16] In a special case $N_I = N_S = 1$, $I = S = 1/2$ one gets the Solomon expression for $1/T_1$ in the presence of isotropic reorientations.[17]

The above general formalism can be also applied for the theoretical description of proton spin–lattice relaxation times T_1 in oxygen-doped polymers. In such a case one takes $I = 1/2$ for the proton spins and $S = 1$ for the resultant electron spin of the paramagnetic oxygen molecule in the ground state[18] $^3\Sigma_g^-$ and $\omega_S \gg \omega_I$. To adapt this theoretical formalism to computer calculation and to the least squares fit of the experimental results, it was necessary to introduce several simplifying assumptions which reduce the number of fitting parameters.

1. Molecular motions are quasi-isotropic; i.e. correlation times and lattice sums $\sum_{i\neq k}\langle |X_m^{ik}|^2\rangle$ are independent of m. In fact, in the presence of quasi-isotropic molecular motions, average values of the lattice sums can be expressed by average squares of Racah functions, which in turn are independent of m.[19,20]

2. There is fast spin diffusion between the fraction of protons, which are strongly coupled to oxygen spins S in the complex (adsorption effect) and the remaining fraction of protons, where the **I** − **S** interaction is only intermolecular within the same domain. This spin diffusion is modulated by translational motion of oxygen molecules whose closest distance of approach is a.

3. We consider average effective correlation times for molecular motions (dependent on the temperature T), which obey the Arrhenius law

$$1/\tau_a = a_0 \exp(-E_a/RT) \qquad (a = R, L, E) \tag{25}$$

In particular, we consider the following correlation times: (a) τ_R, correlation time for isotropic motion,

$$\frac{1}{\tau_R} = R_0 \exp\left(-\frac{E_R}{RT}\right)$$

where E_R is the activation energy for motions of the polymeric backbone (crankshaft, torsional motions, local jumps, ...); (b) τ_L, correlation time for the phenyl ring libration,

$$\frac{1}{\tau_L} = L_0 \exp\left(-\frac{E_L}{RT}\right)$$

where E_L is the activation energy for librational motion; (c) τ_{O_2}, the effective correlation time for the oxygen in the complex (aromatic ring)·O_2.

Dipolar and scalar proton–oxygen interactions depend on the motion of the oxygen molecules and their paramagnetic relaxation.[21-23] In the presence of nonresonant spins S (unpaired electrons in O_2 molecules), the scalar interaction has been considered as a function of the correlation time τ_{O_2}, where τ_{O_2} is the effective correlation time for the oxygen in the complex (aromatic ring)·O_2. The oxygen correlation rate $1/\tau_{O_2}$ must be considered as a sum of two terms: (1) an Arrhenius-like term accounting for the exchange[24] in the complex (aromatic ring)·O_2 with $1/\tau_E = E_0 \exp(-E_E/RT)$, where E_E is the binding energy of the complex, and (2) a collision-like term accounting for the random motion due to collisions in the oxygen gas. In accordance with the literature[25] this term has the form

$$\frac{1}{\tau_S} = pT^n \tag{26}$$

If other processes occur which modulate the scalar proton–oxygen interaction,[26] correlation rates can be added to the collision term which generally can be written as follows:

$$\frac{1}{\tau_S} = pT^n + s \tag{27}$$

Under these assumptions the spin–lattice relaxation time for protons is expressed by the following equation:

$$\frac{1}{T_1} = u\left(A_{IS}\frac{C'}{C'^2 + \omega_S^2} + B_{IS}\frac{C}{C^2 + \omega_I^2} + E_{IS}\frac{E}{E^2 + \omega_S^2}\right) + F_{IS}\left(\frac{7}{3}J(\omega_S,K') + J(\omega_I,K)\right) + G_{II}\left(\frac{F}{F^2 + \omega_I^2} + \frac{4F}{F^2 + 4\omega_I^2}\right) \tag{28}$$

$$J(\omega,x^{-1}) = \frac{x^{-1}}{x^{-2} + \omega^2}, \qquad x^{-1} = (K,K') \tag{29}$$

$$A_{IS} = \frac{7}{3}B_{IS} = \frac{14}{3}S(S+1)N_I^{-1}\sum_{i\neq s}\langle(X_0^{is})^2\rangle \tag{30}$$

$$E_{IS} = \frac{2}{3}S(S+1)N_I^{-1}\sum_{i\neq s}\langle J'(t)^2\rangle \equiv \frac{8\pi^2}{3}S(S+1)J_e^2 \tag{31}$$

$$F_{IS} = \frac{8\pi n_0}{5d^3}\left(\frac{\gamma_S\gamma_I\hbar\mu_0}{4\pi}\right)^2 S(S+1) \tag{32}$$

$$G_{II} = 2I(I+1)N_I^{-1}\sum_{i\neq j}\langle(X_0^{ii})^2\rangle \tag{33}$$

$$F = R_0\exp\left(-\frac{E_R}{RT}\right) + L_0\exp\left(-\frac{E_L}{RT}\right) \tag{34}$$

$$E = E_0\exp\left(-\frac{E_E}{RT}\right) + pT^n + s \tag{35}$$

$$C' = C = D + pT^n + s \tag{36}$$

$$K' = K = pT^n + s + f \tag{37}$$

where J_e is an effective spin–spin coupling constant in hertz. In the case of fast translational diffusion,[26,27] when $K = K' = 1/\tau$, and for arbitrary mean squared flight distances one should insert into eq 28 the following general expressions for the translational spectral density:

$$J(\omega,\tau) = 6Re\left[\int_0^\infty \frac{1 + D\tau\varrho^2}{2D\varrho^2 - i\omega(1 + D\tau\varrho^2)} J_{1/2}^2(a\varrho)\frac{d\varrho}{\varrho}\right] \tag{38}$$

where D = diffusion constant,

$$J_{1/2}(a\varrho) = \left(\frac{2}{\pi a\varrho}\right)^{1/2}\sin(a\varrho)$$

is a Bessel function, and a is the distance of the closest approach of oxygen and protons. It is worth noticing that the weak collision case applies well to solid polymeric systems even at rather low temperatures;[4] however at sufficiently low temperatures (for instance, for degassed polystyrenes at $T \leq 150$ K) the strong collision region is reached.

For oxygen-rich aromatic polymers, at low temperatures, T_1 relaxation is mostly due to proton–oxygen interactions and the dipolar H–H term is negligible. However in the case of fully or partly degassed aromatic polymers, at low temperatures, the H–H dipolar term must be introduced, with a strong collision treatment.[28]

Best Fit of Experimental Data and Parameters Discussion

Equation 28 can be written in a parametric form and optimized by introducing the terms discussed above. In all cases the optimization procedure must begin with the data relative to the degassed polymer.

In this case the only term to be introduced is the dipolar proton–proton interaction

$$G_{II}\left(\frac{F}{F^2 + \omega_I^2} + \frac{4F}{F^2 + 4\omega_I^2}\right)$$

i.e. the term derived from BPP theory.

In the case of degassed syndiotactic polystyrenes (see Figure 1), relative to a γ form, best-fit experimental data lead to the values of E_R and E_L. In this respect, data relative to degassed samples for polystyrenes do not differ from previously published data on other polymers.[4]

The parameters E_R and E_L obtained in this way can be used as starting values for the best fit of eq 28.

Best fit functions relative to α, β, and γ undegassed polymorphous forms are shown in Figures 2a–c and 3a–c (solid lines). The obtained parameters are shown in Tables 1 and 2. Table 1 is relative to physicochemical parameters obtainable from the proton dipole–dipole interaction. The parameters shown in Table 2 are relative to the specific interaction aromatic polymer and oxygen. It must be also noted that, due to the particular temperature dependence of experimental data, the two sets of parameters reported in Tables 1 and 2 are almost totally uncorrelated. Before the actual values found for each parameter and their physicochemical meaning are discussed, it is worth noting that using "ab-initio" calculations,[29] it has been recently shown that the ground state energy of the complex (aromatic ring)-O_2 is lower than the energy for separate C_6H_6 and O_2. *As a consequence it is not surprising that oxygen molecules are selectively adsorbed on aromatic rings.*

E_R has been previously defined as the activation energy for motions of the polymeric backbone. These motions become relevant to the relaxation process at high temperatures. As a consequence this energy must show little or no dependence on the polymorphism and on the presence or absence of oxygen. In fact, as shown in Table 1 all values relative to E_R are the same within experimental error and are not sensitive to the presence of oxygen. At temperatures higher than the T_g it has been previously shown[1,2] that all relaxation values for all polymorphous polystyrenes, degassed or undegassed, are the same within experimental error.

E_L has been previously defined as the activation energy for the libration motion of the aromatic ring. From Table 1 it can be seen that different values for E_L are obtained in different polymorphous forms. In fact the following order is obtained: $\beta > \alpha > \gamma$. It is also worth noting that the libration energies obtained on degassed or undegassed samples are the same. Since the spin diffusion process is inactive only at rather low temperatures, the libration energies obtained in this way are the average value between the actual value for the crystalline fraction and the value of its amorphous counterpart. Even with this limitation the obtained ordering is consistent with crystallographic data. In fact, the β polymorphous form is characterized by a tighter molecular packing than the α form[30] (crystallographic density of the α form is 1.033 g/cm^3 while it is 1.076 g/cm^3 for the β form).

In the above expression, R_0 and L_0 are pre-exponential terms, in units of 10^9 s^{-1} and G_{II} is the proton–proton dipolar coupling, in kilohertz. It must be noted that the energies relative to the backbone overall motion (E_R) and to the phenyl ring libration can be obtained from the data relative to degassed polymers. These energies are quite well determined (see Table 1). The value of these energies is determined only in the portion of the curves where the spin-like interaction is the dominant term. Thus, data relative to degassed or undegassed polymers give best-fitted energies with the same value (see Table 1). On the contrary the portion of the experimental curves, at low temperature, where the scalar spin-unlike term dominates, is mostly sensitive

Table 1. Physico-Chemical Best-Fitted Parameters, E_R, E_L, R_0, and L_0 Obtained from the Proton Dipole–Dipole Interactions, for α, β, and γ Polymorphous Polystyrenes[a]

	α	β	γ	γ degassed
		30 MHz		
E_R	31.3 ± 0.5	31.4 ± 0.5	31.1 ± 0.5	31.1 ± 0.5
E_L	5.5 ± 0.3	6.7 ± 0.3	4.6 ± 0.3	4.6 ± 0.3
R_0	0.06 ± 0.02	0.15 ± 0.04	0.13 ± 0.04	0.10 ± 0.04
L_0	$3 \times 10^{-5} \pm 1 \times 10^{-5}$	$6 \times 10^{-6} \pm 2 \times 10^{-6}$	$3 \times 10^{-5} \pm 1 \times 10^{-5}$	$2 \times 10^{-5} \pm 1 \times 10^{-5}$

[a] The last column in the table refers to a well-degassed γ polymorphous form. Reported values result from the best fit of experimental data collected at 30 MHz.[36]

Table 2. Physico-Chemical Best-Fitted Parameters E_0, E_E, u, and p Obtained from the Proton–Oxygen Scalar Interaction, for α, β, and γ Polymorphous Polystyrenes[a]

	α_c	β_c	γ_c	α_a	β_a	γ_a
			57 MHz			
E_0	$3.6 \times 10^6 \pm 0.5 \times 10^6$	$1.0 \times 10^5 \pm 0.5 \times 10^5$	$5.2 \times 10^5 \pm 0.5 \times 10^5$	$4.1 \times 10^6 \pm 0.5 \times 10^6$	$3.2 \times 10^5 \pm 0.5 \times 10^5$	$4.1 \times 10^5 \pm 0.5 \times 10^5$
E_E	14 ± 1	11 ± 2	11 ± 1	13 ± 2	12 ± 2	12 ± 1
u	7.0 ± 2	1.3 ± 0.3	15 ± 5	20 ± 6	3.3 ± 0.8	65 ± 15
p	12 ± 5	50 ± 20	14 ± 6	17 ± 7	129 ± 50	22 ± 9
			30 MHz			
E_0	$3.6 \times 10^6 \pm 0.2 \times 10^5$	$1.3 \times 10^6 \pm 0.1 \times 10^5$	$5.2 \times 10^5 \pm 0.3 \times 10^5$	$4.1 \times 10^6 \pm 0.2 \times 10^6$	$3.2 \times 10^5 \pm 0.2 \times 10^5$	$2.8 \times 10^6 \pm 0.1 \times 10^5$
E_E	16 ± 2	13 ± 1	10 ± 1	14 ± 1	12 ± 2	10 ± 1
u	3.0 ± 1	0.8 ± 0.2	8 ± 3	11 ± 4	4 ± 1	54 ± 16
p	20 ± 8	47 ± 18	30 ± 12	89 ± 35	49 ± 20	20 ± 8

[a] Reported values result from the best fit of experimental data collected at 30 and 57 MHz.

to the energy relative to the complex oxygen–aromatic ring. This means that the two sets of parameters, E_R and E_L, relative to the polymer motions, and E_E relative to the complex oxygen–aromatic ring are almost independent.

Table 2 shows the results of optimization of parameters associated with eq 28 for terms due to the aromatic polymer–oxygen complex.

Before the actual values of the parameters are discussed, two fundamental remarks must be made:

(i) The introduction of the dipolar term regarding the spin-unlike interaction leads to a best fit of eq 28. However the parameters obtained from this best-fitting procedure are fully uncorrelated not only within the class of polymorphous polystyrenes but also within the amorphous part of each polymorph and its crystalline counterpart.

(ii) The introduction of the term containing the translational correlation time of oxygen and its rate, which is proportional to the oxygen diffusion constant, leads to an optimized coefficient F_{IS} lower by at least 2 orders of magnitude than any other coefficient. Thus in the case of syndiotactic polymorphous polystyrenes this term can be omitted. In fact the amount of adsorbed oxygen is sufficient to act as a relaxation contrast agent but not sufficient to require a term which implies the presence of a large number of oxygen molecules frequently jumping from one aromatic ring to another one.

The introduction of the proton–oxygen scalar term into eq 28 allows for coherent optimization, as reported in Table 2 and discussed in the following.

The scalar term itself contains two terms, reported in eq 35.

The term $pT^n + s$ derives from a collision term[31,32] of the type

$$\frac{1}{\tau} = pT^n \exp\left(-\frac{E}{RT}\right)$$

with $n = 1/2$ and E an activation energy for molecular motions of the oxygen itself.

Note that the model can be further simplified. In fact in the collision term

$$\frac{1}{\tau} = pT^{1/2} \exp\left(-\frac{E}{RT}\right)$$

the term $\exp(-E/RT)$ can be considered constant; i.e. the activation energy for vibrational motions of the oxygen can be supposed constant in the experimental temperature range.

As a consequence, the collision term becomes simply

$$\frac{1}{\tau_{O_2}} = \frac{1}{\tau_E} + \frac{1}{\tau_S} = E_0 \exp\left(-\frac{E_E}{RT}\right) + pT^{1/2}$$

The numerical results are represented as continuous lines in Figures 2a–c and 3a–c, in order to be seen with the corresponding experimental points.

The physico-chemical parameters derived from the best fit procedure and shown in Table 2 are u, E_0, E_E, and p.

Here, u has been defined as the maximal molar fraction, ‰, of adsorbable oxygen in each phase. The evaluation of the term u constitutes an important chemical application of the outlined theory. In fact a scale of u terms gives an evaluation of the polymer as an oxygen scavenger. *Thus, this evaluation is fundamental in the study of membranes used for gas separation.*

The evaluation of u in different polymorphs is outlined in Table 3. In this way the following scale of oxygen adsorption can be obtained:

$$\beta_c < \beta_a \leq \alpha_c < \gamma_c \leq \alpha_c \ll \gamma_a$$

where the index "c" means crystalline phase and the index "a" means amorphous phase; this scale relates well to the permeability scale[33,34] for organic solvents, thereby showing that $\beta < \alpha < \gamma$.

The parameter E_E has been defined as the binding energy for the complex (aromatic ring)·O_2.

The evaluation of E_E in different polymorphs is reported in Table 4. The mean value of E_E over all polymorphous forms is about 12 kJ/mol. The value of the binding energy for the complex C_6H_6·O_2 resulting from "ab initio" calculation[29] or from UV spectroscopy[35] was about 6 kJ/mol. A factor of 2 in energy was found in the complexes with aromatic polymers. Thus it might

Table 3. Mean Values $\bar{u}$ over Best Fit Values of Parameter u Obtained from Experimental Data Collected at 30 and 57 MHz, for Crystalline ("c") and Amorphous ("a") Fractions of α, β, and γ Polymorphous Polystyrenes

α_c	5 ± 2	α_a	15 ± 5
β_c	1.1 ± 0.2	β_a	3.6 ± 0.3
γ_c	12 ± 3	γ_a	59 ± 5

Table 4. Mean Values $\bar{E}_E$ over Best-Fitted Values of Parameter E_E Obtained from Experimental Data Collected at 30 and 57 MHz, for Crystalline ("c") and Amorphous ("a") Fractions of α, β, and γ Polymorphous Polystyrenes

α_c	15 ± 1	α_a	13.5 ± 0.5
β_c	12.0 ± 0.6	β_a	11.7 ± 0.3
γ_c	10.4 ± 0.5	γ_a	11.2 ± 0.7

Table 5. Mean Value of the Ratio E_0(cp)/E_0(ap) Due to the Crystalline Phase ("cp") and Amorphous Phase ("ap") within the Same Polymorphous form for α, β, and γ Polymorphous Polystyrenes

	30 MHz	57 MHz
α	0.88	0.88
β	0.41	0.31
γ	0.18	0.13

be reasonable to advance the hypothesis that the complex is due to two interfacing aromatic rings and one oxygen molecule. It must be noted that in the γ crystalline form the distance between two aromatic rings is 7.7 Å. This distance is long enough to insert an oxygen molecule whose distance from each aromatic ring is ~3.9 Å. This distance matches well the minimum found by ab initio calculations.[29]

The parameter E_0 has been defined as the preexponential factor in the term accounting for the exchange in the complex (aromatic ring)-O_2. The mean values of the ratio E_0(cp)/E_0(ap) between E_0 values due to the crystalline phase (cp) and amorphous phase (ap) within the same polymorphous form are reported in Table 5.

These values are independent of frequency. In fact experimental values at 30 and 57 MHz are the same within experimental errors, although the ratio E_0(cp)/E_0(ap) is dependent upon the polymorphism.

The parameter p has been defined as the coefficient of the collision term. Errors in this parameter are much higher than errors observed in the previously discussed parameters. Measurements at different magnetic fields are necessary in order to verify if this parameter shows some kind of dependence on the frequency or if the high error is only due to experimental errors.

Finally, for the sake of clarity, the parametric equation used for the final best fit has been reported:

$$\frac{1}{T_1} = u\left(E_{IS}\frac{E}{E^2 + \omega_S^2}\right) + G_{II}\left(\frac{F}{F^2 + \omega_I^2} + \frac{4F}{F^2 + 4\omega_I^2}\right)$$

where

$$E = E_0 \exp\left(-\frac{E_E}{RT}\right) + pT^{1/2}$$

It can be seen that the number of parameters used to fit the experimental data is quite reasonable and much lower than the theoretical number shown in eq 28.

Conclusions

The good match between the previously outlined theory and the experimental relaxation values allows the accurate determination of physico-chemical parameters related to oxygen adsorbed on aromatic polymers. Oxygen acts as a powerful relaxation contrast agent. As a consequence those motional parameters which are active in the Larmor frequency range can be evaluated. In aromatic polymers, and in particular for the case of polymorphous polystyrenes, these parameters are of two types, i.e. parameters relative to motions of the polymer, such as backbone motions or phenyl ring librations, and physico-chemical parameters relative to the binding of the oxygen in the complex with the aromatic polymer. The differentiation of libration energies in different polymorphs of syndiotactic polystyrene demonstrates the strength of the method. The possibility of measuring the actual amount of adsorbed oxygen as a function of temperature is the most important application of the theory. In this regard, examples will be discussed from other aromatic polymers able to act as oxygen scavengers.[10]

The quench of the dipolar interaction between protons and oxygen is not fully understood and will be investigated further.

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