Studies of the Antenna Effect in Polymer Molecules. 20. Effect of Molecular Weight on the Solubilization and Photocatalytic Activity of Poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene)

B. White, M. Nowakowska,[†] G. J. Vancso, and J. E. Guillet*

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Received August 8, 1990; Revised Manuscript Received December 13, 1990

ABSTRACT: The effect of molecular weight on the solubilization and photocatalytic activity of a series of copolymers of poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS-VN) in aqueous solution has been investigated. Preliminary light-scattering results, which suggest that PSSS-VN behaves as a random coil in aqueous solution, are also presented. The average number of molecules of perylene (P) and 9,10-dimethylanthracene (DMA) solubilized per macromolecular coil was observed to be proportional to the molecular weight of PSSS-VN. With the exception of the copolymer of highest molecular weight, a given mass of each copolymer solubilized the same amount of probe. On the basis of the rate of singlet oxygen addition to P and DMA, the photocatalytic activity of PSSS-VN was found to be independent of its molecular weight.

Introduction

Poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS-VN) belongs to a novel class of polyelectrolytes containing photosensitive, hydrophobic moieties that display photon harvesting properties when dissolved in aqueous solution. Due to the large hydrophobic content (60 mol %) of PSSS-VN, the interior of the coil is less polar than water. The resulting "hydrophobic pocket" can be considered analogous to the active site of certain enzymes in that it will collect other hydrophobic molecules from aqueous media and, in the presence of light of a suitable wavelength, induce rapid and often specific chemical reactions.[1-3] These synthetic polymers displaying such photocatalytic activity have been termed "photozymes" by Guillet and co-workers.[1]

PSSS-VN has been shown to photosensitize the unimolecular photolysis of 2-undecanone[1] in aqueous solution. Unlike small-molecule solvents, only Norrish type II products were detected in the photozyme. The rate of photolysis in aqueous PSSS-VN solution was about an order of magnitude greater than in hexadecane.[1] The photocatalytic activity was attributed to the greater photon capture cross section of the copolymer as compared to 2-undecanone. It has also been demonstrated that PSSS-VN catalyzes the bimolecular oxidation of several polynuclear aromatic compounds (PNA).[2,3] From an analysis of the secondary products, it was concluded that singlet oxygen produced from quenching of excited naphthalene was the active species involved in the reaction. In this case, photocatalytic activity is due to the proximity of the reactant molecules. Performing the equivalent experiment in a small-molecule solvent, below a probe concentration of 1×10^{-6} M, yielded an order of magnitude decrease in the rate of reaction for 9,10-dimethylanthracene (DMA), and no reaction was observed for perylene. These studies also showed that the efficiency of solubilization and photosensitized chemistry is only slightly dependent on the ionic strength and pH of the solution but is drastically affected by the composition of the copolymer.[2] While very little is known about the conformation of PSSS-VN, photophysical studies suggest that the copolymer adopts a pseudomicellar type of structure with the hydrophobic groups concentrated predominantly in the interior of the coil.[4]

The objective of this paper is 2-fold: to present preliminary light scattering results on PSSS-VN in aqueous solution and to determine the effect of molecular weight on the efficiency of solubilization and photocatalytic activity using P and DMA as probes. Rather than using monochromatic light (280 nm), as was the case in the previous study,[2] natural sunlight was used to test the effect of molecular weight on the photocatalytic activity of PSSS-VN.

Experimental Section

Materials. Copolymers of sodium *p*-styrenesulfonate (SSS) and 2-vinylnaphthalene (VN) were synthesized and purified according to the method previously described.[4] In order to obtain copolymers of different molecular weight but of the same composition, each polymerization mixture contained a fixed molar ratio of SSS to VN (1:1.2) but an increasing amount of initiator, 2,2′-azobis(isobutyronitrile) (AIBN) for the series of copolymers labeled 1-5: 0.02, 0.10, 0.25, 0.70, and 2.0 mol %, respectively. The composition of the various copolymers was determined by elemental analysis (Galbraith Laboratories Inc.) and verified by a comparison of the optical density of each copolymer (0.05 g L^{-1}) in aqueous solution at 280 nm.

9,10-Dimethylanthracene (DMA, 99%, Aldrich) was purified by three recrystallizations from ethanol. Perylene (P, 99.9%, Aldrich Gold label) was used without further purification.

Polymer solutions were prepared from distilled water that had been passed through a Millipore Milli-Q water purification system. Ethyl alcohol (Aldrich, anhydrous), acetone (Caledon, spectro grade), and tetrahydrofuran (THF, HPLC, Aldrich) were all used without further purification.

Procedures. Solubilization of Probes. The solubilization of DMA and P in aqueous solutions of PSSS-VN was achieved by slowly injecting microliter quantities of P (2×10^{-3} M) or DMA (5×10^{-3}) dissolved in acetone into milliliter quantities (10 mL) of copolymer (0.48 g L^{-1}) solution. The resulting aqueous copolymer solutions, containing less than 0.10 vol % acetone, were shaken for an additional 5 min and then equilibrated in the dark for 2-4 h. The concentration of probe in aqueous PSSS-VN solution was estimated from the slope of calibration plots of the total fluorescence intensity versus precise concentrations of P or DMA in THF, at excitation wavelengths of 415 and 356 nm, respectively.[2] Since the optical density of the solutions was less than 0.07, fluorescence emission is directly proportional to the concentration of probe solubilized in the core of PSSS-VN. Under these experimental conditions, emission from DMA dissolved in water contributed less than 6% of the total emission, while emission from P dissolved in water was negligible.

Irradiation of Samples. Irradiations in sunlight were performed in Toronto on bright, sunny days in July. To ensure

---

[†] On leave from the Faculty of Chemistry, Jagiellonian University, Krakow, Poland.

0024-9297/91/2224-2903$02.50/0

that each of the samples received an equal dose of light, all of the copolymer solutions were exposed simultaneously. Under these experimental conditions, about 85% of the solar light is absorbed by the copolymer.

Ultraviolet Spectra. UV spectra of the samples were performed on a Hewlett-Packard 8451 A diode array spectrometer.

Fluorescence Spectra. Steady-state emission spectra of PSSS–VN solutions were recorded at room temperature by using an SLM-Aminco fluorescence spectrophotometer. The sensitized photooxidation reactions were followed by monitoring the decrease in the total emission intensity of P or DMA at excitation wavelengths of 415 and 356 nm, respectively.

Light-Scattering Measurements. The weight-average molecular weights, $\bar{M}_w$, of the copolymers were determined by low-angle laser light scattering (LALLS), using a Chromatix KMX-6 photometer at a wavelength of 632.8 nm and a scattering angle of 6–7°. The instrument is equipped with a 15-mm-long static cell designed for aqueous solutions. The aqueous copolymer solutions were filtered twice with Sartorius cellulose acetate membrane filters of 0.2-μm pore size before injection into the sample cell. In order to minimize the experimental error associated with stray light and dust, measurements of the scattering intensity for each copolymer sample were performed on at least 10 solutions of different concentrations.

The values of $\bar{M}_w$ were obtained from the Rayleigh–Debye relationship, which is valid for low scattering angles, θ:[5]

$$Kc/R_\theta = 1/\bar{M}_w + 2A_2c \qquad (1)$$

where c is the concentration of the copolymer, R_θ is the measured Rayleigh factor, A_2 is the second virial coefficient, and K is an optical constant given as

$$K = (4\pi^2n^2/N_0\lambda_0^4)(dn/dc)^2 \qquad (2)$$

where n is the refractive index of the solvent, λ_0 is the wavelength of the light source, N_0 is Avogadro's number, and dn/dc is the refractive index increment of the copolymer.

However, light-scattering measurements performed on copolymers of heterogeneous composition yield an apparent weight-average molecular weight, $\bar{M}_{w,app}$, that is usually different from the true value of $\bar{M}_w$.[6] The magnitude of the difference between $\bar{M}_{w,app}$ and $\bar{M}_w$ depends on the refractive index increments of the respective homopolymers and copolymer in a given solvent.[7] In order to obtain the true value of $\bar{M}_w$ for PSSS–VN copolymers, light-scattering measurements have to be performed on both of the homopolymers and copolymer in at least three solvents of different refractive index.[5] Due to the different solubility properties of SSS and VN, it was not possible to find three such solvents. The light-scattering measurements for PSSS–VN were thus performed in aqueous solution, and an $\bar{M}_{w,app}$ was obtained. Since the $\bar{M}_{w,app}$ value for copolymer 2 determined by light scattering and the true value of $\bar{M}_w$ obtained previously[4] from ultracentrifuge measurements agreed to within 5%, and the expected error for static light scattering in aqueous solution is about ±10%, values of $\bar{M}_{w,app}$ measured by light scattering will be considered as true $\bar{M}_w$ values.

On the basis of the experimentally determined refractive index increment of copolymer 2 in water, the value of the optical constant K in eq 2 is equal to 0.218 ± 0.006 cm^3 g^{-1}.

The refractive index increment of the copolymer was determined by using a Chromatix KMX-16 differential refractometer operating at a wavelength of 632.8 nm. The instrument was calibrated with NaCl solutions. The measurements were performed for aqueous solutions of copolymer 2 at five different concentrations.

Dynamic light-scattering measurements were performed by using the photon correlation spectroscopy technique (PCS). The experimental setup includes a Brookhaven laser-light-scattering goniometer system, a Brookhaven BI2030-AT correlator, and a Lexel Excel 3000 Ar-ion laser emitting light at 514.5 nm. All dynamic light-scattering measurements were carried out at a scattering angle of θ = 90°. The samples were filtered in the same way as described for LALLS measurements.

Table I
Composition, Weight-Average Molecular Weight, and Size of PSSS–VN Copolymer in Aqueous Solution

copolymer	SSS, mol %	VN, mol %	$10^5\bar{M}_w$	$\bar{R}_{h,eff}$, nm
1	37	63	6.94 ± 0.05	
2	44	56	3.36 ± 0.14	18.7 ± 0.5
3	42	58	2.36 ± 0.13	14.2 ± 0.7
4	42	58	1.21 ± 0.11	9.1 ± 0.1
5	42	58	0.72 ± 0.07	6.1 ± 0.1

All of the above-mentioned measurements were performed at a constant temperature of 22 °C.

Results and Discussion

I. Polymer Characterization. Copolymerization of SSS with VN in the presence of different amounts of initiator produced five water-soluble copolymers of PSSS–VN. Characteristic features of the copolymers, such as molecular weight, composition, and effective radius, are summarized in Table I. The compositions of copolymers 3–5 are identical and contain 58 mol % VN. Copolymer 2 contains 2 mol % less VN, while copolymer 1 contains 5 mol % more VN. Due to the low solubility of copolymer 1 in water, its molecular weight could not be evaluated experimentally. The value of $\bar{M}_w$ quoted in Table I was calculated from a plot of the dependence of $\bar{M}_w$ on the initiator concentration ($\bar{M}_w \propto 1/[I]^{1/2}$), based on experimentally determined values of $\bar{M}_w$ for the other copolymers. The values of $\bar{M}_w$ range from 755 000 for copolymer 1 to 70 000 for copolymer 5. The number-average molecular weight, $\bar{M}_n$, of the copolymers was estimated by assuming a polydispersity of 2, which is the predicted polydispersity for a purely statistical distribution of chain lengths.[8]

Another important parameter characterizing a macromolecule is the average Stokes effective hydrodynamic radius, $\bar{R}_{h,eff}$, which can be determined by using dynamic light-scattering measurements.[9] This was accomplished by measuring the time autocorrelation function of the scattered light intensity and analyzing the data in terms of cumulants.[10] The value of the first cumulant, Γ, was determined from a cumulant expansion series of the field autocorrelation function truncated at the quartic term. The magnitude of Γ at infinite dilution is related to $\bar{R}_{h,eff}$ through the following relationship:[10]

$$\lim_{c\to 0} (\Gamma/\mathbf{q}^2) = kT/6\pi\eta\bar{R}_{h,eff} \qquad (3)$$

where $\mathbf{q}$ is the scattering vector, k is Boltzmann's constant, T is the absolute temperature, and η is the viscosity of the solvent.

It has been shown that the value of $\bar{R}_{h,eff}$ depends on the scattering angle if $\mathbf{q} > q_{lim}$, where q_{lim} is of the order of $1/\bar{R}_{h,eff}$.[11] In order to fulfill this condition, the scattering angle θ should be less than 45°. Measurements, however, had to be performed at an angle of 90° since a further decrease in θ resulted in an abrupt decrease in the signal-to-noise ratio, caused by problems with dust.

The values of $\bar{R}_{h,eff}$ determined for copolymers 2–5 are summarized in Table I. Since $\bar{R}_{h,eff}$ for copolymer 2 is in good agreement with the value of $\bar{R}_h$ obtained from viscosity measurements,[12] i.e., 6% difference, the above procedure was thought to be satisfactory.

An analysis of the relationship between $\bar{R}_{h,eff}$ and molecular weight can provide further information regarding the conformation of PSSS–VN in aqueous solution. For a monodisperse polymer, the effective hydrodynamic radius is related to the molecular weight through a power

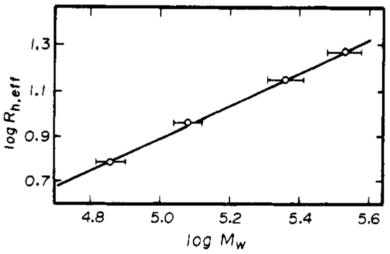

Figure 1. Plot of log $\bar{R}_{h,eff}$ versus log $\bar{M}_w$ for PSSS–VN copolymers in aqueous solutions. $\bar{R}_{h,eff}$ is the effective hydrodynamic radius, and $\bar{M}_w$ is the weight-average molecular weight.

law[13]

$$R_{h,eff} = CM^b \tag{4}$$

where b and C are constants.

The value of b is related to the exponent α in the Mark–Houwink equation through[14]

$$b \cong (\alpha + 1)/3 \tag{5}$$

It is known that for Gaussian coils $^1/_2 < \alpha < 1$, i.e., $^1/_2 < b < {}^2/_3$. The value of b varies from $^1/_2$ in Θ-solvents to $^2/_3$ in good solvents.

The scaling exponent b for PSSS–VN was determined from a log–log plot of $\bar{R}_{h,eff}$ as a function of $\bar{M}_w$, as shown in Figure 1. A linear dependence was observed with values of C and b equal to $(1.5 \pm 0.8) \times 10^{-3}$ and 0.75 ± 0.06, respectively. The value of b obtained from the slope of the line in Figure 1 is slightly greater than the maximum value for a Gaussian coil in a good solvent. This deviation indicates that the increase in size of the coil with molecular weight is greater than the increase predicted for typical polymers in good solvents. The statistical distribution of charged SSS units renders the coil unusually stiff compared with uncharged synthetic polymers. It should be stressed, however, that a more reliable value of b would have been obtained for a monodisperse sample of PSSS–VN. It was also observed that the depolarization ratio (ratio of the intensity of polarized light scattered in the parallel and perpendicular directions) was less than 1%. These results seem to suggest that PSSS–VN behaves as a random coil in aqueous solution and not as a compact or hypercoiled structure, which seemed to be the case from photophysical studies. More detailed results of this investigation are available elsewhere.[15]

II. Effect of Molecular Weight on the Solubilizing Ability of PSSS–VN Copolymers in Aqueous Solution. Studies of the effect of molecular weight on the solubilizing ability of PSSS–VN copolymers were performed by using DMA and P as probes. Polynuclear aromatic compounds (PNAs) are very convenient for this work since they are sparingly soluble in water, very efficiently solubilized in aqueous PSSS–VN solution, and can be easily detected by fluorescence emission.[2] For instance, P displays essentially negligible fluorescence from the aqueous phase but very strong and structured emission when it is solubilized in the core of PSSS–VN.[2,16]

On the basis of a simple two-phase thermodynamic model for the description of the solubilization process,[12] the distribution coefficients of DMA and P between the polymeric pseudophase and aqueous phase can be determined. The distribution coefficient can be defined based on the mole fraction or weight fraction as reference functions for partitioning of the probe between each phase:

$$K = x_p^c/x_p^{aq} \tag{6}$$

where x_p^c and x_p^{aq} are the mole fraction of the probe in the polymer pseudophase and aqueous phase, respectively, or

$$K^* = w_p^c/w_p^{aq} \tag{7}$$

where w_p^c and w_p^{aq} now represent the weight fraction of the probe in each phase. This dual treatment is proposed for two reasons. Calculations based on the mole fraction are more meaningful on a molecular level since it is possible to compare with literature data for low molecular weight compounds, such as surfactants. The application of this method is, however, limited to polymeric systems of known molecular weight, and its precision is limited by how accurately the $\bar{M}_n$ value has been determined. This can be considered to be a disadvantage of this approach. For practical reasons, the treatment based on weight fraction seems to be more convenient. The value of x_p^{aq} for P and DMA was evaluated from the solubility of the probes in water using literature data.[2]

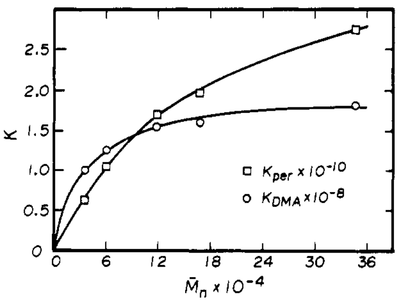

Figure 2. Dependence of the distribution coefficients of P and DMA (K) between polymer pseudophase and aqueous phase on the number-average molecular weight of PSSS–VN copolymers (based on 0.48 g L^{-1} of each copolymer).

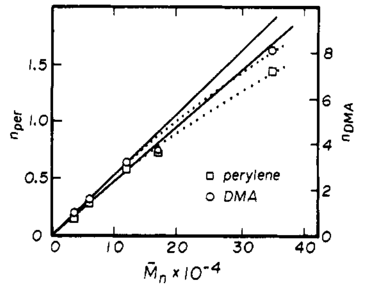

Figure 3. Dependence of the number of molecules of P and DMA statistically solubilized per macromolecule (n) on the molecular weight of the polymer ($\bar{M}_n$) (based on 0.48 g L^{-1} of each copolymer).

Figure 2 displays the dependence of the distribution coefficient, K, for P and DMA on the number-average molecular weight of the five PSSS–VN copolymers. An increase in the molecular weight of the copolymers results in greater values of the distribution coefficient. This implies that the average number of probe molecules solubilized per coil, n, is proportional to the size of the macromolecule. Values of n were calculated by using

$$n = x_p^c/(1 - x_p^c) \tag{8}$$

which requires one to know the total concentration of probe in the saturated aqueous copolymer solution, the solubility of the probe in water, and the copolymer concentration.[2] Figure 3 shows the increase in the number of DMA and P molecules solubilized in aqueous solutions of PSSS–VN as a function of the number-average molecular weight of PSSS–VN. The dependence between n and $\bar{M}_n$ is linear for copolymers 3–5, but the points for copolymers 2 and 1 display a marked deviation from linearity. The fact that copolymer 2 solubilized less than expected, based on this linear behavior, is due to the composition of the

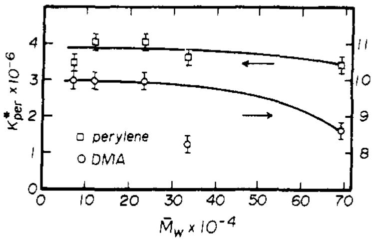

Figure 4. Plot of the distribution coefficient (K^*) of P and DMA on the weight-average molecular weight of PSSS–VN copolymers (based on 0.48 g L^{-1} of each copolymer).

copolymer. As was shown in a previous publication,[2] a copolymer containing more SSS solubilizes less perylene. Presumably the more expanded structure contains a more polar core than the macromolecule with a lower SSS content. Deviation from linearity for copolymer 1 might be a result of its much lower solubility in water. One can imagine the pendant groups in the core of the coil being more tightly packed, making it more difficult for molecules of probe to penetrate within this hydrophobic region.

Statistically one macromolecule of copolymer 1 solubilizes about 5 times more probe than copolymer 5. As one would expect, the number of solubilized molecules per coil is different for each probe and depends on its solubility in water (c_p^{aq}) and distribution coefficient (K).

Figure 4 shows the dependence of the distribution coefficient (K^*), calculated by using the weight fraction as the reference function, on the weight-average molecular weight of PSSS–VN. A change in the value of $\bar{M}_w$ from 7×10^4 to 32.6×10^4 has little influence on the value of K^*. In other words, a defined mass of each copolymer solubilizes essentially the same amount of probe. This indicates that the two-phase model that was proposed to describe the solubilization process in aqueous solution of PSSS–VN is valid. Once again, the distribution coefficient (K^*) is considerably lower for the copolymer of highest molecular weight.

III. Effect of Molecular Weight on the Photocatalytic Activity of PSSS–VN Copolymers. The effect of molecular weight on the photocatalytic activity of PSSS–VN copolymers in aqueous solution was tested for the photosensitized oxidation of P and DMA. The proposed mechanism for this reaction was elucidated by gas chromatographic analysis of the secondary photooxidation products.[2] The low thermal stability of endo peroxides made it impossible to directly detect these compounds. However, the type of secondary products indicated that endo peroxides had to be the primary oxidation products. Based on these results, it was concluded that the sensitized oxidation of P and DMA occurs with participation of singlet oxygen, which is produced when oxygen, dissolved in the core, quenches the electronically excited states of the naphthalene antenna chromophores.[2] The reactions can be described by a pseudo-first-order kinetic equation.[2] The kinetics of the process were compared at the same total concentration of probe in the systems. Table II summarizes the relative rate constants for the photooxidation of P and DMA solubilized in aqueous solutions of PSSS–VN. While the values of the relative rate constants for photooxidation of the two probes are quite different, there is no systematic dependence of the rate constant on the molecular weight for a given probe. This result suggests that only naphthalene chromophores in proximity to PNAs are involved in sensitization and that photon harvesting does not appear to play a significant role in the photocatalytic activity for the oxidation of PNA molecules.

Table II
Relative Rate Constants for the Photosensitized Oxidation of P and DMA Solubilized in Aqueous Solutions of PSSS–VN of Different Molecular Weight

copolymer	$10^3 k_P$, min^{-1}	$10^2 k_{DMA}$, min^{-1}
1	4.4 ± 0.3	7.6 ± 0.2
2	4.2 ± 0.3	7.9 ± 0.2
3	4.8 ± 0.3	8.1 ± 0.3
4	4.2 ± 0.3	8.3 ± 0.3
5	4.4 ± 0.3	7.8 ± 0.2

Conclusions

Copolymers consisting of about 40 mol % SSS and 60 mol % VN in the molecular weight range of $\bar{M}_w$ 7.0×10^4–75.5×10^4 are water soluble. Above a value of $\bar{M}_w$ of about 25×10^4, however, the solubility of the copolymer in water decreases sharply. Preliminary studies using dynamic light scattering suggest that PSSS–VN behaves as a random coil in aqueous solution. The number of molecules that can be solubilized per coil is proportional to the size of the macromolecule. This finding may be important for practical applications of the copolymer as a photocatalyst. By preparing copolymers of specific molecular weight, one can control the number of reactant molecules that are solubilized within the macromolecular coil. This type of control could be used to isolate a molecule and perform chemistry in the absence of competing reactions. The distribution coefficient, calculated based on mole fraction, increases with molecular weight. The same mass of each copolymer, however, solubilizes the same amount of probe. It was also shown that all copolymers display photocatalytic activity. The efficiency of the photosensitized oxidation of P and DMA solubilized in aqueous solutions of PSSS–VN is independent of the molecular weight of PSSS–VN.

Acknowledgment. The financial support of this research by the Natural Sciences and Engineering Research Council of Canada and the Ontario Centre for Materials Research is gratefully acknowledged.

References and Notes

(1) Nowakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1988**, *21*, 3430.
(2) Nowakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1989**, *22*, 2317.
(3) White, B.; Nowakowska, M.; Guillet, J. E. *J. Photochem. Photobiol.* **1989**, *50*, 147.
(4) Nowakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1989**, *22*, 3903.
(5) Elias, H. G. *Macromolecules 1, Structure and Properties*; Plenum Press: New York, 1984.
(6) Bashuk, W.; Benoit, H. *Can. J. Chem.* **1958**, *36*, 1616.
(7) Kerker, M. *The Scattering of Light and Other Electromagnetic Radiation*; Academic Press: San Diego, 1969.
(8) Tanford, C. *Physical Chemistry of Macromolecules*; Wiley: New York, 1963.
(9) Berne, B. J.; Pecora, R. *Dynamic Light Scattering*; Wiley: New York, 1976; Chapter 8.
(10) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
(11) Vancso, G. J. *Macromol. Chem.* **1989**, *190*, 1119.
(12) Nowakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1990**, *21*, 3375.
(13) Schaefer, D. W.; Han, C. C. In *Dynamic Light Scattering*; Pecora, R., Ed.; Plenum Press: New York, 1985.
(14) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(15) Vancso, G. J.; White, B., submitted for publication.
(16) Patterson, L. K.; Vieil, E. *J. Phys. Chem.* **1973**, *77*, 1191.