ABA triblock copolymers containing polyhedral oligomeric silsesquioxane pendant groups: synthesis and unique properties

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Abstract

The synthesis and characterization of POSS containing ABA triblock copolymers is reported. The use of atom transfer radical polymerization (ATRP) enabled the preparation of well-defined model copolymers possessing a rubbery poly(n-butyl acrylate)(pBA) middle segment and glassy poly(3-(3,5,7,9,11,13,15-heptaisobutyl-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane-1-yl)propyl methacrylate(p(MA-POSS)) outer segments. By tuning the relative composition and degree of polymerization (DP) of the two segments, phase separated microstructures were formed in thin films of the copolymer. Specifically, dynamic mechanical analysis and transmission electron microscopy (TEM) observations reveal that for a small molar ratio of p(MA-POSS)/pBA (DP \textsubscript{p(MA-POSS)}/\textsubscript{pBA} = 6/481/6) no evidence of microphase separation is evident while a large ratio (10/201/10) reveals strong microphase separation. Surprisingly, the microphase-separated material exhibits a tensile modulus larger than expected (ca. 2 \times 10^8 Pa) for a continuous rubber phase for temperatures between a pBA-related \( T_g \) and a softening point for the p(MA-POSS)-rich phase. Transmission electron microscopy (TEM) images with selective staining for POSS revealed the formation of a morphology consisting of pBA cylinders in a continuous p(MA-POSS) phase. Thermal studies have revealed the existence of two clear glass transitions in the microphase-separated system with strong physical aging evident for annealing temperatures near the \( T_g \) of the higher \( T_g \) phase (p(MA-POSS)). The observed aging is reflected in wide-angle X-ray scattering as the strengthening of a low-angle POSS-dominated scattering peak, suggesting some level of ordering during physical aging. The \( T_g \) of the POSS-rich phase observed in the microphase separated triloblock copolymer was nearly 25°C higher than that of a POSS-homopolymer of the same molecular weight, suggesting a strong confinement-based enhancement of \( T_g \) in this system.

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1. Introduction

The synthesis of linear organic/inorganic hybrid polymers containing polyhedral oligomeric silsesquioxane (POSS) groups has recently gained attention as a route to prepare novel nanocomposite materials [1]. In the pursuit to understand the effect of POSS inclusions in polymeric hybrids, the synthesis of well-defined model copolymers of precise molar mass, composition and architecture is required [2]. Numerous approaches have been reported in the preparation of POSS containing copolymers, namely, condensation polymerization [3–5], ring-opening metathesis polymerization (ROMP) [6–8], metallocene-mediated processes [9] and free radical polymerization [10,11] techniques. Additionally, recent advances in controlled/living radical polymerization [12,13] have offered a versatile tool to prepare model copolymers from a wide range of monomers (e.g. styrenes, (meth)acrylates), enabling investigation of structure-property relationships [14]. Our group demonstrated the ability to introduce methacrylate functional POSS monomers into polyacrylate materials for the synthesis of well-defined star diblock and ABA triblock copolymers using atom transfer radical polymerization (ATRP) [15–18]. In these block copolymers, POSS moieties are attached to the copolymer backbone as pendant side chain groups.

Several studies reported the presence of POSS groups to effect both thermal and rheological properties of
polystyrene [19], polyurethane [4,20], polynorbornene [6,7] and polypropylene-based blends and copolymers [9,21].

2.1. Materials

2. Experimental

2.1. Materials

n-Butyl acrylate (Acros) was stirred overnight with calcium hydride and distilled before use. Copper(I) bromide (Aldrich) and 4,4’-(di-5-nonyl)-2,2’-bipyridine (dNbpy) were purified and prepared according to previously reported procedures [24]. Copper(II) bromide, N,N,N’,N”-tetramethyldiethylenetriamine (PMDETA), dimethyl-2,7-dibromo-methanediolate were purchased from Aldrich and used as received. 3-(3,5,7,9,11,13,15-heptacyclopentyl-pentacyclo[9.5.1.13,9.15,15.17,13]octasiloxane-1-yl)propyl methacrylate (cyclopentyl MA-POSS) and 3-(3,5,7,9,11,13,15-heptaisobutyl-pentacyclo[9.5.1.13,9.15,15.17,13]octasiloxane-1-yl)propyl methacrylate (isobutyl MA-POSS) were purchased from Hybrid Plastics and used as received.

2.2. Characterization

(i) Size exclusion chromatography (SEC). Was performed in tetrahydrofuran using a Waters 510 pump, 3 Styragel columns (Polymer Standards Service, pore sizes 10^3 Å, 10^4 Å, 10^5 Å) and a Waters 2410 refractive index detector. Calculations of apparent molar mass were determined using the PSS software from a calibration based on linear polystyrene standards (from PSS). 

H NMR analysis was done on a 300 MHz Bruker spectrometer using the Tecmag software.

(ii) Dynamic Mechanical Analysis. A TA Instruments 2980 DMA was run in tensile mode at an oscillation frequency of 1 Hz with a static force of 0.010 N, an oscillation amplitude of 5.0 µm and an automatic tension of 125%. Samples were heated from T = 50 °C (below T_g for pBA) to T = 100 °C (above p(MA-POSS) softening) with a heating rate of 4 °C/min. The sample geometry was a thin film in tension.

(iii) Thermal Analysis. The thermal properties of both POSS homopolymer and triblock copolymers were investigated using DSC with variation in thermal history so as to age the samples to varying degrees.

For this purpose, a TA Instruments DSC 2920 was employed with samples (5–15 mg) prepared from powders and sealed in aluminum pans. Heating experiments were conducted with a nitrogen atmosphere and using a heating rate of 20 °C/min. For isolated cases a slower heating rate of 10 °C/min was employed with negligible differences observed. As our annealing periods extended to several days, annealing was performed on a custom-built hot-stage with temperature control to ± 0.2 °C.

(iv) Wide-Angle X-ray Scattering. In order to assess microstructure and aging-induced microstructural changes in the POSS-triblock polymer, we have used wide-angle X-ray scattering (WAXS). For this purpose, we have employed a Bruker D5005 X-ray diffractometer with angular range 20 = 5° and 2θ = 80° using Cu Kα radiation with wavelength, λ = 1.5418 Å. Samples were prepared as fine powders (after aging treatment) prior to WAXS data collection.

(v) Microscopy. Investigations of morphology were performed using a Philips EM300 transmission electron microscope operated at 80 kV. Samples were cast from chloroform and the ultrathin sections for TEM with a thickness of about 50 nm were cryo-microtomed at...
2.3. Synthesis of difunctional poly(n-butyl acrylate) macroinitiator (Mₙ 61,700 g/mol)

To a 25 ml round bottom flask with magnetic stir bar was added Cu(II)Br₂ (2.0 mg, 0.009 mmol) and then the flask was fitted. The reaction flask was evacuated (1–5 mm Hg) and then added via syringe to the reaction vessel, followed by PMDETA (39 μl, 0.187 mmol). To a separate 4 ml vial with magnetic stir bar was added dimethyl-2,6-dibromo-heptanedioate (60 mg, 0.173 mmol). The vial was then fitted with a rubber septum and evacuated/backfilled with nitrogen (3 cycles). Nitrogen purged n-butyl acrylate (1 ml, 8.7 mmol) was then added via syringe to the vial to dissolve the initiator. The initiator solution was then transferred to the 25 ml round bottom flask containing the catalyst solution and the reaction vessel was placed in a 70 °C oil bath. The reaction was allowed to proceed for 16 hrs and 16 min. ¹H NMR analysis of the polymerization mixture revealed that a monomer conversion of 57% was obtained. The polymer solution was diluted in THF and filtered through neutral alumina to remove the catalyst. The polymer solution was then concentrated via distillation of THF in vacuo and precipitated into a ten-fold excess of methanol/water (4:1 by volume). SEC against linear pS standards indicated a molar mass of Mₙ = 61,700; Mₚ/Mₙ = 1.31.

2.4. Synthesis of p(MA-POSS)-b-pBA-b-p(MA-POSS) from cyclopentyl functional POSS methacrylate monomer

To a 4 ml vial with magnetic stir bar was added 1 g of difunctional pBA macroinitiator (Mₙ = 61,700), cyclopentyl MA-POSS (0.32 g, 0.3 mmol) and Cu(I)Cl (2.96 mg, 0.03 mmol). The vial was fitted with a rubber septum and deoxygenated by evacuation (1–5 mm Hg) and backfilling with nitrogen (3 cycles). PMDETA (6.26 μl, 0.03 mmol) was then added via syringe and the reaction vessel was placed in an oil bath set at 60 °C. Polymerization allowed to proceed for 14 h and 32 min and ¹H NMR analysis of the reaction mixture indicated that a monomer conversion of 90% was achieved. The polymer was then diluted in THF and passed through neutral alumina to remove catalyst. Following concentration of the polymer solution by vacuum removal of THF, precipitation into a 10-fold excess of methanol/water (4:1 by volume) was conducted. Using this procedure, residual cyclopentyl MA-POSS could not be separated from the p(MA-POSS)-b-pBA-b-p(MA-POSS) triblock copolymer. Trituration of the crude product in 20 ml of nonane overnight at room temperature quantitatively removed MA-POSS monomer as confirmed by SEC.

2.5. Synthesis of poly(3-(3,5,7,9,11,13,15-heptaisobutylpentacyclo[9.5.1.1³⁸.1⁵.1²,1².1³.1³]-octasioxane-1-yl)propyl methacrylate (isobutyl MA-POSS) homopolymer

Isobutyl MA-POSS (1 g, 1.06 mmol) and AIBN (1.74 mg, 0.0106 mmol) were weighed into a 5 ml round bottom flask with magnetic stir bar. The flask was then fitted with a septum and was evacuated (1–5 mm Hg) and backfilled with nitrogen (3-cycles). Nitrogen sparged (30 min) toluene (2 ml) was then added to the flask via syringe, and the flask was put into a 60 °C oil bath. Polymers were recovered by precipitation into methanol. The presence of residual monomer required fractionation of the higher molar mass homopolymer. Fractionation was conducted by dissolving 1 g of the p(MA-POSS)/MA-POSS crude mixture in 20 ml of THF, followed by the gradual addition of methanol. The first fraction was collected after the addition of 5 g of methanol. SEC analysis of the fractionated polymer revealed a molecular weight of Mₙ = 12,000 g/mol and a polydispersity of Mₚ/Mₙ = 1.8.

2.6. Synthesis of difunctional poly(n-butyl acrylate) macroinitiator (Mₙ = 25,800 g/mol)

To a 100 ml round bottom flask with magnetic stir bar
was added Cu(I)Br (50 mg, 0.35 mmol) and 1,4-dimethoxy-
benzene (1 g) and then the flask was fitted with a rubber
septum. The reaction flask was then evacuated (1–5 mm
Hg) and backfilled with nitrogen for three cycles. n-Butyl
acrylate (50 mL, 349 mmol) was bubbled with nitrogen for
1 h before use and then added via syringe to the reaction
vessel, followed by PMDETA (60 mg, 0.35 mmol) and
dimethyl-2,6-dibromohexanedioate (603 mg, 1.745 mmol).
The reaction vessel was placed in an 80°C oil bath. The
reaction was allowed to proceed for 3 hrs and 39 min. 1H
NMR analysis of the polymerization mixture revealed that a
monomer conversion of 91% was obtained. The polymer
solution was diluted in THF and filtered through neutral
alumina to remove the catalyst. The polymer solution was
then concentrated via distillation of THF under vacuum and
precipitated into a ten-fold excess of methanol/water (4:1 by
volume). SEC against linear polystyrene standards indicated
a molar mass of $M_n = 25,800$; $M_w/M_n = 1.20$.

2.7. Synthesis of p(MA-POSS)-b-pBA-b-p(MA-POSS) from
isobutyl functional POSS methacrylate monomer

To a 10 mL Schlenk flask with magnetic stir bar was
added isobutyl MA-POSS (1.27 g, 1.34 mmol) and Cu(I)Cl
(1.4 g, 0.014 mmol). The flask was then fitted with a
rubber septum and deoxygenated by evacuation (1–5 mm
Hg) and backfilling with nitrogen (3 cycles). To a separate
vial was added difunctional pBA macroinitiator
($M_n = 25,800$ g/mol) (1 g, 0.03 mmol Br) and then a rubber
septum was fitted over the vial. Deoxygenation of the vial
was performed by evacuation (1–5 mm Hg) and backfilling
with nitrogen (3 cycles). o-Xylene (2.5 mL) was bubbled
with nitrogen for 1 hr before use and then added to the vial
via syringe. The pBA macroinitiator solution was then
transferred to the 10 mL Schlenk flask via syringe. PMDETA
(3.6 mL, 0.014 mmol) was added to reaction vessel via
microliter syringe and the flask was placed in an oil bath set
to 60°C for 22 h and 54 min. Monomer conversion was
determined via 1H NMR and proceeded to 90%. The
product was then diluted in 5 mL of THF and precipitated
into 100 mL of methanol. To remove residual isobutyl MA-
POSS monomer, ultrafiltration was employed using the
Millipore Solvent Resistant Stirred Cell (XFUF 07601).
The crude triblock copolymer of p(MA-POSS)-b-pBA-b-p(MA-
POSS) was dissolved in toluene (120 mL) and methanol
(60 mL). Ultrafiltration at 15–20 psi of nitrogen using RO
filters (MWCO 100,000; Millipore, PLGC07610) was done
for 60 min until approximately 50 mL of the solution
remained. The solution from the cell was decanted and
allowed to dry first in air, then under vacuum. After drying,
750 mg of the triblock copolymer was recovered. SEC
against linear pS standards was used to determine molar
mass ($M_n = 43,010$ g/mol; $M_w/M_n = 1.20$) of the triblock
copolymer and confirmed quantitative removal of the POSS
monomer.

3. Results and discussion

3.1. Synthesis of ABA triblock copolymers using ATRP

The synthesis of ABA triblock copolymers possessing a central segment of poly(n-buty acrylate)(pBA) and outer blocks of poly(methacrylate-POSS)(p(MA-POSS)) was conducted using a two-step ATRP strategy [16]. Compositions of approximately 10–20 wt% of p(MA-POSS) were targeted for the design of a spherical morphology of phase separated p(MA-POSS) domains in a matrix of pBA. In the first stage of the synthesis, the ATRP of n-butyl acrylate
(BA) was conducted using dimethyl-2,6-dibromohexanedi-
dioate as the initiator for the preparation of a difunctional
pBA macroinitiator (Scheme 1). To retain high chain end
functionality, the polymerization was stopped at 57% monomer conversion (1H NMR) while targeting a high degree of polymerization ($M_{n_{\text{sec}}} = 200,000$ g/mol). SEC of the
macroinitiator relative to linear pS standards was used to
calculate molar mass ($M_w = 61,700$ g/mol; $M_w/M_n = 1.31$). Comparison of theoretical molar mass values based on
conversion and the ratio of monomer to initiator (i.e.
$M_w$ theoretical $= \text{conversion} \times (M_1/M_{1_0}) \times M_{\text{BA}}$) $= 58,400$ g/mol versus those from SEC ($M_w$ SEC $= 61,700$ g/mol)
demonstrated that an initiation efficiency in the polymerization
was 94%.

Chain extension of the pBA macroinitiator was
then conducted by the ATRP of 3-(3,5,7,9,11,13,15-heptacyclo-
pentyl-pentaecyclonore[9.5.1.13,9.15,17,13]octasiloxane-1-
yl)propyl methacrylate (cyclopentyl MA-POSS). In the
ATRP reaction, a monomer conversion of 92% was
achieved, as determined from 1H NMR. SEC of the triblock
copolymer against linear pS standards confirmed a small
increase in molar mass ($M_w = 64,010$; $M_w/M_n = 1.39$) after
the ATRP of cyclopentyl MA-POSS. Composition of the
triblock copolymer and DP of each segment was
determined via 1H NMR in conjunction with corrected $M_w$
SEC values of the pBA macroinitiator (2.5 mol%; 16 wt% of p(MA-POSS)). The overall molar composition of the
triblock copolymer was determined to be $p(\text{MA-POSS})_c$-
$b-pBA_{b_{\text{sec}}}-b-p(\text{MA-POSS})_o$.

Initial morphological investigations of thin films pre-
pared from the $p(\text{MA-POSS})_c$-$b-pBA_{b_{\text{sec}}}$-$b-p(\text{MA-POSS})_o$
triblock copolymer was conducted using small angle X-ray
scattering (SAXS) and (TEM). Both techniques confirmed
that morphology of triblock copolymer thin films were
featureless, indicating that phase separation was not induced
at this composition and molar mass. Efforts to prepare
phase-separated structures by increasing the DP of the
p(MA-POSS) were not successful, as limiting degrees of
polymerization were observed in the ATRP of MA-POSS
monomers ($DP_n < 15$) [16]. This observation is consistent
with similar reports of limiting DP in the ROMP of dendritic
macromonomers, presumably due to inaccessibility of the
ruthenium complexed chain-ends shielded by bulky
dendron side chain groups [25]. Thus, in the ATRP of
MA-POSS monomers, bromine-end groups from growing p(MA-POSS) chains may also be inaccessible to copper(I) complexes after a certain DP is reached in the polymerization.

An alternative approach to preparing phase-separated microstructures was devised by preparing a difunctional pBA macroinitiator of lower molar mass. While the overall DPn of the block copolymer was reduced, increasing the relative composition (i.e. volume fraction, f) of pBA to p(MA-POSS) segments was anticipated to yield phase-separated morphologies assuming large values for the interaction parameter (χ) [26]. Additionally, the isobutyl MA-POSS monomer was chosen in this case over the cyclopentyl MA-POSS due to observation of a glass transition in isobutyl p(MA-POSS) homopolymer, as will be discussed in later sections.

The synthetic route to prepare phase separated materials was similar to that used for the higher molar mass POSS triblock, except a lower monomer to initiator ratio ([M]o/[I]) was employed in the ATRP of BA for the synthesis of the difunctional macroinitiator. The polymerization of BA reached a conversion of 90% and SEC relative to pS standards confirmed the synthesis of lower molar mass pBA (Mn = 25,800; Mw/Mn = 1.20). A high initiation efficiency (>90%) was also observed in the polymerization as for the higher molar mass pBA macroinitiator. Chain extension of the macroinitiator with 3-(3,5,7,9,11,13,15-heptaisobutylpentacyclo-[9.5.1.18,14.18,11,15.1]-octasiloxane-1-yl)propyl methacrylate (isobutyl MA-POSS) was then conducted and proceeded to high conversion (92%) as measured using 1H NMR. Monomer conversion was determined by monitoring consumption of vinyl protons (δ = 6.10, 5.50 ppm) from isobutyl MA-POSS relative to resonances from pBA macroinitiator protons.

1H NMR of the p(MA-POSS)-b-pBA-b-p(MA-POSS) triblock copolymer purified by ultrafiltration indicated the presence of protons from both n-butyl and POSS side chain groups. Resonances from the poly(methylacrylate backbone (δ = 0.7–2 ppm) were poorly resolved due to the abundance of protons from side chain groups, with the exception of methine protons (δ = 2.35 ppm, 6, Fig. 1) from the pBA segment. Resonances observed at δ = 0.60 ppm (1 and 4, Fig. 1) were clearly assigned to methylene protons from p(MA-POSS) segments. Methyly protons (δ = 1.0 ppm, 2, Fig. 1) and methine protons (δ = 1.95 ppm, 2, Fig. 1) from isobutyl groups in p(MA-POSS) were distinguishable in addition to methyl protons (δ = 1.0 ppm, 10, Fig. 1) and methylene groups from n-butyl groups in the pBA macrorinitiator (δ = 1.5 and 1.8 ppm, 9 and 10 Fig. 1). At higher chemical shift, methylene protons from both pBA (δ = 4.0 ppm, 7, Fig. 1) and p(MA-POSS) (δ = 3.8 ppm, 5, Fig. 1) were observed indicating successful chain extension had occurred. Calculations of molar composition of each component was conducted by comparison of integration from p(MA-POSS) methylene protons (δ = 0.60 ppm, 1 and 4, Fig. 1) and pBA methine protons (δ = 2.35 ppm, 6, Fig. 1). Overall, the composition of p(MA-POSS) from 1H NMR was determined to be 9.7 mol%, corresponding to 44 wt%. The DPn was also calculated, beginning from Mw SEC values of the pBA macroinitiator (Mw = 25,800 g/mol) yielding molar ratios of p(MA-POSS)10-b-pBA201-b-p(MA-POSS)50 for the final triblock copolymer. This corresponds to a SEC-determined composition of 9.1 mol% and 42.4 wt% of p(MA-POSS). Thus, both estimations of the triblock copolymer composition (1H NMR and SEC) yield a substantial POSS weight fraction that we expected to strongly modify morphological and rheological properties relative to the lower POSS-content triblock with 16 wt% p(MA-POSS).

SEC of the triblock copolymer against linear pS standards confirmed the incorporation of p(MA-POSS) as a small but clear increase in molar mass (Mw = 43,010;
Relative to the macroinitiator was obtained (Fig. 2). Importantly, no change in polydispersity was observed for ATRP chain extension of the pBA macroinitiator with MA-POSS.

3.2. DMA observation of melt-pressed triblocks of varying PBA molecular weight

To begin our characterization comparison of the two triblocks, we conducted DMA temperature sweeps on tensile specimens, the results being shown in Fig. 3. Such measurements are sensitive to changes in thermal transitions, observed through loss tangent peaks, and are connected to morphology differences through storage modulus magnitude. Comparison of the DMA spectra between the higher molar mass p(MA-POSS)\textsubscript{10}-b-pBA\textsubscript{201}-b-p(POSS-MA)\textsubscript{10} and the p(MA-POSS)\textsubscript{10}-b-pBA\textsubscript{201}-b-p(MA-POSS)\textsubscript{10} copolymers also provided greater insight into the organization of p(MA-POSS) segments in the microphase separated system. For the homogeneous p(MA-POSS)\textsubscript{10}-b-pBA\textsubscript{201}-b-p(MA-POSS)\textsubscript{10} system, a plateau tensile modulus above the \( T_g \) of PBA of...
approximately 0.4 MPa was observed. Taking the glass transition temperature to be the onset of tensile modulus decrease (for comparison with DSC) we measure a value of $T_g = \sim -48^\circ C$ for the high molecular weight sample (trace (i)) and $T_g = \sim -42^\circ C$ for the lower molecular weight (trace (ii)). We note that the entanglement molecular weight for pure pBA has been reported [27] to be 28,800 g/mol (substantially larger than the 8,800 value for pMA [28,29]), from which we have estimated the plateau modulus in shear, $G'_N$, to 0.1 MPa or 0.3 MPa in tension. By comparing our observed value with that estimated from $M_e$ measurements of others [27], we reason that this material behaves as an ordinary entangled poly(n-butyl acrylate).

For the phase separated p(MA-POSS)$_{10}$-b-pBA$_{201}$-b-p(MA-POSS)$_{10}$ sample, however, a significantly higher plateau modulus was observed (200 MPa) in the same temperature range as for the homogeneous system. The large difference in the plateau moduli of the two copolymer systems cannot be solely attributed to an increase in the physical crosslink density due to microphase separation of p(MA-POSS) domains in a matrix of pBA. Instead, the enhanced value of the plateau modulus suggests the formation of a microphase separated structure (to be clarified by TEM) composed, surprisingly, of a continuous phase of solid p(MA-POSS) - glassy or semicrystalline - and dispersed domains of pBA. The inverse morphology would be expected to yield a much lower tensile modulus ~1 MPa. This assessment is further supported by the larger magnitude of the loss tangent transition at 70°C relative to the value at ~30°C. Assignments of these transitions correspond to the $T_g$ of the pBA phase at ~30°C and softening of the p(MA-POSS) phase at 50°C. Furthermore, the effect of a larger weight fraction of POSS in the p(MA-POSS)$_{10}$-b-pBA$_{201}$-b-p(MA-POSS)$_{10}$ copolymer was also seen in the DMA by doubling of the cryogenic modulus (below $T_g$ of pBA) relative to the p(MA-POSS)$_{10}$-b-pBA$_{201}$-b-p(MA-POSS)$_{10}$, which is consistent with previous reports for random copolymer systems containing POSS [6]. Finally, no significant difference in the pBA-rich $T_g$ is observed for the two block copolymers, indicating a negligible influence of POSS on pBA softening in either the single or two phase systems.

As we will show below, these results are consistent with TEM analysis and limited SAXS observations (data not shown) for the two triblock copolymer systems. Collectively, these characterization data reveal that microphase separated structures can be formed by optimizing the length of central pBA block provided the DP of p(MA-POSS) block is constant.

### 3.3. Morphology of POSS triblock copolymer thin films

Morphological investigations of p(MA-POSS)$_c$-b-pBA$_{48}$-b-p(MA-POSS)$_c$ triblock copolymer thin films prepared with pBA macroinitiator of higher molar mass ($M_e$ = 64,010; $M_e/M_n = 1.39$) by using SAXS and TEM indicated that no microphase separation was induced during sample preparation; i.e. the resulting morphology and SAXS scattering patterns were completely featureless. However, the morphology of p(MA-POSS)$_{10}$-b-pBA$_{201}$-b-p(MA-POSS)$_{10}$ triblock copolymer thin films prepared with a difunctional pBA macroinitiator of lower molar mass ($M_e$ = 25,800 g/mol; $M_e/M_n = 1.20$) show remarkably well-defined microphase separated structures. In Fig. 4, we show typical microphase separated block copolymer structures imaged by TEM by employing ultrathin sections of thickness ~50 nm that were stained with RuO$_4$ vapor. In a relatively low magnification TEM image (Fig. 4a), well-defined white cylinders are clearly discernible ordered both in and out of the sample plane. In our previous TEM studies on POSS incorporated thermostets, we found that the POSS moiety can be selectively stained with RuO$_4$, although the chemical details of this staining have not been revealed [30]. On this basis, we are confident that the continuous dark phase consists of the p(MA-POSS) block, whereas the bright cylinders consist of pBA. The micrographs of Fig. 4(b) and (c) show higher magnification imaging of local areas in Fig. 4(a). The bright domains originating from pBA are locally well ordered in dark continuous p(MA-POSS) matrix phase, but macroscopically disordered. The fast Fourier transform (FFT) power spectrum was computed...

![Fig. 4. Transmission electron microscopy (TEM) of thin sections of POSS-triblocks prepared with cryomicrotomy at T = ~80°C to yield samples of thickness ~50 nm. The micromotmed sections were chemically treated with RuO$_4$, an agent selective for POSS. (a) Low magnification micrograph showing overall morphology, (b)–(c) Higher magnification micrographs revealing cylindrical morphology, (d) Fourier transform of selected area from micrograph (a) revealing symmetry consistent with local hexagonal packing of the cylinders.](image-url)
POSS containing homopolymers showing the absence of low temperature, or even at all, based on prior reports on melting transition for a p(MA-POSS) rich phase at such a precipitated powder. However, we were surprised to find a phase transition (Fig. 3) and in DSC results we now present.

By comparison, the thermal transition behavior of p(MA-POSS)_{10}-b-pBA_{201}-b-p(MA-POSS)_{10} is quite sensitive to thermal history, but generally shows two strong transitions. As shown in Fig. 5, trace (i), near \( T = -48 \, ^\circ\mathrm{C} \) (onset), we observe a strong \( T_g \) signal indicated by a dramatic step in heat capacity at that temperature. This temperature is to be compared with the \( T_g \) for pure pBA of \( T = -54 \, ^\circ\mathrm{C} \) [31].

Less obvious is a second transition with an onset of \( T = 65 \, ^\circ\mathrm{C} \) (\( \Delta H = 0.71 \, \mathrm{J/g}\)) that appears to be first order melting during the first heating of the as-synthesized (and precipitated) powder. However, we were surprised to find a melting transition for a p(MA-POSS) rich phase at such a low temperature, or even at all, based on prior reports on POSS containing homopolymers showing the absence of crystallization. Therefore, we sought to determine whether

\[ T_g = \frac{\Delta H}{\Delta C}_{p} \]

or not this observation was a true melting point, a first heating artifact, or the manifestation of significant physical aging present in the POSS phase. If the latent heat feature of Fig. 5(i) could be enhanced via thermal treatment at \( T < 65 \, ^\circ\mathrm{C} \) or removed by quenching to leave a strictly second-order transition, then physical aging would be implicated. Thus, following the first heating scan, the triblock copolymer sample was cooled to \( T = 45 \, ^\circ\mathrm{C} \) and annealed at that temperature for 40 hours under nitrogen and then re-scanned from \( T = -100 \, ^\circ\mathrm{C} \) to \( 100 \, ^\circ\mathrm{C} \) as shown in Fig. 5(ii). We observed that this thermal history enhanced latent heat endotherm while maintaining the transition temperature beginning near 65 \( ^\circ\mathrm{C} \). However, the DSC trace of this annealed sample has further revealed a significant heat capacity offset above and below the thermal transition, an aspect discussed further below.\(^2\)

\(^2\) We note that the slight fluctuation in the DSC thermogram at \( T = 0 \, ^\circ\mathrm{C} \) was an artifact of our DSC for those runs.
Following this heating run, the sample was again cooled to $T = -100^\circ$C, this time without intermediate aging. In this case, trace (iii), two clear $T_g$ transitions are observed with the following onset temperatures: $T_g^{\text{pBA}} = -52^\circ$C and $T_g^{\text{POSS}} = 75^\circ$C. $T_g^{\text{pBA}}$, associated with the softening of the pBA-rich phase is about 3–4 °C lower than the value measured in trace (i) (virgin sample) and features a larger step change in heat capacity across the transition. We note that the DMA data show a slightly lower temperature for the second transition.

To our knowledge, the phenomena observed in Fig. 5 are thus far unique for POSS-based systems in revealing a clearly detectable glass transition for a POSS homopolymer phase, albeit within a microphase morphology. Thus, we were prompted to examine the thermal response of a p(MA-POSS) homopolymer of similar molecular weight to that of the block contained in the p(MA-POSS)$_{10}$-b-pBA$_{201}$-b-p(MA-POSS)$_{10}$ triblock. Does such a polymer reveal an accessible glass transition in contrast to p(MA-POSS) homopolymers with cyclopentyl or cyclohexyl[11] corner groups? The DSC results for such a p(MA-POSS) homopolymer with $M_n = 12,000$ g/mol are shown in Fig. 6, this time focusing on a single transition observed near $T = 60^\circ$C. Specifically, the first scan of the precipitated polymer sample, trace a (i), reveals a strong endotherm at $T = 63.6^\circ$C with $\Delta H = 1.76$ J/g. A second scan taken immediately after cooling to $T = 0^\circ$C (trace a (ii)) shows reduction of this complex transition to a simple glass transition with a low onset $T_g = 40.5^\circ$C. We immediately see that $T_g$ of the POSS homopolymer is significantly lower ($\Delta T_g \approx 25^\circ$C) than that of the POSS-rich phase in the p(MA-POSS)$_{10}$-b-pBA$_{201}$-b-p(MA-POSS)$_{10}$ triblock copolymer. Following this thermal history, enthalpy relaxation was attempted by annealing the sample at $T = 45^\circ$C (like for the triblocks in Fig. 5), for four days, the resulting heating scan being shown as trace b (i) in Fig. 6. Clearly, no latent heat endotherm is observed to indicate enthalpy relaxation, but instead a simple $T_g$ is observed at $47^\circ$C. A second heat with no intervening heat treatment (trace b (ii)) shows no alteration of the thermal behavior. Annealing at a temperature closer to $T_g$, however, does result in the appearance of a slight endotherm at $T_g$, as shown in trace c (i) of Fig. 6. Here, annealing was conducted at $T = 55^\circ$C for seven days, resulting in a peak after $T_g$ (onset $T_g = 46.5^\circ$C) at $T = 58^\circ$C. This feature is largely erased on cooling and reheating without annealing (trace c (ii)), but not entirely.

By comparison of Figs. 5 and 6, we make the following salient observations: (i) the $T_g$ for p(MA-POSS) homopolymer is 20–25 °C lower than that observed in a triblock copolymer bearing the same MA-POSS repeating unit (isobutyl corner groups), (ii) in both cases, enthalpy relaxation is indicated for thermal annealing at $T < T_g$, and (iii) enthalpy relaxation for p(MA-POSS) homopolymer is rapid only quite close to $T_g$ in contrast to the triblock copolymer, where relaxation was indicated for annealing 40 °C below $T_g$. While we do not have a definitive explanation for this large $T_g$ difference in aging behavior, recent studies by Zhu et al. [32] revealed an analogous sensitivity of PEO crystal stability on the matrix $T_g$ of PEO/PS cylindrical diblocks. Specifically, it was observed on the basis of DSC, WAXS, and SANS analyses that PEO crystallization was enhanced for ‘soft confinement’; i.e. when the PS matrix was plasticized to a $T_g < T_{\text{cryst.}}$, relative...
to crystallization within glassy PS confinement. It was 
argued that the enhanced stability for soft confinement is 
related to increased dimensionality (in the Avrami sense) of 
the crystals perhaps afforded by a mechanically compliant 
environment. We suggest an analogous explanation for the 
contrast in physical aging behavior between the p(MA-
POSS) homopolymer (slow aging) and p(MA-POSS)_{10}-
\text{pBA}_{201}-\text{p(MA-POSS)}_{10} triblock (faster aging). While 
aging in the p(MA-POSS) homopolymer sample transpires 
in a rigid environment relatively devoid of surface or 
interface, the triblock copolymer ages with proximity to an 
interface with compliant pBA \( T_g \sim -55 \, ^\circ C \). Recall from 
Fig. 4 that we observe a cylindrical morphology of 
continuous p(MA-POSS) and pBA cylinders; apparently, 
such a ‘soft confinement’ enhances the physical aging 
process while raising \( T_g \) significantly.

3.5. WAXS studies of triblock copolymers

To further elucidate the aging of the POSS containing 
homopolymer samples, we have examined the local 
structure of our polymers using WAXS and compare the 
results with scattering patterns of the POSS monomer and 
a triblock copolymer \( (p(MA-POSS)_{6}-\text{pBA}_{481}-\text{p(MA}-
POSS)_{6}) \) sample. The results are shown in Fig. 7. For 
reference, we show in trace (iv) the WAXS pattern for a 
representative MA-POSS monomer (\( R = \) cyclopentyl, 
others are virtually identical) revealing a rhombohedral 
unit cell by comparison with a previous report [4].

Polymerization yielding the p(MA-POSS) homopolymer,
destroys crystallinity to leave four broad scattering peaks in 
the WAXS patterns (trace (ii)), one of which is sensitive to 
aging. In particular, the unaged sample (ii) shows very 
strong scattering at angles, \( 2\theta = 9.12, \ 18.76 \), weak 
scattering at \( 2\theta = 23.22 \) deg, and very weak scattering 
near \( 2\theta = 12 \) deg. These peaks correspond grossly to the 
101, 030, 312, and 110 \( hkl \) reflections of the rhombohedral 
unit cell of the POSS monomer [4], but with significant shift 
in the 101 and 110 reflections. We note that such 
comparison is not meant to suggest that this polymer is 
crystalline, nor that it would have the same unit cell as 
the monomer. Upon aging at \( T = 55 \, ^\circ C \) for seven days, as for 
the case of trace c (i) in Fig. 6, we observe near-doubling of 
the peak at 11.27 deg (110,7.85 \( \AA \)) from 6.2% of the total 
wide-angle scattering to 12.4% (trace (i)), indicating some 
enhanced alignment of POSS ‘faces’ with respect to each 
other. Meanwhile, peaks 1 and 4 are observed to reduce in 
size while peak 4 also shifts to smaller \( d \)-spacing. Table 1 
summarizes the WAXS data for the p(MA-POSS) homo-
polymer sample, with area-% being calculated using 
deconvolution with Peakfit™ software and assuming a 
Lorentzian form for each peak.

While beyond the scope of the present study, preliminary 
investigation of triblock microstructure by WAXS of both 
triblock copolymers has shown behavior intermediate 
between the high level of ordering in POSS monomer and 
low ordering of POSS homopolymer, but very similar to 
previously reported observations on POSS-based multi-
block polyurethanes (Fig. 6) [4]. Trace (ii) of Fig. 7 shows a 
WAXS pattern typical of the triblocks, but in this case for 
\( (p(MA-POSS)_{6}-\text{pBA}_{481}-\text{p(MA-POSS)}_{6}) \).

3.6. Rheological behavior of triblock copolymers

Finally, we have characterized the rheological behavior 
of the microphase separated \( (p(MA-POSS)_{10}-\text{pBA}_{201}-b-
\text{p(MA-POSS)}_{10}) \) triblock copolymer using dynamic 
oscillatory shear for temperatures spanning 
\( 80 \, ^\circ C < T < 170 \, ^\circ C \); i.e. above the softening points 
of both phases: \( T_g \) of \( p(MA-POSS) \gg T_g \) of \( pBA \). Thus, Fig. 8 shows a 
master curve for shear storage and loss moduli where a

<table>
<thead>
<tr>
<th>Peak</th>
<th>2( \theta ) (deg), ( d )-spacing (( \AA ))</th>
<th>Area(%)</th>
<th>2( \theta ) (deg), ( d )-spacing (( \AA ))</th>
<th>Area(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.12 (9.71) 32.4</td>
<td>9.10 (9.72) 27.9</td>
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</tr>
<tr>
<td>2</td>
<td>11.27 (7.85) 6.2</td>
<td>11.93 (7.42) 12.4</td>
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<td></td>
</tr>
<tr>
<td>3</td>
<td>18.76 (4.73) 15.3</td>
<td>18.52 (4.79) 17.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>23.22 (3.83) 46.1</td>
<td>23.60 (3.77) 41.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \) Obtained by Lorentzian deconvolution.
The synthesis and characterization of POSS containing homopolymers and ABA triblock copolymers was conducted. ABA triblock copolymers possessing a soft middle pBA segment and outer p(MA-POSS) segments were prepared using ATRP. We demonstrate that optimization of composition and DP of each segment enabled the preparation of microphase separated structures, but with surprising morphologies. In particular, thin films of ABA triblock copolymers of p(MA-POSS)$_{10}$-p(POSS)$_{10}$-p(MA-POSS)$_{10}$ were characterized using TEM to reveal the formation of a pBA cylinders in a p(MA-POSS) matrix. Thermal analysis indicated the presence of two clear glass transitions in the microphase-separated system with strong physical aging observed in samples annealed at temperatures near the $T_g$ of the (MA-POSS) phase. The occurrence of physical aging was further supported by wide-angle X-ray scattering indicating that rearrangement of POSS moieties was observed in glassy domains. It was found that the $T_g$ of the (MA-POSS) phase from triblock copolymers sequestered in microphase separated domains was nearly 25°C higher relative to a p(MA-POSS)-homopolymer of the comparable molar mass, suggesting a strong confinement-based enhancement of $T_g$ in this system.

4. Conclusions

The synthesis and characterization of POSS containing homopolymers and ABA triblock copolymers was conducted. ABA triblock copolymers possessing a soft middle

**References**