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RESEARCH ARTICLE

Poly(N-vinylimidazole): A biocompatible, efficient, and highly recyclable heterogeneous catalyst for the preparation of bis(3-indolyl) methanes

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Abstract

Poly(N-vinylimidazole) (PVIm), as a biocompatible, efficient, halogen-free, and reusable catalyst, was applied for the solvent-free synthesis of a library of bis(3-indolyl) methanes. The reaction was smoothly carried out under mild conditions, and the crude products were purified easily, and the pure products were obtained in high to excellent yields

Keywords: Heterogeneous catalysis, Functional Polymer, Multicomponent reaction, Bis(3-indolyl)methanes, Ball mill Solvent-free technique

1. Introduction

Indole and its natural and synthetic derivatives are important nitrogen-heteroaromatic scaffolds due to diverse biological properties in the drug synthesis and pharmaceutical industry [1-5]. Bis-indolylalkanes are an essential class of bioactive metabolites of terrestrial and marine origin [6-8]. They are active cruciferous ingredients that promote beneficial estrogen metabolism [9]. Owing to the significant and unique biological properties of BIMs, numerous methods and catalysts have been reported for their synthesis [10-12]. The catalytic synthesis of BIMs is often conducted by condensing two moles of indoles with one mole of carbonyl compound using a Brönsted or Lewis acid catalyst. Many homogeneous and heterogeneous catalysts have been reported for this synthesis route in the literature [13-23]. It is well-known that nitrogen-based catalysts, reagents, and reactants can deactivate and/or decompose Lewis acids [23, 24]. However, Lewis acids are often expensive, and their use in stoichiometric amounts and large scale may not be economical.

Furthermore, the catalyst leakage in pharmaceutical processes can cause serious health problems for human beings. Some other drawbacks include the formation of by-products, prolonged reaction time, corrosion, and waste acid pollution problems [25, 26]. The research finds a safe and green methodology using stable and reusable catalysts under mild conditions to overcome the mentioned disadvantages and develop sound and green methods.

Functional polymers are macromolecules containing functional groups [27]. Poly(N-vinylimidazole) (PVIm) is a biocompatible [28], biodegradable [29], thermal stable [30], and water-soluble linear polymer with pKa around 6.0 [31]. PVIm, as a pH-sensitive functional polymer, can be protonated at acidic pH and de-protonated under basic conditions [32]. PVIm and its copolymers have been applied in the suppressing gene expression, as drug and protein delivery carriers [31], heavy metal removal via metal-binding chelating [33, 34], catalysis [35-38], pervaporation [39], fuel cell [40], CO2 separation [41], and nanofiltration separation [42].

2.0 Experimental

2.1 General procedure

The chemicals, reagents, and solvents were analytical grade and purchased from Sigma Aldrich, ACROS organic, Alfa Aesar, and Fisher Chemical Companies and used as purchased. The purity determination of the products was accomplished by TLC on silica gel polygram SIL G/UV 254 plates. The MS was measured under GC (70 eV) conditions. The IR spectra were recorded on a Perkin Elmer 781 Spectrophotometer. In all the cases, the 1H NMR spectra were recorded with Bruker Avance 400 MHz instruments. Chemical shifts are reported in parts per million in DMSO-d6 and CDCl3 with tetramethylsilane as an internal standard.

2.2 General Procedure for the Synthesis of BIMs

Poly(N-vinylimidazole) (PVIm) was fabricated through free radical polymerization of N-vinylimidazole in toluene at N2 atmosphere with azobisisobutyronitrile (AIBN) as the initiator [37]. The Mv value of PVIm was determined to be 302,000 g mol through viscometry using the Mark–Houwink–Sakurada equation [51]. PVIm (20 mg) was mixed and stirred at 80 °C with a mixture of a carbonyl compound (1) (1 mmol) and indole (2a) or 2-methylindole (2b) (2 mmol) under solvent-free conditions. After appropriate reaction time (monitored by TLC), cold diethyl ether (30 mL) was added into the reaction mixture, and the catalyst was separated by simple filtration. Next, PVIm was washed with Et2O (5 mL) and acetone (5 mL) and dried at ambient temperature. The recovered PVIm was reused for the next run. The ethereal solution was dried at reduced pressure by a rotary evaporator, and the crude product was purified by recrystallization from a mixed solvent of ethanol: water (95:5 %). The physical and spectral data of the pure products were in good agreement with those previously reported in the literature [43].

2.3 Color, melting point, and ^{1}H NMR data of the selected products:

3r: Orange solid, m.p. = 243-244 °C; ^{1}H NMR (CDCl3, 400 MHz) δ = 8.80 (s, 3H), 8.35 (d, J = 7.8 Hz, 3H), 7.88 (s, 3H), 7.49-7.42 (d, J = 7.8 Hz, 3H), 7.38-7.34 (m, 6H), 6.14 (s, 1H) ppm.

3s: Pale yellow needles, m.p. = > 300 °C; ^{1}H NMR (CDCl3, 400 MHz) δ = 8.11 (s, 2H), 7.74 (s, 1H), 7.38-7.31 (m, 5H), 7.14 (dd, J = 7.6 and 8.0 Hz, 3H), 6.94-6.98 (m, 6H) ppm.

3f': Yellow solid, m.p. = 298-299 °C; ^{1}H NMR (DMSO-d6, 300 MHz) δ = 10.92 (s, 1H), 10.88 (s, 1H), 10.58 (s, 1H), 7.26-7.21 (m, 3H), 7.17 (d, J = 7.4 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.90-6.82 (m, 3H), 6.74 (d, J = 8.2 Hz, 1H), 6.67-6.62 (m, 2H), 6.48 (d, J = 7.4 Hz, 1H), 2.12 (s, 3H), 1.96 (s, 3H) ppm.

3g': Orange solid, m.p. = 258-259 °C; ^{1}H NMR (DMSO-d6, 300 MHz) δ =10.69 (s, 1H), 10.66 (s, 2H), 7.36 (d, J = 7.4 Hz, 1H), 7.20-7.18 (m, 2H), 6.90-6.86 (m, 5H), 6.67-6.64 (m, 2H), 6.18 (s, 1H), 6.12 (s, 1H), 1.94 (s, 6H) ppm .

2.4 Recovering and reusing of PVIm

PVIm was filtered and washed with hot ethanol (2 × 5 mL) and then dried overnight at 80 ºC by a vacuum oven. The study of FT-IR spectra of fresh and 4th recovered PVIm demonstrated the chemical and thermal stability of PVIm during the reaction, workup, and recycling conditions.

3.0 Results and discussion

Developing cost-effective and eco-friendly processes and performing reactions with safe and greener reagents, solvents, and catalysts are crucial issues of organic synthesis research. In continuation of our recent studies [35-37], herein, the efficient catalytic activity of PVIm, as a functional polymer, for the synthesis of various bis(3-indolyl)methanes (BIMs) is described. Initially, the synthesis of BIMs was carried out in different solvents using PVIm, and the results are summarized in Table 1. These results suggest that solvent-free was the best condition for the synthesis of BIMs. It may be because polar protic solvents tend to inactive the base sites, and polar aprotic solvents tend to favor attack at the nitrogen, whereas nonpolar solvents prefer C-3 attack.

Table 1. Optimization of the solvent effect on the model reaction.[a]

Entry	Solvent	Yield [b] (%)
1	Dichloromethane	45
2	Toluene	55
3	Acetonitrile	50
4	Ethanol	21
5	Methanol	22
6	Solvent-free	60[c]

[a] Reaction condition: 4-chlorobenzaldehyde (1.0 mmol), indole (2.0 mmol), PVIm (10 mg), temperature (reflux), reaction time (2 h).

[b] Determined by GC.

[c] Reaction condition: 4-chlorobenzaldehyde (1.0 mmol), indole (2.0 mmol), PVIm (10 mg), temperature (80 °C), reaction time (2 h).

Then, the effect of the catalyst loading was studied on the model reaction. As shown in Table 2, the catalytic efficiency of PVIm enhanced in the presence of more amount of the catalyst, and the best result was observed with 20 mg of the catalyst loading (14 wt. % per 4-chlorobenzaldehyde), which afforded the desired product 3b in 95% yield. No improvement was observed in the product yield using more catalyst loading above 20 mg of PVIm. In the case of PVIm, the catalytic activity can be mainly attributed to the basicity of free imidazole rings attached to the backbone of the functional polymer. The pKa value of PVIm was estimated at around 6.0 [31]. A linear relationship was observed between the catalyst loading and 3b yield at a range of 5 mg to 20 mg of PVIm.

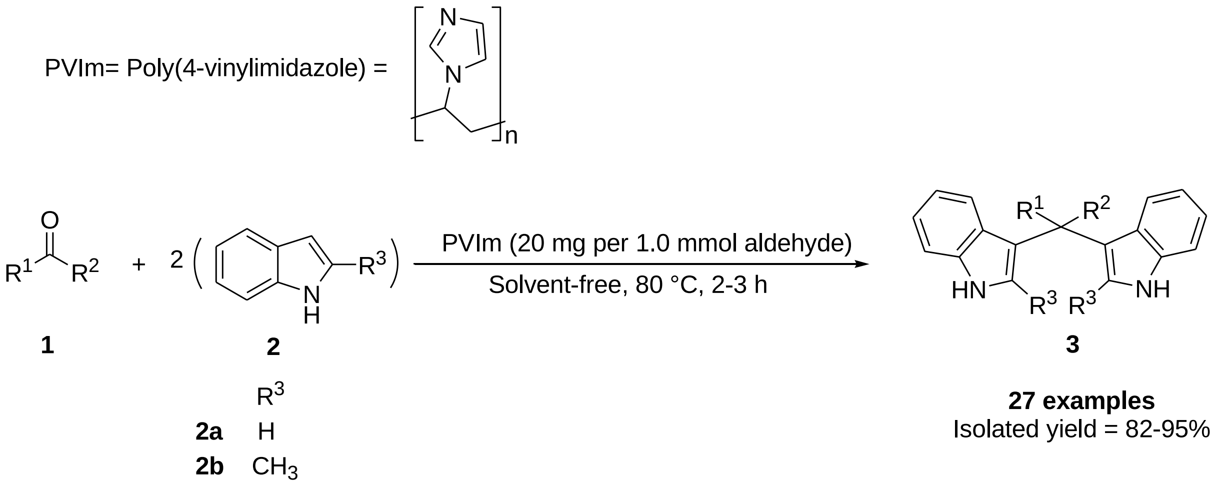
Table 2. Screening of PVIm loading in the model reaction.[a]

Entry	Amount of poly(4-vinylpyridine) (mg)	Yield [b] (%)
1	-	No reaction
2	5	41
3	10	60
4	20	95
5	30	96
6	40	96

a Reaction condition: 4-chlorobenzaldehyde (1.0 mmol), indole (2.0 mmol), temperature (80 °C), reaction time (2 h).

b Determined by GC.

The substrate scope of the new catalytic process was investigated by the reaction of various carbonyl compounds (1) with indole (2a) and 2-methylindole (2b) under optimized reaction conditions (Scheme 1).



Scheme 1. Synthetic conditions of BIMs using PVIm.

Table 3. The substrate scope of the new catalytic process for the synthesis of BIMs.[a]

Entry	Aldehyde	R^3	Product	Time (min)	Yield (%)[b]	M.p. (°C)	
						Found	Reported (43)
1	C_6H_5-CHO	H	3a	135	94	127-128	123-125
2	4-Cl-C_6H_4-CHO	H	3b	120	95	87-88	87-89
3	2-Cl-C_6H_4-CHO	H	3c	124	93	76-78	77-78
4	4-CH_3O-C_6H_4-CHO	H	3d	135	90	191-192	195
5	3,4-$(CH_3O)_2$-C_6H_4-CHO	H	3e	140	90	200-201	197-199
6	4-CH_3-C_6H_4-CHO	H	3f	120	93	96-97	99-100
7	4-NO_2-C_6H_4-CHO	H	3g	120	95	243-244	245-246
9	4-Br-C_6H_4-CHO	H	3h	125	95	110-111	111-113
10	C_6H_5-CH=CH-CHO	H	3i	135	91	99-100	100-102
11	Furfural	H	3j	120	95	320-321	322-324
12	4-OH-C_6H_4-CHO	H	3k	135	90	208-209	210-212
13	2-OH-C_6H_4-CHO	H	3l	145	89	100-101	103-105
14	$CH_3CH_2CH_2CHO$	H	3m	165	90	Oil	Oil
15	$CH_3(CH_2)_5CHO$	H	3n	160	91	65-66	68-70
16	C_6H_5-CO-CH_3	H	3o	180	82	167-168	169-171
17	4-Cl-C_6H_4-CO-CH_3	H	3p	175	84	108-109	109-110
18	4-NO_2-C_6H_4-CO-CH_3	H	3q	170	89	271-272	274-276
19	Indol-3-carbaldehyde	H	3r	140	94	243-244	245-247
20	Isatin	H	3s	140	94	> 300	244-245
21	C_6H_5-CHO	CH_3	3a'	140	94	239-240	244-246
22	3,4-$(CH_3O)_2$-C_6H_4-CHO	CH_3	3b'	160	90	200-201	204-206
23	4-NO_2-C_6H_4-CHO	CH_3	3c'	140	95	242-243	240-242
24	4-OH-C_6H_4-CHO	CH_3	3d'	155	89	237-238	240-242
25	4-CH_3-C_6H_4-CHO	CH_3	3e'	135	91	179-180	175-177
26	Isatin	CH_3	3f'	160	91	298-299	300-301
27	Indol-3-carbaldehyde	CH_3	3g'	165	90	258-259	260-262

a The desired products were characterized by comparing their melting point and/or 1H NMR spectra with those of the known compounds.

b Isolated yield.

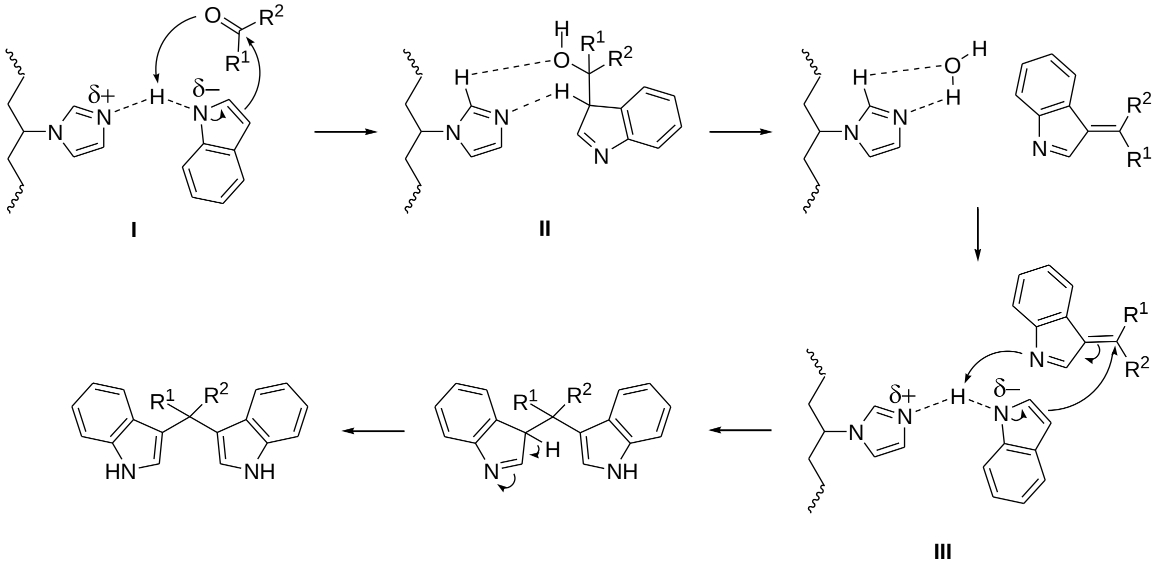
As seen in Table 3, a variety of substituted aromatic and heteroaromatic aldehydes smoothly reacted with indole (2a) or 2-methylindole (2b) using PVIm as a heterogeneous catalyst under the optimized reaction conditions, and the respective BIMs were isolated in 82-95% within 2-3 h.

Table 4. The superiority of our catalytic process for the preparation of 3,3'-bis-indolylphenylmethane compared with some previously reported methods.

Entry	Catalyst	Reaction condition	Time (min)	Catalyst loading	Yield (%)[a]	Ref.
1	CAN	CH_3CN (N_2 atm)	30	0.3 mol	89	44
2	Lanthanide triflate	EtOH / H_2O	720	0.1M solution	95	45
3	Acetic acid	H_2O	10 days	0.01 mol	71	46
4	Indium trichloride	CH_3CN	240	0.2 mol	96	47
5	Zeokarb-225	CH_3CN	450	0.5 g	95	48
6	[Hmim]HSO_4	EtOH	60	0.01 mol	97	14
7	Aminosulfonic acid	EtOH/H_2O (N_2 atm)	30	1.5 mol	93	49
8	Ammonium chloride	Solvent-free	120 h	0.5 mol	96	50
9	Poly(*N*-vinylimidazole)	Solvent-free (80 °C)	135 min	20 mg	94	This work

a Isolated yield.

Based on previously reported mechanisms in the literature [14, 46], a schematic reaction route was proposed, as shown in Scheme 2.



Scheme 2. A plausible mechanism of the synthesis of bis(3-indolyl)methanes in the presence of a catalytic amount of PVIm.

The reusability was investigated to show the worth of PVIm as an easy separable and recyclable heterogeneous catalyst. For this purpose, the model reaction was carried out several times consecutively. The first run gave the conversion of 95% after two hours. Then, the catalyst was collected by filtration, washed with Et2O and acetone, and dried at room temperature overnight. The subsequent runs were carried out in the same procedures four times, and the catalytic activity of PVIm remained almost constant, as shown in Table 5.

Table 5. Reusability of PVIm

Run	Time (min)	Isolated yield (%)
1	120	95
2	120	95
3	126	93
4	126	92

Conflicts of interest

There are no conflicts to declare.

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