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Structure and Re-orientation in the First Stage for Polyamide/Iodine Complex.

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Introduction

Polyamide-6 (PA-6, Nylon$^{@}$-6) is a popular hydrophilic polymer and it easily realizes some states with relatively higher order or orientation.[1] However, while numerous, effective works have been reported about the polymer, unsolved and interesting problems have been also raised about the structures of the ordered states, which are not always equal to "crystallites" in the polymeric system. For investigation of the structure and functionality for this polymer, we have to consider various environmental parameters, comprehensively. And, considering ordered structures of PA-6, not only to parameters for molecular dynamics attributed to hydrogenbonding, attention has to be paid to macroscopic parameters, too.

As one of characteristic behaviors of the ordered structures in PA-6, we have been investigating structures and functionality of "iodine-doped PA-6 (PA-6/polyiodide complex)". Even though "iodine doping" is achieved easily and quickly with an I_2-KI aqueous solution at room temperature, we can see various structures and response: rapid diffusion and coordination by dopant ions (polyiodide or cation) into PA-6, some stages of intercalation, modified orientation, enhanced ionic conduction, etc.[2,3] Due to the previous results suggested with a synchrotron radiation, diffusion of the dopants advances or "modified orientation" is observed within very short time less than one second.[4] Then, we expected more accurate and rapid *in-situ* investigation for the complex on the first stage of doping with an 1-dim PSPC counter.

Experiments

Sample preparation : Doubly-oriented PA-6 film:

PA-6 used was a commercial polymer (M_W=4.2x10^5) and a melt-pressed film was quenched in ice water. The film was drawn three times to be a "doubly-oriented" film. (χ~ 25%) This film (0.15 mm in thickness) was cut to be a strip which could be set in a quartz capillary of 2.0 mm in diameter.

Pouring system : housing, dispenser pump, solution:

The quartz capillary tube was also a guide tube for the I_2-KI aqueous solution. The tube was connected with Teflon$^{@}$ tubes to introduce the solution flow with a dispenser pump and its controller. All parts and a solution reservoir which might contaminate surrounding instruments with the damaging solution or I_2 vapor were perfectly enclosed in a acrylic housing while the pump was not enclosed with in the housing.(Fig.1) Remote-controlled operation of the pump introduced the 0.4N I_2-KI solution into the capillary and the flow was synchronized to start of time-sliced measurement.

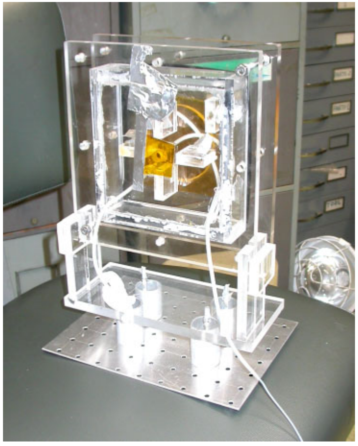

Fig.1. Housing for in-situ observation without damage by corrosive solution or volatile I_2 gas.

Beam, detector, layout:

As an incident, a monochromatized beam (λ = 0.15 nm) on BL-15A was used and diffraction profile was measured with 1-dim PSPC.[5] Significant change of diffraction for the doubly oriented PA-6 on doping had been observed along a layer line normal to the meridian, which was shifted with Q (=4πsinθ/λ) ~0.52 nm^{-1} from the equator.[6] Then, the detector was set shifted from the incident to catch diffraction along the layer line: shifted for 2θ = 1.25x10^{-2} rad. Exposure time was 10 sec.

Results

Unfortunately, we could not detect significant profiles nor drastic change of diffraction during this adopted machine time. The reasons for unsuccess were assumed; (1) too large absorption by the I_2-KI solution to detect diffraction, (2) balance of sensitivity of the detector and an interval of the time-sliced system, (3) fluctuation of the sample film by introduction of the solution. Following experiments may be achieved with more dilute solution or long interval time.

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References

[1] H. Arimoto,et.al., J. Polym. Sci., A3, 317 (1965).
[2] A. Kawaguchi. Polymer, 33, 3981(1992).
[3] A. Kawaguchi., Sens. Act. B. 73, 174 (2001).
[4] A. Kawaguchi, et.al., SPring-8 User Exp. Rep. 5, 354 (2000).
[5]http://pfwww.kek.jp/users_info/station_spec/bl15/bl15a.html
[6] A.Kawaguchi,et.al., Polym.Prep.Jpn., 49, 2414 (2000).

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