RECENT DEVELOPMENTS IN NOVEL CELLULOSE DERIVATIVES

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Recently a fairly large number of studies on the newer functionalization and processings of cellulosics have been made again. There are several reasons for the activities of cellulose chemistry. From the view point of functionalization of cellulose, they are due to that the structural characteristics of cellulose have been re-recognized. As there are three hydroxyl groups in each pyranose ring, cellulose is hydrophilic, reactive but biodegradable. The derivatives in most cases are nontoxic. Although far from rigid, the cellulose backbone is sufficiently stiff to allow formation of ordered phases. Cellulose can be converted into thermally flowable materials by simple chemical modification. Other reasons are the developments of nonaqueous solvent systems, the discovery of super absorbents based on starch, and recent progress in analytical methods and instruments such as high-resolution NMR, DSC and so on.

As shown in Table, the topics can be roughly classified into seven categories. In this lecture, I will explain only the content of the topics concerned with novel cellulose derivatives. Especially, emphasis is put on that the novel functionalization of cellulosics would be achieved by utilizing conventional polymer reaction.

Table. Functionalization of Cellulose : Resent Trends

I. Denaturalization of Cellulose by Chemical Modification.
   (Functionalization by Introducing Substitutents having Non-specific Function)

2. Functionalization by Introducing Specific Groups.
   Specific groups: Biocatalysts, Ligands, Reactive Groups, etc.

3. Plasticization and Composite Materials.

4. Super Absorbents and Hydrogels.

5. Functionalization by Shaping.
   Preparation of High Performance and/or High Functionality Materials(Fibers, Membranes, Beads, Powders) by Shaping.

6. Functionalization by Surface Modification.
   Fibers, Membranes and Gels.

7. Biotechnology.
   Bacterial Cellulose.
   Modification of Cellulose Fibers by Enzyme Treatment.

Functionalization by Substituents Distribution Control

Substituents distribution is characteristics of chemical modification of cellulose, and its control provides one of the useful methods for cellulose functionalization. For example, water solubility of cellulose acetate and methyl cellulose strongly depends on the substituents distribution. The substituents distribution control was also found useful in the high grade functionalization of the physiological properties of cellulose sulfate and carboxymethyl cellulose.

Etherification and Esterification

Highly substituted alkyl ether derivatives can be prepared by the use of nonaqueous solvents, though hardly achieved by heterogeneous reactions. The functional properties of alkyl ether derivatives are markedly different from those of ester derivatives even with long alkyl substituents, as demonstrated in the thermotropic mesophase formation and the formation of monolayer films (spread on the water surface) from tri-O-alkyl ether and corresponding ester derivatives.

Functionalization by Use of Chirality

In the functionalization of cellulosic materials, the use of their chirality is also very interesting problems. In fact several derivatives having chiral discrimination ability have been developed as stationary phases for optical resolution, and a number of interesting thermotropic cholesteric cellulose derivatives have been prepared.

New Cellulose Derivatives

New cellulose derivatives reported recently include conventional but interesting derivatives such as high-DS carboxymethyl celluloses, discarboxyalkyl and dihydroxyalkyl cellulose derivatives, and high-DS aminopropyl celluloses. Cellulose derivatives, which have useful solubility characteristics as coating materials for drugs, have been already commercialized. High-performance dielectric polymers, namely, cellulose derivatives with a high dielectric level and high binding power have been prepared by cyanoethylation of methylcellulose and hydroxyethyl cellulose (HEC). A hydrophobically modified HEC and a quaternary ammonium derivatives of HEC are known to be a novel surface-active polymer and a very useful cationic polymer, respectively. As described above, the use of commercial cellulose derivatives as starting materials provides one of the effective approaches for high-grade functionalization of cellulosics.

Fucntionalization by Introducing Specific Groups

From these topics, I will explain two examples which have been recently developed in Japan. One is on the immobilization of tannine onto cellulose powder. The other is on the rayon fibers having deodorization function.

Block and Graft Copolymers

Narayan developed a new way to prepare controlled cellulose-synthetic polymer graft copolymers by the reaction of the synthetic polymer anion with the modified cellulose under homogeneous conditions. These graft copolymers are of practical interest as biodegradable plastics. We succeeded in the preparation of cellulose graft copolymers having polypeptide side chains. The oligopeptide-grafted copolymers with approximate hydrophobic-hydrophilic balance were found to be blood compatible.