Functionalization on Polyamide Complex with Iodide: A Review

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Summary: Application with iodinated polyamide-6 (iodine/PA-6 complex) is introduced for modification of structure and functionality on the polyamide. Coordination between polyiodides (I_n^- , $n = 3, 5, \ldots$) and the polyamide advances rapidly and drastically within polyiodide solutions even in bulky samples of the polyamide, and responsiveness in the complex with other molecules such as water is enhanced by coordination. Such response and variation of the structure of the complex can introduce novel functionality with other molecules or ions or salts into the polyamide or hydrophilic polymers.

Keywords: complex; iodine; modification; polyamides; structure

Introduction

Doping of iodine into polyamide-6 (PA-6, nylon 6) can be introduced by an easy procedure with a I_2-KI aqueous solution, but a complex consequently prepared by doping ("nylon 6/iodine complex") shows various structures and some complicated activation. While the doping procedure and following reduction process (releasing iodine) were applied for conversion of hydrogen-bondings in PA-6 (α–γ transition), the intermediate state in which polyiodides ions (I_n^-; $n = 3, 5, \ldots$) are coordinated with the polyamide has not been clarified adequately for the complicated structures or chemical reactions.[1,2]

The doping process can be achieved by immersing PA-6 (bulk or oriented film) into aqueous solutions containing polyiodides (for example, I_2-MI aqueous solutions, where MI is an alkali-iodide), and the complex can be prepared easily and rapidly at a room temperature. However, the structures or reaction of the complex are complicated by various processes, such as diffusion of polyiodides or alkali cations (maybe, adsorbed simultaneously), adsorption/release of moisture, transition of the doped polyamide within crystalline region, etc.[3-6] Since the structures of the complex are attributed to coordination of polyiodides with amide groups on the PA-6 chains, it is frequently required on investigation for physical structures of the complex to consider chemistry. In previous researches, we have found some points to consider this complex; (1) PA-6 is a crystalline polymer with comparatively high crystallinity due to the hydrogen-bonding by amide

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groups; (2) nevertheless, the original polyamide is also a hydrophilic polymer with high ability for adsorption of moisture; (3) on the other hand, adsorption of iodine from the aqueous solutions should be estimated considering coordination of polyiodide ions, not a mono-iodide ion (I^-; $n = 1$).[6-9] These points indicate that the structures of the complex should originate from coordination and hydrophilicity. Then, it is considered that, in the complex, coordination in the crystalline region (not only in the amorphous region) causes variation of intercalated structures and activated responses to environments in the ordered states. In following reports, we introduce some characteristic behaviours of the iodinated complex and views for application to functionalization with the complex.

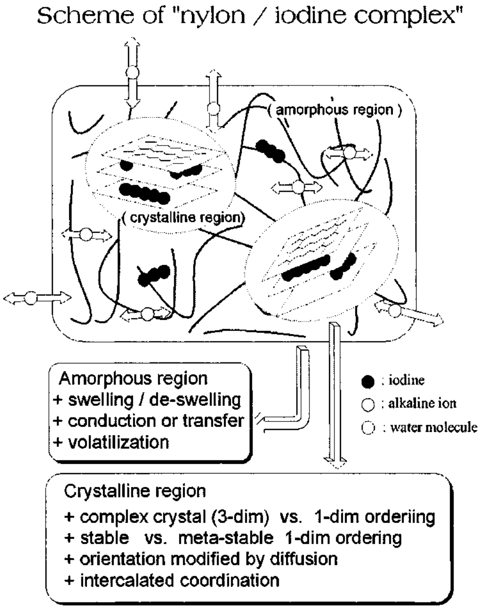

Fig. 1. Scheme of structures in iodinated PA-6 complex.

Preparation

Melt-crystallized plane samples (non-oriented or doubly oriented) or commercial films ("Rayfan^{TM} NO", Toray Plastic Film Co.Ltd.) were used as starting materials. These non-doped samples were annealed in vacuum and their crystalline structure was estimated as the α-phase.

The cut pieces of the samples were immersed into the I_2-MI aqueous solutions (M^+: K^+, Na^+, NH_4^+,,, etc.) which contain the polyiodides of condensation of 0.2-1.0 N at 5-20 °C. If necessary, the doping process was interrupted by rinsing the samples in water. In investigation for response to humidity, doped samples were aged in vacuum to minimize influences by volatilized elements. Or, for the time-sliced investigation with a synchrotron radiation (SR), droplets of the solution were poured into the sample cells at room temperature.

Structures and Characteristic Behaviours

Modification of Diffracted Intensities with Swelling

At first, the term of the "hydrogen-bonded sheets" in the complex does not mean normal hydrogen-bondings between the anti-parallel polyamide chains but is used to support us to understand the layered structure; the structures in the complex are constructed by coordinate bonds. Whereas, the "crystalline region" is not equal to a complex crystal which is attributed to three dimensional symmetry; the "crystalline region" may be the crystallites of the α-phase of PA-6 before doping but, in the complex, it contains various structures (complex crystal with three dimensional symmetry, meta-stable structures, one dimensional ordered structures,,, etc.) and transition among them also exists.

The hydrogen-bondings in PA-6 construct layer structures of the α form in the crystalline region of the non-doped samples.[10] And, the layer structures in the iodine-doped complex attributed to the "hydrogen-bonded sheets" provide sites for coordination with the polyiodides in the crystalline region; the amide groups or hydrogen-bondings are introduced as the host sites with "long range order" which actively interact with the polyiodides, cations or water molecules. Such coordination between the amide groups and the polyiodides is also expected in the amorphous region and it is achieved actually. However, it is regarded that an amount of the doped iodine in the amorphous region is less than that in the crystalline region,[7] or, as static structures, stability of the amorphous complex is relatively lower than that for the crystalline complex. Functionality of the amorphous complex will not be mentioned in detail here while it will induce some interests in view of ionic conduction.[6]

The most elementary and stable coordination is that all layer sites between the "hydrogen-bonded sheets" are occupied with the dopants; this scheme reveals a spacing of 1.56 nm and it is indicated both in comparatively swollen samples and dried ones, i.e., in fresh samples just after rinsing with water or in ones aged in vacuum for a several months, though there is observed transition in intensities of the orders on the 1.56 nm-spacing between the swollen samples and dried ones.[4] Investigation with Raman spectroscopy and WAXD showed that the polyiodides doped in the complex are I_3^- and I_5^- and that they are oriented on the tilt to the chain axis of PA-6 and parallel to it, respectively.[5,6] Furthermore, each complex prepared with the I_2-MI aqueous solutions (M^+: K^+, Na^+, NH_4^+) shows the 1.56 nm-spacing while there is also deviation in intensities of the orders on the spacing depending on the cations; the cations are sure to be doped simultaneously and there should be deviation for their structures and functionality.[11] Therefore, we may require more discussion for modification of the intercalated polyiodides with ageing or swelling since the previous results of Raman spectroscopy indicate information only from the surface of the samples where drying and volatilization take the lead.

Modification of Orientation

On investigation with the "doubly oriented samples", the double orientation can be changed by diffusion of the dopants. It is that, while chain orientation is held parallel to drawn direction, there are two schemes of orientation of the "hydrogen-bonded sheets"; the sheets in the complex can be either parallel or normal to surface of the filmy samples even though the sheets were oriented parallel to the surface in the original non-doped doubly oriented PA-6 samples.(Fig. 2)[12] On the other hand, on investigation with the non-oriented samples, Murthy reported re-orientation of the chain axis normal to the surface of the samples.[3] The two cases may seem to make a conflict for each other, but we should consider that the results with the drawn samples indicate too strict orientation of the chain direction for the PA chains to reconstruct their orientation. On the other hand, a restraint for the chains would not be so strict around the crystallites in the non-oriented PA-6, and then it is possible to reconstruct the chain direction with doping. If so, considering the oriented structures with the polyiodides, we can expect deviation of ability of the polyiodides on diffusion. And the most fundamental point is that diffusion of the dopants into the polyamide can induce re-orientation of the chain direction or the "hydrogen-bonded sheets". Such modification of the orientation is confirmed by a time-sliced observation with the SR at SPring-8 in Nishi-harima, Japan; in the earliest stages on diffusion of the polyiodides, we can observe both creation of the complex structures and, simultaneously, re-orientation of the chains normal to surface of the non-oriented samples or modification of the "hydrogen-bonded sheets" in the doubly oriented samples.[13] Furthermore, it is interesting that the structures formed on the early stage of the doping seem to neither be the most stable intercalation of the spacing of 1.56 nm nor other intercalated structures induced by swelling.(following) Research is going on with the SR.

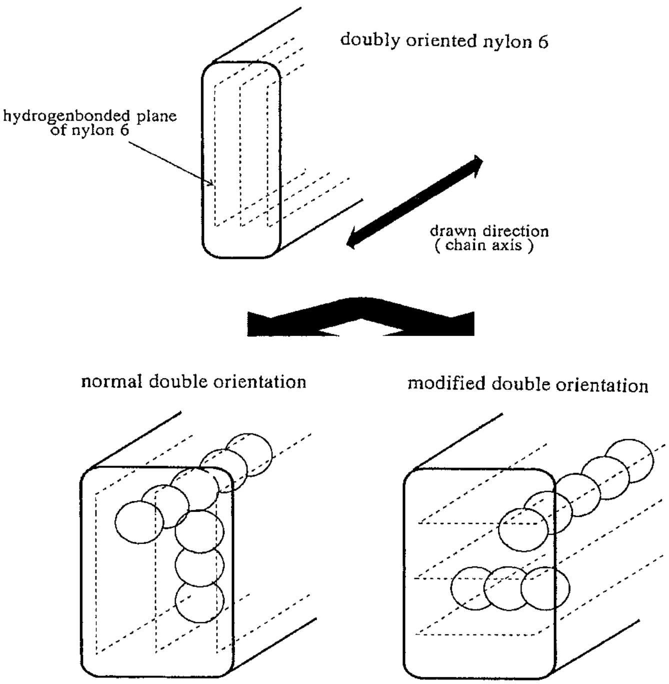

Fig. 2. Modified orientation in doubly oriented complex.

Effects by Moisture-activated Conduction and Modification of Intercalation

As a prior response to moisture, conduction in the amorphous region of the dried complex is activated in a few minutes after transfer into a moist environment. Conduction is ionic and has dependence on cations, M^+, which are doped simultaneously with the polyiodides from the I_2-MI solutions.[14,15] In the view of ionic conduction, however, composition of the polyiodides may not be proper as an application for an electric devices because of problems of volatilization of the iodine.[16]

In the crystalline region, as mentioned above, the most popular intercalation of the polyioidides between the "hydrogen-bonded sheets" shows the spacing of 1.56 nm, where all of the layer-sites between the sheets are occupied with polyiodides or ions. On the other hand, other spacing can be observed by additional procedures. One of them is immersion of the complex samples into an KI aqueous solution, and other is re-swelling by moisture. The former treatment leads "1.95 nm spacing" which is estimated as a one of the layer structures of intercalation with the dopants occupying the sites partially. That is applied with an "elimination effect" by monoiodide ions, I^-.[9] On the other hand, swelling by moisture induces slower and calmer elimination of the dopants from the crystalline region of the complex, and then the swelling process induces not only the "1.95 nm spacing" but also other intercalation with longer spacings.[17] Consequently, modified intercalated layer structures are achieved within the complex system swollen by moisture. And the modified structures vanish in dry condition and are reversed into the most stable intercalation with the spacing of 1.56 nm.

Application for Advanced Doping with other Ions or Salts

Generally, the crystalline region are not so active for conduction or transfer in polymeric systems; they are comparatively static in general swollen systems and occasionally behave as static cross-linking points in a gel. In the iodine complex as mentioned above, however, swelling induces not only the activated ionic conduction in the amorphous regions but also transition of the ordered structure in the crystalline region. It suggests that swelling or the "elimination effect" with the monoiodide ion can be available for "secondary doping" of other ions or molecules which can not be doped directly into the polymeric systems or their crystalline regions of them. And, if the "secondary doping" can be introduced, we can expect novel functionalities and behaviours.

For example, it is possible to import micro composites of AgI through the iodinated PA-6 complex. AgI is a hardly soluble salt and is hard to be dispersed on hydrophilic polymers. However, treatment with Ag^+ solutions to the iodinated complex can induce extraction of micro particles of AgI into it, and the nano-composite of AgI within PA-6 shows characteristic behaviours. For example, the composite shows response of structures to humidity in spite of hard-solubility of AgI for water.[18] And Gotoh et.al. have been researching condution of AgI crystallites and indicated interests in relation between orientation of the crystallites and the polymeric system.[19,20] Iodination may not be always available for modification of general hydrophilic polymers, but, if possible, it will induce novel structures and functionalities standing on coordination and activation with polyiodides.

Conclusion

Iodinated PA-6 complex should be investigated not only as the intermediate state on $\alpha-\gamma$ transition of PA-6 but also as the activated states complicated by multi-components. The procedure of iodination has a potential to introduce characteristic structures and activated functionality on the polyamide or other hydrophilic polymers.

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