

Rapid Communication

SYNTHESIS OF HYPERBRANCHED CONJUGATIVE
POLY(ARYLENEETHYNYLENE)S BY ALKYNE POLYCYCLOTTRIMERIZATION*

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Abstract A series of new hyperbranched poly(aryleneethynylene)s are synthesized by the copolycyclotrimerizations of tetraynes (**I** and **II**) with aliphatic monoynes (**A–C**) catalyzed by tantalum-, niobium-, and cobalt-based catalysts. All the reactions proceed smoothly and soluble polymers of high molecular weights (M_w up to 3.8×10^4) are obtained in high yields (up to 97%).

Keywords: Polycyclotrimerization; Hyperbranched polymers; Poly(aryleneethynylene)s.

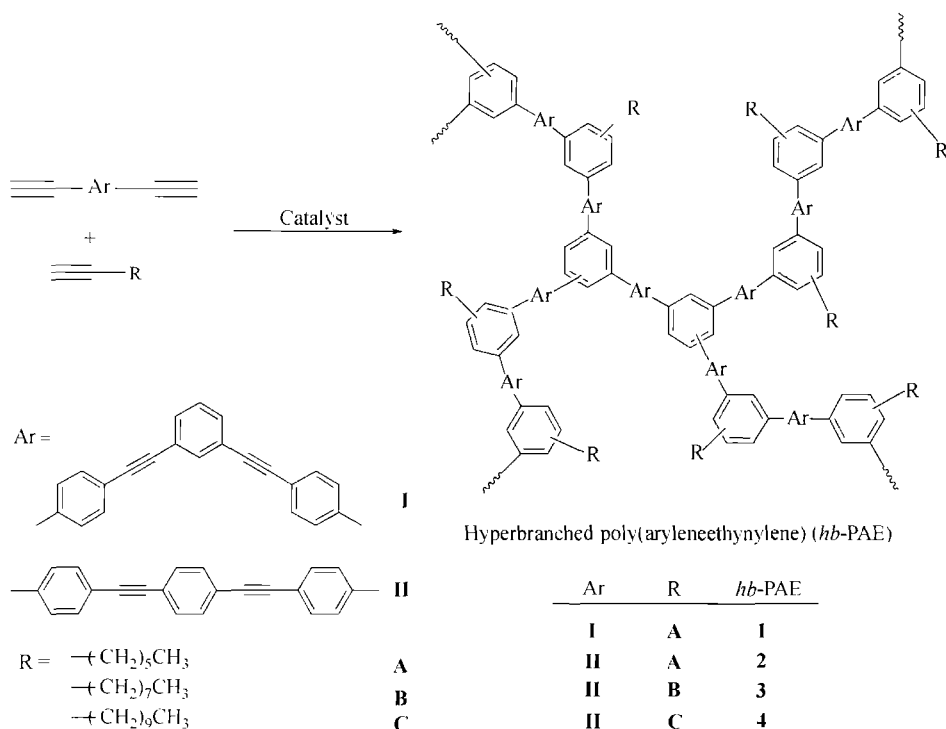
Poly(aryleneethynylene)s (PAEs) are conjugated polymers consisting of aromatic rings and ethynylene rods. The novel properties such as thermal curing, metal complexation and pyrolytic ceramization of PAEs make them a class of promising materials for high-technology applications^[1, 2]. Linear unsubstituted PAE is, however, infusible and insoluble. Different strategies have been developed to improve its processability and the most common approach is to attach linear alkyl or alkoxy pendants to the rigid-rod polymer backbone, which often seriously perturb the electronic structures of the PAEs. We have recently synthesized a variety of hyperbranched polyarylenes (PAs) by simple, one-pot polycyclotrimerizations of aromatic diynes with monoynes^[2, 3]. The resultant polymers show excellent light-emitting and optical-limiting properties as well as outstanding thermal stability. In this work, we tried to utilize the polycyclotrimerization technique to construct new conjugated macromolecules of hyperbranched PAEs (Scheme 1).

We first attempted to copolymerize tetrayne 1,3-bis(4-ethynylphenylethynyl)benzene (**I**) or 1,4-bis(4-ethynylphenylethynyl)benzene (**II**) with 1-octyne (**A**) using TaX_5 – or $NbCl_5$ – Ph_4Sn as catalyst in toluene. The copolymerization of **II** with **A** gives no or insoluble polymer, while that of **I** with **A** produces an hyperbranched poly(arylene thynylene) (*hb*-PAE) with a high molecular weight ($M_w = 28600$) in a high yield (97%; Table 1, No. 1). The reactions catalyzed by $TaBr_5$ – and $NbCl_5$ – Ph_4Sn , however, give polymers with lower M_w s in lower yields. All the polymerizations catalyzed by $CpCo(CO)_2$ –*hν* proceed smoothly and polymers of high molecular weights (M_w up to 3.8×10^4) are obtained in high yields (up to 92%). Almost all of the *hb*-PAEs are completely soluble in common solvents such as toluene, tetrahydrofuran (THF), chloroform, and dichloromethane.

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Scheme 1 Syntheses of hyperbranched poly(aryleneethynylene) by copolycyclotrimerizations of tetraynes with monoynes

Table 1. Copolymerizations of tetraynes (T) with 1-alkynes (M)^a

No.	<i>r</i> ^b	Catalyst	Yield (%)	<i>M_w</i> ^c	<i>M_w</i> / <i>M_n</i> ^c
1	1.5 (A/I)	TaCl ₅ -Ph ₄ Sn	97.0	28600	1.7
2	1.5 (A/I)	TaBr ₅ -Ph ₄ Sn	27.0 ^d	7700	2.4
3	1.5 (A/I)	NbCl ₅ -Ph ₄ Sn	58.9	7000	3.4
4	1.5 (A/I)	CpCo(CO) ₂ - <i>hν</i>	89.6	20700	3.1
5	2.0 (A/I)	CpCo(CO) ₂ - <i>hν</i>	92.0	22300	2.8
6	2.5 (A/I)	CpCo(CO) ₂ - <i>hν</i>	77.4	27800	3.8
7	3.0 (A/I)	CpCo(CO) ₂ - <i>hν</i>	78.4	24300	3.4
8	1.0 (A/II)	CpCo(CO) ₂ - <i>hν</i>	83.3	26600	3.1
9	1.5 (A/II)	CpCo(CO) ₂ - <i>hν</i>	77.3	22900	2.7
10	2.0 (A/II)	CpCo(CO) ₂ - <i>hν</i>	61.5	21400	2.4
11	1.5 (B/II)	CpCo(CO) ₂ - <i>hν</i>	87.5	18600	2.1
12	2.0 (B/II)	CpCo(CO) ₂ - <i>hν</i>	85.5	13500	3.9
13	3.0 (B/II)	CpCo(CO) ₂ - <i>hν</i>	89.6	8850	1.8
14	1.5 (C/II)	CpCo(CO) ₂ - <i>hν</i>	58.3	37900	2.7
15	2.0 (C/II)	CpCo(CO) ₂ - <i>hν</i>	60.4	32200	2.5
16	3.0 (C/II)	CpCo(CO) ₂ - <i>hν</i>	58.7	23190	2.2

^a Carried out under nitrogen for 12 h in toluene at room temperature (Nos. 1–3) or in THF at 65 °C (Nos. 4–16). [T] = 72 mmol/L, [CpCo(CO)₂] = 12 mmol/L, [M₁X₅] = 5 mmol/L (M₁ = Ta, Nb; X = Cl, Br), [Ph₄Sn] = 5 mmol/L

^b Monomer molar ratio *r* = [M]/[T]

^c Estimated by GPC in THF, on the basis of a polystyrene calibration

^d Soluble fraction

The *hb*-PAEs are characterized by spectroscopic methods^[5] and satisfactory analysis data corresponding to their expected molecular structures are obtained. Polymer **1** (Table 1, No. 1), for example, shows no absorption

band at 3267 cm^{-1} , where the $\text{H}-\text{C}\equiv$ stretching band of its monomer **I** locates. The ^1H and ^{13}C -NMR spectra of **1** show no unexpected signals and all the resonance peaks can be readily assigned. The resonance peaks of the acetylenic protons of **I** and **A** locate at δ 1.92 and 3.26, respectively, which completely disappear in the spectrum of **1**. In the ^{13}C spectrum of **1**, no peaks associated with terminal acetylenic carbons are observed in the spectral region of δ 84.6–68.0. The resonance peaks of the internal acetylenic carbons, however, appear at δ 100.8 and 90.3. These spectral data confirm that the terminal triple bonds of the tetraynes have been consumed but their internal ones remain unharmed by the polycyclotrimerization reaction.

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