Macromolecules 1988, *21*, 2643–2644

Polymer Diffusion by Small-Angle Neutron Scattering. An Apparent Paradox

G. C. SUMMERFIELD and ROBERT ULLMAN*

Department of Nuclear Engineering, The University of Michigan, Ann Arbor, Michigan 48109.

Received October 30, 1987

Introduction

Recently, we proposed a procedure for measuring very small diffusion constants in a blend of a polymer and its deuteriated homologue, using small-angle neutron scattering[1]. The key result was

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

$I(\mathbf{q},t)$ is the elastic coherent scattering intensity at wave vector $\mathbf{q}$ and time t, D is the diffusion constant, and $\alpha(\mathbf{r},t)$ is a correlation function. The wave vector $\mathbf{q}$ equals $(2\pi/\lambda)$ $(\mathbf{k} - \mathbf{k}_0)$ where λ is the neutron wavelength, and $\mathbf{k}_0$ and $\mathbf{k}$ are unit vectors in the directions of the incident and scattered neutron beams. The magnitude of $\mathbf{q}$, designated as q, equals $(4\pi/\lambda)\sin(\theta/2)$ where θ is the scattering angle. If $c(\mathbf{r},t)$ is the concentration of molecular centers of the deuteriated (D) species at $\mathbf{r}$ and t, its average value is φ, and the average concentration of the protonated (H) species is $1 - \varphi$. Then, $\alpha(\mathbf{r},t)$ is defined by

$$\alpha(\mathbf{r},t) = \frac{\langle c(\mathbf{R}+\mathbf{r},t)c(\mathbf{R},t)\rangle - \varphi^2}{\varphi - \varphi^2}$$

The angle brackets signify an ensemble average. Equation 1 is based on the assumption that Fick's laws of diffusion are valid and that H and D components are initially well separated and randomly mixed at $t = \infty$. It follows that $\alpha(0,0) = 1$.

Cook, in a classic paper, developed scattering equations for spinodal decomposition of metal alloys.[2] His equations can be and have been applied to polymer diffusion[3] and when specialized to the case of an ideal solution take the form

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

Equations 1 and 2 differ in an important way. The second term, the decay of initial scattering, is the same in both, but the growth of the equilibrium scattering given by the coefficient of $I(\mathbf{q},\infty)$ is very different. In eq 1, this coefficient does not depend on q but does depend on the initial condition of the specimen through the pair correlation function, $\alpha(0,t)$. By contrast, the growth of the equilibrium scattering in eq 2 is a function of q and is independent of the initial condition of the system.

In trying to understand how and why two quite different results can be obtained for the same problem, it is necessary to focus on the assumptions used in the respective derivations.

In the derivation of eq 1, a distinction was drawn between intramolecular and intermolecular scattering. Monomer units i and j within a polymer molecule do not diffuse with respect to each other, but monomer units i and j on different molecules do. In the derivation of eq 2, no such distinction was made. The growth term (the coefficient of $I(\mathbf{q},\infty)$) appears as a consequence of a stochastic fluctuation in the diffusive flux. The equilibrium scattering intensity is identified with the time-independent component of scattering which arises from the fluctuations.

Generalization of Equation 1

A weakness of eq 1 is its restriction to a system in which both components are well separated at $t = 0$. A more general result is obtained by consideration of a broader class of initial conditions. Consider the equation

$$I(\mathbf{q},t) = I_1(\mathbf{q})(1 - \alpha(0,t)) + I_2(\mathbf{q})e^{-2q^2Dt} \tag{3}$$

This is identical with eq 1 except that $I_1(\mathbf{q})$ and $I_2(\mathbf{q})$ are not identified as final and initial scattering intensities. Let the initial pair correlation function be generalized to

$$\alpha(0,0) = \frac{\beta - \varphi}{1 - \varphi} \tag{4}$$

where $\varphi \leq \beta \leq 1$. If $\beta = 1$, the initial state is that of well-separated components as in eq 1. If $\beta = \varphi$, the initial system is randomly mixed, and the scattering does not change with time.

Suppose that the initial state is intermediate between these extremes. Then

$$I(\mathbf{q},0) = \left(\frac{1-\beta}{1-\varphi}\right)I_1(\mathbf{q}) + I_2(\mathbf{q}) \tag{5a}$$

$$I(\mathbf{q},\infty) = I_1(\mathbf{q}) \tag{5b}$$

Equations 3, 5a, and 5b yield

$$I(\mathbf{q},t) = I(\mathbf{q},\infty)\left(1 - \alpha(0,t) - \frac{1-\beta}{1-\varphi}e^{-2q^2Dt}\right) + I(\mathbf{q},0)e^{-2q^2Dt} \tag{6}$$

Equation 6 reduces to eq 1 for β equal unity. If, however, the system is near equilibrium, β differs only slightly from φ, and $\alpha(0,0)$ is only marginally greater than zero. In that limit, eq 6 approaches Cook's result.

Further Generalization

Equations 1, 3, and 6 were developed for a system in which diffusion is accurately described by Fick's laws in which case

$$\partial C/\partial t = D\nabla^2 C$$

In this way, specific predictions of the theory can be directly compared with experiment. In fact, theory is easily extended to include materials in which the dependence of diffusive flux upon concentration is not so simple.

The final term in eq 3 is defined explicitly in ref 1 as eq 15a:

$$I_2(\mathbf{q},t) = n^2\rho^2|A(\mathbf{q})|^2(a_\mathrm{H} - a_\mathrm{D})^2\left|\int (c(\mathbf{r},t) - \varphi)\exp[i\mathbf{q}\cdot\mathbf{r}]\,\mathrm{d}\mathbf{r}\right|^2 \tag{1-15a}$$

There are n monomer units in each polymer molecule, ρ is the number density of polymer molecule, a_H and a_D are scattering lengths of the unlabeled and labeled molecules, respectively, and $A(\mathbf{q})$ is a scattering function

$$A(\mathbf{q}) = (1/n)\sum e^{i\mathbf{q}\cdot\mathbf{r}} \tag{7}$$

where $\mathbf{r}$ is the vector from the center of mass to monomer i.

Defining $\tilde{\alpha}(\mathbf{q},t)$ as the Fourier transform of $\alpha(\mathbf{r},t)$ (ref 1, eq 5), one obtains in place of eq 3

$$I(\mathbf{q},t) = I_1(\mathbf{q})(1 - \alpha(0,t)) + n^2\rho^2V|A(\mathbf{q})|^2(a_\mathrm{H} - a_\mathrm{D})^2\varphi(1-\varphi)\tilde{\alpha}(\mathbf{q},t) \tag{8}$$

By setting $t = 0$ and combining that result with eq 8 for arbitrary t, one finds

$$I(\mathbf{q},t) = I(\mathbf{q},\infty)\left(1 - \alpha(0,t) - \frac{\tilde{\alpha}(\mathbf{q},t)}{\tilde{\alpha}(\mathbf{q},0)}(1 - \alpha(0,0))\right) + I(\mathbf{q},0)\frac{\tilde{\alpha}(\mathbf{q},t)}{\tilde{\alpha}(\mathbf{q},0)} \tag{9}$$

The time-dependent scattering, $I(\mathbf{q},t)$, appears, in general, as the linear superposition of the initial and final

0024-9297/88/2221-2643$01.50/0

scatterings. The coefficients are mutually dependent through the function $\alpha(\mathbf{r},t)$ and its Fourier transform. Note that eq 9 is a direct generalization of eq 6 to a system in which the dependence of diffusion on concentration is not specified.

Experimental Considerations

In many experiments, $I(\mathbf{q},0)$ is much greater than $I(\mathbf{q},\infty)$, and therefore the difference between eq 1 and 2 is not large. Under such circumstances, it becomes difficult to determine from an experiment whether eq 1 or eq 2 provides a better fit, and in many cases, reasonable diffusion constants can be obtained by setting $I(\mathbf{q},\infty) = 0$.

Ideal experiments for comparison with the equations are the investigations of Bartels et al.[4,5] of diffusion in hydrogenated polybutadiene (HPB). In these studies, thick (several micrometers) alternate layers of HPB and its deuteriated homologue (DPB) were prepared, and diffusion was brought about by heating for various lengths of time. In any measurable q range, $I(\mathbf{q},0)$ was equal to zero, and scattering intensities increased with time. The growth of scattering intensity was entirely independent of q and dependent on the initial thickness of layers of the polymer. See Figure 1 of ref 4 and Figure 5 of ref 5. Incidentally, the equations of Bartels et al. are identical with eq 1 if $I(\mathbf{q},0)$ is set equal to zero.

A recent investigation of polystyrene (PSH) and polydeuteriostyrene (PSD) by small-angle neutron scattering was carried out by Anderson and Jou.[6] In their experiment, $I(\mathbf{q},0)$ is much greater than $I(\mathbf{q},\infty)$ at low q. However, in the range of $\mathbf{q}$ where reasonable estimates were possible, the growth of the equilibrium scattering curve showed no dependence on q. This is consistent with Bartels et al.[4,5]

In an experimental arrangement similar to that used by Bartels et al., Stamm[7] has presented small-angle neutron scattering measurements of diffusion from alternating layers of PSH and PSD. His measurements show a growth of scattering intensity which is also independent of q.

Conclusions

1. The original equations of Summerfield and Ullman[1] for determination of diffusion constants by small-angle scattering have been generalized. The generalized result includes the original results and the Cook equation as limiting cases.

2. Measurements of diffusion of polymer in the melt by small-angle neutron scattering by different groups all yield scattering growth terms which are independent of q, consistent with the previous work of Summerfield and Ullman.[1]

Acknowledgment. Professor A. Z. Akcasu called the authors' attention to the contradiction between the Cook–Binder and Summerfield–Ullman equations. His comments and criticisms provided valuable guidelines for this work. Support of the National Science Foundation under Grant DMR8217460 is gratefully acknowledged.

Registry No. PSH, 9003-53-6; neutron, 12586-31-1.

References and Notes

(1) Summerfield, G. C.; Ullman, R. *Macromolecules* **1987**, *20*, 401.
(2) Cook, H. *Acta Metall.* **1970**, *18*, 297.
(3) Binder, K. *J. Chem. Phys.* **1983**, *79*, 6387.
(4) Bartels, C. R.; Crist, B.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2707.
(5) Bartels, C. R.; Crist, B.; Graessley, W. W. *Macromolecules* **1986**, *19*, 785.
(6) Anderson, J. E.; Jou, J. H. *Macromolecules* **1987**, *20*, 1544.
(7) Stamm, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1987, *28*, 2, 56.

Communications to the Editor

A Novel Route to Polypyrazoles

Introduction. Polymers composed of heterocyclic repeat units in the backbone have proven to be among the most thermally stable materials produced to date.[1] A particularly interesting subclass of heterocyclic polymers are polypyrazoles. Among the routes available to these materials, a commonly used approach is cycloaddition. The addition of bis-nitrilimines[2a], bis-sydnones[2b] and bis-azides[2c] to diacetylenes have all successfully produced polypyrazoles. Recently, Bass[3] and coworkers have used the addition of bis-hydrazines to acetylenic ketones and esters to prepare thermally stable polypyrazoles.

We have been studying the polymerization of relatively easily prepared bis-chlorovinylidene cyanides with diamines to give exceptionally stable polyenaminonitriles.[4] We were interested to see if we could prepare the analogous enhydrazinonitriles and subsequently cyclize them to pyrazoles (Scheme I).

Experimental Section. All solvents were purified and dried by standard laboratory procedures.

Instrumentation. Infrared (IR) and Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer Model 298 spectrophotometer and a Perkin-Elmer Model 1800 Fourier transform infrared spectrometer, respectively. NMR spectra were recorded on a Varian Model XL-200 spectrometer operating at 200 MHz for ^1H and 50.3 MHz for ^{13}C spectra. Some ^{13}C NMR were also obtained on an IBM Model WP/SY 100 spectrometer operating at 25.1 MHz. Chemical shifts are recorded in parts per million from hexamethyldisiloxane, used as an internal standard, when DMSO-d_6 was the solvent. Viscosities of polymer solutions were measured by using Cannon-Ubbelohde viscometers. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with a Perkin-Elmer System 7 instrument interfaced with a Perkin-Elmer Model 7500 computer. Heating rates were 10 or 20 °C/min for DSC and 10 °C/min for TGA. Elemental analyses were performed by Galbraith Laboratories, Inc., P.O. Box 51610 Knoxville, TN 37950-1610, and Robertson Laboratory, Inc., 29 Samson Ave., P.O. Box 761, Madison, NJ 07940. The presence of thermally stable structural moieties in the compounds under discussion leads to carbonaceous residues causing low carbon values to be obtained in some instances.

Monomer Syntheses. 1,4-Bis(1-chloro-2,2-dicyanovinyl)benzene and 1,3-bis(1-chloro-2,2-dicyanovinyl)benzene,[4] 4-hydrazinophenyl ether dihydrochloride,[3] and (4-hydrazinophenyl)sulfone[5] were prepared by previously reported procedures.

Model Compound Syntheses. 3,3′-(1,4-Phenylene)bis[1-(4-(phenylsulfonyl)phenyl)-4-cyano-5-amino-