Local dynamics of isotactic and syndiotactic polypropylene in solution

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The local dynamics of polypropylene (PP) in solution is studied by $^{13}$C NMR relaxation and by molecular dynamics (MD) simulation via the orientational autocorrelation function (OACF) of C-H bonds. The interpretation protocol of this function proposed by Dejean de la Bâtie, Lauprétre and Monnerie (DLM) [R. Dejean de la Bâtie, F. Lauprétre, and L. Monnerie, Macromolecules 21, 2045(1988)] is applied and tested on new NMR measurements of the various microstructures of polypropylene. This interpretation scheme of the OACF is supported by a detailed study employing simulated PP trajectories in an atomistic heat bath. MD simulations indicate that, quite generally, the correlation time for segmental motions, $\tau_s$, extracted from the DLM motional model is closely linked with the mean time between conformational jumps. Both experiments and simulations suggest a slightly higher mobility of meso sequences by comparison with racemic sequences. Our analysis of the microscopic aspects of the segmental dynamics and its manifestation in motional models allows us to trace the microscopic origin of the larger mobility of meso sequences. © 2000 American Institute of Physics.

I. INTRODUCTION

The dynamics of a few monomer units within a polymer chain is a highly specific property which, for melts or for blends, is strongly correlated to their material properties and in particular to the glass transition. This local dynamics, which results from main chain librations, isolated or correlated conformational jumps, side group rotations . . . , is the object of intensive research efforts aimed at unraveling the peculiar microscopic aspects of the main $\alpha$ transition and the various secondary $\beta$ and $\gamma$ transitions in polymeric melts.1

For melts well above $T_g$ and for polymers in solution, the local dynamics takes place on time and space scales of $[10^{-1} \text{s}–10^{-8} \text{s}]$ and [0.05–2 nm]. These ranges are relevant to various techniques of NMR and neutron scattering (e.g., quasielastic or neutron spin echo). These time and space scales are also suited for computer simulation studies of polymers modeled at the atomistic level, as we deal with a sub-Rouse dynamical regime.

More particularly, the $^{13}$C $T_1$ spin-lattice measurements in the melt and in solution have been widely used to probe librations and large-amplitude jump motions through the orientational autocorrelation function (OACF) of a unit vector $\mathbf{u}$ lying along the $^{13}$C–$^1$H spin pair, namely $G(t) = \langle (3/2) \cos^2 \theta(t) - 1/2 \rangle$, where $\cos \theta(t) = \mathbf{u}(t) \cdot \mathbf{u}(0)$. To interpret these NMR data in terms of specific motions, one ideally needs a realistic elementary dynamical model, characterized by a small set of physically relevant parameters (denoted collectively as $\gamma_k$) which is suited for an analytical derivation of $G^{\text{mod}}(t; \gamma_k)$. Quite generally, for the orientational dynamics of bonds in large flexible molecules, this is a very difficult task as usual standard motional models such as the isotropic diffusion on a sphere or instantaneous jumps between a small set of well defined orientations are not adequate. In some favorable cases, like in the dynamics of a flexible short chain attached to a quasirigid large molecule, it has been possible to follow the above mentioned ideal program in the interpretation of the NMR data.2 For the local dynamics of linear polymers in the liquid phase, one knows no analytical expression of $G(t)$ which would have been derived rigorously for a dynamical model combining the elementary types of motions. One major difficulty lies in the incorporation in the dynamical model of correlations between successive conformational jumps or between a conformational jump and subsequent dihedral angle cooperative damped counterrotations in the neighborhood of the jumping one. These dynamical correlations, which are well documented by numerous simulations,3–5 are qualitatively important because of the severe restrictions on the skeleton dihedral angle dynamics imposed by the connectivity of a polymer chain and by the impossibility for a large chain fragment to perform large-amplitude motions against solvent viscous forces.

For the interpretation of NMR data probing the local dynamics of polymers, it has therefore been customary to
rely on more phenomenological motional models. Hall and Helfand first derived an analytical expression relative to the time correlation functions for the conformation dynamics of a simplified one-dimensional chain model where bonds can adopt two states and where both correlated and isolated jumps between both states coexist with some specific kinetic rates. On the basis of tests on simulated OACF’s obtained through a realistic single chain Brownian dynamics of polyethylene, Helfand proposed the use of the above mentioned analytical function as a phenomenological expression enabling the description of the bond reorientational dynamics in polymers. This function was later found adequate to describe the fluorescence anisotropy decay of anthracene labeled polybutadiene chains dispersed in a polybutadiene matrix, a further test of the pertinence of this function to represent the reorientational dynamics process of a bond subject to restrictions from chain connectivity. The application of this functional form in the interpretation of $^{13}$C NMR relaxation data required the adjunction of an additional faster decorrelation process modeling the fast librational motions, hence leading to the so-called DLM model. The application of this phenomenological approach to the interpretation of NMR relaxation data on a wide variety of polymers (in solution or in melts well above the glass transition) has been generally quite successful.

Molecular dynamics simulations are nowadays more and more integrated in a multidisciplinary effort aimed at linking the local dynamics of polymers with their chemical structure. In this field, simulations have provided much insight about the nature of conformational transitions, about the limitations of the Kramers theory when describing single bond rotation, about the validity of Langevin dynamics for macromolecules in solution or about many jumps features like geometrical aspects or the size of the moving polymer segment. As illustrated by the work of Bremi et al. on side chain dynamics, simulations can also be used to test an experimental interpretation protocol based on a particular analytical model. The molecular dynamics data provide a consistency check if the model parameters (diffusion coefficient, jump rates . . . ), extracted from a fit of the computed relevant NMR correlation function with the analytical expression $G^{\text{model}}(\tau)$, are in agreement with their value calculated directly from the same trajectory. Such a validated protocol can then be used to interpret experimental data with a definite superiority over model functions which may give equally good fits of experimental data but without providing a reliable physical basis for the interpretation of the parameters.

Using both NMR experiments and molecular dynamics computer simulations, we develop in the present paper a joint study on the local dynamics of polypropylene (PP) in solution. We report a series of new $^{13}$C NMR relaxation experiments which probe the methine/methylene bond reorientational dynamics within specific microstructures and we interpret these NMR data with the DLM motional model. In parallel, we analyze a series of molecular dynamics experiments performed at three temperatures on isotactic (iPP) and syndiotactic (sPP) oligomers in an explicit solvent.

Two main points are developed in the present paper:

(a) We explore the possibility of unraveling within the OACF’s the effects due to conformational jumps and to librational motions in order to test the interpretation protocol of $^{13}$C relaxation data based on the DLM phenomenological model.

(b) Both experiments and simulations indicate a slight but noticeable difference between the local dynamics of meso and racemic microstructures, in agreement with previous experimental indications. We will use our OACF analysis to pinpoint the microscopic origin of this difference.

We finally note that the direct quantitative comparison between simulation results and experimental measurements is not the object of the present study. The force-field model was selected to capture the essential features of PP in solution like relative effects due to tacticity but, in particular for the solvent, no attempt was made to represent realistically the particular solvent used in the NMR relaxation experiments.

The paper is organized as follows. Section II covers our NMR relaxation experiments on various tactic forms of PP in solution and their analysis in terms of a motional model. In Sec. III, we establish a new united atom model for simulations of the PP/CCl$_4$ solution. Section IV deals with the simulation results on PP fragments of different tacticities, first at a unique temperature. We then discuss the temperature dependence of relevant parameters and conclude on the origin of tacticity effects on the local dynamics. We finally perform a jump analysis for PP backbone dynamics and look for jump specificities in segments of different tacticities. The last section, Sec. V, summarizes the connection between experimental observations and molecular dynamics simulations and stresses the interest of the latter in getting a microscopic understanding of the dynamics of complex systems.

II. NMR SECTION

A. Experiments

The isotactic (iPP) and syndiotactic (sPP) polypropylene samples were kindly supplied by Solvay Research and Technology Centre (Brussels, Belgium) and Fina Research (Féry, Belgium), respectively. The meso contents in the iPP and sPP samples were of the order of 95% and 5%, respectively. The iPP and sPP samples are soluble only at temperatures higher than 80 °C, whereas the atactic polypropylene (aPP) is soluble at temperatures higher than −40 °C. Therefore, the aPP sample was obtained by extracting the small amount of atactic chains contained in the iPP sample. The iPP sample was dissolved in boiling xylene, then after 12 h at room temperature, the xylene-insoluble isotactic polypropylene chains were removed and the xylene-soluble aPP was isolated by xylene evaporation. The characteristics of the sample thus obtained are: $M_n = 5840$, $M_w = 118400$, which is indicative of a very large polydispersity. As shown by the NMR spectrum of its methyl carbons (see Fig. 1), the aPP sample exhibits a large variety of stereosequences.

The solutions used for the NMR experiments were prepared by dissolving the polypropylene samples (0.2 g) in a
mixture of orthodichlorobenzene (2 cm$^3$) and benzene-d6 (0.25 cm$^3$) as the lock solvent. $^{13}$C NMR spectra at 25.18 and 50.3 MHz were obtained by using a Bruker AC-100 and a Bruker AC-200 spectrometer, respectively. $^{13}$C spin-lattice relaxation times, $T_1$, were measured under conditions of continuous proton noise decoupling using the standard (180°-t-90°) inversion recovery pulse sequence, with a 10 μs 90° pulse duration and repetition times between pulse sequences greater than five times the longest $T_1$ of the considered nuclei. For each $T_1$ measurement at a well-resolved peak, the accuracy is to within 5%.

B. Link with molecular observables

With the assumption of a purely $^{13}$C-$^1$H dipolar relaxation mechanism, the spin-lattice relaxation time, $T_1$, obtained from a $^{13}$C experiment under $^1$H decoupling conditions is given by the following expression:

$$\frac{1}{nT_1} = \frac{\hbar^2}{10^6_{\text{CH}}} J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C),$$

(1)

where $n$ is the number of protons directly bound to the considered carbon, $\omega_H$ and $\omega_C$ are the $^1$H and $^{13}$C resonance frequencies and $r_{\text{CH}}$ is the internuclear distance. $J(\omega)$ is the spectral density defined by

$$J(\omega) = \frac{1}{\pi} \int_{-\infty}^{+\infty} G(t) e^{i\omega t} dt.$$

(2)

$G(t)$ is the normalized second-order spherical harmonic orientation autocorrelation function (OACF) already introduced in Sec. I, defined by

$$G(t) = \langle P_2(\mathbf{u}(0) \cdot \mathbf{u}(t)) \rangle = (3\cos^2 \theta(t) - 1)/2,$$

(3)

where $\mathbf{u}(t)$ is a unit vector lying along the internuclear vector.

The mean correlation time, or effective correlation time, $\tau_c$, is expressed as

$$\tau_c = \int_0^{+\infty} G(t) dt.$$

(4)

The detailed analysis of relaxation data determined in a number of polymer systems,9,15-22 either in solution or in bulk at temperatures well above the glass transition temperature, has shown that the local motions observed by $^{13}$C spin-lattice relaxation can be satisfyingly described in terms of damped diffusion of bond orientation along the chain sequence, which represents the segmental motions, and independent fast bond librations.9 The corresponding orientation autocorrelation function is written as

$$G_{\text{DLM}} = (1-a)\exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1)$$

$$+ a \exp(-t/\tau_0)\exp(-t/\tau_1)I_0(t/\tau_1),$$

(5)

where $I_0$ is the zero order modified Bessel function, $\tau_1$ is the characteristic time responsible for the diffusion of bond orientation along the chain, $\tau_2$ is the damping term corresponding to the orientation loss process and $\tau_0$ is the characteristic time of the fast librations. $a$ is related to the half-angle $\theta$ of the libration cone through the relation

$$1-a = \frac{\cos \theta - \cos^3 \theta}{2(1-\cos \theta)}.$$

(6)

Assuming that $\tau_0$ is much shorter than $\tau_1$ and $\tau_2$ (a situation which is often encountered), the second term in the $G(t)$ expression can be simplified and $G(t)$ can be written as

$$G_{\text{DLM}} = (1-a)\exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1)$$

$$+ a \exp(-t/\tau_0).$$

(7)

The corresponding spectral density is written as

$$J_{\text{DLM}}(\omega) = (1-a) \frac{1}{(\alpha+i\beta)^{1/2}} + a \frac{\tau_0}{1 + \omega^2 \tau_0^2},$$

(8)

where $\alpha = \tau_2^{-2} + 2 \tau_1^{-1} - \omega^2$ and $\beta = -2 \omega (\tau_1^{-1} + \tau_2^{-1})$. For fast librations, the second term in the $J_{\text{DLM}}(\omega)$ expression can be neglected.

C. Results

The line assignment of the $^{13}$C NMR spectrum of atactic polypropylene was reported previously.12-14,23-26 The high-field CH$_2$ lines were assigned to carbons located in meso-centered tetrads, whereas the low-field CH$_2$ lines corresponded to CH$_2$ groups in racemic-centered tetrads. The opposite behavior was observed for the CH lines: the low-field lines correspond to meso sequences whereas the high-field lines belong to racemic-enriched sequences.

As an example, the temperature dependence of the spin-lattice relaxation times, $T_1$, determined for the 47.5 and 46.4 ppm CH$_2$ lines (racemic-centered tetrads and meso-centered tetrads, respectively) and 28.6 and 28.0 ppm CH lines (meso-centered pentads and racemic-centered pentads, respectively) of the aPP sample at 25 MHz are shown in Figs. 2 and 3. In the low temperature range, the $T_1$ values exhibit a minimum. The position and height of the $T_1$ minimum are independent of the microstructure of the tetrad considered within the accuracy of the experiment. At high temperature, the $T_1$ of the two CH carbons, as well as the $T_1$ of the two CH$_2$ carbons,
are significantly different: the higher values are observed for the CH and CH$_2$ carbons situated inside the meso-centered units. Similar behaviors were observed at 50 MHz. Such differences in the $T_1$ values of the stereosequences of atactic polypropylene were already reported by other authors.$^{12-14}$

The identical values determined for the $T_1$ minimum of the CH carbons (or for the $T_1$ minimum of the CH$_2$ carbons) in the different stereosequences in the aPP polymer can be interpreted in terms of the DLM motional model as an independence of the fast librational motion on the microstructure. Since the contribution of the librations to the $^{13}$C spin-lattice relaxation time $T_1$ for methine carbon in aPP meso (■) and racemic (▲) microstructures; high temperature data for iPP (○) and sPP (●) are indicated. Curves providing the DLM fits for aPP meso (—not shown) and racemic (---) are also shown.

The model used is extended to the segmental motions in the different stereosequences in the aPP polymer by using the DLM model. The fit was achieved by treating simultaneously the 25 and 50 MHz $T_1$ data assuming for the motional model a time scale separation between the fast librations and the segmental motions, as was systematically observed in previously studied polymer chains.$^{9,15-17}$ The parameters $\tau_2/\tau_1$ and $\alpha$ are kept constant over the whole temperature range while $\tau_1$ is assumed to vary according to Arrhenius’ law $\tau_1 = A \exp(E_a/k_B T)$. For a given microstructure, common values of the activation energies $E_a$ and prefactors $A$ are adopted for both methylene and methine carbons. The curves corresponding to the best fits are shown in Figs. 2 and 3. The corresponding parameters are $\tau_2/\tau_1=5.0$, $a_{\text{CH}}=0.55$, $a_{\text{CH}_2}=0.54$, $A=0.04$ ps, $E_a=22.3$ kJ/mol for the meso microstructure and $\tau_2/\tau_1=2.6$, $a_{\text{CH}}=0.51$, $a_{\text{CH}_2}=0.53$, $A=0.10$ ps, $E_a=21.4$ kJ/mol for the racemic microstructure. When taking into account the error bars on experimental data, the parameters extracted from the fit by the DLM model must be analyzed with care, allowing for uncertainties of the order of 5%–10%. We observe that the activation energy of $\approx 22$ kJ/mol and fast librational amplitudes [of the order of 39° using Eq. (6)] are similar for both meso and racemic sequences, while no significant difference between the fast libration amplitudes of methine and methylene carbons can be detected. The major difference between the local C-H orientation dynamics in meso and racemic microstructures seems to be associated with the prefactor in $\tau_1$.

Although experimentally well evidenced by our $T_1$ data, the slightly larger mobility of meso with respect to racemic microstructures for aPP in solution has a molecular origin which appears extremely difficult to assess on the basis of the chemical formulas of the different stereosequences only. In the following, we present a molecular dynamics study of PP in solution which helps to unravel the geometrical and dynamical aspects of the orientational motions of C-H bonds.

III. MODELING AND MOLECULAR DYNAMICS EXPERIMENTS

A. Model for a polypropylene chain in solution

The model system consists of a single C$_{34}$H$_{70}$ oligomer, either iPP or sPP, embedded in an explicit CCl$_4$ solvent. The chain skeletal carbons are indexed from 0 to 22, the skeletal bonds from 1 to 22 with bond $i$ connecting carbons $i-1$ and $i$ denoted as $C_{i-1}$ and $C_i$. The methyl pendant groups, ar-
ranged to form either meso or racemic diads, are connected to the odd numbered (methine) carbons of the main chain. The PP fragment is simulated as a semi-flexible chain where methine, methylene and methyl side groups are modeled as pseudoatoms, thus acting as single force centers coincident with single mass point particles. Similarly, solvent molecules are treated as single pseudoatoms. The C units are interconnected by rigid C-C bonds of length $l_{CC} = 1.53 \text{ Å}$. The C-C-C bending motions are explicitly considered in the chain model: in addition to a bending term associated with any pair of adjacent skeleton bonds, there are two C-C-C bending terms per methine carbon which involve each of the adjacent C-C skeleton bonds and the lateral C-C covalent bond connecting the methyl side group. Denoting bending angles as $\theta_{j,k}$ between adjacent C-C bonds $j$ and $k$, the total bending potential associated with the four bending angles of a propylene monomeric unit is expressed as

$$V_b = \frac{1}{2} \kappa (\Delta_{j,j+1}^2 + \Delta_{i,i+1}^2 + \Delta_{j,i}^2 + \Delta_{i,j+1}^2),$$

where $\kappa$ is the bending force constant, $\Delta_{j,j+1}$ is the dihedral angle formed by the four consecutive C-C bonds between the $j$th and $(j+1)$th methine carbons, with the $j$th carbon being the first atom of the new unit, and $\Delta_{i,i+1}$ is the dihedral angle formed by the four consecutive C-C bonds between the ith and $(i+1)$th methine carbons, with the ith carbon being the first atom of the new unit.

$\kappa$ is the bending force constant, and $\Delta_{j,j+1}$ is the dihedral angle formed by the four consecutive C-C bonds between the $j$th and $(j+1)$th methine carbons, with the $j$th carbon being the first atom of the new unit, and $\Delta_{i,i+1}$ is the dihedral angle formed by the four consecutive C-C bonds between the ith and $(i+1)$th methine carbons, with the ith carbon being the first atom of the new unit.

The last term of $V_b$, with the adopted choice for $\kappa'$, does not affect small amplitude vibrations but has been added in an ad hoc way to prevent the onset of accidentally large amplitude fluctuations leading to the occurrence of a planar conformation of the three bonds $i$, $i+1$ and $i'$, an intermediate conformation toward the inversion of a methylene carbon. We note that a similar strategy was found to be necessary in the independent work of Antoniadis et al. who devoted to a study of atactic polymer melts by molecular dynamics. For the potential term governing the internal rotation around a C-C skeleton bond, we adopt the torsion potential of isopentane proposed by Jørgensen which reads

$$V(\phi_j) = V_0 + \frac{1}{2} V_1 (1 + \cos \phi_j) + \frac{1}{2} V_2 (1 - \cos 2 \phi_j) + \frac{1}{2} V_3 (1 + \cos 3 \phi_j),$$

where $\phi_j$ is the torsion angle defined in the Jørgensen convention whereas the zero angle of torsion in isopentane corresponds to the double gauche conformation for which, in the Newman projection, the C-C bond linking the methyl to the methylene carbon lies along the bissector of the pair of C-C bonds connecting the methyl groups to the methine carbon. The energy parameters, expressed in kJ/mol, are $V_0 = 11.3403$, $V_1 = 6.3787$, $V_2 = 2.2279$, $V_3 = 14.435$. As Fig. 4 shows, this potential displays two degenerated minima for $\phi_j = 124^\circ$ and $\phi_j = 236^\circ$ which are adopted as zero of potential through the suitable choice of $V_0$.

For polymers, one generally uses the Flory convention whereby a dihedral angle $\phi$ is defined by three adjacent skeleton bonds, with angle zero being the trans conformation. The geometry of the molecule leads to an angle of $\phi = \pm 116.6^\circ$, i.e., a gauche state in the Flory convention, for the Jørgensen isopentane double gauche reference state. The link between Jørgensen and Flory conventions is thus $\phi_j = \phi = \pm 116.6^\circ$, depending upon the chirality of the methine carbon in a PP fragment. We further note that, in Flory convention, the two lowest potential minima in Fig. 4 correspond to a slightly shifted trans conformation ($\pm 7.4^\circ$) and to the second gauche state ($\pm 119.4^\circ$).

In our model, the solvent molecules and the PP methine, methylene and methyl groups are modeled as Lennard-Jones (LJ) particles. In the present case, we took a common set of two parameters for all types of C groups and a set for tetrachloride, using Lorentz-Berthelot rules for cross terms. Note that, as suggested by the optimization of parameters for longer alkane chains, we treat the 1–5 interactions in the chain (C groups separated by four C-C bonds) with different LJ parameters from those specific for more distant C groups. All relevant adopted Lennard-Jones parameters are gathered in Table I. In order to speed up calculations, a cutoff distance $d = 2.5 \sigma$ was introduced in the calculation of the Lennard-Jones energies and forces, where $\sigma$ depends upon the particular pair in interaction (see Table I).

In order to link simulation data to the experimental observations discussed in the NMR section, we will need to compute the OACF defined by Eq. (3) on the basis of the C-H bond orientations. The latter need to be expressed in terms of the positions of the united atoms, i.e., center of forces/masses located at the carbon nuclei positions, given that hydrogen atoms are not explicitly considered by the microscopic model. Methylene C-H bond unit vectors are specified by the orientation of the isocell triangle formed by the ith carbon nucleus and the two connected hydrogens, as follows:

![Fig. 4. Isopentane dihedral angle potential expressed in terms of $\phi_j$ (see text). The horizontal dashed line indicates RT energy (in kJ/mol at $T = 400$ K).](image)

### Table I. The chosen parameters for the Lennard-Jones interaction potential between carbon pseudoatoms (either CH, CH$_2$ or CH$_3$ groups) and solvent pseudoatoms S (tetrachloride). Parameters valid for C...C 1-5 interactions only are specified by (1-5) symbol.

<table>
<thead>
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<th></th>
<th>$\epsilon/k_B$ (K)</th>
<th>$\sigma$ (Å)</th>
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<tbody>
<tr>
<td>C...C (1-5)</td>
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<td>4.00</td>
</tr>
<tr>
<td>C...C</td>
<td>60.2</td>
<td>4.00</td>
</tr>
<tr>
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<td>5.27</td>
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<tr>
<td>S...C</td>
<td>149.8</td>
<td>4.64</td>
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</table>
the bissector of the 106° HCH angle is taken coincident with the bissector of the skeleton C\(_i\)-C\(_{i+1}\) bending angle with the HCH plane being taken to be perpendicular to the C\(_i\)-C\(_{i+1}\) plane. The methine C\(_i\)-H orientation is specified as opposite to the vectorial sum of three unit vectors pointing along the C\(_i\)-C bonds and directed away from C\(_i\).

In order to single out the effect of torsion librations on the C-H OACF, we have computed the same C-H OACF on molecules enclosed in a cubic box with side 5\(\times\)5\(\times\)5 Å, starting from normal initial conditions (i.e., sampled from the usual PP + solvent equilibrium ensemble at the required temperature) but in which jumps are artificially prevented to occur. Technically, this is obtained by adding to the regular torsion potential \(V(\phi_j)\) of the PP model unphysical well functions \(\exp(k^{(6)}(\phi_j-\phi_j^{(6)})^6-1)\) centered on the \(i\)th minimum \(\phi_j^{(i)}\) of \(V(\phi_j)\), as shown in Fig. 4. The chosen parameters \((k^{(1)}=2, k^{(2)}=4, k^{(3)}=4)\) are chosen to make those wells sufficiently flat in the minimum region to allow perturbing the torsion potential significantly for energies below a few \(k_BT\) but sufficiently steep at further distances to act as infinite walls and hence prevent any conformational jumps from occurring: the polymer internal moves are then limited to bending and large-amplitude librations.

For all runs, the Cartesian equations of motion are integrated numerically using the velocity version of the Verlet algorithm combined with the method of constraints known as the RATTLE algorithm.\(^{31}\) The time step is fixed to 2.3 fs.

### B. Molecular dynamics experiments of either an IPP or a sPP oligomer in solution

All our molecular dynamics calculations on PP in tetrachloride have been performed on a system consisting of a single oligomer C\(_{34}\)H\(_{70}\) and 239 CCl\(_4\) Lennard-Jones molecules enclosed in a cubic box with side \(L=32.0\) Å, leading to an overall density of 1.51 g/cm\(^3\). We note that the radius of gyration of the oligomer, being typically 6–7 Å in our experiments, is such that \(R_g/L<0.25\), which guarantees minor interferences with image chains generated by periodic boundary conditions.\(^{32}\) Table II gives a complete list of the experiments which are discussed in this paper.

The total length of the simulations, denoted as \(t_{DM}\), is three or four orders of magnitude longer than the relaxation time \(\tau_c\) of the relevant correlation function \(G(t)\). It is more pertinent, although a bit severe when probing a local property, to judge the statistics in our MD experiments in terms of the number of independent chain configurations in the sampling calculated as the ratio between the total time of simulation and the chain global relaxation time \(\tau_R\). At 418 K, the relaxation time of the end-to-end vector correlation function is \(\tau_R\approx150\) ps, leading to \(\approx700\) independent configurations. For the lower temperature runs, the statistics is somewhat poorer, but we estimate that the number of independent configurations remains above 100.

The comparison between time scales \(\tau_c\) and \(\tau_R\) at 418 K shows that, for the adopted oligomer size, there is a factor of \(\approx15\) between the global chain dynamics and the relevant local dynamics time scale: throughout this study, we will assume that the influence of the global rotation of the chain can be neglected in the interpretation of the OACFs.

We finally note in Table II that, for the 418 K temperature case, we performed a series of 50 (iPP) or 70 (sPP) MD trajectories of time length \(\approx0.56\) ns, with jumps artificially forbidden.

### IV. SIMULATION RESULTS ON THE LOCAL DYNAMICS

#### A. End chain effects on orientational autocorrelation functions

Due to obvious computer limitations, our study deals with oligomers and not with long polymers chains. Finite size effects induce a larger mobility of atomic groups at the chain ends. To appreciate these effects on the OACF as defined by Eq. (3) in a quantitative way, we show in Fig. 5 the effective correlation time \(\tau_c\), as defined in Eq. (4), as a function of the C chain index in the case of the \(T=418\) K IPP oligomer simulation. We observe a systematic increase of the correlation times from the chain end toward the center, the mobilities of methine and methylene C-H bonds showing a unique trend within our statistics. The onset of a plateau in the central region indicates that the correlation time becomes

<table>
<thead>
<tr>
<th>Experiment type</th>
<th>(T) (K)</th>
<th>(\tau_c) (ns)</th>
<th>(t_{DM}) (ns)</th>
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<td></td>
<td></td>
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<td>50</td>
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<td>normal</td>
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<tr>
<td>blocked jumps</td>
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</tbody>
</table>
nearly constant for the four or five central C-H bonds. In the following, we will assume that the dynamics of these central C-H bonds is representative of the local dynamics of longer chains. More precisely, the calculation of $G(t)$ for methine C-H bonds uses the bond, implying the central carbon (the C$_{11}$ methine) of the oligomer only, while the corresponding calculation for bonds implying the methylene carbon uses the four C-H bonds linked to carbon atoms adjacent to the central one.

**B. Detailed analysis of orientational autocorrelation function of iPP and sPP at 418 K**

Figure 6 shows the methine C-H $G(t)$ curves for both iPP and sPP solutes at three temperatures. Results derived from this figure are summarized in Table II. In addition to the usual trend whereby relaxation is faster as the temperature increases, one notes a slight but systematic faster orientational decorrelation for the iPP segment with respect to the sPP one, in qualitative agreement with the NMR experimental observations described in Sec. II. We postpone for later discussions both the temperature dependence of the relaxation and the comparison of the mobilities of the two tactic forms. We first concentrate on some possible functional forms for the $G(t)$ function and try to relate them to the molecular motions which give rise to the local chain dynamics.

A closer examination of the $G(t)$ curves indicates a first initial decay over a short time ($\approx 0.2$ ps) due to high frequency modes combining probably bending and fast librational motions. At longer times, the reorientation of the C-H bond in space results from two mechanisms related to the main chain torsional motions around the C-C bonds, namely conformational jumps and random low frequency/large-amplitude librations. It is reasonable to assume that these two contributions act independently on the C-H reorientation and therefore we propose, as a conjecture, the partition

$$G(t) = G^{\text{jump}}(t)G^{\text{lib}}(t),$$

where the two new functions represent the decay induced by a specific mechanism.

The function $G^{\text{lib}}(t)$ can be accessed by considering the C-H reorientation for time windows (portions of trajectories) over which no jump is observed in the neighborhood of the particular C-H bond under consideration. Following a suggestion of Moe and Ediger, we have alternatively performed MD runs for iPP and sPP oligomers at the same temperature/density state point in which jumps were forbidden. The OACF $G^{\text{lib}}(t)$ was evaluated as an average over all the different 50 (iPP) or 70 (sPP) initial conformations.

Figure 7 shows the functions $G^{\text{lib}}(t)$ for iPP and sPP in the case of the methine C-H vector. Identical results were obtained for methylene C-H vectors. This function is apparently independent of the tacticity. It decays on two time scales. The fast decay on the time scale of a few 0.1 ps already noticed for $G(t)$ (see inset of Fig. 7) is followed by a nonexponential decay characterized by a typical time of about 50 ps. Our calculation stresses, as was first noticed by Moe and Ediger on polyisoprene, that in the case of polymers in solution, large-amplitude/low frequency librations are responsible for a large part of the decay of the OACF.

Continuing with our assumption that $G(t)$ is a product of a function reflecting ‘natural’ low frequency/large-amplitude torsional librations in the bottom of potential wells and, on the other hand, a function reflecting the effects of the jumps together with possible correlated large-amplitude torsional librations preparing or damping the jump events, the functions $G^{\text{jump}}(t)$ can be obtained from $G(t)$ and $G^{\text{lib}}(t)$ using Eq. (11). Figure 8 shows $G^{\text{jump}}(t)$ function for the methine and methylene C-H vectors in the cases of iPP and sPP oligomers. As expected from our previous analysis, these rather noisy curves exhibit a faster decay for iPP, the origin of which has to be related to some distinction in the jump events. This point will be discussed shortly.

We now discuss the pertinence of various analytical OACF’s to interpret the observed relaxation functions. By analyzing the decay of $\langle P_2(\cos(\theta(t))) \rangle$ for a linear array of rigid rotors coupled by harmonic angular forces, it has
expression $G$ and $2$ by an exponential decay $\exp(-t/\tau)$.

Effects on the relaxation function of correlated and isolated original one-dimensional model of Hall and Helfand, to the

rotator model at intermediate and long times, respectively. It has been shown that the associated OACF would follow an $\exp(-t/\tau)$ decay at intermediate times ($t \simeq \tau$) followed by an exponential decay $\exp(-t/\tau)$ at longer times. Looking at Fig. 7, the shape of the relaxation function $G_{\text{HH}}(t)$ lends itself to a stretched exponential functional form and we therefore consider in an ad hoc way the form

$$G_{SE}(t) = (1 - a') \exp(-t/\tau_3)^\beta,$$

where $\beta$ is an effective power and the initial value $(1 - a') < 1$ accounts for the rapid initial decorrelation. Figure 7 shows the quality of the best fit of $G_{\text{HH}}(t)$ obtained with expression (12) using the parameters listed in Table III. In particular, the value of $\beta$ seems reasonable as it is intermediate between the values $0.5$ and $1$ predicted for the simple rotator model at intermediate and long times, respectively.

On the other hand, it is interesting to analyze the function $G_{\text{HH}}^\text{jump}(t)$ in terms of the analytical expression of Hall-Helfand (HH),

$$G_{\text{HH}}^\text{jump}(t) = \exp(-t/\tau_1) I_0(t/\tau_1),$$

where $I_0$ is the modified Bessel function of order zero, where the characteristic times $\tau_1$ and $\tau_2$ correspond, at least in the original one-dimensional model of Hall and Helfand, to the effects on the relaxation function of correlated and isolated jumps, respectively.

A tentative fit of $G_{\text{HH}}^\text{jump}(t)$ by $G_{\text{HH}}(t)$ gives the result that a two parameters fit is not signification better than a single parameter fit based on the two last factors of Eq. (13), implying $\tau_1$ only. So we chose to fit the $G_{\text{HH}}^\text{jump}(t)$ data with the function $G_{\text{HH}}^\text{jump}(t)$ defined by

$$G_{\text{HH}}^\text{jump}(t) = \exp(-t/\tau_1) I_0(t/\tau_1).$$

We report in Table III the fitting parameters obtained for the iPP and sPP functions from both methine and methylene curves and the resulting curves are shown in Fig. 8.

Returning to the global OACFs, we have tried a direct fit of $G(t)$ for iPP and sPP by the combined (four parameters) trial function,

$$G_{\text{SEHH}}(t) = (1 - a') \exp(-t/\tau_3)^\beta \exp(-t/\tau_1) I_0(t/\tau_1),$$

the SEHH acronym indicating a merging of a stretched exponential and the Hall-Helfand functions. We find that the parameters $a'$, $\beta$, and $\tau_3$ are not significantly different for the iPP and sPP cases and therefore we preferred to perform the fit by taking a unique set of these three parameters for both tacticities (both methylene and methine carbons) leaving $\tau_1$ as the only parameter sensitive to tacticity. Resulting parameters values are given in Table III. It is remarkable that the global fit of $G(t)$ leads to parameters in very close agreement with values extracted from separate fits on $G_{\text{HH}}^\text{ip}(t)$ and $G_{\text{HH}}^\text{jump}(t)$. The corresponding curve is shown in Fig. 9, together with the simulation data.

In the NMR section, we interpreted the relaxation data in terms of the DLM model [see Eq. (5)]. In Fig. 9, we observe that a tentative fit of the simulated $G(t)$ for iPP and sPP based on the three parameters DLM functional form (using a unique set of parameters $\tau_2$ and $a$ for both tacticities) appears to be as good as the more flexible fit with the four parameters SEHH model function (15). Table IV gathers values of DLM parameters for both iPP and sPP oligomers. We note that the $\tau_1$ parameters extracted from both models are reasonably close to each other.

### C. Temperature dependence of the local dynamics

We have analyzed the global OACF $G(t)$ obtained for iPP and sPP, for both methine and methylene carbons, at three temperatures for the same density (see Table II) in terms of the DLM and the SEHH model functions. The fits for 300 and 350 K data were performed according to the

<table>
<thead>
<tr>
<th>MD function</th>
<th>Fit model</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_3$ (ps)</th>
<th>$\beta$</th>
<th>$a'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{\text{HH}}^\text{ip}(t)$ 418 K</td>
<td>$G_{\text{HH}}^\text{ip}(t)$ [Eq. (14)]</td>
<td>15±1</td>
<td>19±1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$G_{\text{HH}}^\text{ip}(t)$ 418 K</td>
<td>$G_{\text{HH}}^\text{ip}(t)$ [Eq. (12)]</td>
<td>29±2</td>
<td>75±0.03</td>
<td>0.17±0.03</td>
<td></td>
</tr>
<tr>
<td>$G_{\text{HH}}^\text{ip}(t)$ 148 K</td>
<td>$G_{\text{HH}}^\text{ip}(t)$ [Eq. (12)]</td>
<td>29±2</td>
<td>75±0.03</td>
<td>0.17±0.03</td>
<td></td>
</tr>
<tr>
<td>$G(t)$ 418 K</td>
<td>$G_{\text{SEHH}}(t)$ [Eq. (15)]</td>
<td>16±1</td>
<td>20±1</td>
<td>30±2</td>
<td>0.77±0.03</td>
</tr>
<tr>
<td>$G(t)$ 351 K</td>
<td>$G_{\text{SEHH}}(t)$ [Eq. (15)]</td>
<td>26±3</td>
<td>34±3</td>
<td>60±2</td>
<td>0.83±0.03</td>
</tr>
<tr>
<td>$G(t)$ 302 K</td>
<td>$G_{\text{SEHH}}(t)$ [Eq. (15)]</td>
<td>63±3</td>
<td>72±3</td>
<td>77±10</td>
<td>0.85±0.03</td>
</tr>
</tbody>
</table>
procedure explained in the previous section for the 418 K data of the global OACF $G(t)$. All resulting fits are good. The best fit parameters are gathered in Tables III and IV for the SEHH and the DLM models, respectively.

The molecular dynamics technique also offers the possibility to test directly whether the $\tau_1$ parameter is indeed closely related to the mean time between jumps, namely the inverse jump frequency. Accordingly, we have counted the number of jumps in the central part of the oligomer (the ten central skeleton bonds). A jump is defined as the move of a dihedral angle from one torsional potential well to the bottom of a neighboring one (more precisely whenever the angle enters a $\sim 15^\circ$ range centered on the new well bottom). In Table V, we give the number $\lambda$ of individual bond conformational jumps per nanosecond for the two oligomers at the various temperatures.

In Fig. 10, all $\tau_1$ estimates and mean times between jumps are presented on a log time-inverse temperature plot. For the mean time between jumps, we get very convincing linear plots with almost identical slopes for iPP (12.5 kJ/mol) and sPP (12.4 kJ/mol). Within the accessible precision, $\tau_1$ estimates obey an Arrhenius behavior with a slope compatible with the activation energy extracted from the temperature dependence of the jump frequency. This common slope corresponds almost exactly to one barrier height in the isopentane potential (see Fig. 4). Moreover, the analysis of Tables III, IV, and V indicate that the mean times between jumps is approximately twice the $\tau_1$ estimates from the $G(t)$ OACF’s. This strongly suggests a physical interpretation of $1/\tau_1$ as a measure (up to a factor of $\approx 1$) of the jump frequency with a global jump contribution to $G(t)$ given by the $G_{\text{HH}}(t)$ expression [Eq. (14)].

The unique activation energy extracted from the slopes of the Arrhenius plots in Fig. 10, which amounts to a single torsional barrier height, apparently lacks a significant contribution from the temperature dependence of the solvent viscosity.36,37 The reason for this should be related to the fact that, in our simulations, we do not follow a temperature dependence at a constant pressure but at a constant density: the latter situation should be characterized by a much weaker temperature dependence of the viscosity.

### D. iPP versus sPP local dynamics

In Table V we see that, at any temperature, the number of individual bond jumps for iPP systematically exceeds by $\approx 10\%$ the corresponding number for sPP. This observation is consistent with the values of $\tau_1$ derived from the fits of $G(t)$ which are, at any temperature, systematically smaller for iPP than for sPP, irrespective of the adopted functional form in the fit. Since the stretched exponential decay repre-

![FIG. 9. Methine C-H OACF and fits with the SEHH (---) and the DLM expression (- - -) for the iPP oligomer at 418 K. In inset, the initial decay is magnified.](Image)

![FIG. 10. Relaxation times $\tau_1$ extracted from the SEHH model for both iPP (□) and sPP (▲) and from the DLM model for iPP (○) and sPP (●). The inverse jump frequency 1A. for both oligomers (△ or iPP and ▲ for sPP) at various temperatures is also shown. For relaxation times and inverse jump frequencies, use the ordinate scale indicated, respectively, on the left side or the right side of the figure.](Image)

### Table IV. The parameters relative to the fits of the simulated C-H OACF with the DLM expression.

<table>
<thead>
<tr>
<th>MD model</th>
<th>$\tau_1$ (ps)</th>
<th>$\alpha$</th>
<th>$\tau_2$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G(t)$ 418 K</td>
<td>11±1 14±1</td>
<td>22±0.05 25±5</td>
<td>45±5</td>
</tr>
<tr>
<td>$G(t)$ 351 K</td>
<td>21±2 24±2</td>
<td>21±0.05 23±0.05</td>
<td>73±10</td>
</tr>
<tr>
<td>$G(t)$ 302 K</td>
<td>45±2 55±2</td>
<td>20±0.05 23±0.05</td>
<td>97±20</td>
</tr>
</tbody>
</table>

### Table V. Jumps frequencies (per bond) in iPP and sPP at 418 K. The fractions of isolated and correlated jumps are expressed in percent (see text for the definition of isolated and correlated jumps).

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\lambda$ (ns$^{-1}$)</th>
<th>Isolated jumps</th>
<th>Correlated jumps</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$i=0$</td>
<td>$i=2$</td>
</tr>
<tr>
<td>iPP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>418</td>
<td>36.2</td>
<td>51</td>
<td>20</td>
</tr>
<tr>
<td>350</td>
<td>17.8</td>
<td>69</td>
<td>12</td>
</tr>
<tr>
<td>303</td>
<td>8.7</td>
<td>75</td>
<td>11</td>
</tr>
<tr>
<td>sPP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>418</td>
<td>31.5</td>
<td>54</td>
<td>22</td>
</tr>
<tr>
<td>350</td>
<td>16.1</td>
<td>69</td>
<td>16</td>
</tr>
<tr>
<td>303</td>
<td>8.0</td>
<td>75</td>
<td>11</td>
</tr>
</tbody>
</table>
senting the effect of low frequency librations on the relaxation was found to be identical for both tacticities, the distinction between the $\tau_1$ values is then most probably responsible for the faster decorrelation of the orientational correlation function for the iPP oligomer at each temperature (see Fig. 6). More precisely, as activation energies extracted from the jump frequency and from $\tau_1$ estimates are similar for both tactic forms, it means that ultimately, the origin of the relatively faster local dynamics of iPP has to be found in the jump frequency prefactor, which is usually related to entropic effects in the thermodynamic interpretation of kinetic constants. This is a plausible explanation as meso and racemic diads lead to different energy maps as a result of the tacticity dependent 1–5 interactions.

This simulation analysis on the somewhat faster local dynamics of the purely meso stereosequence with respect to racemic sequences and its origin are qualitatively in good agreement with NMR results presented in Sec. II. Both experimental and simulation results are, however, difficult to quantify more precisely as the tacticity effects are rather weak, of the order of a few error bars only.

E. The DLM model and its molecular interpretation

On the basis of the previous sections, which were devoted to a refined analysis of simulated OACF’s, we hereby summarize arguments which demonstrate the relevance of the DLM functional form, closely linked to the original Helfand version, at the price of a partial reinterpretation of the underlying molecular mechanisms.

The HH expression was originally interpreted in terms of a diffusional process of discrete orientations along the chain due to correlated jumps, characterized by a time $\tau_1$, and a damping exponential term characterized by a time $\tau_2$, resulting from all additional orientational relaxation processes (librations, bendings, isolated jumps ...). Our analysis suggests two major points. First, the OACF relaxation mechanism due specifically to jumps can be represented by the $\tau_1$ contribution only, namely the $G_{\text{HH}}(t)$ expression [Eq. (14)]. Next, the remaining relaxation effects due to librational motions split into fast and slow libration effects. The initial drop of the OACF occurring on a time scale shorter than 1 ps, which precisely distinguishes the DLM form from the HH one, can effectively be taken into account by a $(1-a)$ or $(1-a^t)$ prefactor [see Eqs. (5), (12), and (15)]. The large-amplitude/low frequency contributions of libration motions which must originate from cooperative effects, take place on a time scale $\tau_3 \gg 1$ ps. On runs performed with jumps prevented from occurring by artificial barriers, the OACF decay due to these torsional modes is best represented by a stretched exponential. Summarizing, the DLM model function therefore differs from the SEHH functional form [Eq. (15)] by the stretched (versus simple) exponential when we identify both $\tau_2$ (DLM) and $\tau_3$ (SEHH) relaxation times. Three parameters fits of the simulated OACF using the DLM form are, however, practically indistinguishable from fits with the SEHH form, which offers the additional freedom to fix the stretched exponential exponent. A fortiori, fits of experimental data of $T_1$ with the SEHH form are not significant, given the error bars on data. We finally stress that the previous sections have shown that the $\tau_1$ parameter extracted from a DLM fit is indeed well representative of the mean time between jumps.

F. Refined jump analysis

Correlated jumps play an important role in local chain dynamics. These jumps involve at least two single bond conformational jumps (and two successive energy barrier crossings) occurring at closely spaced times around neighboring bonds. It is the mechanism which allows a particular chain segment to modify its structure in a viscous medium without inducing the rotation of large portions of the chain.

In order to define the concept of correlated jumps, we start by computing for the iPP run at 418 K the number of jumps (using the definition previously given) that occur around bond $k \pm l$ between time $t$ and $t+\Delta t$, knowing that at time 0 bond $k$ undergoes a jump: let this number be converted into a frequency $\lambda_{\pm i}(t)$ by dividing the above number of jumps by $\Delta t$. Note that our correlated jump definition is not based on first passage times as is the case in the Helfand et al. paper.

This jump statistics was accumulated for the central part of the oligomer, namely for index $k$ in the range $10 \leq k \leq 13$ and index $i$ in the range $0 \leq i \leq 5$. Figure 11 shows the frequency $\lambda_{\pm i}(t)$ as a function of time $t$ for different neighboring bonds: $i=0$ means that the two jumps, which are considered, occur around the same bond; $i=1$ or 2 means that both jumps occur around first or second neighbor bonds, respectively. If the jumps were occurring independently of one another, then $\lambda_{\pm i}(t)$ would simply be the average jump frequency around one bond, namely 0.036 jumps/ps as reported in Table VI. On the other hand, if two jumps (close to each other in time and in space) are coupled to each other, it will enhance the $\lambda_{\pm i}(t)$ function at short time.

In Fig. 11, we observe a strong peak in the $\lambda_{\pm 2}(t)$ function at a very short time of $\approx 0.05$ ps which shows the presence of immediate and thus directly correlated jumps at the second neighbor bond level. The $\lambda_{\pm 2}(t)$ function indicates
further, although attenuated, correlation which persists for times up to 10 ps. This can result from late direct correlated jumps or, possibly, from indirectly correlated jumps due to a sequence of directly correlated jumps possibly involving other bonds.

An important correlation is also observed for the \( i = 0 \) case (self-correlated jumps) which culminates at a slightly longer time of \( \approx 0.5 \) ps, easily explained as the time required by the dihedral angle to perform the second jump. A closer analysis shows that most of the self-correlated jumps are of the ‘‘return’’ type, namely \( A \rightarrow B \rightarrow A \). It means that the first transition is often not accommodated by the chain and is followed by the reversed transition: this occurs predominantly across the low barrier of the dihedral angle potential.

We note that the time over which self-correlation occurs is rather long [at 10 ps, the \( \lambda_0(t) \) function has not yet reached its asymptotic value]. Again, this can be due to late ‘‘return’’ single jumps or to indirect effects due to a succession of correlated jumps.

The correlation between two jumps around first neighbor bonds appears to be weak and is quickly lost in less than two ps. The same analysis for further neighboring bonds showed no important correlation between conformational jumps.

In order to analyze quantitatively the amount and the type of ‘‘directly’’ correlated jump pairs, better denoted as cooperative jumps pairs, we need an \textit{ad hoc} operational definition of them. We will distinguish them by selecting those pairs which take place within a short time interval corresponding to twice the corresponding \( \lambda(t) \) maximum. Accordingly, all detected jumps (using our original definition) will be classified into three classes: those correlated with a jump on the same bond if these two jumps take place within an interval of 0.9 ps, those correlated with a jump on the second neighbor bond if the two jumps take place within an interval of 0.1 ps, while all other jumps will be considered as isolated ones.

Table V gathers the proportion of the different kinds of jumps for iPP and sPP at various temperatures. For both iPP and sPP, a large proportion of correlated jumps with the second neighbor bond is found. The number of isolated jumps seems to increase as the temperature decreases, but the criteria being rather arbitrary and temperature independent in our analysis, no obvious conclusion can be stressed about the temperature dependence of the type of transitions.

A deeper analysis of the nature of correlated transitions and their possible relationship to tacticity can be done by considering the sequence of three bonds \( i-1, i, i+1 \) involved in a particular correlated jump. For a self-correlated jump, the jumping bond is taken as the \( i \)th one. For correlated jumps between second neighbor bonds, the two jumping bonds are taken to be the \( i-1 \) and \( i+1 \) ones. We then rename one of the two bond sequences \( (i-1, i, i+1) \) or \( (i+1, i, i-1) \) as 1, 2, 3 in such a way that the 1-2 bond pair is an inter-diad and 2-3 bond pair an intra-diad. In the case of iPP, the most frequent transition (\( \approx 60\% \) out of the second neighbor-correlated jumps) is of the type \( g g \) migration: \( ttt \rightarrow t g \rightarrow g \rightarrow t t \). In the case of sPP, the most frequent transition (\( \approx 60\% \) of the second neighbor-correlated jumps) is the \( g \) pair creation-annihilation: \( t t t \rightarrow g g \rightarrow t t \). Other types of correlated transitions at the second neighbor level never exceed a few percent. Concerning pairs of correlated jumps on the same bond, we find a dominance of \( t t t \rightarrow t g \rightarrow t t t \) (\( \approx 40\% \) for sPP and \( \approx 20\% \) for iPP) and \( t g \rightarrow t t t \rightarrow t g \rightarrow t t t \) (\( \approx 20\% \) for sPP and \( \approx 40\% \) for iPP). The dominance of the quoted types of correlated jumps for both tacticities is related to the fact that they require, for each jumping dihedral angle, the passage over the lowest isopentane potential barrier separating the two lowest minima (see Fig. 4). For self-correlated jumps, we see the trace of the larger fraction of \( t t t \) sequence in sPP and the larger fraction of the ‘‘helix’’ \( t g \rightarrow t t \) sequence in iPP.

V. CONCLUSIONS

We now conclude with a series of relationships between the experiments detailed in Sec. II and the simulation work reported in this paper. The comparison between NMR \(^{13}\)C relaxation measurements on PP in solution and our data obtained by molecular dynamics experiments on segments of iPP and sPP requires a preliminary comment: the PP/solvent model used had not been optimized toward a realistic representation of the solution studied experimentally. Our aim was to build a simple efficient PP model, appropriate for the liquid phase, which contains the basic PP chemical details in order to achieve at minimum computational costs two main goals: first, we wanted to single out the main microscopic effects affecting the shape of OACFs probed by NMR and second, we were interested, in a quantitative way, in the relative dynamical effects between different tactic forms. Adopting therefore the Lennard-Jones solvent model for its simplicity, we developed a united atom/constraints PP model, taking care to ensure a fair representation of local interactions. To appreciate the quality of the local potential model, we checked in a previous paper\(^{39}\) the PP structural single chain properties using Monte Carlo methods on long single chains at \( \theta \) point.\(^{40}\) In particular, the Kuhn segment estimates for the various tactic forms of PP at theta point (400 K) were determined as \( 6.1 \pm 0.1 \) \( \AA \) for iPP, \( 7.9 \pm 0.3 \) \( \AA \) for sPP and \( 6.3 \pm 0.2 \) \( \AA \) for aPP, in rather good agreement with experimental data\(^{41}\) and with earlier theoretical estimates based on rotational isomeric state (RIS) calculations.\(^{42}\) These results already suggest a smaller static flexibility (larger persistence length) of sPP with respect to iPP, the 1–5 interactions forcing more \( tt \) correlations between successive dihedral angles in the sPP form. This also explains the large number of self-correlated jumps of the type \( t t t \rightarrow t g \rightarrow t t t \) in the sPP oligomer.

The new \(^{13}\)C relaxation NMR data on iPP, sPP and specific microstructures in aPP which are reported in this paper for two frequencies over a large temperature range confirm the differences in the \( T_1 \) values of particular stereosequences of atactic polypropylene already reported by other authors.\(^{12–14}\) With our PP/solvent model, the slightly higher dynamical flexibility of iPP fragments with respect to the sPP ones seen by NMR is indeed reproduced by our calculations. A quantitative point of comparison can be done through the ratio of \( \tau_c^{\text{aPP}}/\tau_c^{\text{iPP}} \) using values of \( \tau_c \) reported in Table II. At temperatures higher than 80°, this ratio is equal to 1.4±0.1 both for the methine and the methylene carbons,
while we get ratios of $\approx 1.1$ in the simulations, irrespective of the temperature. The smaller effect found in simulations could be due to a deficiency in the united atom type of model but it cannot be excluded that this ratio is somehow solvent specific.

Our results on PP chains in solution indicate that the local relaxation contains quite important contributions from vibrations extending over the whole time range of the OACF. At short times, both experiments and simulations show a rapid decrease of the OACF as a result of all types of fast libration motions. Our united atom model, however, eliminates from the description all faster librational motions implying hydrogen atoms. It is not surprising that the angle characterizing the librational cone is only 22° in the simulations by comparison with 38° in the experiment, according to the DLM analysis. In both the experiments and simulations, we find no significant difference between the methine and methylene librational cones of the CH bonds. At longer times, large-amplitude low frequency torsional motions contribute for a large part to the relaxation of the relevant OACF, a point recently observed by Moe and Ediger in polyisoprene simulations.33

Thanks to our simulation analysis of $G(t)$ in terms of the respective influences on the relaxation of the librational motions on one hand and the skeleton jumps on the other hand, namely $G(t) = G^{lib}(t)G^{jump}(t)$, we are able to test the validity of the phenomenological DLM approach. We find that the $\tau_1$ parameter extracted from the DLM fit on the OACF is not very far from the $\tau_1$ estimate based on the direct fit of $G^{jump}(t)$. The DLM $\tau_1$ value is found to scale with temperature as the mean time between jumps, i.e., as an Arrhenius law with one torsional barrier height as activation energy. This consistence, found within the present PP simulation study, gives much credit to the interpretation of the $G^{HH}(t)$ expression [Eq. (14)] as the jump contribution to the OACF. We also find that the time $\tau_2$ has to be related to large-amplitude librations. However, in the DLM model, the exponential term $\exp -t/\tau_2$ is probably not optimal for representing the effect of low frequency librations which seems to be better described by a stretched exponential. The global fit of the OACF to the three parameters DLM model appears, however, as good as the more realistic SEHH model function [derived from a stretched exponential representation of $G^{lib}(t)$]. As observed in the simulations, the ratios $\tau_2/\tau_1$ are temperature dependent.

When considering NMR data over a large temperature range, even at two frequencies, we probably have less precision and thus less information on the OACF than what a model and intensive numerical calculations can provide, as illustrated in the present work with the availability of simulated time functions $G(t)$ with minute statistical noise, at three temperatures. Therefore, to treat the experimental data, the DLM approach appears sufficient for the interpretation of the local dynamics of polymers in solution even if the simplification which consists of adopting a temperature independent ratio $\tau_2/\tau_1$ as a unique additional parameter is not justified.

Our analysis of simulated OACFs led us to detect the origin of the faster relaxation of iPP OACF with respect to the sPP one as a result of a systematically larger number of conformational jumps in the former case. We attribute it to different entropy contributions to the jump rates, the origin lying in the different static probability maps of two consecutive dihedral angles which are sensitive to tauticity.42

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