

Molecular Simulation of Physical Properties of Hindered-Amine Light Stabilizers in Polyethylene

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Received November 30, 1998. Revised Manuscript Received March 2, 1999

Abstract: Novel Monte Carlo methods are used to simulate the excess chemical potential of commercial hindered-amine light stabilizers (HALS) in polyethylene. The solubility change incurred by increasing the size of the pendant tail of HALS molecules by a single methylene segment is estimated using simulations. Our results indicate that HALS molecules undergo a conformational transition at intermediate pendant-tail chain lengths. Our results also indicate that, above the boiling temperature of a particular stabilizer HALS, a segmental chain length increase raises its solubility in polyethylene. Similar phenomena are observed for small alkanes in polyethylene both theoretically and experimentally. The relative solubility of HALS of different lengths appears to increase with decreasing temperature. Results of molecular dynamics simulations yield diffusion coefficients that are consistent with available experimental data.

Introduction

Polymers can be highly reactive toward their environment; chain scissions and crosslinking can alter the molecular weight of a material considerably, thereby leading to deterioration of mechanical properties. In general, condensation polymers containing functional groups in their backbone, most notably polyesters, polyamides, and polyurethanes, are more prone to hydrolytic and biodegradation than polymers containing a carbon–carbon backbone (polyolefins). Polyolefins are not too susceptible to biodegradation unless they are first oxidized. Exposure to light, however, accelerates oxidation. The more oxidizable polyolefins (e.g., polyethylene or polypropylene) are highly sensitive to photooxidation, and the rate of physical deterioration of these polymers can be accelerated by almost an order of magnitude in the presence of light.

The use of polymeric materials for increasingly demanding applications has led to numerous studies of polymer stability;^{1–4} a number of effective stabilizers have now been developed. Hindered-amine light stabilizers (HALS) represent some of the most widely used photostabilizers for polyolefins, and several experimental studies of their properties have appeared in the literature.^{5–7}

For a stabilizer to be effective in preventing oxidation, it has to be chemically reactive and it has to meet certain physical requirements when dispersed in the host polymer. The stabilizer must be present at sufficiently high concentrations for effective protection of the polymer. One of the major problems encountered in polymer stabilization is the physical loss of stabilizers

from the polymer, which is directly related to their affinity for the polymer and their diffusion in the polymeric matrix. In some cases the loss of a stabilizer from the polymer can be accelerated if the stabilizer has a strong affinity for the surrounding medium (compared to that of the polymer); such effects, however, are not considered in this work.

In the polymer stabilization community, the efficiency of a stabilizer is loosely defined as its ability to protect a polymer from degradation (under weathering conditions, accelerated or otherwise) over time. Empirically, the efficiency of a stabilizer for protection of a polyolefin (the so-called “protection time”) has been found to be correlated to the logarithm of the ratio S^2/D , where S is the solubility (in wt %) of the stabilizer in the polymer and D is its diffusion coefficient (in cm^2/s).^{8,9} Protection time is determined experimentally by exposing polymer samples, stabilized with a known amount of the relevant additive, to accelerated weathering, followed by mechanical testing against failure at various times. Experimental studies have shown that this relationship is approximately valid for HALS-stabilized polyolefins.^{9–11} Additives with a higher S^2/D are indeed found to have a higher efficiency.

In order to design better, more effective stabilizers, it would be useful to understand the factors which govern the solubility and diffusion behavior of such molecules in polyolefins. This will permit screening of promising additives before they are actually synthesized in the laboratory. In this work we demonstrate that molecular simulations can provide valuable information toward that goal. We do so by examining the solubility of a particular class of hindered-amine light stabilizers in polyethylene. Novel Monte Carlo methods are employed to calculate the relative solubility of a homologous series of HALS

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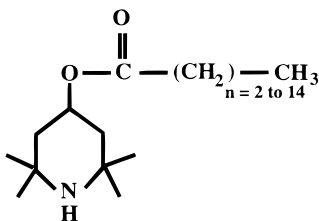


Figure 1. Schematic diagram of the HALS molecule studied in this work.

in linear polyethylene. The main building block of the HALS studied in this work is an ester of 2,2,6,6-tetramethyl-piperidin-4-ol and *n*-butyric acid. The chemical structure is illustrated in Figure 1. The homologous series of HALS is created by varying the length of the pendant chain of the molecule. The rationale behind this work is provided by the fact that in practice there is little incentive to alter the “active” part of the molecule (i.e., the hindered amine), which over the years has been shown to provide effective protection against light; however, modifications of the pendant chain can be achieved experimentally with modest efforts and can influence significantly the efficiency of the stabilizer.

In addition to their engineering importance, solubility studies of HALS-like molecules in polymers are also important from a scientific point of view. Most of the published simulation studies of solubility of penetrants have been concerned with small molecules (e.g., methane, nitrogen, or oxygen).^{12–16} A few exceptions are provided by the simulations of solubility of ethanol and water of Tamai et al.¹⁷ and of short-chain alkanes in polyethylene by de Pablo et al.^{18,19} The study of HALS provides an opportunity to push forward the limits of size and complexity that have prevailed until now toward simulation of solubility and diffusion of industrially relevant systems.

The solubility of a chemical species in a polymer is determined by its excess chemical potential. One of the simplest and most effective methods for the calculation of excess chemical potentials is the Widom particle insertion technique.²⁰ In this method, the “host” fluid is frozen in a particular equilibrium configuration, and a “ghost” or “test” particle is inserted at a random point in that system. The excess chemical potential, μ_{ex} , is calculated from the interaction energy between the guest molecule and the host structure, U_{g} , according to

$$\mu_{\text{ex}} = -\beta^{-1} \ln \langle \exp(-\beta U_{\text{g}}) \rangle_{\text{N}} \quad (1)$$

where $\beta = (k_{\text{B}}T)^{-1}$ (k_{B} is the Boltzmann’s constant) and the brackets denote an average performed over a canonical ensemble comprising *N* particles. Unfortunately, Widom’s method becomes ineffective for high densities of the host system or for large ghost molecules. Alternative methods have subsequently been proposed to alleviate some of these problems.

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The continuum configurational-bias (CCB) method^{21,22} has extended the range of applicability of Widom’s method by allowing complex, articulated test particles to grow, segment by segment, into favorable (low) energy configurations within the host system. The bias introduced by growing molecules into low-energy configurations is subsequently removed by including appropriate weights into the calculation of the chemical potential. Simulations of the solubility of flexible alkanes in polyethylene have become possible through the use of CCB techniques; simulations of solubility of ethanol and water in polyethylene and poly(dimethylsiloxane) by Tamai et al.¹⁷ also resorted to the CCB method. Unfortunately, the computational efficiency of CCB decreases as the size and complexity of the simulated molecules increases.

Other, recently developed methods for simulation of the chemical potential include the chain-increment method of Kumar and co-workers,^{23–25} the expanded ensemble method of Wilding and Müller,²⁶ and the expanded variable chain length (EVALENCH) method of Escobedo and de Pablo.²⁷ To date, however, all of these methods have in general been used to study highly idealized models (e.g., athermal chains), and have not been applied to systems with more realistic interactions. The chain-increment method of Kumar et al. relies on the idea that, for long homonuclear chain molecules, the excess chemical potential associated with appending one additional site at the end of a molecule is independent of chain length. The method proposed by Wilding and Müller relies on an expanded ensemble in which a “tagged” chain is gradually coupled and decoupled from the system by varying an interaction strength parameter; the chemical potential is determined from the probability of finding the tagged chain in a particular coupling state. The third method, EVALENCH, combines elements from CCB, chain-increment, and expanded-ensemble methods. Chain insertions and deletions of a “tagged” chain are performed with CCB. A preselected number of intermediate lengths of the tagged chain define the different states of an expanded ensemble, and a single simulation is sufficient to estimate a segmental chemical potential for the entire tagged chain. In this paper we use both CCB and EVALENCH methods to calculate the segmental chemical potential, and hence the relative solubility of HALS molecules of different sizes dissolved in amorphous polyethylene. As discussed later in this work, our results indicate that simple configurational-bias methods or incremental-chemical potential methods would lead to incorrect results for the total chemical potential of HALS dissolved in polyethylene.

In this work, we also use conventional molecular dynamics (MD) simulations to estimate the diffusion of HALS molecules in polyethylene. In the past, MD methods have been applied extensively to study the diffusion of small penetrants (e.g., oxygen, hydrogen, helium, methane) in polymers. For simple liquids, diffusion coefficients can be calculated from relatively short simulations. However, as the size of the diffusing agent increases, the duration of the MD runs required to estimate diffusion coefficients also increases. Recently, MD techniques have been employed to calculate the diffusion coefficient of

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relatively large penetrants by Tamai et al.²⁸ and by Müller-Plathe.²⁹ Tamai et al. studied the diffusion of methane, water, and ethanol in PDMS from MD runs of about 2–5 ns. Müller-Plathe conducted simulations of benzene diffusion in swollen polystyrene from MD runs of up to 7.4 ns. To the best of our knowledge, however, MD calculations of the diffusion of larger, HALS-like penetrants in polymers have not been attempted before; in this work we use much longer (e.g., 30 ns) trajectories to estimate the diffusion coefficients of such molecules.

Previous studies of the diffusion of small penetrants in polymers indicate that simulated diffusion coefficients are often lower than the corresponding experimental values (they can differ by as much as 2 orders of magnitude); Müller-Plathe³⁰ and Pant et al.³¹ have attributed those deviations to the united-atom representation of the polymers. Note, however, that for their simulations of diffusion of methane in PDMS Sok et al.¹⁶ employed a united-atom model and obtained good agreement with experiment. More recently, Müller-Plathe has proposed that the discrepancies between simulated and experimental diffusion coefficients introduced by a united-atom representation of the molecules diminish as the size of the penetrant molecules increases.³² Considering the complexity of our system and Müller-Plathe's remarks, in this study we model both the HALS molecules and the polymer molecules in the united-atom representation. We study the diffusion of two different HALS molecules: one with a pendant alkyl tail of three carbon atoms (C₃), and another one with a tail of 15 carbon atoms (C₁₅), both dissolved in polyethylene at various temperatures.

System Models

In this work both the polyethylene and the HALS molecules are modeled using a united-atom representation. Within this representation, interaction sites in an alkane chain correspond to a methylene or a methyl group. The alkane model employed in this work is based on the recently proposed NERD force field,³³ which provides good overall agreement between simulated results and available experimental orthobaric densities, second virial coefficients of small alkanes, *P*, *V*, *T* data for short and long alkanes, and vapor–liquid equilibria for various alkane mixtures.^{33,34} The structure (e.g., equilibrium bond lengths and interatomic angles) of the HALS molecule was obtained from ab initio density functional calculations. Sites on different molecules and sites on the same molecule but separated by more than three bonds interact through a Lennard-Jones (LJ) 6-12 potential energy function. In addition to LJ interactions, a torsional potential energy function is imposed on rotations about carbon–carbon bonds of polyethylene chains and of the pendant part of the HALS molecule. The Lennard-Jones parameters for the CH group, as well as those for C atoms (carbon site) employed here are inferred from the values reported by Jorgensen et al.³⁵ Potential energy parameters for the O (oxygen site) and the NH groups are inferred from the universal potential

Table 1. Potential Energy Functions

bond stretching potential
$V(r) = \frac{K_r}{2}(r - b_{\text{eq}})^2$
bond bending potential
$V(\theta) = \frac{K_\theta}{2}(\theta - \theta_{\text{eq}})^2$
torsional potential:
$V(\phi) = V_0 + V_1(1 + \cos \phi) + V_2(1 - \cos 2\phi) + V_3(1 + \cos 3\phi)$
nonbonded interaction potential
$V(r) = 4\epsilon \left[\left(\frac{r}{\sigma} \right)^{12} - \left(\frac{r}{\sigma} \right)^6 \right]$

energy model of Rappe et al.³⁶ Note, however, that since we have gathered LJ interaction parameters for different sites from various sources, we modify some of these following the suggestions of Khare et al.³⁷ Potential energy parameters for interaction sites other than those in the alkane chain are adjusted by requiring that the ratios of σ and ϵ (from Jorgensen to this work) be the same as they are for the CH₂ groups. For interactions between unlike pairs we use Lorentz-Berthelot combining rules, i.e., $\sigma_{AB} = (\sigma_A + \sigma_B)/2$ and $\epsilon_{AB} = (\epsilon_A \epsilon_B)^{0.5}$.

It is important to emphasize that, for quantitative thermodynamic-property calculations, the hindered-amine part of the HALS molecules would require additional refinement of its potential energy function. However, since this work is concerned with the more industrially relevant study of *relative* solubilities and diffusivities of HALS molecules having different pendant chain sizes and given that reportedly accurate potential energy parameters for the pendant chain are available, we believe that our current model is sufficient for the purposes of this study. Also note that, in order to verify the accuracy of the potential energy parameters employed here, we have calculated Henry's constants for small alkanes dissolved in polyethylene, and we have verified that our results compare favorably with experimental values. The details of the interaction potential model used for both polyethylene and HALS molecules are given in Tables 1 and 2.

Simulation Methods

Continuum Configurational Bias (CCB) Method. To estimate the relative solubility of HALS molecules as the size of the pendant chain is varied, we must calculate the segmental chemical potential of that chain. The minimum size of the HALS molecule considered here has a tail consisting of 3 carbon atoms (C₃).

In the CCB method, the penetrant molecule is grown (in a polyethylene sample) from its minimum size, segment by segment, until the whole molecule is completed. The orientation of a growing segment is chosen from a set of N_{samp} random trial configurations with probability

$$W_i = \frac{w_i}{\sum_{j=1}^{N_{\text{samp}}} w_j} \quad (2)$$

where w_j is the Boltzmann weight, $\exp(-\beta U_j)$, corresponding to the *j*th trial orientation. The energy U_j between the appended site (in the *j*th trial orientation) and the host polymer system includes the already existing part of the ghost chain.

By appending a segment of the ghost molecule according to eq 2, low-energy configurations are favored over high-energy configurations, thereby facilitating the growth of long chains in the host system. To account for the bias introduced by this chain growing scheme, Widom's

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Table 2. Potential Energy Parameters^a

bond stretching potential			bond bending potential						
constituents	spring constant,	equilibrium bond length, Å	constituents	spring constant,	equilibrium bond angle, deg	torsional potential constants	Lennard-Jones potential		
	K/Å ²			K/rad ²			species	ε, K	σ, Å
NH-CH _n	144750	1.47	CH _n -NH-CH _n	62500	113.0	V(0) = 0 K	NH	34.7	3.70
CH-CH _n	96500	1.54	NH-CH _n -CH _n	62500	109.4	V(1) = 355.03 K	CH ₂	45.8	3.93
CH _n -O	131300	1.47	CH _n -CH _n -CH _n (ring)	62500	109.4	V(2) = -68.19 K	C	53.0	3.851
CH _n =O	262600	1.22	CH _n -CH _n -CH _n (chain)	62500	114.0	V(3) = 701.32 K	CH ₃	104.0	3.91
			CH _n -O-CH _n	62500	129.5		CH	31.84	3.875
			O=CH _n -CH _n	62500	118.0		O	30.0	3.50

^a "n" refers to 1, 2, or 3.

original expression (eq 1) is modified according to

$$\mu = -\beta^{-1} \ln \langle W^{(m)} w^{(m)} \rangle_N \quad (3)$$

where

$$w^{(m)} = \prod_{j=n_{\min}}^m w_j \quad (4)$$

is the product of the individual-segment Boltzmann weights of the m -segment test molecule, where

$$W^{(m)} = \prod_{j=n_{\min}}^m \left(\frac{1}{W_j N_{\text{samp}}} \right) \quad (5)$$

is the product of individual-segment probabilities for an m -segment solute chain molecule and where n_{\min} is the minimum size of the solute molecule, always present in the host polyethylene melt. To obtain the excess chemical potential, intramolecular contributions to the chemical potential must be subtracted from eq 3.

Expanded Variable-Length Chain (EVALENCH) Method. The EVALENCH method proposed by Escobedo and de Pablo²⁷ uses the configurational bias scheme described above along with the benefits of an expanded ensemble. In this method, an ensemble is defined in which each state corresponds to a different size of the penetrant chain; the partition function for such ensemble is given by

$$\Omega = \sum_{k=1}^M Q(N, V, T, m_k) \exp(\psi_k) \quad (6)$$

where $m_1 = n_{\min}$, $m_M = n_{\max}$, and for any other intermediate state, m_k is an integer number such that $n_{\min} < m_k < m_{k+1} < n_{\max}$. In eq 6, $Q(N, V, T, m_k)$ denotes a canonical partition function corresponding to a particular state having a tagged penetrant chain of size m_k . To each of the variable-length chain states corresponds a preweighting factor ψ_k , whose purpose is to maintain a somewhat uniform probability distribution over the states to the expanded ensemble.

An EVALENCH simulation requires two types of moves, thermal equilibration moves within a state and transition moves between neighboring states. For the equilibration moves we use a hybrid Monte Carlo procedure (discussed in a later section). To facilitate transition moves, configurational bias is introduced during both insertion or deletion of segments according to eq 2. Within this scheme, the probability of proposing a position in which to insert segment i (or to delete segment i from that position), given that one orientation must be chosen from N_{samp} possibilities, is

$$q_i = N_{\text{samp}} W_i \quad (7)$$

Metropolis-type acceptance criteria for a transition attempt from state m_y to state m_x are imposed according to

$$P_{\text{accp}}(m_y \rightarrow m_x) = \min \left[1, \frac{T(x \rightarrow y) p(x)}{T(y \rightarrow x) p(y)} \right] \quad (8)$$

where $T(x \rightarrow y)$ is the probability of proposing a transition from x to

y , and $p(x)$ is the probability of finding the system in state x . In practice, $p(x)$ is estimated from histograms of visits to each state. For two consecutive states of our HALS molecule we write

$$\frac{p(x+1)}{p(x)} = \exp\{-\beta[U_i(m_{x+1}) - U_i(m_x)]\} \exp(\psi_{x+1} - \psi_x) \quad (9)$$

$$T(x \rightarrow x+1) = \frac{q}{s_x} \quad (10)$$

and

$$T(x \rightarrow x+1) = \frac{1}{s_x} \quad (11)$$

where s_x is the number of neighboring states to x (it is always 2, except for states 1 and M in which case it is equal to 1). The segmental chemical potential associated with this scheme is given by²⁷

$$\beta \Delta \mu = \beta \mu(m_\alpha \rightarrow m_{\alpha+1}) = \ln \left[\frac{p(m_\alpha)}{p(m_{\alpha+1})} \right] + \psi_{\alpha+1} - \psi_\alpha \quad (12)$$

Henry's Law and Relative Solubility. At infinite dilution, Henry's law can be used to estimate the solubility of a solute in a solvent according to

$$H_\alpha = \frac{P}{S} \quad (13)$$

where P is the pressure, S is the solubility, and H_α is the Henry's constant. In this work, we estimate Henry's constants for alkanes dissolved in polyethylene to establish the accuracy of the forcefield employed for the tail part of HALS molecules. For a monatomic solute, Henry's constant is related to the infinite-dilution excess chemical potential through

$$\lim_{x_\alpha \rightarrow 0} \exp(\beta \mu_{\text{ex}}) = \frac{\beta}{\rho} H_\alpha \quad (14)$$

where x_α denotes the mole fraction of the solute in the solvent and ρ is the solvent density. For the monatomic case, the excess chemical potential is given by the difference between the chemical potential of the solute dissolved in the solvent and that of an ideal gas at the same temperature. To account for the internal degrees of freedom of the polyatomic molecule, the reference (ideal) system is defined as a system of noninteracting molecules (intramolecular interactions between different molecules are absent, but intermolecular interactions are included). With these modifications, Henry's constant for the solute is given by,¹⁸

$$H_\alpha = \beta^{-1} \rho \frac{\langle \exp(-\beta U_{\text{intra}}) \rangle_0}{\langle \exp(-\beta[U_{\text{inter}} + U_{\text{intra}}]) \rangle} \quad (15)$$

where U_{intra} corresponds to the intramolecular energy of the solute molecule and U_{inter} results from interactions between the solute particle

and the solvent. Using the definitions from eq 1 we can rewrite eq 15 as

$$H_{\alpha} = \beta^{-1} \rho \frac{\exp(-\beta\mu_{\text{intra}})}{\exp(-\beta\mu)} \quad (16)$$

For calculations of solubility in polymers, it is customary to express Henry's constants on a weight-fraction basis. On that basis, eq 16 can be rewritten as

$$H_{\alpha}^w = \beta^{-1} \rho \frac{M_s \exp(-\beta\mu_{\text{intra}})}{M_{\alpha} \exp(-\beta\mu)} \quad (17)$$

where M_{α} , and M_s , denote the molecular weights of the solute and the polymer, respectively.

In this study we are interested in the relative solubility of HALS molecules of different lengths in polyethylene. An expression for the relative solubility change that arises upon addition of one segment (methylene group) to the pendant chain of a HALS molecule can be obtained by combining eqs 13 and 17 according to

$$\frac{S_{\alpha+1}}{S_{\alpha}} = \frac{M_{\alpha+1}}{M_{\alpha}} \exp(-\beta[\Delta\mu - \Delta\mu_{\text{intra}}]) \quad (18)$$

where S_{α} denotes the solubility of an α -site long solute additive.

Molecular Dynamics Simulations. Diffusion coefficients are determined from the mean-squared displacement of the molecules according to

$$D = \frac{1}{6t} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle \quad (19)$$

where $\mathbf{r}(t)$ denotes the coordinates of the center of mass of the HALS molecule at time (t). The density is fixed at the value corresponding to the pure polymer at 1 bar, and a simple Nosé-Hoover thermostat³⁸ is implemented to control the temperature of the system.

Simulation Details

All simulations were carried out at constant density and temperature. At any given temperature, the density of the system at atmospheric pressure (1 atm) was set to the corresponding values obtained from NPT Monte Carlo simulations of pure alkanes using the NERD model.³³ Initial configurations for dense polyethylene melts were generated by CCB Monte Carlo methods. In this study, polyethylene chains were modeled as linear alkane chains of 70 carbon units. In calculating the excess chemical potential at infinite dilution, we restricted our system to 20 polyethylene chains (of 70 segments each) and a single HALS molecule. The minimum-size HALS is inserted into polyethylene at a low density through a trial and error method; the density of the whole system is then brought to the desired value (corresponding to the pure polymer) in several steps using molecular dynamics MD simulations.

Segmental chemical potentials are calculated here using both the CCB and the EVALENCH methods. In using the CCB method, a sequence of configurations for the host system is generated using a hybrid Monte Carlo method (see discussion below). During the CCB calculations, the value of N_{samp} was set to 30. A total of 10^5 CCB insertions were averaged to obtain the reported results for segmental chemical potentials using eq 3.

The hybrid Monte Carlo (HMC) method was also used in this work for molecular rearrangements during EVALENCH simulations.³⁹ The HMC method combines the ease of calcula-

Table 3. Properties of C_{70} , at 1 atm

temperature, °C	ρ (simulation), g/cm ³	ρ (experiment), g/cm ³
250	0.703 (6)	0.701
200	0.732 (7)	0.729
150	0.76 (10)	0.759
120	0.779 (9)	0.776

Table 4. Preweighting Factor $\psi(m)$

number of carbon unit	$\psi(m)$
3	0
4	-0.416
5	-0.667
6	-0.963
7	-1.255
8	-1.546
9	-1.791
10	-2.036
11	-2.281
12	-2.526
13	-2.771
14	-3.016
15	-3.261

tion of an MD method and the exactness of a Monte Carlo (MC) scheme. Unlike a conventional MC method, HMC involves global updates of the coordinates of all interaction sites followed by an accept/reject decision for the whole configuration. There are no discretization errors in HMC and, in principle, the time step size can be larger in HMC than MD, while keeping the method exact. One global move in configuration space consists of a number of MD moves; here we combine 10 MD moves to generate a global move. After each global move, the new system coordinates $\mathbf{r}^{\text{trial}}$ are accepted according to

$$P = \min\left[1, \exp\left(-\frac{\delta H}{kT}\right)\right] \quad (20)$$

where $\delta H = H^{\text{trial}} - H^{\text{old}}$ is the difference in Hamiltonian between the trial and the original configurations. Within this scheme, the trial configuration $\mathbf{r}^{\text{trial}}$ starting from \mathbf{r} depends only on the momenta at the beginning of the global move. These initial momenta are drawn from a Maxwellian distribution of velocities before every attempted global move.

During our EVALENCH simulations, a transition between neighboring states was attempted after every trial global move. For transition moves, we adopted a single-site increment scheme to define the states of the expanded ensemble. As explained by Escobedo and de Pablo,²⁷ for a perfectly uniform distribution $p(m)$, the preweighting factors in eq 11 directly translate into values of incremental chemical potentials. We take this concept and determine the preweighting factors for expanded ensemble simulations from segmental chemical potentials estimated from short CCB Monte Carlo simulations (Table 4). Furthermore, since CCB estimates are relatively inaccurate for long pendant chains, we estimate these factors from intermediate-size pendant-chain results. This idea can be justified from the fact that for sufficiently long chains the segmental chemical potential is essentially constant.

To determine diffusion coefficients for the HALS molecules, MD simulations of about 30 ns were conducted in the NVT ensemble. The HALS-polymer systems were equilibrated for 500 ps prior to averaging. The equations of motion were integrated using a velocity Verlet algorithm; a time step of 2.345 fs was used for the MD moves. During production runs, configurations were stored every 23.45 fs (10 time steps) for subsequent analysis.

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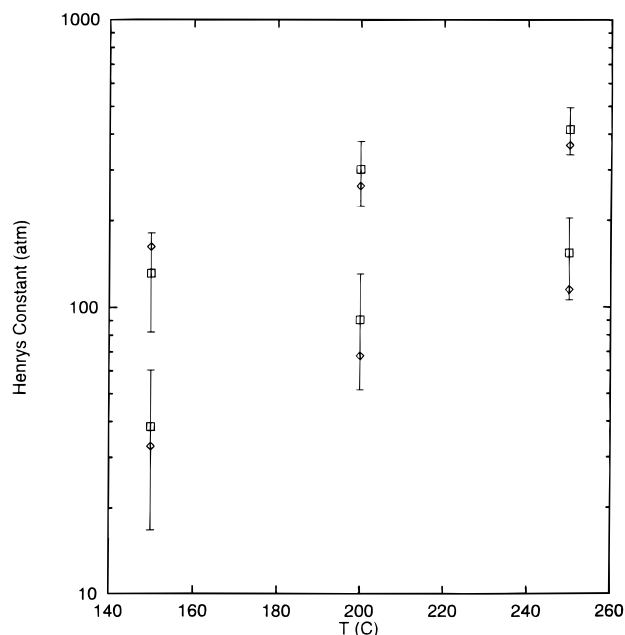


Figure 2. Simulated and experimental Henry's constants for butane and hexane, dissolved in polyethylene at 1 atm and various temperatures. The squares correspond to experimental data of Maloney and Prausnitz,⁴⁰ and the diamonds represent simulated values.

For all of the simulations reported here the Lennard-Jones terms of the potential functions were cut off at 9.825 Å. Simulated chemical potentials were subsequently corrected to include long-range interactions. We also use periodic boundary conditions in all of our simulations.

Results and Discussions

Alkanes. To demonstrate the performance of the methods and the accuracy of the force fields employed in this work, we begin by simulating Henry's constants for short and intermediate-length linear alkanes in polyethylene and compare our results to available experimental data.⁴⁰ The interaction parameters for these lower alkanes are identical to those cited in Table 2 for polyethylene. We postulate that if good results are obtained for the solubility of intermediate molecular weight alkanes (e.g., hexane) in polyethylene, we can expect to obtain results of comparable quality when such alkanes are bonded to our HALS molecules. The set of state conditions used for different parts of this study are given in Table 3. Both the total chemical potential (μ) and the intramolecular chemical potential (μ_{intra}) required for eq 17 are calculated using CCB monte carlo simulations.

Figure 2 shows simulated and experimental Henry's constants for linear alkanes dissolved in polyethylene. Results are given for butane and hexane at atmospheric pressure and at several temperatures; agreement between simulation and experiment is satisfactory. It is interesting to note that, in spite of the fact that the NERD force field was derived from pure component data, it provides satisfactory results for binary mixtures without a need for adjustable interaction parameters.

Our results for the solubility of small alkanes in polyethylene are consistent with those of de Pablo et al.,¹⁸ who used a similar model for both polyethylene and small alkanes, and obtained comparable agreement between their calculations and experimental data.

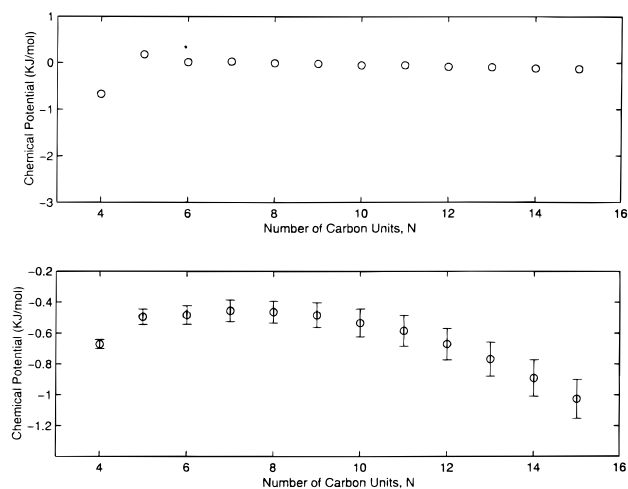


Figure 3. Intramolecular excess chemical potential of HALS molecules at 200 °C from CCB Monte Carlo simulations. The top figure corresponds to the incremental chemical potential with respect to a C₃-HALS, and the bottom figure corresponds to the segmental chemical potential for adding an individual segment to the pendant tail of the HALS molecule.

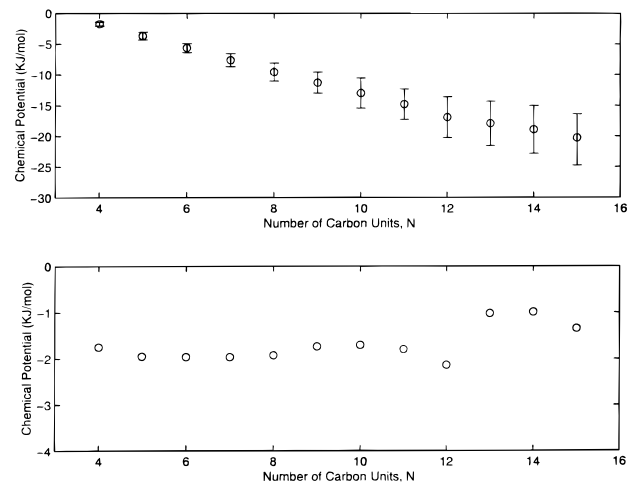


Figure 4. Total excess chemical potential of HALS dissolved in polyethylene, at 1 atm and at 200 °C, from CCB Monte Carlo simulations. The top figure shows the incremental chemical potential with respect to a C₃-HALS, and the bottom figure gives the segmental chemical potential for adding an individual segment to the pendant tail of the HALS molecule.

HALS. Excess Chemical Potential and Relative Solubility.

We study the relative solubility of HALS molecules having different pendant tails in polyethylene at three different temperatures and at atmospheric pressure. An intramolecular chemical potential, required for calculation of relative solubilities (eq 18), is determined from CCB simulations of an isolated HALS molecule. Figure 3 shows how the segmental and the total intramolecular chemical potential change when sites C₄ to C₁₅ are added to an isolated HALS molecule at 200 °C.

The incremental chemical potential associated with insertion of an additional segment of the pendant chain into the polymer melt is calculated using both the CCB and the EVALENCH methods. In Figure 4, results are shown from CCB Monte Carlo simulations of the segmental chemical potential (at 200 °C) of the pendant tail of HALS molecules ranging from C₃ to C₁₅. The monotonically decreasing line in the top figure corresponds to the incremental chemical potential with respect to a C₃ HALS. The bottom figure shows how the segmental chemical potential changes as a function of the size of the HALS molecule. The

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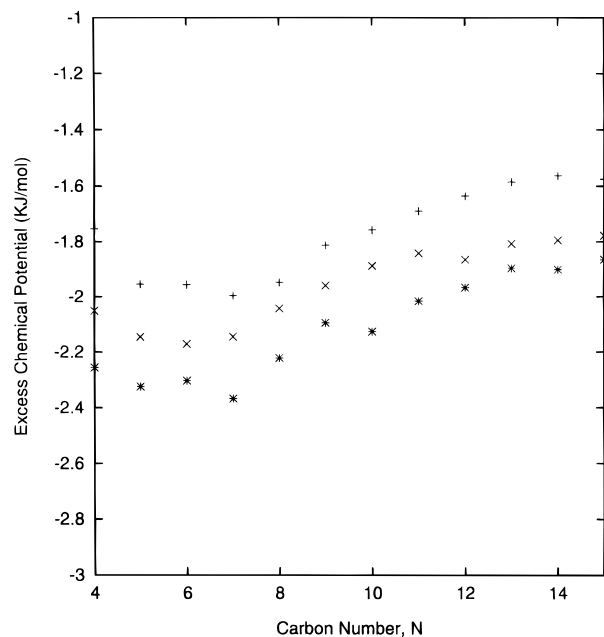


Figure 5. Segmental excess chemical potential of HALS molecules dissolved in polyethylene at 1 atm. The pluses show results at 200, the crosses at 150, and the stars at 120 °C.

accuracy of the CCB method deteriorates as the size of the solute molecule increases; more importantly, as discussed in the literature,⁴¹ important size effects lead to incorrect results for long side chains beyond about 12 methyl groups (note the sudden jump in $\Delta\mu$ for C_{12}).

In Figure 5 results are shown for the excess segmental chemical potential ($\Delta\mu - \Delta\mu_{\text{intra}}$) of sites C_4 through C_{15} of a HALS molecule in polyethylene, calculated by means of EVALENCH simulations. Results are shown at 1 bar for three temperatures, namely 200, 150, and 120 °C. In contrast to results for simple homopolymer melts, where the segmental chemical potential becomes constant (chain-length independent) after just a few sites, the segmental chemical potential of the pendant chain of our HALS molecule exhibits a distinct, nonmonotonic character. For sites C_4 to C_7 it decreases slightly; it then increases gradually and reaches a plateau after site C_{13} . Assuming a constant segmental chemical potential, as is often done in simulations of polymer melts (e.g., when using the “chain-increment method”²³), would be incorrect for the HALS molecules studied in this work; it is precisely for this type of system that the EVALENCH method is of greatest use.

According to these findings, the solubility of HALS molecules increases much more rapidly in going from C_3 to C_7 than from C_7 to C_{15} . The nonmonotonic results of Figure 5 also suggest that HALS molecules could be undergoing a transition as their chain length is increased. In Figure 6, results are shown for the approximate end-to-end distance of the HALS pendant chain as a function of chain length; for these calculations we measure distance in angstroms from the C_1 site (the first methyl group of the pendant chain). Two distinct regimes can be identified in the figure. For the first regime, from C_1 to C_7 , the distance increases rapidly to a value of about 4 Å; for the second, the distance increases more slowly from 4 to about 7 Å. For the first six sites the pendant chain is fairly stretched; after that, as the following eight sites are added, the chain coils up. On the basis of this qualitative picture of molecular configurations, we would expect diffusion coefficients to also exhibit some kind

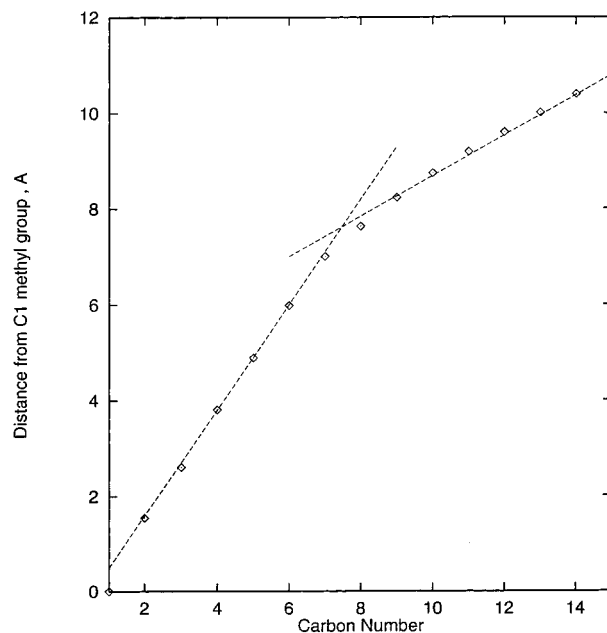


Figure 6. Approximate end-to-end distance of the HALS pendant chain as a function of chain length calculated at 200 °C from EVALENCH simulation. The distances are measured from the first methyl group of the pendant chain.

of transition around C_7 ; unfortunately, the uncertainty of simulated diffusion coefficients is too large to determine with sufficient precision how distinct that transition is.

Henry’s Law provides a simple and useful relationship between residual chemical potential and solubility, when the concentration of the solute is low. We use eq 18 to estimate the relative solubility of two HALS molecules differing by one site in the pendant chain. At atmospheric pressure, in the long-chain limit, a relative solubility of 1.49 is found at a temperature of 200 °C. In other words, at 200 °C the solubility of the HALS increases by about 49% when the length of the pendant tail is increased by one segment. Note that, to generalize our calculations, we have used $M_\alpha = M_{\alpha+1}$ in eq 18, which is essentially true in the long-chain limit. This result is important for optimization of the efficiency of stabilizers, but unfortunately a direct comparison with experiment is not possible because, to the best of our knowledge, such data are not available. Figure 7 shows that in the long-chain limit of the HALS molecule its relative solubility decreases as temperature is raised. Note, however, that this trend of decreasing relative solubility may not be true over a different temperature range. Also note that it is consistent with data for n -alkanes, both in terms of the temperature dependence and the chain-length dependence.

Diffusion. Previous MD studies of transport of small molecules through amorphous polymers have shown that diffusion proceeds by a hopping of the penetrants from one cavity to another in the polymer matrix.⁴² The simplest way of analyzing the diffusion of an individual penetrant is to inspect its path through the host system. We follow the path of the carbonyl carbon of a HALS molecule. A typical trace of the motion of the HALS molecule is shown in Figure 8. The top figure shows the trace projected onto the xy plane, and the bottom figure shows the projection onto the xz plane. Figure 8 shows that there is no jumplike motion, as has been observed in studies of small penetrants;⁴² instead, the HALS motion

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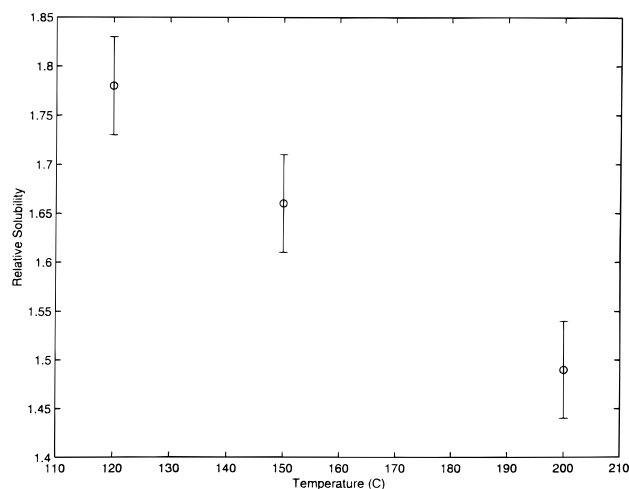


Figure 7. Relative solubility of HALS having a pendant tail that differs by one site only, in polyethylene (in the long chain limit) as a function of temperature.

proceeds by small random-walk steps, which are indicative of liquid-like diffusion.

Figure 9 shows mean-square displacements for a C_3 -HALS and a C_{15} -HALS in polyethylene at 200 °C in a log-log plot. Clearly, the curve shifts downwards as the size of the penetrant molecule is increased. In earlier studies of small-penetrant diffusion in polymers, MD trajectories ranging from a few picoseconds to about 2 ns were used to calculate diffusion coefficients. Müller-Plathe et al.³⁰ pointed out that the linearity of the mean-square displacement vs time curve was not properly attained in many of those studies. These authors also emphasized the need for long MD simulations to ensure that a truly diffusive regime is established. As stated earlier, the results reported in Figure 9 were obtained from simulation trajectories of about 30 ns. We observe from Figure 9 that a clear diffusive mode of transport is reached in our simulations, where the slope of the mean square displacement curve is unity in a logarithmic scale.

Figure 10 shows diffusion coefficients extracted from the long time regime of the mean-square displacement curves. Malik et al.⁹ have measured the diffusion of C_{15} -HALS in polyethylene using UV-spectroscopy between 25 °C and 75 °C. For computational reasons we are constrained to carry out our simulations at higher temperatures; direct comparison of our results with available experiments is therefore not possible.

However, the temperature dependence of the diffusion data can be correlated using a simple William-Landel-Ferry (WLF)⁴³ relation. According to the WLF form, the diffusion coefficient of small molecules above the glass transition temperature is given by

$$\log\left(\frac{D}{D_0}\right) = \frac{c_1(T - T_g)}{c_2 + (T - T_g)} \quad (21)$$

where c_1 and c_2 are the WLF parameters. Since experimental and simulated results for C_{15} -HALS cover a wide range of temperature, we can fit the combined data using eq 21. Following Pant and Boyd,⁴⁴ we use $T_g = 248.5$ K for polyethylene. A good WLF fit is achieved with $c_1 = 26.5$, $c_2 = 45.8$ K, and $D_0 = 10^{-15}$ cm²/s. The WLF fit, shown in Figure

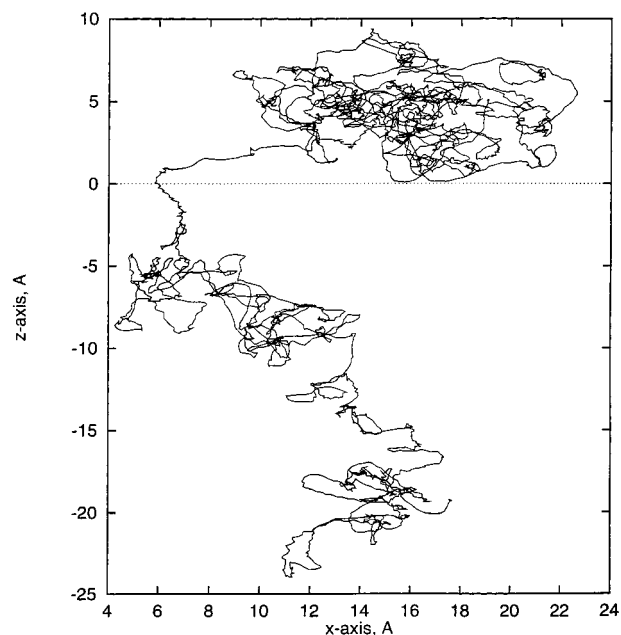
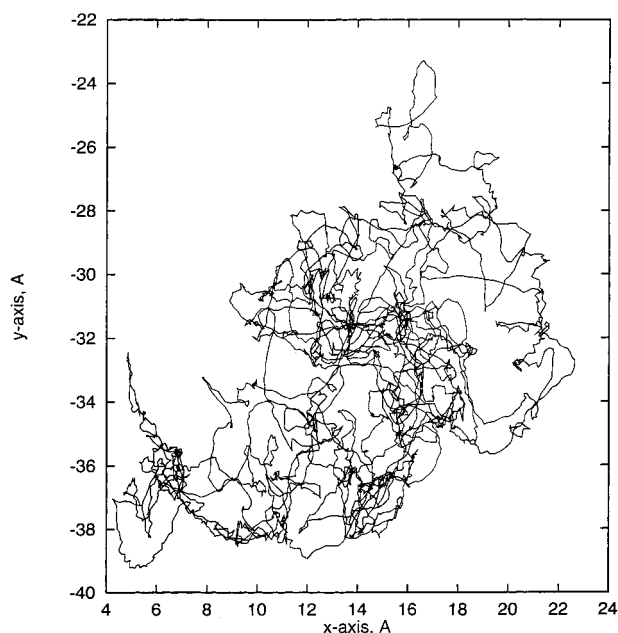


Figure 8. Two dimensional view of the trace of the motion of a C_3 -HALS in polyethylene. The dimensions are in the units of the simulation box length. The top figure gives the view in the xy -plane and the bottom figure gives the view in the yz -plane.

10, suggests that our simulation results are consistent with experimental data. The same parameters are used for C_3 -HALS and for C_{15} -HALS; only D_0 is changed to $D_0 = 2.5 \times 10^{-15}$ cm²/s for the former.

From our simulation studies for diffusion of two different HALS in polyethylene we can obtain an estimate of the effects of penetrant size on their diffusion coefficient. At $T = 200$ °C, a C_3 -HALS has a diffusion coefficient of $D = 8.7 \times 10^{-6}$ cm²/s, which is about 2 times larger than that of the C_{15} -HALS, $D = 4.3 \times 10^{-6}$ cm²/s. Experimental data for the HALS studied here with two different pendant chain lengths are not available; however, useful conclusions can be drawn from a related set of experiments by Al-Malaika et al.⁴⁵ These authors investigated

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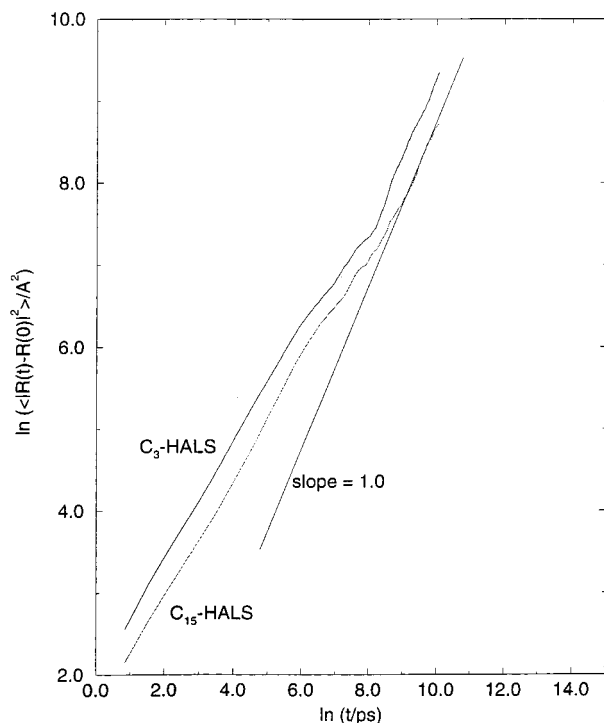


Figure 9. Log-log plot for the center-of-mass mean-square-displacement of a C_3 -HALS molecule and a C_{15} -HALS molecule, in polyethylene.

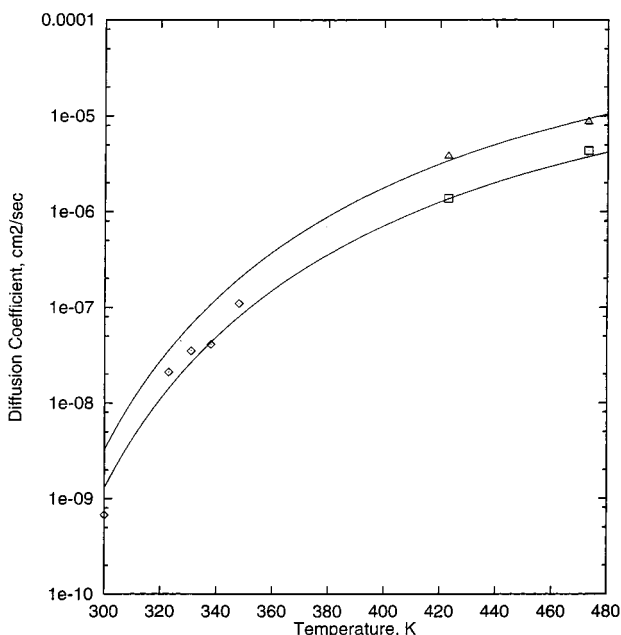


Figure 10. Diffusion coefficients of HALS molecules in polyethylene. The diamonds (C_3 -HALS) and the squares (C_{15} -HALS) are the simulated results, the squares are the experimental results (C_{15} -HALS) of Malik et al.,⁹ and the lines are the WLF fitting curves.

the diffusion of a series of ultraviolet (UV) stabilizers (namely, 2-hydroxybenzophenone with a side group of $-\text{OCH}_2\text{CH}_2\text{OCOCH}_2\text{S}-\text{C}_n\text{H}_{2n+1}$) in low density polyethylene. Their results show that, at 100 °C, the diffusion coefficient for a C_4 -stabilizer in polyethylene is $1.4 \times 10^{-8} \text{ cm}^2/\text{s}$ and that for a C_{18} -stabilizer is $0.4 \times 10^{-8} \text{ cm}^2/\text{s}$. That is, by increasing the length of the side group by 14 methylene groups, the diffusion coefficient of the stabilizer is reduced by almost a factor of 3, which is consistent with our observations.

Conclusions

A combination of CCB and EVALENCH Monte Carlo simulations was used to calculate the excess chemical potential and to estimate the relative solubility of HALS molecules of different lengths in linear polyethylene, at atmospheric pressure. This combination appears to provide a highly effective method for calculation of excess chemical potentials of complex molecules; it was used here to study a chemically detailed molecular model.

To validate the methods and energy parameters employed in this work, the solubility of small alkanes in polyethylene was estimated prior to investigating the behavior of HALS molecules. Excellent agreement was found between simulated and experimentally determined Henry's law constants.

We also studied the relative solubility associated with an increase of the length of the pendant tail of a HALS molecule in linear polyethylene. Our calculations indicate that the pendant chain of HALS molecules undergoes an interesting conformational transition as its length increases. This transition can be used as a criterion for optimization of efficiency and ease of manufacture of HALS molecules. Our simulations indicate that at intermediate temperatures (above the boiling temperature of the HALS), a segmental increase in the size of the additive pendant alkyl chain increases its solubility. In addition, the relative solubility of two HALS molecules differing by one additional methylene group in the pendant alkyl chain increases with decreasing temperature. At this point, comparison to experimental data for the relative solubility of HALS is not possible. However, similar trends are observed in the relative solubility of HALS and that of short alkanes in polyethylene, for which data are available.

Although the studies reported here were conducted at relatively high temperatures, these can in general be used to understand the influence of chain structure on the solubility of an additive in a polymer. The solubility of an additive in contact with a polymer melt is often estimated from⁴⁶⁻⁴⁸

$$-\ln \phi_1 = \frac{\Delta h_f}{RT} \left(1 - \frac{T}{T_m} \right) + \left(1 - \frac{r_1}{r_2} \right) + \chi \quad (22)$$

where ϕ_1 is the volume fraction of the additive in the polymer, Δh_f is the heat of fusion of the additive, r_1/r_2 is the size ratio between an additive and a polymer molecule, T_m is the melting temperature of the additive, and χ is the Flory-Huggins polymer-additive interaction parameter. In terms of excess chemical potential of the solute particle, eq 22 can be written as

$$-\ln \phi_1 = \frac{\Delta h_f}{RT} \left(1 - \frac{T}{T_m} \right) + \frac{\mu_{ex}}{RT} \quad (23)$$

The first term on the right hand side of eq 23 represents an ideal-mixing contribution.

To arrive at a quantitative estimate of the importance of ideal and nonideal contributions in estimating solubility of an additive from our system, we rearrange eq 23 to calculate the relative solubility of additives differing by a single segment

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(48) Billingham, N. C.; Calvert, P. D.; Manke, A. S. *J. Appl. Polym. Sci.* **1981**, 26, 3453.

$$\ln \frac{S_{\alpha+1}}{S_{\alpha}} = \frac{\Delta h_f}{R} \left(\frac{1}{T_{m,\alpha+1}} - \frac{1}{T_{m,\alpha}} \right) - \frac{\Delta \mu}{RT} \quad (24)$$

where $T_{m,\alpha}$ is the melting temperature of an α -site long additive. If we substitute typical values for the additive's heat of fusion, e.g., $\Delta h_f = 40$ KJ/mole, and a difference in melting temperature of 2 °C for a single-site increment of the additive size, we obtain a value of about 0.106 for the ideal contribution term, which, at 120 °C, is about one-seventh of the nonideal contribution term (see Figure 5). This emphasizes the fact that nonideal contributions are important in trying to develop a clear understanding of the solubility of HALS molecules in polymeric systems.

Diffusion coefficients for HALS molecules of two different lengths in polyethylene were estimated from conventional molecular dynamics simulations. To confirm that an "Einstein" diffusion regime was attained in our study, we performed extremely long simulations. Our simulated diffusion coefficients are consistent with experimental data and can be correlated with a WLF-type expression to estimate diffusion coefficients at lower temperatures (than those employed for simulations).

Unlike the motion of small penetrants in polymeric solvents, the diffusion of HALS molecules in polymers does not proceed through a hopping mechanism. Instead, we find that the motion of HALS molecules in polyethylene appears to follow a purely

diffusive mechanism, in agreement with recent experimental observations for intermediate size penetrants.^{49,50}

Finally, we must emphasize that our work has been limited in that we have only studied the chemical potential of a pendant chain and used this to calculate *relative* solubilities of HALS molecules of various sizes in polyethylene. To estimate the *absolute* solubility of HALS-like molecules in polyolefins, two obstacles must be addressed. First, an efficient expanded-ensemble algorithm is necessary to insert the piperidinyl portion of the HALS molecule into the polymer. Second, some of the force field parameters for the HALS molecule must be optimized. To gain a broader understanding of the efficiency of HALS, we are also currently investigating the effect of branching (of the pendant chain of the HALS and of polyethylene) on solubility.

Acknowledgment. The authors are grateful to the Additives Division of Ciba Specialty Chemicals for their permission to publish this work. The authors also thank P. Solera and R. Seltzer for their interest and help with this work.

JA984107M

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