삼차원적으로 배향한 Poly(α, α, α′, α′-tetrafluoro-p-xylylene) 필름의 구조 연구

박수영, S. Chvalun*, John Blackwell*
경북대학교, 고분자공학과
*Case Western Reserve University, Department of Macromolecular Science

A Three-Dimensionally Oriented Texture for Poly(α, α, α′, α′-tetrafluoro-p-xylylene)

Soo-Young Park, S. Chvalun* and John Blackwell*
Kyungpook National University, Department of Polymer Science
*Case Western Reserve University, Department of Macromolecular Science

1. Introduction

Poly(p-xylylene) (PPX) is most easily prepared by a vapor deposition polymerization (VDP) of [2,2]paracychophane, as described by Gorham.[1] Poly(tetrafluoro-*p*-xylylene) (F-PPX) is of interest in view of its potential applications as an interlayer dielectric material in high-speed integrated circuits, since it has an extremely low dielectric constant (<2.35).[2] Two polymorphic crystal structures, designated as α- and β-PPX exist in PPX. X-ray and electron diffraction studies by Iwamoto et al. showed that α-PPX is monoclinic with space group C2/m; the unit cell has dimensions a=5.92Å, b=10.64Å, c=6.55Å, and β=134.7° and contains two monomer units.[3] Isoda et al. reported that the β form has a large trigonal unit cell containing 16 monomers, with dimensions a=b=20.52Å, c=6.55Å, γ=120° , and space group P3.[4] In this paper, we will address the oriented texture of drawn films of F-PPX produced by the VDP process. The X-ray intensity data for these specimens have also been used to analyze the crystal structure.

2. Experiments

F-PPX was prepared from its paracyclophane monomer by the VDP process.[5-6] The resultant films (10-12 ㎛ thick) were drawn X10 in an oven at 350℃ and annealed for 30 min at 500℃. Wide angle diffraction patterns were recorded on film using Ni-filtered Cu K_α radiation, with the beam (a) parallel to the draw direction (designated the OD pattern), (b) normal to the film surface (the ND pattern), (c) perpendicular to both drawing and normal directions (the TD pattern). Molecular mechanics modeling was performed using SYBYL software package (Tripos Inc.) and the crystal structure amplitude for the proposed structure were calculated using Cerius software.

3. Results and Discussion

The ND and TD wide-angel X-ray patterns of a drawn annealed film show distinct layer lines at orders of 6.57Å pointing to high axial orientation. The data in the ND and TD pattern contain many reflections with the same d spacings but with very different relative intensities. These differences indicate that the planar texture of the as-deposited film persists after drawing and annealing, i.e., the drawn film has double orientation. This double orientation was confirmed from the OD pattern where we observe a number of arced reflections. The degree of orientation both in axial and planar orientation is so good that the drawn F-PPX film is similar to that of a single crystal. From ND, TD and OD patterns, the triclinic unit cell parameters of F-PPX were determined with dimensions of a=5.36Å, b=5.92Å, c=6.57Å α=97.0°, β=63.1°, and γ=73.1°. If the unit cell contains one monomer unit, the density of the crystalline structure is 1.71 g/cm^3, which compares very favorably with the observed density of 1.69 g/cm^3 for a highly crystalline polymer. Inspection of the unit cell shows that the chains pack with the phenyl rings approximately perpendicular to the ac plane. This model is energetically stable and shows the excellent agreement between observed and calculated

intensities. Interestingly, we found a major difference between PPX and F-PPX polymer in terms of the orientation of the molecules during deposition. The planes of the phenyl groups in F-PPX are inclined at 23° from the film surface although those in PPX are perpendicular to the surface.

3. Conclusions

The F-PPX film made by the VDP process has a well-developed planar texture. This planar texture is maintained during drawing at 350 C, when a high degree of chain orientation is developed. The resultant film has a doubly oriented, single-crystal texture, with the *100* plane parallel to the planes of the film and the chains axis parallel to the draw direction. The three dimensional wide angle X-ray data show that the unit cell of F-PPX is triclinic, with dimensions of a=5.36Å, b=5.92Å, c=6.57Å α=97.0°, β=63.1°, and γ=73.1° and contains one monomer units. Molecular mechanics modelings predicts a minimum energy conformation in which the trans-planar *"zigzag"* $-CF_2-CF_2-$ unit is inclined perpendicular to the phenylene groups. Packing such a chain in proposed lattice leads to excellent agreement between the observed and calculated structure amplitude (R=0.18). The *ab* projection of the crystal structure is very similar to that observed for the α-form of PPX. However, the structure of F-PPX is more dilated in the a direction as compared to α-PPX, due primarily to the presence of the large fluorine atoms. The planes of phenyl rings of F-PPX are perpendicular to the *ac* plane and tilted 23 degree out of the *100* plane. In this regard the texture is different from that reported for PPX, where the phenylene units are normal to the *100* plane.

5. References

1. W.F. Gorham, *J. Polym. Sci., Part A-1*, **4**(12), 3027 (1966)
2. J.A. Moore, C.I. Lang, T.M. Lu, G-R. Yang, *Polym. Mater. Sci. Eng.* **72**, 437 (1995)

3. R. Iwamoto, B. Wunderlich, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 2403 (1973)
4. S. Isoda, M. Tsuji, M. Ohara, *Polymer,* **24**, 1155 (1983)
5. K.A. Milyan, A.V. Pebalk, E.I. Mishina, I.E. Kardash, *Polym. Sci., Ser. A,* **34**(9), 761 (1992)
6. E.V. Grechkina, V.A. Sochilin, A.V. Pebalk, I.E. Kardash, *Zh. Org. Khim. (Russian)*, **29**(10), 1999 (1993)