

Synthesis of a Hyperbranched Aromatic Polyether ketone Functionalized with Catalytically Active Terminal Groups

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Introduction

In recent years, hyperbranched polymers have drawn much attention for their unique properties such as its flexible structure and large amount of functional terminal groups whose number increases with the increasing molecule weight. For these advantages, hyperbranched polymer can be a good support to immobilize catalytically active groups to form a heterogeneous catalyst.

Experimental

A hyperbranched aromatic polyetherketone with carboxylic acid terminal groups was synthesized by the polycondensation of a AB₂ monomer (**1**), 4,4'-(*m*-phenylenedioxy)-bis(benzenecarboxyl acid), at 110 °C with Eaton's reagent (PPMA) as catalyst. Weight-average molecular weights were determined by gel permeation chromatography (GPC) using a Viscotek TDA 302 system with a TSK-GEL α -M column and N,N-dimethylformamide (DMF) as eluent. This GPC was carried out after converting the acid terminal groups to ethyl ester form. NMR, FT-IR and elemental analysis were conducted to determine the polymer structure.

Results and Discussion

The AB₂ monomer was synthesized as Scheme 1. The yields of the first and second steps were 90% and 96% respectively. The structure of AB₂ monomer **1** was confirmed by NMR and IR, showed in Figure 1 a and b. ¹H NMR (DMSO-d₆, δ , ppm): 6.89 (d, 1H, e), 6.95(m, 2H, d), 7.10 (m, 4H, b), 7.48 (m, 1H, c), 7.95(m, 4H, a), 12.89(s, 2H, f). IR (KBr, cm⁻¹): 1672 (C=O, stretching), 2500-3000 (O-H, vibration, broadband).

After polymerization, the peak of carboxyl acid (f, 12.89 ppm) decreased and a new peak g (7.28 ppm) appeared (Figure 2), which demonstrated the polycondensation process. Moreover, the titration for the hyperbranched polymer showed the remained hydrogen contained in polymer was 2.28mmol/g. Meanwhile the theoretical value was 2.854mmol/g.

With different polymerization conditions, the molecule weight of polymer could be controlled. Some results were summarized in Table 1. The molecule weight would increase as the reaction time, temperature and the amount of PPMA increases. Sample 4, the polymer with low aggregation and insoluble in some organic solvent such as acetone, was preferred to be used for loading TEMPO in the following step as a catalyst.

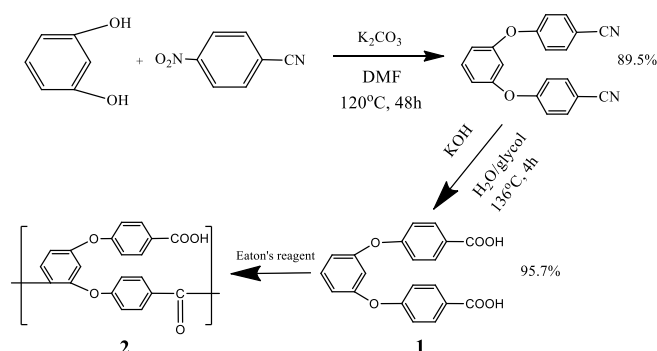
The hyperbranched polymer was linked with TEMPO as Scheme 2. After fully washed with acetone and dried, element analysis was taken. The EA result showed the content of C, H and N was 5.47%, 68.42% and 4.64%. By the content of Nitrogen, the TEMPO loading rate was known as 1.66 mmol/g. With a rough calculation, over 70% terminal was linked with TEMPO.

Conclusions

A new type of hyperbranched aromatic polyetherketone with functional terminal groups was successfully synthesized. The molecular weight can be controlled by changing the polymerization conditions. The catalysis of such polymer will be studied aiming for developing new type of catalyst materials.

Reference

1. K. Matsumoto, M. Ueda, *Chem. Letters*, **35**, 10(2006).
2. J. Hao, M. Jikei, M. Kakimoto, *Macromolecules*, **35**, 5372(2002).



Scheme 1. Synthesis and structures of hyperbranched polymer with carboxyl acid terminal groups

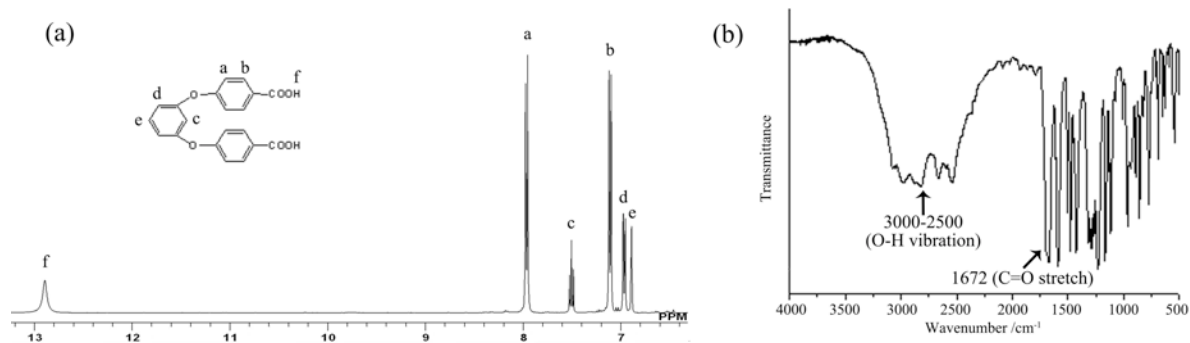


Figure 1. NMR and IR spectroscopy of AB₂ monomer 1

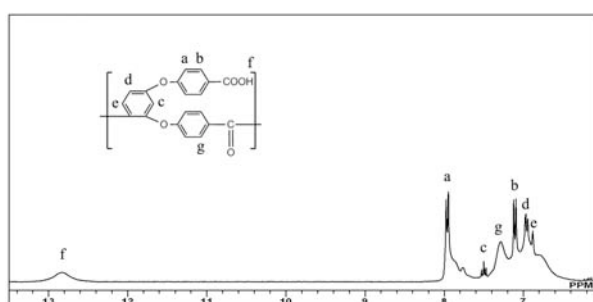
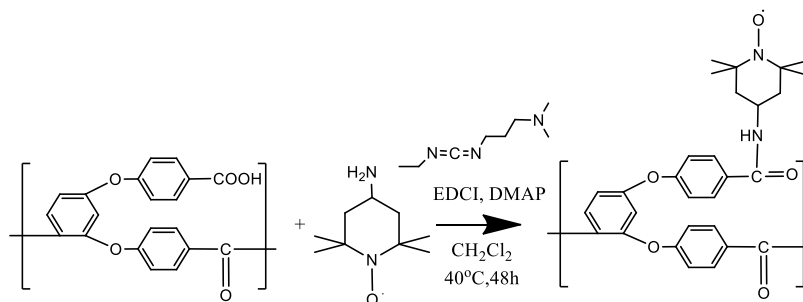


Figure 2. ¹H NMR (DMSO-d₆) of polymer 2. The decreased carboxyl acid peak at 12.89 ppm and the new peak at 7.28 ppm demonstrated the process of polycondensation.

Table 1. Different conditions for polymerization

Sample	PPMA	T/°C	Time	Mw
	/mL			
1	3	110	6	285944
2	3	110	4	399923
3	3	110	2	48619
4	2	110	2	25862
5	1.5	110	2	47800
6	1	110	2	32876
7	3	70	3	30395
8	2	70	2	16067
9	3	40	2	7601

For all the samples, the amount of monomer was 0.3g



Scheme 2. Hyperbranched polymer linked with TEMPO