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Ultrasmall Nanoparticles Diluted Chain Entanglement in Polymer Nanocomposites

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Electronic Supplementary Information

Abstract Nanoparticle-polymer composites exhibit unusual mechanical properties and chain dynamics when the nanoparticle size is smaller than the entanglement mesh size of the matrix polymer chains, corresponding to the ultrasmall regime defined by de Gennes. However, the mechanism is still ambiguous due to the lack of suitable model systems. Here, we develop an ultrasmall nanoparticle system by using a bimodal grafting strategy to graft both short alkyl chains and long polystyrene chains onto the polyoxometalate molecular nanoparticles with a tunable repulsive potential between the nanoparticles, thus facilitating their uniform dispersion in polystyrene matrices. Linear viscoelasticity of the resultant nanocomposites changes with increasing the filler content, which shows a decrease in both plateau modulus and terminal relaxation time, indicative of a dilution effect of the nanoparticles. Namely, the entanglement network becomes sparser with increasing the filler content.

Keywords Polymer nanocomposites; Ultrasmall nanoparticles; Chain entanglement; Polyoxometalates

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INTRODUCTION

The incorporation of nanoparticles (NPs) into polymer matrices can form polymer nanocomposites (PNCs) with improved mechanical, optical, electrical, and thermal properties.^[1,2] To optimize the performance and facilitate the processing of PNCs, many investigations have been devoted to understanding the synergy between NPs and polymer matrices, in particular, the NP-altered dynamics of matrix chains in PNCs.^[3] Recently, the NP size has been found to play an important role in determining the rheological behaviors of PNCs. For instance, the micron-sized particles would increase the viscosity of neat polymer melt from η_p to η , as predicted by the Einstein-Bachelor law as $\eta = \eta_p \times (1 + 2.5\phi + 6.2\phi^2)$, where ϕ is the particle volume fraction.^[4,5] However, for the NPs with size approaching to or smaller than the dimension of matrix polymer chains, η could be reduced, which is referred to as a non-Einstein-like decrease in viscosity in the literature.^[6–10] This unusual phenomenon appeared to arise from the dilution of polymer entanglement mesh that had been predicted as an ultrasmall regime by de Gennes *et al.* in 2000.^[11] Intensive theoretical and simulation

studies have been given to this ultrasmall regime in the recent decade. These studies together revealed that the ultrasmall NPs could show non-Stokes-Einstein diffusion in polymer matrices,^[12–16] swell the matrices, expand the entanglement mesh size,^[17,18] and reduce the melt viscosity of matrices.^[19] However, only a few experimental works have been reported probably because the actual interaction potential between nanoparticles could not be tuned as easily as in the simulation and theoretical studies.^[10,20] To address this issue, it is highly demanded to develop the model systems of ultrasmall NPs with well tunable interaction potential.

Polyoxometalates (POMs) are nanoscale metal-oxide clusters with the sizes from 0.5 nm to 6 nm.^[21] POMs have well-defined framework structures, abundant chemical compositions, and a wide range of functions in catalysis, optics, magnetics, *etc.*, which enable them to be both structural synthon and functional synthon in preparation of hybrid materials and nanocomposites.^[22–29] Moreover, the rigid and compact inorganic frameworks also allow POMs to serve as molecular NPs^[30,31] and suitable moieties of model ultrasmall NPs. However, it is difficult to incorporate POMs into polymer matrices, particularly the low polar matrices like polystyrene, due to the discrepancy of surface chemical properties, which would lead to serious phase separation accordingly.^[32]

In this work, we developed a type of bimodal grafted POMs that can be well dispersed in polystyrene matrices. By

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studying linear viscoelasticity of this model system, we elucidate a dynamic role of the ultrasmall NPs: the plateau and terminal relaxation time decrease owing to an entanglement dilution effect of the ultrasmall NPs, which is instructive to understand the dynamical nature in ultrasmall NP-based PNCs.

EXPERIMENTAL

Materials

2,2'-Azobis(2-methylpropionitrile) (AIBN, 99%, Aladdin) was recrystallized from methanol. Styrene (99%, Aladdin) and dimethylformamide (DMF, analytical grade, Beijing Chemical Plant) were both dried with CaH_2 and then distilled under reduced pressure. Trioctylamine (98%, Aldrich), 1,3-dicyclohexylcarbodiimide (DCC, Sigma-Aldrich), 4-(dimethylamino)pyridine (DMAP, Alfa Aesar), carbon disulfide (99.9%, Aladdin), 1-butanethiol (99%, J&K), 11-bromo-1-undecanol (98%, J&K), 2-bromopropanoic acid (98%, Aladdin), and polystyrene ($M_n = 15.0 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$, PDI = 1.09, Polymer Source) were used as received. $\text{K}_6\text{CoW}_{12}\text{O}_{40}$ (CoW) was synthesized according to the literature.^[33] All used solvents were of analytical grade.

Synthesis of Cationic Chain Transfer Agent

A chain transfer agent was synthesized by using a modified method as reported in our previous work.^[34] The whole synthetic route is shown in Scheme S1 (in electronic supplementary information, ESI), which includes three steps as follows.

Synthesis of 1,2-(butylthiocarbonothioylthio) propanoic acid (abbreviated as BCTA)

1-Butanethiol (9.5 mL) and triethylamine (16 mL) were added to 70 mL of dichloromethane. The mixture solution was cooled to 0 °C by ice bath and stirred for 30 min under the protection of nitrogen. Then carbon disulfide (7 mL) in dichloromethane (30 mL) was added. The ice bath was removed after another 30 min, followed by dropwise addition of 2-bromopropanoic acid (10 mL) in dichloromethane (25 mL). After 2-h reaction, the solvent was removed by rotary evaporation. The raw product was dissolved in chloroform, washed with 10% HCl, and dialyzed in water for three times. The solvent was then removed through rotary evaporation, and pure product was obtained by silica gel column chromatography (petroleum ether:ethyl acetate = 20:1, V/V ; yield: 81%). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 25 °C, TMS, δ , ppm, Fig. S1 in ESI): 4.87 (q, 1H, $-\text{SCH}-$), 3.39 (t, 2H, $-\text{CH}_2\text{S}-$), 1.72 (m, 2H, $-\text{CH}_2\text{CH}_2\text{S}-$), 1.66 (d, 3H, $-\text{SCHCH}_3$), 1.50 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 0.98 (t, 3H, $-\text{CH}_2\text{CH}_3$).

Synthesis of 11-hydroxy- N,N,N -trioctylundecan-1-aminium bromide (abbreviated as HTOA)

11-Bromo-1-undecanol (2.13 g) and trioctylamine (2 g) were dissolved in 50 mL of ethanol and stirred under reflux condition. After 48 h, the reaction solution was concentrated and added dropwisely to frozen diethyl ether to obtain a precipitate. The precipitate was re-dissolved in ethanol and re-predicated by diethyl ether for three times. The pure product was obtained as a white powder with a yield of 60%.

$^1\text{H-NMR}$ (500 MHz, d-DMSO, 25 °C, TMS, δ , ppm, Fig. S2 in ESI): 4.33 (t, 2H, $-\text{CH}_2\text{O}-$), 3.16 (t, 8H, $(-\text{CH}_2)_4\text{N}$), 1.57 (s, 8H, $(-\text{CH}_2\text{CH}_2)_4\text{N}$), 1.40 (t, 2H, $-\text{CH}_2\text{CH}_2\text{O}-$), 1.36–1.22 (br, 44H, $(-\text{CH}_2)_5\text{CH}_3$), $-(\text{CH}_2)_7\text{CH}_2\text{CH}_2\text{O}-$), 0.88 (t, 9H, $(-\text{CH}_2)_5\text{CH}_3$).

Synthesis of 11-((2-(((butylthio)carbonothioylthio)propanoyl)oxy)- N,N,N -trioctylundecan-1-aminium bromide (abbreviated as BTOA)

BCTA (1 g) and HTOA (2.54 g) were dissolved in 80 mL of dichloromethane and stirred for 30 min under ice bath. Then, DCC (1.03 g) in dichloromethane was added into the solution. After stirring for 10 min, DMAP (0.06 g) dissolved in 5 mL dichloromethane was added. After stirring for 30 min, the ice bath was removed. The solution gradually turned from red to yellow. After 12 h, the reaction was stopped, and the solvent was removed through rotary evaporation. The raw product was dissolved in frozen diethyl ether, the white sediment was removed, and then the solvent was removed through rotary evaporation. The pure product was obtained by silica gel column chromatography (chloroform:methanol = 15:1, V/V) with a yield of 75%. $^1\text{H-NMR}$ (500 MHz, d-DMSO, 25 °C, TMS, δ , ppm, Fig. S3 in ESI): 4.80 (q, 1H, $-\text{SCH}(\text{CH}_3)-$), 4.11 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 3.38 (m, 10H, $(-\text{CH}_2\text{CH}_2)_4\text{N}$, $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.70 (m, 8H, $(-\text{CH}_2\text{CH}_2)_4\text{N}$), 1.65 (m, 4H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$, $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.61 (d, 3H, $-\text{SCHCH}_3$), 1.42 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 1.37 (m, 2H, $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.29 (m, 42H, $-\text{N}(\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3)_3$, $-(\text{CH}_2)_6\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 0.94 (t, 3H, $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.90 (t, 9H, $-\text{N}(\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3)_3$). IR (KBr, ν , cm^{-1} , Fig. S4 in ESI): 2955 (CH_3), 2926 (CH_2), 2855 (CH_3), 1734 ($\text{C}=\text{O}$), 1662 ($\text{C}-\text{N}$), 1058 ($\text{C}=\text{S}$). The MALDI-TOF spectrum of BTOA shows a dominant peak at m/z of 745.4, well consistent with the cationic part of BTOA ($\text{C}_{43}\text{H}_{86}\text{NO}_2\text{S}_3^+$) whose molecular weight is 745.3, thus confirming the expected composition of BTOA (Fig. S5 in ESI).

Synthesis of Chain Transfer Agent Modified CoW

BTOA (0.2 g) was dissolved in 70 mL of chloroform, and $\text{K}_6\text{CoW}_{12}\text{O}_{40}$ was dissolved in 70 mL of water. The BTOA chloroform solution was added dropwise into the $\text{K}_6\text{CoW}_{12}\text{O}_{40}$ aqueous solution and stirred intensely at room temperature for 2 h. After that, the chloroform solution was separated and washed with dialyzed water for three times. After removing the chloroform by vacuum evaporation, the pure CoW-BTOA complex was obtained with a yield of 60%. $^1\text{H-NMR}$ (500 MHz, d-DMSO, 25 °C, TMS, δ , ppm, Fig. S3 in ESI): 4.80 (q, 1H, $-\text{SCH}(\text{CH}_3)-$), 4.15 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 3.38 (m, 10H, $(-\text{CH}_2\text{CH}_2)_4\text{N}$, $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.70 (m, 8H, $(-\text{CH}_2\text{CH}_2)_4\text{N}$), 1.65 (m, 4H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$, $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.61 (d, 3H, $-\text{SCHCH}_3$), 1.46 (m, 4H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$, $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.27 (br, 42H, $-\text{N}(\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3)_3$, $-(\text{CH}_2)_6\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 0.94 (t, 3H, $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.89 (br, 9H, $-\text{N}(\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3)_3$). IR (KBr, ν , cm^{-1} , Fig. S4 in ESI): 938 ($\text{W}=\text{O}_a$), 874 ($\text{W}-\text{O}_b-\text{W}$), 764 ($\text{W}-\text{O}_c-\text{W}$); Elemental analysis (%): Calcd. for $(\text{CoW}_{12}\text{O}_{40}(\text{C}_{22}\text{H}_{44}\text{NO}_2\text{S}_3))_6$, 5609.7): C 42.01, H 7.05, N 1.14; Found: C 42.04, H 6.72, N 1.40.

Synthesis of Polystyrene Grafted CoW

The CoW-BTOA complex (0.025 mmol) was dissolved in 2 mL of DMF first, and then styrene and AIBN were added. The molar ratio of [AIBN]/[trithioester terminal group of BTOA] was set as 0.1 to minimize the termination by surface anchored polymeric radical recombination. The molar ratio of styrene to the trithioester groups of BTOA was adjusted at 150:1. The mixture solution was placed into an ampoule, degassed by the freeze-pump-thaw cycle for three times, backfilled with nitrogen, and then reacted at 65 °C in an oil bath for 10 h. The pure grafted-CoW was precipitated from diethyl ether and denoted as g-CoW. ¹H-NMR (500 MHz, CDCl₃, 25 °C, TMS, δ , ppm, Fig. S6 in ESI): 7.3–6.3 (5H, C₆H₅–), 1.0–0.8 (3H, –S(CH₂)₃CH₃); IR (KBr, ν , cm^{–1}, Fig. S7 in ESI): 940 (W=O_d), 876 (W–O_b–W), 698 (benzene ring wag); Elemental analysis (%): Calcd. for (CoW₁₂O₄₀(C₂₂H₄₄NO₂S₃(C₈H₈)₃₀)₆, 23106.7): C 77.52, H 7.05, N 0.35; Found: C 77.07, H 7.43, N 0.31.

Preparation of Nanocomposites

g-CoW was dissolved in chloroform and mixed with the matrix polystyrene. The mixtures were sonicated for 5 min, placed at room temperature for 1 day, and then dried in vacuum at 150 °C for 7 days to remove the solvent completely, yielding transparent nanocomposites.

Measurements

¹H-NMR spectra were recorded on a Bruker UltraShield 500 MHz spectrometer. Elemental analysis was carried out on a Flash EA1112 instrument from Thermo-Quest Italia S.P.A. FTIR spectra were collected on a Bruker Vertex 80v spectrometer equipped with a deuterated triglycine sulfate detector for 32 scans at a resolution of 4 cm^{–1}. MALDI-TOF spectra were measured on a Bruker autoFlexTM MALDI-TOF mass spectrometer. Dynamic light scattering (DLS) measurements were performed by utilizing a Malvern Zetasizer NanoZS instrument with 20 runs per measurement at room temperature. DSC measurements were carried out at temperature ramp rates of 10 K·min^{–1} using a TA Instruments DSC Q20 device. Transmission electron microscopy (TEM) images were acquired on a JEM-2100F electron microscope operated at 200 kV. The thin sections of nanocomposites were microtomed using a Leica EM UC7 microtome into films of 80 nm thickness. Linear viscoelasticity (LVE) measurements were conducted on the ARES-G2 rheometer (TA Instrument) with 8 mm parallel plates geometry. The samples were dried in a vacuum oven at 120 °C for 1 week and subjected to the frequency sweep measurements (0.1–100 rad/s) under nitrogen protection in a temperature range of 120–220 °C. The strain amplitude was kept in a linear regime ($\leq 10\%$) determined through the strain-sweep measurements.

RESULTS AND DISCUSSION

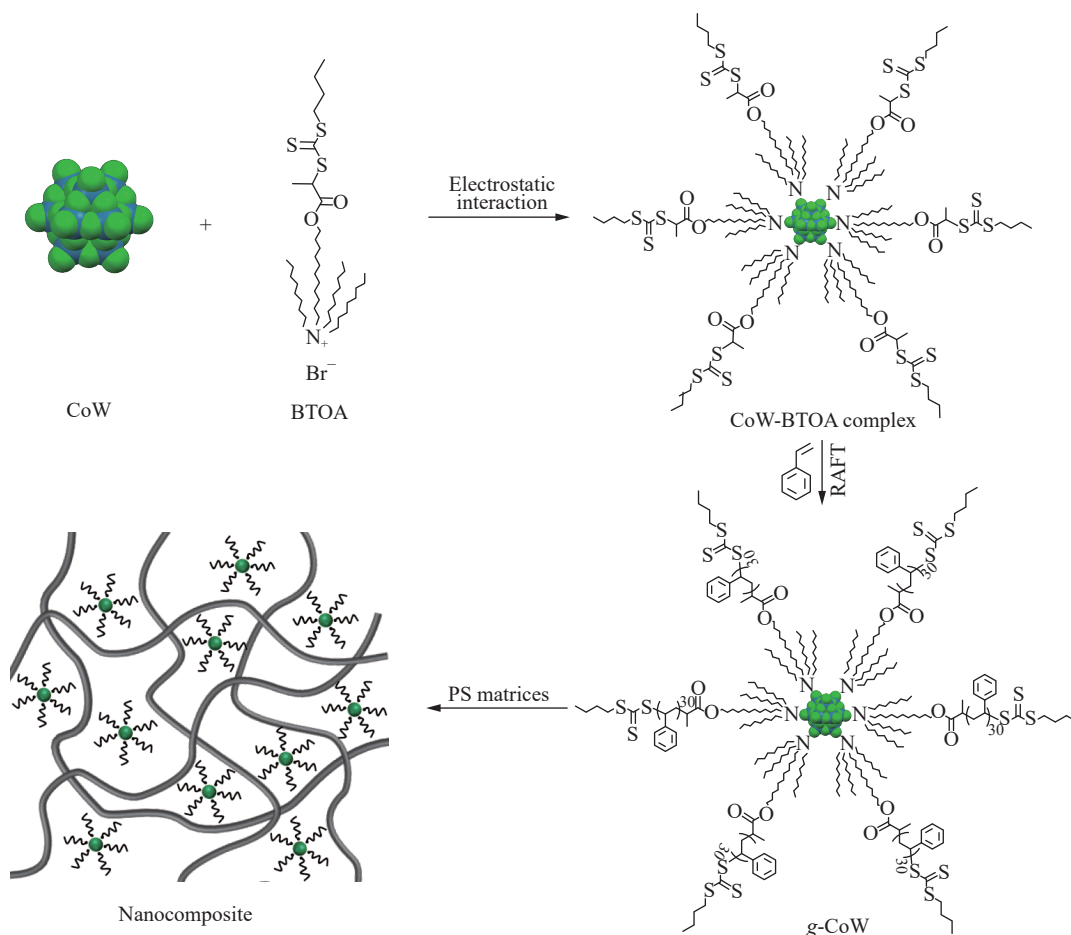
Design and Synthesis of Matrix-dispersible Molecular Nanoparticles

POMs generally exhibit high interfacial energy due to their small sizes, thereby tending to aggregate particularly in low polar polymer matrices. The modification of POMs with polymer moieties is widely used to improve the compatibility

between POMs and polymer matrix. In general, two main strategies are available based on covalent modification^[35–41] and noncovalent modification,^[23,27] respectively, which have been systemically summarized in several reviews.^[42–44] In this work, we developed a noncovalent bimodal grafting strategy with a high grafting density feature to modify the surface of POMs, so as to achieve their dispersion in polymer matrices. To realize the highly grafting density, we selected the highly negatively charged Keggin-type POM [CoW₁₂O₄₀]^{6–} (CoW) of a sphere shape with a diameter of *ca.* 1 nm.

A two-step grafting procedure was adopted as shown in Scheme 1. In the first step, a bifunctional chain transfer agent (BTOA), which contains a quaternized trioctylamine group and a trithioester group, was grafted onto the surface of CoW *via* electrostatic interaction to form a CoW-BTOA complex. The complex is no longer soluble in water but well dissolved in organic solvents like chloroform, suggesting that the hydrophilic surface of CoW has been encapsulated by the hydrophobic alkyl chains of BTOA. The successful electrostatic complexation is also confirmed by NMR shown in Fig. S3 (in ESI). The proton resonance signals of the CoW-BTOA complex are broader and split weaker compared with those of BTOA. This phenomenon indicates the limited mobility of BTOA tethered on CoW surface because of the strong electrostatic complexation, as reported in the literature.^[27] The IR spectra of CoW-BTOA complex display the individual vibrational bands of both CoW and BTOA, reflecting their coexistence in the complex. Furthermore, the characteristic tungsten-oxygen vibration bands of CoW appear at 938 cm^{–1} (W=O_d), 874 cm^{–1} (W–O_b–W), and 764 cm^{–1} (W–O_c–W),^[45] confirming that the framework of CoW is well retained in the complex (Fig. S4 in ESI). Based on the elemental analysis results in the Experimental Section, the chemical composition of CoW-BTOA complex is determined to be (BTOA)₆CoW, indicating that the six negative charges of CoW anions have been completely neutralized by BTOA cations. Based on this composition, the total number of octyl chains surrounding one CoW is 18, corresponding to an extremely high grafting density of 5.7 nm^{–2}.

In the second step of bimodal grafting, the trithioester groups were used to implement the RAFT polymerization to graft PS chains onto CoW, forming g-CoW. The successful grafting is confirmed by NMR, IR, and MALDI-TOF results. The ¹H-NMR spectrum of g-CoW displays characteristic proton signals of the aromatic ring of PS chains at 6.3–7.2 ppm and the terminal methyl groups of BTOA at 0.8–1.0 ppm (Fig. S6 in ESI). The IR spectrum of g-CoW shows the benzene ring wagging vibration of PS chains at 698 cm^{–1}; meantime, the tungsten-oxygen vibration of CoW component is also observed between 1000 and 800 cm^{–1}, which indicates that the CoW framework is intact during the RAFT polymerization process (Fig. S7 in ESI). MALDI-TOF measurement was further used to characterize the molecular weight of the grafted PS chains, which shows a normal distribution (Fig. 1). The difference between adjacent peaks in MALDI-TOF spectrum is 104.1, consistent with a repeating unit of PS, *i.e.*, C₈H₈. The calculated *M_n* is 3.9 kg·mol^{–1},



Scheme 1 Synthesis route to g-CoW and its nanocomposite formation with PS matrices

which reflects the M_n value of a whole ensemble of cationic polymer chain that contains BTOA part and PS part. This value corresponds to the degree of polymerization (DP) of 30. The polydispersity index (PDI) value is 1.04, reflecting a well-controlled polymerization. By using the DP value to fit the elemental analysis results of g-CoW, a chain number of 6 is obtained, which means that the six trithioester groups on the periphery of CoW-BTOA complex were all initiated during the RAFT polymerization. Based on this, the grafting density of PS chains surrounding one g-CoW is 1.9 nm^{-2} .

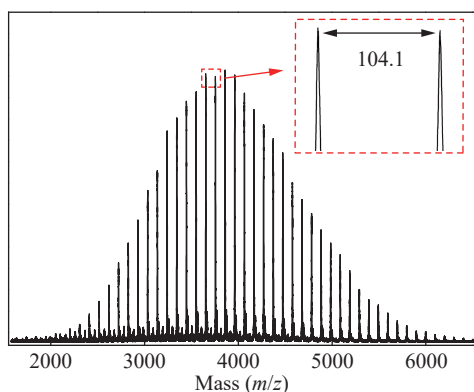


Fig. 1 MALDI-TOF spectrum of g-CoW

DLS and TEM measurements were used to characterize the size of g-CoW in solution and in dry state, respectively. DLS (Fig. 2a) shows a distribution of the hydrodynamic diameters (D_h) of g-CoW in chloroform that peaks at around 7.5 nm. TEM images (Fig. 2b) of dry g-CoW casted on a copper grid and stained by RuO_4 reveal nanospheres with a diameter of *ca.* 7.2 nm. This value is slightly smaller than D_h , probably because the g-CoW chains are fully solvated in the DLS measurement whereas collapsed after casting. For both cases, the size of g-CoW is smaller than the entangled mesh size (around 8.5 nm) of PS.^[46] Therefore, the g-CoW particles meet the requirement of model ultrasmall NPs in PS matrices.

Phase Morphology and Rheological Behavior of Nanocomposites

g-CoW is well soluble in the low polar solvents such as chloroform and toluene, which enables it to be incorporated into PS matrices *via* the solution blending method to form nanocomposites after solvent evaporation. In this work, a linear PS sample of $M_n = 15.0 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$ (PDI = 1.09) was chosen and denoted as PS150k. This molecular weight is much larger than the entanglement molecular weight of $1.8 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$ evaluated from the plateau modulus and a critical entangled molecular weight of $3.5 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$.^[46,47] By adjusting the mass percentage of CoW in PS150k matrix to be 1 wt%, 3 wt%, and 5 wt%, three nanocomposites, *i.e.*

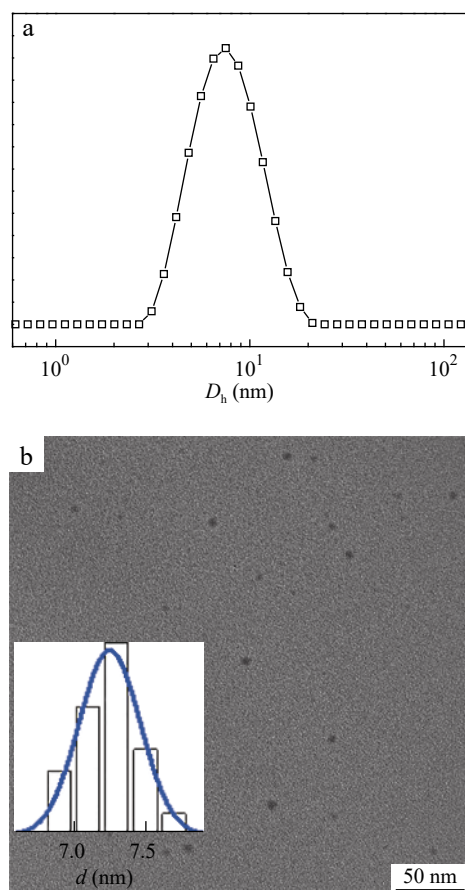


Fig. 2 (a) DLS data of *g*-CoW in chloroform with the concentration of $1 \text{ mg} \cdot \text{mL}^{-1}$ and (b) TEM image of dry *g*-CoW stained by RuO_4

PS150k-1%, PS150k-3%, and PS150k-5%, were obtained, as listed in Table 1. The nanocomposites are all transparent, as exemplified by the photo of PS150k-3% in the inset of Fig. 3, indicative of no detectable phase separation occurring in the samples. Meanwhile, the TEM image of microtomed PS150k-3% also exhibits a uniform phase morphology without any agglomerated regions of *g*-CoW, as shown in Fig. 3. Similar features were also observed for the other two nanocomposites.

Table 1 Summary of the nanocomposites, including CoW content, glass transition temperature (T_g), and terminal viscosity (η_0) at T_{iso}

Sample	CoW (wt%)	T_g ($^{\circ}\text{C}$)	T_{iso} ($^{\circ}\text{C}$)	η_0 ($\text{Pa} \cdot \text{s}$)
PS150k	0	108	170	8.1×10^4
PS150k-1%	1	105	168	6.6×10^4
PS150k-3%	3	102	164	6.3×10^4
PS150k-5%	5	101	163	3.3×10^4

The intrinsic T_g of *g*-CoW ($= 79^{\circ}\text{C}$, see Fig. S8 in ESI) is $\sim 30^{\circ}\text{C}$ lower than that of PS150k matrix ($= 108^{\circ}\text{C}$), probably because the grafting chains have much lower molecular weight and accordingly higher density of chain ends, leading to the larger free volume. The intrinsic T_g of *g*-CoW cannot be found in the nanocomposites. Instead, each nanocomposite sample shows a single glass transition process (DSC traces are shown in Fig. S9 in ESI) and the T_g value (sum-

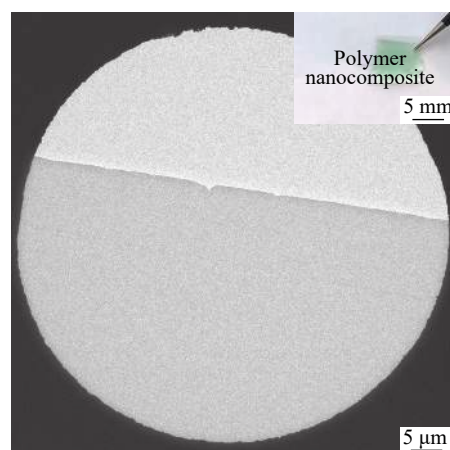


Fig. 3 TEM image of an ultrathin section of PS150k-3% nanocomposite on copper grids (Inset is a photo of the nanocomposite.)

marized in Table 1) decreases with increasing *g*-CoW content. This result indicates good miscibility of *g*-CoW and matrix, and the latter is plasticized by the former.

Fig. 4 compares the master curves of storage and loss moduli (G' and G'') of PS150k and the related nanocomposites at the same reference temperature $T_r = 170^{\circ}\text{C}$. To construct the master curve, raw G' and G'' data at T are normalized by an intensity factor $b_T = T_r/T$ (A factor of $b_T = T_r \rho_r / T \rho$ should be chosen in principle for the rubbery moduli having

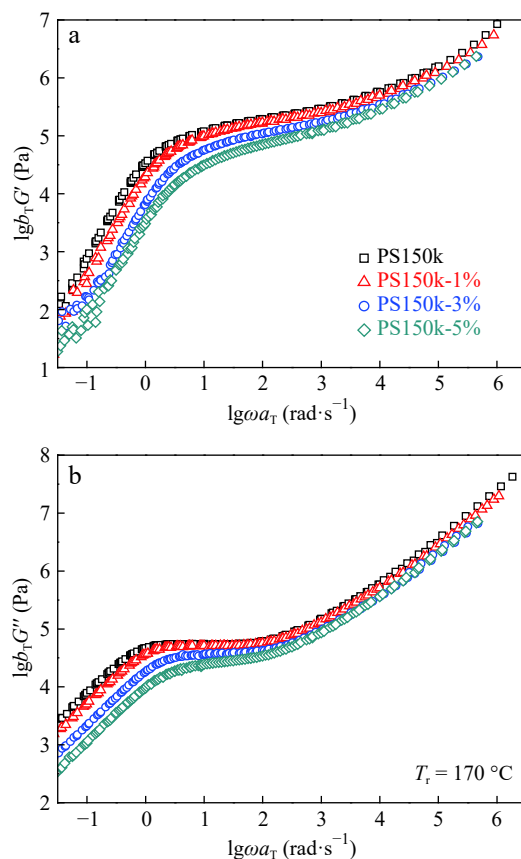


Fig. 4 Plots of (a) storage moduli G' and (b) loss moduli G'' against ω (All data points are reduced at $T_r = 170^{\circ}\text{C}$.)

the entropic origin. However, a change of ρ with T is much weaker than a change of T itself. Therefore, it is safe to ignore a change of ρ here.), and plotted against a reduced angular frequency ωa_T , where a_T is a horizontal shift factor to give the best superposition of G' and G'' .

In Fig. 4, it is noted that both the Rouse regime and the terminal relaxation regime have been accelerated and shifted to higher frequency with increasing content of g-CoW. This acceleration would reflect two effects. Firstly, g-CoW has $\sim 30^\circ\text{C}$ lower T_g than PS150k and can plasticize the latter, which has been explained earlier as the decreased T_g . Second, g-CoW may dilute the entanglement mesh, because the size of g-CoW is considerably smaller than the entanglement mesh size of PS150k matrix.

To explicitly illustrate the dilution effect, we should first normalize the T_g change. One frequently adopted approach is the standard Williams-Landel-Ferry (WLF) analysis,^[48–50] as explained in Fig. 5. Fig. 5(a) compares the plots of horizontal shift factor a_T (in Fig. 4.) against $(T - T_r)$. The plots of a_T against $(T - T_r)$ of the nanocomposites are increasingly weaker than that of neat PS150k matrix with increasing content of g-CoW, reflecting the plasticization effect of g-CoW. To normalize this effect, a new reference temperature $T_{\text{iso}} = T_r + T_g - T_{g,0}$ is chosen (T_g and $T_{g,0}$ are the glass transition temperature of nanocomposite and PS, respectively), and the reduced shift factor a_{iso} is plotted against $(T - T_{\text{iso}})$ in Fig. 5(b). It is noted that the proper choices of T_{iso} (guided

by a change of T_g) would enable the plots to coincide. These plots agree with the WLF curve of PS:

$$\lg a_T = -7.0(T - T_r) / (137 + T - T_r) \quad (1)$$

which means that the plasticization effect has been properly normalized.

Fig. 6 compares the plots of moduli G' and G'' , and complex viscosity $\eta^* = \sqrt{G'^2 + G''^2} / \omega$ obtained as functions of ω and reduced at T_{iso} . The Rouse regime of $G' \sim \omega^{1/2}$ shown in solid line in panel (a) are well superposed, indicating that a change of segmental friction owing to the T_g change has been properly normalized. In contrast, the plateau modulus and terminal relaxation behavior seen in Figs. 6(a) and 6(b) change systematically with increasing content of g-CoW; a decrease of plateau means that the number density of entanglements decreases, and the shift of the terminal relaxation to higher frequency means that the reptation of polymer chains has been accelerated. The changes of plateau and relaxation time together lead to decrease of the zero shear viscosity seen in Fig. 6(c).

The plateau modulus G_N is proportional to the number density of entanglements as:

$$G_N(\phi, T) = \phi \rho RT / M_e(\phi) \quad (2)$$

where ϕ is the volume fraction of PS150k, ρ is the density of nanocomposites, and R is the gas constant. The terminal relaxation time τ_d changes with a change of M_e as:

$$\tau_d(\phi, T) = \tau_0(\phi, T) M^3 / [M_0^2 M_e(\phi)] \quad (3)$$

where τ_0 and M_0 are the relaxation time and molecular weight of the Rouse segments, respectively. $\tau_0(\phi, T)$ has been normalized at T_{iso} . In other words, a change of τ_0 caused by the difference of ϕ can be well compensated through choosing a new reference T_{iso} ($\approx T_g + 62^\circ\text{C}$) that enables $\tau_0(\phi, T_{\text{iso}})$ to remain the same, as explained earlier in Figs. 5(b) and 6. In Eqs. (2) and (3), we found that changes of G_N and η_0 ($G_N \tau_d$) have two molecular origins, i.e., the reduction of polymer volume fraction ϕ , and a dilution effect of the entanglement mesh to increase $M_e(\phi)$ as a function of ϕ . To explicitly examine the dilution effect, we should examine extra decrease of G_N and τ_d in addition to that expected from a change of ϕ itself.

To this end, we replot in Fig. 7 the master curves shown earlier in Fig. 6. Namely, we plot storage and loss moduli normalized by the plateau modulus, G'/G_N and G''/G_N , against a reduced frequency $\omega \tau_d$. Here, τ_d is chosen as an inverse of the cross frequency of G' and G'' in Fig. 6. For the neat PS150k matrix, G_N is chosen to be G' at the frequency where $\tan \delta$ shows the minimum. For the nanocomposite samples, G_N is chosen to superpose the terminal relaxation part of moduli (contributed exclusively from the PS chains) to that of neat PS150k. We do not analyze the high-frequency Rouse part of moduli because this part is attributed to g-CoW as well. The inset in Fig. 7 shows G_N and τ_d plotted against ϕ . Detailed calculation of ϕ is shown in ESI (Table S1). If we assume that g-CoW is a pure solvent, we would have $M_e(\phi) = \phi^{-1 \text{ to } -1.3}$, and accordingly $G_N = \phi^2 \text{ to } 2.3$ and $\tau_d = \phi^1 \text{ to } 1.3$.^[47] The solid lines in the inset show the power law $G_N = \phi^2$ and $\tau_d = \phi^1$, in which G_N of the nanocomposites

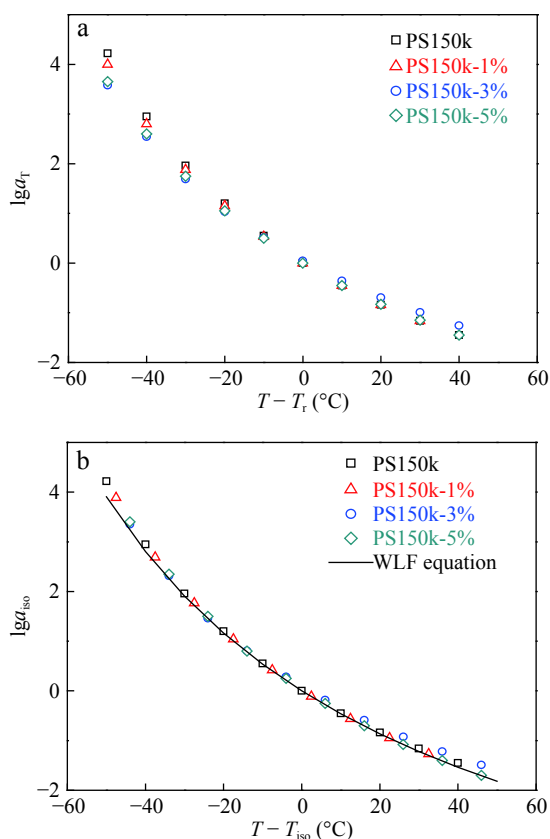


Fig. 5 Plots of (a) shift factor a_T against $(T - T_r)$ and (b) reduced shift factor a_{iso} against $(T - T_{\text{iso}})$, with $T_r = 170^\circ\text{C}$ and T_{iso} being an iso-frictional temperature

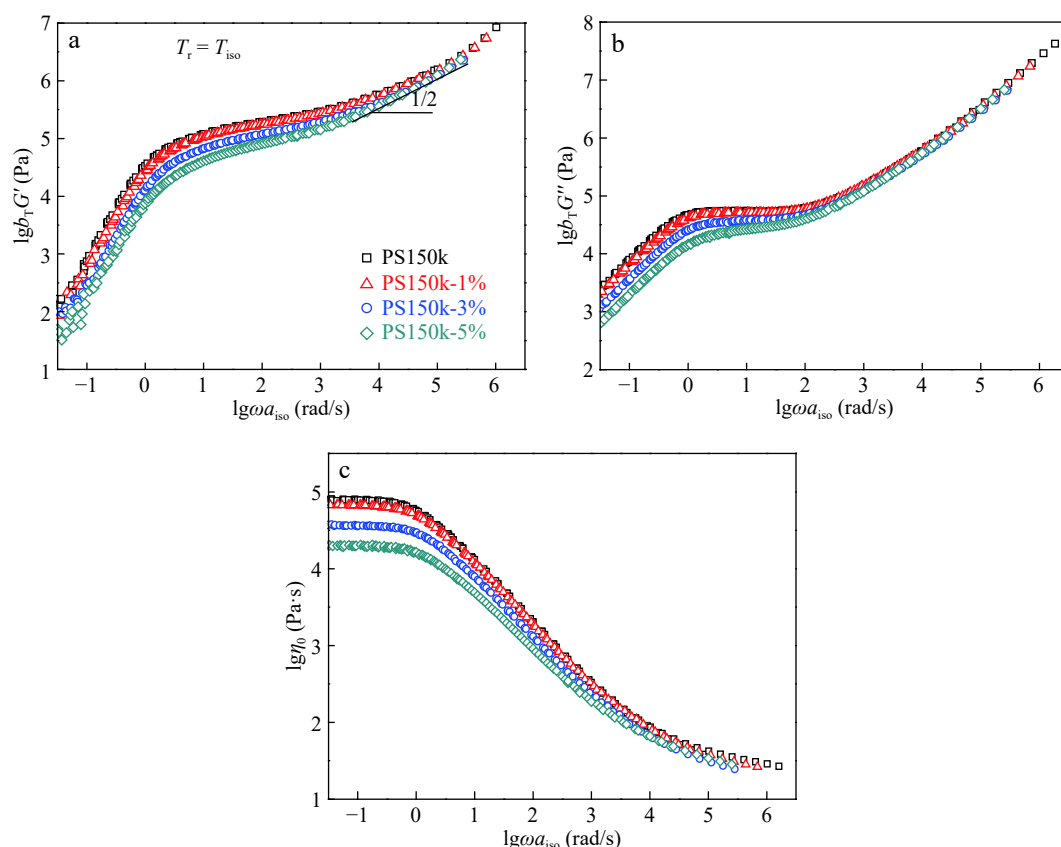


Fig. 6 Plots of (a) storage moduli G' and (b) loss moduli G'' , and (c) complex viscosity η^* against ω (All data points are reduced at T_{iso} .)

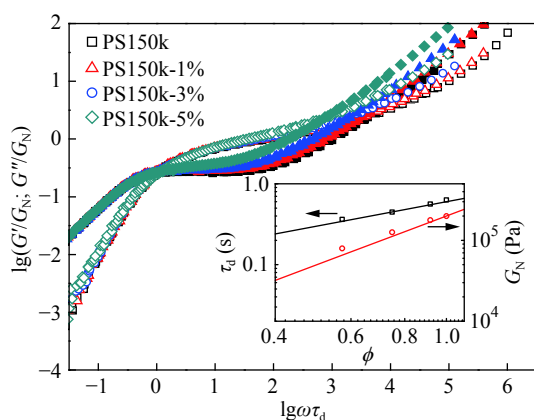


Fig. 7 Plots of reduced storage and loss moduli, G'/G_N and G''/G_N , against reduced frequency $\omega\tau_d$ at T_{iso} . The inset shows a change of G_N and τ_d with ϕ . Solid lines are $G_N = \phi^2$ and $\tau_d = \phi^1$ expected from the pure solvent effect.

shows ϕ dependence weaker than the case of considering g-CoW as a pure solvent. A possible explanation is that g-CoW does not simply serve as a solvent but somehow exhibits the filler effect, *i.e.*, to increase the local strain due to the non-deformable nature of CoW core and polymer segments in the vicinity of the core.^[51–56] This effect would intensify if there is local condensation of g-CoW induced by the segregation. For instance, Wang *et al.* reported an increased storage modulus of poly(ethylene glycol) (PEG) matrices in the presence of PEG-grafted POM which formed aggregates and

performed as enhancing fillers.^[40] To quantitatively and separately study the dilution and the filler effects in our system, a larger parameter space needs to be tested, including the PS size, filler size, filler content and so on, which is considered as interesting future work.

CONCLUSIONS

In conclusion, we have developed a bimodal grafting approach to grafting both short alkyl chains and longer PS chains onto CoW molecular NPs with a high grafting density. The resultant g-CoW shows a diameter smaller than the mesh size of entangled linear PS, performing as model ultrasmall NPs for the PS matrices. Moreover, g-CoW is compatible with the PS matrices and can form transparent g-CoW/PS nanocomposites with a uniform dispersion state. As-prepared g-CoW can impose the entanglement dilution effect on the PS matrices, which leads to a remarkable reduction of plateau modulus and terminal relaxation time. This dilution effect is weaker than an expectation by regarding g-CoW as a pure solvent, implying the existence of certain filler reinforcement. Considering the noncovalent grafting feature of POMs, it is possible to precisely tune the repulsive potential of POMs through adjusting the rearrangement of mobile chains on the POM surface, thus may lead to a controllable distribution state of POMs in the polymer matrices and endow the nanocomposites with mechanical properties different from those of covalently grafted nanoparticles, which

is considered as an interesting future research subject.

Electronic Supplementary Information

Electronic supplementary information (ESI), which includes the detailed synthesis and DSC results of g-CoW and nanocomposites, is available free of charge in the online version of this article <http://dx.doi.org/10.1007/s10118-019-2262-8>.

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