Convergent Synthesis of Polyimide Dendrimers from an ABB' Type Intermediate

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Introduction:

Dendritic polymers have many interesting and desirable physical characteristics that are needed in their linear counterparts. Particularly, they often exhibit low viscosity and high solubility in high molecular weights which could be advantageous during their processing[1-4]. However, most if not all of the synthetic approaches leading to the dendritic polymers are cumbersome and could not give high yields with structural consistency especially in high generations [5]. This shortcoming is particularly true for the prior syntheses of dendritic polyimdes (PIs)[6], although their physical properties do show some desirable attributes over the linear PIs.

In this study, we have designed and prepared an unsymmetrical ABB' intermediate, 4-(2,4-diaminophenoxy)phthalic acid ethyl esters (DAPPAcE), in high yield shown in Scheme 1, and uses it as the building block to construct each PI dendritic generation. Moreover, the two simple essential synthetic reactions were straightforward in our dendritic PI construction which involved addition of diamino groups of DAPPAcE to an anhydride rings (Step 1) first followed by a thermal imidization step (Step 2) leading to imide-anhydride formation, [G-X][A] . This two-step convergent strategy is simple, efficient and quite versatile for syntheses of three generations of PIs such as [G-X][A].

Results and Discussion:

A typical transformation of this convergent synthesis was carried out in dimethyl acetamide (DMAc) at room temperature for step 1 and at 170℃ in butryric anhydride for step 2. The IR absorption changes from an anhydride showing the disappearance of the initial absorptions at 1850 cm^{-1} into those of imide groups at 1778, 1726, 1367 and 718cm^{-1} is exemplified in Fig 1. These IR absorption changes were used as convenient monitoring for the synthesis. In general, the step 1 and 2 were run consecutively and the highly pure dendritic imide-anhydride intermediates [G-X][A] could then be obtained in the second step as a precipitate in about 80% for the two steps from the solution and ready for the construction of the next PI synthesis sequence (see Scheme 2). The imide-anhydrides in [G-X][A] can also be terminated with aniline to form three generations of nearly pure PI-dendrimers from the solution in 93% yield ([G-X][B]) by the anhydride treatment at 170℃(Step 3).

As indicated in Table 1, all generations of imide-anhydrides [G-X][A] and dendritic PIs [G-X][B] (where x=1~3) synthesized possess good solubility and can be dissolved in polar solvents such as NMP, DMSO, DMAc or DMF readily at room temperature (~25℃) and in THF or chloroform with a slight heating to about 40~45℃.

Three generations of [G-X][B] showed PDI of 1.02,1.04 and 1.07 (Table 2) for [G-1][B],[G-2][B],and [G-3][B] of PI dendrimers, respectively. From Table 3, the thermal analysis data indicates that T_g (DSC) and T_d (TGA) of [G-X][A] and [G-X][B] both increased with increasing molecular weight or generations, but the all imdie dendrimers [G-X][B] do outperform those of respective counterpart [G-X][A] due to the presence of the hydrolytic sensitive anhydride groups in the latters. T_d of [G-3][B] is the highest in this study, which reaches 414℃(5%wt loss) and 440℃(10% wt loss) with a T_g of 132.3℃.

Conclusion:

We have synthesized a versatile ABB' polymer intermediate,DAPPAcE, in high yield for the construction of PI dendrimers. Through two-step reaction involving ring-opening of anhydride with DAPPAcE followed by a imidization with butyric anhydride, each dendritic products,[G-X][B] and [G-X][A], could be isolated in greater than 80% from the reaction solvent by precipitation. All synthesized dendrimers showed great thermal stability and high solubility. We are now extending this convergent strategy toward syntheses of PI dendrimers with peripheral functional groups such as anilines.

Reference

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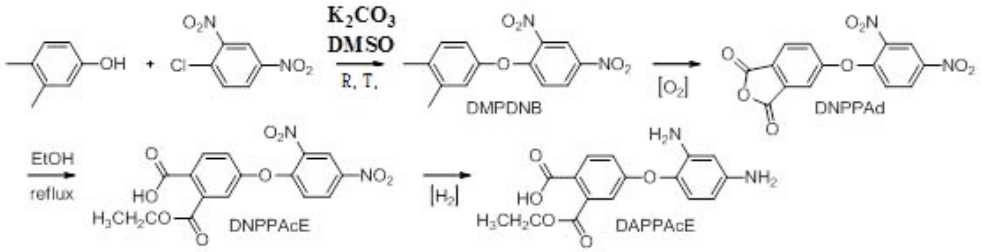
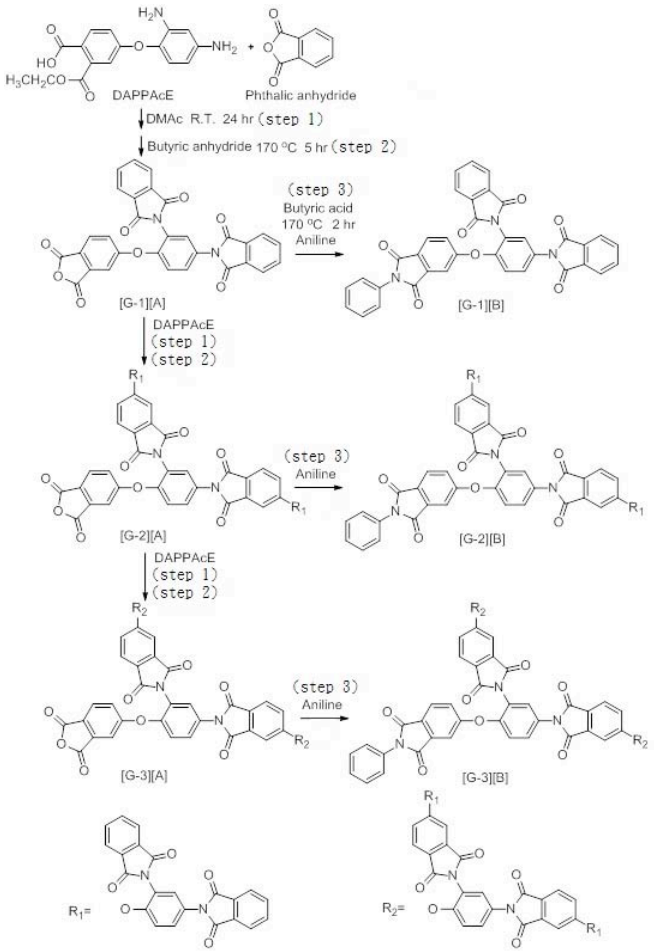


Scheme 1. Synthesis and structures of hyperbranched ABB'poly(ether imide)intermediates.



Scheme 2. Synthesis and structures of Polyimide Dendrimers.

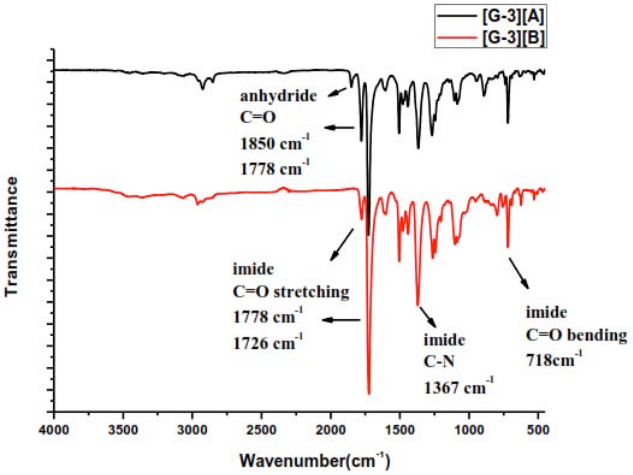


Figure 1. The FTIR analysis of [G-3] [A] and [B]

Table 1. [G-X] [B] (X = 1,2, and 3) of the solubility analysis

	solvent							
	NMP	DMSO	DMAc	DMF	$CHCl_3$	THF	Toluene	Methanol
[G-1][B]	++	++	++	++	++	++	+−	−−
[G-2][B]	++	++	++	++	++	++	+−	−−
[G-3][B]	++	++	++	++	++	++	+−	−−

++ : soluble at room temperature +− : soluble at hot solvent −− : insoluble C : 0.01 g/mL

Table 2. [G-X] [B] (X = 1,2, and 3) of the GPC analysis

[G-X][B]	Mn	Mw	PDI	%Area
[G-1][B]	554	562	1.02	90.89
[G-2][B]	570	595	1.04	92.82
[G-3][B]	577	615	1.07	91.63

Table 3. [G-X] [A], [B] (X = 1,2, And 3) of the thermal properties analysis

	T_g[a] (℃)	T_5[b] (℃)	T_{10}[c] (℃)
[G-1][A]	94.4	390	413
[G-1][B]	111.8	421	444
[G-2][A]	116.9	385	413
[G-2][B]	124.8	412	437
[G-3][A]	122.2	383	413
[G-3][B]	132.3	414	440

a : Determined by DSC at a heating rate of 10℃/min in nitrogen on second heating

b: T_5 (5 wt % loss temperature) was determined by TGA at a heating rate of 10℃/min

c: T_{10} (10 wt % loss temperature) was determined by TGA at a heating rate of 10℃/min