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Melting and α Relaxation Effects on the Kinetics of Polypropylene Thermooxidation in the Range 80−170 °C

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ABSTRACT: An isotactic polypropylene (iPP) sample (100% by FTIR) has been thermooxidized in the temperature range 80−170 °C and the kinetics of the degradation followed by measuring the chemiluminescence intensity along the induction and autoacceleration stages. From those curves, the parameter p_0, related to the initial concentration of oxidizable sites, has been calculated and compared to previous results on other PP of different tacticity. A relationship between the relaxations and/or phase transitions taking place in the temperature range under study and the temperature dependence of parameter p_0 in the four samples of fully or predominantly i-PP has been found. It is proposed that the discontinuities in the rate of release of interchain interactions caused by these phase transitions or relaxations are responsible for the slope of the temperature dependence of log p_0. Polymers bearing α-relaxation show a strong decrease in p_0 at temperatures under 115 °C which is absent in polypropylene samples where the α-relaxation is not resolved. As the α-relaxation has been attributed to the diffusion of chains from the amorphous to the crystalline phase and through the interphase, it is proposed that the α-relaxation makes it possible for crystals to act as radical scavengers and thus contribute to stabilize iPP at temperatures under 115 °C.

Introduction

The oxidation rate of polyolefins is strongly dependent on both the history of the sample and the oxidation conditions, and comparison of absolute values of induction period usually suffers from a large scatter among respective laboratories, even if unstabilized samples and routine oxidation conditions are used.[1−3] This is so in part because the exact mechanisms and thus kinetics of the oxidative degradation of polypropylene are still not unequivocally determined;[4−8] in addition, not well-characterized polymer samples are used partly due to nonuniformity of experimental conditions of the oxidation test including the not well-defined temperature gradients in the sample and ventilation conditions. However, if well-characterized polymer samples are used and the geometry of experiment is kept constant, the reproducibility of the measurements is satisfactory.

In a former work[2] we found that, if represented in adequate reduced coordinates, the autoacceleration chemiluminescence (CL) curves characteristic of the isotactic polypropylene oxidation at different temperatures seemed to be temperature independent. The normalization was numerically performed by dividing the kinetic chemiluminescence curve by the coordinates of the point of inflection. An analytical function describing these normalized kinetic curves was obtained by dividing an equation that describes the oxidation kinetics by its analytical inflection point. The equation chosen for this purpose was that proposed by George and coworkers[8] to describe the intensity of chemiluminescence at any time during the thermooxidation:

$$p_i = p_r p_0 \mathrm{e}^{(b-\alpha)t} = \frac{p_0 \mathrm{e}^{(b-\alpha)t}}{1 + \mathrm{e}^{bt-a}} \qquad (1)$$

This equation is derived from what is known as the "spreading model", and in it p_i stands for the oxidizing fraction, p_r and p_0 stand for the unoxidized fraction and the initial fraction of infectious zones, b is the rate coefficient of the oxidation spreading, α is the rate coefficient for the generation of zones in which oxidation is no longer possible, and $a = \ln[(1 - p_0)/p_0]$. Surprisingly, in reduced coordinates the equation describing the intensity of CL at any time showed that the whole oxidation curve (eq 2) depends only on parameter a:

$$I' = \frac{2}{1 + \mathrm{e}^{a(1-t')}} \qquad (2)$$

where I' and t' are the intensity and the time in reduced coordinates. Furthermore, a relationship was found[9] between parameter a of eq 2 or rather between p_0 ($a = \ln[(1 - p_0)/p_0]$) and the ratio between the initial concentration of hydroperoxides, $[\mathrm{POOH}]_0$, and their concentration in an advanced stage of the reaction, $[\mathrm{POOH}]_\infty$, so that $p_0 \propto ([\mathrm{POOH}]_0/[\mathrm{POOH}]_\infty)^{3/2}$. While $[\mathrm{POOH}]_0$ is located mainly at the crystalline interphase, $[\mathrm{POOH}]_\infty$ is rather related to the amorphous regions. A description of p_0 in terms of both initiating and propagating hydroperoxides seems to be very appropriate as it explains why in reduced coordinates eq 2 is able to describe both the induction and the autoacceleration stages.

If the above relationship is an adequate description of p_0, then strong variations of this parameter should be expected when the polymer suffers phase transitions or relaxations, as when this occurs the actual nature of the "oxidizable" polymer fraction may vary, specially if

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Table 1. Physicochemical Characterization of Samples 1−4

sample	% iso[b]	X_c (%)	T_m (°C)[c]	M_μ[a]
1a	100	57.9	168.5	180 000
1b	100		167.0	180 000
2	100	48.8	164.5	80 000
3	82.2	28.9	150.1	45 000
4	76.6	26.9	143.8	40 000

[a] Measured from the intrinsic viscosity in decalin at 135 °C. [b] Measured from FTIR. [c] DSC.

relaxations and/or transitions involve the crystalline phase or the crystalline interphase. The aim of this work is to present a thorough study of the temperature effect on p_0 in a highly isotactic polypropylene, which has been oxidized in the range 80−170 °C, at least every 5 °C, and frequently every 3.5 °C. Specifically, the influence on p_0 of the relaxations or transitions in that temperature range was looked for; comparison is performed with former work on other three predominantly isotactic polypropylene samples obtained from the fractionation of a commercial isotactic polypropylene.

Experimental Section

Materials. Four polypropylene samples are compared in the current work which were already referred to.[2,9] Sample 1b is a commercially available additive-free polypropylene supplied by Repsol (PP050), which has been purified with the pair of solvent/nonsolvent (*o*-dichlorobenzene/methanol) at 125 °C, under N_2 and with the stabilizer Irganox 1010. This sample has been oxidized from 80 to 170 °C at least every 5 °C. Sample 1a is exactly the same as sample 1b, but oxidized at the same time as samples 2−4, i.e., about a year before the oxidation experiments corresponding to sample 1b. Samples 2−4 are polypropylenes studied in a previous work.[9] They were obtained through consecutive fractionation with the pair of solvents 2-ethoxyethanol/xylene. This method allows the low molecular weight fractions to be separated according to their tacticity. Sample 4 is obtained after the third fractionation step corresponding to the volume ratio 40/60 in the mixture of solvents; sample 3 is the fourth fractionation step, the volume ratio being 50/50, and sample 2 is the sixth fractionation step, the volume ratio being 70/30.

Sample Characterization. The physicochemical characteristics of the four samples appear in Table 1. The characterization of crystallinity, molecular weight, and tacticity have been done as described in former work.[9]

Melting Point. The DSC measurements have been carried out in a Perkin-Elmer DSC-7 calorimeter at 10 °C min^{-1} between 40 and 210 °C in nitrogen. A first scan is recorded, after which the sample is quickly cooled, and a second scan is performed. It is usually the result of this second scan which is used to characterize materials, but in this case, as the scope of this technique is to characterize the state of the sample exactly as it is before performing the CL oxidation experiments, the crystallinity and melting point after the first scan have been calculated (Table 1). In Figure 1, the DSC scans from 50 to 200 °C of all five samples appear.

Mechanodynamical Relaxations. The temperature dependence of the mechanodynamical properties of the samples was studied using a Thermal Instruments DMA 983 analyzer. The loss and storage moduli of each sample were determined at 0.1 Hz from −150 to 130 °C at a heating rate of 5 °C/min. The DMA spectra of samples 1−3 are shown in Figure 2; the DMA spectrum of sample 4 could not be obtained because of its brittleness.

Equipment. The equipment has been fully described elsewhere.[9] The chemiluminescence has been measured by using a Lumipol 2, which is produced at the Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovak Republik. This apparatus has a level of discrimination of 2 count/s at 40 °C. About 4 mg of polymer in powder is placed inside an aluminum pan, which is placed inside the oven of the chemiluminescence device. The flow of the gas oxygen 3.4 L/h passes through the reactor during the measurement.

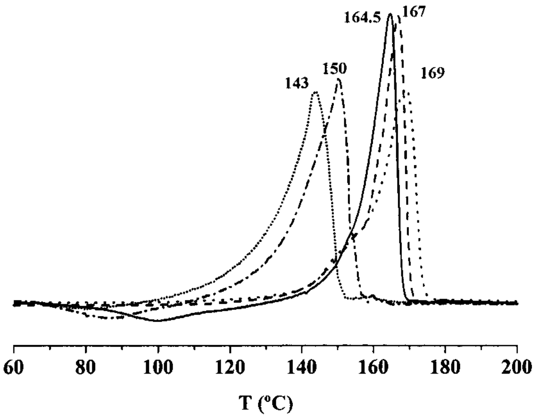

Figure 1. DSC scans from 50 to 200 °C of sample 1a (dot), sample 1b (dash), sample 2 (solid), sample 3 (dash dot), and sample 4 (short dot).

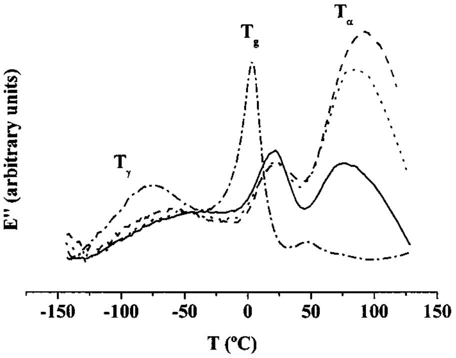

Figure 2. Mechanodynamical spectrum from −150 to 100 °C for sample 1a (dot), sample 1b (dash), sample 2 (solid), and sample 3 (dash dot).

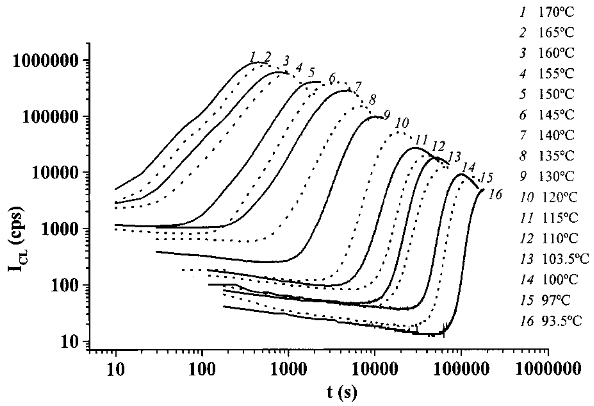

Figure 3. CL curves along the thermooxidation of sample 1b from 80 to 170 °C.

Sample 1 has been oxidized at least every 5 °C between 80 and 170 °C and in some temperature ranges even every 3.5 °C. An example of the results obtained for sample 1b appears in logarithmic scale in Figure 3. Overall, the samples show a very wide range of reaction rates, being the slowest that of sample 1a at 80 °C and the quickest that of sample 4 at 150 °C and sample 1b at 170 °C.

Two possible relaxation/transitions can appear in the range 80−170 °C in predominantly isotactic polypropylene, the α-relaxation, and the melting/crystallizing processes. Our choice of the samples' characteristics has been determined by the interest in studying samples in which melting and α relaxation vary in position and/or intensity, while the oxidation

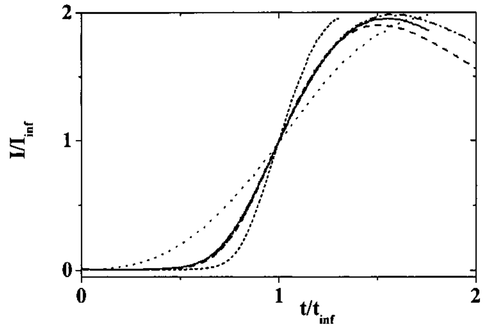

Figure 4. CL curves in reduced coordinates for oxidation experiments at 150 (short dash), 113.5 (solid), 117 (dash dot), 130 (dash), and 93.5 °C (dot).

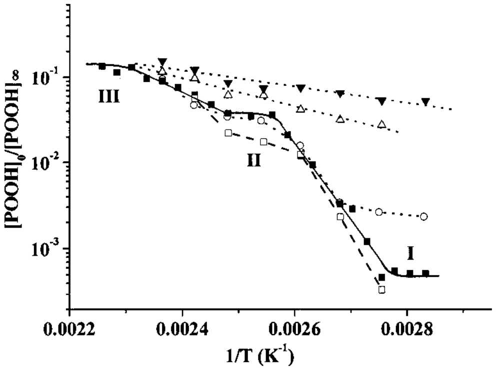

Figure 5. Parameter p_0 as a function of temperature for sample 1a (□), sample 1b (■), sample 2 (○), sample 3 (△), and sample 4 (▲).

temperature range has been kept over 80 °C to avoid changes in the oxidation mechanism.

This temperature range covers then very important morphological changes, as 80 °C is at (samples 1 and 2) or over the α relaxation, and 150 °C/170 °C are above the melting points for samples 3 and 4 and samples 1 and 2 respectively (Figures 1 and 2).

Results

As explained in the Introduction, up to a fairly good approximation, we can fit all the polypropylene oxidation CL reduced curves by using a simple expression (eq 2) with just one adjustable parameter, which is the parameter *a*. We find, in addition, that in reduced coordinates many oxidation experiments coincide (Figure 4), irrespective of the temperature and of the type of sample; i.e., experiments performed on different samples and at different temperatures may yield CL curves in reduced coordinates which follow eq 2 with the same *a* value. For example, as shown in Figure 4, in reduced coordinates the CL curves of sample 1b at 113.5, 117, and 130 °C are exactly the same, and just one parameter is necessary to characterize these oxidation experiments. Examples of this superimposition in the case of samples 2−4 were shown in our former work.[9] That two samples have the same p_0 does not obviously mean that they have the same concentration of initiating hydroperoxides or propagating hydroperoxides, but rather that their ratio is the same, as p_0 is proportional to $[POOH]_0/[POOH]_\infty$.

After fitting all the new CL curves in reduced coordinates, the values of p_0 obtained have been represented in Arrhenius coordinates for the five samples, and the results appear in Figure 5. As shown in the figure, p_0 diminishes with temperature, and more so the more regular the sample. By more regular, both more isotactic and more crystalline are meant. At the same temperature, then, p_0 decreases in the following order: 1a = 1b ≈ 2 < 3 < 4. A given p_0 value is attained at lower temperatures by more irregular samples. For example, $p_0 = 0.01$ is attained by sample 4 at 83 °C, by sample 3 at 113 °C, and by the other three samples at 140 °C. However, the most interesting feature shown in Figure 5 is that samples 1 and 2 strongly change slope at about 115 °C, which is absent in samples 3 and 4. The reproducibility of the results has been checked by the coincidence in the values of p_0 in the set of experiments called 1a and 1b. In sample 1, especially in sample 1b where a large number of experiments has been performed, in addition to the strong change in slope at about 115 °C, three short plateaus are seen in Figure 5, which have been numbered I−III. Plateaus I and II are apparent also in sample 2.

Discussion

Slope Changes in the Arrhenius Representation of p_0. This set of results shows that the four samples under study behave in two qualitatively different ways: samples 1 and 2, which show the strong change in slope at roughly 115 °C, and samples 3 and 4, where the change in slope does not exist. This implies that the difference in stability between the two groups of samples is much greater at $T < 115$ °C than at $T > 115$ °C. In what follows, some considerations on the origin of the temperature dependence of p_0 will be made.

The fact that in highly isotactic polyolefins there is a change in the oxidation mechanism at about 80−100 °C has for long been known. A change in the slope of the representation of the induction time in Arrhenius coordinates has been found in many experimental data.[10−12] Achimsky et al.[10] discussed physical and chemical processes which could be responsible for this mechanism change. A possible relationship with the α-relaxation was discussed in terms of the effect of molecular mobility on the rate constants (initiation, termination, and propagation) though this relationship was rightfully disregarded. However, the change in slope of the Arrhenius representation of p_0 is not related to a modification of the oxidation mechanism, but rather to a variation of the concentration of the species involved in the oxidation reaction. In fact, none of the four samples presented in this work show a change in slope of the Arrhenius representation of the induction time in the temperature range under study.

To understand the p_0 trend shown in Figure 5 for samples 1 and 2, it is necessary to remember what the true meaning of this parameter is. Former work[9] has shown that this parameter cannot be considered as merely the initial concentration of infectious centers in virgin PP, as defined in the infection model,[8] but rather as a parameter which depends both on initiating centers and on the fraction that can propagate oxidation at each degradation temperature.

The homogeneity and/or heterogeneity in the course of oxidation is closely related and dependent on whether a microscopic or a macroscopic study of the system is performed. As a matter of fact, formally the infection model and the homogeneous model involving bimolecular decomposition of hydroperoxides are the same. If thermooxidation is considered as a homogeneous process limited to local “infected” regions in which a steady hydroperoxide concentration exists, then

$$p_0 \approx \left(\frac{[\mathrm{POOH}]_0}{[\mathrm{POOH}]_\infty}\right)^{3/2} \tag{3}$$

where $[\mathrm{POOH}]_0$ and $[\mathrm{POOH}]_\infty$ are the initial concentration of hydroperoxides and the steady concentration of hydroperoxides in an advanced stage of the reaction, respectively.

In this context, the increase of p_0 with temperature can be explained in all cases as a consequence of an increase of the units taking part in the oxidation initiation with respect to the number of units involved in propagation. As the degradation temperature is raised, the interchain interactions which hinder mobility are released and the availability of oxygen increases, and both initiating and propagating POOH functions are more easily formed; apparently, the former increase more quickly than the latter, and consequently log p_0 increases with temperature. In the proximity of a relaxation or phase transition, the discontinuities in the rate of release of interchain interactions and/or in the availability of initiating centers bring about the strong changes in the slope of the temperature dependence of log p_0.

Effect of the Melting Point and the α Relaxation on p_0. Accordingly, in the case of samples 3 and 4, as the oxidation experiments have been performed at temperatures well above T_g and as they do not exhibit other resolved relaxation in the temperature range under study, it is to be expected that the increase in T_{oxid} brings about just the progressive melting of crystallites with increasing cohesive energy. Between 80 and 150 °C log p_0 gently augments as a consequence of a slightly higher increase of $[\mathrm{POOH}]_0$ than of $[\mathrm{POOH}]_\infty$ when performing the oxidation experiments at progressively higher temperatures. It can be checked in Figure 1 that, in fact, 80−90 °C are near the beginning of the melting endotherm in these two polymers. From our point of view, no discontinuities in the rate of release of intermolecular interactions occur in the range 80−150 °C for these two PP samples.

However, in the case of the more regular samples 1 and 2, the situation is very different, as the oxidation temperature range under study coincides to a certain extent with the temperature range in which the α relaxation takes place. Figure 6 shows how the temperature range in which p_0 decreases strongly coincides in both samples 1 and 2 with the temperature range in which the α relaxation is detected by DMTA; in fact, the p_0 change in slope begins at a temperature slightly above that of α relaxation as defined by the maximum of the DMTA peak. There is, then, an apparent correlation between the α relaxation and a stabilization of the polymer detected by a decrease in p_0.

In the literature the onset of this relaxation is related to the peak in the loss modulus which appears at about 90 °C in the DMTA experiments, and for long it has been known that it is caused by motions in the interphase of crystallites.[13−19] It has been shown that the α relaxation in isotactic PP has two components, and the high-temperature one is strongly affected by orientation[20,21] and by the length of chain foldings at the interphase,[22,23] which depends on molecular weight.

Very recent work has shown that the motion occurring at the interphase, and which is responsible for the mechanodynamical α peak, is chain diffusion taking place from the amorphous regions through the crystalline interphase and into the crystals,[24,25] and it has been proved that at and over the α relaxation temperature considerable chain diffusion takes place. This means that in the time scale of the induction period, i.e., from a few minutes to a few days, and at temperatures about 80 °C and over, the interphase cannot be considered as "static", as chain segments progressively diffuse through it. If oxidation is taking place at the same time, then the radicals formed at the interphase because of the decomposition of the hydroperoxides might diffuse into the crystallite, where no oxygen exists and where mobility is highly restricted. Then, the crystallite can behave as a radical scavenger, in a way similar to common polyolefin stabilizers, and thus stop the increase of the p_0 value by decreasing the $[\mathrm{POOH}]_0$, that is, the initiating radical concentration.

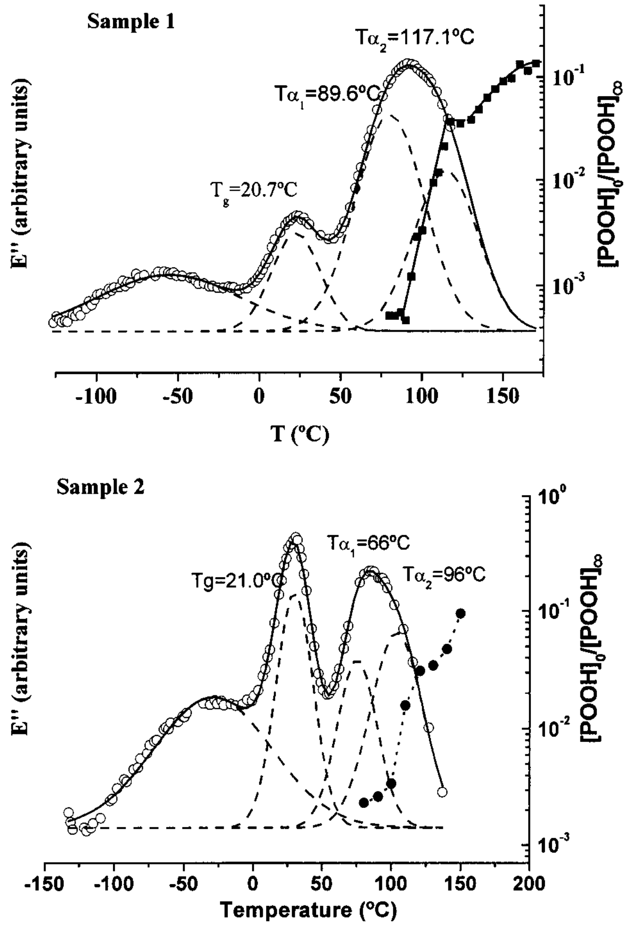

Figure 6. Samples 1 and 2 temperature dependence of p_0 (solid symbols) and DMTA spectrum. DMTA spectrum (○), fitted DMTA spectrum (solid), and fitted components of the DMTA spectrum (γ relaxation, T_g, α_1 and α_2) (dash).

This hypothesis would explain why, in the temperature range of the α relaxation, samples 1 and 2 show such an important decrease of p_0 as compared to samples 3 and 4. For oxidation temperatures over roughly 120 °C, the melting of the crystallites of increasing cohesive energy begins and not only $[\mathrm{POOH}]_0$ increases but also $[\mathrm{POOH}]_\infty$, similarly to what happens in samples 3 and 4. It is at this stage that both the initiation and propagation hydroperoxide concentration increase, as the length of the isotactic chain which is free of intermolecular interactions does so. The gradual release of intermolecular interactions and the subsequent progressive increase of the length of free isotactic chain brings about an increase in the concentration of propagating hydroperoxides, as it is this free isotactic chain where the backbiting propagation mechanism, responsible for the oxidizability of isotactic PP, is possible.[26] All four samples behave similarly in this last stage, which begins at about 80 °C for both samples 3 and 4 and about 115 °C for samples 1 and 2. It is noteworthy that the slope of this final stage decreases in the order sample 1 ≥ sample 2 > sample 3 > sample 4. This must be obviously the case, for $[\mathrm{POOH}]_0$ tends to be higher and $[\mathrm{POOH}]_\infty$ tends to be lower as the isotacticity of the sample decreases.

Effect of Molecular Weight on the Low-Temperature Values of p_0. The only difference between the behavior of samples 1 and 2 is the value attained by p_0 at the low temperature plateau (I in Figure 5) (97−80 °C for sample 2 and 90−80 °C in sample 1). This can be attributed to their different molecular weight. In effect, both samples differ very little in crystallinity (9%), not at all in isotacticity as measured by FTIR and strongly in molecular weight. In a former work[27] it was shown that for these same four PP samples the lower the molecular weight, the lower the induction period, and the log−log representation of both parameters is linear in a broad temperature range (80−150 °C). This relationship has enabled us to relate the induction time to the number of chain end groups, especially to unsaturations of the type $-\mathrm{CH}{=}\mathrm{CH}-\mathrm{CH}_3$ and $-\mathrm{C(CH_3)}{=}\mathrm{CH}_2$, whose ability to interact with oxygen is as important as that of the tertiary carbon in the chain. This would be the reason why at low temperatures $[\mathrm{POOH}]_0$ is higher the lower the molecular weight, and consequently p_0 would increase on diminishing molecular weight.

The results presented in this work evidence a correlation between the temperature dependence of p_0 and the discontinuities in the rate of release of interchain interactions caused by phase transitions or relaxations. We have been able to show how in the vicinity of the melting points the four samples show similar increasing trends of log p_0 with temperature, while a strong decrease of log p_0 occurs in the temperature range of the α relaxations, in those samples in which it is resolved. This p_0 decrease has been related to the possibility of the crystals acting as radical scavengers.

Up to now, the need to use fractions of commercial samples has somewhat limited the available polymeric structures. The use of polyolefins synthesized in our laboratory by means of metallocene catalysts (polypropylene and ethylene−propylene copolymers) to obtain samples in which structural parameters such as crystallinity, molecular weight, and tacticity can be varied in a wider range and in a controlled fashion will help us to get a deeper insight into the effect of the α relaxation in parameter p_0 and the origin of plateaus I and II. The data summarized in Figure 6 indicate that these plateaus could be related to the well-documented presence of two components in the α relaxation, as indicated in the deconvoluted DMTA spectra of samples 1 and 2, which appear in Figure 6.

Conclusions

In fully or predominantly isotactic PP, a correlation has been found between relaxations and phase transitions in the range 80−170 °C and the temperature dependence of parameter p_0. The discontinuities in the rate of release of interchain interactions caused by these phase transitions or relaxations are proposed to be the cause of the changes in the slope of the temperature dependence of log p_0.

Samples of highly isotactic PP, where the α relaxation is conspicuous, show a p_0 concentration which varies with temperature in two clearly defined stages, gently for temperatures over 115 °C and strongly for temperatures under 115 °C. In samples of tendentially atactic iPP, where no α relaxation is resolved, log p_0 varies with temperatures according to one straight line in the temperature range 80−150 °C, a straight line of slope similar to that of highly iPP at high temperatures. It is proposed that the α-relaxation makes it possible for crystals to act as radical scavengers and thus stabilize iPP at temperatures under 115 °C.

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References and Notes

(1) Livanova, N.; Zaikov, G. E. *Int. J. Polym. Mater.* **2000**, *46*, 757.

(2) Tiemblo, P.; Gómez-Elvira, J. M. *Polym. Degrad. Stab.* **2000**, *67*, 49. Corrigendum: *Polym. Degrad. Stab.* **2000**, *72*, 187.

(3) Broska, R.; Rychly, J.; Csomorova, K. *Polym. Degrad. Stab.* **1999**, *63*, 231.

(4) Billingham, N. C. *Makromol. Chem., Macromol. Symp.* **1989**, *28*, 145.

(5) Gijsman, P.; Hennekens, J.; Vincent, J. *Polym. Degrad. Stab.* **1993**, *42*, 95.

(6) Gugumus, F. *Polym. Degrad. Stab.* **1998**, *62*, 245.

(7) Gugumus, F. *Polym. Degrad. Stab.* **1998**, *62*, 235.

(8) George, G. A.; Celina, M.; Lerf, C. J.; Cash, G.; Weddell, D. *Macromol. Symp.* **1997**, *115*, 69.

(9) Tiemblo, P.; Gómez-Elvira, J. M.; Navarro, O.; Matisova-Rychla, L.; Rychly, J. *Polym. Degrad. Stab.* **2001**, *72*, 23.

(10) Achimsky, L.; Audouin, L.; Verdu, J.; Rychly, J.; Matisova-Rychla, L. *Polym. Degrad. Stab.* **1997**, *58*, 283 and references cited therein.

(11) Gijsman, P.; Hennekens, J.; Vincent, J. *Polym. Degrad. Stab.* **1993**, *39*, 271.

(12) Richters, P. *Macromolecules* **1970**, *2*, 262.

(13) Sauer, J. A.; Wall, R. A.; Fuschillo, N.; Woodward, A. E. *J. Appl. Phys.* **1958**, *29*, 1385.

(14) McCrum, N. G. *Makromol. Chem.* **1959**, *34*, 65.

(15) Miller, R. L. *Polymer* **1960**, *1*, 135.

(16) McCrum, N. G. *J. Polym. Sci., Part B* **1964**, *2*, 495.

(17) Turley, S. S.; Keskkula, H. *J. Appl. Polym. Sci.* **1965**, *9*, 2693.

(18) Crissman, J. M. *J. Polym. Sci., Part* C **1968**, *23*, 583.

(19) Owen, A. J.; Ward, I. M. *J. Macromol. Sci., Phys.* **1973**, *B7*, 417.

(20) Jarrigeon, M.; Chabert, B.; Chatain, D.; Lacabanne, C.; Nemoz, G. *J. Macromol. Sci., Phys.* **1980**, *B17*, 1.

(21) Nemoz, G.; Jarrigeon, M.; Vallet, G. *Rev. Phys. Apliquée* **1977**, *12*, 49.

(22) Takayanagi, M. *Pure Appl. Chem.* **1967**, *15*, 555.

(23) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley: New York, 1967.

(24) Hu, W. G.; Schmidt-Rohr, K. *Acta Polym.* **1999**, *50*, 271.

(25) Schmidt-Rohr, K.; Spiess, H. W. *Macromolecules* **1991**, *24*, 5288.

(26) Kato, M.; Osawa, Z. *Polym. Degrad. Stab.* **1999**, *65*, 457.

(27) Rychly, J.; Matisova, L.; Tiemblo, P.; Gómez-Elvira, J. M. *Polym. Degrad. Stab.* **2001**, *71*, 253.

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