# Chain Conformations and Bound-Layer Correlations in Polymer Nanocomposites

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Small angle neutron scattering studies on polystyrene loaded with spherical silica nanoparticles under contrast-matched conditions unequivocally show that chain conformations follow unperturbed Gaussian statistics independent of chain molecular weight and filler composition. Liquid state theory calculations are consistent with this conclusion and also predict filler-induced modification of interchain polymer correlations which have a distinctive scattering signature that is in nearly quantitative agreement with our observations.

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The topic of nanocomposites is of great interest, since the addition of nanoparticles to polymers can yield materials with significantly improved properties [1–6]. Here we focus on two simple, but unresolved, questions which underpin our understanding in this area: (i) What is the effect of filler on chain conformation? (ii) How is interchain packing perturbed by filler-monomer attractions? While most simulations show that chain conformations are hardly affected by the addition of particles [7], a few [8] find significant chain deformation. While this last class of simulations does not appear to be relevant to filled melts [9], they agree with the results of some experiments on corresponding systems [10]. Other experiments [11], which used cross-linked melts, suggest that chain conformation is unaffected by particles. However, their relevance to the more general case of uncross-linked polymers is unclear. The current situation on this question is thus controversial. We performed small angle neutron scattering (SANS) on nanocomposites with model uncross-linked polymers to unequivocally resolve this issue. Polymer reference interaction site model (PRISM) calculations [12] are used to interpret these data and reveal the underlying physics. Our results show that polymers are unperturbed Gaussian coils in the presence of filler. We thus stress that polymers in nanocomposites and thin films behave analogously [13], a result that is bolstered by experiments on thin films [14,15].

Three sets of protonated and deuterated polystyrenes (hPS and dPS, respectively), of roughly equal molecular weight and narrow polydispersities, and silica particles (Nissan, diameter 14 ± 4 nm) were used as obtained (Table I). We consider blends with 66 wt % hPS and 34 wt % dPS, which almost contrast match the silica [16]. This implies that the silica has a mean scattering length density of $3.0 \times 10^{-6}$ Å$^{-2}$ corresponding to a density of 1.90 g/cm$^3$, which is less than the bulk value of 2.2 g/cm$^3$ [17]. This low density is consistent with Ref. [11], which reported that the apparent density of fumed silica was only 60% of the bulk. This is probably because, both in our experiments and in Ref. [11], the particles are imperfectly mixed with the polymers, with the particles being surrounded by "voids" especially at large filler content [Fig. 1(a)]. While these density numbers are low, we shall show that they do not affect our primary conclusions on chain conformations. Nanocomposites with 0, 2.9, 6.0, and 9.1 vol % silica were prepared for each molecular weight. We also prepared 15.9 and 27.4 vol %

TABLE I. Molecular weights ($M_w$) and polydispersities (PDI) for polystyrenes used in this work. Light scattering data provided by Polymer Laboratories.

| dPS | | hPS | |
|---|---|---|---|
| $M_w$ (kg/mol) | PDI | $M_w$ (kg/mol) | PDI |
| 90 | 1.02 | 98 | 1.03 |
| 250 | 1.03 | 243 | 1.02 |
| 620 | 1.05 | 557.5 | 1.03 |

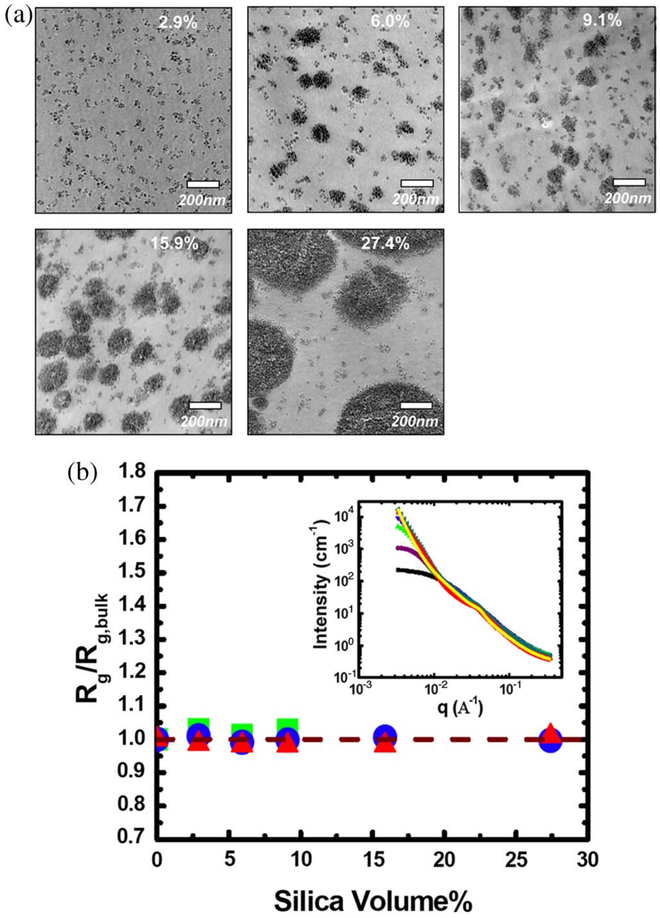

FIG. 1 (color online). (a) TEM micrographs of nanocomposites formed from PS of molecular weight 250 kg/mol indicating vol % loading of silica in each sample. (b) Ratio of the radii of gyration of polymers in the presence of particles to the corresponding pure blend for PS 90 kg/mol (green squares), PS 250 kg/mol (blue circles), and PS 620 kg/mol (red triangles) as functions of silica volume fraction. Inset: Plots of "raw" SANS intensities $I_{\mathrm{expt}}(q)$ in absolute units as a function of $q$ for the PS 250 kg/mol nanocomposites. The black squares, purple circles, green triangles, blue inverse triangles, dark cyan "left" triangles, and red "right" triangles correspond to a particle vol % of 0, 2.9, 6.0, 9.1, 15.9, and 27.4, respectively. The yellow line show fits to the 27.4 vol % data as discussed in the text.

silica nanocomposites with the 250 and 620 kg/mol PS matrices. The nanocomposite preparation technique affects particle dispersion. While the chain dimensions are found to be practically insensitive to dispersion, we chose to use the best achievable dispersion. This was obtained by first dissolving the polymers in methylethylketone. Silica particles were then added, and the mixture sonicated for 2 minutes. The solutions were poured into petri dishes, and the solvent evacuated under vacuum. Further drying in a vacuum oven at 120 °C for 24 hours is followed by premolding at room temperature and final molding at 160 °C for 30 minutes. TEM images [Fig. 1(a)] show that particles are reasonably dispersed for filler loadings $<10$ vol % but that particle agglomeration is the norm for larger loadings.

SANS was conducted at the National Institute of Standards and Technology, with neutrons of 6 Å wavelength [18]. Data, which were time-independent and reproducible, were collected at 140 °C over the wave vector range $q = 0.0033$–$0.5$ Å$^{-1}$. These were corrected for background, empty cell scattering, and detector efficiency and converted to an absolute scale. In parallel, we have applied the PRISM theory of polymer nanocomposites as in Ref. [12]. Fillers were modeled as hard spheres of diameter $D$ (14 nm) and polymers as freely jointed chains with monomers of diameter $d$ (0.53 and 1 nm) and a realistic persistence length of $4/3d$. Since a fully self-consistent PRISM theory is presently unavailable for polymer nanocomposites, chain conformations are assumed to be unperturbed relative to the unfilled melts. Polymer-polymer and particle-particle interactions are taken to be hard-core, while monomers and fillers interact via an exponentially decreasing attraction of contact strength $\varepsilon_{\mathrm{pc}}kT$ and (short) spatial range $\alpha d$. Calculations were performed for $\varepsilon_{\mathrm{pc}} = 1$–$2.5$ and $\alpha = 0.5$–$1$. The total mixture packing fraction was set to 0.45 and chain length to 2360. These parameters closely correspond to the experimental density, backbone persistence length, and radius of gyration of a PS chain of molecular weight ~250 kg/mol.

Figure 1(b) (inset) shows representative "raw" SANS intensities $I_{\mathrm{expt}}(q)$ in absolute units for several filler loadings with 250 kg/mol PS. The low-$q$ intensity increases dramatically with increasing silica content, especially for loadings $\leq 10$ vol %. This implies that the matrix is not totally contrast-matched to the filler, an unsurprising result in light of voids surrounding particles [[11] and Fig. 1(a)]. The $q < 0.009$ Å$^{-1}$ data apparently follow a $q^{-4}$ dependence in all cases, i.e., a Porod form. Because of these extra scattering contributions, we cannot unequivocally determine chain dimensions from the low-$q$ data ["Zimm" regime]. However, since the high-$q$ intensity is expected to be independent of filler structure [11], chain dimensions are determined from this regime. We construct an intensity $I(q)$: $I(q) = [I_{\mathrm{expt}}(q)/\phi_p] - I_{\mathrm{incoherent}}$, where $\phi_p$ is the polymer volume fraction. This scaling of $I_{\mathrm{expt}}(q)$ by $\phi_p$ allows us to examine the scattering intensity per unit polymer volume, a quantity that can be immediately compared across all nanocomposites and with the theory. We now consider Kratky plots, i.e., $q^2I(q)$ vs $q$ [Fig. 2(a)]: The signature of Gaussian statistics is a "Kratky plateau" for $qR_g \gg 1$, where $R_g$ is the radius of gyration. Figure 2(a) shows the presence of well-defined plateaus, as well as their insensitivity to nanoparticle loading. In this analysis, $I_{\mathrm{Incoherent}}$ was treated as a constant, which was assigned to the value (0.32 cm$^{-1}$) derived from the unfilled polymer blends. [This follows since the silica possesses essentially no incoherent cross section.] To test for the robustness of this assumption, we have also independently adjusted the

$I_{\text{incoherent}}$ for each sample. The resulting values of $I_{\text{incoherent}}$ varied by less than 10% from the bulk value ($I_{\text{incoherent}} \sim 0.31$–$0.35\ \text{cm}^{-1}$) verifying the robustness of the analysis procedure. For Gaussian chains, the plateaus are directly related to the statistical segment length $\sigma$ [15]:

$$\sqrt{\frac{[q^2 I(q)]_{\phi_p=1}}{[q^2 I(q)]_{\phi_p}}} = \frac{\sigma_{\phi_p}}{\sigma_{\phi_p=1}} \equiv \frac{R_g(\phi_p)}{R_g(\phi_p = 1)}. \tag{1}$$

Figure 1(b) shows that the chain size is unaltered in all nanocomposites within our uncertainty limits of 5%. Note that the chain $R_g$ varies from ~8 nm (90 kg/mol) to 22 nm (620 kg/mol). These $R_g$'s bracket the nanoparticle diameter (~14 nm), suggesting that the ratio of the particle size to $R_g$ is not an important variable in this context. We have also varied the density of the silica from 1.9 to 2.2 g/cm$^3$, and again the results were practically identical. We believe that our results unequivocally show that the chains follow unperturbed Gaussian statistics. These results are in good agreement with our previous results for chain dimensions in thin films [14,15], which found that the chain conformations parallel to the surface assumed their unperturbed values even for film thickness $< R_g$.

The presence of a small angle peak around $q = 0.04$ Å$^{-1}$ [Fig. 2(a)], which becomes more pronounced with increasing silica content, is a novel feature of these data. The peak position is essentially independent of filler volume fraction and polymer molecular weight. To understand its physical origin, we turn to theory. Figure 2(b) presents theoretical Kratky plots for $\varepsilon_{\text{pc}} = 1$, $\alpha = 0.5$, and $D/d = 26.4$. Motivated by experiments, the calculated $I(q)$ is defined only per unit polymer volume. To clearly show relative changes with filler volume fraction, the Kratky curves are normalized to the plateau level of the *pure* polymer system. The theoretical plateau values are invariant to loading, since the polymer conformations are assumed to be unperturbed. Qualitatively, the theory and the experiment show the same features and trends, although the theoretical higher order oscillations are not observed experimentally, likely because the silica particles are rather size polydisperse, amplified by agglomeration at higher volume fractions. Based on our past theoretical work [12], the low angle peak is clearly identified as due to the perturbation of *interchain* packing of polymer segments near filler surfaces due to the combined influences of monomer-particle attraction and excluded volume interactions. It is significant that all features of the theoretical scattering curves, including the location of the small angle peak, are nearly independent of the precise values of $\varepsilon_{\text{pc}}$, $\alpha$, and $N$, as long as the nanocomposite is miscible. An example of this robustness is shown in Fig. 2(c). The peak intensity varies roughly linear with $D$, a consequence of the filler-induced enhancement of the low-$q$ collective polymer structure factor being proportional to $(D/d)^3$ (excluded volume). Thus, $q^2 I(q) \sim (1/D)^2 D^3 \sim D$ [12].

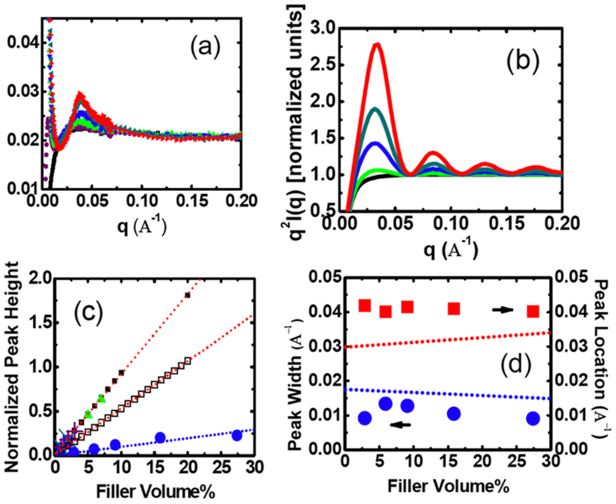

FIG. 2 (color online). (a) Experimental Kratky plots (symbols same as in the inset in Fig. 1) of the PS 250 kg/mol systems using intensity values defined as $I(q) = I_{\text{expt}}(q)/\phi_p - I_{\text{incoherent}}$. (b) Kratky plots from PRISM theory with $D/d = 26.4$, $\varepsilon_{\text{pc}} = 1$, and $\alpha = 0.5$. The black, green, blue, dark cyan, and red lines correspond to filler vol % of 0, 1, 5, 10, and 20, respectively. (c) Plots of peak intensity from Kratky plots as a function of filler volume fraction. Lines are guides to the eye. Theoretical results used $D/d = 26.4$ (upper red line) and $D/d = 14$ (lower red line), respectively. For $D/d = 26.4$, along with $\varepsilon_{\text{pc}} = 1$ and $\alpha = 0.5$ (black squares), four other combinations are represented—$\varepsilon_{\text{pc}} = 1.5$ and $\alpha = 0.5$ (green triangles), $\varepsilon_{\text{pc}} = 2.5$ and $\alpha = 0.5$ (blue squares), $\varepsilon_{\text{pc}} = 1$ and $\alpha = 0.75$ (dark cyan crosses), and $\varepsilon_{\text{pc}} = 1.5$ and $\alpha = 1$ (purple plusses), respectively. For $D/d = 14$, $\varepsilon_{\text{pc}} = 1$ and $\alpha = 0.5$ (open black squares). The blue circles and lines are the results from the experiments. (d) Peak locations and peak widths corresponding to experiments (symbols) and theory (lines), respectively.

We now compare the theory and experiment in a more detailed manner. The data are fit to the form: $I(q) = [A/(1 + q^2 s^2)^2] + (C/q^2)\exp\{-[(q - q_{\max})^2/(\Delta q)^2]\} + B I_{\text{polymer}}(q)$, inspired by the unified model of Beaucage, Kammler, and Pratsinis [19]. The first term is the Debye-Bueche contribution from the particles, which does fit the low-$q$ data. The last contribution comes from the unfilled blend and utilizes the fact that the chains remain unperturbed. The second contribution has a peak, whose location and width are in surprisingly good agreement with the theory [Fig. 2(d)]. The peak heights vary linearly with filler content, as in the theory, but the experimental amplitudes ($C$ parameter) are about 5–10 times smaller than the calculations [Fig. 2(c)]. It is likely that this discrepancy arises because the experiments have particle agglomeration, while the equilibrium theory corresponds to complete filler dispersion. As an alternative approach, we have modeled the second contribution as the form factor of polydisperse hard spheres. Good agreement is obtained (not shown) by assuming that the distribution of particle diameters is a Gaussian with a mean of 16 nm and a deviation of 2 nm.

Again, the form factor properly fits the first peak of the scattering at $\sim 0.04\ \text{Å}^{-1}$ but predicts the existence of higher order peaks, which are absent in the experiments. These results are consistent with the PRISM prediction that the presence of particles and an adsorbed polymer layer results in the imprinting of a ''correlation hole'' type of contribution in the collective polymer structure factor with features closely related to the particle form factor [12]. Further credence for this assignment comes from the fact that the theoretical results depend primarily on the particle diameter and not on the detailed nature of filler-polymer attractions as long as they are neither too weak nor too strong, which can result in depletion or bridging-induced phase separation, respectively [12].

Finally, we comment briefly on the potential sources for the qualitatively different trends deduced by us and by previous workers for the role of particles on chain dimensions [10,20]. Nakatani *et al.* considered filled polydimethylsiloxane and found that the chain size either increased or decreased on adding particles. We attribute these findings to the following: (i) most of the polymers used had significant polydispersity; (ii) the molecular weights of the isotopic polymers blended with the filler were quite different in at least one case; (iii) particle dispersion/agglomeration, which was not characterized. The compounded effect of these factors could result in significant uncertainty in the chain dimensions deduced. Similarly, Mackay *et al.* [20] utilized soft nanoparticles, which may behave differently than the ''hard'' silica nanoparticles utilized by us. Additionally, it is possible that the low-$q$ data, which are used to characterize chain dimensions, could be affected by particle agglomeration (which was not characterized) [10,20]. In conclusion, we emphasize that our experimental results on chain conformations are in good agreement with a broad class of molecular simulations, e.g., [7,9]. We strongly recommend that these simulations be employed to clearly delineate the role of nanoparticles on chain behavior, especially in regimes where it is hard to perform experiments.

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