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Poly(vinylpyrrolidinium) perchlorate as a new and efficient catalyst for the promotion of the synthesis of polyhydroquinoline derivatives via Hantzsch condensation

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Abstract A green approach for the promotion of the synthesis of Hantzsch products using poly(vinylpyrrolidinium) perchlorate {[PVPH]ClO_4} as a new modified polymeric catalyst in the absence of solvent is reported. The title catalyst is easily prepared and characterized using a variety of techniques including infrared spectra, X-ray diffraction, thermal gravimetric analysis, scanning electron microscopy, pH analysis, and Hammett acidity function. Some of the advantages of this novel synthetic method are: easy preparation of the catalyst, short reaction times, high to excellent yields of the products, simple and easy work-up procedure, and reusability of the catalyst.

Keywords Poly(vinylpyrrolidone) (PVP) · Poly(vinylpyrrolidinium) perchlorate {[PVPH]ClO_4} · Polyhydroquinoline derivatives · Hantzsch condensation · Solvent-free conditions

Introduction

Polyhydroquinoline derivatives are among the most important classes of organic compounds, which show a wide range of biological and pharmaceutical properties [1–13]. In addition, they can be used as reducing agents for the direct reductive amination of aldehydes and ketones [14]. These significant properties attracted the attention of many organic chemists to the synthesis of these types of compounds. These attempts resulted in the introduction of a variety of reagents for the promotion

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of the Hantzsch reaction, as a classical method used for this purpose. Some of these reagents are: ceric ammonium nitrate (CAN) [15], $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [16], $Hf(NPf_2)_4$ [17], Grinding [18], Polymer [19], $K_7[PW_{11}CoO_{40}]$ [20], MCM-41 [21], molecular iodine [22], nickel nanoparticle [23], ionic liquids [24], organocatalyst [25], *p*-TSA [26], BINOL-phosphoric acid derivatives [27], $HClO_4 \cdot SiO_2$ [28], HY-zeolite [29], and montmorillonite K-10 [30].

Although, each of these methods have their own advantages, some of them often suffer from one or more disadvantages such as use of stoichiometric amounts of reagents, acidic or basic catalysts, expensive metal precursors, tedious work-up, long reaction times, unsatisfactory product yields, excess of organic solvent, high temperatures, harsh reaction conditions, and difficulty in preparation of the catalyst, which limit the use of these methods. Therefore, it is important to find more convenient methods for the synthesis of polyhydroquinoline derivatives.

Herein and in continuation of our previous report on the preparation and use of the polymer-supported reagents in various organic reactions [31–33] we wish to report the use of poly(vinylpyrrolidone) as a support for $HClO_4$ and the applicability of the prepared reagent in the promotion of the synthesis of the polyhydroquinoline derivatives via the Hantzsch condensation reaction.

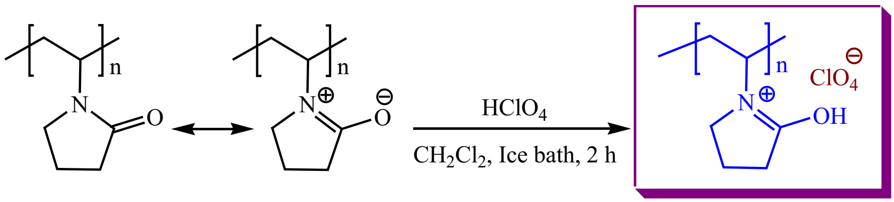
Experimental

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. Cross-linked poly(vinylpyrrolidone) we purchased it from BASF, the chemical company, Germany. All products were characterized by comparison of their physical constants, IR, and NMR spectroscopy with authentic samples and those reported in the literature.

The FT-IR spectra were run on a VERTEX 70 Bruker company (Germany). Thermogravimetric analyses (TGA) were performed on TG/DTA6300 Sll-Nanotechnology Wide-angle X-ray diffraction (XRD) with measurements performed at room temperature on a Siemens D-500 X-ray diffractometer (Germany), using Ni-filtered Co–Kα radiation ($\lambda = 0.15418$ nm). Company (Japan). Samples were heated from 25 to 800 °C at ramp 10 °C min^{-1} under N_2 atmosphere. Scanning election microphotographs (SEM) were obtained on a SEM-Philips XL30. The purity determination of the substrate and reaction monitoring were accompanied by TLC on silica gel polygram SILG/UV 254 plates.

Catalyst preparation

$HClO_4$ (5 mmol, $\cong$0.43 mL) was added to a suspension of the powdered poly(vinylpyrrolidone) (0.5 g) [crosslinked poly(vinylpyrrolidone) with MW >1,000,000] in 10 mL dry CH_2Cl_2 over a period of 10 min in an ice bath. After the addition was completed, the mixture was stirred for 2 h and then the mixture was filtered. The solid residue was washed with diethyl ether (10 mL) and dried at 80 °C to afford $[PVPH]ClO_4$ as a white powder (Scheme 1).



Scheme 1 Preparation of [PVPH]ClO_4

General procedure for the synthesis of the Hantzsch polyhydroquinoline derivatives

A mixture of aldehyde (1 mmol), cyclic diketone (1 mmol), β-ketoester (1 mmol), ammonium acetate (2 mmol), and [PVPH]ClO_4 (40 mg, 0.09 mmol) was heated at 100 °C in an oil-bath for the appropriate time (Table 2). After completion of the reaction [monitored by TLC: *n*-hexane: ethyl acetate (4:1)], the reaction mixture was cooled to room temperature and EtOH (5 mL) was added to it and filtered to separate the catalyst. After evaporation of the solvent from the filtrate, the crude solid product was recrystallized from ethanol to give the pure product. The spectral (IR and ^{1}HNMR) data of a new compound is presented below.

Diethyl 3,3′-(1,3-phenylene) bis (2,7,7-trimethyl-5-oxo-1,4,5, 6,7,8-hexa hydro quinoline-3-carboxylate): Yellow solid; Isolated yield (90 %); Melting point: 323–327 °C; IR (KBr): 3295, 3214, 2959, 1692, 1614, 1489, 1379, 1218 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d6): 0.8 (s, 3H, CH_3)–0.82 (s, 3H, CH_3)–1 (s, 3H, CH_3)–1.01 (s, 3H, CH_3)–1.07 (t, $J = 7.2$ Hz, 3H,CH_3)–1.17 (t, $J = 7.2$ Hz, 3H, CH_3)–1.92 (d, $J = 16$ Hz, 1H)–1.98 (d, $J = 16$ Hz, 1H)–2.14 (d, $J = 5.2$ Hz, 1H)–2.18 (d, $J = 5.2$ Hz, 1H)–2.23 (d, J = 16 Hz, 1H)–2.25 (s, 3H, CH_3)–2.29 (d, J = 16 Hz, 1H)–2.3 (s, 3H, CH_3)–2.39 (d, $J = 14.4$ Hz, 1H)–2.43 (d, $J = 16.8$ Hz, 1H)–3.9–4.1 (m, 2xCH_2)–4.77 (s, 1H)–4.83 (s, 1H)–7 (s,1H) 6.81–7 (m, 3H, ArH), 9.1 (s, 1H, NH)–9.4 (s, 1H, NH).

Results and discussion

Catalyst characterization

IR analysis

The infrared spectra of PVP and [PVPH]ClO_4 are shown in Fig. 1. As can be seen, the FT-IR spectra of PVP are considerably changed after modification as [PVPH]ClO_4.

In the FT-IR spectrum of the prepared reagent the characteristic absorption bands at 1090 and 624 cm^{-1} are assigned to asymmetric and symmetric stretching and bending vibration of ClO_4, respectively [31]. Furthermore, in this spectrum, the bands at 1429 (C–N) and 650 (N–C=O) cm^{-1} disappeared and a moderate

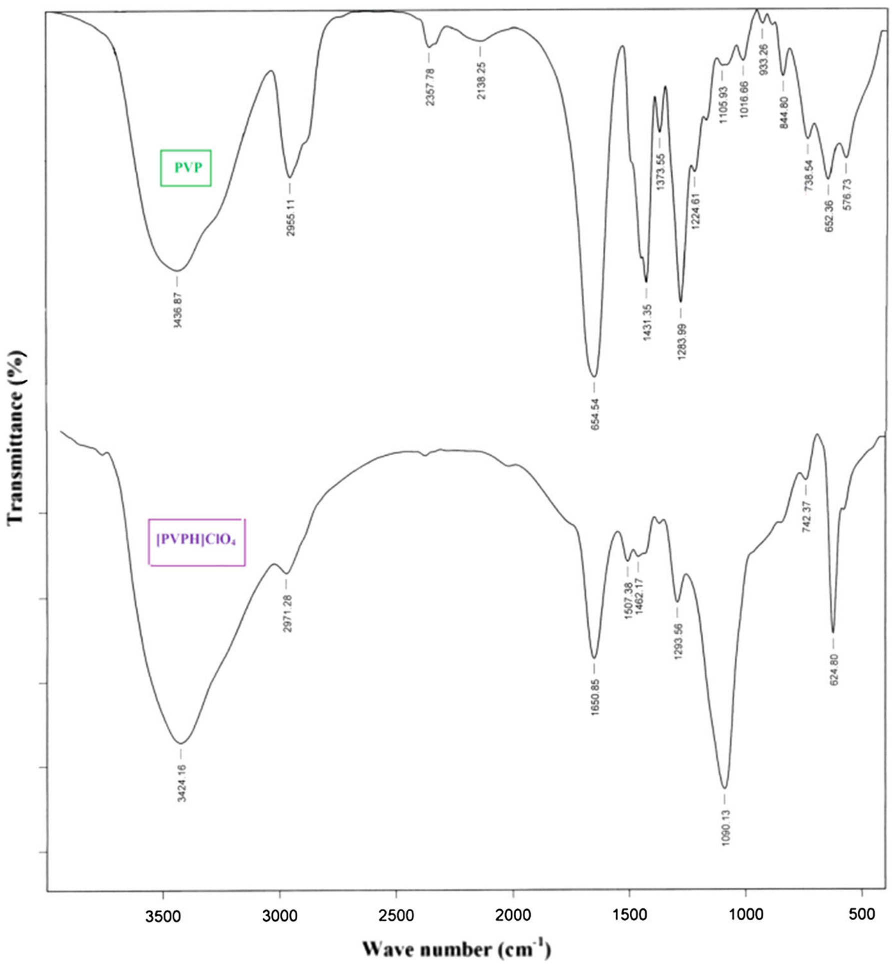


Fig. 1 FT-IR spectra of PVP and [PVPH]ClO_4

absorption at 1650 cm,$^{-1}$ which can be related to the internal imine groups of the pendant rings of the polymer, appeared [33].

XRD analysis

The X-ray diffraction (XRD) patterns of the PVP and [PVPH]ClO_4 samples are shown in Fig. 2. On the basis of this figure it can be concluded that incorporation of $HClO_4$ leads to some changes in the diffractogram of PVP. The PVP diffraction exhibits a diffused background pattern with two diffraction halos appearing around 2θ equal to 18 and 25 indicating that the polymer is amorphous [34]. After modification of PVP by $HClO_4$, the first peak (2θ around 18) disappeared, and the broad peak at 2θ around 25 is slightly reduced. These observations imply that the crystalline size of PVP is decreased after reaction with $HClO_4$ [31, 33].

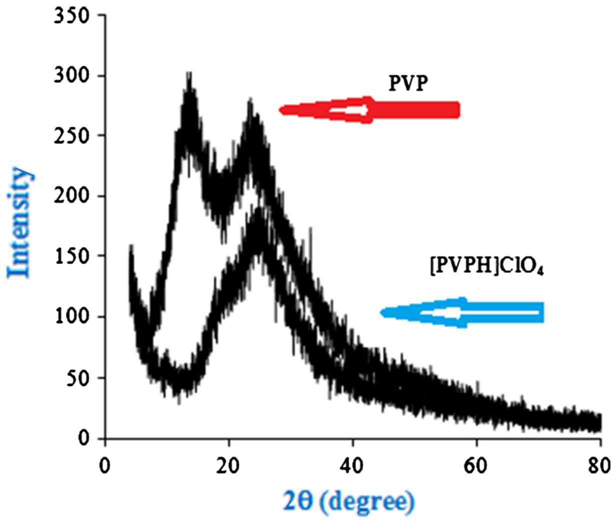


Fig. 2 XRD patterns of PVP and [PVPH]ClO_4

TGA analysis

The thermal stability of PVP and [PVPH]ClO_4 was determined by thermogravimetric analysis (TGA) curves, as shown in Fig. 3. The TGA curve of PVP displayed a weight loss below 120 °C, which corresponded to the loss of the physically adsorbed water and bonded H_2O within the gallery of PVP. The large proportion of polymer underwent degradation in the range of 350–470 °C. The TGA analysis of [PVPH]ClO_4 shows one-stage decomposition, completely different from PVP. The first weight loss, which appeared at <120 °C, was attributed to the loss of moisture contents. The second weight loss, which started from 250 °C, can be a result of the thermal decomposition of the pendant ClO_4 groups [31, 33].

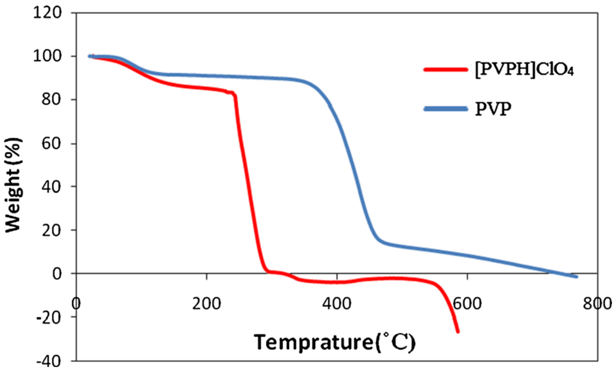


Fig. 3 TGA curves for PVP and [PVPH]ClO_4

SEM analysis

The samples of PVP and $[PVPH]ClO_4$ were also analyzed by scanning electron microscopy (SEM) with various magnifications for determining the particle shape, surface morphology and size distribution, as represented in Fig. 4. These images show that with chemical modification the primary morphology of PVP was completely changed, and the particles were aggregated. It should be noted that after the reaction of PVP with $HClO_4$ the polymer became swollen, which increased the surface area of the catalyst and finally its catalytic activity.

pH analysis

To 25 mL of an aqueous solution of NaCl (1 M) with a primary pH 5.65, $[PVPH]ClO_4$ (0.5 g) was added and the resulting mixture was stirred for 2 h at room temperature after which the pH of the solution decreased to 1.34. This is equal to a loading of 2.28 mmol H^+/g of the catalyst [33].

Hammett acidity

The Hammett acidity method is an effective way to strengthen the acidity of an acid in organic solvents, using the UV–Vis technique [33]. The Hammett function is defined as:

$$H_0 = \mathrm{p}K\,(\mathrm{I})_{\mathrm{aq}} + \log\left([\mathrm{I}]_{\mathrm{s}}/[\mathrm{IH}^+]_{\mathrm{s}}\right).$$

The $\mathrm{p}K\,(\mathrm{I})_{\mathrm{aq}}$ is the $\mathrm{p}K_{\mathrm{a}}$ value of aqueous solution of the indicator and $[\mathrm{IH}^+]_{\mathrm{s}}$ and $[\mathrm{I}]_{\mathrm{s}}$ are the molar concentrations of protonated and unprotonated forms of the indicator in the solvent. According to Lambert–Beer's Law, the value of $[\mathrm{I}]_{\mathrm{s}}/[\mathrm{IH}^+]_{\mathrm{s}}$ can be determined and calculated through the UV–Visible spectrum. For this

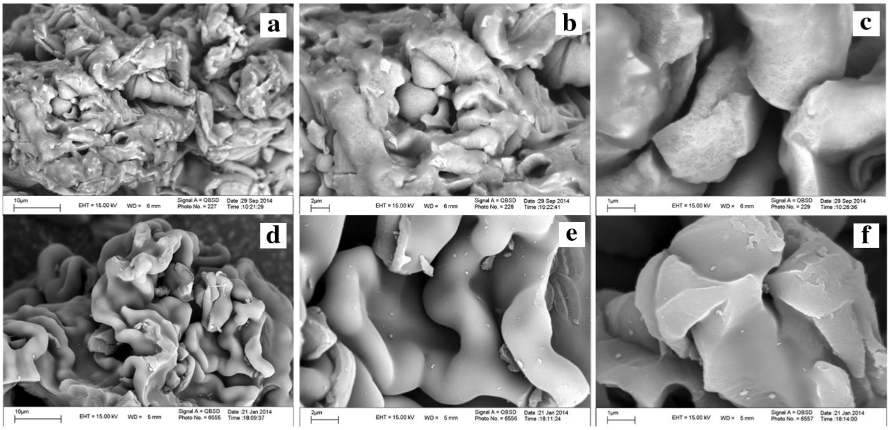


Fig. 4 SEM micrographs of $[PVPH]ClO_4$ (**a**–**c**) and PVP (**d**–**f**)

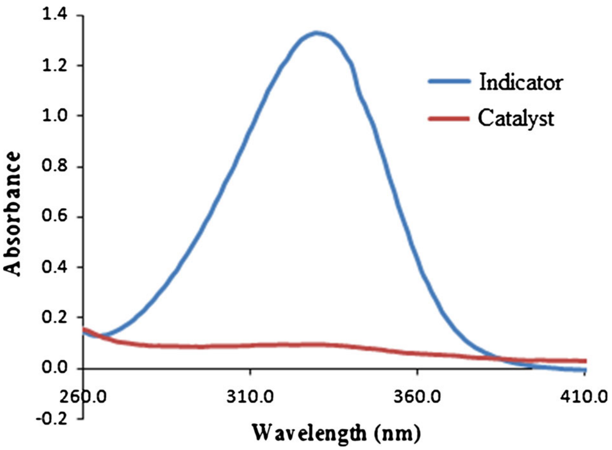


Fig. 5 Absorption spectra of 4-nitroaniline (*indicator*) and $[PVPH]ClO_4$ (*catalyst*) in CCl_4

Table 1 Calculation of Hammett acidity function (H_0) for $[PVPH]ClO_4$

Entry	Catalyst	A_{max}	$[I]_s$ (%)	$[IH^+]_s$ (%)	H_0
1	–	1.329	100	0	–
2	$[PVPH]ClO_4$	0.096	7.22	92.78	−0.12

Condition for UV–Visible spectrum measurement: solvent: CCl_4, indicator: 4-nitroaniline ($pK\ (I)_{aq} = 0.99$), 1.44×10^{-4} mol/L (10 mL); Catalyst: $[PVPH]ClO_4$ (10 mg), 25 °C

purpose, 4-nitroaniline ($pK(I)_{aq} = 0.99$) as the basic indicator and CCl_4 as the solvent were chosen. As can be seen in Fig. 5, the maximal absorbance of the unprotonated form of the indicator was observed at 330 nm in CCl_4. When $[PVPH]ClO_4$ as a catalyst was added to the indicator solution, the absorbance of the unprotonated form of the indicator decreased, which indicated that the indicator was partially in the form of $[IH^+]$. The obtained results are listed in Table 1.

Catalytic activity

On the basis of the above mentioned studies, we anticipated that $[PVPH]ClO_4$ could be used as an efficient catalyst for the promotion of the reactions, which need the use of an acidic catalyst to speed-up. In order to confirm this decision, we started to study the applicability of this polymeric catalyst in the acceleration of the Hantzsch reaction.

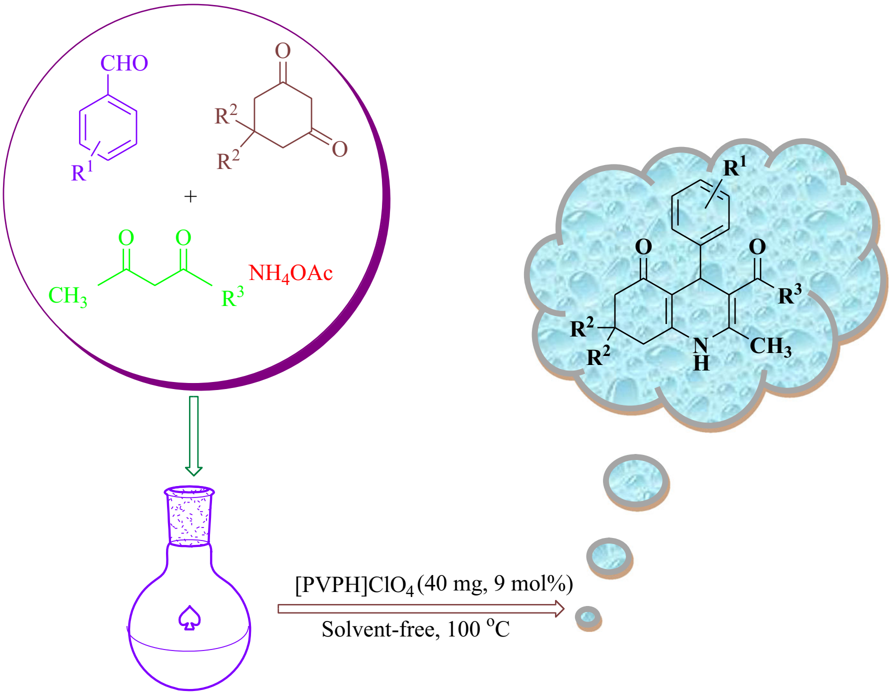
At first step, optimization of the reaction conditions was done by studying the reaction of 4-chlorobenzaldehyde with ethylacetoacetate, 5,5-dimethyl-1,3-cyclohexanedione (dimedone), and ammonium acetate in the presence of various amounts of $[PVPH]ClO_4$ in the absence of solvent and also in different solvents such as dichloromethane, acetonitrile, and ethanol under thermal conditions (Table 2). In this study different ratios of substrates were also examined. The

Table 2 Effect of temperature, solvent and amount of the catalyst on the synthesis of polyhydroquinoline derivative of 4-chlorobenzaldehyde

Entry	Catalyst (mg)	Solvent	Time (min)	Yield (%)[a]	Temperature (°C)
1	40 (9 mol%)	CH_2Cl_2	25	20	Reflux
2	40	EtOH	25	Unidentified mixture	Reflux
3	40	CH_3CN	25	Unidentified mixture	Reflux
4	20 (4.5 mol%)	–	70	75	100
5	30 (6.8 mol%)	–	27	85	100
6	40	–	13	98	100
7	40	–	50	80	70
8	40	–	100	80	30

Reaction conditions: 4-chlorobenzaldehyde (1 mmol); ethylacetoacetate (1 mmol), dimedone (1 mmol) and ammonium acetate (2 mmol)

[a] GC yield



Scheme 2 Optimized condition for the preparation of the polyhydroquinoline derivatives

optimum amounts were found to be 1:1:1:2:0.09 for 4-chlorobenzaldehyde, ethylacetoacetate, dimedone, ammonium acetate, and the catalyst, respectively (Scheme 2).

Table 3 Synthesis of polyhydroquinoline derivatives catalyzed by [PVPH]ClO_4

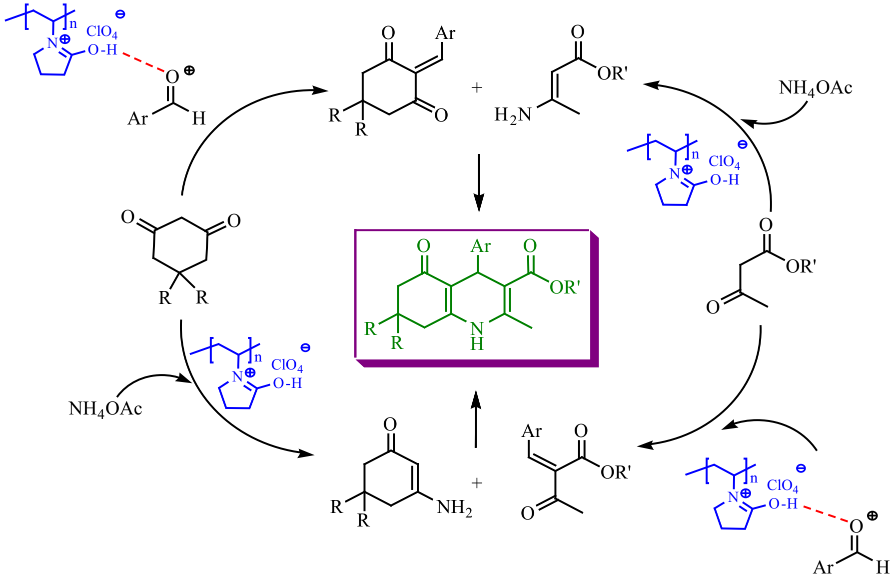
Entry	Aldehyde	R^2	R^3	Time (min)	Yield (%)	Melting point (°C)	
						Found	Reported references
1	C_6H_5CHO	CH_3	OEt	8	97	203–205	206–208 [35]
2	$4\text{-}ClC_6H_4CHO$	CH_3	OEt	13	97	241–243	244–246 [36]
3	$4\text{-}BrC_6H_4CHO$	CH_3	OEt	10	96	250–252	255–256 [35]
4	$4\text{-}CH_3OC_6H_4CHO$	CH_3	OEt	15	95	254–256	255–257 [35]
5	$4\text{-}HOC_6H_4CHO$	CH_3	OEt	4	97	230–232	234–236 [35]
6	$4\text{-}CH_3C_6H_4CHO$	CH_3	OEt	2	97	258–259	256–258 [35]
7	$4\text{-}NO_2C_6H_4CHO$	CH_3	OEt	27	96	243–245	247–249 [35]
8	$3\text{-}CH_3OC6H4CHO$	CH_3	OEt	8	95	198–200	201–203 [37]
9	$2\text{-}ClC_6H_4CHO$	CH_3	OEt	10	97	203–205	207–209 [37]
10	$2\text{-}CH_3OC_6H_4CHO$	CH_3	OEt	7	97	250–253	257–259 [36]
11	$2\text{-}CH_3C_6H_4CHO$	CH_3	OEt	4	97	199–201	201–205 [38]
12	$2\text{-}NO_2C_6H_4CHO$	CH_3	OEt	25	96	200–202	204–206 [37]
13	C_6H_5CHO	H	OEt	10	98	242–245	240–242 [39]
14	$4\text{-}ClC_6H_4CHO$	H	OEt	5	96	233–234	234–236 [39]
15	$4\text{-}HOC_6H_4CHO$	H	OEt	3	96	220–222	222–224 [39]
16	$4\text{-}CH_3C_6H_4CHO$	H	OEt	12	96	240–242	241–243 [39]
17	$4\text{-}CH_3C_6H_4CHO$	CH_3	OMe	3	95	270–273	274–276 [39]
18	$4\text{-}CH_3OC_6H_4CHO$	CH_3	OMe	5	97	248–252	249–251 [39]
19	$4\text{-}CNC_6H_4CHO$	CH_3	OMe	5	97	222–225	220–222 [40]
20	$4\text{-}ClC_6H_4CHO$	CH_3	OMe	10	93	218–219	220–221 [39]
21	$4\text{-}CHOC_6H_4CHO$	CH_3	OEt	7	90	298–300	294–296 [36]
22	$3\text{-}CHOC_6H_4CHO$	CH_3	OEt	15	90	325–327	

The desired products were characterized by their physical data, comparison with melting points, IR and/or ^{1}H NMR spectroscopy

Isolated yield

After optimization of the reaction conditions and in order to show the general applicability of the method, different types of aldehydes were subjected to the same reaction under the determined conditions. The obtained results showed that in all cases the corresponding polyhydroquinolines were obtained in good to excellent yields in appropriate times (Table 3, entries 1–12). We have also found that the same results were obtained when methylacetoacetate is used in place of ethylacetoacetate (Table 3, entries 17–20). It can be easily seen that in all cases, regardless of the substituent, the reaction gave the products in good to high yields during relatively short reaction times.

To investigate the versatility of the selected method, the reaction of 1,3-cyclohexanedione with various aldehydes was also carried out in the presence of



Scheme 3 Plausible mechanism of the reaction

this reagent. Short reaction times and high yields of the products showed that this substrate also reacted well under the selected conditions (Table 3, entries 13–16).

The reaction of dimedone with *p*-phthaldialdehyde and/or *m*-phthaldialdehyde in the presence of [PVPH]ClO_4 (0.18 mmol) was also successful and the desired bis-products were obtained after short reaction times in high yields (Table 3, entries 21 and 22).

A plausible mechanism of the reaction is shown in Scheme 3. On the basis of this mechanism, the main role of the catalysts is the activation of carbonyl group for nucleophilic attack. This proposed mechanism is found in the literature [36, 37].

Table 4, compares the efficiency of [PVPH]ClO_4 with other catalysts in the synthesis of the polyhydroquinoline derivative of 2-chlorobenzaldehyde. In this Table the following points should be considered: (a) Although the same reaction can be carried out in the absence of catalyst, in this situation the reaction time is very long (Table 4, entry 1), and (b) Although the same reaction can be carried out using lower amounts of some of the reported catalysts, the main drawback is that their preparation is difficult and time consuming (Table 4, entries 7, 8), and/or starting material is expensive (Table 4, entries 3–5, 7, 8). On the other hand, easy preparation of the catalyst, use of inexpensive supporter polymer, and lower amounts of [PVPH]ClO_4 are the most important advantages of the present method.

The reusability of the catalyst was checked in the reaction of 4-hydroxybenzaldehyde (Table 3, entry 5) under the optimized reaction conditions. After the separation of the product, the catalyst was washed with EtOH, dried, and reused for the same reaction. This process was carried out over five runs and all reactions led to the desired products with high efficiency (Fig. 6). It should be noted that the pH

Table 4 Comparison of various solid catalysts in the synthesis of the polyhydroquinoline derivative of 2-chlorobenzaldehyde (Table 3, entry 9)

Entry	Catalyst (amounts of the catalyst)	Conditions	Time (min)	Yield (%)	References
1	Catalyst-free	H_2O, reflux	4 h	93	[41]
2	P(4-VPH)HSO_4 (20 mg)	H_2O, reflux	15	92	[42]
3	Co_3O_4–CNTs (30 mg)	EtOH, reflux	45	93	[43]
4	SBA-15/SO_3H (4 mol%)	Solvent-free, 60 °C	30	85	[38]
5	MCM-41 (1 mol%)	Solvent-free, 90 °C	25	88	[21]
6	$HClO_4$–SiO_2 (50 mg)	Solvent-free, 90 °C	13	94	[28]
7	Fe_3O_4@chitosan (30 mg)	EtOH, r.t.	60	95	[44]
8	γ-Fe_2O_3@HAp@Melamine (150 mg)	Solvent-free, 80 °C	10	89	[45]
9	[PVPH]ClO_4 (40 mg, 9 mol%)	Solvent-free, 100 °C	10	97	This work

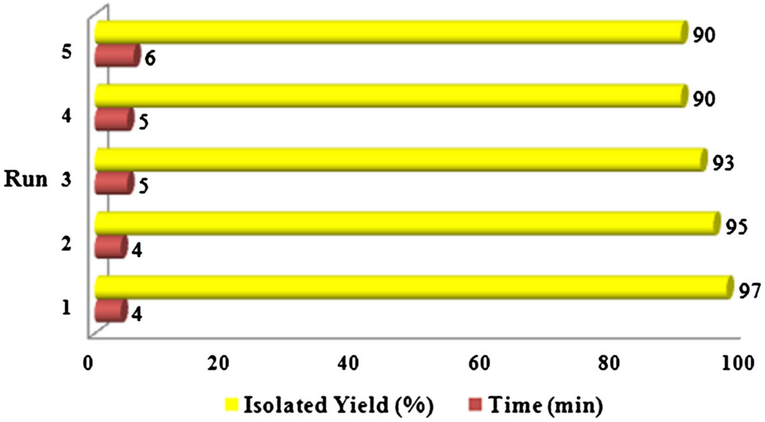


Fig. 6 Reusability of [PVPH]ClO_4 (Table 3, entry 5)

analysis of the recovered catalyst showed nearly the same loading of H^+ as the freshly prepared catalyst. These results suggest that changing the catalyst and/or leaching of the acid species does not occur during the course of the reaction.

Conclusion

In this paper, [PVPH]ClO_4 is prepared using commercially available starting materials and characterized with a variety of techniques. In continuation, this modified polymeric catalyst is used for the synthesis of polyhydroquinoline derivatives in the absence of solvent. Handling of the catalyst is easy, and this method is safer than the other ways, which, in them, the mineral acids like H_2SO_4 or $HClO_4$, are used as the catalysts. [PVPH]ClO_4 is very stable in the presence of moisture compared with some of the other forms of the modified PVP (e.g., [PVP–SO_3H]Cl) and even after several days it is not destroyed and its color is not changed at all. Also, this catalyst could be successfully recovered and recycled at least for five runs without significant loss in its activity.

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References

1. T. Godfraid, R. Miller, M. Wibo, Pharmocol. Rev. **38**, 321 (1986)
2. A. Sausins, G. Duburs, Heterocycles **27**, 279 (1988)
3. P.P. Mager, R.A. Coburn, A.J. Solo, D.J. Triggle, H. Rothe, Drug Des. Discov. **28**, 273 (1992)
4. R. Mannhold, B. Jablonka, W. Voigt, K. Schonafinger, K. Schraven, Eur. J. Med. Chem. **27**, 229 (1992)
5. F. Bossert, H. Meyer, E. Wehinger, Angew. Chem. Int. Ed. Engl. **20**, 762 (1981)
6. H. Nakayama, Y. Kasoaka, Heterocycles **42**, 901 (1996)
7. V. Klusa, Drugs Future **20**, 135 (1995)
8. R.G. Bretzel, C.C. Bollen, E. Maester, K.F. Federlin, Am. J. Kidney Dis. **21**, 54 (1993)
9. R.G. Bretzel, C.C. Bollen, E. Maester, K.F. Federlin, Drugs Future **17**, 465 (1992)
10. R. Boer, V. Gekeler, Drugs Future **20**, 499 (1995)
11. Y.L. Chen, K.C. Fang, J.Y. Sheu, S.L. Hsu, C.C. Tzeng, J. Med. Chem. **44**, 2374 (2001)
12. G. Roma, M.D. Braccio, G. Grossi, M. Chia, Eur. J. Med. Chem. **35**, 1021 (2000)
13. M.P. Maguire, K.R. Sheets, K. McVety, A.P. Spada, A. Zilberstein, J. Med. Chem. **37**, 2129 (1994)
14. T. Itoh, K. Nagata, A. Kurihara, M. Miyazaki, A. Ohsawa, Tetrahedron Lett. **43**, 3105 (2002)
15. Sh Ko, Ch-F. Yao, Tetrahedron **62**, 7293 (2006)
16. H. Khabazzadeh, E. Tavakilinejad Kermani, D. Afzali, A. Amiri, A. Jalaladini, Arabian J. Chem. **5**, 167 (2012)
17. M. Hong, C. Cai, W.-B. Yi, J. Fluor Chem. **131**, 111 (2010)
18. S. Kumar, P. Sharma, K.K. Kapoor, M.S. Hundal, Tetrahedron **64**, 536 (2008)
19. A. Dondoni, A. Massi, E. Minghini, V. Bertolasi, Tetrahedron **60**, 2311 (2004)
20. M.M. Heravi, K. Bakhtiari, N.M. Javadi, F.F. Bamoharram, M. Saeedi, H.A. Oskooie, J. Mol. Catal. A Chem. **264**, 50 (2007)
21. L. Nagarapu, M. Dharani Kumari, N.V. Kumari, S. Kantevari, Catal. Commun. **78**, 1871 (2007)
22. S. Ko, M.N.V. Sastry, C. Lin, C.F. Yao, Tetrahedron Lett. **46**, 5771 (2005)
23. S.B. Sapkal, K.F. Shelke, B.B. Shingate, M.S. Shingare, Tetrahedron Lett. **50**, 1754 (2009)
24. S.J. Ji, Z.Q. Jiang, J. Lu, T.P. Loh, Synlett **5**, 831 (2004)
25. A. Kumar, R.A. Maurya, Tetrahedron **63**, 1946 (2007)
26. A. Kumar, R.A. Maurya, Synlett **6**, 883 (2008)
27. C.G. Evans, J.E. Gestwicki, Org. Lett. **11**, 2957 (2009)
28. M. Maheswara, V. Siddaiah, G.L.V. Damu, C.V. Rao, ARKIVOC **ii**, 201 (2006)
29. B. Das, B. Ravikanth, R. Ramu, B. Vittal Rao, Chem. Pharm. Bull. **54**, 1044 (2006)
30. G. Song, B. Wang, X. Wu, Y. Kang, L. Yang, Synth. Commun. **35**, 2875 (2005)
31. N.G. Khaligh, F. Shirini, Ultrason. Sonochem. **20**, 26 (2013)
32. F. Shirini, O.G. Jolodar, J. Mol. Catal. A Chem. **356**, 61 (2012)
33. F. Shirini, P.N. Moghadam, S. Moayedi, M. Seddighi, RSC Adv. **4**, 38581 (2014)
34. X.Y. Li, X. Wang, D.G. Yu, S. Ye, Q.K. Kuang, Q.W. Yi, X.Z. Yao, J. Nanomater. **2012**, 7 (2012)
35. A. Zare, F. Abi, A.R. Moosavi-Zare, M.H. Beyzavi, M.A. Zolfigol, J. Mol. Liq. **178**, 113 (2013)
36. A. Khazaei, M.A. Zolfigol, A.R. Moosavi-Zare, J. Afsar, A. Zare, V. Khakyzadeh, M.H. Beyzavi, Chin. J. Catal. **34**, 1936 (2013)
37. M. Tajbakhsh, H. Alinezhad, M. Norouzi, S. Baghery, M. Akbari, J. Mol. Liq. **177**, 44 (2013)
38. S. Rostamnia, F. Pourhassan, Chin. Chem. Lett. **24**, 401 (2013)
39. M. Nasr-Esfahani, S.J. Hoseini, M. Montazerozohori, R. Mehrabi, H. Nasrabadi, J. Mol. Catal. A Chem. **382**, 99 (2014)

40. R. Surasani, D. Kalita, A.V.D. Rao, K. Yarbagi, K.B. Chandrasekhar, J. Fluorine Chem. **135**, 91 (2012)
41. B.P. Bandgar, P.E. More, V.T. Kamble, J.V. Totre, ARKIVOC **xv**, 1 (2008)
42. B. Janardhan, B. Rajitha, P.A. Crooks, J. Saudi. Chem. Soc. (2014). doi:10.1016/j.jscs.2014.01.009
43. Z. Zarnegar, J. Safari, Z. Mansouri-Kafroudi, Catal. Commun. (2014). doi:10.1016/j.catcom.2014.10.023
44. A. Maleki, M. Kamalzare, M. Aghaei, J. Nanostruct. Chem. (2014). doi:10.1007/s40097-014-0140-z
45. S. Igder, A.R. Kiasat, M.R. Shushizadeh, Res. Chem. Intermed. (2014). doi:10.1007/s11164-014-1808-1