Low Dielectric Poly(imide siloxane) Films Enabled by a Well-Defined Disiloxane-Linked Alkyl Diamine

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ABSTRACT: This paper presents an efficient pathway to achieve the dielectric constant as low as 2.48 @ 25 °C, 1 MHz for nonporous poly(imide siloxane) films with mechanical and thermal robustness. A symmetric disiloxane-linked alkyl diamine, bis(aminopropyl)tetramethyldisiloxane (BATMS) with a well-defined molecular formula NH2CH2CH2CH2Si-(CH3)2OSi(CH3)2CH2CH2NH2, has been used to controllably reduce the dielectric constant of the polymer films by adjusting the loading of BATMS. The thermal stability of all the polymer films remains robust with T5 and T10 no less than 458 and 472 °C, respectively, while the glass-transition temperature decreases with increasing incorporation of flexible disiloxane-alkyl segments into a polymer backbone. There exists a consistent regularity between the thermal, optical, and dielectric properties with the loading amount of BATMS in the polymer films, inferring that the disiloxane-alkyl segments are homogeneously distributed in the polymer backbone. Charge-transfer complex inhibition of polymer films by disiloxane segments has been revealed by an enlarged d-spacing in wide-angle X-ray diffraction spectra and a blue shift in film fluorescence emission spectra. The combined low dielectric constant, robust mechanical and thermal stability, and improved hydrophobicity make the series of BATMS-resulting poly(imide siloxane) films promising candidates for sophisticated flexible microelectronic application.

1. INTRODUCTION

Polymides (PIs) are regarded as high-performance polymers because of their excellent chemical, thermal, and irradiation stability; high mechanical strength; and reliable electrical insulation and therefore widely used in aerospace, microelectronics, optoelectronics, and civil engineering in different forms including films, composite resins, fibers, and plastics.1,2 However, every coin has two sides. While possessing these remarkable performances, PIs suffer from inherent drawbacks such as poor processability, intense coloration, and particularly high dielectric constant for nowadays state-of-the-art microelectronic application because of strong polarized chain packing that results from the charge-transfer complexes (CTCs) formed between the alternate electron-accepting and electron-donating aromatic rings of the neighboring chains.3,4 On the other hand, polysiloxane represents another category of high-performance polymers widely used as electronic packaging, which is skeletally composed of an alternate Si–O bond that is the most prevalent bond in our terrestrial environment with high bond energy (BDE = 445 kJ/mol).5 Despite the strong Si–O bond, the backbone of linear polysiloxane is noodle-like “soft” with negligible interchain interaction because of the surrounding apolar alkyl groups, predominantly methyl, along the polymer backbone, which offers polysiloxane with great chain rotation ease and superior hydrophobicity simultaneously.6 The typical structural characteristics of rigid PI’s and flexible polysiloxane’s backbone are integrally depicted in Figure 1.

It is intriguing to explore the results if the polysiloxane with nearly zero interchain interaction combines with PI having polarized interchain CT interaction. Actually, the incorporation of polysiloxane with PI has long attracted the research interests in a wide range of applications including adhesives,7 metal anticorrosion coating,8 epoxyc-mediated ternary copolymers,9 fuel cell proton exchange membranes,10 gas permeation membranes,11 and atomic oxygen erosion-resistant materials.12

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Figure 1. Structural characteristic illustration of rigid PI with interchain CTCs (left) and flexible polysiloxane with nearly zero interchain interaction (right).

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The effective practice of modifying PI by polysiloxane is to create covalent connection with imide linkage, which could generally be classified into three approaches according to the structure of the obtained polymers: thermoplastic copolymers by using a siloxane-containing dianhydride,13−15 thermoplastic copolymers by using a siloxane-containing diamine,16−23 and cross-linked copolymers by using a trifunctional aminosilane,24−26 most probably aminopropyl triethoxysilane.25 The siloxane-containing PI monomers have usually been synthesized via the core reaction of hydrosilylation that creates C−Si connection. The siloxane-containing dianhydride has hardly been used in preparing PI films, and the synthetic routes of siloxane-containing dianhydride involve complicated multi-step procedures, thus difficult to achieve high purity. In comparison, the siloxane-containing diamine is readily accessible with high yield and purity. However, the traditional siloxane-containing diamine is the methyl siloxane oligomer with two terminal propylamines. Hence, it is uncertain whether the telechelic amino groups remain synchronously reactive toward condensation with the dianhydride because the “immiscibility” probably occurs with an elongated siloxane chain, which would become impedimental to the condensation of the telechelic amino toward the dianhydride. These disadvantages would aggravate for preparing PI films where the polymerization degree is very important to achieve PI films with high quality.

Herein, we present an unoligomerized, symmetric siloxane diamine monomer bis(aminopropyl)tetramethyldisiloxane (BATMS) synthesized following a process developed in our laboratory, in which two aminopropyls are connected by minimized disiloxane linker (see Scheme S1 and Figure S1 in the Supporting Information). Poly(siloxane imide) films were therefrom prepared by copolymerizing BATMS with a commercial diamine 4,4′-oxydianiline (ODA) in different compositions toward a commercial dianhydride 4,4′-oxydiphthalic dianhydride (ODPA) through a two-step process. In this work, the diamine monomer (BATMS) has a well-defined molecular formula NH2CH2CH2(CH3)2Si(CH3)2O(CH3)2CH2CH2NH2, unlike the traditional oligomerized siloxane diamine in which multiple siloxane segments are not precisely controlled but with just an average chain length depending on different oligomerization formulations. The strategy of the minimized disiloxane linkage in BATMS aims at facilitating the synchronous condensation reactivity of the two terminal amino groups toward the dianhydride, which otherwise might not be guaranteed for telechelic amino in the oligomerized siloxane diamine. According to the BATMS molar percentage (χ) in diamine comonomers, the copolymer films were coded as PI-χ in which χ is one of 10, 25, 40, 50, 60, 75, and 90. The use of the disiloxane-linked alkyl diamine BATMS in the synthesis of copolymer films is illustrated in Scheme 1.

2. RESULTS AND DISCUSSION

2.1. Polymer Synthesis. All the polymerizations were carried out by condensing the dianhydride ODPA with an equimolar diamine mixture of ODA and BATMS in one portion, following a two-step thermal imidization process to generate copolymer films peeled from a glass plate. Nylon salt formation in some cases occurred during the first step of poly(amic acid) (PAA) process because of the basicity of...
BATMS, but the nylon salts could generally be reversed (redissolved) by moderately increasing the temperature, and robust PI films were obtained after the following thermal treatment. The exception is PI-90, in which case, because of the high molar percentage of BATMS, the reversion of nylon salt demonstrated great difficulties with partial redissolution achieved, which eventually led to the reduced mechanical properties of the copolymer films.

### 2.2. Mechanical and Thermal Properties

Except for PI-90, which was fragile and unable to generate the mechanical test results, the copolymer films exhibit tensile strength ranging from 124.4 to 61.8 MPa, tensile modulus ranging from 2.77 to 1.74 GPa, and elongation at break ranging 28.4 to 17.0%. The mechanical properties of the copolymer films show gradual decrease with increasing \( \chi \), which could be attributed to the increasing degree of nylon salt formation that decreases the degree of polymerization of copolymer films, even if the redissolution of precipitated nylon salts was achievable. Another probable reason is that the increasing disiloxane and alkyl segment decreases the structural regularity and rigidity of the polymer main chain, thus reducing the chain orientation and eventually the mechanical properties of the copolymer films.

The glass-transition temperature (\( T_g \)) was measured by dynamic mechanical analysis (DMA), as shown by loss tan \( \delta \) curves in Figure 2a, where the transitions are explicitly seen with sharp peaks. The copolymer films present a consecutive decrease from 230 °C to 108 °C with an increasing \( \chi \) from 10 to 75. Understandably, the increasing introduction of flexible disiloxane and alkyl segments reduces the rigidity and imparts greater rotation ease with the copolymer backbone, which together contribute to the decreasing \( T_g \). The thermal decomposition curves of the films in \( \text{N}_2 \) are displayed in Figure 2b, where the 5% weight loss temperature \( (T_5) \) and 10% weight loss temperature \( (T_{10}) \) values present a similar regular decrease with increasing BATMS, which could be attributable to the increasing presence of thermally labile aliphatic propyl linkage between amino functionality and disiloxane segment in BATMS. Despite the decreasing trend with increasing BATMS percentage, \( T_5 \) and \( T_{10} \) values of all the seven films are higher than 458 and 472 °C, showing robust thermal stability that is favorable to withstand a high-temperature fabrication process.

The general mechanical and thermal properties of the copolymer films are shown in Table 1.

| mechanical properties<sup>a</sup> | TGA | CTE (ppm K<sup>−1</sup>) |
|---|---|---|
| X | TS (MPa) | TM (GPa) | Eb (%) | \( T_5 \) (°C) | \( T_{10} \) (°C) | residual mass (%) | \( T_L \) (°C) by DMA | ND<sup>b</sup> |
| 10 | 124.4 | 2.77 | 28.4 | 485 | 518 | 57.3 | 234 | 21.5 |
| 25 | 116 | 2.63 | 25 | 479 | 496 | 50.6 | 206 | 22.2 |
| 40 | 111 | 2.39 | 21.5 | 476 | 488 | 46.2 | 173 | 25.2 |
| 50 | 84.4 | 2.34 | 21.4 | 470 | 481 | 40.1 | 151 | 25.1 |
| 60 | 69.8 | 2.26 | 21.2 | 470 | 478 | 34.8 | 134 | 25.4 |
| 75 | 61.8 | 1.74 | 17 | 468 | 476 | 28.1 | 108 | 27.2 |
| 90 | ND<sup>a</sup> | ND<sup>a</sup> | ND<sup>a</sup> | 458 | 472 | 20.5 | ND<sup>b</sup> | 29.6 |

<sup>a</sup>TS: tensile strength, TM: tensile modulus; and Eb: elongation at break. <sup>b</sup>ND: not determined.

| Figure 2b | Figure 2a | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 |
|---|---|---|---|---|---|---|---|---|
| Figure 2a | Figure 2b | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 |
| Figure 2a | Figure 2b | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 | \( \chi \) from 10 to 75 |
disiloxane segments were homogeneously inserted into the polymer chain as anticipated.

2.3. Inhibited Polymer CTC. PI’s typical interchain CTC would be weakened by the inserted disiloxane segments because of the intrinsic negligible interchain interaction of polysiloxane. Meanwhile, disiloxane incorporation leads to the increased polymer chain flexibility that further inhibits the CTC by the enlarged interchain distance (d-spacing), as derived from wide-angle X-ray diffraction (WAXD) spectra in Figure 3a. According to the Bragg equation, the smaller the diffraction angle is, the larger the average interchain spacing is. It can be seen that the diffraction 2θ decreases with increasing disiloxane percentage, indicating that the presence of disiloxane enlarges the copolymer interchain distance. The enlarged interchain distance leads to improvement in the solubility of copolymer films, as shown in Table 2.

The film fluorescence is another supporting evidence for CTC inhibition. The PI film fluorescence is associated with its aggregate state. In the presence of strong CTC in PI, the polymer chains would pack together and form an ordered aggregate structure, which tend to emit CT fluorescence at a shorter wavelength when the CTC was weakened. In general, a typical CT fluorescence wavelength is usually longer than 450 nm, and fully aromatic PI emits fluorescence at a longer wavelength than alicyclic PI. Although the difference between peak wavelength is slight, the gradual “blue shift” of CT fluorescence is observed from PI-10 (497 nm) to PI-90 (473 nm), as shown in Figure 3b.

The increasing insertion of flexible disiloxane segments increases the rotation capability of the polymer backbone; therefore, the interchain π–π stacking associated with the rigid and highly coplanarized polymer structure is weakened. As a consequence, consecutive “blue shifts” in the emission fluorescence of the copolymer films on increasing the percentage of BATMS are generated. As shown in Table 3, besides the blue shift in fluorescence emission, the reduced CTC is also manifested by enhancement of optical transparency (increasing λ0) of copolymer films with increasing χ.

2.4. Dielectric Properties, Moisture Absorption, and Polymer Chain Volume. PI films have been integrated into microelectronic devices such as flexible printed circuits for several decades. At the forefront of this research field has been how to reduce the dielectric constant (ε′) of PI films with an aim to achieve the high-speed and high-fidelity signal transmission. As microelectronic miniaturization continues to develop according to the dictation by “Moore’s law”, the degraded performances of electronic components have become increasingly translated into resistance-capacitance time delay (RC delay) during signal transmission, which would be alleviated only by lowering the ε of the insulating materials. The proposed roadmap to reduce the ε of the insulating materials so far seems a little aggressive in practical microelectronic fabrication, but the trend remains undoubted, and considerable research interests have thus been inspired in devising new PI films to reduce the ε. For instance, sacrificial thermable components have been introduced into PI films with an aim to introduce air (εair = 1) by making porous voids. Nevertheless, these approaches remain industrially impractical because of the complicated fabrication process and the compromised flexural strength of the composite PI films as well. The appealing approach toward low dielectric constant PI films for practical microelectronic application is polymer backbone structure optimization, like introducing bulky group, fluorinated and aliphatic structure via the functionalized monomers. Recently, Fang and co-workers have prepared the fluorinated polysiloxane with thermally induced cross-linking network structure, which exhibited a low dielectric constant at high frequency. Ando reported the use of the trifunctional organosilicon to prepare low dielectric constant at high frequency. Ando reported the use of the trifunctional organosilicon to prepare low dielectric constant PI films with silica and even investigated the effects of BATMS-ODPA segment in the cross-linked PIs.

Our present work focuses on the thermoplastic poly(amide siloxane) films, in which each disiloxane-alkyl is alternated by the imide ring in the BATMS-ODPA chain segments. Even

| Table 2. Solubility and WAXD Properties of Copolymer Films with Different χ |
| --- |
| χ | NMP | DMAc | DMF | THF | acetone | DMSO | CHCl3 | d-spacing (Å) |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 10 | -- | -- | ± | -- | -- | -- | -- | |
| 25 | ± | ± | ± | -- | -- | -- | -- | 5.3513 |
| 40 | + | + | + | ± | ± | ± | -- | 5.8977 |
| 50 | + | + | + | -- | ± | ± | -- | 5.9757 |
| 60 | + | + | + | -- | + | + | -- | 5.9915 |
| 75 | + | + | + | ++ | + | + | -- | 6.0236 |
| 90 | + | + | + | ++ | + | + | -- | ND+ |

*a*: soluble at room temperature; +h: soluble on heating; ±: partially soluble or swelling on heating; and --: insoluble even on heating.

\[ d = \frac{n\lambda}{2\sin \theta} \]

**Table 3. Optical Properties, Water Absorption, Dielectric Properties, and Polymer Chain Volume Characteristics of Copolymer Films with Different χ |
| --- |
| X | λ0 | λem | WA | ε′ | ε″ | V | FFV | FFV |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 10 | 410 | 497 | 1.68 | 3.15 | 0.011 | 228.16 | 0.1988 |
| 25 | 404 | 495 | 1.12 | 2.92 | 0.011 | 237.56 | 0.1994 |
| 40 | 401 | 493 | 0.91 | 2.79 | 0.012 | 246.96 | 0.2015 |
| 50 | 383 | 492 | 0.60 | 2.69 | 0.013 | 253.22 | 0.2041 |
| 60 | 385 | 491 | 0.56 | 2.61 | 0.012 | 259.48 | 0.2107 |
| 75 | 383 | 497 | 0.55 | 2.48 | 0.014 | 268.88 | 0.2215 |
| 90 | 378 | 473 | 0.33 | ND | ND | 272.82 | 0.2304 |

λ0: UV–vis cutoff wavelength of the films; λem: fluorescence emission peak wavelength of the films. WA: water absorption of the films @ 60 °C for 48 h. Dielectric constant (ε′) and dielectric loss (ε″) of the films measured at 25 °C, 1 MHz. V: van der Waals volume calculated. FFV: fractional free volume. ND: not determined.
though the chain segments of BATMS-ODPA and ODA-ODPA might be randomly distributed along the copolymer mainchain, the BATMS-ODPA segments are certainly composed of structural alternation of disiloxane-alkyl and imide ring. Besides, the disiloxane is structurally well defined in BATMS, instead of a roughly mean chain length in the traditional oligomerized siloxane diamine. The minimized disiloxane structure in BATMS eliminated the microphase separation that may occur with an oligomerized siloxane diamine during the polycondensation with a dihydride. This further explains the consistent regularity between the content of BATMS-ODPA segment in polymer mainchain and the properties of the copolymer films.

The well-defined disiloxane-alkyl segments that alternate with an imide ring structure, and the absence of phase separation as well, provide a desired polymer backbone structure for investigating the dielectric properties of this series of poly(imide siloxane) films. The general dielectric properties @ 25 °C, 1 MHz and moisture absorption of the three poly(imide siloxane) films are summarized in Table 3, which shows that increasing $\chi$ leads to smaller $\epsilon'$ and stable dielectric loss $\epsilon''$. Although the copolymer films have the $\epsilon''$ values slightly larger than 0.01, they are favorable for microelectronic application, considering their substantially lowered $\epsilon'$. The reducing water absorption (WA @ 60 °C for 48 h) with increasing disiloxane percentage in the polymer backbone was observed because of the inherent hydrophobicity of disiloxane segments, which is an important compensating advantage to pristine PI that is insufficiently water-repelling because of the hydrophilicity of the polar imide ring.

Here, we chose three copolymer film samples PI-40, PI-60, and PI-75 for detailed exploration of the effects of the disiloxane-alkyl segment on the $\epsilon'$ by dynamic dielectric measurements. As illustrated in Figure 4a, the $\epsilon'$ plots as a function of temperature ($\epsilon' - T$) for three samples at frequencies of 1 MHz and 1 Hz were recorded in the range between −150 and 200 °C. The content of incorporated siloxane-alkyl segments is found to exert a remarkable effect on reducing the dielectric constant of the copolymer films. With $\chi$ increasing from 40 to 60 and 75, the copolymer film presents a consecutive and obvious decrease in $\epsilon'$. The remarkable reduction in $\epsilon'$ would be ascribed to the comprehensive effects of the intrinsic nonpolarizability of disiloxane segments and the altered aggregate state of the copolymer films. The homogeneously inserted disiloxane-alkyl segments reduce the CT chain packing and break the interchain coplanarization by enlarging the chain spacing and increasing the backbone flexibility. With increasing temperature, the $\epsilon'$ gradually increases because of the increasing mobility of the polymer backbone, and when the temperature is approaching $T_g$, the $\epsilon'$ increases remarkably. Because higher disiloxane-alkyl content leads to lower $T_g$ of the copolymer films, there appears an overlap zone in the temperature range in the proximity of $T_g$ in the dielectric spectra for the three samples. $\epsilon'$ variation with frequency ($\epsilon' - F$) curves at 25 °C is displayed in the inset of Figure 4a, which shows that the $\epsilon'$ value of all the samples decreases with increasing frequency correspondingly. The frequency dependency of $\epsilon'$ can be accounted for by the dipole orientation movement of the copolymer that would gradually become outpaced and then stagnant when the electric field alternation keeps escalating toward higher frequency. The frequency effect is also seen in the $\epsilon' - T$ curves at 1 Hz and 1 MHz. It is found that at starting measurement temperature (−150 °C), the $\epsilon'$ at 1 Hz and 1 MHz remains basically the same value, and when the temperature increases, the difference

Figure 4. Dynamic dielectric measurement results of the poly(imide siloxane) films of the first heating (a) $\epsilon'$ of PI-40, PI-60, and PI-75 as a function of temperature under 1 Hz and 1 MHz. Inset: $\epsilon'$ of three films as a function of frequency under 25 °C. (b) 3-D spectrum of dielectric constant variation with frequency and temperature for PI-40. (c) 3-D spectrum of dielectric constant variation with frequency and temperature for PI-60. (d) 3-D spectrum of dielectric constant variation with frequency and temperature for PI-75.
between the ε′ at 1 Hz and 1 MHz becomes more appreciable, with the former larger than the latter. The relaxation at low temperature is more clearly seen in the ε′−T curves at 1 Hz than at 1 MHz, and these relaxations present receding tendency with increasing χ.

The dielectric relaxations also reflect the intrinsic structure of the polymers. The 3-dimensional (3-D) spectra of ε′ variation with temperature and frequency for PI-40, PI-60, and PI-75 are displayed in Figure 4b−d, respectively, and the relaxations have been assigned in the diagrams. The γ relaxation of PI films occurring at low temperature is generally believed to correlate with the phenyl and imide ring motions strongly influenced by water absorption content, and such relaxation was reported to recede when the samples had been completely dried before measurement in dry nitrogen. By comparing the slope of γ relaxation of PI-40 with those of PI-60 and PI-75 for the first heating, with increasing χ, the increasing presence of hydrophobic disiloxane segments in the polymer backbone is explicitly observed to lead to the depression of γ relaxation at about −100 °C. The γ relaxation for PI-60 is weaker than that of PI-40, and particularly for PI-75, the γ relaxation totally disappeared because of its lowest water absorption with highest disiloxane content among the three samples. Our observations in this work support the suggestion that the γ relaxations existing in the PI’s dielectric spectra are associated with the water absorption and could be inhibited by reducing the presence of water in PI films. Furthermore, it confirms that the disiloxane is homogeneously distributed in the copolymer backbone without the presence of siloxane phase separation. Otherwise, the separated siloxane phase relaxation usually at about −100 °C, which is located in the range of γ relaxation, would become more clear, other than receding with increasing content of disiloxane content in the copolymer from PI-40 to PI-75.

At a higher temperature range than γ relaxation, there are two secondary relaxations correlated with local movement, weak β1 and β2 relaxation. This transition is generally associated with local bond rotations along the polymer backbone. These motions are considered to be primarily a function of the PI structure. Some studies reported that β relaxations are related with rotation of phenylene and imide groups around the linkages as −O− and −CH−. The magnitude of the activation energy of a secondary relaxation depends on rotational potential energy barriers, internal frictions, and the volume and environment of the moving repeat units. The stronger the energy barrier and internal friction are, the more appreciable the β relaxations are. With an increase in χ, the interchain CT interaction is reduced because of the increase of nonpolar and flexible disiloxane-alkyl segments in the polymer backbone, which leads to increased rotation ease, decreased internal friction, and enlarged free volume of the repeat units along the polymer chain. As a result, β1 and β2 relaxations present receding tendency with increasing disiloxane content in PI films. Similar to the case of γ relaxation, the β1 and β2 relaxations of PI-60 are weaker than those of PI-40. PI-75 shows an absence of such β1 and β2 relaxations.

α-Transition at higher temperature than β1 and β2 relaxation is the main transition that arises from polymer mainchain movement. The mainchain motion determines the dielectric behavior of α-transition. With more disiloxane-alkyl incorporation, the copolymer mainchain is more flexible and the dipole orientations along the mainchain are more responsive in the alternating electric field. Therefore, it is observed in the dielectric spectra that PI-75 has the most responsive α-transition, manifested by the highest maximum ε′ at the same measurement temperature upper limit of 200 °C for all the three samples. For the same reason, the maximum ε′ of PI-60 is larger than that of PI-40.

The above detailed analyses of the dielectric relaxations reveal that with the incorporation of more disiloxane segments, the poly(imide siloxane) backbone presents greater depression in relaxation at low temperature, including γ relaxation at about −100 °C and β1 and β2 relaxations at about ambient temperature. Combining these results with the unanimous sharp peaks in DMA tan δ−T curves (Figure 2a) for all the measured poly(imide siloxane) films, it can be assumed that the siloxane phase separation at about −100 °C (typically characterized by relaxation spectra43) commonly observed with oligosiloxane segments could be fully eliminated by adopting the minimized disiloxane segment in this work.

Free-volume analysis has been employed in studying the effect of a bulky group such as triptycene in enabling microporous PIs for gas separation and low dielectric application. It was reported that the hierarchical triptycene structure enlarges the free volume of the polymer chain by the contribution of its steric bulkiness. Fractional free volume (FFV) is an established parameter to evaluate whether a specific group or substructure contributes to enlarge the free volume of the polymer. Here, we calculated the van der Waals volume and FFV of film samples with different χ based on group contribution Bondi method, as presented in Table 1.
3 (see the Supporting Information for details). Compared with wholly aromatic ODPA-ODA moiety, ODPA-BATMS is more flexible because of the lubricating effect of noodle-like disiloxane segments. Therefore, it can be seen that increasing \( \chi \) leads to larger van der Waals volume \( (V_\omega) \) of the resulting PI. As \( V_\omega \) increases, the polarizable group per volume decreases correspondingly, consistent with decreasing \( \varepsilon' \). Furthermore, the FFV presents an increase with an increase in \( \chi \), indicating that disiloxane segment insertion is efficient in reducing interchain interaction, consistent with improved solubility and higher transparency.

3. CONCLUSIONS

In summary, an unoligomerized, symmetric disiloxane-containing diamine with well-defined structure, BATMS, was synthesized to copolymerize with ODA toward ODPA to prepare poly(amide siloxane) films. As shown in Figure 5, the properties of copolymer films show a perfectly regular variation with the content of BATMS, inferring the homogeneous insertion of disiloxane segments into the copolymer backbone. The incorporated flexible and high-temperature-resistant disiloxane segments decrease the \( T_g \) of copolymer films but offer robust thermostability with high values of \( T_g \) and \( T_{10} \) even when the molar percentage of BATMS is as high as 90.

4. EXPERIMENTAL SECTION

4.1. Materials. Commercially available \( N,N' \)-dimethylacetamide (DMAc) was purified by vacuum distillation over \( P_2O_5 \) and stored over 4 Å molecular series prior to use, and tetrahydrofuran was freshly distilled in nitrogen over sodium. ODA and 4,4′-oxydiphthalic dianhydride (ODPA) were purified by sublimation before use. Other reagents and solvents were obtained commercially and used as received.

4.2. Preparation of Polymer Films. The diamine mixture of ODA and BATMS with a certain molar percentage was dissolved in dry DMAc under stirring, and then equimolar dianhydride ODPA in dry DMAc was dropped into the mixture with gradually increasing stirring intensity. The solid content of the polycondensation solution was 12–15 wt %. For the cases of high molar percentage of BATMS such as 60, 75, and 90, the nylon salt precipitation was observed; on increasing the reaction temperature to 40–70 °C depending on the molar percentage of BATMS, the nylon salt could be dissolved and reverted toward the polycondensation. The fully soluble PAAs were rapidly cast onto the preheated glass plate and then subjected to thermal imidization following the process of 4 h @ 100 °C, 2 h @ 150 °C, 2 h @ 200 °C, and 2 h @ 250 °C. The poly(amide siloxane) films were stripped from the glass plates after being soaked in boiled water and dried for measurements.

4.3. Characterization. \(^1\)H NMR spectra were recorded on a Bruker DRX 400 spectrometer with DMSO-d_6 as the solvent and tetramethylsilane as the internal reference. An Instron universal tester model 1122 (GB/T1040.1-2006) was used to study the stress–strain behavior of the PI film samples, and the measurements were performed at room temperature with a stretching rate of 2.5 mm/min, and the data were the average value of five experiments except for the maximum and minimum value. Thermogravimetric analysis (TGA) measurements were conducted with a PerkinElmer TGA-2 in flowing nitrogen at a heating rate of 10 °C/min. DMA measurement was conducted with DMA Q800V20.22 Build 41 using tensile mode at a frequency of 1 Hz and heating rate of 3 °C/min.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03302.

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DEDICATION

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