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Supplementary Material Available: Listings of positional and thermal parameters for **2**–**4** (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This paper is part XXXIX of the series Haloaldehyde Polymers.

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(22) Crystal data for **3** ($C_{12}H_{15}O_5Cl_9$); monoclinic, $P2_1/n$; $a = 16.120$ (5), $b = 27.27$ (1), $c = 10.566$ (5) Å; $\beta = 98.14$ (3)°; $V = 4599$ (3) Å^3; $Z = 8$; D(calcd) = 1.613 g cm^{-3}. The 469 variables were refined with 3066 unique reflections (3° $< 2\theta <$ 45°) with $F_o > 3\sigma(F_o)$ to yield $R = 7.45\%$ and $R_w = 4.72\%$.

(23) Crystal data for **4** ($C_{14}H_{16}O_6Cl_{12}$); monoclinic, $P2_1/a$; $a = 16.795$ (5), $b = 10.952$ (4), $c = 16.587$ (6) Å; $\beta = 113.65$ (3)°; $V = 2795$ (2) Å^3; $Z = 4$; D(calcd) = 1.677 g cm^{-3}. The 353 variables were refined with 2290 unique reflections (3° $< 2\theta <$ 45°) with $F_o > 4\sigma(F_o)$ to yield $R = 4.29\%$ and $R_w = 3.43\%$.

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Estimation of the Free Volume in Polymers by Means of a Monte Carlo Technique

Introduction. During the past 30–40 years, a number of investigators have shown that the diffusion coefficients of small penetrant molecules in polymers, as well as the viscosity of polymers, can be correlated with the polymer free volume (or "empty volume").[1-14] A basic difficulty in such correlations lies in the estimation of the free volume. Bondi and Haward[15,16] have reviewed several definitions of the free volume of condensed phases. The evaluation of the free volume is based at the present time on indirect methods, in some cases involving adjustable parameters, because of the inherent difficulties involved in the determination of the free volume by experimental techniques.

The objective of this study was to develop a more rigorous theoretical method for determining the free volume available within polymers for the diffusion of small penetrant molecules. The method described here is based on the Monte Carlo simulation of the polymer microstructure, such as conceived by Suter and his co-workers.[17-19] Ultimately, this method, in conjunction with molecular dynamics, may allow the prediction of diffusion coefficients of gases in polymers from physicochemical properties of the polymers and of the penetrant gas molecules.

Simulation of Polymer Microstructure. A theoretical determination of the free volume requires an accurate description of the microscopic (atomistic) structure of the polymer. Suter and co-workers[17-19] have recently developed a methodology for obtaining a detailed structure of glassy polymers near their glass transition temperature. The model system was a cube with periodic boundaries, filled with segments from a single "parent" chain. Monte Carlo simulation of a single chain involves the generation of a chain conformation, i.e., a sequence of rotation angles.

The conformation statistics of unperturbed polymer chains are well described by the rotational isomeric state (RIS) theory.[20,21] This theory provides a priori probabilities $p_{\eta;i}$ (bond i in state η) and conditional probabilities $q_{\zeta\eta;i}$ (bond i in state η, given bond $i - 1$ in state ζ). The probabilities $p_{\eta;2}$ and $q_{\zeta\eta;i}$ define an "equivalent Markov process" for the Monte Carlo generation of chain conformations.

The structures obtained with chains generated by this scheme are characterized by excessively high energies. Hence, an initial structure is obtained by using a *modified* Markov process, based on the RIS theory, and incorporating long-range interactions. These interactions are modeled with a finite range modification of the Lennard-Jones potential function in which the potential tail is replaced by a quintic spline. The quintic spline is fitted between the interatomic distances of 1.45σ and 2.30σ, where σ is the interatomic distance where the Lennard-

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Table I
Run-Time Statistics for the Computation of Polymer Microstructure

scaling for atomic radii	rotational barrier	Lennard-Jones potential quintic spline range		starting structure		ending structure		iters.	function eval	CPU time, h
		R_1	R_2	objective function, kcal/mol	gradient norm, kcal/mol·E	objective function, kcal/mol	gradient norm, kcal/mol·K			
				Poly(propylene)						
0.5	none	0.94	1.04	0.195×10^4	0.210×10^4	0.135×10^{-17}	0.112×10^{-11}	43	127	0.03
1.0	full	0.94	1.04	0.28×10^5	0.400×10^5	388.130	0.736×10^{-4}	2170	4196	1.23
1.0	full	1.45	2.30	101.714	6.196	95.940	0.791×10^{-4}	198	447	0.71
				Poly(vinyl chloride)						
0.5	none	0.94	1.04	984.25	0.135×10^5	0.316×10^{-14}	0.528×10^{-8}	42	124	0.03
0.7	full	0.94	1.04	396.118	892.00	102.314	0.142×10^{-4}	1532	3114	0.73
1.0	full	0.94	1.04	0.417×10^4	0.219×10^4	567.484	0.274×10^{-4}	1266	2561	0.77
1.0	full	1.45	2.30	34.353	20.408	−67.997	0.115×10^{-4}	1166	2267	3.71

Jones potential is zero. In addition, for polar polymers, the electrostatic interactions are modeled with a Block–Walker[22] approximation of the dielectric constant in the coulombic potential function. In this case, a quintic spline is fitted between the interatomic distances of $0.7r_{ij}$ and 2.30σ, where r_{ij} is the sum of the van der Waals radii of two interacting atoms i and j.

The initial structure thus obtained is "relaxed" by potential energy minimization using analytical derivatives. The computing time can be kept relatively small by stagewise minimization, employing a technique of "blowing up" the atomic radii.

A polymer is not in true thermodynamic equilibrium below its glass transition temperature. Therefore, glassy polymers show volume relaxation; i.e., the volume gradually decreases with time. However, at temperatures slightly below the glass transition temperature, T_g, the unrelaxed volume in a polymer is negligible or nonexistent (if the polymer has had sufficient time to relax at that temperature). Hence, the above method yields a true description of a glassy polymer at temperatures in the vicinity of T_g. Molecular structures were obtained by the above method for atactic poly(propylene) (PP) at −40 °C and for poly(vinyl chloride) (PVC) at +70 °C. The glass transition temperatures of the two polymers are −18 °C and +80 °C, respectively. It may be noted that PP is a nonpolar polymer, whereas PVC is polar.

The structure of the polymer depends strongly on the value of the polymer density used. In this study, the periodic cube mentioned above was filled with chain segments at a density corresponding to the experimental value for the polymers studied. The densities of PP and PVC at the temperature of the investigation are 0.892 and 1.373 g/cm[3,23] respectively. For a polymer chain consisting of 76 monomer units, these correspond to cube edge sizes of 18.15 and 17.98 Å. Typical run-time statistics are presented in Table I. A model structure of relaxed poly(propylene) is shown in Figure 1.[18]

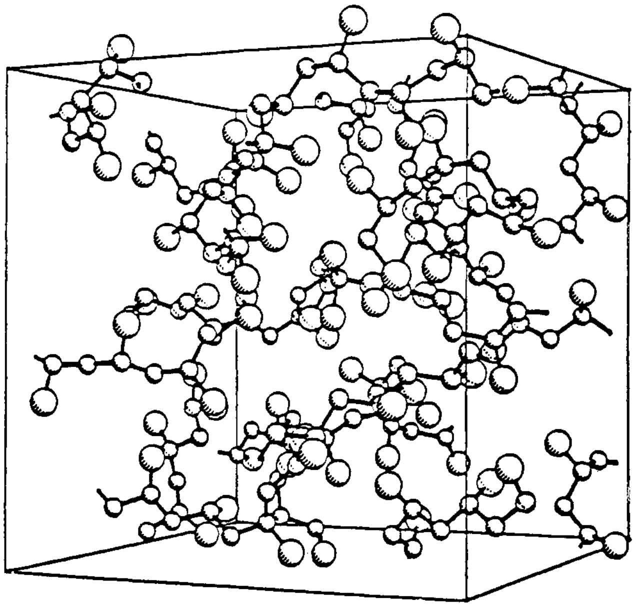

Figure 1. "Relaxed" model structure of poly(propylene) in detailed mechanical equilibrium. The small spheres denote skeletal carbon atoms. The large spheres indicate methyl groups. Hydrogen atoms have been omitted for clarity.[18] Reprinted with permission from ref 18. Copyright 1985 American Chemical Society.

Evaluation of Free Volume. The free volume in the polymer available to penetrant molecules of different sizes was obtained from the polymer microstructure. To obtain a statistical average, 10 different structures of the polymer were generated. These structures were obtained by simulating different configurations of the polymer chain within a periodic box. For each of these structures, the free volume available to spherical penetrant molecules of different sizes was evaluated using the Monte Carlo technique.

Each of the atoms of the polymer chain (the CH_3 group was considered as a "quasi" atom) was visualized as a hard sphere with its respective van der Waals radius. A large number of points [say, N ($=10^6$)] representing the centers of the penetrant molecules were randomly chosen within the periodic box. These random points were tested for uniformity and reproducibility. From a knowledge of the exact location of the atoms of the polymer it was determined whether a chosen point (coordinate position) was located in an unoccupied volume or in a volume already occupied by the polymer.

Registers (or counters) were set up for spheres of different diameters. The maximum size of a sphere, d_m, that can be inserted *without* disturbing the polymer structure was obtained for each point in the unoccupied volume. All registers corresponding to diameters less than d_m were incremented by 1, implying thereby that any hard sphere of size less than d_m can be inserted at that point. If N_d is the total number of points in the unoccupied volume at which a sphere of diameter d can be inserted, then the ratio of N_d to N is the fractional free volume available to a penetrant molecule of diameter d. Let $f'(d)$ denote this fraction. Accordingly, values of $f'(d)$ were obtained for various values of penetrant diameter d.

Three Monte Carlo simulations were performed for every microstructure, each with a different initial point (random number). The results of the simulations did not differ significantly. The average of the three values of the available free volume, $f'(d)$, was used for each microstructure. Finally, the available free volume for the poly-

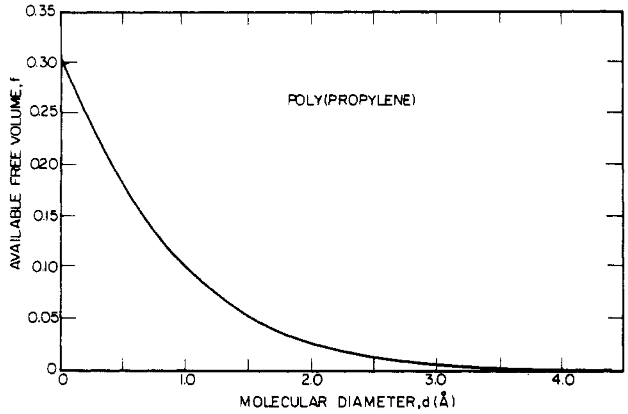

Figure 2. Available free volume in poly(propylene) as a function of the hard-sphere diameter of penetrate molecules at −40 °C.

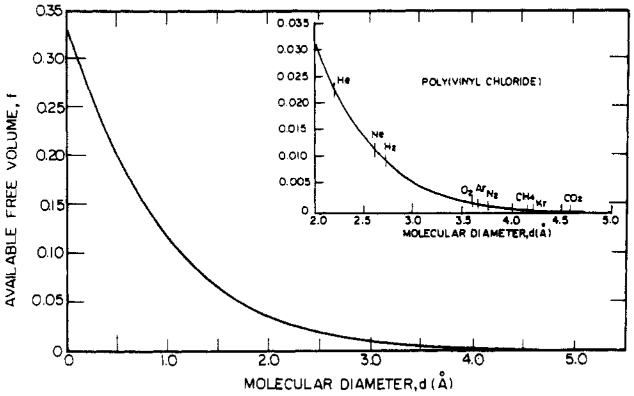

Figure 3. Available free volume in poly(vinyl chloride) as a function of the hard-sphere diameter of penetrant molecules at 70 °C.

mer, $f(d)$, was obtained from an arithmetic average of $f'(d)$ for the 10 different structures of the polymer. This average was used as a representative value of the fractional free volume available to a penetrant molecule of diameter d in a glassy polymer at temperatures closely below T_g.

Results. Plots of $f(d)$ versus d for PP and PVC are presented in Figures 2 and 3, respectively. As expected, the fraction of the free volume available to larger penetrant molecules is smaller than that available to smaller penetrants. The *total* free-volume fraction of the two glassy polymers studied (PP and PVC) is 0.31 and 0.32, respectively. These values are so close because of the similarity in the chemical structures of PP and PVC. The free-volume fractions for PP and PVC, obtained from Bondi's[24] approximate group contribution method, are 0.35 and 0.37, respectively. The agreement is satisfactory.

Several investigators have tried to correlate experimental diffusion coefficients of simple gases through polymers with their molecular diameters. However, no consistent relationships between these properties have been observed because the diffusion coefficients of gases in polymers depend both on the nature of the gas *and* that of the polymer. The ease with which a noninteracting penetrant molecule diffuses through a polymer matrix depends upon the free volume available to it. Therefore, this volume is a better parameter than the molecular diameter for the correlation of diffusion coefficients and can be calculated by the method outlined before.

Future studies must determine the topology of the free volume, i.e., the "channels" through which penetrant molecules might diffuse in the polymer. The calculations described above only determine the locations in the selected polymer volume that can accommodate penetrant molecules of different sizes, but not whether or how these locations are interconnected. The calculations must also be extended to other polymers. Eventually, it should be possible to predict diffusion coefficients for different penetrants and glassy polymers, at least near T_g, by the methods of molecular dynamics.

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