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Synthesis and characterization of hexafluoroisopropylidene bisphenol poly(arylene ether sulfone) and polydimethylsiloxane segmented block copolymers

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ABSTRACT

A series of hexafluoroisopropylidene bisphenol poly(arylene ether sulfone) (BAF PAES) segmented block copolymers with varying fractions of polydimethylsiloxane (PDMS) were synthesized by a condensation reaction of hydroxyl-terminated BAF PAES and dimethylamino endcapped PDMS. The segmented block copolymers have high thermal stability. The BAF PAES homopolymer exhibits a tensile modulus of 1700 MPa and an elongation at break of 16%. Copolymerizing BAF PAES with increasing molecular weight amounts of PDMS results in tensile properties ranging from plastic to elastomeric where the elongation is 417% for a segmented block copolymer with 64 wt% PDMS incorporated. The morphological properties of these segmented block copolymers were characterized by atomic force microscopy (AFM), small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM). AFM and TEM images show the segmented block copolymers were microphase separated, and comparison with bisphenol A (BA) PAES-*b*-PDMS segmented block copolymers revealed complex differences between the morphological behavior of the two systems. SAXS data of the segmented block copolymers supports AFM and TEM images, indicating microphase separation but little long-range order.

1. Introduction

Segmented block copolymers have been long studied for their mechanical, chemical, and thermal properties. Considerable research that has been conducted on segmented block copolymers has gone into developing polymeric structure–property relationships. The resulting materials based on high performance thermoplastics have been found to have a combination of impact resistance and toughness that can serve in high impact applications [1,2]. In order to achieve high impact and toughness, segmented block copolymers typically encompass oligomers with well-defined properties—good thermal stabilities and excellent mechanical properties. These high performance thermoplastics include polycarbonates, polyimides, polyketones, and poly(arylene ether sulfone)s [3].

Vaughn et al. [4] reported the synthesis of segmented block copolymers with bisphenol A-polycarbonate–polydimethylsiloxane (PDMS) in the late 1960s. This research showed these materials had a two-phase morphology, demonstrated thermal stability to 390 °C, and had mechanical properties ranging from elastomeric to rigid depending on the polysiloxane content. Holub et al. [5] also synthesized similar materials using polyimide as the thermoplastic with PDMS. These segmented block copolymers possessed good processability, low water absorption, atomic oxygen resistance, low dielectric constants, and excellent adhesion. These materials have the potential to be used for applications in the microelectronics, automobiles, and aerospace areas. Segmented block copolymers with polyetheretherketone and polystyrene have also provided promising results for high performance applications [6–8].

Poly(arylene ether sulfone) (PAES) has been one of the most studied thermoplastics to be incorporated into segmented block copolymers. PAESs are amorphous thermoplastics that have exceptional thermal, mechanical, chemical properties and have been studied for their use in medical applications, substrates for cookware, and tubing for pump housings [3]. PAESs have also been modified by sulfonation or by chloromethylation for their use in reverse osmosis [9], materials for environmental applications [10,11], and extensively for their use in proton exchange membranes (PEMs) in fuel cell applications [12–14]. However, the most common PAES based on bisphenol A is a relatively brittle polymer which limits its use in many applications. Previous research by Noshay et al. [15,16] showed that incorporating an elastomer like PDMS improves the impact resistance of the polymer because the soft domains can inhibit crack propagation in the material. Tensile properties of these materials suggested that as

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more polysiloxane was added into the PAES, the materials became more elastic and the elongation increased. Further research by McGrath and Wilkes et al. [17] studied the phase separation of bisphenol A PAES–PDMS segmented block copolymers (BA PAES-*b*-PDMS) and determined the polymer segment with the highest content was the continuous phase and predominated on the film surface as shown by transmission electron microscopy (TEM).

While these materials and other segmented block copolymers often produce transparent films, it is important to control the size and distribution of the elastomeric domains as transparency is dependent on the size of the domains. Elastomeric domains with sizes larger than the wavelength of visible light can scatter visible light and result in hazy or opaque materials. We have interest in exploring these properties of PAES–PDMS segmented block copolymers where the bisphenol in the PAES is changed from bisphenol A to bisphenol AF. It is well known that incorporation of fluorine into a polymer backbone can improve the T_g of the polymer, enhance the thermal stability, and optimize the mechanical properties such as modulus, yield stress and strain at break [18]. Our desire is to understand the mechanical, thermal, and morphological properties of segmented block copolymer systems. In this report, we synthesize and characterize hexafluoroisopropylidene bisphenol poly(arylene ether sulfone) (BAF PAES) segmented block copolymers with PDMS (BAF PAES-*b*-PDMS) by varying the molecular weight of the two segments. This report will summarize our work on studying the morphological properties of BAF PAES-*b*-PDMS in comparison with BA PAES-*b*-PDMS. Morphology was studied by small-angle X-ray scattering (SAXS), atomic force microscopy (AFM), and transmission electron microscopy (TEM). We have also evaluated the mechanical and thermal properties of the segmented block copolymers.

2. Experimental section

2.1. General considerations

Anhydrous dimethylacetamide (DMAc), chlorobenzene, tetramethylammonium hydroxide pentahydrate ($TMAH \cdot 5H_2O$), and toluene were purchased from Aldrich and used as received. Anhydrous potassium carbonate (K_2CO_3) and isopropylidene bisphenol monomer (BA) were purchased from Aldrich in highly pure monomer grade and dried overnight under vacuum at 60 °C before use. Hexafluoroisopropylidene bisphenol monomer (BAF) and dichlorophenylsulfone (DCDPS) were graciously provided by Solvay Advanced Polymers and dried overnight under vacuum at 60 °C before use. Udel® was also provided by Solvay Advanced Polymers. Octamethylcyclotetrasiloxane (D_4), purchased from Aldrich, was vacuum distilled before use. 1,5-Bis(dimethylamino)hexamethyltrisiloxane was purchased from Silar Laboratories.

2.2. Preparation of hydroxyl-terminated PAES

2.2.1. Hexafluoroisopropylidene bisphenol PAES (BAF PAES)

Hydroxyl-terminated BAF PAES oligomer was prepared following a pervious literature method [19]. Synthesis of the oligomers was conducted in a three-neck, 250-mL round-bottom flask equipped with a mechanical stirrer, gas inlet, Dean–Stark trap, and condenser. The polymerization was carried out in a metal bath capable of high temperature reactions. For preparation of a 5000 g/mol oligomer, the round-bottom flask was charged with BAF (5.06 g, 0.015 mol), DCDPS (3.83 g, 0.013 mol), and K_2CO_3 (5.40 g, 0.039 mol) as a base. DMAc (80 mL) was added to the flask in a 2:1 v:v ratio with toluene as an azeotroping agent.

The reaction was started at 140 °C for 1–2 h. The temperature of the reaction was increased gradually from 140 to 152 °C over 3–4 h to allow the toluene to reflux. Within 5 h of reaction, all toluene/water had been removed. The temperature was increased to 160 °C and maintained for 20–24 h. Upon completion, the polymer was coagulated by pouring the reaction mixture gradually into a stirred solution of 10% aqueous HCl (800 mL). The polymer was filtered and dried overnight under vacuum at 90–110 °C. The polymer was dissolved in dichloromethane, precipitated into methanol, and dried under vacuum overnight at 80 °C.

2.2.2. Isopropylidene bisphenol PAES (BA PAES)

For preparation of a 5000 g/mol oligomer, the round-bottom flask was charged with BA (5.06 g, 0.015 mol), DCDPS (3.83 g, 0.013 mol), and K_2CO_3 (5.40 g, 0.039 mol) as a base. DMAc was added in a 2:1 ratio with toluene as an azeotroping agent. Reaction conditions were identical to the preparation of BAF PAES oligomers.

2.3. Preparation of dimethylamine-terminated PDMS (PDMS)

The dimethylamine-terminated PDMS oligomers were prepared following a previous literature method [17,20–22]. To synthesize the tetramethylammonium disiloxanolate catalyst, D_4 (13.3 g, mol) and $TMAH \cdot 5H_2O$ (0.71 g, 0.0039 mol) were added to a reactor with an attached Dean–Stark trap with condenser linked to a drying tube equipped with an overhead mechanical stirrer. The mixture was heated to 80 °C in a silicone oil bath for 24 h under a rapid stream of Argon bubbled through the reaction mixture. The solution became homogeneous within 2 h. The reaction was conducted for 24 h.

For the synthesis of a 10,000 g/mol PDMS oligomer, D_4 (60.3 g, 0.00603 mol) and 1,5-bis(dimethylamino)hexamethyltrisiloxane (1.78 g, 0.00603 mol) were added to a 250-mL round-bottom flask equipped with a magnetic stir bar and condenser, and stirred under Argon. The catalyst (3.73 g, 0.0105 mol) was removed from the reactor and was added to the reaction mixture using a clean, dry 12-gauge needle. The reaction was allowed to proceed at 80 °C for 2–3 days. The temperature was increased to 150 °C under Argon for 2–3 h to remove any residual catalyst. The solution was vacuum distilled at 70 °C to remove any residual end-capping reagent.

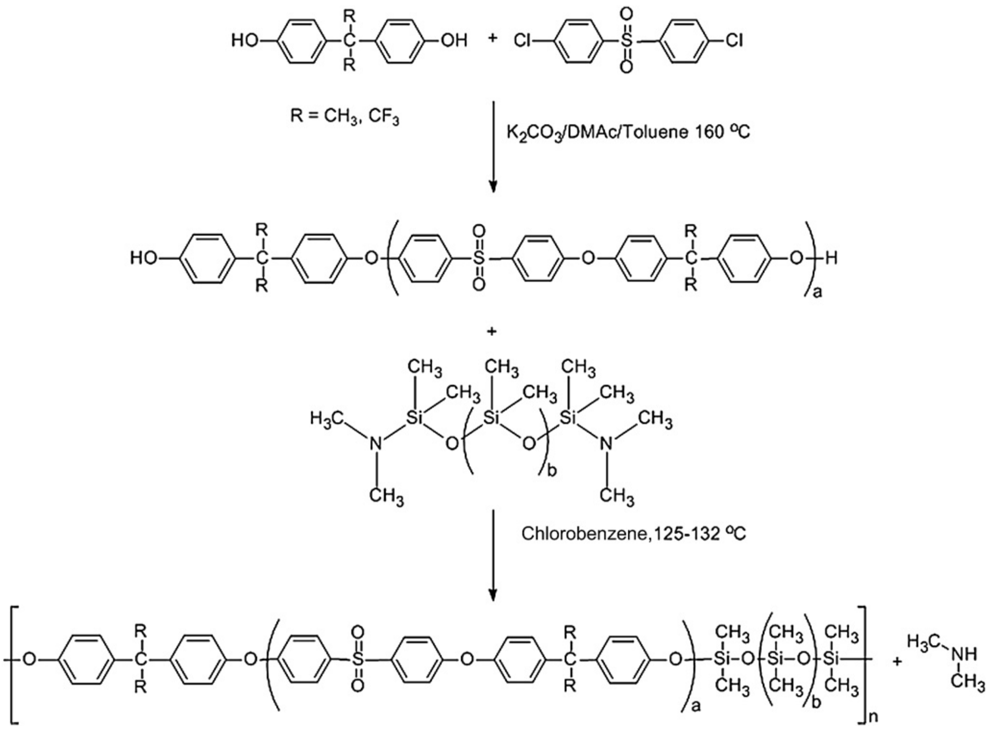
2.4. Preparation of segmented block copolymers

2.4.1. Hexafluoroisopropylidene bisphenol PAES segmented block copolymers (BAF PAES-b-PDMS)

Segmented block copolymers were prepared with BAF PAES and PDMS in a 1:1 molar ratio following a modified previous literature method [15]. BAF PAES oligomer 5400 g/mol (1.04 g, 0.000193 mol) and chlorobenzene (40 mL) were charged to a three-neck, 100-mL round-bottom flask equipped with a magnetic stir bar, gas inlet, Dean–Stark trap, and condenser in a silicone oil bath. The solution was stirred for 1 h at 125–132 °C. The PDMS oligomer 10,000 g/mol (1.93 g, 0.000193 mol) were added to the reaction mixture using a clean, dry 18-gauge needle in increments. The reaction was allowed to proceed at 125–132 °C for 8–12 h. The reaction was cooled and the product was precipitated into methanol (800 mL). The product was dried overnight under vacuum at 90–110 °C.

2.4.2. Isopropylidene bisphenol PAES segmented block copolymers (BA PAES-b-PDMS)

Identical preparation conditions were used for the segmented block copolymers prepared with BA PAES and PDMS. Segmented block copolymers were prepared in a 1:1 molar ratio, using BA PAES oligomer 5500 g/mol (1.04 g, 0.000193 mol) and PDMS oligomer 10,000 g/mol (1.93 g, 0.000193 mol).



Scheme 1. Synthesis of segmented block copolymers.

2.5. Film preparation of segmented block copolymers

The segmented block copolymers were dissolved in THF to afford transparent solutions with 5, 10, or 15 wt% solids, and the solutions were cast onto clean glass substrates. The films were dried for 2–3 days at ambient temperature, and then dried overnight under vacuum at 90–110 °C.

2.6. Thermogravimetric analysis (TGA)

Measurements were conducted by TA Instruments Thermogravimetric Analysis Q500 at temperatures from 35 °C to 600 °C under nitrogen at a heating rate of 10 °C/min.

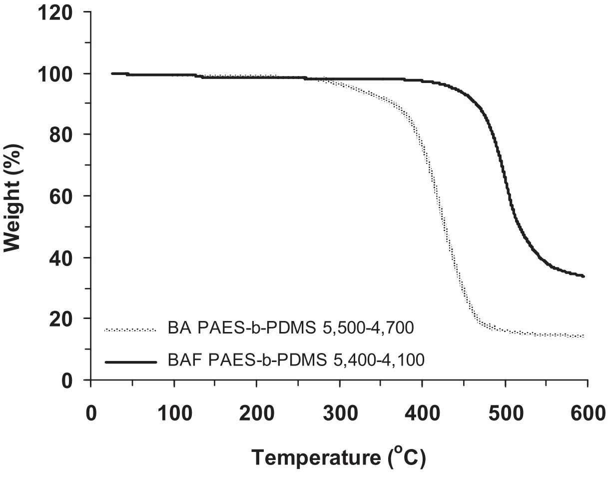


Fig. 1. TGA thermograms of PAES segmented block copolymers, at 10 °C/min.

2.7. Mechanical analysis

Stress–strain tests were preformed on an Instron Model 1123 Universal Testing system with a Bluehill software package using a 20-lb load cell at room temperature at a rate of 10 mm/min. Tests were done on dog-bone-shaped specimens (15 mm gauge length and 3.93 mm width) cut by a standard bench-top die from films (0.09 mm thickness). Prior to testing, specimens were dried under vacuum overnight at 90–110 °C.

2.8. Tapping mode atomic force microscopy (TP-AFM)

Images of the BAF PAES-*b*-PDMS were obtained using a Digital Instruments MultiMode scanning probe microscope with a NanoScope Iva controller. A silicon probe (Veeco) with an end radius of <10 nm and a force constant of 5 N m^{-1} was used to image samples.

2.9. Small-angle microscopy (SAXS)

Small-angle X-ray scattering profiles of films of various thicknesses were collected using a Molecular Metrology multiwire area detector. X-rays having wavelength of 1.542 Å were generated using a Rigaku Ultrax18 rotating anode X-ray generator operated at

Table 1
Thermal stabilities of BAF PAES and PDMS homopolymers and BAF PAES-*b*-PDMS.

Segmented block copolymers		T_d – 5% wt. loss (°C)
BAF PAES	PDMS	
5400	1600	410
5400	4100	439
5400	10,000	406
9700	4100	467

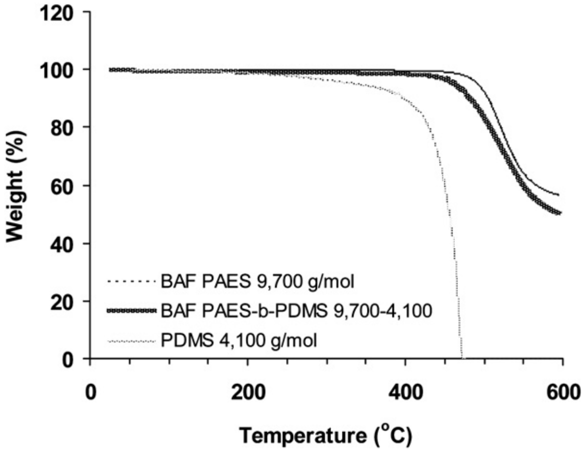


Fig. 2. TGA thermograms of BAF PAES-*b*-PDMS and homopolymers.

45 kV and 100 mA, with a Cu anode and a Ni filter. Data collected at camera lengths of 1.5 m and 0.5 m were combined to span an effective q-range of 0.007 Å^{-1} to 0.45 Å^{-1}, where q is the magnitude of the scatter vector defined by $q = 4\pi \sin(\theta)/\lambda$ for scattering angle, 2θ, and wavelength, λ. Camera length and beam center were determined using a silver behenate calibration standard. The data were corrected for background noise and transmission before azimuthal averaging. The azimuthally averaged data were placed on an absolute scale using type-2 glassy carbon as a secondary intensity standard. For samples where thickness and transmission measurements were thought to be inaccurate, data were scaled to a background level of 0.1 cm^{-1} and subsequently presented with intensity in arbitrary units (a.u.). The average interdomain spacing, d, of the segmented block copolymers was calculated as $d = 2\pi/q_{\max}$, where $q_{\max}$ is the position of maximum intensity for a given scattering peak. All data manipulation, data evaluation, and scattering calculations were done in WaveMetrics IGOR Pro v. 6 using data analysis packages written by Jan Ilavsky, Argonne National Laboratory [23].

2.10. *Transmission electron spectroscopy (TEM)*

Non-equilibrium segmented block copolymers films were observed and imaged using a Philips EM 420 TEM equipped with a tungsten filament, 100 kV maximum accelerating voltage, single and double axis sample tilt, and a CCD camera for recording images. Staining of the segmented block copolymer films was not necessary due to the sufficient contrast between the PAES and PDMS phases.

Finally, in this report, the nomenclature used for these materials will refer to the PAES type (BA or BAF) followed by the volume fraction of PDMS incorporated in the segmented block copolymer.

3. Results and discussions

3.1. *Synthesis of segmented block copolymers*

The synthesis of the segmented block copolymers is shown in Scheme 1. Segmented block copolymers were achieved by a nucleophilic aromatic substitution reaction between the phenol (BA or BAF) and DCDPS monomers with a molar excess of phenol (BA or BAF) to afford hydroxyl end-groups on the PAES oligomers. Systematically varied molecular weights of these oligomers were prepared. The hydroxyl-terminated BAF PAES structure was determined by ^{1}H NMR and their molecular weights were determined by SEC. The dimethylaminesilyl-terminated PDMS oligomers were synthesized by an equilibrium reaction as described in detail by Kantor et al. [20]. The dimethylaminesilyl end-groups and molecular weights of these oligomers were determined by NMR end-group analysis. Synthesis of the segmented block copolymers was done by a condensation reaction in chlorobenzene between the hydroxyl-terminated PAES oligomers and the silylamine end-groups of the PDMS at a 1:1 molar ratio with the release of the dimethylamine by-product. Noshay et al. [15] synthesized BA PAES-*b*-PDMS in both chlorobenzene and THF. Their work determined that chlorobenzene was a better reaction solvent as high molecular weight copolymers could be synthesized in a shorter reaction time [15]. With slow and gradual addition of PDMS to the PAES solution the viscosity increased. This addition process is also described by Noshay in order to gradually reach a stoichiometric end-point to achieve high molecular weight segmented block copolymers. Precipitation into methanol provided fluffy white material characterized by NMR to determine their structural compositions and functional groups. NMR also provided measure of the molecular weight content and volume fraction of PDMS which was incorporated into the segmented block copolymer. Intrinsic viscosity measurements (in chloroform at 25 °C) for these segmented block copolymers were as high as 0.4 dL/g. We also note the silicon–oxygen–carbon linkage in these segmented block copolymers is hydrolytically stable under various conditions as described by previous studies [24].

3.2. *Thermal stability of segmented block copolymers*

The TGA profile, in Fig. 1, shows thermal stability of two segmented block copolymers systems. The BA PAES-*b*-PDMS (5500–4700) has a thermal decomposition at 5% weight loss at 320 °C. The BAF PAES-*b*-PDMS showed thermal stability to 439 °C at 5% weight loss. This increased stability for these fluorinated segmented block copolymer systems can be attributed to the higher bond strength of the C–F bond over the C–H bond and the shielding effect of the high electronegativity of the fluorine atoms in the polymer [25,26].

We also show the thermal decomposition temperatures of several other BAF PAES-*b*-PDMS in Table 1. The thermal stabilities

Table 2
Mechanical properties of BAF PAES-*b*-PDMS.

Segmented block copolymers		Siloxane (wt%)[a]	Intrinsic viscosity[b] (dL/g)	Tensile stress at break (MPa)	Tensile strain at break (%)	Tensile stress at yield (MPa)	Young's modulus (MPa)
BAF PAES	PDMS						
40,000	–	0	0.215	16 ± 3	16 ± 4	38 ± 6	1713 ± 62
5400	4100	35	0.194	15 ± 3	16 ± 14	16 ± 3	520 ± 98
6800	5800	46	0.289	9 ± 3	172 ± 54	13 ± 0.61	245 ± 21
5400	10,000	64	0.367	8 ± 0.9	417 ± 67	8 ± 0.96	36 ± 3

[a] Calculated by ^{1}H NMR.
[b] 0.2 dL/g in chloroform at 25 °C.

Table 3
Mechanical properties of BA PAES-*b*-PDMS.

Segmented block copolymers		Siloxane (wt%)[a]	Intrinsic viscosity[b] (dL/gm)	Tensile stress at break (MPa)	Tensile strain at break (%)	Tensile stress at yield (MPa)	Young's modulus (MPa)
BA PAES	PDMS						
Udel P-3500		–	0.342	28 ± 20	6 ± 1	48 ± 12	1201 ± 350
10,000	5600	36	0.197	15 ± 8	8 ± 7	24	800 ± 7
7800	5800	47	0.340	9 ± 4	134 ± 49	12 ± 2	355 ± 25
5500	10,000	65	0.307	14 ± 0.8	631 ± 170	14 ± 0.6	8 ± 2

[a] Calculated by ^{1}H NMR.
[b] 0.2 dL/gm in chloroform at 25 °C.

range from 400 to 467 °C, these values are also consistent with many other fluorinated-based polysulfones [27,28] copolymers and polyimides siloxane copolymers [18,29,30] that are in the range of 400–500 °C. The influence of the BAF PAES oligomer on the thermal stability of the segmented block copolymer is illustrated in Fig. 2. The thermal stability of the segmented block copolymer at 5% weight loss is 467 °C. This high stability is resultant of the BAF PAES 9700 g/mol oligomer incorporated, which has a T_d of 491 °C rather than the PDMS oligomer which has a T_d at 5% weight loss of 343 °C.

3.3. Mechanical analysis of segmented block copolymers

Segmented block copolymers are unique in that excellent properties can result from their multiphase structures. We synthesized BAF PAES homopolymer (41,000 g/mol) and then prepared films cast from THF. The tensile properties of the homopolymer and segmented block copolymers are presented in Table 2. The data show the homopolymer had a modulus of 1700 MPa. BAF PAES-*b*-PDMS, with increasing PDMS content from 35 to 64%, showed a decrease in the modulus from 520 to 36 MPa. The material properties transition from being plastic to more elastomeric. The segmented block copolymers also showed an increase in the tensile strain at break from 16 to 417% with increase in PDMS content. These tensile properties were consistent with the BA PAES-*b*-PDMS materials synthesized in our labs as well as to the original work by Noshay et al. [15].

Similarly, Udel® homopolymer obtained from Solvay Advanced Polymers was cast from THF and the mechanical properties were determined. The homopolymer had a modulus of 1200 MPa compared to the 1700 MPa for the fluorinated analog. BA PAES-*b*-PDMS was prepared and films cast from THF gave mechanical properties ranging from plastic to elastomeric upon increasing the amount and molecular weight of PDMS in the segmented block copolymer.

The mechanical properties of segmented block copolymers were also explained by Noshay and McGrath in their review. They suggested that at a certain M_n of PDMS (correlating to a high PDMS composition) incorporated into the segmented block copolymer system, PAES no longer influences the modulus and merely acts as a “pseudo crosslink,” and the PAES oligomer only reinforces the copolymers [1,31]. These values are consistent with other segmented block copolymers. Therefore, incorporating fluorine into the bisphenol unit has only a moderate effect on the modulus of the homopolymer and the segmented block copolymer (Table 3).

3.4. Morphological characteristics of segmented block copolymers

AFM was used to show that these materials form phase-separated morphologies. Images of the as cast, non-equilibrium PAES segmented block copolymers BAF-72 (BAF PAES-*b*-PDMS 5400/10,000) and BA-71 (BA PAES-*b*-PDMS 5500/10,000) in Fig. 3 showed that these materials were microphase separated. In these phase (surface) images, dark features are representative of the soft material (PDMS) and light features are indicative of the hard material (PAES). BA-71 showed finer dimensions than the BAF-72.

The microphase separation that is evident in these segmented block copolymers is indicative of the incompatibility between the PAES, an amorphous thermoplastic, and PDMS, an elastomer. The phase separation of polysulfone segmented block copolymers incorporating various flexible units such as poly(tetramethylene oxide) and polyester was studied by Pospiech et al. [32]. Their research showed that phase separation is enhanced by the incorporation of flexible units due to their higher mobility and incompatibility between the two phases. Segmented block copolymers with highly amorphous segments show a high degree of intermixing and no phase separation [33].

We further analyzed the morphology of a series of segmented block copolymers using TEM. Images were obtained from cryosections of un-stained, non-equilibrium films solution-cast from THF at room temperature over 3 days. The BAF PAES-*b*-PDMS micrographs, in Figs. 4 and 5, show microphase separation, with the PDMS domains appearing dark because of their higher electron density than BAF PAES. BAF-72 showed a disordered morphology. In the samples where the composition is approximately balanced

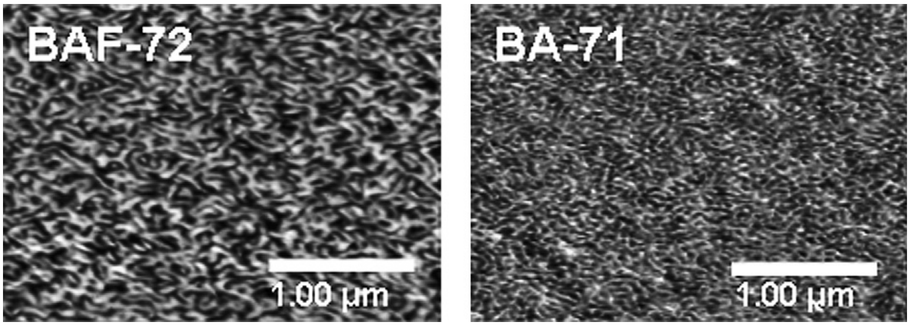


Fig. 3. AFM images of PAES segmented block copolymers BAF-72 and BA-71 showing the surface of the film.

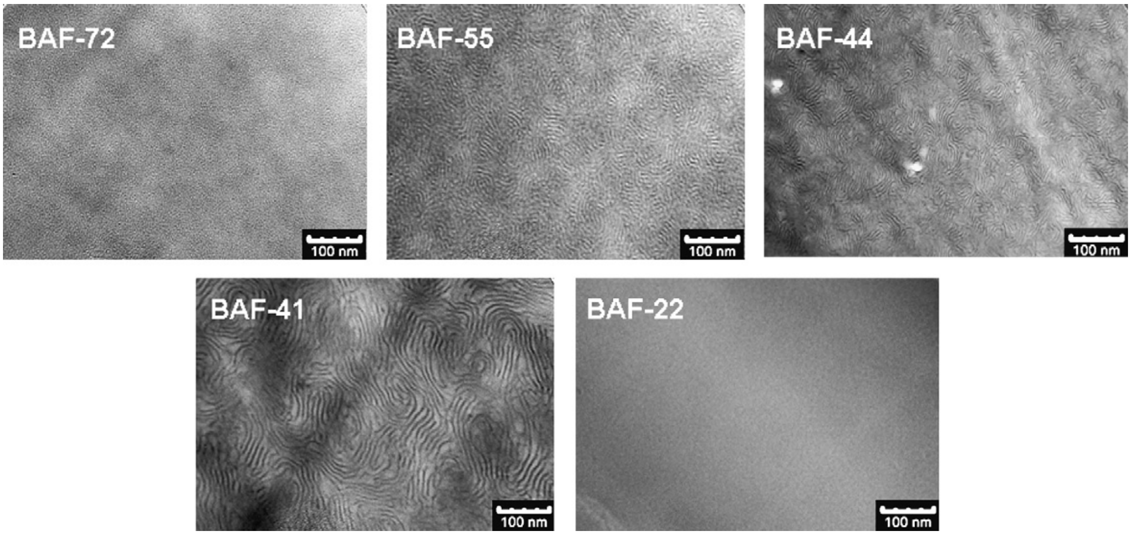


Fig. 4. TEM images of BAF PAES-*b*-PDMS (BAF-72) 5,400/10,000, (BAF-55) 6,800/5,800, (BAF-44) 5,400/4,100, (BAF-41) 9,700/4,700, (BAF-22) 5,400/1,600.

between the two polymers, BAF-55 and BAF-44, the formation of small, weakly ordered lamellar domains was observed. Surprisingly, BAF-41 showed the most well-ordered lamellar morphology despite being more asymmetric in composition than BAF-55. Where the composition heavily favored either constituent, BAF-72 and BAF-22, the morphology was disordered.

In comparison with selected BAF PAES-*b*-PDMS micrographs, Fig. 6 shows the TEM micrographs for BA PAES-*b*-PDMS with PDMS volume fractions of 71, 52, and 20%. The BA PAES-*b*-PDMS all exhibited microphase separation. As was seen for BAF-72, the micrograph of BA-71 shows a disordered, microphase-separated morphology. The roughly equal volumes of BA PAES and PDMS in BA-52 give rise to the development of lamellar-like morphology with some order, roughly equivalent to that found for BAF-55.

Unlike the fluorinated analog, the morphology for the sample with the lowest PDMS volume fraction, BA-20, was clearly microphase separated, and appears to show the formation of spherical domains of PDMS. Previous work by McGrath and Wilkes et al. [17] and follow-up research by Patel et al. [34] on the bulk morphology of a series of BA PAES-*b*-PDMS found spherical microdomain structures where the interdomain spacing increased as the molecular weight percent of the PDMS segments increased. The morphologies also illustrated continuity for both phases where the segment compositions were nearly equal.

Based on the AFM and TEM results of the BAF PAES-*b*-PDMS, we further evaluated these materials by SAXS in Figs. 6 and 7. Well-defined peaks in the SAXS data for BAF-72 and BA-71, shown in Fig. 6, indicate microphase separation, consistent with the AFM and TEM images. The lack of second-order Bragg reflections indicates no long-range ordering, also consistent with microscopy data. The data also indicate that the incorporation of fluorine into the PAES unit led to an increase in the scattered intensity for BAF PAES-*b*-PDMS, due in part to the higher electron density of BAF PAES over BA PAES. The scattering term $(\Delta\rho)^2$, a measure of the X-ray scattering contrast in a two-phase material, is increased approximately 40% by the substation of fluorine for hydrogen in the bisphenol A. Sample BAF-72 has an interdomain spacing of 21.9 nm, while BA-71 has an interdomain spacing of 19.3 nm.

The remaining BAF PAES-*b*-PDMS materials were also characterized by SAXS, as shown in Fig. 7. The interdomain spacings of the segmented block copolymers were determined and are given in Table 4. The data agree well with the microscopy data for the disordered samples, with at most a single characteristic scattering maximum. Sample BAF-41, which was clearly lamellar by TEM, does not show the characteristic Bragg diffraction peaks one would expect for a strongly lamellar morphology. This discrepancy may be the result of preferential orientation of the lamella in the plane of the cast films, a likely result of the very low surface tension of the PDMS constituent. Attempts to collect SAXS data with the specimen geometry rotated such that the incident beam of photons would be parallel to the lamellae were unsuccessful due to minimal film thickness (22 μm).

The exact effect of fluorination on morphology in these materials remains unclear. The BAF PAES-*b*-PDMS materials appear to show stronger microphase separation behavior, with BAF-41 forming well-defined lamellae. However, where direct comparisons are possible the effects are not clearly discernable. While BAF-55 and BA-52 have very similar morphologies, BA-20 is more

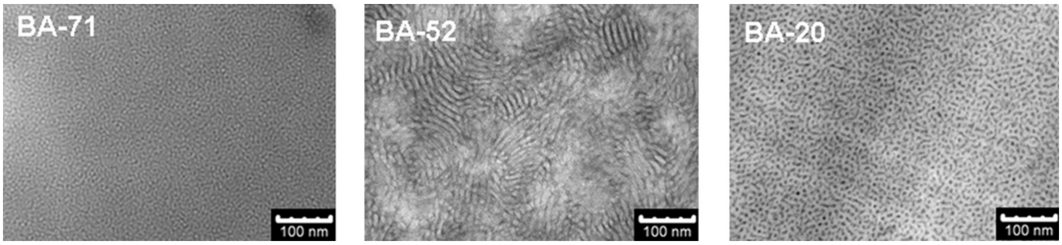


Fig. 5. TEM images of BA PAES-*b*-PDMS (BA-71) 5500/10,000, (BA-52) 10,000/10,000, (BA-20) 10,000/1600.

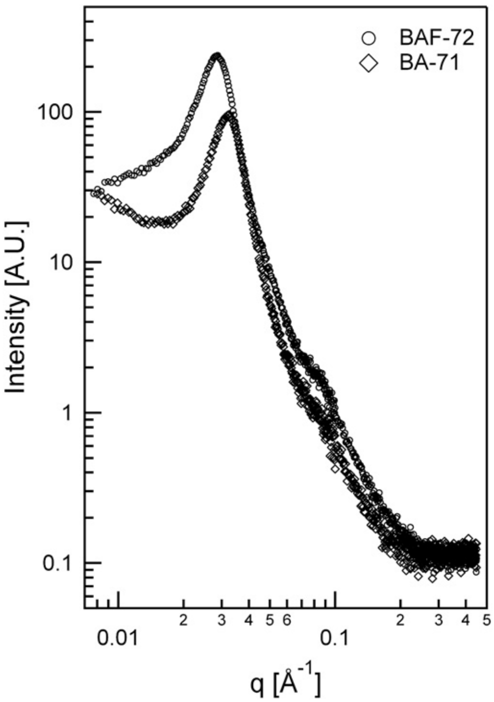


Fig. 6. SAXS data for PAES segmented block copolymers BAF-72 and BA-71.

strongly phase separated than BAF-22. A number of complex explanations for the observed morphological behaviors are possible, but outside the scope of this work. It is worth noting that many parameters play an important role in determining bulk morphology, including molecular weight [35,36], casting solvent [37,38], annealing temperature and time [39–42].

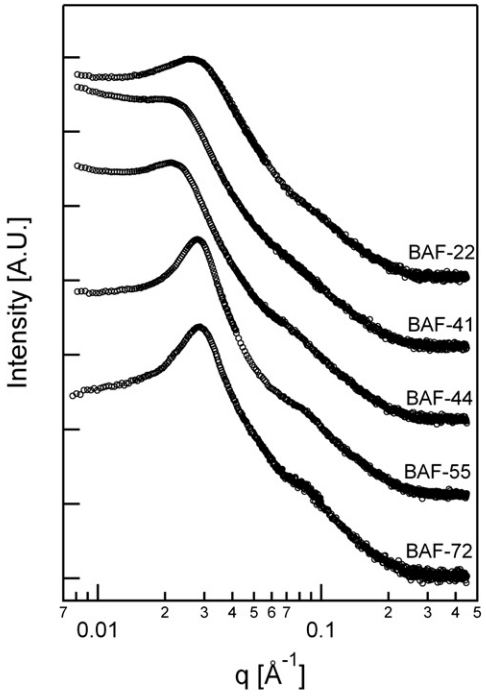


Fig. 7. SAXS data for BAF PAES-*b*-PDMS of various PDMS volume fractions. The data have been scaled vertically for clarity of presentation.

Table 4
Interdomain (ID) spacing between scattering domains from SAXS for BAF PAES-*b*-PDMS.

Image	BAF PAES	PDMS	ID Spacing (SAXS Bragg, nm)
BAF-72	5400	10,000	21.9
BAF-55	6800	5800	25.9
BAF-44	5400	4100	29.9
BAF-41	9700	4700	26.6
BAF-22	5400	1600	24.7

4. Conclusions

We have synthesized and characterized a new family of BAF PAES-*b*-PDMS and compared them to BA PAES-*b*-PDMS synthesized in our lab. The incorporation of fluorinated methyl groups in the PAES unit gives these segmented block copolymers thermal stability to nearly 500 °C, which is greater than the BA PAES-*b*-PDMS. The BAF PAES homopolymer has a higher tensile modulus than the Udel$^{®}$ homopolymer, 1700 MPa compared to 1200 MPa. The tensile properties of the two families of segmented block copolymers were similar with properties ranging from elastomeric and plastic depending on the molecular weight composition of the oligomer. Both segmented block copolymer systems were transparent and colorless. They were also microphase separated, as indicated by AFM, SAXS, and TEM. There were distinct differences in the morphological properties of these segmented block copolymers analyzed by TEM. The BA PAES-*b*-PDMS materials formed weakly ordered lamellae at a symmetric composition and were disordered at asymmetric compositions, but were thought to have characteristics in agreement with those reported previously for this class of segmented block copolymers. The BAF PAES-*b*-PDMS displayed increased morphological order with decreasing PDMS content, with a clearly lamellar morphology formed by the sample with 41 vol% PDMS. Without a direct comparison to BAF-41, these results do not conclusively reveal the effect of fluorination on the driving force for microphase separation in these segmented block copolymers.

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