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Study of the correctness of the solubility parameters obtained from indirect methods by molecular dynamics simulation

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Abstract

Conformational energies of models of polyethylene (PE), isotactic-polypropylene (i-PP), atactic-polypropylene (a-PP) and polyisobutylene (PIB) with different chain lengths in their unperturbed liquid state (E_l), unperturbed isolated state (E_{iu}) and perturbed isolated state (E_{ip}) at 190 °C were computed using molecular dynamics simulation. The computed E_l, E_{iu} and E_{ip} were then used to calculate the solubility parameters of the polymers (δ). Our results indicate that there exists a cutoff chain length (~20 backbone carbons) above which the differences between the solubility parameters ($\Delta\delta$) computed based on ($E_{iu} - E_l$) and ($E_{ip} - E_l$), respectively, become significant. In addition, it was found that the higher the degree of shrinkage of the polymer in vacuum is, the larger the $\Delta\delta$ is. Since PE and PIB exhibited considerable shrinkage in vacuum, their $\Delta\delta$ are much higher than those of the PPs. It seems that, at 190 °C, vacuum acts more or less like a Θ solvent for both types of polypropylenes but a bad solvent for PE and PIB. Our results also suggest that the characteristic ratio of the polymer has little effect on $\Delta\delta$ and that it was the long range attractive interactions between the monomers distant along the backbone contour of the same molecule that led to the formation of fairly compact globule in the cases of PE and PIB. Since δ of the high molecular weight models computed from ($E_{iu} - E_l$) agree with experiment better than those from ($E_{ip} - E_l$), it implies that δ obtained from indirect measurements correspond to a hypothetical vaporization process where the conformations of polymer coils do not undergo significant changes. In other words, δ of a polymer that is determined by the currently available indirect methods may deviates significantly from their 'true' value if the polymer exhibits a high degree of swelling or shrinkage in vacuum at the temperature of the experiment.

Keywords: Hildebrand solubility parameter; Molecular dynamics; Conformational energy

1. Introduction

The concept of solubility parameter was first introduced by Hildebrand in an attempt to calculate activity coefficients of small molecules in a solution environment [1]. It has also been used quite extensively to predict miscibility of binary solutions since the difference in the components' solubility parameters is related to the enthalpy change on mixing. In fact, non-polar small molecules having comparable solubility parameters are found to be thermodynamically miscible. Solubility parameter (δ) is defined as the square root of the cohesive energy density which basically corresponds to the amount of energy that is required to vaporize a mole of liquid as shown in the following equation:

$$\delta = \sqrt{\frac{\Delta E}{V}} \tag{1}$$

where ΔE is the internal energy change of vaporization (i.e. $E_i - E_l$, the difference between the internal energy of a mole of molecules in the ideal vapor or isolated state (E_i) and that in the liquid state (E_l)). And V is the molar volume of the liquid at the temperature of vaporization. According to Hildebrand, both the interaction potential of the molecules and the radial distribution function of the liquid determine ΔE and therefore δ. For small molecules, ΔE simply equals the amount of energy needed to overcome the intermolecular interactions that hold the molecules in the liquid state. And the energy associated with the change in the shape (or dimension) of the molecules during the vaporization is not included. This is reasonable for small

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molecules since they do not undergo significant conformational changes as they are vaporized.

However, as Choi pointed out in one of his recent articles, omitting such an internal conformational energy is not valid for macromolecules and would lead to an incorrect estimation of δ [2]. This is due to the fact that, in general, the shape of a macromolecule in its isolated state differs significantly from that in the liquid state [3]. In other words, if one were able to vaporize a polymer, he/she would find that the average radius of gyration of the polymer molecules in their isolated state would be different from that in the liquid state, the unperturbed state. Since different polymers would have different degrees of swelling or shrinkage in vacuum due to the excluded volume effect or long range attractive interaction, it is speculated that omitting the energy associated with the conformational change process in the ΔE estimation would have different effects on the resultant δ. In this regard, we selected four saturated hydrocarbon polymers including linear polyethylene (PE), isotactic-polypropylene (i-PP), atactic-polypropylene (a-PP) and polyisobutylene (PIB) to address such an issue. The rationale of choosing these polymers is twofold. First of all, since they are the simplest hydrocarbons, one could neglect the electrostatic and hydrogen bonding interactions without introducing large errors to the calculations. Secondly, since their characteristic ratios are different (see Table 1), it is expected that they would exhibit a range of dimensions in both the liquid and isolated states [4].

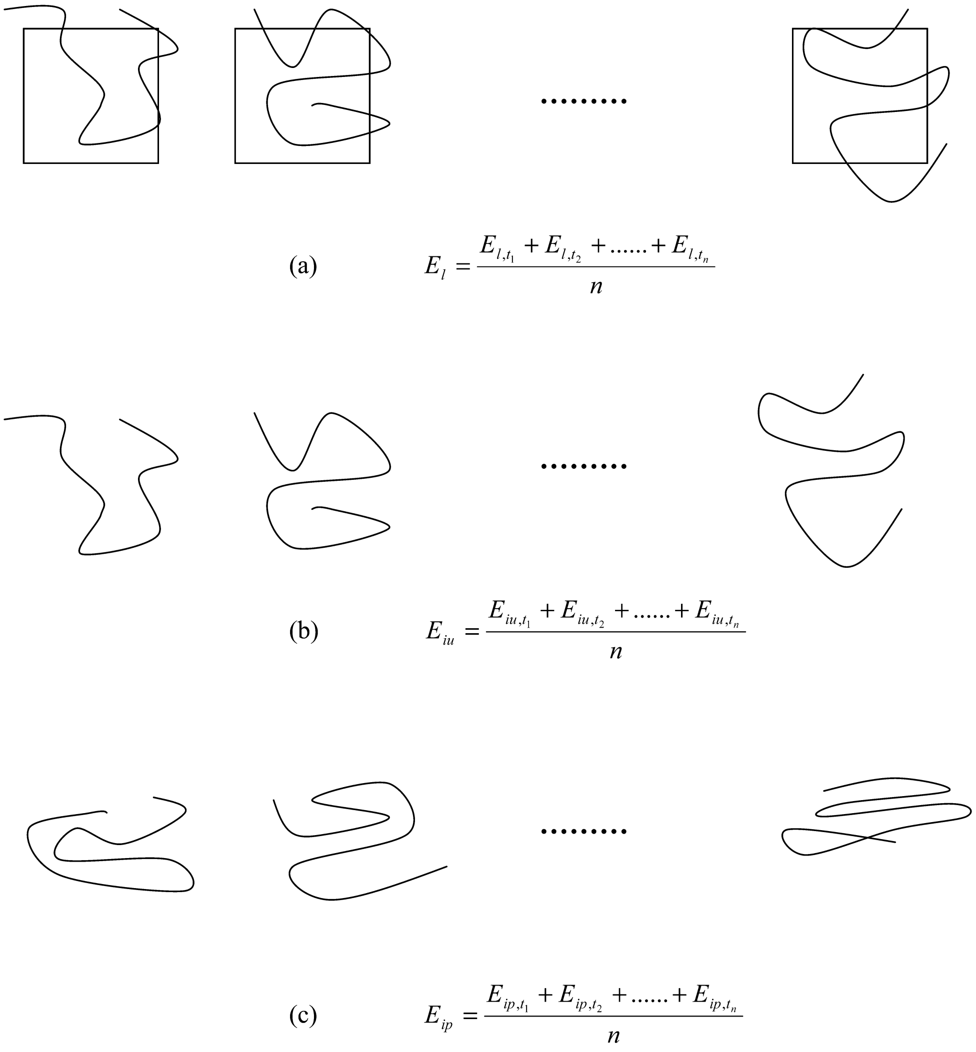
2. Simulation methodology

As discussed earlier, solubility parameter is related to the difference in the internal energy of a mole of molecules in their isolated and liquid states. This basically requires the computation of the conformational energy of the model polymer of interest in its isolated state E_i and that in the liquid state E_l. With the use of the experimental molar volume of the liquid at the temperature used to compute E_i and E_l as well as Eq. (1), δ can then be calculated. It should be noted that the molar volume of the liquid could also be computed from simulation with the use of a constant number of particles-pressure-temperature (NPT) molecular dynamics (MD) scheme. However, such an approach was not used in the present work simply because the force field we used, Dreiding 2.21, which will be discussed in more detail latter in this section, has been found to be incapable of accurately reproducing liquid density—the parameter used to calculate molar volume. Fortunately, it has been found that the force field is able to reproduce solubility parameters of polyethylenes (the most basic hydrocarbons) fairly accurately using the constant number of particles-volume-temperature (NVT) MD scheme [5,6].

The conformational energy of a model polymer in the liquid state, E_l, can be calculated as the time average of the sum of the bonded and non-bonded interaction energies of the system under periodic boundary conditions as shown in Fig. 1(a). Here, it should be noted that the term conformational energy we use here differs from the one defined in the polymer literature. In the latter case, conformational energy usually refers to the energy associated with the rotation about bonds and non-bonded interactions are not included in the calculation. In reference [2], two different methods for calculating E_i are presented. In one approach, the equilibrium conformations of the model system in the liquid state, generated by the NVT MD simulation, are copied and placed in vacuum and their average conformational energy is then computed as shown in Fig. 1(b). It is obvious that these conformations are identical to those used to calculate E_l. We refer this artificial state of the molecules to as the unperturbed isolated state and the corresponding average conformational energy to as E_{iu}. The other method to obtain E_i is to carry out a separate MD simulation of the same model used in the liquid state simulation in vacuum as depicted in Fig. 1(c). Since vacuum essentially acts as a solvent, the long-range interactions may swell or shrink the molecule during such MD annealing. However, as can be seen in the Section 3, all the polymer models studied in the present work shrunk, to different degrees, in vacuum. As a result, the equilibrium conformations that are used to calculate the average conformational energy would be different from those of the unperturbed isolated state. And we refer such average conformational energy to as E_{ip}. Since E_{iu} and E_{ip} are different except under the theta condition, it is expected that δ calculated based on E_{iu} and E_{ip} would be different as well. To quantify such differences,

Table 1
Melt densities and characteristic ratios at the corresponding experimental temperatures and temperature coefficients of unperturbed dimensions of the model polyolefins

Model	Experimental density (g/cm^3) at 190 °C	Characteristic ratio at the experimental temperature	Temperature coefficient of unperturbed dimension	Characteristic ratio at 190 °C
PE	0.759	6.7 (140 °C) [13]	-1.1×10^{-3} [13]	6.34
i-PP	0.762	4.73 (183 °C) [14]	-4.0×10^{-3} [14]	4.60
a-PP	0.762	5.34 (130 °C) [13]	-1.34×10^{-3} [13]	4.92
PIB	0.780	6.6 (297 °C) [13]	-0.27×10^{-3} [13]	6.30



(a) $$E_l = \frac{E_{l,t_1} + E_{l,t_2} + ... + E_{l,t_n}}{n}$$

(b) $$E_{iu} = \frac{E_{iu,t_1} + E_{iu,t_2} + ... + E_{iu,t_n}}{n}$$

(c) $$E_{ip} = \frac{E_{ip,t_1} + E_{ip,t_2} + ... + E_{ip,t_n}}{n}$$

Fig. 1. Schematic representations of a model polymer molecule simulated in the liquid state (a), copied from the liquid state and placed in vacuum (b) and simulated separately in the vacuum state (c).

we computed $\Delta\delta = \delta_u - \delta_p$ for the polymers. Here, δ_u and δ_p simply refer to as the solubility parameters calculated based on ($E_{iu} - E_l$) and ($E_{ip} - E_l$), respectively.

Molecular dynamics simulations were carried out using a commercial software package Cerius2, version 4.4, developed by Accelrys Inc. [7]. For each polymer, models with 10, 16, 20, 30, 40, 50, 60, 70, 80, 90, 100, and 120 carbons were built. To save computer efforts, a united-atom approach was used for all models. The liquid state of the model polymers was constructed using the method of Theodorou and Suter [8]. The dimension of the cubic periodic unit cell was determined by the experimental density and the molecular weight of the polymer being simulated. The experimental densities of the four model polymers at the simulation temperature (190 °C) were obtained from literature and are summarized in Table 1 [9]. Since the polymers of interest are usually processed over the temperature range of 170–210 °C and their melt indexes are measured at 190 °C, 190 °C was chosen. Here, the melt index is a commonly used parameter in the plastics industry to characterize the processability of polymers. It should be noted that, for each polymer, we used the same density value for the models of the same type but with different chain lengths. This is because for both PPs and PIB, liquid densities of the low molecular weight systems at 190 °C are not available. In the case of PE, the liquid density only changes from 0.69 (10 backbone carbons) to 0.75 g/cm^3 (120 backbone carbons). In the construction of the models in the liquid and isolated states, we used a random torsion angle distribution scheme to generate the initial conformations simply because the simulation temperature is fairly high.

The critical molecular weights for entanglement (M_c) of PE, i-PP, a-PP and PIB are 5,300, 6,200, 5,800 and 10,000 g/mol, respectively, which are significantly higher than the molecular weights of even the highest molecular weight models used in our simulations [10]. Therefore, our models, in a sense, correspond to melts without entanglements. The question here is that would entanglements affect the computed solubility parameters? In other words, would

Table 2
Equations and parameters used in the Drieding 2.21 force field

Interaction		Equation	Parameter	
Bonded energy (kJ/mol)	Bond energy	$E_b = 1/2K_b(R - R_0)^2$	$K_b = 2.93 \times 10^5$ kJ/mol/nm^2, $R_0 = 0.15$ nm	
	Angle energy	$E_\theta = 1/2K_\theta(R - R_\theta)^2$	$K_\theta = 418$ kJ/mol/rad^2, $R_\theta = 1.91$ rad	
	Torsion energy	$E_\phi = \sum_{n=1}^{2} 1/2K_{\phi,n}[1 \pm \cos(n\phi)]$	$K_\phi = 20.9$ kJ/mol	
	Inversion energy	$E_{inv} = K_{inv}(\cos\chi - \cos\chi_0)^2$	$K_{inv} = 20.9$ kJ/mol, $\chi_0 = 2.09$ rad	
Non-bonded energy (kJ/mol)	Van der Waals energy	$E_{vdw} = \varepsilon_0[(\sigma_0/R)^{12} - 2(\sigma_0/R)^6]$	C with one implicit H	$\varepsilon_0 = 0.615$ kJ/mol, $\sigma_0 = 0.3983$ nm
			C with two implicit H	$\varepsilon_0 = 0.829$ kJ/mol, $\sigma_0 = 0.4068$ nm
			C with three implicit H	$\varepsilon_0 = 1.047$ kJ/mol, $\sigma_0 = 0.4152$ nm

extra energy be required to remove the entanglements during the vaporization process? In our view, one will never be able to obtain the answer for this question with 100% confidence unless he/she could vaporize polymers. However, it is noteworthy that the concept of entanglement can only be defined when a polymer melt is under shear. In such a situation, it is conceivable that entanglements could add extra resistance to the imposed deformation. Since solubility parameter is a purely thermodynamic concept that shear is not part of it, entanglements may not have any significant effect on polymers' solubility parameters.

For all MD simulations, a generic force field, Drieding 2.21, developed by Mayo et al., was adopted [11]. Since we are only interested in the relative differences in the $\Delta\delta$ of the polymers, not their absolute values, we feel justified to use such a simple force field considering the number of systems needed to be simulated. In Drieding 2.21, the total (conformational) energy of a system is described as the summation of the bonded and non-bonded interaction energies. The bonded interaction energies include bond stretching, bond angle bending, torsion, and inversion energies. In terms of the non-bonded interaction energy, only the van der Waals interaction energy is considered in the present study. The expressions that are used to describe the above interactions and the corresponding parameters used in such expressions are summarized in Table 2. In general, each model created was subjected to energy minimization before the MD annealing. The Nose method was used for all NVT MD simulations which were carried out for a period of 800 picoseconds (ps) with a time step of 1 femtosecond (fs) to ensure the stability of the MD trajectories [12]. All simulations showed that the conformational energy leveled off at the last few hundreds ps, indicating that the simulation time was long enough for the systems to relax to their equilibrium state. The bonded and non-bonded energies as well as the radii of gyration (R_g) were calculated by averaging the corresponding values of the systems using the conformations obtained from the last 100 ps of the MD simulations.

3. Results and discussion

Following the foregoing described MD strategies, the average bonded, non-bonded, and total energies (i.e. bonded plus non-bonded energies) of the model polyolefins at 190 °C were calculated and are summarized in Tables 3–6. It should be noted that models with chain lengths other than 120 backbone carbons are omitted here for clarity. As shown in each table, the average bonded energy values are fairly close to each other in the unperturbed liquid, unperturbed isolated and perturbed isolated states. It is expected that the bonded energies of the models in the unperturbed states are identical since the conformations used to calculate such energies are identical. It was also observed that the bonded energies of the perturbed isolated state are so close to those of the other two states. This simply means that if there are differences between the dimensions of the model molecules in the perturbed isolated state and the other two unperturbed states, the differences are not attributed to the bonded energies but the non-bonded energy. In fact, this is the case in the present study. And

Table 3
Bonded and non-bonded energy terms of PE (120 backbone carbons) in the unperturbed liquid, unperturbed isolated and perturbed isolated states at 190 °C

Polyethylene		Molecule in the unperturbed liquid state	Molecule in the unperturbed isolated state	Molecule in the perturbed isolated state
Bonded energy (kJ/mol)	Bond energy	222	222	247
	Angle energy	234	234	238
	Torsion energy	284	284	309
	Inversion energy	0	0	0
Non-bonded energy (kJ/mol)	Van der Waals energy	−752	−155	−481
Total energy (kJ/mol)		−12	585	313

Table 4

Bonded and non-bonded energy terms of i-PP (120 backbone carbons) in the unperturbed liquid, unperturbed isolated and perturbed isolated states at 190 °C

i-PP		Molecule in the unperturbed liquid state	Molecule in the unperturbed isolated state	Molecule in the perturbed isolated state
Bonded energy (kJ/mol)	Bond energy	359	359	372
	Angle energy	510	510	523
	Torsion energy	539	539	518
	Inversion energy	59	59	63
Non-bonded energy (kJ/mol)	Van der Waals energy	−832	−435	−543
Total energy (kJ/mol)		635	1032	933

Table 5

Bonded and non-bonded energy terms of a-PP (120 backbone carbons) in the unperturbed liquid, unperturbed isolated and perturbed isolated states at 190 °C

a-PP		Molecule in the unperturbed liquid state	Molecule in the unperturbed isolated state	Molecule in the perturbed isolated state
Bonded energy (kJ/mol)	Bond energy	376	376	380
	Angle energy	510	510	514
	Torsion energy	531	531	531
	Inversion energy	59	59	63
Non-bonded energy (kJ/mol)	Van der Waals energy	−794	−385	−543
Total energy (kJ/mol)		681	1091	945

Table 6

Bonded and non-bonded energy terms of PIB (120 backbone carbons) in the unperturbed liquid, unperturbed isolated and perturbed isolated states at 190 °C

PIB		Molecule in the unperturbed liquid state	Molecule in the unperturbed isolated state	Molecule in the perturbed isolated state
Bonded energy (kJ/mol)	Bond energy	627	627	627
	Angle energy	2408	2408	2420
	Torsion energy	288	288	288
	Inversion energy	1	1	1
Non-bonded energy (kJ/mol)	Van der Waals energy	−543	63	−234
Total energy (kJ/mol)		2781	3387	3103

it is the lowering of van der Waals energy (compare the van der Waals energy of the models in their unperturbed and perturbed isolated states as shown in Tables 3–6) that led to the conformational changes of these molecules. Since the bonded energies of the models in different states are comparable, the average van der Waals energies were used as E_l, E_iu and E_ip to calculate the corresponding solubility parameters.

The average van der Waals energies of the model polyolefins with different chain lengths calculated in the three different states are shown in Figs. 2–5. In all cases, the average van der Waals energy in the unperturbed isolated state tends to be the highest while that in the liquid state the

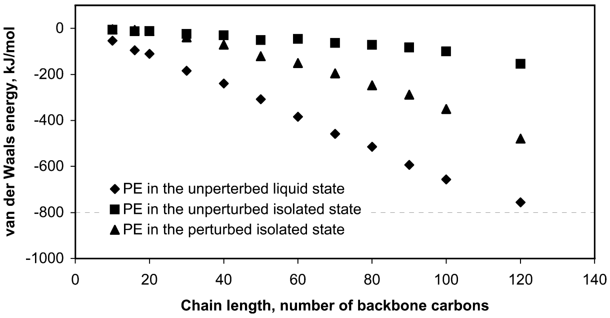


Fig. 2. Chain length dependence of the van der Waals energy of PE in its unperturbed liquid, unperturbed isolated and perturbed isolated states at 190 °C.

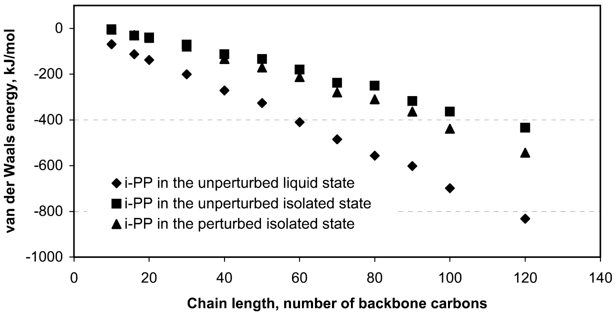


Fig. 3. Chain length dependence of the van der Waals energy of i-PP in its unperturbed liquid, unperturbed isolated and perturbed isolated states at 190 °C.

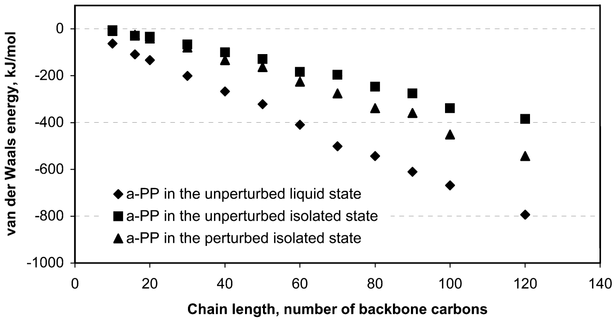


Fig. 4. Chain length dependence of the van der Waals energy of a-PP in its unperturbed liquid, unperturbed isolated and perturbed isolated states at 190 °C.

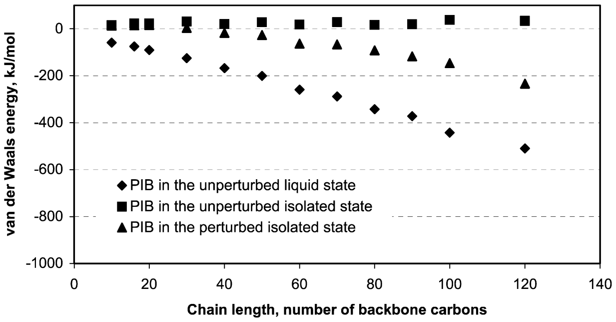


Fig. 5. Chain length dependence of the van der Waals energy of PIB in its unperturbed liquid, unperturbed isolated and perturbed isolated states at 190 °C.

lowest and that in the perturbed isolated state in between. And both ($E_{iu} - E_l$) and ($E_{ip} - E_l$) increase with increasing chain length of the model, indicating that more energy is required to vaporize the higher molecular weight models, as expected. However, there exist no significant differences in E_{iu} and E_{ip} for the models with chain lengths below 20 backbone carbons. This simply means that, for all the model polyolefins with chain lengths above the aforementioned value, the equilibrium conformations in the perturbed isolated state are energetically more favorable than those in the unperturbed isolated state. Both high molecular weight PE and PIB exhibited much larger differences in E_{iu} and E_{ip} than the polypropylenes, indicating that conformations of polypropylene used in the unperturbed liquid, unperturbed isolated and perturbed isolated states are very similar. These results are best illustrated by Figs. 6 and 7 and Table 7. It is obvious in the figures that the conformations and the calculated radii of gyration of both types of PPs in the liquid and isolated perturbed states are fairly similar. In contrast, both PE and PIB exhibited conformations that are much more compact than those of PPs as well as larger differences in the calculated R_g in the perturbed and unperturbed states. Based on the above results, it seems that at 190 °C, vacuum

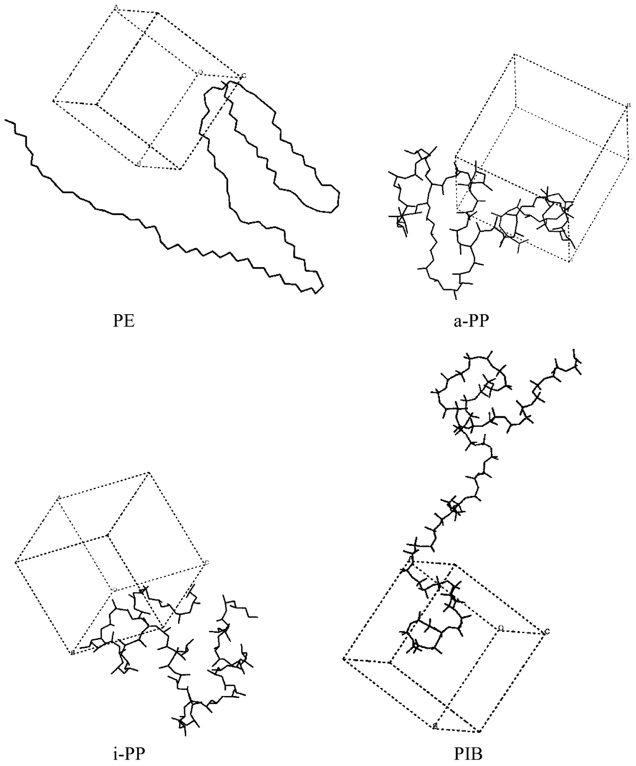

PE a-PP
i-PP PIB

Fig. 6. Representative equilibrium conformations of PE, i-PP, a-PP and PIB (120 backbone carbons) in the unperturbed liquid state at 190 °C. It should be noted that the equilibrium conformations of the polymers in their unperturbed isolated states are identical to those shown here.

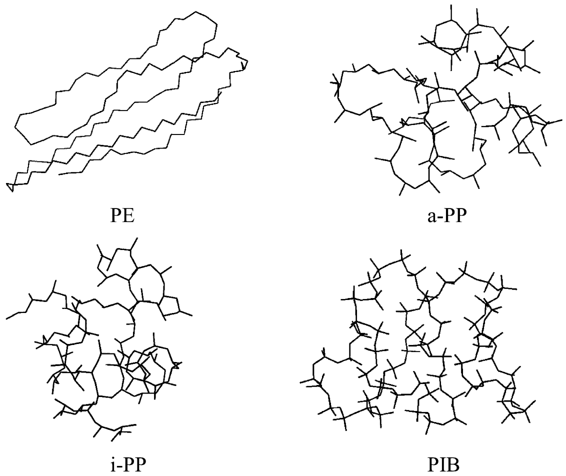

PE a-PP
i-PP PIB

Fig. 7. Representative equilibrium conformations of PE, i-PP, a-PP and PIB (120 backbone carbons) in the perturbed liquid state at 190 °C.

Table 7
Calculated radii of gyration of the model polyolefins (120 backbone carbons) at 190 °C

Model	R_g in the unperturbed liquid and unperturbed isolated states (Å)	R_g in the perturbed isolated state (Å)
PE	15	9
i-PP	9	8
a-PP	10	8
PIB	17	9

acts more or less like a Θ solvent for i-PP and a-PP but a bad solvent for both PE and PIB.

By substituting the average van der Waals energies along with the experimental molar volumes into Eq. (1), the corresponding solubility parameters and $\Delta\delta$ were calculated. Fig. 8 shows the results of such calculations. It is evident in the figure that $\Delta\delta$ of all models stay very close to zero up to a chain length of approximately 20 backbone carbons and increase linearly with increasing chain length thereafter. Except PE, $\Delta\delta$ of the remaining models started to level off at a chain length of 60 backbone carbons. However, it is expected that the trend observed in the case of PE does not continue indefinitely. When one compares the solubility parameters computed based on E_{iu} and E_{ip} with the experimental values (Table 8), it was found that the values obtained based on E_{iu} are much closer to the values obtained from indirect methods than the ones on E_{ip}, especially in the case of PE. This indicates that δ obtained from indirect measurements correspond to a vaporization process that conformations of the macromolecules do not undergo significant changes. This is not unreasonable since all experimental δ values are inferred from polymers in their unperturbed solution or melt state. And since the computed $\Delta\delta$ reflects the difference between E_{iu} and E_{ip}, the higher the $\Delta\delta$, the less accurate the δ obtained from indirect measurements. Furthermore, since the difference between E_{iu} and E_{ip} depends on the degree of shrinkage of the polymer in vacuum at a given temperature, it is believed that the correctness of the experimental solubility parameter depends on the swelling coefficient of the polymer in vacuum at the temperature at which δ is measured. However, we do not have sufficient data here to propose a quantitative relation between the swelling coefficient and $\Delta\delta$ as well as temperature and $\Delta\delta$. More data with the use of a more accurate force field are needed for such a purpose. Nonetheless, the present data do not support the idea that the characteristic ratio plays a role in determining $\Delta\delta$. It seems that the systems with low characteristic ratios appear to yield smaller $\Delta\delta$. However, it is difficult to explain the difference in $\Delta\delta$ between PE and PIB even though they have comparable characteristic ratio.

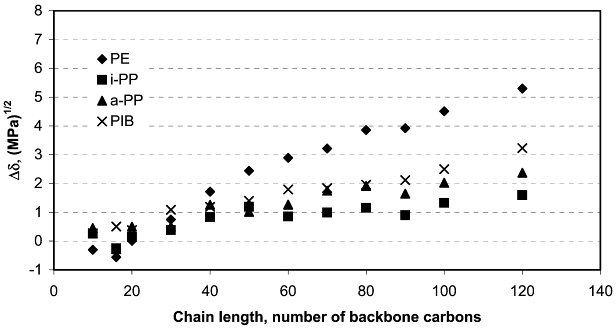


Fig. 8. Chain length dependence of $\Delta\delta$ for PE, i-PP, a-PP and PIB at 190 °C.

Table 8
Computed solubility parameters of PE, i-PP, a-PP and PIB (120 backbone carbons) at 190 °C

Model	Experimental solubility parameter, $(\mathrm{MPa})^{1/2}$	δ_u $(\mathrm{MPa})^{1/2}$	δ_p $(\mathrm{MPa})^{1/2}$
PE	17.2–18.3 (at 166 °C) [15]	16.5	11.2
i-PP	16.8–18.8 (at 25 °C) [9]	11.1	8.1
a-PP	16.8–18.8 (at 25 °C) [9]	11.0	9.4
PIB	16.0–16.6 (at 25 °C) [9]	11.8	8.5

4. Conclusions

The conformational energies of four industrially important polyolefins with different chain lengths in their unperturbed liquid, unperturbed isolated and perturbed isolated states at 190 °C were calculated using molecular dynamics simulation. The conformational energies were then used to calculate the respective solubility parameters of the polymers. It was found that the use of different isolated states in the calculations of solubility parameters yield different values for models with chain lengths above 20 backbone carbons. It seems that such difference depends critically on the degree of shrinkage of the polymer in vacuum at a given temperature. In particular, polymers exhibiting significant shrinkage in vacuum show relatively large $\Delta\delta$.

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