Dynamics of Polypropylene Chains in Their Binary Blends of Different Stereochemical Sequences Studied by Monte Carlo Simulations[*]

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Abstract The conformational and dynamic properties of polypropylene (PP) for both pure melts and blends with different chain tacticity were investigated by Monte Carlo simulation of isotactic (*i*PP), atactic (*a*PP) and syndiotactic (*s*PP) polypropylenes. The simulation of coarse-grained PP models was performed on a high coordination lattice incorporating short- and long-range intramolecular interactions from the rotational isomeric state (RIS) model and Lennard-Jones (LJ) potential function of propane pairs, respectively. The dynamics of chains in binary PP/PP mixture were investigated with the composition of $C_{150}H_{302}$ with different chain tacitity. The diffusion rates of PP with different stereochemistry are generally in the order as: *i*PP > *a*PP >> *s*PP. For PP/PP blends with 50:50 wt% binary mixtures, immiscibility was observed when *s*PP was introduced into the mixtures. The diffusion rate of *i*PP and *a*PP became slower after mixing, while *s*PP diffuses significantly faster in the binary mixtures. The mobility of PP chains depends on both intramolecular (molecular size and chain stiffness) and intermolecular (chain packing) interactions. The effect of intramolecular contribution is greater than that of intermolecular contribution for *i*PP and *a*PP chains in binary mixtures. For *s*PP chain, intermolecular interaction has greater influence on the dynamics than intramolecular contribution.

Keywords: Binary blends of PP with different stereochemical sequences; Dynamics; Tacticity effect; Monte Carlo Simulation.

INTRODUCTION

Blending is one of the most effective methods to develop new materials for special applications by mixing two or more components together. This strategy is usually used to produce new polymeric materials. It is well known that the micro-phase separation structure of a polymer blend is controlled by its compositions[1−5]. Small differences in the covalent structure of the chains are subject to strong changes in the qualitative appearance of the phase diagram[6−10]. The mixing behavior of polymeric hydrocarbon melts of minor structure change is illustrated by various experimental and theoretical investigations of conventional polyolefins[11−14].

The behavior of simple polymeric hydrocarbon pairs in polyethylene (PE) and polypropylene (PP) blends is generally known to be incompatible[15−17]. Phase separation in the melts is consistent with short range order in liquid state of PE and PP. For PE chains, their radius of gyration remains constant in crystal and melt states[18−20]. Immiscibility of PE/PP blends is also illustrated by pair correlation functions (PCFs), the solubility parameter and Flory-Huggins interaction parameter[21, 22].

PP/PP blend melt provides a very interesting example of the sensitivity of the mixing of polymeric hydrocarbon polymers. A binary mixture of short chains of atactic polypropylene (*a*PP) and isotactic polypropylene (*i*PP) is miscible in the melts[23] but not for long chains due to minor mixing entropy. Moreover, immiscibility was observed only by replacing either species by syndiotactic polypropylene (*s*PP)[23, 24]. The mechanism responsible for immiscibility in PP was found to be different from PE/PP blends in melt states. The chain dimension and the cohesive energy of PP mixtures in both two- and one-component melts are approximately the same[25]. Moreover, the change in the mixing energy of the two-component, ΔE_{AB}, is zero in *a*PP and *i*PP but if either component is replaced by *s*PP, ΔE_{AB} is positive[26]. These results agree with the behavior of PP chain with zero chemical potential, $\Delta\mu$, for the transfer of *i*PP and *a*PP chains. However, $\Delta\mu$ of *s*PP is positive for the transfer change of *s*PP/*i*PP and *s*PP/*a*PP melts[27]. In addition, another reason for the immiscibility in the binary blends of PP with different stereochemical sequences could be the component-selective crystallizability[28]. In addition, PCFs are also utilized to characterize the intermolecular interaction of polymer blends, and *s*PP tends to avoid close contact with *i*PP more than with *a*PP[26]. For these binary blends of PP with different stereochemical sequences, the immiscibility in *i*PP/*s*PP is stronger than that in *a*PP/*s*PP blends[29–31].

Waheed *et. al.*[32] showed that the average mobilities of *i*PP and *s*PP are similar but individual bead in each chain can depart greatly from the average value. Every bead in *i*PP melt can move in a short time period whereas for *s*PP melt, a few beads could rarely move. The correlation times for conformational transitions of *s*PP were also slower than that of *i*PP[33]. Even though there are some past simulation works on structural and thermodynamic properties of binary blends of PP with different stereochemical sequences, there is still no detailed study about the dynamic properties reported for binary blends of PP with different stereochemical sequences with different chain tacticity from those previous reports[27, 30, 32–34].

In this article, the structure and dynamic change for PP chains are investigated for binary blends of PP with different stereochemical sequences. Monte Carlo simulation would be utilized to examine the dynamic properties of PP chains in both pure melts and binary blends of PP with different stereochemical sequences (50:50 wt% mixtures) with different chain tacticity.

MODEL AND METHOD

The Second Nearest Neighbor Diamond Lattice (2nnd)

PP molecules were modeled by a chain of beads, and each bead was represented by $-CH_2CH(CH_3)-$ unit. The coarse-grained beads were represented by two backbone carbons, which can be placed on the second nearest neighbor diamond lattice (2nnd). This lattice was constructed by removing all second alternating sites from the tetrahedral diamond lattice. The lattice has $10i^2 + 2$ sites in the ith shell, identical to the closest packing of hard spheres. These coarse-grained beads were at the center of the backbone carbon atoms that were bonded to the methyl side group. The step length of the PP melts simulation on the lattice was 0.25 nm obtained from the standard C$-$C bond length. So, the simulation was performed in a manner that retained the memory of the underlying diamond lattice with all carbon atoms in the backbone being mapped[25–27].

System Description

The simulation was performed with 64 PP independent parent chains and each of 50 beads in periodic boundary condition of $30 \times 30 \times 30$ unit cell. This unit cell produced a density of 0.750 g/cm^3 with 11.85% of bead occupancy on 2*nnd* lattice (but the remaining from bead occupancy (88.15%) was not freely accessible). The density of the system was determined by the geometry of the high-coordination lattice and the associated mass of a $-CH_2CH(CH_3)-$ unit on which each bead is placed. Simulations were reported for six compositions consisting of three systems of pure melts and of binary mixtures as expressed in Table 1.

Table 1. Number of chains for polypropylene (PP) pure melts and binary mixtures (50:50 by weights)

Systems	Number of chains		
	*i*PP	*a*PP	*s*PP
*i*PP pure melts	64	–	–
*a*PP pure melts	–	64	–
*s*PP pure melts	–	–	64
*i*PP/*a*PP mixture	32	32	–
*i*PP/*s*PP mixture	32	–	32
*a*PP/*s*PP mixture	–	32	32

Interactions

The energetics of the system was derived from two parts. The local intramolecular interactions were described by the modified Rotational Isomeric State(RIS) model of Suter *et al.*[35], which was mapped onto the coarse-grained PP model. In this model, there were three short-range interactions with statistical weights denoted by η, τ, and ω. Two successive bonds of *meso* diads in *i*PP contributed to the conformational partition functions *via* the product of the two statistical weight matrices as follows:

$$\begin{bmatrix} \eta & 1 & \tau \\ \eta & 1 & \tau\omega \\ \eta & \omega & \tau \end{bmatrix} \begin{bmatrix} \eta\omega & \tau\omega & 1 \\ \eta & \tau\omega & \omega \\ \eta\omega & \tau\omega^2 & \omega \end{bmatrix} \quad (1)$$

In *s*PP case, four successive bonds in *s*PP chains contributed *via* the product of four statistical weight matrices.

$$\begin{bmatrix} \eta & 1 & \tau \\ \eta & 1 & \tau\omega \\ \eta & \omega & \tau \end{bmatrix} \begin{bmatrix} \eta & \omega & \tau\omega \\ \eta\omega & 1 & \tau\omega \\ \eta\omega & \omega & \tau\omega^2 \end{bmatrix} \begin{bmatrix} \eta & \tau & 1 \\ \eta & \tau & \omega \\ \eta & \tau\omega & 1 \end{bmatrix} \times \begin{bmatrix} \eta & \tau\omega & \omega \\ \eta\omega & \tau\omega^2 & \omega \\ \eta\omega & \tau\omega & 1 \end{bmatrix} \quad (2)$$

The *a*PP was described by the statistical weight matrices defined by

$$\begin{bmatrix} \eta\omega & 1 & \tau\omega \\ \eta\omega & \omega & \tau\omega^2 \\ \eta & \omega & \tau\omega \end{bmatrix} \quad (3)$$

These statistical weights were formulated as Boltzmann factors with energies $E_\eta = 0.29$ kJ/mol, $E_\tau = 3.8$ kJ/mol, and $E_\omega = 8.0$ kJ/mol. The description with a 3×3 statistical weight matrix was mapped into a precisely equivalent model for each propane $-CH_2CH(CH_3)-$ unit. The probability for any PP chain conformation of specified stereo-chemical sequence can be deduced from the 9×9 statistical weight matrices using the RIS model techniques. The ratio of these probabilities for the current and proposed conformation was obtained by Metropolis techniques for acceptance or rejection.

The intermolecular interaction was treated by a discretized Lennard-Jones (LJ) potential energy. This was also used to specify the value of the second virial coefficient for the pair-wise interaction of a propane bead pair using the Mayer *f* function. The effective interaction energy for the ith shell, u_i, was specified by its average Mayer *f* function. The input LJ potential used $\sigma = 0.512$ nm and $\varepsilon/k_B = 237$ K, and reproduced the experimental density of the melt at 473 K (well above the melting point of PP)[36]. Asymmetric perturbation was added in the second shell interaction to represent the repulsive interaction of two methyl groups oriented toward each other[37, 38]. The intermolecular interaction was utilized for all bead pairs from different chains. For pairs of beads that were not the nearest or the next-nearest to each other, intramolecular interaction was treated, instead. The bonded nearest neighbors were separated by a constant distance and the interaction of intramolecular next-nearest neighbors was evaluated separately using the RIS model.

Moves

The fundamental move was chosen so that the sample configuration space is efficient. Single bead moves were employed in this simulation. On a local scale, a single bead may move to an unoccupied neighboring site provided that the distance to the two (one, for end beads) neighboring beads to which it was bonded was unchanged. Local moves would lead to a collapse of the carbon-atom pairs.

The Metropolis criterion (incorporating both the short- and long-range intermolecular interactions) was used to determine the move acceptance. A Monte Carlo step (MCS) was defined as the length of the simulation. One MCS consisted of an average number of moves required to move every bead once. Then, move acceptance was determined by comparing the probabilities of initial and final states through the standard Metropolis criterion. Intra- and inter-molecular contributions to the energy of the system converge to constant values within 2×10^7 MCS. Snapshots obtained from a subsequent 2×10^7 MCS were used in the analysis reported here.

RESULTS AND DISCUSSIONS

Neat Polypropylene Melts

Rotational and translational motion of each pure PP melts are compared in Figs. 1 and 2, respectively. The rotational motion is represented by the orientation autocorrelation functions of the end-to-end vector of the chain ($< \bar{R}(t) \cdot \bar{R}(0) >$). iPP and aPP ($P_m = 0.5$) exhibit a complete decay from an initial value to zero within 10^7 Monte Carlo Step (MCS) while sPP chains decay to about 0.6. The decay rate of sPP melts is considerably slower than iPP and aPP due to longer *trans* sequences in sPP chain. In addition, the translational motion as presented by the mean-square displacement of the center-of-mass (MSD) of PP melts with different chain tacticity is shown in Fig. 2. Similar trends to ($< \bar{R}(t) \cdot \bar{R}(0) >$) are seen. From MSD data, iPP diffuses faster than aPP and sPP, and the diffusion rate can be ordered as; iPP > aPP >> sPP.

A comprehensive study of the effect of stereochemistry on the diffusion of iPP, aPP and sPP was also previously conducted by the same Monte Carlo simulation used in this work. It was also observed that iPP diffuses faster than sPP but a maximum in the diffusion rate at an intermediate stereochemical composition (aPP) was found. Sequences of meso and racemo diads diffuse faster in aPP due to quenched randomness of stereochemical sequences than in iPP and sPP. Comparison to isolated chain acceptance rates suggests that intermolecular cohesiveness of stereochemically pure sequences lowers mobility but can be overcome by the randomness of atactic stereochemistry[32].
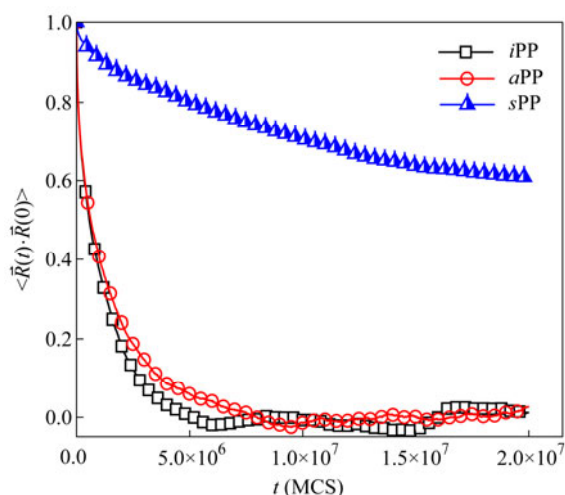
Fig. 1 Orientation autocorrelation function (OACF) for the end-to-end vector $< \bar{R}(t) \cdot \bar{R}(0) >$ for polypropylene pure melts at $T = 473$ K and density $\rho = 0.75$ g/cm^3 as a function of MCS
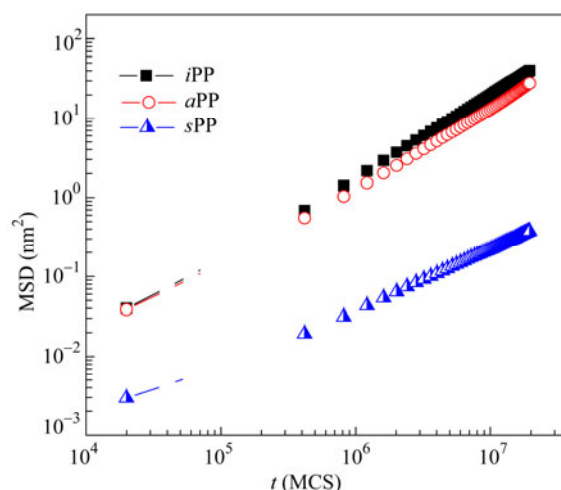
Fig. 2 Mean-square displacement (MSD) of the center-of-mass (COM) in nm^2 for polypropylene pure melts at $T = 473$ K and density $\rho = 0.75$ g/cm^3 as a function of MCS

In addition to simulation works, pulsed-gradient diffusion (D) experiments were also performed to study the effect of stereochemical composition on diffusion in PP melts. For the proton NMR diffusion measurements, three PP specimens of differing molecular weight M and dispersity, with the probability of a meso diads P_m = 0.02 (syndiotactic), 0.23 (atactic), and 0.89 (nearly isotactic) were studied. Both simulation and M-scaled experiment found D at high P_m several times faster than at low P_m. The constant-M simulation also showed a maximum near $P_m = 0.8$ due to quenched randomness[39].

In this work, typical parameters to characterize the properties of PP melts including the diffusion coefficient (D), the mean square radius of gyration $<R_g^2>^{1/2}$ and the characteristic ratio (C_n) representing the mobility, molecular size and chain stiffness are presented in Table 2. The molecular size (the mean square radius of gyration) and chain stiffness (the characteristic ratio) of sPP are the largest as the *racemo* diads prefer to hold up the *trans-trans* conformation. This also leads to the slowest diffusion rate for sPP compared to iPP and aPP.

Table 2. Mean square radius of gyration $<R_g^2>^{1/2}$ (nm), the characteristic ratio $<r^2>_0/nl^2$ and diffusion coefficient D (nm²/MCS) of polypropylene pure melts

Chain	$<R_g^2>^{1/2}$ (nm)	C_n	D (nm²/MCS)
iPP	1.30	4.40	3.42E−3
aPP	1.27	4.23	2.35E−3
sPP	1.35	4.80	2.98E−5

The mean square radius of gyration and the characteristic ratio of iPP are larger than those of aPP because most of meso diads in iPP chains prefer to form helix conformation rather than an extended trans conformation. In addition, Chen *et. al.* have used the same simulation technique to study iPP crystallization and the amount of helix conformation at different temperature. Fraction of iPP repeating units in helical conformation at 473 K is around 0.7[40].

Helix conformation in iPP chains is related to smaller chain dimension and lower chain stiffness. iPP has an intermediate chain dimension and chain stiffness compared to aPP and sPP. However, the diffusion rate of iPP is the fastest; therefore, the intra-chain effect (chain dimension and chain stiffness) may not be the only key factor to control the dynamics of iPP melts. Another factor such as chain packing and intermolecular cohesiveness should play an important role for iPP dynamics. The overall mobility of PP melts can be ordered as: iPP > aPP >> sPP for both rotational and translational modes.

These results suggest that not only the intra-chain effect (molecular size and chain rigidity) but also the inter-chain effect (molecular packing) can influence the mobility of PP chains. Intermolecular pair correlation functions (PCFs) of iPP, aPP and sPP melts were previously reported by Haliloglu *et. al.*[34], PCFs data are more distinguishable in the range of 0.5−0.8 nm and sPP has the highest PCFs at the distance 0.5−0.8 nm compared to aPP and iPP. Furthermore, sPP chain prefers to interact with other sPP chains and has the highest packing density while aPP and iPP have less efficient intermolecular packing. These results suggest that sPP melts retain more "structured" than aPP and iPP melts[26]. Intermolecular packing in sPP makes the chain more difficult to move. Both intra- and inter-molecular contributions should influence on sPP, but, in the case of aPP and iPP, the inter-molecular contribution seem to be greater than the intra-molecular contribution.

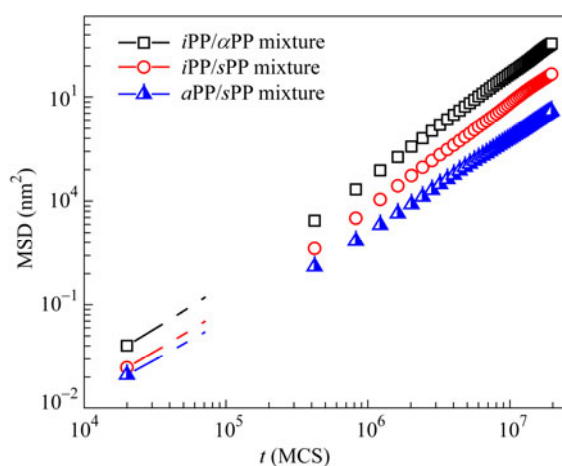### Binary blends of PP with different stereochemical sequences

For binary blends of PP with different stereochemical sequences, the mobility of each PP chain is compared to that of both pure melts. The dynamic behaviors of overall binary blends of PP with different stereochemical sequences were studied without differentiating theirs tacticity. All binary blends of PP with different stereochemical sequences show a $< \bar{R}(t) \cdot \bar{R}(0) >$ decay (Figs. 3 and 4) of about half of the initial value within 5×10^6 MCS, and their rates are distinguished from each other. The overall diffusion rate of each PP mixture decreased when half of iPP or aPP was replaced by sPP chains.

Similar to pure PP melts, the chain interaction between itself in binary blends of PP with different stereochemical sequences is stronger than that between chains with different tacticity and this leads to denser

intermolecular packing. In addition, PCFs of binary mixture indicate that beads in each chain prefer to be surrounded by beads of PP chains with the same tacticity[31]. Similarly, *i*PP chains consisting of meso diads strongly avoid trans conformation as they prefer helix conformation and stay apart from *s*PP chains in which the racemo diads in *s*PP prefer trans conformation. *i*PP and *a*PP chains contain some meso portions and these cause poorer chain packing in *s*PP/*i*PP binary mixture and phase separation for *i*PP/*s*PP and *a*PP/*s*PP mixtures. The observed de-mixing in *i*PP/*s*PP is stronger than that in *a*PP/*s*PP mixture. *i*PP/*s*PP and *a*PP/*s*PP mixtures are immiscible while *i*PP/*a*PP mixture is miscible. *s*PP is immiscible to both *i*PP and *a*PP when they are mixed[26, 34]. In general, the dimension of PP chains in the binary PP mixture is slightly decreased (less than 4% except 17% decrease for *s*PP) after mixing with PP with different chain tacticity. The chain mobility of *i*PP/*a*PP is greater than that of *a*PP/*s*PP mixture, and the magnitude of the overall diffusion rate can be ordered as: *i*PP/*a*PP > *i*PP/*s*PP > *a*PP/*s*PP. The overall mobility indicates that the diffusion of *i*PP and *a*PP in the mixture is slightly decreased while the mobility of *s*PP shows significantly increasing rate up to 2 and 3 times for *s*PP in *i*PP/*s*PP and *a*PP/*s*PP binary mixtures, respectively.
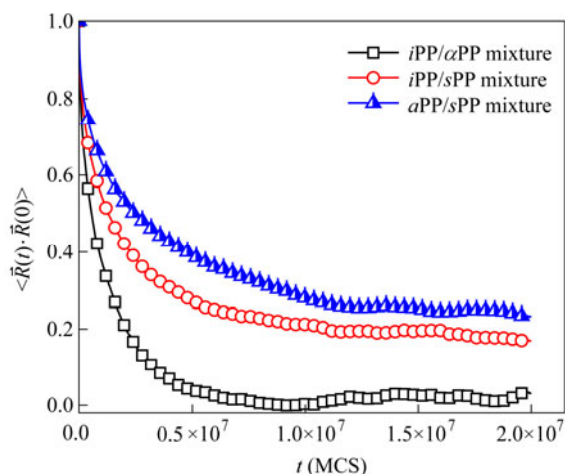
Fig. 3 Orientation autocorrelation function (OACF) for the end-to-end vector $< \bar{R}(t) \cdot \bar{R}(0) >$ for polypropylene binary mixtures at $T = 473$ K and density $\rho = 0.75$ g/cm^3 as a function of MCS

Fig. 4 Mean-square displacement (MSD) of the centers-of-mass (COM) in nm^2 for polypropylene binary mixtures at $T = 473$ K and density $\rho = 0.75$ g/cm^3 as a function of MCS

iPP Chains in Binary Blends of PP with Different Stereochemical Sequences

$< \bar{R}(t) \cdot \bar{R}(0) >$ and MSD of *i*PP chains in pure melts and binary mixtures are compared (figure not shown). All *i*PP chains in binary mixtures decay at slightly different rate. MSD also exhibits similar trends with $< \bar{R}(t) \cdot \bar{R}(0) >$. For example, *i*PP chains in *i*PP/*s*PP mixture diffuse slightly slower than other systems (ordered as: pure *i*PP ≈ *i*PP/*a*PP > *i*PP/*s*PP) for both rotational and translational motions.

The relative values of chain dimension ($<R_g^2>^{1/2}$), chain stiffness (C_n) and diffusion coefficient (D) of PP chains in binary mixtures compared to those in pure system are presented in Table 3. The diffusion rate of *i*PP chains in binary mixtures is smaller. Interestingly, molecular size and chain stiffness of *i*PP in both *i*PP/*a*PP and *i*PP/*s*PP mixture are slightly decreased as: *i*PP > *i*PP/*a*PP > *i*PP/*s*PP. Even though molecular dimension and chain stiffness are decreased, the diffusion rate of *i*PP is decreased in binary mixture. These data indicate that the intra-chain effect (molecular size and chain stiffness) is not the key factor to control the dynamic behavior of *i*PP chains in binary mixtures.

The local intermolecular packing can be obtained from PCFs of binary mixtures and have been previously reported[26, 34]. Accordingly, the presence of *s*PP causes *i*PP chains to aggregate slightly with other *i*PP chains compared to the situation in which *i*PP shares the melt with *a*PP. A more preferential interaction of *s*PP with

other *s*PP chains provides the reason that *i*PP and *s*PP chains try to avoid contacting each other in the melts[34, 38]. This implies that there is less inter-chain packing in *i*PP/*s*PP and *i*PP/*a*PP binary mixtures. *i*PP chains in *i*PP/*s*PP mixture should give the evidence for a preferential contact to themselves more than those in *i*PP/*a*PP system which is quite similar to pure *i*PP melts. These results should be related to smaller diffusion rate of *i*PP component in *i*PP/*s*PP and *i*PP/*a*PP binary mixtures.

Table 3. Relative values of the mean square radius of gyration $<R_g^2>^{1/2}$, the characteristic ratio $<r^2>_0/nl^2$ and the diffusion coefficient D of the chains in binary blends of PP with different stereochemical sequences (50:50 by weights)

Chain	Mixture system	$<R_g^2>_{mix}/<R_g^2>_{pure}$	$C_{n(mix)}/C_{n(pure)}$	D_{mix}/D_{pure}
*i*PP	*i*PP/*a*PP	0.98	0.95	0.94
	*i*PP/*s*PP	0.95	0.91	0.74
*a*PP	*i*PP/*a*PP	0.98	0.97	0.91
	*a*PP/*s*PP	0.96	0.93	0.43
*s*PP	*i*PP/*s*PP	0.83	0.68	2.06
	*a*PP/*s*PP	0.94	0.89	2.90

Moreover, these results can be described in terms of intrachain stereochemical sequences. Because the consecutive *meso* diads in *i*PP chains have significantly less mobility than in the presence of a small amount of *racemo* diads mixed randomly in the chain *i.e.* *a*PP[32, 41, 42]. In binary mixtures, when the neighboring chains of *i*PP are either *a*PP or *s*PP, the [mmm] tetrad in *i*PP chains in the mixture has slightly slower mobility than that of pure *i*PP melts. *i*PP chains in *i*PP/*a*PP mixture have greater mobility than in *i*PP/*s*PP mixture. This is because *s*PP has longer consecutive *r* diads than *a*PP. Hence, *s*PP should have more all-*trans* crystal-like sequence which retards the mobility of other chains in binary mixture.

*a*PP Chains in Binary Blends of PP with Dferent Stereochemical Sequences

$< \bar{R}(t) \cdot \bar{R}(0) >$ of *a*PP chains decays differently from other PPs. Similar trends are also observed for MSD (figure not shown). The mobility of *a*PP chains in *a*PP/*s*PP mixture (rotational and translational modes) is slower than that of pure *a*PP melts and *i*PP/*a*PP mixture whereas the mobility of *a*PP in pure melts and in *i*PP/*a*PP system is indistinguishable from each other.

Generally, the mobility of *a*PP chains in binary mixtures is slower than that of *a*PP in pure melts. Both molecular size and chain stiffness are decreased in the blended systems *i.e.* these properties of *a*PP in *i*PP/*a*PP mixture are slightly greater than in *a*PP/*s*PP mixture. This should be related to slower diffusion rate of *a*PP chains in *i*PP/*a*PP and *a*PP/*s*PP mixtures. *a*PP in *a*PP/*s*PP mixture diffuse slower than in *i*PP/*a*PP mixture even though they have approximately the same molecular size and chain rigidity. These results indicate that intra-chain properties (molecular size and chain rigidity) are not the only factors that affect the dynamic behavior of *a*PP chains in binary mixtures.

It was reported that PCFs are slightly decreased in binary blends of PP with different stereochemical sequences when half of all chains are replaced by *a*PP chains[34]. From those PCFs data, *i*PP/*a*PP melt is miscible while *a*PP/*s*PP blend is immiscible leading to inhomogeneity of *a*PP/*s*PP system. This makes the diffusion rate of *a*PP in *a*PP/*s*PP become smaller than that in *i*PP/*a*PP mixture.

These results can also be described by the effect of the stereochemical configuration of tetrad sequences in PP chains. The mobility of some tetrad sequences in *a*PP depended on their counterpart environment. When tetrad sequences are surrounded by the same tetrads from different *a*PP chains, there is lower intermolecular interaction resulting in poorer chain packing. In addition, the mobility of the random tetrad in *a*PP chains in *a*PP/*s*PP binary mixtures is smaller than that of pure *a*PP melts.

### *s*PP Chains in Binary Blends of PP with Different Stereochemical Sequences

Figures 5 and 6 present $< \bar{R}(t) \cdot \bar{R}(0) >$ and MSD for *s*PP chains in pure melts and binary blends of PP with different stereochemical sequences, respectively. Similar dynamical features of *s*PP are observed in both rotational and translational motion. The mobility of *s*PP in PP/PP binary blends is greater than that of their pure

melts. For *i*PP/*s*PP mixture, due to an aggregation of *i*PP chains, this binary mixture exhibits a demixing. Hence, *s*PP chains in *i*PP/*s*PP system diffuse significantly faster than *s*PP in *a*PP/*s*PP mixture.

The relative values of molecular size, chain stiffness and diffusion coefficient of *s*PP chains in binary PP/PP mixture are presented in Table 2. The data have quite similar trends for *i*PP and *a*PP in their binary mixtures. Both chain dimension and chain stiffness of *s*PP chains in *i*PP/*s*PP mixture are more decreased than those in *a*PP/*s*PP binary mixture. Accordingly, *s*PP chains in binary mixtures can diffuse faster than those of pure *s*PP melts in the order as: *a*PP/*s*PP > *i*PP/*s*PP > pure *s*PP melts. The dynamic behavior of *s*PP chain in binary mixture does not mainly result from an intrachain effect (molecular size and chain stiffness).
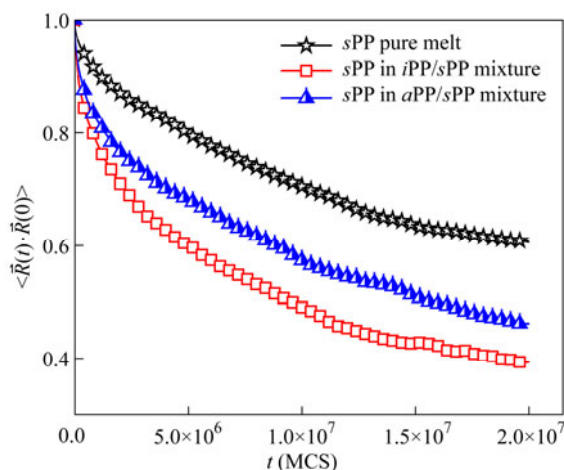
Fig. 5 Orientation autocorrelation function (OACF) for the end-to-end vector $< \bar{R}(t) \cdot \bar{R}(0) >$ of *s*PP chains in pure melts and binary mixture at $T = 473$ K and density $\rho = 0.75$ g/cm^3 as a function of MCS
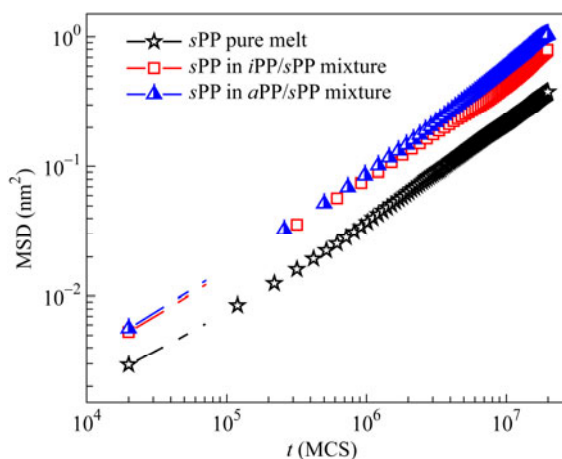
Fig. 6 Mean-square displacement (MSD) of the centers-of-mass (COM) in nm^2 of *s*PP chains in pure melts and binary mixture at $T = 473$ K and density $\rho = 0.75$ g/cm^3 as a function of MCS

The PCFs of binary mixtures depict the general features for the *s*PP chains similar to those of *i*PP chains, but all three PCFs are clearly distinguishable[34]. The chain packing of *s*PP in *i*PP/*s*PP mixture is better than that in *a*PP/*s*PP mixture and pure *s*PP melts. In addition, both *i*PP and *s*PP chains avoid to contact each other. This leads to an self-aggregation of *i*PP and *a*PP chains in binary mixture. An inhomogeneity of binary PP/PP mixtures is caused by preferential interaction among *s*PP chains. This preferential interaction forces *s*PP chains to separate from *i*PP chains in *i*PP/*s*PP more than *a*PP chains in *a*PP/*s*PP system[38].

The intra-molecular effect of tetrad in PP molecules is also utilized to describe the mobility of PP chains. When the neighboring chains consist of random tetrad, the [rrr] tetrad has more mobility than pure stereochemical PP chains. *s*PP chains have more mobility in *a*PP/*s*PP mixture than in *i*PP/*s*PP mixture. An increased mobility of *s*PP (2−3 times higher than that of the pure *s*PP melts) in blends may be related to both a reduction of molecular size and intermolecular contribution when [rrr] tetrad*s* are surrounded by different type of tetrad*s*. All these effects cause the diffusion rate of *s*PP chains in *i*PP/*s*PP mixture smaller than that in *a*PP/*s*PP mixture.

CONCLUSIONS

The structural and dynamic properties of PP melts with different chain tacticity were studied by Monte Carlo simulation. Molecular size, chain stiffness, chain packing and the diffusion of chains were investigated in both pure melts and binary blends of PP with different stereochemical sequences. The diffusion coefficients obtained from simulation are related to both intermolecular (pair correlation function) and intramolecular (molecular size and chain stiffness) contributions.

In pure melts, the diffusion rate of PP with different tacticity is generally ordered as *i*PP > *a*PP >> *s*PP. Both molecular size and chain stiffness provide no clear correlation to the diffusion of PP melts. The mobility is depended not only on the intramolecular contribution but also on the intermolecular interaction among neighboring chains.

Miscibility was observed for *i*PP/*a*PP mixture but not in *i*PP/*s*PP and *a*PP/*s*PP blends. In general, molecular size and chain stiffness became lower when chains with different tacticity were added to binary blends of PP with different stereochemical sequences. The diffusion rates of *i*PP and *a*PP chains in binary mixtures were decreased which should be related to the intramolecular contribution (molecular size and chain stiffness) and intermolecular interaction (chain packing). The diffusion rate of *s*PP chains in the mixtures is higher than that in pure *s*PP melts. This implies that intermolecular contribution affects the chain dynamics more than intramolecular contribution.

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