The Flexibility and Unusual Low Thermal Expansion Exhibited by Block Copolymers of Polyimide and PDMS and the Observation of Their Microdomain Structural Changes Using Synchrotron Radiation X-rays

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Introduction: Block copolymers of polyimide (PI) and polydimethylsiloxane (PDMS), PI/PDMS, have great potential for applications of flexible devices due to the ductility. Despite the large thermal expansion of PDMS, block copolymer films of polyimide: PMDA-TFDB and PDMS (PI/PDMS-1, **Fig. 1**) show unexpectedly lower coefficient of volumetric thermal expansion (CVE) than PMDA-TFDB homopolymer (Homo-PI). In this study, investigated were the mechanism of the low CVE of PI/PDMSs by analyzing the structural changes during heating/cooling by in-situ small-angle X-ray scattering (SAXS) method.

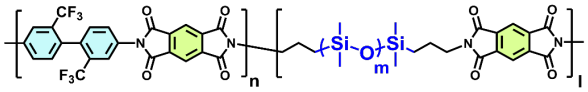

Fig. 1 Chemical structure of PI/PDMS-1.

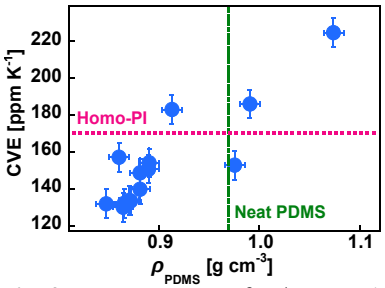

Fig. 2 ρ_{PDMS} vs. CVE of PI/PDMS-1.

Results and Discussion: Synthetic scheme of PI/PDMS-1 and methods measuring CVE were previously reported[1]. PI/PDMS-1 with the same PDMS fraction showed decreasing CVE with increasing molecular weight of the PDMS and the CVE was minimized at a specific fraction. The weight density of the PDMS in PI/PDMS-1 (ρ_{PDMS}) was significantly lower than that of neat PDMS. Furthermore, the ρ_{PDMS} and CVE in each PI/PDMS-1 show positive correlation, which is unusual for normal materials (**Fig. 2**). TEM observation of unstained PI/PDMS-1 films clarified segregated nanodomains of the PDMS in the PI matrix. In-situ SAXS analyses of the PI/PDMS-1 and their precursor films revealed that the volume of the PDMS nanodomain in PI/PDMS-1 decreases (increases) with heating (cooling). The PDMS nanodomain swollen with the solvent formed in the film precursors and the shape of the swollen nanodomain was memorized during drying and thermal imidization. The low-density PDMS nanodomain possibly causes to the negative thermal expansion leading to reduced CVE of PI/PDMS-1.

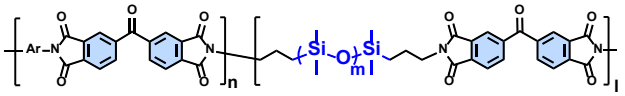

Fig. 3 Chemical structure of PI/PDMS-2.

Furthermore, novel block copolyimides, PI/PDMS-2 (**Fig. 3**), containing benzophenone moiety was synthesized and the films exhibited lower CVE similar to the PI/PDMS-1 (**Fig. 4**), although the PI matrix had isotropic orientation. The benzophenone moiety is crosslinkable by UV irradiation and expected to enhance the shape-memory effect. The effect of crosslinking on the CVE will be discussed in the presentation.

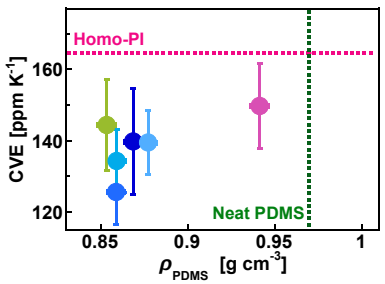

Fig. 4 ρ_{PDMS} vs. CVE of PI/PDMS-2.

References: [1] Momoze et al. *Fiber preprints, Japan* **2024**, 79, 1, 1A01.

Keywords: Polyimide, PDMS, Block Copolymer, volumetric Thermal Expansion, SAXS