Macromolecules **1987,** *20,* 401-404

Analysis of Diffusive Processes in Bulk Polymer by Small-Angle Neutron Scattering†

G. C. Summerfield* and Robert Ullman

Department of Nuclear Engineering, The University of Michigan,
Ann Arbor, Michigan 48109. *Received March 14, 1986*

ABSTRACT: The diffusion of clusters of polymer molecules labeled by deuterium dispersed in an unlabeled matrix changes the angular dependence of neutron scattering as a function of time. Equations are derived for extracting the diffusion constant from the scattering data for a system where Fick's law applies. The method is of particular importance where diffusion is very slow with diffusion constants of the order of 10^{-16} cm^2/s. This domain is difficult to reach by other experimental methods.

Introduction

The diffusion of polymer molecules in bulk is slow, and procedures that permit measurement over short distances are required to observe it. Among the methods that have been used are radioactive tracer studies,[1-3] infrared microdensitometry,[4,5] nuclear magnetic resonance,[6-10] fluorescent photobleaching and recovery,[11-14] forward recoil spectrometry,[15,16] and small-angle neutron scattering.[17-19] Here we concentrate on the small-angle neutron scattering method.

Diffusion constants in metallic alloys[20] and in polymers have been studied by scattering of X-rays and neutrons. This is achieved by observing the time variation of the scattering patterns as atoms or molecules of different cross sections change their positions. However, the methods used in metallurgy and in past polymer work are distinctly different. In metallurgy, what is observed is the decay of the Fourier components of the radial distribution function with time. In previous work on polymers, and here we refer specifically to the experiments of Bartels, Crist, and Graessley,[18,19] the scattering arises from an assembly of single polymer molecules, the scattering increasing as a function of time. The collective scattering term, which decreases with time and has been used in the metallurgical experiments, was not seen because the wavelength of concentration fluctuations was too large in their sample. It is crucial to the method of Bartels et al. that the geometry of the initial arrangement of molecules be precisely known, which in their experiments was alternating layers of deuteriated and protonated polymer. In dealing with the collective scattering of the sample, the initial scattering must be known, and this is sufficient to characterize the geometric arrangement of the components in the determination of diffusion by scattering. Our contribution to the problem is to combine the two methods in such a way that both the collective scattering of clusters of polymer molecules and the single-molecule contribution are observed, and to separate the two terms of the scattering by a straightforward experimental procedure. The initial clusters must be sufficiently small so that they are clearly observable in a small-angle neutron scattering measurement. In some cases, this requires that some of the clusters be of a size comparable to that of a single macromolecule. As in the metallurgical problem, the geometry of the initial cluster is given by the *initial* scattering. Accordingly, the experimentalist does not have to prepare samples in which the initial geometric distribution of the interdiffusing species is precisely controlled.

Since the initial clusters of polymer molecules should be not much bigger than the dimension of a single molecule, the method is particularly useful when diffusion constants are of the order of 10^{-16} cm^2/s. This represents a difficult regime to attain by other methods.

Diffusion and Correlation Functions

For simple diffusion, the concentration of diffusing material, $c(\mathbf{r},t)$, obeys the diffusion equation

$$\partial c/\partial t = D\nabla^2 c \tag{1}$$

If the mean concentration of diffusing material is ϕ, $c(\mathbf{r},\infty) = \phi$. Both $c(\mathbf{r},t)$ and ϕ are expressed as volume fractions. If $c(\mathbf{q},t)$ is the Fourier transform of $c(\mathbf{r},t)$ defined by

$$\tilde{c}(\mathbf{q},t) = \int (c(\mathbf{r},t) - \phi) \exp(i\mathbf{q}\cdot\mathbf{r})\, \mathrm{d}\mathbf{r} \tag{2}$$

it is easy to show that

$$\tilde{c}(\mathbf{q},t) = \tilde{c}(\mathbf{q},0) \exp(-Dq^2t) \tag{3}$$

One can define a spatial correlation, $\alpha(\mathbf{r},t)$, by

$$\alpha(\mathbf{r},t) = (\langle c(\mathbf{R},t)c(\mathbf{R} + \mathbf{r},t)\rangle - \phi^2)/(\phi - \phi^2) \tag{4}$$

The angular brackets indicate an ensemble average, which in this case is equivalent to an average with respect to $\mathbf{R}$. Note that for $t = \infty$ the two species should be completely mixed, and $\alpha(\mathbf{r},\infty) = 0$. Also, if the two species are initially completely segregated, $\alpha(0,0) = 1$. The latter result implies that $\langle c^2(\mathbf{R},0)\rangle = \phi$.

Equation 1 describes the diffusion of the center of mass of a molecule. In a polymeric system, in which the dimensions of particles containing many polymer molecules are comparable to the span of a single polymer molecule, the concentration of molecular centers is not the same as the concentration of polymer segments. The correlation function $\alpha(r,t)$ is defined in terms of the centers of mass and is not appropriate for the overall segmental concentration.

The Fourier transform of $\alpha(\mathbf{r},t)$, designated as $\alpha(\mathbf{q},t)$, takes the form

$$\tilde{\alpha}(\mathbf{q},t) = \tilde{c}(\mathbf{q},t)\tilde{c}(-\mathbf{q},t)/(\phi - \phi^2) \tag{5}$$

If eq 3 is substituted into eq 5, the following is obtained:

$$\tilde{\alpha}(\mathbf{q},t) = \tilde{c}(\mathbf{q},0)\tilde{c}(-\mathbf{q},0) \exp(-2q^2Dt)/(\phi - \phi^2) \tag{6}$$

Equation 6 is useful in studying diffusion since the time dependence is contained only in the exponential term. This is the result referred to earlier that has been used for the study of alloy structure by X-ray scattering,[19] for which $\alpha(\mathbf{q},t)$ is directly proportional to the scattering intensity.

Small-angle neutron scattering from polymers is composed of two terms, one of which is similar to that derived in eq 6 and a second which originates from scattering from a single molecule. These equations are derived in the next section.

---

† Work supported by the National Science Foundation, Grant DMR 8217460.

0024-9297/87/2220-0401$01.50/0 © 1987 American Chemical Society

Polymer Diffusion and Small-Angle Neutron Scattering

The system under consideration contains deuteriated (D) polymer molecules and normal (H) polymer molecules of the same degree of polymerization, n, N_p molecules in a volume V. The volume fraction of D molecules is ϕ. The properties of the H and D species are assumed to be identical except for neutron scattering lengths. Define these to be a_D and a_H per monomer for the deuteriated and normal species, respectively. The coherent, elastic scattering is given by

$$I(\mathbf{q},t) = \langle \textstyle\sum_{i,j,M} a_{Mi}a_{Mj} \exp(i\mathbf{q}\cdot\mathbf{r}_{ij}) + \sum_{M\neq N,ij} a_{Mi}a_{Nj} \exp(i\mathbf{q}\cdot\mathbf{r}_{ij})\rangle \tag{7}$$

The sums are taken over all pairs of monomer units, i and j, which are, for convenience, separated into sums within a single molecule (M) and on different molecules (M and N). The wave vector, $\mathbf{q}$, equals $(2\pi/\lambda)(\mathbf{k} - \mathbf{k}_0)$, where $\mathbf{k}_0$ and $\mathbf{k}$ are unit vectors in the directions of the incident and scattered neutron beams, and λ is the neutron wavelength. The magnitude of $\mathbf{q}$, designated q, equals $(4\pi/\lambda) \sin(\theta/2)$, where θ is the scattering angle, a_{Mi} and a_{Nj} are scattering lengths, and $\mathbf{r}_{ij}$ is the vector connecting segment i with segment j. The first term of eq 7 contains the scattering from pairs of segments within a single polymer molecule. In that term $\mathbf{r}_{ij} = \mathbf{r}_i^0 - \mathbf{r}_j^0$, where $\mathbf{r}_i^0$ and $\mathbf{r}_j^0$ are vectors from the center of mass of the molecule to segments i and j. The intermolecular scattering is contained in the second term of eq 7. There $\mathbf{r}_{ij} = \mathbf{R}_{MN} + \mathbf{r}_i^0 - \mathbf{r}_j^0$, where $\mathbf{R}_{MN}$ is the vector distance between the centers of molecules M and N, segment i is on molecule M, and segment j is on molecule N.

In this system, the probability, P_D that a monomer is deuteriated is equal to ϕ. Correspondingly, $P_H = 1 - \phi$. The joint probability, P_{DD}, is the probability that both the i and j monomers are deuteriated. P_{HD} and P_{DH} are similarly defined. These quantities are related by the equations

$$P_{DD} + P_{DH} = P_D = \phi \tag{8a}$$

$$P_{HH} + P_{HD} = P_H = 1 - \phi \tag{8b}$$

$$P_{HD} = P_{DH} \tag{8c}$$

The mean value and mean squared value of the scattering length are

$$\langle a \rangle = P_D a_D + P_H a_H^2 \tag{9a}$$

$$\langle a^2 \rangle = P_D a_D^2 + P_H a_H^2 \tag{9b}$$

In general $\langle a_{Mi}a_{Nj}\rangle$ is given by

$$\langle a_{Mi}a_{Nj}\rangle = P_{DD}a_D^2 + 2P_{DH}a_Da_H + P_{HH}a_H^2 \tag{9c}$$

In the intramolecular case, $P_{DD} = P_D$, $P_{HH} = P_H$, and $P_{HD} = 0$. Therefore $\langle a_{Mi}a_{Mj}\rangle = \langle a^2\rangle$. In the intermolecular case, P_{DD} tends to ϕ^2 as $\mathbf{R}_{MN}$ becomes large. The excess probability over the average, $P_{DD} - \phi^2$, is proportional to the correlation function $\alpha(\mathbf{R}_{MN},t)$. Using the limiting condition that $\alpha(0,0) = 1$, one finds that

$$P_{DD} = \phi^2 + \phi(1 - \phi)\alpha(\mathbf{R}_{MN},t) \tag{10a}$$

By combining the results of the intra- and intermolecular probabilities in a single expression, one finds

$$P_{DD} = \phi\delta_{MN} + (1 - \delta_{\mathrm{MN}})(\phi^2 + \phi(1 - \phi)\alpha(\mathbf{R}_{MN},t)) \tag{10b}$$

Equations 8a–c and 10b yield the other joint probabilities P_{HH} and P_{HD}. Using these in eq 7, one finds

$$I(\mathbf{q},t) = \underset{\text{intramolecular}}{N_p\langle a^2\rangle \textstyle\sum_{ij}\langle \exp(i\mathbf{q}\cdot\mathbf{r}_{ij})\rangle} + \underset{\text{intermolecular}}{\textstyle\sum_{M\neq N,ij}\langle((\langle a\rangle^2 + (a_H - a_D)^2\phi(1-\phi)\alpha(\mathbf{R}_{MN},t)) \exp(i\mathbf{q}\cdot\mathbf{r}_{ij})\rangle} \tag{11}$$

If the term

$$N_p\textstyle\sum_{ij}\langle((\langle a\rangle^2 + (a_D - a_H)^2\alpha(0,t)) \exp(i\mathbf{q}\cdot\mathbf{r}_{ij})\rangle$$

is added and subtracted on the right-hand side of eq 11, a more convenient form for $I(\mathbf{q},t)$ is obtained

$$I(\mathbf{q},t) = I_1(\mathbf{q},t) + I_2(\mathbf{q},t) \tag{12a}$$

where

$$I_1(\mathbf{q},t) = N_pn^2(a_H - a_D)^2\phi(1 - \phi)(1 - \alpha(0,t))S_s(\mathbf{q}) \tag{12b}$$

$S_s(\mathbf{q})$ is the scattering function for a single molecule.

$$S_s(\mathbf{q}) = \underset{\text{intramolecular}}{(1/n^2)\textstyle\sum_{ij}\langle \exp(i\mathbf{q}\cdot\mathbf{r}_{ij})\rangle} \tag{12c}$$

The molecular conformation of single molecules is assumed not to change with time. This is implicit in the omission of the time dependence in $S_s(\mathbf{q})$. The second term in eq 12a is

$$I_2(\mathbf{q},t) = \langle \textstyle\sum_{M,N,ij}(a_H - a_D)^2\phi(1 - \phi)\alpha(\mathbf{R}_{MN},t) \exp(i\mathbf{q}\cdot\mathbf{r}_{ij})\rangle \tag{12d}$$

where the contribution from density fluctuations has been taken equal to zero.

The factor $(1/n)\sum_i\exp(i\mathbf{q}\cdot\mathbf{r}_i^0)$ is taken to be insensitive to the relative positions of neighboring molecules. Making the assumption that it is, in fact, independent of the positions of centers of mass and defining its ensemble average by

$$A(\mathbf{q}) = (1/n)\langle \textstyle\sum_i\exp(i\mathbf{q}\cdot\mathbf{r}_i^0)\rangle \tag{13}$$

reduce $I_2(\mathbf{q},t)$ to

$$I_2(\mathbf{q},t) = (a_H - a_D)^2\phi(1 - \phi)n^2A^2(\mathbf{q})\langle \textstyle\sum_{M,N}\alpha(\mathbf{R}_{MN},t) \exp(i\mathbf{q}\cdot\mathbf{R}_{MN})\rangle \tag{14}$$

In eq 14, the sums are taken over all pairs of the molecular centers, and the intramolecular modulation is contained in $A(\mathbf{q})$. If these sums are replaced by integrals, $I_2(\mathbf{q},t)$ is given by

$$I_2(\mathbf{q},t) = n^2\rho^2A^2(\mathbf{q})(a_H - a_D)^2\left|\int (c(\mathbf{r},t) - \phi) \exp(i\mathbf{q}\cdot\mathbf{r})\, \mathrm{d}\mathbf{r}\right|^2 \tag{15a}$$

where ρ is the number of polymer molecules per unit volume.

Equations 2 and 3 taken together with eq 15a yield

$$I_2(\mathbf{q},t) = n^2\rho^2A^2(\mathbf{q})(a_H - a_D)^2|\tilde{c}(\mathbf{q},0)|^2 \exp(-2q^2Dt) \tag{15b}$$

Note that the time dependence of $I_1(\mathbf{q},t)$ is proportional to $1 - \alpha(0,t)$, $\alpha(0,0) = 1$, and therefore $I_1(\mathbf{q},0) = 0$. Also, the entire time dependence of I_2 is contained in the factor $\exp(-2q^2Dt)$. It follows that $I(\mathbf{q},0) = I_2(\mathbf{q},0)$ and $I(\mathbf{q},\infty) = I_1(\mathbf{q},\infty)$. Accordingly

$$I(\mathbf{q},t) = I(\mathbf{q},\infty)(1 - \alpha(0,t)) + I(\mathbf{q},0) \exp(-2q^2Dt) \tag{16}$$

$I(\mathbf{q},0)$ is the scattering from an original segregated sample, $I(\mathbf{q},\infty)$ is obtained from a sample that is completely interdiffused, and $I(\mathbf{q},t)$ is measured at any intermediate time. Since for any particular time, there are data points for many values of q, D and $\alpha(0,t)$ can be obtained by a least-squares fit. The function $\alpha(0,t)$ depends on the shape, size, and distribution of initial clusters as well as on the diffusion constant. A knowledge of $\alpha(0,t)$ makes it possible to extract further useful information from $I_1(\mathbf{q},t)$. An example of how this might be achieved is suggested in the following section.

Some Properties of $\alpha(0,t)$

Equation 4, specialized to the case where $r = 0$, becomes

$$\alpha(0,t) = \int (c(\mathbf{R},t) - \phi)^2 \,\mathrm{d}\mathbf{R}/(\phi(1-\phi)V) \qquad (17)$$

After some manipulation this may be written as

$$\alpha(0,t) = (8\pi Dt)^{-3/2} \int \alpha(\mathbf{R},0) \exp(-R^2/8Dt) \,\mathrm{d}\mathbf{R} \qquad (18)$$

provided that diffusion is simple and eq 1 applies.

A knowledge of the initial configurations of the segregated clusters permits the determination of $\alpha(\mathbf{R},0)$ and therefore of $\alpha(0,t)$ for particular values of D, yielding another determination of the diffusion constant. For example, if the clusters are randomly arranged in the manner described by Porod[21] and Debye,[22] then $\alpha(\mathbf{R},0) = \exp(-R/b)$, where b is a constant characterizing the size and interpenetration of the deuterium-rich and deuterium-poor phases. In this case $\alpha(0,t)$ takes the form

$$\alpha(0,t) = (2p^2 + 1) \exp(p) \operatorname{erfc}(p) - 2p/\pi^{1/2} \qquad (19)$$

where erfc (p) is

$$\operatorname{erfc}(p) = 1 - (2/\pi)^{1/2} \int_0^p \exp(-x^2) \,\mathrm{d}x$$

and $p = (2Dt)^{1/2}/b$.

The combination of eq 4 and 15a results in an expression for I_2 that is convenient for comparison with eq 19

$$I_2(\mathbf{q},t) = n^2\rho N_p(a_\mathrm{H} - a_\mathrm{D})^2 A^2(\mathbf{q})\phi(1-\phi) \int \mathrm{d}\mathbf{r}\, \alpha(\mathbf{r},t) \exp(i\mathbf{q}\cdot\mathbf{r}) \qquad (20)$$

To the extent that the approximations in this picture are valid, $A^2(\mathbf{q})$ may be replaced by $S_\mathrm{s}(\mathbf{q})$ (obtainable from $I(\mathbf{q},\infty)$). Then $I_2(\mathbf{q},0)$ reduces to

$$I_2(\mathbf{q},0) = I(\mathbf{q},0) = n^2\rho N_p(a_\mathrm{H} - a_\mathrm{D})^2\phi(1-\phi)(8\pi b^3 S_\mathrm{s}(\mathbf{q}))/(1 + (qb)^2)^2 \qquad (21)$$

which provides a second method to determine experimentally the values of b for this model of the segregated species.

Discussion

The particular virtue of the small-angle neutron scattering method of measuring diffusion constants is that it is capable of measuring smaller diffusion constants than are easily accessible by other techniques.[11,15,16] The decay of the initial scattering, which appears as the second term in (16), is largest for the smallest sizes of segregated regions. These volumes are observable in the experimentally available q range, and the cluster sizes should be of the order of 100–300 Å. Very large clusters, $\sim 10^4$ Å, make negligible contributions to the experiment. Thus the scattering at small times is dominated by contributions from the desegregation of small regions. This is a relatively rapid process and is especially useful in measuring very small diffusion constants. Some preliminary experiments by Jou and Anderson[23] on polystyrene tend to confirm our expectation of the power of this method.

The simplicity of the result given in the second term of eq 16 is surprising since it is obvious that large clusters will disappear upon diffusion more slowly than small. What must be kept in mind is that the Fourier components of scattering of a large particle and of a small particle at a particular $\mathbf{q}$ value decay at the same rate. Since most of the contribution to scattering of the larger particle occurs at lower $\mathbf{q}$, the overall decay of the scattering of the larger particle is slower.

The equations of Bartels et al.[18,19] differ from ours owing to different initial geometries. In their studies, the samples are composed of plane layers. These layers are relatively thick, and the scattering from these layers, $I_2(\mathbf{q},t)$, appears at values of q that are below the experimentally available range. They extract the diffusion constant from $\alpha(0,t)$ which, as we have said, requires a detailed and accurate knowledge of the original geometry of the H and D layers. By contrast, it is easy to prepare samples in which the segregated clusters are three-dimensional and small enough that the initial scattering is easily measurable. Then, as was discussed earlier, the diffusion constant can be extracted without knowledge of the initial configuration of the segregated clusters.

The results derived here are dependent on the crucial assumption that Fick's law, i.e., eq 1, applies. This is quite restrictive since the free energy of mixing of H and D polymer is not always ideal.[24,25] The equations are derived for polymers of the same degree of polymerization; deviations from that requirement will have some effect. Diffusion can be stress dependent, and internal stresses do exist in glassy polymers. We cannot always be sure that these stresses are completely relaxed in systems where diffusion is very slow. In deriving eq 15a, monomer distribution about the center of mass is taken to be independent of the relative position of different molecular centers. This is probably correct in bulk polymer, but in a system containing solvent, it probably is not. If these several constraints are not satisfied, an apparent diffusion constant is still obtained. Its relation to the true diffusion constant requires a deeper analysis.

These general ideas have had application to the early stages of phase separation of polymer mixtures. A particularly elegant example has been presented by Izumitani and Hashimoto,[26] who dealt with mixtures of polybutadiene and styrene–butadiene random copolymers. The particle sizes they observed were large, and appropriately their measurement was carried out by the scattering of light. From the point of view of scattering theory, their results and ours are the same. One difference is that the free energy of mixing is ideal (or almost so) for a solution of H and D polymer; it is highly nonideal when phase separation takes place.

Registry No. Neutron, 12586-31-1.

References and Notes

(1) Bueche, F.; Cashin, W.; Debye, P *J. Chem Phys.* **1952**, *20*, 1978.
(2) Bueche, F. *J. Chem. Phys.* **1968**, *48*, 1410.
(3) Kumagai, Y.; Watanabe, H.; Miyasake, K.; Hata, J. *J. Chem. Eng. Jpn.* **1979**, *12*, 1.
(4) Klein, J.; Briscoe, B. J. *Proc. R. Soc. London, A* **1979**, *A365*, 53.
(5) Klein, J.; Fletcher, D.; Fetters, L. J. *Nature (London)* **1983**, *304*, 526.
(6) Tanner, J E. *Macromolecules* **1971**, *4*, 748.
(7) Kimmich, R.; Bacchus, R. *Colloid Polym. Sci.* **1982**, *260*, 911.
(8) Bacchus, R.; Kimmich, R. *Polymer* **1983**, *24*, 964.
(9) Fleischer, G. *Polym. Bull. (Berlin)* **1983**, *9*, 152.
(10) Fleischer, G. *Polym. Bull. (Berlin)* **1984**, *11*, 75.
(11) Smith B. A. *Macromolecules* **1982**, *15*, 469.
(12) Smith, B. A.; Samulski, E. T.; Yu, L. P.; Winnik, M. A. *Phys. Rev. Lett.* **1984**, *52*, 45.
(13) Antonietti, M.; Coutandin J.; Gritter, R.; Sillescu, H. *Macromolecules* **1984**, *17*, 798.
(14) Antonietti, M.; Coutandin, J.; Sillescu, H. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 525.
(15) Kramer, E. J.; Green, P.; Palmstron, C. *Polymer* **1984**, *25*, 473.

(16) Green, P. F.; Mills, P. J.; Palmstron, C. J.; Mayer, J. W.; Kramer, E. J. *Phys. Rev. Lett.* **1984**, *53*, 2145.
(17) Stamm, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1983**, *24*(2), 380.
(18) Bartels, C. R.; Graessley, W. W.; Crist, B *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 495.
(19) Bartels, C. R.; Crist, B. J.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2702.
(20) Cook, H. E.; Hilliard, J. E. *J. Appl. Phys.* **1969**, *40*, 2191.
(21) Porod, G. *Kolloid-Z.* **1951**, *124*, 83; **1952**, *125*, 51, 109.
(22) Debye, P.; Bueche, A. M. *J. Appl. Phys.* **1949**, *20*, 518.
(23) Anderson, J. E.; Jou, J., submitted to *Macromolecules*.
(24) Bates, F S.; Wignall, G. D.; Koehler, W. C. *Phys. Rev Lett.* **1985**, *55*, 2425.
(25) Bates, F. S.; Wignall, G. D. *Macromolecules* **1986**, *19*, 932.
(26) Izumitani, T.; Hashimoto, T. *J. Chem. Phys.* **1985**, *83*, 3694.

X-ray Photoelectron Spectroscopy Study of an Ion Sputtering Process of Fluoro Polymers Using Monte Carlo Simulation

T. Takahagi and A. Ishitani*

Toray Research Center, Inc., 1-1, 1-Chome, Sonoyama, Otsu, Shiga 520, Japan.
Received May 21, 1986

ABSTRACT: The sputtering of Ar ion bombarded poly(tetrafluoroethylene) (PTFE) and poly(vinylidene fluoride) (PVDF) was studied by X-ray photoelectron spectroscopy (XPS). Monte Carlo simulation of the Ar ion sputtering process of both polymers is performed to understand the variation of XPS spectra during sputtering. In both polymer systems, fluorine atoms are preferentially sputtered away from the polymer chains, leaving carbon atoms behind. The damaged layer produced by the process has a homogeneous composition within the sampling depth of XPS. Observed XPS spectra of both polymers are explained by random elimination of fluorine atoms from a polymer chain, although better fitting is acquired by also taking a double fluorine atom elimination mechanism into account.

Introduction

Ion sputtering is frequently used in surface analysis. It is used to obtain signals in secondary ion mass spectroscopy (SIMS) and also for surface cleaning and depth profiling in X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and ultraviolet photoelectron spectroscopy (UPS). It is important to obtain new information for better understanding of the sputtering mechanism in SIMS, especially for organic polymers. It is also desirable to have detailed knowledge of the change of surface composition in depth profiling or in cleaning by sputtering, especially in quantitative analysis.

XPS is expected to be a useful tool for investigation of the change of surface composition induced by the ion sputtering process because of its good surface sensitivity and capability of providing chemical bonding information. The effects on inorganic materials induced by ion sputtering have already been studied in detail by XPS by many authors.[1-10] On the other hand, not many studies[5,11-13] have concerned ion sputtering on organic materials. An understanding of the mechanism of sputtering is particularly important for SIMS measurement of polymer materials;[13-17] however, it is far from satisfactory.

In this paper, we examine the change of chemical composition on the surface of poly(tetrafluoroethylene) (PTFE) and poly(vinylidene fluoride) (PVDF) by Ar ion bombardment with XPS because these fluoro polymers have already been extensively studied by XPS[18-22] and SIMS.[13,15,17] Thickness of a damaged layer on the sputtered polymer surface is estimated by the photoelectron takeoff angle variation measurement of XPS. Change of XPS spectra of the polymers by Ar ion bombardment is interpreted by a simple calculation based on Monte Carlo simulation.

Experimental Section

PTFE and PVDF used in this study are commercially available as 50-μm-thick sheets. These sheets were washed well with an ultrasonic cleaner in *n*-heptane to remove organic contamination from the surface before use.[23] A sample was attached to a holder by double-sided adhesive tape. The AEI-Kokusai Denki Model ES-200 was used for the XPS study with an Al K$\alpha_{1,2}$ X-ray source ($h\nu$ = 1486.6 eV) in a vacuum of 1×10^{-8} Torr.

XPS spectra were recorded at the takeoff angle of 90° in the ordinary measurement and at takeoff angles of 90°, 60°, 40°, 30°, and 20° in the angle-resolved measurement. The takeoff angle here is the angle of observation of photoelectrons relative to the sample surface. All XPS spectra were collected and stored with 1.0-eV steps using a Kratos Model DS-300 data system based on a PDP11/03 computer from Digital Equipment Corp. Sputtering was done by using an ion beam with a 500 nA/cm^2 density and a 1-keV energy at 2×10^{-4} Torr of Ar pressure in the preparation chamber of the ES-200.

Models of Sputtering Process for Monte Carlo Simulation

The simulation is executed on a cyclic polymer chain containing 2500 monomeric units, which is safely considered to be large enough for statistical calculation. It is assumed that only fluorine atoms are sputtered away, whereas all carbon atoms are left intact because of the great difference in their sputtering rates. Another model based on simultaneous elimination of both fluorine and carbon with different rates is also tried but showed little difference from the simpler one. Sputtering of hydrogen atoms in the PVDF system is also neglected since hydrogen cannot be detected in XPS measurement and its elimination brings about very little chemical shift on a carbon atom.[24]

Ar ion sputtering is simulated with the two models shown in Figure 1. In model A, elimination of only a single fluorine atom by one encounter with an activated particle is assumed; that is, any fluorine atom in a polymer chain is independently sputtered away in complete randomness. On the other hand, in model B, it is assumed that both single and double fluorine atom elimination concurrently occur, where the second process happens in a probability of *r*%. The double elimination here means that two fluorine atoms bonding to a carbon atom are broken off

© 1987 American Chemical Society