Korea Polymer Journal, Vol. 8, No. 3, pp 142 – 146 (2000)

Notes

Hyperbranched Poly(ether sulfone) with 1,3,5-*s*-Triazine Moiety

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Received April 26, 2000

Abstract : Hyperbranched poly(ether sulfone) analogs with the 1,3,5-*s*-triazine moiety were prepared by the direct polymerization of AB_2 type monomer, 2,4-bis(4-hydroxyphenyl)-6-(4-(4-(4-fluorobenzenesulfonyl)phenoxy)phenyl)-1,3,5-*s*-triazine (**3**). The selective reactivity of three chlorine atoms on cyanuric chloride toward nucleophiles provides an efficient route for the systematic synthesis of AB_2 type triazine monomers and their hyperbranched polymers. The triazine rings influenced the structural and material characteristics of these hyperbranched polymers. The hyperbranched poly(ether sulfone) analog **4** showed a glass transition at 295 °C, and was soluble in THF, 1,4-dioxane, and DMSO. An excellent thermal stability of polymer **4** was exhibited by a TGA analysis, which showed that 5% weight loss occurred at 480°C.

Introduction

Recently, dendrimers and hyperbranched polymers have attracted much attention due to their unique structural characteristics and consequent novel properties.[1-3] Dendrimers are well-defined globular macromolecules with highly functionalized surface and monodispersity in size. However, laborious and iterative synthetic steps give rise to many practical difficulties in the synthetic process.[4-6] On the other hand, hyperbranched polymers, as an analog of dendrimers, are generally prepared by a direct polymerization of AB_x type monomers.[7-10] Therefore, there have been increasing interests in hyperbranched polymers because these polymers are expected to have globular structures with highly functionalized peripheral branch-end groups, although the hyperbranched structure is not as well-defined as that of dendrimers. In 1952, Flory predicted that AB_x type monomers, where x is 2 or greater, would produce highly branched polymers possessing one unreacted A functional group and (x-1)n+1 unreacted B functional groups at the periphery, where n is the degree of the polymerization.[11] However, these hyperbranched polymers have been rather neglected subjects until recently, in part due to their poor mechanical properties. Interests in hyperbranched polymers grew again after Kim and Webster reported on the hyperbranched polyphenylenes in 1990.[12,13] Furthermore, the functionalization of hyperbranched polymers can be performed in a number of ways using end-group modification. Hawker and Chu have reported the hyperbranched poly(ether ketone)s and their end-group functionalization which influences the solubility and glass transition behavior of hyperbranched polymers.[14] Frey *et al.* described the use of hyperbranched polyglycerols for the preparation of amphiphilic molecular nanocapsules for hydrophilic guests.[15] In addition, unimolecular micelle behavior is also observed in some amphiphilic hyperbranched polymers.[16]

Recently, we reported on the hyperbranched polymers based on the common structural skeleton, namely, 1,3,5-*s*-triazine moiety. The hyperbranched polyethynylenes, poly(benzyl ethers), and poly(ether ketones) were synthesized. In addition, their structural characteristics and unusual aggregation behavior of the amphiphilic hyperbranched polymers due to the triazine moiety also have been discussed.[17-19]

In this work, as a part of an effort described above, we report the synthesis of a hyperbranched poly(ether sulfone) with the heterocyclic 1,3,5-*s*-

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triazine moiety. Their structural characteristics and thermal properties are discussed.

Experimental

Materials. Cyanuric chloride, 4-bromodiphenyl ether, aluminum chloride, and magnesium turning from Aldrich were used as received. 4-Fluorobenzenesulfonyl chloride from Tokyo Kasei was used as received. THF was distilled from Na/benzophenone under N_2 prior to use. Other solvents, such as nitrobenzene, toluene, and DMF were purified by the procedure described in the literature.[20]

Equipment. ^1H (250 MHz) and ^{13}C NMR (56 MHz) spectra were obtained from a Bruker AC 250 spectrometer. Infrared spectra were recorded on an FTS-4 (Digilab) FT-IR spectrophotometer. Mass spectra were recorded on a VG Trio-2000 (Fisons Instrument) with EI ionization. Elemental analyses were performed on a CE instruments EA 1110 (CHNS/O). Molecular weights and molecular weight distributions were determined using a GPC (at 30 °C) equipped with a Waters Associates 410 RI detector, 510 HPLC pump and μ-Styragel columns with pore sizes of 10^2, 500, 10^3 and 10^4 Å. The eluent was THF and the molecular weights were calibrated with polystyrene standards. UV-VIS spectra were obtained using a Hewlett-Packard 8452A spectrophotometer. Glass transition temperatures were recorded on Perkin Elmer DSC 7 at a heating rate of 20 °C/min. Thermogravimetric analyses were performed under N_2 atmosphere on a PL-TGA (Polymer Laboratories) at a heating rate of 20 °C/min.

2,4-Dichloro-6-(4-phenoxyphenyl)-1,3,5-*s*-triazine (1). A THF solution (200 mL) of 4-phenoxyphenylmagnesium bromide (90 mmol) was added to a THF solution (200 mL) of cyanuric chloride (21.58 g, 120 mmol). The reaction mixture was stirred at -5 °C for 5 h. The solvent was removed at reduced pressure to obtain the crude product, which was then dissolved into methylene chloride, and washed with water. The organic layer was dried over anhydrous magnesium sulfate, and then evaporated. The product was recrystallized from methylene chloride/*n*-hexane. Yield 94%, mp=167-169 °C, UV (THF): λ_{max}=320 nm, MS: *m/z*=317, 319, 321, IR (KBr) 1245, 1486, 1522, 1607, 3015 cm^{-1}, ^1H NMR ($CDCl_3$) δ 7.04 (d, J=9.1 Hz, Ph-O-Ph- (o), 2H), 7.11 (d, J=8.1 Hz, Ph-O-Ph- (o), 2H), 7.23 (t, J=7.4 Hz, Ph-O-Ph- (1), 1H), 7.42 (t, J= 7.9 Hz, Ph-O-Ph- (2), 2H), 8.45 (d, J=9.1 Hz, Ph-O-Ph-triazine (m), 2H), ^{13}C NMR ($CDCl_3$) δ 117.5, 120.4, 124.9, 126.5, 130.1, 132.1, 154.9, 163.7, 171.7, 173.9, Anal. Calcd for $C_{15}H_9N_3OCl_2$ C, 56.63; H, 2.85; N, 13.21. Found C, 56.79; H, 2.90; N, 13.32.

2,4-Bis(4-methoxyphenyl)-6-(4-phenoxyphenyl)-1,3,5-*s*-triazine (2). A THF solution (150 mL) of compound **1** (17 g, 53.4 mmol) was added to a THF solution (300 mL) of 4-methoxyphenylmagnesium bromide (182 mmol). The reaction mixture was stirred at reflux for 10 h. After cooling to room temperature, the solvent was removed at reduced pressure. The crude product was dissolved in methylene chloride, and then washed with water. The organic layer was dried over anhydrous magnesium sulfate and evaporated. The product was column chromatographed with methylene chloride and *n*-hexane on a silica gel. Further purification was performed by recrystallization from methylene chloride/*n*-hexane. Yield 68%, mp=143-144 °C, UV (THF): λ_{max}=380 nm, IR (KBr) 1031, 1251, 1372, 1520, 1604, 2950, 3015 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.88 (s, CH_3O-Ph-, 6H), 7.02 (d, J=8.9 Hz, CH_3O-Ph- (o), 4H), 7.12-7.21 (m, Ph-O-Ph- (o), Ph-O-Ph- (o), and Ph-O-Ph- (1), 5H), 7.39 (t, J=7.9 Hz, Ph-O-Ph- (2), 2H), 8.67-8.75 (m, CH_3O-Ph-triazine (m), and Ph-O-Ph-triazine (m), 6H). ^{13}C NMR ($CDCl_3$) δ 55.4, 113.8, 117.9, 119.7, 124.0, 129.9, 130.7, 161.1, 163.3, 170.7. Anal. Calcd for $C_{29}H_{23}N_3O_3$ C, 75.47; H, 5.02; N, 9.11. Found C, 75.13; H, 5.26; N, 8.74.

2,4-Bis(4-hydroxyphenyl)-6-(4-(4-(4-fluorobenzenesulfonyl)phenoxy)phenyl)-1,3,5-*s*-triazine (3). A solution of compound **2** (3.0 g, 6.5 mmol) and 4-fluorobenzenesulfonyl chloride (1.77 g, 9.1 mmol) in nitrobenzene (20 mL) was added dropwise to a nitrobenzene solution (20 mL) of aluminum chloride (5.2 g, 39 mmol) at 0°C. The reaction mixture was stirred at 80°C for 8 h. After cooling to room temperature, the mixture was poured into dilute aqueous acid and washed with water. The solution was dried over anhydrous magnesium sulfate and the solvent was removed at reduced pressure. The product was column chromatographed

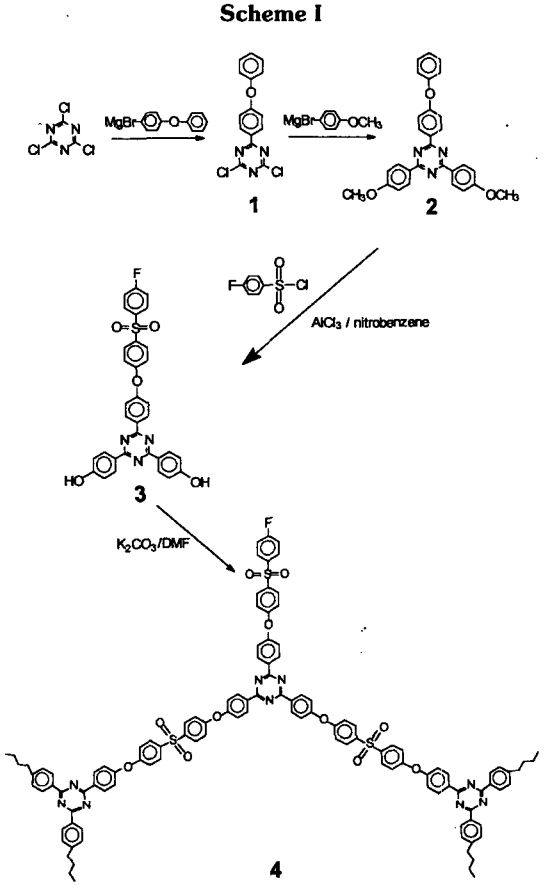
with THF and *n*-hexane on a silica gel. Further purification was performed by recrystallization from toluene/methanol to produce pale red crystal. Yield 20%, mp=303-305°C, UV (THF): λ_{max} =314 nm, MS: *m/z*=592. IR (KBr) 3422, 3015, 1608, 1438, 1318, 1240, 1106 cm^{-1}. ^1H NMR (DMSO-d_6) δ 6.96(d, *J*=8.8 Hz, HO-Ph- (o), 4H), 7.22 (m, -Ph-O-Ph- (o), 4H) 7.32 (t, F-Ph- (o), 2H), 7.98 (m, -Ph-SO_2-Ph- (o), 4H), 8.56 (d, *J*=8.8 Hz, HO-Ph-triazine (m), 4H), 8.75 (d, *J*=8.8 Hz, -Ph-O-Ph-triazine (m), 2H). ^{13}C NMR (DMSO-d_6) δ 115.7, 116.8, 117.2, 118.8, 120.0, 126.3, 130.2, 130.8, 132.4, 135.4, 137.8, 158.3, 160.7, 162.1, 166.8, 169.5, 170.4. Anal. Calcd for $C_{33}H_{22}N_3O_5FS$ C, 66.99; H, 3.75; N, 7.16; S, 5.42. Found C, 66.82; H, 3.96; N, 6.82; S, 5.47.

Hyperbranched Poly(ether sulfone) Analogue (4). A solution of AB_2 monomer **3** (1.26 g, 2.3 mmol) and potassium carbonate (0.59 g, 4.27 mmol) in DMF (15 mL) and toluene (10 mL) was stirred for 4 h at 140°C. Toluene was removed using a Dean-Stark apparatus and the reaction mixture was refluxed for 4 h. After cooling to room temperature, the reaction mixture was precipitated into dilute aqueous acid solution and neutral water. Further purification was carried out by repeated precipitation from THF into methanol. The polymer was filtered and dried to yield gray powder. Yield 70%; IR (KBr) 1241, 1366, 1440, 1498, 1519, 1592, 1651, 3070, 3372 cm^{-1}; ^1H NMR (THF-d_8) δ 6.92 (br, HO-Ph- (o)), 7.18 (br, F-Ph- (o), -Ph-O-Ph- (o)), 7.95 (d, *J*=8 Hz, -Ph-SO_2-Ph- (o)), 8.53 (br, HO-Ph- (m)), 8.72 (br, -O-Ph-triazine (m)), 10.06 (s, HO-Ph-); ^{13}C NMR (THF-d_8) δ 116.5, 118.8, 119.6, 120.5, 121.3, 127.2, 131.0, 131.9, 133.0, 133.5, 133.9, 137.9, 160.1, 161.7, 163.9, 171.2, 172.2.

Results and Discussion

The selective reactivity of three chlorine atoms on cyanuric chloride toward a variety of nucleophiles was found to provide synthetic versatility for AB_2 molecules and their one-pot polymerized hyperbranched polymers which contain 1,3,5-*s*-triazine units.[17-19] The AB_2 type triazine monomer for the hyperbranched poly(ether sulfone) was synthesized following the synthetic route described in Scheme I. The chlorine atoms of cyanuric chloride were sequentially substituted by 4-phenoxyphenyl and 4-methoxyphenyl groups to yield 2,4-bis(4-methoxyphenyl)-6-(4-phenoxyphenyl)-1,3,5-*s*-triazine (**2**). The AB_2 monomer **3** was prepared by the sulfonylation of **2** with 4-fluorobenzenesulfonyl chloride and the deprotection of the methoxy groups in the presence of aluminum chloride. At first, we tried to prepare an AB_2 monomer, 2,4-bis(4-hydroxyphenyl)-6-(4-(4-fluorobenzenesulfonyl)phenoxy)-1,3,5-*s*-triazine by the sulfonylation of 2,4-bis(4-methoxyphenyl)-6-phenyl-1,3,5-*s*-triazine. However, the sulfonylation on the phenyl ring of 2,4-bis(4-methoxyphenyl)-6-phenyl-1,3,5-*s*-triazine was not successful due to the electron-withdrawing characteristics of the triazine ring. Therefore, 4-phenoxyphenyl unit was introduced, instead, of the phenyl group on the triazine ring.[18]

Scheme I



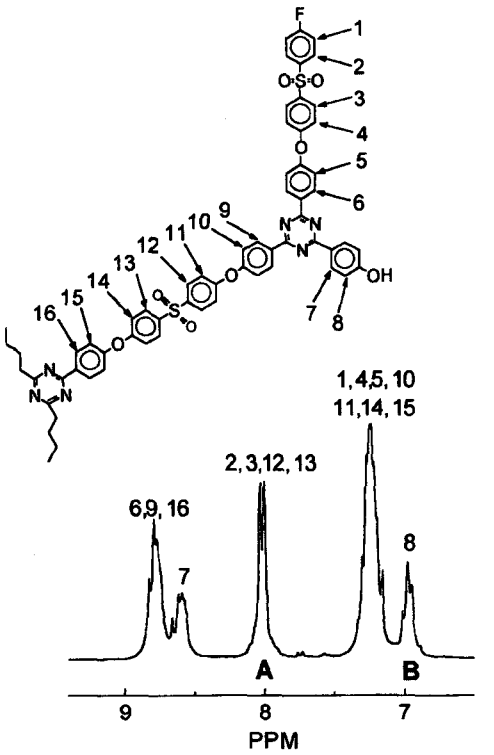


Figure 1. ^{1}H NMR spectrum of polymer **4** in THF-d_8.

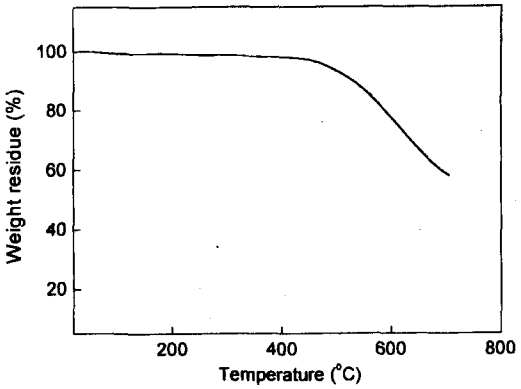


Figure 2. TGA thermogram of polymer **4**.

The one-pot polymerization of the AB_2 monomer **3** was carried out in DMF in the presence of potassium carbonate to yield hyperbranched polymer **4**. The polymer was soluble in THF, 1,4-dioxane, and DMSO, but insoluble in other organic solvents such as acetone, methylene chloride, DMF, and NMP. The molecular weight of the polymer estimated by GPC was $M_n = 5200$ with $M_w/M_n = 2.0$. When the polymerization time was increased to increase the molecular weight, insoluble product was obtained. Structural characterization was carried out by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. In particular, the ^{1}H NMR spectrum of polymer **4** in Figure 1 provided an information on the molecular weight of the hyperbranched poly(ether sulfone) **4**. Peak A was generated by the protons which are ortho to the sulfonyl groups, and peak B from the protons which are ortho to the peripheral hydroxyl units. Thus, the integration ratio of peak B to A equals (2n+2)/4n, where n is the degree of polymerization. From this ^{1}H NMR analysis, the M_n value of the polymers **4** was evaluated to be 4800.

This hyperbranched polymer **4** showed a glass transition at 295°C. Crystallinity was not observed by DSC or optical polarizing microscope. The excellent thermal stability of polymer **4** is shown in Figure 2. Thermogravimetry analysis showed that a 5% weight loss occurred at approximately 480°C and 10% loss at 530°C. The overall char yield after heating to 700°C was approximately 58%.

Conclusions

Hyperbranched poly(ether sulfone) analogs with the 1,3,5-s-triazine moiety were prepared by the direct polymerization of AB_2 type triazine monomers. The hyperbranched poly(ether sulfone) with triazine ring was soluble in THF, 1,4-dioxane, and DMSO and showed a glass transi-

Table I. Polymerization of AB_2 Monomer 3

Polymer	Time (h)	Yield (%)	M_n		M_w/M_n[a]	DP_n
			GPC[a]	^{1}H NMR[b]		
4	6	70	5200	4800	2.0	9

[a]GPC values with polystyrene standards. [b]Calculated from ^{1}H NMR spectra.

tion at 295 °C. An excellent thermal stability was exhibited by a TGA analysis, which showed that 5% weight loss occurred at about 480°C. The selective reactivity of three chlorine atoms of cyanuric chloride provided an opportunity for a systematic synthesis of a variety of AB_2 type monomers and their hyperbranched polymers.[17-19]

Acknowledgement. This work was supported by Korea Science and Engineering Foundation (981-1110-056-2).

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