Poly(1,4-cyclohexanediyldimethylene 2,6-naphthalate)의 합성, 열적성질 및 결정구조

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Synthesis, Thermal Property and Crystal Structure of Poly(1,4-cyclohexanediyldimethylene 2,6-naphthalate)

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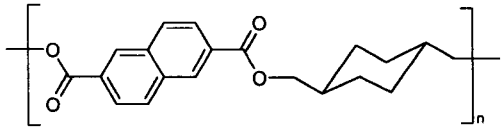
1. Introduction

Engineering thermoplastics with useful properties at elevated temperatures usually contain aromatic units[1] in its chemical structure, especially symmetrical aryl groups such as 1,4-phenylene[2], 4,4'-biphenylene[3,4], and 2,6-naphthalene[1]. Aromatic groups often impart molecular rigidity, which contributes to high glass transition temperature and good thermal stability, and also to high melting point in semicrystalline polymers.

Rigid, thermally stable, but symmetrical aliphatic monomers for polycondensation polymers are rare. One class is 1,4-cyclohexanedimethanol (CHDM). This molecular unit can be incorporated into polyesters. CHDM containing isomer composition of 30/70 *cis/trans* is commercially prepared in high yield. Isolation of the pure isomer is tedious and expensive, and therefore *cis/trans* mixtures have usually been used in industry.



In this study, poly(1,4-cyclohexanediyldimethylene 2,6-naphthalate) (PCHDN) with the chemical structure as shown above was synthesized and its thermal property and crystal structure were investigated using DSC, TGA and X-ray powder diffraction. In the crystal structure analysis, the molecular modeling with the aid of molecular mechanics calculation was used.

2. Experimental Section

PCHDN used in this study was synthesized by reacting 1,4-cyclohexanedimethanol (30/70 *cis/trans*) with dimethyl-2,6-naphthalate using titanium butoxide as a catalyst in the mixed solvents of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene. During the reaction, the solution was heated to reflux at 189 ℃ for 24 h under vigorous stirring. Polymer was coagulated by pouring the mixture into a flask containing acetone. The mixture was stirred for 3 h, vacuum filtered, and washed several times with acetone and methanol. The polymer was dried in a vacuum oven at 100 ℃ for several days.

Melting and crystallization points of PCHDN were measured with a Perkin Elmer DSC-7 equipped with intercooler system. The heating and cooling rates were 20 ℃/min. Thermal decomposition behavior of PCHDN was investigated using a themogravimetric analyzer (TA instruments, TGA 2050) under nitrogen flow at 10 ℃/min rate.

The X-ray powder diffractograms of PCHDN powders annealed at various temperatures were obtained using a M18XHF diffractometer (MAC Science Co.) with Ni-filtered Cu-K_α radiation at a scanning rate of 2 °/min.

The crystal structure modeling with the aid of molecular mechanics calculation was carried out using Cerius2 (version 4.0, Molecular Simulation Inc.). The total potential energy of a molecular chain consists of the contribution from the intramolecular and intermolecular interactions. The COMPASS force field was used to calculate the potential energy of crystal structure.

3. Results & Discussion

Figure 1 shows the DSC thermograms of PCHDN on heating and subsequent cooling. The melting and crystallization temperatures of PCHDN is 319 ℃ and 272 ℃, respectively. The TGA thermogram of PCHDN is represented in Figure 2, indicating that the thermal decomposition temperature of PCHDN is approximately 400 ℃.

The X-ray powder diffraction patterns of the PCHDN annealed at various temperatures are shown in Figure 3. As the annealing temperature increase, the diffraction patterns remain unchanged without appearance and disappearance of diffraction peaks. Therefore, the crystal transformation induced by temperature is not expected in PCHDN polymer. The schematic representation and numbering of torsion angles of the PCHDN backbone unit are shown in Figure 4. The energy contour maps are drawn by the conformational energy calculation of the PCHDN

backbone. As shown in Figure 5, it seems reasonable to assume that the conformation of PCHDN backbone is nearly all-*trans*. Indexing of diffraction peaks in the X-ray powder diffractograms yields a triclinic unit cell with a dimension of a=6.24Å, b=6.58Å, c=16.44Å, α=88.06°, β=44.66°, γ=106.08° and the calculated crystal density of 1.319 g/cm^3 indicates that there is only one chain per unit cell. Based on this triclinic unit cell, the crystal structure of PCHDN using computer modeling are generated and then energy-minimized. When the experimentally observed X-ray powder diffractogram is compared with the simulated one for the final crystal structure as shown in Figure 6, It reveals that the final crystal structure obtained using computer modeling and potential energy minimization satisfies well the experimentally observed X-ray powder diffractogram.

3. References

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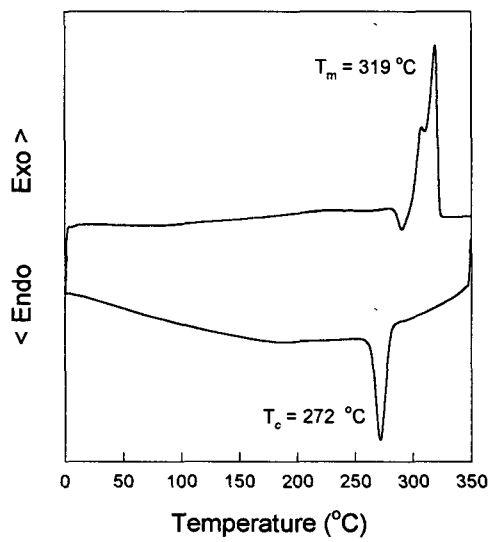


Figure 1. Melting and crystallization thermograms of PCHDN.

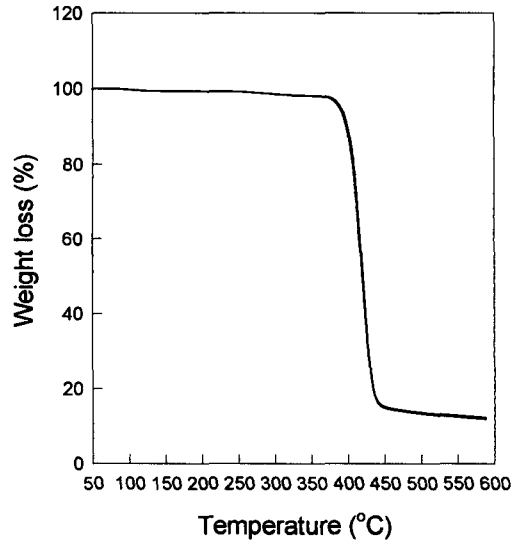


Figure 2. TGA thermogram of PCHDN.

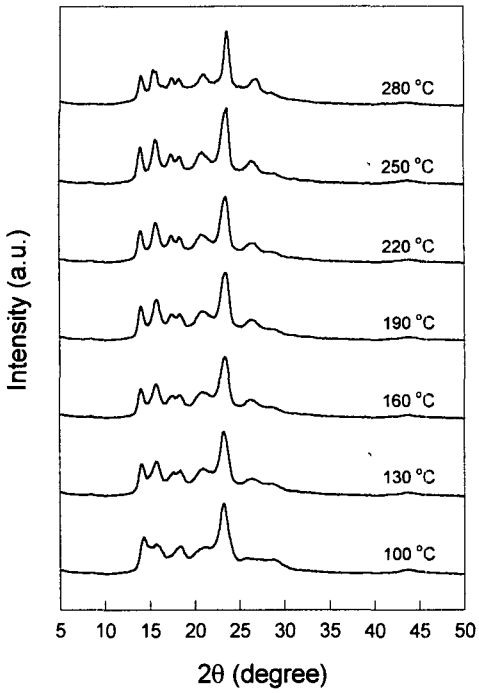


Figure 3. X-ray powder diagrams of PCHDN annealed at various temperatures.

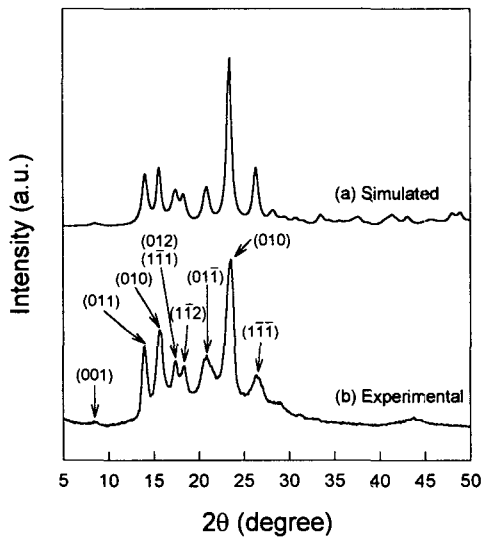


Figure 6. Comparison of the experimental X-ray powder diffractogram with the simulated one.

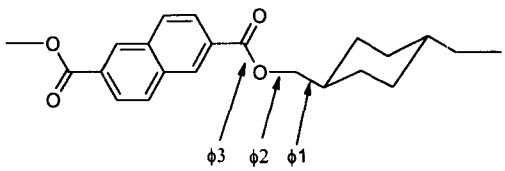
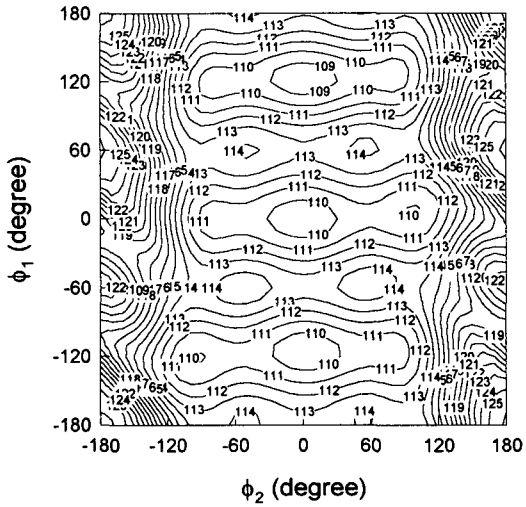


Figure 4. Schematic representation of PCHDN backbone.



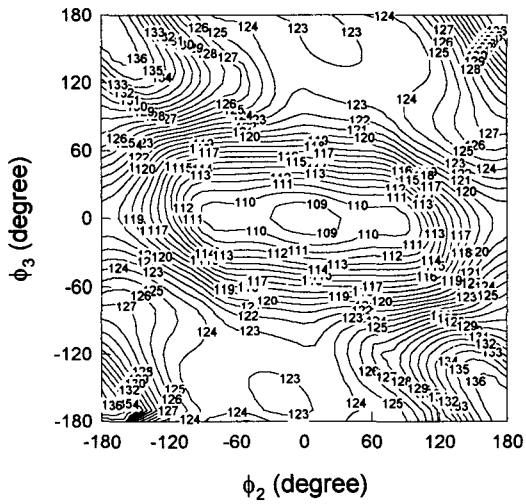


Figure 5. Conformational energy contour maps calculated for each pair of dihedral angles of PCHDN bacbone.