Polymer Bulletin 46, 357–362 (2001)

Polymer Bulletin

Synthesis of palladium clusters with surface initiator for polymerization of 2-methyl-2-oxazoline

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Received: 19 April 2001/Accepted: 2 May 2001

Summary

Palladium clusters were synthesized by reduction of palladium(II) acetate in the presence of a bipyridyl ligand (**1**) with an initiator for polymerization of 2-methyl-2-oxazoline. The **1**-protected palladium clusters were soluble in $CHCl_3$ and CH_2Cl_2. The **1**-protected palladium clusters were combined with 2-methyl-2-oxazoline in chloroform. After polymerization, the reacted bipyridyl ligand was removed from the palladium cluster by suspending the obtained palladium clusters with pyridine. The ^1H NMR measurement indicated that the reacted bipyridyl ligand was formed via surface polymerization of 2-methyl-2-oxazoline.

Introduction

Much attention has been paid to metal clusters as one class of promising nanoscopic materials [1]. The most remarkable feature of nanoscopic metal clusters is that their chemical and physical properties are quite different from those of bulk metals and metal atoms. To prevent agglomeration with the formation of large particles or powders, these nanostructured particles usually need to be protected by stabilizers such as polymers [2-6] or surfactants [7]. Construction of well-defined polymers containing nanometer-size clusters is one of the attractive targets for polymer and material chemistry. Previously we have introduced a new methodology for constructing well-defined polymers containing metal clusters, i.e., polymer-grafted metal clusters which were simply produced by reduction of palladium ions with a bipyridyl-terminated polymer [8]. A more promising approach for the preparation of the polymer-grafted metal clusters might be given by the use of immobilized initiators at the surface of the metal clusters for in-situ generation of the grafted polymers. This method should be applied for a variety of monomers utilizing radical, cationic, and anionic polymerizations. To obtain a homogeneous grafted polymer, first the surface grafting density has to be uniform, second the polydispersity index should be near to 1, and finally all chains should be linear. These requirements are easily achieved by living polymerization. Here we present a synthesis of palladium clusters with surface initiator and the surface initiated cationic ring-opening polymerization of 2-methyl-2-oxazoline to construct polymer-grafted metal clusters.

Results and Discussion

Synthesis of palladium clusters with surface initiator

A bipyridyl ligand (**1**) with an initiator for polymerization of 2-methyl-2-oxazoline was prepared from 4,4'-dimethyl-2,2'-bipyridine with 1,10-dibromodecane. A palladium cluster was synthesized by stirring an ethanol solution (150 ml) of palladium(II) acetate and **1** (molar ratio 8:1) at room temperature for 72 h. Reduction of palladium ions was monitored by UV-vis absorption spectrum. After reduction was continued, the homogeneous black reaction mixture gave an unstructured UV-vis spectrum without maximum of typical palladium clusters [9-10]. After the solvent was removed under reduced pressure, the black residue was washed with benzene for several times to remove the free ligand. The obtained palladium cluster was soluble in $CHCl_3$ and CH_2Cl_2. These solutions were stable without precipitation for more than half a month at room temperature under air.

To confirm the interaction of the bipyridyl ligand with the palladium cluster, the ^1H NMR of the sample was measured in $CDCl_3$. The ^1H NMR spectrum of the bipyridyl ligand showed aromatic protons of the bipyridyl ring at 7.0-8.5 ppm as well as aliphatic protons at 1.2-3.4 ppm (Figure 1a). The ^1H NMR spectrum of the palladium complex of **1**, which was prepared by mixing of palladium(II) acetate with the bipyridyl ligand in $CDCl_3$, shows that the peak of aromatic protons of the bipyridyl ring shifted due to complexation (Figure 1b, inset). Although a similar shift of aromatic protons was observed in the ^1H NMR spectrum of the palladium clusters (Figure 1b), the 6- and 6'-position's aromatic protons of the bipyridyl ring were hardly recognized compared with the aliphatic protons. These results indicate that the bipyridyl ligand was fixed at the surface of the palladium cluster.

Quantitative size information of metal particles can be obtained using transmission electron microscopy (TEM). The TEM investigation of the obtained clusters, deposited on a grid from an alcohol solution, indicated the average particle size of 4.2 nm with narrow size distribution (Figure 2). The average particle size of 4.2nm was near to so-called “magic atom number” of 2869 atoms, i.e., nine-shell clusters [1].

The elemental analysis of the palladium cluster gave values as follows: C, 6.81; H, 0.82; N, 1.28; O, 4.09; Br, 3.66; Pd, 83.34. This corresponded to a molar ration of Pd:**1** of 19.0:1. The calculated formula for the **1**-protected palladium cluster was $Pd_{2869}\mathbf{1}_{151}O_{ca.900}$ as nine-shell clusters.

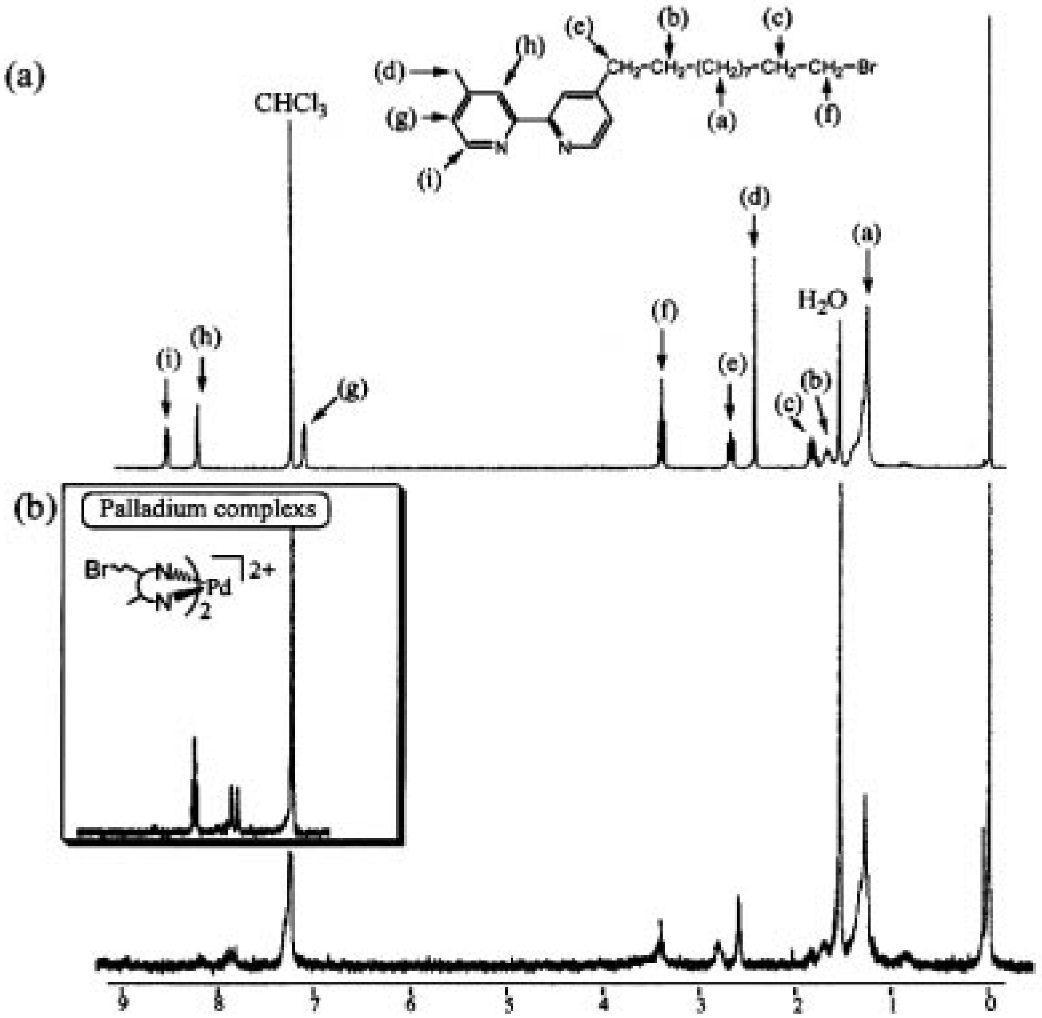


Figure 1. ^{1}H NMR spectra of (a) the bipyridyl ligand, (b) the palladium cluster, and the palladium complex (inset).

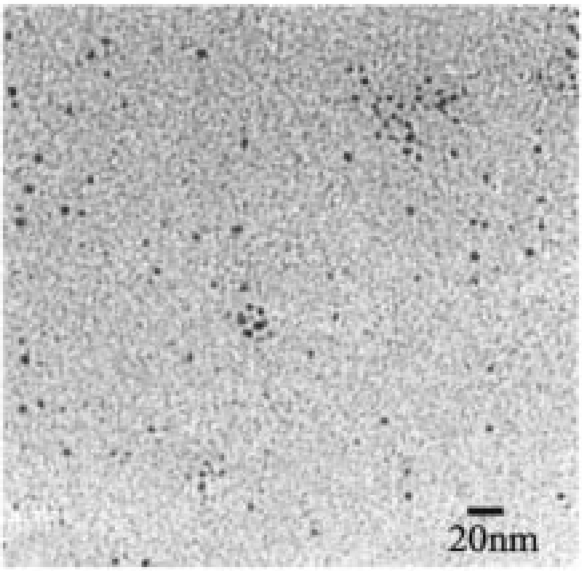
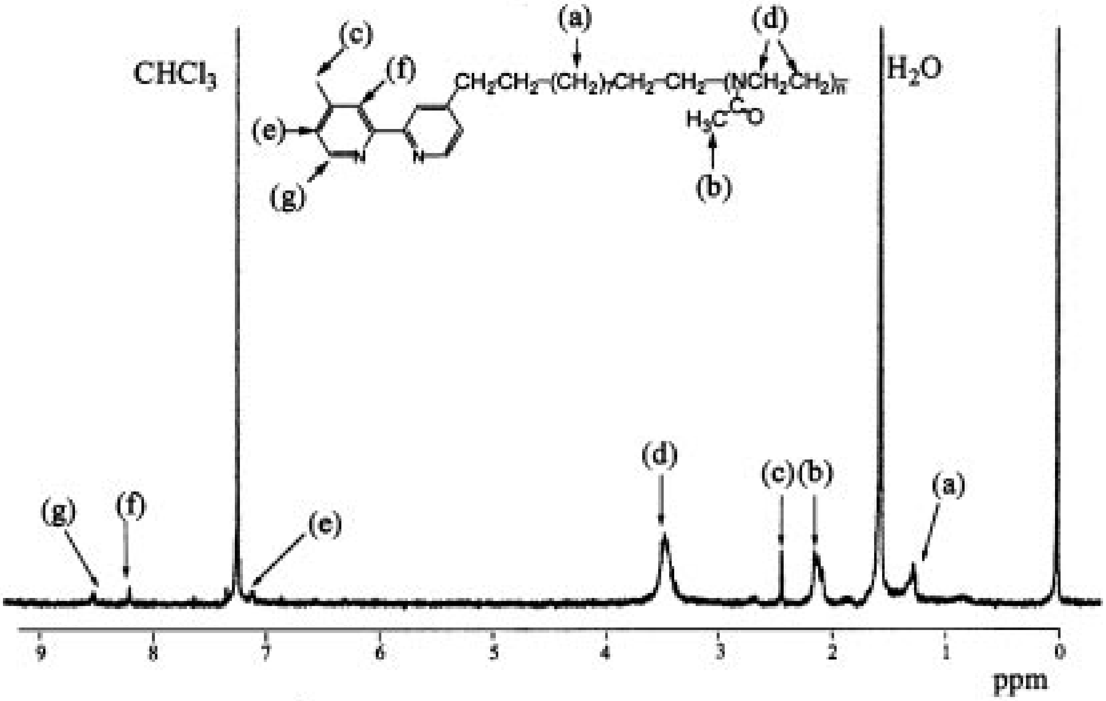


Figure 2. TEM of the **1**-protected palladium cluster

Surface polymerization

The resulting palladium clusters were combined with 2-methyl-2-oxazoline in dry $CHCl_3$ at 70 °C for 48 h. After polymerization, the solvent was removed under reduced pressure. The resulting product was not soluble in common solvents. To consider the reason for insolubility of the resulting product, the palladium cluster was synthesized by stirring an ethanol solution of palladium(II) acetate and poly(2-methyl-2-oxazoline) (M_n=4000) at room temperature for 72 h. After removal of the solvent, the palladium cluster was insoluble in common organic solvents. Comparison of these results suggested that the insolubility of the resulting product was affected by the grafted polymers obtained in the surface polymerization process. To make the grafted polymers available for standard techniques of polymer analysis, degrafting of the polymers from the palladium clusters is required. The bipyridyl ligand would be removed by adding a large excess amount of pyridine. The obtained palladium clusters were suspended with pyridine to remove the reacted bipyridyl ligand. After the precipitate was removed by filtration, the solvent was removed under reduced pressure. The high molecular weight part (M_n=1040, M_w=1070, polystyrene standard) was fractionated by gel permeation chromatography (GPC). The ^{1}H NMR was measured in $CDCl_3$ for characterization of the obtained high molecular weight product. The ^{1}H NMR spectrum of the obtained product showed the methylene protons of poly(2-methyl-2-oxazoline) at 2.1ppm and the methyl protons of poly(2-methyl-2-oxazoline) at 3.4ppm as well as the aromatic protons and the aliphatic protons of the bipyridyl ligand (Figure 3). From the ^{1}H NMR spectrum, the number-average molecular weight (M_n) of the obtained product was 1100. The value was in good



Fiugre 3. ^{1}H NMR spectrum of the reacted bipyridyl ligand

agreement with that from GPC analysis. These results indicate that the obtained product was formed via surface polymerization of 2-methyl-2-oxazoline.

In conclusion, we have demonstrated a new approach using surface polymerization for preparation of the polymer-grafted palladium cluster. The strategy could be easily extended to other monomers.

Experimental Section

Instruments

^{1}H NMR spectra were obtained with a JOEL JNM-EX270 spectrometer (270MHz) in $CDCl_3$. FT-IR spectra were recorded on a Hitachi 260-50 grating spectrophotometer. Gel permeation chromatographic analyses were carried out on a Shodex K-803L column by using chloroform as an eluent after calibration with standard polystyrene samples. UV-visible spectra were measured in EtOH on a Jasco V-530 spectrometer. Transmission electron microscopy was preformed using a JOEL JEM-100SX operated at 100kV. One drop of the solution of the sample was placed for 1 min on a copper grid. Then, the drop of the solution was removed with filter paper.

Materials

Tetrahydrofuran (THF) was distilled under nitrogen over sodium diphenylketyl. Chloroform was distilled under nitrogen from P_2O_5. 2-Methyl-2-oxazoline was distilled under nitrogen. Other solvents and reagents were commercially supplied and used without further purification.

Synthesis of 4-(1-bromoundecyl)-4'-methyl-2,2'-bipyridyl (**1**)

To a pre-cooled (-78 °C) mixture of 2.0 M heptane/THF/ethylbenzene solution (3 ml, 6.0 mmol) of lithium diisopropylamide (LDA) in 20 ml of dry THF was added a solution of 4,4'-dimethyl-2,2'-bipyridyl (1 g, 5.4 mmol) in 100 ml of dry THF for 30 min. The resulting dark brown solution was stirred for 2 h at -78 °C. The lithiated bipyridyl solution was added dropwise to a solution of 1,10-dibromodecane (12.1 ml, 54 mmol) in dry THF (40 ml). The mixture was allowed warm to room temperature and stirred overnight. After the insoluble part was filtered off, the orange solution was concentrated under reduced pressure. The residue was extracted with *n*-hexane, and the solution was applied to an alumina column chromatography, using ethyl acetate/hexane (1/15, v/v) as an eluting solvent. The first fraction containing the product was concentrated by evaporation and dried under reduced pressure. The product was obtained as a white solid. Yield was 1.0 g (45%). ^{1}H NMR ($CDCl_3$): δ1.27 (br, 14H), 1.68 (m, 2H), 1.84 (m, 2H), 2.43 (s, 3H), 2.68 (t, 2H), 3.40 (t, 2H), 7.13 (t, 2H), 8.23(s, 2H), 8.54(m, 2H). IR (KBr,

cm^{-1}): 2929, 1598, 1548, 1464, 1429, 1107, 992, 829. Anal Calcd. for $C_{29}H_{31}BrN_2$ (487.21): C, 65.51; H, 7.69; N, 6.95; Br, 19.85. Found : C, 65.23; H, 7.64; N, 6.92; Br, 20.13.

Synthesis of palladium cluster

1 (10 mg, 2.47 x 10^{-2} mmol) and $Pd(OAc)_2$ (44,9 mg, 2.0 x 10^{-1} mmol) were dissolved in 50 ml of ethanol and the resulting mixture was stirred for 72 h at room temperature. After removing the solvent by evaporation, benzene (50 ml) was added to a black residue and the precipitate was isolated by centrifugation. ^1H NMR ($CDCl_3$): δ1.27 (br, 14H), 1.68 (m, 2H), 1.84 (m, 2H), 2.43 (s, 3H), 2.68 (t, 2H), 3.40 (t, 2H).

Polymerization of 2-methyl-2-oxazoline from surface initiator

The obtained palladium cluster (50 mg) and 2-methyl-2-oxazoline (10 ml) were placed in chloroform (80 ml) and stirred for 48 h at 70 °C under nitrogen. After polymerization, the resulting solution was poured into a large amount of diethyl ether and the precipitate was isolated by centrifugation.

Removal of the reacted ligand from surface of palladium cluster

To the obtained black residue was added pyridine (50 ml) and the mixture was stirred for 48 h at room temperature. After removing the solvent by evaporation, the mixture was fractionated by GPC. ^1H NMR ($CDCl_3$): δ1.27 (br, 14H), 2.1 (br), 2.43 (s, 3H), 3.4 (br), 7.13 (t, 2H), 8.23 (s, 2H), 8.54 (m, 2H).

References

1. Schmid G (1992) Chem Rev 92: 1709
2. Mayer A B R, Mark J E, Morris R E (1998) Polym J 30: 197
3. Mayer A B R, Mark J E (1997) J Polym Sci Part A Polym Chem 35: 3151
4. Yonezawa T, Toshima N (1995) J Chem Soc Faraday Trans 91: 4111
5. Moffitt M, Eisenberg A (1995) Chem Mater 7: 1178
6. Chen C -W, Akashi M (1997) J Polym Sci Part A Polym Chem 35: 1329
7. Bönnemann H; Braun G, Brijoux W, Brinkmann R, Tilling A S, Seevogel K, Siepen K.(1996) J Organomet Chem 520: 143
8. Naka K, Yagushi M, Chujo Y (1999) Chem Mater 11: 849
9. (a) Creighton J A, Eadon D G (1991) J Chem Soc Faraday Trans 87: 3881
10. Mayer A B R, Mark J E (1997) J Polym Sci Part A Polym Chem 35: 3151