Molecular Structural Characterization of Properties of Polymethacrylates by Molecular Modeling Techniques

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Abstract : We simulated the conformational changes of polymethacrylates which have side chains with different lengths (methyl and butyl) by molecular dynamics simulation technique. Bulk states of atactic amorphous polymers relaxed at a higher temperature were generated. The chain behaviors of polymethacrylates were investigated upon varying temperatures. Molecular structural information was then obtained by characterizing radial distribution function(RDF), mean square displacement, self diffusion constant, and Connolly surfaces, among others. The estimated self diffusion constants and RDF values of PMMA and PBMA were found to be in good agreement with our expectation in view of the chain flexibility.

Introduction

Polymer properties are directly related to their structures and the understanding of the relationship between structures and properties is the ongoing subject of polymer materials research and development. During the past three decades, significant progress in the polymer characterization has been achieved mainly due to the development of instrumental techniques. In relation to this, computer simulation or molecular modeling for the study of polymers has been emerged as an extremely valuable tool to provide detailed information and basis of understanding for the structure-property relationship on the molecular level.[1-6] Among the computer simulation methods, the two most widely used methods for atomic-level modeling of molecules are Monte Carlo statistical mechanics(MC) and molecular dynamics(MD).[7,8] The principal differences between them are in the modes of sampling the configuration space available to the system.[9,10] For MD, new configurations are generated by application of Newton's equation of motion to all atoms simultaneously over a small time step to determine the new atomic positions and velocities.[11] It would be possible, therefore, to get the molecular information of dynamic properties of polymers such as mean square displacement (MSD), self diffusion constant, and radial distribution function(RDF), etc.. In the case of acrylic resins, the rich combination of monomers with different side chains produces a variety of industrially important homo- and copolymers. In this study, to gain some fundamental understanding of the effect of side chains on the macroscopic properties in terms of the molecular structures, we applied molecular dynamics simulation to polymethacrylates which have side chains with different lengths (methyl and butyl). To obtain detailed information on the molecular level, we simulated poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate)(PBMA) by using MD method instead of MC simulation method.[12,13] A large number of papers have been published on the conformational characteristics of PMMA.[14-18] The published data related to PMMA and PBMA, however, are scarce. In the present

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study, we focused on two typical polymers, PMMA and PBMA which differ in the glass transition temperature by 38°C, which means that the latter is more flexible than the former due to the longer side chain of the latter. The microstructure of a molecule determines its macroscopic properties. The in-depth conformational microstructure of a polymer is hard to determine experimentally. To prove the chain flexibility of molecules, there are many instrumental measurements available. They include thermal analysis that can yield the glass transition temperature of polymers and heat capacity(Cp), dynamic mechanical analysis (DMA) that can tell us about some kinds of thermal properties of polymers in dynamic environment instead of static environment, and diffusion constants of polymers and so on. However, limited information of molecules can be obtained by these experimental measurements. Data from experiments determine the rules and models used for the interactions between polymer chains. Simulation results should agree with experimental ones to validate a chain model.

Experimental

Measurements. Thermal and physical properties of the two samples of PMMA[poly(methyl methacrylate)] and PBMA[poly(butyl methacrylate)] purchased from Aldrich were investigated by several measurements. For the quantitative analysis of tacticities, ^{13}C NMR as well as ^{1}H NMR spectra were recorded. The two samples were found to contain similar amount of meso dyad fraction. The average value of 27.5% was used in the subsequent molecular modeling procedure for both polymers. Average molecular weights and polydispersity were measured using GPC. Thermal analysis was also performed with DSC to determine Tg's.

Models and Simulation. All the calculations were performed on an SGI Irix 6.3 O_2 workstation using the commercial software package of Cerius.[2] Details of the modeling are described below. In all cases, the number of repeating units was fixed to 20 in the model molecules with the chain end group set as CH_3.[19] For the molecular mechanical force field, the formalism of AMBER was used

with proper modification.[20,21] For the dynamics runs, Verlet leapfrog algorithm was employed with the pressure fixed. (NPT molecular dynamics simulation)[22,23] In molecular modeling to simulate the bulk properties, the generation of a representative model molecule is probably the most important step to get a reasonable result. Thus, the initial configurations were prepared as follows. First, linear molecules, whose tacticity is adjusted as the one measured by NMR, were generated. They were built into amorphous cells with periodic boundary condition to eliminate surface effects. The bulk state of polymers was generated by rotational isomeric state(RIS) Metropolis Monte Carlo (RMMC) scheme, which is very useful when generating initial configuration even though their statistical weights are unknown.[24] The RIS ratio of PMMA and PBMA were obtained by summation of dihedral distribution of polymers, and the system was then energy minimized.[25] In order to achieve statistically distributed conformations overcoming the local minimum energy barrier, the system was subjected to dynamics run at an elevated temperature of 1000K for 100 ps. Then the system was minimized again. For the calculation of various properties, dynamics were performed at 300K for 200 ps with the time step of 1 fs. It was found that the system developed to equilibrium very quickly as determined by monitoring the energy of the system. The first 10 ps was discarded and all the properties were calculated for the rest 190 ps. Various properties were calculated by extracting information of polymers from the molecular dynamics trajectory. Among them are the mean square displacement, self diffusion constant, radial distribution function(RDF), structure factor, and Connolly surfaces.[26,27] For the detailed analysis of the behavior of the different polymethacrylates systems, these property calculations were performed separately on selected portions of each molecule including backbone, carbonyl groups, the carbons directly attached to the carbonyl groups (to be called C_1 carbons), and the end carbons of the side chains (C_e carbons) in case of the longer side chain (PBMA). Initial configurations obtained after model preparation and final ones after the dynamics run are shown in Figure 1. The overall shapes of the mol-
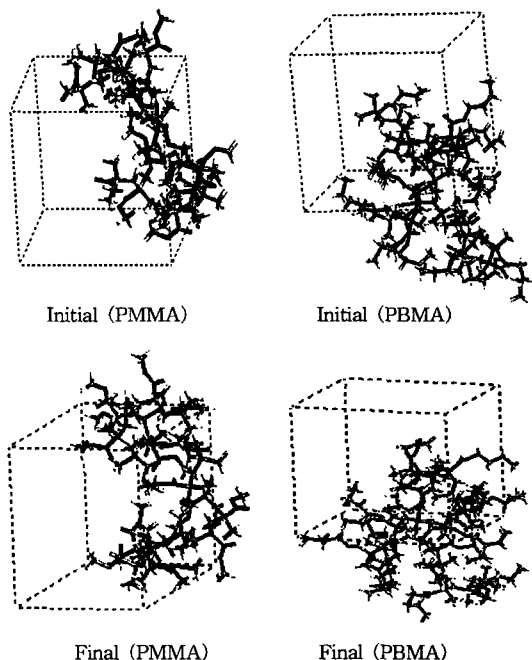
Initial (PMMA)   Initial (PBMA)

Final (PMMA)   Final (PBMA)

Figure 1. Initial and final configurations of PMMA and PBMA amorphous periodic boundary cells in the preparation stage.

ecules were significantly changed, which means that initial configuration generated by RMMC scheme was quite reasonable.

Results and Discussion

Mean square displacements. MSD of selected portions were calculated from MD simulations with averaging trajectory for every 10 ps of total 200 ps MD runs. Self diffusion constants were determined as the slopes of the fitting of the linear part of MSD data. MSD defined as the average displacements of a given portion of atoms (or whole atoms) on a polymer chain relative to their initial positions can be calculated from the trajectory after solving Newton's equation of motion. MSD is calculated as follows :

$$msd(m) = \langle |r(t)-r|^2 \rangle = \frac{1}{n}\sum_{i=1}^{n} |r(m+i)-r(i)|^2 \quad (1)$$

where m runs to maximum number of points allowed for the MSD calculation, n is number of data points used for averaging. Self diffusion con-
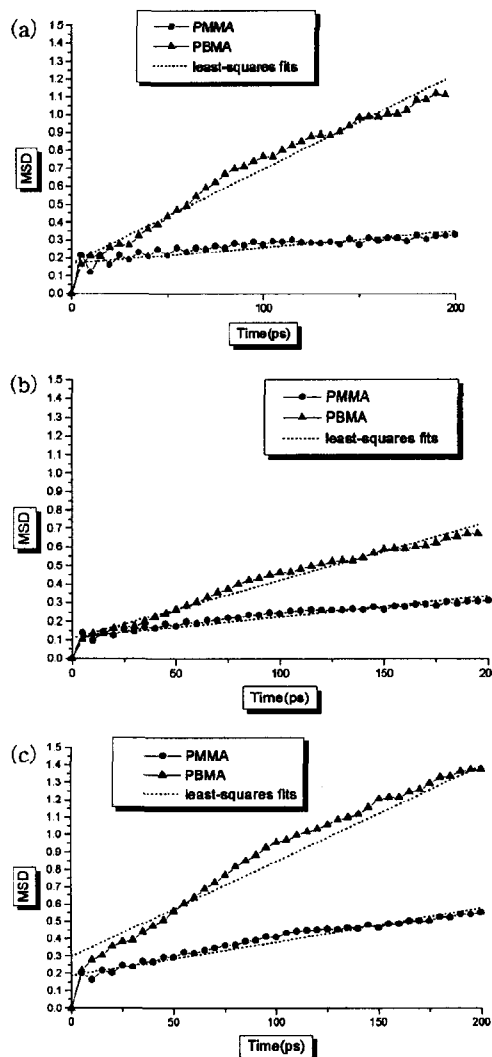
Figure 2. Mean-square displacements of PMMA and PBMA as a function of time; (a) backbone atoms, (b) COO atoms, and (c) C atoms.

stant is obtained using the Einstein relation :

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

where N is number of atoms, r is position of the particle and t represents time. It can be readily observed that, as one goes farther toward the end of the side chain starting from backbone, the extent of motion gets larger and also this effect becomes more pronounced in case of PBMA than in PMMA. As shown in Figure 2 and Table I, in

Table I. Self Diffusion Constants

Group*	PMMA	PBMA
Backbone	0.08	0.67
COO	0.11	0.18
C	0.17	0.81
End C		1.34

unit : $10^{-6}[cm^2/sec]$ per atom

*For detail, see text

case of backbone atoms of PMMA and PBMA, there is a significant difference in the values of self diffusion constants, which means backbone atoms of PBMA have higher mobility than that of PMMA. Whereas, in the case of COO atoms of the two, we found slight difference in their mobility. For C_e of PBMA, the mobility of atoms was very high as we expected. The data of MSD and self
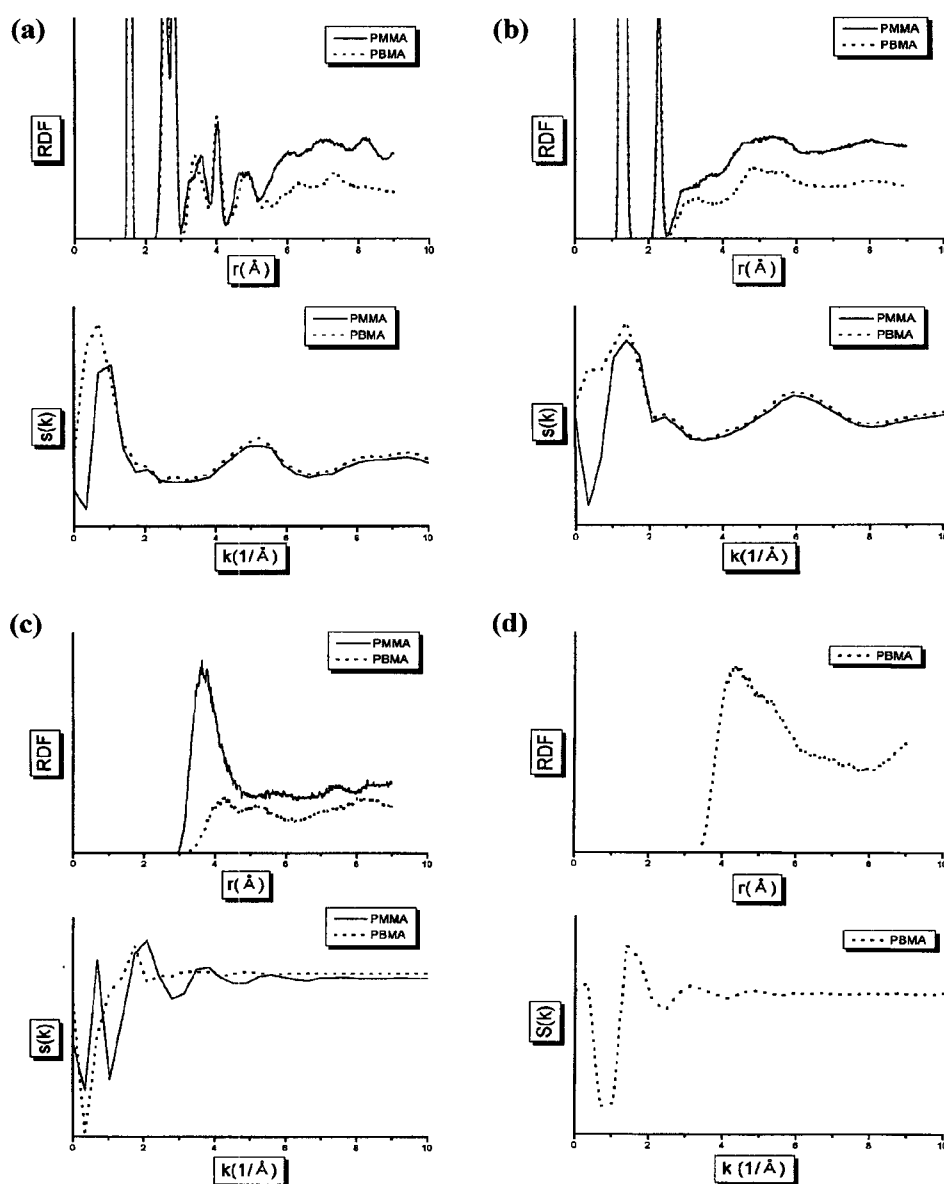

Figure 3. Radial distribution function and structure factor of each selected portion of chains; (a) backbone atoms, (b) COO atoms, (c) C atoms, and (d) End-C atoms(PBMA).

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diffusion constant can provide quantitative evidence for the differences in the mobility of atoms as representing chain flexibility.

Radial distribution function. RDF describes the spatial correlation between any two chains or chain segments. The value of RDF is a relative measure rather than an absolute one. RDF is usually assumed to be isotropic in the system, it should be centrosymetric. The following expression was used to calculate the RDF $G_{AB}(r)$ between two selected groups A and B :

$$G_{AB}(r) = \frac{N_{AB}(r) \times V}{(N_A N_B - N_{AB}) 4\pi r^2 dr} \qquad (3)$$

where N_A and N_B represent number of atoms in group A and B respectively, N_{AB} is number of atoms common to both groups A and B, and V is the unit cell volume(for nonperiodic systems V=1). A Fourier transform of an RDF can be performed to obtain the structure factor for the mode. The structure factor, $S_{AB}(k)$, between two selected groups A and B is related to the radial distribution function $G_{AB}(r)$ through a 3D Fourier transform :

$$S_{AB}(k) = \frac{N_{AB}}{N} + \frac{(N_A \times N_B) - N_{AB}}{V \times N} \times \int dr G_{AB}(r) e^{ik \cdot r} \qquad (4)$$

where k is a wave factor. As shown in Figure 3, there is higher contact probability in PMMA backbone chains than in PBMA backbone chains after 5Å. In the COO atoms of PMMA and PBMA, the same trend was found but different range was observed due to the rigidity. On the other hand, in the C_1 atoms of PMMA and PBMA, we observed strong repulsion when approaching closer than 3Å due to their steric hindrance and conformational energy, and after 3Å, PMMA shows a higher probability in C_1 contact than PBMA. The C_e atoms of PBMA(Figure. 3d) showed collectively similar tendency to the C_1 atoms of PMMA. The differences just mentioned between the estimated RDF values seem reasonable considering the conformational difference and free volume of the two polymers.

Connolly surfaces. For the calculation of free space in two polymers, Connolly surface of selected parts of a molecule were introduced.[26,27] The surface was generated by rolling a spherical probe of a specified radius over the van der Waals

surface of the model system, which was generated when the probe radius was zero. Radius value of 0.75Å was used to get cavities that would be filled by adding one carbon atom to a residue, and 1.4Å to get the surface available to solvents, respectively. Two different radii of probe sphere were used in order to get more quantitative results. As shown in Table II and III, there are three terms of surface which are contact, saddle,

Table II. Connolly Surface of Each Selected Portion When the Probe Radius is 0.75 Å

Group	species($Å^2$)	PMMA	PBMA
Backbone	contact	28.9	64.2
	saddle	69.2	82.5
	concave	77.9	58.7
	total	176.1	205.4
COO	contact	95.5	84.8
	saddle	152.8	117.5
	concave	115.7	79.3
	total	363.2	281.6
C	contact	202.2	115.3
	saddle	227.7	123.6
	concave	127.2	67.7
	total	557.2	306.5
End C	contact		245.8
	saddle		227.5
	concave		86.3
	total		559.6

Table III. Connolly Surface of Each Selected Portion When the Probe Radius is 1.4 Å

Group	species ($Å^2$)	PMMA	PBMA
Backbone	contact	1.3	21.7
	saddle	10.0	54.9
	concave	48.6	72.8
	total	59.9	149.3
COO	contact	7.7	23.8
	saddle	42.9	68.2
	concave	145.2	111.8
	total	195.7	203.8
C	contact	35.0	38.9
	saddle	128.6	88.1
	concave	265.3	130.3
	total	429.0	257.3
End C	contact		102.1
	saddle		193.2
	concave		235.5
	total		530.8

and concave.[26,27] In case of radius = 1.4Å, there was a large difference in backbone, which indicates that the chain of PBMA has enough space to roll the probe sphere in view of chain flexibility. In COO, same phenomena were observed except the case of concave points which might be interpreted as that the COO groups were more stretched in PBMA than in PMMA, even though PBMA chains possess higher contact probability than PMMA. On the contrary, in COO groups when radius = 0.75, values of contact, saddle and concave points in PMMA are much higher than these in PBMA, as we expected. Therefore, it can be elucidated from the results of Connolly surface calculation that in case of COO groups, there is more space to get into the water-sized molecule in PBMA than in PMMA.

Conclusions

In the present study, we investigated the chain behavior of polymers, by applying the molecular dynamics simulation on the molecular level to acrylic resins, especially two typical polymers, PMMA and PBMA which differ in the lengths of the side chains. Comparable results were obtained from the other types of calculations but they allowed various other aspects of detailed interpretation. Although computer simulation of polymers has limitations in the viewpoint of simulation time and step size, we could get a glimpse of the changes of microstructure of polymers by calculating mean square displacement, self diffusion constant, and normalized radial distribution function and structure factor of the two polymers. The estimated self diffusion constants and RDF values of PMMA and PBMA are in good agreement with our expectation in view of chain flexibility at least qualitatively. In addition to these analyses, we introduced the Connolly surface calculation by using the two different radii of spherical probe put into PMMA and PBMA. Although some properties of polymers were calculated by the method of molecular dynamics simulation as a function of time, their exact estimation is quite difficult for experimental measurements as well as computer simulation so that it may be inevitable to be subject to some extent of error and depends strongly

on the accuracy of the force field determining the interaction of both bond and non-bonded interactions. As a preliminary study for polymer blend system, we simulated chain behaviors of PMMA and PBMA which differ in some degree of chain flexibility due to the length of side chain. It will be our future study to predict the miscibility of these two polymer systems according to the length of side chain from the viewpoint of conformational changes as we did in this study.

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