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Registry No. *rac*-$Et[Ind]_2ZrCl_2$, 100080-82-8; propylene, 115-07-1; polypropene, 9003-07-0.

Forced Rayleigh Scattering on a Soluble Conducting Polymer

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ABSTRACT: Forced Rayleigh scattering (FRS) is used to probe the dynamics of a conducting polymer, poly(3-octylthiophene), in solution. The optical labels employed are photoexcited states on the chains themselves; chemical addition of a photochromic labeling attachment is not required. The main feature of the time dependence of the diffracted intensity is an exponential time decay; from the quadratic dependence of the decay time on the grating wave vector, we find a translational diffusion coefficient in the dilute regime of $(8 \pm 1) \times 10^{-8}$ cm^2/s, corresponding to a hydrodynamic radius of $R_h = 130 \pm 15$ Å. It is shown that the mean value measured in the experiments is the *z*-average diffusion coefficient, in contrast with FRS experiments in which photochromic labels are chemically attached to the ends of the chains. We propose that bipolarons are the excited states responsible for chain labeling, based in part on the photoinduced absorption spectra for poly(3-alkylthiophenes).

Introduction

The technique of forced Rayleigh scattering (FRS), which has alternatively been called holographic grating relaxation spectroscopy and the holographic grating technique,[1-4] has proved to be a powerful tool in the measurement of the diffusive dynamics of condensed phases. The experiment employs an optical pump-and-probe technique: Two coherent, absorbed laser beams (the pump beams) are used to form interference fringes within a sample, resulting in a spatially periodic excited-state

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concentration profile. Such a distribution will, quite generally, form a grating that can be used to diffract a monochromatic probe beam at a wavelength known a priori to be sensitive to the presence of these excited states. If the crossing angle between the two pump beams is θ_c, then the grating period d and the diffraction angle θ_d are, respectively

$$d = \lambda_0/(2 \sin (\theta_c/2)) \tag{1a}$$

$$\theta_d = \sin^{-1} (\lambda_1/d) \tag{1b}$$

where λ_0 (λ_1) is the wavelength of the pump (probe), which, for small θ_c, may be taken as in vacuo.[1c] If the excited states are sufficiently long-lived, then when the pump beam is switched off, the grating will decay as the excited and unperturbed regions diffuse into one another. By monitoring the diffracted beam intensity as a function of time, one can infer the relevant diffusion coefficient.

FRS and other transient grating techniques have been employed in many systems. In particular, Hervet et al.[2] and Léger et al.[3] pioneered the use of FRS as a probe of polymer diffusion by labeling some of the chains with a photochromic dye molecule at each end. Since the labeled chains differ from the others only by the addition of this small molecule, it is valid to assume that the diffusive motion of the labeled chains represents a good approximation to the diffusion properties of the polymer of interest. FRS has since been used (for example) to probe the diffusion dynamics of dilute, semidilute, and entangled polymer solutions,[3-6] as well as polymer gels[7] and polyballs.[8]

Our objective in the present work is to demonstrate the feasibility of FRS experiments for a soluble conducting polymer, poly(3-octylthiophene), in solution. Polymers of this type have attracted much interest recently[9] because of the unique properties of their electronic excited states, which (in the case of a nondegenerate ground state, as in the poly(3-alkylthiophenes)), are generally ascribed to polarons and bipolarons,[10] with associated electronic states within the π–π^* band gap. Our work was motivated by a previous spectroscopic CW photoinduced absorption study[11] of poly(3-hexylthiophene) in solution, which suggested that the preferred excited states were bipolarons. Furthermore, significant ($\sim 10°$) phase shifts and attenuation of the signal with increasing chopping frequency were observed even at chopping frequencies as low as 23 Hz, implying that at least some of these bipolarons were quite long-lived (with lifetimes at least on the order of a few milliseconds). Thus, we reasoned that an FRS-type of experiment should be possible on such systems, using the excited gap states associated with the photogenerated bipolarons as labels. The results reported here are of interest since (i) they provide insight into the dynamics of a conducting polymer in solution and (ii) they suggest that the chemical addition of a labeling molecule is not necessary for conducting polymers, since the requisite nonlinear resonant optical properties are evidently already provided by the photoinduced excited states associated with the backbone itself.

Experimental Section

The poly(3-octylthiophene) (P3OT) used in these studies was provided by Dr. J.-E. Österholm of Neste Corp.; the number-average and weight-average molecular weights, based on GPC, were M_n = 27 000 and M_w = 89 000, respectively. (The monomer molecular weight is 194.) Methods of polymer synthesis and preparation have been reported elsewhere.[12] The solvent employed was spectroscopic-grade 1,2,4-trichlorobenzene (TCB). The P3OT solutions were prepared by stirring the polymer plus solvent at 45 °C for ca. 10 min. The solutions were then filtered through a 5-μm glass mesh into precleaned, sealable UV–vis spectrophotometric cells, with a 1-mm path length and a volume of 0.3 cm^3. When not in use, the solutions were kept in sealed, light-shielded containers. Our FRS apparatus is similar to the one reported by Wesson et al.[7] The pumping irradiation is provided by a 488-nm, 50-mW argon ion laser beam controlled by either a shutter or a chopper. This beam is split into two equally intense portions, which are then crossed at the sample; the range of crossing angles employed for this work was $3° \leq \theta_c < 8°$. The grating is probed with a 4-mW helium–neon laser incident normally; the beams illuminate an area of ca. 0.1 cm^2. The sealed sample cell sits within a copper block in which holes were machined to allow the passage of the beams, and this block is positioned such that the sample sits at the center of a goniometer. A photomultiplier (EMI 9781R) equipped with a notch filter (λ = 632.8 nm, $\Delta\lambda$ = 4 nm) and a 1-mm aperture is placed on the goniometer arm ca. 1 m from the sample; such an arrangement allowed the diffraction angles to be measured to ± 0.1°. The signals were amplified with a current-to-voltage converter with a gain of 4.7 V/μA; the photomultiplier tube current was always <1 μA. The overall bandwidth for the detection apparatus was ca. 50 kHz. Single pump-beam pulses were generated by a mechanical shutter; the resultant diffracted signal was stored on a digital storage oscilloscope and transferred to a computer. Typically, at a given angle, 10–15 signals were averaged in order to increase the signal-to-noise ratio. In the most concentrated of our samples, the 1/10 absorption depth of the pump beam was about 50 μm, which is significantly greater than the largest fringe spacing of 9 μm. All experiments were performed at room temperature. In order to ensure that no permanent changes were introduced by the absorbed pump beam, a control sample was exposed to ~2000 50-mW pulses of 50-ms duration (typically, a total of ~200 pulses are used in our FRS experiments). This extended exposure produced no noticeable changes in the UV–vis absorption spectra.

The pump and probe energies were chosen in accordance with UV–vis and CW photoinduced absorption spectra for these solutions. Thus, P3OT in TCB has an absorption edge at ca. 2.25 eV, and, for a pump energy of 2.54 eV, its highest energy photoinduced absorption peak is at ca. 1.44 eV, with a fwhm of ca. 0.3 eV.[11a] (These results are not significantly different from our previously reported work involving poly(3-hexylthiophene) in methylene chloride).[11b] Photoinduced absorption is directly sensitive only to changes in the imaginary part of the index of refraction. However, both real and imaginary changes in the index of refraction will produce excited-state gratings in an FRS experiment.[13] Since the probe energy is located just below the band edge on the tail of a photoinduced absorption peak, one expects (from Kramers–Kronig analyses) that changes in the real part will be significant as well. Thus, we expect both amplitude and phase-grating contributions to the diffracted signal.

In an FRS experiment, the photoinduced grating can relax via inter- or intramolecular relaxation of the excited states, or diffusion, or a combination of these modes.[5,6] If the first spatial harmonic c_q of the excited-state concentration profile (at wave vector $q = 2\pi/d$, where d is the grating spacing given in eq 1a) decays as $e^{-t/\tau}$, then the resultant diffracted intensity will be given by[2-5]

$$I(t) = (Ae^{-t/\tau} + B)^2 + C^2 \tag{2}$$

where A, B, and C are time-independent: A^2 is the grating efficiency (in appropriate units), while B and C represent coherent and incoherent base-line scattering, respectively. In our analyses, B is set to zero in all cases. Also, the base-line contribution C^2 is obtained by using the pretrigger feature of the oscilloscope. If the relaxation rates for diffusion across a fringe spacing are very much shorter than the intrinsic excited-state decay rates, then diffusion is the dominant mode for grating relaxation, and the rate constant is given by $1/\tau = Dq^2$, where D is the diffusion coefficient of the labeled species. If, on the other hand, intra- or intermolecular decay rates ($1/\tau_{in}$) become comparable to q^2D, then the deviations from the pure q^2 dependence are observed; for example, if the excited-state decay is intramolecular (with a decay rate of $1/\tau_{in}$), the grating relaxation rate becomes $1/\tau$ =

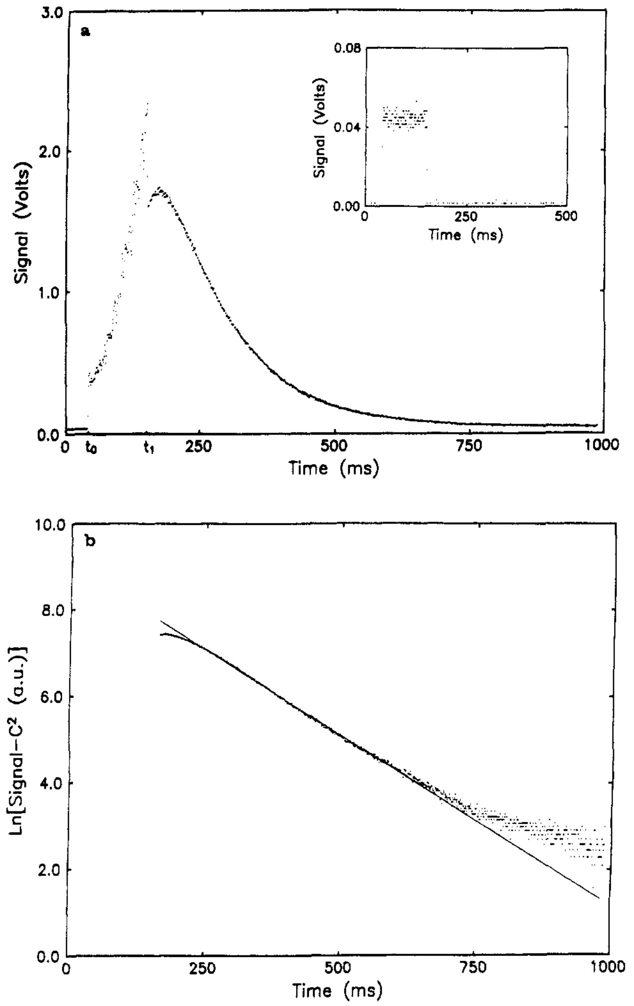

Figure 1. (a) Photomultiplier voltage as a function of time for a photoexcited grating, with $q^2 = 5.6 \times 10^7$ cm^{-2}. The pump beam shutter is opened at time t_0 and closed at time t_1. The inset shows the fluorescent contribution to the signal, obtained with the probe beam blocked. (b) Natural logarithm of the signal depicted in (a) for $t > t_1$. The solid line shows a best fit to the linear region and has a slope of $2/\tau = 7.9 \times 10^{-3}$ Hz. Note that the signal decreases exponentially for 2.5–3 decay times.

$1/\tau_{\text{in}} + Dq^2$. In any case, the role of diffusion can be ascertained by determining the dependence of the rate constant on the grating wave vector q.

Results

In Figure 1a we show the profile for the diffracted intensity vs time for a 3.1 mg/mL P3OT/TCB solution for a fringe spacing of $d = 8.4$ μm ($q^2 = 5.6 \times 10^7$ cm^{-2}). The pump beam was controlled by a shutter opened at time t_0 and closed at time t_1. The pulse width $t_1 - t_0$ was varied in order to obtain the maximum signal-to-noise ratio; we found that the optimum signal was obtained for a pulse width of ca. 80% of the approximate $1/e$ decay time of the signal. In a separate experiment, we verified that the decay time itself was independent of the pulse width. The signal has several distinct parts: (a) a fast rise at $t = t_0$, limited by the shutter speed (ca. 0.5 ms); (b) a slower increase in the signal for $t_0 < t < t_1$; (c) a fast decay at $t = t_1$, also limited by the shutter speed; (d) a small increase in the signal after $t = t_1$; and (e) a much longer time-scale decay. That the signal depicted arises from the formation of a grating is evidenced by the following observations: (i) The signal disappears if one of the pump beams is blocked or (ii) if the detector is intentionally mispositioned at an angle that differs by more than 0.2° from the diffraction angle predicted by eq 1b. (iii) If the probe beam is blocked, the resultant signal is a much smaller square pulse that follows the pump beam, as shown in the inset of Figure 1a. The amplitude of this square pulse is independent of angle; it is evidently due to luminescence radiation at the wavelength passed by the notch filter.

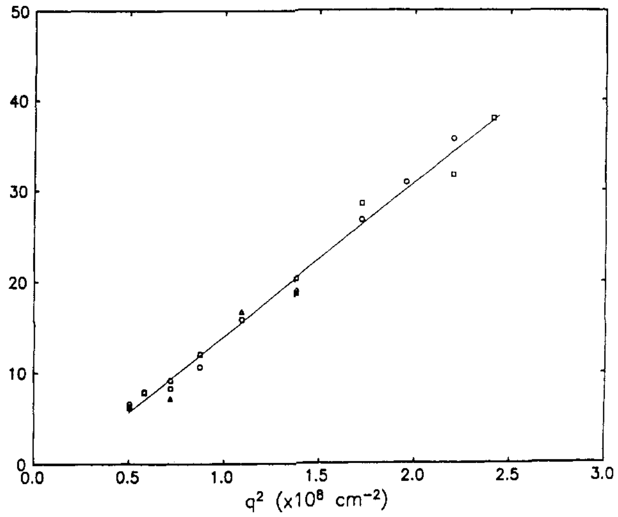

Figure 2. Rate constant $2/\tau$ of the slow decay as a function of the square of the grating wave vector, $q^2 = 4\pi^2/d^2$, for various concentrations. From the slope of the best-fit line we obtain the diffusion coefficient $D = (8 \pm 1) \times 10^{-8}$ cm^2/s. Key: (□) $c = 5$ mg/mL; (○) 3.1 mg/mL; (△) $c = 1.7$ mg/mL.

In Figure 1b, the natural logarithm of the signal, with the pretrigger base line subtracted away, is shown vs time. Obviously, the small increase in the amplitude after the shutter is closed cannot be explained by eq 2. However, the subsequent slow decay is seen to be exponential for 2.5–3 time constants and hence is well described by eq 2 with $B = 0$ in this region. As the signal approaches the base line, the error associated with setting $B = 0$ in eq 2 becomes more serious, and nonexponential behavior appears. From a best fit to the linear portion we obtain the rate constant $2/\tau = 7.9$ Hz ± 5%.

In order to determine the role of diffusion in the temporal behavior of the signal, we plot the rate constant $2/\tau$ vs q^2 for several different concentrations of P3OT in TCB in Figure 2. The rate constant is seen to be proportional to q^2 in the range $5 \times 10^7 < q^2 < 2.4 \times 10^8$ cm^{-2}; evidently, the grating relaxation mechanism is purely diffusive in this region. From the slope of the best fit line we obtain the diffusion coefficient $D = (8 \pm 1) \times 10^{-8}$ cm^2/s. Further, it is also seen that this diffusion constant is independent of the concentration in the region $1.5 < c < 5.0$ mg/mL. This confirms that the experiments probe the dilute regime. From the measured diffusion coefficient and the relation $D = kT/(6\pi\mu R_{\text{h}})$, where kT is the temperature and μ is the viscosity of TCB[14] at room temperature, we obtain an effective hydrodynamic radius $R_{\text{h}} = 130 \pm 15$ Å.

Discussion

It seems clear from the data that the slow-decay portion of the signal arises from macromolecular diffusion. Thus, we first consider the question of which mean value of the diffusion coefficient is measured in our FRS experiments. This follows from the expression for the grating efficiency η as a function of the peak-to-peak changes in the real and imaginary parts of the index of refraction ($\Delta\tilde{n}$ and Δk, respectively):[13]

$$\eta(\omega) = f(\theta,\omega)(\Delta\tilde{n}^2 + \Delta k^2) \qquad \eta \ll 1 \qquad (3)$$

where $f(\theta,\omega)$ is a function of the diffraction angle θ and the probe energy ω but is independent of the molecular properties of the sample. $\Delta\tilde{n}$ and Δk are proportional to the number of excited states per unit volume[13] that label the grating, N_1: $\Delta\tilde{n} = (\partial\tilde{n}/\partial N_1)N_1$, $\Delta k = (\partial k/\partial N_1)N_1$, so that

$$\eta(\omega) = f(\theta,\omega)((\partial\tilde{n}/\partial N_1)^2 + (\partial k/\partial N_1)^2)(N_1)^2 \qquad (4)$$

Hence, the grating efficiency scales with the square of the excitation density N_1. If the probability of excitation *per monomer* is independent of molecular weight, then the number of these excitations created on a given chain will be proportional to that chain's molecular weight. Thus we infer from (4) that the diffracted intensity $I_q(t)$ for a polydisperse sample is

$$I_q(t) \sim \sum_i n_i(M_i)^2 \exp(-D_i q^2 t) \Big/ \sum_i n_i(M_i)^2 \qquad (5)$$

where n_i and D_i are the number per unit volume and the diffusion coefficient for chains of length i, respectively. Following Léger et al.,[4] we develop $I_q(t)$ in a cummulant expansion:[15]

$$I_q(t) \sim \exp(-\bar{D}_s q^2 t)\Big(1 - q^2 t \sum_i n_i(M_i)^2 (D_{si} - \bar{D}) \Big/ \sum_i n_i(M_i)^2 + q^4 t^2 \sum_i n_i(M_i)^4 (D_{si} - \bar{D})^2 \Big/ \sum_i n_i(M_i)^2 + \dots\Big) \qquad (6)$$

where $\bar{D}$ is the mean that results in the vanishing of the second term in the series; i.e.

$$\bar{D} = \sum_i n_i(M_i)^2 D_i \Big/ \sum_i n_i(M_i)^2 \qquad (7)$$

Thus, we conclude our FRS experiments are sensitive to the z-average diffusion coefficient, contingent upon the following conditions: (1) The change in the real (or complex) diffraction coefficient is proportional to the number of excited states produced and (2) the probability of excitation per monomer is independent of molecular weight. Equation 7 is, of course, familiar from quasi-elastic light scattering (QELS), which measures the same average.[16] This result is quite different, however, from the FRS experiment considered by Léger et al.[4] in which the chains are labeled chemically. In that case photochromic molecules are attached to the ends of the chains; all chains have the same probability of becoming labeled. Thus, Léger et al. find that FRS experiments using polymers labeled in this fashion will measure the number-average diffusion coefficient, in sharp contrast to present considerations.

It is evident that the excited states serving to label the chains have intrinsic lifetimes in excess of 0.2 s since, as shown in Figure 2, we observe $2/\tau \sim q^2$ down to $2/\tau = 5$ Hz. As mentioned previously, the CW photoinduced absorption spectra of solutions of poly(3-alkylthiophenes) imply that bipolarons are photoproduced and that at least some of the bipolarons have lifetimes on the order of or greater than a few milliseconds. In fact, it should be noted that because of various forms of disorder (e.g., chain kinks), one expects a rather large range of characteristic excitation lifetimes. Indeed, although fast photoinduced absorption (FPA) data are not available for conducting polymers in solution, several studies of FPA for thin films of polyacetylene[17] and other conducting polymers show a much faster decay mode (<1 ns) associated with intrachain recombination of the gap states. Thus we suggest that the fast, "discontinuous" portions of the signal (at t_0 and t_1) arise from subnanosecond photoproduction and decay of the bipolarons. The slower rise during the pump pulse is indicative, we believe, of much longer lifetimes attributable to trapping of the bipolarons by chain kinks or impurities. These "frozen" excitations would then serve as labels as the chains diffuse. Forced Rayleigh scattering at a single probe wavelength cannot, of course, independently confirm or refute these ideas; future experiments involving FPA in solution and/or a spectroscopic study of the FRS signal as one changes the probe wavelength should prove quite useful in further exploring the precise nature of the excitations.

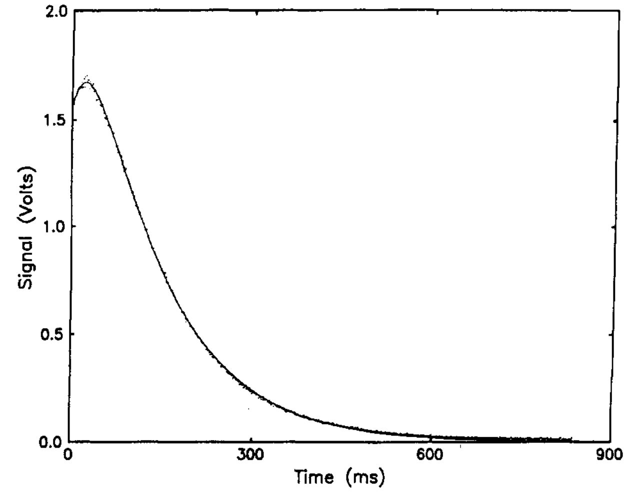

Figure 3. The same data as in Figure 1a, this time fit to the function $f(t) = (A_1 \exp(-t/\tau_1) - A_2 \exp(-t/\tau_2))^2$. The origin ($t = 0$) has been shifted to coincide with closing of the pump beam shutter. The fit yields $A_1 = 1.64$ $\mathrm{V}^{1/2}$, $1/\tau_1 = 4.05$ Hz, $A_2 = 0.38$ $\mathrm{V}^{1/2}$, and $1/\tau_2 = 28.7$ Hz.

It is important to address the possible role of local heating in our experiments. Thus, Eichler et al.[19] and others[20] have used the FRS technique to pump a *thermal* grating in various organic solvents doped with an absorbing dye. Certainly there is no reason to rule out thermal gratings in our experiments a priori; however, organic solvents typically have thermal diffusivities[21] of $D_T \sim 10^{-3}$ cm^2/s (as seen, for example, in the FRS experiments of Eichler et al.). Since this differs from our result by 3 orders of magnitude or more, we can safely conclude that heating plays no role in the slower rise and decay processes comprising our signal. However, since the faster portions at t_0 and t_1 are limited by the shutter response, we cannot rule out thermal processes contributing to these signatures. While important, these considerations do not affect our calculation of the diffusion coefficient corresponding to the slow decay time nor its assignment to polymer diffusion.

The short interval during which the signal increases slightly after the pump is switched off is somewhat more difficult to interpret. Such features have been frequently reported in the literature[5b,22-24] and are generally attributed to the presence of two diffusants that form gratings which are 180° out of phase.[6,23,24] In this case, eq 2, representing the diffracted intensity as a function of time, must be replaced with

$$I(t) = (A_1 \exp(-t/\tau_1) - A_2 \exp(-t/\tau_2))^2 + C^2 \qquad (8)$$

In Figure 3 we present again the data of Figure 1 (with the pretrigger base line C^2 subtracted away), this time fit to eq 8, using A_1, A_2, $1/\tau_1$, and $1/\tau_2$ as the adjustable parameters in a nonlinear least-squares routine. We see that (8) provides a good fit except in the base-line region where, as argued above, the neglect of the coherent base-line contribution becomes unjustified. The fit yields $A_1 = 1.64$ $\mathrm{V}^{1/2}$, $1/\tau_1 = 4.05$ Hz, $A_2 = 0.38$ $\mathrm{V}^{1/2}$, and $1/\tau_2 =$

28.7 Hz. We note that $2/\tau_1$ is quite close to the rate constant determined from the slope of the linear region of the semilogarithmic plot (see Figure 2). Fits for intensity profiles at other values of q^2 yielded similar results, with approximately the same ratio of τ_1/τ_2. Thus, from a phenomenological standpoint, the maximum in the data can be explained by the presence of a smaller fraction of faster ($D_2/D_1 \cong 6.3$), hydrodynamically smaller diffusant, which forms a grating 180° out of phase with the one considered above. Although the precise identity of this additional participant is unclear, effects of this type are perhaps not surprising when one considers the polydisperse nature of our samples.

Conclusion

We have demonstrated that forced Rayleigh scattering can be used to measure the z-average diffusion coefficient of a conducting polymer in dilute solution, using excited states on the chains themselves as optical labels. For P3OT in trichlorobenzene we obtain $D = (8 \pm 1) \times 10^{-8}$ cm^2/s and (hence) a hydrodynamic radius of $R_h = 130 \pm 15$ Å. We suggest that the excitations are bipolarons, since (i) bipolaron-type signatures are observed in photoinduced absorption measurements of the same system and (ii) this hypothesis offers a fairly straightforward explanation of the rather disparate features seen in the time decay of the grating. The experiments employ the oft-studied nonlinear/photochromic optical properties of conducting polymers in a new manner. Since the system we have studied is by no means atypical, this technique should be applicable to other soluble conducting polymers as well.

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