

Synthesis of Chiral Poly(norbornene carboxylic acid ester)s and Their Characteristic Properties in The Thin Film

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Introduction

Addition polymerization of cyclic olefins with functional groups, particularly norbornenes with polar substituents have been of great interest because of the pronounced characteristics of the resulting polymers such as high glass transition, optical transparency, low birefringence etc.[1] Multiple applications are considered such as flexible flat panel display, dielectric material, microfluidic system.[2]

Stereochemical study of substituted norbornenes may provide not only polymers of different properties but also helpful information for the understanding of unusual polymerization of the norbornenes with polar substituents. Therefore, we recently reported that the synthesis of chiral norbornene carboxylic acid methyl ester and its polymerization via addition polymerization gave highly regular structured polynorbornene with substituents and the ¹³C NMR DEPT study was confirmed that C-PNME exhibited the highest tacticity. [3]

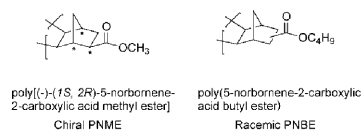


Figure 1. Structures of C-PNME and R-PNBE

We discuss optical birefringence ($\Delta n = n_{\text{in-plane}} - n_{\text{out of plane}}$) change depending on annealing condition in terms of change in amorphous polymer structure and polymer molecular structure dependency. Amorphous structure was investigated by grazing incidence X-ray scattering (GIXS). Thickness and refractive index were measured by ellipsometry.

Experimental

Material and Film Preparation All the polymers were synthesized and supported by Byun et al. [3] Thin films with different thicknesses (20–450 nm) were prepared by spin-coating solutions of the polynorbornenes in chloroform (0.5–5 wt%) onto Si(100) wafers.

Measurement Grazing incidence X-ray scattering (GIXS) measurements were carried out at the 4C2 beam line at the Pohang Light Source (PLS), Korea. In order to investigate the optical anisotropy of poly norbornene thin films, anisotropic measurement was carried out at room temperature in a variable-angle spectroscopic ellipsometer (VASE) system (Model VASE, Woollam, Lincoln, NE, USA). Film thickness was determined by model fitting the VASE spectroscopic data to multiple Fresnel reflectivity of a polymer/SiO₂/Si three-layer using the analysis software built into the VASE.

Results and discussion

Figure 2a clearly shows that intensity of out-of-plane direction for C-PNME dried at 80 °C is relatively more intense than that of in-plane direction, indicating that when C-PNME film formed through spin casting process, the main chains of C-PNME polymer were almost aligned parallel to surface of confined film with a constant dimension. In other words, C-PNME has anisotropic character within the film. It was found, in addition, that molecular chain orientation

within the film of C-PNME annealed at 200 °C is closely similar to that of C-PNME dried at 80 °C, remaining unchanged anisotropic property.

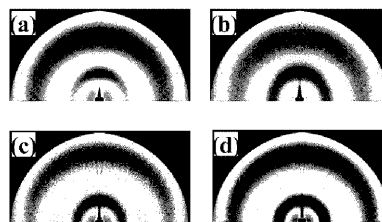


Figure 2. 2D GIXD patterns measured at $\alpha_i = 0.22^\circ$ for poly(norbornene carboxylic acid alkyl ester)s films with thickness of about 450 nm of (a) C-PNME drying at 80 °C. (b) C-PNME annealed at 200 °C. (c) R-PNBE drying at 80 °C. (d) R-PNBE annealed at 200 °C.

R-PNBE has a strong tendency toward random orientation chain conformation in the film after undergoing thermal annealing treatment.[4] This result is thought to be due to improved chain mobility because of alkyl side chain linked to rigid main backbone chain along with racemic mixture composition, as a consequence, leading much more random coil conformation when compared to prior to the thermal annealing treatment Figure 3, shows optical anisotropy of sample at about 450 nm thickness at 630 nm wavelength. It is clear that C-PNME has more optical birefringence than R-PNBE for 80 °C drying, 150 and 200 °C annealing sample. Birefringence of two polymers decreased with increase of annealing temperature. For R-PNBE, birefringence dropped down to zero, but for C-PNME has still small value birefringence after annealing at 200 °C. This result is exactly identical with X-ray data in terms of anisotropy.

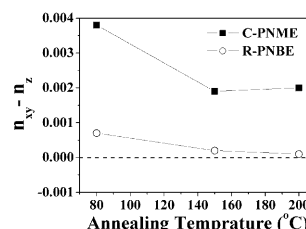


Figure 3. Change of birefringence for (a) C-PNME and (b) R-PNBE films with change in annealing temperature.

Conclusions

In this study, we have investigated annealing effect on amorphous structure of C-PNME and R-PNBE using GIXS and ellipsometry. The structure of C-PNME induced strong anisotropy of X-ray pattern and optical birefringence in confined as-deposited thin film and after annealing anisotropic property was reduced but still remained to large extent. However, R-PNBE showed almost isotropic amorphous halo in X-ray pattern and very little uniaxial birefringence in ellipsometry measurement. It was proved that X-ray pattern and optical birefringence of ellipsometry data have strong correlation with each other. Besides, they reflected polymer conformation structure. C-PNME is expected to have main chains which are parallel to surface of substrate due to intrinsic chain stiffness of C-PNME and residual stress induced during spin casting process. Conversely, R-PNBE is expected to have random coil chain structure in the confined film. This difference is caused from polymer repeat unit structure (i.e. chiral compound and racemic mixture).

References

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