Concentration Dependence of the Diffusion of Poly(propylene oxide) in the Melt

Barton A. Smith* and Stephen J. Mumby

IBM Research Laboratory, San Jose, California 95193

Edward T. Samulski and Li-Ping Yu

Chemistry Department, University of Connecticut, Storrs, Connecticut 06268.
Received March 26, 1985

ABSTRACT: Fluorescence redistribution after pattern photobleaching has been used to measure the translational diffusion coefficient of labeled poly(propylene oxide) (PPO) chains in molten PPO at 25 °C. Labeled PPO was synthesized with exactly one fluorophore per molecule, starting from the dye 4-diethanolamino-7-nitrobenzofurazan. A narrow molecular weight distribution fraction with M_n = 33 600 (M_w/M_n = 1.1) was prepared by gel permeation chromatography. The labeled PPO was dissolved in mixtures of high (M_w = 32 000) and low (M_w = 1000) molecular weight PPO. Diffusion coefficients were from 4.8×10^{-9} cm^2 s^{-1} in 100% M_w = 1000 to 1.1×10^{-10} cm^2 s^{-1} in 100% M_w = 32 000. The dependence of the diffusion coefficient upon concentration of the higher molecular weight PPO is discussed in terms of scaling plus reptation theories. It is concluded that the reptation model does not provide an accurate prediction of the concentration dependence of the diffusion coefficient for this system.

Introduction

Theories based on the reptation model have been used extensively in recent years to predict the scaling behavior of the diffusion of polymer molecules.[1] In particular, scaling plus reptation theories have been used to predict the concentration dependence of diffusion of polymer chains in solution with concentration $c > c_e$, where c_e is the concentration for onset of entanglement.[2-4] These theories predict that the diffusion coefficient is proportional to $c^{-7/4}$, in agreement with data from forced Rayleigh scattering (FRS) experiments.[2,3] Agreement between the scaling behavior of the diffusion coefficients measured by the FRS technique and those predicted by the reptation model appears to be good even for the diffusion of a polystyrene sample having a molecular weight (M_w = 78 300) as little as twice that for entanglement ($M_c \simeq$ 31 000–36 200).[5,6] A conclusion drawn from these results[2,3] was that reptation is the essential process in the diffusion of polymer chains in an entangled semidilute solution and that constraint release does not make a significant contribution. Measurement of diffusion coefficients of polystyrene in solution in good solvents has since been made by several other workers,[7-11] using a variety of experimental techniques, which suggest that the power law $c^{-1.75}$ is obeyed only in a rather limited concentration range just exceeding the critical concentration for entanglement.[12] This concentration dependence is not expected to persist to very high concentrations, as excluded volume effects are reduced. However, at very high concentrations, the slope of the available data[11] exceeds even the slope predicted for unperturbed chain dimensions. This may be due to a substantial concentration dependence of the monomeric friction coefficient.[6] Nemoto et al.[13] have measured diffusion coefficients for a tracer dye in a polymer solution in order to evaluate that dependence.

Measurement of diffusion coefficients in the melt or in Θ solvents are not complicated by a concentration crossover between good- and poor-solvent behavior. Wesson et al.[11] employed the FRS technique to study polystyrene in cyclohexane at 34.5 °C, but the concentration range investigated by these workers was limited. Dynamic light scattering (DLS) measurements have been used by Amis et al.[14] in an attempt to measure the diffusion coefficient of polystyrene ($M_w = 1.79 \times 10^5$ to 1.05×10^6) in cyclohexane at 35 °C. The DLS measurements were made over a larger concentration range (~0.03–0.3 g cm^{-3}) than those made with the FRS technique,[11] and the values of diffusion coefficient appear to scale with concentration as predicted by reptation theory. However, DLS measures the mutual diffusion coefficient of the solution, rather than the tracer diffusion coefficient which is predicted by the theory.

We have investigated the dependence of the diffusion coefficient upon concentration in the melt as a test of the reptation model. For these measurements, poly(propylene oxide) having a molecular weight (M = 33 000) approximately 5 times the critical molecular weight for entanglement ($M_c \simeq$ 6000–7000)[15,16] was diluted to various concentrations with PPO of much lower molecular weight (M_w = 1000).

Diffusion Measurements

Diffusion measurements were made by fluorescence redistribution after pattern photobleaching (FRAPP). Details of this technique may be found elsewhere.[16-20] Polymer molecules, labeled with fluorescent dye which can be irreversibly photochemically bleached, are initially mixed in a low (~0.1%) uniform concentration throughout the sample. In the present study, a sinusoidal variation in the concentration of this fluorescent dye was produced by bleaching a small circular spot (diameter ~0.5 mm) of the sample using two intersecting high-intensity coherent light beams. The light source was an argon ion laser producing 0.5 W at 488 nm. Total power incident on the sample for photobleaching was 0.2 W. The power of the two beams was then greatly attenuated and used to monitor the diffusion of unbleached fluorescent-labeled polymer into the bleached areas. The pitch of the periodic pattern was varied within the range 6–16 μm by changing the angle of intersection of the beams. Measured diffusion coefficients were independent of the pitch over this range. The fluorescence intensity was observed as a function of time after photobleaching. Diffusion coefficients were deduced from a least-squares fit of a single-exponential function to the fluorescence recovery data. All measurements were made at 25 °C.

Materials

Fluorescent-dye-labeled PPO was synthesized with exactly one fluorophore in the polymer backbone. This was achieved by initiating the polymerization of propylene oxide with the dye 4-diethanolamino-7-nitrobenzofurazan with zinc hexacyanocobaltate as catalyst in tetrahydrofuran.[16,21] A fraction of this dye-labeled polymer having molecular weight M_n = 33 600 and a narrow molecular weight distribution (M_w/M_n = 1.1) was selected by gel permeation chromatography. Of the two unlabeled PPO samples used in the current investigations, the low molecular weight (M_w = 1000, M_w/M_n = 1.1) polymer was purchased from Polysciences. The higher molecular weight polymer (M_w = 32 000, M_w/M_n = 1.6) had approximately the same molecular weight as the labeled material. Samples were prepared for diffusion measurements by mixing the three PPO components in di-

0024-9297/86/2219-0470$01.50/0

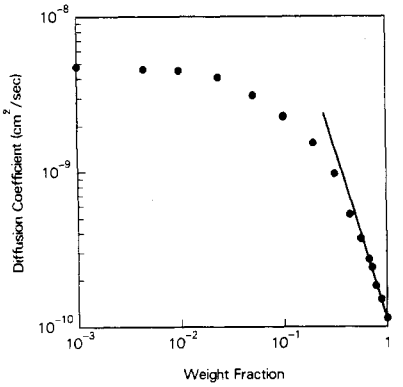

Figure 1. Diffusion coefficient ($cm^2\ s^{-1}$) as a function of the total weight fraction of the high molecular weight (M_w = 32000) PPO in the lower molecular weight (M_w = 1000) polymer solvent.

chloromethane solution and then removing the dichloromethane under vacuum at 50 °C. The fluorescent-dye-labeled PPO was always present in the sample at a concentration that produced an absorbance of 0.5 cm^{-1} at 488 nm.

Results

Diffusion coefficients of the fluorescent-dye-labeled PPO are plotted in Figure 1 as a function of the total weight fraction of the high molecular weight PPO in the solution. The diffusion coefficients span almost 2 orders of magnitude. The extremities of this range are $D = 1.1 \times 10^{-10}$ $cm^2\ s^{-1}$ for the self-diffusion of labeled PPO in unlabeled PPO of the same molecular weight and $D = 4.8 \times 10^{-9}$ $cm^2\ s^{-1}$, corresponding to the diffusion of labeled PPO in the low molecular weight solvent. The straight line in Figure 1 is the best fit by least squares to the five points corresponding to concentrations of the high molecular weight polymer exceeding 65% by weight. (By drawing this line, we do not mean to imply that a strict scaling law applies to this range of concentrations.) The slope of this line is −2.2. Thus, the dependence of the diffusion coefficient on concentration at the limit of high concentration is given by $D \propto c^{-2.2}$.

The measured diffusion coefficients may be corrected for a change in free volume with molecular weight by means of the WLF equation.[6,22,23] We measured the glass transition temperatures of the two polymer samples by differential scanning calorimetry to be T_g = 185 K (M_w = 1000) and T_g = 190 K (M_w = 32000). This small difference in the glass transition temperatures, together with the fact that the measurements were made over 100 K above T_g, gives a negligible WLF free volume correction to the diffusion coefficients. The magnitude of this correction to the slope of the line in Figure 1 would be approximately 1%.

Discussion

Scaling plus reptation arguments have been used previously to predict the concentration dependence of the diffusion coefficient of a linear polymer molecule dissolved in a good solvent.[3,4] The regime of interest is that above the critical concentration for the polymer molecules to be entangled. According to these arguments

$$D \propto \frac{k_B T}{\eta_s \xi}\left(\frac{g}{N}\right)^2 \qquad (1)$$

where D is the diffusion coefficient, k_B is Boltzmann's constant, T is the temperature, η_s is the solvent viscosity, ξ is the screening length for both excluded volume and hydrodynamic interactions, g is the number of monomers per independent subunit, and N is the total number of monomers in the polymer chain. The number of monomers in each subunit, g, may be expressed as $g = c\xi^3$. It is assumed that ξ is independent of N and depends on only the monomer concentration. It is further assumed that ξ scales as the end-to-end distance of the independent subunit, and thus $g \propto \xi^{5/3}$ in a good solvent. It follows that, for a good solvent: $\xi \propto c^{-3/4}$, and $g \propto c^{-5/4}$. Therefore, from eq 1, $D \propto c^{-7/4}$.

Some of the assumptions in the above argument are of questionable validity for semidilute (where chains begin to overlap) or concentrated solutions.[11,12] In particular, it is known that polymer chains do not retain good-solvent dimensions in semidilute or higher concentrations, thus changing the relationship between g and ξ as concentration is increased.[24] In addition, eq 1 contains the assumption that only the solvent viscosity contributes to the viscous drag on the chain diffusion in its tube and that other polymer chains only affect D by introducing topological constraints. It seems likely that the friction coefficient experienced by the chain will depend upon the polymer concentration, at least in the high-concentration limit. Therefore, we do not expect diffusion in polymer solutions to scale according to this rather simple model[25] over a wide range of concentrations. Indeed, most experiments have yielded very different results.[12]

In the melt, the argument is not complicated by the change in chain dimensions as a function of concentration. For the case of a low molecular weight polymeric solvent, as employed in the present investigation, some swelling of the longer chains is to be expected.[26] However, this is a small effect which we believe is negligible in the limit of high concentration of the high molecular weight polymer. In addition for melts, the friction coefficient is not expected to change with concentration. Therefore, measurements of the diffusion coefficient as a function of concentration in the melt should be a good test of the basic assumption of the reptation model.

Predictions of the distance between entanglements (and thus D) as a function of concentration in the melt cover a considerable range.[27] The prediction $D \propto c^{-2}$ by Rubinstein and Helfand[28] is in agreement with our results. However, $D \propto c^{-1}$ is in closer agreement with viscoelastic response data.[29] We expect that constraint release may contribute significantly to the diffusion of these molecules.

Acknowledgment. We thank Dr. Robert J. Herold of the General Tire and Rubber Co. Research and Development Division for the catalyst and high molecular weight PPO samples, Dr. Leo Kadehjian for synthesis of the initiator dye, and Richard Siemens for the DSC measurements. We also thank Dr. G. Ronca and Dr. Patricia M. Cotts for helpful discussions.

Registry No. PPO (SRU), 25322-69-4.

References and Notes

(1) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(2) Hervet, H.; Léger, L.; Rondelez, R. *Phys. Rev. Lett.* **1979**, *42*, 1681.
(3) Léger, L.; Hervet, H.; Rondelez, F. *Macromolecules* **1981**, *14*, 1732.
(4) de Gennes, P.-G.; Léger, L. *Annu. Rev. Phys. Chem.* **1982**, *33*, 49.
(5) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 55.
(6) Ferry, J. D. "Viscoelastic Properties of Polymers", 2nd ed.; Wiley: New York, 1970; p 406.
(7) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1980**, *13*, 1085.
(8) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1981**, *14*, 1334.
(9) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1984**, *17*, 431.
(10) Wesson, J. A.; Takezoe, H.; Yu, H.; Chen, S. P. *J. Appl. Phys.* **1982**, *53*, 6513.
(11) Wesson, J. A.; Noh, I.; Kitano, T.; Yu, H. *Macromolecules* **1984**, *17*, 782.
(12) Tirrell, M. *Rubber Chem. Technol.* **1984**, *57*, 523.

(13) Nemoto, N.; Landry, M. R.; Noh, I.; Kitano, T.; Wesson, J. A.; Yu, H. *Macromolecules* **1985**, *18*, 308.
(14) Amis, E. J.; Han, C. C.; Matsushita, Y. *Polymer* **1984**, *25*, 650.
(15) Van Krevelen, D. W. "Properties of Polymers", 2nd ed.; Elsevier: Amsterdam, 1976; p 339.
(16) Smith, B. A.; Samulski, E. T.; Yu, L.-P.; Winnik, M. A., *Macromolecules*, in press.
(17) Smith, B. A.; Samulski, E. T.; Yu, L.-P.; Winnik, M. A. *Phys. Rev. Lett.* **1984**, *52*, 45.
(18) Smith, B. A. *Macromolecules* **1982**, *15*, 469.
(19) Smith, B. A.; McConnell, H. M. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 2759.
(20) Smith, L. M.; Smith, B. A.; McConnell, H. M. *Biochemistry* **1979**, *18*, 2256.
(21) Livigni, R. A.; Herold, R. J.; Eliner, O. C.; Aggarwal, S. L. In "Polyethers"; Vandenberg, E. J., Ed.; American Chemical Society, Washington, DC, 1975; Adv. Chem. Ser. No. 6, p 20.
(22) von Meerwall, E.; Grigsby, J.; Tomich, D.; van Antwerp, R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1037.
(23) Antonietti, M.; Coutandin, J.; Sillescu, H. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 525.
(24) Fixman, M.; Peterson, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 3524.
(25) de Gennes, P.-G. *Phys. Today* **June 1983**, *36*, 33.
(26) Flory, P. G. *J. Chem. Phys.* **1949**, *17*, 303.
(27) Evans, K. E.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1913.
(28) Rubinstein, M.; Helfand, E. *J. Chem. Phys.* **1985**, *82*, 2477.
(29) Graessley, W. W.; Edwards, S. F. *Polymer* **1981**, *22*, 1329.

A Long, Regular Polypeptide 3_{10}-Helix†

C. Toniolo* and G. M. Bonora

Biopolymer Research Center, C.N.R., Department of Organic Chemistry, University of Padova, 35131 Padova, Italy

A. Bavoso, E. Benedetti,* B. Di Blasio, V. Pavone, and C. Pedone

Department of Chemistry, University of Naples, 80134 Naples, Italy.
Received August 1, 1985

ABSTRACT: The infrared absorption and ^1H nuclear magnetic resonance analyses of chloroform solutions of the terminally blocked homooctapeptide from the $C_{\alpha,\alpha}$-dimethylated α-aminoisobutyric acid residue are consistent with the presence of a 3_{10}-helical structure of high thermal stability. The crystal structure of the octapeptide, obtained by X-ray diffraction, indicates the formation of a 3_{10}-helix, stabilized by six consecutive intramolecular N—H···O=C H bonds of the C_{10}-III (or III′) type. This represents the first observation at atomic resolution of a *regular* 3_{10}-helix larger than two complete turns. Packing of the octapeptide molecules gives rise to a channel in which the solvent (methanol and water) molecules are accommodated.

1. Introduction

The polypeptide 3_{10}-helix, first proposed by Donohue in the early 1950s[15] has a three-residue repeat and a H bond between the C=O group of residue i and the N–H group of residue $i + 3$ [type III (or III′) C_{10}-form or β-bend].[53,55,62] Its ϕ,φ torsion angles are approximately ±60°, ±30°, within the same energy minimum in the conformational map as the α-(3.6_{13}) helix.[13,47,63] However, the H-bonding schemes are significantly different in the two types of helices, being of the $i \leftarrow i + 4$ (C_{13}-form or α-bend[55]) in the α-helix. For a long periodic structure formed by C^{α}-*mono*alkylated α-amino acid residues with the same chirality at the α-carbon atom, the 3_{10}-helix is energetically considerably less favorable than the α-helix.[13,47,63] Therefore, it is not surprising that only short pieces of approximately 3_{10}-helix (particularly at the C terminus of an α-helix) have been found in protein crystal structure analyses[11,13,34,47,49] (for recent examples, see ref 14, 27, and 65).

More recently, by theoretical[1,4,10,33,38,40,42,60,61] as well as experimental[3,8,9,22,23,26,36,44,50,52,56,58,61] studies it has been shown that the ϕ,φ angles of the achiral Aib (α-aminoisobutyric acid) residue, the prototype of the $C^{\alpha,\alpha}$-*di*alkylated α-amino acids, are restricted to values near those associated with either right- or left-handed α- or 3_{10}-helices, unless it is part of a strained cyclic compound.[21] The X-ray diffraction structures of Aib homopeptides to the pentamer have provided examples of short (less than two complete turns) 3_{10}-helical conformations in the solid state.[3,44,52,56,61] Our recent solution conformational analysis of monodispersed, terminally blocked $(Aib)_n$ homooligopeptides to the dodecamer is strongly in favor of the formation of fully developed, stable 3_{10}-helices in chloroform, starting from the octamer.[58]

In this paper we present the results of a conformational investigation in $CDCl_3$ solution of the terminally blocked Aib homooctapeptide, *p*-BrBz-$(Aib)_8$-O-*t*-Bu (*p*-BrBz = *p*-bromobenzoyl, O-*t*-Bu = *tert*-butoxy) by using infrared (IR) absorption and ^1H nuclear magnetic resonance (NMR). We extended the study of the structural preferences of this octapeptide to the crystal state by means of X-ray diffraction. This investigation represents the first observation at atomic resolution of a long (more than two complete turns), *regular* 3_{10}-helix and allowed us to characterize this important peptide ordered secondary structure in detail.

2. Materials and Methods

(a) Peptide Synthesis. *p*-BrBz-Aib-OH. This compound was synthesized from *p*-BrBz-Cl and H-Aib-OH in an aqueous NaOH–acetone mixture: yield 95%; mp 226–227 °C (from ethyl acetate–petroleum ether); thin-layer chromatography (silica gel plates 60F-254, Merck Darmstadt) R_{f1} (9:1 $CHCl_3$–ethanol) 0.10, R_{f2} (3:1:1 1-butanol–acetic acid–water) 0.80. Anal. Calcd for $C_{11}H_{12}NO_3Br$: C, 46.2; H, 4.2; N, 4.9; Br, 27.9. Found: C, 46.2; H, 4.2; N, 4.9; Br, 28.0. The crystal structure has recently been solved by X-ray diffraction.[59]

Oxazolone from *p*-BrBz-Aib-OH. This compound was synthesized from *p*-BrBz-Aib-OH in acetic anhydride at 120 °C for 20 min:[58] yield 96%; mp 106–107 °C (from hot benzene); R_{f1} 0.95. Anal. Calcd for $C_{11}H_{10}NO_2Br$: C, 49.3; H, 3.8; N, 5.2; Br, 29.8. Found: C, 48.8; H, 3.9; N, 5.1; Br, 29.2. The crystal structure of this compound has recently been solved by X-ray diffraction.[59]

† This is part 143 in the series "Linear Oligopeptides". For part 142, see ref 57.

0024-9297/86/2219-0472$01.50/0