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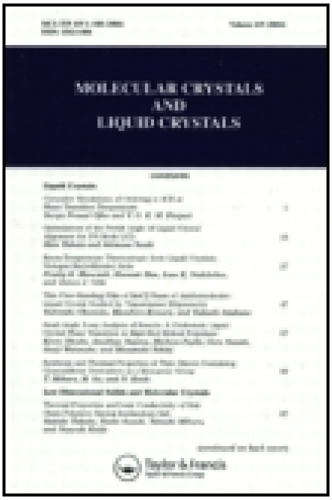

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Synthesis of Hyperbranched Platinum-Poly(yne) Polymers by Self Polycondensation

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A hyperbranched polymer constructed by platinum-acetylide units has been synthesized by self polycondensation of a dinuclear platinum complex having one terminal acetylene and two platinum-chloride groups as an AB_2 monomer in the presence of a copper catalyst in amine. The hyperbranched polymer is soluble in common organic solvents and characterized by means of spectral analyses and GPC.

INTRODUCTION

Highly branched polymers such as dendrimers and hyperbranched polymers have recently received much attention as materials with unique physical and chemical properties.[1] It has been reported that hyperbranched polymers show properties similar to those of dendrimers.[2] Since the same reaction sequences are repeated for the stepwise growth of dendrimers, much endeavor may be required for the synthesis of dendrimers having a well-defined structure. In contrast, hyperbranched polymers may be easily prepared in a large quantity though the structure of hyperbranched polymers is not so well-controlled as those of dendrimers.[3]

In attempts to develop novel functional materials some organometallic dendrimers have been prepared, but hyperbranched polymers composed of organometallic compounds are quite rare in spite of the synthetic advantage of hyperbranched polymers over dendrimers.[4] As an extension of our study on organometallic polymers constructed with group 10 metals and acetylenes,[5] we recently reported the synthesis of platinum-acetylide dendrimers up to the third generation containing 45 platinum atoms in the molecule.[6,7] Herein we present the one-pot synthesis of novel hyperbranched organometallic polymers with a backbone composed of platinum-acetylide units by self polycondensation of a dinuclear platinum-acetylide complex.

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RESULTS AND DISCUSSIONS

First, we attempted to prepare hyperbranched platinum-acetylide polymers by polycondensation between triethynylmesitylene (A_3 monomer) and dichlorobis(phosphine)platinum (B_2 monomer) in a 2:3 molar ratio (SCHEME 1). Treatment of triethynylmesitylene **1** with dichloroplatinum complex **2** in the presence of a catalytic amount of CuCl in diethylamine at room temperature gave polymer **3**, of which molecular weight was confirmed by GPC analysis to be M_w = 62,000 (polystyrene standards). The IR spectrum of **3** showed absorptions at 3246 and 2093 cm^{-1}, which are assignable to $\nu_{\equiv C-H}$ and $\nu_{C\equiv C}$, respectively. Further characterization, however, was difficult due to low solubility of **3**. Similar results have been reported by Lewis and co-workers several years ago.[8] By varying the molar ratio of **1** to **2**, the molecular weights of the resulting polymers became smaller than that of

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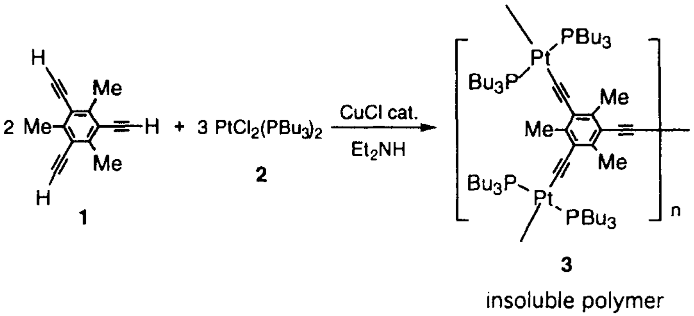
3. Poor solubility, however, did not improve, suggesting that polymer **3** has a highly cross-linking structure with a three-dimensional network.



SCHEME 1

To avoid the formation of cross-linked polymers, methodology for the synthesis of hyperbranched platinum-acetylide polymers was changed into self polycondensation of AB_2 type monomer.[3] Dinuclear platinum-acetylide complex **4**, which has two platinum-chloride moieties and one terminal acetylene, was selected as an AB_2 type monomer. Complex **4** was prepared as shown in SCHEME 2, using two kinds of trialkylsilyl groups, trimethylsilyl and tri-*iso*-propylsilyl groups, for protection of terminal acetylenes.[7] Stepwise cross-coupling reaction of 1,3-dibromo-5-iodobenzene **5** with equimolar amounts of tri-*iso*-propylsilylacetylene and then with excess trimethylsilylacetylene by Pd-Cu catalysts gave a triethynylbenzene derivative **6**.[9] Selective removal of the trimethylsilyl group was performed by treatment of K_2CO_3 in aqueous methanol to give compound **7**. Platinum moieties were introduced by the reaction with excess dichloroplatinum complex in the presence of a CuCl catalyst in piperidine-tolunen under reflux to give dinuclear platinum-acetylide **8**. Desilylation of **8** by treatment of Bu_4NF afforded the target complex **4**.

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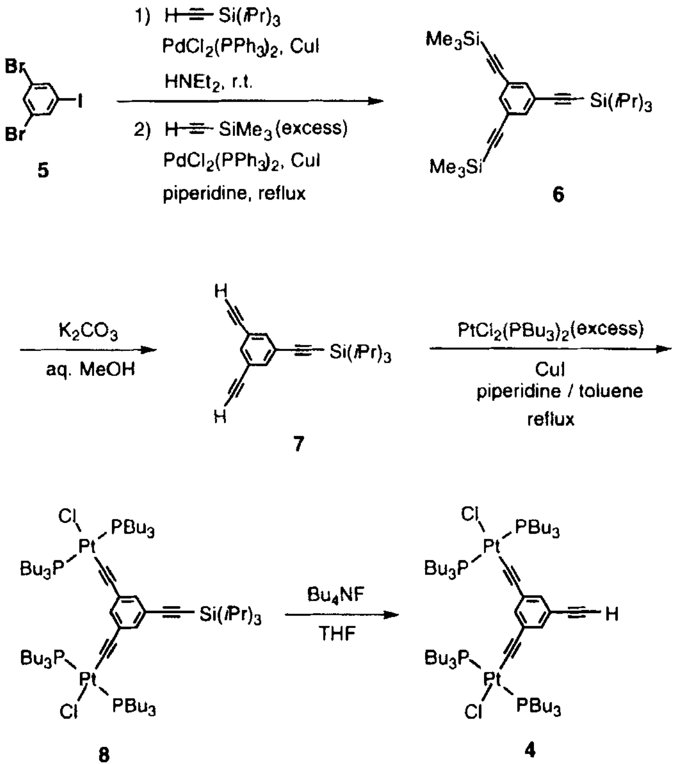

SCHEME 2

Self polycondensation of **4** was carried out in the presence of a CuCl catalyst in diethylamine at room temperature (SCHEME 3). Pale yellow polymer **9**, which is soluble in common organic solvents, was isolated by column chromatography on alumina as highly viscous oil in 91% yield. The GPC analysis of polymer **9** showed the average molecular weight M_w = 16,000 (polystyrene standards) and the polydispersity index M_w / M_n = 1.28. Though the concentration of monomer was varied from 12.3 mmol/L to 2.0 mmol/L, no significant difference was observed in the molecular weight of the resulting

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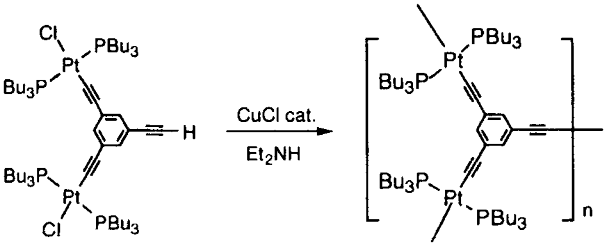
polymer. Since we have already found that the GPC analysis using polystyrene standards apparently shows about a half value of the real molecular weights of platinum-acetylide dendrimers,[6,7] the molecular weight of **9** should be estimated to be about 32,000, which corresponds to about 20 units of monomer **4**.

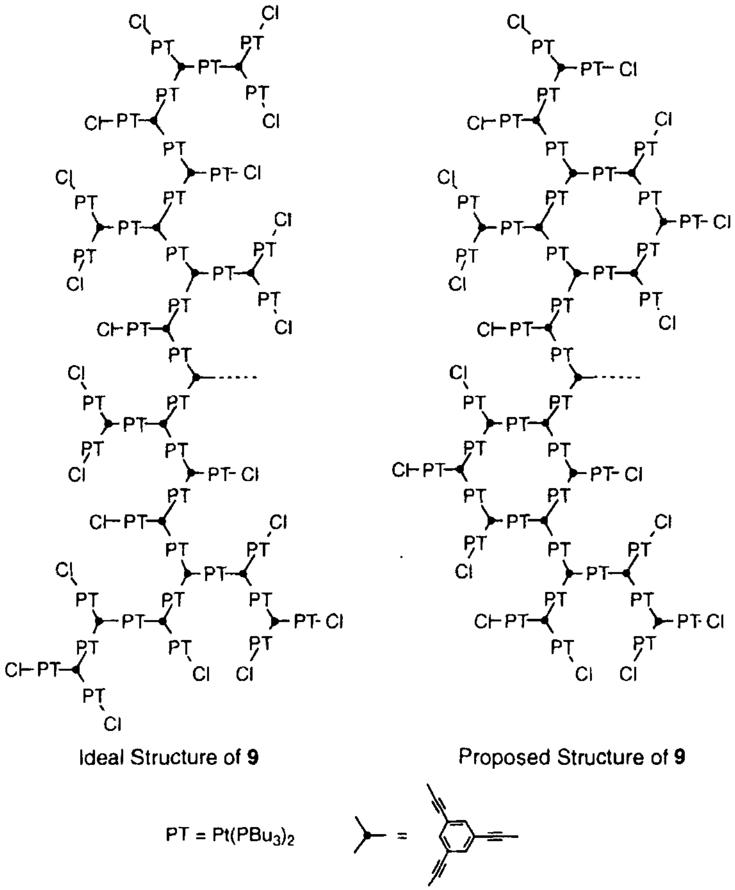


4

9
soluble polymer

SCHEME 3

In the IR spectrum of **9**, an absorption due to $\nu_{C\equiv C}$ was found at 2096 cm^{-1}, while no $\nu_{\equiv C-H}$ absorption was observed. The ^1H NMR spectrum of **9** was similar to that of monomer **4** except for the absence of a signal assignable to the proton of terminal acetylene. The ^{31}P NMR spectrum of **9** showed two singlet signals at δ 7.11 (J_{Pt-P} = 2381 Hz) and 3.58 (J_{Pt-P} = 2371 Hz) in a 1:1.2 intensity ratio. The former was assigned to the phosphines bound to a chloroplatinum moiety $C{\equiv}CPt(PBu_3)_2Cl$ and the latter to those bound to a diethynylplatinum moiety $C{\equiv}CPt(PBu_3)_2C{\equiv}C$. However, the ratio of chloroplatinum and diethynylplatinum moieties must be 1:1 in an ideal hyperbranched polymer prepared from **4**. This results may admit of two interpretations. One ascribes the structural defect to the loss of the terminal chloroplatinum moieties and the other to the formation of a cyclic structure. Since no signals attributed to the terminal groups converted from chloroplatinum moieties were observed in the ^{1}H NMR spectrum of **9** as mentioned above, the former does not seem reasonable. Therefore, polymer **9** is proposed to be a hyperbranched polymer with a partial cyclic structure as shown in SCHEME 4.



Ideal Structure of **9**

Proposed Structure of **9**

SCHEME 4

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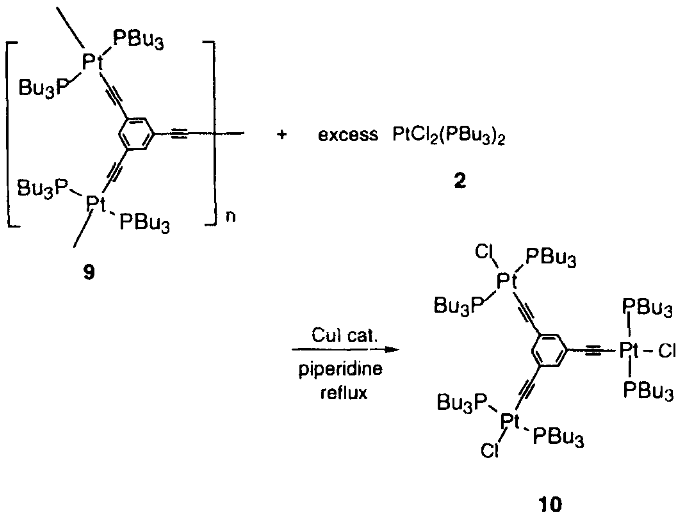
The thermogravimetric analysis showed that **9** is thermally stable up to about 350 °C. Reaction of **9** with **2** in refluxing piperidine in the presence of a CuI catalyst resulted in the depolymerization of **9** to give trinuclear platinum complex **10** (SCHEME 5).



SCHEME 5

In conclusion, the self polycondensation of AB_2 monomer **4** successfully produces a hyperbranched platinum-acetylide polymer **9** though there are a little structural defects like a cyclic structure in the molecule.

ACKNOWLEDGMENTS

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