Relaxometric Study of Secondary Transitions in Aromatic Polymers

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ABSTRACT: An accurate description of minor transitions occurring at low temperatures in aromatic polymers can be obtained by a combination of relaxometric methods. In each technique, suitable contrast agents will be chosen, the most suitable for each detection. In this paper, the method will be applied to SAN (styrene−acrylonitrile) copolymers. Oxygen can be selectively absorbed on aromatic polymers. The selective absorption of paramagnetic oxygen causes numerous effects well observable by the ^{1}H NMR relaxometric method since it acts as a relaxation contrast agent. In SAN copolymers, the above observations allow a precise measurement of γ transitions due to the phenyl ring libration. Another small molecule well adsorbed by aromatic rings is water. Due to its strong dipole moment, water acts as a contrast agent for dielectric relaxation measurement. In SAN copolymers, γ transitions, barely observable at low temperature with extreme uncertainty, appear strong and well resolved in the presence of water. Thus a combination of these two relaxometric methods allows a precise description of the interruption of phenyl ring libration, the true cause of the relaxometric behavior. Dielectric and NMR relaxations are also in agreement with weak transitions observed by dynamic mechanical tan δ measurements.

Introduction

Low-temperature transitions present in polystyrene homo- and copolymers are supposedly due to phenyl ring libration.

In fact, in the case of atactic polystyrene homopolymer, dynamic mechanical measurements performed by various authors[1−3] gave evidence of a number of secondary relaxation processes, one of which, identified as a γ transition, was ascribed by Yano and Wada[3] to the rotation of the phenyl groups. The attribution was based on the fact that the γ peak does not appear in dielectric loss, this being explained by considering that no electric dipole orientation is associated with the rotation of the phenyl ring.

The occurrence of a secondary relaxation process in styrene−acrylonitrile (SAN) random copolymers has been reported by Cook et al.[4] They detected a β transition by dielectric spectroscopy in a temperature range of −80 to −40 °C and in a frequency range of 10^1−10^5 Hz. The process was found to exhibit an Arrhenius type temperature dependence, with an activation energy of 39 kJ/mol. The authors tentatively ascribed the process to local motion of the dipolar C−N groups. In the same work, dynamic mechanical measurements were carried out by a torsion pendulum with a frequency of about 1 Hz, but no evidence was found of any relaxation processes other than the α one (corresponding to the glass transition).

More recently, Paciello et al.[5] reported a dielectric investigation on SAN-based blends: a β process was found in pure SAN in the ranges 20−80 °C and 10^3−10^6 Hz, with an activation energy of 70 kJ/mol.

Such a problematic situation may be due to the relatively low relaxation strength of these secondary processes, resulting in low intensity of the mechanical and dielectric signals. Nevertheless, a comparison of the results of different techniques such as NMR relaxometry, dynamic mechanical analysis, and dielectric spectroscopy can be extremely useful in the identification of the molecular processes responsible for the observed relaxations and is therefore worth attempting.

We will show that the use of suitable contrast agents allows precise, well-defined, unambiguous measurements.

Oxygen can be selectively adsorbed on aromatic systems.[6]

The selective absorption of paramagnetic oxygen on aromatic polymers causes numerous effects well observable by ^{1}H NMR relaxometric methods. The main effect is that, when the temperature is lowered, a marked shortening of the spin−lattice relaxation (T_1) is observed.[7] Moreover, in some aromatic polymers, at temperatures adequately low, a full interruption of the spin diffusion process is observable. As a consequence, protons belonging to the aromatic rings relax much faster than backbone or aliphatic protons.[8] The amount of sorbed oxygen is different in different polymorphs and much higher in the amorphous fractions with respect to their crystalline counterparts.[9] Since different polymorphs exhibit very different T_1 relaxation times, their differentiation is very clear and they can be efficiently studied by NMR relaxometric methods. Moreover, in semicrystalline aromatic polymers, NMR relaxometry

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Table 1. SAN Samples Characterization[a]

sample	AN content (wt %)	AN content (molar ratio)	M_w	M_n
SAN A	25	0.395	100 300	59 100
SAN B	33	0.490	80 600	47 900

[a] Samples: SAN A and SAN B, obtained by a continuous bulk polymerization process. (AN) = acrylonitrile content; weight average (M_w) and number average (M_n) molecular weights. Uncertainties better than 3% of nominal value.

can be efficiently used to obtain the crystalline/amorphous ratio. Another advantage is that the extreme spread of T_1 values, induced by oxygen absorption, can be used to measure second-order transitions.[10] In fact, even small effects may cause variations in the amount of adsorbed oxygen; thus high-order transitions, barely observable with other physical methods, can be studied by NMR relaxometry.

In connection with the possible absorption of dipole-bearing molecules on aromatic polymers, dielectric relaxometry may be of particular interest. The interaction of water with the aromatic rings can give rise to strong electric dipoles able to act as contrast agents for the measurements of dielectric losses. Thus, again, high-order transitions can be detected by dielectric relaxation measurements obtained in the presence of water used as a contrast agent.

In the present work, SAN samples have been studied by dynamic mechanical spectroscopy, by NMR relaxometry, and by dielectric spectroscopy in order to obtain accurate information on the secondary processes occurring in SAN and on the interactions of small molecules with aromatic rings.[11]

Materials and Methods

Two SAN samples have been considered, SAN A and SAN B, obtained by a continuous bulk polymerization process and supplied by Enichem (Mantova Plants). Their acrylonitrile (AN) content and weight average (M_w) and number average (M_n) molecular weights, with uncertainties better than 3% of nominal value, are reported in Table 1.

Dynamic mechanical measurements were carried out by a Rheometrics mechanical spectrometer (RMS 800) in the torsion rectangular geometry, with an imposed sinusoidal strain wave (maximum strain 0.5%, frequency 1 Hz) in the temperature range −150 to +150 °C. Specimens (dimensions: 2 mm × 12 mm × 50 mm) were compression molded at 200 °C.

NMR Relaxation. All pulse low-resolution ^{1}H NMR spectra were measured at 81 MHz on a commercial spectrometer "Spinmaster" (Stelar, Mede, and Pavia, Italy). The instrument dead-time is 8 μs. The 90° pulse width was 3.5 ± 0.1 μs.

Samples were contained in standard 5 mm diameter NMR tubes. To ensure a suitable oxygen source,[10] with an amount always much larger than the maximum adsorbed fraction, a big glass cylinder was sealed on the top of each tube. The cylinder, volume ≈250 cm^3, contained air, which at room temperature has a pressure ≈1 atm.

All samples were finely powdered and slightly compressed in the NMR tube. The height of the sample was always kept well within the NMR coil (4−5 mm).

A variable-temperature unit (Stelar VTC90) equipped with a N_2 evaporator system was used in the temperature range 125−300 K. A chromel−alumel thermocouple placed in the probe head, at a distance less than 1 mm from the coil, ensured good temperature control (±0.1 °C).

Spin−lattice relaxation times T_1 were measured with the aperiodic saturation recovery sequence consisting of a train of 15 (π/2) pulses spaced out in an aperiodic way. The sequence was run according to a multiblock, multiscan procedure; in each experiment, the number of blocks, corresponding to the number of different τ delays, was at least 64 for single exponential decays and 128 for multiple exponential decays. The first 12 points after the dead time, in each block, were considered for the evaluation of the magnetization, obtained as a result of the aperiodic saturation recovery experiment; to minimize the experimental errors, their mean value was used for the calculation of relaxation values.

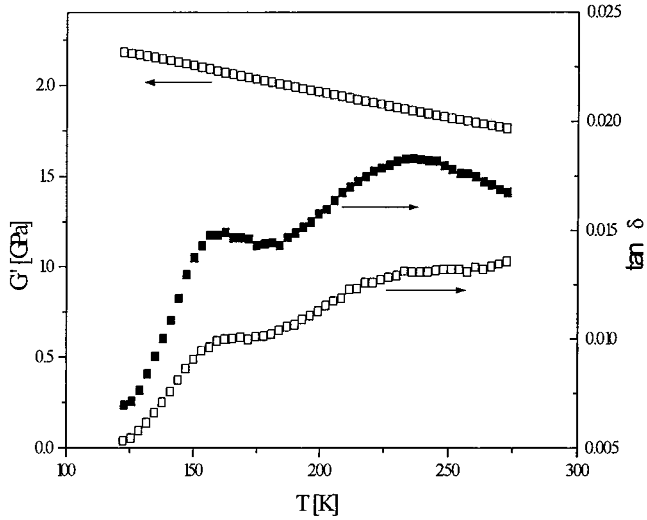

Figure 1. Storage elastic shear modulus G′ (upper curves) and the loss factor tan δ (bottom curves) resulting from dynamic mechanical measurements, plotted vs temperature for SAN A (open symbols) and SAN B (solid symbols).

NMR Data Analysis. Aperiodic saturation 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 having relative spin densities A_i, while A_0 is the value of the magnetization after a single π/2 pulse. This equation was fitted with a commercial computer program "STEFIT",[12] which uses a "Simplex" algorithm.[13] The experimental points deviation was compared with the calculated one and their compatibility tested to a 99% 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 evaluated and compared with a binomial distribution: only distributions within 99% confidence level were accepted.

Reported data are to be considered with the following limits: single exponential, error within 2%; multiple exponentials, error on the longest T_i value and on the other T_i values within 2% and 5%, respectively; error on A_i values less than 10% for each component.

Dielectric measurements were performed with spectrometer built by TNO (Netherlands organization for applied scientific research) around a Schlumberger type 1250 frequency response analyzer. A temperature range of −160 to +130 °C and a frequency range of 10^{-2}−10^3 Hz were used. Specimens, in the form of compression-molded disks (thickness about 0.1 mm, diameter about 38 mm), were gold plated by vacuum sputtering before the tests.

Results and Discussion

Dynamic Mechanical Measurements. The storage shear modulus G′ and the loss factor tan δ for the two samples SAN A and SAN B are plotted as functions of temperature in Figure 1.

A limited portion of the measured data, from 110 to 273 K, is here shown, the only significant feature appearing in the higher temperature range being the glass transition, which is not relevant to the present discussion.

Two secondary relaxations are clearly apparent in Figure 1, with maximum tan δ values at about 243 K

(β transition) and 158 K (γ transition), respectively. The strength of both the observed relaxations is larger for the higher AN content sample, SAN B.

NMR Relaxation in the Presence of Paramagnetic Species. As previously mentioned, oxygen, selectively sorbed on aromatic rings, causes a strong shortening of relaxation times. The effect usually is well observable on T_1 relaxation while the spin–spin relaxation T_2 is usually too short to be measured and its value can be obtained only by line width studies.

At temperatures below the glass transition, $T_{1,\mathrm{diamagnetic}}$, in the absence of oxygen, is very long, of the order of few seconds. In the presence of air, the observed values can be ascribed almost completely to the scalar term of the oxygen–polymer interaction. A full treatment of the T_1 relaxation in the presence of sorbed O_2 has been given in detail elsewhere;[8,9,14] however, for the sake of clarity, a brief discussion is reported in the following.

The equation for the relaxation rate results as a sum of three terms.

First term:

$$\frac{1}{T_{1d}^{\mathrm{II}}} = G_{\mathrm{II}}\left(\frac{\mathrm{F}}{\mathrm{F}^2 + \omega_{\mathrm{I}}^{\,2}} + \frac{4F}{F^2 + 4\omega_{\mathrm{I}}^{\,2}}\right)$$

where G_{II} is the coupling constant for the dipole–dipole proton interaction and

$$F = R_0 \exp\left[-\frac{E_{\mathrm{R}}}{RT}\right] + L_0 \exp\left[\frac{E_{\mathrm{L}}}{RT}\right]$$

E_{R} being the activation energy for motions of the polymeric backbone and E_{L} the activation energy for phenyl ring libration.

Second term:

$$\frac{1}{T_{1d}^{\mathrm{IS}}} = \frac{4}{15} G_{\mathrm{IS}}\left(\frac{7C}{C^2 + \omega_{\mathrm{S}}^{\,2}} + \frac{3C}{C^2 + \omega_{\mathrm{I}}^{\,2}}\right)$$

where G_{IS} is the coupling constant for the dipole proton–oxygen interaction and $C = F + pT^{1/2}$, where $pT^{1/2}$ is a collision term taking into account the random motion due to collisions in the oxygen gas.

Third term:

$$\frac{1}{T_{1s}^{\mathrm{IS}}} = E_{\mathrm{IS}} \frac{E}{E^2 + \omega_{\mathrm{S}}^{\,2}}$$

E_{IS} is the coupling constant for the scalar proton–oxygen interaction $E = E_0 \exp[-E_{\mathrm{E}}/RT] + pT$, E_{E} being the binding energy for the complex |aromatic ring·O_2|.

Thus the spin–lattice relaxation rate can be written as

$$\frac{1}{T_1} = \frac{1}{T_{1d}^{\mathrm{II}}} + u\left(\frac{1}{T_{1d}^{\mathrm{IS}}} + \frac{1}{T_{1s}^{\mathrm{IS}}}\right)$$

The coefficient u is the maximum molar fraction of absorbable oxygen; thus a scale of u terms for different polymers gives an evaluation of the polymer as oxygen scavenger. The term

$$\frac{1}{T_{1d}^{\mathrm{IS}}} = E_{\mathrm{IS}} \frac{\mathrm{E}}{E^2 + \omega_{\mathrm{S}}^{\,2}}$$

takes into account the interaction between nuclear spins (protons) and unpaired electrons ($S = 1$) belonging to O_2 molecules and, at low temperature, is the dominant term.

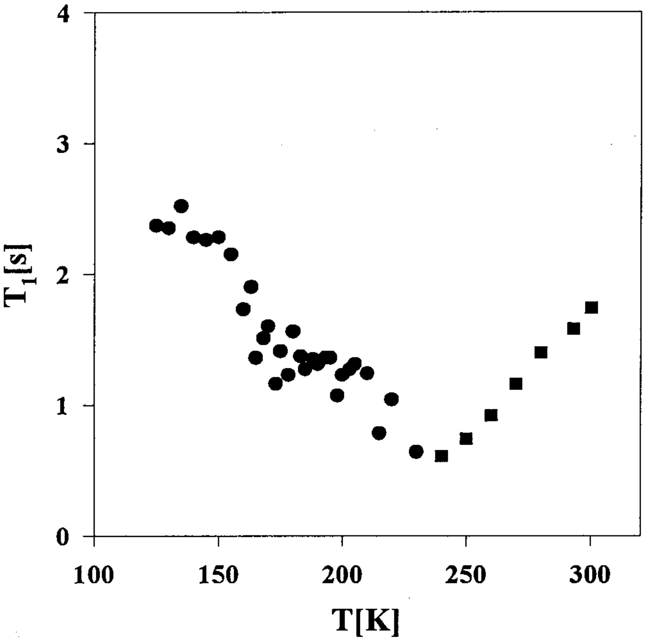

Figure 2. T_1 measurements at 81 MHz. From 130 to 230 K the data reported with the ● symbol are relative to T_1 values of backbone protons. In the same range of temperature, T_1 values of aromatic protons are shorter than 30 ms.

$T_{1\rho}$ is a parameter sensitive to slow motions; in fact, its general expression[15] is

$$1/T_{1\rho} = A\left[\frac{3\tau_{\mathrm{c}}}{1 + 4\omega_1^{\,2}\tau_{\mathrm{c}}^{\,2}} + \frac{5\tau_{\mathrm{c}}}{1 + \omega_0^{\,2}\tau_{\mathrm{c}}^{\,2}} + \frac{2\tau_{\mathrm{c}}}{1 + 4\omega_0^{\,2}\tau_{\mathrm{c}}^{\,2}}\right]$$

since $\omega_1 = 61$ kHz, corresponding to $B_1 = 14$ G and $\omega_0 = 40$ MHz; thus $\omega_0^2\tau_c^2 \gg 1$ and only the first term is active. For a phenyl ring libration (which is a high-frequency motion) one should expect full insensitivity of $T_{1\rho}$, as in Figure 4.

In the case of T_2, a full treatment of relaxation in the presence of oxygen has yet to be given. It must be noted that, below the glass transition, even in the absence of oxygen, $T_{2,\mathrm{diamagnetic}}$ is very short,[16] of the order of 10^{-5} s.

In some cases, however, when the phenyl ring libration is interrupted, the effect of the oxygen is so strong that the line widths (inversely proportional to T_2) are strongly broadened, with a full loss of the signal. This is the case of SAN copolymers, where an interruption of the spin diffusion occurs not only in T_1, as previously described,[17] but also in T_2.

If the rate of exchange of the paramagnetic oxygen on the aromatic rings is slow enough and the amount of oxygen high enough, an abrupt interruption of the spin diffusion process occurs. This process usually is well observable with T_1, which assumes different values for phenyl ring protons and for the backbone ones. In regard to T_2, it must be noted that, in suitable conditions, in the presence of oxygen, and upon interruption of the phenyl libration, a large broadening of the phenyl resonance occurs. Thus the paramagnetic contribution of the oxygen gives rise to very broad lines that can be also shifted with respect to their diamagnetic counterparts.[18] In this way the fraction of the signal due to

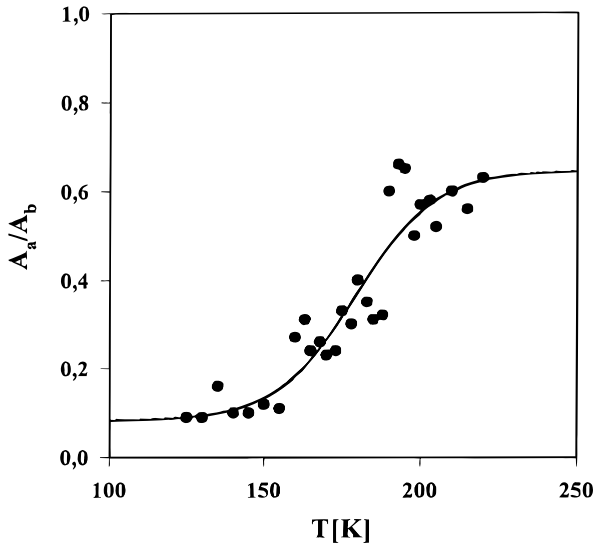

Figure 3. Ratio between the spin densities of fast (A_a) and slow (A_b) T_1 relaxing components in SAN. The carrier frequency is 81 MHz. Five protons (aromatic) contribute to the fast relaxing component and six protons to the slow relaxing component (backbone protons; three of polystyrene and three of the equimolar acrylonitrile).

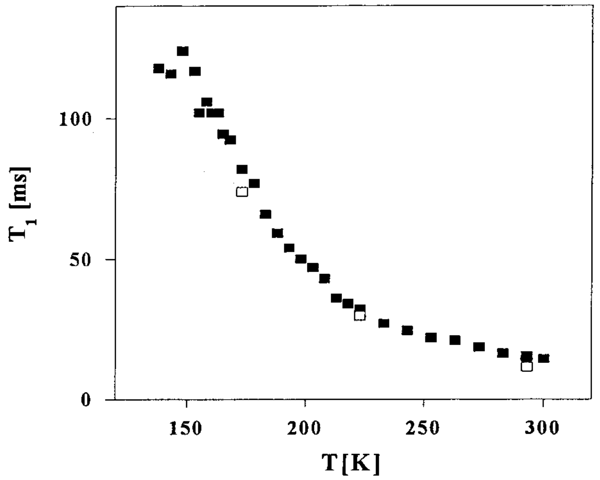

Figure 4. $T_{1\rho}$ measurements: (■) 61 kHz; (□) 53 kHz. The carrier frequency is 40 MHz.

aromatic protons can fully disappear from the spectral region in which the broad resonance of the "normal" spectrum lies. This is the way in which NMR data reported in Figure 3 can be intuitively understood. A full theoretical study of all dynamic parameters in the presence of sorbed oxygen is in progress.

Second-Order Transitions. T_1 of SAN A was studied by lowering the temperature; see Figure 2.

Note that the minimum at ≈240 K is related to the interaction between nuclear spins and O_2 unpaired electrons. In fact, in the absence of oxygen (degassed samples), the minimum is not present.

As usual, when the amount of oxygen is high enough, the spin diffusion process is ineffective and aromatic protons of styrene show a T_1 relaxation much shorter than the value ($T_{1,\text{aliphatic}}$) of backbone protons; however, the spin diffusion process is still operating between aliphatic protons of styrene units and aliphatic protons of acrylonitrile. From a full simulation and data analysis the spin density of the short T_1 component, due to aromatic rings (A_a), and the spin density of the long T_1 component, due the backbone protons (A_b) can be studied. Their ratio is reported as a function of the temperature; see Figure 3.

It must be noted that, in a sample styrene/acrylonitrile 1/1, the maximal theoretical value of this ratio is 0.8 (corresponding to 5 aromatic protons vs 3 + 3 aliphatic protons). However, if, for some reason, the absorption of oxygen increases, the line width of the signal due to aromatic protons becomes too broad to be detected, disappearing into the dead time of the instrument. This is the case of SAN where, in Figure 3, a second-order transition becomes apparent, corresponding to a hindered libration of phenyl rings. This transition, previously described by mechanical losses,[4,19] was quite difficult to measure and even more difficult to ascribe. The NMR relaxometric method shows that the attribution of this secondary transition to the loss of the phenyl libration movement is indeed correct. In fact, phenyl ring libration has the effect of easing the loss of oxygen, while when the ring libration is interrupted, the absorption of oxygen is more efficient and its paramagnetism causes a broadening of the NMR resonance whose FID is lost in the dead time of the instrument. It must be noted that a γ transition observed in atactic polystyrene[20,21] was tentatively attributed to the loss of libration movement. Again, the same type of transition has been also observed in unsaturated polyester resins containing polystyrene[22] and attributed to the loss of the libration movement.

However, the only indication about this type of transition derives from dynamical mechanical investigation, i.e., the loss tangent vs temperature, while the storage modulus seems completely unaffected. The ^{13}C spectra, performed in CP-MAS, do not seem sensitive, it is even possible that some relaxation parameter might give further information; this type of measurement, however, is not trivial.

Phenyl ring libration gives rise to transitions so small that most techniques are unable to perform its observation. This is the case of $T_{1\rho}$ measurements, which, performed as a function of the temperature, do not show any γ transition; see Figure 2 and Figure 4.

The plot shown in Figure 4 confirms that the observed transition is related to a high-frequency motion, fully inactive in the kilohertz region and only observable with *ad hoc* methods.

Dielectric Measurements. To make a direct comparison of the dielectric data to the dynamic mechanical ones, specimens were first measured in the same temperature range in which the mechanical secondary relaxations are observed (110−273 K).

Curves plotted by solid symbols in Figure 5 show the results of such measurements expressed by tan δ (the ratio of the imaginary to the real part of the complex permittivity, ϵ''/ϵ') as a function of temperature for the two samples.

Data shown in Figure 5 are measured at 1 Hz, the same frequency used for dynamic mechanical testing (see Figure 1). The same two relaxation processes are revealed by the two experimental techniques, with a remarkable similarity in the position of the tan δ maxima and in the relative height, shape, and width of the loss factor peaks. On the basis of the dielectric data, the high-temperature (β) process and the low-temperature (γ) one result frequency−temperature dependences of the Arrhenius type with activation energies of about 70 and 42 kJ/mol, respectively.

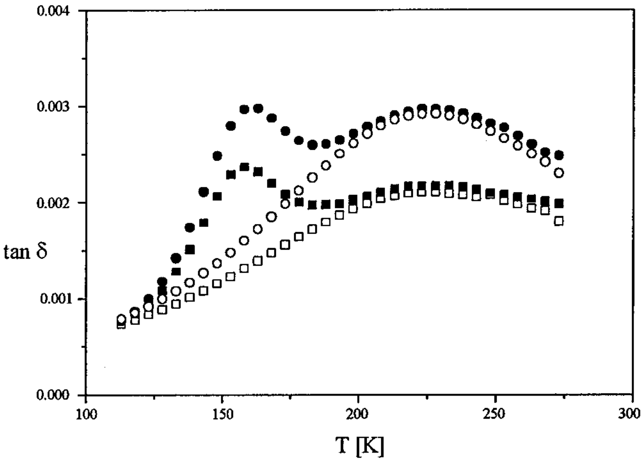

Figure 5. Dielectric loss factor (tan δ) at 1 Hz plotted vs temperature for SAN A (squares) and SAN B (circles). Solid symbols refer to the specimens measured when molded in the presence of humidity; open symbols, to the same specimens measured after thermal treatment in nitrogen flux at 400 K for 1 h.

As previously described, the γ process occurs at temperatures close to that of the secondary transition observed by NMR spectroscopy and is due to the same molecular transition.

The attribution to the motion of the phenyl rings is also confirmed by the not too great difference of the temperature and frequency location of the process here observed with that of the γ relaxation in polystyrene homopolymer, also attributed to the motion of the phenyl groups, which was found by different authors[1-3] to be 133 K at 11.3 Hz, 132 K at 1 Hz, and 193 K at 34 kHz: the activation energy of this relaxation is reported[3] to be 38 kJ/mol, a value close to the one found in SAN.

Even so, a difficulty is encountered in this line of reasoning, due to the fact that no dipole moment is associated with the phenyl group and that, therefore, its motion should not be detected by dielectric spectroscopy (the same consideration was used[3] to confirm the attribution of the γ transition in PS, as mentioned above).

It is well-known from the literature[11] that aromatic polymers are able to adsorb small molecules coordinated to phenyl rings; in particular, the ability of adsorbing water molecules gives rise to a strong electric dipole suitable to be used in dielectric relaxation studies. Again, it must be observed that, when the temperature is lowered, when oxygen adsorption increases,[9] most small molecules are well absorbed by aromatic systems.[11]

If a suitable amount of water molecules is absorbed on phenyl rings, any motion related to the phenyl rings can be observed by dielectric measurements.

Following this hypothesis, we performed a second dielectric measurement on the same specimens previously tested in the low-temperature range: before the new test, however, the specimens were kept for about 1 h at 400 K (that is, about 15 K above the glass transition temperature) in flowing nitrogen, to remove the humidity contained in the material. The result of the second measurement is shown by the open symbols in Figure 5: the γ process has now completely disappeared, while the β relaxation appears almost exactly the same as in the first test run.

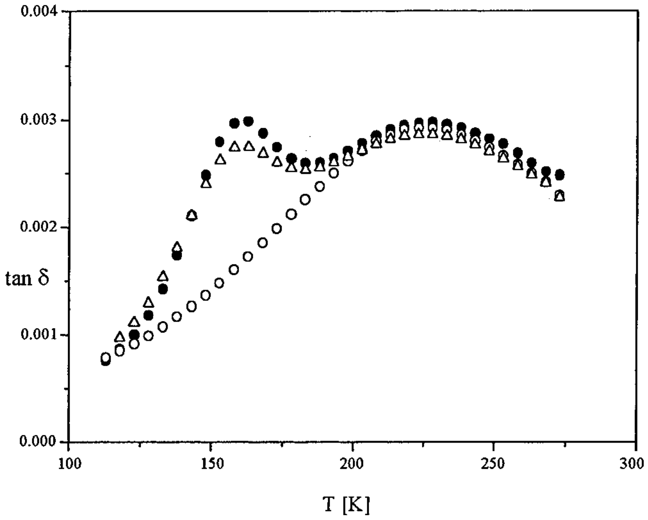

Figure 6. Dielectric loss factor (tan δ) at 1 Hz plotted vs temperature for SAN B. Solid circles refer to the specimen measured as molded, open circles refer to the same specimen measured after thermal treatment in flowing nitrogen at 400 K for 1 h, and open triangles refer to the same specimen measured for the third time after being kept in flowing humid (relative humidity ~75%) air at 400 K for 30 min.

The phenomenon is reversible: In Figure 6 the open triangles show the result of a third measurement on the same SAN B specimen used for the tests reported in Figure 5. Before the third measurement, the specimen was kept for 30 min in humid air flux at 400 K (relative humidity ~75%). By comparing the tan δ vs temperature curve obtained from the third test run with the curves from the previous runs (also plotted in Figure 6), one can observe that the annealing in air makes the γ relaxation appear again, with an intensity very close to that obtained in the first run. The same results were obtained on SAN A.

The permanence in air at $T > T_g$ is likely to restore in the specimen the absorbed humidity that was removed by the annealing in flowing nitrogen before the second test run.

In agreement with previous findings and according to the interpretation of NMR results, we can rationalize the γ relaxation observed in SAN as due to the libration of the phenyl rings.

When humidity is absorbed, giving rise to a complex with an electric dipole bound to phenyl rings, strong dielectric relaxations can be detected. The absorption of humidity on the phenyl rings is reversible, and when it is removed from the specimen, the γ relaxation cannot be detected any more.

The theory of correlation times as used in NMR and in dielectric relaxations can be found in the literature.[23,24]

Conclusions

The detection of secondary transitions in solid polymeric systems is often quite difficult. Even more difficult is the correct attribution of the observed transitions to conformational variations, free or hindered flips, and small motions such as ring librations.

A combination of relaxometric methods may help in the detection and correct attribution of small transitions. In particular, T_1 measurements that are sensitive to high-frequency motions can be extremely useful to detect any variation in the O_2 content.

The line width of NMR resonances can be used to reveal the presence of paramagnetic species.[15] A high absorption of a paramagnetic species can produce a broadening of lines to such an extent that a line becomes unobservable. In the time domain this effect is seen as a loss of spin density. Thus the study of the FID itself in the time domain is useful to assess the presence of a high absorption of O_2.

Motions in the kilohertz region can be efficiently studied by the field cycling method, which, however, can be used only on quite sharp and well-defined NMR signals. Broad NMR lines as present in polymeric solids below the glass transition can be studied in the kilohertz region only by performing $T_{1\rho}$ measurements; these must be performed at a frequency corresponding to at least the natural line width, i.e., at least 50 kHz. Thus the full range at frequencies lower than this limit must be studied by non-NMR techniques. One of the best techniques fulfilling these requirements appears to be the dielectric relaxometry, particularly on account of its sensitivity to the electric dipole induced on the phenyl ring by absorption of water molecules.[23,24] Thus, in the presence of aromatic systems and water, this technique seems the most apt to observe any low-frequency motion.

All experimental methods described in this paper do not use isotopically substituted or labeled polymers. We are aware of the possibility of performing detailed studies of molecular motions using ^{2}H NMR.[25] Aim of our work is to show that it is possible to obtain information on second-order transitions working directly on commercial polymers, without the need of deuterated polymers.

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