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Communications to the Editor

Dendritic Hyperbranched Polyethynylenes with the 1,3,5-*s*-Triazine Moiety

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Dendritic hyperbranched polymers have recently attracted much attention because of their unique structural characteristics and consequent novel properties.[1,2] Highly branched polymers in this area can be categorized into two parts. The first one is the structurally well-defined dendritic macromolecules prepared by stepwise divergent or convergent approaches. Although these approaches generate highly monodisperse and regularly branched macromolecules, laborious iterative synthetic steps give rise to many practical difficulties in synthetic process.[3] The second one is based on Flory's prediction that direct polymerization of AB_x type monomers would produce hyperbranched polymers with one unreacted A functional group and $(x - 1)n + 1$ unreacted B functional groups, where n is the degree of polymerization.[4−10] One of the important issues in this area is to rationally design the structures of AB_2 type molecules and their polymers so that the structure−property relationship of hyperbranched polymers can be systematically investigated.

Here we report the synthesis of new hyperbranched polymers obtained by one-pot polymerization of AB_2 type monomer with the 1,3,5-*s*-triazine moiety. Selective reactivities of three chlorine atoms on cyanuric chloride toward a variety of nucleophiles provide synthetic versatility for AB_2 monomers and their one-pot polymerized hyperbranched polymers which have 1,3,5-*s*-triazine units.

Our initial work involved the synthesis of AB_2 type 1,3,5-*s*-triazine molecules that have 3-ethynylphenoxy substituent as A and a 4-iodophenoxy substituent as B. In this system, the Heck coupling reaction was employed to synthesize hyperbranched polyethynylenes. As outlined in Scheme 1, cyanuric chloride was reacted with 4-iodophenol in CH_2Cl_2/H_2O (1:1, v/v) with sodium hydroxide for 5 h at room temperature to yield 2-chloro-4,6-bis(4-iodophenoxy)-1,3,5-*s*-triazine (**1**), which was purified by recrystallization from *n*-hexane/methylene chloride.[11]

Compound **1** was then allowed to react with 3-ethynylphenol in $CHCl_3/H_2O$ with NaOH for 24 h at reflux to give the desired AB_2 type molecule, 2-(3-ethynylphenoxy)-4,6-bis(4-iodophenoxy)-1,3,5-*s*-triazine (**2**).[12,13] The polymerizations of compound **2** to produce hyperbranched polymers are based on the Heck coupling reaction of aryl ethynyl and aryl iodide units to yield ethynylene branching moieties.[14−16] The polymerizations were carried out in triethylamine/THF (1:1, v/v) in the presence of $Pd(PPh_3)_2Cl_2$ and CuI. Polymerization results are summarized in Table 1. The products were purified by repeated precipitation from THF into methanol or methanol/water. The polymers were soluble in organic solvents such as CH_2Cl_2, $CHCl_3$, THF, DMF, and DMSO. Molecular weights of the polymers were estimated by GPC to be in the range $M_w = 6000−10000$ with M_w/M_n values in the range 1.6−3.0.[17]

Scheme 1

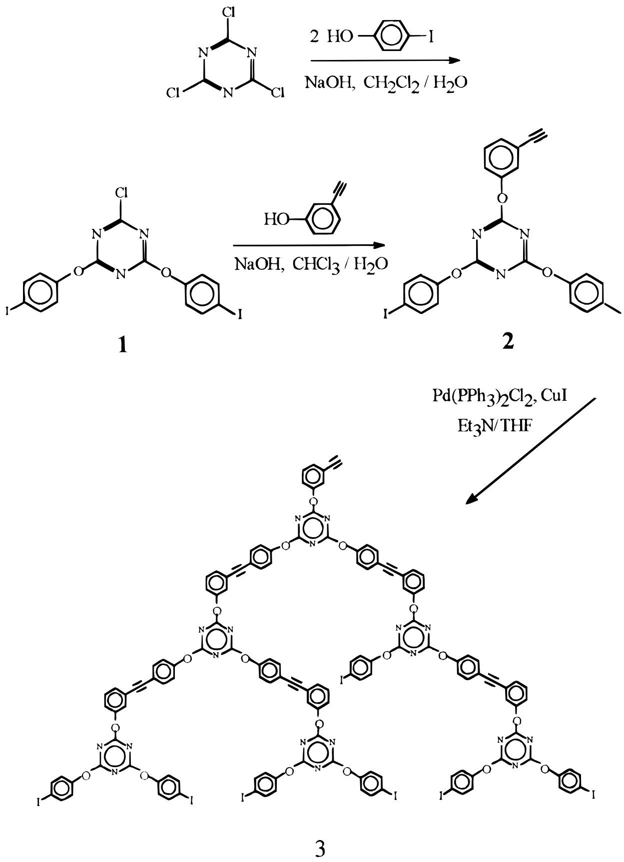

Table 1. Polymerization of 2-(3-Ethynylphenoxy)-4,6-bis(4-iodophenoxy)-1,3,5-*s*-triazine

polymer	temp (°C)	time (h)	yield (%)	M_w[a]	M_w/M_n
3a	0	3	58	10 000	1.6
3b	RT	6	60	6 000	2.5
3c	60	3	35	10 000	3.0

[a] GPC values versus polystyrene standards.

The structural characterization was carried out by ^1H NMR, ^{13}C NMR, and Raman spectroscopy. The ^1H NMR spectrum of compound **2** in Figure 1 showed resonances of the aromatic protons of the iodophenoxy units at 6.89 (d, $J = 8.4$ Hz) and 7.68 ppm (d, $J = 8.4$ Hz). Aromatic protons of the ethynylphenoxy moiety gave resonance peaks between 7.10 and 7.40 ppm.[13]

As the polymerization proceeds, the coupling of ethynyl moieties with aryl iodides produced aryl ethynylene units and reduced the population of iodophenoxy groups, which exist on the periphery of the polymer branches. Therefore, as Figure 1 shows, the polymerization reduced the relative integration of iodophenoxy proton

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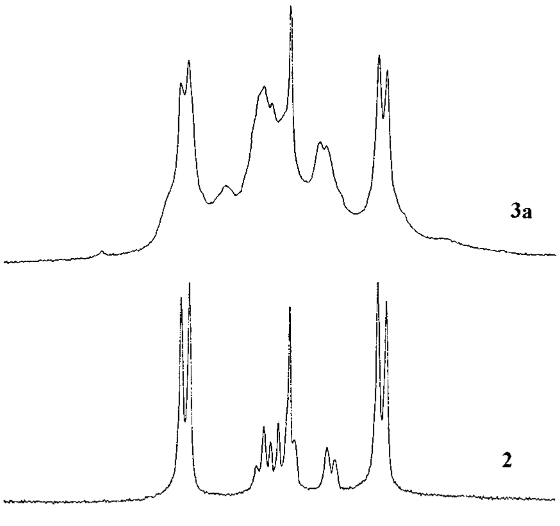

Figure 1. ^{1}H NMR spectra of monomer **2** and polymer **3a** in $CDCl_3$.

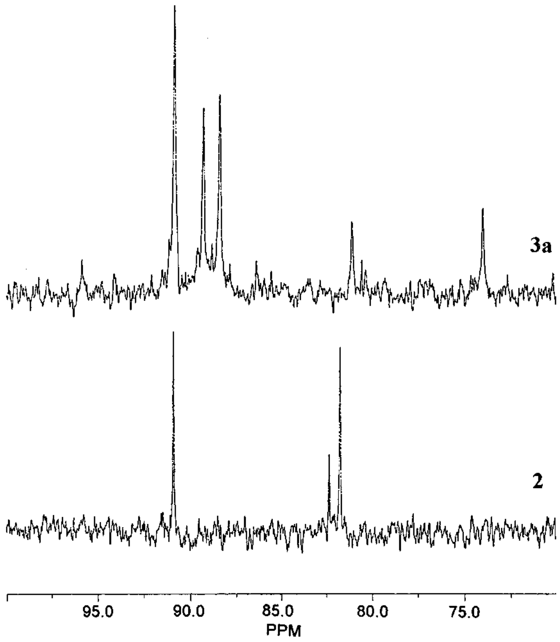

Figure 2. ^{13}C NMR spectra of monomer **2** and polymer **3a** in DMSO-d_6.

peaks at 6.89 (d) and 7.68 ppm (d) compared with other aromatic proton peaks between 7.10 and 7.60 ppm. The ^{13}C NMR spectrum of compound **2** showed two resonance peaks of ethynyl carbons at 81.8 and 82.4 ppm (Figure 2).

Polymerization of compound **2** generated two ethynylene carbon peaks at 88.4 and 89.3 ppm with disappearance of the peaks of the ethynyl carbons. The peak at 90.8 ppm is due to the C−I of the iodophenoxy units which are at the end of branches. Two additional peaks were present at 74.7 and 80.8 ppm, possibly due to two different carbons of symmetric diacetylenic moieties which could be formed by the oxidative coupling of two aryl ethynyl units during the polymerization.[18] The formation of diacetylenic moieties was further evidenced by Raman spectra in Figure 3. Monomer **2** showed an ethynyl absorption band at 2105 cm^{-1}. Polymers showed two absorption bands at 2218 and 2208 cm^{-1}, which are due to ethynylene and diacetylenic units, respectively. The Raman spectra indicated that lower polymerization temperature produced hyperbranched polymers with higher content of ethynylene units. The ratio of diacetylenic units to ethynylenes in polymer **3a** was estimated to be ∼25% by using the inverse gated decoupling technique of ^{13}C NMR. This type of structural irregularity in hyperbranched polymers was also reported by Fréchet et al.[19] The one-pot polymerization of Fréchet's AB_2 monomer, 5-(bromomethyl)-1,3-dihydroxybenzene, produced not only O-alkylated but C-alkylated branches. The thermal properties of the polymers were studied by DSC and TGA. Polymers **3a**, **3b**, and **3c** showed very similar thermal behavior. The polymers have a glass transition temperature at around 130 °C, while they do not have any melting behavior before cross-linking near 240 °C.[15] When the polymers were heated in a nitrogen atmosphere, 3% weight loss occurred approximately at 315 °C and 10% loss at 400 °C. The overall char yields after heating to 700 °C were approximately 30%.

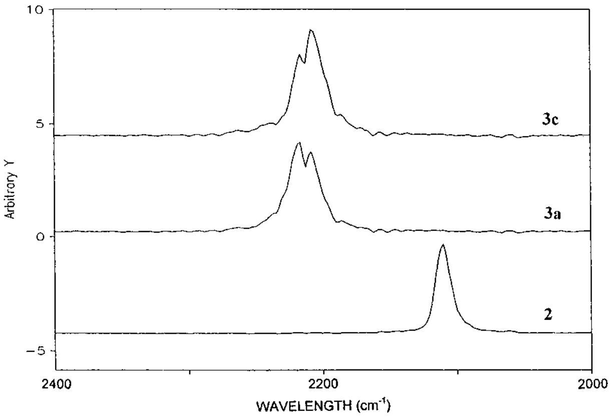

Figure 3. Raman spectra of monomer **2**, polymer **3a**, and polymer **3c**.

In summary, hyperbranched polyethynylenes with the 1,3,5-*s*-triazine moiety can be prepared by one-pot polymerization of an AB_2 type monomer, 2-(3-ethynylphenoxy)-4,6-bis(4-iodophenoxy)-1,3,5-*s*-triazine (**2**), which was synthesized from cyanuric chloride. The polymers, in this case, have structural irregularity due to incorporation of diacetylenic branches during the polymerization. However, the sequential replacement of three chlorines on cyanuric chloride with nucleophiles provides an efficient route to systematic synthesis of a variety of AB_2 type 1,3,5-*s*-triazine monomers, which could be one-pot polymerized to easily produce high molecular weight hyperbranched materials. Current efforts are focused on extending the scope of the structures of AB_2 type 1,3,5-*s*-triazine molecules and their polymers without structural irregularity in order to investigate the detailed structure−property relationship of these types of hyperbranched polymers.

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(11) For **1**: yield 89%; mp 211−213 °C; $\lambda_{\max}$ ($CHCl_3$) = 254 nm; IR (KBr) 3086, 1574, 1527, 1385, 1292, 951 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.89 (d, $J = 8.3$ Hz, 4H), 7.69 (d, $J = 8.3$ Hz, 4H); ^{13}C NMR (DMSO-d_6) δ 91.62, 124.01, 138.48, 151.16, 168.27, 171.80; MS m/z 551, 553. Anal. Calcd for $C_{15}H_8N_3O_2ClI_2$: C, 32.67; H, 1.46; N, 7.62. Found: C, 32.75; H, 1.50; N, 7.17.

(12) (a) 3-Ethynylphenol was obtained by trimethylsilylethynylation on 3-iodophenol and deprotection of the trimethylsilyl groups of 3-((trimethylsilyl)ethynyl)phenol. ^1H NMR ($CDCl_3$) δ 2.98 (s, 1H), 4.91 (s, 1H), 6.75 (d, $J = 7.1$ Hz, 1H), 6.88 (s, 1H), 6.99 (d, $J = 8.0$ Hz, 1H), 7.12 (t, $J = 6.2$ Hz, 1H); MS m/z 119. (b) Bohlmann, F.; Albrecht, K. D.; Schmidt, G. *Ber.* **1966**, *99*, 2822. (c) Stille, J. K.; Nilb, R. G.; Norris, S. O. *Macromolecules* **1976**, *9*, 516.

(13) For **2**: yield 78%; mp 137−139 °C; $\lambda_{\max}$ ($CHCl_3$) = 240 nm; IR (KBr) 3298, 1593, 1386, 1209, 1013 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.14 (s, 1H), 6.89 (d, $J = 8.4$ Hz, 4H), 7.10 (d, $J = 6.9$ Hz, 1H), 7.26 (s, 1H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.36 (t, $J = 6.1$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (DMSO-d_6) δ 81.80, 82.39, 90.89, 121.99, 123.49, 124.98, 129.45, 130.02, 138.57, 151.05, 151.25, 173.35; MS m/z 634. Anal. Calcd for $C_{23}H_{13}N_3O_3I_2$: C, 43.63; H, 2.07; N, 6.64. Found: C, 43.45; H, 2.55; N, 6.21.

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(17) To increase the molecular weights, more vigorous polymerizations at higher temperature or with longer polymerization time compared to those in Table 1 were performed. In those conditions, insoluble products were obtained, probably due to the extended coupling of ethynyl groups to form diacetylene units.

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