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Immiscibility of Poly(ethylene) and Poly(propylene): A Molecular Dynamics Study

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ABSTRACT: In this article, we report the results of molecular dynamics simulations for models of poly(ethylene), isotactic poly(propylene), and mixtures of the two to understand the possible origin of melt state incompatibility. At temperatures well above the crystal melting points of the homopolymers, isolated poly(ethylene) and poly(propylene) chains formed high-density collapsed states. The poly(ethylene) and poly(propylene) chains were found to segregate into distinct domains even when the initial state was highly interpenetrating. The poly(ethylene) phase shows a significant amount of local order at the simulation temperature. In the case of poly(propylene), some helical segments were found in the collapsed structure. We speculate that the immiscibility of these two nonpolar polymers, in the melt state, may be due to the differences in local morphology that are present in the melt state.

Introduction

Poly(ethylene) and poly(propylene) are known to be incompatible in general (ref 1 is a recent literature review). This is usually understood in terms of the differences in the crystal habits of the two polymers. Since the two polymers are simple olefins, it might be expected that miscibility would be observed in melted mixtures. If the melt is truly isotropic, the fully entangled, highest entropy state would be one in which the polymers are mixed on a molecular level. While experimental studies are scanty, there is some evidence for incompatibility in the melt state for blends of poly(ethylene) (PE) and isostatic poly(propylene) (i-PP).

Alle and Lyngaee-Jorgensen[2] were able to reduce the capillary flow behavior of such blends to a single master plot of reduced viscosity versus reduced shear rate. From this, it was concluded that the PE/i-PP system formed either a miscible blend under shear flow conditions or a melt structure that did not change much over the temperature range studied. On the basis of the simulation results reported here and other experimental evidence, we believe that the latter explanation is correct.

Small angle neutron scattering has been used to study the phase morphology of a 50/50 blend of high-density poly(ethylene) (HDPE)/i-PP, using deuterium labeling to enhance contrast. A phase-segregated morphology was observed at temperatures as high as 200 °C, which is well above the melting temperatures of the two polymers. The domain dimensions were found to be about the same as those observed in blends crystallized from the melt.[3] Incompatibility between PE and PP was indicated also by observation of mutual solutions in a common solvent.[4]

Phase separation in the melt would be consistent with the existence of short range order in the liquid state of semicrystalline polymers like PE and i-PP. In the case of PE, there is considerable experimental evidence for nonhomogeneous segment densities in its melts. One example is dynamical mechanical measurements, where plots of log G' versus temperature show no terminal zone at temperatures higher than T_m.[5] The elasticity observed in these systems is not due to chemical cross-links; the polymer can be fully soluble. It suggests the pinning of mobile segments of the polymer attached to more ordered regions.

Aharoni and co-workers[6] studied the crystallization of ultra-high molecular weight poly(ethylene) (UHMWPE) and reported that the radius of gyration of the macromolecules was the same in the melt state as in the crystalline material. It was concluded that the crystallization process does not require any large scale reeling in of chain segments. Therefore, in the reverse process of melting, it is expected that relative segmental densities will be retained, especially in the absence of shear. Ballard et al.[7] also used SANS to show that the radius of gyration of a poly(ethylene) sample remained constant in the melt and crystalline states.

In this article, we report the results of molecular dynamics simulations for models of poly(ethylene), isotactic poly(propylene), and mixtures to understand the possible origin of melt state incompatibility. The calculations are based on single- and two-chain models and are not necessarily representative of the bulk state. However, the chains are sufficiently long that, under the influence of induced-diple or van der Waals forces, they form a high-density collapsed state. These preliminary simulations suggest that melt state incompatibility may arise from strong local or short-ranged order in the melt state of poly(ethylene) and is therefore similar to the cause of the immiscibility of the two materials in the solid state.

Molecular Dynamics Simulation

Molecular dynamics simulations were carried out for single-chain models of poly(ethylene) (PE, isotactic poly(propylene) (i-PP), and two-chain models of blends in vacuum. The PE and i-PP models consisted of single chains with 250 and 170 monomer repeat units, respectively. Four two-chain structures were constructed. One consisted of two identical 250-mer PE chains and another of two identical 170-mer i-PP chains. The two remaining systems consisted of one 250-mer PE chain and one 170-mer i-PP chain. In three of our systems, straight chain conformations, i.e., with all skeletal bonds

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Table 1. Lennard-Jones Parameters Used for the Simulations Described in the Text

	σ_0 (nm)	ϵ_0 (kJ/mol)
carbon with one implicit hydrogen	0.3983	0.615
carbon with two implicit hydrogens	0.4068	0.829
carbon with three implicit hydrogens	0.4152	1.047

being in the trans state, were used as the starting conformation. The one exception is a model of a PE/i-PP mixture in which poly(ethylene) and poly(propylene) chains were in a highly entangled state initially.

The model construction and molecular dynamics simulations were performed by using POLYGRAF version 3.2.1, a commercial polymer modeling software.[8] In all of our models we have used united-atom representations, in which hydrogen atoms are not modeled explicitly, to reduce the model complexity. The united-atom approximation may introduce some errors into our results, since the total torsional potential is not modeled as well with united-atom models. However, since we carried out the simulations at an elevated temperature (500 K), where the molecules will sample more of its phase space, we feel justified in using a united-atom simplification.

For a molecular mechanics force field we adopted the Drieding II force field,[9] which has been used recently in studies of poly(ethylene) crystallization.[10] In the Drieding II force field, the total potential energy is described by the summation of bonded and nonbonded energies. The bond and bond angle distortion energies are described by quadratic functions with the equilibrium bond length and bond angle as the reference points, respectively. The equilibrium bond lengths and force constants used were 0.153 nm and 2.93×10^5 (kJ/mol)/nm^2, respectively, for the skeletal backbone bonds. Equilibrium bond angle values of 109.82° and 108.98° were used for all bond angles of PE and i-PP molecules, respectively. The torsional angle energy is described by a summation of cosine functions in the torsion angle defined by four consecutive atoms. A Lennard-Jones 12-6 potential was used to describe the van der Waals interaction with a cutoff distance of 1.05 nm. The Lennard-Jones parameters used for the simulations are summarized in Table 1. Off-diagonal van der Waals parameters are obtained by using the geometric mean rule. Electrostatic interactions were neglected in all models, as one would expect that these types of interactions are not significant in hydrocarbon polymers such as poly(ethylene) and poly(propylene).

Since we are forming compact collapsed structures, our simulation results will depend on the choice of van der Waals parameters. We have not attempted to optimize this choice for melt state or mixture equations of state behavior. We have simply used the Drieding II parameters, which were estimated from lattice spacing measurements and heat of sublimation data for low molecular weight hydrocarbons.[11] Comparable parameters were used by other researchers to model poly(ethylene) and poly(propylene).[10,12] These simulations reproduce certain physical properties of these two polymers reasonably well. As a result, we feel justified that our choice of these parameters should be appropriate for this study.

All initial structures were energy minimized to a residual root mean square force below 2.4 kJ/mol·nm on all atoms by using a conjugate gradient method. Canonical molecular dynamics simulations at 500 K were carried out for each structure until the total energy of the system leveled off. Nosé dynamics,[13] coupled with the summed Verlet algorithm,[14] was used to create the canonical molecular dynamics trajectories using a dynamics time step of 1 fs. The final morphology of each structure was then examined visually. During the course of these MD simulations, the polymer chains have multiple opportunities to reorient their segments drastically because of the absence of a density constraint.

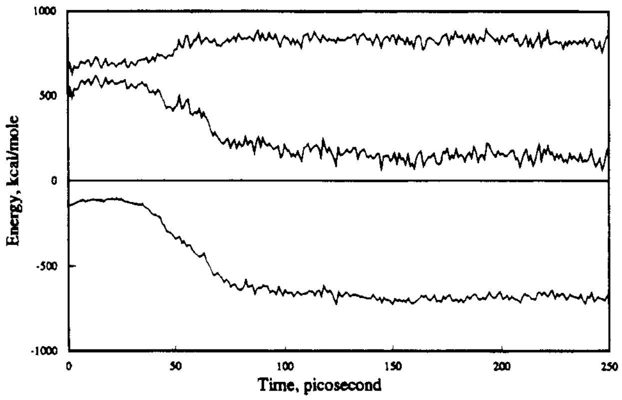

Figure 1. Variation of bonded, van der Waals, and total energies as a function of time for the isolated poly(ethylene) molecule (a 250 ps MD simulation at 500 K). The highest and lowest curves correspond to the bonded and nonbonded energies, respectively. The middle curve corresponds to the total energy.

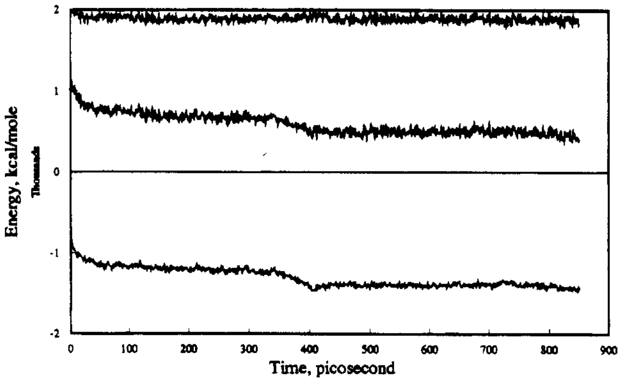

Figure 2. Variation of bonded, van der Waals, and total energies as a function of time for the blend with a well-entangled initial conformation (a 850 ps MD simulation at 500 K). The highest and lowest curves correspond to the bonded and nonbonded energies, respectively. The middle curve corresponds to the total energy.

Results and Discussion

As described in the previous section, all initial structures were subjected to an energy minimization step before the molecular dynamics simulations. MD annealing was then performed on each structure. In each simulation, we observed a collapse to form a densely packed state. The formation of this state in vacuum is not too surprising since the molecular segments are strongly attracted by the van der Waals interactions. Shortly after collapse, the total energy of each structure leveled off. The annealing period required for achieving the constant energy state varied from system to system. The bulk of the reduction in energy is attributed to a decrease in the van der Waals energy.

Figures 1 and 2 show the time variations of the bonded, van der Waals, and total energy curves of the isolated PE chain and the PE/i-PP mixture with a well-entangled initial conformation. The shrinkage of the

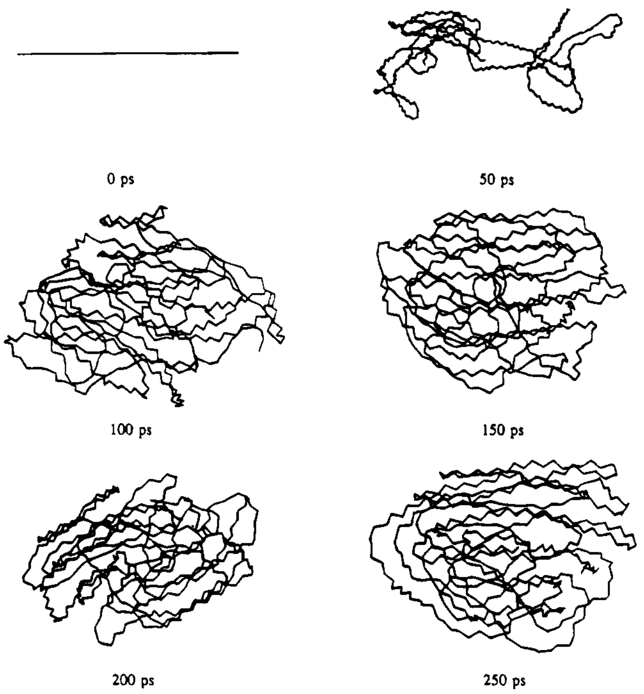

Figure 3. Conformational evolution of an isolated poly(ethylene) molecule with 250-mers at 500 K.

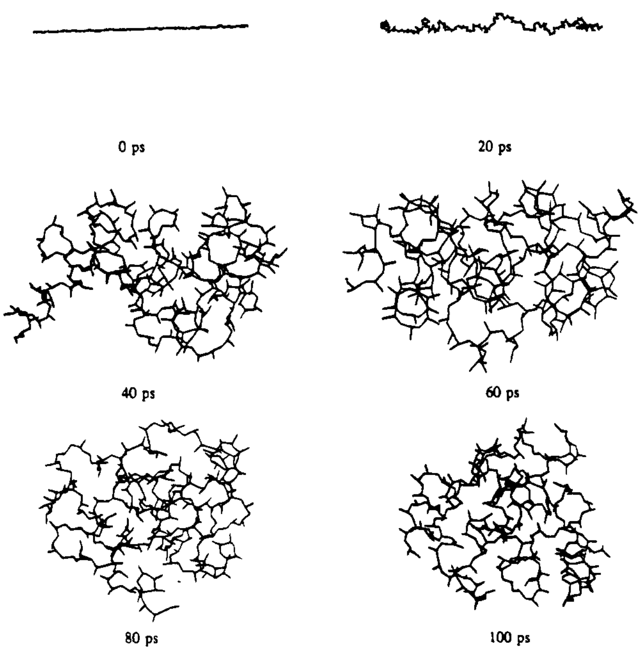

Figure 4. Conformational evolution of an isolated isotactic poly(propylene) molecule with 170-mers at 500 K.

isolated poly(ethylene) chain, as shown in Figure 3, followed the global collapse mechanism that has been described by Kavassalis and Sundararajan.[8] The total energy of this structure started to level off at around 100 ps, and a more ordered, perhaps paracrystalline-type structure, developed after about 200 ps. This simulation was stopped at 250 ps.

Similar collapse behavior was also observed for the isolated i-PP chain. Here, the collapse rate of the i-PP molecule was faster than that of the PE chain. In fact, it took a shorter period of time, 50 ps, to reach the state in which the total energy of the molecule leveled off. As shown in Figure 4, an amorphous structure was formed in this simulation. This structure, which corresponds to the state after 100 ps, is not as compact as the collapsed structure of the isolated PE molecule, but does contain a small number of helical segments.

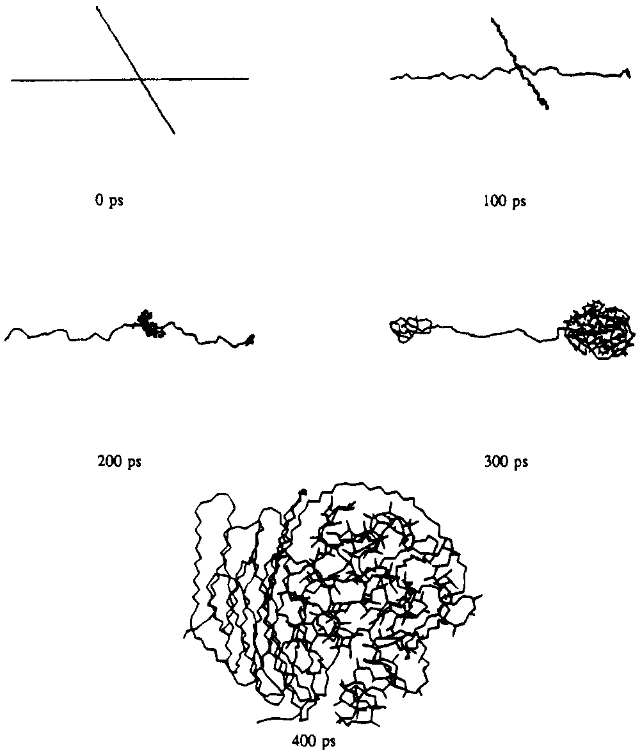

Figure 5. Selected snapshots of a mixture containing a 250-mer poly(ethylene) and 170-mer isotactic poly(propylene) molecules over a 500 ps MD annealing.

These observations coincide with practical experience with these two polymers. Poly(ethylene)s quenched from the melt always exhibit some crystallinity, while quenched poly(propylene) is amorphous, as judged by X-ray crystallography. The agreement with experiment here may be purely coincidental since we have not repeated the collapse simulation multiple times to confirm that the two collapse rates are indeed different.

The difference in the collapse rate between PE and i-PP is also evident in the case where they were assembled together. As a result, the poly(ethylene) and poly(propylene) chains do not have opportunities to entangle during the MD annealing. Figure 5 shows that the poly(propylene) chain collapsed in about 200 ps, while the poly(ethylene) chain was still in the early stage of the collapse. The whole mixture formed a compact structure in about 400 ps. During this time, the total energy of the system leveled off with a significantly lower van der Waals energy. From the snapshot of the simulation of 400 ps, we see that these two polymers collapse into two separate domains with a small amount of interpenetration and entanglement. This separation was not observed, on the same time scale, in simulations of two poly(ethylene) or two isotactic poly(propylene) chains assembled together.

Since the initial conformation of the blend shown in Figure 5 is not likely to exist in the melt, the observed segregation in the previous simulation may be due to the way the initial structure was constructed. To test this, we constructed a model in which the initial state consisted of a well-entangled PE and i-PP system, as shown in the first snapshot of Figure 6. By using this initial state, a molecular dynamics simulation was carried out under the same annealing conditions. Surprisingly, the well-entangled chains also transformed into a configuration showing two distinct regions, but

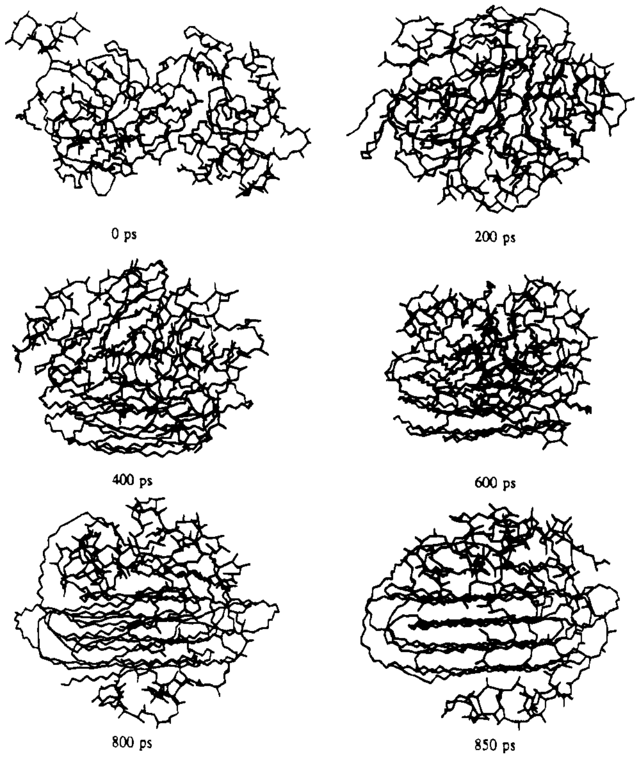

Figure 6. Selected snapshots of a mixture containing a 250-mer poly(ethylene) and 170-mer isotactic poly(propylene) molecules over a 850 ps MD annealing. Note that the initial configuration was highly intertwined.

this time over a longer annealing period, 800 ps. The locally ordered structure seen in the simulations of the isolated PE molecule and the previous two-chain model was also observed for the PE molecule in this blend. Moreover, it was observed that the degree of order in the collapsed state increased with annealing time. Note that the annealing time of this blend is the longest among the simulations carried out here. In fact, the simulation was performed up to 850 ps, which required 25 days of CPU time on a single processor system.

The size of the collapsed poly(ethylene) chain in the blend is more or less comparable with the size of the collapsed structure formed by the isolated poly(ethylene) molecule. In this case, more monomer units were found in the trans state than in that of the isolated poly(ethylene) molecule. The distance between the chains in the PE-rich region ranges from 0.4 to 0.5 nm, and the number of monomer units in each run of all-trans segment is about 15.

What we observed in these simulations is essentially a segregation into two domains of two chains. Note that the chains do not separate at infinity because of the initial entanglements and finite simulation times. It is not clear to what extent this behavior is related to either macrophase or microphase separation since our models consisted of only two chains and were simulated in a vacuum environment. We speculate that the origin of the segregation in these simulations is due to the differences in the local structures of the polymers that form as they are annealed. In particular, the PE species can form a locally ordered fluid state in which an overall lower energy is formed from the presence of approximately six nearest neighbor PE segments.

It has long been recognized that local structural effects are important to the phase behavior of polymer mixtures and block copolymers. The Flory–Huggins lattice theory has been generalized by several researchers. These extensions generally decompose the interaction parameter, χ, into two components,[15-17] with one component corresponding to the enthalpic effect on mixing while the other represents the entropic contribution to the excess free energy of mixing. This supplement reflects the fact that the mixing of two polymers cannot be described sufficiently by a purely statistical process as in the Flory–Huggins lattice theory. Rather, a "local structure" term is needed to better describe the excess thermodynamic properties of mixing. This addition corrects, in part, for the mean field approximation made in the Flory–Huggins theory. To what extent local structure persists into the melt state has been debated numerous times.[18] Some local structure will exist in all polymer liquids. What is not understood is to what extent the local order can disrupt phase behavior in liquid polymer mixtures. For the two-chain simulations reported here, PE was found to have a strong tendency to self-associate into a locally ordered structure at 500 K. It is difficult to assess, on the basis of these simulations alone, whether this may be the root cause of both microphase and macrophase separation behavior in this polymer pair. One concern is the presence of a large amount of surface area, which could be the driving force for the separation. We are confident, however, that we can rule out that surface effects as the cause of the formation of the local order. The formation of locally ordered domains is more pronounced for longer chains and, hence, for larger structures with overall lower surface/volume ratios.[19] Simulations with more chains, within periodic boundary conditions, will address some of these open questions.

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