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Synthesis of a pyridine substituted polycarbodiimide and its use as a solid support for chemical reagents

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ABSTRACT

Optically active, polycarbodiimides **3**(**a, b** & **c**) with pyridine pendant groups were synthesized using [(R) – 2,2′- binaphthoxy] (di-isopropoxy) titanium(IV) catalyst. The polymers were characterized by ^{1}H and ^{13}C NMR, and IR. Thermal stability of these polymers (up to 162 °C by TGA), allows thermally demanding chemical transformations on their side chains without decomposition. Advantages include fine-tunability of the other pendant group of the carbodiimide monomer. This allows one to optimize the properties of the polymer without undergoing copolymerization or further post-polymerization modifications. Borane (BH_3) was coordinated to poly **3** (**a** & **b**) to prepare the functional polymers **4** (**a** & **b**) respectively. A strong IR signature peak at 2368 cm^{-1} supports BH_3 coordination. Gravimetric analysis indicates 97–99% borane complexation of the pyridine units. In addition, the thermal stability increased to 194 °C in poly **4a** is consistent with the incorporation of BH_3 to the pendant pyridine of the helical polycarbodiimide **3a**. Poly **4** (**a** & **b**) can be used as supported reagents and successfully reduced the carbonyl compounds (**5 a**–**e**) in moderate to excellent yields (60–100%) and are shown to be efficient, non-volatile, stable, and mild supported-reducing reagents. Upon completion of the reduction reaction, the polymer support was quantitatively recycled as required for a green solid catalyst support.

1. Introduction

A strategy of modern chemistry has been to exploit the advantages of polymer supported reagents [1] and this has been proven to be an important tool for the synthesis of small molecules [2]. The immobilized reagents are generally more stable, easy to handle and can easily be separated by filtration or other techniques during work-up procedures after the reaction [3,4]. Supports have the potential to be recycled, thereby offering both a green and economic approach for many chemical transformations [5]. Even in a large excess of solid supported reagents used to drive reactions to completion, products require minimum or no further purification which has driven continued interest in the solid supported reagents.

Pyridine and its derivatives; such as bipyridine, terpyridine and pyridine containing reagents exemplified by pyridinium chlorochromate, pyridine-borane, and pyridine dichromate have been extensively used in organic synthesis [6–8]. Lewis acid–base type of complexes of pyridine with a variety of Lewis acids [9–11] offered unique and versatile chemistry [12–14]. However, to the best of our knowledge, there are few examples of functional pyridine containing polymers [15,16] and polymers derived from them [17–20] which have been used as supports for catalytic reactions. A limitation of poly(vinylpyridine) supports is the fact that they are prepared using free radical techniques that provide atactic chains which are highly disordered and offer a range of different catalytic environments. Globally, we would like to form well-organized polymers (helical rods in this case) that should offer more uniform catalytic sites along their length. To do so calls for the use of different polymerization techniques. This can itself be problematic because of the incompatibility of Lewis basic groups and the metal catalyst used to synthesize the polymer. In particular, most pyridine or heteroatom containing monomers often prove problematic during polymerization using transition metal catalysts. Heteroatoms, be they oxygen, sulfur, phosphorus or nitrogen coordinate and deactivate many metal catalysts. The insertion polymerization of carbodiimides via transition metal catalysts (Ti, Zr, Ni, Cu, etc.) is not an exception.

Herein we explore the advantages of immobilization of a pyridine reducing reagent on a novel series of helical polycarbodiimides. [21–24] These are the first polycarbodiimides that possess heterocyclic side chains and that can be used as recyclable supports for reagents.

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2. Experimental

2.1. General

The chemicals were purchased from Aldrich (Sigma–Aldrich, Milwaukee, WI) and Fisher Scientific, Fair Lawn, NJ and used as received unless stated otherwise. 6-nitropiperonal was received from Tokyo Chemical Industry, Japan. The solvents, tetrahydrofuran (THF) dichloromethane and chloroform were distilled prior to use. ^{1}H and ^{13}C NMR data were recorded on a Varian or Mercury 300 MHz or 400 MHz spectrometers (300 or 400 MHz for ^{1}H, 75 or 100 MHz for ^{13}C NMR) at room temperature. The chemical shift values were reported relative to TMS ($\delta = 0.00$ ppm) as an internal standard. IR spectra were obtained from JASCO FT/IR-410. Wave numbers in cm^{-1} are reported for characteristic peaks. Melting points of the compounds were recorded using a Mel-Temp apparatus. Mass spectra were obtained at the NCSU Department of Chemistry Mass Spectrometry Facility using electrospray ionization (ESI) on an Agilent Technologies 6210 LC-TOF mass spectrometer. Specific optical rotation was recorded on a JASCO P-1010 polarimeter. Thermo Gravimetric Analysis (TGA) was performed on Hi-Res TGA 2950 Thermogravimetric Analyzer under nitrogen atmosphere from 25 °C to 600 °C at a heating rate of 10 °C per minute. All the manipulations for polymerizations were done inside an MBraun UNIlab drybox under nitrogen atmosphere.

2.2. Synthesis of monomers

2.2.1. Preparation of urea derivatives, *1 a–c*

The urea compounds **1a**, **1b** and **1c** were prepared from commercially available amino pyridine derivatives; 3-aminopyridine or 3-(methyl amino)pyridine; and alkyl isocyanates; n-hexylisocyanate or n-dodecylisocyanate. In a typical procedure, the aminopyridine derivative (1.0 equivalent) was dissolved in dichloromethane. The solution was cooled to 0 °C and an alkyl isocyanate (1.3 equivalents) diluted in dichloromethane was added to the reaction mixture drop wise via addition funnel. The reaction mixture was allowed to warm to room temperature and then refluxed overnight. Solvent was removed and the resulting urea derivatives were purified by recrystallization from ethanol at 0 °C. The reactions were performed in 1–6 g scales.

*2.2.1.1. Compound **1a**; 1-hexyl-3-(pyridin-3-yl) urea; yield: 96%, white solid, mp: 92 °C.* ^{1}H NMR, 300 MHz ($CDCl_3$, δ ppm): 8.30 (Ar–H, $J = 2.4$ Hz, 1H, d), 8.19 (Ar–H, $J = 3.3$ Hz, 1H, dd), 8.04–8.00 (Ar–H, 1H, m), 7.80 (CONH, 1H, s), 7.22–7.18 (Ar–H, 1H, m), 5.46 (CONH, $J = 5.4$ Hz, 1H, t), 3.26–3.19 (2H, m), 1.50–1.43 (2H, m), 1.31–1.25 (6H, m), 0.85(3H, -CH3, $J = 6.9$, t). ^{13}C NMR, 100 MHz ($CDCl_3$, δ ppm): 156.66, 143.05, 140.56, 136.93, 126.55, 123.95, 40.30, 31.57, 30.17, 26.68, 22.65 and 14.10.

*2.2.1.2. Compound **1b**; 1-hexyl-3-(pyridin-3-ylmethyl) urea; yield: 99%, white solid, mp: 93 °C.* ^{1}H NMR, 300 MHz ($CDCl_3$, δ ppm): 8.49–8.47 (Ar–H, 2H, m), 7.66–7.62 (Ar–H, 1H, m), 7.25–7.21 (Ar–H, 1H, m), 5.05 (CONH, 1H, br), 4.70 (CONH, 1H, br), 4.36 (ArCH2-, 2H, $J = 6.0$ Hz, d), 3.17–3.11 (2H, m), 1.48–1.44 (2H, m), 1.29–1.26 (6H, m), 0.87(3H, $-CH_3$, $J = 6.9$, t). ^{13}C NMR, 100 MHz ($CDCl_3$, δ ppm): 159.19, 148.61, 148.31, 135.72, 135.13, 123.56, 41.50, 40.42, 31.63, 30.33, 26.68, 22.67 and 14.12.

*2.2.1.3. Compound **1c**; 1-dodecyl-3-(pyridin-3-yl) urea; yield: 98%, white solid, mp: 92 °C.* ^{1}H NMR, 300 MHz ($CDCl_3$, δ ppm): 8.30 (Ar–H, $J = 2.4$ Hz, 1H, d), 8.19 (Ar–H, $J = 3.3$ Hz, 1H, dd), 8.05–8.01 (Ar–H, 1H, m), 7.78 (CONH, 1H, s), 7.22–7.18 (Ar–H, 1H, m), 5.45 (CONH, $J = 5.1$ Hz, 1H, t), 3.23 (2H, $J = 6.9$ Hz, dd), 1.51–1.47 (2H, m), 1.24 (17H, br), 0.87(3H, –CH3, $J = 6.9$, t). ^{13}C NMR, 100 MHz ($CDCl_3$, δ ppm): 156.63, 143.10, 140.49, 137.08, 126.69, 124.11, 40.46, 32.15, 30.39, 29.91, 29.89, 29.85, 29.60, 27.19, 22.92 and 14.35.

2.2.2. Preparation of carbodiimides, *2a–c*

The substituted urea derivatives (compounds **1a–c**) were dehydrated to the corresponding carbodiimides using known procedures [25] with slight modifications. In a typical procedure, dibromotriphenyl phosphorane (1.3 equivalents) was suspended in 5 mL dichloromethane at 0 °C under nitrogen atmosphere and triethyl amine (2.5 equivalents) was added drop wise. The mixture was stirred at low temperature in an ice bath for 10 min and then urea derivative (**1a, 1b** or **1c**, 1–3 g scale, 1.0 equivalent) was added in four equal portions at an interval of 10 min. The reaction mixture was allowed to warm to room temperature and stirred overnight under inert atmosphere. The solvent was removed by rotavaporation and the carbodiimide was extracted from the solid by pentane. The crude carbodiimide monomer sample was purified by column chromatography on silica gel using ethyl acetate and hexane (1:1) mixture to provide colorless oils in all cases.

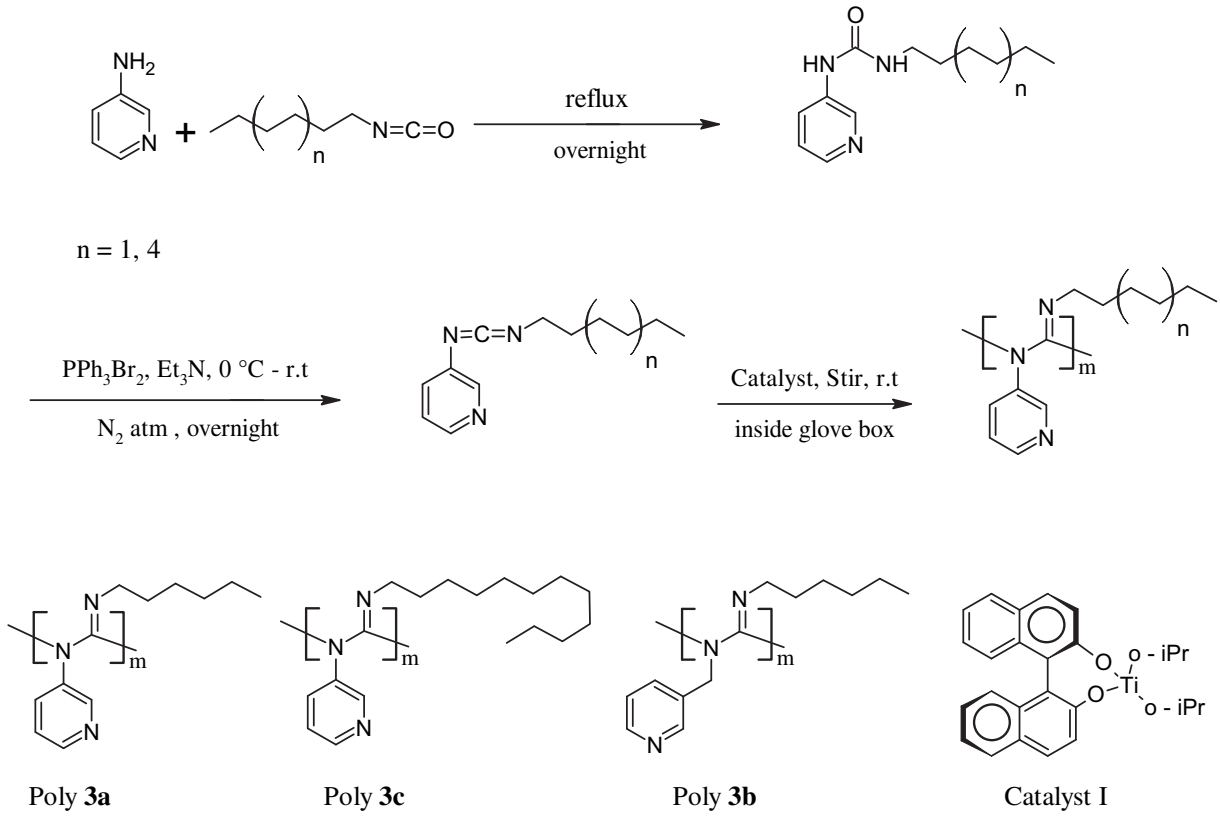
*2.2.2.1. Compound **2a**; N-hexyl-N′-pyridin-3-ylcarbodiimide; yield: 70%, colorless oil.* ^{1}H NMR, 300 MHz ($CDCl_3$, δ ppm): 8.40 (Ar–H, $J = 2.4$ Hz, 1H, d), 8.32 (Ar–H, $J = 3.6$ Hz, 1H, dd), 7.38–7.34 (Ar–H, 1H, m), 7.23–7.18 (Ar–H, 1H, m), 3.44 (2H, $J = 6.9$ Hz, t), 1.74–1.64 (2H, m), 1.44–1.37 (2H, m), 1.33–1.28 (6H, m), 0.88(3H, –CH3, $J = 6.9$, t). ^{13}C NMR, 100 MHz ($CDCl_3$, δ ppm): 145.55, 145.44, 138.30, 130.35, 124.03, 46.71, 31.25, 26.42, 22.51 and 13.98. IR(cm^{-1}): 2146 (carbodiimide). HRMS [M+1] *m*/*z*: 204.15.

*2.2.2.2. Compound **2b**; N-hexyl-N′-(pyridin-3-ylmethyl)carbodiimide; yield: 72%, colorless oil.* ^{1}H NMR, 300 MHz ($CDCl_3$, δ ppm): 8.56–8.52 (Ar–H, 2H, m), 7.66–7.63 (Ar–H, 1H, m), 7.30–7.26 (Ar–H, 1H, m), 4.38 (ArCH2-, 2H, s), 3.16 (2H, J = 6.9 Hz, t), 1.49–1.45 (2H, m), 1.28–1.24 (6H, m), 0.87(3H, –CH3, $J = 6.9$, t). ^{13}C NMR, 100 MHz ($CDCl_3$, δ ppm): 149.10, 140.41, 135.58, 135.30, 123.64, 48.14, 46.67, 31.46, 31.32, 26.54, 22.69 and 14.17. IR (cm^{-1}): 2127 (carbodiimide). HRMS [M+1] *m*/*z*: 218.16.

*2.2.2.3. Compound **2c**; N-dodecyl-N′-pyridin-3-ylcarbodiimide; yield: 84%, colorless oil.* ^{1}H NMR, 400 MHz ($CDCl_3$, δ ppm): 8.40–8.39 (Ar–H, 1H, m), 8.32 (Ar–H, $J = 3.2$ Hz, 1H, dd), 7.37–7.34 (Ar–H, 1H, m), 7.22–7.18 (Ar–H, 1H, m), 3.44 (2H, $J = 6.8$ Hz, t), 1.72–1.65 (2H, m), 1.31–1.25 (17H, m), 0.87(3H, –CH3, $J = 6.8$, t). ^{13}C NMR, 100 MHz ($CDCl_3$, δ ppm): 145.34, 145.26, 138.09, 134.08, 130.13, 123.81, 46.71, 31.92, 31.29, 29.63, 29.55, 29.49, 29.35, 29.06, 26.76, 22.70 and 14.13. IR (cm^{-1}): 2140 (carbodiimide). HRMS [M+1] *m*/*z*: 288.24.

2.3. Synthesis of polymers, *3a–c*

All the mentioned polymers Poly **3a, 3b** and **3c** were synthesized inside an inert atmosphere dry box. In a typical procedure, the monomer sample (0.50–2.0 g in scale) was mixed with catalyst (**I**) [22]; with a monomer to catalyst ratio 100:1 or 200:1. The polymerizations were performed at room temperature and without any solvent. The reaction mixture transformed into a dark red viscous liquid and solidified within 48 h. The reaction mixture was allowed to remain at room temperature inside the dry box for 7 days for any secondary monomer diffusion. The resulting light orange solid was dissolved in chloroform and precipitated in methanol to remove the catalyst and unreacted monomer. The light yellow solid thus obtained was washed with several volumes of methanol and then dried under vacuum overnight.



Synthesized polymers and the catalyst

Scheme 1. Synthesis of polycarbodiimides.

*2.3.1. Poly-**3a**; Poly(N-hexyl-N′-pyridin-3-ylcarbodiimide), yield: 55%*

^{1}H NMR, 300 MHz ($CDCl_3$, δ ppm): 8.36–8.04 (Ar–H, 2H, br), 7.26–6.90 (Ar–H, 2H, br), 3.34–2.40 (2H, br), 1.29–0.37 (11H, br). ^{13}C NMR, 75 MHz ($CDCl_3$, δ ppm): 148.69, 144.67, 143.21, 128.52, 123.70, 123.17, 47.38, 31.48, 28.09, 26.54, 22.61 and 13.95. IR(cm^{-1}): 1621 (imine stretch). $[\alpha]_{435}^{25} = +68.43$ ($c = 0.2$ in $CHCl_3$, $l = 0.5$ dm).

*2.3.2. Poly-**3b**; Poly(N-hexyl-N′- (pyridin-3-ylmethyl) carbodiimide), yield: 74%*

^{1}H NMR, 400 MHz ($CDCl_3$, δ ppm): 8.80–7.90 (Ar–H, 2H, br), 7.60–6.40 (Ar–H, 2H, br), 5.25–3.80 (2H, br), 3.70–2.60 (2H, br), 1.24–0.75 (11H, br). ^{13}C NMR, 100 MHz ($CDCl_3$, δ ppm): 148.89, 148.05, 134.99, 122.71, 50.00, 31.49, 30.21, 28.94, 26.53, 22.56 and 13.99. IR (cm^{-1}): 1637 (imine stretch). $[\alpha]_{435}^{25} = +56.75$, ($c = 0.2$ in $CHCl_3$, $l = 0.5$ dm).

*2.3.3. Poly-**3c**; Poly(N-dodecyl-N′-pyridin-3-ylcarbodiimide), yield: 78%*

^{1}H NMR, 300 MHz ($CDCl_3$, δ ppm): 8.13 (Ar–H, 2H, br), 7.01 (Ar–H, 2H, br), 3.87–2.57 (2H, br), 1.26–0.88 (23H, br). ^{13}C NMR, 100 MHz ($CDCl_3$, δ ppm): 148.62, 147.72, 144.68, 143.18, 128.36, 123.30, 47.38, 31.97, 29.71(br), 29.42, 26.91, 22.72 and 14.15. IR (cm^{-1}): 1619 (imine stretch). $[\alpha]_{589}^{23} = +25.21$ ($c = 0.3$ in $CHCl_3$, $l = 0.5$ dm).

2.4. Synthesis of supported polymer-borane reagents

Poly-**3a** was dissolved in chloroform and poly-**3b** was dissolved in THF solvent and cooled to 0 °C. BH_3•Me_2S (2 M solution in THF) was added drop wise to the cold stirring polymer solution under nitrogen atmosphere so that the ratio of borane to pyridine in the polymer was 1:1. The mixture was stirred at room temperature for 18 h and then precipitated by addition of hexane, stirred overnight and filtered to yield a yellow solid. The solid was washed with hexanes several times and dried under vacuum 24 h (yield 97–99%).

IR (cm^{-1}): 2368 (B–H stretch) poly-**4a**, 2366 (B–H stretch) poly-**4b**.

2.5. Reduction of carbonyl compounds

In a typical reduction reaction, 0.2 g (2.0 equivalents) of poly-**4a** or poly-**4b** dissolved in 10 mL THF solvent was cooled to 0 °C in an ice bath. To this cold solution, the carbonyl compound, (1.0 equivalent) dissolved in 2 mL THF, was added drop wise followed by addition of $BF_3.OEt_2$ (2 M in THF), 1.0 equivalent. The reaction mixture was stirred until completion (ranging from 3 h to overnight) of reaction as monitored by TLC on silica gel plate (solvent: petroleum ether: Ethyl acetate; 5:1). Saturated solution of $NaHCO_3$ was added, the mixture was stirred for 30 min and the solid polymer support was separated by filtration. The filtrate was extracted with $CHCl_3$ (15 mL × 2) and the organic layer was washed with water (10 mL), brine (10 mL), dried using anhydrous Na_2SO_4, filtered, and the solvent was removed by rotavaporation to obtain the corresponding alcohols.

3. Results and discussion

Starting from commercially available 3-aminopyridine or 3-(methylamino)pyridine and n-alkyl isocyanates (n-hexyl- or

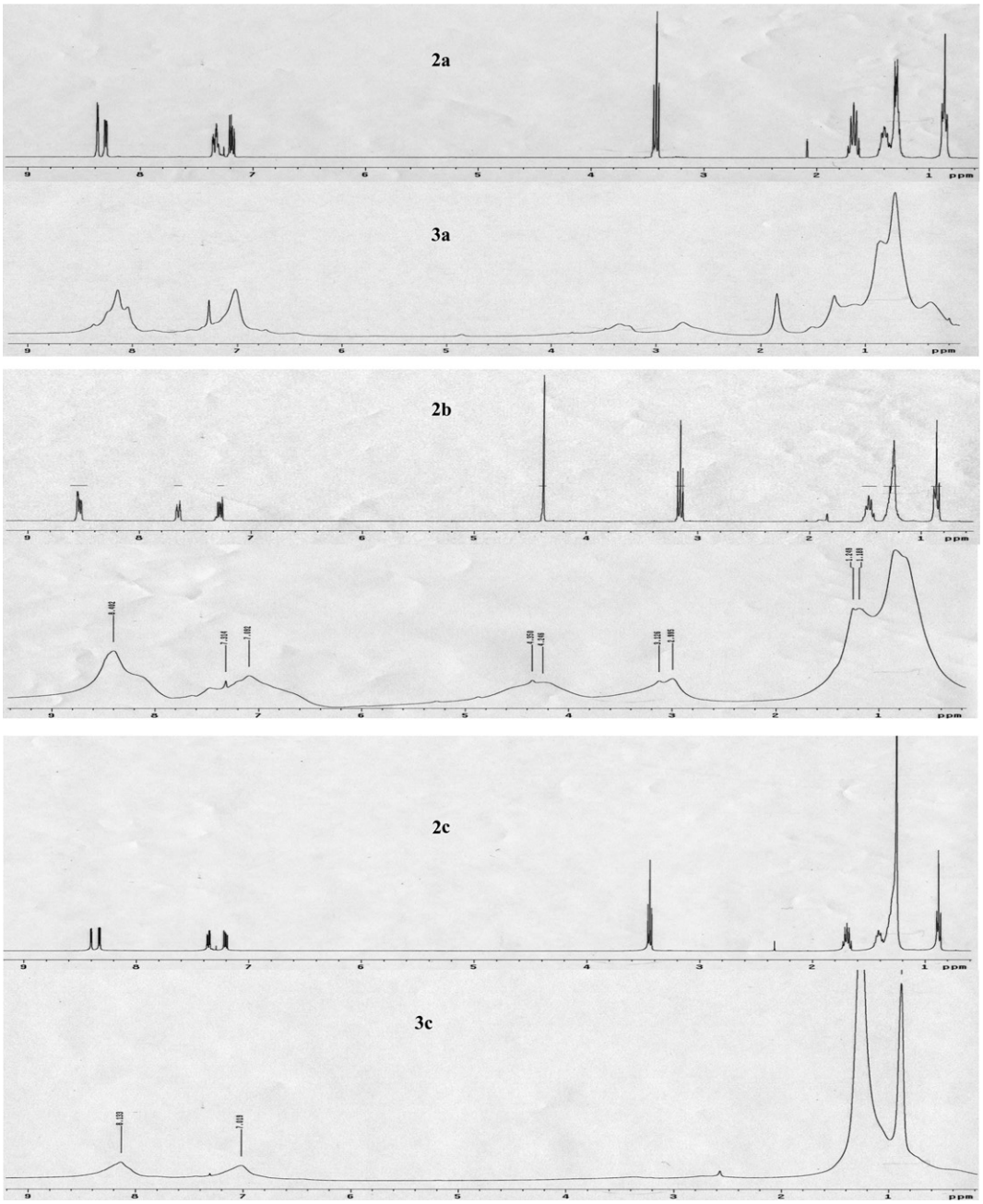


Fig. 1. ^{1}H NMR spectra of monomers [2a–c] and the polymers [3a–c].

n-dodecylisocyanate), polycarbodiimides (**3a**–**c**) with pyridine pendant groups were synthesized in three steps using [(*R*)–2,2′-binaphthoxy](di-isopropoxy)titanium(IV) catalyst (**I**) [27] as shown in Scheme 1.

Both 3 -aminopyridine and 3-(methyl amino)pyridine were found to undergo facile reaction with the isocyanates to form the expected ureas. Likewise, the 4-(methyl amino)pyridine proved equally effective. Interesting, however, and for reasons not understood, the ureas formed from 4-(methyl amino)pyridine with either n-hexylisocyanate or n-dodecylisocyanate would not dehydrate under standard conditions. All the 3-aminopyridine and 3-(methylamino) pyridine ureas could be readily dehydrated to their corresponding carbodiimides using standard conditions. These 3-pyridinyl monomers became the basis of this study.

Before preparation of monomers **3a**–**c**, we did some exploratory polymerizations of phenyl-hexylcarbodimide, bearing no heterocyclic groups, with the titanium catalysts in the presence of one equivalent (relative to monomer) of pyridine. Although the rate was retarded, the polymerization proceeded in a normal fashion. This experiment gave us confidence that the pyridine side chains would be tolerated by the very Lewis acidic Ti(IV) catalysts that are frequently used in these polymerizations. As expected, all 3 monomers were successfully polymerized using catalyst **I**. Time to gel in these neat polymerizations (ca. 48 h) were approximately twice as slow as the analogous polymerization of phenyl-hexylcarbodiimide (ca. 24 h).

Formation of polymers **3a**–**c** from their corresponding monomers **2a**–**c** were confirmed and characterized by IR, ^{1}H and ^{13}C

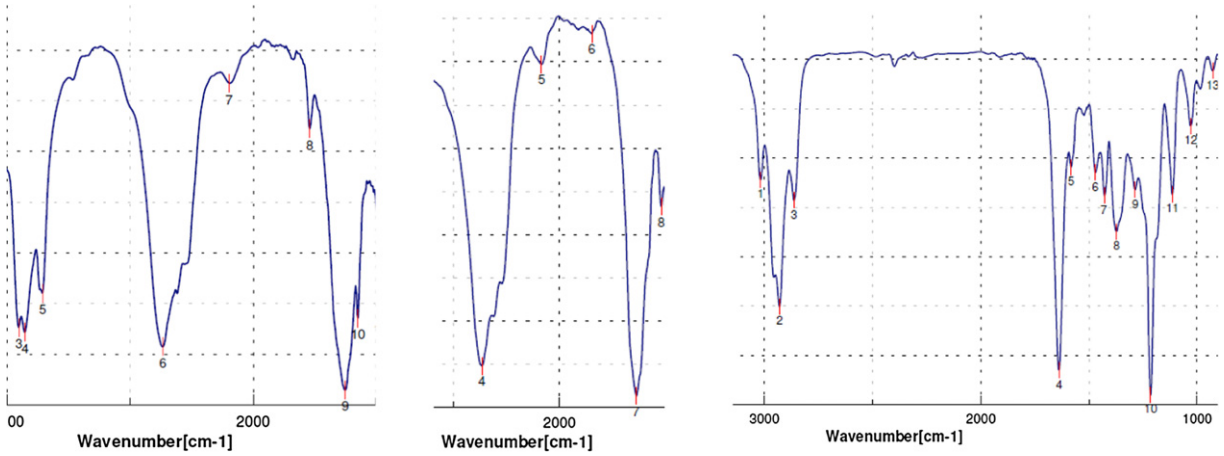


Fig. 2. IR spectra showing B–H stretching in Poly **4a** (left), poly **4b** (middle) and the recycled polymer (right).

NMR. The polymers are stable at room temperature for several months. All the monomers show very strong peaks for the carbodiimide stretch (2146–2127 cm^{-1}), which can be used to monitor the course of the reaction as these peaks disappeared completely during polymerization. New IR peaks emerged at 1621 cm^{-1} (poly-**3a**), 1619 cm^{-1} (poly-**3b**), and 1637 cm^{-1} (poly-**3c**) for the imine stretch corresponding to the guanidine of the polymer backbone. All three polymers **3a-c** are soluble in halogenated solvents such as chloroform and dichloromethane. Poly-**3a** and -**3b** are insoluble in THF whereas poly-**3c** is soluble in THF. The ^1H NMR spectra of polymers were broad but the chemical shifts are consistent with the corresponding monomers (Fig. 1).

Determining the molecular weights of these polymers has proved elusive to date: these nitrogen-rich polymers adhere strongly to GPC columns and will not elute, a suitable MALDI-TOF matrix has not been identified, and their liquid crystalline nature prevents standard viscometry measurements. However, similar monomers (e.g., phenyl hexylcarbodiimide, di-n-hexylcarbodimide) have been shown to proceed via a living polymerization using titanium catalysts and there is no a priori reason to assume the same general control is not maintained with these monomers.

These polymers **3a**–**c** offer new and versatile chemical supports; compared to other commercially available pyridine containing polymers like poly(vinylpyridine) [28]. Advantages include uniform reaction sites and fine-tunability of the solubility using the other pendant group of the carbodiimide monomer. This allows one to optimize the properties of the polymer without undergoing copolymerization or further post-polymerization modifications.

We investigated the reactivity of functional polycarbodiimide pyridine polymers as solid supports as in Lewis acid–base interactions with BH_3 [29,30]. As an example, poly-**3a** was allowed to react with BH_3•Me_2S to prepare a new pyridine-borane coordinated polymer (poly-**4a)** in which nitrogen-borane coordination was evidenced by a very strong signature peak in IR at 2368 cm^{-1} (B–H stretch). The characteristic B–N stretches reported in the literature around 1090 cm^{-1} [31,32] for pyridine-borane itself was not distinct in this polymer probably due to peak shifting and overlap in this fingerprint region. The yield for borane complexation in the polymers, as determined by mass difference, is 97–99%. Because of the presence of basic nitrogens in the polycarbodiimide backbone, control experiments were performed. Reactions to determine whether the BH_3 could coordinate with the backbone of poly(N-phenyl-N′-hexylcarbo diimide) [33] and poly(di-N-hexylcarbodiimide) with BH_3•SMe_2 reagent showed that the polycarbodiimide backbone is completely stable under the reaction conditions and does not participate in Lewis acid–base interactions with the boron nor is the imine functional group reduced by this mild reducing agent.

Poly-**4a** shows remarkable solubility differences from its parent (poly-**3a**) and related polymers as it is insoluble in halogenated organic solvents like chloroform and dichloromethane but dissolves in THF. The IR data of poly-**4a** shows the characteristic very strong B-H stretching band at 2368 cm^{-1} (Fig. 2). TGA was measured at a heating rate of 10 °C per minute under the nitrogen atmosphere for these polymers. The temperature for 5% weight loss is 165 °C for poly-**3a**, 196 °C for poly-**3b**, 162 °C for poly-**3c** and 194 °C for poly-**4a** (Fig. 3). The two polymers: poly-**4a** and poly-**3a**

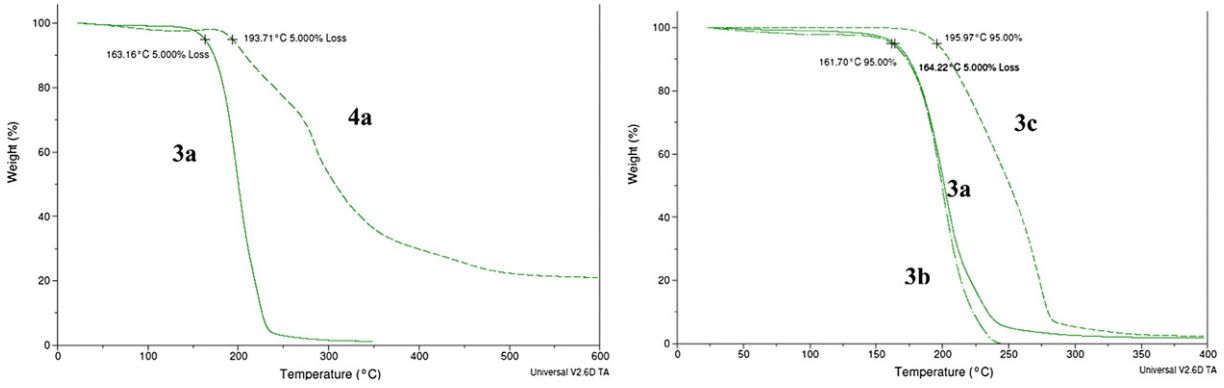
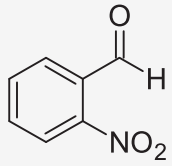
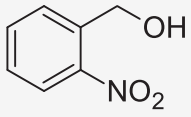
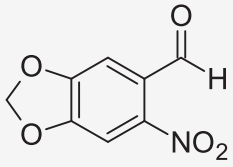
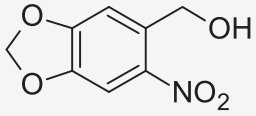
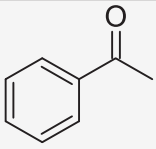
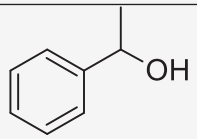
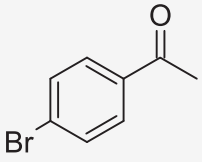
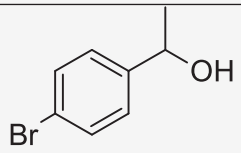
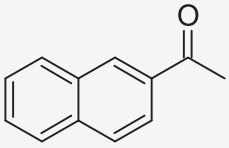
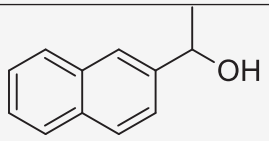


Fig. 3. TGA of polymers **3a**, **3b**, **3c** and **4a**.

Table 1
Reduction of carbonyl compounds with poly **4a**.

Entry	Carbonyl compound		Product		% yield
1	**5a**		**6a**		100%
2	**5b**		**6b**		
3	**5c**		**6c**		75%
4	**5d**		**6d**		80%
5	**5e**		**6e**		60 %

showed remarkable differences in their thermal properties as indicated in the Fig. 3 which is further consistent to borane coordination in the polymer. The thermal stability of these polymers allows heat demanding chemical transformations along their backbones and their side chains without decomposition thereby providing an excellent means of polymer support for conducting various chemical transformations.

Poly **4a** was used as a polymer supported reducing agent and was used to reduce a variety of aldehydes and ketones (**5a**–**e**) and the results are shown in Table 1.To recycle the polycarbodiimide support and to cleave any B–N bond remained, the polymer support was treated with 1 N HCl [26], washed and dried.

After the reduction and standard aqueous work-up the polymer support was quantitatively recovered and characterized by IR spectroscopy.

4. Conclusions

In summary, we have designed and synthesized the pyridine containing polycarbodiimides and we quantitatively incorporated borane (BH_3) into the polymer along the pendant groups via well-known pyridine-borane coordination reaction. This polymer-supported reagent was found to be a stable, mild reagent for the reduction of aldehydes and ketones. The polymer support was efficiently regenerated after aqueous work-up.

This study suggests that the polycarbodiimides with pyridine as pendant group can be used as an important and versatile green solid support for a variety of reagents capable of forming complex with pyridine moiety. Currently, work is in progress on developing variety of functional polymers derived from polycarbodiimides with pyridine and its derivatives as pendant groups.

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