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Introduction of *O*-sulfonated poly(4-vinylpyrrolidonium) chloride as a polymeric and reusable catalyst for the synthesis of xanthene derivatives

Farhad Shirini,*[a] Peyman Najafi Moghadam,[b] Simin Moayedi[ab] and Mohadeseh Seddighi[a]

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O-Sulfonated poly(4-vinylpyrrolidonium) chloride is prepared from the reaction of poly(4-vinylpyrrolidone) [PVP], as a cheap and commercially available reagent, and neat chlorosulfonic acid at room temperature. A variety of techniques including infrared spectra (IR), thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD), pH analysis and Hammett acidity (H_o) were used to characterize this solid acid. This polymeric reagent showed excellent catalytic activity for the synthesis of xanthene derivatives including 1,8-dioxooctahydroxanthenes, 14-aryl-14*H*-dibenzo[*a*,*j*] xanthenes and 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones under solvent free conditions. The products were formed in excellent yields over short reaction times and the catalyst can be reused several times without any appreciable loss in its activity.

Introduction

Replacement of conventional, toxic and polluting Brönsted and Lewis acid catalysts with eco-friendly reusable heterogeneous catalysts is an area of current interest. In this context, there has been renewed interest in the synthesis of solid acid catalysts that function as an acid under a solid state.[1] These materials have many advantages compared to traditional liquid acids such as their efficiency, operational simplicity, easy recyclability and recoverability, non-corrosive nature and friendly to the environment, all factors which are important in industry. Therefore, solid acid catalysts can play a significant role in the development of clean technologies.

Among various supports, polymers are becoming important and useful tools in chemistry. Both soluble and cross-linked polymers have been used as support materials in organic synthesis. The soluble polymer supports provide a more homogeneous reaction mixture, so they generally require a more complicated separation procedure that limited their common use, while the cross-linked materials can be separated with simple filtration.[2] One of the key goals in the design of a new catalyst is to combine high efficiency of the catalyst with its easy separation from the reaction products and the possibility of recycling, so in this aspect cross-linked polymers create a perspective type of support materials.

One of the most widely used heterogeneous and polymeric supports for numerous reagents and catalysts is cross-linked poly(vinylpyrrolidone) (PVP) because of its commercial availability, stability, reasonable high loading capacity, good physicochemical structure and facile functionalization. It is One of the most widely used excipients in pharmaceuticals, for example as a binder in tablets, granulates and capsules. Stabilizer of suspensions, ophthalmic preparation, sugar coating, film coating and miscellaneous applications are the other applicabilities of this reagent.[3] Also, it seems to an attractive support to immobilize mineral acids because of the basic nature of pyridyl group. Therefore, various PVP-supported reagents have been designed to catalyze some of the organic reactions.[4–7]

During the last decade, xanthenes and their derivatives have been the subject of considerable levels of interest because of their numerous applications in pharmaceutical and biological research such as antimicrobial,[8] antiviral,[9] antitumor,[10] and anticancer[11] activities. Additionally, these heterocyclic compounds can be used in laser technology,[12] fluorescent material for visualization of biomolecules,[13] and also as dyes.[14,15] Thus, the synthesis of xanthene derivatives currently is of much importance. The most common protocols for the one pot multi-component preparation of symmetric and asymmetric xanthenes are as follow:

• The reaction of aldehydes (1 eq.) with cyclic 1,3-dicarbonyl compounds (2 eq.) for the preparation of 1,8-dioxooctahydroxanthenes.

[a]*Department of Chemistry, College of Sciences, University of Guilan, 41335, Rasht, Iran. E-mail: shirini@guilan.ac.ir; Fax: +98 131 3233262; Tel: +98 131 3233262*
[b]*Department of Chemistry, Faculty of Sciences, Urmia University, Urmia, Iran*

• The reaction of aldehydes (1 eq.) with β-naphthol (2 eq.) for the preparation of 14-aryl-14*H*-dibenzo[*a*,*j*] xanthenes.

• The reaction of aldehydes (1 eq.) with β-naphthol (1 eq.) and cyclic 1,3-dicarbonyl compounds (1 eq.) for the preparation of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones.

A variety of catalysts such as $FeCl_3\ 6{\cdot}H_2O$,[16] sulfamic acid,[17] amberlyst-15,[18] silica sulfuric acid,[19] selectfluor™,[20] poly-tungstozincate acid,[21] $H_3PW_{12}O_{40}$,[22] I_2,[23] pTSA,[24] cellulose sulfonic acid,[25] NH_2SO_3H,[26] β-cyclodextrin,[27] nano-TiO_2,[28] saccharin sulfonic acid,[29] succinimide-*N*-sulfonic acid,[30] poly(4-vinylpyridinium)hydrogen sulfate [P(4-VPH)HSO_4],[31] SO_3H-functionalized MCM-41,[32] 1-butyl-3-methylimidazolium hydrogen sulfate [bmim][HSO4],[33] trityl chloride (TrCl),[34] silica-bonded S-sulfonic acid (SBSSA),[35] *N*-sulfonic acid poly(4-vinylpyridinium) chloride,[36] PVPP-BF_3,[37] have been used to facilitate the preparation of xanthene derivatives. Although these procedures provide an improvement, many of them suffer from disadvantages such as long reaction times, harsh reaction conditions, need to excess amounts of the reagent, use of organic solvents, use of toxic reagents and non-recoverability of the catalyst. Additionally, only some of them are useful for the synthesis of all of the above mentioned xanthenes. Therefore, introduction of simple, efficient and mild procedures with easily separable and reusable solid catalysts to overcome these problems is still in demand.

Experimental section

Reagents and materials

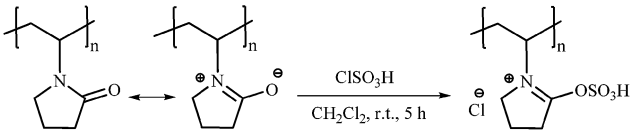
Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. Cross-linked poly(4-vinylpyrrolidone) we purchased it from BASF the chemical company, Germany. All yields refer to the isolated products. Products were characterized by comparison of, their physical constants, IR and NMR spectroscopy with authentic samples and those reported in the literature.

Characterization

The FT-IR spectra were run on a VERTEX 70 Bruker company (Germany). Thermogravimetric analyses (TGA) were performed on TG/DTA6300 Sll-Nonotechnology 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. Wide-angle X-ray diffraction (XRD) measurements were performed at room temperature on a Siemens D-500 X-ray diffractometer (Germany), using Ni-filtered Co-Kα radiation ($\lambda = 0.15418$ nm).

Catalyst preparation [PVP-SO_3H] Cl

Chlorosulfonic acid (1.2 mL, 18 mmol) was added to a suspension of powdered poly(4-vinylpyrrolidone) (2.0 g) [cross-linked poly(4-vinylpyrrolidone) with $M_W > 1\ 000\ 000$] in 10 mL dry CH_2Cl_2 over a period of 15 min. The mixture was stirred at room temperature for 5 h and then the mixture was filtered. The solid residue was washed with ethyl acetate (20 mL) and dried at 80 °C to afford [PVP-SO_3H] Cl as a pale yellow powder (Scheme 1).



Scheme 1 Preparation of the catalyst ([PVP-SO_3H] Cl).

General procedure for the synthesis of 1,8-dioxooctahydroxanthenes

A mixture of dimedone or cyclohexadione (2.1 mmol), aldehyde (1 mmol) and [PVP-SO_3H] Cl (10 mg) was stirred in an oil-bath at 120 °C under solvent-free conditions. After completion of the reaction (monitored by TLC), the reaction mixture was cooled, EtOH (10 mL) was added and the catalyst was removed by filtration. Then, water was added and the precipitated product was collected by filtration in high purity.

General procedure for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*] xanthenes

A mixture of β-naphthol (2 mmol), aldehyde (1 mmol) and [PVP-SO_3H] Cl (40 mg) was stirred in an oil-bath at 120 °C under solvent-free conditions. After completion of the reaction (monitored by TLC) the reaction mixture was cooled to room temperature, EtOH (10 mL) was added to it and filtered to separate the catalyst. Then the crude product was recrystallized from EtOH to give the pure product.

General procedure for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones

A mixture of β-naphthol (0.144 g, 1 mmol), dimedone or cyclohexadione (1.2 mmol), aldehyde (1 mmol) and [PVP-SO_3H] Cl (40 mg) was stirred and heated in an oil-bath at 120 °C for an appropriate period of time. After completion of the reaction, as monitored with TLC, the reaction mixture was cooled to room temperature, EtOH (10 mL) was added to it and filtered to separate the catalyst. Then the crude product was recrystallized from EtOH to give the pure product.

The spectral data of the selected compounds are as follow:

9-(2-Mehtoxyphenyl)-3,3,6,6-tetramethyl-1,8-dioxooctahydro xanthene. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.97$ (s, 6H), 1.11 (s, 6H), 2.14 and 2.23 (d, $J = 16.4$ Hz, 2H), 2.39 and 2.48 (d, $J = 17.4$ Hz, 2H), 3.79 (s, 3H), 4.87 (s, 1H), 6.77 (d, $J = 8$ Hz, 1H), 6.89 (dt, $J_1 = 7.4$ Hz, $J_2 = 1.2$ Hz, 1H), 7.12 (m, 1H), 7.43 (dd, $J_1 = 7.4$ Hz, $J_2 = 1.6$ Hz, 1H) ppm.

9-(3-Bromophenyl)-1,8-dioxo-octahydroxanthene. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$; 1.95–2.1 (m, 4H), 2.30–2.44 (m, 4H), 2.55–2.63 (m, 2H), 2.66–2.73 (m, 2H), 4.79 (s, 1H), 7.11 (t, $J = 7.6$ Hz, 1H), 7.26 = 7.36 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 20.3$, 27.2, 31.6, 36.9, 116.3, 122.3, 127.7, 129.6, 131.0, 146.6, 164.3, 196.4 ppm.

9-(3-Mehtoxyphenyl)-1,8-dioxo-octahydroxanthene. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.99$–2.10 (m, 4H), 2.30–2.45 (m, 4H),

2.54–2.71 (m, 4H), 3.81 (s, 3H), 4.83 (s, 1H), 6.69–6.71 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 6.89–6.95 (m, 2H), 7.17 (t, J = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3, 27.2, 31.5, 37.0, 55.2, 111.5, 114.5, 116.8, 121.0, 129.0, 146.0, 159.4, 164.0, 196.5 ppm.

14-(2-Chlorophenyl)-14*H*-dibenzo[*a*,*j*]xanthenes. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.85 (s, 1H), 6.93–6.99 (m, 2H), 7.30 (d, J = 7.1 Hz, 1H), 7.44(d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.54(d, J = 8.8 Hz, 2H), 7.67 (t, J = 7.5 Hz, 2H), 7.83–7.87 (m, 4H), 8.79 (d, J = 8.5 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 34.6, 117.9, 118.0, 123.4, 124.3, 126.8, 127.7, 127.8, 128.5, 129, 129.5, 130.1, 130.8, 131.6, 131.7139.5, 148.9 ppm.

14-(3-Nitrophenyl)-14H-dibenzo[*a*,*j*]xanthenes. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.64 (s, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.48 (t, J = 7.44, 2H), 7.55 (d, J = 8.8, 2H), 7.65 (t, J = 7.55 Hz, 2H), 7.84–7.90 (m, 6H), 8.35 (d, J = 8.5 Hz, 2H), 8.46 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.1, 116.3, 118.5, 122.1, 122.4, 123.1, 125.0, 127.7, 129.5, 129.9, 130, 131.5, 131.8, 134.7, 147.4, 148.6, 149.2 ppm.

12-(2-Naphthyl)-9,9-dimethyl-8,9,10,12-octahydrobenzo[*a*] xanthene-11-one. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (s, 3H), 1.14 (s, 3H), 2.32 and 2.36 (AB system, J = 16.4 Hz, 2H), 2.61 (s, 2H), 5.92 (s, 1H), 7.28–7.44 (m, 5H), 7.50 (d, J = 8 Hz, 1H), 7.67–7.82 (m, 6H), 8.08 (d, J = 8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.2, 29.3, 32.3, 34.9, 41.5, 50.9, 114.1, 117.1, 117.6, 123.7, 124.9, 125.4, 125.7, 126.7, 127.1, 127.2, 127.4, 128.0, 128.4, 129.0, 131.4, 131.5, 132.1, 133.3, 142.1, 147.8, 164.0, 196.9 ppm.

Results and discussion

Catalyst characterization

The infrared spectra of PVP and [PVP-SO_3H] Cl are shown in Fig. 1. As can be seen, presence of an extra sulfonic acid group on the pyrrolidine nitrogen in the [PVP-SO_3H] Cl increased the number of vibrational modes and brought completely different FTIR spectrum. In the case of [PVP-SO_3H] Cl, the broad band around 2600 to 3700 cm^{-1} can be attributed to the OH stretching of the SO_3H group Additional bands at 1170, 1066, 882 and 578 cm^{-1} are assigned to the S=O asymmetric and symmetric stretching, S–OH bending and symmetric S–O stretching vibrations, respectively.[38,39] Furthermore, the bands at 1429 (C–N) and 650 (N–C=O) cm^{-1} are disappeared, a moderate absorption at 1648 cm^{-1} that corresponds to the internal imine groups present in the pendant rings of the polymer is appeared.[6,7] These observations confirm the functionalization of pyrrolidine oxygen with sulfonic acid.

Fig. 2 represents the X-ray diffraction (XRD) patterns of the PVP and [PVP-SO_3H] Cl samples. As shown in this figure, incorporation of $ClSO_3H$ leads to some changes in the diffractogram of PVP. The PVP diffraction exhibits a diffused background pattern with two diffraction halos appeared around 2θ equal to 13 and 22 indicating that the polymer is amorphous.[40] After modification of PVP by $ClSO_3H$ the first peak (2θ around 13) is disappeared, and the broad peak at 2θ around 22 is slightly reduced. These observations imply that the crystalline size of PVP is decreased after reaction with $ClSO_3H$.[38]

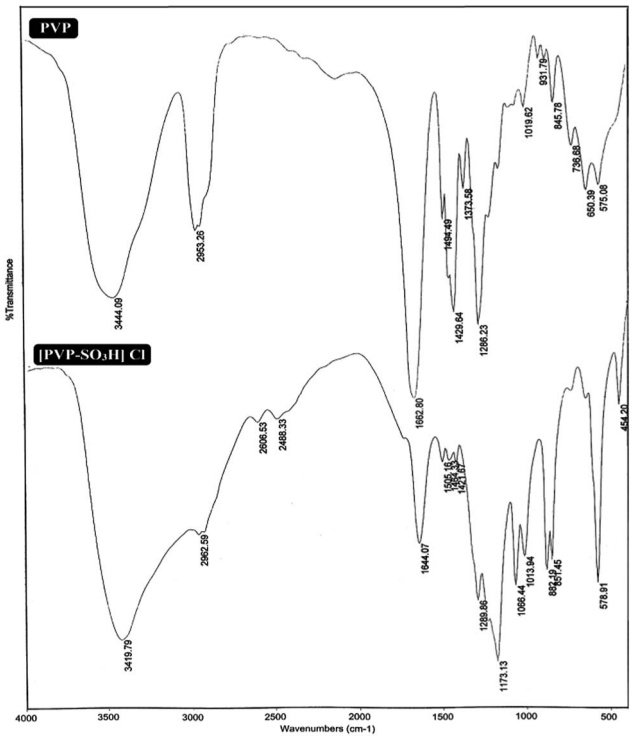


Fig. 1 FT-IR spectra of PVP and [PVP-SO_3H] Cl.

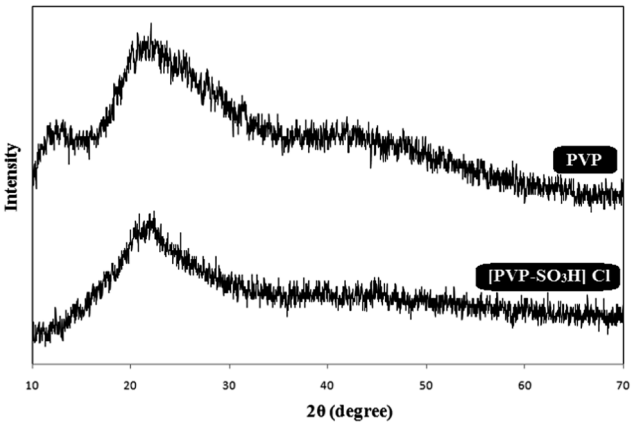


Fig. 2 XRD patterns of PVP in comparison of [PVP-SO_3H] Cl.

The samples of PVP and [PVP-SO_3H] Cl were also analyzed by scanning electron microscopy (SEM) with various magnifications for determining the size distribution, particle shape and surface morphology, as represented in Fig. 3. These images showed 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 chlorosulfonic acid the polymer was became swollen. This increased the surface area of the catalyst and finally its catalytic activity. Furthermore, in the SEM images of [PVP-SO_3H] Cl the pendant sulfonic groups were observed on the surface PVP polymer.

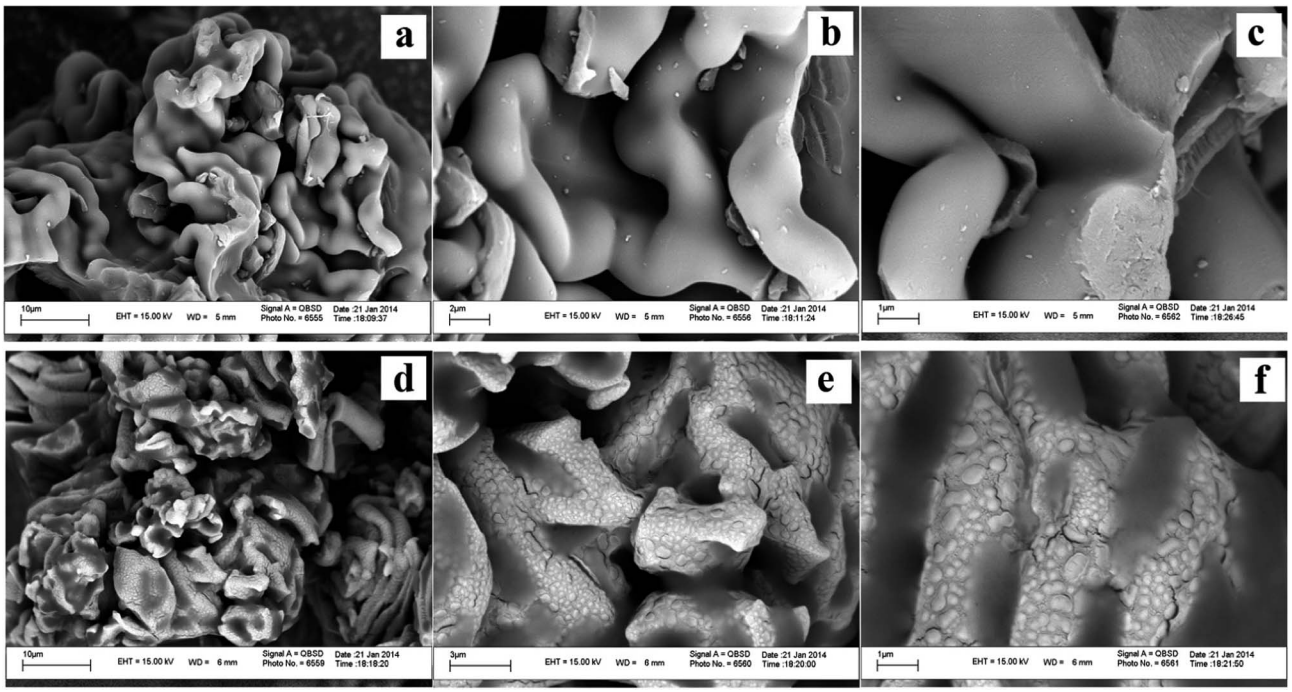


Fig. 3 SEM micrographs of PVP (a–c) and [PVP-SO_3H] Cl (d–f).

The thermal stability of PVP and [PVP-SO_3H] Cl was determined by Thermogravimetric analysis (TGA) and differential thermogravimetry analysis (DTGA) curves, as shown in Fig. 4. The TGA curve of PVP displayed a weight loss below 120 °C which is corresponding 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 and DTG analysis of [PVP-SO_3H] Cl show four-stage decomposition, completely different from PVP. The first weight loss appeared at <120 °C attributed to the loss of moisture contents. The second weight loss which started from 200 °C (210–280 °C, $T_{max} = 260$ °C) can be a result of the thermal decomposition of the pendant sulfonic groups. The sulfonated PVP moiety undergoes intermolecular bonding interactions in the solid state, leading to the formation of a rigid network structure which requires higher temperature for decomposition. This is confirmed by the third (310–360 °C, $T_{max} = 330$ °C) and fourth (380–480 °C, $T_{max} = 430$ °C) decomposition stages.[38] The DTGA-TGA data show that the [PVP-SO_3H] Cl catalyst is stable to 210 °C.

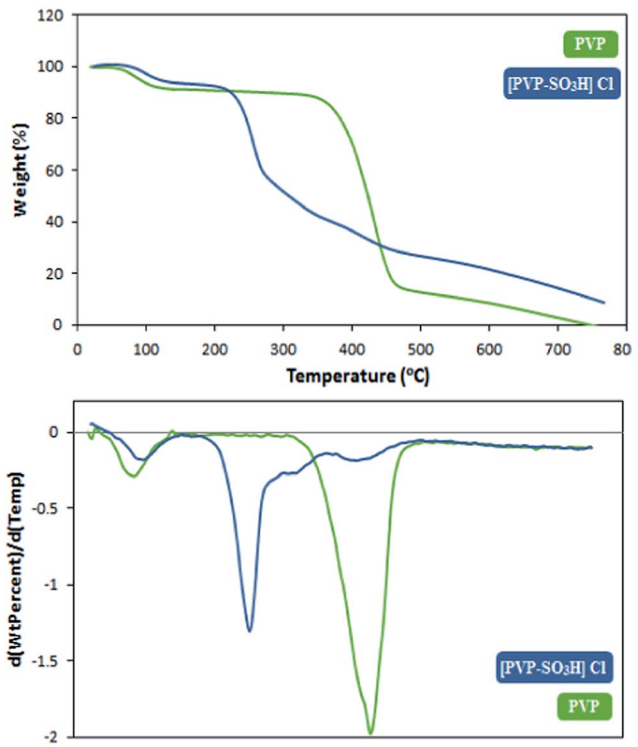


Fig. 4 TGA curves (up) and DTGA curves (down) for PVP and [PVP-SO_3H] Cl.

The Hammett acidity method is an effective way to the acidity strength of an acid in organic solvents, using UV-vis technique.[39] The Hammett function is defined as:

$$H_0 = pK\,(I)_{aq} + \log\,([I]_s/[IH^+]_s)$$

where the $pK\,(I)_{aq}$ is the pK_a value of aqueous solution of the indicator, and $[IH^+]_s$ and $[I]_s$ are the molar concentrations of protonated and unprotonated forms of the indicator in the solvent, respectively. According to Lambert–Beer's Law, the value of $[I]_s/[IH^+]_s$ can be determined and calculated through UV-visible spectrum. For this 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 [PVP-SO_3H] Cl as a solid acid catalyst was added to

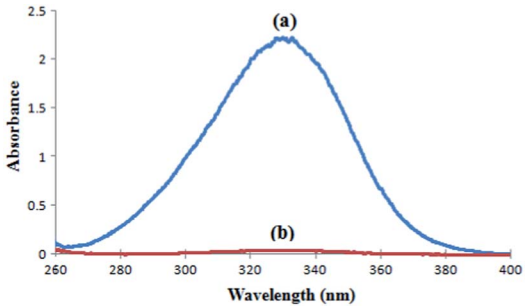


Fig. 5 Absorption spectra of 4-nitroaniline (indicator) (a) and [PVP-SO_3H] Cl (catalyst) (b) in CCl_4.

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^+]. These results that have listed in Table 1, show the acidity strength of [PVP-SO_3H] Cl.

To 25 mL of an aqueous solution of NaCl (1 M) with a primary pH 5.6, [PVP-SO_3H] Cl (0.5 g) was added and the resulting mixture was stirred for 2 h at room temperature after which the pH of solution decreased to 1.21. This is equal to a loading of 3.0 mmol H^+ per gram of the catalyst.[39]

Catalytic activity

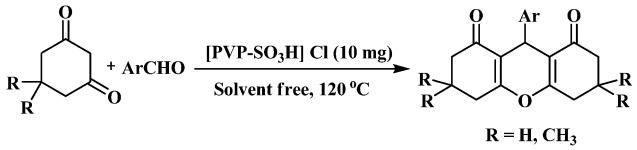
On the basis of the information obtained from the above mentioned studies, we anticipated that *O*-sulfonated poly(4-vinylpyrrolidonium) chloride can be used as an efficient catalyst for the promotion of the reactions which need the use of an acidic catalyst to speed up. So we were interested to investigate the applicability of this reagent in the preparation of the xanthenes derivatives.

At first, we focused our attention to study the synthesis of 1,8-dioxooctahydroxanthenes. For optimization of the reaction conditions, the condensation of 4-chlorobenzaldehyde with dimedone (5,5-dimethyl-1,3-cyclohexanedione) to the corresponding product was selected as a model reaction and the various conditions using different amounts of catalyst at various temperatures under solvent-free conditions were examined. Finally the optimal reaction conditions for this reaction was as follow: 1 mmol aldehyde, 2.1 mmol dimedone and 10 mg [PVP-SO_3H] Cl as catalyst at 120 °C under solvent-free conditions (Scheme 2). Any further increase of the catalyst or temperature did not improve the reaction time and yield.

Table 1 Calculation of Hammett acidity function (H_0) for [PVP-SO_3H]-Cl[a]

Catalyst	A_{max}	$[I]_s$ %	$[IH^+]_s$ %	H_0
—	2.2254	100	0	—
[PVP-SO_3H] Cl	0.0374	1.68	98.32	−0.78

[a] Condition for UV-visible spectrum measurement: solvent: CCl_4, indicator: 4-nitroaniline ($pK_{(I)aq} = 0.99$), 1.44×10^{-4} mol L^{-1} (10 mL); catalyst: [PVP-SO_3H] Cl (10 mg), 25 °C.



Scheme 2 Synthesis of 1,8-dioxooctahydroxanthenes catalyzed by [PVP-SO_3H] Cl.

After optimization of the reaction conditions and in order to establish the effectiveness and the acceptability of the method, we explored the protocol with a variety of simple readily available substrates under the optimal conditions. As presented in Table 2, different aromatic aldehydes (containing electron-withdrawing or electron-donating groups) were condensed with cyclic 1,3-diketones (dimedone or 1,3-cyclohexadione) under the optimal conditions in high yields and very short reaction times. As can be seen, the nature of the substituents on the aromatic ring did not show strongly obvious effects in terms of yields and times under the selected reaction conditions, while the steric effects increased the reaction times (Table 2, entry 8).

In the next step, [PVP-SO_3H] Cl solid acid catalyst was used in the condensation of β-naphthol with aldehydes leading to 14-aryl-14*H*-dibenzo[*a*,*j*] xanthenes. Our observations showed that under the same conditions used for the preparation of 1,8-dioxooctahydroxanthenes, this reaction was not completed. We found that higher amounts of the catalyst was need and 40 mg [PVP-SO_3H] Cl was adequate to accomplish the reaction effectively at 120 °C (Scheme 3). Under this optimum conditions, various aldehydes were reacted with β-naphthol in short reaction times with high yields that confirms the efficiency of this method (Table 3).

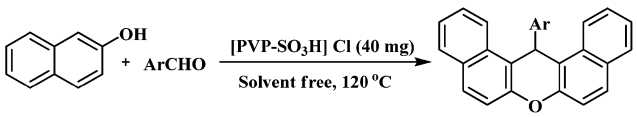
After the successful application of [PVP-SO_3H] Cl as a solid acid catalyst in the synthesis of symmetric xanthenes, we decided to use it in the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones as asymmetric xanthenes. For this purpose and to obtain the optimum reaction conditions, the reaction between 4-chlorobenzaldehyde, β-naphthol and dimedone to its corresponding xanthene was investigated as a model reaction in different conditions. We found that the best result was obtained using 1 mmol aldehyde, 1 mmol β-naphthol, 1.2 mmol dimedone and 40 mg [PVP-SO_3H] Cl at 120 °C under solvent-free conditions (Scheme 4). Subsequently, to reveal the generality of this method, the condensation was carried out with a variety of substrates using [PVP-SO_3H] Cl under the optimal conditions. The results show that these conversions were also occurred with excellent yields in very short times (Table 4).

In order to highlight the merits of our newly developed procedures, we have compared our result obtained from the synthesis of 9-phenyl-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthenes, 14-phenyl-14*H*-dibenzo[*a*,*j*]xanthenes and 12-(4-chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*] xanthene-11-one catalyzed by [PVP-SO_3H] Cl with other results reported in the literature. As shown in Table 5, this method is superior in

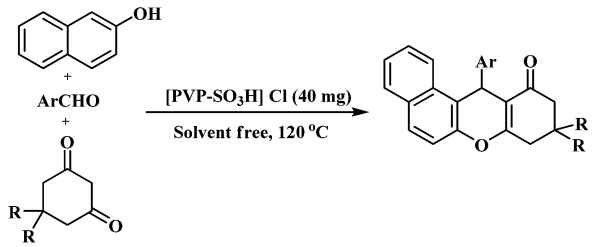
Table 2 synthesis of 1,8-dioxooctahydroxanthenes in the presence of [PVP-SO_3H] Cl

					Mp (°C)	
Entry	Ar	R	Time (min)	Yield[a] (%)	Found	Reported
1	C_6H_5–	Me	3	94	198–200	201–202 (ref. 20)
2	4-ClC_6H_4–	Me	3	95	229–231	230–232 (ref. 20)
3	3-BrC_6H_4–	Me	3	92	282–284	281–282 (ref. 36)
4	4-BrC_6H_4–	Me	3	95	235–237	236–238 (ref. 16)
5	3-$CH_3C_6H_5$–	Me	3	94	198–200	205–207 (ref. 41)
6	2-$CH_3OC_6H_5$–	Me	4	91	185–186	188–190 (ref. 42)
7	3-$CH_3OC_6H_5$–	Me	3	95	190–191	192–194 (ref. 30)
8	2-$NO_2C_6H_4$–	Me	20	92	251–252	251–252 (ref. 36)
9	3-$NO_2C_6H_4$–	Me	9	93	162–164	164–165 (ref. 36)
10	4-$NO_2C_6H_4$–	Me	3	96	220–222	222 (ref. 41)
11	C_6H_5–	H	3	90	262–264	265–267 (ref. 43)
12	2-ClC_6H_4–	H	3	91	247–249	248–249 (ref. 36)
13	4-ClC_6H_4–	H	3	96	281–283	282–285 (ref. 43)
14	3-BrC_6H_4 –	H	3	92	278–280	280–281 (ref. 36)
15	4-BrC_6H_4–	H	2	95	286–288	284–285 (ref. 27)
16	3-$CH_3OC_6H_5$–	H	2	94	190–192	192–194 (ref. 43)
17	3-$NO_2C_6H_4$–	H	2	94	281–283	280–282 (ref. 43)
18	4-$NO_2C_6H_4$–	H	2	95	250–252	254–256 (ref. 43)

[a] Isolated yields.



Scheme 3 Synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*] xanthenes catalyzed by [PVP-SO_3H] Cl.



Scheme 4 Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*] xanthen-11-ones catalyzed by [PVP-SO_3H] Cl.

the term of the reaction time. Furthermore, this avoids some of the disadvantages associated with the other procedures such as toxic reagents, organic solvents and low yields.

To check the reusability of the catalyst, the reaction of 4-chlorobenzaldehyde (1 mmol) with dimedone (2.1 mmol) under the optimized reaction conditions was studied again. When the reaction completed, ethyl acetate was added and the catalyst was separated by filtration. The recovered catalyst was washed with ethyl acetate, dried and reused for the same reaction. This process was carried out over five runs and all reactions were led to the desired products without significant changes in terms of

Table 3 Synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*] xanthenes in the presence of [PVP-SO_3H] Cl

				Mp (°C)	
Entry	Ar	Time (min)	Yield[a] (%)	Found	Reported
1	C_6H_5–	6	93	184–186	184–185 (ref. 37)
2	2-ClC_6H_4–	18	90	208–211	206–209 (ref. 36)
3	4-ClC_6H_4–	5	96	288–291	290–292 (ref. 37)
4	3-BrC_6H_4–	7	94	187–189	190–191 (ref. 28)
5	4-BrC_6H_4–	7	96	295–297	296–298 (ref. 19)
6	2-$CH_3OC_6H_5$–	40	90	250–252	258–259 (ref. 37)
7	4-$CH_3OC_6H_5$–	20	92	196–198	199–201 (ref. 36)
8	3-$NO_2C_6H_4$–	3	96	212–214	211–212 (ref. 37)
9	4-$NO_2C_6H_4$–	4	94	313–315	312–313 (ref. 37)
10	4-OHC_6H_4–	10	94	135–137	130–133 (ref. 36)

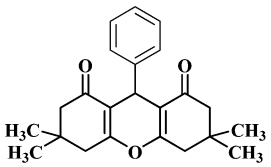
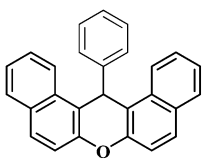
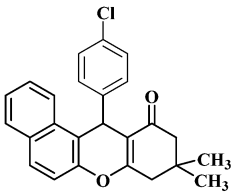
[a] Isolated yields.

Table 4 Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*] xanthen-11-ones catalyzed by [PVP-SO_3H] Cl

					Mp (°C)	
Entry	Ar	R	Time (min)	Yield[a] (%)	Found	Reported
1	4-ClC_6H_4–	CH_3	5	94	185–187	185–187 (ref. 26)
2	3-BrC_6H_4–	CH_3	10	93	163–165	161–164 (ref. 34)
3	4-BrC_6H_4–	CH_3	4	96	179–181	180–182 (ref. 36)
4	2-$CH_3OC_6H_5$–	CH_3	20	91	159–161	163–165 (ref. 44)
5	4-$CH_3OC_6H_5$–	CH_3	10	94	198–200	201–203 (ref. 34)
6	4-OHC_6H_4–	CH_3	30	93	149–151	150–151 (ref. 22)
7	2-Naphtyl-	CH_3	10	95	214–216	213–215 (ref. 36)
8	4-ClC_6H_4–	H	10	93	201–203	205–206 (ref. 22)
9	4-BrC_6H_4–	H	10	94	199–201	208–209 (ref. 45)
10	4-OHC_6H_4–	H	35	93	262–264	269–270 (ref. 45)

[a] Isolated yields.

Table 5 Comparison of the results obtained from the synthesis of 9-phenyl-3,3,6,6-tetramethyl-1,8-dioxooctahydro xanthenes, 14-phenyl-14*H*-dibenzo[*a*,*j*]xanthenes, 12-(4-chlorophenyl)-8,9,10,12-octahydrobenzo[*a*]xanthene-11-one in the presence of [PVP-SO_3H] Cl with those obtained using other catalysts

Product	Catalyst (loading)	Reaction conditions	Time (min)	Yield (%)
	$FeCl_3 \cdot 6H_2O$ (10 mol%)	80 °C/[bmim][BF_4]	6 h	92 (ref. 16)
	Amberlyst-15 (200 mg)	Reflux/CH_3CN	5 h	92 (ref. 18)
	Silica sulfuric acid (30 mg)	80 °C/Solvent free	60	97 (ref. 19)
	Selectfluor™ (10 mol%)	120 °C/Solvent free	60	95 (ref. 20)
	Polytungstozincate acid (50 mg)	80 °C/Solvent free	40	94 (ref. 21)
	Cellulose sulfonic acid (50 mg)	110 °C/Solvent free	5 h	94 (ref. 25)
	β-cyclodextrin (1 mmol)	60 °C/H_2O	10 h	96 (ref. 27)
	Succinimide-*N*-sulfonic acid (5.6 mol%)	80 °C/Solvent free	35	92 (ref. 30)
	[bmim][HSO_4] (42 mol%)	80 °C/Solvent free	3 h	85 (ref. 33)
	SBSSA (30 mg)	Reflux/EtOH	10 h	98 (ref. 35)
	N-sulfonic acid PVP Cl (20 mg)	100 °C/Solvent free	10	97 (ref. 36)
	[PVP-SO_3H] Cl (10 mg)	120 °C/Solvent free	3	94 (This work)
	Sulfamic acid (10 mol%)	125 °C/Solvent free	8 h	93 (ref. 17)
	Silica sulfuric acid (30 mg)	80 °C/Solvent free	45	89 (ref. 19)
	Polytungstozincate acid (50 mg)	80 °C/Solvent free	60	81 (ref. 21)
	Saccharin sulfonic acid (15 mol%)	120 °C/Solvent free	70	94 (ref. 29)
	P(4-VPH)HSO_4 (10 mg)	100 °C/Solvent free	55	94 (ref. 31)
	SO_3H-functionalized MCM-41 (20 mg)	80 °C/Solvent free	60	90 (ref. 32)
	N-sulfonic acid PVP Cl (20 mg)	100 °C/Solvent free	30	80 (ref. 36)
	PVPP-BF_3 (50 mg)	120 °C/Solvent free	90	94 (ref. 37)
	[PVP-SO_3H] Cl (40 mg)	120 °C/Solvent free	6	93 (This work)
	$H_3PW_{12}O_{40}$ (5 mol%)	60 °C/Solvent free	60	92 (ref. 22)
	I_2 (10 mol%)	60 °C/Solvent free	60	95 (ref. 23)
	*p*TSA (20 mol%)	120 °C/Solvent free	35	86 (ref. 24)
	NH_2SO_3H (20 mol%)	120 °C/Solvent free	95	84 (ref. 26)
	TrCl (7 mol%)	110 °C/Solvent free	45	90 (ref. 34)
	N-sulfonic acid PVP Cl (20 mg)	130 °C/Solvent free	30	90 (ref. 36)
	[PVP-SO_3H] Cl (40 mg)	120 °C/Solvent free	5	94 (This work)

the reaction times and yields which clearly demonstrates practical recyclability of this catalyst (Fig. 6).

The simple and efficient preparation of symmetric and asymmetric xanthenes including 1,8-dioxooctahydroxanthenes, 14-aryl-14*H*-dibenzo[*a*,*j*] xanthenes and 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones. The catalyst shows high thermal stability and was recovered and reused without any noticeable loss of activity. Furthermore, high reaction rates, no side reactions, ease of preparation and handling of the catalyst, simple experimental procedure, use of inexpensive and reusable catalyst with lower loading and solvent free conditions are the other advantages of this method. Further studies on some more practical applications of the [PVP-SO_3H] Cl catalyst in the other organic reactions are currently underway in our laboratory.

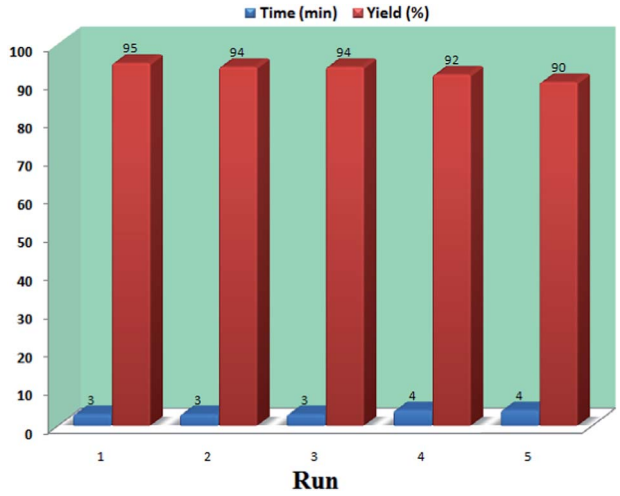


Fig. 6 Recyclability of [PVP-SO_3H] Cl in the synthesis of 9-(4-chlorophenyl)-3,3,6,6-tetramethyl-1,8-dioxooctahydro xanthene (Table 2, Entry 2).

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