

Note

HYPERBRANCHED AROMATIC POLYMERS OBTAINED VIA SELF-CONDENSATION*

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Abstract Hyperbranched aromatic polymers were prepared by Friedel-Crafts reaction with Lewis acid, AlCl_3 and ZnCl_2 , as the catalysts. In this work, hyperbranched polybenzyl (PB) and poly(methylene)naphthalene (PN) were synthesized and characterized by $^1\text{H-NMR}$ and GPC. In addition, their fluorescence properties were measured with steady-state fluorescence spectra in THF and ethylene dichloride. The quantum yields of polybenzyl and poly(methylene)naphthalene in ethylene dichloride are much larger than those in THF.

Keywords Hyperbranched polymer, Polybenzyl, Poly(methylene)naphthalene, Fluorescent spectra

INTRODUCTION

Flory^[1] first predicted that AB_n ($n \geq 2$) type of monomer would produce the highly branched polymer possessing one unreacted A and $(n - 1) \text{DP} + 1$ number of unreacted B at the surface of polymer. Many papers pertinent to the preparation and characterization of hyperbranched polymers have been published in recent years^[2-10].

In general, the synthesis of the monomers used in the preparation of hyperbranched polymers is relatively complicated though their polymerization reactions usually are simple. Thus it would be interesting if the commercially available monomers can be used to prepare the hyperbranched polymers.

In this paper, benzyl chloride (B) and chloromethyl naphthalene (N) were selected and underwent the Friedel-Crafts reaction with the Lewis acid, such as AlCl_3 and ZnCl_2 , as the catalyst to synthesize hyperbranched polymers.

EXPERIMENTAL

Materials

Ethylene dichloride and nitrobenzene were dried by usual procedures. Tetrahydrofuran (THF) was distilled from a sodium diphenyl ketyl solution before use. Anhydrous AlCl_3 was obtained by sublimation and anhydrous zinc chloride was obtained by fusion to remove water. Benzyl chloride was distilled under reduce pressure before use. 1-Chloromethylnaphthalene (containing 5% 2-chloromethyl naphthalene) was purchased from Acros and used without purification.

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Preparation of Polybenzyl (PB4)

Into a three-necked flask equipped with a dropping funnel and a nitrogen gas inlet, 0.064 g (0.48 mmol) of anhydrous AlCl_3 and 20 mL of ethylene dichloride were added. With stirring 5.5 mL (47.80 mmol) of benzyl chloride solution (in 10.3 mL of ethylene dichloride) was added dropwise to the flask within ten minutes and the polymerization reaction was carried out at about 15 °C for 1 h. The reaction was terminated with dilute hydrochloric acid until the red color disappeared. Then the organic layer was collected and the aqueous layer was extracted with ethylene dichloride. The combined extract was washed with water until neutral and dried over anhydrous MgSO_4 . The solution was evaporated to remove a part of solvent with a rotatory evaporator and then poured into methanol to precipitate out the product. The crude product was reprecipitated with methanol from ethylene dichloride and dried under vacuum at 50 °C for two days. An orange powdery polymer was obtained in 55.0% yield.

Preparation of Polymethylene Naphthalene (PN4)

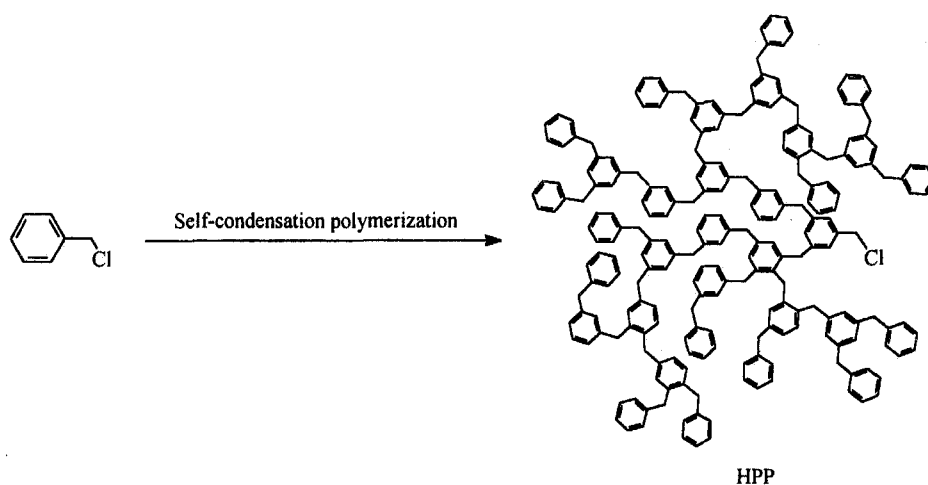
A solution of 8.48 g (48.0 mmol) of 1-chloromethylnaphthalene in 20 mL of nitrobenzene was added dropwise to 0.32 g (2.4 mmol) of ZnCl_2 and 9.0 mL of nitrobenzene within five minutes under nitrogen. The color of the solution turned from green to deep black throughout the reaction. After 6 h the reaction mixture was poured into methanol to precipitate out the product. The crude product was reprecipitated with methanol from ethylene dichloride and then dried under vacuum at 50 °C for two days. The white powdery product was obtained with 58.0% yield.

Characterization

The ^1H -NMR spectra of the polymers were recorded on a Varian NMR spectrometers. The GPC (gel permeation chromatography) measurements were carried out on a Waters chromatograph connected to a Waters 410 differential refractometer using THF as the eluent and standard polystyrenes for calibration. Fluorescence spectra were obtained from a Perkin-Elmer Luminescence Spectrometer LS 50B. Fluorescence quantum yields were determined by referring to naphthalene in cyclohexane^[11].

RESULTS AND DISCUSSION

In the Friedel-Crafts alkylation of aromatic ring, benzyl chloride is a very active alkylation agent through self-alkylation. The introduction of the first benzyl group, which acts as an electron-donating group, would activate the aromatic ring for further substitution reaction. It is very difficult to obtain polybenzyl with disubstitution pattern, like a linear polymer, through the self-condensation of benzyl chloride, because the aromatic ring has many potentially active sites to be attacked by electrophilic species.



Scheme 1 Synthesis of hyperbranched polybenzyl by self-condensation polymerization

Table 1 summarizes the results of polymerization of benzyl chloride (B) and 1-chloromethylnaphthalene (N). The PB obtained is soluble in CH_2Cl_2 , CHCl_3 , $\text{ClCH}_2\text{CH}_2\text{Cl}$, THF and C_6H_6 , but insoluble in hexane and methanol. The polymerization of 1-chloromethylnaphthalene carried out in ethylene dichloride or nitromethane by using strong Lewis acid, such as AlCl_3 and TiCl_4 , gave an insoluble product. When nitrobenzene was used as a solvent and the weak Lewis acid ZnCl_2 was employed as a catalyst at low concentration (5% molar ratio to monomer), however, it was found that the polymerization could proceed and the soluble poly(methylene)naphthalene with relatively low molecular weight and low polydispersity was obtained.

Table 1 Self-condensation polymerization of benzyl chloride (B) and 1-chloromethyl naphthalene (N) in room temperature^a

Sample	AlCl_3 or ZnCl_2^b (mol%)	t (h)	Yield (%)	M_w^c ($\times 10^{-3}$)	M_w/M_n^c
PB1	10	1.0	55.0	18.70	11.26
PB2	5	1.0	54.0	66.50	28.92
PB3	2	1.0	61.6	9.88	4.60
PB4	1	1.0	55.0	6.01	2.75
PB5	0.5	1.0	7.5	2.96	1.67
PN1	1	1.0	24.0	0.99	1.28
PN2	5	2.0	42.3	1.38	1.29
PN3	5	4.0	60.8	1.76	1.44
PN4	5	6.0	58.0	2.01	1.34
PN5	5	8.0	60.4	1.80	1.38
PN6	5	12.0	48.2	2.66	1.39

^a Conditions: Concn. = 20% (W/V); Solvent: ethylene dichloride for benzyl chloride- AlCl_3 and nitrobenzene for 1-chloromethyl naphthalene- ZnCl_2 systems, respectively

^b Molar ratio with respect to benzyl chloride, or 1-chloromethyl naphthalene, respectively

^c Measured by GPC

$^1\text{H-NMR}$ spectrum of hyperbranched polybenzyl (PB2) is shown in Fig. 1. There are two broad peaks, *i.e.* the chemical shifts at $\delta = 3.3\text{--}4.0$ and at $\delta = 6.4\text{--}7.3$ which can be assigned to the methylene groups and the phenyl groups, respectively. The broad peaks appearing here might be due to the presence of various isomers and are difficult to be resolved.

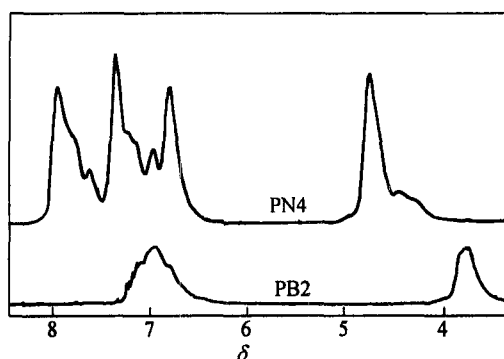


Fig. 1 $^1\text{H-NMR}$ spectra of PB2 and PN4 (CDCl_3 , 200 MHz)

The steady state fluorescence spectra of PB and PN measured in ethylene dichloride were shown in Figs. 2 and 3, respectively. PB shows intense emission at about 425 nm, while PN emits in the shorter wavelength region of 350 nm.

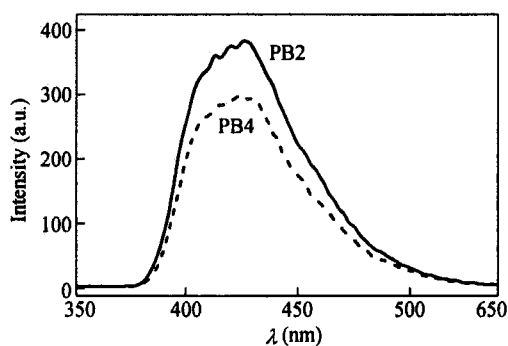


Fig. 2 Fluorescence spectra of PB2 and PB4 in ethylene dichloride at $\lambda_{\text{ex}} = 278$ nm

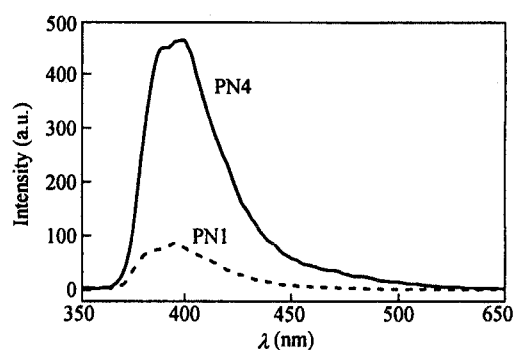


Fig. 3 Fluorescence spectra of PN1 and PN4 in ethylene dichloride

Table 2 Fluorescence quantum yields (ϕ_f) of PB and PN in THF and ethylene dichloride at $\lambda_{\text{ex}} = 278$ nm

	PB2b ^a	PB2d ^b	PN4a ^c	PN1 ^d
ϕ_f (ED)	0.64	0.66	0.32	0.074
ϕ_f (THF)	0.0085	0.0055	0.0041	0.0023

^a PB2b: second fraction of PB2, $M_w = 33.3 \times 10^3$, $M_w/M_n = 1.63$

^b PB2d: fourth fraction of PB2, $M_w = 9.81 \times 10^3$, $M_w/M_n = 1.84$

^c PN4a: first fraction of PN4a, $M_w = 3.29 \times 10^3$, $M_w/M_n = 1.28$

^d PN1: no fractionation, $M_w = 0.99 \times 10^3$, $M_w/M_n = 1.28$

The fluorescence quantum yields were determined in THF and ethylene dichloride, respectively (see Table 2). The quantum yields of PBs and PNs in ethylene dichloride are much larger than those in THF, and in the PN case the molecular weights also exhibit an obvious effect on the quantum yield. It is expected that the PB probably have potential applications as fluorescence material because of their good light-harvesting properties.

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REFERENCES

- 1 Flory, P.J., *J. Am. Chem. Soc.*, 1952, 74: 2718
- 2 Kim, Y.H. and Webster, O.W., *Macromolecules*, 1992, 25: 5561
- 3 Kricheldorf, H.R. and Stukenbrock, T., *J. Polym. Sci., Part A: Polym. Chem.*, 1998, 36: 31
- 4 Suzuki, M., Yoshida, S., Shiraga, K. and Saegusa, T., *Macromolecules*, 1998, 31: 1716
- 5 Kennedy, J.P. and Isaacson, R.B., *J. Macromol. Chem.*, 1996, 1: 541
- 6 Montaudo, G., Bottino, F., Caccamese, S., Finocchiaro, P. and Bruno, G., *J. Polym. Sci., Part A-1*, 1970, 8: 2453
- 7 Montaudo, G., Finocchiaro, P., Caccamese, S. and Bottino, F., *J. Polym. Sci., Part A-1*, 1970, 8: 2475
- 8 Grassie, N. and Meldrum, I.G., *Euro. Polym. J.*, 1971, 7: 629
- 9 Pinkus, A.G. and Lin, W.H., *J. Macromol. Sci., Chem. Ed.*, 1979, A13: 133
- 10 Tsonis, C.P. and Hasan, M.U., *Polymer*, 1983, 9: 349
- 11 Eaton, D.F., *Pure Appl. Chem.*, 1988, 60: 1107