

Rapid Communication

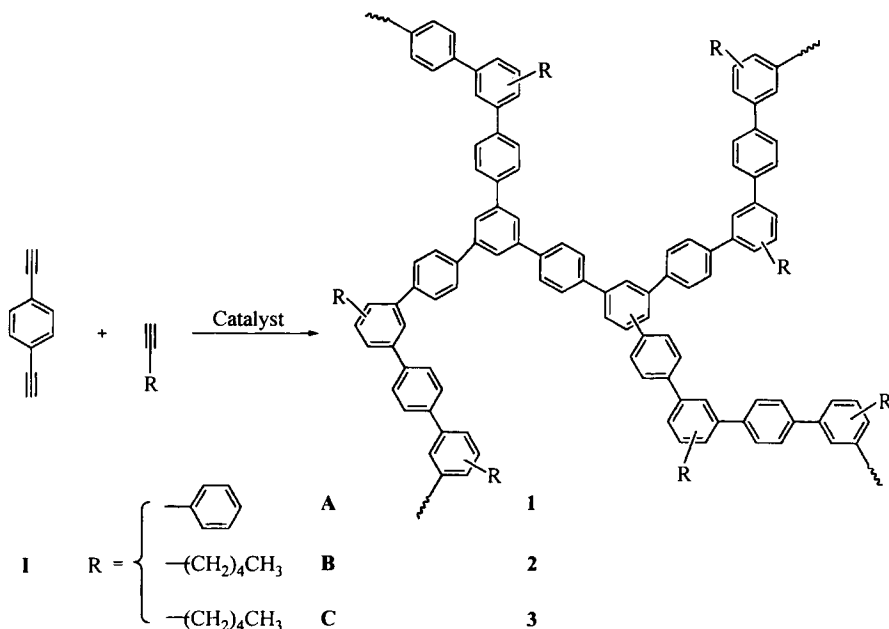
SYNTHESES AND CHARACTERIZATIONS OF HYPERBRANCHED POLYPHENYLENES*

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Abstract New hyperbranched polyphenylenes with high molecular weights are synthesized by the copolycyclotrimerizations of 1,4-diethynylbenzene (**I**) with phenylacetylene (**A**), 1-octyne (**B**), and 1-dodecyne (**C**) catalyzed by TaCl₅-Ph₄Sn. The polymers are completely soluble in common solvents such as toluene, THF, chloroform, and dichloromethane. The polymers are characterized by spectroscopic methods and all of the polymers give satisfactory analysis data corresponding to their expected molecular structures.

Keywords Alkyne polycyclotrimerization, Hyperbranched polymers, Polyphenylenes

Hyperbranched polymers have attracted much attention over the past decade because of the expectation that their unique molecular shape, branching pattern and surface functionality may impart unusual properties. Methods for the synthesis of hyperbranched polymers are, however, rather limited. Cyclotrimerization of alkynes to aromatic



Scheme 1

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rings is a century-old reaction. Although chemists have intensively investigated cyclotrimerization of various diynes in the last century, their attention was mainly focused on low molecular weight compounds. We have explored the possibility of using the alkyne cyclotrimerization for the construction of hyperbranched polymers and succeeded in synthesizing hyperbranched polyarylenes from diyne polycyclotrimerizations^[1-5]. The target of this work is to prepare soluble hyperbranched polyphenylenes by copolycyclotrimerizations of a diyne (**I**) with monoynes (**A–C**; Scheme 1).

The copolymerizations of **I** with **A–C** in different feeding ratios were carried out using TaCl₅–Ph₄Sn as catalyst and the polymerization results are summarized in Table 1. Whereas the homopolymerization of **I** gives only insoluble gel, its copolymerizations with enough amounts of **A** yield complete soluble polyarylenes (Table 1, Nos. 3 and 4), demonstrating that copolymerization with an aliphatic monoyne is an effective way for synthesizing soluble polyphenylenes. Similarly, soluble polymers of high molecular weights are obtained in high yields when **I** is copolymerized with appropriate amounts of **B**. The copolymerizations of **I** with less amounts of **C** produces soluble polyarylenes, thanks to the higher solublizing power of **C**, a monoyne with a longer alkyl “tail”.

Table 1. Copolymerizations of diyne with monoynes^a

No.	<i>r</i> ^b	Yield (%)	Solubility ^c	<i>M_w</i> ^d	<i>M_w/M_n</i> ^d
1	0.0 (A/I)	gel	×		
2	1.0 (A/I)	22.7	∇	4201	9.0
3	1.4 (A/I)	83.9	O	1383	2.4
4	2.8 (A/I)	53.9	O	855	1.8
5	0.6 (B/I)	Gel	×		
6	0.8 (B/I)	100	O	15320	5.2
7	0.9 (B/I)	99.8	O	12660	4.2
8	1.0 (B/I)	88.9	O	32330	6.7
9	1.2 (B/I)	93.7	O	7500	3.9
10	0.8 (C/I)	76.1	O	67190	9.6
11	0.9 (C/I)	85.2	O	21630	7.1
12	1.0 (C/I)	74.0	O	24960	6.6

^a Carried out in toluene at room temperature under nitrogen for 12 h using TaCl₅–Ph₄Sn as catalyst, [TaCl₅] = [Ph₄Sn] = 20 mmol/L; ^b Monomer molar ratio $r = [M_I]/[M_{II}]$; ^c Tested in common organic solvents such as toluene, THF, chloroform, and dichloromethane; ×: Insoluble (gel), ∇: Partially soluble; O: Completely soluble; ^d Estimated by GPC in THF on the basis of a polystyrene calibration

The polymers show no resonance peaks of terminal acetylene protons at δ ~3.2, where their monomers do. The polymers exhibit broad resonance peaks at δ 7.1–7.9. The multiple peaks suggest diversified connection patterns of the polyphenylene structure in the polymers. The ¹³C-NMR spectra of the polymers confirm their polyphenylene structure by the strong resonance peaks in the aromatic spectral region (δ 125.6–143.2) and the complete absence of the acetylenic resonance at δ 83.7 and 79.8. No signals of other structures are observed, revealing that the polycyclotrimerization is the only reaction taking place in the system.

The FT-IR spectra of the polymers show typical aromatic absorption bands at 3030, 2924, 2852, 1595 and 1496 cm⁻¹. The peaks at 822, 758 and 698 cm⁻¹ indicate the existence of the benzene derivatives with 1,2,4- and 1,3,5-substitutions. Whereas strong absorption bands of acetylenic triple bonds (3267 and 2106 cm⁻¹) can be clearly observed in the IR spectrum of the homopolymers, these bands are absent in the spectra of the copolymers. The end-capping of the triple bonds by the monoynes effectively suppresses the cross-linking reactions, making the copolymers soluble.

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