Macromolecules 1984, 17, 1284–1285

Notes

Center-of-Mass Diffusion of Reptating Polymer Molecules

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In connection with our current investigation of the diffusion of bulk polymer across an interface,[1,2] we have examined more carefully the predictions made by the Doi–Edwards model for the center-of-mass motion of a reptating polymer.[3] The system we are studying involves two samples of the same bulk polymer which are brought together and interdiffuse. In this system, the configuration of a polymer close to the interface when the samples are first brought together is not Gaussian since the component of the mean square end-to-end vector in the direction perpendicular to the interface will be compressed in order to maintain the constant-density requirement.[4] As interdiffusion progresses, the configuration of this molecule will gradually become Gaussian since each element of new tube created is oriented randomly. The coil becomes completely Gaussian when it has relaxed once.

We can follow the interdiffusion process using the mean square center-of-mass displacement of a molecule as calculated by Doi and Edwards:[3]

$$\langle \Delta R_G^2(t) \rangle = \frac{a^2}{N(\Delta t)} \int_0^t \mathrm{d}t' \left[\frac{\langle V(t')^2 \rangle}{\langle V(\infty)^2 \rangle} \right] = \frac{a^2}{N(\Delta t)} \int_0^t \mathrm{d}t'\, G_0(t') \quad (1)$$

Here, $V(t)$ is the end-to-end vector at time t, N is the degree of polymerization, a is the bond length, and Δt is the time between jumps of the chain in the discrete model. As in simple fluid diffusion, this analysis is valid only for times large compared to Δt. This is not especially restrictive since Δt is very small compared to the characteristic time describing the relaxation of a chain from its original tube. According to Doi and Edwards,[3] this relaxation time $\tau_r = (2/\pi)N^2(\Delta t)$.

When the polymer configurations are Gaussian at all times (molecules far from the interface), $G_0(t') = 1$ and $\langle \Delta R_G^2(t) \rangle$ is proportional to t at *all* times large compared to Δt, which is the same as the result from random walk theory. Specifically, $\langle \Delta R_G^2(t) \rangle = 6D_G t$, where D_G is the polymer center-of-mass diffusion coefficient and is equal to $a^2/6N(\Delta t)$. When the polymers do not start out in Gaussian configurations (polymers close to the interface), $G_0(t')$ is an increasing function of time during the first relaxation and the center-of-mass motion cannot be described by a simple random walk over times comparable to a relaxation time.

Since an examination of the Doi and Edwards results shows that $\langle \Delta R_G^2(t) \rangle$ for Gaussian polymers is exactly equivalent to that for Brownian particles for all times $t \gg \Delta t$, we originally intended to use random walk theory in our interdiffusion problem to describe the motion of polymers which always have Gaussian configurations. That is, we originally believed that the center-of-mass diffusion of these molecules exactly followed the results derived from the theory of Brownian motion. However, as shown below, this is not strictly true since the higher moments of the polymer center-of-mass displacement are not equivalent to those from random walk theory.

Following the same procedure by which $\langle \Delta R_G^2(t) \rangle$ was found, it is seen that to highest order in N the 2mth moment of the center-of-mass displacement is

$$\langle \Delta R_G^{2m}(n\Delta t) \rangle = \langle [\sum_{i=0}^{n-1} \xi(i\Delta t)\mathbf{V}(i\Delta t)]^{2m} \rangle / N^{2m} \quad (2)$$

where $\xi(t)$ is randomly 1 or −1. For $m = 2$, this can be simplified to

$$\langle \Delta R_G^4(t) \rangle = \frac{5a^4}{3N^2}\left(\frac{t}{\Delta t}\right) + \frac{4a^4}{N^2(\Delta t)^2} \int_0^t \mathrm{d}t' \int_0^{t-t'} \mathrm{d}t'' \left[\frac{\langle (\mathbf{V}(0)\cdot\mathbf{V}(t''))^2 \rangle}{\langle V^2 \rangle^2} \right] + \frac{2a^4}{N^2(\Delta t)^2} \int_0^t \mathrm{d}t' \int_0^{t-t'} \mathrm{d}t'' \left[\frac{\langle V(0)^2 V(t'')^2 \rangle}{\langle V^2 \rangle^2} \right] \quad (3)$$

$$= \frac{5a^4}{3N^2}\left(\frac{t}{\Delta t}\right) + \frac{2a^4}{N^2(\Delta t)^2} \int_0^t \mathrm{d}t' \int_0^{t-t'} \mathrm{d}t'' \, [2G_1(t'') + G_2(t'')] \quad (4)$$

$G_1(t)$ and $G_2(t)$ are measures of the correlation between the end-to-end vectors of a molecule at different times. It is easy to show that

$$G_1(0) = G_2(0) = 5/3, \qquad G_1(\infty) = 1/3, \qquad G_2(\infty) = 1 \quad (5)$$

so over the first relaxation time, G_1 and G_2 are decreasing functions of time. When t is much greater than a relaxation time, all moments of the polymer center-of-mass displacement converge to those from random walk theory. For instance, at long times, eq 4 reduces to

$$\langle \Delta R_G^4(t) \rangle = \frac{5}{3}\frac{a^4}{N^2}\left(\frac{t}{\Delta t}\right)^2 = 60(D_G t)^2 \quad (6)$$

which is the Brownian motion result.

We see then that, even for polymers which always maintain Gaussian characteristics, the center-of-mass motion does not follow the results from random walk theory over times comparable to a relaxation time due to correlations in the end-to-end vectors. Unlike the deviations of polymer center-of-mass motion from random walk theory in dilute solution,[5,6] the Doi–Edwards reptating molecule *always* has a second moment, $\langle \Delta R_G^2(t) \rangle$, proportional to time, and the deviation from Brownian motion does not appear until higher moments are examined. We feel that an interesting result in itself is that the non-Brownian character of this diffusion process does not show in the second moment while it does in the fourth and higher moments. In any case, only if a description of the diffusion of bulk polymers in the first few relaxation times is unimportant is it safe to use the simplification that the center-of-mass diffuses as a Brownian particle.

Acknowledgment. I thank Matthew Tirrell and Stephen Prager for discussions on this topic and the University of Minnesota Corrosion Research Center (Grant DE-AC02-79ER10450) for support of this work.

0024-9297/84/2217-1284$01.50/0

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Urethane-Substituted Poly(diacetylene): Electrical Conductivity of Poly[5,7-dodecadiyne-1,12-diol bis([(*n*-butoxycarbonyl)methyl]urethane)] in Amorphous and Single-Crystalline Forms

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Received June 1, 1983

This note is concerned with anisotropic electrical conductivities of a single-crystalline form poly(diacetylene). In our previous papers,[2,3] we reported the synthesis, characterization, and mechanical and electrical properties of poly[4,6-decadiyne-1,10-diol bis([(*n*-butoxycarbonyl)-methyl]urethane)], which has a highly conjugated poly(ene–yne) backbone with the substituent R = $-(CH_2)_3OCONHCH_2COO(CH_2)_3CH_3$. The polymer abbreviated as poly(3BCMU) is soluble in common organic solvents such as $CHCl_3$. $CHCl_3$-cast films of this polymer exhibited an enhancement of the electrical conductivity by doping with iodine from 10^{-12} to 10^{-5} Ω^{-1} cm^{-1}, although the films were poorly crystalline.[3] Another member of this class of poly(diacetylene)s, poly[5,7-decadiyne-1,12-diol bis([(*n*-butoxycarbonyl)methyl]urethane)], having the substituent R = $-(CH_2)_4OCONHCH_2COO(CH_2)_3CH_3$ [abbreviated as poly(4BCMU)] has an intriguing property. Namely, we can obtain, besides solvent-cast amorphous specimens of this poly(4BCMU), single crystals with fully extended chains by a solid-state polymerization of the monomer single crystals.[4] We prepared $CHCl_3$-cast and single-crystalline form specimens of this polymer and compared their electrical properties in the undoped and iodine-doped states.

Experimental Section

4BCMU monomer was prepared through the following four-step reactions: (i) Addition of 4-chloro-1-butanol to ethyl vinyl ether; (ii) reaction of the ether with sodium acetylide in liquid ammonia to obtain 5-hexyne-1-ol [bp 72 °C (10 torr)];[5] (iii) oxidative coupling of the monoalcohol by Hay's method[6] to obtain 5,7-dodecadiyne-1,10-diol; and finally (iv) reaction of the diol with *n*-butyl isocyanatoacetate to obtain 4BCMU (mp 72 °C).

Needlelike and plateletlike single crystals of 4BCMU monomer (typical sizes = 6 × 1 × 0.2 and 3 × 2 × 0.2 mm^3, respectively) were grown from acetone/hexane solution by slowly evaporating the solvent. Powder-form monomer crystallites were obtained by precipitating the monomer from acetone solution in *n*-hexane. These single-crystalline and powder-form specimens were allowed to polymerize by irradiating them with 48-Mrd ^{60}Co γ-rays in high-vacuum ampules (10^{-5} Torr) at room temperature. Unreacted monomer was extracted with acetone. The polymer conversion determined from the absorbance at 470 nm of the $CHCl_3$ solutions (ϵ_{max} = 17000 L/(mol·cm)) was 94.4% for single crystals and 74.1% for powder-form samples. This method has been shown to give accurate values for the polymer conversion of poly(4BCMU).[7] Poly(4BCMU) films were obtained by casting the powder-form polymer from $CHCl_3$ solution. Both the single-crystalline and powder-form poly(4BCMU)s showed metallic black-gold luster, while the color of the films was red with metallic brilliancy.

Table I
Characteristics of Poly(4BCMU) Samples in Various Forms

samples	$10^{-3}\cdot M_n{}^a$	$10^{-3}\cdot M_w{}^a$	$M_w/M_n{}^a$	ΔH_t, J g^{-1} 380 K	410 K
powder form	93	623	6.7	18.47	4.77
$CHCl_3$ cast	56	339	6.1	6.25	4.16
single crystal	152	984	6.5	21.39	6.66

[a] Molecular weights based on polystyrene standards.

All the samples were characterized with a gel permeation chromatograph (Model HLC-801A, Toyo Soda Mfg. Co.) by using $CHCl_3$ carrier and polystyrene elution standards. Table I lists the molecular weights M_w and M_n of these samples. The single-crystalline sample has the highest M_w, while the $CHCl_3$-cast specimen the lowest among the samples examined. Presumably, as pointed out by Wenz and Wegner,[8] UV-induced chain scission and/or degradation due to oxygen or impurities in $CHCl_3$ had taken place during the casting and film handling processes.

The samples were tested on a differential scanning calorimeter (DSC Model 8055, Rigaku-Denki Co.) with a heating rate of 10 K min^{-1} to estimate the degree of crystallinity. Color change accompanied by crystalline melting was observed by a micromelting point apparatus (Yanagimoto Seisakusho, Kyoto).

A preliminary X-ray diffraction study was carried out on single crystals by using a cylindrical camera with Cu Kα radiation.[9] The relation between the unit cell and habitus of the crystal was determined by two rotation photographs around the mutually perpendicular axes along the length and width of plateletlike crystals. The fiber (*c*) axis is parallel in the width direction and *b* axis (the side groups) in the thickness direction, and thus, the poly(4BCMU) chains are stacked along the length direction of the crystal.

Conductivity experiments were performed in two-electrode configuration. For $CHCl_3$-cast films, two platinum wires were connected to a specimen (usually 9 × 3 × 0.15 mm^3 size) with carbon black containing conductive paste (Dotite XC-12, Fujikura Kasei Co.). On the other hand, single-crystalline specimens were prepared as follows: Plateletlike crystals with good quality were selected by examining them with a polarizing microscope. Gold was evaporated onto each specimen to form electrodes so that we could measure the conductivities $\sigma_\parallel$ and $\sigma_\perp$ in the directions parallel to the *c* and *a* axes of the crystal, respectively. The area and distance between the electrodes were measured with a Peacock dial thickness gauge (0.01 mm) and Ocular micrometer attached to a polarizing microscope. Current was measured from a 1.5- or 130-V dry cell with a Keithley 640 electrometer. Doping of specimens with iodine was carried out by exposing specimens to iodine vapor at 10^{-3} Torr at room temperature. The amount of iodine absorbed in the specimen was determined either by weighing or by elemental analysis. The dopant concentration is expressed by *Y* as the number of moles of I_3^- ions per mol of the monomer unit, because dopant iodine is known to exist mostly in I_3^- form at low dopant concentration level from the measurement of Raman spectra.[3]

The current for the doped specimens under both applied voltages of 1.5 and 130 V was almost constant during more than 200 h as previously shown in the case of poly(3BCMU).[3] This means that the observed conductivity is mostly due to electronic rather than ionic conduction. However, for the undoped specimens, transient current was observed for a few minutes, which may be attributed to the orientation of polar side groups and/or ionic conduction due to a small amount of impurities. Therefore, the current at 5 min after applying the voltage was used for the calculation of conductivity.

Results and Discussion

In DSC tests, $CHCl_3$ cast films and single-crystalline samples usually exhibit two endothermic peaks at about 380 and 410 K, although the 380 K peak for the former is rather weak. The red color of the former slightly changes its tone at 380 K and, further, to yellow at 410 K, while

0024-9297/84/2217-1285$01.50/0