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Novel Synthesis of Polycinnamamides by Palladium-Catalyzed Carbon–Carbon Coupling Polycondensation of Bis(acrylamide)s with Aromatic Diiodides

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

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan.
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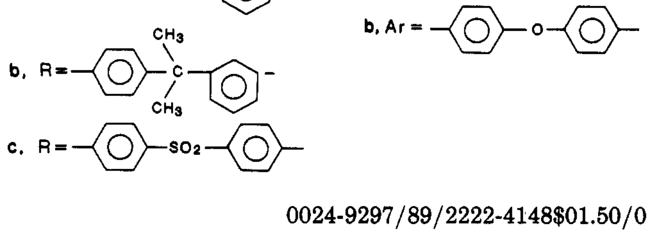
ABSTRACT: A novel method for the synthesis of polycinnamamides of high molecular weights has been developed by the palladium-catalyzed carbon–carbon coupling polycondensation of bis(acrylamide)s with aromatic diiodides. The effects of reaction variables, such as reaction temperature, reaction time, kinds and amounts of base and catalyst, and reaction medium, on the polycondensation were investigated in detail. Inherent viscosities of the polycinnamamides obtained were between 0.22 and 2.60 dL·g^{-1}, depending on the chemical structure of the polymers. The polycinnamamides had glass transition temperatures ranging from 230 to 270 °C and were thermally and photochemically cross-linkable through the double bonds in the polymer backbone.

Introduction

Most condensation polymers such as polyamides, polyesters, and polyethers have been synthesized by carbon–nitrogen and carbon–oxygen bond-forming polycondensation with the elimination of such small molecules as water and hydrogen halides.[1,2] However, only a few carbon–carbon bond-forming polycondensations have been known to date, despite the fact that many effective carbon–carbon bond-forming reactions have been developed by use of transition-metal catalysts in the field of synthetic organometallic chemistry.[3,4] Yamamoto et al. reported the nickel-catalyzed carbon–carbon coupling polymerization of the Grignard reagents of dihalogeno aromatic compounds such as *p*-dibromobenzene and 2,5-dibromothiophene yielding poly(*p*-phenylene) and poly(2,5-thienylene), respectively.[5,6] Synthesis of poly(arylene–acetylenes) by the palladium-catalyzed carbon–carbon coupling polycondensation of aromatic dibromides with aromatic diacetylenes was reported by Havens and Hergenrother[7] and Trumbo and Marvel,[8] independently. More recently we have successfully developed the palladium-catalyzed carbonylation polycondensation for the synthesis of polyamides[9,10] or polyesters[11] of high molecular weights from aromatic dibromides, carbon monoxide, and diamines or bis(phenol)s, respectively.

Heck found in the late 1970's a novel palladium-catalyzed carbon–carbon coupling reaction for the synthesis of arylalkenyl compounds from aromatic halides and vinylic compounds.[12–15] This reaction, called the Heck reaction, seemed to constitute another promising polymer-forming carbon–carbon coupling reaction using bifunctional monomer pairs. We report herein a novel successful synthesis of polycinnamamides by the palladium-catalyzed carbon–carbon coupling polycondensation of bis(acrylamide)s 1 with aromatic diiodides 2 (eq 1).

$$\underset{1}{H_2C{=}CHC(O)NHRNHC(O)CH{=}CH_2} + \underset{2}{IArI} \xrightarrow[\text{solvent}]{\text{Pd catalyst base}} \underset{3}{[-CH{=}CHC(O)NHRNHC(O)CH{=}CHAr-]_n} \quad (1)$$



Experimental Section

Monomers. *N,N'*-(3,4'-Oxydiphenylene)bis(acrylamide) (1a). To a solution of 27.08 g (135 mmol) of 3-aminophenyl 4-aminophenyl ether and 30.16 g (298 mmol) of triethylamine in 300 mL of dichloromethane was added dropwise with stirring at 0 °C over a period of 60 min under nitrogen atmosphere a solution of 26.93 g (298 mol) of acryloyl chloride in 70 mL of dichloromethane. The solution was stirred at room temperature for 21 h. After the reaction, the solution was washed successively with 1 M aqueous hydrochloric acid and water and dried over anhydrous sodium sulfate. The solvent was removed from the organic layer in vacuo. The raw product was dissolved in methanol and precipitated with water. The white precipitate was filtered, washed with water, and dried at room temperature in vacuo. The yield was 31.1 g (75%): mp 197–200 °C; IR (KBr) 3275 (N—H), 1665 (C=O), 1605 cm^{-1} (C=C); ^{1}H NMR (DMSO-d_6) δ 5.60–5.80 (t, 2 H, CH=), 6.28–6.44 (d, 4 H, CH$_2$=), 6.95–7.78 (m, 8 H, Ar), 10.14 (s, 2 H, NH). Anal. Calcd for $C_{18}H_{16}N_2O_3$: C, 70.12; H, 5.23; N, 9.09. Found: C, 69.81; H, 5.08; N, 9.09.

***N,N'*-(3,4'-Isopropylidenediphenylene)bis(acrylamide) (1b).** To a solution of 11.32 g (50 mmol) of 2-(3-aminophenyl)-2-(4-aminophenyl)propane and 12.14 g (120 mmol) of triethylamine in 100 mL of dichloromethane was added dropwise with stirring at 0 °C over a period of 15 min a solution of 10.86 g (120 mmol) of acryloyl chloride in 10 mL of dichloromethane. The solution was stirred at room temperature overnight. The crude product isolated was purified by chromatography with ethyl acetate to give 9.41 g (56%) of **1b** as a white powder: mp 74–77 °C; IR (KBr) 3275 (N—H), 1665 (C=O), 1605 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ 1.57 (s, 6 H, CH$_3$), 5.61–5.77 (t, 2 H, CH=), 6.29–6.38 (d, 4 H, CH$_2$=), 6.97–7.36 (m, 8 H, Ar), 8.36, 8.68 (s, 1H, NH). Anal. Calcd for $C_{21}H_{22}N_2O_2$: C, 75.42; H, 6.63;, N, 8.38. Found: C, 75.51; H, 6.95; N, 7.84.

***N,N'*-(4,4'-Sulfonyldiphenylene)bis(acrylamide) (1c).** To a solution of 2.483 g (10 mmol) of bis(4-aminophenyl) sulfone and 2.226 g (22 mmol) of triethylamine in 30 mL of *N,N*-dimethylacetamide (DMAc) was added dropwise at 0 °C a solution of 1.991 g (22 mmol) of acryloyl chloride in 5 mL of DMAc. The solution was stirred at room temperature for 20 h. The reaction mixture was then poured into 1 M aqueous hydrochloric acid. The precipitate was filtered, washed with water, and dried at room temperature in vacuo. The yield was 3.001 g (84%): mp 112–116 °C; IR (KBr) 3300 (N—H), 1680 (C=O), 1595 (C=C), 1330, 1150 cm^{-1} (SO$_2$); ^{1}H NMR (DMSO-d_6) δ 5.56–5.77 (t, 2 H, CH=), 6.30–6.43 (d, 4 H, CH$_2$=), 7.85 (s, 8 H, Ar), and 10.62 (s, 2 H, NH). Anal. Calcd for $C_{18}H_{16}N_2O_4S$: C, 60.66; H, 4.52; N, 7.86; S, 9.00. Found: C, 60.08; H, 4.38; N, 7.94; S, 8.78.

Bis(4-iodophenyl) ether (**2b**) was prepared according to the method reported by Suzuki et al.[16] in 57% yield by the halogen-exchange reaction of bis(4-bromophenyl) ether with copper(I) iodide and potassium iodide in hexamethylphosphoramide at 150 °C for 8 h; mp 138–140 °C (lit.[17] mp 140–141 °C).

Other Materials. Iodobenzene was purified by vacuum distillation. *N*-Phenylacrylamide was prepared by the conven-

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tional method from aniline and acryloyl chloride: mp 103 °C (lit.[18] mp 101–102 °C); IR (KBr) 3315 (N—H), 1665 (C═O), 1605 cm^{-1} (C═C).

p-Diiodobenzene (**2a**) was purified by recrystallization from ethanol. Palladium acetate [$Pd(OAc)_2$], palladium chloride ($PdCl_2$), and 1,4-bis(diphenylphosphino)butane (dppb) were used as received. Dichlorobis(triphenylphosphine)palladium [$PdCl_2(PPh_3)_2$][19] and tri(*o*-tolyl)phosphine ($PTol_3$)[20] were prepared by the reported procedures. Triphenylphosphine (PPh_3) was purified by recrystallization from hexane.

Tri-*n*-butylamine and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) were purified by vacuum distillation. 4-(Dimethylamino)pyridine, 1,8-bis(dimethylamino)naphthalene (BDMAN), lithium acetate, potassiusm acetate, sodium acetate, and sodium carbonate were used as received.

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

Model Reaction. Synthesis of *N*-Phenylcinnamamide. In a three-necked flask equipped with a nitrogen inlet, a reflux condenser with a calcium chloride drying tube, and a stirrer, 0.3679 g (2.5 mmol) of *N*-phenylacrylamide, 0.5100 g (2.5 mmol) of iodobenzene, 0.0056 g (0.025 mmol) of $Pd(OAc)_2$, 0.0304 g (0.10 mmol) of $PTol_3$, and 0.6429 g (3.0 mmol) of BDMAN were dissolved in 5 mL of DMF, and then the reaction solution was stirred at 100 °C for 4 h under nitrogen. The mixture was poured into 300 mL of 1 M aqueous hydrochloric acid and extracted with dichloromethane. The organic layer was dried with anhydrous sodium sulfate and removed in vacuo. The product was dried under vacuum. The yield was 0.5545 g (99%): mp 149–150 °C (lit.[21] 151 °C); IR (KBr) 3335 (N—H), 1660 (C═O), 980 cm^{-1} (trans C═C); ^{1}H NMR (DMSO-d_6) δ 6.86 (d, 16 Hz, 1 H, trans-C(O)C═).

Polymerization. Polymer 3ab from 1a and 2b. In a three-necked flask equipped with a stirrer, a nitrogen inlet, and a reflux condenser with a calcium chloride drying tube were placed 0.3854 g (1.25 mmol) of **1a**, 0.5275 g (1.25 mmol) of **2b**, 0.0028 g (0.0125 mmol) of $Pd(OAc)_2$, 0.0152 g (0.05 mmol) of $PTol_3$, 0.6965 g (3.25 mmol) of 1,8-bis(dimethylamino)naphthalene, and 5 mL of DMF. The reaction solution was stirred at 100 °C for 4 h under nitrogen. The viscous solution thus formed was diluted with 50 mL of DMF and poured into 450 mL of methanol. The precipitated polymer was filtered, washed with hot methanol, and dried at room temperature in vacuo. The yield was 0.5877 g (99%). The inherent viscosity of the polymer was 2.60 dL·g^{-1}, measured at a concentration of 0.5 g·dL^{-1} in DMAc at 30 °C; IR (film) 3275 (N—H), 1665 (C═O), 980, 685 cm^{-1} (C═C); ^{1}H NMR (DMSO-d_6) δ 6.71 (d, 7 Hz, cis C(O)CH═), 6.77 (d, 15 Hz, trans C(O)CH═), 7.05–7.76 (m, ═CHPh), 10.26 (s, NH). Anal. Calcd for $(C_{30}H_{22}N_2O_4)_n$: C, 75.94;, H, 4.67; N, 5.90. Found: C, 74.55; H, 4.50; N, 5.80; I, 0.40.

Other polymers were prepared by analogous procedures.

Measurements. Infrared (IR) spectra were recorded on a Hitachi EP-G3 spectrophotometer and a JASCO FT/IR-5000 Fourier transform infrared spectrophotometer. ^{1}H nuclear magnetic resonance (NHR) spectra were recorded on a JEOL JNM-PMX60 NMR spectrometer (60 MHz) and a JEOL JNM-JX270 NMR spectrometer (270 MHz). Thermogravimetry (TG), differential scanning calorimetry (DSC), and thermomechanical analysis (TMA) were performed with Shimadzu thermal analyzers TGA-40M, DSC-41M, and TMA-40M (penetration method), respectively. Number-average molecular weight ($\bar{M}_n$) and weight-average molecular weight ($\bar{M}_w$) were determined by means of gel permeation chromatography (GPC) on the basis of a polystyrene calibration on a JASCO HPLC BIP-I apparatus (column, Shodex GPC AD-80M/S polystsyrene gel; eluent, DMF containing 0.01 mol·L^{-1} of lithium bromide).

Results and Discussion

Polymer Synthesis. New bis(acrylamide) monomers **1a–c** were synthesized by the reactions of the corresponding diamines were acryloyl chloride.

Before the polymerization, the model reaction of *N*-phenylacrylamide with iodobenzene was carried out in the presence of $Pd(OAc)_2$, $PTol_3$, and BDMAN. The reaction proceeded smoothly and the yield of *N*-phenylcinnamamide was quantitative.

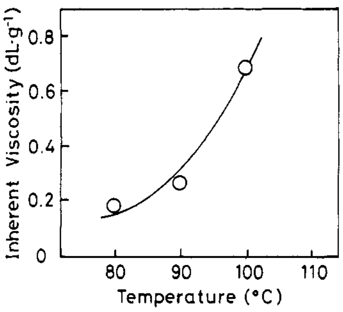

Figure 1. Effect of reaction temperature on inherent viscosity of polycinnamamide **3ab** formed by the polycondensation of **1a** with **2b** under nitrogen for 4 h. Monomers, 2.5 mmol; CH_3COONa, 5.5 mmol; $Pd(OAc)_2$, 0.025 mmol; $PTol_3$, 0.1 mmol; DMF, 10 mL.

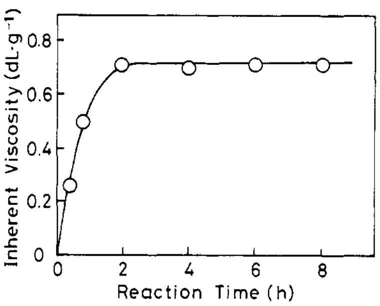

Figure 2. Time dependence of inherent viscosity of polycinnamamide **3ab** formed by the polycondensation of **1a** with **2b** at 100 °C under nitrogen. Monomers, 2.5 mmol; CH_3COONa, 5.5 mmol; $Pd(OAc)_2$, 0.025 mmol; $PTol_3$, 0.1 mmol; DMF, 10 mL.

Table I
Synthesis of Polycinnamamide 3ab with Various Catalysts[a]

catalyst	η_{inh},[b] dL·g^{-1}	catalyst	η_{inh},[b] dL·g^{-1}
$Pd(OAc)_2$	0.74[c]	$Pd(OAc)_2$/2dppb	0.10
$Pd(OAc)_2$/2$PTol_3$	0.22	$PdCl_2$/4$PTol_3$	0.19
$Pd(OAc)_2$/4$PTol_3$	0.84	$PdCl_2(PPh_3)_2$/4$PTol_3$	0.06
$Pd(OAc)_2$/4PPh_3	0.26		

[a] Polymerization was carried out with 2.5 mmol of **1a**, 2.5 mmol of **2b**, 6.5 mmol of CH_3COONa, and 0.025 mmol of the catalyst in 10 mL of DMF at 100 °C for 4 h under nitrogen. [b] Measured at a concentration of 0.5 g·dL^{-1} in DMAc at 30 °C. [c] Palladium black precipitated during the polymerization.

The carbon–carbon coupling polycondensation of bis(acrylamide) **1a** with bis(4-iodophenyl) ether (**2b**) in the presence of a palladium catalyst and a base in an organic solvent giving polycinnamamide **3ab** was investigated in detail as a typical polycondensation reaction.

Figure 1 shows the effect of reaction temperature on the inherent viscosity of the polycinnamamide. The molecular weight of the polymer tended to increase gradually with increasing reaction temperature, judging from the viscosity values. At a temperature above 110 °C, however, gelation of the reaction solution occurred. Figure 2 reveals the time dependence of the inherent viscosity of the polymer. The polymerization proceeded rapidly at 100 °C in DMF and was almost completed within 2 h.

Table I summarizes the catalytic effect of various palladium compounds on the polymerization. Among the palladium catalysts employed, $Pd(OAc)_2$ coupled with 4 equiv of $PTol_3$ was exceptionally effective, giving the highest inherent viscosity of the polymer. In the case of $Pd(OAc)_2$, which was the second effective catalyst, palladium black precipitated during the polymerization, thus

Table II
Synthesis of Polycinnamamide 3ab with Various Bases[a]

base	η_{inh},[b] dL·g^{-1}	base	η_{inh},[b] dL·g^{-1}
tri-*n*-butylamine	*c*	CH_3COOLi	0.14
DBU	*d*	CH_3COONa	0.84
4-(dimethylamino)pyridine	*d*	CH_3COOK	0.32
BDMAN	1.01	Na_2CO_3	0.09

[a] Polymerization was carried out with 2.5 mmol of **1a**, 2.5 mmol of **2b**, 6.5 mmol of the base, 0.025 mmol of $Pd(OAc)_2$, and 0.1 mmol of $PTol_3$ in 10 mL of DMF at 100 °C for 4 h under nitrogen. [b] Measured at a concentration of 0.5 g·dL^{-1} in DMAc at 30 °C. [c] Gelation occurred. [d] Polymer was not obtained.

Table III
Synthesis of Polycinnamamide 3ab in Various Solvents[a]

solvent	yield, %	η_{inh},[b] dL·g^{-1}	solvent	yield, %	η_{inh},[b] dL·g^{-1}
DMF	99	2.60	HMPA	100	0.68
DMAc	99	2.45	DMSO	98	0.32
NMP	100	0.81	pyridine	0	
DMI	100	1.28			

[a] Polymerization was carried out with 1.25 mmol of **1a**, 1.25 mmol of **2b**, 3.25 mmol of BDMAN, 0.0125 mmol of $Pd(OAc)_2$, and 0.05 mmol of $PTol_3$ in 5 mL of the solvent at 100 °C for 4 h under nitrogen. [b] Measured at a concentration of 0.5 g·dL^{-1} in DMAc at 30 °C.

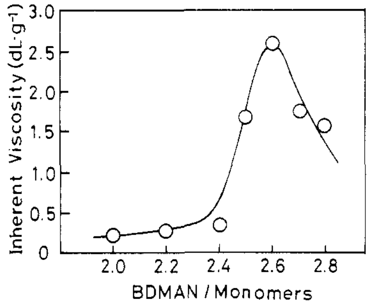

Figure 3. Effect of amount of 1,8-bis(dimethylamino)naphthalene on inherent viscosity of polycinnamamide **3ab** formed by the polycondensation of **1a** with **2b** at 100 °C for 4 h under nitrogen. Monomers, 1.25 mmol; $Pd(OAc)_2$, 0.0125 mmol; $PTol_3$, 0.05 mmol; DMF, 5 mL.

contaminating the resulting polymer The precipitation was efficiently circumvented by the addition of 4 equiv of the phosphine compounds based on $Pd(OAc)_2$. Therefore this catalytic system was used as the catalyst for further polymerizations. Only 1 mol % of the palladium catalyst based on the monomers was enough to give the polymer with high inherent viscosity.

The presence of a base was essential as an acceptor of the hydrogen halide formed in the Heck reaction. Table II summarizes the effect of the base on the polymerization. Among eight bases employed, 1,8-bis(dimethylamino)naphthalene (BDMAN) was the most effective, judging from the highest viscosity value of the obtained polymer. Because the hydroiodide of BDMAN, which was formed during the polymerization, remained in solution and dissolved readily in many organic solvents, it was completely removed from the resulting polymer by pouring the reaction solution into methanol to precipitate the polymer.

Figure 3 shows the effect of amount of BDMAN on the inherent viscosity of the polymer. Although the polycondensation theoretically required 2 equiv of the base on the basis of the bifunctional monomers, the highest inherent viscosity was obtained when a 30% excess of BDMAN was used.

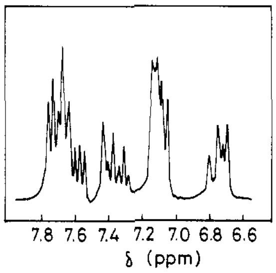

Figure 4. 270-MHz ^1H NMR spectrum of polycinnamamide **3ab** in DMSO-d_6.

Table IV
Inherent Viscosities of Various Polycinnamamides[a]

monomers		polymer		
bis(acrylamide)	diiodide		yield, %	η_{inh},[b] dL·g^{-1}
1a	**2a**	**3aa**	99	1.51
1a	**2b**	**3ab**	99	2.60
1b	**2a**	**3ba**	97	1.32
1b	**2b**	**3bb**	94	0.89
1c	**2a**	**3ca**	97[c]	0.26[d]
1c	**2b**	**3cb**	96[c]	0.22[d]

[a] Polymerization was carried out with 1.25 mmol of the monomers, 3.25 mmol of BDMAN, 0.0125 mmol of $Pd(OAc)_2$, and 0.05 mmol of $PTol_3$ in 5 mL of DMF at 100 °C for 4 h under nitrogen. [b] Inherent viscosity was measured at a concentration of 0.5 g·dL^{-1} in DMAc at 30 °C. [c] Polymer precipitation occurred during the polymerization. [d] Inherent viscosity was measured in concentrated sulfuric acid.

Table III lists the solvent effect on the polymerization. DMF and DMAc gave the polymer with an inherent viscosity higher than 2.0 dL·g^{-1}. This is probably attributable to the fact that these amide-type solvents were good solvents for the polycinnamamides. In the Heck reaction, it is known that aromatic iodides are more effective than aromatic bromides. When bis(4-bromophenyl) ether was used in place of bis(4-iodophenyl) ether (**2b**), polycinnamamide **3ab** with a low inherent viscosity of 0.14 dL·g^{-1} was obtained, even if longer reaction time of 24 h was applied.

The polymer thus obtained was confirmed to be the corresponding polycinnamamide **3ab** by means of infrared (IR) spectroscopy, ^1H NMR spectroscopy, and elemental analysis. The IR spectrum exhibited absorption bands at 3275 (N—H), 1665 (C═O), 980 (trans C═C), 685 cm^{-1} (cis C═C). The ^1H NMR spectrum of polymer **3ab** is shown in Figure 4. Polycinnamamide **3ab** consisted of a configurational mixture of double bonds, as evidenced by two doublet peaks at 6.71 (J = 7 Hz) and 6.77 ppm (J = 15 Hz), which were assigned to be olefinic protons of cis and trans configuration, respectively, and had almost the same integrated areas as each other. In contrast, only the trans isomer was obtained in the model reaction product, *N*-phenylcinnamamide, synthesized from *N*-phenylacrylamide and iodobenzene under the same reaction conditions. The reason for this difference in stereochemistry is not yet clear. The elemental analysis values were in good agreement with the calculated values, with no trace of metallic ash. The molecular weight of polycinnamamide **3ab** having an inherent viscosity of 2.60 dL·d^{-1} was found to be 93 200 and 488 100 for $\bar{M}_n$ and $\bar{M}_w$, respectively, for standard polystyrene.

A variety of polycinnamamides **3aa–cb** were prepared from combinations of bis(acrylamide)s **1a–c** and aromatic diiodides **2a** and **2b** under the same reaction conditions as that for the polymerization producing polycinnamamide **3ab**. The results are summarized in Table IV. Poly-

Table V
Solubility of Polycinnamamides[a]

polymer	NMP	DMAc	DMF	HMPA	pyridine	DMSO	H_2SO_4
	solvent						
3aa	±	±	±	●	–	±	++
3ab	++	++	++	++	++	●	±
3ba	++	±	++	++	±	●	++
3bb	++	++	++	++	++	++	±

[a] Solubility: ++, soluble at room temperature; ±, partially soluble or swelling; –, insoluble.

Table VI
Thermal Behavior of Polycinnamamides

polymer	T_g,[a] °C		T_{10},[b] °C	
	DSC	TMA	in air	in nitrogen
3aa			445	450
3ab	232	227	445	445
3ba	269	268	395	385
3bb	238	243	395	395

[a] Determined at a heating rate of 10 °C·min^{-1} under nitrogen. [b] Determined by TG at a heating of 10 °C·min^{-1}.

cinnamamides **3aa,ab,ba,bb** had high inherent viscosities (0.89–2.60 dL·g^{-1}), while the inherent viscosity values of **3ca** and **3cb** were not high enough (0.22 and 0.26 dL·g^{-1}, respectively), probably due to the precipitation of the resulting polymer during the polymerization. The addition of inorganic salts such as lithium chloride and lithium iodide, which usually prevents polymer precipitation in many cases of the preparation of polyamides, was not effective in the present polycondensation.

Polymer Characterization. Table V lists the solubility behavior of polycinnamamides **3aa**–**bb**. These polycinnamamides except **3aa** dissolved in pyridine, DMSO, and amide-type solvents such as NMP, DMAc, and DMF. Transparent and tough films of the polycinnamamides could be cast from the DMF solutions.

Table VI summarizes the thermal behavior data of polycinnamamides **3aa**–**bb**. These polymers did not decompose below 300 °C and the 10% weight loss temperatures for polycinnamamides **3aa** and **3ab** prepared from **1a** were higher than those of polycinnamamides **3ba** and **3bb** prepared from **1b**. This is probablay based on higher thermal stability of the ether bond compared with the isopropylidene group. The glass transition temperatures (T_g) of polycinnamamides were observed between 230 and 270 °C by the DSC measurement.

Since the polycinnamamides possess carbon–carbon double bonds in their backbone, they were expected to cross-link thermally and photochemically. Figure 5 shows the results of the thermal curing of polycinnamamide **3ab**, which was carried out with film specimens by heating under nitrogen. The T_g values of the polymer increased from 227 to 271 °C by the thermal curing at 250 °C, and the polymer became insoluble in the organic solvents. These facts apparently indicated that the thermal cross-linking had occurred on the double bond between the polymer chains. Since the thermal curing below T_g did not show a remarkable increase in the T_g of the polymer, a temperature above the T_g was essential to ensure thermal cross-linking.

The polycinnamamide **3ab** film became also insoluble by irradiation with UV light of the high-pressure mercury lamp for 30 min. Figure 6 shows the IR spectrum of polycinnamamide **3ab** before and after the irradiation by UV light. The transmittance of the trans C=C bond at 980 cm^{-1} decreased gradually with increasing the irradiation time. This phenomenon was caused by the photochemical cross-linking of the double bond in the polymer backbone.

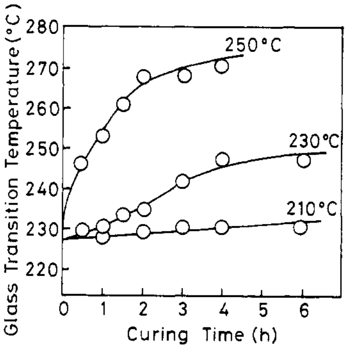

Figure 5. Effect of thermal curing time and temperature on the T_g of polycinnamamide **3ab** under nitrogen.

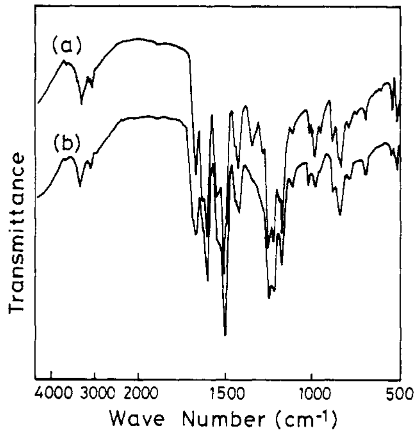

Figure 6. (a) IR spectrum of polycinnamamide **3ab** and (b) spectrum after irradiation by UV light for 8 h of a film cast on calcium fluoride.

Thus, we have successfully developed a novel and alternative route for the synthesis of polycinnamamides from bis(acrylamide)s and aromatic diiodides by the palladium-catalyzed carbon–carbon coupling polycondensation. This method has some advantages over the classic route for polycinnamamide synthesis using biscinnamic acids and their derivatives coupled with aromatic diamines. The preparation of biscinnamic acids and their acid chlorides includes many reaction steps, whereas bis(acrylamide)s are simply prepared by the reaction of acryloyl chloride with diamines. Polycinnamamides thus obtained may be accepted as one of the thermally and photochemically cross-linkable high-temperature plastics.

Registry No. **1a**, 121414-76-4; (**1a**)(**2a**) (copolymer), 121414-77-5; (**1a**)(**2b**) (copolymer), 121414-80-0; **1b**, 121414-78-6; (**1b**)(**2a**) (copolymer), 121414-79-7; (**1b**)(**2b**) (copolymer), 121414-81-1; **1c**, 121988-06-5; (**1c**)(**2a**) (copolymer), 121988-27-0; (**1c**)(**2b**) (copolymer), 121988-28-1; **3aa**, 121988-30-5; **3ab**, 121988-29-2; **3ba**, 121546-38-1; **3bb**, 121546-44-9; **3ca**, 121988-31-6; **3cb**, 121988-32-7; BDMAN, 20734-58-1; dppb, 121988-07-6; $H_2C{=}CHCOCl$, 814-68-6; $Pd(OAc)_2$, 3375-31-3; $PTol_3$, 26834-21-9; PPh_3, 603-35-0; $PdCl_2$, 7647-10-1; $PdCl_2(PPh_3)_2$, 13965-03-2; CH_3CO_2Li, 546-89-4; CH_3CO_2Na, 127-09-3; CH_3CO_2K, 127-08-2; Na_2CO_3, 497-19-8; 3-aminophenyl 4-aminophenyl ether, 2657-87-6; 2-(3-aminophenyl)-2-(4-aminophenyl)propane, 60201-75-4; bis-

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

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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

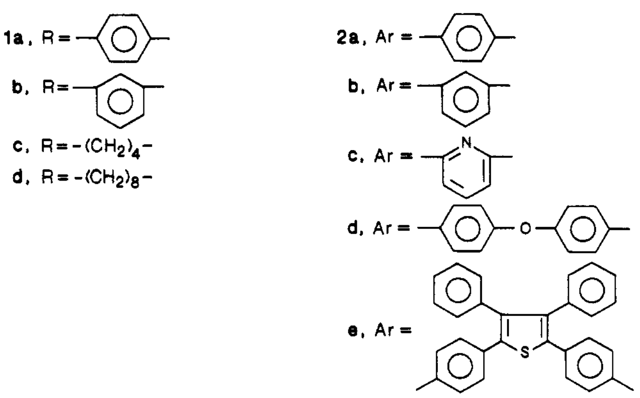
Recently much attention has been given to C_1 chemistry. Carbon monoxide is an inexpensive and important starting material for the industrial production of methanol, acetaldehyde, acetic acid, etc.[1] In these reactions transition-metal catalysts such as cobalt and ruthenium complexes were necessary 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 polycondensation of dihydrazides and aromatic dibromides with carbon monoxide (eq 1).

$$\underset{\mathbf{1}}{H_2NNHC(O)RC(O)NHNH_2} + CO + \underset{\mathbf{2}}{BrArBr} \xrightarrow[\text{solvent}]{\text{Pd catalyst base}} \underset{\mathbf{3}}{[-NHNHC(O)RC(O)NHNHC(O)ArC(O)-]_n} \qquad (1)$$



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

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