Reduction of Thermal Expansion and Improvement of Elongation Based on Microphase-Separated Structure of Siloxane-Containing Block Copolymerized Polyimides

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Introduction

Polyimide (PI) has excellent heat resistance, mechanical strength, and electrical insulation properties, and is used as an insulating film for electronic device substrates. With the recent development of flexible devices, PI is also required to have higher toughness and ductility. Therefore, copolymerization of PI with polydimethylsiloxane (PDMS) has been used to improve the toughness of PI. However, copolymerization with PDMS, which has a particularly large thermal expansion coefficient among polymers, leads to a decrease in thermal dimensional stability and causes warping and cracking of the substrate due to the mismatch in thermal expansion coefficient with the substrate. On the other hand, we recently found that a multi-block copolymer of PMDA-TFDB, a fluorinated fully aromatic PI, and PDMS (MBC-PI) (**Fig. 1**) exhibits a smaller coefficient of volumetric thermal expansion (CVE) than the crystal lattice of PMDA-TFDB alone (homo-PI). In this study, we compared the CVE and phase-separated structure of MBC-PI under different heat treatment conditions to elucidate the mechanism of low CVE.

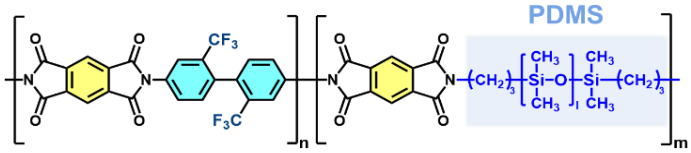

Fig. 1 Chemical structure of MBC-PI.

Experiment

A PAA solution of the MBC-PI precursor (molecular weight of PDMS: 4380 g mol^{-1}, volume fraction of PDMS: 11 vol%) was blade-coated onto a glass substrate, dried at 70°C, and heated to 400°C to form a PI film. Drying and heating process were performed under a nitrogen atmosphere. The PI film formation was performed by adjusting the heating rate in the range of 2-24°C min^{-1}. Here, samples prepared at a heating rate of 2 and 24°C min^{-1} are referred to as Slow-MBC and Fast-MBC, respectively. Slow-MBC films was cut into strips and subjected to tensile testing. Also, cross sections of MBC-PI film were observed by transmission electron microscopy (TEM) without staining. The in-plane and out-of-plane linear thermal expansion coefficients $CTE_{//}$ and $CTE_{\perp}$ of each PI film were evaluated by TMA and near-infrared interference spectroscopy, respectively, and CVE was calculated with the equation $CVE = 2\,CTE_{//} + CTE_{\perp}$. Variable temperature small-angle X-ray scattering (VT-SAXS) measurements were also performed, and the SAXS intensity curves were transformed into a one-dimensional autocorrelation

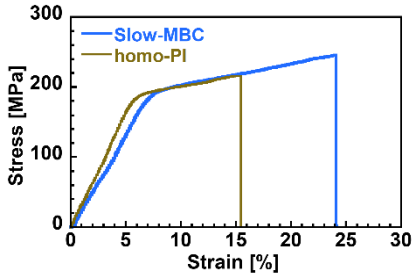

Fig. 2 Mechanical property of homo-PI and Slow-MBC.

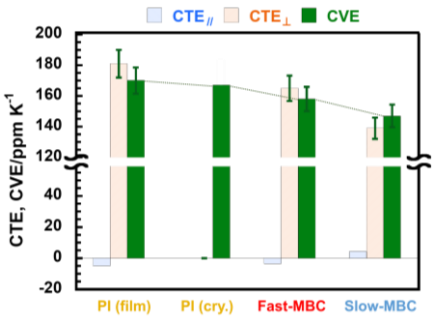

Fig. 3 Thermal deformations of film and crystalline homo-PI, Fast-MBC, and Slow-MBC.

function to analyze the size change of the segregated structures as heating.

Results and Discussion

Compared with homo-PI, MBC-PI exhibited increased ductility and tensile strength while Young's modulus was almost the same (**Fig. 2**), confirming the improved flexibility and mechanical properties due to copolymerization with PDMS. The CVEs of Slow-MBC and Fast-MBC were 147 ± 5 ppm K^{-1} for Slow-MBC and 158 ± 5 ppm K^{-1} for Fast-MBC, both significantly lower than the CVE of homo-PI film (170 ppm)[1] and crystal lattice (168 ppm)[2] (**Fig. 3**). The TEM image shown in **Fig.4** shows the formation of a phase-separated structure with one-dimensional repeats in the in-plane direction. The VT-SAXS measurements showed a significant decrease in the invariant Q with heating (**Fig.5(a)**), indicating that the electron density difference between the PI and PDMS phases decreases with heating. One-dimensional autocorrelation function curves were used to evaluate the long period D and the domain size L of the PDMS phase. For this analysis, we used the one-dimensional phase-separated structure model shown in **Fig.5(b)**. As temperature rises, the size of the PDMS phase, which should have expanded greatly, shrank, and the length of the long period expanded (**Fig. 5 (c)**). Since $D/L > 0.3$ is much larger than 11% of the composition ratio, we proposed a model in which the unblocked PI occupies 60% of the membrane as a sea region and the phase-separated island region between PI and PDMS occupies the remaining 40% (**Fig. 6 (a)**). As the temperature increases, the PDMS phase shrinks in the in-plane direction and expands in the out-of-plane direction, and the long period D increases due to the increased orientation of the PI chains in the island region. Focusing on the sea-island interface, the PI chains in the sea region are compatible with the PDMS chains in the island region to avoid mismatch in the interfacial area (**Fig. 6 (b)(c)**). The above mechanism suppresses the out-of-plane linear expansion, and this is consistent with the decrease in Q with increasing temperature. The above discussion reveals the mechanism of uniquely low $CTE_{\perp}$ and CVE of MBC-PI.

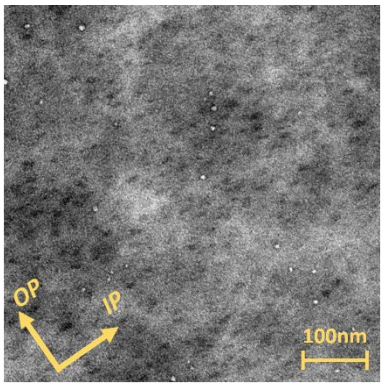

Fig. 4 TEM image in cross section of Slow-MBC film observed without staining. The black area and the bright area correspond to PDMS phase and PI matrix phase.

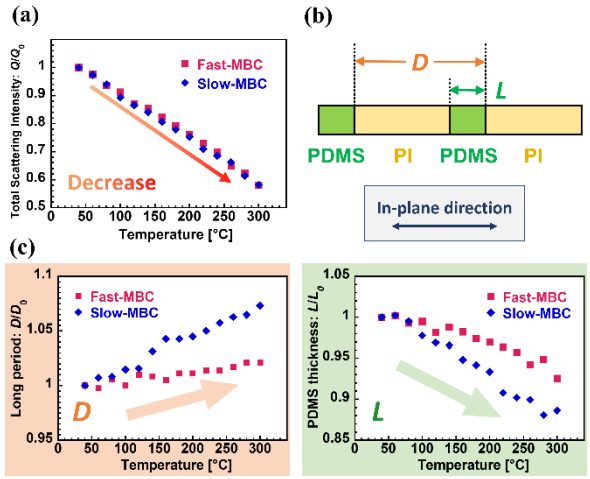

Fig. 5 (a) Temperature dependence of Q. (b) One-dimensional phase-separated structure model in MBC-PI. (c) Thermal deformations of normalized L and D.

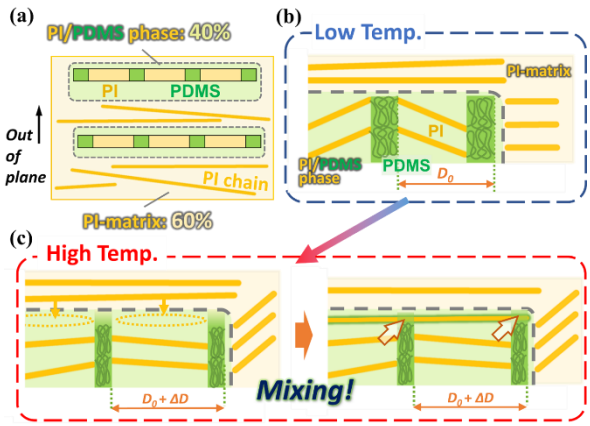

Fig. 6 Schematic models of (a) phase separation and (b)(c) temperature-induce phase mixing mechanism model in MBC-PI .

References

[1] S. Ando, K. Sekiguchi et al., *Macromol. Chem. Phys.* **2018**, 219, 1700354. [2] R. Ishige, S. Ando et al. *Macromolecules* **2017**, 50, 2112-2123.