Structural Effects of a Benzene Inclusion into a Polyethylene Matrix: A Monte Carlo Simulation

Oscar Ahumada* and Manuel Laso

Department of Chemical Engineering, ETSII, UPM, José Gutiérrez Abascal, 2 E-28006 Madrid, Spain

Received July 10, 2001; Revised Manuscript Received September 26, 2001

ABSTRACT: The detailed conformational analysis of a polymeric system containing a benzene inclusion is presented. Monte Carlo simulations of several polymeric systems, based on polyethylene, PE, have been used in order to investigate the structural perturbation induced in the polymeric matrix by the presence of the benzene molecule. Polymeric chains with different degrees of rigidity have been simulated, and the structural parameters have been compared with their analogue systems without the inclusion of benzene. An initial study performed on conventional PE showed that, thanks to its high flexibility, PE was able to accommodate the benzene inclusion, keeping the conformation of the chains virtually unaffected by the presence of the aromatic ring. The perturbation induced by the ring is an approximately ellipsoidal region centered on the inclusion and of a thickness of about 2 Å. In this region a greater occupancy of mers is found. This perturbation relaxes, in a nonmonotonic way, with increasing distance from the benzene. When higher chain rigidity is imposed, the polymeric chains accommodate the ring by modifying their conformations, mainly through an increase in the number of gauche states. The conformational perturbation induced by the benzene was found to become much stronger, showing the polymeric chains less favorable interaction with the benzene. It is worth to mention that the persistence length of the systems containing the benzene, in the cases where extra rigidity is imposed, is reduced as compared with their analogue systems without the ring. As consequence, it was possible to conclude that even in the absence of any specific interaction between the benzene and the polymeric matrix, the rigidity of the chains plays an important role in the affinity between the benzene and the polymer and in the flexibility of the whole composite.

1. Introduction

Industrially manufactured plastics often contain a certain amount of low molecular weight components,[1] e.g., initiators and catalysts from the polymerization precess, or additives that provide specific properties.[2] Examples are the inclusion of plasticizer to lower the glass transition temperature of the polymer and therefore to expand the range of applications or to improve processability[3] and the effect of filler and additives as flame retardants, antioxidants, or UV stabilizers. In same cases the low molecular weight compound inserted into the material is directly responsible for the new properties. In the latter type of systems, the polymer behaves as the container where the active molecules display their abilities. For such applications polymers are taken because of their general good mechanical properties, the versatility of synthesis, and the low cost of processing. Organic nonlinear optical (NLO) materials[4] are a good example of that kind of application. In this materials a chromophore is included into a polymeric matrix in order to produce NLO effects such as to double the frequency of an input source of light or to modulate the refractive index of light of a waveguide through the electrooptical (Pockels) effect.[5] Many problems lurk behind this simple way of creating NLO devices. First and foremost is the amount of chromophore that can be dispersed into the matrix. Since the NLO response is proportional to the number of such entities, it is desirable to increase the concentration of chromophores. However, at high concentration of the NLO molecules the composite undergoes phase separation and the chromophore molecules crystallize, making their orientation impossible.

For these reasons, it is interesting to study the effect produced by the inclusion of benzene-like molecules into polymeric matrices from the microscopic point of view. It is, in some cases, difficult to determine experimentally at the molecular level the structural effect of these inclusions in order to find the necessary key properties that determine the phase separation or the plasticizer effect. Under these circumstances, molecular simulations are a powerful tool which allows a detailed analysis of the structure of such polymeric systems.

As a model of a chromophore−polymer binary system, we have taken a molecule of benzene immersed in a matrix of amorphous polyethylene. Obviously, benzene does not have a dipole moment, and therefore does not show NLO properties, but the aim of this study is to investigate on an atomic scale and without any specific interaction the perturbation produced by the inclusion and the length scale of this perturbation. An important parameter on the miscibility of this composites is the flexibility of the polymeric chains. We have therefore studied the effect of polymer flexibility on the mechanisms by which a molecule of benzene is accommodated in an amorphous polymer matrix. To this end, we have used a Monte Carlo simulation based on a suite of advanced moves including the very poweful end-bridging algorithm of Mavrantzas et al.[6]

In the section 2 we will describe the model used. We will also show some results on structural and thermodynamic properties of both the pure polymer and polymer plus benzene. In section 3 we will address the question of the effect of chain flexibility on the structural properties of the polymer−benzene system.

2. Molecular Model

The model system used here consisted of $N_{\mathrm{ch}} = 5$ molecules of linear polyethylene of average degree of

10.1021/ma011178o CCC: $22.00

polymerization 100 with a uniform chain length distribution with a corresponding polydispersity index of 1.08 and one molecule of benzene placed in a cubic box of around 22 Å edge length, with periodic boundary conditions. The united-atom representation is used for both polyethylene and benzene molecules, with the methylene group along the chain of PE and the CH groups of benzene regarded as the interacting sites. Nonbonded interactions are described by a Lennard-Jones potential of the form

$$V_{ij}^{\mathrm{LJ}}(r) = 4\epsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \quad (1)$$

with r_{ij} being the scalar minimum image distance between sites i and j. There are two types of nonbonded interactions: between two CH_2 pseudoatoms and between a CH and a CH_2 pseudoatoms. The latter represents the interaction between the benzene sites and the PE sites. For the interaction between unlike atoms we have used the Lorentz–Berthelot mixing rule,[7]

$$\sigma_{ij} = \frac{1}{2}[\sigma_{ii} + \sigma_{jj}]$$

$$\epsilon_{ij} = [\epsilon_{ii}\epsilon_{jj}]^{1/2} \quad (2)$$

Along a PE chain all pairs of sites separated more than three bonds along the chain and all intermolecular sites interact with the Lennard-Jones pair potential. Potential tails are cut at 1.45 σ_{PE} and brought smoothly to zero at 2.33 σ_{PE} using a quintic spline.[8] Bond lengths are kept constant, whereas bond angles are assumed to fluctuate around an equilibrium angle θ_0 of 112° subject to the Van der Ploeg and Berendsen bending potential[9] of the form

$$V_{\mathrm{bending}}(\theta) = {}^{1}/_{2}K_{\theta}(\theta - \theta_0)^2 \quad (3)$$

with K_0 482.23 kJ/mol. Associated with each dihedral angle ϕ is also a torsional potential of the form[10]

$$V_{\mathrm{torsion}}(\phi) = c_0 + c_1\cos(\phi) + c_2(\cos(\phi))^2 + c_3(\cos(\phi))^3 + c_4(\cos(\phi))^4 + c_5(\cos(\phi))^5 \quad (4)$$

with $c_0 = 9.28$, $c_1 = 12.16$, $c_2 = -13.12$, $c_3 = -3.06$, $c_4 = 26.25$, and $c_5 = -31.51$ in kJ/mol.

The benzene ring is considered completely rigid, and it remains static during the whole simulation; therefore, the only interaction they experience is intermolecular via the Lennard-Jones potential with the PE sites. The model used for the united atom of the benzene molecule is based on the work of Bartell et al.[11]

All simulations were conducted in the NPT (1 atm and 450 K) ensemble using a Monte Carlo procedure. A combination of reptation, rotation, flip, volume fluctuations, concerted rotation (CONROT), and end-bridging (EB)[6] moves was used. The reptation move consists of the displacement of a trimer from one randomly chosen end of the chain to the opposite one. The rotation move is performed by rotating of one of the two ends of the chain. The flip is a very simple and very local move involving the random selection of an internal chain segment and its rotation about the axis joining its two neighboring segments on the same chain by a small random angle. This move leaves the bond lengths unchanged but modifies up to two bond angles and up to four dihedral angles. Volume fluctuations are initiated by randomly expanding or contracting all edge lengths of the periodic box by a random amount. The starts of all chains are affinely displaced following the isotropic deformations of the periodic box, with all bond lengths, bond angles, and torsions left unchanged.

MC moves can be made to tunnel through energetic barriers in the configurational space of the polymer, circumventing the limitations of dynamic algorithms. This feature has been exploited in polymers simulations in moves that alter connectivity[12] as EB.[6,13] The appeal of such moves is readily apparent: small alterations to the connectivity result in large jumps in the configuration space of the polymer, especially accelerating the rate of evolution of long-range structural features such as the end-to-end vector of the chain.

The geometric problem of *bridging* a pair of dimers with a trimer, given all intervening bond lengths and angles, forms the basis of CONROT and EB. In the case of CONROT an internal trimer is excised from the chain, and then the bonds penultimate to the bridge are rotated by a small amount and then rebridged, inducing local fluctuations in the structure. The end-bridging move alters the connectivity by *bridging* a chain end to an interior segment on another chain with a trimer. In addition, one of the trimers adjoining the bridged internal segment is cut, preserving the total mass of the system. EB Monte Carlo simulations induce a certain polydispersity with a relative chemical potential profile designed to give a uniform chain length distribution.

Since it is difficult to completely change the initial three-dimensional shape during the simulation of dense atomistically detailed polymer, one should start with a reasonably “good” conformation. The main problem consists of creating a packing of chains that do not intersect and whose three-dimensional shape corresponds to statistical data derived from experiments. The starting configuration used here was generated with a homemade modified version of PolyPack[14] which includes the possibility of packing polymeric chains under the presence of an inclusion. PolyPack is a set of algorithms for generating polymer structures used as initial configurations in simulations of dense phases. These algorithms generate polymer systems that avoid severe overlaps and guarantee the chains to obey the proper conformational statistics. There are two main ideas behind PolyPack: first, the packing algorithm starts from a random configuration which is improved iteratively by means of a heuristic search algorithm which ultimately furnishes the target configuration. In contrast to energy minimizations and simulated annealing techniques, the search does not necessarily follow a path driven by physical forces. It rather tries to solve the combinatorial problem regardless of the physical problem it is derived from. The second idea is the *principle of horizon*. Since it is difficult to manipulate an atomistically detailed, highly connected system, an incremental modification of the nonbonded interaction is used. A horizon value defines the scope beyond which the atoms are “ghosts” to each other. It is increased to eventually attain its full range where each atom can “see” all others.

3. Results and Discussion

In this work several simulations have been performed in order to study the structural perturbation induced in the polyethylene matrix by the presence of a benzene inclusion. All the simulations were performed at a pressure of 1 atm and a temperature of 450 K.

Structural Properties of a Binary System (PE and Benzene). The first step in this study was to simulate the PE matrix in the absence of the benzene inclusion. This initial simulation was used, first, as a reference to discriminate the structural effects produced by the inclusion and, second, as a check of the ability of the algorithm to equilibrate the system. After that initial simulation, the binary system compoused by five PE chains and a sigle molecule of benzene was performed. The most relevant structural parameters are represented in Figure 1.

In Figure 1 four magnitudes have been represented: the bending and torsional angle distributions and the inter- and intramolecular pair distribution function. The model includes the possibility to vary the bending angle to have a model as flexible as possible. The distribution of bending angles (Figure 1a) shows a Gaussian-like profile centered at θ_0 as expected from the bending potential used. Figure 1b shows the distribution of the torsional angles. The Ryckaert−Bellemans[21] potential (eq 4), used here, is a 3-fold torsional potential that mainly distributes the torsions in the vicinity of 0° or trans, +120° or gauche+, and −120° or gauche−.

The structure of liquid PE can be examined by calculating the intermolecular pair distribution function $g_{\text{inter}}(r)$. This is shown in Figure 1c. At short distances $g_{\text{inter}}(r)$ is zero (the "correlation hole" effect). This happens because the segment cloud of the chain partially excludes units of other chains from coming close to the reference mer on the chain. Figure 1d shows the intrachain pair distribution $g_{\text{intra}}(r)$. The first sharp peak is due to pairs of mers covalently linked and separated by a bond length. The second peak represent mers two bonds apart, while the other peaks reflect similar conformational preferences of the chain.

The structural properties of the PE plus benzene system represented in Figure 1 do not show evidences of relevant differences in these quantities.

Thermodynamic Properties. Figure 2a represents the evolution of the total energy together with its components: bending, torsional, intrachain, and interchain nonbonded energies for pure PE. It is interesting to show the evolution of the different terms of the energy from the initial configuration (obtained from PolyPack) (Figure 2b) to illustrate how efficiently the MC procedure reaches the production phase. The total energy of the initial configuration (generated by PolyPack) is less than 3 orders of magnitude larger (the initial configuration has an energy of 28746 kcal/mol while the plateau value of the energy fluctuates around 50 kcal/mol) than the equilibrium value obtained by end-bridging MC. This is consistent with the philosophy of PolyPack, which gives good structural properties at the expense of concentrating the energy in a few overlaps. Therefore, the torsional energy of this initial configuration is at the equilibrium value, while the Lennard-Jones part is much larger just because of these overlaps. The MC procedure needs about 3 million MC steps for the equilibration of PE.

The first difference between pure PE and the system consisting on PE with an inclusion of benzene comes up in the energy as is evidenced in Figure 3, where the total energy distributions are plotted. In this figure a shift toward higher energies is found in the system containing the molecule of benzene.

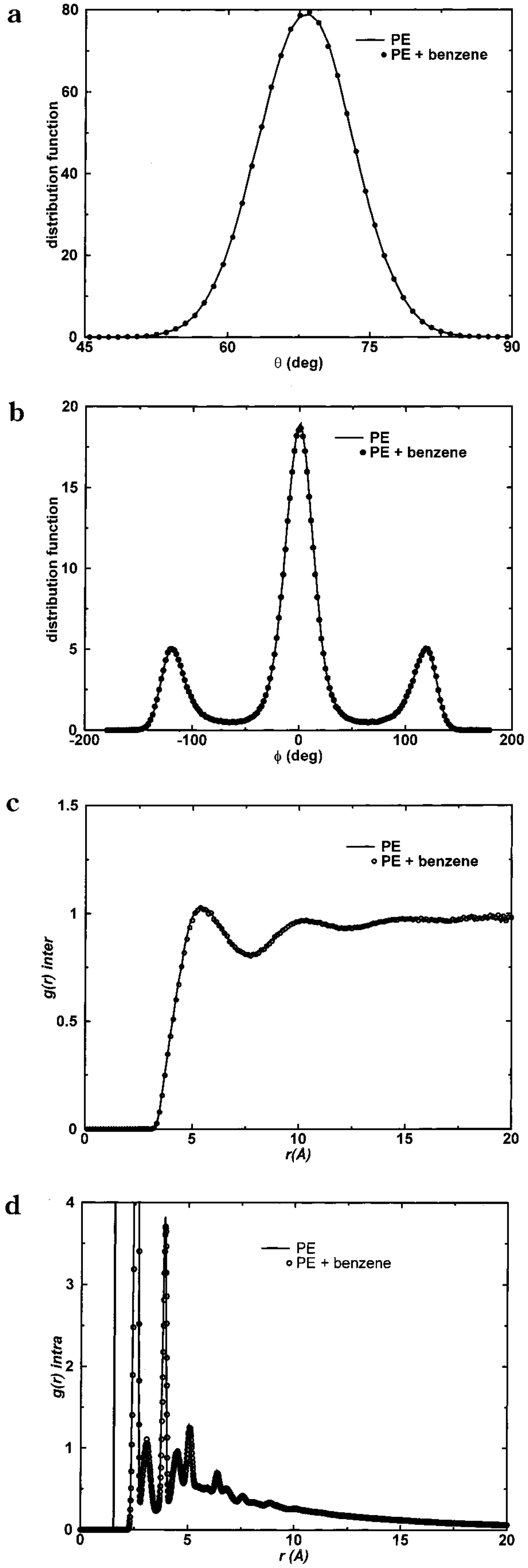


Figure 1. Structural parameter of PE with an inclusion of benzene compared with pure PE: (a) bending angle distribution; (b) torsional angle distribution; (c) intermolecular pair distribution function; (d) intramolecular pair distribution function.

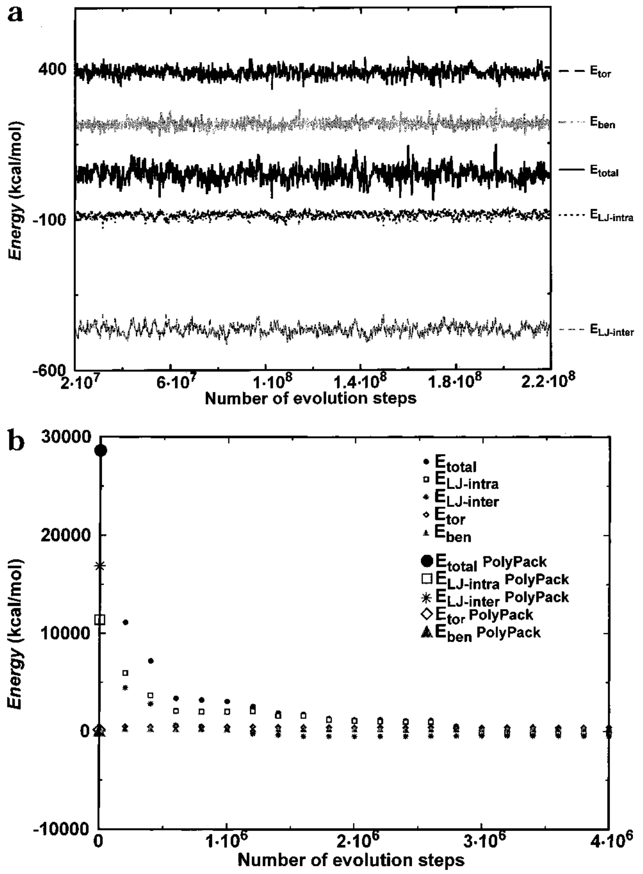


Figure 2. (a) Evolution of the total energy together with its components for pure PE; bending, torsional, intrachain and interchain no bonded energies. (b) The initial decay of the energy and its components.

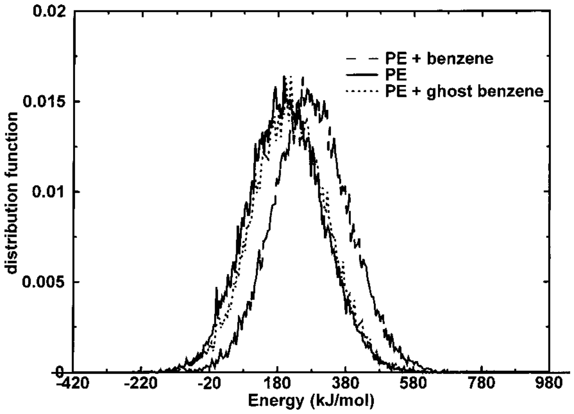


Figure 3. Total energy distribution is plotted for the system PE + benzene compared with the distribution for the pure PE and for PE + benzene where the Lennard-Jones interspecies contribution has been eliminated (ghost benzene).

This shift has its origin in the Lennard-Jones intermolecular interaction. To check whether the displacement of the position of the maximum of the distribution is caused by the extra Lennard-Jones interaction between PE and the benzene molecule, the Lennard-Jones intermolecular contribution has been subtracted. (The benzene has been considered as a "ghost" for the Lennard-Jones energy calculation.) The shift disappears thus implying that it has its origin in the extra intermolecular interaction between the PE and the benzene molecules.

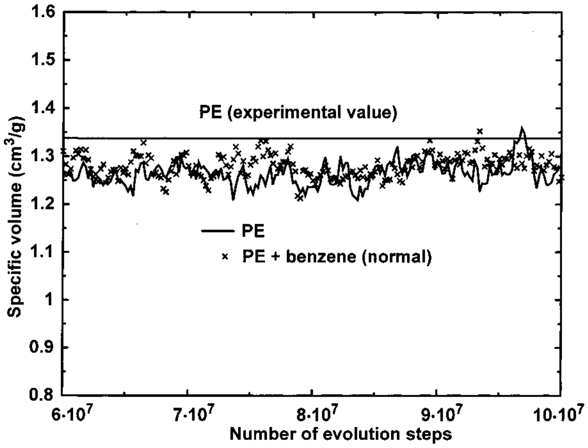


Figure 4. Specific volume of PE plus benzene has been represented and compare with pure PE and with the experimental value of pure PE taken from ref 15.

Table 1. Specific Volume for Polyethylene PE (Experimental Value), PE (Simulated), and PE plus the Benzene Molecule (Simulated)

system	specific volume (cm^3/g)
PE (experimental)	1.337 ± 0.005
PE (sim)	1.25 ± 0.03
PE + benzene (sim)	1.29 ± 0.03

The evolution of the specific volume during the simulation is represented in Figure 4 for the binary system PE + benzene and compared with pure PE. The decrease of the specific volume ν with the average chain length $\bar{X}$ is usually correlated by a relation of the form

$$\nu = \nu_\infty + \frac{\nu_0}{\bar{X}} \tag{5}$$

where ν_∞ is the value of ν at infinite chain length and ν_0 a proportionality constant describing the rate with which ν falls with increasing $\bar{X}$. The experimental data for PE[15,16] were fitted using eq 5 in order to obtain the value of the specific volume that corresponds to the degree of polymerization used during the simulation (see Table 1).

Figure 4 shows that the specific volumes obtained from the simulation of the both systems (PE and PE + benzene) are almost equal.

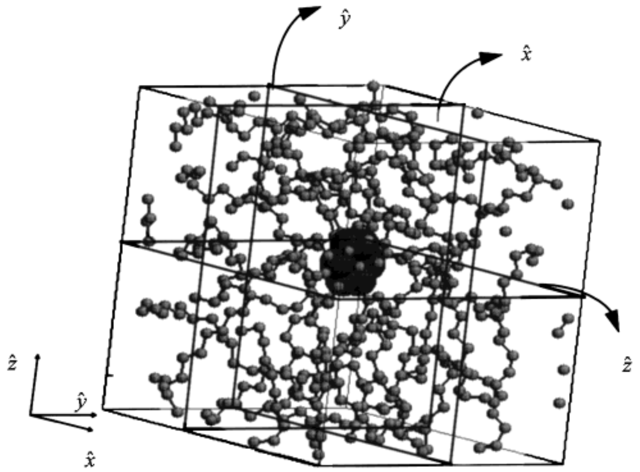
Our MC simulations clearly overpredict the density (Figure 4) as expected by the use of the united atom representation.

From similar analyses of other thermodynamic and structural properties we could conclude that the combination of MC moves was perfectly able to equilibrate these systems.

It seems that due to the high flexibility of PE chains these are able to accommodate the benzene molecules without disturbing very much their structural properties.

To investigate whether the inclusion induces some degree of local ordering, we seeked to find the points where a bond of the polyethylene chain intersects some characteristic planes in the vicinity of the benzene molecule. An obvious choice for these planes was the one on which the benzene molecule lies and two planes perpendicular to this one and also mutually perpendicular as represented in Scheme 1. We have defined the planes by their normal vectors: the planes perpen-

Scheme 1. Schematic Representation of the Simulation Box and the Planes Chosen To Calculate the Intercession between Such Planes and the Chain Bonds



dicular to the plane of the ring are $\hat{y}$ and $\hat{z}$ while the plane containing the benzene ring is $\hat{x}$. The intersections were obtained from 260 configuration separated each other by 10^6 (1 million) MC moves.

The intersection points of PE bonds with these planes also help define the shape of the cavity created by the benzene molecule. The intersection points of the three planes are represented in parts a, b, and c of Figure 5 for $\hat{y}$, $\hat{z}$, and $\hat{x}$, respectively.

The cloud of intersection points in the two planes perpendicular to the plane of the benzene ring has an elliptical shape (as corresponds to side views of the ring) while the cavity produced by the benzene in the plane of the ring $\hat{x}$ is consistent with the higher symmetry of the top view of the ring. The shape of the cavity can be characterized by a oblate ellipsoid such as the one represented in Scheme 1. A remarkable feature of the clouds of intersection points is that they display density fluctuations with increasing distance from the ring: an accumulation of points in the immediate vicinity of the benzene ring is followed by a less densely populated region. Even a second region of higher concentration of points can be detected. In Figure 5a three ellipses have been drawn at the approximate boundaries of these regions in order to guide the eye.

To quantify the distribution of intersection points, a square grid of 0.5 Å spacing was constructed on the $\hat{y}$ and $\hat{z}$ planes, and the number of intersection points was counted on every cell. Given their equivalence, planes $\hat{y}$ and $\hat{z}$ were overlapped and treated as a single plane. The surface plot is represented in Figure 6.

The center "hole" produced by the ring is first surrounded by an elliptical ridge that represents an accumulation of intersection points and then followed by a valley and a second weak ridge.

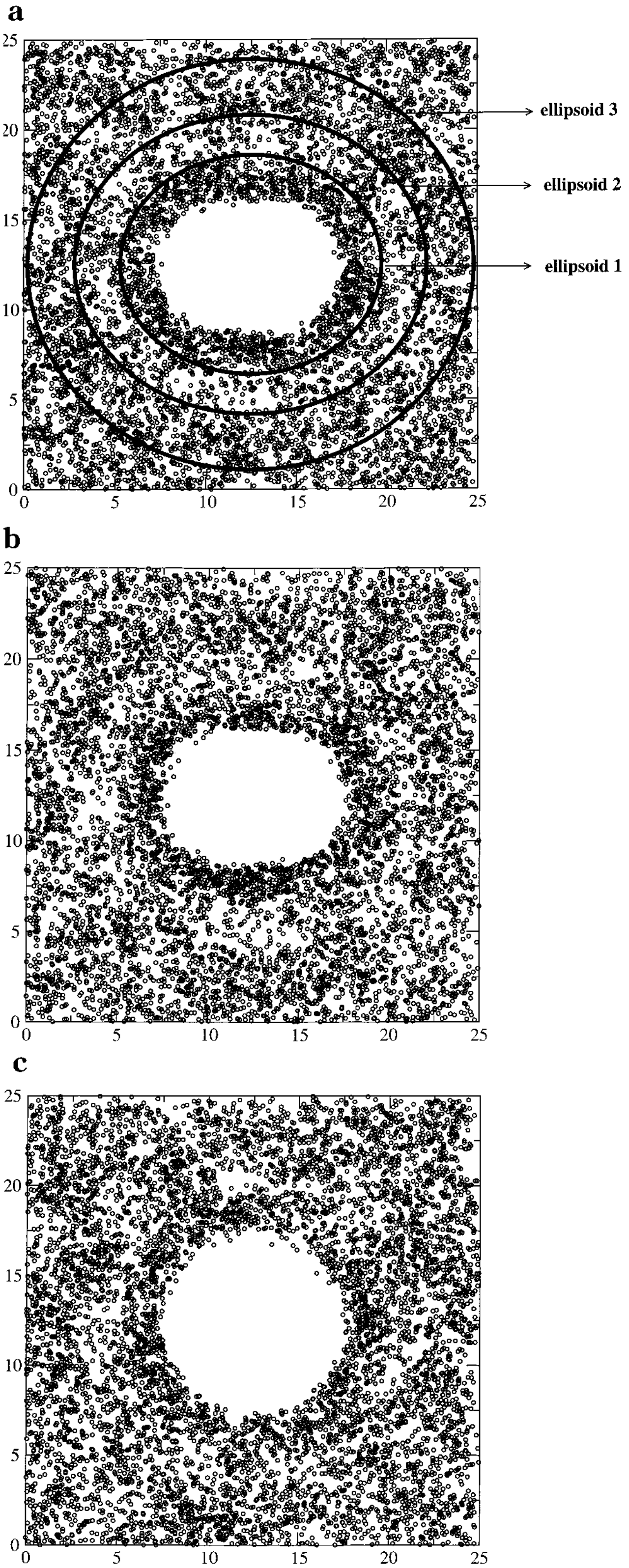


Figure 5. Intersection points between polymeric backbones and the two planes perpendicular to the plane of the benzene ring $\hat{y}$ and $\hat{z}$ (a) and (b) and the plane of the ring $\hat{x}$ (c). Ellipsoids 1, 2, and 3 are plotted as a guide to the eye.

The presence of the benzene obviously causes the chains to pack in a more compact way in the immediate vicinity of the ring, thus depleting the outward neighborhood. This wavy perturbation on the packing of the chains is, of course, not appreciable in pure PE. While this way of packing the chains is consistent with the specific volume observed in Figure 4 (an accumulation of mers in the vicinity of the ring is followed by a less dense region in order to keep the same specific volume as in pure PE), the nonmonotonic radial variation of mer density is a somewhat unexpected feature of the PE + benzene system.

It is interesting to see to what extent the average size of the chains changes in order to make compatible a high concentration of mers close to the benzene ring and, simulataneously, virtually unmodified overall struc-

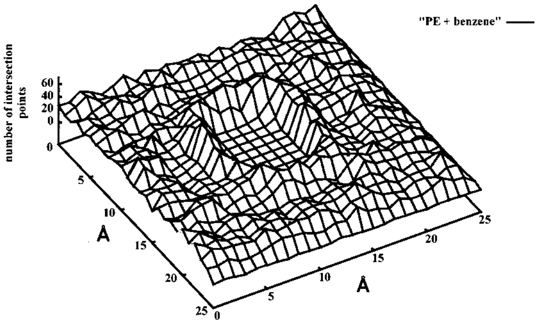


Figure 6. Distribution of intersection points of the planes of Figure 5a,b. To have better statistics and based on the assumption that the planes $\hat{y}$ and $\hat{z}$ are equivalent, the intersection points for these two planes were accumulated and are presented as a unique plane.

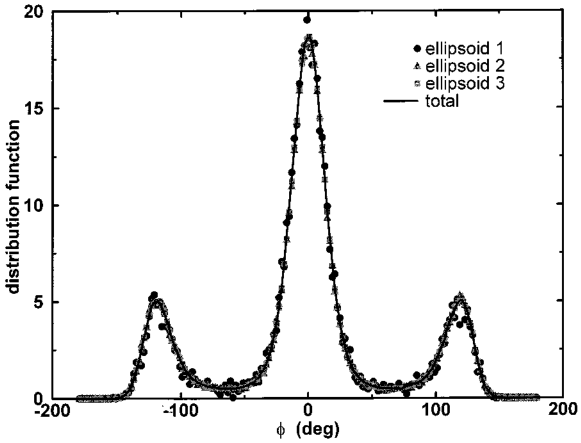


Figure 7. Torsional distribution has been calculated for all bonds lying within the three concentric ellipsoids whose projection onto the plane $\hat{x}$ is plotted.

tural parameters. A typical property to characterize the shape of the polymeric chains is the characteristic ratio $C_N = \langle R^2\rangle/(N - 1)$, where $\langle R^2\rangle$ represents the mean-square end-to-end distance and $(N - 1)$ is the number of bonds. The values for both systems are given in Table 2. They are very close to the value of $C_\infty = 8.3$ reported by Fetters et al.[17] measured by small-angle neutron scattering (SANS) directly on PE melts. This value is larger than the value of 6.7 tabulated by Flory[18] and experimentally measured in solution under Θ-conditions. More important than how close these results are to the experimental value is the fact that both values are undistinguishable within the statistical error bars.

Values of the characteristic ratio are related to the occupancy of the trans state. Figure 1b shows that both systems have exactly the same torsional distribution, which is consistent with the same characteristic ratio found here.

In view of the unexpected nonmonotonic decay of mer concentration shown in Figure 6, we studied the distribution of torsion angles within the three concentric ellipsoidal regions, to see whether differences in mer concentration are correlated with conformational preferences (e.g., an enrichment of gauche states). The results of the distribution of torsions are plotted in Figure 7, showing that independent of the differences in mer density, the distribution of torsional angles is indistinguishable from that of normal PE.

Structural Effect of the Benzene Inclusion as a Function of Chain Flexibility. Our goal was to investigate the structural effect of the rigidity of the polymer on the miscibility of PE with other molecules such as benzene. Sometimes the solubility of low molecular weight compounds in polymeric matrices, independent of any particular interaction, can be just a consequence of the flexibility of the polymer chains. To vary the degree of rigidity of the system, we modified the torsional potential as represented in Figure 8. The main differences of those potentials with respect to the Ryckaert−Bellemans' potential are the height of the barriers that separate the trans and the gauche states and the depth of the wells. We have called the two modified potentials used in this work *mild* and *rigid*, as the barrier that separates the trans and the gauche states is successively increased. All the c_i coefficients of the modified torisonal potentials are the same than the ones of eq 4, less the c_1 coefficient, that is, $c_1 = 8.83$ kJ/mol for the *mild* system and $c_1 = 6.08$ kJ/mol for the *rigid*. As a consequence of the modifications, the population of the trans state grows at the expense of the gauche conformation. The global size of the chains tends to increase, the persistence length, L_P,[19] will be augmented, and therefore the flexibility of the chains will be reduced.[20] We will refer to these two systems with modified chain rigidity as pseudo-PE or p-PE: they retain the Lennard-Jones, geometry, and binding potential of PE, but higher rigidity has been imposed, through the modification of the torsional potential.

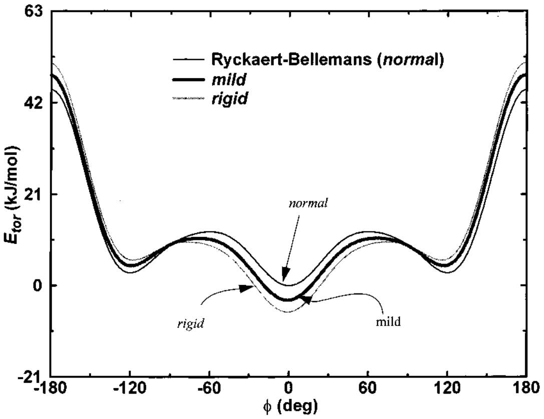


Figure 8. Torsional potential used here for the *normal*, *mild*, and *rigid* systems.

Table 2. Characteristic Ratio for PE and PE + Benzene Obtained from the Simulation

system	C_N
PE	8.45
PE + benzene	8.19

Two full simulations were carried out with each potential: one considering the binary system p-PE plus benzene and the other on pure p-PE. The latter, as previously, was used as reference. The first structural difference appears immediately when extra rigidity is imposed to the system. In Figure 9 the torsional angle distribution is plotted for the p-PE and p-PE + benzene systems for the *mild* torsional potential. In this case the rigidity imposed on the system reduces the number of trans states to favor the gauche with respect to the same system without the presence of the aromatic ring.

The intramolecular pair distribution function is represented in Figure 10 for the *mild* system. New peaks become visible in this distribution function as compared with Figure 1d. They are the consequence of having larger portions of the chains in all-trans. When the comparison is established between the system with and

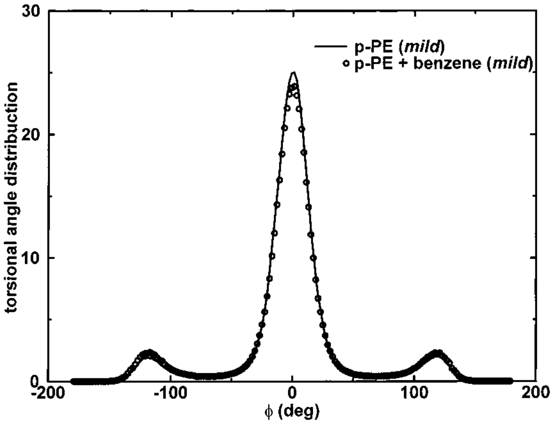


Figure 9. Torsional angle distribution for the p-PE and p-PE + benzene systems for the *mild* torsional potential.

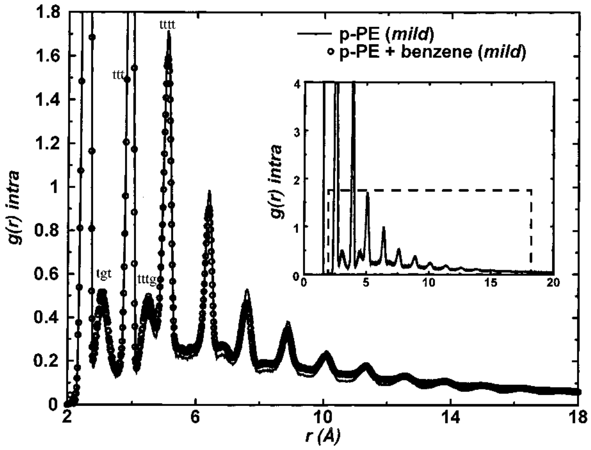


Figure 10. Intramolecular pair distribution function is represented for the *mild* system for both systems: p-PE + benzene and p-PE. Inside the whole plot is represented.

without the ring, it is obvious that some peaks in the system containing the benzene are more intense, while others show a lower population of such conformations. The peak at 1.54 Å has been omitted in the plot (only visible in the inset of Figure 10, where the whole plot is represented) because it corresponds to two consecutive mers and is equal for both systems. The first difference emerges in the second peak around 3.1 Å, which is due to triads *tgt* and which is more intense in the system with the benzene. The same happens for the peak at 4.3 Å, coresponding to *tttg*. On the contrary, the peak at 5.1 Å, which corresponds to *tttt*, is more intense for the case of pure p-PE. The consequence of incorporating a benzene ring into the material is the increases of the gauche states, as is evidenced in Figure 9 as well, to accommodate the insertion. This is the reason why the peaks corresponding to distances between mers that are separated by conformations containing gauche states are more populated in the case of the system containing the benzene, while when the peak contains only trans states the occupancy is higher for the pure p-PE. Similar results were obtained for the *rigid* torsional potential.

Additional insight into the structural changes induced by the rigidity can be gained by studying the intermolecular pair-distribution function, represented in Figure 11 for both the *mild* and the *rigid* systems. According to Figure 11, the imposition of rigidity causes a noticeable shift in the position of the shells of intermolecular neighbors when the benzene is present into the system. The shift is more relevant as the rigidity of the system is increased. The displacement of the peaks toward larger distances indicates that the increase of population of gauche states around the benzene inclusion reduces the ability of p-PH chains to pack efficiently. Another noticeable effect is the decrease of intermolecular neighbors relative to the pure p-PE system.

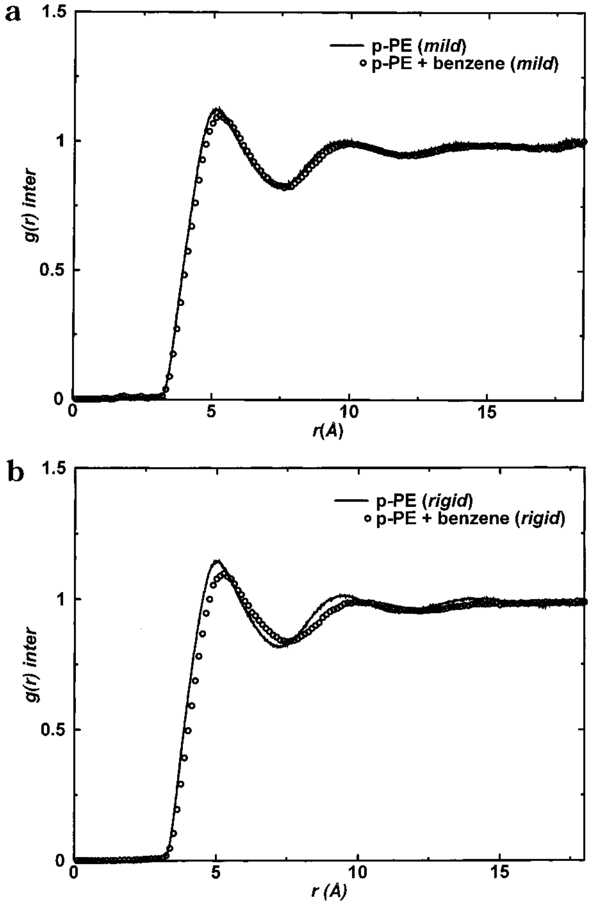


Figure 11. Intermolecular pair-distribution function for both the *mild* (a) and the *rigid* (b) systems. Comparison is established between the system with and without the benzene.

Once the structural differences, due to the presence of the benzene molecule, have been evidenced for the systems housing *extra* rigidity, the intersection points of the bonds of the p-PE chains with planes perpendicular to the plane of the benzene molecule have been plotted in a similar fashion as in Figure 5 for the system with the normal torsional potential. Figure 12a,b represents the mentioned intersection points for the *mild* and *rigid* systems. It is clear how these diffused rings showed in Figure 5 start to be more defined as in the *mild* case to end up with a system having a ring containing many intersection points followed by an essentially empty space (*rigid* system). The appearance of empty space is evidence of the less favorable interaction between the polymer and the benzene. This empty space is as well a consequence of the fact that when the chain are stiffer, longer segments of the chains adopt the trans state. This higher population of the trans state is reflected in Figure 10 where more peaks on the pair distribution funtion are present. The long segments of all trans bonds tend to pack together as in crystallize samples producing empty spaces. The persistence length was calculated for the three different degrees of rigidity, *normal*, *mild*, and *rigid* and both with and without the

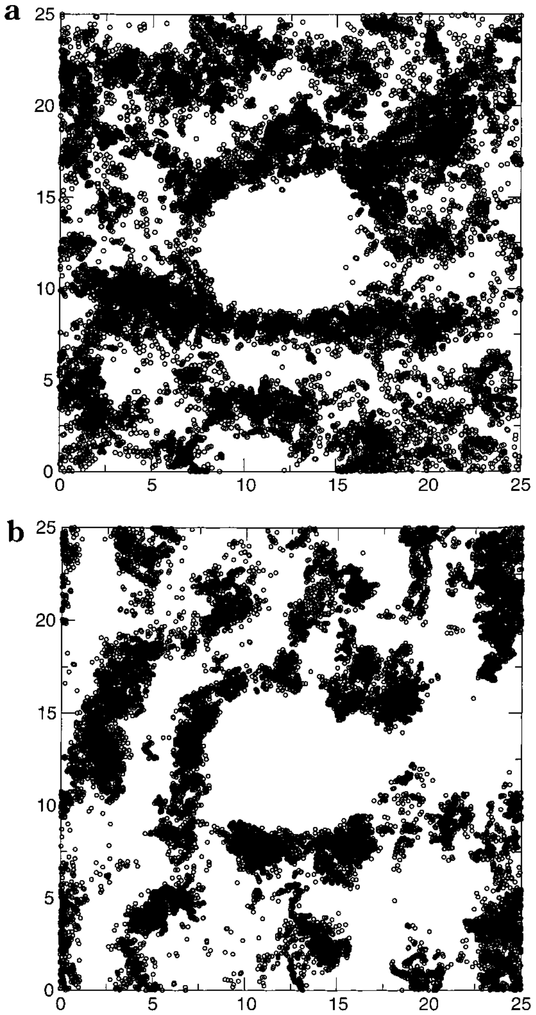


Figure 12. Intersection points between polymeric backbones and the plane perpendicular to the plane of the benzene ring $\hat{x}$ plotted together for the *mild* (a) and *rigid* (b) systems.

Table 3. Persistence Length for the Six Systems Simulated Here; Systems with and without the Benzene Molecule for the Normal, Mild, and Rigid Torsional Potentials

system	persistence length (Å)
PE (normal)	8.3 ± 0.2
PE + benzene (normal)	8.2 ± 0.2
p-PE (mild)	9.7 ± 0.4
p-PE + benzene (mild)	8.9 ± 0.4
p-PE (rigid)	10.7 ± 0.4
p-PE + benzene (rigid)	9.5 ± 0.4

presence of the benzene. The results are tabulated in Table 3. The systems with the normal torsional potential show almost the same persistence length, while when the system becomes more rigid, the persistence length increases. Interestingly, when the system starts to be more rigid, the persistence length for the system with the inclusion of the molecule of benzene is lower than the L_P of the system without the inclusion. The difference in L_P between the system with and the one without the benzene is larger as the rigidity increases. This result clearly points to the plasticizer effect of the inclusion when the system in not flexible enough to accommodate the low molecular weight inclusion.

4. Conclusion

The effect of a benzene inclusion in PE does not change very much the conformations of the chains although it produces a bulk distortion because in the same volume (see Figure 4) as the one occupied by the pure PE, an extra molecule is inserted. The presence of the benzene causes the spatial mer density to vary in a damped oscillatory fashion in the vicinity of the ring. The first high-mer-density ellipsoidal shell is about 2 Å thick. This is is followed by a low-mer-density shell of roughly equal thickness. The high flexibility of the PE chains allows them to efficiently pack around the benzene molecular without significantly modifying their conformational paramters. Very different behavior is however found when more rigid chains are considered. Through a modification of the torsional potential, *pseudo*-PE's of increased rigidity can be studied as model systems for more rigid polymers. Increased chain rigidity is found to make it increasingly difficult for the amorphous matrix to accommodate the benzene inclusion. The oscillatory variation in mer density with increasing distance from the inclusion becomes more pronounced. For the most rigid chains considered, there is a clearly tendency for chains to leave relatively large regions close to the ring unoccupied. Although the appearance of such large empty pockets in well-equilibrated simulations of rigid chains may not quantitatively represent a specific real system, it is compellingly indicative of the less favorable interation between the benzene and the polymer. It clearly shows the relationship between chain flexibility and the ability of an amorphous polymer matrix to accommodate a low molecular weight inclusion. The increase of flexibility induced by the benzene molecule is more pronounced when the system is more rigid than the actual PE. Rigid p-PE chains are more perturbed by the presence of the inclusion. They are forced to occupy more gauche states in order to make place for the benzene molecule. As a consequence, both the radius of gyration of the system and the persistence length are lowered. The aforementioned effect of increase of flexibility is reflected in more compact molecular configurations.

References and Notes

(1) Brydson, Ed.; *Plastic Materials*, 5th ed.; Butterworths: London, 1989.
(2) Grossman, R. F.; Lutz Jr., L. T. In *Polymer Modifiers and Additives*; Lutz, J. T., Ed.; Marcel Dekker: New York, 2000.
(3) Bergquist, P.; Zhu, Y.; Jones, A. A.; Inglefield, P. T. *Macromolecules* **1999**, *32*, 7925.
(4) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley Interscience: New York, 1991.
(5) Ahumada, O.; Weder, Ch.; Neuenschwander, P.; Suter, U. W.; Herminghause, S. *Macromolecules* **1997**, *30*, 3256.
(6) Mavrantzas, V. G.; Boone, T. D.; Zervopoulou, E.; Theodorou, D. N. *Macromolecules* **1999**, *32*, 5072.
(7) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford University Press: New York, 1987.
(8) Theodorou, D. N.; Suter, U. W. *Macromolecules* **1985**, *18*, 1467.
(9) Van der Ploeg, P.; Berendsen, H. J. C. *J. Chem. Phys.* **1982**, *76*, 327.
(10) Ryckaert, J. P.; Bellemans, A. *Chem. Phys. Lett.* **1975**, *30*, 123.
(11) Bartell, L. S.; Sharkey, L. R.; Shi, X. *J. Am. Chem. Soc.* **1988**, *110*, 7006.
(12) Lastoskie, C. M.; Madden, W. G. In *Computer Simulations of Polymers;* Roe, R.-J., Ed.; Prentice Hall: Englewood Cliffs, NJ, 1991; p 233.
(13) Pant, P. V. K.; Theodorou, D. N. *Macromolecules* **1995**, *28*, 7224.
(14) Muller, M. The Structure of Dense Polymer Systems; Geometry, Algorithms, Software. Ph.D. Thesis, ETH Zürich No. 13096, 1999.

(15) Pearson, D. S.; Ver Strate, G.; von Meerwall, E.; Schilling, F. C. *Macromolecules* **1987**, *20*, 1133.
(16) Dee, G. T.; Ougizawa, T.; Walsh, D. J. *Polymer* **1992**, *33*, 3462.
(17) Fetters, L. J.; Graessley, W. W.; Krishnamoorti, R.; Lohse, D. J. *Macromolecules* **1996**, *30*, 4973.
(18) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.
(19) Kratky, O.; Porod, G. *Recl. Trav. Chim. Pays-Bas* **1949**, *68*, 1106.
(20) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon: Oxford, UK, 1986.

MA011178O