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Poly(*N*-vinylimidazole) as efficient recyclable catalyst for the Michael addition of CH-acids to electron deficient alkenes in water*

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Efficiency of poly(*N*-vinylimidazole) as the basic recyclable catalyst for the Michael addition of CH-acids to acrylonitrile, methyl acrylate, methyl vinyl ketone and methyl vinyl sulfone in water at ambient temperature was studied. In these reactions, formation of both 1 : 1 and 1 : 2 adducts is possible.

Key words: poly(*N*-vinylimidazole), CH-acids, electron deficient alkenes, basic catalysis, recyclable catalyst, the Michael addition.

The Michael addition is one of the most important and widely used methods for the carbon—carbon bond formation.[1,2] Catalysis by strong bases commonly used in this reaction often led to formation of side products.[3] Therefore, more selective catalysts were currently suggested, *e.g.*, soft bases,[4—7] Lewis acids, including salts and complexes of transition metals and lanthanides,[8,9] ionic liquids,[10—12] enzymes,[13] Amberlyst 15,[14] SiO_2.[15] Among them, chiral organic catalysts giving rise to non-racemic products[16—19] are of particular value.

From the economical and ecological viewpoints, the catalysts which could be used repeatedly have major advantages.[20] Often enough, such catalytic systems contain synthetic polymers acting as supports for catalyst.[21] Among them, the catalysts suitable for the Michael addition are also known.[22—24] So-called smart polymers capable of changing physicochemical properties, especially solubility, depending on the conditions[20,21] are of great importance. This property makes it possible, on the one hand, to perform the reaction in the homogeneous conditions, and, on the other hand, to use the catalytic system repeatedly. In some cases, the polymers themselves can exhibit catalytic properties similar to biopolymers. We have previously shown that polymers bearing basic imidazole moieties catalyzed the Michael addition of thiols[25] and nitrogen heterocycles[26] to electron deficient alkenes.

In the present work, we studied the possibility to apply poly(*N*-vinylimidazole) with molecular weight 75300 as the basic catalyst for the Michael addition of the CH-acids to electron deficient alkenes.

Results and Discussion

In the presence of poly(*N*-vinylimidazole), CH-acids such as malononitrile, ethyl nitroacetate, acetylacetone, and 2-nitropropane react with electron deficient alkenes, *e.g.,* methyl acrylate, acrylonitrile, methyl vinyl sulfone, and methyl vinyl ketone (Scheme 1). Depending on the nature of the CH-acid, these reactions give predominantly the 1 : 1 (**3a—h**) or the 1 : 2 adducts (**4a—e**) (Table 1). The reactions proceed in water at ambient temperature.

It was found that in the case of excess of alkene, malononitrile yielded exclusively 1 : 2 adducts (see Table 1, entries *1—3*). Acetylacetone gave rise to the 1 : 1 adducts (entries *4—6*), whereas ethyl nitroacetate gave products, whose composition depended on the nature of alkene and the reactant ratio (entries *7—11*). Ethyl (3-acetyl-4-hydroxy-4-methyl-1-nitrocyclohexane)carboxylate (**5**) was synthesized with the excess of methyl vinyl ketone in 73% yield. Apparently, compound **5** formed *via* addition of the second molecule of methyl vinyl ketone to 1 : 1 adduct **3f** followed by intramolecular aldol-crotonic condensation (Scheme 2).

It is of note that in contrast to other studied Michael acceptors, acrylonitrile readily reacts with malononitrile

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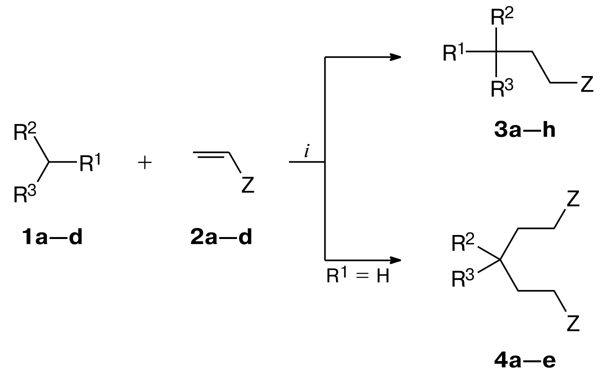
Scheme 1

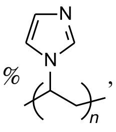


1	R^1	R^2	R^3
a	H	CN	CN
b	H	C(O)Me	C(O)Me
c	H	NO_2	CO_2Et
d	Me	Me	NO_2

2: Z = CO_2Me (**a**), CN (**b**), SO_2Me (**c**), C(O)Me (**d**)

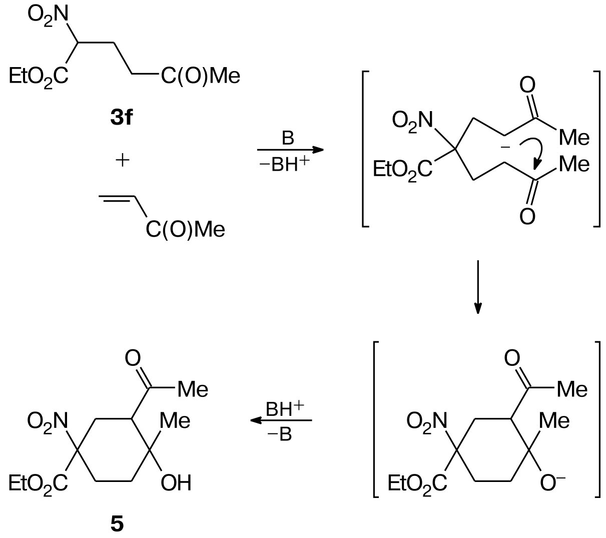
3	R^1	R^2	R^3	Z
a	H	C(O)Me	C(O)Me	CO_2Me
b	H	C(O)Me	C(O)Me	CN
c	H	C(O)Me	C(O)Me	SO_2Me
d	H	NO_2	CO_2Et	CO_2Me
e	H	NO_2	CO_2Et	CN
f	H	NO_2	CO_2Et	C(O)Me
g	Me	Me	NO_2	SO_2Me
h	Me	Me	NO_2	C(O)Me

4	R^2	R^3	Z
a	CN	CN	CO_2Me
b	CN	CN	CN
c	CN	CN	SO_2Me
d	NO_2	CO_2Et	SO_2Me
e	NO_2	CO_2Et	C(O)Me

i. 10 mol.% 

, H_2O, 20—25 °C.

Scheme 2



to give exclusively 1 : 2 adduct (see Table 1, entry *2*); in the cases of acetylacetone and ethyl nitroacetate, the yields were low (entries *5* and *8*).

In the present work, we studied the possibility of the catalyst recyclization on an example of the reaction between malononitrile and methyl acrylate (see Table 1, entry *1*). It was found that at least the second cycle proceeded without loss of the catalyst activity. After completion of the reaction (TLC monitoring), the product was extracted with ethyl acetate, the organic layer was separated, and the reactants and water in the amounts required for the next step were added to the water phase. In the second catalytic cycle, dimethyl 4,4-dicyanoheptanedioate (**4a**) was obtained in the yield of 90%.

In summary, poly(*N*-vinylimidazole) can be used as cheap, efficient, and most importantly easy-separable recyclable organic catalyst for the addition of CH-acids to the Michael acceptors. Poly(*N*-vinylimidazole) provides performing these reactions under simple and cost-effective conditions, *e.g.*, with water as a solvent at ambient temperature.

Experimental

The course of the reactions was monitored by TLC on silica gel precoated plates 60 F_{254} (Merck), visualization in iodine vapor or in the $KMnO_4$ solution. Silica gel Merck 60 (0.040—0.063 mm) was used for column chromatography. ^1H and ^{13}C NMR spectra were run on a Bruker AMX-400 instrument in $CDCl_3$ and DMSO-d_6 at working frequencies of 400.13 and 100.61 MHz, respectively; the chemical shifts are given in the δ scale relative to the residual signals of the solvents ($CHCl_3$, δ_H 7.27, δ_C 77.00; DMSO, δ_H 2.50, δ_C 39.51) as internal standards. The starting methyl vinyl ketone (Aldrich) was purified by vacuum distillation (b.p. 34—35 °C (120 Torr)), other starting compounds (Aldrich, AlfaAesar) were used as purchased. Poly(*N*-vinylimidazole) with *M* 75300 was synthesized by the known procedure.[27]

Addition of CH-acids (1a—d) to alkenes (2a—d) in the presence of poly(*N*-vinylimidazole) (general procedure). To a stirred solution of poly(*N*-vinylimidazole) (14.1 mg, 0.15 mmol per monomer unit) in distilled water (4 ml), CH-acid **1a**—**d** (1.5 mmol) was added followed by addition of alkene **2a**—**d** (4.5 mmol) after 5 min of stirring. The reaction mixture was stirred at ambient temperature until complete consumption of the reactants (see Table 1). In the case of formation of insoluble products (**3g**, **4c**, and **4d**), the precipitates were separated by filtration or centrifugation, washed with water and diethyl ether and dried *in vacuo*. Compound **4d** was additionally recrystallized from AcOEt. All other products were extracted with AcOEt, the organic layer was dried with Na_2SO_4, the solvent was removed *in vacuo*, the residues were purified by column chromatography (elution with petroleum ether—AcOEt (2 : 1) for **3a**, **3f**, **3h**, **4a**,

4e, and **5**, petroleum ether—AcOEt (1 : 1) for **4b**, petroleum ether—AcOEt (1 : 2) for **3c**, petroleum ether—CH_2Cl_2 (1 : 1) for **3d**). Compounds **3a**, **3c**, **3d**, **3f**, **3h**, **4a**, **4e**, and **5** are colorless oils, compound **4b** is colorless crystals. Compounds **3b** and **3e** were not isolated, their yields were determined by ^{1}H NMR spectroscopy of the mixtures obtained by extraction and removal of the volatiles. Structures of known compounds were confirmed by the comparison of the ^{1}H and ^{13}C spectra with published data (references are given in Table 1). The ^{1}H and ^{13}C spectra and elemental analysis data for hitherto unknown compounds are given below.

3-(2-Methylsulfonylethyl)pentane-2,4-dione (3c). Colorless oil. ^{1}H NMR ($CDCl_3$), δ: 2.19 (s, 1.8 H, CH_3, enol); 2.25 (s, 6 H, CH_3, keto-form); 2.29—2.36 (m, 2 H, CH_2, keto-form); 2.81—2.84 (m, 0.6 H, CH_2, enol); 2.93 (s, 3 H, CH_3S, keto-form); 2.96 (s, 0.9 H, CH_3S, enol); 3.01 (t, 2 H, CH_2, keto-form, *J* = 7.4 Hz); 3.05—3.06 (m, 0.6 H, CH_2, enol); 4.02 (t, 1 H, CH, keto-form, *J* = 6.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 19.97 (CH_3, enol); 20.33 (CH_3, keto-form); 22.96 (enol); 29.74 (keto-form); 40.86 (keto-form); 41.03 (enol); 51.69 (keto-form); 54.33 (enol); 65.12 (CH, keto-form); 106.38 (C=C, enol); 191.41 (C=C, enol); 202.82 (C=O, keto-form). Found (%): C, 46.78; H, 6.73. $C_8H_{14}O_4S$. Calculated (%): C, 46.58; H, 6.84.

3-Methyl-1-methylsulfonyl-3-nitrobutane (3g). M.p. 108—110 °C (purified by washing with water and diethyl ether). ^{1}H NMR (DMSO-d_6), δ: 1.58 (s, 6 H, CH_3); 2.29—2.34 (m, 2 H, CH_2); 3.01 (s, 3 H, CH_3S); 3.12—3.16 (m, 2 H, CH_2). ^{13}C NMR (DMSO-d_6), δ: 25.06 (CH_3); 31.68 (CH_3); 40.14 (CH_2); 48.93 (CH_2); 87.17 (C). Found (%): C, 37.13; H, 6.65; N, 7.01. $C_6H_{13}NO_4S$. Calculated (%): C, 36.91; H, 6.71; N, 7.17.

Table 1. Addition of CH acids **1a—d** to electron deficient alkenes **2a—d** in the presence of poly(*N*-vinylimidazole) in water at 20—25 °C

Entry	CH-acid	Alkene	Reagents ratio[a]	*t*/h[b]	Product	Yield[c] (%)
1	**1a**	**2a**	1 : 3 : 0.1	8	**4a**[28]	90 (92[d]) 90[d](cycle 2)
2	**1a**	**2b**	1 : 3 : 0.1	24	**4b**[e]	61 (90[d])
3	**1a**	**2c**	1 : 3 : 0.1	1	**4c**	98
4	**1b**	**2a**	1 : 3 : 0.1	48	**3a**[29]	69
5	**1b**	**2b**	1 : 3 : 0.1	24	**3b**[30]	20[d]
6	**1b**	**2c**	1 : 3 : 0.1	48	**3c**	30 (35[d])
7	**1c**	**2a**	1 : 3 : 0.1	48	**3d**[31]	80
8	**1c**	**2b**	1 : 3 : 0.1	120	**3e**[32]	34[d]
9	**1c**	**2c**	1 : 3 : 0.1	144	**4d**	87
10	**1c**	**2d**	1 : 1.1 : 0.1	2	**3f**[33]	84
11	**1c**	**2d**	1 : 3 : 0.1	2	**4e**[34] **5**[34]	25 73
12	**1d**	**2c**	1 : 1.1 : 0.1	120	**3g**	47 (55[d])
13	**1d**	**2d**	1 : 1.1 : 0.1	12	**3h**[35]	65 (87[d])

[a] Molar ratio CH-acid : alkene : poly(*N*-vinylimidazole) (per monomer unit).

[b] Reaction time.

[c] Yield of the isolated product.

[d] Yield by the ^{1}H NMR data using dimethyl fumarate as an internal standard.

[e] M.p. 90—92 °C (*cf.* Ref. 11: 90—92 °C).

2,2-Bis(2-methylsulfonylethyl)malononitrile (4c). M.p. 209—211 °C (purified by washing with water and diethyl ether). ^{1}H NMR (DMSO-d_6), δ: 2.65—2.70 (m, 4 H, CH_2); 3.12 (s, 6 H, CH_3S); 3.43—3.47 (m, 4 H, CH_2). ^{13}C NMR (DMSO-d_6), δ: 28.32 (CH_3); 35.37 (C(2)); 40.44 (CH_2); 49.38 (CH_2); 114.33 (CN). Found (%): C, 39.10; H, 4.95; N, 10.15. $C_9H_{14}N_2O_4S_2$. Calculated (%): C, 38.83; H, 5.07; N, 10.06.

Ethyl 4-methylsulfonyl-2-(2-methylsulfonylethyl)-2-nitrobutanoate (4d). M.p. 110—114 °C (from AcOEt). ^{1}H NMR (DMSO-d_6), δ: 1.24 (t, 3 H, CH_3, *J* = 7.1 Hz); 2.59—2.68 (m, 4 H, CH_2); 3.06 (s, 6 H, CH_3S); 3.16—3.31 (m, 4 H, CH_2); 4.30 (q, 2 H, OCH_2, *J* = 7.1 Hz). ^{13}C NMR (DMSO-d_6), δ: 13.59 ($CH_2\underline{C}H_3$); 26.72 (CH_3S); 40.11 (CH_2); 48.19 (CH_2); 63.75 (OCH_2); 93.20 (C(2)); 164.83 (C=O). Found (%): C, 34.92; H, 5.41; N, 3.88. $C_{10}H_{19}NO_8S_2$. Calculated (%): C, 34.77; H, 5.54; N, 4.06.

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References

1. M. E. Jung, in *Comprehensive Organic Synthesis*, Eds B. M. Trost, I. Fleming, Pergamon Press, 1991, **4**, 1.
2. P. Perlmutter, *Conjugate Addition Reactions in Organic Synthesis*, Oxford, Pergamon Press, 1992, 394 p.
3. E. D. Bergman, D. Ginsburg, R. Pappo, *Org. React.*, 1959, **10**, 179.
4. Z. Zhang, Y.-W. Dong, K. Komatsu, *Synlett*, 2004, 61.
5. W. Wang, M. Yu, *Tetrahedron Lett.*, 2004, **45**, 7141.
6. C. Xu, J. K. Bartley, D. I. Enache, D. W. Knight, G. J. Hutchings, *Synthesis*, 2005, 3468.
7. K. Ko, K. Nakano, S. Watanabe, Y. Ichikawa, H. Kotsuki, *Tetrahedron Lett.*, 2009, **50**, 4025.
8. J. Christoffers, *Eur. J. Org. Chem.*, 1998, 1259.
9. J. Comelles, M. Moreno-Macas, A. Vallribera, *Arkivoc*, 2005, **9**, 207.
10. B. C. Ranu, S. Banerjee, *Org. Lett.*, 2005, **14**, 3049.
11. B. C. Ranu, S. Banerjee, R. Jana, *Tetrahedron*, 2007, **63**, 776.
12. E. A. Mistryukov, *Mendeleev Commun.*, 2007, **17**, 230.
13. G. A. Strohmeier, T. Sovic, G. Steinkellner, F. S. Hartner, A. Andryushkova, T. Purkarthofer, A. Glieder, K. Gruber, H. Griengl, *Tetrahedron*, 2009, **65**, 5663.
14. B. Das, M. Krishnaiah, K. Laxminarayana, K. Damodar, D. N. Kumar, *Chem. Lett.*, 2009, **38**, 42.
15. S. Banerjee, S. Santra, *Tetrahedron Lett.*, 2009, **50**, 2037.
16. *Asymmetric Organocatalysts — from Biomimetic Concepts to Applications in Asymmetric Synthesis*, Eds A. Berkessel, H. Gröger, Wiley-VCH, Weinheim, 2005, 440 p.
17. *Enantioselective Organocatalysis: Reactions and Experimental Procedures*, Ed. P. I. Dalko, Wiley-VCH, 2007, 536 p.
18. *Organocatalysis*, Eds M. T. Reetz, B. List, S. Jaroch, H. Weinmann, Springer-Verlag, Berlin—Heidelberg, 2008, 341 p.
19. *Top. Curr. Chem.*, Ed. B. List, Springer-Verlag, Berlin—Heidelberg, 2010, **291**, 460 p.

20. *Recoverable and recyclable catalysts*, Ed. M. Benaglia, John Wiley and Sons Ltd., 2009, 471 p.
21. *Top. Curr. Chem.*, Ed. A. Kirschning, Springer-Verlag, Berlin—Heidelberg, 2004, **242**, 337 p.
22. D. Benza, T. Constantieux, J. Rodriguez, *Synthesis*, 2004, 923.
23. C. Reddy, V. Reddy, J. G. Verkade, *J. Org. Chem.*, 2007, **72**, 3093.
24. R. Ballini, L. Barboni, L. Castrica, F. Fringuelli, D. Lanari, F. Pizzo, L. Vaccaro, *Adv. Synth. Catal.*, 2008, **350**, 1218.
25. I. P. Beletskaya, E. A. Tarasenko, A. R. Khokhlov, V. S. Tyurin, *Zh. Org. Khim.*, 2007, **43**, 1732 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2007, **43**, 1733].
26. I. P. Beletskaya, E. A. Tarasenko, A. R. Khokhlov, V. S. Tyurin, *Zh. Org. Khim.*, 2010, **46**, 473 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2010, **46**, 461].
27. I. P. Beletskaya, A. R. Khokhlov, E. A. Tarasenko, V. S. Tyurin, *J. Organomet. Chem.*, 2007, **692**, 4402.
28. S. Paganelli, A. Schionato, C. Botteghi, *Tetrahedron Lett.*, 1991, **32**, 2807.
29. R. Chong, P. S. Clezy, *Aust. J. Chem.*, 1967, **20**, 123.
30. G. R. Zellars, R. Levine, *J. Org. Chem.*, 1948, **13**, 1911.
31. A. A. Smirnova, V. V. Perekalin, V. A. Shcherbakov, *Zh. Org. Khim.*, 1968, **4**, 2245 [*J. Org. Chem. USSR* (*Engl. Transl.*), 1968, **4**, 2166].
32. A. Dornow, A. Frese, *J. Liebigs Ann. Chem.*, 1953, **581**, 211.
33. R. E. Moskalyk, A. L. C. Mak, L. G. Chatten, R. A. Locock, *J. Pharm. Sciences*, 1981, **70**, 496.
34. M. Picquet, C. Brineau, P. H. Dixneuf, *Tetrahedron*, 1999, **55**, 3937.
35. P. B. Kisanga, P. Ilankumaran, B. M. Fetterly, J. G. Verkade, *J. Org. Chem.*, 2002, **67**, 3555.

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