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Atomistic Modeling of the Formation of Radical Pairs in Irradiated Amorphous Poly(propylene)

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ABSTRACT: Radiation-induced radical-pair formation has been modeled in a simple atomistic study, utilizing Molecular Simulations Inc., (MSI) amorphous macrocells, containing the three poly(propylene) tacticities; isotactic (i-PP), syndiotactic (s-PP), and atactic (a-PP). For all three tacticities, the ratios of secondary "partner" radical probabilities, generated following hydrogen atom ejection from the primary radical site, were found to deviate only a little from the availability of hydrogen atoms of the PP "a"-, "b"-, and "c"-type carbons ($-C^aH_2C^bHC^cH_3-$). It is demonstrated that b-type partners have the lowest probability of being formed, and therefore, b-type primary radical initiation is required to produce the ESR spectra generally observed, which is predominantly composed of b-type radicals. It is reasoned that the hydrogen atom on the b-carbon is most easily ejected, either following ion−molecule−electron recombination, or as proton ejection. Radical-pair distance distribution functions demonstrate that most partners are formed on immediately adjacent chains, because ejected hydrogen atoms or protons have little possibility to travel much further. Mean radical-pair distances were found not to differ greatly at $\rho \approx 0.90 \times 10^3$ kg m^{-3}, being 6.15, 6.20, and 6.26 Å, from b-type radical initiation in i-PP, s-PP, and a-PP, respectively. Density variation had only a small effect on the mean radical-pair distance in i-PP, except when the polymer was completely amorphous, a condition which never occurs in reality. Similarly, only small mean radical-pair distance variations are expected in s-PP and a-PP, over the range of densities normally encountered.

Introduction

Following our previous modeling of the formation of radical pairs in amorphous high-density poly(ethylene) (HDPE),[1] and subsequent successful use of the radical-pair generator in the analysis of gel fraction curves obtained from irradiated LLDPE,[2−4] we believe it to be important to explore further the ideas of these studies in other linear and branched polyalkanes. The next obvious choice is poly(propylene). Before the radical-pair generator can be applied to the analysis of PP gel fraction curves, it is necessary to study radical-pair formation in the three PP tacticities: isotactic (i-PP), syndiotactic (s-PP), and atactic (a-PP). The key parameter used in building the generator for polyethylene (PE) was the mean radical-pair distance, which had been determined experimentally by Dubinskii et al.[5] and Iwasaki et al.[6,7] Mean radical-pair distances for PP are not available in the literature.

Mean radical-pair distances are usually calculated from electron spin resonance (ESR) data in one of two ways: either by comparing the size of the shift of the saturation curve of the "forbidden" $\Delta M_S = 2$ signal, due to paired spin centers, relative to the total single radical $\Delta M_S = 1$;[5] or from the peaks at separations $d_{||} = 2d_{\perp}$ in the $\Delta M_S = 1$ component of the ESR spectrum.[6,7] In PP there are three types of nonterminal alkyl radicals possible (Figure 1), whereas in PE there is only one. Although b-type radicals predominate in the ESR spectra of i-PP,[6,8] there are significant proportions of other radicals present, rendering it impossible to determine the number of coupling protons from the resultant poorly resolved hyperfine lines. In view of this, the present study is used to establish mean radical-pair distances, for the three PP tacticities, using the hydrogen atom ejection model developed in our previous paper.[1] Further to this, the probabilities of the types of secondary partner radicals formed by the initiating radical are examined. In addition, density variation is considered for the most important PP tacticity, i-PP.

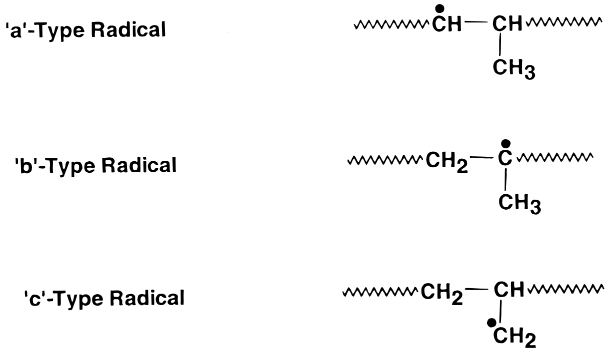

Figure 1. The three types of radical that may occur in PPs.

A brief overview of the radiation chemistry that ensues following the deposition of ionizing radiation was given in the earlier work on HDPE.[1] In particular the ion−molecule electron recombination reaction, leading to a secondary excited state, was considered to be the predominant precursor to radical-pair formation:

$$R_aH^{\bullet +} + e^- \rightarrow R_aH^* \qquad (1)$$

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Radical pairs are generated by hydrogen atom ejection following the recombination reaction:[5,7]

$$R_a^{*} \rightarrow R_a^{\bullet} + H^{\bullet} \tag{2}$$

$$H^{\bullet} + R_bH \rightarrow R_b^{\bullet} + H_2 \tag{3}$$

An alternative mechanism, which was given in the overview but not thought to be significant, is that of proton or hole transfer between precursor radical cations and neighboring alkyl chains:

$$R_aH^{\bullet +} + R_bH \rightarrow R_a^{\bullet} + R_bH_2^{+} \tag{4}$$

A large body of information exists implicating such charge-transfer reactions as radical migration processes.[9,10] The cation produced in reaction 4 is liable to electron capture, either before ejection of a hydrogen molecule

$$R_bH_2^{+} + e^{-} \rightarrow R_bH_2^{\bullet *} \rightarrow R_b^{\bullet} + H_2 \tag{5}$$

or after ejection of a hydrogen molecule

$$R_bH_2^{+} \rightarrow R_b^{+} + H_2 \tag{6}$$

$$R_b^{+} + e^{-} \rightarrow R_b^{\bullet *} \rightarrow R_b^{\bullet} \tag{7}$$

The net result is similar to that predicted in the H atom ejection model used in the generator of our previous HDPE study, in that partner radicals are produced predominantly between carbon atoms of adjacent chains. However, unlike hydrogen atom abstraction by ejected H atoms, proton transfer, from cation radicals in the ionic mechanism of partner radical formation, is bound to be site selective, because the proton affinity of neighboring acceptor C−H bonds is expected to decrease in the order of tertiary C > secondary C > primary C.[9] Site selectivity of this nature would affect preferred partner ratios and radical-pair distance distribution functions, being more apparent in PP than in PE, because the pendant methyl groups, which are primary carbon atoms, ensure that every other carbon of the PP main-chain backbone is tertiary, whereas in PE secondary main-chain carbons predominate almost exclusively.

To include the mechanisms of proton transfer into the radical-pair generator would necessitate intensifying what is already a lengthy and complex program, and employing estimates of probabilities for the various reaction pathways which are as yet not accurately defined for PP. Hence, in this paper, as in the previous work on amorphous HDPE,[1] a first approximation for radical-pair data was obtained using the simple H atom ejection model. It should be remembered that this simple radical-pair generator amply reproduced the experimental results of Dubinskii et al.[5] in the modeling of amorphous HDPE. Also, at low numbers of cross-links per number-average molecule, the number of “gel-effective” cross-links determined in LLDPE using the same radical-pair generator[2] proved to be in good agreement with the total numbers of cross-links determined by rheology.[3,4] Some of the inaccuracies incurred by not invoking proton transfer may have been accommodated for in the cone angle of hydrogen atom ejection ($\phi = 15°$) used in the simple generator. Nevertheless, the reproduction of experimental results indicates that proton transfer is of minor importance in radical-pair formation, at least for PE, and hence, we believe for related poly(alkenes) also.

Table 1. Probabilities of Partner-Radical (r_p) Formation in Amorphous PP (Head to Tail, $\rho = 0.90 \times 10^3$ kg m^{-3}):[a] i-PP

initiating radical	a-type partners	b-type partners	c-type partners
a-type radical	0.3066	0.1744	0.5189
b-type radical	0.3150	0.1584	0.5266
c-type radical	0.3004	0.1614	0.5381
mean	0.3073	0.1647	0.5279

[a] Mean ≡ completely random a-, b-, c-type radical initiation.

Table 2. Probabilities of Partner-Radical (r_p) Formation in Amorphous PP (Head to Tail, $\rho = 0.90 \times 10^3$ kg m^{-3}):[a] s-PP

initiating radical	a-type partners	b-type partners	c-type partners
a-type radical	0.3305	0.1409	0.5286
b-type radical	0.3033	0.1623	0.5344
c-type radical	0.3066	0.1478	0.5456
mean	0.3135	0.1503	0.5362

[a] Mean ≡ completely random a-, b-, c-type radical initiation.

Table 3. Probabilities of Partner-Radical (r_p) Formation in Amorphous PP (Head to Tail, $\rho = 0.90 \times 10^3$ kg m^{-3}):[a] a-PP

initiating radical	a-type partners	b-type partners	c-type partners
a-type radical	0.2976	0.1464	0.5560
b-type radical	0.2840	0.1591	0.5569
c-type radical	0.3065	0.1559	0.5376
mean	0.2960	0.1538	0.5502

[a] Mean ≡ completely random a-, b-, c-type radical initiation

Computational Model

Essentially, the model is as outlined in our previous publication on HDPE,[1] but with modifications for PP. Hydrogen atom ejection was modeled in amorphous PP macrocells (MSI, Insight II, Version 400).[11] Chains consisting of 1000 propylene monomer units, with two end groups per chain, were packed into amorphous subcells at densities of (0.85−0.94) × 10^3 kg m^{-3}. Each unit subcell contained one chain, equilibrated for greater than 1000 molecular dynamics steps (293 K) under periodic boundary conditions. The macrocells contained 24 000 carbon atoms in 8 interlocking unit subcells. Hence, there were 72 016 atoms in total, inclusive of hydrogen atoms.

A program was written in “C” to read the Cartesian coordinates of the individual atoms in the equilibrated MSI macrocell and store the coordinates, relative to the center of the cell, in one-dimensional arrays. Radical-pair formation was considered to take place in the macrocell under static rather than dynamic conditions, because hydrogen atoms are ejected within the lifetime of a single vibration (∼10^{-15} s), and move at least 4 orders of magnitude faster than the polymer segmental motions (>1 ns). The minimum velocity of a hydrogen atom moving under random thermal motion is ∼2 × 10^4 Å ns^{-1}. Hence, the “initiating” hot-hydrogen atoms reach neighboring chains and react with them before chain motions takes place.

The method of radical-pair generation used in this study has been well-described previously, with the following constants applied to the generator: van de Waals radii for hydrogen and carbon, 1.0 and 1.7 Å, respectively, and the cone angle of hydrogen atom ejection (ϕ) was taken to be 15°, being the angle which most closely reproduced experimental results in HDPE.[1] The distance of atomic screening from the ejection site was increased up to 40 Å. To improve accuracy of the radical-pair distribution functions, the generation off possible partner radicals was repeated 10 000 times. After 10 000

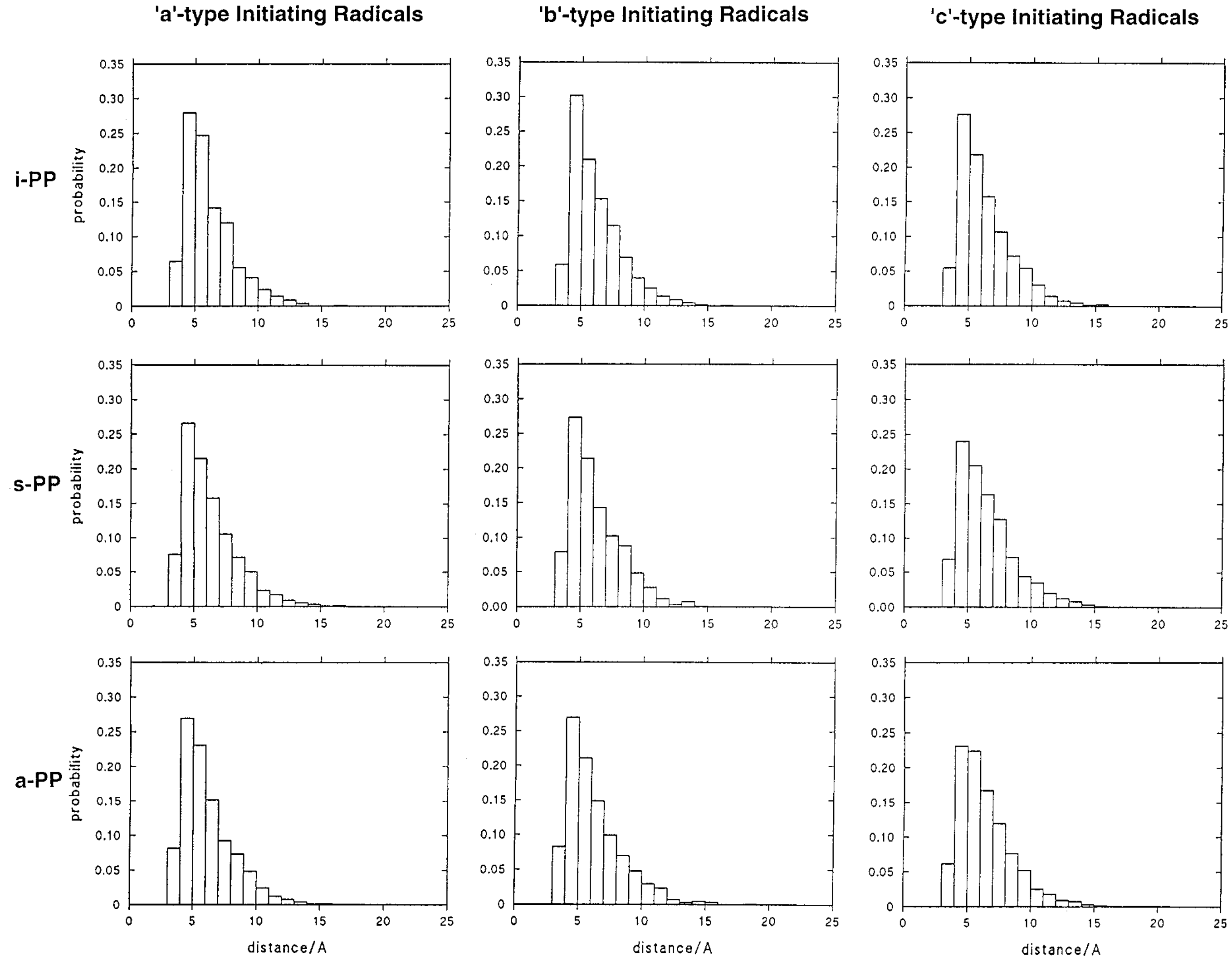

Figure 2. Atomistic radical-pair distance probability distribution functions for available partners in amorphous i-, s-, and a-PP ($\rho = 0.90 \times 10^3$ kg m^{-3}).

Table 4. Statistical Availability of Hydrogen Atoms in PP

	C_a-hydrogen atoms	C_b-hydrogen atoms	C_c-hydrogen atoms
available H atoms	2	1	3
ratio of availability	0.3333	0.1667	0.5

Table 5. Probabilities of Combined Radical Formation (Initiating Radicals plus Partner Radicals) in Amorphous PP (Head to Tail, $\rho = 0.90 \times 10^3$ kg m^{-3}):[a] i-PP

initiating radical	a-type combined radicals	b-type combined radicals	c-type combined radicals
a-type radical	0.6534	0.0872	0.2595
b-type radical	0.1575	0.5792	0.2633
c-type radical	0.1502	0.0807	0.7691
mean	0.3204	0.2490	0.4306

[a] Mean ≡ completely random a-, b-, c-type radical initiation.

iterations, the sum of the frequencies in the histogram intervals was normalized, such that the total frequency was unity with respect to radical initiation, to give the fractional number of partner radicals per initiating radical generated.

Results and Discussion

1. Probabilities of Radical Sites. The probabilities of partner-radical formation, as found by our atomistic statistical model applied to i-PP, s-PP, and a-PP, are shown in Tables 1—3, respectively, for radical initiation from the a-, b-, and c-type initiating radicals. The mean probability of a-, b-, and c-type partner-radical formation, taken from all three PP tacticities combined, differ by only approximately −8.31, −6.30, and +7.62% from the numerical availability of hydrogen atoms on the respective a-, b-, and c-type carbons (Table 4). Hence, the ratio of partner-radical probabilities is generally close to the numerical availabilities of hydrogen atoms. Deviations from the numerical availabilities in Table 4 therefore, reflect screening effects. The atomistic model yields of b-type partner-radicals are only slightly less than statistically expected on the basis of availability. Hence, b-type partner radicals have the lowest probability of being formed in all three PPs, because there is only one H atom available on the b carbon.

The atomistic probabilities of combined radical (r_c) formation, initiating radicals (r_i) plus partner radicals (r_p), ($r_c = r_i + r_p$), are shown for i-PP, s-PP, and a-PP, in Tables 5, 6, and 7, respectively, for radical initiation from the a-, b-, and c-type initiating radicals, calculated according to the following equation:

$$p(r_c)_x = \frac{1}{2}\cdot(p(r_i)_x + p(r_p)_x) \tag{i}$$

where x is the type of radical (a-, b-, or c-type) under

Table 6. Probabilities of Combined Radical Formation (Initiating Radicals plus Partner Radicals) in Amorphous PP (Head to Tail, $\rho = 0.90 \times 10^3$ kg m^{-3}):[a] s-PP

initiating radical	a-type combined radicals	b-type combined radicals	c-type combined radicals
a-type radical	0.6653	0.0705	0.2643
b-type radical	0.1517	0.5811	0.2672
c-type radical	0.1533	0.0739	0.7728
mean	0.3234	0.2418	0.4348

[a] Mean ≡ completely random a-, b-, c-type radical initiation.

Table 7. Probabilities of Combined Radical Formation (Initiating Radicals plus Partner Radicals) in Amorphous PP (Head to Tail, $\rho = 0.90 \times 10^3$ kg m^{-3}):[a] a-PP

initiating radical	a-type combined radicals	b-type combined radicals	c-type combined radicals
a-type radical	0.6488	0.0732	0.2780
b-type radical	0.1420	0.5795	0.2785
c-type radical	0.1533	0.0779	0.7688
mean	0.3147	0.2435	0.4418

[a] Mean ≡ completely random a-, b-, c-type radical initiation.

Table 8. Mean Radical-Pair Distances in Amorphous PP (Head to Tail, $\rho = 0.90 \times 10^3$ kg m^{-3}):[a] i-PP

initiating radicals	$\overline{r_{i,p}}$/Å
a-type radicals	6.1185
b-type radicals	6.1470
c-type radicals	6.2834
mean	6.1830

[a] Mean ≡ completely random a-, b-, c-type radical initiation.

analysis. (N.B.: $p(r_i)_x = 1$ when r_i and r_p are the same type, otherwise $p(r_i)_x = 0$.)

Since b-type partners have the lowest probability of being formed (Tables 1−3), and ESR spectra observed experimentally predominantly contain b-type combined radicals,[6,8] then nearly all the initiating radicals must be b-type in order to produce the spectra. This is demonstrated in Tables 5−7. The above premise is in keeping with excitation energy transfer theory of PP,[12] where most of the exciton energy is predicted to exist in the lowest exciton level ($K = 0$), corresponding to pure main-chain C−C bond excitation. Somewhat less than 9% of the exciton energy is believed to exist with nonzero K values, but even then excitation of the side bond is not localized on the methyl group. Hence, most excitons do not "see" the methyl group and scission of it from the main chain is not expected. Of the main chain hydrogen atoms, the b-carbon H atom is then most easily ejected either following ion−molecule−electron recombination or as a proton ejection.

2. Radical-Pair Distances. The radical-pair probability-distance distribution functions, summed over all initiating radical to possible partner-radical distances, resulting from atomistic modeling the interactions of ejected hydrogen atoms from the three types of initiating radicals in the three tacticities of amorphous PP ($\rho = 0.90 \times 10^3$ kg m^{-3}), are given in Figure 2. They all peak between 4 and 5 Å and then decay exponentially to zero at around 15 to 16 Å. The corresponding mean radical-pair distances ($\overline{r_{i,p}}$), are given in Tables 8−10. The values in these tables are not greatly different for the three tacticities and in all cases c-type initiating radicals give the largest mean radical-pair distances. The interchain carbon−carbon correlation functions (Figure 3) show probabilities for the interchain carbon−carbon distances ($g(r)$), as given by MSI software,[11] from all pairs of carbon atoms on adjacent chains. It can be seen that the $g(r)$ values at the mean radical-pair distances, taken over all types of initiating radicals, are 0.722, 0.656, and 0.621 for i-PP, s-PP, and a-PP, respectively. Hence, as was found for HDPE previously,[1] the mean radical-pair distances are only a little greater than the mean interchain distances, and most of the partner radicals are formed on immediately adjacent chains, because the ejected hydrogen atoms or protons get little

Table 9. Mean Radical-Pair Distances in Amorphous PP (Head to Tail, $\rho = 0.90 \times 10^3$ kg m^{-3}):[a] s-PP

initiating radicals	$\overline{r_{i,p}}$/Å
a-type radicals	6.2367
b-type radicals	6.2017
c-type radicals	6.4373
mean	6.2919

[a] Mean ≡ completely random a-, b-, c-type radical initiation.

Table 10. Mean Radical-Pair Distances in Amorphous PP (Head to Tail, $\rho = 0.90 \times 10^3$ kg m^{-3}):[a] a-PP

initiating radicals	$\overline{r_{i,p}}$/Å
a-type radicals	6.1586
b-type radicals	6.2642
c-type radicals	6.4350
mean	6.2859

[a] Mean ≡ completely random a-, b-, c-type radical initiation.

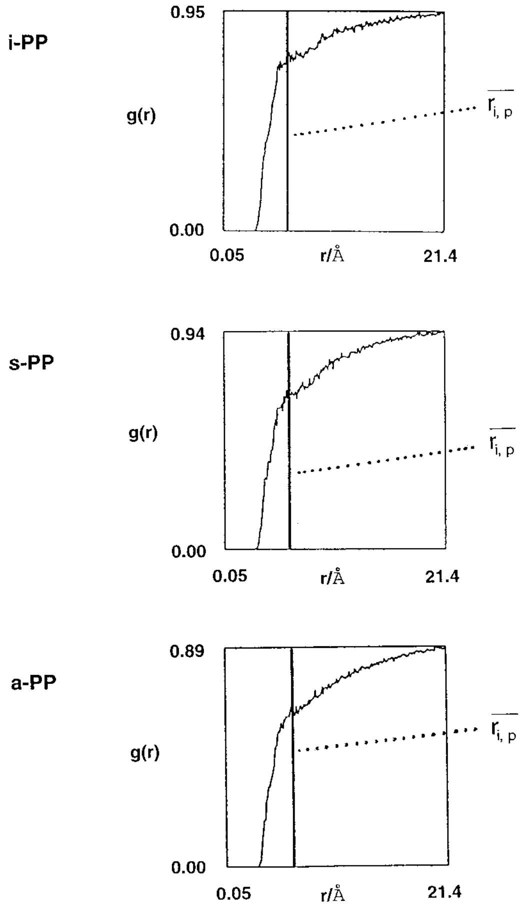

Figure 3. MSI[11] interchain carbon−carbon correlation functions for the amorphous i-, s-, and a-PP cells ($\rho = 0.90 \times 10^3$ kg m^{-3}) used in this study, together with mean radical-pair distances ($\overline{r_{i,p}}$).

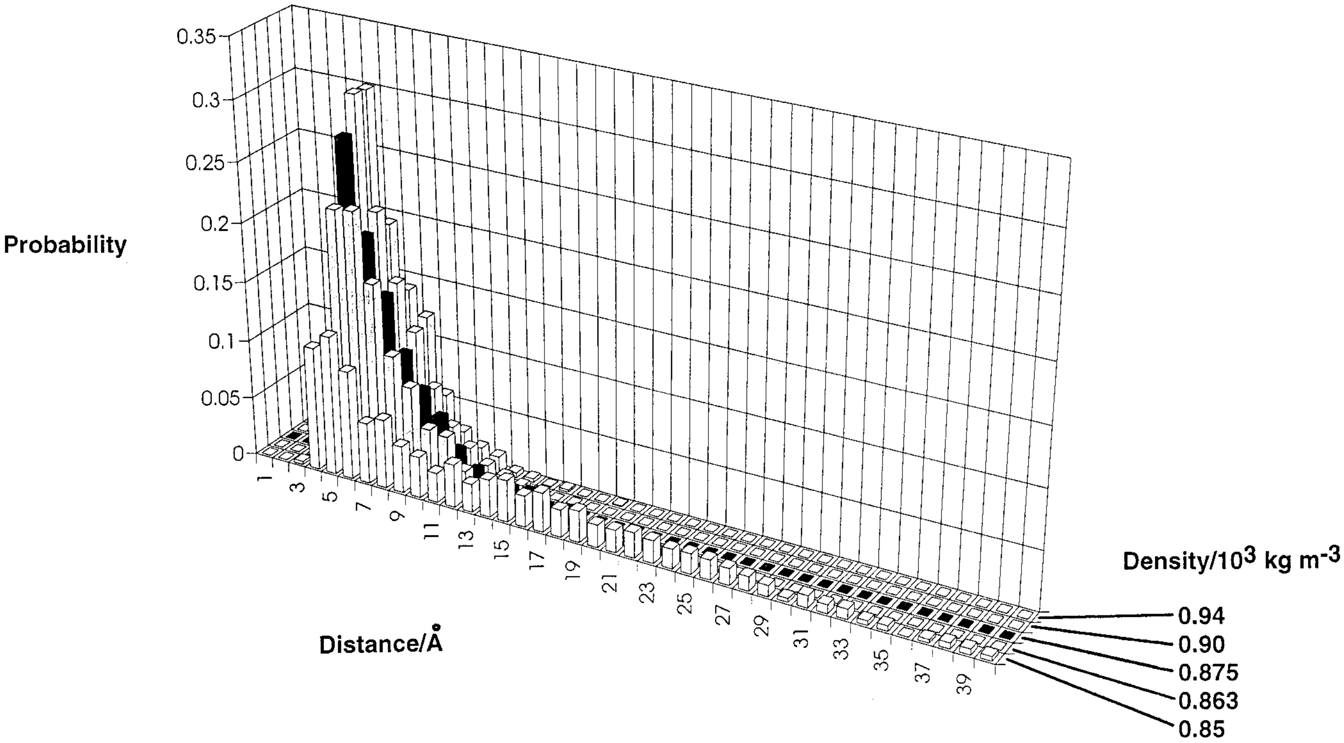

Figure 4. Atomistic radical-pair distance probability distribution functions for amorphous i-PPs of varying density (ρ = (0.85−0.94) × 10^3 kg m^{-3}), generated by b-type initiating radicals.

chance to travel much further. For generation of partner radicals from b-type initiating radicals, which has been demonstrated to occur in reality, the mean radical-pair distances increase a little in the order i-PP < s-PP < a-PP.

3. Effect of Density Variation on Mean Radical-Pair Distances. Having established that only b-type initiating radicals produce sufficient b-type combined radicals to generate the ESR spectra observed experimentally by other authors, it was decided to examine the effect of density variation in i-PP on mean radical-pair distances. Macrocells were built of different densities from 0.85 × 10^3 to 0.94 × 10^3 kg m^{-3}, and the radical-pair probability-distance distribution functions, simulated by b-type initiating radicals, were generated (Figure 4). This density range was chosen because completely amorphous PP is believed to have a density of (0.85−0.854) × 10^3 kg m^{-3}, while completely crystalline PP has a density of (0.932−0.943) × 10^3 kg m^{-3}.[13] Although the modeling here was carried out in completely amorphous macrocells, parameters were set to yield results obtainable for polycrystalline systems. Hence, the complete range of PP densities found in normal use was covered. In Figure 4, the lowest density 0.85 × 10^3 kg m^{-3}, has a very blunt peak at 4−5 Å and a long tailing distribution to around 40 Å. The long tail is immediately lost by 0.863 × 10^3 kg m^{-3} where an exponential decay to zero probability at around 15−16 Å occurs. Thereafter, the peak probability becomes sharper and the curve returns to the form seen previously for the three tacticities at 0.9 × 10^3 kg m^{-3} (Figure 2). The mean radical-pair distances, corresponding to the distribution functions shown in Figure 4, are plotted in Figure 5 as a function of density. It can be seen from Figure 5 that density variation has only a small effect on the mean radical-pair distance except in the completely amorphous density region. Since the density of completely amorphous i-PP had to be calculated from liquid i-PP data,[13] it is hardly ever likely to be encountered in solid i-PP. s-PP and a-PP are expected to produce similar mean radical-pair distance versus density variation profiles over the same range of densities.

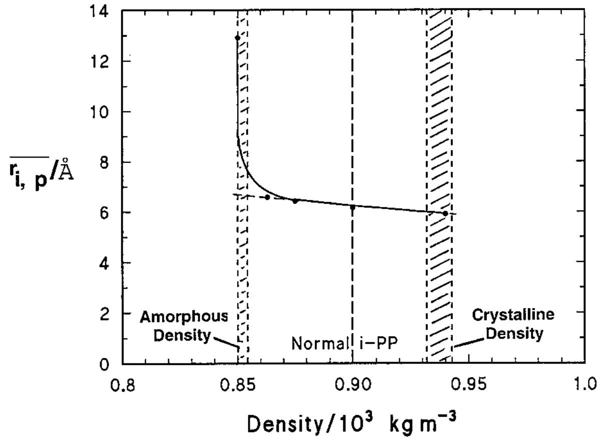

Figure 5. Atomistic mean radical-pair distance ($\overline{r_{i,p}}$) variation in amorphous i-PP of varying density (ρ = (0.85−0.94) × 10^3 kg m^{-3}), generated from b-type initiating radicals.

Conclusions

b-Type partners have the lowest probability of being formed in all three PPs, because there is only one H atom available on the b carbon. The atomistic ratio of partner probabilities deviated only a little from the numerical availability of hydrogen atoms on the respective a-, b-, and c-type carbons of the three tacticities of PP. The deviations resulted from geometrical screening effects. Since b-type partners have the lowest probability of being formed, nearly all the initiating radicals must be b-type, in order to produce the combined radical ESR spectra observed experimentally.[6,8] This is in keeping with the theory of exciton energy transfer in PP,[12] which demonstrates that the hydrogen on the b carbon is most easily ejected or transferred, and scission of the methyl side group is not expected.

The atomistic radical-pair distance distribution functions, resulting from all types of radical initiation in the three tacticities of amorphous PP ($\rho = 0.90 \times 10^3$ kg m^{-3}), all peak between 4 and 5 Å and then decay exponentially to zero at around 15–16 Å. Most of the partner radicals are formed on immediately adjacent chains, because the ejected hydrogen atoms, or proton transfers, get little chance to travel much further. This is in keeping with the results obtained from PE.[1] The mean radical-pair distances ($\overline{r_{i,p}}$) are not greatly different for the three tacticities, being 6.15, 6.20, and 6.26 Å for b-type radical initiation in i-PP, s-PP, and a-PP, respectively. The effectiveness of radiation-induced cross-linking observed in polyalkanes, particularly in the presence of gaseous bridging agents such as acetylene, is predominantly a consequence of the close proximity of radical pairs on adjacent chains.[2] Density variation had only a small effect on the mean radical-pair distance in i-PP, except when completely amorphous which is never found in the solid state. Similarly, only small mean radical-pair distance variations are expected in s-PP and a-PP, over the range of densities normally encountered in the solid state.

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