Correlation among ordered Structure, degree of crosslinking and thermal expansion of thermally cross-linkable polyimide

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I. Introduction

In recent years, reducing the coefficient of volumetric thermal expansion (CVE) of polyimides (PI) used as insulating films is demanded due to development of electronic devices. Ordered structure and crosslinking are believed effective to reduce CVE. Poly(amic ester)s (PAEs) with rigid main chains and bulky substituents form a smectic liquid crystal (Sm LC) in the solution and can be converted in PI keeping the orientation order[2]. In this study, thermally crosslinkable PAE exhibiting Sm LC phase were synthesized for the efficient thermal crosslinking reaction (**Fig. 1**), and we discussed the correlation among the ordered structure of the precursor and the degree of crosslinking reaction and thermal expansion behavior.

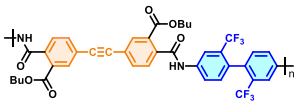

Fig. 1 Chemical structure of PAE.

II. Experimental

PAEs was synthesized as previously reported[2]. PAEs films were prepared on Si substrates and imidized by annealing at 270°C for 1.5 hours under N_2 gas flow. The degree of crosslinking (χ_c) of PI was evaluated from the far infrared spectrum. The coefficient of linear thermal expansions of in-plane and out of plane directions ($CTE_{//}$, $CTE_{\perp}$) of the PI films were evaluated separately.

III. Result & Discussion

In the grazing-incidence x-ray scattering (GI-WAXS) image (**Fig. 2** (a)), a sharp peak corresponding to 1/4 of the repeat unit length of the PI was observed in the equatorial direction, indicating that the layered structure of PI film prepared from PAE film exhibitting liquid crystal phase (LC PI) was maintained after imidization. **Fig. 2** (b) shows a GI-WAXS image of LC PI after cross-linking by thermal curing at 400°C (LC PI-C). After crosslinking, the diffuse scattering peaks concentrated around the meridian with d-spacing corresponding to the distance between adjacent molecular chains are shifted to a small angle, and the [004] diffraction attributed to the layer reflection disappeared. This result indicates that the layer structure of LC PI is disarranged by crosslinking reaction, and the inter-molecular spacing of in-plane oriented chains increases. The value of χ_c of LC PI-C was evaluated at 68 %, while that of the crosslinked PI film (N-LC PI-C) prepared from amorphous PAEs without controlling isomerism was 57%. This is because of the improved efficiency of the cross-linking reaction, due to the confinement effect of DPAs in the smectic layer.

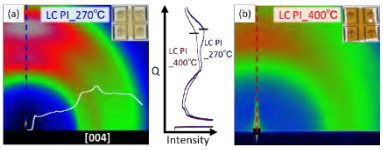

Fig. 2 2D GI-WAXD patterns and photographs of (a)LC PI_270 °C, (b) LC PI_400 °C films on hydrophilic Si wafers.

Table. 1 Thermal exoansion, thermal anisotropy and in-plane orientation of LC PI and Non LC PI before and after crosslinking.

Sample	$\alpha_{//}$	$\alpha_{\perp}$ [ppm/K]	β	η	S
LC PI[a]	39	117	195	0.40	−0.39
LC PI-C[a]	29	164	222	0.61	−0.25
N-LC PI[b]	27	110	164	0.51	−0.16
N-LC PI-C[b]	28	51	127	0.10	−0.09

[a)]LC PI and LC PI-C represent PI films prepared from PAE exhibitting Sm LC and cured at 270 and 400°C respectively.
[b)] N-LC and N-LC PI-C represent PI films prepared from amorphous PAE without Sm LC and cured at 270 and 400°C respectively

Table 1 compares the $CTE_{//}$ ($\alpha_{//}$), $CTE_{\perp}$ ($\alpha_{\perp}$), coefficient of volumetric thermal expansion (CVE, β), CTE anisotropy $\eta = (\alpha_{//} - \alpha_{\perp})/\beta$, and the degree of orientation order (S, smaller S toward −0.5 indicates more in-plane orientation) of N-LC PI and LC PI before and after crosslinking. The CVE of LC PI increased by crosslinking, and the GI-WAXS and the change in S indicate that the crosslinking induces bending in the main chains to decrease the persistence length and S, and increase the interchain distance in the film thickness direction and free volume. Since the CVE of polymers is generally proportional to the compressibility of the free volume [5], in the present LC PI, the effect of the free volume which increases CVE would exceed the effect of the generated covalent bond which suppress CVE. In contrast, N-LC PI shows a lower CVE after cross-linking, similarly to the previously reported amorphous PIs [1] Furthermore, the CVE of LC PI is larger than that of N-LC PI, even though LC PI can be fully ordered. In the amorphous PIs involving N-LC PI, the CTE of each molecular chain is interacted each other to suppress CVE through strong attraction and entanglement between polar groups, resulting in the lower CVE than a simple linear sum of the inherent CTEs of the PI chain. In contrast, LC PIs form the polydomain structure and each domain can thermally expand independently. As the results, CVE becomes a simple linear sum of the CTEs of each domain, which would be larger than that of the amorphous PIs.

References

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