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# Homopolymer and Random Copolymer of Polyhedral Oligomeric Silsesquioxane (POSS)-Based Side-Chain Polynorbornenes: Flexible Spacer Effect and Composition Dependence

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Supporting Information

ABSTRACT: A series of homopolymers and random copolymers of polyhedral oligomeric silsesquioxane (POSS)based side-chain polynorbornenes were prepared using ringopening metathesis polymerization. For the homopolymer P-z-POSS (z represents the spacer length, z = 5, 12, and 17), the POSS groups tethered to the side chain are linked to the polynorbornene backbone through the flexible spacer with different lengths. For the random copolymer P-6-co-17(X/Y)(X/Y = 1/1, 3/1, 6/1, and 9/1), the composition was regulated by adjusting the molar feed ratio X/Y of the norbornene monomer with butyl ester side group (M-6) to the POSS containing monomer with the longest spacer (M-17-POSS).



Using various techniques, we studied the spacer length effect on POSS crystallization of the homopolymers and the composition dependence of physical properties of the copolymers. It is found that P-5-POSS is amorphous. On the contrary, POSS crystallization is observed in P-12-POSS and P-17-POSS, and the longer the spacer is, the higher the POSS crystallization ability is. With the comonomer of M-17-POSS, all the P-6-co-17(X/Y) samples can have the POSS group to crystallize, resulting in a nanosegregation similar to the lamellar morphology. The lamellar period is inversely proportional to the POSS volume fraction. The POSS crystallites are raft-like, containing two layers of POSS groups stacked together. Uniaxial stretching can well align the POSS crystallites in the copolymers to be parallel to the stretching direction, and the lamellar period is decreased with increasing the strain. Varying X/Y from 1/1 to 9/1 changes the copolymer from plastic to thermoplastic elastomer, wherein the latter takes the POSS crystallites as the physical cross-links.

## INTRODUCTION

Introduction of inorganic components to polymer matrixes is one of the most important strategies to fabricate polymeric materials with desired properties.<sup>1,2</sup> Upon careful tuning the interactions and morphologies of the polymer host and the inorganic substances, the resultant composites are able to present excellent properties in mechanical, optical, thermal, electromagnetical or biological aspects.<sup>3-5</sup> For the past decades, organic-inorganic hybridization of polymers on the molecular level has aroused great interest.<sup>6-8</sup> In this respect, many works have been focused on inorganic nanoparticles of polyhedral oligomeric silsesquioxanes (POSSs).9-15 POSS molecules are cage-like (e.g., cubic), and at the corners of the cage, different functional groups can be introduced using advanced synthetic strategies.<sup>16-19</sup> POSS can be placed at chain ends,<sup>20</sup> used as cross-link points,<sup>21</sup> or tethered to the main chain as pendant

groups,  $2^{2-24}$  etc., resulting in a fascinating class of polymer nanocomposites. Incorporation of POSS into polymer chains can remarkably alter chain dynamics and molecular packing and thus materials properties.<sup>25-27</sup> Often POSS molecules crystallize into hexagonal (or rhombohedral) structures,<sup>28-33</sup> with the lattice parameters vary more or less depending on the vertex substituents applied. After integrating into polymers, POSS groups can retain the ability to crystallize in many cases.<sup>34–36</sup> To manipulate the properties of POSS-based polymeric nanocomposites, one should pay close attention to crystallization of POSS groups that is highly dependent on the chemical structure of hybrid polymers and also to morphologies

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Scheme 1. Chemical Structures of P-z-POSS and P-4-co-17(X/Y)



of the nanocomposites that is associated with the POSS crystallization.

Various synthetic methods can be employed to produce polymers bearing pendent POSS groups.<sup>22-24</sup> Introducing vinyl or norbornene groups to one corner of the POSS cage can result in the monomers suitable for free radical polymerization or ring-opening metathesis polymerization (ROMP).<sup>25,26,37</sup> In this case, POSS-based side-chain homopolymers or random copolymers can be readily synthesized, wherein the POSS groups are located on the side chain. Considering that the size of POSS group is usually larger than the repeat unit on the main chain, strong steric hindrance existing in the homopolymer can prevent POSS crystallization to a large extent. On the other hand, POSS crystallization can frequently be observed in random copolymers when the comonomers, the vertex group, and the composition are properly selected.<sup>38,39</sup> For copolymers, POSS groups can be diluted if comonomers are inserted between POSS monomers. This will effectively reduce steric hindrance and thus facilitate POSS crystallization. It is noted that in many POSS-based side-chain polymers the POSS group is attached through a rather short linkage (e.g., 2 or 4 methylene units). Recently, it has been reported that POSS crystallization is greatly enhanced when the side chain contains a longer spacer between the POSS end group and the main <sup>13</sup> The molecular design can be analogous to the chain.40 "flexible spacer" concept proposed for side-chain liquid crystalline polymers (SCLCP).<sup>44</sup> In SCLPC, the flexible spacer can decouple the motions of the main chain and the mesogenic side chain and thus promote the liquid crystal formation. Similar decoupling effect may take place in the POSS-based side-chain polymers. Given POSS groups tethered on the main chain, their crystallization occur under constrained conditions. In this case, the POSS groups form raft-like crystallites.<sup>34-</sup> The "raft" is composed of just two layers of POSS stacked together; however, the ordered packing can still present the feature of the hexagonal (or rhombohedral) structure.<sup>34-36</sup>

In this work, we synthesize a series of POSS-based side-chain polynorbornenes, of which the chemical structures are shown in Scheme 1. For the homopolymer (denoted as P-z-POSS, z is the number of atoms on the spacer backbone that connect main-chain backbone and POSS end group, z = 5, 12, and 17), the investigation is targeted to further elucidate the "spacer length effect" on POSS crystallization. Using various characterization techniques including thermal analysis and X-ray diffraction (XRD), we demonstrate that the longer flexible

spacer can dramatically promote POSS crystallization. Considering that POSS crystallites can reinforce more significantly the mechanical properties of nanocomposites in comparison with the disordered POSS aggregates or molecularly dispersed POSS groups,<sup>25,27</sup> we chose the monomer of P-17-POSS (M-17-POSS) to copolymerize with the norbornene monomer bearing butyl ester group (M-6), resulting in the random copolymer of P-6-co-17(X/Y) (X/Y is the molar feed ratio of M-6 to M-17-POSS, X/Y = 1/1, 3/1, 6/1, and 9/1). It is identified that the physical properties of the random copolymer are highly dependent on the composition. With increasing X/Y, the copolymers switch from plastic to thermoplastic elastomer; for the latter the POSS crystallites serve as the physical cross-links. A nanosegregation structure similar to lamellar morphology is observed, of which the lamellar period is inversely proportional to the volume fraction of POSS in the nanocomposites. The two-dimensional (2D) XRD results indicate that upon uniaxial stretching the POSS raft-like crystallites can be highly orientated, which are parallel to the stretching direction with a remarkably reduced lamellar period.

#### EXPERIMENTAL SECTION

**Materials.** Aminopropylisobutyl-POSS ( $NH_2$ -iBuPOSS) was purchased from Hybrid Plastic. The Grubbs third generation catalyst and *exo*-5-norbornenecarboxylic acid (Nb-COOH) were obtained from Sigma-Aldrich. 6-Bromohexanoic acid (Br-C6-COOH) and 11-bromoundecanoic acid (Br-C11-COOH) were purchased from Heowns. Dichloromethane (DCM, J&K Chemicals) was dried over calcium hydride and then distilled before use. Other reagents were obtained from J&K Chemicals without further purification.

**Instruments and Measurements.** <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Bruker ARX400 spectrometer at room temperature using deuterated chloroform (CDCl<sub>3</sub>) as the solvent and tetramethylsilane (TMS) as the internal standard. To determine the degree of polymerization (DP) of the polymers synthesized, <sup>1</sup>H NMR (500 MHz) experiment was carried out on a Bruker AVANCE III spectrometer. Elemental analysis was performed with an Elementar Vario EL instrument. Mass spectra were recorded on a Bruker APEX IV mass spectrometer. Gel permeation chromatography (GPC) was carried out on a Waters 515 GPC instrument using THF as eluent at a flow rate of 1.0 mL/min at 35 °C. The GPC calibration curve was obtained with linear polystyrene standards.

Differential scanning calorimetry (DSC, TA Q100 with a mechanical refrigerator) was used to investigate the thermal transitions of the polymers. The temperature and heat flow were calibrated with benzoic acid and indium. The sample was encapsulated in a hermetically sealed aluminum pan with a weight of  $\sim$ 3 mg. In DSC

## Table 1. Molecular Characterization of P-z-POSS and P-6-co-17(X/Y)

				X/Y		POSS content	
	DP <sup>a</sup>	$M_{\rm n}  imes 10^{-5} ({ m g/mol})^{b}$	PDI <sup>b</sup>	molar feed ratio	measured by <sup>1</sup> H NMR	weight fraction (%)	volume fraction (%)
homopolymer							
P-5-POSS	330	3.3	1.2				
P-12-POSS	280	2.5	1.4				
P-17-POSS	150	1.8	1.3				
random copolymer							
P-6-co-17(1/1)	430	2.9	1.2	1:1	1.1:1	63	60
P-6-co-17(3/1)	520	2.5	1.2	3:1	3.0:1	49	47
P-6-co-17(6/1)	670	2.2	1.3	6:1	5.9:1	38	35
P-6-co-17(9/1)	750	2.3	1.2	9:1	9.0:1	30	28
<sup><i>a</i></sup> Measured by <sup>1</sup> H NMR. <sup><i>b</i></sup> Measured by GPC.							

experiments, the samples were first heated to above the melting temperature to erase the thermal history. Afterward, the first cooling and second heating curves were recorded at a rate of 10  $^{\circ}$ C/min.

One-dimensional (1D) XRD experiments of the powder samples were performed with a high-flux small-angle X-ray scattering instrument (SAXSess, Anton Paar) which was equipped with a temperature control unit of Anton Paar TCS300. The diffraction patterns were recorded on an imaging plate covering the q range from 0.06 to 29 nm<sup>-1</sup> ( $q = 4\pi \sin \theta / \lambda$ , where  $\lambda$  is the X-ray wavelength and  $2\theta$  is the scattering angle). 2D XRD of the oriented samples was recorded using a Bruker D8 Discover diffractometer with a Vantec 500 detector. The orientated samples were prepared by mechanical shearing at above the melting point of the samples followed by quenching to room temperature. The 2D XRD patterns were obtained through a transmission mode, with the X-ray incident beam aligned perpendicular to the shearing direction. The background scattering was recorded and then subtracted. For both 1D and 2D XRD experiments, the diffraction peak positions were calibrated with silicon powder for wide angle region and silver behenate for low angle region, respectively.

To follow the structure evolution of the copolymer samples upon uniaxial stretching, 2D XRD experiments were also conducted on a modified Xeuss system (Xenocs SA, France) with a semiconductor detector of Pilatus 100K (DECTRIS, Swiss). The rectangular-shaped film specimens with the width of 4 mm and thickness of ~0.2 mm, which were obtained by hot compression, were uniaxially stretched using a Linkam TST350 tension stage which was mounted on the sample stage of the Xeuss system. The sample-to-detector distance was 301.30 mm. At each selected strain, the 2D XRD pattern was collected for 10 min. To clearly identify the low angle scattering, we also used the Xeuss system to perform the small-angle X-ray scattering (SAXS) experiment by setting the sample-to-detector distance to be 586.18 mm. The SAXS pattern was acquired for 30 min.

Rheology temperature sweep measurements were carried out on a TA ARES-G2 rheometer with 8 mm parallel plate and approximately 1 mm gap under nitrogen flow. The heating rate was of 5 °C/min. The storage modulus and loss modulus were measured in the small-amplitude oscillatory shear mode with a constant frequency of 1 rad/s and oscillation strain of 1%. The stress–strain curves of the copolymers were also measured using the ARS-G2 rheometer utilizing its solid tensile fixture to grip the dumbbell-shaped specimen. The dumbbell-shaped specimens with the width of 4 mm and thickness of ~0.2 mm were prepared by hot compression. The tensile experiments were carried out at 25 °C with a rate of 15 mm/min.

**Synthesis.** The details of monomer synthesis and the molecular characterization data are shown in the Supporting Information.

The homopolymer P-*z*-POSS and random copolymer P-6-*co*-17(X/Y) were prepared using the same ROMP method. The polymerization condition is shown in Table S1. Using P-6-*co*-17(9/1) as the example, described below is the polymerization procedure. With the molar ratio of 9/1, monomer M-6 (244.6 mg, 1.26 mmol) and monomer M-17-POSS (161.0 mg, 0.14 mmol) were loaded in a dry Schleck flask with a magnetic stirring bar. After three pump–purge cycles with high purity

nitrogen, 8 mL of dry DCM was injected to the mixture under vigorous stirring to dissolve the monomers, and then a solution of Grubbs third generation catalyst (1.7 mg,  $2 \times 10^{-3}$  mmol) in 1 mL of dry DCM was injected to initiate the polymerization. After the reaction mixture was stirred overnight at room temperature, a few drops of vinyl ethyl ether were added to the reaction mixture to quench the polymerization. The reaction mixture was passed through a short alumina column to remove the catalyst, and then the polymer solution was added dropwise to methanol (100 mL) under stirring. The dissolution and precipitation process was repeated three times. Finally, the product was collected by centrifugation and dried under vacuum to a constant weight. The resultant P-6-co-17(9/1) was obtained as white solid in yield of 92%.

# RESULTS AND DISCUSSION

Synthesis and Molecular Characterization of Homopolymers and Random Copolymers. The homopolymer Pz-POSS was synthesized using ROMP of the norbornene monomer M-z-POSS. As shown in the synthetic route (Scheme S1 in the Supporting Information), M-5-POSS was directly obtained by amidation of NH2-iBuPOSS and Nb-COOH. For the monomers with longer spacers, M-12-POSS or M-17-POSS was synthesized via two steps: NH2-iBuPOSS was first reacted with Br-C6-COOH or Br-C11-COOH followed by the reaction with Nb-COOH. After purification, all the monomers were characterized using various techniques with the satisfactory analysis data. ROMP of M-z-POSS resulted in the homopolymers with a good yield of ~90%. Table 1 summarizes the values of DP of P-z-POSS measured by <sup>1</sup>H NMR (see the Supporting Information) and the apparent number-average molecular weight  $(M_n)$  and polydispersity index (PDI) measured by GPC. It can be seen that under the same reaction condition ROMP of the monomer with longer spacer produces the polymer with lower DP. This suggests that the steric hindrance caused by the large substituent on norbornene can hamper the polymerization. Nevertheless, as the DPs for all the P-z-POSSs are large enough, the molecular weight dependence of phase structure can be avoided. Note that the chemical structure of the side chain of P-5-POSS is somewhat different from that of P-12-POSS and P-17-POSS. However, as will be shown below, this difference will not affect the flexible spacer length effect that we discuss in this work.

To prepare the random copolymers by ROMP, we synthesized the monomer M-6 and copolymerized it with the POSS containing monomer M-17-POSS. M-6 has small butyl ester group attached to the norbornene group, which should have a higher reactivity than M-17-POSS in ROMP. We controlled the molar feed ratio X/Y of two monomers to regulate the copolymer composition. Figure 1 depicts the <sup>1</sup>H

#### Macromolecules



Figure 1. <sup>1</sup>H NMR spectra of M-6, M-17-POSS, and P-6-co-17(1/1).

NMR spectra of M-6, M-17-POSS, and P-6-co-17(1/1). As shown by the spectrum of the copolymer, disappearance of resonance signal at 6.15 ppm, which is the characteristic for the protons on the double bond of norbornene, and the broadened signal at 5.35 ppm indicate the successful polymerization of the monomers. The polymerization resulted in the copolymers with  $M_{\rm n}$  of around 2.5 × 10<sup>5</sup> g/mol and relatively low polydispersity of 1.2–1.3. The values of DP increase with increasing X/Y (see Table 1), which should be due to that M-6 possesses higher reactivity than M-17-POSS. Considering the interchain crossmetathesis may occur during the polymerization process,<sup>27</sup> we prolonged the reaction time to 24 h to promote the formation of random copolymer. On the basis of <sup>1</sup>H NMR result, we calculated the molar ratio of M-6 to M-17-POSS in the copolymers synthesized (see Supporting Information). It is found that the values of X/Y measured experimentally are almost identical to the feed ratios (see Table 1), suggesting that the copolymers should be random. In Table 1, the weight fractions of POSS in copolymers are also listed. The POSS groups form crystallites in the random copolymers (see below). Assuming POSS in the nanocomposites possesses the density of nearly 1.15  $g/cm^{3}$ ,<sup>36</sup> and taking the copolymer densities measured by a floatation technique, we estimated the POSS volume fraction (see Supporting Information), which is changed from 60% to 28% when X/Y is varied from 1/1 to 9/1 (see Table 1).

Spacer Length Effect on the Phase Structure of Homopolymers. Phase transitions of P-z-POSS were studied by DSC. The DSC traces of first cooling and subsequent heating at a rate of 10 °C/min of the three homopolymers are shown in Figure 2, and that of monomers is given in Figure S3 for comparison. P-17-POSS presents the thermal transition similar to M-17-POSS (see Figure S3). Therefore, its exotherm and endotherm on the cooling and heating curve, respectively, shall correspond to the crystallization and melting of POSS units on the side chains. The melting temperature  $(T_m)$  of P-17-POSS is 132 °C, nearly 10 °C higher than that of M-17-POSS which may be due to that the polymer has lower entropy in the isotropic state. P-12-POSS only shows a small and broad exothermic process upon cooling, overlapping with a glass transition at around 84 °C, different from M-12-POSS that shows a strong crystallization peak at around 90 °C. Upon heating of P-12-POSS, an exothermic peak is observed after glass transition, which is immediately followed by an endotherm peaked at 130 °C. By comparison with P-17-



Figure 2. DSC traces P-z-POSS samples recorded during (a) first cooling and (b) second heating at a rate of 10  $^{\circ}$ C/min.

POSS, it can be seen that P-12-POSS crystallizes slower. The nucleation barrier of P-12-POSS is relatively higher, making crystallization to be hampered during the normal cooling process, and the exothermic process corresponds to the cold crystallization of P-12-POSS. For P-5-POSS, only the glass transition is detected during the DSC cooling and heating scan. The glass transition temperature ( $T_g$ ) of P-5-POSS is 15 °C higher than that of P-12-POSS, implying that with shorter spacer P-5-POSS becomes more rigid. While the M-5-POSS crystal has the highest  $T_m$  among the three monomers (see Figure S3), the POSS groups in P-5-POSS can no longer crystallize.

The DSC results in Figure 2 reveal that variation of spacer length can greatly influence the crystallization of POSS groups on the side chains. This was also verified by the XRD experiments. Figure 3 depicts the 1D XRD profiles of three P-z-



Figure 3. 1D XRD profiles of P-z-POSS samples recorded at room temperature.

POSS samples recorded at room temperature, wherein the data of M-17-POSS are also shown for comparison (the XRD profiles of other two monomers are shown in Figure S4). The crystalline small molecule of M-17-POSS exhibits the characteristic sharp diffractions, similar to other octaalkyl-substituted POSS molecules.<sup>32,33</sup> It is interesting to note that there are two diffractions at q of 2.03 and 4.05 nm<sup>-1</sup>. With the q ratio of 1:2, these two diffractions suggest a layer structure existing in M-17-POSS. Given the chemical structure of M-17-POSS, the substituent at one corner of POSS containing long flexible spacer and norbornene group cannot pack into the hexagonal

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lattice of POSS. In this case, a nanosegregation can occur, resulting in the layer structure which is smectic-like. Compared with the monomer, P-17-POSS renders the diffractions much broader, indicating that the crystal size and crystallinity of POSS were reduced. Nevertheless, as pointed by the arrows, the diffractions at the q of 5.92, 7.84, 8.83, and 13.62  $\text{nm}^{-1}$  can be recognized. They can be assigned to  $(101)/(\overline{1}11)$ , (110), (102), and (113) plane of the hexagonal lattices with a = b =1.61 nm and c = 1.65 nm. P-12-POSS can provide the diffraction profile similar to that of P-17-POSS. However, the sufficiently crystallized P-12-POSS still has the diffractions obviously broader than P-17-POSS. On the other hand, the amorphous halo underneath the major diffraction at q of  $\sim$ 5.9 nm<sup>-1</sup> is larger for P-12-POSS, indicative of lower crystallinity. This outcome is consistent with the heats of fusion detected by DSC heating scan, which are 5.2 and 14.6 J/g for P-12-POSS and P-17-POSS, respectively. For P-5-POSS, the amorphous halo centered at q of 6.1 nm<sup>-1</sup> manifests the lack of crystalline order of POSS, in agreement with the DSC results.

To further identify the packing of POSS-based side-chain polynorbornenes, we performed 2D XRD experiments. Figure 4a describes the 2D XRD pattern of the orientated P-17-POSS



**Figure 4.** (a) 2D XRD of P-17-POSS recorded at room temperature. (b) Azimuthal scanning data of diffraction 2 shown in (a). The dashed lines indicate the result of peak deconvolution.

sample prepared by mechanical shearing at 140 °C followed by quenching to room temperature. With the shear direction indicated in the figure (the equator), a pair of diffraction spots (diffraction 1 in Figure 4a) on the meridian locates at the q of 5.9 nm<sup>-1</sup>. Another pair of arcs (diffraction 2 in Figure 4a), which have a much wider azimuthal distribution, shows near the equator, of which the q position is same as that of 1. Careful examination reveals that the arc should be separated into two, of which the peak maximum 12° apart from each other (Figure 4b). Therefore, the angle between the diffractions of 1 and 2 is 84°. Note that for POSS crystals with the hexagonal structure the dihedral angle between (101) and (T11) plane is usually around 83°.<sup>33</sup> Therefore, we presume that diffractions 1 and 2 can be assigned as (101) and (T11), respectively, for the POSS crystal formed in P-17-POSS.

For crystallization of the POSS groups linked to polymer chains as the pendant groups, a 2D raft-like crystallites is proposed,<sup>34–36</sup> since the main chains and the spacers that cannot crystallize with POSS can impose the confinement effect. It is further suggested that the "raft" contains two planes of POSS units stacked together. We think that this packing model is appropriate for the samples which can form POSS crystallites studied in this paper. From Figure 4a, it can be seen

that diffraction 1 in fact is broadened along the meridian direction. Its full width at half-height in terms of q is relatively larger in comparison with that of diffraction 2. This should be attributed to the limited (101) layers (two layers as suggested)<sup>34–36</sup> of POSS that form the "raft". For P-17-POSS with a relatively high molecular weight, mechanical shearing can align the "rafts" or "bilayer lamellae" to be parallel to the shear direction.

The aforementioned experiments elucidate that increasing the flexible spacer length can substantially enhance the POSS crystallization of P-z-POSS. The pendant POSS units of P-5-POSS cannot crystallize. After inserting a longer flexible spacer between the polynorbornene main chain and the POSS group, P-12-POSS and P-17-POSS show the crystalline packing of POSS. Our molecular design in fact follows the "decoupling" concept that is widely applied for SCLCP.<sup>44</sup> For SCLCP, Ringsdorf and Finkelmann have proposed that the reasonably long flexible spacer can effectively decouple the dynamics of the main and side chain, facilitating the liquid crystal ordering of side-chain mesogenic groups. The same "decoupling" effect works for the POSS containing side-chain polymers. Moreover, the longer the spacer is, the higher the crystallization ability of POSS is. Accordingly, when preparing the random copolymers, we chose M-17-POSS as the comonomer.

**Composition Dependence of Phase Structures of Random Copolymers.** As mentioned, the composition of P-6-co-17(X/Y) can be well controlled by the feed ratio X/Y. The phase transitions of the copolymers were investigated using DSC. As shown in Figure 5, exothermic and endothermic



**Figure 5.** DSC traces of P-6-*co*-17(X/Y) samples recorded during (a) first cooling and (b) second heating at a rate of 10 °C/min.

peaks are observed upon the cooling and heating scan, respectively, indicating the reversible first-order phase transition. The homopolymer P-6 obtained from ROMP of M-6 is amorphous with a low  $T_{\rm g}$  at around -20 °C. Therefore, the first-order transition detected comes from the POSS groups. It is found that the transition process becomes diffuse, and the peak temperature moves toward the lower temperature when the content of M-6 is increased. While the  $T_{\rm m}$  of P-6-co-17(1/1) locates at 123 °C, close to that of P-17-POSS, P-6-co-17(9/1) exhibits an endothermic hump on the heating curve with the peak temperature at 75 °C. These results imply that the copolymer with fewer POSS groups form the crystallites with smaller size and broader distribution.

Shown in Figure 6a are the 1D XRD results of the copolymers with different compositions. Similar to that for P-17-POSS, the strongest diffraction of the copolymers is



**Figure 6.** (a) 1D XRD profiles of P-6-*co*-17(X/Y) samples recorded at room temperature. (b) 1D XRD profiles of P-6-*co*-17(1/1) recorded at various temperatures upon heating and cooling.

observed at q of ~6.0 nm<sup>-1</sup>. In addition, the peaks at the q of 7.9, 8.7, and 13.8 nm<sup>-1</sup> can be recognized. The outcome confirms that the POSS units pack into the hexagonal crystal structure. Increasing the amount of M-6 can gradually broaden the diffractions and enhance the amorphous scattering. Moreover, it is worth mentioning that the major diffraction at ~6.0 nm<sup>-1</sup>, which should originate from the (101) and (T11), intends to split into two when the X/Y values are 6/1 and 9/1 (see the discussion below). This also reflects that changing the composition can alter more or less the POSS packing in the copolymers.

From Figure 6a we can observe that besides the diffractions of POSS crystal there is some scattering existing at  $q < 2 \text{ nm}^{-1}$ , indicating the density fluctuation or a sort of ordered

morphology on the sub-10 nm scale. This low angle scattering is associated with the POSS crystallization. Figure 6b presents the thermal 1D XRD curves of P-6-*co*-17(1/1) recorded during the heating and cooling process. Upon heating, the low angle scattering peak at q of 1.32 nm<sup>-1</sup> slightly shifts to left. When the intensity of POSS diffractions starts to reduce at 100 °C, the low angle scattering becomes broad and weak accordingly. It almost fully disappears at 120 °C as a large amount of the POSS crystallites are melted. Upon cooling, the low angle scattering restores. The similar temperature dependence of low angle scattering can be found for the other copolymers.

In order to observe the low angle scattering more clearly, we performed SAXS experiments, of which the data are shown in Figure 7a. The SAXS result indicates that the low angle scattering shifts to lower angle with increasing X/Y from 1/1 to 9/1, corresponding to the *d*-spacing ( $L_{POSS}$ ) changing from 4.7 to 10.0 nm. Considering the POSS in copolymers can form raftlike crystallites, their interference should be the origin of the low angle scattering. Assuming a lamellar morphology, we can estimate the thickness of "raft"  $(t_{POSS})$  based on the  $L_{POSS}$  and the POSS volume fraction  $(f_{POSS})$ . For P-6-co-17(1/1), the volume fraction of POSS is estimated to be 60% (see Table 1). Therefore, the value of  $t_{POSS}$  obtained for P-6-co-17(1/1) is of  $\sim$ 2.8 nm, fairly double the molecular size of isobutyl-substituted POSS. This supports the bilayer POSS crystallite proposed by Coughlin et al.<sup>35,36</sup> Figure 7b describes the TEM image obtained from the microtomed sample of P-6-co-17(1/1), which confirms the lamellar morphology. Without staining, the dark line with the thickness of  $\sim$ 3 nm corresponds to POSS crystallite possessing the higher electron density than the other organic components. The dark lines are locally parallel to each other with the spacing of ~5 nm, consistent with the SAXS result.

It is interesting to note that for other three copolymers the thicknesses of "raft" POSS crystallites are all estimated to be ~2.8 nm based on the assumption of lamellar morphology. Figure 7c describes the plot of  $(L_{POSS})^{-1}$  vs  $f_{POSS}$ , showing a linear line with the slope of  $(2.8 \text{ nm})^{-1}$ . Therefore, we consider that all P-6-co-17(X/Y)s undergo nanosegregation caused by POSS crystallization, resulting in the lamellar phase-like morphology as shown by the schematic drawn in Figure 8a. While the POSS raft-like crystallites remain the thickness of bilayer structure unchanged, increasing the content of comonomer M-6 enlarges the distance between the adjacent POSS "rafts". Namely, the lamellar period  $L_{POSS}$  is inversely proportional to the POSS volume fraction  $f_{POSS}$ . Since only the



**Figure 7.** (a) SAXS profiles of P-6-*co*-17(X/Y) samples recorded at room temperature. (b) TEM image of P-6-*co*-17(1/1). (c) Plot of ( $L_{POSS}$ )<sup>-1</sup> vs  $f_{POSS}$ .  $L_{POSS}$  is the lamellar period, and  $f_{POSS}$  is the volume fraction of POSS in the copolymers.



Figure 8. Schematics of P-6-co-17(X/Y). (a) POSS packing and nanosegregation morphology. (b) Morphology changing upon uniaxial stretching.

first order of low angle scattering is observed, the "lamellar phase" of the copolymers should lack the long-range order.

Mechanical Properties and Stretching-Induced Morphology Evolution of Random Copolymers. The random copolymers with different compositions exhibit different mechanical properties. Figure 9 shows the rheological temper-



Figure 9. Rheological temperature sweep curves of P-6-co-17(X/Y).

ature sweep curves of P-6-*co*-17(X/Y). At 30 °C, the shear storage modulus (G') decreases with the increase of X/Y, in accordance with the reduction of POSS crystal amount. The values of G' for P-6-*co*-17(1/1) and P-6-*co*-17(9/1) are 1.62 × 10<sup>8</sup> and 2.64 × 10<sup>6</sup> Pa, respectively, indicating that the copolymers can be changed from plastic to rubber upon decreasing the POSS content. During heating, all the samples exhibit the decrease of G', wherein the drastic change happens in the temperature range of POSS crystal melting. For example, the G' value of P-6-*co*-17(1/1) drops nearly 4 orders of magnitude when the temperature is increased from 110 to 130 °C. This result manifests that the POSS crystallization determines the mechanical properties of the copolymers.

It is worthy to point out that after melting the copolymers can be separated into two groups in terms of G'. Namely, the G' values of the samples with X/Y of 3/1, 6/1, and 9/1 are close to each other, which are more than 1 order of magnitude larger than that of P-6-co-17(1/1). For P-6-co-17(1/1), the loss modulus (G'') is higher than G' at above 120 °C (see Figure S5), and thus the sample starts to flow. We presume that for P-6-co-17(1/1) with the highest POSS content the pendant POSS groups wrap the polynorbornene main chain to a large extent, leading to the thick chain and thus the large entanglement molecular weight. Without enough entanglements, P-6-co-17(1/1) is easy to flow. On the other hand, it is observed that the other three samples show G' larger than G'' (see Figure S5) after POSS melting, giving a rubber-like plateau in the high temperature range. Furthermore, the G' value of P-6-co-17(9/1) is the highest and that of P-6-co-17(3/1) is the smallest. This

reflects that for the copolymer with less POSS content the entanglement molecular weight is smaller. It was found that the homopolymer P-6 entered terminal flow at around 95  $^{\circ}$ C (Figure S5). Therefore, the results shown here indicate that incorporating a small amount of POSS units (such as 10%) to tether on the main chain through a long spacer can drastically modify the rheological properties. The detailed investigation is undergoing currently.

We used the hot compression method to make the film samples, which are optically transparent, for the uniaxial stretching experiment. The film of P-6-co-17(1/1) was hard and rather brittle; we just measured the stress-strain curves for the other three samples at room temperature. As shown in Figure 10, the copolymers exhibit yielding and strain hardening,



**Figure 10.** Stress-strain curves of P-6-co-17(X/Y) samples measured at room temperature. The strain rate is 15 mm/min.

similar to semicrystalline polymers. As the POSS content decreases, the stress at yield point decreases, showing the same trend observed for the storage modulus; on the other hand, the strain at yield point and the strain at break increase. Particularly, P-6-co-17(9/1) presents the high strain approaching 1000%. This sample renders the properties of thermoplastic elastomer with the dynamic recovery of 91% at 70 °C (see Figure S6). Compared with the homopolymer P-6 without POSS, of which the stress—strain curve is also shown in Figure 10, the copolymers demonstrate much better mechanical properties that shall be attributed to the existence of POSS crystallites.

As mentioned above, the copolymers adopt a sort of lamellar phase morphology due to POSS crystallization. We applied 2D XRD to monitor the morphology change of the copolymers under uniaxial stretching at room temperature. Shown in Figure 11a are the experimental results of P-6-co-17(6/1); the data of the other samples are presented in the Supporting Information (Figures S7 and S8). The *X*-axis (equator direction) in Figure



Figure 11. 2D XRD (a) and SAXS (b) of P-6-co-17(6/1) recorded at various strains during uniaxial stretching. In both (a) and (b), the X-axis is the stretching direction.

11a indicates the stretching direction. For the original sample, a uniform diffraction ring at ~6.0 nm<sup>-1</sup>, which corresponds to the (101) and ( $\overline{1}11$ ) diffractions of POSS crystal, is observed. The uniaxial stretching can first induce the diffraction near the X-axis to be stronger, indicating that the POSS crystallites start to orientate. After the yield point at the strain of ~30%, the diffraction at the meridian (i.e., Y-axis in Figure 11a) increases in intensity gradually. When the strain turned to be larger than 100%, the sample was subjected to strain hardening. Meanwhile, the meridional diffraction becomes spot-like, although it looks more or less diffusive. In this case, the POSS crystallites in the copolymer are well aligned by stretching.

The 2D XRD pattern of P-6-co-17(6/1) at the large strain, for example, at the strain of 300%, shares the same feature with that shown in Figure 4a of the sheared P-17-POSS. Namely, with the stretching (shear) direction along the equator, the diffraction on the meridian (indicated as 1 in Figures 4a and 11a) is relatively broad in q along the meridian and narrow in azimuth angle distribution. On the other hand, the diffraction near the equator has a wide azimuth distribution (indicated as 2 in Figures 4a and 11a). In Figure 11a, it can be identified that diffraction 2 has the maximum positon  $6^{\circ}$  away from the X-axis, in consistence with that found from Figure 4a. Same as that for the sheared P-17-POSS, apparently, diffractions of 1 and 2 for the stretched P-6-co-17(6/1) may be assigned to (101) and  $(\overline{1}11)$ , respectively. Close examination indicates that diffraction 1 locates at  $q = 6.03 \text{ nm}^{-1}$  while diffraction 2 is at 5.91 nm<sup>-1</sup>. As mentioned above, for P-6-co-17(6/1), the major diffraction tends to split into two (Figure 6), of which the two positions are actually the same as that two found from the stretched sample. Note that for the hexagonal (or rhombohedral) crystal structure of POSS the (101) and  $(\overline{1}11)$  diffractions are identical, of which the *d*-spacing is 1.06 nm for P-17-POSS. The diffraction peak splitting indicates that the packing of POSS groups in the copolymer with large X/Y deviates a little from the rhombohedral one. Diffraction 1 that slightly spreads on the meridian direction indicates that the bilayer POSS crystallites have the "raft" surface parallel to the stretching

direction. Its *d*-spacing (1.04 nm) is smaller than that of diffraction 2 (1.06 nm). In other words, the *d*-spacing of the nominal (101) planes is compressed a little bit. We presume that this is due to the composition effect. Note that P-6-co-17(6/1) possesses just one POSS group per 7 repeat units on average. When the POSS groups of a same chain intend to pack together, the main-chain segments with the majority of M-6 have to adjust their conformations, resulting in a loss of conformational entropy. In this case, the entropy elasticity of the main chain increases, which may make a compression on the POSS "raft" and thus the smaller *d*-spacing of (101) plane.

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In Figure 11a, the low angle scattering corresponding to the lamellar morphology appears rather close to the beamstop. To clearly detect the change of low angle scattering, we performed SAXS measurement when P-6-co-17(6/1) was stretched. The isotropic scattering ring at q of 0.79 nm<sup>-1</sup> is observed for the original sample (Figure 11b). The uniaxial stretching moves the scattering to be concentrated on the *Y*-axis (meridian direction) that is perpendicular to the stretching direction (X-axis). After the yield point, a two-point pattern is observed. The scattering spots on the meridian increase in intensity with increasing the strain, manifesting that the POSS "rafts" are oriented more and more parallel to the stretching direction. Interestingly, it is found that the position of low angle scattering moves outward as the strain is increased. Consequently, the lamellar period  $L_{POSS}$  is reduced. This phenomenon was also found for P-6-co-17(3/1) and P-6-co-17(9/1) (see Figures S7 and S8). Given that the POSS "rafts" are rigid, the decrease of  $L_{POSS}$  shall come from the thickness reduction of the amorphous layer siting between the POSS "rafts". While the P-6-co-17(X/Y) specimen is elongated under uniaxial stretching, the lateral dimension is shrunk. In this case, a compression acts on the soft amorphous layer which is composed of polynorbornene main chains and also the flexible spacers. For P-6-co-17(6/1), when the strain is increased from 0% to 200%, the value of  $L_{\rm POSS}$  changes from 7.9 to 6.3 nm. To account for such a remarkable reduction of  $L_{POSS}$  we presume that the stretching and compression can cause the lamellar morphology to be sheared. As schematic in

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Figure 8b, while keeping the POSS "rafts" parallel to the stretching direction, the main chains are elongated and the flexible spacers can be more titled toward the stretching direction, resulting in the smaller  $L_{POSS}$ .

#### CONCLUSIONS

In summary, we have successfully synthesized a series of organic-inorganic nanocomposites of POSS-based side-chain polynorbornenes, namely, the homopolymer P-z-POSS and the random copolymer P-6-co-17(X/Y), using the ROMP method. Our molecular design of the homopolymer follows the concept of "flexible spacer" proposed for side-chain liquid crystalline polymer. The experimental results of DSC and XRD indicate that using the reasonably long spacer to link the POSS groups to the main chain can make POSS groups crystallizable. Moreover, increasing the spacer length can enhance the POSS crystallization ability. The POSS groups in the side-chain polynorbornene form raft-like crystallites, while the packing scheme of POSS remains the features of hexagonal (or rhombohedral) crystal structure. We selected the POSS containing monomer M-17-POSS, which has the longest flexible spacer, to copolymerize with a norbornene monomer with the small side group of butyl ester (M-6). The random copolymers possess the composition well controlled by the molar feed ratio X/Y of M-6 to M-17-POSS. In all the P-6-co-17(X/Y) samples prepared, POSS groups can form crystallites, of which the crystal lattice is compressed a little bit when X/Ybecomes 6/1 and 9/1. The POSS crystallization forms again the raft-like crystallites in the copolymers and causes a nanosegregation similar to lamellar morphology. Given the "raft" thickness of two POSS layers unchanged, the lamellar period of copolymer is found to be inversely proportional to the POSS volume fraction. When the X/Y ratio varies from 1/1to 9/1, the copolymer changes from plastic to thermoplastic elastomer that takes the POSS crystallites as physical crosslinking points. Upon uniaxial stretching, the copolymers can exhibit the yielding and strain hardening behavior, similar to semicrystalline polymers. The POSS raft-like crystallites can be well oriented along the stretching direction after yielding. The lamellar period is decreased with increasing strain, suggesting that the flexible spacers incline toward the stretching direction. Our work confirms that introducing long flexible spacer is indeed an effective way to promote the crystallization of POSS groups in the side-chain polymers. With the POSS crystallization, the mechanical properties of the random side-chain copolymer can be further well-tuned by adjusting the composition. We anticipate that the molecular design strategy demonstrated here using POSS-based side-chain polynorbornenes can be employed in other polymeric systems to fabricate the organic-inorganic nanocomposites.

## 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.8b00302.

Experimental details of monomer synthesis and characterization, determination of the composition and POSS volume fraction, and additional experimental data (PDF)

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#### Notes

The authors declare no competing financial interest.

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