Temperature-Dependent Conformational Change and Intramolecular Energy Transfer of Polysilylenes

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Received May 2, 1991; Revised Manuscript Received September 12, 1991

ABSTRACT: Fluorescence and fluorescence excitation as well as absorption spectra of dilute organic solutions of poly(di-*n*-butylsilylene) and poly(di-*n*-hexylsilylene) have been measured at different temperatures, and the dependence of the relative fluorescence quantum yields on temperature was determined. Evidence is presented showing that the energy transfer is occurring intramolecularly from helical to rodlike conformational segments for these polysilylenes. Analysis of the temperature dependence of the relative fluorescence quantum yields reveals that the transfer yield increases sharply with decreasing temperature at the temperatures near the conformational transition temperature. It is inferred that the transfer yield and rate increase as the rod segment content in the chain increases.

Introduction

A detailed understanding of the electronic process of polysilylenes is the foundation on which an understanding at the molecular level of many important properties must rest. These include the charge-transfer mechanism in doped polysilylenes, photoconducting properties, and thermochromism as well as photodegradation.[1] Symmetrically substituted poly(dialkylsilylenes) such as poly(di-*n*-hexylsilylene) are known to exhibit distinct thermochromism in organic solvents, showing a marked spectral change in the absorption spectrum with decreasing temperature.[2-4] For example, the absorption maximum of poly(di-*n*-hexylsilylene) shifts abruptly from about 320 to 350 nm, when the temperature is lowered (−20 to −30 °C). In contrast to this, thermochromism of unsymmetrically substituted poly(dialkylsilylenes) such as poly(hexylmethylsilylene) is observed merely as a smooth spectral change.[2] There is general agreement that these phenomena are caused by the conformational change of the $-(SiR_2)_n-$ backbone from helixlike to rodlike (or planar zigzag) conformations.[4-8] Organic polymers such as polydiacetylene also are known to exhibit thermochromism based on the conformational change of the $-(CH{=}CHC{\equiv}C)_n-$ backbone.[9,10] However, these π-conjugated organic polymers emit only weakly or, in general, show no emission.[11] Moreover, for most of the organic polymers, the thermochromism is observed as a rather smooth spectral change. Thus, symmetrically substituted poly(dialkylsilylenes) are unique polymers in the sense that they not only exhibit a high quantum yield fluorescence associated with the σ–σ^* electronic transition of the σ electrons on the backbone atoms but do exhibit distinct thermochromism caused by the conformational change.

Although a large number of studies have been carried out on the fluorescence as well as thermochromism of polysilylenes in solutions, there seems to be almost no publication concerning the temperature dependence of the emission properties at temperatures near the conformation transition temperature. In order to understand the nature of the abrupt thermochromism of polysilylenes, it is of importance to investigate how the emission properties change with temperature. Quite recently, Isaka and Matsumoto[12] investigated the emission properties of a bulk polysilylene polymer and observed fluorescence from both the helical and rod conformations at temperatures in the neighborhood of the transition temperature (~40 °C). They interpreted the emission in terms of a heterojunction model. However, it seems to be still not clear whether or not the electronic energy is transferring intramolecularly, since the measurements were carried out for the solid polymer.

In the present work, we have investigated the emission properties of dilute solutions of typical symmetrically substituted poly(dialkylsilylenes), poly(di-*n*-hexylsilylene) (PDHS) and poly(di-*n*-butylsilylene) (PDBS), at different temperatures. Dual fluorescence from the electronic states corresponding to helical and rod conformations was observed at temperatures where the two conformational segments coexist. Evidence is presented showing that the energy-transfer process is occurring intramolecularly from helical to rod segments for these polymers. Analysis of the temperature dependence of the relative fluorescence intensities provides estimates for the relative rates that characterize the excited-state dynamical behavior of isolated polysilylenes. The energy transfer yield from helical to rod segments is found to increase markedly with decreasing temperature. This observation is interpreted in terms of the increase of the transfer rate which is related to the rod segment content in the polysilylene chain.

Experimental Section

Materials. Poly(di-*n*-hexylsilylene) (PDHS) and poly(di-*n*-butylsilylene) (PDBS) were synthesized from the corresponding dichloroalkylsilanes by means of a Wurtz-type condensation reaction in a toluene reflux. The polysilylenes thus obtained were reprecipitated by isopropyl alcohol. The molecular weights were determined relative to polystyrene calibration standards. The values for M_w are found to be 1.86×10^6 with $M_w/M_n = 28.4$ for PDHS and 1.20×10^5 with $M_w/M_n = 6.56$ for PDBS.

Measurements. Emission and excitation spectra were measured with a Spex Fluolog-2 (Model 211-340) fluorescence spectrophotometer. This photometer is equipped with a double-grating excitation monochromator, a high-pressure 450-W xenon lamp for excitation, and a photomultiplier tube (Hamamatsu R928-P) in a water-cooled housing operated in photon-counting mode to monitor the emission signals. The linear reciprocal dispersion of the excitation monochromator is 1.8 nm/mm and that of the emission monochromator is 2.5 nm/mm. Each emission or excitation spectrum can be corrected for the wavelength dependence of the detector response or the excitation light intensity. Absorption spectra were obtained with a Hitachi U-3210 spectrophotometer. In the spectral measurements, the sample solution in a quartz tube with a diameter of 3.0 mm was put into a quartz Dewar vessel which was cooled by suitable coolants. The optical density of the samples, measured with a 10-mm-path-length cell, was always kept below 0.1. In order to

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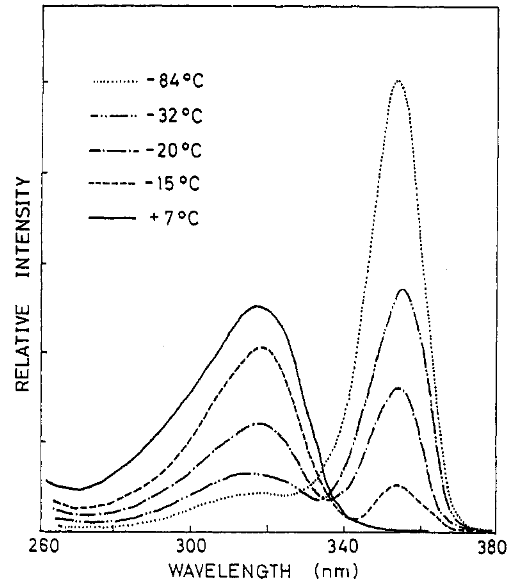

Figure 1. Absorption spectra of PDBS in hexane measured at different temperatures.

avoid unnecessary photodegradation of the samples, each of the emission and excitation measurements was carried out within 30 s, and the excitation slit was always kept as small as 1.0 nm. The temperature of the samples was measured with a digital thermometer (Iuchi Model 245S) with the accuracy of ±0.5 °C. Molecular weight distribution of the polysilylenes was measured with a Shodex GPC system 11, using toluene as the solvent.

Results

Figure 1 shows absorption spectra of PDBS in hexane measured at different temperatures. It is clearly seen that as the temperature is lowered the intensity of the absorption band at about 350 nm increases, while that at 320 nm decreases. The band at 318 nm is considered to be due to an electronic transition of segments with the helical conformations, while the band at 353 nm is considered to be due to that for the rod conformations of the polysilylene.[4-8] When the intensities at the absorption maxima corresponding to the two conformational segments are plotted as a function of temperature, that for the helical conformations exhibits an abrupt decrease followed by a gradual decrease with decreasing temperature, although that of the rod conformations shows a rather monotonous and rapid increase following an abrupt appearance of the band at a temperature near −10 °C. At temperature near −20 °C, the intensities of the two absorption bands become almost equal for both PDBS and PDHS.

Figure 2 shows the fluorescence spectra obtained by the excitation of the helix absorption band and the excitation spectra obtained by monitoring the fluorescence from the rod conformations for PDHS in an isopentane–methylcyclohexane mixture at different temperatures. The fluorescence band at 363 nm can be regarded as the emission from the rod segments, while that at 340 nm can be regarded as the emission from the helical segments of the isolated polysilylene.[13] The fluorescence band positions are found to be almost invariant with temperature. When this sample was cooled down to 77 K, the fluorescence center was still observed at 358 nm, indicating that the fluroescence originates neither from aggregates nor microcrystals but rather from isolated polymer[13] (the fluorescence band from aggregates is reported to be observed at 380 nm). As is clearly seen in Figure 2, when the helical segments of the polysilylene is excited, the fluorescence emission from both the helix and rod segments is observed over the temperature range from −16 to −42 °C. Furthermore, the band corresponding to the helical conformations is observed, in addition to that of the rod conformations, in the excitation spectra obtained by monitoring the fluorescence from the rod conformations. It follows from these observations that the energy transfer from the helical to rod segments and the fluorescence emission from the helical segments are occurring in parallel in dilute solutions. Since the concentration of the sample solution is always maintained as low as 10^{-6} Si–Si unit mol/L, the energy-transfer process is considered to be occurring intramolecularly.

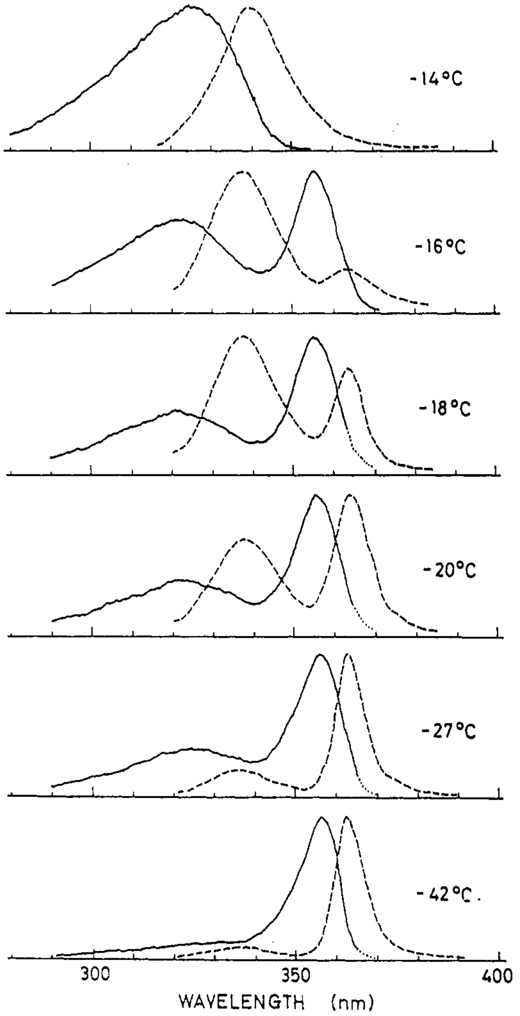

Figure 2. Corrected fluorescence spectra obtained by excitation at 315 nm (broken-line curves) and corrected excitation spectra obtained by monitoring the fluorescence at 365 nm (solid-line curves) for PDHS in an isopentane–methylcyclohexane (1:1) mixture at different temperatures. All spectra are normalized to a common value.

Relative fluorescence band intensities are plotted in Figure 3 as a function of temperature for PDBS in hexane. These plots are obtained by the excitation at the absorption band corresponding to the helical conformations. As the temperature is decreased, the intensity of the fluorescence from the rod segments increases, while that from the helical segments decreases. The decrease of the fluorescence intensity for the helical segments seems to correspond to the decrease of the absorption intensity with decreasing temperature. We have obtained also relative intensities of the helix and rod bands in the fluorescence excitation spectra obtained by monitoring the fluorescence from the rod segments at different temperatures. The intensity of the rod band in the excitation spectra is found to increase

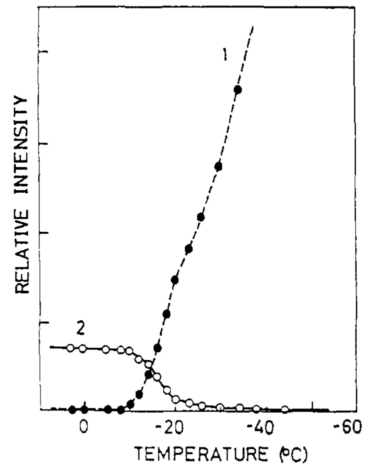

Figure 3. Relative fluorescence intensities of the rod (1) and helix bands (2) for PDBS in hexane at different temperatures, obtained by excitation at 318 nm.

monotonously, while that of the helix band increases at first and then reaches a plateau value with decreasing temperature.

As is mentioned, we have obtained semiquantitative data for the dependence of the observed spectra on temperature. These data can provide estimates for the relative rates that characterize the excited-state dynamical behavior of isolated polysilylenes. This is discussed below in detail.

Discussion

The Model. The details of the conformation of polysilylenes dissolved in solutions do not seem to be fully understood, since NMR and X-ray diffraction data are not available. However, in light of the results obtained for the solid polymer, a similar conformational change is expected to occur also for isolated polysilylenes in solutions at temperatures near the transition temperature. Hence, it is not unreasonable to ascribe the absorption band near 320 nm to the electronic transition for helical segments in which the gauche conformations predominate and the band near 350 nm to that for rod segments in which the trans conformations predominate. This is supported also by the results of the band-structure calculations for polysilylenes having helical and all-trans conformations.[14] On the basis of the fact that only two distinct absorption bands appear in these wavelength regions, we consider that, as a first approximation, the two absorption bands of the polysilylenes are mostly due to the existence of two kinds of segments, helical and rod, although at present these assignments are not definite. Each of the segments is considered to consist of a significant number of linked Si atoms, e.g., at least 30,[15] since the band positions are almost independent of temperature. Of course, the segments showing conformations other than helical and rod may exist, e.g., those of a random mixture of gauche and trans conformations, i.e., random coil.

Our results indicate that the energy transfer is occurring intramolecularly from helical to rod segments of polysilylenes. The most probable transfer process would be the one from one segment to the neighboring segments, since the transfer probability to remote segments is expected to be low. Of course, the energy transfer may occur at the chain contact or crossing points, but its probability is expected to be low as compared with that between the neighboring segments. We assume that the energy transfer is taking place intramolecularly from one helical segment to neighboring rod segments, only when the latter is nearly directly attached to the former. When random-coil conformations exist between the helical and rod segments, the energy-transfer process is not considered to proceed easily.

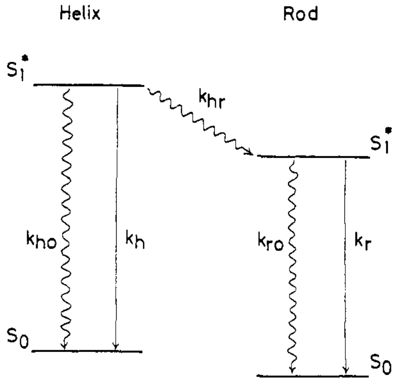

Figure 4. Scheme showing the relaxation processes in isolated polysilylenes dissolved in solutions.

A crude model interpreting the electronic relaxation processes in symmetrically substituted poly(dialkylsilylene) is described in Figure 4, where k_h and k_{h0} are, respectively, the radiative and nonradiative rate constants of the lowest excited singlet state of the helical segment and k_r and k_{r0} are, respectively, those of the rod segment. The averaged energy-transfer rate constant from the excited states of the helical segments to those of the neighboring rod segments is denoted by k_{hr}. According to this simplified model, the fluorescence quantum yield from the excited states of the rod segments, obtained by the excitation at the helix absorption band, Φ_{hr}, is expressed by

$$\Phi_{hr} = [k_{hr}/(k_h + k_{h0} + k_{hr}P_r(T))][k_r/(k_r + k_{r0})] \quad (1)$$

where $P_r(T)$ is attributed to the probability that a rod segment is located inside a certain transfer radius. In similar way, we can obtain the relations

$$\Phi_{hh} = k_h/(k_h + k_{h0} + k_{hr}P_r(T)) \quad (2)$$

$$\Phi_{rr} = k_r/(k_r + k_{r0}) \quad (3)$$

where Φ_{hh} is the fluorescence quantum yield from the helix segments obtained by the excitation at the helix absorption band and Φ_{rr} is the yield from the rod segments obtained by the excitation at the rod absorption band. As will be discussed later in detail, the value for $k_{hr}P_r(T)$ is considered to be roughly proportional to the rod-segment content in the chain.

Temperature Dependence of the Transfer Yield and Rate. We have obtained fluorescence, fluorescence excitation, and absorption spectral data at different temperatures. At a particular temperature T, when the intensity of the helix band in the excitation spectrum obtained by monitoring the rod fluorescence, $I_{hr}(T)$, is divided by that of the helix absorption band, $A_h(T)$, the resultant ratio corresponds to the relative fluorescence quantum yield from the rod segments obtained by the excitation at the helix absorption band. That is

$$\Phi_{hr}(T) \propto I_{hr}(T)/A_h(T) \quad (4)$$

In a similar way, the relative value for Φ_{rr} can be obtained from the relation

$$\Phi_{rr}(T) \propto I_{rr}(T)/A_r(T) \quad (5)$$

where $I_{rr}(T)$ is the intensity of the rod band in the excitation

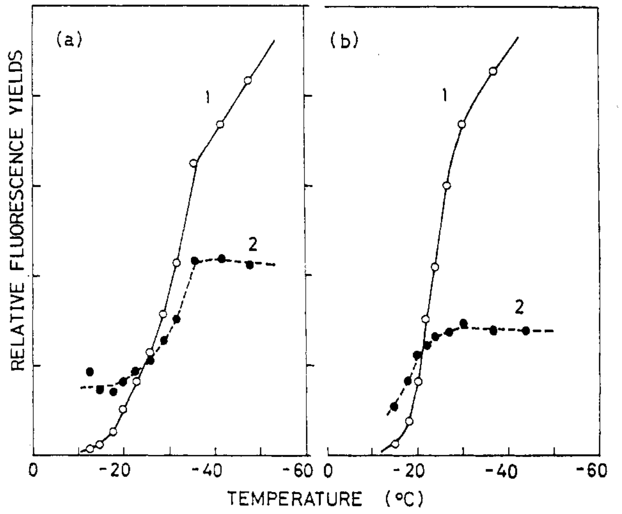

Figure 5. Relative fluorescence quantum yields, Φ_{hr} (1) and Φ_{rr} (2), plotted as a function of temperature for PDBS in hexane (a) and PDHS in an isopentane–methylcyclohexane (1:1) mixture (b). These plots are obtained from the excitation spectral data.

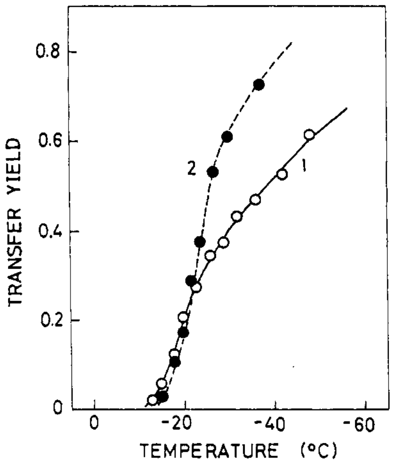

Figure 6. Energy-transfer yields, χ_{hr}, from the helical to rod segment plotted as a function of temperature for PDBS in hexane (1) and PDHS in an isopentane–methylcyclohexane (1:1) mixture (2).

spectrum obtained by monitoring the rod fluorescence, and $A_r(T)$, that of the rod absorption band, both measured at a temperature T. Utilizing the data already obtained, together with the relations (4) and (5), we can evaluate the relative values for Φ_{hr} and Φ_{rr} at different temperatures, which are plotted in parts a and b of Figure 5, respectively, for PDBS and PDHS. It is clearly seen that the value for Φ_{hr} increases almost exponentially with decreasing temperature, although Φ_{rr} does not show a marked increase.

It follows from eqs 1 and 3 that

$$k_{hr}P_r(T)/(k_h + k_{h0} + k_{hr}P_r(T)) = \Phi_{hr}/\Phi_{rr} \qquad (6)$$

where the left-hand side corresponds to the energy-transfer yield, $\chi_{hr}(T)$, from the helix to rod segments. Although it is not easy to obtain the absolute values for Φ_{hr} and Φ_{rr}, the ratio, Φ_{hr}/Φ_{rr}, can be evaluated rather quantitatively as a function of temperature using the absorption and excitation spectral data. As is seen in Figure 6, the transfer yields show a marked increase with decreasing temperature for both PDBS and PDHS, presumably reaching to a saturated value upon further decrease of temperature.

The radiative rate constant, e.g., k_h, is normally treated as a constant for most fluorescent molecules. With polysilylenes, it is possible to consider that this value changes with the length of the segment, since the molar extinction coefficient varies depending on the Si–Si chain length.[16,17] However, the facts that the fluorescence and absorption centers for the helix segment, as well as the fluorescence lifetime,[12] are almost invariant with temperature and that the value for Φ_{rr} $(=k_r/(k_r + k_{r0}))$ varies with temperature only by a factor of 2 support the contention that the radiative rate constant k_h or k_r does not vary markedly with temperature, if at all.

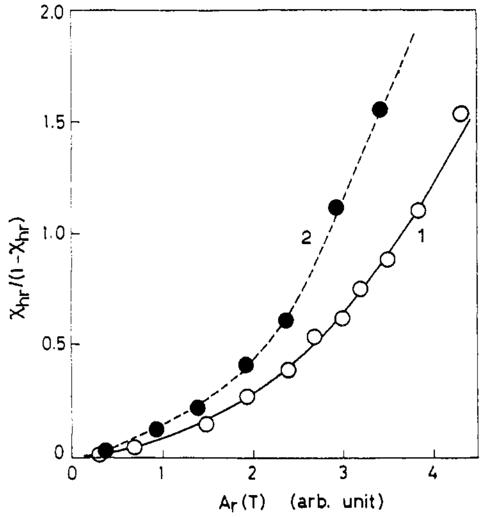

Figure 7. Value for $\chi_{hr}(T)/(1 - \chi_{hr}(T))$ plotted as a function of the rod absorption intensity, $A_r(T)$, for PDBS in hexane (1) and PDHS in an isopentane–methylcyclohexane (1:1) mixture (2).

Now, let us discuss the temperature dependence of the intramolecular energy-transfer yield or rate in some detail. As is shown in Figure 6, the relative transfer yield, $\chi_{hr}(T)$ $(=\Phi_{hr}/\Phi_{rr})$, increases significantly with decreasing temperature. If all the rate constants involved in eq 6 are almost independent of temperature, then the temperature dependence of the transfer yield or rate should be caused mainly by the temperature dependence of $P_r(T)$. One can recognize, by comparing the data in Figure 5 with those in Figure 1, that $P_r(T)$ is related to the content of the rod segments. Rearranging eq 6, we have

$$\chi_{hr}(T)/(1 - \chi_{hr}(T)) = k_{hr}P_r(T)/(k_h + k_{h0}) \qquad (7)$$

Hence, if the left-hand side of eq 7 is plotted against the intensity of the rod absorption band, $A_r(T)$, we can find the relation between $P_r(T)$ and the rod segment content. Figure 7 shows the values of $\chi_{hr}(T)/(1 - \chi_{hr}(T))$ plotted against $A_r(T)$ for PDBS and PDHS. It is seen that these plots provide roughly a linear relation, although there is an apparent deviation from the linearity. That is, the transfer does not seem to proceed efficiently when the rod-segment content is very small. The deviation may be due to the changes in the σ-conjugation length which could change the transfer rate constant k_{hr}.

In our treatment, the energy-transfer rate is related to the rod-segment content in the polysilylene chain. This treatment resembles formally the one for the intermolecular energy-transfer process in which the transfer rate changes with the increase of the acceptor concentration, but it is essentially different from the intermolecular treatment in the sense that the energy transfer is occurring along the backbone $-(SiR_2)_n-$ chain of isolated polysilylenes. If all the helical segments are attached directly to the rod segments, the value $P_r(T)$ should not vary strongly with temperature. At temperatures near the transition temperature, however, $P_r(T)$ increases sharply with decreasing temperature or increasing rod-segment content. This seems to indicate that all of the helical segments are not attached directly to the rod segments at this temperature range.

Conclusions

We have presented evidence showing that energy transfer is taking place intramolecularly from helical to rodlike segments for PDBS and PDHS dissolved in organic solvents. A crude model interpreting the observed electronic relaxation processes is presented. Analysis of the temperature dependence of the relative fluorescence quantum yields, based on the model, reveals that the transfer yield as well as the transfer rate increases markedly with decreasing temperature at the temperatures near the transition temperature, where the rod-segment content also increases sharply with decreasing temperature. It is inferred that the energy-transfer yield and rate increase as the content of the rod segments in the chain increases.

Note Added in Proof. Quite recent investigation suggests that the thermochromism is related to conformational change due to intramolecular chain association, rather than coil to rod transition (Shukla, P.; Cotts, P. M.; Miller, R. D.; Rusell, T. P.; Smith, B. A.; Wallraff, G. M.; Baier, M.; Thiyagarajan, P. *Macromolecules* **1991**, *24*, 5606).

Acknowledgment. We thank Dr. Gordon Fearon for encouragement, Drs. Donald Weyenberg and Stelian Grigoras for careful reading of the manuscript, and Mr. Toshio Suzuki for introductory advice in sample preparation.

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Registry No. PDHS (homopolymer), 97036-67-4; PDHS (SRU), 94904-85-5; PDBS (homopolymer), 97036-65-2; PDBS (SRU), 95999-72-7.