

Rapid Communications

POLYCYCLOTRIMERIZATION OF DIYNES, A NEW APPROACH TO HYPERBRANCHED POLYPHENYLENES*

Kai-tian Xu and Ben-zhong Tang**

*Department of Chemistry, The Hong Kong University of Science and Technology
Clear Water Bay, Kowloon, Hong Kong, China*

Abstract Polycyclotrimerization of diynes was explored as a new route to hyperbranched polymers in this investigation. Polymerization of terminal diynes of 1,8-nonadiyne and 1,9-decadiyne was studied using TaCl_5 , NbCl_5 , $\text{Mo}(\text{CO})_4(\text{nbd})$ and $[\text{Mo}(\text{CO})_3\text{cp}]_2$ as catalysts (where nbd = 2,5-norbornadiene, cp = cyclopentadiene). A soluble polymer was obtained when the polymerization of 1,9-decadiyne was initiated by TaCl_5 at low temperature (0°C). The polymer, however, became partially soluble after purification, possibly due to the postpolymerization-induced crosslinking. NbCl_5 -catalyzed polymerization of 1,9-bis(trimethylsilyl)-1,8-nonadiyne gave a completely soluble polymer. Soluble polymers were also obtained from the polymerization of 3,9-dodecadiyne initiated by NbCl_5 , $\text{Mo}(\text{CO})_4(\text{nbd})$, $[\text{Mo}(\text{CO})_3\text{cp}]_2$, $\text{PdCl}_2\text{-ClSiMe}_3$ and Pd/C-ClSiMe_3 . IR, UV, and NMR spectroscopic analysis revealed that different catalysts gave polymers with different structures, ranging from linear polyenes to hyperbranched polyphenylenes. The polymers absorb UV light at around 250 nm and emit fluorescence at 340 nm when they are excited at 248 nm.

Keywords Polycyclotrimerization, Diyne, Hyperbranched polymer

INTRODUCTION

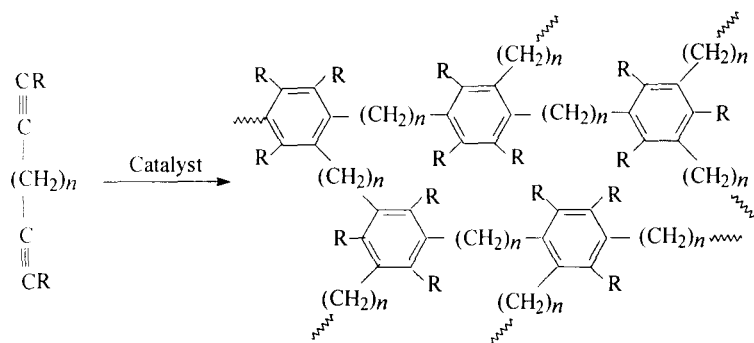
Cyclotrimerization of alkynes was discovered in 1864 by Berthelot^[1, 2]. Since Reppe revealed that some transition metal complexes could catalyze the cyclotrimerization effectively under mild conditions in 1948^[3, 4], this category of reactions has attracted extensive research efforts and has become a versatile tool for the synthesis of complex organic molecules^[5-8]. Diynes or diacetylenes also undergo cyclotrimerization. Although chemists have investigated intensively the cyclotrimerization of various diynes during the last half century^[9-12], their attention was mainly focused on low molecular weight compounds, such as cyclodimers and cyclotrimers. Up to now, there have only been very few scattered investigations concerning polymers of diynes^[13-17].

Recently, we launched an investigation on polymer formation via cyclotrimerization of diynes. The purpose of our present study is to develop a new methodology for the synthesis of hyperbranched polymers (Scheme 1). Polymers with unique structures unattainable by other routes could be prepared in this way, through tailoring the structures of diynes and selecting appropriate catalysts. We report here the preliminary results of our investigation. To our knowledge, our work represents the first successful example in preparing completely soluble hyperbranched polyphenylenes via polycyclotrimerization.

* This work was in part supported by the Earmarked Research Grants of the Hong Kong Research Grants Council (HKUST6062/98P and HKUST6149/97P).

** Corresponding author: Ben-zhong Tang (唐本忠), E-mail: tangbenz@ust.hk

Received February 25, 1999



Scheme 1

EXPERIMENTAL

All diynes were purchased from Farchan and distilled over CaH_2 before use. 1,9-bis(trimethylsilyl)-1,8-nonadiyne was prepared by the coupling reaction of $\text{LiC}\equiv\text{C}(\text{CH}_2)_5\text{C}\equiv\text{CLi}$ and ClSiMe_3 ^[18], and satisfactory analytical data were obtained. All catalysts were purchased from Aldrich and used without further purification. The solvents used in the polymerization reactions were distilled from sodium benzophenone ketyl or CaH_2 prior to use.

Polymerization was carried out in a Schlenk tube with glass stopcock on side arm under nitrogen atmosphere. The detailed experimental procedures can be found in our previous publications^[19, 20]. The reaction was quenched by the addition of a small amount of MeOH. The polymer solution was added into a large amount of MeOH via a cotton filter under magnetic stirring, and the precipitant formed was filtrated and dried in vacuo at room temperature. Yield was estimated from the weight of the MeOH-insoluble products. The solubility of the polymers was tested in various common organic solvents, such as toluene, THF, chloroform, dichloromethane, and ethyl acetate.

FTIR spectra of the polymers were recorded on a Perkin Elmer PC 16 spectrometer. NMR spectra were recorded in chloroform- d on a Bruker ARX 300 NMR spectrometer. UV and fluorescence spectra were recorded in THF on a Milton Ray 3000 Array spectrophotometer and a SLM 8000C spectrofluorometer, respectively. Molecular weights were estimated by Waters 510 gel permeation chromatography (GPC), using THF as the eluent at a flow rate of 1.0 mL/min.

RESULTS AND DISCUSSION

Polymerizations of both terminal and internal diynes were investigated. Table 1 summarizes the experimental results of the terminal diynes. Polymerization of 1,8-nonadiyne catalyzed by $[\text{Mo}(\text{CO})_3\text{cp}]_2$ in toluene was unsuccessful. In CCl_4 , a polymer was obtained in quantitative yield, which was, however, completely insoluble. Similar results were obtained when $\text{Mo}(\text{CO})_4(\text{nbd})$ was used as the catalyst. NbCl_5 - and TaCl_5 -catalyzed polymerizations yielded only partially soluble products. While the polymerization of 1,9-decadiyne catalyzed by NbCl_5 produced little polymer, the TaCl_5 catalyst gave a completely insoluble gel in 60% yield. When the polymerization was conducted at 0°C at a high catalyst concentration, a soluble polymer was produced (Table 1, No. 9). However, the purified polymer became only partially soluble after drying *in vacuo*.

The IR spectrum of the poly(1,8-nonadiyne) obtained from TaCl_5 shows the absorption bands of $\text{C}\equiv\text{H}$ and $\text{C}\equiv\text{C}$ at 3310 and 2130 cm^{-1} , respectively. The ^1H -NMR spectrum of the soluble fraction of the poly(1,8-nonadiyne) shows absorption peaks in the region of $\delta = 6.6\text{--}7.2$, suggesting that the polymer contains aromatic rings. The ^{13}C -NMR spectrum of the soluble fraction exhibits two absorption peaks of the terminal acetylene triple bond ($\text{C}\equiv\text{CH}$) at $\delta = 68.9$ and 85.3 ,

as well as multiple peaks of the aromatic carbons in the region of $\delta = 126.5\sim 143.3$. All the spectroscopic data indicate that the monomer has undergone cyclotrimerization and that the polymer possesses a hyperbranched structure.

Table 1 Polymerization of terminal diynes^{a)}

No.	Catalyst	Solvent	Yield (%)	Solubility
1, 8-Nonadiyne				
1	[Mo(CO) ₃ cp] ₂	toluene	0	Insoluble
2	[Mo(CO) ₃ cp] ₂	CCl ₄	100	
3	Mo(CO) ₄ (nbd)	toluene	0	
4	Mo(CO) ₄ (nbd)	CCl ₄	64	Insoluble
5	NbCl ₅	toluene	82	partially soluble
6	TaCl ₅	toluene	70	partially soluble
1, 9-Decadiyne				
7	NbCl ₅	toluene	Trace	Insoluble
8	TaCl ₅ ^{b)}	toluene	60	
9	TaCl ₅ ^{c)}	toluene	72	Soluble

a) carried out under nitrogen for 24 h at 65 °C; [M]₀ = 0.5 mol/L, [cat.] = 20 mmol/L; abbreviation: cp = cyclopentadiene, nbd = 2,5-norbornadiene; b) polymerized for 8 h; c) polymerized at 0 °C for 2 h; [M]₀ = 0.25 mol/L, [cat.] = 80 mmol/L

In order to prepare soluble polymers, we selected internal diynes as the objects of investigation. For internal diynes, the steric hindrance of the two substituted groups connected to triple bonds might hamper the intermacromolecular reaction between chains (crosslinking) leading to insoluble polymers. We thus replaced the terminal hydrogens of 1,8-nonadiyne by trimethylsilyl groups. The resulting monomer (1,9-bis(trimethylsilyl)-1,8-nonadiyne) showed somewhat lower polymerizability, but the NbCl₅-catalyzed polymerizations at 30 °C offered completely soluble polymers (Table 2, Nos. 7 and 8).

Table 2 Polymerization of 1,9-bis(trimethylsilyl)-1,8-nonadiyne^{a)}

No.	Catalyst	<i>T</i> (°C)	Yield (%)	Solubility	<i>M</i> _w ^b	<i>M</i> _w / <i>M</i> _n ^b
1	Mo(CO) ₄ (nbd) ^c	65	60	Partially soluble		
2	NbCl ₅	65	4	Insoluble		
3	TaCl ₅	65	trace			
4	NbCl ₅	30	trace			
5	TaCl ₅	30	trace			
6	NbCl ₅ ^{d)}	30	8	soluble	9900	2.0
7	NbCl ₅ ^{e)}	30	10	soluble	16300	3.2

a) Carried out under nitrogen for 24 h in toluene; [M]₀ = 0.25 mol/L, [cat.] = 20 mmol/L; abbreviation: nbd = 2,5-norbornadiene; b) Estimated by GPC on the basis of a standard polystyrene calibration; c) Solvent: CCl₄; d) Polymerized for 72 h; [M]₀ = 0.5 mol/L, [cat.] = 80 mmol/L; e) Polymerized for 72 h; [M]₀ = 0.5 mol/L, [cat.] = 160 mmol/L

The polymerization results of another internal diyne, 3,9-dodecadiyne, are listed in Table 3. Quite a few catalysts gave soluble polymers from this monomer. Spectroscopic analysis, however, reveals that different catalysts gave polymers with different structures.

When Mo(CO)₄(nbd), [Mo(CO)₃cp]₂ and PdCl₂-ClSiMe₃ were used as the polymerization catalysts, the polymer products did not show absorption peaks of the acetylene triple bonds. An example of the ¹³C-NMR spectrum of the polymers is given in Fig. 1a. The polymers absorbed UV light below 250 nm, indicating that the polymers may possibly have linear polyene structures as shown in Chart 1a. The ring structure reduces the conjugation length, therefore, the polymers do not absorb in the long wavelength region.

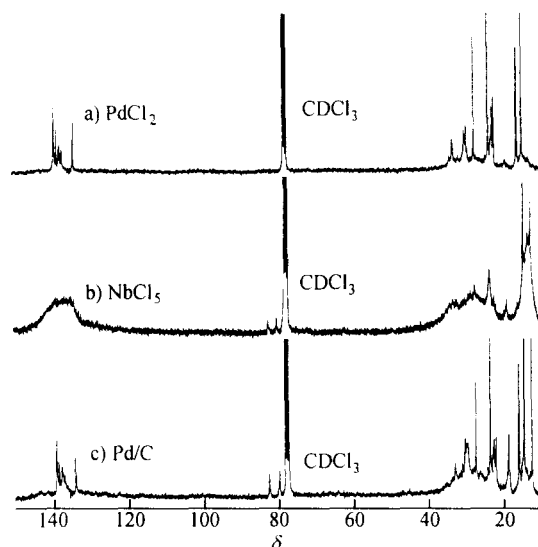
Table 3 Polymerization of 3, 9-dodecadiyne^a

No.	Catalyst	<i>T</i> (°C)	Yield (%)	Solubility	<i>M_w</i> ^b	<i>M_w</i> / <i>M_n</i> ^b
1	Mo(CO) ₄ (nbd) ^c	65	50	soluble	238300	6.6
2	[Mo(CO) ₃ cp] ₂ ^c	65	24	soluble	40300	8.1
3	NbCl ₅	65	100	insoluble		
4	TaCl ₅	65	16	partially soluble		
5	NbCl ₅	50	79	insoluble		
6	NbCl ₅	rt	38	soluble	33600	2.3
7	Co(CO) ₂ cp	120	50	partially soluble		
8	PdCl ₂ -ClSiMe ₃ ^d	65	52	soluble	4500	3.0
9	Pd/C-ClSiMe ₃ ^d	65	50	soluble	3600	2.2

a) carried out under nitrogen for 24 h in toluene; [M]₀ = 0.5 mol/L, [cat.] = 20 mmol/L; abbreviation: nbd = norbornadiene, cp = cyclopentadiene;

b) estimated by GPC on the basis of a polystyrene calibration;

c) solvent: CCl₄; d) Solvent: THF; [Pd] = 55 mmol/L, [ClSiMe₃] = 1.0 mol/L

**Fig. 1** ¹³C-NMR spectra of poly(3,9-dodecadiyne)s obtained from different catalysts

a) PdCl₂-ClSiMe₃ (sample from Table 3, No. 8; linear structure)

b) NbCl₅ (Table 3, No. 6; linear + hyperbranched structure)

c) Pd/C-ClSiMe₃ (Table 3, No. 9; hyperbranched structure)

When NbCl₅ was used, the ¹³C-NMR spectrum of the resulting polymer clearly shows the absorption peak of the terminal triple bonds (Fig. 1b). Compared with the poly(3,9-dodecadiyne) obtained from PdCl₂-ClSiMe₃ (Table 3, No. 8), the polymer from NbCl₅ has much higher molecular weight (Table 3, No. 6). The terminal triple bonds should thus not only come from the ends of the linear chains, but also from those of the branches. The polymer was also oxidized by *m*-chloroperoxybenzoic acid in CH₂Cl₂^[21] and many hydroxyl groups and some carbonyl groups could be detected from the oxidized products. This hints that the initial unoxidized polymer contains many double bonds and some triple bonds. UV adsorption indicates no high conjugation in the polymer ($\lambda_{\text{max}} < 250$ nm). Thus NbCl₅ probably initiated both polycyclo-trimerization (giving hyperbranched polyphenylene structure) and metathesis polymerization (giving linear polyene structure) of 3,9-dodecadiyne, and the resulting polymer may contain both linear and branched segments as shown in Chart 1b.

For all the poly(3,9-dodecadiyne)s discussed above, postpolymerization reactions were observed. The molecular weights and polydispersity of the polymers increased continuously during

the isolation, purification, and storage processes. The GPC curves changed from unimodal to bimodal, with the appearance of a new peak in the high molecular weight region. This might be caused by the reaction of the double bonds in the chains, which eventually leads to crosslinking products.

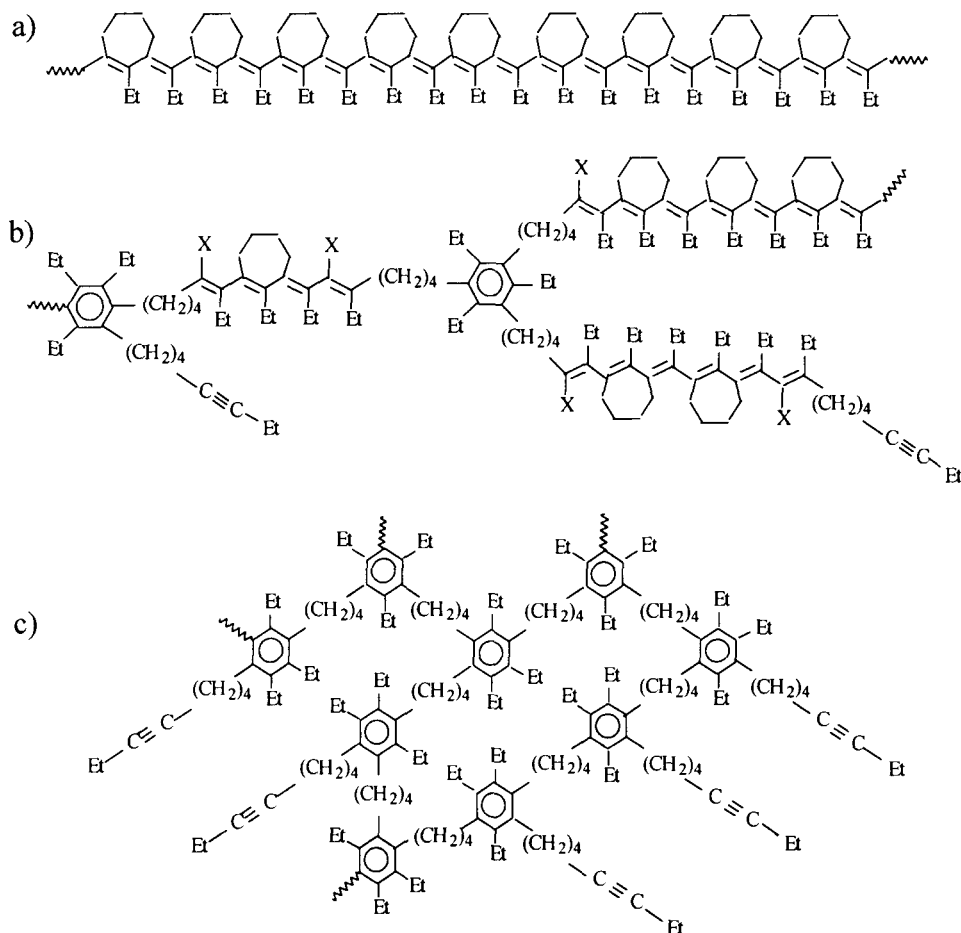


Chart 1

When Pd/C–ClSiMe₃ was used, the ¹³C-NMR spectrum of the resulting poly(3,9-dodecadiyne) showed strong signals of terminal acetylene triple bonds at $\delta = 79.9$ and 82.5 (Fig. 1c). The structure of the polymer thus should be hyperbranched. No obvious post-polymerization reactions were noted for the polymer. The GPC curve of the polymer remained unimodal and no insoluble polymers were induced by postpolymerization reactions. UV spectra of the polymer show a λ_{max} at 217 nm. For further comparison, Co(CO)₂cp, an effective catalyst for cyclotrimerization of both terminal and internal alkynes^[3], was used for the polycyclotrimerization of 3,9-dodecadiyne. Oligomers were obtained at the catalyst concentrations of 20–50 mmol/L, and partially soluble polymers were obtained at the catalyst concentration of 80 mmol/L. The polymers from Pd/C–ClSiMe₃ and Co(CO)₂cp show similar ¹H and ¹³C-NMR spectra, suggesting that the polymerization catalyzed by Pd/C–ClSiMe₃ proceeds by polycyclotrimerization mechanism. A schematic structural representation of the polymer is given in Chart 1c.

All the poly(3,9-dodecadiyne)s emitted fluorescence at 340 nm when excited at 248 nm.

Summarizing, in this study, we have developed a new methodology for the synthesis of

hyperbranched polyphenylenes. Polymers of terminal diynes underwent postpolymerization in the solid state. Since the polymer prepared at low temperatures was soluble, the crosslinking reaction occurred in the film state would make the polymer a promising candidate for coating materials. Soluble polymers were prepared from internal diynes. The nature of the catalysts played a key role in determining the molecular structures of polymers. The hyperbranched polyphenylenes may possess interesting electronic and optical properties. This is currently under active investigation in our laboratory.

REFERENCES

- 1 Berthelot, M., *Ann. Chim. Phys.*, 1866, 9: 446
- 2 Berthelot, M., *Liebigs Ann. Chem.*, 1866, 139: 273
- 3 Reppe, W., Schlichting, O., Klager, K. and Toepel, T., *Liebigs Ann. Chem.*, 1948, 560: 1
- 4 Reppe, W. and Schweckendiek, W.J., *Liebigs Ann. Chem.*, 1948, 560: 104
- 5 Nicholas, K. M., *Acc. Chem. Res.*, 1987, 20: 207
- 6 Vollhardt, K. P. C., *Pure Appl. Chem.*, 1993, 64: 153
- 7 Saa, C., Grotts, D., Hsu, G. and Vollhardt, K.P.C., *Synlett.*, 1994, 487
- 8 Winter, M.J., "Alkyne Oligomerization", In "The Chemistry of the Metal-Carbon Bond, Carbon-Carbon Bond Formation Using Organometallic Compounds", eds. by Hartley, F.R. and Patai, S., Wiley, Chichester, 1985, Vol. 3, p. 259
- 9 Colthup, E.C. and Meriwether, L.S., *J. Org. Chem.*, 1961, 26: 5169
- 10 Perkins, P. and Vollhardt, K.P.C., *Angew. Chem.*, 1978, 90: 643
- 11 Perkins, P. and Vollhardt, K.P.C., *Angew. Chem., Int. Engl. Edn.*, 1978, 17: 615
- 12 Vollhardt, K.P.C. and Bergman, R.G., *J. Am. Chem. Soc.*, 1974, 96: 4996
- 13 Stille, J.K. and Frey, D.A., *J. Am. Chem. Soc.*, 1961, 83: 1697
- 14 Hubert, A.J. and Dale, J., *J. Chem. Soc.*, 1965, 3160
- 15 Gibson, H.W., Bailey, F.C., Epstein, A.J., Rommelmann, H., Kaplan, S., Harbour, J., Yang, X.-Q., Tanner, D.B. and Pochan, J.M., *J. Am. Chem. Soc.*, 1983, 105: 4417
- 16 Sergeyev, V.A., Shitikov, V.K., Chernomordik, Y.A. and Korshak, V.V., *Appl. Polym. Symp.*, 1975, 26: 237
- 17 Srinivasan, R. and Faron, M.F., *Polym. Bull.*, 1988, 20: 359
- 18 Tang, B.Z. and Kotera, N., *Macromolecules*, 1989, 22: 4388
- 19 Tang, B.Z., Kong, X., Wan, X., Peng, H., Lam, W.Y., Feng, X.D. and Kwok, H.S., *Macromolecules*, 1998, 31: 2419
- 20 Tang, B.Z., Kong, X., Wan, X. and Feng, X.D., *Macromolecules*, 1997, 30: 5620
- 21 Lewars, E.G., *Chem. Rev.*, 1983, 83: 519