Preparation of Hyperbranched Polyimides from Tri(phthalic acid methyl ester) and 1,4-Phenylene Diamine

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Dendrimers and hyperbranched polymers, which have been termed as 'dendritic polymers' now, are of interest for many researchers in recent years due to their unique characteristic of low solution viscosity, low density and excellent solubility despite of their comparable high molecular weight. These characteristics are mainly derived from their intrinsic highly branched structure, globular shape and entanglement-free status to a certain extent.

Aromatic polyimides are one of the most important high performance polymers due to their outstanding thermal stability, mechanical strength and dielectric characteristic. Synthesis and properties of hyperbranched polyimides from AB_2 monomers have already reported in literatures.[1] Recently, polymerizations of A_2 and B_3 monomers were also attempted to form hyperbranched polyimides.[2] However, the polymerization of A_2 and B_3 monomers essentially results in gelation over a certain conversation of functional groups. Insoluble polyimides were actually isolated from the polymerization of A_2 and B_3 monomers except for the case of fluorinated ones.[2] To overcome the intrinsic problem, we tried a direct polycondensation involving of *in-situ* activation of a B_3 monomer to synthesize A_2+B_3 type hyperbranched polyimides.

Considering the thermal stability of resulted polymers, we have designed a new B_3 monomer, i.e. isomeric tri(phthalic acid methyl ester)s, as shown in Scheme 1. 1,3,5-Benzenetriol and 4-nitrophthalonitrile were allowed to react through nucleophilic substitution in the presence of potassium carbonate to give 1,3,5-tri(3,4-dicyanophenoxy)benzene(**1**). Then basic hydrolysis reaction successfully converted the compound (**1**) to 1,3,5-tri(3,4-dicarboxylphenoxy)benzene(**2**). Subsequent dehydration reaction of compound (**2**) afforded 1,3,5-tri(3,4-dicarboxylic anhydride phenoxy)benzene(**3**). The tri(phthalic anhydride) (**3**) was reacted with methanol to give isomeric mixture of tri(phthalic acid methyl ester) (**4**). The new B_3 monomers are characterized by using of ^{1}H NMR, ^{13}C NMR, IR and elemental

analysis. The monomer (4) contains isomers of *p*- and *m*-methyl esters (*p-p-p, p-p-m, p-m-m, m-m-m*). The overall ratio of *m*- and *p*-methyl ester was estimated to be about 3:1.

As shown in Scheme 2, the polymerization of the tri(phthalic acid methyl ester) (4) and 1,4-phenylene diamine in the presence of condensation agent gives poly(amic acid methyl ester)s (**PAAMEs**) precursors. After isolation, **PAAMEs** were end-capped with 4-toluidine by adopting the same reaction conditions as the precursor synthesis to afford 4-toluidine end-capped poly (amic acid methyl esters) (**TE-PAAMEs**). **TE-PAAMEs** were then converted into 4-toluidine end-capped polyimides (**TEPIs**) by cyclodehydration in the presence of acetic anhydride and pyridine.

The polymerization conditions and results of tri(phthalic acid methyl ester) (B_3) and 1,4-phenylene diamine (A_2) are summarized in Table 1. It is noted that the A_2+B_3 polymerization could successfully achieve high molecular weight and soluble polymers as the monomer concentration was below 0.11g/ml. A weight average molecular weight ranging from 33,600 to 125,000 was achieved for this polymerization approach. It was pointed by Flory that the A_2+B_3 polymerization in 1:1 mol statistically results in gelation over a certain conversation of functional groups.[3] This prediction is based on the exclusive reactivity between functional group A and B during polymerization. However in our case, the starting B_3 monomer is inactive in its original form and the condensation agent are necessary for the polycondensation. The polymerization includes *in-situ* activation of carboxyl groups of the B_3 monomers by DBOP,[4] which affords two kind of intermediates sequentially. Due to the reactivity difference of the intermediates, the oligomer with low dendritic content might be formed at the early stage of polymerization, which causes the deviation of this work from Flory's ideal A_2+B_3 polymerization toward gelation.

The **PAAMEs**, **TE-PAAMEs** and **TEPIs** were soluble in DMAc, DMF, DMSO and NMP at ambient temperature. The solutions of **TE-PAAMEs** in NMP or DMAc could pass the filter with 0.2μm diameter mesh and no gel portion was observed. The thermal properties of the hyperbranched polyimides by chemical imidization were investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA). Their glass trasition temperatures by DSC ranges from 212 to 235°C and 5%

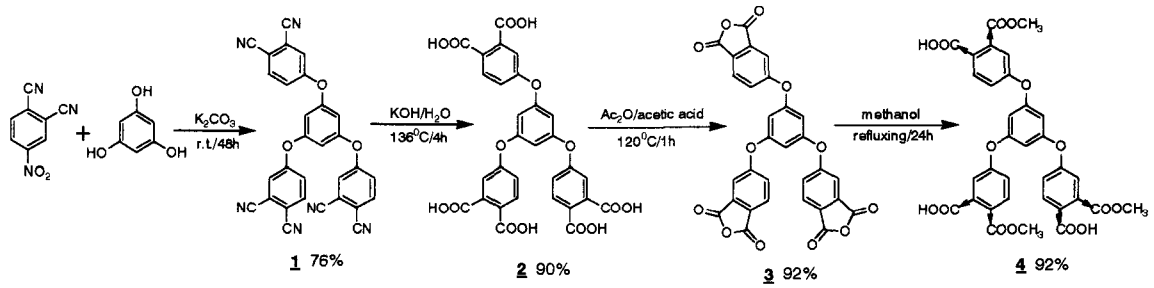
weight loss temperatures of films by TGA are around 480-500°C.

Hyperbranched polymers are generally unsuitable for the preparation of self-standing films due to lack of chain entanglements. This certainly limits their application as bulk materials. Hyperbranched polyimide films from **TE-PAAMEs** were successfully prepared by casting the DMAc solutions onto glass plates upon heating. The transparent yellow films from **TE-PAAMEs** were flexible, tough and with smooth appearance. As concerns about the brittleness of the AB_2 type hyperbranched polyimide films having the similar chemical structure, one can recognize the existence of entanglement in hyperbranched polyimides prepared by A_2+B_3 approach. It is interesting to note that **TE-PAAMEs** with relatively low inherent viscosity could also afford flexible and tough films. The thermal and mechanical properties of the films were investigated by DSC, TGA, thermal mechanical analysis (TMA) and dynamic mechanical analysis (DMA). The T_ss by TMA measurement range from 215 to 231°C for **TEPI** films, similar with their glass transition temperatures. The 5% weight loss temperatures for the films are located in range of 495~510°C, slightly higher than those by chemical imidization. It is interesting to note the tensile storage modulus for the films attained 4.0 GPa, as high as that of their linear analogues.

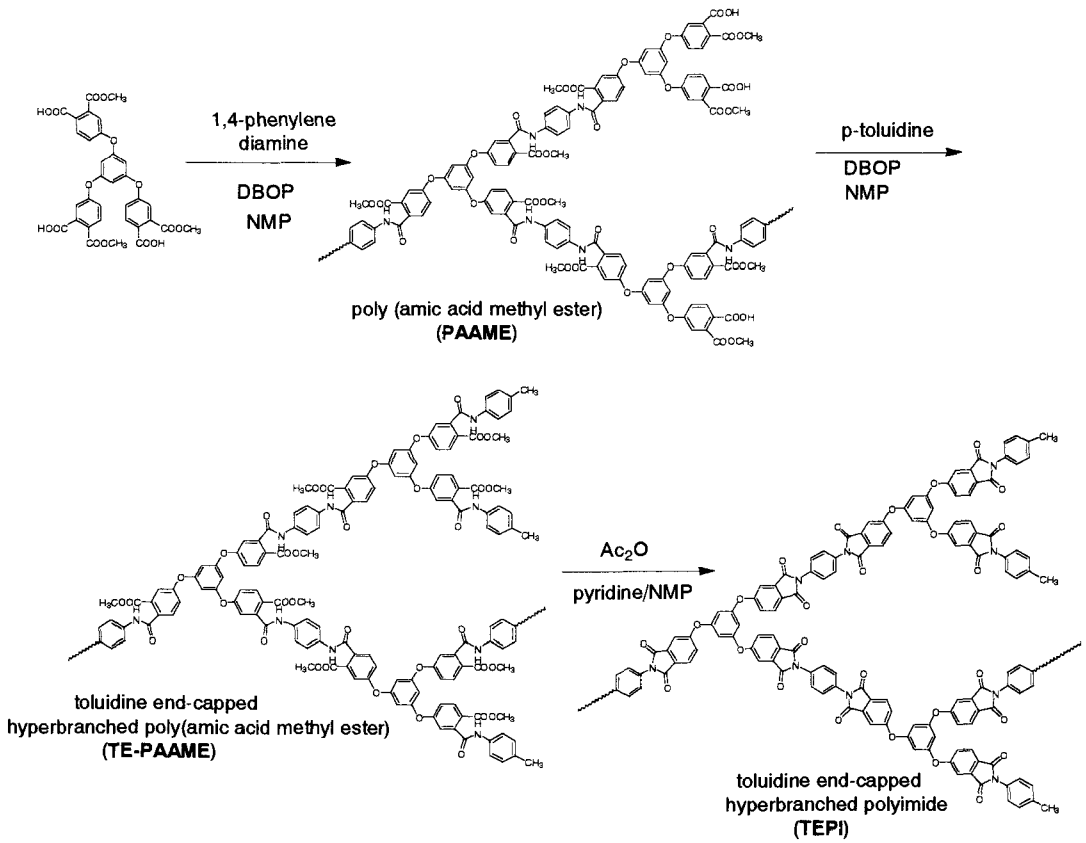
Table 1 Synthesis of Hyperbranched Poly(amic acid methyl ester) (PAAME)[a]

entry	concentration (g/ml)	temperature (°C)	yield %	η_{inh}[b] (dL/g)	M_w[c]	M_w/M_n
1	0.19	r.t.		gel		
2	0.11	r.t.		gel		
3	0.097	r.t.	97	0.97	$1.25x10^5$	2.63
4	0.073	r.t.	90	0.25	$6.74x10^4$	2.08
5	0.058	r.t.	86	0.23	$3.76x10^4$	1.84
6	0.032	r.t.	78	0.17	$3.36x10^4$	2.17

[a] Direct polycondensation of tri(phthalic acid methyl ester) (B_3) and 1,4-phenylene diamine (A_2) in NMP with DBOP as condensation agent. [b] Measured at a concentration of 0.5g/dL at 30°C in NMP. [c] Determined by GPC measurement with a laser light scattering detector in DMF containing lithium bromide (0.01 mol/L). The specific refractive increments (dn/dc) were 0.150 mL/g for **3**, 0.172mL/g for **4**, 0.188mL/g for **5**, and 0.196mL/g for **6**.



Scheme 1



Scheme 2

References

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