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Do Very Small POSS Nanoparticles Perturb s-PMMA Chain **Conformations?**

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Supporting Information

ABSTRACT: Small-angle neutron scattering (SANS) measurements of syndiotactic s-PMMA polymers mixed with weakly attractive 1.0 nm diameter polyhedral oligomeric silsesquioxane (POSS) nanoparticles (NPs) show no observable changes in the chain radius of gyration R_{gy} regardless of the polymer molecular weights, the amount of residual solvent, or the POSS NP loading and dispersion (from 0 to 20 vol %). In retrospect, these results are not surprising since scaling arguments imply that chain size in the concentrated region of the phase diagram of a polymer solution is ideal and independent of the polymer volume fraction ϕ_{i} and only as the semidilute region is entered with decreasing concentration does the chain size for a good



solvent begin to increase due to polymer excluded volume and then scales with concentration as $\phi^{-1/8}$. For typical polymer nanocomposites the NP concentrations are less than 50% v/v, so the polymers are still generally within the concentrated regions of their phase diagrams, where ideal chain conformations are observed for small molecule solvents. By combining the present results with previous results from the literature, we conclude that spherical NPs apparently have little effect on the conformations of polymer chains, especially in typical polymer nanocomposites that only incorporate moderate amounts of NPs.

■ INTRODUCTION

There has been a great deal of recent attention¹⁻¹³ on the effects of nanoparticles (NPs) on polymer chain conformations in polymer nanocomposites (PNCs). In addition to its intrinsic fundamental interest, changes in polymer conformation may significantly influence the practically important mechanical properties of the PNCs. The foundational question of whether the presence of well-dispersed NPs changes the host polymer conformation, characterized by the radius of gyration R_{o} , has unfortunately been the source of considerable controversy. Both experiments and simulations have been used to address this question. Table 1 provides a comprehensive up-to-date summary of existing theoretical and experimental work on the conformation of polymer chains in the presence of spherical NPs, a topic that we shall discuss in more detail in the next

section. If we look only at work published after 2010, the emerging consensus appears to be that polymer chains are hardly affected by the addition of NPs, apparently independent of whether the chains and NPs are athermal toward each other or if they have attractive interactions with each other.

Here we focus on the case of PNCs containing very small NPs (VSNPs, diameters of 1-2 nm) where large chain expansions were observed for two different polymer-NP systems (Table 1).^{1,6} It was proposed in those studies that by analogy with polymer solutions,¹⁴ VSNPs act as good solvents,¹⁵ swelling the chains, plasticizing the polymers, and

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references	sis this work	13	32	without 32	to chain 11	AC 10	⁻ analysis, 7, 12, 33	6	27	34	8	on, Debye 31	35	24	25	30	mples, 1	Vo ZAC 6	n method, 32 Id	2, 3	15	30		on if $R_{\rm g} > 36$	on if $R_{\rm g}$ > 36 on is more 37	on if $R_g > 36$ on is more 37 all SANS $q = 1$
comments	ZAC condition, Guinier, RPA and Kratky analy	Guinier and RPA analysis	extrapolation method, Kratky analysis	extrapolation method, Kratky analysis, with and magnetic field	ZAC condition, extra contribution at low q due adsorption, RPA, and Kratky analysis	NPs are covered with trimethoxyphenylsilane, Z condition, Kratky analysis	ZAC condition or extrapolation method, Kratky remains unperturbated under stretching	ZAC condition, Kratky analysis	RPA analysis, extra contribution at low q	RPA analysis	RPA analysis	extra contribution at low q due to chain adsorptianalysis					max increase: ≈60% for 20% v/v NPs, liquid sa small SANS q range	max increase: 15% at 10% v/v NPs, soft NPs, N condition, Kratky analysis	max increase: 16% at 3% v/v NPs, extrapolatior Kratky analysis, with and without magnetic fie	max increase: 11% for Sharaf	max increase: $\approx 14\%$ at 20% v/v NPs	max increase: ${\approx}18\%$ for 40.9% v/v 1 nm NPs		max expansion: $\approx 7\%$ at 20% 2 nm NPs, expansi distance between NPs	max expansion: ≈7% at 20% 2 nm NPs, expansi distance between NPs max expansion: ≈10% for 60% v/v NPs, expansi pronounced if the NPs are mobile	max expansion: ≈7% at 20% 2 nm NPs, expansi distance between NPs max expansion: ≈10% for 60% v/v NPs, expansic pronounced if the NPs are mobile max contraction: ≈25% for 20% NPs, liquid, sma
experiments or simulations	experiment	experiment	experiment	experiment	experiment	experiment	experiment	experiment and simulation	experiment	experiment	experiment	experiment	simulation	simulation	simulation	simulation	experiment	experiment	experiment	simulation	simulation	simulation		simulation	simulation simulation	simulation simulation experiment
NP dispersion	good dispersion or aggregation depending on NP % v/v	aggregation	coexistence individual NPs and aggregates	aggregation	good dispersion or aggregation depending on $M_{\rm w}$	good dispersion	aggregation	phase separation	aggregation	aggregation	aggregation	aggregation	randomly distributed	cubic or randomly distributed	good dispersion	good dispersion	not determined	good dispersion	aggregation	randomly distributed	good dispersion	good dispersion				not determined
INP/ polymer interaction	weakly attractive	athermal	athermal	athermal	attractive	athermal	repulsive		repulsive	repulsive	attractive	attractive	variable	from weakly to strongly attractive	repulsive, neutral, attractive	repulsive	athermal	athermal	repulsive		attractive	attractive			athermal	athermal athermal
$R_{ m g}/R_{ m NP}$	$R_{\rm g} > R_{\rm NP}$	$R_{ m g} > R_{ m NP}$	$R_{ m g}pprox R_{ m NP}$	$R_{\rm g} > R_{\rm NP}$	$R_{\rm g}^{}_{\rm g} > R_{\rm NP}, R_{\rm g} \approx R_{\rm NP}$	$R_{ m g} > R_{ m NP}, R_{ m g} \approx R_{ m NP}, R_{ m g} pprox R_{ m NP}$	$R_{\rm g} > R_{\rm NP}$	$\frac{R_{\rm g}}{R_{\rm NP}} R_{\rm NP}, R_{\rm g} \approx$	$R_{\rm g} < R_{ m NP}$	$R_{ m g} pprox R_{ m NP}$	$R_{\rm g}$ > $R_{\rm NP}$	$R_{\rm g} > R_{\rm NP}, R_{\rm g} < R_{\rm NP}$	variable	$R_{ m g}pprox R_{ m NP}$	$R_{\rm g} > R_{\rm NP}$	$R_{\rm g} < R_{\rm NP}, R_{\rm g} \approx R_{\rm NP}$	$R_{\rm g} > R_{\rm NP}$	$R_{\rm g} > R_{\rm NP}$	$R_{\rm g} > R_{\rm NP}$	$R_{ m g} > R_{ m NP}$	$R_{\rm g} > R_{\rm NP}$	$R_{\rm g} > R_{\rm NP}$		$R_{\rm g} > R_{\rm NP}$	$R_{ m g} > R_{ m NP}$ $R_{ m g} > R_{ m NP}$	$egin{array}{ll} R_{ m g} > R_{ m NP} \ R_{ m g} > R_{ m NP} \ R_{ m g} > R_{ m NP} \ R_{ m NP} \ R_{ m g} > R_{ m NP} \end{array}$
(mn)	1	1.6	4.0	4.0	6.1	6.5			7.2	7.8	8	5 and 14	variable		variable		1	2-3.6	4.8	0.5 - 20		1, 2, and	4 nm	4 nm 1, 2, 2.7 nm	4 nm 1, 2, 2.7 nm	4 nm 1, 2, 2.7 nm 1
system NP/polymer	POSS NP/PMMA	PEG-POSS NP/PEG	PS grafted Fe ₂ O ₃ /PS	PS grafted Fe ₂ O ₃ /PS	silica NP/PMMA	silica NP/PS			silica NPs/PEP	silica NP/SBR (un-cross- linked and cross-linked)	silica NP/latex	silica NP/PEMA			-/PE		polysilicate/PDMS	cross-linked PS NP/PS	bare Fe ₂ O ₃ /PS	-/PDMS or PE				-/PE	-/PE collapsed PE or POE/PE or PEO	 –/PE collapsed PE or POE/PE or PEO polysilicate/PDMS
conformation	unperturbed																expanded									contracted

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references	27	26	4, 38	37	2, 3	2, 3	36
comments	max contraction: 12% for 50% v/v NPs, RPA analysis, extra contribution at low q	max contraction: 25% for 16% v/v NPs, PI–PS–PI form spherical micelles in a PS core	max contraction: 9% for 1 nm NPs in PE and 11% for 1 nm 20% v/v in PDMS	max contraction: $\approx 18\%$ for 60% v/v NPs	max contraction: 11% for Sharaf	max contraction: 14% for Sharaf at high volume fraction	max contraction: ≈5% only for 10% v/v NPs
experiments or simulations	experiment	experiment	simulation	simulation	simulation	simulation	simulation
NP dispersion	aggregation	good dispersion	randomly distributed		randomly distributed	cubic phase	
NP/polymer interaction	repulsive	athermal	variable	athermal			
$R_{ m g}/R_{ m NP}$	$R_{ m g}pprox R_{ m NP}$	$R_{\rm g} > R_{\rm NP}$	$R_{\rm g} > R_{\rm NP}$	$R_{\rm g} > R_{\rm NP}, R_{\rm g} \approx R_{\rm NP}$	$R_{\rm g} < R_{ m NP}$	$R_{\rm g} < R_{\rm NP}, R_{\rm g} > R_{\rm NP}$	$R_{\rm g} > R_{\rm NP}$
$\mathop{({ m nm}}\limits_{{ m (nm)}}$	7.2	8.4	0.75 to 4 nm		4-20	0.5-20	3.6 nm
system NP/polymer	silica NPs/PEP	Id/dN Id-Sd-Id	-/PE or PDMS	collapsed PE or POE/PE or PEO	-/PDMS or PE	-/PDMS or PE	-/PE
chain conformation							

Fable 1. continued

Article

reducing the melt viscosities η .^{16–19} For example, a 60% decrease in viscosity for 10 wt % cross-linked polystyrene (PS) NPs (3–5 nm in size) in a PS matrix¹⁷ and a 30% decrease for 10 wt % fullerene C_{60} ($R_{\rm NP} = 0.7$ nm) in PS¹⁸ were observed. These experimental results have been rationalized in terms of the $R_{\rm o}/R_{\rm NP}$ ratios by numerical simulations.²⁰

There is a significant problem with this line of thought: if the VSNPs acted akin to solvents, their typical concentrations $(\phi_{\rm NPs} \approx 0.1-0.2)$ are still much too low to lead to significant chain swelling due to polymer excluded volume. In the case of small molecule solvents, chain swelling does not occur until the polymer concentrations enter the semidilute regime. For example, for poly(methyl methacrylate) (PMMA) solutions in the very good solvent chloroform,²¹ swelling only occurs for polymer volume fractions $\phi_{\rm P}$ < 0.15 or solvent/NP volume fractions >0.85. PS solutions behave in a similar fashion.^{22,23} In the semidilute region the polymer chains are swollen, and the swelling scales with polymer volume fraction as $\phi_{\rm P}^{-1/8}$ until the overlap concentration is reached, at which point the chains reach their maximum size, which is proportional to $N^{3/5}$, where N is the polymerization index. In striking contrast to this wellunderstood behavior of classical polymer solutions, large chain swelling has been reported in PNCs that are very concentrated "polymer-in-NP solutions", well above the semidilute region where the chain excluded volume should vanish.^{1,6}

To address this issue, we have extended our earlier work^{11} on larger 13 nm diameter spherical silica NPs to 1 nm diameter polyhedral oligomeric silsesquioxane (POSS) NPs dispersed in poly(methyl methacrylate) (PMMA). We describe the effect of PMMA chain length, and NP dispersion and concentration, on PMMA R_{g} and compare our results with those from previous studies to advance the current state of the art for this important research topic. Our new data include NP/polymer $(R_{\rm NP}/R_{\sigma})$ size ratios between 0.05 and 0.1, similar to the size ratios investigated in the previous studies that reported large chain swellings.^{1-4,6} As in the earlier experimental studies, we used small-angle neutron scattering (SANS) to determine the polymer chain conformations. SANS can determine the polymer form factor and thus radius of gyration (R_{σ}) if one eliminates the scattering due to the NPs by the zero average contrast (ZAC) method, i.e., by matching the average scattering length density (SLD) of the polymer matrix to that of the NPs by using a mixture of hydrogenated and deuterated polymers. We also used small- and wide-angle X-ray scattering (SAXS and WAXS), transmission electron microscopy (TEM), and Raman spectroscopy to characterize the POSS dispersions. By this protocol we systematically show that the PMMA chains do not swell in the presence of POSS NPs, even though the NPs are well dispersed. Thus, we conclude that our original conjecture, that typical NP concentrations are too low to affect chain conformations, applies. More broadly, we conclude that there is little measured effect of spherical NPs on polymer chain conformations over a broad range of NP sizes, interactions, and compositions.

LITERATURE BACKGROUND

In this section we describe in more detail the previous experimental and computational work addressing the question of polymer chain conformations in PNCs. To the best of our knowledge, Table 1 lists these studies according to the effect of the NPs on the chain conformation (unperturbed, expanded, contracted). Probably the earliest SANS experiment on PNCs to determine chain dimensions was performed by Nakatani et al. on polydisperse polydimethylsiloxane (PDMS) polymers filled with polysilicate NPs (radius $R_{\rm NP} = 1$ nm).¹ For $R_{\rm g} > R_{\rm NP}$, they observed a nearly 60% increase of polymer R_{g} at low NP volume fraction ($\phi_{\rm NP} \cong 0.1$), followed by a decrease of $R_{\rm g}$ at larger $\phi_{\rm NP}$ to values still greater than that of the unfilled polymer. On the other hand, for R_{g} close to but still larger than $R_{\rm NP}$ small polymer chain contraction was observed. A qualitative argument was given to explain these results in terms of NP excluded volume, reinforced by simulations from Sharaf et al.^{2,3} However, no information on the quality of the filler dispersions was provided, naturally leading to questions concerning the relative contributions of particle and polymer chain scattering to the data, its possible effect upon their method of data analysis, and thus the validity of their conclusions (scattering from NP aggregates, if not properly accounted for, can lead to misinterpretation of the SANS data and incorrect R_{g} values). In contrast to these experimental and theoretical results, Vacatello⁴ performed simulations and concluded that no increase in R_g appeared under similar conditions, which suggested that the large chain expansions observed could not be explained by NP excluded volume effects alone. Subsequently, Mackay and co-workers⁵ suggested that the solubility of NPs in polymer matrices depends upon the relative sizes of the polymers and NPs (R_{g} vs R_{NP}). If R_{g} < $R_{\rm NP}$, the polymer and NPs are not miscible. However, when $R_{\rm g}$ > $R_{\rm NP}$, miscibility, accompanied by polymer chain expansion, was found using SANS measurements (a 15% increase in polystyrene (PS) R_g at 10% v/v of cross-linked PS NPs).⁶ They thus concluded that NP miscibility and polymer chain swelling are intimately related, with $R_{\rm g}/R_{\rm NP}$ as a key parameter, in rough agreement with Nakatani et al. They also concluded that their results were consistent with the unchanged chain conformations measured in different systems in which NPs arrange in small aggregates^{7,8,12,13} or phase separate.⁹

Recently, Crawford et al. investigated the silica/PS system for polymer/NP size ratios $R_g > R_{NP}^{10}$ where $R_{NP} = 6.5$ nm. Using TEM, they established that the NPs were well dispersed for all concentrations studied (up to 33% v/v silica) and that the polymer chain conformations were unchanged independent of NP loading and chain length. These observations suggested that miscibility and chain swelling were not generally related and that the R_g/R_{NP} ratio was not the primary controlling parameter for chain expansion, contrary to the findings of ref 6. Although chain conformation may be affected locally, depending on the sign of the NP–polymer interaction (attractive or repulsive) and its strength, Monte Carlo calculations show that the global polymer structure characterized by R_g remains unaffected.^{24,25} Finally, in recent work using VSNPs, Rizk et al. did not observe drastic changes in R_g^{-13}

 R_{g}^{13} . In some cases, polymer chain contraction was observed with increasing NP concentration. Westermann et al.²⁶ observed a 15% or 25% decrease of the R_{g} of polyisoprene (PI) in the presence of 9% v/v or 16% v/v PI–PS–PI micellar NPs, respectively (here $R_{g} > R_{NP} = 8.4$ nm). In other work, Nusser and co-workers²⁷ observed a 2%, 8%, or 12% R_{g} decrease for 18% v/v, 35% v/v, or 50% v/v 13 nm silica NPs in PI, respectively (where the NPs formed aggregates).

Polymer chain dimensions were also studied in PNCs containing anisotropic NPs with high aspect ratios, such as single or multiple wall carbon nanotubes (SWCNT or MWCNT), using both simulations²⁸ and experiments.²⁹ The authors observed no changes in R_g for all MWCNT

concentrations and low SWCNT concentrations²⁹ but at the highest concentration studied of SWCNT (10 wt %) found a large chain expansion of approximately 35%. Their simulations showed²⁸ the presence of local polymer density perturbations (i.e., depletion or densification layers around the NPs), which depended upon the sign and strength of the polymer/NP interaction. In more recent work using molecular dynamics simulations,³⁰ the same group found that spherical NPs lead to a small polymer chain expansion (3% at 18.7% v/v NPs and up to 18% for 40.9% v/v NPs) if the polymer-NP interaction is attractive, but no change of R_g occurs when the interaction is repulsive. In related experimental work, SANS measurements were performed on PNCs with attractive interactions and no changes in R_{g} were observed, but the existence of a bound polymer layer surrounding the NPs was responsible for scattering intensity at low scattering vector q.^{11,31} This bound layer could also screen the attractive interactions with the polymer matrix, leading to the observed absence of chain expansion.

The literature on this topic is thus controversial, although the emerging consensus seems to be that there are at most very small changes in chain dimensions when spherical NPs with diameter 10–15 nm are utilized. The situation for VSNPs, the focus of the current work, is less clear both experimentally and theoretically.

MATERIALS AND METHODS

POSS Nanoparticles. The polyhedral oligomeric silsesquioxane (POSS) NPs were obtained from Hybrid Plastics. The chemical structure of the POSS used, MS0815 (phenyl-SiO_{1.5})₇($C_8H_{17}SiO_{1.5}$), is shown in Scheme 1a. The molecular weight M° is 1068 g/mol, and the density was measured by He pycnometry to be 1.298 g/cm³.

POSS MS0815, whose interaction with the PMMA chains is only weakly attractive, was used to investigate the effect of NPs on polymer $R_{\rm e}$. We thus avoided any POSS derivative that could form hydrogen bonds with PMMA. The reasons we believe the net interaction between the POSS and the PMMA is weakly attractive are as follows. PMMA is soluble in benzene or toluene but insoluble in isooctane and other alkanes.³⁹ These solubility observations suggest that if the intermolecular interaction between the POSS NPs and PMMA chains can be viewed as an "average" value over the ligands (seven phenyls vs one isooctyl), then the average interaction should be weakly attractive. The seven phenyl groups should experience attractive interactions with the PMMA chains, while the single isooctyl chain interaction with PMMA should be repulsive. Of course, since the phenyl or isooctyl ligands are now constrained by their chemical bonds to the POSS cages, they are not able to reorient freely, so the comparison of solubility data in this manner is qualitative at best and experiments designed to investigate and quantify these POSS-polymer interactions would be useful.

The presence of the isooctyl chain on the POSS molecule enhances its solubility in various organic solvents such as hexane or THF (note that octaphenyl POSS is not soluble in these, or indeed in most, organic solvents). However, the residual tendency for this POSS to crystallize despite the presence of the bulky isooctyl chain limits its solubility in PMMA. This factor will be discussed further below.

The size of the POSS NPs was determined by SAXS and SANS measurements. Since the NPs are expected to have diameters on the order of 1-2 nm (depending upon the size of the ligands), the high q region is where their scattering signatures will appear. In Figure S1a we show the SAXS data for a solution of 20% v/v of POSS MS0815 in THF. The data have been fitted in the high q region using a hard sphere form factor with a radius of 0.42 nm. The suppression of scattering at lower q values is consistent with the presence of a hard sphere structure factor due to the high concentration of POSS NPs required to obtain a reasonable X-ray scattering signal. In Figure S1b we show a fit of the experimental structure factor, obtained by

Scheme 1. (a) Molecular Structure of the Polyhedral Oligomeric Silsesquioxane (POSS) Nanoparticles MS0815, $Si_8O_{12}C_{50}H_{52}$ (the Si_8O_{12} Cage Is Outlined in Red); (b) PMMA Chain Structure; and (c) Molecular Structure of the Solvent, Tetrahydrofuran (THF)



dividing the experimental scattering intensity by the hard sphere form factor determined by a fit to the high q portion of I(q), to a Percus-Yevick (P-Y) hard sphere structure factor. This yields a P-Y hardsphere diameter of 1.13 nm, in reasonable agreement with the value determined by the form factor fit. In fact, if one considers that the form factor essentially measures the diameter of the high electron density POSS Si₈O₁₂ cage, since the organic ligands on the POSS molecule have little contrast with the solvent, whereas the structure factor measures the average interparticle distance which includes the contribution from the ligands, one would indeed expect the P-Y diameter to be larger than the form factor diameter. Thus, the SAXS data are consistent with a POSS diameter of approximately 1.0 ± 0.2 nm, similar to the NP diameter in the work of Nakatani et al.¹ In addition, the SAXS data also demonstrate that the POSS are molecularly dispersed in THF, even at 20% v/v. The uncertainty on the POSS diameter corresponds to one standard deviation.

Poly(methyl methacrylate) (PMMA). The polymers used for the SANS, SAXS, and WAXS studies were commercial poly(methyl

methacrylate)s (PMMA, Scheme 1b). Most of the polymers were syndiotactic-rich, except for the 193 kDa h-PMMA, which was atactic. The polymers were purchased from Polymer Source and Varian Inc. Table 2 lists the polymer molecular weights (M_w) and polydispersities (M_w/M_p) . Note that "h" and "d" refer to hydrogenated and deuterated, respectively. Thermal gravimetric analyses (TGA) were performed at DuPont as described in the Supporting Information using Sigma-Aldrich h-PMMA with an average molecular weight of 120 kDa determined by gel permeation analysis with a T_{σ} of 105°C was determined by differential scanning calorimetry (DSC). The results of both analyses were supplied by the manufacturer. In-house DSC measurements for these polymers yielded somewhat higher T_{o} values, defined as the glass transition midpoint, of approximately 120 °C. The s-PMMA used to prepare the PNCs is not semicrystalline, as demonstrated by the absence of any sharp Bragg peaks in our WAXS data (see Figure 2) that could be associated with the presence of polymer crystallinity (see below). These data are in general agreement with SAXS and SANS data for s-PMMA,⁴⁰⁻⁴² where the peaks at high q > 0.5 Å⁻¹ have been assigned to intramolecular structural regularities along the PMMA main chains and intermolecular shortrange distance correlations between chains. These short-range correlations will grow into long-range correlations as polymer crystallinity increases.

Sample Preparation. Tetrahydrofuran (THF, Scheme 1c), a good solvent for both PMMA⁴³ and POSS MS0815, was chosen to prepare the POSS/PMMA nanocomposites. Reagent grade THF was purchased from Sigma-Aldrich. Samples of POSS dispersed in PMMA were prepared by dissolving the two components separately in THF and then mixing the two solutions in the correct proportions to generate the desired final POSS concentration in PMMA. After mixing, the samples were poured into small aluminum pans, and the THF was allowed to slowly evaporate at room temperature for a period of several days until the sample weights reached equilibrium. The data displayed in Figure S2 show that after 4 days the samples have reached a constant mass, indicating that any remaining solvent is evaporating very slowly, and we observed that these sample compositions remained stable even after one year of aging. The residual THF content is 10.2 wt % (13.5% v/v), as determined by TGA measurements discussed further below. We return to the effect of the remaining THF on chain conformation and POSS dispersion in the Results and Discussion sections.

Raman Scattering. Raman data were obtained using a Horiba-JY LabRAM spectrometer equipped with a confocal optical microscope. The excitation wavelengths of 532 or 785 nm were generated by a frequency-doubled Nd:YAG laser or a Ti sapphire laser optically pumped by the 532 nm Nd:YAG laser. Raman data were collected to evaluate the POSS concentration uniformity in the samples and the amount of residual solvent (THF) remaining after annealing at various temperatures (see Figure S3).

Transmission Electron Microscopy (TEM). Nanocomposite pieces were sectioned to a nominal thickness of 90 nm by ultramicrotomy using a diamond knife. Each section was floated onto a 90/10 water/acetone mixture and captured onto a copper mesh microscope grid. The sections were observed unstained using a JEOL TEM operated at 200 kV accelerating voltage, and bright field images were recorded with a digital camera.

Small- and Wide-Angle X-ray Scattering (SAXS and WAXS). Small- and wide-angle X-ray scattering were performed to independently characterize the NP dispersions. There are three

Table 2. Characteristics	s of PMMA	Polymers	Used in	This	Study
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	-		-						
		h-PMMA	d-PMMA						
molecular weight (kDa)	$M_{\rm w} \times 10^3 ~({\rm g/mol})$	$M_{\rm w}/M_{\rm n}$	tacticity	$M_{\rm w} \times 10^3 ~({\rm g/mol})$	$M_{\rm w}/M_{\rm n}$	tacticity			
50	51	1.02	syndiotactic	53	1.09	syndiotactic			
193	193	1.17	atactic	193.7	1.15	syndiotactic			
500	477	1.06	syndiotactic	508	1.13	syndiotactic			

^a"h" and "d" refer to hydrogenated and deuterated, respectively.

detectors for the DND-CAT SIDD beamline at the APS, optimized for WAXS, MAXS, and SAXS. Together, these detectors covered the qrange from 0.002 to 3.5 Å⁻¹. In addition, WAXS data were collected using an in-house laboratory diffractometer (Panalytical X'Pert MPD) using 1.54 Å Cu radiation in a typical Bragg–Brentano configuration which included variable slits and X'Celerator detector. Data were collected over a 2θ range of $4-80^{\circ}$ and a step size of 0.0167°.

Small-Angle Neutron Scattering (SANS). SANS data were collected on beamline CG-2 at the High Flux Isotope Reactor at Oak Ridge National Laboratory (Oak Ridge, TN). A typical sample thickness was 0.4–0.8 mm. Four configurations (detector–sample distance/neutron wavelength) were used: 18.5 m/12 Å, 18.5 m/4.72 Å, 4 m/4.72 Å, and 0.25 m/4.72 Å, providing a *q*-range from 0.0012 to 0.327 Å⁻¹ SANS experiments were also performed at the Laboratoire Léon Brillouin (LLB, CEA Saclay, France) on the PACE spectrometer using three configurations: 4.7 m/17 Å, 4.7 m/6 Å, and 1.0 m/6 Å, giving a *q* range from 0.0024 to 0.37 Å⁻¹. The contrast match/scattering length density measurements for POSS MS0815 were performed at the NIST Center for Neutron Research using the SANS instrument on the cold neutron guide NG7.

To determine the polymer radii of gyration in the presence of NPs, we used the zero average contrast (ZAC) method,^{7,9–11,27,29} a routine technique used to directly measure polymer chain conformations.⁴⁴ By preparing a 90.3% v/v mixture of hydrogenated h-PMMA, with a scattering length density (SLD = $N_a(\sum_i b_i/v)$, with N_a the Avogadro number, b_i the bound coherent neutron scattering length of atom *i* in the molecule, and ν the molar volume) of 1.06×10^{10} cm⁻², and 9.7% v/v deuterated d-PMMA, with a SLD of 6.97 × 10¹⁰ cm⁻², the polymer matrix will have the same SLD as the NPs (SLD = 1.56×10^{10} cm⁻²). The latter was determined for POSS MS0815 by a calculation based upon the POSS chemical formula (Si₈O₁₂C₅₀H₅₂) and its mass density measured by He pycnometry (1.298 g/cm³).

The scattering intensity I(q) from a mixture of hydrogenated and deuterated polymer chains in a solvent is given by

$$I(q) = \phi \varphi_{\rm H} \varphi_{\rm D} \Delta \rho^2 V P(q) + (\varphi_{\rm H} \rho_{\rm H} + \varphi_{\rm D} \rho_{\rm D} - \rho_{\rm S})^2 \times [V \phi P(q) + V \phi^2 S(q)]$$
(1)

In eq 1, ϕ is the polymer volume fraction, $\varphi_{\rm H}$ is the hydrogenated chain volume fraction, $\varphi_{\rm D}$ is the deuterated chain volume fraction, $\Delta \rho^2$ is the neutron contrast term, equal to the square of the difference in SLD for h-PMMA vs d-PMMA (= ($\rho_{\rm H} - \rho_{\rm D})^2$), $\rho_{\rm S}$ is the SLD for the solvent, *V* is the polymer specific volume (= $M_{\rm w}/(dN_{\rm a})$), where *d* is the polymer density and $N_{\rm a}$ is Avogadro's number, P(q) is the polymer chain form factor, and S(q) is the interchain structure factor.

A similar expression to eq 1 will also apply if we replace the solvent molecules with VSNPs, i.e., NPs whose form factors are unity over the q range of interest. Then at the ZAC condition the second term of eq 1 vanishes, and the scattered intensity I(q) becomes

$$I(q) = \phi \varphi_{\rm H} (1 - \varphi_{\rm H}) \Delta \rho^2 V P(q)$$
⁽²⁾

Thus, at the ZAC condition one eliminates the scattering from the NPs and directly measures the form factor of the polymer chains.

The ZAC approach is a unique and powerful method to determine the polymer chain conformation in PNCs. Although the measurement is direct, it requires a very accurate match of the polymer and NP SLDs, a condition that is often difficult to achieve with sufficient accuracy. Furthermore, the determination of R_g is also very sensitive to the details of the data treatment and analysis. As we consider this a very important issue we will explain in detail our treatment (see below).

RESULTS

POSS Dispersion in PMMA. The presence of only weakly attractive POSS–PMMA interactions will naturally make it more difficult to uniformly disperse the POSS NPs in the polymer matrix (see Discussion). The quality of the NP dispersions in the polymer matrices would be expected to have

a strong impact on the polymer R_g since the presence of NP aggregates leads to (effectively) larger particles. For that reason it is very important to characterize the POSS dispersions, and we have done so using WAXS, SAXS, SANS, and TEM. The combination of these four techniques provides an accurate evaluation of the POSS NP dispersion quality on subnanometer to micrometer length scales.

Figure 1 shows TEM images for POSS NPs dispersed in 500 kDa PMMA at 5%, 10%, and 20% v/v, respectively. At 5% v/v,



Figure 1. TEM images of 500 kDa 90.3% v/v h-PMMA/9.7% v/v d-PMMA PNCs filled with 5% (top), 10% (middle), and 20% v/v (bottom) POSS.

TEM images only show a gray background similar to pure PMMA. At this concentration individual POSS NPs are not visible (except for a few small aggregates or crystals), likely due to the low TEM contrast between PMMA and POSS and a POSS whose size is below the spatial resolution limit of the microscope.

At the higher concentration of 10% v/v the individual POSS NPs are still not visible by TEM, but a slightly larger number of aggregates/crystals are present. However, at 20% v/v POSS NPs, many faceted POSS crystals appear. Since the POSS are very soluble in THF, and there is no evidence of POSS

crystallization in the initial optically clear THF/polymer solutions, these crystals likely formed during the solvent evaporation process, while the POSS diffusion coefficient was still large enough for the crystals to grow (i.e., while there is still a significant volume fraction of THF present). Perhaps one can control the POSS crystal size and number density by changing the solvent evaporation rate and/or temperature or by selecting a different solvent or solvent mixture, but we did not explore those many possibilities.

In addition to TEM, we used SANS, SAXS, and WAXS to further characterize our samples (Figure 2). In Figure 2a, SANS data are shown for similar samples composed of 5%, 10%, or 20% v/v POSS in deuterated 500 kDa d-PMMA. At 5% v/v the SANS I(q), normalized to directly yield $M_w P(q)$, presents a strong increase at very low q followed by a long plateau in intensity over almost 1 decade in *q* at intermediate *q*. If one extrapolates the intermediate q plateau to q = 0, one obtains a M_w which is close to the molecular weight of an individual POSS molecule, as expected if the primary scatterers are POSS NPs. A Zimm analysis gives a M_w of 1203 g/mol (vs 1068 g/mol actual) and a R_g of 0.52 nm, the latter consistent with our SAXS characterization of POSS in THF solution which yielded a POSS radius of 0.5 ± 0.1 nm (see Figure.S1). The POSS molecular weight deduced from the neutron measurements suggests that most of the POSS NPs are individually dispersed in the polymer, if we assume that the increased neutron scattering intensity at low q is primarily due to crazes, rather than the small number of POSS aggregates that are visible in the TEM images. In further support of the craze hypothesis, we show SAXS data for pure PMMA in Figure 2b and S4. At low q the scattering shows a power law increase for which $I(q) \sim 1/q^3$, as expected for a craze model in which oriented cylindrical fibrils are the source of the scattering.4

In Figure 2c, we show WAXS spectra for the same PNCs (500 kDa 90.3% v/v h-PMMA/9.7% v/v d-PMMA with 5%, 10%, or 20% v/v POSS). There are no significant differences between the data for pure s-PMMA and the data for the 5% v/ v and 10% v/v nanocomposites. There is no evidence for polymer crystallization in the presence of POSS. The absence of sharp Bragg peaks suggests that the POSS NPs are still molecularly dispersed at 10% v/v. The only change induced by the NPs is an increase of the SANS scattered intensity at low *q* and a slight decrease of the plateau level at high q, both suggesting the presence of a small number of aggregates, which also appear in the TEM images. In the 20% v/v sample we clearly observe in the TEM images the presence of crystals for 20% v/v POSS (Figure 1), together with Bragg peaks at high qcorresponding to the WAXS powder diffraction pattern for POSS MS0815 (see Figure 2c). For the 20% v/v sample, the SANS data (Figure 2a) show a large increase of intensity at low q_i and the intermediate plateau is reduced to a mere inflection point. From this plateau decrease, an effective volume fraction of remaining individual POSS NPs can be determined (assuming that in the 5% v/v samples all the POSS are individually dispersed). One finds 7.7% and 7.1% v/v of individual POSS for the 10% and 20% v/v samples, respectively. In summary, at 5% and 10% v/v the POSS NPs are well dispersed except for the presence of a few small aggregates, while at 20% v/v the NPs clearly have formed numerous crystals, although it is likely that there is still a large fraction of molecularly dispersed POSS (more than 7%, although we do not know the precise solubility limit). Note



Figure 2. (a) $M_w P(q)$ as a function of *q* from SANS measurements for PNCs with 500 kDa d-PMMA. The vol % POSS (5%, 10%, or 20%) is also shown in the legend. (b) X-ray scattering data for 500 kDa 90.3% v/v h-PMMA/9.7% v/v d-PMMA nanocomposites (0%, 5%, 10%, and 20% v/v POSS) from SAXS, MAXS, and WAXS detectors combined. The data are plotted on a log-log scale. The straight solid black line has the q^{-3} dependence expected for scattering by crazes. Note that the intensity of the small-angle scattering from the samples varies as a power law with an exponent close to 3, as expected for craze scattering. Such scattering is still evident in the 5 and 10% v/vsamples, but additional scattering appears for the 20% v/v sample due to POSS aggregates and crystals, the latter of which are also responsible for the Bragg peaks at high q. (c) WAXS data for 500 kDa 90.3% v/v h-PMMA/9.7% v/v d-PMMA nanocomposites (0%, 5%, 10%, and 20% v/v POSS). The data are now plotted on a linearlinear scale. The broad peaks due to short-range order of the PMMA chains can be seen in all the diffraction patterns, and at the highest POSS concentration of 20% v/v sharp Bragg peaks appear due to POSS crystals. Note that a similar behavior is observed for 500 kDa d-PMMA (see Figure S4b).

that 50 and 193 kDa PMMA PNCs behave similarly (see Figures S5 and S6).

These are dense NP solutions in PMMA; even for the low NP concentration of 5% v/v, one estimates the average NP surface-to-surface distance to be less than 2 nm. This is much

smaller than the PMMA R_g for any of the polymers we investigated, indicating that the polymer chains should be strongly confined, although these 1 nm diameter NPs might behave more like small molecule solvents than NPs. To confirm it, one can calculate the POSS–POSS interparticle surface-to-surface distance (ID) assuming a random spatial

distribution of NPs: ID = $d_n \left[\left(\frac{2}{\pi \phi_p} \right) \right]$

$$\frac{3}{100} - 1$$
. Thus, for

our

particles with $d_n = 1.0$ nm, at a NP volume fraction of $\phi_P = 0.05$, the average ID is 1.33 nm. These are very dense concentrations of NPs, with the interparticle distances much less than the R_g values of our polymers. These 1.0 nm diameter NPs are only slightly smaller than the 1.39 nm Kuhn length of PMMA but still more than 6 times larger than the segment length of 0.153 nm⁴⁶ and thus must be approaching the size where molecules behave like true solvents. This will be discussed further below.

Residual Solvent in PNCs. As mentioned previously, POSS/PMMA PNCs have approximately 13.5% v/v of residual THF after equilibration at 20 °C, despite the relatively high vapor pressure of 143 mmHg for THF at that temperature. Moreover, since there is no additional small-angle scattering for the pure polymers with similar amounts of residual THF, we believe the THF is uniformly distributed in the polymer and only affects the "average scattering length of PMMA". To determine the conditions necessary to remove all the solvent from the PNC samples, we ran a series of TGA experiments where the samples were rapidly heated in flowing N₂ to a fixed temperature and held at that temperature for 10 h, during which time the weight change due to solvent loss was continuously monitored. The results of these isothermal TGA experiments are shown in Figure S7.

We could fit the TGA data reasonably well with a singleexponential decay function at temperatures below 70 °C, but at higher temperatures a double-exponential decay was required, suggesting that THF/PMMA desorption becomes a more complex process at higher temperatures. Improved fits were obtained using stretched exponential functions $(e^{-(t/\tau)^{\mu}}, see$ Supporting Information), with the stretching exponent β decreasing from a value very nearly equal to 1.0 at 50 °C to values slightly less than 0.5 at 140 °C. This is consistent with our observation of single-exponential decays at 50 °C that evolve to strongly stretched exponential decays at higher temperatures. This dramatic change in relaxation behavior is probably associated with the polymer glass transition near 105 °C (120 °C midpoint) and clearly shows that a simple Fickian diffusion model is not able to describe solvent loss in this system (Figure S8). The various factors that can impact solvent molecular diffusion within polymer films prior to evaporation at the polymer/air interface have been discussed thoroughly, including the effects of sample shape, concentration-dependent diffusion coefficients, moving phase boundaries, and elastic strain in the polymer matrix.^{47,48} Here we simply use the TGA results to estimate the amounts of remaining solvent in the PNC samples characterized by SANS and SAXS in this study. The TGA fits were extrapolated to long times to determine the equilibrium THF contents of the films at each annealing temperature. These equilibrium THF contents are plotted in Figure 3a, showing that annealing temperatures greater than the pure polymer glass transition temperature of about 105 °C are required to fully eliminate the residual THF solvent, as was also confirmed by our Raman scattering measurements (Figure



Figure 3. (a) Limiting equilibrium THF content (by weight in blue and by volume in red) as a function of annealing temperature for 120 kDa PMMA samples, derived from the TGA data shown in the Supporting Information (Figure S7). (b) Raman spectra of 50 kDa PMMA/THF samples annealed under the conditions shown. The peak at 812 cm⁻¹ is a PMMA vibration, and the peak at 912 cm⁻¹ is the strongest Raman mode due to THF (assigned as an A symmetry ring breathing mode⁴⁹). The THF Raman band is barely detectable in the sample annealed at 140 °C.

3b), in which the THF Raman band (peak at 912 cm⁻¹) is no longer detectable in the sample annealed at 140 °C.

However, annealing the samples at high temperatures had the serious side effect of causing aggregation/crystallization of the POSS NPs, even at 5% v/v. Figure 4c shows the WAXS pattern for a 500 kDa 90.3% v/v/9.7% v/v PMMA sample with 5% v/v POSS MS0815 after annealing the sample for 64 h at 92 °C to remove residual solvent (which was estimated to be approximately 5.7% v/v after annealing based upon our TGA measurements). Bragg peaks due to POSS crystals (Figure 4a) that formed while annealing can be seen, similar to the 20% v/v sample (Figure 4b).

To conclude on the POSS dispersion in PMMA, we have found that the presence of residual THF solvent in the nanocomposites stabilizes the POSS dispersions to 10% v/v. At POSS concentrations of 20% v/v or higher appreciable numbers of POSS crystals were observed to form as the THF concentrations decreased at room temperature. The resulting POSS crystals are on the order of 50-200 nm in size (see Figure 1), and their WAXS patterns are consistent with those of pure MS0815 (see Figure 4). It may be possible to

2000

a 1000

0

0.3

0.2

0.1

0.0

6000

4000

0

0.0

PMMA/0.05 MS0815/92 C anneal

0.5

structure due to the annealing conditions.

b

С 2000 MS0815

1.5

2.0

1.0

q(Å-1)

Figure 4. (a) X-ray powder diffraction (WAXS) pattern for pure POSS MS0815 powder. (b) WAXS pattern for a 500 kDa 90.3% v/v h-PMMA/9.7% v/v d-PMMA sample with 20% v/v POSS MS0815,

which was annealed at room temperature (20 °C). Bragg peaks from

small POSS crystals have formed, as also shown in the TEM photo in

Figure 1. (c) X-ray powder diffraction pattern for a 500 kDa 90.3% v/

v h-PMMA/9.7% v/v d-PMMA sample with 5% v/v POSS MS0815

after annealing the sample for 64 h at 92 °C to remove residual solvent, which we estimate to be approximately 5.7% v/v after

annealing based upon our TGA measurements. The apparent shifts in

Bragg peak positions and changes of their intensities compared to pure POSS shown in (a) are likely due to the sensitivity of peak

locations in our $\theta - 2\theta$ scattering geometry to sample height and

possibly some preferred orientation of the POSS crystallites in the

sample. However, we cannot rule out a different POSS crystal

Based upon the calculated POSS SLD of 1.56×10^{10} cm⁻². the individual POSS NPs will scatter weakly due to the small contrast mismatch with the matrix and will not contribute appreciably to the SANS intensity, especially compared to the much stronger scattering from the mixed d-PMMA/h-PMMA chains. To clearly illustrate this, we also performed SANS measurements of samples composed of 25% v/v d-PMMA/ 75% v/v h-PMMA (molecular weight of 500 kDa, SLD = 2.54 $\times 10^{10}$ cm⁻², or 2.22 $\times 10^{10}$ cm⁻² including the contribution from the 13.5% v/v THF), significantly further away from the POSS contrast match condition of SLD = 1.56×10^{10} cm⁻² compared to the 9.7% v/v d-PMMA/90.3% v/v h-PMMA/ THF matrix SLD of 1.44×10^{10} cm⁻². Figure 5 shows that



control the POSS crystal size and polydispersity by, for example, following a certain annealing sequence at elevated temperatures, or adjusting the POSS concentration, or selecting a different solvent or mixture of solvents (chloroform, CHCl₃, would be an interesting choice).

In the following we proceed to determine the PMMA conformations in the unannealed PMMA/THF/POSS systems, where we find that in the absence of POSS, but with residual solvent, the PMMA molecules still adopt their ideal conformations, as in the pure melts. Thus, the presence of the residual THF does not affect the polymer chain conformations, as is generally found for highly concentrated polymer solutions in good solvents, where excluded volume interactions are fully screened. Thus, as in pure polymer melts, the impact of NPs on the ideal polymer conformations can still be determined despite the presence of residual solvent.

Effect of POSS NPs on Polymer Conformations in POSS/PMMA PNCs. We first address the fact that the presence of residual hydrogenated THF in our samples changes the ZAC condition (described above in the Materials and Methods section), so the POSS SLD is no longer precisely matched to the SLD of its surroundings. On the basis of a typical residual THF content in our PNC samples of 13.5% v/ v, determined by TGA measurements, we estimate that the SLD of the 9.7% v/v d-PMMA/90.3% v/v h-PMMA/THF matrix has a SLD of 1.44×10^{10} cm⁻², whereas the POSS NPs are predicted to have a SLD = 1.56×10^{10} cm⁻². This latter value was derived from the POSS elemental composition

Figure 5. $M_w P(q)$ obtained by SANS for 500 kDa PMMA filled with 10% v/v of POSS NPs (SLD = 1.56×10^{10} cm⁻²) under near-ZAC $(9.7\% \text{ v/v d-PMMA}/90.3\% \text{ v/v h-PMMA}/\text{THF}, \text{SLD} = 1.44 \times 10^{10}$ cm^{-2} ; black circles) and further away from ZAC conditions (25% v/v d-PMMA/75% v/v h-PMMA, SLD = 2.22×10^{10} cm⁻²; blue squares).

after normalization the more mismatched SANS spectrum superimposes upon the spectrum collected closer to the ZAC condition. Thus, we observe that there is very little scattering from the POSS NPs contributing to our data, which leads us to the conclusion that the dominant contribution to the scattering must come from the deuterated and hydrogenated polymer chains, and thus our scattering data can be analyzed to determine the polymer conformations (the R_{σ} values).

Figures 6a, 6c, and 6e show the SANS scattering intensity in ZAC conditions as a function of scattering vector q for respectively 50, 193, and 500 kDa PMMA filled with POSS NPs (5%, 10%, and 20% v/v) compared to the pure polymer. The data were normalized by the polymer volume fractions ϕ (also corrected for the residual THF), $\varphi_{\rm h}, \varphi_{\rm d},$ and the contrast term $\Delta \rho^2 = (\rho_{\text{h-PMMA}} - \rho_{\text{d-PMMA}})^2$, and thus we plot $M_w P(q)$, where M_w is the average PMMA molecular weight and P(q)the polymer form factor. We assume that at high q (i.e., ≈ 0.1 Å⁻¹) $\dot{M}_w P(q)$ should be independent of the POSS volume fraction. This will be true if the incoherent scattering from the hydrogenated POSS does not become a major source of background at high q. More explicitly, a multiplicative factor has been applied to the data for the filled systems to

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Figure 6. $M_w P(q)$ obtained by normalizing the scattering intensity (see main text) as a function of q for PMMA filled with 0% v/v (green circles), 5% v/v (red squares), 10% v/v (blue triangles), or 20% v/v (purple crosses) POSS for (a) 50, (c) 193, or (e) 500 kDa PMMA. In the insets in (a, c, e), we show Zimm plots: $1/(M_w P(q))$ vs q^2 . (b, d, f) Here we show the data as Kratky plots: $q^2 M_w P(q)$ vs q. The black dashed arrow in (b) corresponds to the Gaussian coil (Gc) behavior.

superimpose it on the data for the pure polymer at 0.1 Å⁻¹. (All factors used are listed in Table S2; note that this correction was done for the 50 and 500 kDa PMMA data, but not for the 193 kDa data.)

From SANS measurements under ZAC conditions one can determine the $R_{\rm g}$ of a single chain either from the low q region (Guinier range) or from the high q region (Kratky range). The low q analysis depends upon accurately matching the scattering length density of the polymer matrix to that of the NPs. An appreciable mismatch leads to additional scattering in this region if the NPs form large aggregates, preventing the use of the Guinier region for $R_{\rm g}$ determination.^{9,29} Even if the contrast match is good, unexpected scattering may occur^{7,8,11,12} due to isotope-dependent polymer adsorption on the NP surfaces, but this possibility seems unlikely for the VSNPs used in our study. On the other hand, the values for $R_{\rm g}$ extracted from the high q Kratky region are very sensitive to background subtraction and data normalization.

Here we make use of both low and high q regions to determine the polymer chain behavior in the presence of NPs.¹³ For all PMMA molecular weights and POSS volume fractions (0%, 5%, 10%, and 20% v/v), the low q Guinier region is not affected by extra scattering due to POSS aggregates, consistent with a good contrast match. Thus, we used a Zimm analysis to determine each $R_{\rm g}$ value. By plotting $1/(M_{\rm w}P(q))$ as a function of q^2 for $qR_{\rm g} \ll 1$, one can extract both the polymer molecular weight $(M_{\rm w,0})$ and the radius of gyration $R_{\rm g}$:

$$\frac{1}{M_{\rm w}P(q)} = \frac{1}{M_{\rm w,0}} \left(1 + q^2 \frac{R_{\rm g}^2}{3} \right)$$
(3)

Note that here the plot is linear in a larger $qR_{\rm g}$ range (typically $qR_{\rm g} < 5$), not just for $qR_{\rm g} \ll 1$. For all $M_{\rm w}$, the Zimm plots showed a change in slope at very low $qR_{\rm g}$ due to the presence of crazes in the samples.

In the intermediate and high q regions the scattering intensity includes a large contribution from the incoherent scattering from hydrogen in our samples contributed by the h-PMMA and POSS, together with a smaller contribution from coherent scattering due to sample heterogeneity.⁵⁰ We have measured a series of h-PMMA and d-PMMA reference samples and subtracted those data from our sample data. However, some issues have been encountered in the past with scattering measurements for pure PMMA melts, such as the presence of appreciable multiple scattering, which is not directly proportional to the sample thickness or transmission. For that reason the data cannot be normalized to a true cross section that is independent of sample dimension.⁵¹ This implies that one must subtract the scattering from blanks having the same thicknesses as the ZAC samples.⁵²

Another important issue is the aforementioned presence of residual THF solvent in the films. We thus performed SANS measurements on pure h-PMMA with different thicknesses before and after annealing (Figure S10). Before annealing the incoherent intensity depends upon thickness, while after annealing the incoherent intensities are similar. Thus, depending on whether the PNC samples were annealed or not, we subtracted the appropriate h-PMMA incoherent background value. Note that for the 20% v/v samples (50 and 193 kDa) the incoherent background values that were subtracted seem too large, probably because we have not corrected for the presence of the POSS which has a significantly smaller atom % hydrogen (42.6 atom % H) than either h-PMMA (53.3 atom % H) or h

THF (61.5 atom % H). We thus subtracted a lower incoherent background than expected.

We first consider the 50 kDa systems (Figure 6a). At very low q (<0.002 Å⁻¹) the scattering increases roughly as q^{-3} , which we associate with the presence of crazes in the samples due to the solvent evaporation method. At higher q there is a Guinier regime, characterized by an intensity plateau, which if extrapolated to q = 0 yields the average M_w . From a Zimm analysis for the pure PMMA without NPs, we found a M_w of 44 kDa and a R_g of 6.6 nm (see inset in Figure 6a). This M_w is 12% lower than the nominal M_w of 50 kDa. This discrepancy could be due to the presence of the craze scattering at very low q, which impacts the Zimm analysis, or the fact that the Flory-Huggins parameter $\chi_{H/D}$ between h-PMMA and d-PMMA chains is not equal to zero. Indeed, the fitting using the RPA model with a $\chi_{H/D} = 1.1 \times 10^{-3}$ leads to a good agreement with the experimental values of M_w . This value is in reasonable agreement with χ values determined by SANS measurements of syndiotactic d-PMMA and h-PMMA.⁵³ In the following the Zimm analysis will be used to determine R_{σ} .

Turning now to the behavior at high q, Figure 6b shows the 50 kDa PMMA SANS data in Kratky representation, $q^2M_wP(q)$ as a function of q. For pure PMMA, the spectrum exhibits a maximum around 0.06 Å⁻¹, rather than a broad Kratky plateau, indicating that the PMMA chains do not behave as classical Gaussian coils (Gc) at larger q values. This behavior has been previously observed for PMMA and attributed to the effect of chain stiffness and local structure.^{51,54–56} However, the maximum of the Kratky curve still corresponds to the plateau value for Gaussian coils, which is theoretically given by $2M_w/R_g^2 = 27.4 \text{ g/(mol Å}^2)$ for syndiotactic PMMA.^{46,51} We obtained for the pure PMMA a value of 25.3 g/(mol Å²), in reasonable agreement with the expected one.

When adding POSS at different volume fractions (5%, 10%, and 20% v/v), the $M_w P(q)$ for filled samples superimposes on that of the pure PMMA, confirmed by the Zimm analysis from which R_g is determined (insets in Figures 6a, 6c, and 6e). Figure 7 shows the resulting values of $R_g/R_{g,0}$ (green circles) as a function of POSS volume fraction. The values of $R_g/R_{g,0}$ are 1.0 within the experimental uncertainties, estimated to be ±5%, indicating that the presence of these POSS NPs does not affect the polymer chain conformations.



Figure 7. $R_g/R_{g,0}$ for 50 kDa PMMA PNCs as a function of POSS volume fraction from Zimm (green circles) and Kratky (red squares) analyses. The error bars are estimated around ±5% based on uncertainties from the SANS instrument.

One can also evaluate the R_g values from the Kratky analysis by using the relation

$$\frac{R_{\rm g}}{R_{\rm g,0}} = \sqrt{\frac{(q^2 M_{\rm w} P(q))_0}{q^2 M_{\rm w} P(q)}} \tag{4}$$

where $q^2 M_w P(q)$ corresponds to the observed values at the maxima and R_{g0} is the radius of gyration of the pure PMMA. These results are also shown in Figure 7 (red squares) where the $R_g/R_{g,0}$ ratios are again equal to 1 within the error bars. Thus, from these two different methods of extracting R_{σ} values from the scattering data (Zimm and Kratky), we conclude that the presence of the POSS NPs does not modify the PMMA chain conformations. The same conclusions are likewise derived from the 193 kDa (Figures 6c and 6d) and 500 kDa (Figures 6e and 6f) PMMA SANS data. Table 3 summarizes the different results obtained by the Zimm and Kratky analysis for the different PMMA M_ws. Note that for the nonannealed 500 kDa samples the $R_{\rm g}$ and $M_{\rm w}$ are larger than the expected theoretical one. Since the conclusions on chain conformation are obtained by relative comparison to the pure polymer, this observation does not modify our interpretations.

Figures 8a and 8b present the $R_g/R_{g,0}$ values for all the systems we have studied (50, 193, and 500 kDa PMMA) as functions of POSS volume fraction. The $R_g/R_{g,0}$ values are equal to 1 within the error bars, independent of POSS concentration, indicating that the chain conformations are not affected by the POSS NPs. This is the main message of this paper: for $R_{\rm NP} \ll R_g$, the PMMA chain conformation is not affected by the presence of POSS for a wide range of PMMA M_w s and NP volume fractions.

Figure 8c presents the variation of R_g (from Zimm analysis) with polymerization degree N for pure (0%) and filled PNCs (5% and 10% v/v). It has been suggested that VSNPs may behave like solvent molecules and modify the chain conformations depending upon the sign and magnitude of the NP/polymer interaction.¹⁴ In our case the POSS and PMMA have only weak attractive interactions and R_g scales as $N^{0.53}$. This observation reinforces our main conclusion, which is that the conformations of PMMA chains in the presence of POSS NPs is not perturbed from the ideal melt conformations, and thus there are no observable excluded volume effects.

SANS, SAXS, and WAXS Data for Samples Annealed at Higher Temperatures To Reduce the Amount of Residual Solvent. We also performed SANS measurements on 500 kDa samples under ZAC conditions after annealing the samples at 90-92 °C for 64 h under a N₂ atmosphere (Figure 9a). Note that such annealing temperature is well below the POSS temperature decomposition (see Figure S9). No significant changes in the SANS data were observed compared to before annealing; i.e., the scattering intensity remains essentially unchanged when the residual THF is reduced from 13.5% v/v to approximately 7.5% v/v. The Kratky representations reveal a slight decrease of the maximum after annealing (see inset to Figure 9a). Using relation 4, one obtains a $R_g/R_{g,0} = 1.05$ after annealing (compared to 1.03) before annealing; see Figure 7 and Table 3). We also measured a similar sample of NPs in pure d-PMMA, i.e., in scattering conditions that reveal the POSS dispersion quality (Figure 9b). Here the SANS spectrum after annealing is clearly different from that before annealing, with a q^{-4} intensity upturn at intermediate and low q, indicating the presence of dense POSS aggregates after annealing. This low q upturn is also

Table 3. Summary of the Different Parameters	Obtained by t	he Kratky an	d Zimm Ana	alysis of the S	SANS Data for	the Different
PNCs						

	Kratky analysis		Zimm analysis						
$\Phi_{ ext{POSS}}$	Kratky level (g mol ⁻¹ A ⁻²)	$R_{\rm g}/R_{\rm g,0}$	$1/M_{\rm w} (\times 10^{-5} {\rm g}^{-1} {\rm mol})$	$M_{\rm w}~({\rm kDa})$	Zimm slope ($\times 10^{-2}$ g ⁻¹ mol A ²)	$R_{\rm g}~({\rm nm})$	$R_{\rm g}/R_{\rm g,0}$		
			50 kDa						
0	25.3	1.00	2.27	44	3.33	6.63	1.000		
0.05	25.2	1.00	2.20	45	3.20	6.59	0.995		
0.10	26.4	0.98	2.14	47	3.13	6.62	0.998		
0.20	26.4	0.98	2.06	48	3.02	6.62	0.998		
			193 kDa						
0	25.17	1.00	0.55	182	3.18	13.18	1.000		
0.05	24.99	1.00	0.55	181	3.22	13.23	1.025		
0.10	26.53	0.97	0.52	191	3.04	13.22	1.025		
0.20	25.97	0.98	0.50	198	3.20	13.80	1.037		
			500 kDa						
0	32.86	1.00	0.144	696	2.80	24.19	1.00		
0.05	30.75	1.03	0.150	672	3.05	24.79	1.025		
0.10	31.13	1.03	0.147	591	3.47	24.80	1.025		
0.20	31.90	1.01	0.140	622	3.37	25.09	1.037		
0 (after annealing)	31.21	1.00	0.194	516	2.46	19.53	1.000		
0.05 (after annealing)	28.40	1.05	0.212	471	2.89	20.21	1.035		

accompanied by the appearance of Bragg peaks in WAXS data due to the formation of POSS crystals during annealing (Figure 4b). Despite this aggregation or crystallization, no significant change in chain conformation is observed (Figure 9a). We conclude that neither the presence of residual THF solvent nor well-dispersed or poorly dispersed POSS NPs affects the polymer chain conformations in these PNCs.

DISCUSSION

PNCs that incorporate POSS NPs have been the subject of numerous studies despite the difficulty of dispersing POSS in polymers due to their generally low solubilities, especially for POSS NPs that do not have strong attractive interaction with the polymer chains driven, for example, by hydrogen bond formation. On the other hand, POSS with ligands that are chemically similar to the polymer matrix so that $\chi = 0$ might be expected to disperse well, even at high concentrations. Nevertheless, for a recent SANS study, POSS with oligomeric PEO ligands were dispersed in PEO matrices using n-butanol as a common solvent at concentrations only as high as 5% v/ v.¹³ The polymer R_{σ} values showed a small contraction (5% or less) due to the POSS NPs at that concentration, which was judged to be within the range of experimental uncertainty. In other work, POSS NPs with cyclohexyl or isobutyl ligands were dispersed in PMMA using melt blending, but solubilities less than 1% were reported.⁵⁷ The same group also dispersed three distinctly different POSS NPs in PMMA using THF as the solvent.⁵⁸ The three different POSS, which had different cage structures, also had the following different ligands: cyclohexyl groups, methacryl groups, or a combination of three silanol (Si-OH) groups and seven phenyl groups. The silanol group can form a hydrogen bond with the PMMA carbonyl group. The dispersion quality was assessed by optical transparency, with the more transparent PNCs assumed to have better NP dispersions (the important role in light scattering played by the POSS index of refraction compared to that of the host PMMA polymer was not addressed). Cyclohexyl-POSS did not disperse well even at concentrations as low as 2.5 wt %, whereas methacryl-POSS dispersed well up to 10 wt %, and trisilanol/phenyl-POSS dispersed well up to 20

wt %⁵⁸ based upon the optical transparency of each sample (but very little quantitative optical data were presented). In that study the samples were vacuum annealed at 110 °C for 48 h, at which temperature we estimate from Figure 3 that they would still retain about 3% v/v THF. Based upon our observations when annealing our samples at high temperatures, POSS crystallization under these conditions, especially for POSS with well-defined molecular geometries due to eight equivalent small ligands, is very likely to occur. Cyclohexyl-POSS with eight cyclohexyl groups is symmetric enough to readily form crystals. Our MS0815 POSS, with seven phenyl groups and one large isooctyl chain, is less likely to pack easily in crystals due to its lower symmetry and the bulky isooctyl group and is thus more soluble in general but still crystallizes when it becomes concentrated enough in PMMA during annealing.

Several other papers have described the morphologies of POSS PNCs. In a study of the dielectric properties of ethylphenyl POSS dissolved in polystyrene matrices⁵⁹ good dispersions were reported up to 40 wt % POSS based upon optical transparency. Another paper⁶⁰ showed that the chain length of the POSS ligands is important for dispersion of POSS in polypropylene: POSS with methyl groups were nearly insoluble, while POSS with isobutyl groups apparently dispersed at low loading but aggregated at higher concentrations. A liquid mixture of POSS cages of different sizes (cages with 8, 10, or 12 vertices) with isooctyl ligands could be dispersed in polypropylene to concentrations as high as 10 wt %. Together, these results show the influence of the POSS ligands upon NP dispersion quality in specific polymers.

In several recent theoretical studies Grest and collaborators have used molecular dynamics (MD) simulations to model solvent evaporation from polymer⁶¹ and nanocomposite⁶² films cast from solutions. Two important conclusions from these simulations are that a solvent depleted polymer layer forms near the film surface in both cases, slowing solvent evaporation, and the NP distribution in the polymer film after solvent evaporation is more uniform for weak NP–polymer attraction than for strong attraction, relative to the NP–solvent interactions. Thus, our observations of significant retained



Figure 8. $R_g/R_{g,0}$ as a function of POSS volume fraction for 50, 193, and 500 kDa PMMA PNCs from (a) Zimm analysis and (b) Kratky analysis. The error bars are estimated around ±5% based on uncertainties from SANS instrument. (c) A log–log plot showing the evolution of the radius of gyration R_g as a function of polymerization degree N for 0%, 5%, and 10% v/v POSS in PMMA. The black continuous line represents the best fit giving $R_g = 0.27N^{0.53}$, in good agreement with the literature.²¹

solvent, likely due to a relatively impermeable surface layer, leading to a uniform NP dispersion are consistent with these MD simulations. Furthermore, measurements of solvent loss using ellipsometry for PMMA films spin-coated from toluene solutions show that at approximately 19 vol % solvent the PMMA glass transition increases above room temperature, at which point the rate of solvent loss decreases dramatically.⁶³ For our samples, with 13.5% v/v THF, we surmise that T_g has also increased to a value above room temperature, leading to very slow solvent diffusion and evaporation rates and thus the stable residual solvent concentrations we observe. We emphasize, however, that our PNCs are probably not at true thermodynamic equilibrium but are instead kinetically frustrated from reaching equilibrium. Given a sufficiently



Figure 9. (a) Normalized SANS scattering intensity, $M_wP(q)$, of 500 kDa PMMA/5% v/v POSS under ZAC condition before (red squares) and after (blue triangles) annealing (90–92 °C for 64 h under a N₂ atmosphere). The inset shows the Kratky representations in which the pure PMMA after annealing (green circles) has been added for comparison. (b) SANS scattering intensity of similar sample in pure d-PMMA revealing the POSS structure before (red squares) and after (blue triangles) annealing.

long equilibration time we would indeed expect all the THF solvent to evaporate.

Another important question relates to the relative diffusion coefficients of the THF molecules and the larger POSS NPs in PMMA. Clearly the growth of crystals or amorphous aggregates during solvent evaporation requires diffusion of POSS molecules to the crystal nucleation sites, leading to diffusion-limited aggregation/crystallization. Measurements of the diffusion of small molecules in polymers, including PMMA,⁶⁴ show a strong inverse relationship between molar volume and diffusion coefficient: large molecules diffuse much more slowly than small molecules. Based upon an extrapolation of data shown in ref 62 and using the POSS molar volume of 0.82 L mol⁻¹, the POSS diffusion coefficient in PMMA below $T_{\rm g}$ should be very small ($D < 10^{-15} \, {\rm cm}^2 \, {\rm s}^{-1}$) in the absence of residual solvent. On the other hand, the THF diffusion coefficient would be expected to be much larger based upon its much smaller molar volume (0.089 $L \text{ mol}^{-1}$). In the Supporting Information we have estimated the diffusion coefficients of THF in PMMA as a function of temperature using TGA to observe the weight losses due to solvent evaporation in samples of 120 kDa PMMA cast from THF solution. The diffusion coefficients range from about 4×10^{-9} cm² s⁻¹ at 50 °C to 4×10^{-8} cm² s⁻¹ at 140 °C, showing the significant effect of the increased polymer chain mobility as the glass transition is approached from below ($T_{\rm g} \sim 105~^{\circ}{\rm C}$ in pure PMMA). However, these values represent averages during

the solvent evaporation at each temperature. Since the diffusion coefficients are likely to be not only temperature dependent, but also concentration dependent,^{47,48} the resulting instantaneous evaporation rates will clearly decrease with time as the solvent content of the film decreases, leading to the formation of a relatively impermeable polymer surface layer with low solvent concentration that will impede solvent diffusion to the air/polymer interface, especially at temperatures below T_g . The molecular dynamics results of Grest and co-workers support this scenario.⁶² As the THF solvent concentration decreases, the POSS concentration increases and exceeds the solubility limit in the PMMA/THF matrix, leading to crystal growth. This will continue until the POSS diffusion constant in the matrix becomes too small to support further crystal nucleation or growth.

Although the presence of residual solvent would be expected to have a large impact on mechanical properties and is thus undesirable for studies of those properties, $^{65-67}$ the presence of 10 wt % residual THF (a value typical of a number of solvent cast polymers that are dried at room temperature⁶⁸) should not impact the polymer chain conformations since the polymers are still well within the concentrated, ideal chain conformation regions of their phase diagrams. In fact, our SANS data for unfilled PMMA samples show that the polymer chains in the presence of 10 wt % residual solvent (THF) indeed retain their ideal conformations for the three molecular weights we studied (see Figure 8c).

Finally, we return to our primary objective-to determine the effect of POSS NPs on the polymer radius of gyration in our PNCs. As described in the Introduction, Nakatani et al.¹ and Tuteja et al.⁶ reported very large polymer chain expansions (60% increase of polymer $R_{\rm g}$ at 40% v/v of NPs for Nakatani and 20% increase at 10% v/v for Tuteja) in PNCs containing VSNPs. These authors proposed that NP miscibility and polymer chain swelling are closely related: well-dispersed VSNPs act as a solvent and swell the polymer chains when $R_{\rm NP}/R_{\rm g}$ < 1. In our case, both conditions, $R_{\rm NP}/R_{\rm g}$ < 1 and good POSS dispersion (at 5 and 10% v/v), are fulfilled, but no changes in R_{σ} are observed. How can we reconcile these different results? First, in that study¹ no information on the quality of the NP dispersions was provided, despite the fact that scattering from NP aggregates can lead to erroneous R_{g} values. In their experiment the investigated q-range was also small, 0.008-0.06 Å⁻¹, and the data in that range will likely be impacted by the scattering from NP aggregates. In comparison, in our study we evaluate the quality of the POSS dispersions, use a much larger SANS q-range, and minimize POSS-PMMA SLD mismatch and thus the scattering from POSS aggregates. Second, simulations suggest that attractive NP/polymer interactions, combined with $R_{\rm NP} < R_{\rm g}$, are necessary to cause an increase in $R_{\rm g}$. Karatrantos et al.³⁰ showed using simulations that only PNCs with attractive NP/polymer interactions lead to chain expansion consistent with NP excluded volume for high VSNP volume fractions (less than 20% expansion for 40% v/v NP concentration), but no changes are predicted for repulsive polymer-NP interactions even at that volume fraction. However, at 10-20% v/v, the calculations predict almost no change of polymer R_g , independent of the sign of the interaction. Although we believe our NP/polymer interactions should be weakly attractive, we cannot rule out that they are weakly repulsive instead. In either case, our experimental work is roughly in agreement with the predictions of Karatrantos et

al. since we observe no measurable change in R_g due to the POSS NPs. We have recently investigated an attractive silica NP/PMMA PNC and did not observe any changes in R_g .¹¹ However, in that case the NPs were larger in size (13 nm diameter) and the PMMA chains were found to adsorb on their surfaces. The case of very small (~1 nm) NPs with strongly attractive NP-polymer interactions has yet to be carefully investigated, especially at high concentrations where the calculations predict chain expansions scaling with NP excluded volume alone, $R_g/R_{g,0} = (1 - \phi_{\rm NP})^{-1/3}$, while SANS measurements^{1,6} showed much larger expansions.

CONCLUSION

We have investigated the PMMA polymer chain conformations in the presence of ~1.0 nm diameter POSS NPs. The POSS dispersions in PMMA were characterized using SAXS, WAXS, and TEM. At low POSS concentrations (5% and 10% v/v), and in the presence of residual THF solvent, the POSS NPs are well dispersed, while at higher concentrations (20% v/v), or without residual solvent, the POSS are found to crystallize or form aggregates. Using SANS, we measured the polymer radius of gyration R_g as a function of POSS concentration and PMMA $M_{\rm w}$ in samples with well-dispersed POSS NPs. We observed no deviation of R_g from ideal chain behavior. Since there is no specific attractive interaction between the POSS NPs and the PMMA chains, our results agree with recent simulation work but are in striking contrast to other experimental studies that found large effects of VSNPs on polymer chain conformations. Whether this is due to the specific polymer systems and nanoparticles used, including their relative sizes and the nature of the interactions between them (attractive, repulsive or athermal), remains unknown. Whether "universal" behavior is to be expected is an important question for future studies to address.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.8b00432.

SAXS and SANS of POSS NPs and pure PMMA, TGA measurements (isotherm experiments and pure POSS), Raman spectra of POSS PNCs with THF, TEM, and WAXS data of 50 and 193 kDa POSS PNCs, diffusion coefficient of THF in PMMA (PDF)

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