

論文 / 著書情報
Article / Book Information

題目(和文)	Synthesis and Characterization of Hyperbranched Aromatic Poly(ether ketone) Functionalized with Actively Catalytical Terminals
Title(English)	触媒末端を有するハイパーブランチポリエーテルケトンの合成と特性評価
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第9621号, 授与年月日:2014年9月25日, 学位の種別:課程博士, 審査員:柿本 雅明,手塚 育志,高田 十志和,早川 晃鏡,道信 剛志
Citation(English)	Degree:, Conferring organization: Tokyo Institute of Technology, Report number:甲第9621号, Conferred date:2014/9/25, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

Summary

The objective of this study is to introduce functional terminal groups on a novel designed hyperbranched aromatic poly(ether ketone) (HBPEK) to synthesize new catalysts with the benefit of hyperbranched structure. Moreover, the TEMPO terminated HBPEK was grafted to insoluble supports to form an insoluble catalyst.

Firstly, a new type of hyperbranched aromatic poly(ether ketone) terminated with carboxylic acid groups (P2) was synthesized via a one-step polycondensation of a symmetric AB₂ monomer, 4,4'-(*m*-phenylenedioxy)-bis(benzenecarboxylic acid) using phosphorous pentoxide-methanesulfonic acid (PPMA) as a condensing agent and solvent. Subsequently, the terminal carboxylic acid functional group of P2 was converted to an ethyl ester functional group by treatment with thionyl chloride followed by ethanol in the presence of triethylamine. The weight-average molecular weight (M_w) of the ethyl ester-terminated hyperbranched poly(ether ketone) (P3) was measured by gel permeation chromatography (GPC). By changing the reaction time and the amount of PPMA, M_w can be controlled in the range of 4.2×10^4 to 1.6×10^5 . P2 was soluble in polar solvents, and P3 was soluble in less-polar solvents. The thermal stabilities of the poly(ether ketone)s were investigated using TGA, which indicated that the decompositions of P2 and P3 start at around 150°C and 200°C, respectively. The inherent viscosities of P2 were in the range of 0.101 and 0.171, while those of P3 ranged from 0.067 to 0.112. The ion exchange capacities (IEC) calculated by titration were in the range of 2.2-2.8 mol kg⁻¹ according to the difference in molecular weights. P2 was tested as a weak-acid catalyst and exhibited a certain catalytic activity for the hydrolysis of cellulose to glucose.

Then, several kinds of monomer was discussed in order to synthesize a linear type or less

branched type of poly(ether ketone), concluding 4-phenoxybenzoic acid, 4-phenoxy-1,3-benzenedicarboxylic acid, 4-phenoxyphthalic acid, 4-phenoxyphthalic anhydride and 4-phenoxyphthalic acid, 2-methyl ester. The side carboxylic acid terminal groups showed a considerable influence on the activity and solubility of the system. By comparing the yield of polymerization of various structures, the originally designed AB₂ monomer shows an outstanding high activity for polymerization, and that was utilized in the following study for catalysis.

Next, a nitric radical, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was introduced to the terminal groups of HBPEK. TEMPO/HBPEK was studied as a novel heterogeneous catalyst for aerobic oxidation of alcohols. The synthesized TEMPO/HBPEK has 2 mmol g⁻¹ of TEMPO and exhibits good catalytic activity and selectivity for the aerobic oxidation of benzyl alcohol with only a small amount of nitric acid (2 mol %). The catalytic activity of TEMPO/HBPEK, which is still a homogenous system, was slightly lower than molecular TEMPO. The lower catalytic activity is probably due to a lower mobility of the TEMPO terminals on HBPEK. Since the TEMPO/HBPEK is soluble in the current reaction condition, it has been grafted onto insoluble supports: carbon black (TEMPO/HBPEK/CB) and polyimide nano-particles (TEMPO/HBPEK/PI). The TEMPO loading was calculated as 1.32 mmol g⁻¹ and 0.96 mmol g⁻¹ separately, from the result of CHN elemental analysis. Those two heterogeneous catalysts show lower activity than TEMPO/HBPEK because of the solubility, but they are still catalytically active. The initial catalytic activity of TEMPO/HBPEK/CB was better than that of TEMO/HBPEK/PI, whereas the durability of TEMPO/HBPEK/PI is better than that of TEMPO/HBPEK/CB.

However, we also observed that not all insoluble compounds can be easily collected. The polyimide particle, for instance, is easy to be stuck on glassware and bring a difficulty for 100 % collection. The ketjen black, in contrast, does not have such problems that could always reach a high collection yield. But inevitably, the Ketjen Black faces a problem by the deactivation of TEMPO in the recyclability test, which is probably caused by its surface radicals. Thus, other carbon materials with fewer radicals are worth trying. Hereby, graphene, a two dimensional material with single layer sp^2 hybridized carbon atoms arranged in honeycomb lattice, which theoretically has no radicals, has been investigated. as a support to graft TEMPO/HBPEK. HBPEK was demonstrated that can be used for modification of graphene by Friedel–Crafts reaction with a polymer loading of 44 wt%. The polymer was dispersed on the surface as small bulks observed by TEM. After functionalized with TEMPO, it was used as a heterogeneous catalyst. The TEMPO loading rate was calculated as 0.96 mmol g^{-1} . 2-adamantanol was used as a more challenging reactant in the aerobic oxidation. The TEMPO/HBPEK/graphene shows good recyclability and activity for at least 5 runs. The performance of the 2-adamantanol oxidation also proved the potential for different substrates.