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Hyperbranched poly(arylene ether phosphine oxide)s

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Summary

New AB_2 and A_2B monomers, bis(4-fluorophenyl)-4'-hydroxyphenylphosphine oxide and bis(4-hydroxyphenyl)-4'-fluorophenyl-phosphine oxide were prepared and converted to corresponding hyperbranched poly(arylene ether phosphineoxide)s with hydroxyphenyl and fluorophenyl end functional groups. While the dihydroxy monomer gave a low molecular weight polymer, the difluoro monomer produced a high molecular weight hyperbranched polymer. The glass transition temperature of the obtained polymers was 266°C and 230°C, and 5% weight loss temperature was 491 °C and 391 °C, respectively. The fluorophenyl-terminated hyperbranched polymer was soluble in $CHCl_3$, but the hydroxyphenyl-terminated polymer was not soluble in CHCl3 even though it has lower molecular weight than the fluorophenyl-terminated polymer, indicating that properties of the hyperbranched polymers markedly depend on end functional groups as well as their molecular weight.

Introduction

Dendrimers and hyperbranched polymers have attracted considerable attention recently owing to their highly branched, globular structure and consequent novel properties [1-4]. While dendrimers require careful multistep synthesis, hyperbranched polymers are easily obtained by one step polymerization of AB_x type monomer that produce highly branched structures containing a large number of chain end functional groups - one unreacted A functional group and (x-1)n + 1 unreacted B functional groups, where n is degree of polymerization [5]. These large number of chain end functional groups present in hyperbranched polymers significantly affect physical properties of polymers such as glass transition temperature and solubility [6-8].

It has been reported that hyperbranched poly (aryl ether)s [9-12] could be obtained through nucleophilic aromatic substitution between aromatic halide group and phenol group in AB_x type monomer. In this polymerization, aryl halide is activated toward a substitution by an electron-withdrowing group such as sulfone, ketone, imide and heterocycles. Phosphine oxide [13-14], which is also known as an effective activating group in nucleophilic aromatic substitution has three more valence bonds that make it

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ideal for a trifunctional structure of AB_2 type monomer. In addition, phosphorus-incorporated polymers are known to have flame retardance and oxygen plasma resistance [15-16].

In this paper, we report the synthesis of two new AB_2 and A_2B type monomers and corresponding fluorophenyl-terminated and hydroxyphenyl-terminated hyperbranched poly(arylether phosphine oxide)s. These monomers contain one hydroxyphenyl group and two fluorophenyl or two hydroxyphenyl groups and one fluorophenyl group, respectively. In both cases, the aryl fluoride is activated toward nucleophilic aromatic substitution by phosphine oxide moiety. The effect of chain end functional groups on the physical properties and structures of the hyperbranched poly(arylether phosphine oxide)s is also investigated.

Experimental

Monomer synthesis

Bis(4-fluorophenyl)-4'-methoxyphenylphosphine(**2**) To a flame dried 3-neck round bottom flask fitted with nitrogen inlet were added 2.94g(0.121 mol) of magnesium turnings and 50ml of dry THF. To this solution was added dropwise 12ml(0.109mol) of 4-bromofluorobenzene at 0°C and this solution was stirred at room temperature overnight to give slightly cloudy gray solution. 10.4g(0.0497mol) of dichloro-4-methoxyphenylphophine **1** [17] was added dropwise at 0°C and the solution was stirred overnight at room temperature. The mixture was quenched with enough amount of 10% aqueous H_2SO_4 solution and water, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered, and concentrated in *vacuo* to give yellow liquid. The crude product was purified by column chromatography on silica gel with n-hexane to give colorless clear oil(12.9g, 79% yield) : FTIR (NaCl, cm^{-1}) : 3063(Ar-H), 2836(O-CH_3), 1588, 1494(Ar C=C), 1461(P-Ar), 1159(Ar-F). ^{1}H NMR(200MHz, chloroform-*d*) δ 7.30-7.19(m, 6H),7.02(t, 4H), 6.91(d, 2H), 3.80(s, 3H). ^{13}C NMR(50MHz, chloroform-*d*) δ 163.22(d,J_{C-F}=247Hz,2C), 160.51(s,1C), 135.34(dd,J_{C-P}=11.4,J_{C-F}=8.8Hz, 4C), 134.97(d,J_{C-P}=11.3Hz, 2C), 133.10(d,J_{C-P}=105Hz, 2C), 127.29(d,J_{C-P}=107HZ, 1C), 115.66(dd,J_{C-P}=20.7,J_{C-F}=7.4Hz, 4C), 114.38(d,2C), 55.10(s, 3C) ^{31}P NMR(121MHz, chloroform-*d*) : δ -8.79.

Bis(4-fluorophenyl)-4'-methoxyphenylphosphine oxide (**3**) To aqueous $KMnO_4$(2.48g, 0.0157mol in 130ml H_2O) solution was added 4.93g(0.015mol) of bis(4-fluorophenyl)-4'-methoxyphenylphosphine **2** and the solution was stirred at room temperature for 12hr. The mixture was extracted by chloroform, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give yellow oil. The crude product was purified by column chromatography to give colorless clear oil(4.75g, 92% yield) : FTIR (NaCl,cm^{-1}) : 3067(AR-H), 2841(O-CH_3), 1594, 1500(Ar C=C), 1462(P-Ar), 1179(P=O), 1161(Ar-F). ^{1}H NMR(200MHz, chloroform-*d*) : δ 10.29(s, 1H), 7.69-7.57(m,4H), 7.44-7.31(m,6H), 6.90(dd,2H). ^{13}C NMR(50MHz, chloroform-*d*) : δ 164.98(dd,J_{C-F}=252, J_{C-P}=3.2Hz, 2C), 162.68(d, J_{C-P}=2.8Hz, 1C), 134.38(dd,J_{C-P}=11.4, J_{C-F}=8.8Hz, 4C), 133.76(d,J_{C-P}=11.3Hz, 2C), 129.78(dd,J_{C-P}=103.8,J_{C-F}=3.3, 2C), 124.02(d, J_{C-P}=111.6Hz, 1C), 115.64(dd,J_{C-F}=23.5,J_{C-P}=13.2Hz, 4C), 114.34(d,J_{C-P}=13.2Hz, 2C), 55.30(s, 3C). ^{31}P NMR (121MHz, chloroform-*d*) : δ 28.34.

Bis(4-fluorophenyl)-4'-hydroxyphenylphosphine oxide (**4**) A solution of 5.06g (14.7mmol) of bis(4-fluorophenyl)-4'-methoxyphenyl-phosphine oxide **3** in 150ml CH_2Cl_2 was cooled to -78°C and 30ml of 1M BBr_3 was added over a period of 30min. The resulting mixture was stirred at room temperature for 24hr and quenched by cautiously pouring into 800ml ice/water. The mixture was heated until the organic solvent completely evaporated. The aqueous layer was extracted with 800ml of ethyl acetate, dried over $MgSO_4$, filtered, and concentrated in *vacuo* to give white solid. Recrystallization from ethyl acetate gave 3.98g(82% yield) of pure bis(4-fluorophenyl)-4'-hydroxyphenylphosphine oxide **4** : M.P.: 224-225°C. FTIR (KBr, cm^{-1}) : 3444(br, Ar-OH), 3061(Ar-H), 1591, 1500(Ar C=C), 1434(P-Ar), 1179(P=O), 1164(Ar-F). ^1H NMR (200MHz, DMSO-*d6*) δ 7.80-7.67(m,4H), 7.54(dd, 2H), 7.36(td, 4H), 6.98(dd, 2H). ^{13}C NMR(75MHz, DMSO-*d6*) : δ 164.32(dd,J_{C-F}=249,J_{C-P}=3.3Hz, 2C), 161.04(d,J_{C-P}=2.9Hz,1C), 134.47(dd, J_{C-P}=11.3,J_{C-F}=8.93Hz, 4C), 133.70(d,J_{C-P}=11.3Hz, 2C), 130.31(dd,J_{C-P}=105,J_{C-F}=3.23Hz, 2C), 121.89(d, J_{C-P}=112Hz, 1C), 116.27(dd,J_{C-F}=23.5,J_{C-P}=13.2, 4C), 115.82(d,J_{C-P}=12.8Hz, 2C). ^{31}P NMR (121MHz, DMSO-*d6*) : δ 24.25

Bis(4-methoxyphenyl)-4'-fluorophenylphosphine oxide (**5**) : To a flamed dried 3-neck round bottom flask fitted with nitrogen inlet were added 1.235g(0.051mol) of magnesium turnings and 30ml of dry THF. To this solution was added dropwise at 0°C 5.5ml(0.044mol) of 4-bromo-anisole and the mixture was stirred at room temperature overnight to give slightly cloudy black solution. The mixture was added dropwise to a solution of 2ml (0.022mol) phosphorus oxychloride in 10ml dry THF at 0°C through cannula, and then stirred at room temperature for 5hrs. This solution was filtered and concentrated in *vacuo* to give crude liquid, phosphinic chloride. To a solution of crude bis(4-methoxyphenyl)phosphinic chloride in 10ml dry THF was added dropwise at 0°C through cannula 4-fluorophenylmagnesium bromide, which had been previously prepared from 0.6g(0.0247mol) of magnesium turnings and 2.5ml(0.0228mol) of 4-bromofluorobenzene in 20ml THF. Then, the reaction mixture was allowed to stir at room temperature overnight. The mixture was quenched with enough amount of 10% aqueous sulfuric acid solution, and then extracted with CH_2Cl_2,dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel(n-hexane : ethyl acetate = 1 : 1) to give colorless viscous liquid(3.65g, 45% yield). FTIR (NaCl, cm^{-1}) : 2839(O-CH_3), 1597, 1503(Ar C=C), 1460(P-Ar), 1178(P=O) ^1H NMR(200MHz, chloroform-*d*) : δ 7.67(m, 6H), 7.05(td, 2H), 6.92(dd, 4H), 3.81(s, 6H) ^{13}C NMR(50MHz, chloroform-*d*) : δ 164.96(d, J_{C-F}=252Hz, 2C), 162.64(d,J_{C-P}=2.75Hz, 1C), 134.53(dd,J_{C-P}=11.4,J_{C-F}=8.73Hz, 2C), 133.92(d,J_{C-P}=11.4Hz, 4C), 128.87(d,J_{C-P}=103.4Hz, 2C), 123.13(d,J_{C-P}=111Hz, 1C), 115.80(dd,J_{C-F}=21.2Hz,J_{C-P}=13.2Hz, 2C), 114.17(d,J_{C-P}=13.2, 4C), 55.35(S, 6C) ^{31}P NMR(121MHz, chloroform-*d*) : δ 29.7

Bis(4-hydroxyphenyl)-4'-fluorophenylphosphine Oxide (**6**) A solution of 2.2g(6.18 mmol) of bis(4-methoxyphenyl)-4'-fluorophenyl-phosphine oxide **5** in 25ml CH_2Cl_2 was cooled to -78°C and 2.8ml(30mmol) of BBr_3 was added over a period of 30min. The resulting mixture was stirred at room temperature for 24hr and quenched by cautiously pouring into 400ml ice/water. The mixture was heated until the organic solvent completely evaporated. The aqueous layer was extracted with 100ml portions of ethyl acetate, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography to give white solid (1.64g, 82% yield) : M.P. : 230-

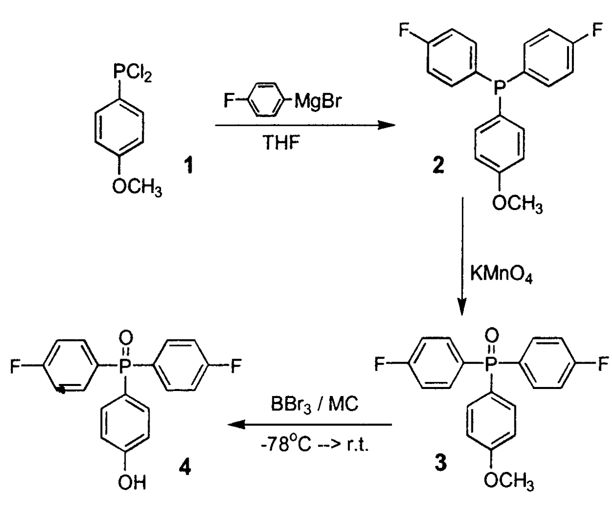
231°C. FTIR (KBr, cm^{-1}) : 3360(br, Ar-OH), 1601, 1504(Ar C=C), 1437(P-Ar), 1161(Ar-F). ^{1}H NMR(200MHz, DMSO-*d6*) : δ 10.19(s,2H), 7.65-7.53(m,2H), 7.41-7.29(m,6H), 6.87(dd,4H). ^{13}C NMR(75MHz, DMSO-*d6*) : δ 163.99(dd,J_{C-F}=250,J_{C-P}=3.1Hz, 2C), 160.59(d,J_{C-P}=2.8HZ, 1C), 133.88(dd, J_{C-P}=11.0,J_{C-F}=8.7Hz, 2C), 133.18 (d,JC-P=11.1Hz, 4C), 129.96(dd,J_{C-P}=104.7,J_{C-F}=3.3Hz, 1C), 121.50(d,J_{C-P}=111Hz, 2C), 115.62-114.94(m, 6C). ^{31}P NMR(121MHz, DMSO-*d6*) : δ 26.68.

Polymerization

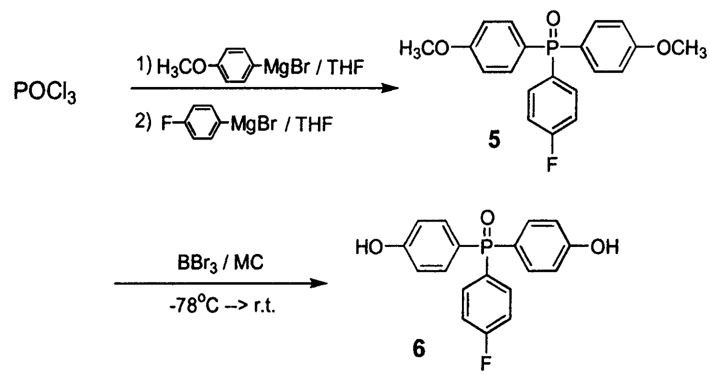
AB_2 and A_2B monomers, **4** and **6**, were polymerized in NMP with K_2CO_3 as a base at 170°C. A representative procedure is as follows. (**PEPO1**): A 25ml three-neck flask fitted with an overhead stirrer and Dean stark trap was charged with 0.50g(1.60mmol) of bis(4-fluorophenyl)hydroxyphenylphosphine oxide **4** and 0.44g(3.20mmol) of K_2CO_3. The polymer concentration was controlled to approximately 25 wt% in N-methylpyrrolidinone(NMP) and small amount of toluene was added to effect the azeotropic removal of water. The mixture was stirred and heated to 140°C, at which toluene was collected and removed from the system. The temperature was maintained for 4hr, and more toluene was periodically added and subsequently collected and drained from the trap. The mixture was then heated to 170°C for 4hr. After that, the mixture was allowed to cool, diluted with 4ml of NMP, and then poured into 300ml water. The solid precipitate was washed MeOH and dried overnight at 100°C in *vacuo*.

Results and discussion

As shown in Scheme 1, bis(4-fluorophenyl)-4-hydroxyphenylphosphine oxide **4** was synthesized through Friedel-Crafts reaction of anisole with PCl_3 in the presence of catalytic amount of anhydrous $SnCl_4$ (**1**), followed by Grignard reaction (**2**), $KMnO_4$ oxidation (**3**), and demethylation with BBr_3. The synthesis of the reversed A_2B type monomer, bis(4-hydroxyphenyl)-4-fluorophenylphosphine oxide **6** was accomplished by successive reactions of the two Grignard reagents, 4-methoxyphenylmagnesium bromide and 4-fluorophenylmagnesium bromide, with phosphorus oxychloride, followed by demethylation with BBr_3 (Scheme 2).

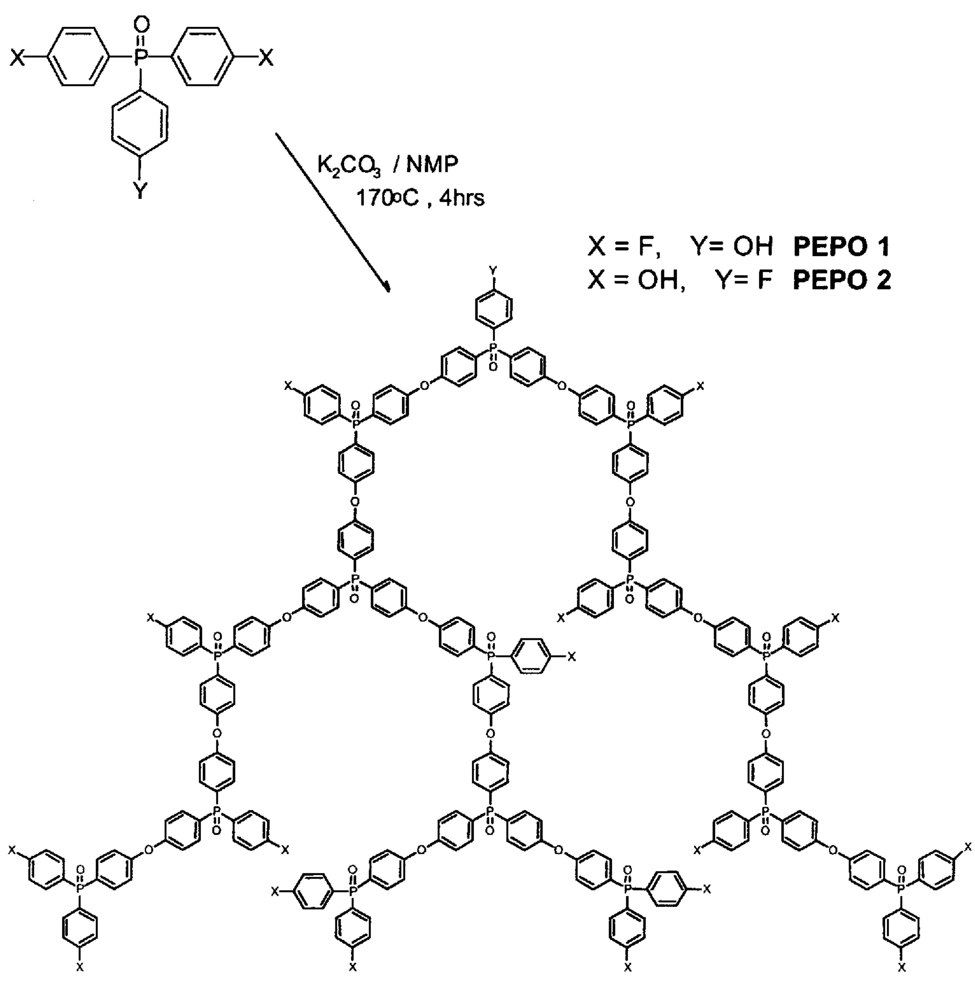


Scheme 1. Preparation of AB_2 difluoro monomer



Scheme 2. Preparation of A2B dihydroxy monomer

The polymerizations were carried out in N-methylpyrrolidone with K_2CO_3 as a base at 170°C for 4hrs as depicted in Scheme 3.



Scheme 3. Preparation of Hyperbranched Polymers

The obtained polymers were purified by precipitation from NMP into water. The recent attempt [18] of the polymerization of AB_2 monomer produced only low molecular weight, but the polymerization of monomer in this study gave a high molecular weight hyperbranched polymer judging from the viscosity, 0.44 (Table 1).

The prolonged polymerization of the monomer yields insoluble product presumably due to the intermolecular reaction. However, the polymerization of A_2B monomer at the same polymerization condition produced relatively low molecular weight polymer ([η]=0.15) due to the premature precipitation during polymerization. The structural characterization was carried out by spectroscopic methods such as ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy.

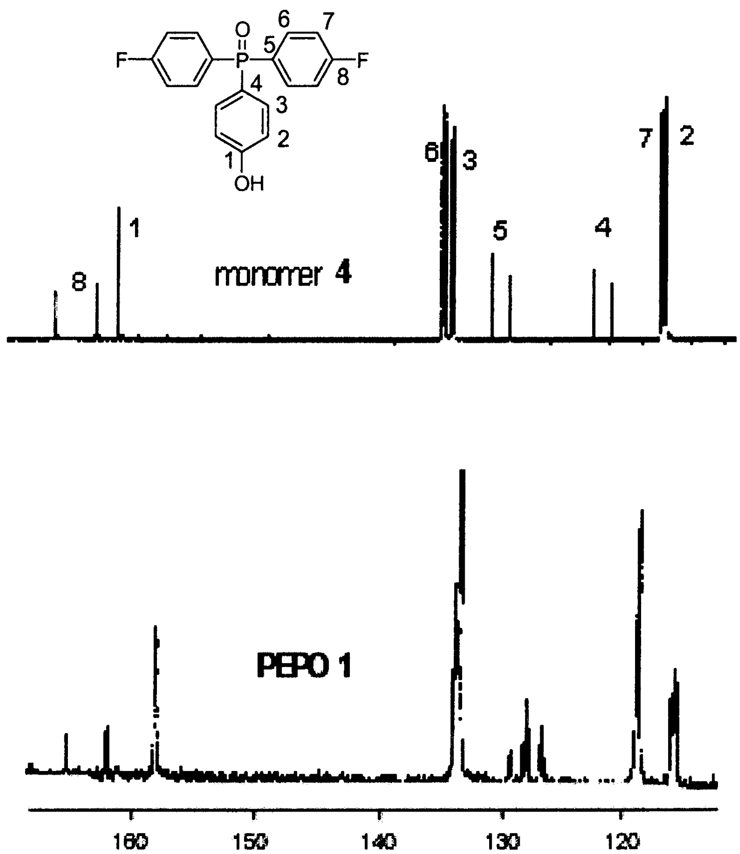


Fig. 1. ^{13}C NMR spectra of monomer **4** and polymer **PEPO 1** in DMSO-d_6

^{13}C NMR spectra of monomers showed characteristic resonance of ipso carbon of fluoride group at 164.3 ppm (dd, $J_{C\text{-}F}$=249,$J_{C\text{-}P}$=3.3Hz) in monomer **4** and at 164.0 ppm (dd,$J_{C\text{-}F}$=250,$J_{C\text{-}P}$=3.1Hz) in monomer **6**, respectively. As polymerization proceeded, substitution of fluoride groups with phenoxide moieties increased the population of aryl ether linkage and decreased that of fluorophenyl groups (**PEPO 1**), which were confirmed by ^{13}C NMR spectra of monomer **4** and polymer **PEPO 1** (Fig. 1).

The hyperbranched polymers with two different end group, hydroxyphenyl or fluorophenyl, exhibited quite different solubility behavior. While the fluorophenyl-terminated hyperbranched polymer **PEPO 1** was soluble in $CHCl_3$, the hydroxyphenyl-terminated hyperbranched polymer **PEPO 2** was not soluble in $CHCl_3$, but soluble in basic aqueous solutions such as K_2CO_3 or 10% NaOH aqueous solution. However, both polymers were also soluble in aprotic polar solvents such as DMSO, DMF and NMP. These solubility behavior of the two polymers clearly showed that the properties of hyperbranched polymers markedly depend on the end functional groups.

Table 1. Hyperbranched Poly(arylene ether phosphine oxides)

POLYMER	$[\eta]^{(a)}$ dL/g	$T_g^{(b)}$ (°C)	$T_d^{(c)}$ (°C)	THF	$CHCl_3$	10% NaOH	DMSO	NMP(d)
PEPO 1	0.44	266	491	X	O	X	O	O
PEPO 2	0.15	230	391	X	X	O	O	O

(a) Intrinsic viscosity was measured in NMP at 25°C.
(b) Measured by DSC at heating rate of 10°C/min.
(c) Temperature at which 5% weight loss occurred at heating rate of 10°C/min..
(d) Soluble : O , Insoluble : X

Thermal behavior of the polymers was studied with TGA and DSC. The fluorophenyl-terminated hyperbranched polymer **PEPO 1** had T_g of 266°C, while the hydroxyphenyl-terminated hyperbranched polymer **PEPO 2** had T_g of 230°C(Fig. 2). 5% weight loss temperature of polymers indicates that the thermal stability of the hydroxyphenyl-terminated polymer is lower than that of fluorophenyl-terminated hyperbranched polymer due to the lower thermal stability of the terminal hydroxy groups as well as its low molecular weight.

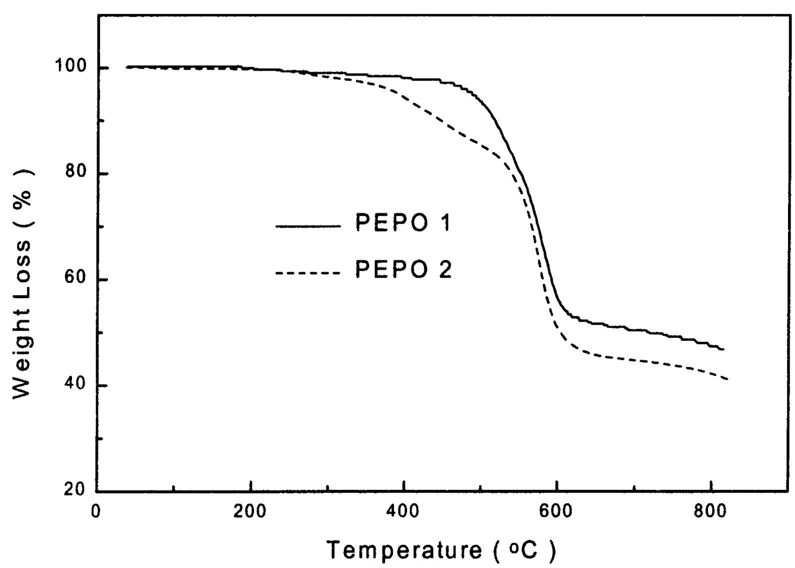


Fig. 2. TGA thermogram of hyperbranched poly(arylene ether phosphine oxide)s

In summary, two types of hyperbranched poly(aryl ether)s containing phosphine oxide were synthesized. While the polymerization of AB_2 monomer **4** produced a high molecular weight polymer, the A_2B monomer **6** with two hydroxy groups gave a relatively low molecular weight polymer due to the poor solubility of corresponding phenoxide salt. It seems that the choice of the A and B groups in the starting monomer significantly affects not only the polymerization but also the physical properties of the corresponding hyperbranched poly(aryl ether phosphine oxide)s.

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