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ORIGINAL PAPER

A novel polymeric catalyst for the one-pot synthesis of xanthene derivatives under solvent-free conditions

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Abstract A simple, efficient, and environmentally benign route was developed for the preparation of 14-aryl or alkyl-14*H*-dibenzo[a,j]xanthene, 1,8-dioxo-octahydroxanthene and 12-aryl—8,9,10,12-tetrahydrobenzo[a]xanthene-11-ones from condensation of various aldehydes with (i) *β*-naphthol, (ii) cyclic 1,3-dicarbonyl compounds and (iii) *β*-naphthol and cyclic 1,3-dicarbonyl compounds, using novel polymeric catalyst [poly(AMPS-co-AA)] under solvent-free conditions. Use of easily available catalyst, shorter reaction times, better yields, simplicity of the reaction, heterogeneous system, and easy work-up are the advantages of the present method.

Keywords *β*-Naphthol · Aldehydes · Poly(AMPS-co-AA) · Cyclic 1 · 3-Dicarbonyl compounds · Solvent-free

Introduction

Xanthene and benzoxanthene have attracted considerable interests because of their wide range of antibacterial, antiviral and anti-inflammatory activities as well as phototoxicity and antagonist activity [1–3]. Some xanthene derivatives are used in industry, such as PH sensitive florescent material for the visualization of biomolecular assemblies [4, 5], in laser technologies due to their useful spectroscopic properties [6], in photodynamic therapy [7], as dyes [8] and antagonists for the paralyzing action of zoxazolamine [9]. Xanthenedione derivatives are valuable synthons because of the inherent reactivity of the inbuilt pyran ring [10]. They are also found as core units in several natural products [11].

Polymer-supported reagents have been in use since 1946, and have been the subject of many review articles [12, 13]. Synthesis using these reagents is attractive and suitable for parallel synthesis because the reactions often proceed with high yields, and the work-up involves simple filtration and evaporation of the solvent. Polymeric reagents can also be used in flow systems [14]. Moreover, the reactions using polymer-supported reagents were carried out with the reagents in "T-bags" so that when each particular reaction was completed the "T-bag" was simply removed and washed [15]. Therefore, it is reasonable to assume that polymeric reagents will be employed with increasing regularity to conduct one to multistage synthetic sequences. To facilitate this mentioned use, the technique requires rapid development, particularly in the following areas: (i) the search for new functionalized polymers, and (ii) the development of new solid supports with properties specifically optimized for the synthetic procedure. Two approaches exist for the preparation of functional polymers, the polymerization or copolymerization of monomers which carry out the desired functionality, and the chemical modification of performed polymers. With these assumptions, during the course of systematic study on the development of supported reagents and catalysts for the organic transformation [16], we decided to investigate poly(2-acrylamido-2-methyl propane sulphonic acid) (AMPS) crosslinked with *N*,*N*′-methylene bisacrylamide (MBA) as a novel catalyst for the synthesis of xanthene derivatives.

Because of their wide range of pharmacological activity and also their industrial and synthetic applications, several

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methods have been reported for the synthesis of xanthene and benzoxanthene, which include trapping of benzynes by phenols [17, 18], cyclodehydration [19], cyclocondensation between 2-hydroxyaromatic aldehydes and 2-tetralone [20], and intramolecular phenyl carbonyl coupling reactions of benzaldehyde and acetophenones [21]. Also, 14-aryl or alkyl-14*H*-dibenzo [a,j]xanthene and related products have been prepared by the reaction of β-naphthol with formamide [22], 2-naphthol-1-methanol [23] and carbon monoxide [24]. Among these methods, the condensation reaction of aldehydes with (i) β-naphthol (ii) cyclic 1,3-dicarbonyl compounds and (iii) β-naphthol and cyclic 1,3-dicarbonyl compounds is one of the most simple and straightforward approaches for the synthesis of 14-aryl or alkyl-14*H*-dibenzo[a,j]xanthene, 1,8-dioxo-octahydroxanthene and 12-aryl—8,9,10,12-tetrahydrobenzo[a]xanthene-11-ones, respectively. A variety of reagents such as P_2O_5/Al_2O_3 under microwave irradiation [25], silica sulfuric acid [26, 27], boric acid [28], $BF_3.SiO_2$ [29], oxalic acid [30], $TaCl_5$ [31], $KAl(SO_4)_2.12H_2O$ (alum) [32], tetrabutylammonium bromide [33], 1-methyl-3-propane-imidazolium hydrosulfate [34], methanesulfonic acid [35], $ZrOCl_2.8H_2O$ [36], polyaniline-*p*-toluenesulfonate salt [37], antimony trichloride. SiO_2 [38], trichloroisocyanuric acid [39], $NaHSO_4.SiO_2$ [40], *p*-TSA in ionic liquid ([bmim]BF_4) [41], $InCl_3$ or P_2O_5 [42, 43], strondium triflate [44], praline triflate [45], $HBF_4.SiO_2$ [46], 1-butyl-3-methylimidazolium hydrogen sulfate [bmim]HSO_4 [47], cellulose sulfuric acid [48], $HClO_4.SiO_2$ [49], $H_{14}[NaP_5W_{30}O_{110}]$ [50], cyanuric chloride [51, 52], Caros acid [53], nano-TiO_2 [54], and selectfluor^{TM} [1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2,2,2]octane bis(tetrafluoroborate) [55] have been employed to accomplish this transformation. Each of these methods involves the use of violent reaction conditions, long reaction times and tedious procedures which afford the product in poor yields. Thus, there is a certain need for the development of an alternative for the production of xanthene derivatives, which surpasses those limitations.

Experimental

IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer (KBr pellets). ^{1}H NMR spectra were obtained using Jeol FT NMR 90 MHz spectrometer in $CDCl_3$ using TMS as an internal reference. Melting points were determined in open capillary tubes in a Stuart BI Branstead Electrothermal Cat No:IA9200 apparatus and uncorrected.

Synthesis of crosslinked poly(AMPS-co-AA)

N,N′-methylene bisacrylamide (MBA, 2 g) as a crosslinker was added to the mixture of 2-acrylamido-2-methylpropane sulphonic acid (AMPS 10 g) and acrylic acid (AA 10 mL) in 100 ml distilled water. The solution was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type). The reactor was immersed in a thermostated water bath at 70 °C. An inert gas (nitrogen) was gently bubbled into the reactor to remove the oxygen. After 15 min, the ammonium persulphate solution (APS 0.2 g in 2 mL H_2O) was added to the mixture, and the mixture was allowed to stir (200 rpm) for 20 min. To remove probably unreacted monomer, 1 g of polymer was added to excess distilled water and the mixture allowed to stir gently for 72 h. Then, the polymer was filtered and poured to excess methanol and remained for 48 h. Then, methanol was decanted and the product divided into small pieces. Finally, the polymer was dried in oven. After grinding, the powdered polymer was kept away from moisture, heat and light. The IR spectrum of the polymer showed the characteristic absorption of acid (O–H) groups at 3,444 cm^{-1}, carbonyl groups at 1,654 cm^{-1} and R_2CH_2-SO_3^- (AMPS) at 1,206 cm^{-1} (Fig. 1).

Instrumental analysis

A simultaneous thermal analyzer (STA-625, Geometric Scientific) was used for thermo gravimetric analysis of

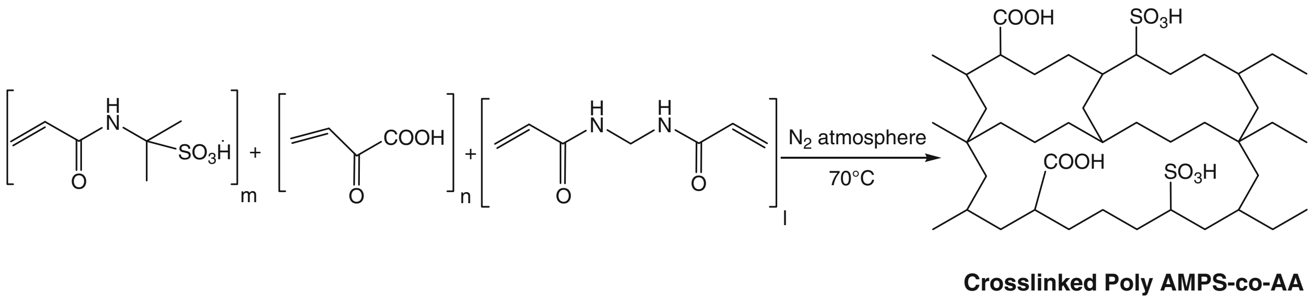


Fig. 1 The synthesis of crosslinked poly(AMPS-co-AA)

AA-co-AMPS polymer under nitrogen atmosphere. The heating rate was 20 °C/min. The sample weight taken for TG was 10.0 mg.

Thermal characterization

Thermal data obtained from TGA and DTGA traces are included in Fig. 2. The copolymer exhibits three distinct weight losses in its thermo gravimetric curve. The first one is in the range of 38–181 °C attributed to loss of water (9.3 wt%), and the two others are in the range of 183–335 °C with maximum decomposition rate at 297 °C (weight loss 47 %) and 187–496 °C with maximum decomposition rate at 416 °C (weight loss 82 %).

General procedure for the synthesis of xanthene derivatives using poly(AMPS-co-AA)

Synthesis of 14-aryl or alkyl-14H-dibenzo [a,j]xanthene

To a mixture of aldehyde (**1**, 1 mmol) and β-naphthol (**2**, 2 mmol), crosslinked poly(AMPS-co-AA) (0.04 g) was added and the mixture was heated on an oil bath at 110 °C for the reasonable time (Table 2). Completion of the reaction was indicated by TLC (hexane:ethyl acetate, 8:2). After completion, appropriate amounts of hot EtOH (96 %) were added and the mixture stirred for 10 min; then, the catalyst was separated by filtration. The filtrate was concentrated in vacuo to remove the ethanol. The residue was washed with cold water and crystallized from hot ethanol to afford the pure products. The desired pure product was characterized by making a comparison between its physical data and that known benzoxanthene.

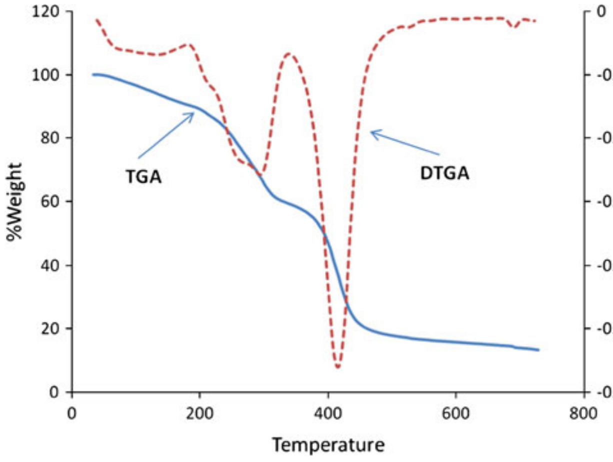


Fig. 2 TGA and DTGA thermo grams of AA-co-AMPS polymers. Heating rate 20 °C/min, under N_2

Synthesis of 1,8-dioxo-octahydroxanthene

To a mixture of β-naphthol (**2**, 1 mmol) and cyclic 1,3-dicarbonyl compounds (**4**, 2 mmol), crosslinked poly (AMPS-co-AA) (0.04 g) was added and the mixture was heated on an oil bath at 110 °C for the reasonable time. After completion of the reaction, hot ethanol was added to the mixture and then filtered. The residue was recrystallized from ethanol. The results obtained are showed in Table 3.

Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-ones

In a separate set of experiments, to a mixture of β-naphthol (**2**, 1 mmol), cyclic 1,3-dicarbonyl compounds (**4**, 1.2 mmol), and aldehyde (**1**, 1 mmol), crosslinked poly (AMPS-co-AA) (0.06 g) was added and the mixture was heated on an oil bath at 110 °C for the reasonable time and these reactions were all repeated exactly under the above same conditions. The results obtained are showed in Table 4.

Spectra data for selected compounds

Compound **3b**: ^1H NMR (100 MHz, $CDCl_3$) δ 6.52 (s, 1H), 7.44–8.40 (m, 19H). IR: (KBr disc) cm^{-1}: 3,010, 2,920, 1,580, 1,510, 1,480, 1,460, 1,420, 1,400, 1,240, 1,132.

Compound **3q**: ^1H NMR (90 MHz, $CDCl_3$) δ 3.64 (s, 3H), 6.48 (s, 1H), 6.94–7.62 (m, 15H), 8.07 (s, 1H). IR: (KBr disc) cm^{-1}: 3,060, 2,930, 1,590, 1,460, 1,420, 1,400, 1,240, 1,110, 800.

Compound **5h**: ^1H NMR (90 MHz, $CDCl_3$) δ 1.01 (s, 6H), 1.14 (s, 6H), 2.24 (m, 4H), 2.50 (m, 4H), 6.14 (s, 1H), 7.12–7.84 (m, 4 H). IR (KBr disc) cm^{-1}: 3,020, 2,982, 1,686, 1,662, 1,460, 1,402, 1,378, 1,240, 1,174.

Compound **5m**: ^1H NMR (90 MHz, $CDCl_3$) δ 1.04 (s, 6H), 1.26 (s, 6H), 2.01 (m, 4H), 2.25 (s, 3H), 2.46 (m, 4H), 5.63 (s, 1H), 6.64–7.16 (m, 4 H). IR (KBr disc) cm^{-1}: 3,040, 2,970, 2,920, 1,660, 1,620, 1,480, 1,460, 1,360, 1,200, 1,140, 1,000, 870.

Compound **5s**: ^1H NMR (90 MHz, $CDCl_3$) δ 2.01 (m, 4H), 2.12 (m, 4H), 2.42 (m, 4H), 4.86 (s, 1H), 7.01–7.92 (m, 3 H), 8.14 (s, 1H). IR (KBr disc) cm^{-1}: 3,005, 2,960, 2,890, 1,660, 1,615, 1,535, 1,460, 1,330, 1,200, 1,180, 1,120, 960, 840.

Compound **5t**: ^1H NMR (90 MHz, $CDCl_3$) δ 2.04 (m, 4H), 2.20 (m, 4H), 2.52 (s, 3H), 2.64 (m, 4H), 5.21 (s, 1H), 6.91–7.98 (m, 4 H). IR (KBr disc) cm^{-1}: 3,010, 2,970, 2,890, 1,646, 1,615, 1,480, 1,420, 1,360, 1,200, 1,180, 1,130, 960, 780.

Compound **5u**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 2.13 (m, 4H), 2.24 (m, 4H), 2.72 (m, 4H), 3.64 (s, 6H), 5.26 (s, 1H), 7.01–8.12 (m, 3 H). IR (KBr disc) cm^{-1}: 3,040, 2,935, 2,878, 1,655, 1,610, 1,520, 1,440, 1,380, 1,260, 1,190, 1,120, 1,040, 960.

Compound **5v**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 2.00 (m, 4H), 2.11 (m, 4H), 2.42 (m, 4H), 5.24 (s, 1H), 6.69–7.23 (d, 2H), 7.46–8.01 (d, 2H). IR (KBr disc) cm^{-1}: 3,002, 2,986, 2,924, 2,894, 1,660, 1,612, 1,510, 1,420, 1,360, 1,220, 1,180, 1,120, 980, 860.

Compound **5w**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.98 (m, 4H), 2.04 (m, 4H), 2.24 (m, 4H), 4.99 (s, 1H), 7.01–8.11 (m, 4H). IR (KBr disc) cm^{-1}: 3,070, 2,992, 2,935, 2,890, 1,650, 1,610, 1,480, 1,420, 1,200, 1,180, 1,120, 960, 870.

Compound **5x**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 2.02 (m, 4H), 2.32 (m, 4H), 2.61 (m, 4H), 3.78 (s, 3H), 5.24 (s, 1H), 6.82–7.68 (m, 4 H). IR (KBr disc) cm^{-1}: 3,040, 2,990, 2,934, 2,886, 1,660, 1,614, 1,510, 1,480, 1,360, 1,280, 1,246, 1,190, 1,040, 960, 780.

Compound **6b**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.98 (s, 3H), 1.06 (s, 3H), 2.28 (s, 2H), 2.55 (s, 2H), 5.70 (s, 1H), 7.18–7.82 (m, 12 H). IR: (KBr disc) cm^{-1}: 3,060, 2,980, 2,880, 1,660, 1,480, 1,400, 1,360, 1,230, 1,140.

Compound **6k**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.01 (s, 3H), 1.13 (s, 3H), 2.24 (s, 2H), 2.35 (s, 2H), 5.78 (s, 1H), 6.84–8.01 (m, 11H). IR: (KBr disc) cm^{-1}: 3,010, 2,980, 2,925, 1,660, 1,590, 1,560, 1,380, 1,230, 1,160, 800.

Compound **6l**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.99 (s, 3H), 1.12 (s, 3H), 2.25 (s, 2H), 2.31 (s, 2H), 2.56 (s, 3H), 5.76 (s, 1H), 6.92–7.91 (m, 10H). IR: (KBr disc) cm^{-1}: 3,010, 2,940, 2,890, 1,650, 1,618, 1,530, 1,480, 1,360, 1,230, 1,040, 820.

Results and discussion

To the best of our knowledge, crosslinked poly(AMPS-co-AA) has not been explored in organic synthesis. In continuation of our interest on application of heterogeneous catalysts for the development of useful synthesis methodology [56–60], we wish to report a simple, efficient and practical method for the synthesis of xanthene derivatives using crosslinked poly(AMPS-co-AA) as eco-friendly catalyst with high catalytic activity under solvent-free condition at 110 °C (Scheme 1).

In recent years, solvent-free organic reactions have caused great interests, which have many advantages such as high efficiency and selectivity, separation and purification, mild reaction conditions, and to benefit industry as well as environment [61–65].

During our investigation, we chose β-naphthol and 4-chlorobenzaldehyde as model reaction and examined the amount of crosslinked poly(AMPS-co-AA) as catalyst in the absence of solvent under various temperatures (Scheme 1; Table 1). Then, in order to determine the

Scheme 1 One-pot synthesis of xanthene derivatives using a novel polymeric catalyst

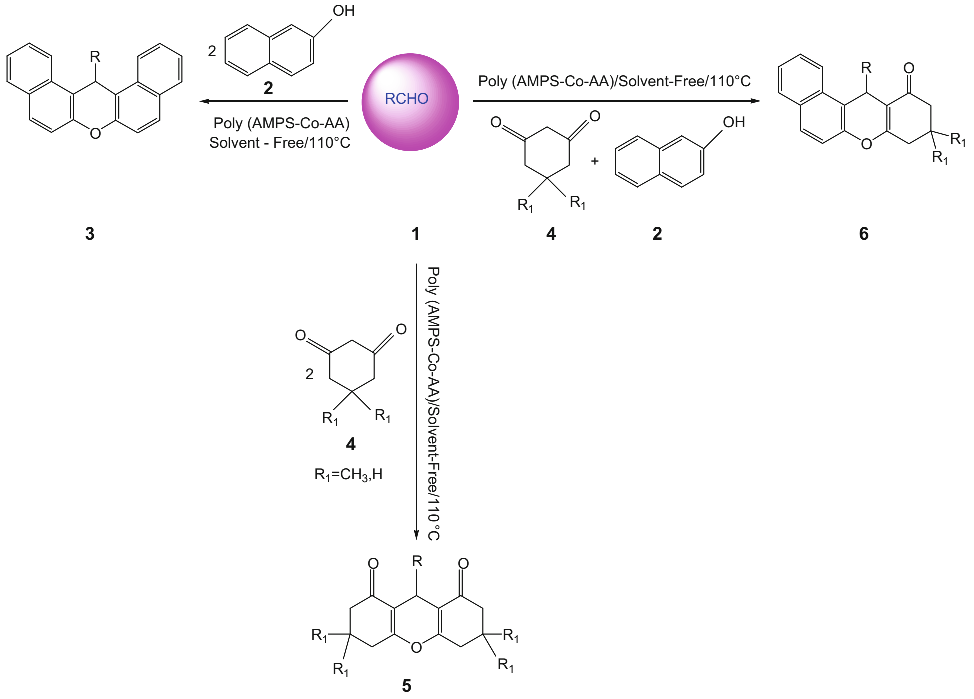


Table 1 Screening of the reaction conditions for the synthesis of 14-(4-chlorophenyl)-14*H*-dibenzo[a,j]xanthene (**3b**)

Entry	Amount poly (AMPS-co-AA) (g)	Temperature (°C)	Times (min)	Yield[a] (%)
1	0.02	90	80	55
2	0.02	100	60	65
3	0.02	110	40	72
4	0.02	120	40	72
5	0.01	110	80	60
6	0.03	110	30	80
7	0.04	110	30	92
8	0.05	110	30	92
9	–	110	120	–[b]

[a] Isolated yields, [b] no reaction

optimum reaction conditions, 2 mol of *β*-naphthol and 1 mol of 4-chlorobenzaldehyde together with a specified amount of crosslinked poly(AMPS-co-AA) were reacted under the different temperatures. The results in Table 1 showed some interesting points. First of all, increasing amount of poly(AMPS-co-AA) did not improve obviously the yields of **3b**. So, the optimum amount of poly(AMPS-co-AA) was found to be 0.04 g relative to reactants. The second important point which could be elicited evidently from these results was that the raising of the reaction temperature from 110 to 120 °C did not increase the yield and also did not improve the reaction rates. Also, in absence of the mentioned catalyst no products could be detected even after 2 h.

After optimization of the reaction conditions, we studied the generality of these conditions to other substrates. Using this method, different kinds of aldehydes were reacted with *β*-naphthol to produce the corresponding 14-aryl or alkyl-14*H*-dibenzo[a,j]xanthene under solvent-free conditions (Table 2). All the reactions proceeded efficiently within 20–30 min at 110 °C to provide the corresponding xanthene derivatives in good yields ranging from 75 to 92 %. Various aromatic, alkyl and hetroaromatic aldehydes containing electron-withdrawing and electron-donating substituent at ortho, meta or para positions show equal ease towards the product formation in good to high yields.

The practical synthetic efficiency of this reaction was highlighted by the reaction of terephtaldehyde with *β*-naphthol to give structurally complex xanthene derivative (**3k**) (Scheme 2).

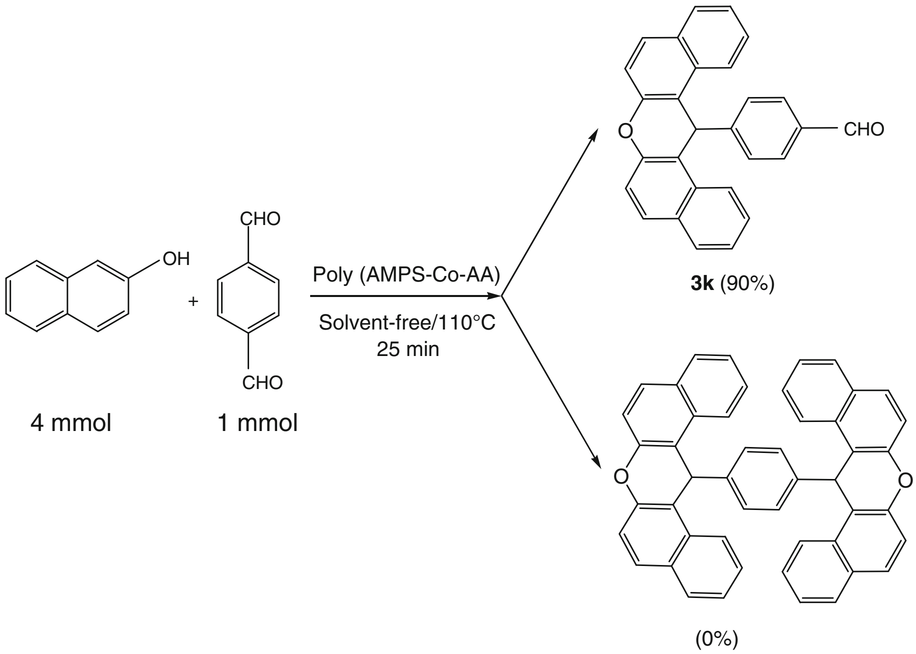
We expected that both of the formyl groups on the aromatic ring of terephtaldehyde would react with *β*-naphthol. However, we observed that one of the formyl groups was condensed with *β*-naphthol and another group was intact because of the steric effects between *o*-hydrogens of benzene ring and the xanthene ring [25]. The most important of this method is that the acid sensitive functionality present in the molecule remains unaffected. This fact was amply demonstrated by the reaction of pyridine-3 or 2-carboxaldehyde with *β*-naphthol, which gave pyridine-3 or 2-yl 14*H*-dibenzo[a,j]xanthene in good yields (Scheme 3).

Table 2 The one-pot synthsis of 14-aryl or alkyl-14*H*-dibenzo[a,j]xanthene using poly(AMPS-co-AA)

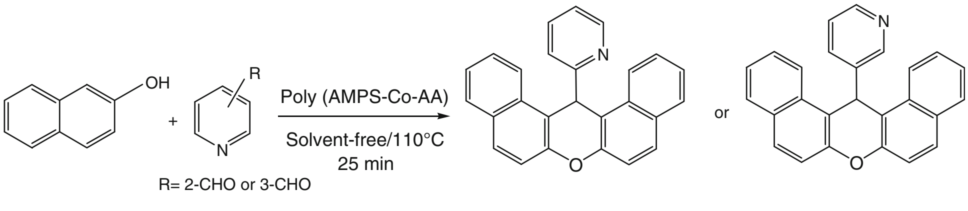
Product (**3**)	R	Time (min)	Yield[a] (%)	Mp (°C)	
				Found	Reported
a	C_6H_5	30	88	182–183	183–185 [25]
b	$4\text{-}ClC_6H_4$	30	92	290–292	289–291 [25]
c	$2\text{-}ClC_6H_4$	30	87	213–215	213–215 [25]
d	$3\text{-}BrC_6H_4$	25	90	190–192	192–193 [31]
e	$4\text{-}BrC_6H_4$	25	92	298–300	298–300 [25]
f	$3\text{-}NO_2C_6H_4$	25	87	213–214	210–211 [25]
g	$4\text{-}NO_2C_6H_4$	25	86	312–313	310–312 [25]
h	$2\text{-}CH_3OC_6H_4$	25	80	259–260	258–259 [25]
i	$4\text{-}CH_3OC_6H_4$	25	86	204–206	203–205 [25]
j	$4\text{-}FC_6H_4$	25	90	238–240	238–240 [25]
k	$4\text{-}CHOC_6H_4^{b}$	25	90	309–311	310–312 [25]
l	Pyridyl-2-yl	30	75	236–237	236–237 [25]
m	Pyridyl-3-yl	30	80	201–203	200–202 [25]
n	$4\text{-}CH_3C_6H_4$	25	83	228–229	226–228 [25]
o	Isipropyl	20	84	157–158	154–156 [25]
p	*n*-Propyl	20	81	152–154	152–154 [25]
q	$3\text{-}CH_3OC_6H_4$	30	89	171–173	–

[a] The yields refer to the isolated pure products which were characterized from their spectral data and were compared with authentic sample, [b] *β*-naphthol/aldehyde (4:1)

Scheme 2 Reaction between terephthaldehyde and excess amount of *β*-naphthol



Scheme 3 Reaction between pyridine-3 or 2-carboxaldehyde with *β*-naphthol



3l

3m

Encouraged by these results, we replaced the cyclic 1,3-dicarbonyl compounds (1,3-cyclohexanedione or 5,5-dimethyl-1,3-cyclohexanedione) instead of *β*-naphthol in same conditions (Scheme 1). Initially, we optimized the amount of poly(AMPS-co-AA) for condensation of the reaction between 5,5-dimethyl-1,3-cyclohexanedione and 4-chlorobenzaldehyde. The best result was obtained with 0.04 g of poly(AMPS-co-AA). To investigate the versatility of the catalyst, the reaction of cyclic 1,3-dicarbonyl compounds was carried out with various aldehydes for the synthesis of 1,8-dioxo-octahydroxanthene under solvent-free conditions at 110 °C (Table 3). All reactions proceeded efficiently within 15–25 min at 110 °C to provide the corresponding xanthene derivatives in good yields ranging from 68 to 86 %.

Following the success from synthesis 1,8-dioxo-octahydroxanthene, we have developed this synthetic method for the preparation of additional extended bis-1,8-dioxo-octahydroxanthene derivative in a 4:1 molar ratio of 5,5-dimethyl-1,3-cyclohexanedione to terephtaldehyde to poly(AMPS-co-AA) (0.08 g) (Scheme 4). As expected, the reaction proceeded smoothly for 25 min with yield 80 % under solvent-free conditions at 110 °C [mp > 300 °C (dec.), Lit. > 300 °C] [47].

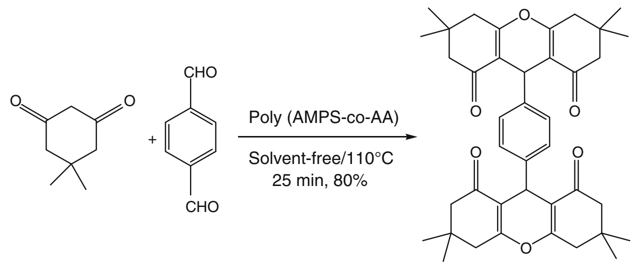
Multicomponent reactions (MCRs) have attracted considerable interest because of their expectational synthetic and practical efficiency [66]. MCRs involve three or more starting materials reacting in a single flask to form a new product [67–70]. One example of an MCRs is a three-component, one-pot synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-ones.

Finally, we have developed this synthetic method for one-pot efficient synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-ones by polycondensation aldehydes with *β*-naphthol and cyclic 1,3-dicarbonyl (1,3-cyclohexanedione or 5,5-dimethyl-1,3-cyclohexanedione). For achieving the optimal reaction condition, the reaction of 4-chlorobenzaldehyde with *β*-naphthol and 5,5-dimethyl-1,3-cyclohexadione in the presence of crosslinked poly(AMPS-co-AA) was selected as a model reaction and

Table 3 Preparation of 1,8-dioxo-dodecahydroxanthene using poly(AMPS-co-AA)

Product **(5)**	R	R^1	Time (min)	Yield[a] (%)	Mp (°C)	
					Found	Reported
a	C_6H_5	CH_3	25	85	204–205	203–204 [47]
b	$\text{4-ClC}_6\text{H}_4$	CH_3	25	85	233–235	230–232 [47]
c	$\text{2-ClC}_6\text{H}_4$	CH_3	25	85	225–227	225–227 [47]
d	$\text{2-NO}_2\text{C}_6\text{H}_4$	CH_3	25	80	251–252	252–254 [47]
e	$\text{4-NO}_2\text{C}_6\text{H}_4$	CH_3	25	82	224–226	222–223 [47]
f	$\text{3-NO}_2\text{C}_6\text{H}_4$	CH_3	25	80	170–172	170–172 [47]
g	$\text{4-CH}_3\text{C}_6\text{H}_4$	CH_3	25	84	215–217	215–217 [47]
h	$\text{4-BrC}_6\text{H}_4$	CH_3	25	86	242–244	240–241 [47]
i	$\text{4-FC}_6\text{H}_4$	CH_3	25	85	225–227	226–227 [36]
j	$\text{2-HOC}_6\text{H}_4$	CH_3	25	70	206–208	202–205 [39]
K	$\text{4-HOC}_6\text{H}_4$	CH_3	25	68	250–252	247–248 [36]
l	2-Thiophene	CH_3	25	74	166–167	164–165 [38]
m	$\text{2-CH}_3\text{C}_6\text{H}_4$	CH_3	25	84	210–212	–
n	C_6H_5	H	15	72	203–205	201–203 [37]
o	$\text{4-ClC}_6\text{H}_4$	H	15	70	229–232	231–223 [37]
p	$\text{4-CH}_3\text{C}_6\text{H}_4$	H	15	80	218–220	216–218 [37]
q	$\text{4-BrC}_6\text{H}_4$	H	15	82	229–231	228–231 [37]
r	$\text{4-HOC}_6\text{H}_4$	H	15	74	249–251	245–247 [37]
s	$\text{3-NO}_2\text{C}_6\text{H}_4$	H	15	76	277–279	–
t	$\text{2-CH}_3\text{C}_6\text{H}_4$	H	15	82	227–228	–
u	$\text{3,4-CH}_3\text{OC}_6\text{H}_3$	H	15	80	180–181	–
v	$\text{4-FC}_6\text{H}_4$	H	15	84	271–273	–
w	$\text{2-ClC}_6\text{H}_4$	H	15	80	249–251	–
x	$\text{2-CH}_3\text{OC}_6\text{H}_3$	H	15	70	216–218	–

[a] Isolated yields



Scheme 4 Reaction between terephthaldehyde with 5,5-dimethyl-1,3-cyclohexanedione

the effects of the reaction parameters such as amount of the catalyst and temperature were studied in detail. The best result was obtained with 0.06 g of poly(AMPS-co-AA) under solvent-free conditions at 110 °C. Several structurally diverse aldehydes (Table 4) were subjected to condensation with *β*-naphthol and cyclic 1,3-dicarbonyl compounds under the catalytic influence of poly(AMPS-co-AA) (0.06 g) and solvent-free conventional heating, and 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-ones were obtained in high yields. Also, the tolerance of the present method towards various functionalities present in the substrates viz. halides, methoxy, hydroxyl and nitro groups generalizes the scope of the present method.

In the next step, we investigated the reusability and recycling of poly(AMPS-co-AA). At first we put 4-chlorobenzaldehyde (1 mmol), *β*-naphthol (2 mmol) and 0.04 g of poly(AMPS-co-AA) together, and then the mixture was stirred at 110 °C for 30 min without any solvent. When the reaction was completed, the poly(AMPS-co-AA) was separated by simple filtration by diluting with hot ethanol, then, dried in oven at 110 °C for 24 h recovered poly(AMPS-co-AA) was reused in subsequent reactions (Table 5).

Table 4 Preparation 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-ones using poly(AMPS-co-AA)

Product **(6)**	R	R^1	Time (min)	Yield[a] (%)	Mp (°C)	
					Found	Reported
a	C_6H_5	CH_3	40	75	150–152	151–153 [42, 43]
b	4-ClC_6H_4	CH_3	40	85	179–181	180–182 [42, 43]
c	2-ClC_6H_4	CH_3	45	80	178–180	179–180 [42, 43]
d	2-$NO_2C_6H_4$	CH_3	50	78	220–223	223–225 [42, 43]
e	4-$NO_2C_6H_4$	CH_3	40	88	174–175	178–180 [42, 43]
f	3-$NO_2C_6H_4$	CH_3	40	80	167–169	168–170 [42, 43]
g	4-FC_6H_4	CH_3	35	80	182–184	185–186 [42, 43]
h	4-$CH_3C_6H_4$	CH_3	30	80	176	176–178 [42, 43]
i	4-$CH_3OC_6H_4$	CH_3	35	85	208–209	204–205 [42, 43]
J	2-$CH_3OC_6H_4$	CH_3	30	88	167–168	163–165 [42, 43]
k	3-BrC_6H_4	CH_3	40	85	173–175	–
l	2-$CH_3C_6H_4$	CH_3	45	86	165–166	–
m	2-Thiophene	CH_3	50	74	182–183	180–181 [44]
n	4-ClC_6H_4	H	25	85	207–208	206–208 [46]
o	4-$CH_3OC_6H_4$	H	25	79	179–181	180–182 [46]
p	3-$NO_2C_6H_4$	H	25	85	233–235	235–236 [46]
q	4-$NO_2C_6H_4$	H	25	75	237–239	234–235 [46]
r	C_6H_5	H	50	80	192–193	189–190 [46]

[a] Isolated yields

Table 5 Reuse of the poly(AMPS-co-AA) for synthesis of **3b**

Entry	Times (min)	Yield[a] (%)
0	30	92
1	30	70
2	40	65

[a] Isolated yields

Conclusions

An efficient, heterogeneous, simple and safe procedure for the preparation of the xanthene derivatives in good yields and short times was reported in this work. The notable advantages of this methodology are operational simplicity, generality, short reaction times and easy work-up.

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