# Diffusion in Polymer Solutions Studied by Fluorescence Correlation Spectroscopy

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We employed fluorescence correlation spectroscopy (FCS) to study the diffusion of molecular and macromolecular tracers in polystyrene solutions over a broad range of concentrations ($c$) and molecular weights ($M_{w,m}$) of the matrix polymer. Molecular tracer diffusion scales only with the matrix concentration and superimposes on a single, nonpolymer specific, curve. On the contrary, the diffusion of macromolecular tracers in solutions of matrix polymers with $M_{w,m}$ sufficiently larger than the tracer molecular weight scales with $c/c_p^*$, where $c_p^*$ is the tracer overlap concentration. We further demonstrate that FCS can address local and global dynamics simultaneously.

## 1. Introduction

A comprehensive understanding of tracer diffusion in nondilute polymer solutions is a longstanding research issue, which has attracted standing interest during several decades.[1−17] Diffusion in polymer solutions and gels is important for many biological and industrial applications, e.g., drug delivery in living tissue, polymer production, doped electrically conducting polymers, and porous chromatography. Small molecule diffusion in polymer solutions can sense the microscopic friction, which for sufficiently large molecular probes is proportional to segmental friction coefficient extracted from viscosity measurements.[13] In semidilute polymer solutions, the reduction of the tracer diffusion is usually discussed in terms of spatiotemporal properties of both the matrix and the tracer species.[12] These properties are expressed by the size ($R$) of the diffusant and the mesh size ($\xi$) for the polymer solution and its global dynamics relative to the time that the diffusant needs to cover the distance $\xi$. The concentration dependence $D(c)$ of the tracer diffusion of a large probe in a matrix with similar size resembles the concentration dependence of the self-diffusion coefficient.[2] It can therefore be represented either by the scaling laws of the matrix self-diffusion in the semidilute and concentrated regime or by a semiempirical exponential law that should depend on the diffusant size.[8,14,15] It is this size-dependent dynamics[11] that is receiving attention[17] since it provides new means to investigate host matrix mobility at different length scales.

A number of experimental techniques have been developed and used to study polymer chains diffusion and/or small tracer diffusion in dilute and nondilute polymer solutions. Most commonly used methods include, for example, pulsed-field-gradient (PFG) NMR,[6,10,18] forced Rayleigh scattering,[2−4] Taylor dispersion,[7] fluorescence recovery after photobleaching (FRAP),[12] dynamic light scattering (DLS),[5] and X-ray photon correlation (XPCS).[17] Each of these techniques is typically tailored for a certain range of concentrations or diffusion coefficient values. In recent years, the fluorescence correlation spectroscopy (FCS) has emerged as a powerful tool for investigation of the diffusion of fluorescent molecules, macromolecules, or nanoparticles in various environments. The method is based on detecting the fluctuations of the fluorescent light intensity caused by the diffusion of the fluorescent species through a small observation volume defined by the focus of a confocal microscope.[19,20] In this respect FCS is a single-molecule spectroscopic technique free of intermolecular interactions and slow contributions, e.g., clusters, as compared to DLS and XPCS possessing in addition species selectivity. Despite its great potential and high versatility in addressing the diffusion and transport properties in complex systems, so far utilization of fluorescent correlation spectroscopy has been limited mainly to biological, i.e., aqueous environments.[19−27] Only very recently FCS was successfully applied to study the size and conformation of macromolecules in organic solvents,[28,29] adsorbed polymers,[30−32] grafted gels,[33] colloidal suspensions,[34] and polymer melts.[35] With respect to nondilute solutions of synthetic polymers in organic solvents, FCS was used to study the small dye diffusion[36] and the polymer self-diffusion[8,36−38] in polystyrene/toluene solutions.

In this work, we utilize FCS to measure the diffusion of tracers with different sizes in polystyrene (PS) solutions in order to address the relation of tracer diffusion to polymer specific properties and examine some unique features of FCS, i.e., diffusion of molecular and polymeric probes simultaneously. As tracers we used functionalized perylene dye *N*-(2,6-diisopropylphenyl)-9-(*p*-styryl)perylene-3,4-dicarboximide (PMI) as well as three PS batches with different molecular weights ($M_w \sim 34$, 255, and 340 kg/mol) labeled with the PMI chromophore, which was chosen on the account of its high quantum efficiency and excellent photostability.[39−41] Acetophenone was used as a good solvent for PS for its low vapor pressure and high boiling temperature. Furthermore, the data for the PS diffusion in concentrated solutions may help to get better inside on the recently reported[42−44] effect of microstructure formation by inkjet drop deposition of solvents on a PS substrate.

## 2. Experimental Section

**2.1. Materials.** Polystyrenes with different molecular weights ($M_w$) (34−1700 kg/mol) and low polydispersities ($M_w/M_n$) were prepared using anionic polymerization technique described elsewhere.[45,46] Three batches of polystyrene, PS-34 ($M_w = 34$

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kg/mol, $M_w/M_n = 1.05$), PS-255 (255 kg/mol, 1.07), and PS-340 (340 kg/mol, $M_w/M_n = 1.17$), were covalently labeled with *N*-(2,6-diisopropylphenyl)-9-(*p*-styryl)perylene-3,4-dicarboximide (PMI), a perylene chromophore bearing styrene functionality.[47,48] In the termination step of polymerization, after obtaining the required molecular weight, a solution of the chromophore in THF (molar ratio of the dye to polystyrene 5:1) was added into the living polystyrene solution (in cyclohexane) and the reaction mixture stirred for 72 h at room temperature. The living anionic ends were quenched by addition of methanol. The polymer was twice precipitated in methanol to remove the excess of dye, and then dried in vacuum for 48 h. It is important to emphasize at this point that we did not precipitate more often, i.e., until complete removal of the unattached dye, because (as shown below) FCS can easily separate the contributions of tracers with different sizes. The fluorescently labeled polystyrenes were characterized by gel permeation chromatography (using PS standards and THF as eluent) and $^1$H NMR.

The tracers PMI, PS-34, PS-255, and PS-340 were dissolved in acetophenone or toluene (Sigma-Aldrich) at concentrations of around $5 \times 10^{-8}$ M. Unlabeled polystyrenes with different molecular weights were gradually added to these solutions as matrix polymers up to the desired host concentration. The solutions were stirred by a magnetic stirrer at 700−1000 rpm for an extended period of time ranging from 4 to 24 h. Due to their very high viscosity, the solutions with PS concentration above 0.1 g/mL could not be mixed with magnetic stirrer and were therefore left at ambient temperature for more than 2 days before they were used.

**2.2. Techniques.** ***Dynamic Light Scattering (DLS).*** DLS experiments were carried out in the angular range $30° < \theta < 150°$ using a commercial instrument (ALV-5000, ALV-GmbH, Langen, Germany). A Krypton-ion laser was used as a light source (wavelength $\lambda = 647.1$ nm). A cylindrical cell having an inner diameter of 18 mm was placed in a thermostatic bath. All studied solutions were filtered directly into the cylindrical cell through 0.45 $\mu$m membrane filters (Millipore). All experiments were performed at room temperature ($T = 25$ °C) at which the viscosity of the neat acetophenone is $\eta = 1.62$ mPa·s.

***Fluorescence Correlation Spectroscopy (FCS).*** FCS experiments were performed on a commercial FCS setup (Carl Zeiss, Jena, Germany) consisting of the module ConfoCor 2 and an inverted microscope model Axiovert 200. A 40× Plan Neofluar objective with a numerical aperture of 0.9 and oil as immersion liquid were used in this study. The fluorescence species were excited by He−Ne laser at 543 nm and the emission was collected after filtering with a BP560-615 band-pass filter. For detection, an avalanche photodiode enabling single-photon counting was used. An eight-well glass chamber (Helma, Germany) was used as sample cell for the polymer/acetophenone solutions. This chamber has a bottom slide with high optical quality surface and thickness of 0.17 mm. To prevent evaporation of the organic solvent during the experiments the sample chamber was covered with a thin glass slide. For each solution, series of 20 measurements with total duration 10 min were performed. The final results were obtained as an average of 2−4 experiments performed with different sample loading and preparation.

## 3. Results and Discussion

In a FCS experiment, the fluorescence light, emitted by chromophores diffusing through a small observation volume, formed by the laser focused into the sample of interest is detected and analyzed. As the fluorescent molecules diffuse in and out of the observation volume, they cause temporal fluctuations of the detected fluorescence intensity $\delta F(t')$ defining the autocorrelation function $G(t) - 1 = \langle \delta F(t')\delta F(t' + t)\rangle / \langle F(t')\rangle^2$.

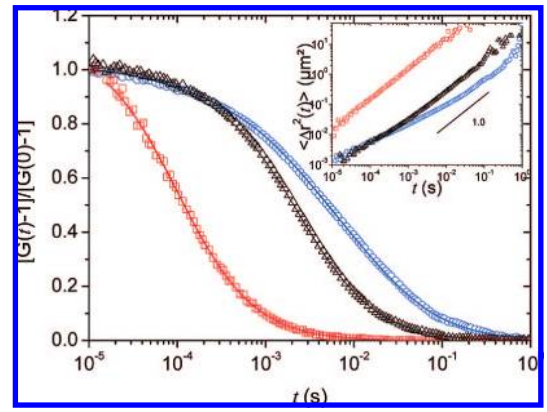


**Figure 1.** Normalized correlation functions of (□) free PMI, (△) PS-34, and (○) mixed probes (PMI, PS-34, and PS-255) present in the PS-220/acetophenone solution with concentration of 0.1 g/mL represented by eq 1 (solid lines). The mean square displacement (eq 2) for the three tracers is shown in the inset.

For an ensemble of $m$ different types of freely diffusing fluorescence species, this autocorrelation function can be analyzed using following analytical equation:[19,20]

$$G(t) = 1 + \left[1 + \frac{T}{1-T}e^{-t/\tau_T}\right]\frac{1}{N}\sum_{i=1}^{m}\frac{f_i}{\left[1+\frac{t}{\tau_{D_i}}\right]\sqrt{1+\frac{t}{S^2\tau_{D_i}}}} \quad (1)$$

where $N$ is the average number of diffusing particles in the observation volume, $T$ and $\tau_T$ are the fraction and the decay time of the triplet state, $\tau_{D_i}$ is the diffusion time of the $i$th species, $f_i$ is the fraction of component $i$, and $S$ is the so-called structure parameter, $S = z_0/x_0$; $z_0$ and $x_0$ represent the axial and radial dimensions of the confocal volume, respectively. Furthermore, the diffusion time $\tau_{D_i}$ is related to the respective diffusion coefficient $D_i$ through[19,20] $D_i = x_0^2/4\tau_{D_i}$.

Figure 1 shows typical normalized autocorrelation functions for the diffusion of PMI, PS-34, and a mixture of PMI, PS-34, and PS-255 in the same polymer matrix (unlabeled PS220/acetophenone at $c = 0.1$ g/mL). The overall concentration of the fluorescent molecules in all three cases was in the order of $5 \times 10^{-8}$ M and $G(t)$ for PMI can be nicely represented by eq 1 (solid red line) assuming only one type of diffusing species ($m = 1$) with diffusion time $\tau_{PMI}$. As mentioned in the Experimental Section the fluorescently labeled PS samples contain free PMI and hence $G(t)$ for PS-34 displays the diffusion of both PS-34 and PMI. For the representation of the experimental $G(t)$ with eq 1 (black solid line in Figure 1) a second component ($m = 2$) is therefore needed. The decay time of the fast component ($i = 2$) deduced from this fit was found to compare very well with $\tau_{PMI}$. The molar fraction ($f_2$ in eq 1) of this fast (PMI) component was 8%. The representation of $G(t)$ for the three-component (PMI, PS-34, and PS-255) solution is addressed below.

For statistically independent freely diffusing fluorescent tracers, $G(t)$ is directly related to the tracer mean square displacement $\langle \Delta r^2(t)\rangle$ through[22,23]

$$G(t) = 1 + \frac{1}{N}\left(1 + \frac{2}{3}\frac{\langle \Delta r^2(t)\rangle}{{x_0}^2}\right)^{-1}\left(1 + \frac{2}{3}\frac{\langle \Delta r^2(t)\rangle}{{z_0}^2}\right)^{-1/2} \quad (2)$$

The inset in Figure 1 displays the mean square displacement $\langle \Delta r^2(t)\rangle$ vs $t$ in a log−log plot exhibiting the characteristic for a random Brownian diffusion slope of 1. The plots for PS-34 and for the mixture of PMI, PS-34, and PS-255 show multiple slopes due to the simultaneous diffusion of species with different sizes recovering, however, the slope of 1 at long times.

The representation of the experimental autocorrelation $G(t)$ by eq 1 yields $\tau_{D_i}$ and hence the diffusion coefficient of the $i$th tracer $D_i = {x_0}^2/4\tau_{D_i}$. However, as the value of $x_0$ depends strongly on the geometrical characteristics of the optical setup, a suitable calibration is required.[34,35] The diffusion coefficients $D_{\text{PS-255}} = 8.9 \times 10^{-8}$ cm$^2$/s and $D_{\text{PS-340}} = 7.4 \times 10^{-8}$ cm$^2$/s in dilute PS-255 and PS-340/acetophenone solutions measured by DLS were used as standards. FCS experiments on the same solutions yielded the diffusion times of $\tau_{\text{PS-255}} = 1365$ $\mu$s and $\tau_{\text{PS-340}} = 1700$ $\mu$s which led to $x_0 \approx 0.22$ $\mu$m used hereafter to calculate the tracer diffusion coefficients.

**3.1. Molecular Dye Diffusion.** The diffusion of the PMI dye in PS ($M_w = 110-450$K)/acetophenone solutions was measured over a very broad range of matrix PS concentrations up to $c = 0.44$ g/mL. The diffusion time $\tau_{\text{PMI}}$ ranges from about 60 $\mu$s in the dilute regime up to 1100 $\mu$s at the highest concentration. The variation of the normalized diffusion coefficient $D(c)/D_0$ with PS concentration is shown in the plot of Figure 2; $D_0 = 2.1 \times 10^{-6}$ cm$^2$/s is the diffusion coefficient of PMI in acetophenone. At low PS concentrations, the diffusion coefficient is virtually constant irrespective of the matrix $M_{w,m}$ in the examined range 110−450 kg/mol. Replacing acetophenone with another good solvent for PS does not alter this behavior as shown by the PMI diffusion data in PS (220K)/toluene solutions. Hence, the results in Figure 2 present a general trend which is independent of the matrix molecular weight and irrespective of good solvents. Such type of "master curves" are commonly represented either by polynomial[13,47] or exponential[12,27] functions. Their fit to the experimental data yields: $D/D_0 = 1 - 5.0c + 8.9c^2 - 5.5c^3$ or $D/D_0 = \exp(-9.9c^{1.35})$. This lack of polymer specificity clearly shows that the diffusion of small tracers ($R \sim 1$ nm) does not relate to the mesh size $\xi$ of the polymer network which for good solvents scales with $(c/c^*)^{-3/4}$ with $c^*$ being the crossover concentration to semidilute solution, i.e., molecular weight dependent. Proposed dependences to $\xi$ would imply a successful superposition only for a plot of $D$ vs $c/c^*$.

The plot of Figure 2 can accommodate reported diffusion coefficients for similar systems obtained by different experimental techniques. Meerwall et al.[1] have studied the diffusion of hexafluorobenzene in PS (10K to 1000K)/THF solutions. Similarly to our results they found that the diffusion of a small probe was independent of the matrix sizes.[1,13] More recently, Chekal and Torkelson[10] reported similar behavior for a styrene monomer diffusing in PS solutions down to a matrix PS molecular weight $M_w$ of 1300 g/mol. The present FCS data in Figure 2 are in very good agreement with the literature results establishing the scaling $D/D_0$ vs $c$ (and not $c/c^*$) for the normalized diffusion of small probes in various polymer/good solvent systems. The polymeric nature of the matrix expressed in the crossover concentration does not affect the small probe behavior. Instead, it is only the crowding effect of the environment molecules that reduces the diffusion rate of the small probes in such solution. Albeit the underlying physics is different, the proximity of the virial coefficient (5.0) in the polynomial fit of $D/D_0$ vs $c$ with the corresponding value (5.3) for the normalized short time diffusion of hard-sphere colloids[49] is quite remarkable.

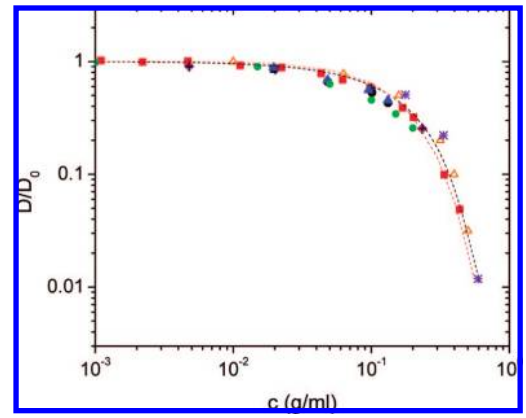


**Figure 2.** Normalized diffusion coefficients of various small molecules in PS solution: PMI in (●) PS (110K), (■) PS (220K) and (◆)PS (450K) in acetophenone, (▲) PMI in PS (220K)/toluene, (△) hexafluorobenzene in PS (10K−1000K)/THF,[1] (●) Rh6G in PNIPAAM/ethanol,[31] and (*) anthracene in PS (50K)/THF.[13] The dashed line represents the fitting (black) polynomial and (red) exponential function.

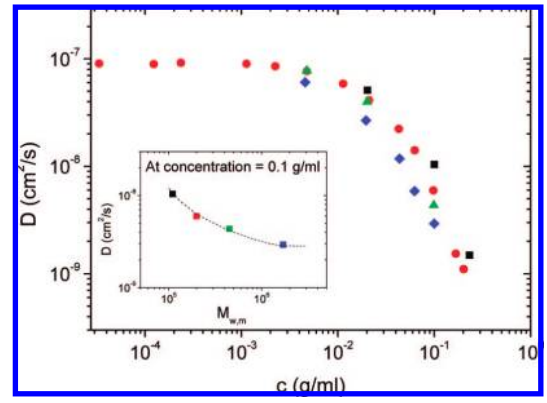


**Figure 3.** Dependence of the diffusion coefficient of PS-255 ($M_{w,p} = 255$k) on the matrix polymer concentration for various matrix PS molecular weights: (■) $M_{w,m} = 110$K, (●) $M_{w,m} = 220$K, (▲) $M_{w,m} = 450$K, (◆) $M_{w,m} = 1700$K. Inset: Diffusion coefficient of PS-255 at $c = 0.1$ g/mL versus matrix molecular weight (dashed line is guide for the eye).

**3.2. Macromolecular Tracer Diffusion.** We studied the diffusion of three polystyrene tracers (PS-34, PS-255, and PS-340 fluorescently labeled with PMI) in unlabeled PS matrices in acetophenone for various molecular weights and polymer matrix concentration. The diffusion coefficient $D_0$ of PS-34, PS-255, and PS-340 in neat acetophenone amounts to $2.5 \times 10^{-7}$, $8.9 \times 10^{-8}$, and $7.4 \times 10^{-8}$ cm$^2$/s, respectively. Figure 3 shows the diffusion coefficient of PS-255 probe as a function of the matrix PS concentrations for four different molecular weights of the PS matrix. As expected, the diffusion coefficient of the polymer probe decreases strongly with matrix concentration.

At a given matrix concentration, the polymer probe diffusion becomes independent of the matrix molecular weight, $M_{w,m}$, when the latter well exceeds the molecular weight of the probe, $M_{w,p}$ as shown for PS-255 in the inset of Figure 3 at polymer matrix concentration of 0.1 g/mL. This finding is in agreement with earlier work which has shown that the probe diffusion would no longer depend on the matrix molecular weight when the latter is 3−5 times larger than the respective probe.[2,4] Consequently, in order to discuss the concentration dependence

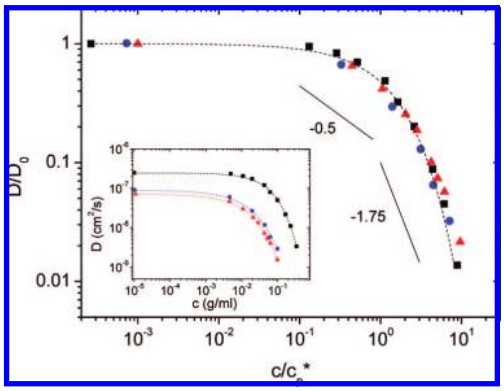


**Figure 4.** Normalized diffusion coefficients of all polymer probes in matrices with 3−5 times larger than polymer probes in acetophenone solutions (■) PS-34 in PS220K, (●) PS-255 in PS1700K, (▲) PS-340 in PS1700K plotted vs $c/c_p^*$. Sold lines indicate the slopes −0.5 and −1.75 from scaling concepts whereas the dashed line describes the empirical equation $D/D_0 = \exp[-0.84(c/c_p^*)^{0.74}]$. The inset shows authentic diffusion coefficients of all labeled PS vs matrix concentration.

of the probe diffusion, we have studied the diffusion of the three polymeric probes in matrices with $M_{w,m} \geq 5M_{w,p}$, i.e., PS-34 in PS220K, PS-255 in PS1700K, and PS-340 in PS1700K, all in acetophenone solutions. The inset in Figure 4 depicts the dependence of the diffusion coefficients of the three tracers on the matrix concentration.

Albeit the implicit $M_{w,p}$ dependence is eliminated and the effect of $M_{w,m}$ is weak ($M_{w,m} \geq 5M_{w,p}$), the slowing down of the tracer diffusion for PS-34 and PS-340 at high matrix concentrations is still rather different. This behavior reflects the different self-diffusion mechanisms in dilute and nondilute polymer solutions. The tracer polymer will fill the polymer matrix ($M_{w,m} \geq 5M_{w,p}$) at a matrix concentration $c$ at which its mesh size $\xi_m$ ($<R_{g,m}$) reaches the diffusant size ($\sim R_{g,p}$), i.e., at the overlap concentration $c_p^* = [3M_{w,p}/(4\pi N_A R_{g,p}^3)]$[50] of a virtual semidilute solution of the polymeric probe; $N_A$ is Avogadro's number, $R_{g,p} = 1.3R_{h,p}$ in good solvent[51] is the radius of gyration of the probe and $R_{h,p} = kT/6\pi\eta D(c=0)$ is the hydrodynamic radius. Hence, $c_p^*$ amounts to 0.037, 0.013 and 0.010 g/mL for PS-34, PS-255, and PS-340 respectively. Indeed, the presentation $D(c)/D(c=0)$ versus $(c/c_p^*)$ leads to a successful superposition as seen in Figure 4. This single "master curve" implies that the tracer diffusion shows a self-diffusion behavior with concentration dependence predicted by scaling concepts,[52,53] i.e., slopes −0.5 and −1.75, respectively, in the semidilute and entangled regimes always referred to $c_p^*$.

The normalized diffusion data of Figure 4 can be represented by a modified version of the exponential concentration dependence

$$D = D_0 \exp(-\alpha(c/c_p^*)^u) \quad (3)$$

with $\alpha = 0.84 \pm 0.03$ and $u = 0.74 \pm 0.04$. The initially proposed[14,15] exponential equation

$$D = D_0 \exp(-\alpha' c^u) \quad (4)$$

where $\alpha'$ is proportional to the polymer size and the exponent $u$ accounts for the interactions (topological) with the environment, also describes the diffusion data for the different polymeric tracers (dashed lines in the inset of Figure 4).The concurrent success of eq 3 suggests that the $N$-dependence of $\alpha'$ compensates that of the overlap concentration $(c_p^*)^u \sim N^{-0.44}$. Indeed, the adjusted values of $\alpha'$ scale as $N^{0.4}$.

FCS technique is a powerful tool that allows investigations of the diffusion of single tracers with different sizes and chemical structures in a very broad range of matrix polymer concentrations. To address its versatility, we examine the possibility to resolve the diffusion of individual tracers in a polymer matrix containing a mixture of fluorophore tracers (Figure 1). For this purpose, acetophenone solutions (~10 nM/L) of PS-34 and PS-255 were mixed in comparable mole fractions in the matrix PS220K at 0.1 g/mL. Since both polymer probes contain an amount of free PMI as well, three different tracers (PMI, PS-34, and PS-255) are present in the solution. The normalized $G(t)$ for this mixture shown in Figure 1 was represented by eq 1 ($m = 3$) using $f_{PMI} = 0.12$; $f_{PS\text{-}1} = 0.44$, $\tau_{PS\text{-}1} = 2400$ $\mu$s; $f_{PS\text{-}2}$=0.44, $\tau_{PS\text{-}2} = 20\,000$ $\mu$s as adjustable parameters whereas $\tau_{PMI}$ (=100 $\mu$s) was fixed to its value obtained from the corresponding autocorrelation function (also shown in Figure 1) of the pure PMI in PS220K at the same matrix concentrations ($c = 0.1$ g/mL). The molar fractions of the three components are in accordance with the preparation procedure, and the diffusion times for PS-34 and PS-255 in the mixture are very close to the values obtained from the separate measurements described above. The mean square displacements of pure PMI and the tracers in the mixture are shown in the inset in Figure 1. The pure PMI shows a free Fickian diffusion slope whereas for the mixture free diffusion is observed at short times for PMI and at long times for PS-255. In the intermediate time range more than one type of tracers contribute simultaneously.

## 4. Conclusion

We have used fluorescence correlation spectroscopy (FCS) to study the diffusion of tracer with different sizes in polystyrene/acetophenone solutions over a broad range of concentrations. Our results show that the diffusion of small molecular tracers ($R_h \sim 1$ nm) in polymeric solutions is controlled by the crowded environment mainly, and it is not affected by the polymeric nature of the matrix expressed in the crossover concentration. Alternatively, the diffusion of polymeric probe in solution of a matrix polymer depends on the molecular weights of both ($M_{w,p}$ and $M_{w,m}$). In the case when $M_{w,m} \geq 5M_{w,p}$ the diffusion of a polymeric probe behaves like a self-diffusion that exhibits the anticipated concentration dependence $D(c/c_p^*)$, where $c_p^*$ is the probe overlap concentration and can be captured by the scaling concepts[52,53] and well described by the Phillies equation.[14,15]

Finally, we have shown that FCS can be employed to investigate simultaneously a multicomponent diffusion in polymer solutions, provided the probes have sufficiently different diffusion times. In this way, in addition to the local friction measurement by means of molecular tracer diffusion, a concurrent access to macromolecular diffusion in multicomponent polymer systems can yield information about thermodynamic interactions. This capability, combined with the extremely small observation volume (<1 $\mu$m$^3$) that allows high-resolution studies of heterogenic systems, emphasizes the role of the FCS as a new, very useful and versatile tool in polymer science.

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## References and Notes

(1) von Meerwall, E. D.; Amis, E. J.; Ferry, J. D. *Macromolecules* **1985**, *18*, 260–6.

(2) Kim, H.; Chang, T.; Yohanan, J. M.; Wang, L.; Yu, H. *Macromolecules* **1986**, *19*, 2737–44.
(3) Landry, M. R.; Gu, Q.; Yu, H. *Macromolecules* **1988**, *21*, 1158–65.
(4) Nemoto, N.; Kojima, T.; Inoue, T.; Kishine, M.; Hirayama, T.; Kuratal, M. *Macromolecules* **1989**, *22*, 3793–8.
(5) Wheeler, L. M.; Lodge, T. P. *Macromolecules* **1989**, *22*, 3399–408.
(6) Piton, M. C.; Gilbert, R. G.; Chapman, B. E.; Kuchel, P. W. *Macromolecules* **1993**, *26*, 4472–7.
(7) Wisnudel, M. B.; Torkelson, J. M. *Macromolecules* **1996**, *29*, 6193–207.
(8) Liu, R.; Gao, X.; Adams, J.; Oppermann, W. *Macromolecules* **2005**, *38*, 8845–9.
(9) Robertson, R. M.; Smith, D. E. *Macromolecules* **2007**, *40*, 3373–7.
(10) Chekal, B. P.; Torkelson, J. M. *Macromolecules* **2002**, *35*, 8126–38.
(11) Brochard-Wyart, F.; de Gennes, P. G. *Eur. Phys. J. E* **2000**, *1*, 93–7.
(12) Cheng, Y.; Prud'homme, R. K. *Macromolecules* **2002**, *35*, 8111–21.
(13) Gisser, D. J.; Johnson, B. S.; Ediger, M. D. *Macromolecules* **1993**, *26*, 512–9.
(14) Phillies, G. D. J. *Macromolecules* **1986**, *19*, 2367–76.
(15) Phillies, G. D. J. *Macromolecules* **1987**, *20*, 558–64.
(16) Tao, H.; Lodge, T. P.; von Meerwall, E. D. *Macromolecules* **2000**, *33*, 1747–58.
(17) Tuteja, A.; Mackay, M. E.; Narayanan, S.; Asokan, S.; Wong, M. S. *Nano Lett.* **2007**, *7*, 1276–81.
(18) Pickup, S.; Blum, F. D. *Macromolecules* **1989**, *22*, 3961–8.
(19) Rigler R. *Fluorescence Correlation Spectroscopy*; Springer-Verlag: New York, 2001.
(20) Eigen, M.; Rigler, R. *Proc. Natl. Acad. Sci. U.S.A.* **1994**, *91*, 5740–7.
(21) Lumma, D.; Keller, S.; Vilgis, T.; Raedler, J. O. *Phys. Rev. Lett.* **2003**, *90*, 218301.
(22) Winkler, R.; Keller, S.; Rädler, J. O. *Phys. Rev. E* **2006**, *73*, 041919.
(23) Shusterman, R; Alon, S.; Gavrinyov, T.; Krichevsky, O. *Phys. Rev. Lett.* **2004**, *92*, 048303.
(24) Walter, N. G.; Schwille, P; Eigen, M. *Proc Natl Acad Sci USA* **1996**, *93*, 12805–10.
(25) Bonné, T. B.; Lüdtke, K.; Jordan, R; Tpánek, P.; Papadakis, C. M. *Colloid Polym. Sci.* **2004**, *282*, 833–43.
(26) Cluzel, P.; Surette, M.; Leibler, S. *Science* **2000**, *287*, 1652–5.
(27) Michelman-Ribeiro, A.; Horkey, F.; Nossal, R.; Boukari, H. *Biomacromolecules* **2007**, *8*, 1595–600.
(28) Kim, B. S.; Lebedeva, O. V.; Koynov, K.; Gong, H.; Glasser, G.; Lieberwith, I.; Vinogradova, O. I. *Macromolecules* **2005**, *38*, 5214–22.
(29) Koynov, K.; Mihov, G.; Mondeshki, M.; Moon, C.; Spiess, H. W.; Müllen, K.; Butt, H-J. *Biomacromolecules* **2007**, *8*, 1745–50.
(30) Sukhishvili, S. A.; Chen, Y.; Müller, J. D.; Gratton, E.; Schweizer, K. S.; Granick, S. *Macromolecules* **2002**, *35*, 1776–84.
(31) Zhao, J.; Granick, S. *Macromolecules* **2007**, *40*, 9564–69.
(32) Wang, W.; Zhang, C.; Wang, S.; Zhao, J. *Macromolecules* **2007**, *40*, 1243–7.
(33) Gianneli, M.; Beines, P. W.; Roskamp, R. F.; Koynov, K.; Fytas, G.; Knoll, W. *J. Phys. Chem. C* **2007**, *111*, 13205–11.
(34) Kang, K.; Gapinski, J.; Lettinga, M. P.; Buitenhuis, J.; Meier, G; Ratajczyk, M.; Dhont, J. K. G.; Patkowski, A. *J. Chem. Phys.* **2005**, *122*, 044905.
(35) Best, A.; Pakula, T.; Fytas, G. *Macromolecules* **2005**, *38*, 4539–41.
(36) Grabowski, C.; Mukhopadhyay, A. *Macromolecules* **2008**, *41*, 6191–94.
(37) Zettl, H.; Häfner, W.; Böker, A.; Schmalz, H.; Lanzendörfer, M.; Müller, A. H. E.; Krausch, G. *Macromolecules* **2004**, *37*, 1917–20.
(38) Zettl, H.; Zettl, U.; Krausch, G. *Phys Rev E* **2007**, *75*, 061804.
(39) Hermann, A.; Müllen, K. *Chem. Lett.* **2006**, *35*, 978–85.
(40) Jung, C.; Müller, B. K.; Lamb, D. C.; Nolde, F.; Müllen, K.; Bräuchle, C. *J. Am. Chem. Soc.* **2006**, *128*, 5283.
(41) Uji-i, H.; Melnikov, S. M.; Deres, A.; Bergamini, G.; de Schryver, F, A.; Hermann, A.; Müllen, K.; Enderlein, J.; Hofkens, J. *Polymer* **2006**, *47*, 2511–8.
(42) Karabasheva, S.; Baluschev, S.; Graf, K. *Appl. Phys. Lett.* **2006**, *89*, 031110.
(43) Bonaccurso, E.; Hankeln, B.; Niesenhaus, B.; Butt, H.-J.; Graf, K. *Appl. Phys. Lett.* **2005**, *86*, 124101.
(44) Li, G.; Butt, H.-J.; Graf, K. *Langmuir* **2006**, *22*, 11395–9.
(45) Ni, S. R.; Zhang, P; Wang, Y. C.; Winnik, M. A. *Macromolecules* **1994**, *27*, 5742–50.
(46) Tcherkasskaya, O.; Spiro, J.; Ni, S.; Winnik, M. *J. Phys. Chem.* **1996**, *100*, 7114–21.
(47) Rohr, U. Dissertation, Johannes-Gutenberg-Universität Mainz, 1999.
(48) Jang, Y-J.; Naundorf, C.; Klapper, M.; Müllen, K. *Macromol. Chem. Phys.* **2005**, *206*, 2027–37.
(49) Nägele, G. *Phys. Rep.* **1996**, *272*, 215–372.
(50) Cotton, J. P.; Nierlich, M.; Boue, F.; Daoud, M.; Farnoux, B.; Jannink, G.; Duplessix, R.; Picot, C. *J. Chem. Phys.* **1976**, *65*, 1101.
(51) Kok, C. M.; Rudin, A. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 655–9.
(52) de Gennes, P. G. *Scaling Concepts in Polymer Physics*, 1st ed.; Cornell University Press: Ithaca, NY, 1979.
(53) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, UK, 1987.

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