(4-aminophenyl) sulfone, 80-08-0; N-phenylcinnamamide, 3056-73-3; N-phenylacrylamide, 2210-24-4; iodobenzene, 591-50-4.

References and Notes

- Morgan, P. W. Condensation Polymers by Interfacial and Solution Methods; Interscience: New York, 1965.
- Billmeyer, F. W.; Jr. Textbook of Polymer Science; Wiley-Interscience: New York, 1984.
- (3) Colqohoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. New Pathways for Organic Synthesis; Plenum: New York and London, 1984.
- (4) Yamamoto, A. Organotransition Metal Chemistry— Fundamental Concepts and Applications; Wiley-Interscience: New York, 1986.
- (5) Yamamoto, T.; Hayashi, Y.; Yamamoto, A. Bull. Chem. Soc. Jpn. 1978, 51, 2091.
- (6) Yamamoto, T.; Sanechika, K.; Yamamoto, A. J. Polym., Sci., Polym. Lett. Ed. 1980, 18, 9.
- (7) Havens, S. J.; Hergenrother, P. M. J. Polym. Sci., Polym. Lett. Ed. 1985, 23, 587.

- (8) Trumbo, D. L.; Marvel, C. S. J. Polym. Sci., Polym. Chem. Ed. 1986, 24, 2311.
- (9) Yoneyama, M.; Kakimoto, M.; Imai, Y. *Macromolecules* 1988, 21, 1908.
- (10) Yoneyama, M.; Kakimoto, M.; Imai, Y. J. Polym. Sci., Polym. Chem. Ed. 1989, 27, 1985.
- (11) Yoneyama, M.; Kakimoto, M.; Imai, Y. Macromolecules, 1989, 22, 2593.
- (12) Heck, R. F. Org. React. (N.Y.) 1982, 27, 345.
- (13) Heck, R. F. Acc. Chem. Res. 1979, 12, 146.
- (14) Heck, R. F. Pure Appl. Chem. 1978, 50, 691.
- (15) Spencer, A. J. Organomet. Chem. 1983, 258, 101.
- (16) Suzuki, H.; Kondo, A.; Inouye, M.; Ogawa, T. Synthesis 1986, 121.
- (17) Merkushev, E. B.; Simakhina, N. D.; Koveshnikova, G. M. Synthesis 1980, 486.
- (18) Reppe, W. Ann. Chem. 1953, 582, 1.
- (19) Heck, R. F. Palladium Reagents in Organic Syntheses; Academic: New York, 1985.
- (20) Ziegler, C. B., Jr.; Heck, R. F. J. Org. Chem. 1978, 43, 2941.
- (21) Johnston, K. M. Tetrahedron 1968, 24, 5595.

Novel Synthesis of Poly(acylhydrazide)s by Palladium-Catalyzed Polycondensation of Dihydrazides, Aromatic Dibromides, and Carbon Monoxide

Masaru Yoneyama, Masa-aki Kakimoto, and Yoshio Imai*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan. Received December 23, 1988; Revised Manuscript Received March 13, 1989

ABSTRACT: A novel and convenient method was found for the synthesis of acylhydrazides by the palladium-catalyzed carbonylation of hydrazide with aromatic bromides. By the extension of this reaction, a new approach to the preparation of poly(acylhydrazide)s was developed. The palladium-catalyzed polycondensation of dihydrazides and aromatic dibromides with carbon monoxide yielded a series of poly(acylhydrazide)s with inherent viscositites between 0.13 and 0.65 dL·g⁻¹.

Introduction

Recently much attention has been given to C_1 chemistry. Carbon monoxide is an inexpensive and important starting material for the industrial production of methanol, acetaldehyde, acetic acid, etc.¹ In these reactions transition-metal catalysts such as cobalt and ruthenium complexes were necessary to activate carbon monoxide. Although new reactions and catalysts for carbon monoxide have been explored extensively, only a few studies have been reported on the synthesis of polymers using carbon monoxide.^{2,3} More recently we have developed a novel carbonylation polycondensation for the synthesis of polyamides or polyesters from carbon monoxide, aromatic dibromides, and diamines or bis(phenol)s in the presence of palladium catalysts.⁴⁻⁶

During the course of our study on carbonylation polycondensation, we have found that the reaction of hydrazides as nucleophiles with aromatic bromides and carbon monoxide in the presence of a palladium catalyst yielded excellent yields of acylhydrazides. This reaction would be suitable for the synthesis of poly(acylhydrazide)s.

Poly(acylhydrazide)s are known to be the precursors for poly(1,3,4-oxadiazole)s, which are one of the high-temperature plastics.⁷ Poly(acylhydrazide)s are generally prepared from dihydrazides and diacid chlorides in amide-type solvents.^{8,9}

This paper describes a novel method for the synthesis of poly(acylhydrazide)s by the palladium-catalyzed poly-

condensation of dihydrazides and aromatic dibromides with carbon monoxide (eq 1).

Experimental Section

Materials. Benzhydrazide was recrystallized from ethanol. p-Bromoanisol, p-bromotoluene, and bromobenzene were purified by vacuum distillation. p-Bromobenzamide, p-bromobenzonitrile, and p-bromochlorobenzene were used as received. Methyl p-bromobenzoate, p-bromoacetophenone, and p-bromobenzoic acid

were recrystallized from methanol.

Terephthalic dihydrazide (1a) and sebacic dihydrazide (1d) were recrystallized from water. Isophthalic dihydrazide (1b) and adipic dihydrazide (1c) were recrystallized from ethanol and aqueous ethanol, respectively. p-Dibromobenzene (2a), 2,6-dibromopyridine (2c), and bis(4-bromophenyl) ether (2d) were recrystallized from ethanol. m-Dibromobenzene (2b) was purified by vacuum distillation. 2,5-Bis(4-bromophenyl)-3,4-diphenylthiophene (2e) was synthesized according to the method reported in our previous paper.4

Tri-n-propylamine and 1.8-diazabicyclo[5.4.0]-7-undecene (DBU) were purifed by vacuum distillation. 1,4-Diazabicyclo-[2.2.2]octane (DABCO) was recrystallized from ethanol. 4-(Dimethylamino)pyridine, 1,8-bis(dimethylamino)naphthalene, and

sodium acetate were used as received.

Palladium chloride (PdCl₂) and palladium acetate [Pd(OAc)₂] were used as received. Dichlorobis(triphenylphosphine)palladium(II) [PdCl₂(PPh₃)₂], ¹⁰ tetrakis(triphenylphosphine)palladium(0) [Pd(PPh₃)₄], ¹¹ dichloro[1,3-bis(diphenylphosphino)-propane]palladium(II) [PdCl₂dppp], ¹² dichloro[1,4-bis(diphenylphosphino)butane]palladium(II) [PdCl₂dppb], ¹³ and diphenylphosphino)butane]palladium(II) [PdCl₂dppb], ¹³ and diphenylphosphino)butane] chloro[1,1'-bis(diphenylphosphino)ferrocene]palladium(II) [PdCl₂dppf]¹⁴ were prepared by the reported procedures.

N,N-Dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP), tetramethylurea (TMU), 1,3-dimethyl-2-imidazolidone (DMI), hexamethylphosphoramide (HMPA), and dimethyl sulfoxide (DMSO) were purified by vacuum distillation over calcium hydride. Pyridine

was purified by distillation over calcium hydride.

Model Reaction. Synthesis of Dibenzoylhydrazine. An ordinary catalytic reduction apparatus with a gas burette was used as the reaction apparatus.4 In a three-necked flask equipped with a stirrer, a carbon monoxide inlet, and a reflux condenser were placed 0.3404 g (2.5 mmol) of benzhydrazide, 0.3925 g (2.5 mmol) of bromobenzene, 0.0089 g (0.05 mmol) of PdCl₂, 0.0525 g (0.2 mmol) of PPh3, and 5 mL of DMF. The flask was purged several times with carbon monoxide and then heated with stirring at 100 °C in an oil bath. To the mixture, 0.45 mL (3.0 mmol) of DBU was added all at once with a syringe. The reaction mixture was stirred at 100 °C until the theoretical amount of carbon monoxide was absorbed. The reaction solution was diluted with 10 mL of DMF and poured into 350 mL of 1 M aqueous hydrochloric acid. The precipitated product was filtered, washed with water, and dried at room temperature in vacuo. The yield was 0.5175 g (86%): mp 239 °C (DTA) (lit. 15 234-238 °C); IR (KBr) 3410, 3210 (N-H), 1635 cm⁻¹ (C=O).

Polymerization. Polymer 3db from 1b and 2d. In a three-necked flask, a mixture of 0.4855 g (2.5 mmol) of 1b, 0.8200 g (2.5 mmol) of 2d, and 0.1460 g (0.125 mmol) of Pd(PPh₃)₄ were dissolved in 10 mL of DMSO. The flask was flushed several times with carbon monoxide and then heated with stirring at 95 °C in an oil bath. To the reaction solution, 0.9 mL (6.0 mmol) of DBU was added all at once with a syringe. The reaction mixture was stirred at 95 °C until the consumption of carbon monoxide stopped. The reaction solution was diluted with 40 mL of DMSO and poured into 450 mL of methanol. The precipitated polymer was filtered, washed thoroughly with hot methanol, and dried at room temperature under vacuum. The yield was 0.9982 g (96%). The inherent viscosity of the polymer in DMSO was 0.46 dL·g⁻¹ measured at a concentration of 0.5 g·dL⁻¹ at 30 °C. The IR spectrum (KBr) exhibited bands at 3255 (N-H) and 1650 cm⁻¹ (C=O). Anal. Calcd for (C₂₂H₁₆N₄O₅)_n: C, 63.46; H, 3.87; N, 13.46. Found: C, 62.89; H, 3.69; N, 12.68.

Other polymers were prepared by analogous procedures. Measurements. IR spectra were recorded on a JASCO FT/IR-5000 Fourier transform infrared spectrophotometer.

Number-average molecular weight (\bar{M}_n) and weight-averaging molecular weight (\bar{M}_w) were determined by means of gel permeation chromatography (GPC) on the basis of a poly(oxyethylene) calibration on a JASCO HPLC BIP-I apparatus (column, Shodex GPC AD-80M/S polystyrene gel; eluent, DMF containing 0.01 mol·L⁻¹ of lithium bromide).

Results and Discussion

Model Reaction. Unsymmetrical acylhydrazide compounds are usually prepared from hydrazides and acid

Table I Reaction of Benzhydrazide with Bromobenzene Derivatives and Carbon Monoxide

| R | reactn time, h | isolated yield, % | R | reactn time, h | isolated yield, % |
|-------------------|-------------------|----------------------|-----------------------|-------------------|----------------------|
| CH ₃ | 7.8 | 90 | H ₂ NC(O) | 4.5 | 93 |
| CH ₃ O | 3.2 | 79 | H ₃ COC(O) | 4.6 | 90 |
| Cl | 2.8 | 92 | HOC(O) | 5.3 | 89 |
| H | 2.6 | 86 | $H_8CC(O)$ | 3.5 | 59 |
| NC | 2.8 | 87 | • , , | | |

^a Reaction was carried out with 2.5 mmol of benzhydrazide, 2.5 mmol of the p-bromobenzene derivatives, 3.0 mmol of DBU, 0.05 mmol of PdCl2, and 0.2 mmol of PPh3 in 5 mL of DMF at 100 °C under carbon monoxide.

Table II Synthesis of Poly(acylhydrazide) 3bd with Various Palladium Catalysts^a

| | | polymer | | |
|---|-------------------|----------|--|--|
| catalyst | reactn time, h | yield, % | $\frac{\eta_{\mathrm{inh}},^{b}}{\mathrm{dL}\cdot\mathrm{g}^{-1}}$ | |
| PdCl ₂ (PPh ₃) ₂ | 21.6° | trace | | |
| PdCl ₂ (PPh ₃) ₂ /2PPh ₃ | 4.3 | 91 | 0.35 | |
| PdCl ₂ /4PPh ₃ | 3.5 | 87 | 0.37 | |
| $Pd(OAc)_2/4PPh_3$ | 3.4 | 83 | 0.34 | |
| Pd(PPh ₃) ₄ | 5.2 | 84 | 0.46 | |
| PdCl ₂ dppp | 6.6 | 78 | 0.32 | |
| PdCl ₂ dppb | 3.1 | 93 | 0.39 | |
| PdCl ₂ dppf | 3.0 | 86 | 0.32 | |

^a Polymerization was carried out with 2.5 mmol of 1b, 2.5 mmol of 2d, 6 mmol of DBU, and 0.075 mmol of the catalyst in 10 mL of DMF at 100 °C under carbon monoxide. b Measured at a concentration of 0.5 g·dL⁻¹ in DMSO at 30 °C. c Palladium black precipitation occurred during the polymerization.

chlorides. 16 However, an alternate approach involving the palladium-catalyzed reaction of hydrazides with bromobenzene derivatives and carbon monoxide has not been reported to date. We studied for the first time this reaction to explore a new synthetic route for unsymmetrical acylhydrazides (eq 2).

An ordinary catalytic reduction apparatus with a gas burette was used as the reaction apparatus.⁴ The reaction was carried out at 100 °C in the presence of PdCl₂ and PPh₃ as the catalyst and DBU as hydrogen bromide acceptor in DMF under atomspheric pressure of carbon monoxide. The progress of the reaction was monitored by the consumption of carbon monoxide in the gas burette.

The results shown in Table I revealed that the palladium-catalyzed carbonylation condensation proceeded smoothly at 100 °C and completed within 8 h. Most of the reactions afforded acylhydrazide compounds in high yields, over 79%. The yield of p-acetylbenzhydrazide was somewhat low, because the acylhydrazide also can react with the ketone moiety. Thus, this palladium-catalyzed reaction was found to be an alternate and conventional method for the synthesis of unsymmetrical acylhydrazides.

Polymer Synthesis. The high-yield model reaction was extended to the polymerization starting from bifunctional intermediates. The carbonylation polycondensation of isophthalic dihydrazide (1b) and bis(4-bromophenyl) ether (2d) with carbon monoxide in the presence of a palladium catalyst and a base in an organic solvent giving poly-(acylhydrazide) 3bd was investigated first to optimize the reaction conditions. The polymerization apparatus and

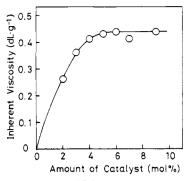


Figure 1. Effect of amount of Pd(PPh₃)₄ on the inherent viscosity of poly(acylhydrazide) **3bd** formed by the polycondensation of **1b** with **2d** under carbon monoxide at 100 °C for 2.4–12.7 h. Monomers, 2.5 mmol; DBU, 6 mmol; DMF, 10 mL.

Table III Synthesis of Poly(acylhydrazide) 3bd in Various Solvents^a

| | poly | | |
|----------|-------------------|-------------|---|
| solvent | reactn time, h | yield, % | $\overset{oldsymbol{\eta_{	ext{inh}}},^b}{\mathrm{dL}\cdot\mathbf{g}^{-1}}$ |
| DMF | 2.4 | 94 | 0.43 |
| DMAc | 3.5 | 94 | 0.41 |
| NMP | 1.8 | 85 | 0.35 |
| TMU | 3.6 | 80 | 0.31 |
| DMI | 5.1 | 89 | 0.38 |
| HMPA | 7.4 | 88 | 0.34 |
| DMSO | 3.8 | 93 | 0.46 |
| pyridine | 2.4 | 84 | 0.39 |

^a Polymerization was carried out with 2.5 mmol of 1b, 2.5 mmol of 2d, 6 mmol of DBU, and 0.125 mmol of Pd(PPh₃)₄ in 10 mL of the solvent at 100 °C under carbon monoxide. ^b Measured at a concentration of 0.5 g·dL⁻¹ in DMSO at 30 °C.

procedure were the same as those used in the model reaction.

Table II summarizes the effect of palladium catalysts on the polycondensation. All the polymerizations using these catalysts were completed within 6.6 h, except for that using PdCl₂(PPh₃)₂. The reaction time required for the completion of the polymerization, however, was somewhat longer compared with the other carbonylation polycondensations for polyamide and polyester syntheses,⁴⁻⁶ because hydrazides had lower nucleophilicities than amines and hydroxylate anion. Among the palladium catalysts employed, Pd(PPh₃)₄ gave the best results, judging from inherent viscosity of the obtained polymer. Moreover, in this case, precipitation of palladium black, which made catalytic activity apparently lower, was not observed during the polymerization without further addition of PPh₃.

Figure 1 shows the effect of amount of Pd(PPh₃)₄ on the inherent viscosity of poly(acylhydrazide) **3bd**. More than 5 mol % of the catalyst based on the monomers was necessary to obtain the polymer with sufficiently high inherent viscosity. This indeed shows that the polymerization proceeded catalytically.

Table III summarizes the solvent effect on the inherent viscosity of the polymer. Most of the solvents employed were suitable solvents for the synthesis of the polymer with reasonably high inherent viscosity, and in particular, DMSO was the most effective reaction medium. This is because DMSO was known to be a good solvent for the poly(acylhydrazide)s.

For the carbonylation polymerization, a base that acts as the hydrogen bromide acceptor was essential. Table IV lists the effect of base on the polymerization. Among six bases employed, DBU was the most effective, judging from the reaction time and the yield and inherent viscosity of the resulting polymer.

Table IV Synthesis of Poly(acylhydrazide) 3bd with Various Bases^a

| | | poly | mer | |
|-----------------------------------|-------------------|-------------|--|---|
| base | reactn time, h | yield, % | $\frac{\eta_{\mathrm{inh}},^{b}}{\mathrm{dL}\cdot\mathrm{g}^{-1}}$ | |
| tripropylamine | 13.8 | 66 | 0.17 | _ |
| DBU | 3.8 | 93 | 0.46 | |
| DABCO | 9.4 | 81 | 0.24 | |
| 4-(dimethylamino)pyridine | 5.1 | 75 | 0.20 | |
| 1,8-bis(dimethylamino)naphthalene | 67.5 | 47 | 0.17 | |
| sodium acetate | 4.2 | 51 | 0.15 | |

^aPolymerization was carried out with 2.5 mmol of 1b, 2.5 mmol of 2d, 6 mmol of the base, and 0.125 mmol of Pd(PPh₃)₄ in 10 mL of DMSO at 100 °C under carbon monoxide. ^b Measured at a concentration of 0.5 g·dL⁻¹ in DMSO at 30 °C.

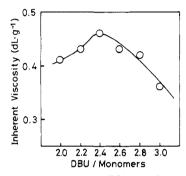


Figure 2. Effect of amount of DBU on inherent viscosity of poly(acylhydrazide) 3bd formed by the polycondensation of 1b with 2d under carbon monoxide at 100 °C for 2.3-6.5 h. Monomers, 2.5 mmol; Pd(PPh₃)₄, 0.125 mmol; DMSO, 10 mL.

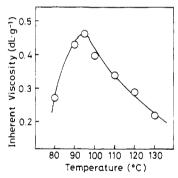


Figure 3. Effect of reaction temperature on inherent viscosity of poly(acylhydrazide) 3bd formed by the polycondensation of 1b with 2d under carbon monoxide for 1.4-8.0 h. Monomers, 2.5 mmol; DBU, 6 mmol; Pd(PPh₃)₄, 0.125 mmol; DMSO, 10 mL.

Figure 2 shows the relationship between the amount of DBU and the inherent viscosity of the polymer. Although a theoretical amount of the base required for the polymerization was 2 equiv on the basis of the monomers, a slight excess amount of DBU was preferable to obtain a higher inherent viscosity of the polymer.

Figure 3 reveals the temperature dependence on the polymerization. The optimum reaction temperature for the poly(acylhydrazide) synthesis was found to be 95 °C. This temperature was somewhat lower than that for the polyamide and polyester synthesis reported previously.⁴⁻⁶

The polymer thus obtained was confirmed to be the corresponding poly(acylhydrazide) **3bd** by means of IR spectroscopy and elemental analysis. The IR spectrum exhibited absorptions at 3255 (N—H) and 1650 cm⁻¹ (C—O), which are the characteristic absorption bands of acylhydrazide bonds. The elemental analysis values were in agreement with the calculated values with no trace of metallic ash. The number-average molecular weight (\bar{M}_n) and weight-average molecular weight (\bar{M}_n) of poly(acylhydrazide) **3bd** having an inherent viscosity of 0.46 dL·g⁻¹,

Table V Inherent Viscosities of Various Poly(acylhydrazide)s by Palladium-Catalyzed Polycondensationa

| | dibromide | | | | |
|-------------|-----------|------|------|------|------|
| dihydrazide | 2a | 2b | 2c | 2d | 2e |
| 1a | ь | 0.43 | 0.27 | 0.65 | 0.23 |
| 1 b | 0.47 | 0.28 | 0.18 | 0.46 | 0.49 |
| 1c | 0.18 | 0.17 | 0.13 | 0.28 | 0.24 |
| 1 d | 0.22 | 0.34 | 0.20 | 0.34 | 0.30 |

^aPolymerization was carried out with 2.5 mmol of the dihydrazide, 2.5 mmol of the dibromide, 6 mmol of DBU, and 0.125 mmol of Pd(PPh₃)₄ in 10 mL of DMSO at 95 °C for 3.0-24.5 h under carbon monoxide. Inherent viscosity was measured at a concentration at 0.5 g·dL⁻¹ in DMSO at 30 °C. b The polymer obtained was insoluble in organic solvents.

determined by means of GPC, were 3900 and 12600, respectively, for standard poly(oxyethylene). The ratio of $\bar{M}_{\rm w}/\bar{M}_{\rm n}$ was 3.2.

A variety of poly(acylhydrazide)s 3aa-de were prepared from combinations of dihydrazides la-d and aromatic dibromides 2a-e under the optimum reaction conditions obtained for poly(acylhydrazide) 3bd. The results are summarized in Table V. A longer reaction time was required to complete the polymerization in the case of 2c, while the other reactions proceeded faster and were completed within 5 h. The wholly aroamtic poly(acylhydrazide)s that resulted had inherent viscosities in the range 0.18-0.65 dL·g⁻¹, whereas the inherent viscosities of aliphatic-aromatic poly(acylhydrazide)s were 0.13-0.34 dL·g⁻¹. This difference may be attributed to the difference in solubility of both types of poly(acylhydrazide)s. Thus, we have found a novel approach to the synthesis of poly-(acylhydrazide)s with moderate molecular weights by the palladium-catalyzed carbonylation polymerization of aromatic dihydrazides and aromatic dibromides.

Registry No. (1a)(2a)(CO) (copolymer), 121988-08-7; (1a)-(2b)(CO) (copolymer), 121988-09-8; (1a)(2c)(CO) (copolymer), 121988-10-1; (1a)(2d)(CO) (copolymer), 121988-11-2; (1a)(2e)(CO) (copolymer), 121988-12-3; (1b)(2a)(CO) (copolymer), 121988-13-4; (1b)(2b)(CO) (copolymer), 121988-14-5; (1b)(2c)(CO) (copolymer), 121988-15-6; (1b)(2d)(CO) (copolymer), 122047-22-7; (1b)(2e)(CO) (copolymer), 121988-16-7; (1c)(2a)(CO) (copolymer), 121988-17-8; (1c)(2b)(CO) (copolymer), 121988-18-9; (1c)(2c)(CO) (copolymer), 121988-19-0; (1c)(2d)(CO) (copolymer), 121988-20-3; (1c)(2e)(CO) (copolymer), 121988-21-4; (1d)(2a)(CO) (copolymer), 121988-22-5; (1d)(2b)(CO) (copolymer), 121988-23-6; (1d)(2c)(CO) (copolymer), 121988-24-7; (1d)(2d)(CO) (copolymer), 121988-25-8; (1d)(2e)(CO) (copolymer), 121988-26-9; (1a)(2a)(CO) (SRU), 122188-56-1;

(1a)(2b)(CO) (SRU), 39278-99-4; (1a)(2c)(CO) (SRU), 122188-57-2; (1a)(2d)(CO) (SRU), 32034-15-4; (1a)(2e)(CO) (SRU), 122188-58-3; (1b)(2b)(CO) (SRU), 81367-22-8; (1b)(2c)(CO) (SRU), 122188-59-4; (1b)(2d)(CO) (SRU), 26100-82-3; (1b)(2e)(CO) (SRU), 122188-60-7; (1c)(2a)(CO) (SRU), 27417-29-4; (1c)(2b)(CO) (SRU), 27251-03-2; (1c)(2c)(CO) (SRU), 122188-61-8; (1c)(2d)(CO) (SRU), 27251-04-3; (1c)(2e)(CO) (SRU), 122188-62-9; (1d)(2a)(CO) (SRU), 27417-30-7; (1d)(2b)(CO) (SRU), 26100-81-2; (1d)(2c)(CO) (SRU), 122188-63-0; (1d)(2d)(CO) (SRU), 27251-06-5; (1d)(2e)(CO) (SRU), 122188-64-1; DBU, 6674-22-2; DABCO, 280-57-9; PdCl₂dppf, 72287-26-4; PdCl₂dppp, 59831-02-6; PdCl₂dppb, 29964-62-3; Pd(PPh₃)₄, $\begin{array}{l} 14221\text{-}01\text{-}3; \ PdCl_2(PPh_3)_2, \ 13965\text{-}03\text{-}2; \ BrC_6H_4\text{-}p\text{-}CH_3, \ 106\text{-}38\text{-}7; \\ BrC_6H_4\text{-}p\text{-}OCH_3, \ 104\text{-}92\text{-}7; \ BrC_6H_4\text{-}p\text{-}Cl, \ 106\text{-}39\text{-}8; \ BrC_6H_4\text{-}p\text{-}CN, \\ \end{array}$ 623-00-7; BrC₆H₄-p-CONH₂, 698-67-9; BrC₆H₄-p-COOCH₃, 619-42-1; BrC₆H₄-p-CO₂H, 586-76-5; BrC₆H₄-p-COCH₃, 99-90-1; PhCO(NH)₂COC₆H₄-p-CH₃, 19338-21-7; PhCO(NH)₂COC₆H₄-p-OCH₃, 6781-59-5; PhCO(NH)₂COC₆H₄-p-Cl, 6828-55-3; PhCO-(NH)₂COC₆H₄-p-CN, 121988-03-2; PhCO(NH)₂COC₆H₄-p-CONH₂, 121988-04-3; PhCO(NH)₂COC₆H₄-p-CO₂CH₃, 66395-10-6; $PhCO(NH)_2COC_6H_4-p-CO_2H$, 109411-44-1; $(NH)_2COC_6H_4$ -p-COCH₃, 121988-05-4; PPh₃, 603-35-0; PdCl₂, 7647-10-1; Pd(OAc)₂, 3375-31-3; 4-(dimethylamino)pyridine, 1122-58-3; 1.8-bis(dimethylamino)naphthalene, 20734-58-1; sodium acetate, 127-09-3; tripropylamine, 102-69-2; dibenzoylhydrazine. 787-84-8; carbon monoxide, 630-08-0; benzhydrazide, 613-94-5; bromobenzene, 108-86-1.

References and Notes

- (1) Falbe, J. New Synthesis with Carbon Monoxide; Springer-Verlag: Berlin, 1980.
- Yamamoto, T.; Yamamoto, A. Chem. Lett. 1977, 353. Sen, A.; Lai, T.-W. J. Am. Chem. Soc. 1982, 104, 3520.
- Yoneyama, M.; Kakimoto, M.; Imai, Y. Macromolecules 1988, 21, 1908.
- Yoneyama, M.; Kakimoto, M.; Imai, Y. J. Polym. Sci., Polym. Chem. Ed. 1989, 27, 1985.
- Yoneyama, M.; Kakimoto, M.; Imai, Y. Macromolecules 1989, 22, 2593.
- Cassidy, P. E. Thermally Stable Polymers; Marcel Dekker: New York. 1980.
- Frazer, A. H.; Wallenberger, F. T. J. Polym. Sci., Part A 1964, 2, 1137.
- (9) Frazer, A. H.; Wallenberger, F. T. J. Polym. Sci., Part A 1964, 2.1147
- (10) Heck, R. F. Palladium Reagents in Organic Syntheses; Academic: New York, 1985.
- Coulson, D. R. Inorg. Synth. 1972, 13, 121.
- Steffen, W. L.; Palenik, G. J. Inorg. Chem. 1976, 15, 2432.
- Tanaka, M.; Kobayashi, T.; Sakakura, T. Nippon Kagakukaishi **1985**, 537.
- (14) Hayashi, T.; Konishi, M.; Kumada, M. Tetrahedron Lett. **1979**, 21, 1871.
- Hatt, H. H. Org. Synth. 1943, 2, 208.
- Zabicky, J., Ed. The Chemistry of Amides; Interscience: New York, 1970.