PRL **100,** 077801 (2008)　PHYSICAL REVIEW LETTERS　week ending 22 FEBRUARY 2008

Polymer Chain Swelling Induced by Dispersed Nanoparticles

Anish Tuteja,[1] Phillip M. Duxbury,[2] and Michael E. Mackay[1,2,*]

[1]*Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan 48824 USA*
[2]*Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824 USA*

(Received 29 October 2007; published 21 February 2008)

The dimensions of individual deuterated polystyrene (d-PS) chains in a well-dispersed mixture of protonated polystyrene and chemically identical nanoparticles was determined by neutron scattering. A 10%–20% increase in the radius of gyration of d-PS was found when the nanoparticles are homogeneously dispersed in the polymer, an effect that occurs only when the radius of gyration of the polymer is larger than the nanoparticle radius. These results are reconciled with the existing literature.

DOI: 10.1103/PhysRevLett.100.077801　PACS numbers: 61.41.+e, 61.05.fg, 61.46.Df

Nanomaterials [1] have the potential for performance that far exceeds traditional materials. Property improvements have been achieved in a variety of polymer-based nanocomposites [2–9] although nanoparticle dispersion remains a key factor dictating properties. If nanoparticles are segregated, performance is usually compromised as aggregates yield performance characteristic of traditional fillers. In contrast, dispersed nanoparticles exhibit unique physical effects, including a non-Einstein viscosity reduction [10,11], and surprisingly fast diffusion [12] where, for example, CdSe quantum dots were found to diffuse ~200 times faster than predicted by the Stokes-Einstein relation [13]. Control of nanoparticle segregation at fine length scales is critical to bulk heterojunction solar cell performance [14], providing further motivation for a more complete understanding of the morphology of nanoparticle-polymer blends.

Extensive experiments on a diverse set of nanoparticle-polymer systems indicate that when the nanoparticle radius (a) is smaller than the polymer radius of gyration (R_g) miscibility is promoted [9,10,15], and multifunctional property enhancements are possible. Analysis of neutron scattering data in the dispersed phase indicates that the Flory χ parameter is negative for nanoparticles dispersed in polystyrene, providing a mechanism for dispersion. However neutron scattering results also revealed that the linear polymer had an R_g increase of order 10%, implying a substantial 30% increase in volume, which is clearly entropically unfavorable. It is the interplay of these two terms, in addition to the usual favorable mixing entropy, that dictates phase stability [16–21].

However, experimental characterization of polymer conformation in the presence of nanoparticles is challenging, as traditional small angle neutron scattering from deuterated samples yields a convolution of nanoparticle and deuterated polymer scattering effects. A particularly attractive system to disentangle these effects is a contrast matched blend where the scattering strength of the nanoparticles is close to that of the undeuterated polymer. As described below (see also [10,15]), we have studied unique systems consisting of polystyrene nanoparticles in polystyrene melts where this contrast matching condition is achieved.

It is reported in the literature that nanoparticles produce an increase or decrease in R_g that is system specific, with some systems having an increase or decrease [22,23] or no change at all [24]. Theoretical reports show similar variations [25–29]. Here, we present experimental evidence of polymer swelling due to dispersed nanoparticles and reconcile this behavior with the existing experimental and theoretical literature.

The nanoparticles employed in this study are formed from linear polystyrene precursors containing 20% cross-linking units that are randomly distributed along the backbone. The nanoparticles are synthesized by dripping a semidilute precursor solution into hot solvent to activate the cross-linking process and collapse the chain. Details of the nanoparticles and linear polymers are given in Table I. The nanoparticles were kindly supplied by Professor Craig Hawker (UC–Santa Barbara) and the linear polymers were purchased from Scientific Polymer, including the deuterated polystyrene (d_8-PS).

Samples were prepared by dissolving the polymers and nanoparticles in a common solvent, usually toluene, then

TABLE I. Systems used in this study, along with their weight average molecular weights (M_w) and polydispersity indices (PDI = weight to number average ratio).

System	Abbreviation	M_w (kD) (PDI)
Nanoparticle	25 kD NP	27.3 (1.24)
	52 kD NP	61.3 (1.19)
	135 kD NP	162 (1.32)
	1700 kD NP	1700 (1.40)
PS	75 kD PS	75.7 (1.17)
	115 kD PS	115 (1.15)
	393 kD PS	393 (1.16)
d-PS	21 kD d-PS	21.1 (1.14)
	65 kD d-PS	65.3 (1.01)
	235 kD d-PS	235 (1.03)

dripping this into methanol, a nonsolvent for all components. The nonsolvent induces rapid precipitation (RP) where the precipitates consist of intimately mixed polymer-nanoparticle blends. The precipitates were filtered and dried at 50 °C for one week to remove any remaining solvent. Note that if the starting solution was allowed to slowly evaporate rather than using RP, we [9,10] and others [30] have found that phase separated structures are produced. This is due to the lower solubility of nanoparticles in most solvents, so that slow drying of the solution yields precipitation of nanoparticle aggregates prior to precipitation of the polymer. The well-mixed blends formed by RP were compression molded under vacuum into 8 mm diameter disks that were 1 mm thick. These disks were aged, also under vacuum, for 24 h at 170 °C to ensure equilibrium was achieved.

Small angle neutron scattering (SANS) was performed at Argonne National Laboratory IPNS where neutrons were produced at a pulse frequency of 30 Hz with a wavelength (λ) range of 1.4–14 Å. The detector was fixed at a distance of 2 m from the sample to provide a wave vector (Q) range of 0.005–0.6 Å^{-1}; $Q = 4\pi/\lambda \sin(\theta/2)$, θ is the scattering angle. The raw intensity data [$I(Q)$] were absolutely calibrated with a silica standard following procedures developed at IPNS [31].

To demonstrate that nanoparticles with $a < R_g$ were homogeneously dispersed in the polymer, a blend of 2% 135 kD NP's with deuterated polymer 235 kD d-PS ($R_g \approx$ 11 nm) was carefully characterized by SANS; see Fig. 1(a). In this system, the contrast is provided by the nanoparticles and the observation of a low-Q plateau indicates that no significant phase separation has occurred, in agreement with our previous studies [10,15]. Furthermore, detailed modeling of these data as polydisperse spheres with a Schultz distribution of their radii reveals a radius of 3.4 ± 0.9 nm, which is consistent with the expected nanoparticle radius of 3.6 ± 0.6 nm, should the nanoparticle collapse to the bulk density of polystyrene [10]. Finally, the inset of Fig. 1(a) shows a Kratky plot (Q^2I versus Q) to reveal a single peak consistent with nanoparticles homogeneously dispersed within the material. Taken together, the SANS evidence for homogeneous dispersion of this system is thus very strong. Conversely, if the nanoparticles are larger that the polymer chains (i.e., $a > R_g$), as illustrated by 1700 kD NP ($a \approx 8.6$ nm), blended with 21 kD d-PS ($R_g \approx 3.8$ nm), then phase separation is found, as shown in Fig. 1(b). Here a power law region is seen over most of the Q range, which is the signature of a phase separated blend. Note we have subtracted a constant background from all these data, which does not alter any of the above conclusions.

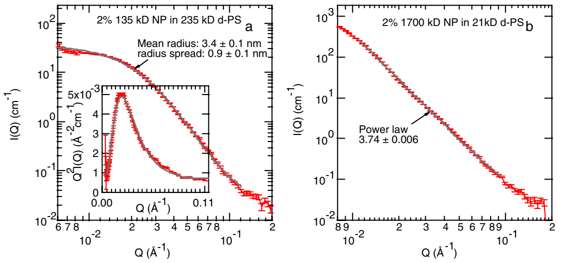

FIG. 1 (color online). (a) Neutron scattering intensity versus wave vector data for 2% 135 kD NP blended with 235 kD d-PS to provide scattering from the nanoparticles. The inset shows a Kratky plot of the same data. (b) Similar data for a larger nanoparticle, 1700 kD NP, blended with a smaller linear polymer, 21 kD d-PS.

To probe the conformation of individual polymer chains in dispersed blends, we use the fact that the nanoparticles and PS used here are essentially chemically identical, so that they have similar neutron scattering length densities (SLD's) and minimal contrast. In this case SANS from a blend consisting of 2 wt % d-PS in a mixture of linear PS and PS nanoparticles is dominated by scattering from the d-PS. Moreover, at this weight concentration the d-PS chains are well separated in the mixture so that the SANS data reflect the conformation of individual d-PS chains.

To probe the d-PS chain conformation, in the absence of nanoparticles, a blend was made with 2 wt % 65 kD d-PS with 98% 75 kD PS yielding the neutron scattering results shown in Fig. 2(a). The data could be modeled as a

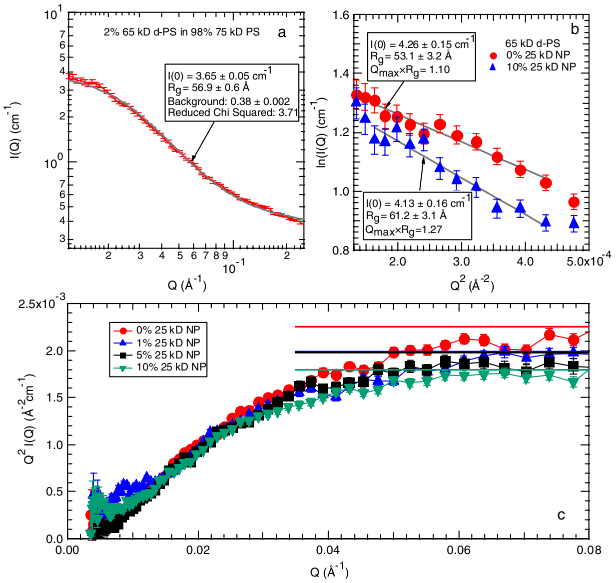

FIG. 2 (color online). (a) Intensity versus wave vector for 2% 65 kD d-PS blended with 98% 75 kD PS with SANS data compared to the Debye model with a constant incoherent background. (b) Intensity versus wave vector for 2% 65 kD d-PS blended with 98% 75 kD PS compared to 2% 65 kD d-PS blended with a 10% 25 kD NP—88% 75 kD PS mixture presented in a Guinier plot and associated analyses. (c) Kratky plot of Q^2I versus Q for 2% 65 kD d-PS blended with 75 kD PS containing 1%, 5%, and 10% 25 kD NP. The solid lines are $2I(0)/R_g{}^2$ determined with the Debye fits discussed in the text.

Gaussian coil (Debye function) with an R_g of 5.7 ± 0.1 nm and a constant background. A similar result is found by performing a Guinier analysis for spherical objects as shown in Fig. 2(b), and an R_g of 5.3 ± 0.3 nm is determined, which is within experimental error of the Debye analysis.

Addition of 10% 25 kD NP's to this system produces an R_g increase to 6.1 nm ± 0.3 nm from a similar Guinier analysis and is consistent with a Debye fit to the entire data set. However, the Guinier analysis in Fig. 2(b) is difficult since the intensity data at the small wave vector is suspect, and it is even more suspect for the higher molecular weight linear polymer discussed below. So, we used the Debye form factor, $I(x) = 2I(0)[x^2 - 1 + \exp(-x^2)]/x^4$, with $x = QR_g$ to determine R_g in all cases discussed below.

From this data analysis we found the intensity at the zero wave vector, $I(0)$, was constant for each of the given linear polymer systems, regardless of the nanoparticle concentration. For example for 65 kD d-PS blended with nanoparticles and 75 kD PS, $I(0) = 3.81 \pm 0.36\ \mathrm{cm}^{-1}$; and for 235 kD d-PS blended with nanoparticles and 115 kD PS, $I(0) = 14.8 \pm 1.7\ \mathrm{cm}^{-1}$. Since $I(0) = NV^2\Delta\rho^2$, where N is the number concentration of scatters, V, the scatterer volume ($NV \equiv \varphi$, the volume fraction), and $\Delta\rho$ the SLD contrast, then in our contrast equivalent system $I(0)$ depends only on the d-PS concentration and molecular weight. Moreover, we expect the ratio of $I(0)$'s for the two examples listed above to be equal to the first power of their molecular weight ratio according to $I(0) = \varphi\Delta\rho^2[V_0/M_0]M_w$, where V_0 and M_0 are a monomer volume and molecular weight, assuming a Schulz molecular weight distribution [32]. Since φ is held constant, the $I(0)$ ratio should be 3.6. The experimentally determined value is 3.9 ± 0.8, which is in good agreement with that expected from their molecular weight ratio.

To further support the R_g analysis, we plotted the data in a Kratky plot to highlight the Gaussian nature of the scatterer for the neat and filled systems as shown in Fig. 2(c). Whereas the Guinier analysis suffers from poor intensity resolution at small wave vector, the Kratky analysis suffers from subtraction of the incoherent background at larger wave vectors, frequently leading to the subtraction of two large numbers to yield a small one. The background is ~ one-half of the total intensity at $Q \approx 0.07\ \text{Å}^{-1}$, where the data approach the Gaussian plateau, and the data for all the systems appear to behave as such. Furthermore, the Gaussian plateau should be equal to $2I(0)/{R_g}^2$, and when results from the Debye fit are placed in the plot (solid lines) the agreement is satisfactory, lending further credence to the analysis procedure. Also, since $I(0)$ is equal for all the systems in the graph, this points to an R_g increase when nanoparticles are added to the polymer melt.

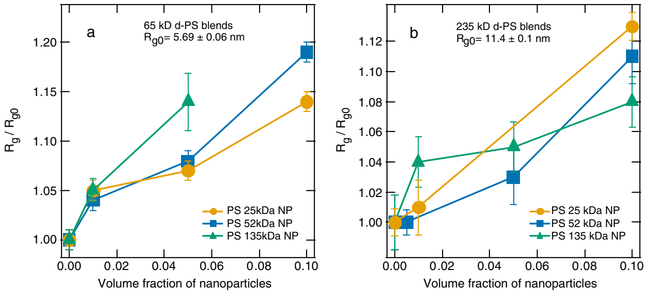

FIG. 3 (color online). Radius of gyration of 65 kD d-PS (a) and 235 kD d-PS (b) for three nanoparticle molecular weights as a function of nanoparticle concentration. The 2% blends in (a) and (b) also contained 75 kD PS and 115 kD PS, respectively. The nanoparticles have radii: 2.0 nm (25 kD); 2.7 nm (52 kD); 3.6 nm (135 kD) if they collapse to the bulk density of polystyrene.

All the results of our study are gathered in Fig. 3 where the radius of gyration is normalized with that of the unfilled polymer, R_{g0}. It is clear that the radius increases with nanoparticle concentration, which is consistent with the results in Fig. 2. There is no clear trend with nanoparticle size although the smaller molecular weight linear polymer swells more relative to R_{g0} than the larger molecular weight. Qualitatively, the nanoparticles behave as a solvent to swell the polymer chains. If excluded volume were the only effect, then R_g/R_{g0} should vary as $[1 + \varphi]^{1/3}$, where in this case φ is the nanoparticle volume fraction [15]. This does not appear to be the case, and the *solid* solvent behavior of the nanoparticles leads to a much larger increase in the polymer dimensions.

The results presented above appear at odds with a recent study [24], where it was found that silica nanoparticles blended with polystyrene produced no change in polymer radius of gyration. However, it is evident from the TEM images of Fig. 1 in their paper that some of the silica nanoparticles have phase segregated. Since our previous study indicates that dispersion is required for chain swelling, our work and that presented in [24] are not inconsistent. Here, as in our previous studies, we have found that the condition $R_g > a$ is essential to dispersion and chain swelling. Nakatani *et al.* [23] in their groundbreaking study of polysilicate nanoparticles blended with PDMS also noted that the condition $R_g > a$ is necessary for chain swelling, and they also observed that low nanoparticle concentrations promote chain swelling, presumably due to better dispersion in this limit [15]. Their results are thus broadly consistent with ours.

Though there have been many molecular dynamics and Monte Carlo studies of chain conformations in the presence of nanoparticles, the regime that is relevant to our experiments remains extremely challenging. Early studies considered the behavior of a single chain in the presence of random nanoparticles [23]. Extensions to treat melt densities emerged, but they still fixed the positions of the nanoparticles and studied chain conformations in the presence of these fixed nanoparticle obstacles, either in regular arrays or in random locations [27,33,34]. However, this approximation neglects nanoparticle mixing entropy that is known to be important in nanocomposites, as exemplified in Flory theories and SCF DFT studies of nanoparticle dispersion [15,19,21]. When nanoparticle mobility is included in simulation studies, along with realistic enthalpic terms, behavior broadly consistent with our results has been found [25].

In conclusion, we demonstrated that nanoparticles of radius a may be dispersed in enthalpically matched polymer melts, provided the melt chain radius of gyration, R_g, obeys $R_g > a$. Many practical nanocomposites are close to the enthalpically matched limit, so a similar behavior is expected. Indeed, we have found that unusual multifunctional behavior results in this limit [9].

We gratefully acknowledge funding from NSF No. CTS0400840 and the use of the neutron scattering facilities at Argonne National Laboratory. The help of Ms. Erin Vogel and Professor Greg Baker in determining the molecular weight for some of the samples is greatly appreciated.

---

[*]Electronic addresses: mackay@msu.edu
http://www.nanoeverything.com

[1] R. W. Siegel, Phys. Today **46**, no. 10, 64 (1993).
[2] L. S. Schadler *et al.*, MRS Bull. **32**, 335 (2007).
[3] F. Gao, Mater. Today **7**, 50 (2004).
[4] R. A. Vaia and E. P. Giannelis, MRS Bull. **26**, 394 (2001).
[5] R. A. Vaia and H. D. Wagner, Mater. Today **7**, 32 (2004).
[6] W. A. Curtin and B. W. Sheldon, Mater. Today **7**, 44 (2004).
[7] R. Krishnamoorti, MRS Bull. **32**, 341 (2007).
[8] R. A. Vaia and J. F. Maguire, Chem. Mater. **19**, 2736 (2007).
[9] A. Tuteja, P. M. Duxbury, and M. E. Mackay, Macromolecules **40**, 9427 (2007).
[10] M. E. Mackay *et al.*, Nat. Mater. **2**, 762 (2003).
[11] A. Tuteja *et al.*, Macromolecules **38**, 8000 (2005).
[12] F. Brochard-Wyart and P. G. deGennes, Eur. Phys. J. E **1**, 93 (2000).
[13] A. Tuteja *et al.*, Nano Lett. **7**, 1276 (2007).
[14] H. Hoppe and N. S. Sariciftci, J. Mater. Chem. **16**, 45 (2006).
[15] M. E. Mackay *et al.*, Science **311**, 1740 (2006).
[16] J. B. Hooper and K. S. Schweizer, Macromolecules **39**, 5133 (2006).
[17] J. B. Hooper and K. S. Schweizer, Macromolecules **38**, 8858 (2005).
[18] J. B. Hooper *et al.*, J. Chem. Phys. **121**, 6986 (2004).
[19] V. V. Ginzburg, Macromolecules **38**, 2362 (2005).
[20] A. C. Balazs, T. Emrick, and T. P. Russell, Science **314**, 1107 (2006).
[21] G. He, V. V. Ginzburg, and A. C. Balazs, J. Polym. Sci. Part. B: Polym. Phys. **44**, 2389 (2006).
[22] A. I. Nakatani *et al.*, Int. J. Thermophys. **23**, 199 (2002).
[23] A. I. Nakatani *et al.*, Polymer **42**, 3713 (2001).
[24] S. Sen *et al.*, Phys. Rev. Lett. **98**, 128302 (2007).
[25] F. M. Erguney, H. Lin, and W. L. Mattice, Polymer **47**, 3689 (2006).
[26] H. Lin, F. Erguney, and W. L. Mattice, Polymer **46**, 6154 (2005).
[27] M. Vacatello, Macromolecules **35**, 8191 (2002).
[28] M. Vacatello, Macromolecules **34**, 1946 (2001).
[29] F. W. Starr, T. B. Schrøder, and S. C. Glotzer, Phys. Rev. E **64**, 021802 (2001).
[30] F. M. Du, J. E. Fischer, and K. I. Winey, J. Polym. Sci. Part. B: Polym. Phys. **41**, 3333 (2003).
[31] P. Thiyagarajan *et al.*, J. Appl. Crystallogr. **30**, 280 (1997).
[32] L. H. Peebles, *Molecular Weight Distributions in Polymers* (Interscience Publishers, New York, 1971), p. 331.
[33] J. E. Mark, Polymer **46**, 8894 (2005).
[34] M. S. Ozmusul *et al.*, Macromolecules **38**, 4495 (2005).