Original Article: An Efficient Procedure for the Synthesis of Xanthenediones and (Arylmethylene) Bis (Naphthalene-2-yl-Sulfane) Derivatives Using PVPP-*p*-TSA as a Catalyst

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Abstract

Extensive biological activities associated with xanthenes, both synthetic and naturally occurring, ensure that the synthesis of these compounds remains a topic of current interest. In this research, efficient methods for the synthesis of some bulky xanthenediones was developed by the reaction of dimedone or 1,3-cyclohexadione with aledydes or bisaldehydes in the presence of polyvinylpolypyrrolidone supported *p*-toluene sulfonic acid (PVPP-*p*-TSA) as a new polymeric catalyst in ethanol at room temperature. Forthermore, a convenient method for the synthesis of (arylmethylene)bis(naphthalene-2-yl-sulfane) derivatives by polyvinylpolypyrrolidone supported *p*-toluene sulfonic acid (PVPP-*p*-TSA) is described. The reaction proceeded via condensation of aldehydes with 2-thionaphthol in the presence of PVPP-*p*-TSA in ethanol at reflux conditions. All synthesized compounds were identified by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. Polyvinylpolypyrrolidone supported *p*-toluene sulfonic acid (PVPP-*p*-TSA) was characterized via Fourier transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Clean methodologies, simple preparation of the catalyst, high yields, environment-friendly and reusable catalyst are some advantages of this work.

Introduction

Xanthenes exhibit a broad biological activities, such as trypanothione reductase enzyme inhibition (Chibale *et al*., 2003), antiviral activity (Jamison *et al*., 1990), antibacterial (Singh *et al*., 2014; Evangelinou *et al*., 2014; Yunnikova *et al*., 2011), antiplasmodial (Azebaze *et al*., 2006: Zelefack *et al*., 2009), anticancer (Tao *et al*., 2009; Rewcastle *et al*., 1991; Niu *et al*., 2012; Lee *et al*., 2003), antimalarial (Laphookhieo *et al*., 2006), antifungal (Djoufack *et al*., 2010), and antihypertensive activities (Diniz *et al*., 2013), and also have industrial usage (Knight *et al*, 1989) and applications such as use as fluorescent dyes (e.g., fluorescein, rhodamine-b and eosin Y) (Li *et al*., 2014). Because of these important biological properties, many preparation methods for xanthenes have been described in the literature. One of the commonly used methods reported for the synthesis of xanthene derivatives involves the condensation of aldehydes with dimedon. This reaction can be carried out in the presence of diammonium hydrogen phosphate (Darviche *et al.,* 2007), InCl3.4H2O (Fan *et al*., 2005), FeCl3.6H2O/[Hmim]BF4 (Fan *et al*., 2005), silica sulfuric acid (Seyyedhamzeh *et al*., 2008), amberlyst-15 (Das *et al*., 2006), Fe3+–montmorillonite (Song *et al*., 2007), SbCl3/SiO2 (Zhang *et al*., 2008), SiO2-R-SO3H (Mahdavinia *et al*., 2009), L-proline (Bhattacharjee et al., 2017), PVPP-BF3 (Mokhtary and Mirfarjood Langroudi 2014), TPA/PAA (Nasr-Esfahani *et al*., 2016), [H-NMP]+[HSO4]- (Naeimi, and Nazifi 2014), [DDPA][HSO4] (Fang *et al*., 2011), SBNPSA (Rashedian *et al*., 2010), CAN/HY-zeolite (Sivaguru and Lalitha 2014), HOSA (Zolfigol, and Yarie 2016), SnCl2.2H2O (Karami *et al*., 2014), FeCl3-rice

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husk (Shirini *et al*., 2013), TiO2 NPs (Eidi *et al*., 2015), nano-ZnFe2O4 (Das *et al*., 2014), and nano-CuFe2O4@SO3H (Vajar and Mokhtary 2019), dicationic Brönsted ionic liquid ([SO3H–Pyrazine–SO3H]Cl2) (Sadati *et al*., 2020), ZnO nanorods decorated graphene oxide (GO/ZnO) (Hasanzadeh Banakar *et al*., 2018), VOSO4 (Ghatak *et al*., 2020), and boric acid under ultrasound conditions (Shashi *et al*., 2021).

The protection of carbonyl groups as dithioacetals is a common and popular practice in organic chemistry (Kocienski 2003). The importance of thioacetals is due in part to their inherent stability under usual acidic or basic conditions and because of their behavior as masked acyl anions or methylene functions (Page *et al*., 1989). In connection of our interest in the utilized of polyvinylpolypyrrolidone as an insoluble solid support for preparation of new polymeric catalyst in some organic reactions (Mokhtary and Refahati 2013; Yosefzadehand Mokhtary 2016; Goudarzvand Cheginiand Mokhtary 2017), herein, an efficient method for the synthesis of some novel xanthenediones and (arylmethylene)bis(naphthalene-2-yl-sulfane) derivatives were developed by the reaction of 1,3-dicarbonyl compounds or 2-thionaphthol with aledydes in the presence of polyvinylpolypyrrolidone supported p-toluene sulfonic acid (PVPP-p-TSA) as a new polymeric catalyst in ethanol respectively (Scheme 1)
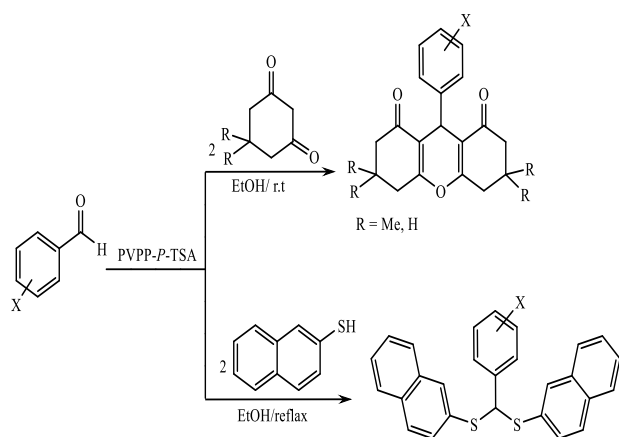
Scheme 1 Synthesis of xanthenediones and (arylmethylene) bis (naphthalene-2-yl-sulfane) derivatives catalyzed by PVPP-*p*-TSA.

Experimental

General

High-purity chemical reagents were purchased from the Merck Chemical Company. Melting points were determined using an Electrothermal Mk3 apparatus and were uncorrected. NMR spectra were recorded in DMSO-d_6 on a Bruker Avance DRX-400 MHz instrument spectrometer using TMS as internal standard. Fourier transform infrared (FT-IR) spectra were performed in the transmission mode (Shimadzu, SP-1100, P-UV-Com instrument) on powder samples which were ground with KBr and compressed into a pellet. The thermal stability was determined by thermogravimetric analysis (TGA, Mettler Toledo). The TGA thermogram were recorded at a heating rate of 10 °C/min in the temperature ranging from the room temperature to 600 °C in an inert atmosphere. Scanning Electron Microscopy (SEM) analysis was performed, in order to investigate the microstructure of the sample using digital scanning microscope VEGA model.

Preparation of the Catalyst

To a suspension of PVPP (1 g) in ethyl acetate (25 mL), a solution of *p*-toluenesolfonic acid (1.72 g, 10 mmol) in ethyl acetate (15 mL) was added dropwise and the mixture was stirred for 1 h at room temperature. The resulting residuum was filtered and washed with ethyl acetate (2×10 mL) and dried in a vacuum desiccator to give PVPP-*p*-TSA as a stable powder.

General Method for the Preparation of Xanthenediones

A mixture of dimedon or 1,3-cyclohexadione (2 mmol), aromatic aldehyde (1 mmol) and PVPP-*p*-TSA (0.05 g) was stirred at room temperature in ethanol (5 mL) for the suitable time, as shown in Table 2. After completion of the reaction, the reaction mixture was cooled to room temperature, and the PVPP-*p*-TSA was filtered off. The crude solid residue was recrystallized from ethanol to obtain pure crystals of the appropriate xanthenediones in 88-97% yields. All products were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and physical constants.

General Method for the Synthesis of (Arylmethylene) Bis (Naphthalene-2-yl-sulfane) Derivatives

A mixture of 2-thionaphthol (2 mmol), aromatic aldehyde (1 mmol) and PVPP-*p*-TSA (0.05 g) was stirred at reflux condition in the ethanol (5 mL) for the suitable time, as shown in Table 5. Completion of

the reaction was indicated by TLC monitoring. The reaction mixture was cooled to room temperature, and the PVPP-*p*-TSA was filtered off. The filtrate was concentrated to dryness, and the crude solid residue was recrystallized from ethanol to obtain pure crystals of the bis (naphthalen-2-yl-sulfane) derivatives in 90-97% yields.

Spectral Data of the New Products

9-(2-hydroxyphenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3i): White solid; m.p. 231-233 °C; FT-IR (KBr) cm⁻¹: v = 773, 1294, 1554, 1573, 1639, 2877, 2950, 3436; ¹H NMR (300 MHz, CDCl₃): δ 1.67-1.78 (m, 2H, CH₂), 1.81-1.99 (m, 2H, CH₂), 2.24-2.26 (m, 6H, 3CH₂), 2.51-2.58 (m, 2H, CH₂), 5.10 (s, 1H, CH), 6.94 (s, 1H, Ar), 6.97-7.00 (m, 3H, Ar), 7.08-7.14 (m, 1H, Ar), 10.53 (s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃): δ 21.3, 27.8, 29.3, 31.7, 36.6, 113.9, 115.8, 121.0, 122.3, 127.1, 131.0, 155.1, 157.0, 198.7.

9-(1H-indol-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3j): Yellow solid; m.p. 173-175 °C; FT-IR (KBr) cm⁻¹: v = 730, 1203, 1454, 1544, 1656, 1676, 2891, 2943, 3055, 3409; ¹H NMR (300 MHz, CDCl₃): δ 1.77-1.86 (m, 2H, CH₂), 1.92-2.00 (m, 2H, CH₂), 2.24-2.31 (m, 4H, 2CH₂), 2.62-2.69 (m, 4H, 2CH₂), 4.89 (s, 1H, CH), 6.93-7.04 (m, 3H, Ar), 7.26 (d, *J* = 7.5 Hz, 1H, Ar), 7.56 (d, *J* = 7.5 Hz, 1H, Ar), 10.80 (s, 1H, NH); ¹³C NMR (75 MHz, CDCl₃): δ 21.1, 29.3, 36.5, 38.6, 105.7, 111.1, 113.9, 118.7, 119.6, 121.7, 123.1, 127.3, 136.4, 155.0, 198.8.

4-(2-(4-(3,3,6,6-tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl) phenoxy) ethoxy)benzaldehyde (3k): Yellow solid; m.p. 198-200 °C; FT-IR (KBr) cm⁻¹: v = 837, 1249, 1575, 1598, 1662, 2720, 2896, 2931; ¹H NMR (300 MHz, CDCl₃): δ 1.01 (s, 6H, 2CH₃), 1.12 (s, 6H, 2CH₃), 2.21-2.24 (m, 4H, 2CH₂), 2.48 (s, 4H, 2CH₂), 4.21-4.40 (m, 2H, CH₂), 4.72 (s, 1H, CH), 6.78-6.84 (m, 2H, Ar), 7.04 (d, 2H, *J* = 8.7 Hz, Ar), 7.20-7.29 (m, 2H, Ar), 7.83 (d, 2H, *J* = 8.7 Hz, Ar), 9.91 (s, 1H, CHO); ¹³C NMR (75 MHz, CDCl₃): δ 27.5, 32.2, 38.1, 39.0, 68.8, 113.9, 114.2, 114.9, 128.4, 129.8, 131.8, 136.8, 155.0, 156.5, 168.3, 191.0, 198.7.

4-(4-(4-(1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl)phenoxy)butoxy)benzaldehyde (3l): Yellow solid; m.p. 165-167 °C; FT-IR (KBr) cm⁻¹: v = 831, 1255, 1575, 1598, 1670, 2720, 2869, 2947; ¹H NMR (300 MHz, CDCl₃): δ 1.94-2.08 (m, 8H, 4CH₂), 2.33-2.39 (m, 4H, 2CH₂), 2.58-2.67 (m, 4H, 2CH₂), 3.95-4.01 (m, 2H, CH₂), 4.11-4.17 (m, 2H, CH₂), 4.78 (s, 1H, CH), 6.75-6.79 (m, 2H, Ar), 7.00-7.04 (m, 2H, Ar), 7.20-7.25 (m, 2H, Ar), 7.84-7.88 (m, 2H, Ar), 9.91 (s, 1H, CHO); ¹³C NMR (75 MHz, CDCl₃): δ 20.3, 25.8, 27.1, 30.7, 37.0, 67.1, 114.0, 114.8, 117.0, 129.3, 132.0, 136.6, 157.4, 163.8, 164.1, 190.9, 196.7.

*2-(4-(2-(1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl)phenoxy)butoxy)benzaldehyde (3m):* Yellow solid; m.p. 221-223 °C; FT-IR (KBr) cm⁻¹: v = 754, 1288, 1598, 1618, 1676, 2710, 2873, 2950; ¹H NMR (300 MHz, CDCl₃): δ 1.78-2.02 (m, 8H, 4CH₂), 2.19-2.26 (m, 4H, 2CH₂), 2.52-2.57 (m, 4H, 2CH₂), 3.96-4.02 (m, 2H, CH₂), 4.25 (m, 2H, CH₂), 4.67 (s, 1H, CH), 6.77-6.82 (m, 1H, Ar), 6.88-6.92 (m, 1H, Ar), 7.05 (t, *J* = 7.5 Hz, 2H, Ar), 7.20-7.29 (m, 2H, Ar), 7.43-7.63 (m, 2H, Ar), 10.40 (s, 1H, CHO); ¹³C NMR (75 MHz, CDCl₃): δ 20.4, 25.9, 27.0, 30.3, 36.9, 56.5, 67.6, 68.5, 112.5, 114.0, 114.5, 119.8, 121.0, 124.7, 127.9, 128.0, 131.0, 132.9, 136.9, 157.7, 161.5, 164.9, 165.0, 189.5, 196.5.

9,9'-((ethane-1,2-diylbis(oxy)) bis (3,1-phenylene)) bis (3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione) (3n): Yellow solid; m.p. 156-158 °C; FT-IR (KBr) cm⁻¹: v = 696, 1195, 1595, 1662, 2682, 2873, 2956; ¹H NMR (300 MHz, CDCl₃): δ 1.03 (s, 12H, 4CH₃), 1.12 (s, 12H, 4CH₃), 2.23 (d, *J* = 2.7 Hz, 8H, 4CH₂), 2.49 (d, *J* = 2.1Hz, 1H), 4.28(s, 4H, 2CH₂), 4.77 (s, 2H, 2CH), 6.70-6.73 (m, 2H, Ar), 6.91-6.96 (m, 2H, Ar), 7.13-7.18 (m, 2H, Ar), 7.29 (s, 2H, Ar); ¹³C NMR (75 MHz, CDCl₃): δ 27.5, 29.1, 32.2, 40.8, 50.7, 66.3, 112.4, 114.9, 115.5, 121.4, 128.9, 145.7, 158.5, 162.3, 196.4.

4-(bis(naphthalen-2-ylthio)methyl)-2-methoxyphenol (3x): White solid; m.p. 129-131 °C; FT-IR (KBr) cm⁻¹: v = 632, 858, 1203, 1458, 1506, 1591, 2923, 3047, 3434; ¹H NMR (300 MHz, CDCl₃): δ 3.68 (s, 3H, OCH₃), 6.36 (s, 1H, CH), 6.72 (d, *J* = 8.1 Hz, 1H, Ar), 7.04 (dd, *J* = 10, 1.8 Hz, 1H, Ar), 7.17 (d, *J* = 1.8 Hz, 1H, Ar), 7.47-7.59 (m, 6H, Ar), 7.82-7.89 (m, 6H, Ar), 9.14 (s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃): δ 55.9, 56.8, 126.7, 127.1, 127.7, 128.7, 129.9, 130.0, 132.2, 132.5, 133.5, 146.9, 147.

Results and Discussion

In this research, PVPP-*p*-TSA was prepared by simple reaction of *p*-toluenesolfonic acid with the polyvinylpolypyrrolidone (Scheme 2).
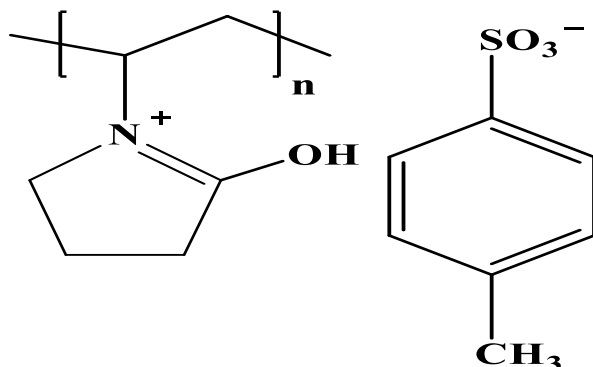
Scheme 2 The chemical structure of PVPP-*p*-TSA

Identification of the polyvinylpolypyrrolidone immobilized *p*-toluenesolfonic acid was performed by recording the Fourier transform infrared spectroscopy (FT-IR) spectrum of PVPP-*p*-TSA. According to FT-IR analysis of PVPP-*p*-TSA, the symmetric and unsymmetric stretching vibrations of SO_2 were observed at 118 and 1215 cm^{-1} respectively. The stretching vibrations of C=O was observed at 1652 cm^{-1}, and the hydroxyl stretching vibrations was observed at 3343 cm^{-1}. These results presented the evidences that *p*-toluenesolfonic acid was successfully connected to the polyvinylpolypyrroli done. Furthermore, the pH of the catalyst solution (0.20 g) in water (5 mL) was equal to 2.1.

The thermal behavior of PVPP-*p*-TSA was shown in Fig. 1. The thermal analysis PVPP-*p*-TSA showed two main decreasing peaks. PVPP-p-TSA thermal analysis data showed that the catalyst was stable up to 240 ° C. With increasing temperature up to 300 °C, due to the removal of the sulfonyl group from the polymer surface, a significant reduction in the thermal stability of the catalyst was created.

Morphological study of PVPP-*p*-TSA surface was examined by scanning electron microscope (Fig. 2). The SEM image of the PVPP-P-TSA catalyst exhibits the same morphology without phase separation at the catalyst surface, which suggests the immobilization of *p*-toluene sulfonic acid on the polyvinylpyrroli done is uniform.

The elemental composition of the SEM PVPP-*P*-TSA image was presented in Figure 3. The EDX spectrum shows the presence of N, O, and S in the catalyst.

To optimize the reaction conditions and obtain the best catalytic activity, the reaction of dime done and 4-chlorobenzaldehyde was investigated as a model reaction in several solvents. In this study, it was observed that PVPP-*P*-TSA is more effective in ethanol at room temperature than the reaction time and yields of the desired product (Table 1).

After optimizing the reaction conditions, a diversity of xanthenediones was prepared using PVPP-*P*-TSA at high yields (Table 2, entries 1-10). Reactions worked well with all aldehyds that had electron donor or electron-withdrawing substituents. In addition, PVPP-*P*-TSA was successfully used to perform the reaction of 2,2'-(butane-1,4-diylbis(oxy)) dibenzaldehyde or 4,4'-(butane-1,4-diylbis(oxy)) dibenzaldehyde or 4,4'-(ethane-1,2-diylbis(oxy)) dibenzaldehyde and dime done or 1,3-cyclohexadione in ethanol at ambiant temperature to provide new xanthenediones with excellent yields (Scheme 3). Furthermore, a new bis xanthenedione 3n was successfully prepared by the reaction of 3,3'-(ethane-1,2-diylbis(oxy)) dibenzaldehyde and dime done (1:4) in ethanol at ambiant temperature after 2h with %95 yields (Scheme 4).

In the next experiment, PVPP-*p*-TSA was used to perform the reaction of arylaldehydes and 2-thionaphthol to obtain a series of (arylmethylene) bis (naphthalene-2-yl-sulfane) derivatives in excellent yields. To optimize the reaction conditions and obtain the best catalytic activity, the reaction of benzaldehyde and 2-thionaphthol was investigated as a sample reaction in several solvents. In this study, it was found that PVPP-*p*-TSA in ethanol at reflux conditions is more effective with respect to the efficiency of the desired product (Table 3).

To evaluate the effect of the catalyst, the model reaction was also performed by different amounts of PVPP-*p*-TSA. It was considered that the variation of the catalyst had an effective influence on the reaction efficiency. The result showed the best amount of PVPP-*p*-TSA is 0.05g which provides the required product with excellent yields (Table 4).
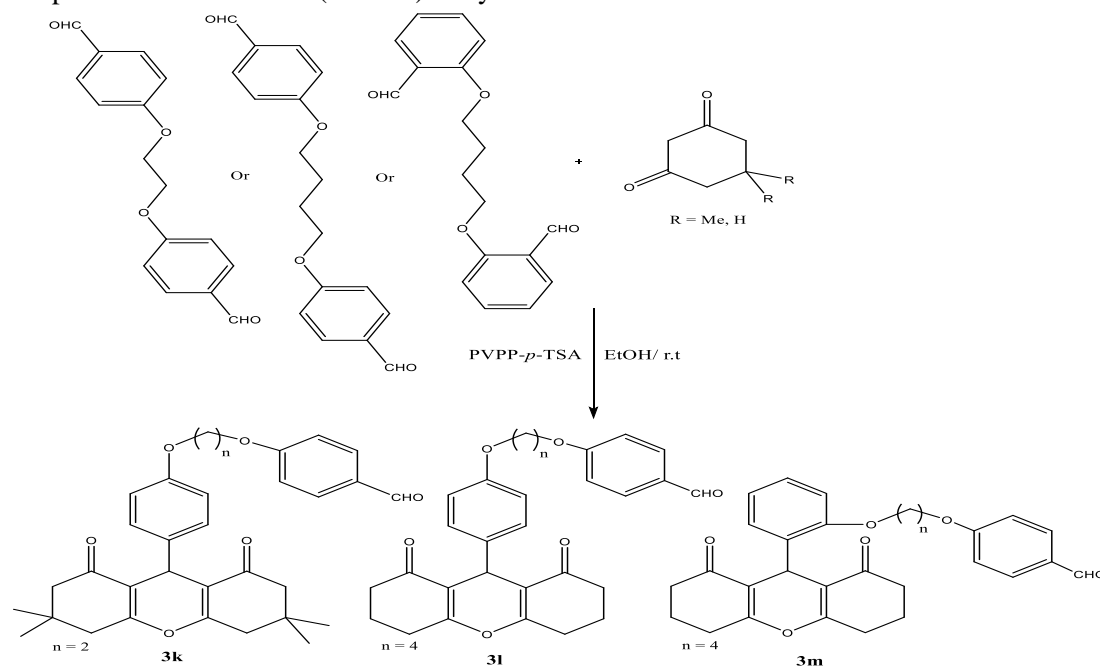
By these optimal reaction conditions, a variety of (arylmethylene) bis (naphthalene-2-yl-sulfane) derivatives were prepared from aldehydes and 2-thionaphthol using of PVPP-*p*-TSA as a reusable catalyst (Table 5).

To evaluate the reusability of the catalyst, it was used in the synthesis of 3a and 3o, four cycles under the optimal conditions. The catalyst powder was

recovered by simple filtration and washed with dichloromethane. Then, depending on the amount of catalyst, the required amount of fresh dime done or 2-thionaphthol and benzaldehyde was added. The results showed that the catalyst could be reused four times without efficiency considerable loss of its catalytic activity (Table 6).

Compounds 3a and 3o were compared with some reported in the literature (Table 7). As you can see, our results show a very good comparison with the previously reported data that all terms, including efficiency, reaction time, and reaction conditions are considered.

To evaluate the efficiency of the present procedure for the synthesis of xanthenediones and (arylmethylene) bis (naphthalene-2-yl-sulfane) derivatives, compounds 3a and 3o were compared with some reported in the literature (Table 7). As you

can see, our results show a very good comparison with previously reported data that all terms, including, reaction times, and reaction conditions are considered.

Table 1 Synthesis of 3b in different solvents[a]

Entry	Solvent	Yield (%) b
1	MeCN	75
2	EtOH (96%)	97
3	MeOH	76
5	H_2O	70
6	$CHCl_3$	60

[a]Reaction conditions: Dimedone (2 mmol), 4. Chlorobenzaldehyde (1 mmol), PVPP-*P* TSA (0.05 g) at room temperature after 1 h. [b]Isolated yields.
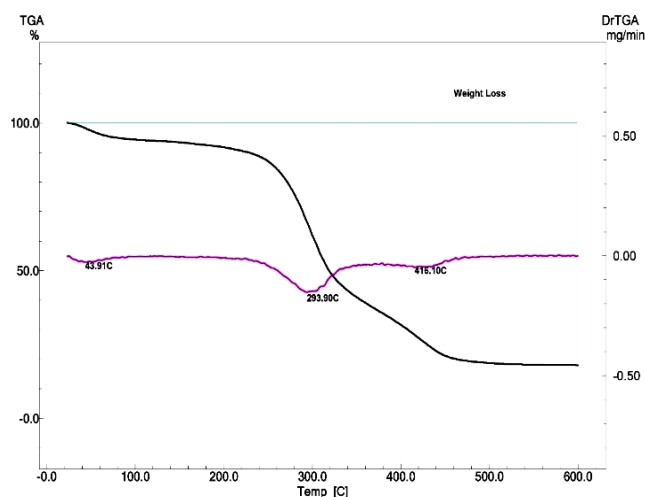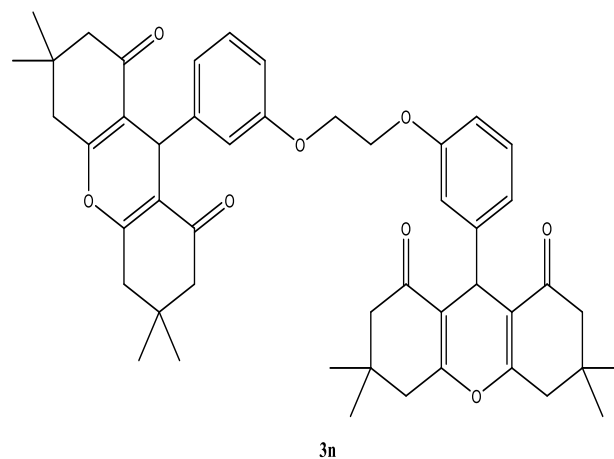

Scheme 3 Synthesis of novel xanthenediones by PVPP-*P*-TSA.

Table 2 Synthesis of xanthenediones by PVPP-*P*-TSA.[a]

R	X	Product	Time (h)	Yields (%)[b]	Mp °C Found	Mp °C Reported
Me	H	3a	1	96	201-202	201-202 [26]
Me	4-Cl	3b	1	97	229-231	230-232 [26]
Me	4-Br	3c	1	97	242-243	242-244 [26]
Me	$3-NO_2$	3d	1	94	165-167	166-168 [26]
Me	$4-NO_2$	3e	1	95	225-226	226-228 [26]
Me	2-OH	3f	1.5	89	204-206	203-206 [35]
Me	4-CHO-Ph	3g	1.5	90	210-212	211-213 [27]
Me	3-Br	3h	2	92	192–194	190–192 [26]
H	2-OH	3i	2	88	231-233	--------
H	Indole	3j	1.5	90	173-175	-------

[a]Reaction conditions: Dimedone or 1,3-cyclohexadione (2 mmol), aldehyde (1 mmol), PVPP-*P*-TSA (0.05 g), ethanol (5 ml) at room temperature. [b]All yields refer to isolated products.

Fig. 1 The thermal analysis diagram of PVPP-*p*-TSA
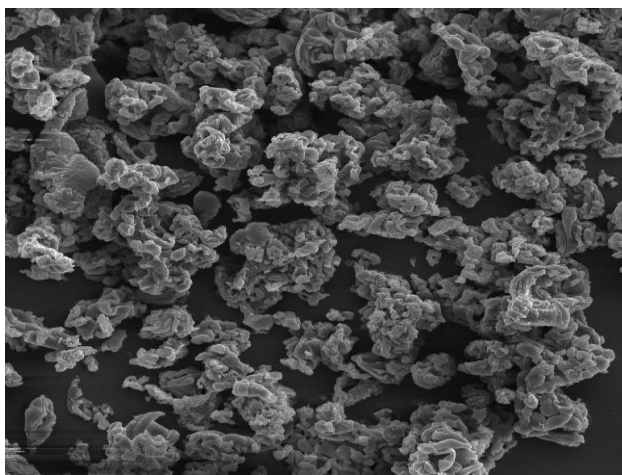

Scheme 4 The chemical structure of bis xanthenedione
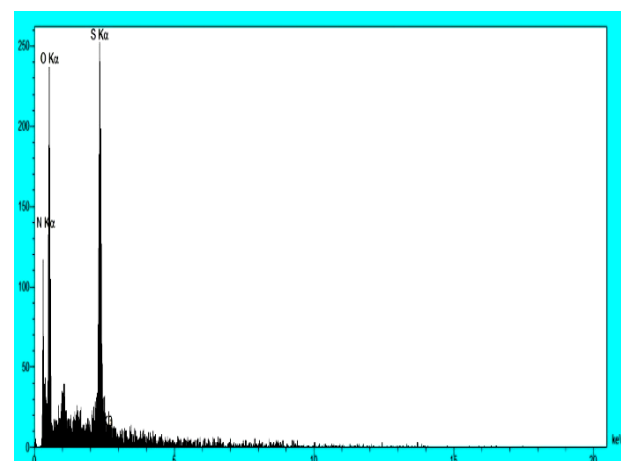

Fig. 2 SEM image of PVPP-*P*-TSA

Table 3 Synthesis of 3o by PVPP-*p*-TSA in different solvents[a]

Entry	Solvent	Yield (%) [b]
1	Solvent-free	55
2	CH$_3$CN	62
3	EtOH	96
4	MeOH	78

[a]Reaction conditions: benzaldehyde (1 mmol) and 2-thionaphthol (2 mmol) at reflux conditions.
[b]Isolated yields.

Table 4 Synthesis of 3o in different amounts of the catalyst[a]

Entry	PVPP-*p*-TSA (g)	Yield (%) [b]
1	0.02	45
2	0.03	60
3	0.04	85
4	0.05	96

[a]Reaction conditions: benzaldehyde (1 mmol) and 2-thionaphthol (2 mmol) in ethanol (5 mL) at reflux conditions.
[b]Isolated yields

Fig. 3 The EDX spectrum of PVPP-*P*-TSA

Table 5 Synthesis of (arylmethylene)bis(naphthalene-2-yl-sulfane) derivatives by PVPP-*p*- TSA[a]

Entry	X	Product	Time (h)	Yield (%) [b]	m.p. °C	
					ound	Reported [44]
1	C_6H_5	3o	2.5	95	136-138	135-138
2	4-Cl-C_6H_4	3p	2	96	109-111	108-110
3	4-Br-C_6H_4	3q	2	97	111-112	110-112
4	2,4-Cl_2-C_6H_4	3r	2	96	88-90	89-90
5	3,5-Cl_2-C_6H_4	3s	2	95	126-128	125-128
6	3-NO_2-C_6H_4	3t	2	97	156-158	155-158
7	2-MeO-C_6H_4	3u	2.5	90	78-80	78-81
8	4-MeO-C_6H_4	3v	2.5	92	94-96	95-96
9	3-MeO-C_6H_4	3w	2.5	94	137-139	138-139
10	4-HO-3-MeO-C_6H_4	3x	2	96	129-131	------

[a]Reaction and conditions: aldehyde (1 mmol), 2-thionaphthol (2 mmol), and PVPP-*P*-TSA (0.05 g), ethanol (5 ml) at reflux conditions.
[b]All yields refer to isolated products.

Table 6 The recycling of PVPP-*P*-TSA for the synthesis of 3a and 3o[a]

Run	1	2	3	4
Yield (%)	96 (95) a	94 (93) a	92 (91) a	90 (89) a

Table 7 Comparison of PVPP-*P*-TSA with some other catalysts for synthesis of 3a and 3o.

Entry Product	Catalyst	Reaction conditions	Time/h	Yield (%)	Ref.
3a	SiO_2-R-SO_3H	80 °C	4.5	75	[24]
3a	Amberlyst-15	CH_3CN/reflux	5	86	[21]
3a	Fe^{3+}-montmorillonite	EtOH/reflux	6	94	[22]
3a	PVPP-BF_3	CH_3CN/rt	4	94	[26]
3a	$FeCl_3.6H_2O$/[Hmim]BF_4	80 °C	6	92	[19]
3a	$SbCl_3$/SiO_2	120 °C	50 min	93	[23]
3a	TPA/PAA	100 °C	30 min	93	[27]
3a	HOSA	90 °C	35 min	92	[32]
3a	TiO_2 NPs	80 °C	20 min	92	[35]
3a	[H-NMP]$^+$[HSO_4]$^-$	H_2O/))))	50 min	86	[28]
3a	$SnCl_2.2H_2O$	100 °C	1	96	[33]
3a	$FeCl_3$-rice husk	100 °C	1	91	[34]
3a	DDPA[HSO_4]	H_2O/100 °C	1	93	[29]
3a	SBNPSA	EtOH/reflux	2	93	[30]
3a	CAN/Zeolit	80 °C	1.5	88	[31]
3o	PVPP-*P*-TSA	EtOH/rt	1	96	This work
3o	PVPP-BF_3	DCE/reflux	3.5	92	[44]
3o	PVPP-*P*-TSA	EtOH/70 °C	2.5	95	This work

Conclusions

Briefly, we present a single-pot prcedure for the preparation of some bulky xanthenediones and (arylmethylene)bis(naphthalene-2-yl-sulfane) derivatives in the presence of polyvinylpolypyrrolidone immobilized *p*-toluene sulfonic acid (PVPP-*p*-TSA) as a novel polymeric catalyst in ethanol at ambient temperature. High efficiency and simple method are the advantages of this prcedure.

Acknowledgements

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