

Polyacrylamide Supported Phenolate as a Heterogeneous, Efficient, Recyclable, and Selective Catalyst for Aza- and Thio-Michael Addition in Aqueous Media

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ABSTRACT

Water mediated reactions offer useful and more environmentally friendly alternatives to their harmful organic solvent versions and have received increasing interest in recent years. Furthermore, water has unique physical and chemical properties, and by its utilization it would be possible to realize reactivity or selectivity that cannot be attained in organic solvents. Polyacrylamide supported phenolate is synthesized, characterized, and introduced as a new basic heterogeneous catalyst for aza- and thio-Michael addition reactions of both aliphatic and aromatic amines and thiols to α,β -unsaturated electrophiles in aqueous media at room temperature. Di-thio-Michael addition of dithiol was performed successfully. Results showed that thio-Michael addition is faster than aza-Michael addition due to higher nucleophilicity of thiolate anion in comparison with neutral amino functionality. Mild reaction condition, low catalyst/substrate ratio, high efficiency, and reusability make this new basic heterogeneous catalyst as one of few reported polymer supported catalysts for aza- and thio-Michael reactions in green aqueous media.

Key Words:

polyacrylamide supported phenolate;
aza-Michael addition;
thio-Michael addition;
 α,β -unsaturated electrophile.

INTRODUCTION

Polymer supported organic catalysts have attracted much attention in organic synthesis owing to easy workup procedures and minimization of cost and waste generation due to reuse and recycling of the catalysts. Therefore, it is not surprising that their applications are covering an ever-increasing part of the spectrum of organic transformations [1].

The use of water as a medium for organic reactions has a number of potential advantages:

- (i) It is the cheapest solvent available on earth;
- (ii) It is non-toxic and non-hazardous to the environment;
- (iii) Isolation of the organic products can be performed by simple phase separation.

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There are beneficial effects of aqueous solvents on rates and selectivities of important organic transformations, e.g., Diels-Alder, aldol, and Michael additions reactions [2-3].

The versatile Michael reaction has numerous applications in synthesis of fine chemicals and is classically catalyzed by a base under homogeneous conditions [4]. In heterogeneous phase various solid catalysts have been found useful, including synthetic diphosphate $\text{Na}_2\text{CaP}_2\text{O}_7$, [5] zeolite, [6] $\text{NiBr}_2/\text{montmorillonite}$, [7] phenolate supported silica [8,9], and other catalysts with more or less success.

Important types of Michael reaction are aza- and thio-Michael reactions and because of the intrinsic importance of β -amino and β -thio carbonyl compounds they have attracted sustained attention in organic synthesis [10,11]. These reactions require either basic [12-15] or acidic catalysts [16-18], and in the past few years many new types of catalysts have been reported in the literature [19-28]. Unfortunately, many of these procedures often require a large excess of reagent, long reaction time and drastic conditions in using toxic organic solvents such as acetonitrile, methylene chloride or 1,2-dichloroethane. As far as we know, there are only a few reports in the literature of heterogeneous catalysis for aza- and thio-Michael addition reactions in aqueous media [20,21,24, 28] and in the case of aza- Michael only aliphatic amine addition are reported. Therefore, the need still exists for a general, facile, and environmentally benign methodology for the conjugate addition of amines and thiols to α,β -unsaturated carbonyl compounds under aqueous condition.

In continuation of our work on catalysis of organic reactions in organic or aqueous phase with modified polyacrylamide [29-34], we now describe the use of the polyacrylamide supported phenolate (PAPh) as a new heterogeneous catalyst in aza- and thio-Michael addition reaction between α,β -unsaturated electrophiles and both aliphatic and aromatic amines and thiols in aqueous solution at room temperature.

EXPERIMENTAL

All solvents and reagents were purchased from Fluka or Merck. The products were characterized by comparison

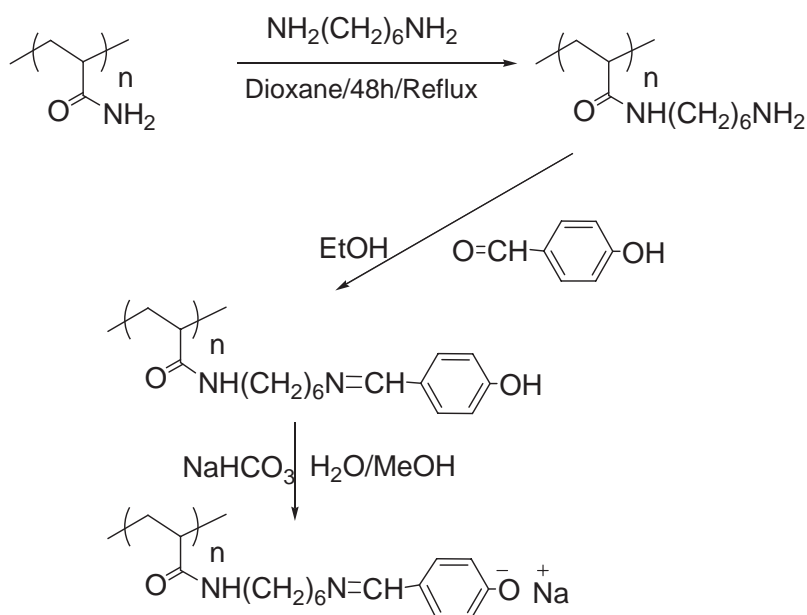
of their spectral data with those reported in the literature. Infrared (IR) spectra were run on a FTIR-8300 Shimadzu spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DPX-250 spectrometers using tetramethylsilane (TMS) as internal standard in pure deuterated solvents. Chemical shifts are given in the δ scale in parts per million (ppm) and the bonds are assigned as singlet (s), doublet (d), triplet (t), quartet (q) multiplet (m) and doublets of doublet (dd). The progress of the reactions were monitored by TLC on silica gel polygram SIL/UV 254 plates or by GLC on Shimadzu model GC-8A and GC-14A instruments with hydrogen flame ionization detectors. The spectral data for some of the products are given in the spectra section.

Preparation of Polyacrylamide Supported Phenolate (PAPh)

The amino functionalized polyacrylamide was synthesized by copolymerization of acrylamide with 2% DVB in ethanolic media and subsequent transamidation with 1,6-diaminohexane according to our previous procedure [29]. The resulting cross-linked polymer (5 g) was stirred at room temperature with 4-hydroxybenzaldehyde (2.44 g, 20 mmol) in ethanol (60 mL), following the reaction up to disappearance of phenol, detected by TLC. The reaction was completed within approximately 30 min at room temperature. The mixture was filtered and the solid washed with ethanol and dried at 50°C. It was stirred with 1.8 g NaHCO_3 in 1:1 water/methanol for 1 h and filtered, washed with water, methanol, and finally dried at 50°C. Gravimetric and titrimetric analyses were in agreement and indicated a loading of 1.5 mmol phenolate/g of polymer.

General Procedure for Aza- or Thio-Michael Addition Reaction

To a flask containing an equimolar mixture (1 mmol) of amine or thiol and α,β -unsaturated carbonyl compound in water (5 mL), PAPh (0.07 g or 0.1 mmol) was added and the mixture was stirred at room temperature until completion of the reaction, as monitored by TLC or GC. The catalyst was filtered, washed with ethyl acetate and the product was separated by extraction with ethyl acetate. The organic layer was evaporated under vacuum on a rotary evaporator and the resulting pure product



Scheme I

was obtained.

In the case when the reaction did not go to completion (Table 1 entries 11, 12, and 13 and Table 2 entries 11 and 12) the final purification was performed by column chromatography using Hexane/THF (5/1) as eluent. Structural assignments of the products are based on their ^1H NMR and ^{13}C NMR.

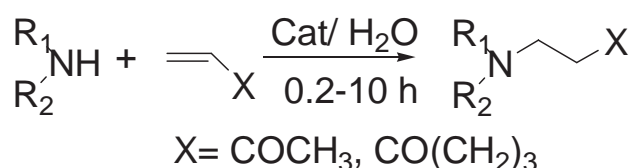
RESULTS AND DISCUSSION

PAPh was prepared by modification of polyacrylamide through transamidation with 1,6-diaminohexane [29] and subsequent reaction with 4-hydroxybenzaldehyde and final treatment with a weak base (Scheme I).

For optimizing the reaction conditions with respect to solvent and substrate/catalyst molar ratio, PAPh catal-


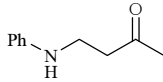
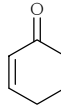
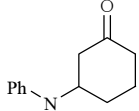

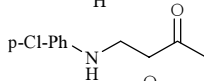
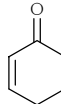
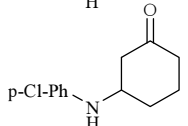

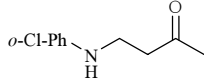
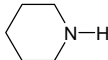

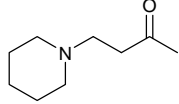
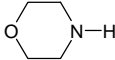

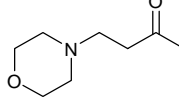


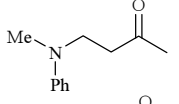


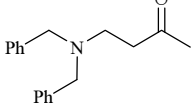


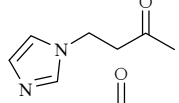

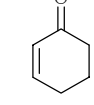
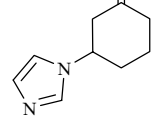


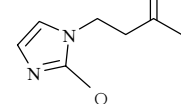

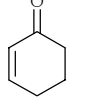
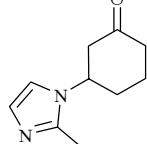
ized reaction of cyclohexenone with aniline as a model reaction was studied. The reaction was carried out in different solvents such as tetrahydrofuran, dichloromethane, cyclohexane, ethanol, and water. The last two solvents proved to be the best. The aza-Michael reaction in water without any catalyst proceeded very slowly with low yield. However, in the presence of PAPh a drastic rate enhancement was observed and proved that 1/0.1 was the optimum substrate/catalyst molar ratio.

In order to show the general applicability of our method, the addition of several aromatic and aliphatic amines to methyl vinyl ketone and cyclohexenone were catalyzed by PAPh and produce mono-substituted aza-Michael adducts in proper time and with good to excellent yields (Scheme II and Table 1). It is notable that no by-products were produced resulting from the undesir-




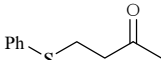
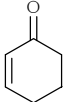
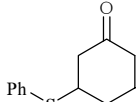
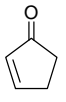
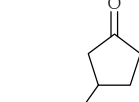
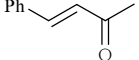
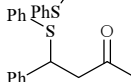

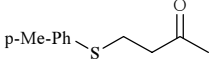
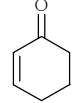
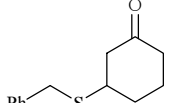

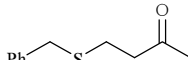
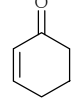
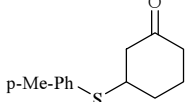
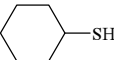

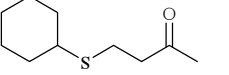
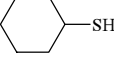
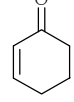
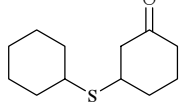

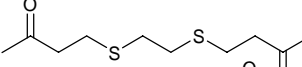
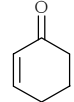
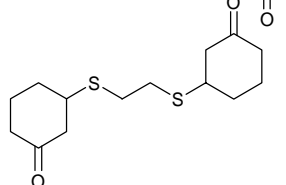
Scheme II

Table1. Conjugative addition of various amines to α,β -unsaturated ketones at room temperature.

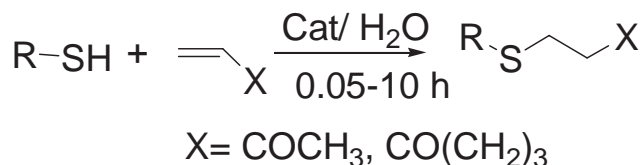
Entry	Amine	α, β -unsaturated ketones	Product	Time (h)	Isolated yield ^a (%)
1.	PhNH ₂			0.25 24	98 40 ^b
2.	PhNH ₂			3	93
3.	<i>p</i> -Cl-PhNH ₂			3	90
4.	<i>p</i> -Cl-PhNH ₂			10	85
5.	<i>o</i> -Cl-PhNH ₂			3	86
6.				0.2	92
7.				0.2	94
8.				3	94
9.				0.3	96
10.				0.8	90
11.				8	79
12.				0.5	74
13.				10	68

^(a) Yields refer to pure isolated products. The products were identified by comparison of their ¹HNMR, ¹³CNMR spectra and physical data with those reported in the literature [18,19,22,23,26,35,36]; ^(b) No catalyst.

Table 2. Conjugative addition of thiols to α,β -unsaturated ketones at room temperature.

Entry	Amine	α, β -unsaturated ketones	Product	Time (min)	Isolated yield ^a (%)
1.	PhSH			5	96
2.	PhSH			4 60	95 13 ^b
3.	PhSH			4	91
4.	PhSH			24h	80
5.	<i>p</i> -MePhSH			3	97
6.	<i>p</i> -MePhSH			6	92
7.	PhCH ₂ SH			5	94
8.	PhCH ₂ SH			7	93
9.				5	89
10.				7	89
11.	HS-CH ₂ -CH ₂ -SH			30	85
12.	HS-CH ₂ -CH ₂ -SH			60	70

^(a) Yields refer to pure isolated products. The products were identified by comparison of their ¹H NMR, ¹³C NMR spectra and physical data with those reported in the literature [19, 37-39]. ^(b) No catalyst.



Scheme III

able 1,2-addition or bis-addition side reactions which are usually observed under classical conditions [4].

The reaction of cyclic amines such as piperidine and morpholine with methyl vinyl ketone gave 92 and 94 % yields, respectively, in 0.2 h (Table 1, Entries 6 and 7). Sterically hindered amine, for example dibenzylamine (Table 1, Entry 9) with methyl vinyl ketone offered 1,4-addition products in 96% yield in 0.3 h

We have also studied the addition of imidazoles as biologically important amines to methyl vinyl ketone and cyclohexenone (Entries 10 and 11) under similar reaction conditions. Imidazole reacted with methyl vinyl ketone and cyclohexenone cleanly to produce the corresponding Michael adducts in 90 and 79 % yields respectively.

The applicability of the method for the addition of structurally diverse thiols to methyl vinyl ketone and cyclohexenone in the presence of PAPH in water was also investigated (Scheme III and Table 2). The reactions progressed well at room temperature and the desired β -thio ketones were produced rapidly (2-60 min) in high yields except the reaction of benzylideneacetone with thiophe-

nol which was sluggish and after 24 h, the desired Michael adduct was isolated in only 80% yield (Table 2, entry 4).

Through this study, we have also investigated the double Michael addition of 1,2-ethane dithiol to vinyl methyl ketone and cyclohexenone. The reactions proceeded well and the desired Michael adducts were isolated in 70-85% yields within 0.5-1 h at room temperature (Table 2, Entries 11 and 12). These double Michael adducts are potential precursors for the preparation of macrocyclic or polymeric compounds carrying sulfur heteroatoms.

For comparison, the performance of our catalyst and a few other catalysts reported in the literature are presented in Table 3 and Table 4. As shown our catalyst has advantages with respect to the reaction medium, time, and ratio of Cat/sub. The possibility of recycling the catalyst is of concern, especially for large-scale operations. Therefore, recyclability of the catalyst was studied and the catalyst proved to be reusable several times without noticeable reduction in its activity. We believe that the good efficiency of the catalyst for the aza-Michael reac-

Table 3. Comparison of the polymeric catalyst (PAPH) with a few others reported catalysts in aza-Michael reaction.

Solid catalyst	Condition	Cat/Sub	Time(h)	Yield(%)
PAPH	Water	0.1:1	0.3 0.2	96 ^a Quant ^b
Bi(NO) ₃ [18]	CH ₂ Cl ₂	0.2:1.36	12-15	78 ^a
CeCl ₃ .7H ₂ O-NaI on Al ₂ O ₃ [23]	Solvent-free	1.35:1	overnight	95 ^a
Cu(OAc) ₂ [20]	Water	0.05:1	12	Quant ^b
FeCl ₃ .7H ₂ O [21]	Water	0.1:1	15	Quant ^b
Ionic liquid [24]	Water	0.1:1	7	97 ^b

(^a) Aza-Michael reaction of dibenzylamine and vinyl methyl ketone. (^b) Aza-Michael reaction of diethylamine and vinyl methyl ketone.

Table 4. Comparison of the polymeric catalyst (PAPh) with a few others reported catalysts in thio-Michael reaction.

Solid catalyst	Condition	Cat/Sub	Time(Min)	Yield(%)
PAPh	Water	0.1:1	4	95 ^a
			5	96 ^b
NaHCO ₃ [28]	Water	0.1:1	45	95 ^a
Supported cinchona alkaloids [25]	Toluene	-	overnight	85 ^a
KF [27]	Toluene	0.02:1	60	57 ^b
IRA-400F [27]	Toluene	0.02:1	60	92 ^b
A10OcCl [27]	Toluene	0.02:1	60	91 ^b

(^a) Thio-Michael reaction of thiophenol and cyclohexenone. (^b) Thio-Michael reaction of thiophenol and vinyl methyl ketone.

tions in water can be due to its polyacrylamide nature and consequently its compatibility with both the solvent and the reactants.

CONCLUSION

PAPh proved to be an excellent selective catalyst for aza- and thio-Michael addition of aliphatic as well as aromatic amines and thiols to α,β -unsaturated electrophiles in water at room temperature without any side reactions, such as condensation, dimerization, or rearrangements. This catalyst brings advantages such as high catalytic activity, recoverability and selectivity under very mild aqueous condition. The separation of the catalyst can be done by simple filtration.

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APPENDIX

Sample Spectroscopic Data:

Entry (8) (Table 1): 4-(Methyl-phenyl-amino)-butan-2-one: ¹HNMR (CDCl₃, 250 MHz) δ (ppm) = 7.24-7.12 (m, 2H), 6.82-6.55 (m, 3H), 3.6 (t, 2H), 2.88 (s, 3H),

2.65 (t, 2H), 2.32.17 (s, 3H); ¹³CNMR (CDCl₃, 63 MHz) δ (ppm) = 207.95, 148.63, 129.25, 116.61, 112.44, 47.25, 40.56, 38.42, 30.63; IR (ν^{-1})= 1710 (C=O).

Entry(12) (Table 1): 4-(2-Methyl-imidazol-1-yl)-butan-2-one: ¹HNMR(CDCl₃, 250 MHz) δ (ppm) = 6.86 (d, 1H), 6.82 (d, 1H), 4.11 (t, 2H), 2.87 (t, 2H), 2.38 (s, 3H), 2.08 (s, 3H); ¹³CNMR (CDCl₃, 63 MHz) δ (ppm) = 205.55, 144.77, 127.68, 119.37, 44.2, 40.43, 30.68, 13.29; IR (ν^{-1})= 1710 (C=O).

Entry(13) (Table 1): 3-(2-Methyl-imidazol-1-yl)-cyclohexanone: ¹HNMR(CDCl₃, 250 MHz) δ (ppm) = 6.94 (dd, 2H), 4.27 (m, 1H), 2.71-2.64 (m, 2H), 2.46-2.35 (m, 5H), 2.2-2.0 (m, 3H), 1.82-1.74 (m, 1H); ¹³CNMR (CDCl₃, 63 MHz) δ (ppm) = 207.5, 151.3, 130.1, 115.48, 54.4, 48.9, 40.74, 32.3, 25.96, 22.35, 13.43; IR (ν^{-1})= 1705 (C=O).

Entry(4) (Table 2): 4-Phenyl-4-phenylsulphanyl-butan-2-one: ¹HNMR(CDCl₃, 250 MHz) δ (ppm) = 7.5-7.7 (m, 3H), 7.15-7.3 (m, 7H), 4.6 (t, 1H), 2.8-3.1 (dd, 2H), 2.15 (s, 3H); ¹³CNMR (CDCl₃, 63 MHz) δ (ppm) = 205.88, 141.51, 137.43, 133.28, 129.44, 129.22, 129.05, 128.18, 128.06, 49.89, 48.45, 30.71; IR (ν^{-1})= 1710 (C=O).

Entry(9) (Table 2): 4-Cyclohexylsulphanyl-butan-2-one: ¹HNMR(CDCl₃, 250 MHz) δ (ppm) = 2.75-2.73 (dd+m, 5H), 2.17-2.18 (m, 2H), 2 (m, 2H), 1.77 (m,

2H), 1.63 (m, 1H), 1.30 (m, 6H); ^{13}C NMR (CDCl_3 , 63 MHz) δ (ppm) = 207.25, 44.08, 34.34, 30.74, 26.10, 24.10; IR (ν^{-1})= 1710 (C=O).

Entry(10) (Table 2): 3-Cyclohexylsulphanyl-cyclohexanone: ^1H NMR(CDCl_3 , 250 MHz) δ (ppm) = 3.15 (m, 1H), 2.71-2.64 (m, 2H), 2.41-2.31 (m, 3H), 2.15-2.11 (m, 2H), 1.92 (m, 2H), 1.74-1.63 (m, 5H), 1.35-1.28 (m, 5H); ^{13}C NMR (CDCl_3 , 63 MHz) δ (ppm) = 209.11, 49.00, 42.36, 41.38, 34.51, 33.11, 26.28, 25.61; IR (ν^{-1})= 1700 (C=O).

Entry(11) (Table 2): 4-[2-(3-Oxo-butylsulphanyl)-ethylsulphanyl]-butan-2-one: ^1H NMR(CDCl_3 , 250MHz) δ (ppm) = 2.76-2.70 (m, 12H), 2.18 (s, 6H); ^{13}C NMR (CDCl_3 , 63 MHz) δ (ppm) = 207.00, 43.97, 32.63, 30.45, 26.01; IR (ν^{-1})= 1710 (C=O).

Entry(12) (Table 2): 3-[2-(3-Oxo-cyclohexylsulphanyl)-ethylsulphanyl]-cyclohexane-1-one: ^1H NMR (CDCl_3 , 250 MHz) δ (ppm) = 3.20-3.10 (m, 2H), 2.76 (m, 4H), 2.7-2.65 (m, 2H), 2.42-2.32 (m, 6H), 2.16-2.13 (m, 4H), 1.74-1.70 (m, 4H); ^{13}C NMR (CDCl_3 , 63 MHz) δ (ppm) = 208.53, 48.27, 42.68, 41.09, 31.74, 30.91, 24.25; IR (ν^{-1})= 1700 (C=O).

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