

## Initial stage of composite structure and ionic conduction in hydrophilic polymer

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**Introduction**

Even below melting point, polymeric material can be modified elastically in  $T > T_g$  and chain direction is also oriented by external strain. And such modification of orientation is induced by diffusion of ion in some cases of hydrophilic polymers. We have investigated rapid diffusion of "polyiodide ion",  $I_n^-$  ( $n = 3, 5, \dots$ ), into polyamide-6 (PA6, Nylon<sup>TM</sup>6) at room temperature; diffusion into polymer advance by support of coordination of ion with affinity with polymer chain and they introduce new oriented structure or modification of polymeric system.[1] It suggests dynamism for both coordination and diffusion in polymeric materials which is permitted even for modification of chain direction.

Furthermore, descent of  $T_g$  induced by coordination with polyiodide ions also makes it easy for additional ion to diffuse into the polymeric structure; we call such treatment "second doping" against previous iodine doping which has realized enhanced mobility in polymer. And, for example, if the additional ion can be fixed through precipitation, innovative preparation of "hybrid composite" can be achieved.[2]

Here, we conducted observation of diffusion and precipitation of ion into hydrophilic polymer on "second doping" with time-sliced diffraction.

**Experiments**

As starting non-doped PA6, commercially produced film ("Rayfan", TORAY Film, Co.Ltd., 0.1mm in thickness) was used. To minimize adsorbed water, drawn sample film was annealed at 200°C in vacuum for more than 48hrs. On (1st) iodine doping,  $I_2$ -KI(aq) was used and the iodine-doped sample was aged in silica-gel for more than 3 months.

We produced a vessel made of acrylic resin with windows of Kapton<sup>TM</sup> films which achieved "in situ" observation for diffraction on inflow of solution.(Fig.1) Filmly sample was fixed by a holder (for edge-view and for thru-view) and a dispenser pump remotely controlled could suck up solution to immerse the

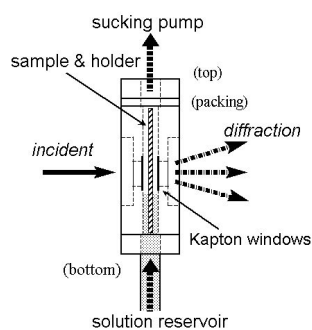


Fig.1: section scheme of acrylic vessel.

samples in. An incident and diffraction could penetrate through the Kapton films. And,  $AgNO_3$ (aq) (0.5M) was used as a solution for "second doping".

Detecting facilities were utilized at BL-15A ( $\lambda = 1.5\text{\AA}$ ): a 2-dim. CCD detector (C4880, Hamamatsu Photonics) supported by an image intensifier (9 in.).

**Results**

On "(1st) iodine doping", diffusion of polyiodide ion into PA6 film is very rapid; coordinated structure or modified orientation advance in time of less than one second even though it is a meta-stable structure observed just after iodine doping or can be modified by following "water rinsing".[3]

On the other hand, though precipitation of silver iodide (AgI) is not so rapid as diffusion of iodine on "1st doping", it was achieved a few decade minutes. (Fig.2) On this precipitation process with "2nd doping", ordering along drawn direction was kept while structure between polymer chains was lost earlier. These results suggest diversity of coordination in polymer.

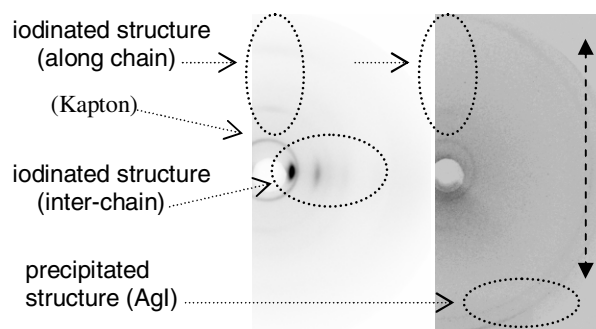


Fig.2: diffraction before injection of  $AgNO_3$ (aq) for "2nd doping" (left) and 30min after injection (right); diffraction by AgI rises up within 30min. or less and horizontal diffraction of iodinated PA6 vanishes while meridian one remains along drawn direction.

**References**

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