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The Effect of Pressure and of Controlled Stretch on the Luminescent Properties of 9,10-Bis(phenylethynyl) Anthracene[‡]

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The luminescence properties of 9,10-bis(phenylethynyl) anthracene have been investigated in solid poly(vinyl acetate) (PVAc) and a copolymer of vinyl chloride (VCl) and vinyl acetate (VAc) as a function of pressure to 65 kbar and of controlled stretch over a range of up to 4 times the original length using the 400 nm line of a frequency-doubled Ti:sapphire laser. With increasing pressure, the intensity (corrected for the absorption at 400 nm) decreases significantly and there is a distinct change in peak shape in the region of 20−40 kbar. In this region, the lifetime increases from 3.5 ± 0.2 to 4.0 ± 0.2 ns. The result can be explained on the basis of the analysis of Levitus and Garcia-Garibay. The red shift of the absorption peak is equivalent to a blue shift of the excitation laser, which results in excitation of a different polarization of the molecule. Up to a stretch of 2, the controlled stretch produces an increase of intensity for laser excitation polarized in the direction of stretch and a decrease for excitation polarized at 90° to the stretch, indicating that molecules are being oriented preferentially with the stretch. At larger stretches, there is a very similar increase in emission intensity for both orientations of the exciting light. Various aspects of the observations are considered but there appears to be no simple explanation for the apparent increase in oscillator strength.

Introduction

The structure of 9,10-bis(phenylethynyl) anthracene (BPEA) is shown in Figure 1. BPEA has had a wide variety of applications because of its high fluorescence yield and its solubility in a variety of liquids and polymers.[1−8] Many of the applications, as well as the techniques for investigation of its behavior, have been reviewed by Levitus and Garcia-Garibay.[9] They also present a thorough and incisive analysis of the photophysics of BPEA with emphasis on the polarization characteristics of the BPEA as a function of excitation wavelength.

In this paper, we present the effect of high pressure and of controlled stretch on the emission of BPEA in dilute solution in poly(vinyl acetate) (PVAc) and a copolymer of vinyl chloride and vinyl acetate (p(VCl-*co*-VAc)).

Experiment

BPEA was purchased from Sigma-Aldrich as were poly(vinyl acetate) (PVAc, medium molecular weight, $T_g \approx 35$ °C) and poly(vinyl chloride-*co*-vinyl acetate) [p(VCl-*co*-VAc)]. The copolymer contains ~86% vinyl acetate and has a $T_g = 72$ °C. The polymers were used without further purification, because neither of them gave any emission when irradiated at the excitation wavelength. BPEA was also used as purchased.

The BPEA and polymers are dissolved in spectral grade chloroform, and then the transparent solution is poured into a glass dish to form a blend film. After the solvent evaporates at room temperature, the film is dried for several days in a vacuum oven. The concentration of BPEA is 0.05 wt %. The operation of the diamond anvil cell (DAC) has been described in detail elsewhere[10] as has the controlled stretch apparatus.[11]

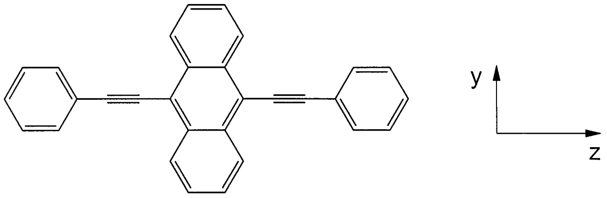

Figure 1. Structure of 9,10-bis(phenylethynyl) anthracene (BPEA). The arrows indicate the direction of the principal axes of the molecule.

For emission, the excitation utilizes the 400 nm (25 000 cm^{-1}) line of a frequency-doubled Ti:sapphire laser. The polarization is established using a quarter wave plate and a calcite polarizer. Our absorption apparatus utilizes a xenon lamp, and the light is brought to and from the surface of the diamonds (or the stretched films) by light fibers, so no control of the polarization is possible. The relative absorption efficiency is established from the strength of absorption at 400 nm (25 000 cm^{-1}). The emission efficiency is approximated by the product of the peak height and full width at half-maximum (fwhm).

For both emission and absorption with the controlled stretch apparatus, as is described in detail in ref 11, the sample width is measured under a microscope at each degree of stretch, so that the absorption or emission efficiency can be normalized to the number of molecules in the light path.

Results

Figure 2a,b shows typical emission spectra for BPEA in PVAc (panel a) and p(VCl-*co*-VAc) (panel b) at a series of pressures taken with the laser beam polarized vertically. The spectra with the laser beam polarized horizontally were similar

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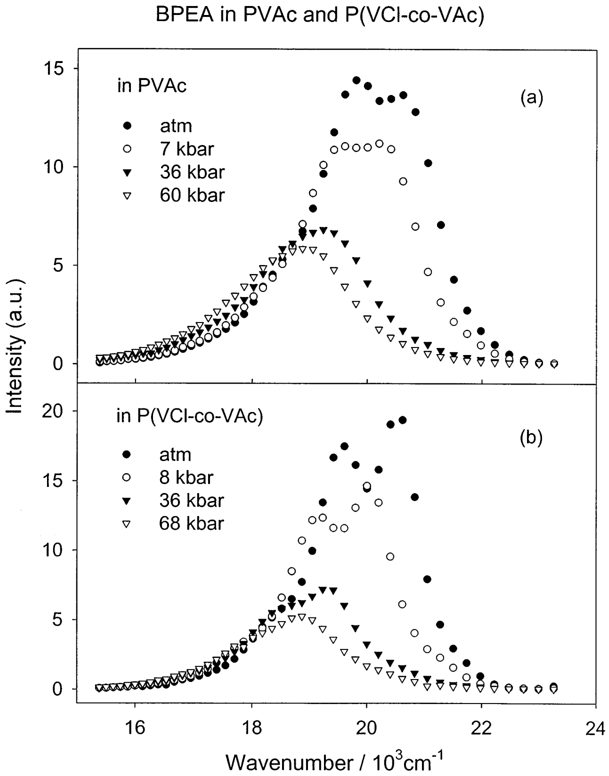

Figure 2. Emission spectra at several pressures for BPEA in (a) PVAc and in (b) p(VCl-*co*-VAc).

but with a slightly larger decrease with pressure (see below). With the use of hydrostatic pressure on the sample, one might expect only a minimal effect of polarization of the exciting laser. The major features include a red shift of 1200−1500 cm^{-1} (200−300 cm^{-1} larger in the copolymer than in PVAc). This is typical for $\pi-\pi^*$ excitation or emission over a range of 60−65 kbar. In addition, there is a definite change of shape of the peak in the region 20−35 kbar. The peak location, peak shape, and intensity are completely reversible upon release of pressure. The lifetime (3.5 ± 0.2 ns) is independent of pressure up to 20−30 kbar. Between 25 and 35−40 kbar, it increases to 4.0 ± 0.2 ns and remains constant at higher pressures.

Figure 3a,b shows the spectra in PVAc at several degrees of stretch for horizontal and vertical polarizations of the exciting laser beam. The stretch is oriented vertically. There is no change in peak location or shape with stretch. The lifetime remains constant at 3.5 ± 0.2 ns. The intensity does not reverse. The spectra in the copolymer are qualitatively similar.

For the spectra shown in Figures 2 and 3, no correction for the absorption efficiency at 400 nm has been made, although the correction is applied for the intensity change presented below. The emission vs stretch spectra in Figure 3 are corrected for the number of molecules in the light path but not for the absorption efficiency. The absorption is relatively weak because of the dilution of the samples and their thinness. For the pressure absorption data, the change in peak location and shape is similar to that observed in emission. For the stretch data, there is no change in peak location and no change in shape.

Figure 4 shows the change in absorption efficiency at 400 nm (25 000 cm^{-1}) as a function of pressure for the two media. Figure 5 shows the corresponding effect of stretch, corrected for the change in the number of molecules in the light path as discussed above. In both cases, these represent the average of 4−5 loads with a scatter of ±5% or less. As mentioned in the Experiment section, the absorption spectra necessarily involved

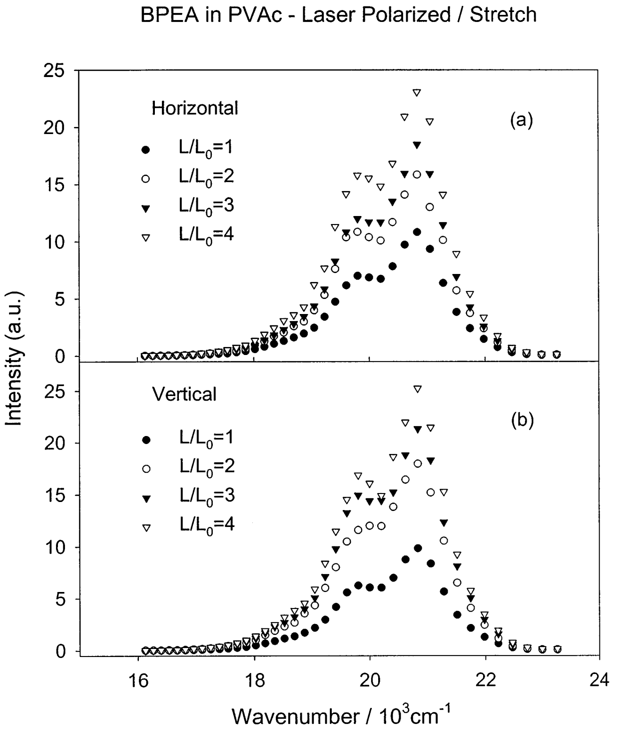

Figure 3. Emission spectra of BPEA in PVAc at several degrees of stretch corrected for the number of molecules in the light path: (a) horizontally polarized exciting light; (b) vertically polarized exciting light.

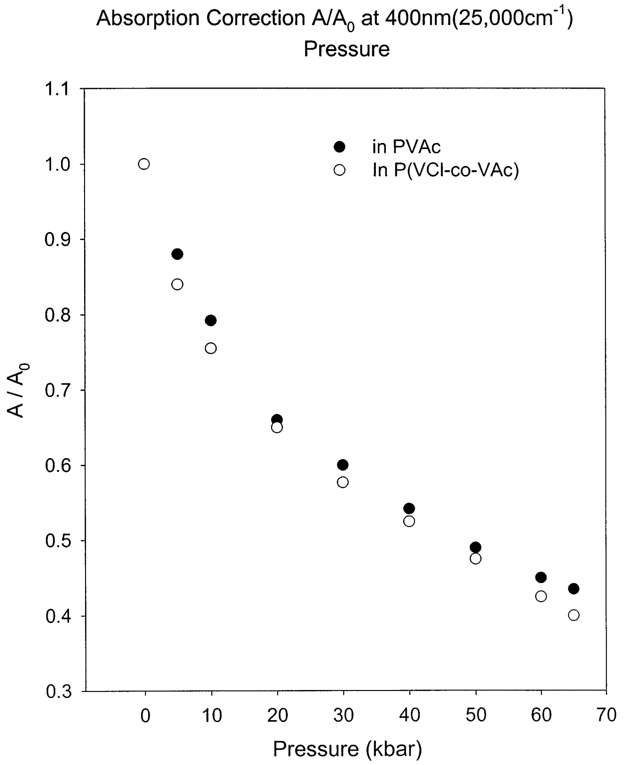

Figure 4. Change in absorption efficiency at 400 nm (25 000 cm^{-1}) as a function of pressure.

unpolarized light. Nevertheless, the changes in the polarized emission spectra discussed below are corrected for the observed changes in absorption efficiency as a first-order correction.

Figure 6 shows the change of emission intensity with pressure in the two media, corrected for relative absorption efficiency. These represent the average of 8−11 loads for both polarizations

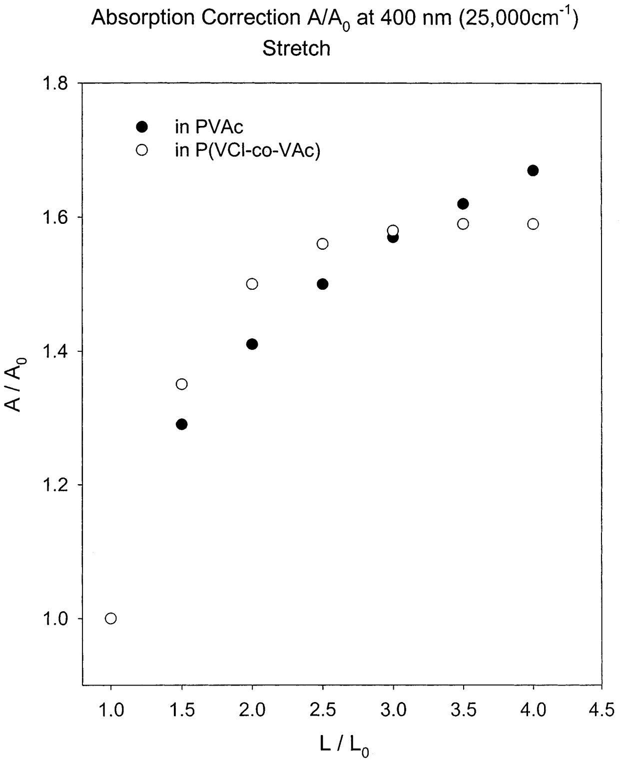

Figure 5. Change in absorption efficiency at 400 nm (25 000 cm^{-1}) as a function of stretch.

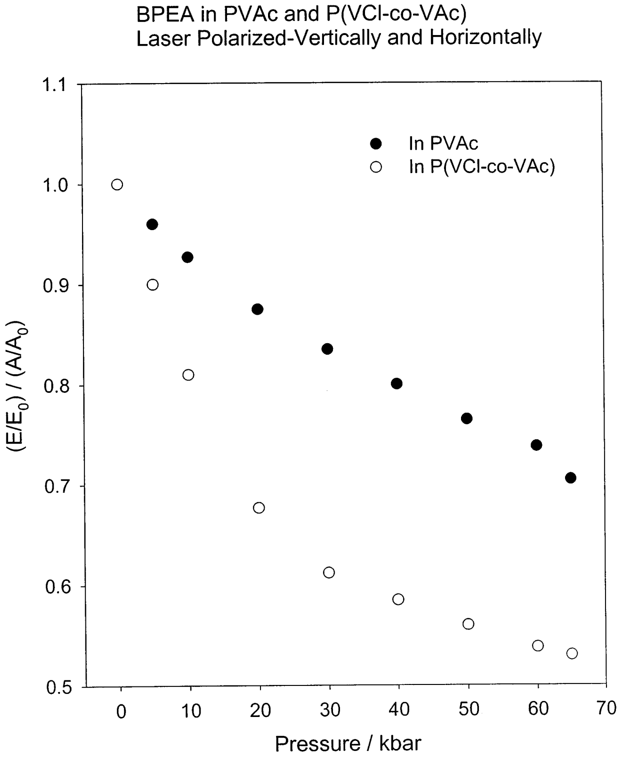

Figure 6. Change in emission intensity with pressure of BPEA (corrected for absorption efficiency).

of the exciting laser beam. The loads with horizontal polarization of the excitation show a marginally (10−15%) greater decrease with pressure than those with the beam polarized vertically. The scatter in the data from load to load is unusually large and approached the apparent difference between polarizations.

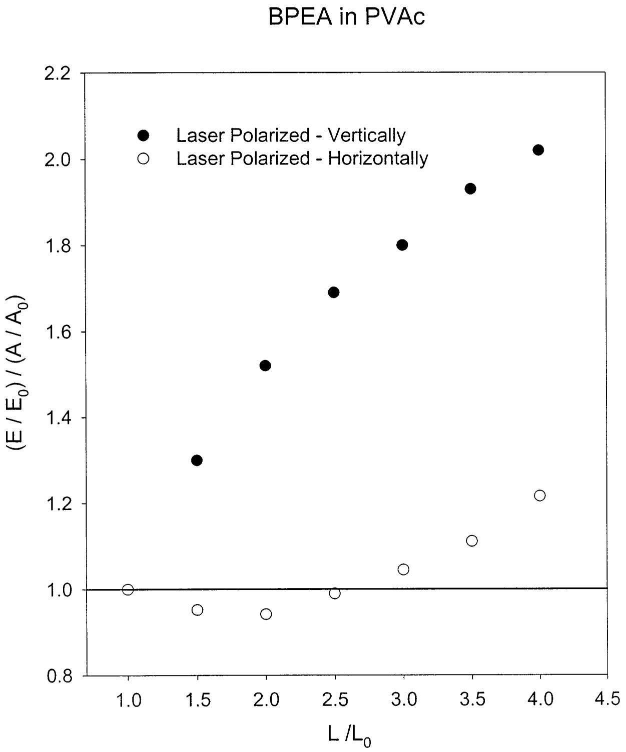

Figure 7. Change in emission efficiency with stretch of BPEA in PVAc for vertically and horizontally polarized exciting light (corrected for the number of molecules in the light beam and normalized to the relative absorption efficiency).

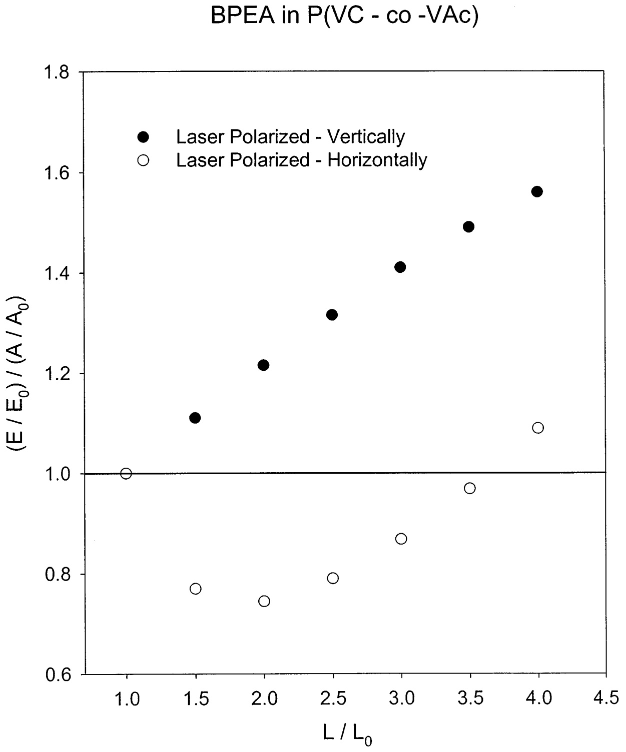

Figure 8. Change in emission efficiency with stretch of BPEA in p(VCl-*co*-VAc) for vertically and horizontally polarized exciting light (corrected for the number of molecules in the light beam and normalized to the relative absorption efficiency).

Figures 7 and 8 exhibit the change in emission intensity with stretch in the two media for both polarizations of the laser beam. Each set of data represents the average of 4−5 loads with each polarization of the laser beam with a scatter of ±5−7%. The emission intensity is corrected for the change in the number of molecules in the light path and normalized to the relative absorption efficiency at 400 nm (25 000 cm^{-1}), which has also been corrected as above.

Discussion

With increasing pressure, the luminescence efficiency decreases to a greater degree in the copolymer than in PVAc. There is a red shift of the absorption and emission peak of 1200−1500 cm^{-1}, ∼300 cm^{-1} greater in the copolymer than in PVAc. A red shift and accompanying decrease in luminescence efficiency is generally associated with the energy gap law.[12] However, in accordance with this law, the nonradiative rate (k_{nr}) should increase and result in a decrease in the lifetime. The lifetime is independent of pressure to 20−25 kbar and then increases by 10−15%. Therefore, this factor cannot be dominant.

The paper of Levitus and Garcia-Garibay[9] provides us with a reasonable explanation. Specifically, in Table 2 of their paper, they show that a change of excitation wavelength from 407.1 to 335.7 nm (a change of ∼5200 cm^{-1}) results in a decrease of the oscillator strength from 1.45 to 0.05 and a change from z to y polarization of the transition. The observed red shift of absorption and emission peaks is equivalent to moving the exciting beam to shorter wavelength by 20−25 nm with a resulting decrease in oscillator strength. The tendency to increase the y component of the polarization could account for the change of peak shape (and possibly of lifetime) observed in the 20−25 kbar pressure range.

For the first factor of 2 in stretch, the intensity increases for the vertically polarized excitation and decreases for the horizontally polarized beam. The stretch is in the vertical direction and an increasing number of molecules are thus oriented with the z axis parallel to the beam polarization. This difference is larger for the copolymer than for PVAc, quite possibly because of the low T_g in PVAc.

At higher degrees of stretch, the intensity increases in an essentially parallel fashion for both polarizations of the excitation beam. Because the lifetime is independent of the stretch and there is no measurable peak shift or change of shape of the emission peak, this could not be due to a decrease in k_{nr} because of the stiffening of the medium. At the higher degrees of stretch and before correction for the change in area fraction exposed to the laser beam, the absorption is relatively weak but there is no measurable change in location or shape of the peak.

In attempting to characterize the increase in emission intensity for stretches greater than 2, it is desirable to summarize the observations. There is no change in the absorption peak location, and the ratio of intensity at 400 nm to that of the peak is constant at ∼0.45, so there is not even a minimal change in peak shape. The corrected relative absorption increases by ∼12−15% over the range of stretch of 2−4 for PVAc and by 6−8% for the copolymer in the same range. In the stretch range 2−4, the ratio of intensities (PVAc/copolymer) is 1.25 ± 0.05% independent of stretch for either vertically or horizontally polarized excitation. In this same range, the ratio of intensities change for vertically over horizontally polarized excitation is 1.7 ± 0.05% for PVAc and 1.6 ± 0.05% for the copolymer (all of these ratios are normalized to 1.00 at zero stretch). Also the ratio of the normalized emission intensity at a stretch of 4 to that at a stretch of 2 is 1.3−1.4 for either medium and for either orientation of the polarization of the exciting laser beam. Thus, it seems that this increase is not associated with the polarization or the medium.

It is possible that this increase in oscillator strength occurs continuously with stretch; for the initial stretch, the reorientation aspect is dominant, but as a higher percentage of the molecules are oriented vertically, the change in oscillator strength becomes the controlling factor. Given the points made in the preceding paragraph, it is not at present possible to assign a cause for the change of oscillator strength.

Summary

The effect of pressure and of controlled stretch has been measured on the luminescence and absorption properties of BPEA in dilute solution of PVAc and in a copolymer of VCl and VAc. With increasing pressure, both emission and absorption peaks shift to lower energy by 1200−1500 cm^{-1} in 60 kbar. The luminescence intensity (corrected for absorption) decreases. The lifetime is independent of pressure to ∼20 kbar and then increases, accompanied by a change in peak shape. The results can be interpreted in terms of the analysis of Levitus and Garcia-Garibay in that the red shift of absorption results in an excitation with a different polarization and lower oscillator strength.

The initial effect of stretch is an increase in emission intensity for laser excitation polarized parallel to the direction of stretch and a decrease for the excitation oriented at 90°, evidently because of a reorientation of the molecules in the direction of the stretch. At larger stretches, there is a parallel increase in intensity for both orientations of the excitation polarization in both media. An increase in oscillator stretch of unknown origin predominates over the orientation effect.

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References and Notes

(1) Lukacs, J.; Lampert, R. A.; Metcalfe, J.; Phillips, D. *J. Photochem. Photobiol. A* **1992**, *63*, 59.

(2) Cicerone, M. T.; Ediger, M. D. *J. Chem. Phys.* **1996**, *104*, 7210.

(3) Cicerone, M. T.; Blackburn, F. R.; Ediger, M. D. *J. Chem. Phys.* **1995**, *102*, 47.

(4) Blackburn, F. R.; Wang, C.-Y.; Ediger, M. D. *J. Phys. Chem.* **1996**, *100*, 18249.

(5) Gisser, D. J.; Johnson, B. S.; Ediger, M. D.; Von Meerwall, E. D. *Macromolecules* **1993**, *26*, 512.

(6) Heitz, M. P.; Maroncelli, M. *J. Phys. Chem. A* **1997**, *101*, 5852.

(7) Hanhela, P. J.; Paul, D. B. *Aust. J. Chem.* **1984**, *37*, 553.

(8) Maulding, D. R.; Roberts, B. G. *J. Org. Chem.* **1972**, *37*, 1458.

(9) Levitas, M.; Garcia-Garibay, M. A. *J. Phys. Chem. A* **2000**, *104*, 8632.

(10) (a) Jurgenson, C. W.; Drickamer, H. G. *Phys. Rev. B* **1984**, *30*, 7202. (b) Yang, G.; Dreger, Z. A.; Drickamer, H. G. *J. Phys. Chem. B* **1997**, *101*, 4218. (c) Dreger, Z. A.; Yang, G.; White, J. O.; Drickamer, H. G. *J. Phys. Chem. B* **1997**, *101*, 9511. (d) Yang, G.; Li, Y.; White, J. O.; Drickamer, H. G. *J. Phys. Chem. B* **1999**, *103*, 5181.

(11) Yang, G.; Li, Y.; Zhu, A.; White, J. O.; Drickamer, H. G. *Macromolecules* **2000**, *33*, 3173.

(12) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145 and references therein.