Synthesis of Aromatic Hyperbranched Polymers and Their Application in Catalysis

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Abstract: Hyperbranched polymers have a large number of end-groups and a dendritic-like structure. Unlike dendrimers, hyperbranched polymers can be synthesized in one step process from AB_x-type monomers, where x is two or more. It means that a large number of catalytically active sites can be introduced if the end-groups are converted into catalytically active functional groups. Our research group has been developing novel hybrid materials of aromatic hyperbranched polymers and carbon and investigating their property as heterogeneous catalysts. This presentation introduces the recent progress of our study on hyperbranched poly(ether sulfone) and hyperbranched poly(ether ketone) with catalytically active terminals such as sulfonic acid and TEMPO.

Keywords: Heterogeneous Catalyst / Solid Acid / Aerobic Oxidation / High Performance Polymer

1. Introduction

Hyperbranched polymers have a large number of end-groups and a dendritic-like structure. Unlike dendrimers, hyperbranched polymers can be synthesized in one step process from AB_x-type monomers, where x is two or more. In terms of the potential applications of hyperbranched polymers, our research group has been particularly interested in the aromatic hyperbranched polymers with catalytically functional groups as illustrated in Figure 1. Such polymers will work in various environments because of their high thermal and chemical stabilities, demonstrating high catalytic activity owing to good interaction between the hyperbranched polymer and the reactant.

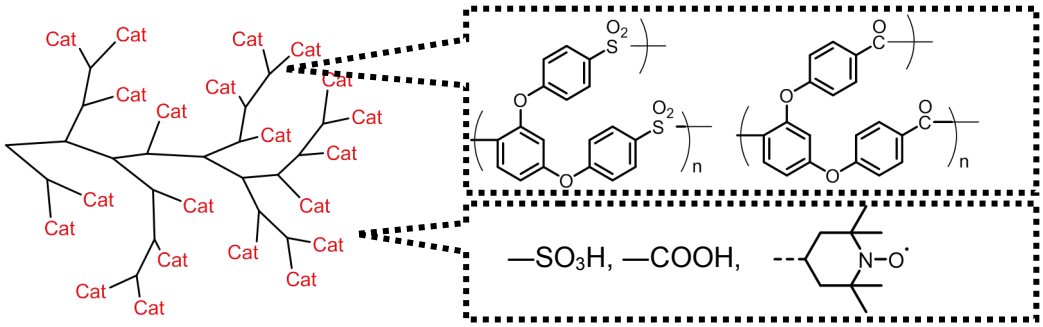

Figure 1. Schematic image of the aromatic hyperbranched polymers for catalysis.

2. Hyperbranched Poly(Ether Sulfone) for Catalysis

Acid catalyzed reactions are widey used currently to produce various chemicals, and the development of active heterogeneous catalysts is quite important in terms of green chemistry. While typical ion exchange polymers such as Amberlyst®-15 are available at below 120 °C, we can expect a higher operating tempaerture by employing aromatic polymers such as poly(ether sulfone). Figure 2 shows the synthetic route of hyperbranched poly(ether sulfone)[1]. As polymerized sulfonated poly(ether

sulfone), SHBPES, can be used as homogeneous catalysts. Besides, this polymer can be used as a heterogeneous catalyst by grafting it onto carbon black (SHBPES/CB)[2]. We have demonstrated that this material is catalytically active for the esterification between 1-butanol and acetic acid, and the Friedel-Crafts alkylation of anisole with benzyl alcohol[2].

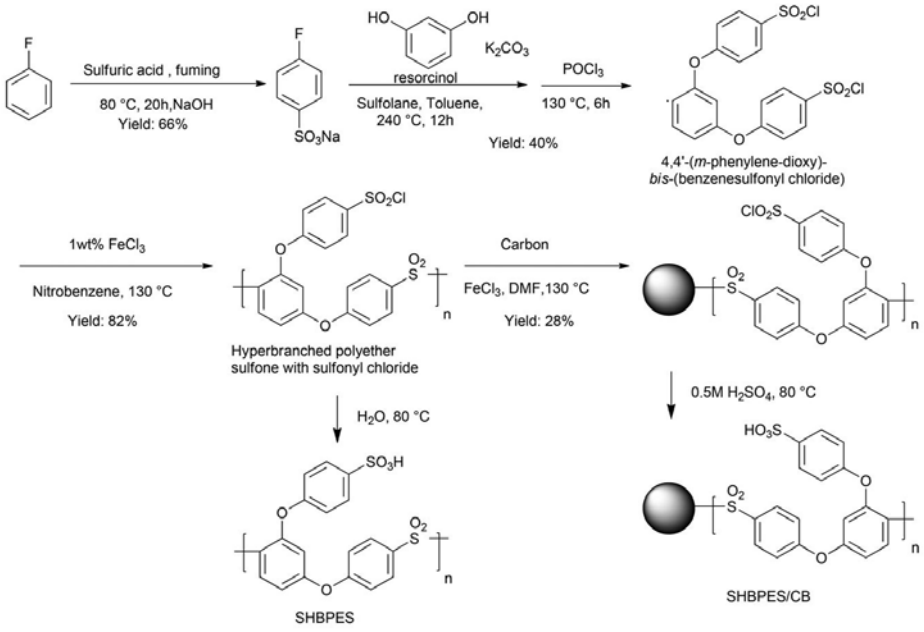

Figure 2. Synthetic route of sulfonated hyperbranched poly(ether sulfone).

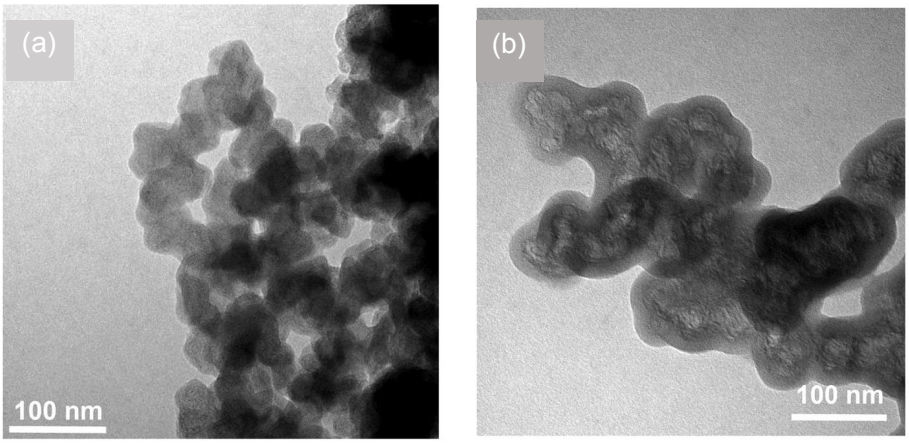

Figure 3. TEM images of the carbon black (a) before and (b) after grafting SHBPES.

3. Hyperbranched Poly(Ether Ketone) for Catalysis

We have expanded the above mentioned concept to other polymer backbone and the application to other catalytic reactions. Figure 4 shows the synthetic route of hyperbranched poly(ether ketone). The polymer with carboxylic acid terminals (HBPEK) was synthesized by a polycondensation reaction of a AB_2 type monomer, 4,4'-(*m*-phenylenedioxy)-bis(benzenecarboxylic acid)[3]. We have demonstrated that this polymer is catalytically active for the hydrolysis of cellulose. Furthermore, this carboxylic acid terminal can be converted into another catalytically functional group, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), which is catalytically active for the aerobic oxidation of alcohols. Indeed, we have demonstrated that the polymer with TEMPO terminals, TEMPO/HBPEK,

is catalytically active for the aerobic oxidation of benzyl alcohol[4], and 2-adamanthanol[5]. This polymer can be utilized as a heterogeneous catalyst by grafting it onto an aromatic support such as carbon black and polyimide nano-particles[6] (Figure 5). Additionally, we have demonstrated that the immobilization of TEMPO is also possible on the terminals of hyperbranched polyimide, synthesized by an $A_2 + B_2$ type polymerization[7].

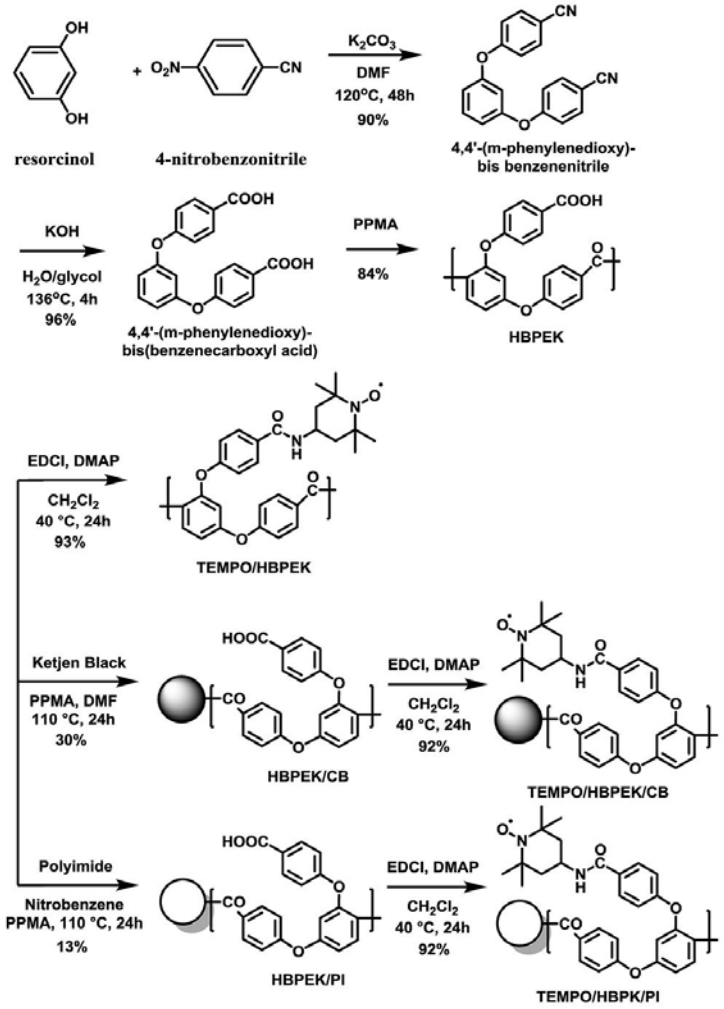

Figure 4. Synthetic route of hyperbranched poly(ether ketone) for application in catalysis.

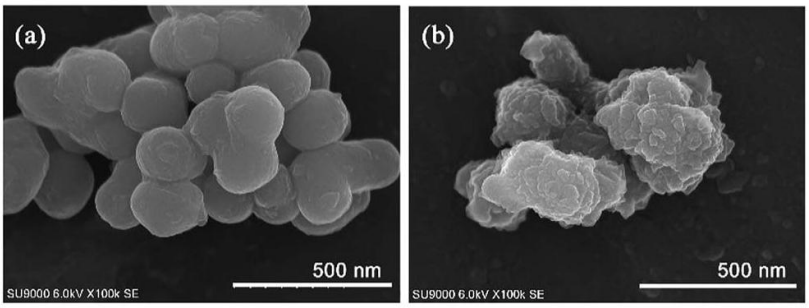

Figure 5. FE-SEM images of the polyimide particles (a) before and (b) after grafting HBPEK.

4. Conclusions

We have demonstrated that aromatic hyperbranched polymers are promising as catalyst materials. This material design concept will be applicable to a wider range of catalytically active sites aiming for

more various catalytic reactions. Further studies will be done to achieve more challenging catalytic reactions using aromatic polymers.

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References

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