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Preparation of Polycinnamamide Catalyzed by Palladium−Graphite through the Heck Reaction

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ABSTRACT: Palladium−graphite (Pd−Gr) was successfully used as a heterogeneous catalyst for the preparation of polycinnamamide through the Heck reaction. The condensation reaction of ethyl acrylate and iodobenzene catalyzed by Pd−Gr proceeded efficiently in the presence of tributylamine in an aprotic polar solvent such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), *N*-methylpyrrolidone (NMP), and dimethyl sulfoxide (DMSO). The polymerization of *N,N′*-(3,4′-oxydiphenylene)bis(acrylamide) and bis(4-iodophenyl) ether catalyzed by Pd−Gr was carried out in the presence of tributylamine in DMF at 100 °C. The polymerization proceeded efficiently to form polycinnamamide, but required a longer reaction time compared to the polycondensation catalyzed by palladium acetate. The structure of the resulting polymer was confirmed as *trans*-polycinnamamide by two-dimensional NMR measurements. The resulting polymer was almost white, which means that it was less contaminated by palladium metal. The removal and recycling of Pd−Gr were much easier than in the case of homogeneous catalysts.

Introduction

Transition metal compounds have been investigated as catalysts for polycondensations in recent years. Especially, many organic reactions catalyzed by palladium complexes are applied to polycondensations, which include the Heck reaction, transmetalations from organotin or organozinc compounds, cross-coupling reactions of alkylboron compounds, the insertion reaction of carbon monoxide, and nucleophilic substitutions with olefins through π-allyl complexes.[1−12] We have reported the palladium-catalyzed polycondensations through the C−C coupling reaction and insertion reactions of carbon monoxide.[2,6,7] Although homogeneous palladium complexes, such as palladium acetate, palladium chloride, and palladium tetrakis(triphenylphosphine), are commonly used as catalysts for these polycondensations, there has been no report about polycondensation reactions using heterogeneous transition metal catalysts. The heterogeneous catalysts can give great advantages, such as removal from the reaction mixture and recycling of the catalysts. In addition, there is the concentration effect by local enrichment of the reagent and lowering of the activation energy is observed in some cases.

Metal−graphite combinations are one of the useful heterogeneous catalysts because of their high reactivity, easy preparation, and manipulation. Umani-Ronchi et al. have reported that transition metal−graphites prepared from potassium-intercalated graphite are useful as heterogeneous catalysts in many organic reactions.[13] Palladium−graphite (Pd−Gr) which is prepared by the metal exchange reaction of potassium-intercalated graphite showed a high reactivity for the hydrogenation of olefins,[14] the Heck reaction,[15] and the nucleophilic substitution reactions through the π-allyl complex.[16] This paper describes the first investigation of polycondensation using the Pd−Gr-catalyzed Heck reaction.

Experimental Section

Palladium−Graphite. Palladium−graphite (Pd−Gr) was prepared by the reaction of potassium-intercalated graphite and palladium(II) chloride as described in the literature.[16]

In a three-necked flask, 0.80 g of potassium in small pieces was added to 1.94 g of graphite powder (99.16%) under an argon atmosphere. The mixture was stirred and heated at 200 °C for 15 min. The powdery mixture turned to brown from black. The formed potassium−graphite was allowed to cool to room temperature. In the flask, 1.77 g of palladium chloride and 1,2-dimethoxyethane (freshly distilled from sodium benzophenone ketyl) were added to a slurry of potassium−graphite. The mixture was stirred and heated at 100 °C for 8 h. After the mixture was cooled, 2 mL of water was added and the solid phase was separated by filtration. The product was washed with 20 mL of dilute HCl (0.1 mol L^{-1}), 200 mL of hot water, 20 mL of methanol, and 20 mL of ether and was finally dried in vacuo at 80 °C for 12 h. The content of palladium in Pd−Gr was determined to be 17 wt % by ICP plasma emission spectroscopy.

Monomers. *N,N′*-(3,4′-Oxydiphenylene)bis(acrylamide) (**1**) was prepared by the condensation of 3,4′-oxydianiline and acrylic acid chloride. The yield was 56%, and the structure was confirmed by spectroscopies, as described in the literature.[2] Bis(4-iodophenyl) ether (**2**) was prepared by the reaction of diphenyl ether, iodine, and bis(trifluoroacetoxy)iodobenzene in carbon tetrachloride at room temperature. The precipitate was filtered out, washed with methanol, and purified by recrystallization from hexane. The yield was 59%, and the structure was confirmed by spectroscopies, as described in the literature.[9]

Other Materials. Ethyl acrylate and iodobenzene were purified by distillation. Palladium chloride, palladium acetate, and palladium-coated active carbon were used without further purification. Triethylamine, tripropylamine, and tributylamine were also purified by distillation. Biphenyl, 1,8-diazabicyclo[5.4.0]-7-undecene (DBU), 1,8-bis(dimethylamino)naphthalene (BDMAN), sodium acetate, sodium carbonate, and tritolylphosphine were used as received. *N,N*-Dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), *N*-methylpyrrolidone (NMP), and dimethyl sulfoxide (DMSO) were purified by distillation.

Model Reaction. In a three-necked flask, 0.24 g (2.4 mmol) of ethyl acrylate, 0.41 g (2.0 mmol) of iodobenzene, 0.48 g (2.6 mmol) of tributylamine, and 0.06 g (9.6×10^{-5} mol) of Pd−Gr (4.8 mol % of Pd with respect to iodobenzene) were added under a nitrogen atmosphere. Biphenyl (40 mg) was also added to the mixture as an internal standard for HPLC measurements. The mixture was stirred and heated to 80 °C. The yield of ethyl cinnamate formed was determined by HPLC measurements without isolation of the product.

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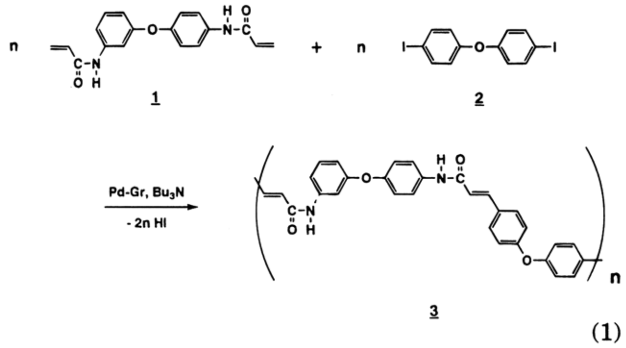
Polymerization Catalyzed by Pd−Gr. A typical procedure for the polymerization is as follows. In a three-necked flask, 0.385 g (1.25 mmol) of *N,N'*-(3,4'-oxydiphenylene)bis(acrylamide) (**1**) and 0.528 g (1.25 mmol) of bis(4-iodophenyl) ether (**2**) were dissolved in 20 mL of DMF. Pd−Gr (4.3 mg, 6.87×10^{-3} mmol/Pd) and 0.77 mL (3.25 mmol) of tributylamine were added to the solution. The mixture was stirred at 100 °C under a nitrogen atmosphere. After 40 h, the mixture was filtered to remove the catalyst and then poured into 300 mL of methanol to precipitate polymer **3**. The polymer was filtered out, washed with hot methanol, and dried *in vacuo*. The yield was 95%. The inherent viscosity of the polymer was 0.95 dL g^{-1}, measured in DMF at a concentration of 0.5 g dL^{-1} at 30 °C. IR (KBr): 1665 (C=O), 976 cm^{-1} (C=C). Anal. Calcd for $(C_{30}H_{22}N_2O_4)_n$: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.83; H, 4.59; N, 5.70.



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Polymerization Catalyzed by Palladium Acetate. In a three-necked flask, 0.385 g (1.25 mmol) of **1**, 0.528 g (1.25 mmol) of **2**, 2.8 mg (1.25×10^{-2} mmol) of palladium acetate, 15.2 mg (5.0×10^{-2} mmol) of tritolylphosphine, and 0.77 mL (3.25 mmol) of tributylamine were dissolved in 5 mL of DMF. The mixture was stirred at 100 °C under a nitrogen atmosphere. After 4 h, the mixture was poured into 300 mL of methanol to precipitate polymer **3**. The polymer was filtered out, washed with hot methanol, and dried *in vacuo*. The yield was 95%. The inherent viscosity of the polymer was 1.11 dL g^{-1}, measured in DMF at a concentration of 0.5 g dL^{-1} at 30 °C.

Measurements. High-performance liquid chromatography (HPLC) measurements were performed by using a C_{18} column with a Shimadzu LC-9A and SPD-6A (UV spectrophotometric detector). Inductively coupled plasma (ICP) spectrometric measurements were carried out by using a SII SPS1500VR plasma spectrometer. Infrared (IR) spectra were recorded on a JASCO FTIR-8100 Fourier transform infrared spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL FX-90Q NMR spectrometer and homo *J*-resolved ^{1}H−^{1}H NMR spectra and homonuclear correlated (HH-COSY) NMR spectra were recorded on a JEOL GSX-500 NMR spectrometer. Gel permeation chromatography (GPC) measurements were carried out by using a JASCO HPLC 880PU, polystyrene−divinylbenzene columns (two Shodex KD806M and KD802), and DMF containing 0.01 mol L^{-1} of lithium bromide as an eluent. The absolute molecular weight was determined by laser light scattering measurement using a miniDAWN apparatus (Wyatt Technology Co.) and a Shimadzu RID-6A refractive index detector. A specific refractive index increment (d*n*/d*c*) of the polymer in DMF at 690 nm was determined to be 0.268 mL g^{-1} by using an Optilab 903 apparatus (Wyatt Technology Co.). XPS measurements were performed by using a ULVAC-PHI-5500MT system. The spectra were acquired using monochromated Al Kα (1486.7 eV) radiation at 14 kV and 200 W. Scanning electron microscope (SEM) back-scattered images were taken by using a JEOL T-220 microscope.

Results and Discussion

Characterization of Pd−Gr. The palladium content by weight in palladium−graphite (Pd−Gr) catalyst was determined to be 17%, which is about half of the reported value (33 wt %).[14] The low content of palladium may be caused by the low conversion of the reaction of potassium and graphite to form potassium−graphite. The XPS spectrum of Pd−Gr showed typical peaks for zero valence palladium, which is the same as palladium-coated active carbon (Pd−C). It was also confirmed that any potassium atom could not be detected in Pd−Gr.

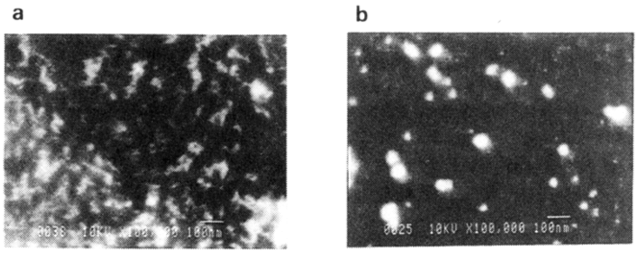

Figure 1. SEM back-scattered images of palladium catalysts: (a) palladium−graphite; (b) palladium-coated active carbon.

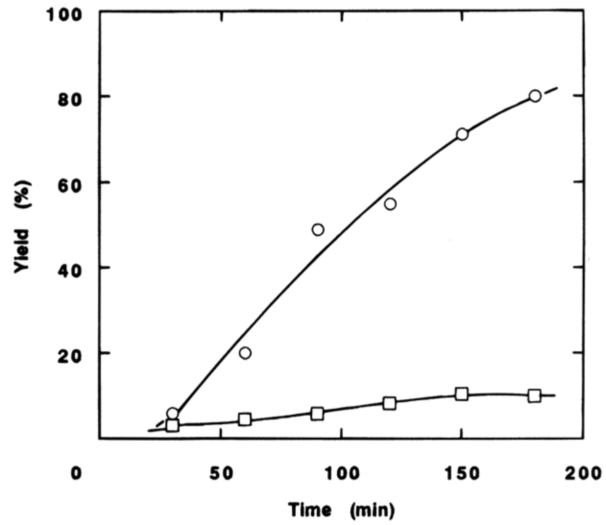

Figure 2. Formation of ethyl cinnamate with Pd−Gr (○) or with Pd−C (□) from the condensation of ethyl acrylate and iodobenzene in the presence of tributylamine at 80 °C.

As it has been reported that palladium is highly dispersed on the graphite surface rather than intercalated between the graphite layers in Pd−Gr,[17] there was no diffraction peak corresponding to the intercalated layer in the X-ray diffraction spectrum of Pd−Gr. The SEM back-scattered images of Pd−Gr and Pd−C are shown in Figure 1. The palladium particles on Pd−Gr which were detected as white spots were smaller than those on Pd−C. This difference must affect the catalytic activity for the Heck reaction and the polycondensation.

Model Reaction. The Heck reaction of ethyl acrylate and iodobenzene was examined in the presence of a catalytic amount of Pd−Gr. The yield of ethyl cinnamate was determined by HPLC measurements and plotted against the reaction time (Figure 2). Pd−C was also used in order to make a comparison. The activity of palladium−graphite was much higher than that of palladium carbon for the Heck reaction. It is obvious that the wide dispersion of the palladium metal on the Pd−Gr catalyst afforded the higher reactivity. Both Pd−Gr and Pd−C were easily removed by filtration after the reaction because they were insoluble in the reaction mixture.

The effect of solvent and base on the Heck reaction catalyzed by Pd−Gr was investigated, as shown in Table

Table 1. Condensation[a] of Ethyl Acrylate and Iodobenzene Catalyzed by Pd–Gr

solvent	base	yield (%)[b]
DMF	tributylamine	63
DMAc	tributylamine	76
NMP	tributylamine	69
DMSO	tributylamine	85
DMAc	triethylamine	37
DMAc	tripropylamine	89

[a] Reaction was carried out with 2.4 mmol of ethyl acrylate, 2.0 mmol of iodobenzene, 2.6 mmol of base, and 0.06 g of Pd–Gr at 80 °C. [b] Determined by HPLC measurement without isolation of the product.

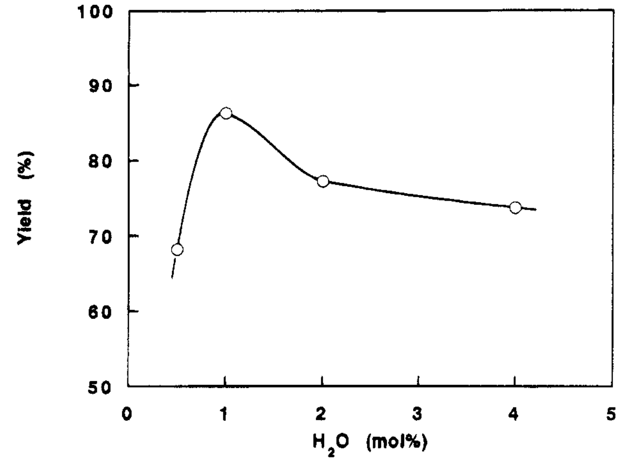

Figure 3. Effect of the amount of water in DMF on the formation of ethyl cinnamate catalyzed by Pd–Gr.

1. Aprotic polar solvents, such as DMF, DMAc, NMP, and DMSO, were available for this condensation. The reaction proceeded fast in high dielectric constant solvents such as DMSO. A base was essential for the Heck reaction. Trialkylamines, such as tripropylamine and tributylamine, were highly effective for the reaction. Triethylamine gave a lower yield of ethyl cinnamate because the reaction temperature at 80 °C was very close to the boiling point of triethylamine.

Figure 3 shows the effect of water content in DMF on the reaction for 3 h. It is reported that small amounts of water do not interfere with the Heck reaction.[18] It is noteworthy that DMF containing 1% (volume) water gave the best yield of ethyl cinnamate. It is clear that a small amount of water accelerates the reaction. The yield of ethyl cinnamate decreased in the case over 1% of water.

Polymerization Catalyzed by Pd–Gr. The results of the polycondensation of bis(acrylamide) **1** and diiodide **2** catalyzed by Pd–Gr carried out in DMF at 100 °C are shown in Table 2. The polycondensation proceeded efficiently in the presence of tributylamine and without any ligand compounds. Polymer **3** was obtained with an inherent viscosity of 0.9 dL g^{-1} after 20 h of polymerization. Among the bases, tributylamine was the most effective for this polymerization, while BDMAN afforded the polymer with the highest molecular weight in the case of previously reported homogeneous catalysts.[2] The aprotic polar solvents were effective for the polymerization, similar to the model reaction. The polymerization in DMF and DMAc gave the polymers with high inherent viscosities. DMSO which afforded the high yield in the model reaction was not suitable for the polymerization because of the poor solubility of the resulting polymer in DMSO. Since Pd–Gr is insoluble in the reaction mixture, it can be easily removed by filtration. In addition, the polymerization with the recovered Pd–Gr catalyst gave the polycinnamamide with an inherent viscosity of 0.7 dL g^{-1}.

Table 2. Synthesis of Polycinnamamide Catalyzed by Palladium–Graphite[a]

no.	base	solvent	time (h)	yield (%)	η_{inh} (dL g^{-1})[b]
1	tributylamine	DMF	4	90	0.25
2	tributylamine	DMF	20	95	0.90
3	tributylamine	DMF	40	95	0.95
4	tributylamine	DMF	20	85	0.30
5	BDMAN[c]	DMF	20	96	0.45
6	DBU[d]	DMF	20	0	
7	CH_3COONa	DMF	20	0	
8	Na_2CO_3	DMF	20	0	
9	tributylamine	DMAc	20	94	0.95
10	tributylamine	NMP	20	97	0.68
11	tributylamine	DMSO	20	86	0.25

[a] Polymerization was carried out with 1.25 mmol of the bis(acrylamide) and 1.25 mmol of the diiodobenzene, 3.25 mmol of base, and 6.87 × 10^{-3} mmol/Pd of Pd–Gr at 100 °C in 20 mL of the solvent. [b] Measured at a concentration of 0.5 g dL^{-1} in DMF at 30 °C. [c] BDMAN: 1,8-bis(dimethylamino)naphthalene. [d] DBU: 1,8-diazabicyclo[5.4.0]-7-undecene.

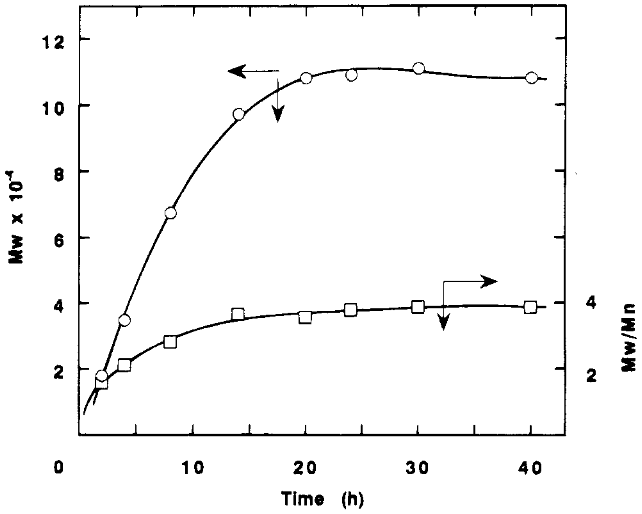

Figure 4. Time dependence of M_w (○) and M_w/M_n (□) of polycinnamamide formed by the polycondensation catalyzed by Pd–Gr at 100 °C. Conditions: monomers, 1.25 mmol; tributylamine, 3.25 mmol; Pd–Gr, 6.87 × 10^{-3} mmol/Pd; DMF, 20 mL.

The weight average molecular weight of the resulting polymer was plotted against the reaction time (Figure 4). The polymers having a molecular weight of about 100 000 formed by the polymerization for 20 h. As shown in Figure 5, the molecular weights of the resulting polymer increased by increasing the feed amount of Pd–Gr and the high molecular weight polymer was obtained when 2.5 mol % of Pd–Gr was used for the polymerization.

The effect of the molar ratio of diiodide/bis(acrylamide) on the polycondensation was investigated, as shown in Table 3. The polydispersity was evaluated by the polydispersity index (M_w/M_n) determined by GPC through a laser light scattering measurement. When the diiodide/bis(acrylamide) ratio was 0.99, the inherent viscosity and the molecular weight of the resulting polymer decreased compared with those prepared by the ratio of 1.00. In the case of the ratio of 1.01, the polydispersity index increased, while the inherent viscosity and the molecular weight were not affected. However, at the ratio of 1.05, the reaction mixture afforded gelation. It is obvious that the equimolar

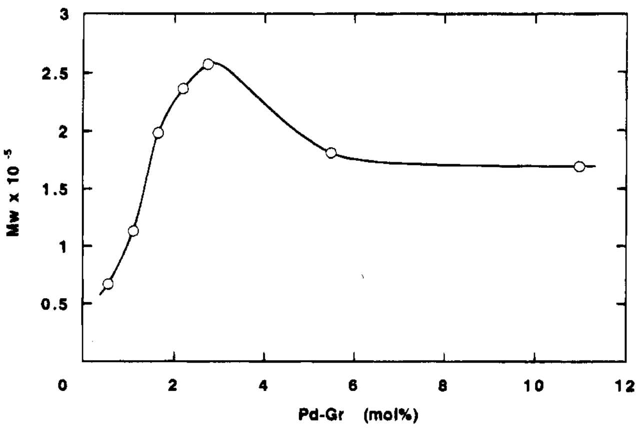

Figure 5. Effect of the feed amount of Pd−Gr on the molecular weight of polycinnamamide. Reaction conditions: 1.25 mmol of monomers and 3.25 mmol of tributylamine in 20 mL of DMF at 100 °C for 8 h.

Table 3. Effect of the Molar Ratio of Diiodide on the Polymerization Catalyzed by Pd−Gr[a]

no.	diiodide/ bis(acrylamide)	η_{inh} (dL g^{-1})[b]	$10^{-5}M_w$[c]	$10^{-4}M_n$[c]	M_w/M_n[c]
12	0.99	0.43	0.24	0.11	2.13
2	1.00	0.90	1.13	3.43	3.28
13	1.01	0.90	1.84	4.17	4.41
14	1.05	*d*	*d*	*d*	*d*

[a] Polymerization was carried out with 1.25 mmol of the bis(acrylamide), the prescribed amount of the diiodide, 3.25 mmol of tributylamine, and 6.87 × 10^{-3} mmol/Pd of Pd−Gr at 100 °C in DMF. [b] Inherent viscosity was measured at a concentration of 0.5 g dL^{-1} in DMF at 30 °C. [c] Absolute molecular weight was determined by GPC with a laser light scattering measurement. The d*n*/d*c* at 690 nm was determined to be 0.268 mL g^{-1}. [d] Gelation of the reaction mixture occurred.

amount of two monomers is essential for the formation of the polymer with a high molecular weight, though the olefin is often used in small molar excess relative to the organic halide in order to achieve exclusive monosubstitution of olefin in the case of many organic syntheses using the Heck reaction. These results suggest that the second substitution of the residual vinyl proton groups by intermediate complex of the aromatic halide and palladium occurred during the polymerization, which enlarged the polydispersity indices. The second substitution was accelerated when an excess amount of aromatic halide was used for the polycondensation, which caused gelation at the ratio of 1.05.

The structure of the resulting polymer was determined by IR and NMR spectra and it was found that polymer **3** had a structure identical to that of the previously prepared polycinnamamide using the homogeneous palladium catalysts. The *J*-resolved two-dimensional ^{1}H NMR spectrum was measured to determine coupling constants of protons around the double bond in the main chain. There were two different pairs of peaks with regard to the double bond, as shown in Figure 6. The coupling constant for the peaks at 6.73 and 7.54 ppm was 15.2 Hz, and the constant for the peaks at 6.69 and 7.57 ppm was 15.6 Hz. Both are typical coupling constants for olefin protons connected by a trans linkage. The two different pairs of peaks for olefin protons were not changed to single peaks by the measurement at 100 °C, which denies that the two pairs arise from restriction of bond rotations. It is suggested that the pairs resulted from the unsymmetrical structure by the introduction of the meta-linked phenylene ring. The HH-COSY NMR spectrum is shown in Figure 7, which gives more information about the pair peaks. The coupling of trans protons appeared as the crosspeak A, which may be mixed with the crosspeak between aromatic protons and vinyl protons. Crosspeak B correlates peaks at 6.69 and 7.28 ppm. Considering the *J*-resolved ^{1}H NMR spectrum (Figure 6), the peak at 7.28 ppm is not a doublet peak. This fact implies that the peak at 7.28 ppm arises from the meta-linked phenylene ring. Therefore, the vinyl proton which shows the peak at 6.69 ppm is close to the meta-linked phenylene ring. From these results, the chemical shifts around the double bond of the polymer would be assigned as shown in Figure 8.

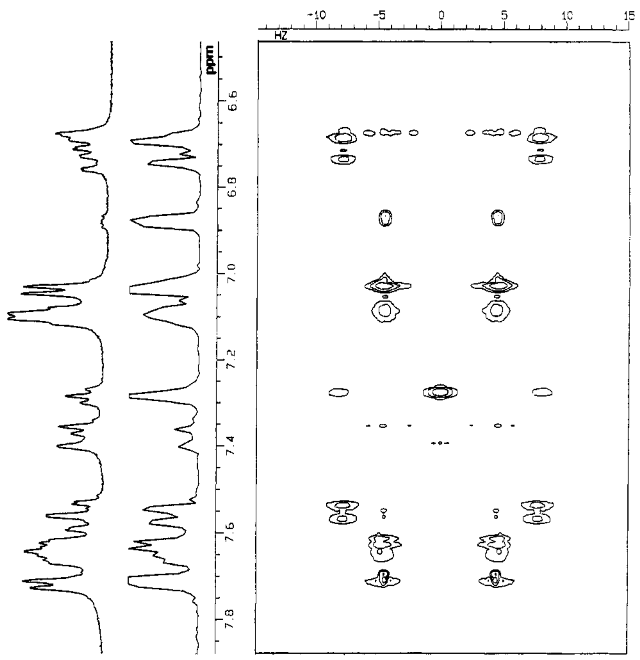

Figure 6. *J*-resolved ^{1}H NMR spectrum of polycinnamamide formed with Pd−Gr.

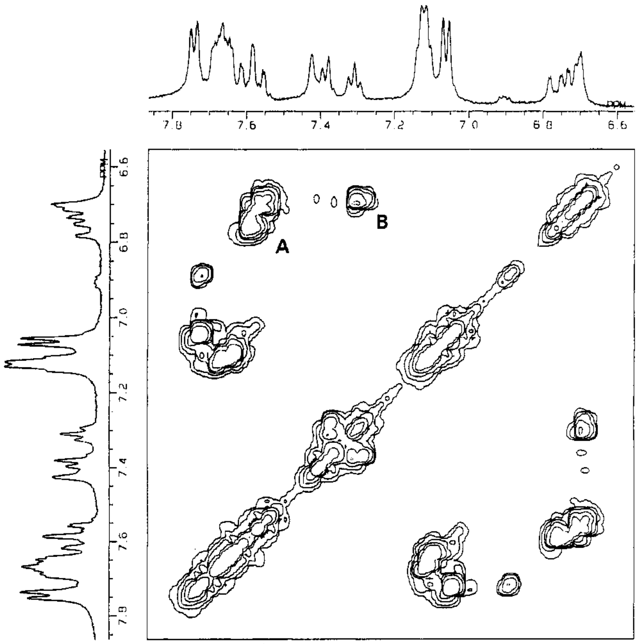

Figure 7. HH-COSY NMR spectrum of polycinnamamide formed with Pd−Gr.

The resulting polymer prepared using Pd−Gr was less colored than the polymer prepared using the homogeneous palladium catalysts. The amount of residual

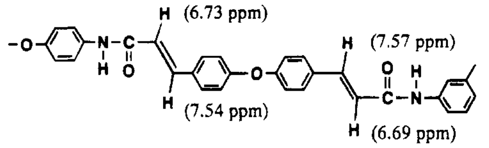

Figure 8. Assignment of chemical shifts to polycinnamamide.

Table 4. Synthesis of Polycinnamamide with Various Palladium Catalysts[a]

no.	catalyst	ligand	time (h)	yield (%)	η_{inh} (dL g^{-1})[b]
1	Pd−Gr		4	90	0.25
2	Pd−Gr		20	95	0.90
15	Pd−Gr	PTol$_3$[c]	20	96	0.81
16	Pd−C		20	94	0.69
17	Pd(OAc)$_2$	PTol$_3$[c]	4	95	1.11

[a] Polymerization was carried out with 1.25 mmol of the bis(acrylamide) and 1.25 mmol of the diiodobenzene, 3.25 mmol of tributylamine, and 6.87×10^{-3} mmol of Pd (nos. 1, 2, 12) or 1.25×10^{-2} mmol of Pd (nos. 13, 14) at 100 °C in DMF. [b] Measured at a concentration of 0.5 g dL^{-1} in DMF at 30 °C. [c] PTol$_3$: tritoylphosphine (5.0×10^{-2} mmol).

Table 5. Polydispersity Indices[a] **of the Polymers Prepared by Using Palladium Catalysts**

no.	catalyst	η_{inh} (dL g^{-1})[b]	$10^{-5}M_w$[c]	$10^{-4}M_n$[c]	M_w/M_n[c]
2	Pd−Gr	0.90	1.13	3.43	3.28
18	Pd−Gr	1.19	2.89	7.51	3.85
17	Pd(OAc)$_2$	1.11	2.20	5.10	4.32
19	Pd(OAc)$_2$		1.12	2.87	3.91

[a] Absolute molecular weight was determined by GPC with a laser light scattering measurement. The d*n*/d*c* at 690 nm was determined to be 0.268 mL g^{-1}. [b] Measured at a concentration of 0.5 g dL^{-1} in DMF at 30 °C.

palladium in the polymer prepared by Pd−Gr was determined to be *ca.* 50 ppm by the ICP plasma emission spectroscopy. However, the residual palladium of *ca.* 500 ppm was detected in the polymer prepared by palladium acetate. The fact that the amount of palladium in the polymer prepared by Pd−Gr was 10 times less than that in the polymer prepared by palladium acetate may affect the color of the polymer.

Polymerization Catalyzed by Various Palladium Compounds. Table 4 contains the results of the polycondensation catalyzed by Pd−C and palladium acetate. Pd−C showed less reactivity for the polymerization than Pd−Gr, similar to the model reaction. It is reported that ligand compounds such as tritolylphosphine accelerate the Heck reaction.[19] In the case of Pd−Gr, tritolylphosphine was not so effective on the inherent viscosity of the polymer. However, the polymerization using Pd−Gr required a longer reaction time than the polymerization catalyzed by palladium acetate. The high molecular weight polymer was obtained within a 5 h reaction time in the latter case.

Table 5 shows the GPC results of the polymerization catalyzed by Pd−Gr and palladium acetate. When Pd−Gr was used as a catalyst, the polydispersity indices were lower than those of the polymer prepared by using palladium acetate. The control experiments using an equimolar amount of ethyl acrylate and iodobenzene with Pd−Gr or palladium acetate were carried out under the same conditions as the polycondensation. In the case of Pd−Gr, the amount of the product by the second substitution was about 3 times less than the case of palladium acetate.[20] This fact supports the lower polydispersity indices for the polycondensation catalyzed by Pd−Gr.

Conclusion

Polycinnamamide was successfully prepared through the Heck reaction in the presence of the heterogeneous Pd−Gr catalyst. Although the polymerization reaction was slower compared with that of the homogeneous palladium catalysts, Pd−Gr possesses some benefits as follows: (1) The Pd−Gr catalyst could be easily separated from the reaction mixture. This fact caused a lower content of the palladium atom in the resulting polymer and gave a less colored polymer. (2) The polycondensation selectively proceeded to afford the smaller molecular weight distribution since the second substitution of the vinyl proton occurred less than in the case of the homogeneous palladium catalyst.

References and Notes

(1) Heitz, W.; Brugging, W.; Freund, L.; Gailberger, M.; Greiner, A.; Jung, H.; Kampschulte, U.; Niebner, M.; Osan, F.; Schmidt, H. W.; Wicker, M. *Makromol. Chem.* **1988**, *189*, 119.
(2) Yoneyama, M.; Kakimoto, M.; Imai, Y. *Macromolecules* **1989**, *22*, 4148.
(3) Bochmann, M.; Kelly, K. *J. Polym. Sci., Part A* **1992**, *30*, 2503.
(4) Bochmann, M.; Lu, J. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2493.
(5) Cramer, E.; Percec, V. *J. Polym. Sci., Part A* **1990**, *28*, 3029.
(6) Yoneyama, M.; Kakimoto, M.; Imai, Y. *Macromolecules* **1988**, *21*, 1908.
(7) Yoneyama, M.; Kakimoto, M.; Imai, Y. *Macromolecules* **1989**, *22*, 4152.
(8) Perry, R. J.; Turner, S. R.; Blevins, R. W. *Macromolecules* **1993**, *26*, 1509.
(9) Perry, R. J.; Wilson, B. D. *Macromolecules* **1994**, *27*, 40.
(10) Suzuki, M.; Sawada, S.; Saegusa, T. *Macromolecules* **1989**, *22*, 1505.
(11) Suzuki, M.; Lim, J.-C.; Saegusa, T. *Macromolecules* **1990**, *23*, 1574.
(12) Suzuki, M.; Sawada, S.; Yoshida, S.; Eberhardt, A.; Saegusa, T. *Macromolecules* **1993**, *26*, 4748.
(13) Savoia, D.; Trombini, C.; Umani-Ronchi, A. *Pure Appl. Chem.* **1985**, *57*, 1887.
(14) Savoia, D.; Trombini, C.; Umani-Ronchi, A.; Verardo, G. *J. Chem. Soc., Chem. Commun.* **1981**, 540.
(15) Savoia, D.; Trombini, C.; Umani-Ronchi, A.; Verardo, G. *J. Chem. Soc., Chem. Commun.* **1981**, 541.
(16) Boldrini, G. P.; Savoia, D.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Organomet. Chem.* **1984**, *268*, 97.
(17) Schaefer-Stahl, H. *J. Chem. Soc., Dalton Trans.* **1981**, 328.
(18) Heck, R. F. In *Organic Reactions*; John Wiley & Sons, Inc.: New York, 1982; Vol. 27, pp 360.
(19) Dieck, H. A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1133.
(20) The amount of the product produced by the second substitution was evaluated by the ratio of the peak areas in HPLC measurements.

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