

Synthesis of polyesteramides by palladium-catalyzed carbonylation–polycondensation of aromatic diiodides and amino alcohols

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Abstract

Polyesteramides were prepared by palladium-catalyzed carbonylation–polycondensation reaction of aromatic diiodides and amino alcohols. Several polyesteramides with moderate intrinsic viscosity were synthesized in excellent yields using different substrates and characterized. All polymers exhibited characteristic infrared absorption frequencies corresponding to amide and ester carbonyl groups. The effects of reaction parameters such as carbon monoxide pressure, solvent, base, temperature, etc. on the yield and intrinsic viscosity of the polyesteramide obtained were investigated using the carbonylation of 4,4'-diiodobiphenyl and 3-aminopropan-1-ol as a model polymerization reaction. The rate of carbonylation as well as intrinsic viscosity of the resulting polyesteramide increased with increase in the carbon monoxide pressure. Under optimized reaction conditions, the catalyst could be recycled efficiently several times without any loss in activity leading to very high cumulative turnover numbers ($>10^3$) that are almost two orders of magnitude higher than those reported for similar reactions.

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Keywords: Polyesteramides; Carbonylation; Polycondensation; Polymerization; Palladium; Catalysis

1. Introduction

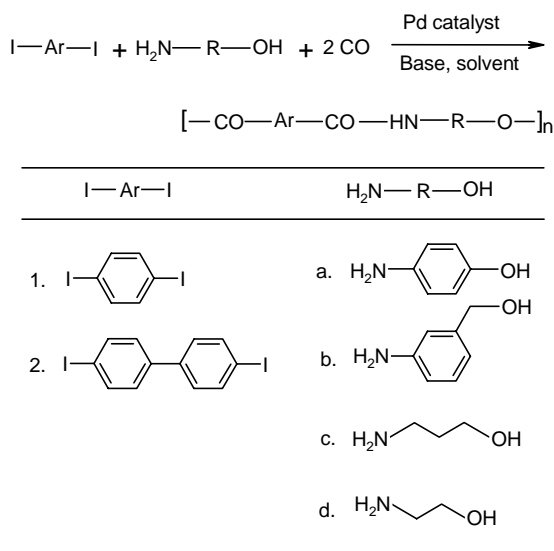
Palladium-catalyzed carbonylation–polycondensation reactions have attracted considerable interest for the synthesis of several high performance polymers like polyamides [1–3], polyesters [4], polyimides [5,6], polybenzoxazoles [7], poly(acylhydrazides) [8], etc. The most advantageous feature of these novel catalytic reactions is that they allow direct use of cheaper and easily available carbon monoxide as a comonomer. Conventionally, most of the above mentioned polymers are prepared by condensation reactions using aromatic diacids or their suitable derivatives such as esters, chlorides, etc. Such condensation methods are suitable only if the appropriate diacid is easily available. However, difficulties may arise when diacids with less common substitution patterns are required. In view of the commercial importance of carbonyl containing high performance polymers, it would be desirable to have a simple alternative procedure for their preparation that does not require

presence of an acid function on the reacting monomers. The palladium-catalyzed carbonylation–polycondensation reaction is emerging as a promising alternative for the preparation of several such macromolecules [9].

As a part of our program on novel polymerization processes using carbon monoxide as a comonomer, we are currently exploring the synthetic utility of transition metal catalyzed carbonylation reactions in the preparation of high value functional polymers. Recently, we have developed for the first time a single step synthesis of polyesteramides using palladium-catalyzed carbonylation–polycondensation reaction of an aromatic diiodide and an amino alcohol (Scheme 1) [10].

Polyesteramides contain both ester and amide functions and are, therefore, hybrid structures of polyester and polyamides. The polyesteramides are of interest because of their excellent heat resistant and gas barrier properties [11]. Until now, polyesteramides have been prepared by condensation of diacids or their derivatives with amino hydroxy compounds [12–15]. The proposed carbonylation route eliminates the need for diacid derivatives and provides a cleaner and efficient synthetic route to polyesteramides. In this article, we report on the detailed investigation into

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Scheme 1. Synthesis of polyesteramides by catalytic carbonylation route.

the effects of various reaction parameters such as carbon monoxide pressure, solvent, base, temperature, etc. on the synthesis of polyesteramides by palladium-catalyzed carbonylation–polycondensation reaction.

2. Experimental

2.1. Materials

4,4'-Diiodobiphenyl (DIBP); 4,4'-dibromobiphenyl (DBBP); 1,4-diiodobenzene (DIB); palladium chloride (PdCl₂); 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU); 1,4,8-diazabicyclo[2.2.0]octane (DABCO); 1,5-diazabicyclo[4.3.0]non-5-ene (DBN); and 4-aminophenol were purchased either from Fluka or Aldrich Chemicals. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA), triethylamine (TEA), 3-aminopropan-1-ol, 3-aminobenzyl alcohol, and ethanolamine were received from Merck Chemicals (India). *N,N*-Dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), chlorobenzene, methanol, toluene, and triphenylphosphine (PPh₃) were purchased from SD Fine Chemicals (India). Carbon monoxide (CO) was purchased from Matheson Gas Co. (USA) and had a stated purity of 99%. All solvents were freshly distilled before use.

2.2. Experimental setup

All polymerization experiments were carried out in a 50 ml capacity stainless steel autoclave (Parr Instruments Company, USA) fitted with a magnetically driven impeller with a four-blade stirrer capable of operations upto 1500 rpm. Temperature of the liquid in the reactor was maintained at a desired value (± 1 °C) with the help of a PID controller, which provided alternate heating and cooling

arrangement. The reactor was also equipped with internal thermocouple and a digital pressure transducer (with the precision of ± 1 psig) for temperature and pressure monitoring, respectively. The relevant safety features such as rupture disc and high temperature–pressure cutoff were also installed as a part of the reactor setup.

2.3. Analytical measurements

Intrinsic viscosity (η) was measured in NMP at a concentration of 0.5 g dl⁻¹ at 30 °C. Infrared spectra were recorded on a Bio-Rad Model FTS 175C using KBr pellets. Thermogravimetric analysis was performed on a Mettler-Toledo STAR system in air medium. NMR spectrum was recorded on a Bruker-200 or 500 MHz machine in a mixture of trifluoroacetic acid and chloroform-d₁. Gas chromatographic analysis was performed on HP 5890 series gas chromatograph equipped with HP-1 column and a thermal conductivity detector using helium as a carrier gas.

2.4. Model polymerization reaction (preparation of polymer 2c)

The autoclave was charged with 4,4'-diiodobiphenyl (2.08 g, 5 mmol); 3-aminopropan-1-ol (0.380 ml, 5 mmol); 1,8-diazabicyclo[5.4.0]undec-7-ene (1.4 ml, 10 mmol); PdCl₂ (2 mg, 0.011 mmol); triphenylphosphine (12 mg, 0.044 mmol), and chlorobenzene (25 ml). The reactor was flushed twice with high purity nitrogen to ensure absence of any traces of air or oxygen in the reactor and then heated to 120 °C under low stirring. When the temperature was stabilized at the set point, CO was introduced to a desired level (3 atm) and the contents were stirred at an agitation speed of 900 rpm. The reactor was operated at constant pressure conditions throughout the reaction by supplying CO from a reservoir vessel using a constant pressure regulator. The pressure drop in the reservoir vessel was measured using a digital pressure transducer as a function of time. After the reaction, the reactor was cooled and the excess gas was vented. The reaction mixture was poured in 100 ml methanol to obtain a solid polymer, which was again dissolved in NMP and reprecipitated using methanol. The product was washed with methanol twice and dried in vacuo. The yield was 1.20 g (85%). Intrinsic viscosity in NMP (measured at a concentration of 0.5 g dl⁻¹ at 30 °C) was 0.25 dl g⁻¹. Analytically found: C, 71.85; H, 5.26; N, 4.65%. Calculated (for C₁₇H₁₅NO₃, 281): C, 72.60; H, 5.34; N, 4.98. IR (KBr): 3350 (amide), 1712 (ester), 1638 (amide I), 1542 (amide II), 1278, 1111 cm⁻¹. ¹H NMR spectrum in a mixture of CF₃COOH and CDCl₃ (20:80% v/v): δ 2.25 (–CH₂–CH₂–CH₂–); 3.76 (–NH–CH₂–); 4.61 (–O–CH₂–); 7.65, 7.81, and 8.09 (aromatic protons); and 11.54 (–NH–CO). Five percent weight loss temperature (*T*₅) was 300 °C and 10% weight loss temperature (*T*₁₀) was 320 °C in air as determined by the thermogravimetric analysis.

Depending on the nature of monomers, polyesteramides were obtained as viscous oils or solids. After initial decantation of the reaction solvent, the contents were dissolved in NMP and precipitated using methanol to obtain the solid polymer products.

3. Results and discussion

The catalytic carbonylation–polycondensation reactions have emerged as an attractive alternative for the synthesis of several carbonyl-containing polymers, which are otherwise prepared by the condensation reactions involving carboxylic acids or their suitable derivatives. A few general observations can be made from the prior literature on similar reactions [1–7]. Thus, both bromo as well as iodo aromatics served as substrates in the carbonylation–polycondensation reactions depending on the reaction conditions whereas the chloro substrates were almost unreactive. The catalyst normally used for these reactions was PdCl₂ modified with phosphine ligands (mostly triphenylphosphine). These reactions were conducted at temperatures between 90 and 130 °C and CO pressures up to 20 atm. Stoichiometric amount of strong organic base like DBU was also employed as an acceptor for the hydrogen halide released during the reaction course. In all these reactions, either amine or hydroxy group acted as a nucleophile, which attacked the intermediate Pd–CO species resulting in the formation of amide or ester, respectively. We, therefore, thought that the use of amino alcohol as a bifunctional nucleophile should in principle result in the formation of an esteramide unit and this chemistry when applied to carbonylation of dihalides should provide polyesteramides.

In order to develop a catalytic carbonylation route for direct single step synthesis of polyesteramides, a few pre-

liminary reactions were carried out using dihaloaromatic compounds and aliphatic amino alcohols in presence of CO and a catalyst. Since there was no prior literature on the preparation of polyesteramides by carbonylation route, we used the combination of PdCl₂ and PPh₃ as catalyst for the initial exploratory reactions, since this combination was successfully used in the synthesis of several other polymers (e.g. polyesters, polyamides, polyimides, etc.) by carbonylation–polycondensation reaction [1–8]. The first experiment was conducted using 4,4'-diiodobiphenyl and 3-aminopropan-1-ol as substrates. The catalyst used was PdCl₂ in combination with 4 equivalents of triphenylphosphine (TPP) and the reaction was conducted at CO pressure of 3 atm and 120 °C in presence of chlorobenzene solvent (details are given in Experimental section). The CO consumption was completed within first 18 min. The reaction was continued for 1 h and then the autoclave was cooled to room temperature, the excess CO was vented and the reaction mixture was poured into 100 ml of methanol. The solid obtained was collected by filtration, dissolved in NMP, and reprecipitated using methanol. The white solid, thus, obtained was washed with methanol and dried overnight under vacuum. The yield was 1.20 g.

Before proceeding to further investigations, it was important to confirm that the product obtained was polyesteramide. This was accomplished by several characterizations (see Experimental section for details). The infrared spectrum of the product in KBr pellets (Fig. 1) showed characteristic absorption peaks clearly indicating the presence of an ester (1712 cm⁻¹) and amide (3350, 1638, and 1542 cm⁻¹) carbonyl functions. The proton NMR spectrum of the product in a mixture of trifluoroacetic acid and chloroform-d₁ is shown in Fig. 2. The aliphatic protons appear at δ 2.25 (–CH₂–CH₂–CH₂–), 3.76 (–NH–CH₂–), and 4.61

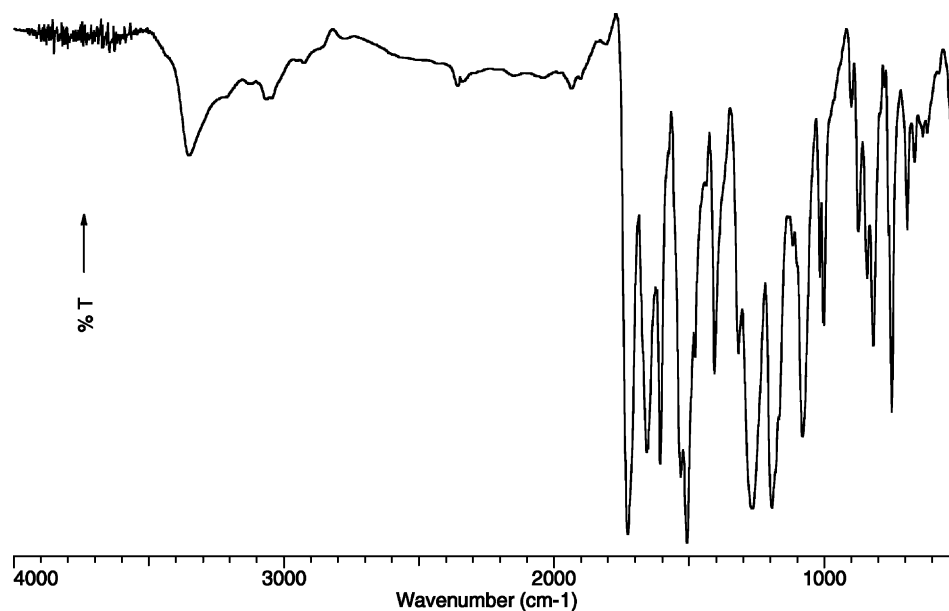


Fig. 1. Infrared spectrum of polyesteramide 2c in KBr.

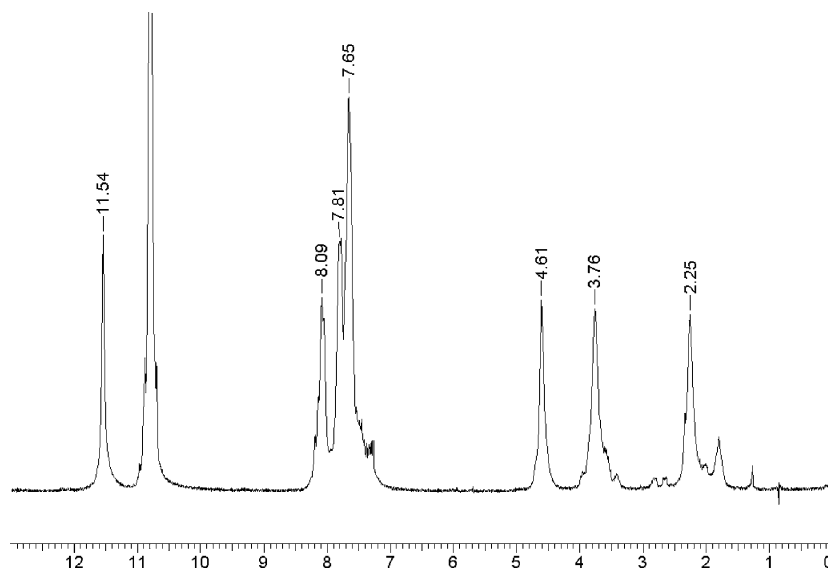


Fig. 2. ^1H NMR spectrum of polyesteramide **2c** in a mixture of trifluoroacetic acid and chloroform- d_1 (20:80% v/v).

($-\text{O}-\text{CH}_2-$). The aromatic protons appear at δ 7.65, 7.81, and 8.09. The signal at δ 11.54 is due to the amide proton ($-\text{NH}-\text{CO}$). The ^1H NMR spectrum clearly indicated the absence of any amine linkages, which would result in a signal around δ 5–6. This NMR data was consistent with the proposed structure for polyesteramide **2c** (Fig. 3). The partial $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum presented in Fig. 4 also clearly indicated peaks at δ 177.62 and 174.16 corresponding to ester and amide carbonyl groups. This is the first report on the synthesis of polyesteramides via catalytic carbonylation–polycondensation reaction of dihaloaromatic compounds with amino alcohols.

Once it was established that the polymer obtained was the desired polyesteramide, we repeated the above experiment except that 4,4'-diiodobiphenyl was replaced by 4,4'-dibromobiphenyl. In this case also we obtained 0.240 g of polyesteramide with consistent characterization data but the yield based on the dihalide was very low (17%). Furthermore, the intrinsic viscosity was just 0.086 dl g^{-1} , which was substantially lower than that obtained using 4,4'-diiodobiphenyl. The reaction using dichloroderivative did not give any polymer. These preliminary experiments suggested that the diiodo substrates efficiently underwent the carbonylation–polycondensation reaction with 3-aminopropan-1-ol to give polyesteramide in excellent yield and moderate molecular weight. Therefore, further studies were carried out using diiodoaromatic substrates. Following this procedure, we prepared several polyesteramide derivatives using

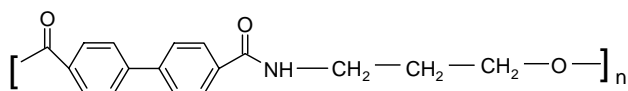


Fig. 3. Structure of polyesteramide **2c**.

different combinations of diiodo substrates and amino alcohols (see Scheme 1 for polymer identification codes). The results are presented in Table 1.

We then investigated the effect of various reaction parameters on the efficiency of the carbonylation–polycondensation reaction for the polyesteramide synthesis. For this purpose, the carbonylation–polycondensation of 4,4'-diiodobiphenyl and 3-aminopropan-1-ol in presence of catalytic amount of $\text{PdCl}_2/4\text{PPh}_3$ was investigated at 120°C as the standard polymerization reaction. In these reactions, the amount of CO consumed was compared with the final amounts of 4,4'-diiodobiphenyl and 3-aminopropan-1-ol consumed, which indicated almost stoichiometric material balance as shown in Scheme 1. Therefore, the absorption of CO was taken as a direct measure of polymerization progress for comparing different reactions. Two parameters, t_{50} and t_{95} (defined as the time required for the absorption of 50 and

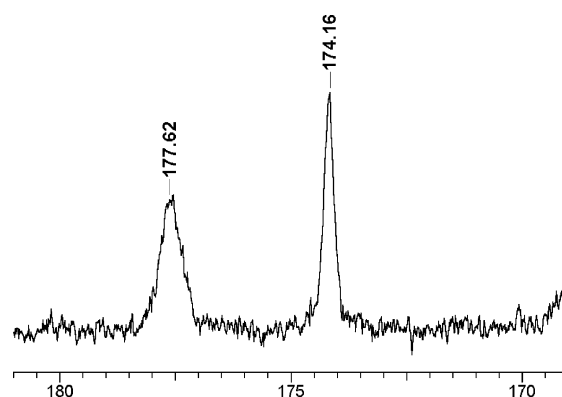


Fig. 4. $^{13}\text{C}\{^1\text{H}\}$ NMR (in a mixture of trifluoroacetic acid and chloroform- d_1 , 20:80% v/v) resonance of the carbonyl groups in polyesteramide **2c**. The peak at δ 177.62 is due to ester carbonyl and at δ 174.16 is due to the amide carbonyl.

Table 1
Synthesis of polyesteramides by catalytic carbonylation–polycondensation reaction^a

Polymer code ^b	Molecular formula	Yield (%) ^c	η (dl g ⁻¹) ^d	Elemental analysis (%)			Thermal properties (°C) ^e		IR spectra (ν) (cm ⁻¹)	
				C	H	N	T_5	T_{10}		
1a	C ₁₄ H ₉ NO ₃	90	f	Calculated	70.29	3.76	5.86	380	430	3351, 1729, 1653, 1509, 1268, 1196, 1078, 720.
				Found	69.50	3.52	5.30			
1b	C ₁₅ H ₁₁ NO ₃	25	0.17	Calculated	71.15	4.35	5.53	342	392	3436, 1716, 1645, 1542, 1370, 1107, 783.
				Found	70.80	4.22	5.43			
2a	C ₂₀ H ₁₃ NO ₃	95	f	Calculated	76.19	4.13	4.44	375	410	3354, 1727, 1653, 1531, 1266, 1194, 1082, 750.
				Found	75.48	4.06	4.12			
2b	C ₂₁ H ₁₅ NO ₃	40	0.20	Calculated	76.60	4.56	4.25	360	385	3371, 1714, 1648, 1541, 1489, 1274, 1111, 753.
				Found	75.90	4.48	4.21			
2c	C ₁₇ H ₁₅ NO ₃	85	0.25	Calculated	72.60	5.34	4.98	300	320	3350, 1712, 1638, 1542, 1278, 1111.
				Found	71.85	5.26	4.65			
2d	C ₁₆ H ₁₃ NO ₃	35	0.18	Calculated	72.91	4.87	5.24	316	331	3321, 1718, 1639, 1541, 1273, 1108, 843.
				Found	71.89	4.42	5.12			

^a Reaction conditions—diiodide: 5 mmol; aminohydroxy compound: 5 mmol; PdCl₂: 0.011 mmol; triphenylphosphine: 0.044 mmol; DBU: 10 mmol; chlorobenzene: 25 ml, CO pressure: 3 atm; temperature: 120 °C; agitation: 900 rpm; reaction time: 1 h.

^b Scheme 1.

^c Isolated yields.

^d Intrinsic viscosity measured at a concentration of 0.5 g dl⁻¹ in NMP at 30 °C.

^e 5% (T_5) and 10% (T_{10}) weight loss temperature in air determined by TGA.

^f Insoluble in NMP.

95% of the total theoretical CO, respectively) were used to compare different reactions. Unless otherwise mentioned, all reactions were completed (>98% conversion) in the specified reaction time as indicated by the CO absorption profiles and further confirmed by the liquid phase analysis.

The effect of solvent on the carbonylation–polycondensation reaction was also investigated and the results are summarized in Table 2. Considering the reaction time, yield, and intrinsic viscosity of the polyesteramide, chlorobenzene appears to be the most suitable solvent. It is interesting to note that despite better solubility of the resulting polyesteramide in NMP, lower yield and viscosity was obtained compared to other solvents when NMP was used as

Table 2
Effect of solvent on the carbonylation–polycondensation polymerization^a

Entry	Solvent	t_{50}/t_{95} (min)	Yield (%) ^b	η (dl g ⁻¹) ^c
1	Chlorobenzene	4.5/17	85	0.25
2	DMF	6/20	60	0.17
3	DMAc	8/30	62	0.16
4	NMP	6/24	20	0.11
5	Toluene	14/50	43	0.15
6	Dichloromethane	–	0	0

^a Reaction conditions—4,4'-diiodobiphenyl: 5 mmol; 3-aminopropan-1-ol: 5 mmol; PdCl₂: 0.011 mmol; triphenylphosphine: 0.044 mmol; DBU: 10 mmol; solvent: 25 ml; CO pressure: 3 atm; temperature: 120 °C; agitation: 900 rpm; reaction time: 1 h.

^b Isolated yields.

^c Intrinsic viscosity measured at a concentration of 0.5 g dl⁻¹ in NMP at 30 °C.

reaction solvent (Table 2, entry 4). No polymer was obtained in dichloromethane. Further reactions were, therefore, conducted in chlorobenzene solvent.

It is known that Pd(0) complexes can oxidatively add the aryl iodide even in the absence of the added phosphine ligand because of higher reactivity of the iodo derivatives [16,17]. In order to investigate the role of ligand, we did the standard reaction without adding any phosphine ligand. It was observed that polyesteramide **2c** was still obtained but in very low yield (14%) and intrinsic viscosity (0.06 dl g⁻¹). However, we preferred using phosphine ligand during these studies for efficient separation and recycling of the catalyst. The polymers were often insoluble in chlorobenzene and, therefore, could be separated by simple filtration or decantation. In a control run (for the synthesis of polyesteramide **2c**), the filtrate containing the soluble Pd-phosphine complex was recycled with fresh charge of reactants. We found that even after four recycles, there was no appreciable loss in the catalytic activity, yield, and the intrinsic viscosity of the resulting polymer (Fig. 5). The successful recycle of the catalyst under standard reaction conditions (monomers: 5 mmol; PdCl₂: 0.011 mmol; temperature: 120 °C; and CO pressure: 3 atm) gave a total cumulative TON of 2275 (455 × 5). This TON is almost two orders of magnitude higher than those reported earlier for other carbonylation–polycondensation reactions [1–8].

The base plays a key role during the carbonylation–polycondensation reaction and no polyesteramide could be obtained in the absence of a base. The base acts as a

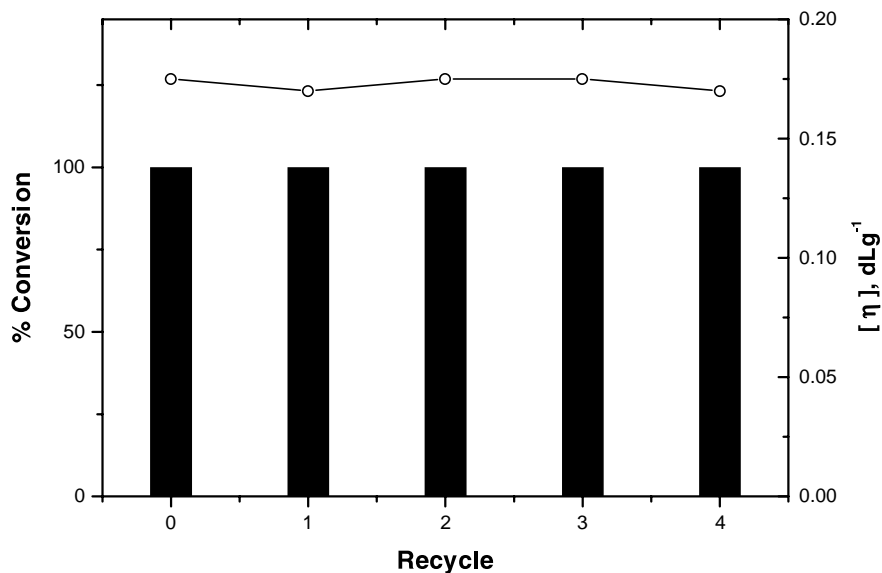


Fig. 5. Catalyst recycle experiments. Bar graph shows conversion of dihalide, and line graph shows intrinsic viscosity of the polyesteramide **2c**.

scavenger for HI produced during the reaction. The experimental results showing effect of various bases for the carbonylation–polycondensation reactions are summarized in Table 3. Use of a strong and hindered organic base like DBU was particularly effective for better yields and higher intrinsic viscosities. The inorganic bases like NaOH and NaOAc were almost ineffective in these reactions. The effectiveness of DBU compared to other bases could be because of its ability to swell the resulting polymer apart from acting as an acid acceptor, as has been suggested previously [1,4]. It is interesting to note that the amine ($-\text{NH}_2$) function in the amino alcohol can also efficiently trap HI released in the reaction. Indeed, in a reaction without the addition of any base, only 25% of the total theoretical CO was consumed. This indicated that the carbonylation con-

tinued until sufficient free amine was available for trapping the released HI. As expected, no polyesteramide could be obtained in this case owing to disturbed reaction stoichiometry due to removal of active $-\text{NH}_2$ groups from reaction. We further investigated the effect of DBU amount on the polymerization. The results presented in Fig. 6 suggest that a little more than two equivalents of DBU was required for synthesis of polyesteramide with higher viscosity. Use of even higher amount of the base rather resulted in lowering the intrinsic viscosity of the polyesteramide.

Table 3
Effect of base on the carbonylation–polycondensation polymerization^a

Entry	Base	pK _a ^b	t ₅₀ /t ₉₅ (min)	Yield (%) ^c	η (dl g ⁻¹) ^d
1	DBU	11.9	4.5/17	85	0.25
2	DBN	11.0	8/17	80	0.20
3	DABCO	9.15	15/55	65	0.14
4	Et ₃ N	10.75	20/50	20	0.09
5	TMEDA	9.15	22/56	15	0.08
6	NaOH	–	45	20	0.09
7	NaOAc	–	50	18	0.07

^a Reaction conditions—4,4′-diiodobiphenyl: 5 mmol; 3-aminopropan-1-ol: 5 mmol; PdCl₂: 0.011 mmol; PPh₃: 0.044 mmol; base: 10 mmol; chlorobenzene: 25 ml; CO pressure: 3 atm; temperature: 120 °C; agitation: 900 rpm; reaction time: 1 h.

^b Values for aqueous solutions of the corresponding conjugate acids [18–20].

^c Isolated yields.

^d Intrinsic viscosity measured at a concentration of 0.5 g dl⁻¹ in NMP at 30 °C.

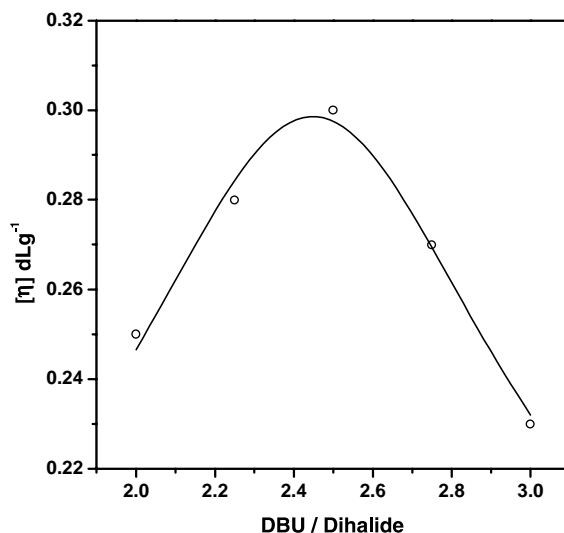


Fig. 6. Effect of amount of DBU on the carbonylation–polycondensation reaction. Reaction conditions—4,4′-diiodobiphenyl: 5 mmol; 3-aminopropan-1-ol: 5 mmol; PdCl₂: 0.011 mmol; PPh₃: 0.044 mmol; chlorobenzene: 25 ml; CO pressure: 3 atm; temperature: 120 °C; agitation: 900 rpm; reaction time: 1 h; intrinsic viscosity measured at a concentration of 0.5 g dl⁻¹ in NMP at 30 °C.

Table 4
Effect of CO pressure on the carbonylation–polycondensation polymerization^a

Entry	CO pressure (atm)	Yield (%) ^b	η (dl g ⁻¹) ^c
1	1	87	0.23
2	3	85	0.25
3	5	86	0.27
4	7	85	0.26
5	11	89	0.29

^a Reaction conditions—4,4'-diiodobiphenyl: 5 mmol; 3-aminopropan-1-ol: 5 mmol; PdCl₂: 0.011 mmol; PPh₃: 0.044 mmol; DBU: 10 mmol; chlorobenzene: 25 ml; temperature: 120 °C; agitation: 900 rpm; reaction time: 1 h.

^b Isolated yields.

^c Intrinsic viscosity measured at a concentration of 0.5 g dl⁻¹ in NMP at 30 °C.

Next, we investigated the effect of CO pressure on the polymerization reaction and the results are presented in Table 4. The carbonylation–polycondensation reaction proceeds smoothly even at very low CO pressure (1 atm) producing the polyesteramide **2c** in excellent yield (87%) with intrinsic viscosity of 0.23 dl g⁻¹ (Table 4, entry 1). Further increase in the CO pressure resulted in only marginal increase in the intrinsic viscosity but the reaction rate was significantly increased, as observed from the typical CO absorption profiles at different CO pressures (Fig. 7).

Finally, we examined the effect of temperature on the carbonylation–polycondensation reaction in a range of 90–130 °C. The results presented in Table 5 suggest that there was no substantial change in the yield of the polyesteramide produced at the end of 1 h, but the intrinsic viscosity was strongly influenced by the temperature. The

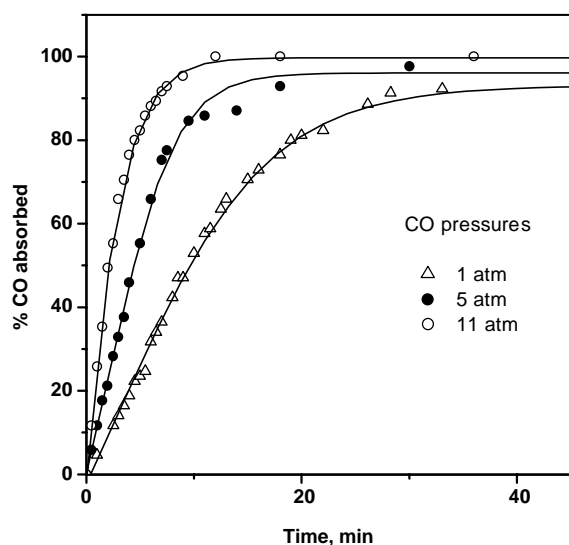


Fig. 7. CO absorption profile at different pressures. Reaction conditions—4,4'-diiodobiphenyl: 5 mmol; 3-aminopropan-1-ol: 5 mmol; PdCl₂: 0.011 mmol; PPh₃: 0.044 mmol; DBU: 10 mmol; chlorobenzene: 25 ml; temperature: 120 °C; agitation: 900 rpm; reaction time: 1 h.

Table 5
Effect of temperature on the carbonylation–polycondensation polymerization^a

Entry	Temperature (°C)	Yield (%) ^b	η (dl g ⁻¹) ^c
1	90	87	0.12
2	100	85	0.13
3	110	86	0.18
4	120	85	0.25
5	130	89	0.20

^a Reaction conditions—4,4'-diiodobiphenyl: 5 mmol; 3-aminopropan-1-ol: 5 mmol; PdCl₂: 0.011 mmol; PPh₃: 0.044 mmol; DBU: 10 mmol; chlorobenzene: 25 ml; CO pressure: 3 atm; agitation: 900 rpm; reaction time: 1 h.

^b Isolated yields.

^c Intrinsic viscosity measured at a concentration of 0.5 g dl⁻¹ in NMP at 30 °C.

intrinsic viscosity was highest at 120 °C and decreased on either increasing or decreasing the temperature. The low intrinsic viscosities (and hence the lower molecular weights) of the polymers at lower temperatures could be because of the low reaction rates. On the other hand, the increased side reactions at higher temperatures result in the lowering of the polyesteramide chain lengths. The typical CO absorption profiles for the model reaction at different temperatures (Fig. 8) indicate increase in the rate of carbonylation with temperature as expected. The apparent energy of activation calculated from the Arrhenius plot of ln *R* versus 1/*T* (Fig. 9), where *R* is the initial rate of carbonylation reaction, is 18 kJ mol⁻¹. Such a low value for activation energy suggests that the reaction may be mass transfer controlled and requires detailed investigation of reaction engineering aspects.

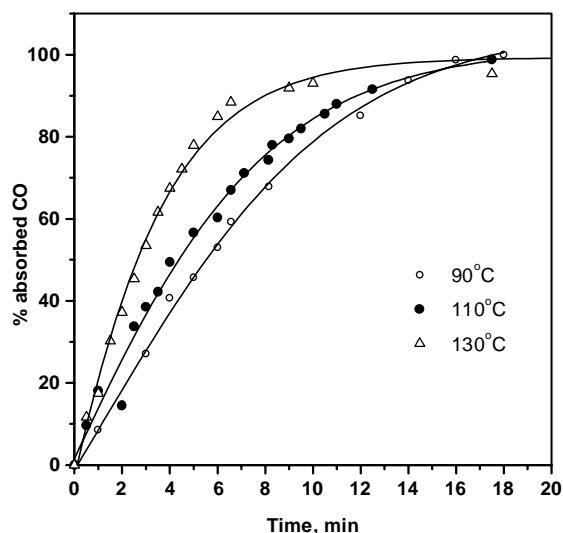


Fig. 8. Effect of temperature on the carbonylation–polycondensation reaction. Reaction conditions—4,4'-diiodobiphenyl: 5 mmol; 3-aminopropan-1-ol: 5 mmol; PdCl₂: 0.011 mmol; PPh₃: 0.044 mmol; DBU: 10 mmol; chlorobenzene: 25 ml; CO pressure: 3 atm; agitation: 900 rpm; reaction time: 1 h.

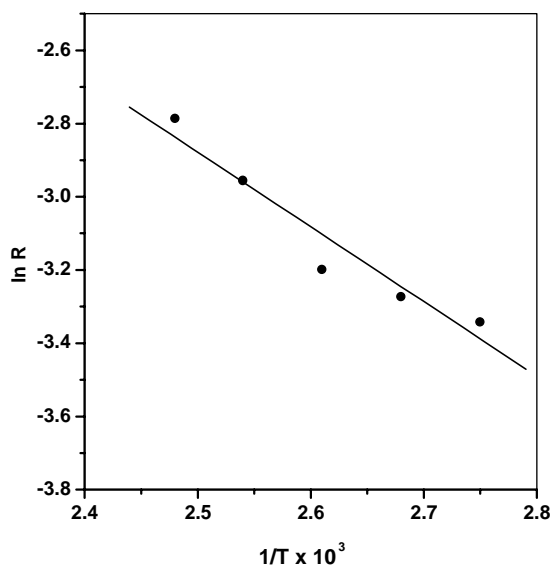


Fig. 9. Arrhenius plot.

The mechanism of carbonylation–polycondensation reactions is not clearly understood at present but it may be similar to the classical Heck type carbonylation of aryl halides. The mechanism of Heck type carbonylation has been investigated in elaborate details previously [16,21–24] and based on these investigations, a probable mechanism may be proposed for the present carbonylation–polycondensation poly-

merization reaction (Fig. 10). The catalytically active species during the catalytic cycle is believed to be a Pd(0) complex **1**, which can be formed during the reaction in presence of CO and phosphine ligand, e.g. Pd(PPh₃)₄, (PPh₃)₂Pd(CO), etc. [21]. The oxidative addition of aromatic iodide to this zero-valent palladium complex forms the arylpalladium (II) halide complex **2**. Subsequent coordination and insertion of CO into arylpalladium (II) halide species leads to the Pd-acyl intermediate **3** which on a nucleophilic attack by either OH or NH₂ moiety results in the formation of corresponding ester or amide. The Pd(II)–HI complex **4** then reductively eliminates HI and regenerates Pd(0) complex marking the completion of the catalytic cycle. The observed effect of CO pressure on the carbonylation provides support for this proposed mechanism. The oxidative addition of aryl iodide is a comparatively fast step [25] and, therefore, the insertion of CO into the Pd-aryl complex becomes rather slow and the rate-limiting step [3]. Increase in the CO pressure, therefore, results in the increase in the rate of carbonylation.

While other carbonylation–polycondensation reactions, e.g. those used in the polyamide or polyester synthesis involve only one type of nucleophile, i.e. either amine or alcohol, the polyesteramide synthesis involves both. Certainly, the difference in reactivity between individual amine and hydroxyl group would influence the placement of individual amide and ester units in almost the same way as during the conventional condensation reaction using diacid and needs detailed investigation.

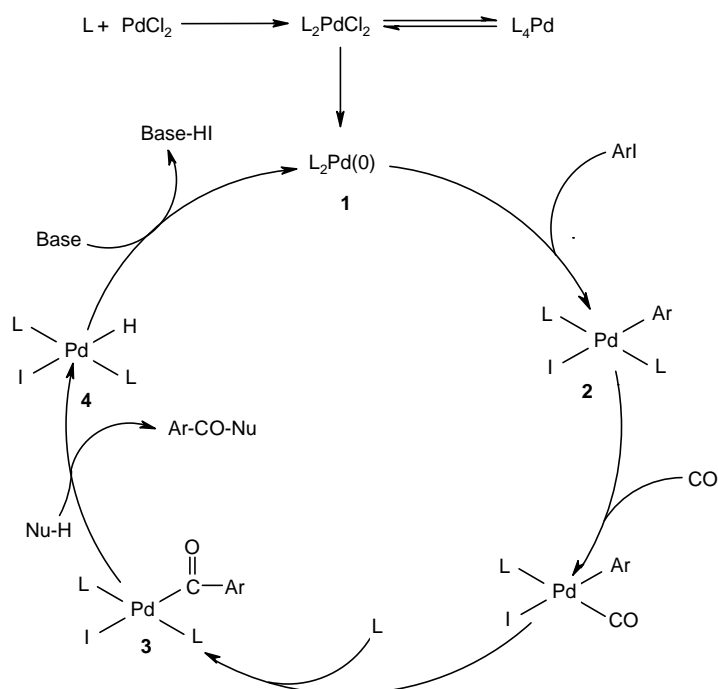


Fig. 10. Proposed reaction mechanism for the synthesis of polyesteramides by catalytic carbonylation–polycondensation reaction (Nu = HN– or O– and L = PPh₃).

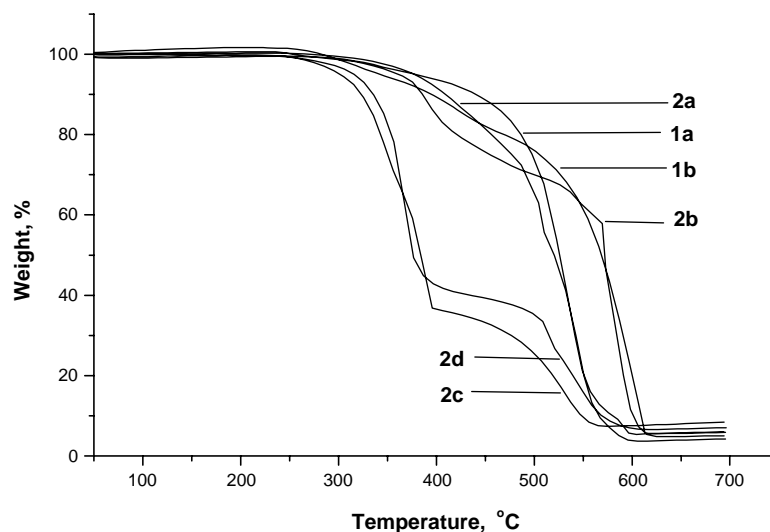


Fig. 11. TGA curves for polyesteramides prepared by catalytic carbonylation route.

4. Properties of the polyesteramides

A wide variety of alternating polyesteramides were prepared using the proposed catalytic carbonylation route (Table 1). The wholly aromatic polyesteramides were insoluble in common solvents while those containing flexible alkyl units were soluble in NMP. The molecular weight of a THF soluble fraction of polymer **2c** determined using GPC (polystyrene standards) was 5000. The reaction of fully aromatic monomers was faster than those carried out using aliphatic amino alcohols and the former gave comparatively higher yields. All the polymers obtained by carbonylation–polycondensation had distinct and characteristic IR absorption peaks due to the ester (around 1720 cm^{-1}) and amide (around 1630 cm^{-1}) carbonyl groups. Thermogravimetric analysis in air indicated that all polymers had good thermal stability in air. The TGA curves for all polymers are shown in Fig. 11.

Finally, it is interesting to note that the proposed catalytic route does not require the presence of acid function on the monomers and has three major advantages, viz. (1) easy access to a wide variety of diiodoaromatics [26–28]. (2) the iodide released during the reaction can be oxidized back to iodine and recycled in the process for preparation of iodoaromatics by catalytic iodination outlined above [9]. This recycling partly compensates for the high cost of iodoaromatics. (3) Availability of simple and highly efficient catalysts with very high activity at comparatively milder reaction conditions that can be efficiently recycled. The key issue in the synthesis of polyesteramides by the proposed carbonylation route is, however, the low molecular weights. All polyesteramides obtained in the present study have lower intrinsic viscosities and suggest the formation of low molecular oligomers in considerable amounts. Like in conventional polycondensation reactions, the high molecular weights could only be obtained at a very high and selec-

tive conversion of substrates. We are currently investigating these issues in more details.

5. Conclusions

We have successfully demonstrated that linear polyesteramides can be efficiently prepared by the carbonylation–polycondensation reactions of aromatic dihalides and suitable amino alcohols in high yields. In some cases, it was possible to recycle the catalyst efficiently and very high turnover numbers have been obtained that are two orders of magnitude higher than those reported to date for similar reactions. It should be noted that although the proposed catalytic route offers a potential alternative to conventional polycondensation reactions, the relatively lower degree of polymerization seems to be the important drawback at present. We are currently investigating different methodologies, which will allow synthesis of high molecular weight polyesteramides by carbonylation route.

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