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Poly(*N*-vinylimidazole) as an Efficient and Recyclable Catalyst of the Aza-Michael Reaction in Water

I. P. Beletskaya[a], **E. A. Tarasenko**[a], **A. R. Khokhlov**[b], and **V. S. Tyurin**[a]

[a] *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences,*
Leninskii pr. 31, Moscow, 119991 Russia
e-mail: beletska@org.chem.msu.ru

[b] *Faculty of Chemistry, Moscow State University, Vorob'evy gory 1, Moscow, 119992 Russia*

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Abstract—Poly(*N*-vinylimidazole) effectively catalyzed Michael addition of 1*H*-1,2,4-triazole, 3,5-dimethyl-1*H*-1,2,4-triazole, uracil, oxazolidin-2-one, and succinimide to but-3-en-2-one, cyclohex-2-en-1-one, methyl acrylate, and methyl vinyl sulfone in water at room temperature. The catalyst can readily be regenerated and repeatedly used at least five times without loss in activity, as shown in the reaction of 1*H*-1,2,4-triazole with but-3-en-2-one as an example.

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Organic polymers constitute the basis of all living organisms; they play the role of construction materials at both macro and micro levels and make cell organelle space structured. Another function of organic polymers as a part of enzymatic systems is to catalyze all biochemical reactions and hence the life process as a whole. The use of synthetic polymers is related primarily to the design of different types of materials. However, starting from the Merrifield solid-phase synthesis in 1963 [1], organic polymers have found wide application as supports for reagents and catalysts [2, 3]. In the recent time, interest in such polymers became stronger, and specific attention was given to so-called "smart" polymers due to their ability to change their physicochemical properties, primarily solubility, depending on the conditions. Especially promising is simulation of biopolymers by simple synthetic polymers whose behavior is similar to the behavior of polypeptides and that are capable of acting as catalysts.

Imidazole ring is a structural fragment of the side chain in the amino acid residue of histidine which constitutes a part of almost all enzymes. Imidazole is known to catalyze a number of biochemical reactions [4, 5]; therefore, the catalytic activity of poly(*N*-vinylimidazole) was studied while simulating some biological processes [6, 7]. We previously found that polymers having imidazole groups catalyze hydrolysis of *p*-nitrophenyl acetate [6] and Michael addition of thiols to electron-deficient alkenes [8], acting as base catalysts.

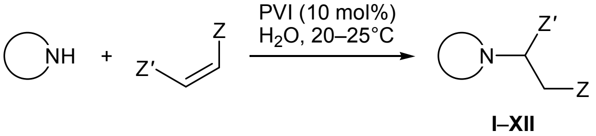
An important advantage of polymeric catalysts is that they can readily be separated from the products due to considerable difference in the properties of high- and low-molecular compounds. As a result, such catalysts may be used repeatedly, which is profitable from the economic viewpoint and is environmentally benign. Thus the use of poly(*N*-vinylimidazole) is promising from the viewpoint of "green chemistry" [9].

In the present work we examined the activity of poly(*N*-vinylimidazole) with a molecular weight of 75300 [10] as base catalyst in the aza-Michael reaction. The aza-Michael reaction is one of the most general and widely used methods for building up new carbon–nitrogen bonds, especially in the synthesis of β-aminocarbonyl compounds. This reaction may be catalyzed by various Lewis acids [11], combinations $BF_3 \cdot OEt_2$–R_4NX [12], MCl_3–Me_3SiCl (M = Ru, Fe) [13], Brønsted acids [14], acidic clays [15], amines [16, 17], *N*-methylimidazole [18], coordination compounds of metals of the platinum group [19], ionic liquids [20, 21], quaternary ammonium salts [20, 22] and bases [23], KF–Al_2O_3 [24], borax [25], Amberlyst-15 [26], tributylphosphine [27], R_3P–Me_3SiCl [28], $Cu(acac)_2$–[bmIm]BF_4 [29], copper nanoparticles [30], Hβ-SnA zeolite [31], silica gel [32], β-cyclodextrin [33], sugars [34], sodium dodecyl sulfate [35], and in the recent time by organic catalysts, e.g., of peptide type [36]. Data were also reported on the aza-Michael reactions performed in water in the absence of a catalyst [37, 38]. However, these reactions occurred only with fairly nucleophilic primary and secondary amines. Only one example of the use of polymeric bases as catalysts in the aza-Michael reactions was reported: poly(*N*-vinylpyridine) catalyzed the addition of secondary amines and carbamates to α,β-unsaturated esters, nitriles, and ketones [39]. The reactions were carried out under solvent-free conditions in heterogeneous medium. On the other hand, as noted above, secondary amines are capable of reacting in the absence of a catalyst. For example, the reactions of piperidine and diethylamine with methyl acrylate in water in the absence of catalyst [37] and in the presence of 5 wt % (with respect to amine) of poly(*N*-vinylpyridine) in the absence of a solvent [39] occurred under comparable conditions and afforded the corresponding addition products in almost similar yields. Secondary amines are much stronger bases than poly(*N*-vinylpyridine); therefore, the use of the latter as base catalyst in this case is likely to be redundant.

In our study on the aza-Michael reaction catalyzed by poly(*N*-vinylimidazole) we used as substrates aza heterocycles (see table) that are weaker bases than imidazole, otherwise the substrate itself can catalyze its addition to electron-deficient alkenes. As Michael acceptors we selected α,β-unsaturated ketones (methyl vinyl ketone and cyclohex-2-en-1-one), methyl vinyl sulfone, and methyl acrylate. The reactions were carried out in water. 1*H*-1,2,4-Triazoles reacted with the above alkenes in the presence of 10 mol % of poly(*N*-vinylimidazole) (PVI) under mild conditions (room temperature), and the corresponding addition products were obtained in high and good yields (Scheme 1; see table, run nos. 1, 2, 4–7). An exception was less reactive methyl acrylate (run no. 3).

We examined the possibility for repeated use of the catalyst in the reaction of 1*H*-1,2,4-triazole with methyl vinyl ketone (run no. 1). In each cycle, when the reaction was complete (according to the TLC data), the mixture was evaporated, the residue was extracted with ethyl acetate, the organic layer was removed from the polymer, and water and reactants required for the next cycle were added. The yields of 4-(1*H*-1,2,4-triazol-1-yl)butan-2-one in five successive cycles were 88, 90, 85, 92, and 86% (according to the ^{1}H NMR data); thus almost no loss of catalytic activity was observed.

Scheme 1.



I–XII

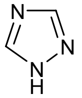
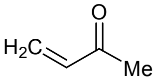
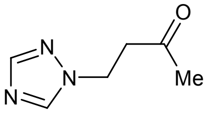
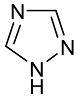
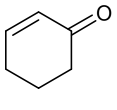
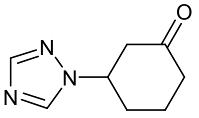
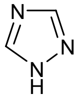
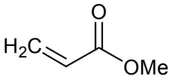
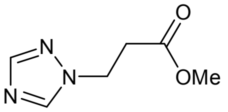
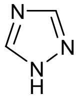
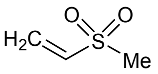
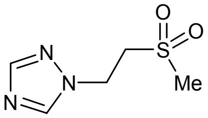
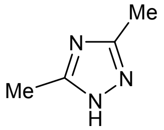
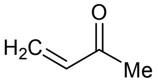
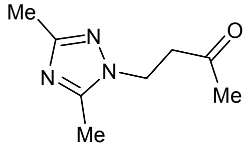
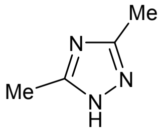
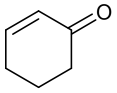
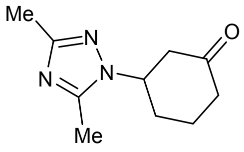
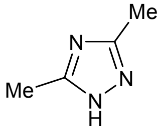
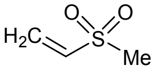
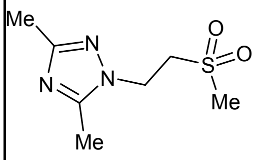
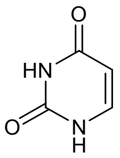
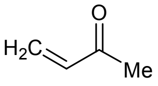
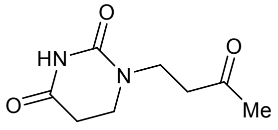
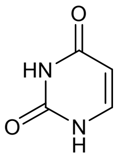
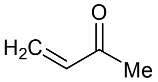
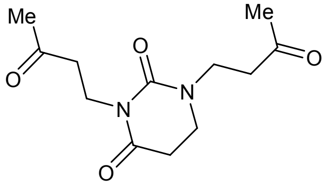
Z = C(O)Me, SO_2Me, CO_2Me, Z′ = H;
ZZ′ = $CH_2CH_2CH_2C(O)$.

Unlike 1*H*-1,2,4-triazoles, least nucleophilic nitrogen-containing heterocycles, such as uracil, oxazolidin-2-one, and succinimide, readily reacted under analogous conditions only with most reactive methyl vinyl ketone (run nos. 8, 9, 11, 12). In the reaction with uracil 1 : 1 and 1 : 2 adducts can be formed (run nos. 8, 9). The use of poly(*N*-vinylimidazole) as catalyst allowed us to obtain 1 : 1 or 1 : 2 adduct, depending on the amount of the alkene taken. Up to now, no catalyst was found to ensure selective formation of the above adducts. For example, the reactions catalyzed by sodium dodecyl sulfate and $NaHCO_3$ in water [35] or by DABCO in acetonitrile [17] lead to preferential formation of the 1 : 1 adduct, whereas the 1 : 2 adduct was formed as the major product in the presence of tributylphosphine [27] or benzyl(triethyl)ammonium hydroxide [17]. In the reactions of methyl acrylate with 1*H*-1,2,4-triazole and uracil, the yields of the corresponding addition products were not satisfactory even on prolonged heating (run nos. 3, 10).

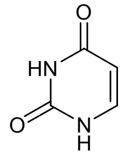
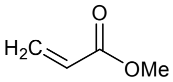
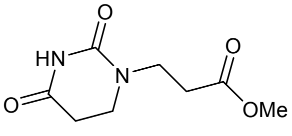
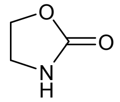
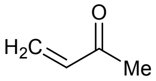
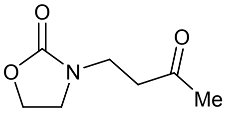
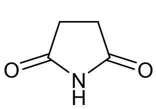
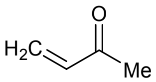
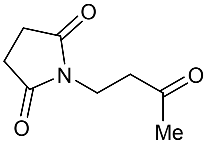
Presumably, poly(*N*-vinylimidazole) as catalyst favors polarization of the N–H bond in heterocyclic substrates, thus increasing their nucleophilicity. This is especially important for weakly nucleophilic substrates (run nos. 8–12). Here, the polymer, which is not a strong base, readily donates proton to the emerging carbanion (Scheme 2). The role of water in the reactions under study is essential. It also favors proton transfer; therefore, reactions with even weakly basic nitrogen-containing heterocycles may occur in the absence of a catalyst, though at a considerably lower rate. For example, the yields of the addition products of 1*H*-1,2,4-triazole to methyl vinyl ketone (run no. 1) and methyl vinyl sulfone (run no. 4) in the presence of poly(*N*-vinylimidazole) are 82 and 87%, respectively, and in the absence of catalyst (other conditions being equal), 47 and 36%.

Thus we have shown that poly(*N*-vinylimidazole) is a low-expensive, efficient, and (what is important) readily recyclable organic catalyst for the addition of

Addition of nitrogen-containing heterocycles to alkenes in the presence of poly(*N*-vinylimidazole) in water at 20–25°C[a]

Run no.	NH compound	Alkene	Reaction time, h	Product	Yield,[b] %	Reference
1			2	 **I**	82 (47)	[18]
2			24	 **II**	92	–
3			18 (60°C)	 **III**	20[c]	[18]
4			30	 **IV**	87 (36)	-
5			5	 **V**	91	-
6			48	 **VI**	90	–
7			24	 **VII**	94	–
8			4	 **VIII**	83 (6)[d]	[35]
9[e]			24	 **IX**	90	[27]

(Contd.).

10			16 (70°C)	 **X**	10[c]	[18]
11			8	 **XI**	75 (0)	[40]
12			24	 **XII**	81	[41]

[a] Molar ratio NH-compound–alkene–poly(*N*-vinylimidazole) 1.0 : 1.2 : 0.1 (per monomer unit).

[b] Yield of the isolated product; in parentheses is given the yield in the absence of catalyst.

[c] According to the ^{1}H NMR data using dimethyl fumarate as internal standard.

[d] Apart from 1 : 1 adduct, 11% of 1 : 2 adduct was isolated.

[e] Molar ratio NH-compound–alkene–poly(*N*-vinylimidazole) 1.0 : 2.4 : 0.1 (per monomer unit).

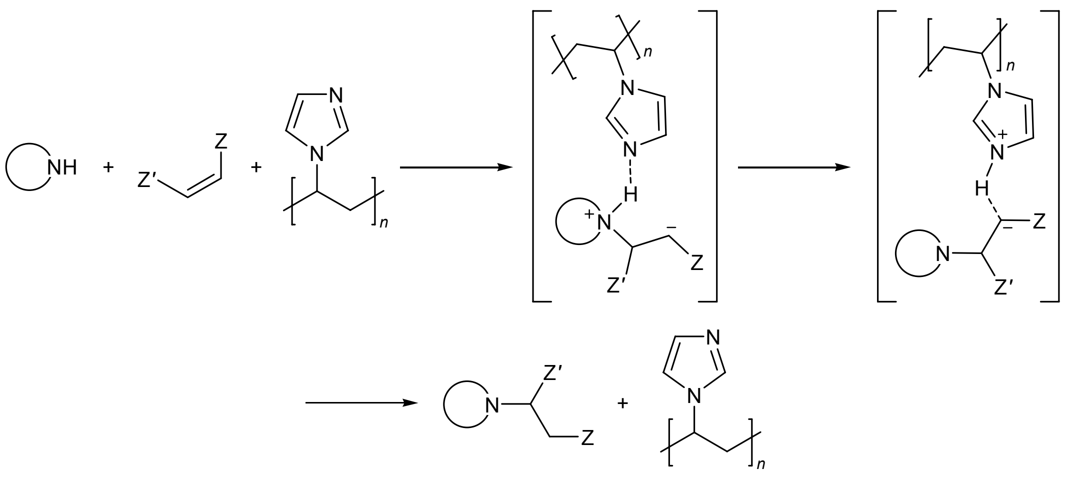
nitrogen-containing heterocycles to Michael acceptors. The use of poly(*N*-vinylimidazole) is advantageous due to experimental simplicity and economically safe conditions: the reactions are carried out in water at room temperature.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer at 400.13 and 100.61 MHz, respectively, using $CDCl_3$ as solvent. All reactions were carried out under argon. Their progress was monitored by TLC on silica gel 60 F_{254} plates (Merck). Silica gel Merck 60 (0.04–0.063 mm) was used for column chromatography. Poly(*N*-vinylimidazole), *M* 75300, was synthesized according to the procedure reported in [10].

Addition of nitrogen-containing heterocycles to alkenes in the presence of poly(*N*-vinylimidazole) (*general procedure*)**.** Water, 4 ml, was added to 14.1 mg (0.15 mmol per monomer unit) of poly(*N*-vinylimidazole) and 1.5 mmol of nitrogen-containing heterocycle, and the mixture was stirred for 10 min. The corresponding alkene, 1.8 mmol, was then added,

Scheme 2.



the mixture was stirred at room temperature until the reaction was complete (see table), evaporated to a minimal volume, and extracted with ethyl acetate, the extract was dried over Na_2SO_4, the solvent was distilled off under reduced pressure, and the residue was subjected to column chromatography using methylene chloride–methanol as eluent. The products were identified by ^1H and ^{13}C NMR spectroscopy, and elemental compositions were also determined for the newly synthesized compounds.

3-(1*H*-1,2,4-Triazol-1-yl)cyclohexan-1-one (II). Colorless viscous liquid. ^1H NMR spectrum, δ, ppm: 1.71–1.82 m (1H, CH_2), 2.04–2.12 m (1H, CH_2), 2.21–2.29 m (2H, CH_2), 2.38–2.49 m (1H, CH_2), 2.83 d.d (1H, CH_2, J = 14.4, 4.3 Hz), 2.95 d.d (1H, CH_2, J = 14.4, 9.9 Hz), 4.65 m (1H, 3-H), 7.94 s (1H, CH=N), 8.10 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 21.46 (CH_2), 31.22 (CH_2), 40.38 (CH_2), 46.94 (CH_2), 57.80 (C^3), 141.53 (C=N), 151.94 (C=N), 206.66 (C=O). Found, %: C 57.88; H 6.76; N 25.69. $C_8H_{11}N_3O$. Calculated, %: C 58.17; H 6.71; N 25.44.

1-[2-(Methylsulfonyl)ethyl]-1*H*-1,2,4-triazole (IV). White solid, mp 91°C. ^1H NMR spectrum, δ, ppm: 2.66 s (3H, CH_3), 3.65 t (2H, CH_2, J = 6.2 Hz), 4.70 t (2H, CH_2, J = 6.2 Hz), 8.00 s (1H, CH=N), 8.23 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 41.99, 43.10, 53.45, 144.27 (C=N), 152.82 (C=N). Found, %: C 34.37; H 5.21; N 23.76; S 18.22. $C_5H_9N_3O_2S$. Calculated, %: C 34.28; H 5.18; N 23.98; S 18.30.

4-(3,5-Dimethyl-1*H*-1,2,4-triazol-1-yl)butan-2-one (V). Colorless oily liquid. ^1H NMR spectrum, δ, ppm: 2.14 s (3H, CH_3CO), 2.27 s (3H, CH_3), 2.43 s (3H, CH_3), 3.03 t (2H, CH_2, J = 6.3 Hz), 4.17 t (2H, CH_2, J = 6.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.66 (CH_3), 13.68 (CH_3), 30.09 (**C**H_3CO), 41.88 (CH_2), 42.27 (CH_2), 152.48 (C=N), 159.47 (C=N), 205.34 (C=O). Found, %: C 57.19; H 7.97; N 24.92. $C_8H_{13}N_3O$. Calculated, %: C 57.46; H 7.84; N 25.13.

3-(3,5-Dimethyl-1*H*-1,2,4-triazol-1-yl)cyclohexan-1-one (VI). White solid, mp 93°C. ^1H NMR spectrum, δ, ppm: 1.63–1.75 m (1H, CH_2), 2.06–2.27 m (2H, CH_2), 2.31 s (3H, CH_3), 2.38 s (3H, CH_3), 2.40–2.47 m (2H, CH_2), 2.62 d.d (1H, CH_2, J = 14.4, 4.8 Hz), 3.02 d.d (1H, CH_2, J = 14.4, 11.1 Hz), 4.34 m (1H, CHN). ^{13}C NMR spectrum, δ_C, ppm: 11.64 (CH_3), 13.79 (CH_3), 21.81 (CH_2), 31.01 (CH_2), 40.32 (CH_2), 47.28 (CH_2), 55.63 (CHN), 150.85 (C=N), 159.47 (C=N), 207.39 (C=O). Found, %: C 62.19; H 8.03; N 21.63. $C_{10}H_{15}N_3O$. Calculated, %: C 62.15; H 7.82; N 21.74.

3,5-Dimethyl-1-[2-(methylsulfonyl)ethyl]-1*H*-1,2,4-triazole (VII). White solid, mp 118°C. ^1H NMR spectrum, δ, ppm: 2.32 s (3H, CH_3), 2.48 s (3H, CH_3), 2.64 s (3H, CH_3S), 3.61 t (2H, CH_2, J = 6.2 Hz), 4.46 t (2H, CH_2, J = 6.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.67 (CH_3), 13.71 (CH_3), 41.52, 41.98, 53.36, 153.29 (C=N), 160.50 (C=N). Found, %: C 41.59; H 6.45; N 20.76; S 15.86. $C_7H_{13}N_3O_2S$. Calculated, %: C 41.36; H 6.45; N 20.67; S 15.78.

Reaction of 1*H*-1,2,4-triazole with but-3-en-2-one with regeneration of the catalyst (see table, run no. 1**).** Water, 0.5 ml, was added to a mixture of 1.9 mg (0.02 mmol per monomer unit) of poly(*N*-vinylimidazole) and 13.8 mg (0.2 mmol) of 1*H*-1,2,4-triazole, and the mixture was stirred for 10 min. But-3-en-2-one, 16.8 mg (0.24 mmol), was added, and the mixture was stirred for 2 h at room temperature. The mixture was then evaporated, the residue was extracted with ethyl acetate, the extract was separated from the polymer, dried over Na_2SO_4, and evaporated, dimethyl fumarate was added as reference, and the mixture was analyzed by ^1H NMR. The polymer was washed with diethyl ether and dried under reduced pressure, the above indicated amounts of water and the reactants were added, and the next reaction cycle was performed in a similar way. The yields of 4-(1*H*-1,2,4-triazol-1-yl)-butan-2-one in five successive cycles were 88, 90, 85, 92, and 86%.

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