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Phenacylpyridinium Oxalate as a Novel Water-Soluble Photoinitiator for Free Radical Polymerization

M. Atilla Tasdelen, Bunyamin Karagoz, Niyazi Bicak (✉), Yusuf Yagci (✉)

Department of Chemistry, Istanbul Technical University, Maslak, Istanbul 34469, Turkey

E-mails: bicak@itu.edu.tr, yusuf@itu.edu.tr

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Summary

Phenacylpyridinium oxalate (PPOx) was synthesized by counter anion exchange reaction of phenacylpyridinium bromide (PPBr) with potassium oxalate. Radicals formed from the photolysis of PPOx in aqueous solutions were capable of initiating polymerization of hydrophilic monomers such as acrylamide (AAm), 2-hydroxyethyl methacrylate (HEMA) and *N*-vinyl pyrrolidone (NVP). Direct decomposition of excited phenacylpyridinium ion as well as electron transfer and cleavage reactions involving both pyridinium and oxalate ions were proposed for the initiation step.

Keywords

Photopolymerization, free radical polymerization, phenacyl salts, aqueous polymerization, water soluble monomer

Introduction

Photopolymerization is the basis of several industrial applications in the preparation of films and coating, inks, adhesives, fiber optics, and biomaterials [1-5]. There is an increasing, legislation-led drive away from organic solvents towards water-borne formulations in the paints and coatings industry. Water as a green solvent has several attractive properties such as non-toxicity, cheap cost, readily availability for coatings technology. Various radical initiation techniques, including thermal [6-8], redox [9-12], photochemical [13-17], electrochemical [18] and radiolysis [19, 20] methods have been employed for aqueous solution polymerizations. Among them photoinduced polymerizations, which utilize light energy to initiate chain reactions to form polymer materials, offer a number of advantages: solvent-free formulations, low energy input, room temperature treatment and low costs. Photoinitiators play a vital role in the photopolymerization. The introduction of water solubilising groups (quaternary ammonium salts, sulfonates, thiosulfates, and phosphinate carboxylic acids or hydrophilic chain) onto a conventional photoinitiator is a relatively simple manner for polymerization of water soluble monomers. Direct substitution of such a group on to the photoinitiator affects the nature of the chromophore and its photoactivity. Generally, water soluble photoinitiator have reduced photoactivity to that of its parent oil soluble initiator. Example of the typical structure of water-soluble photoinitiators are derivatives of benzophenones [21], thioxanthones [22], benzyl [23] and hydroxy alkyl ketones [24], and phenyl trimethyl benzoyl phosphinates [25].

Phenacylonium salts are shown to be efficient latent photoinitiators with non-nucleophilic counter ions for polymerization of acrylates and epoxides [26]. Phenacyl radicals formed from the homolytic cleavage of carbon-heteroatom bond initiate the free radical polymerization [27, 28] while phenacylium cations formed from both heterolytic directly and/or homolytic cleavage of carbon-heteroatom followed by intermolecular electron transfer, initiate the cationic polymerization [29-31].

In this paper, we report the synthesis and characterization of phenacylpyridinium oxalate (PPOx) and its application to photopolymerization of water-soluble monomers such as acrylamide (AAm), 2-hydroxyethyl methacrylate (HEMA), *N*-vinyl pyrrolidone (NVP).

Experimental

Materials

2-Bromoacetophenone (98 %, Acros), oxalic acid (98 %, Acros) and acrylamide (AAm, 97 %, Aldrich) were used as received. 2-Hydroxyethyl methacrylate (HEMA, 96%, Acros), and *N*-vinyl pyrrolidone (NVP, 98 %, Acros) were passed through basic alumina column to remove the inhibitor. All solvents were purified by conventional procedures.

Synthesis of Phenacylpyridinium Bromide (PPBr)

Phenacyl bromide is lachrymatory. The reaction should be conducted under efficient fume cupboard. PPOx was synthesized as follows: Phenacyl bromide 7.5 g (3.77×10^{-2} mol) was dissolved in 15mL acetone in a 100 mL volume of Erlenmeyer flask. The flask was placed in an ice bath. To the cold solution 3 g (3.77×10^{-2} mol) pyridine was added drop wise while stirring. The mixture was stirred for 1 h at 0°C and stirring was continued for another 1 h at room temperature. The quaternary product, phenacylpyridinium bromide was obtained as voluminous precipitate. It was filtered and washed with 10 mL diethyl ether as quickly as possible to avoid humidity of air. The white crystalline mass was collected by filtering and dried under vacuum at room temperature for 24 h (yield = 96.2 %).

UV (H_2O): λ_{max}., nm (ε, mol^{-1} L cm^{-1}); 246 (20090) and 282 (2125).
FTIR (ATR): 3460, 3010, 1695, 1590, 1580, 1490, 1450, 1340, 1230, 1220, 1200, 1150, 1080, 990, 850, 800, 760, 650, cm^{-1}

Synthesis of Phenacylpyridinium Oxalate (PPOx)

Phenacylpyridinium bromide was dissolved in 10 mL water. Meanwhile, potassium oxalate solution was prepared by neutralization aqueous solution of 2.28 g (1.81×10^{-2} mol) oxalic acid dehydrate (20 mL) with 2.1 g (3.75×10^{-2} mol) KOH in 5 mL water. The above solution was added to this solution. No precipitate was observed. About ¾ of the solution was evaporated by rotavapor and left to stand for 2 weeks at room temperature. The white crystalline mass was collected by filtering and dried under vacuum at room temperature for 24 h (yield = 26.2 % and mp. 65°C).

UV (H_2O): $\lambda_{max.}$, nm (ε, mol^{-1} L cm^{-1}); 252 (20150) and 288 (1520).
FTIR (ATR): 3340, 1720, 1600, 1450, 1380, 1220, 1045, 870, 770, 680, cm^{-1}
^{1}H-NMR (200 MHz, $CDCl_3$, ppm): 5.6 (s, 2H, $^+NCH_2$), 7.4-8.0 (m, 5H, C_6H_5 and m, 5H, C_5H_5N).

Photopolymerization

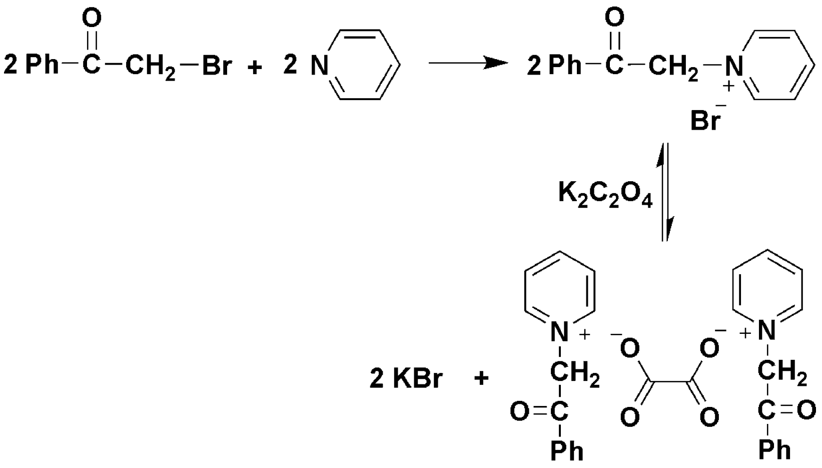
Typical procedure; first, a mixture of PPOx (0.012 mol L^{-1}), monomer (1.7 mol L^{-1}) and water (2 mL) was contained in a quartz tube and filled with dry nitrogen prior to irradiation from Rayonet merry-go-round photoreactor equipped with 16 lamps emitting nominally at $\lambda > 300$ nm with a light intensity of 3×10^{-3} mW cm^{-2}. The light intensity was measured by Delta ohm HD-9021 power meter. At the end of irradiation for one hour, polymers were precipitated in 10-fold excess appropriate nonsolvent for each monomer (methanol, cold water and acetone, for AAm, HEMA and NVP respectivley) and dried in vacuum. All the other polymerization of different monomers was performed under identical conditions. Conversions for all samples were determined gravimetrically.

Analysis

^{1}H-NMR spectra were recorded on a Bruker 250 MHz spectrometer using $CDCl_3$ as solvent and tetramethylsilane as the internal standard. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. FT-IR spectra were recorded on a Perkin Elmer FT-IR Spectrum One spectrometer.

Results and Discussion

A simple two-step procedure was used for the synthesis of the phenacylpyridinium oxalate (PPOx). Accordingly, phenacyl bromide was first reacted with pyridine to yield the respective salt with bromide anion. In the second step, the counter anion exchange with potassium oxalate yielded the desired final product. The overall synthesis was presented in Scheme 1.



(1)

(2)

Scheme 1. Synthesis of Phenacylpyridinium Oxalate (PPOx)

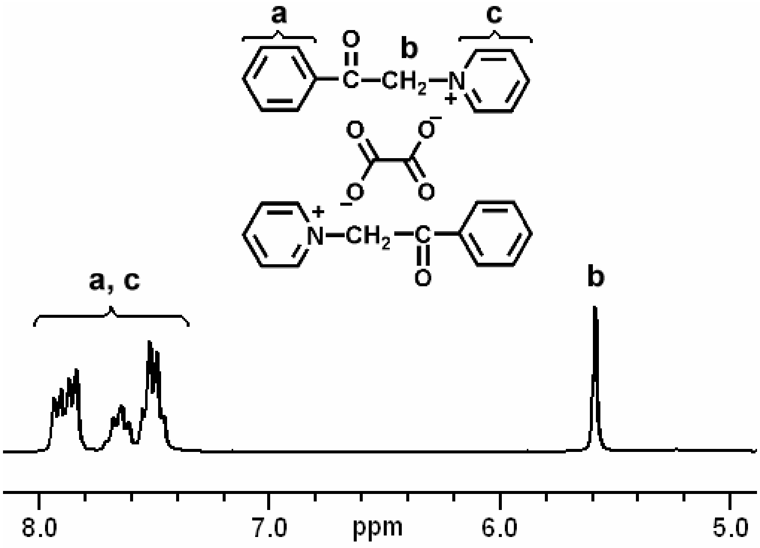


Figure 1. ^{1}H-NMR spectrum of phenacylpyridinium oxalate

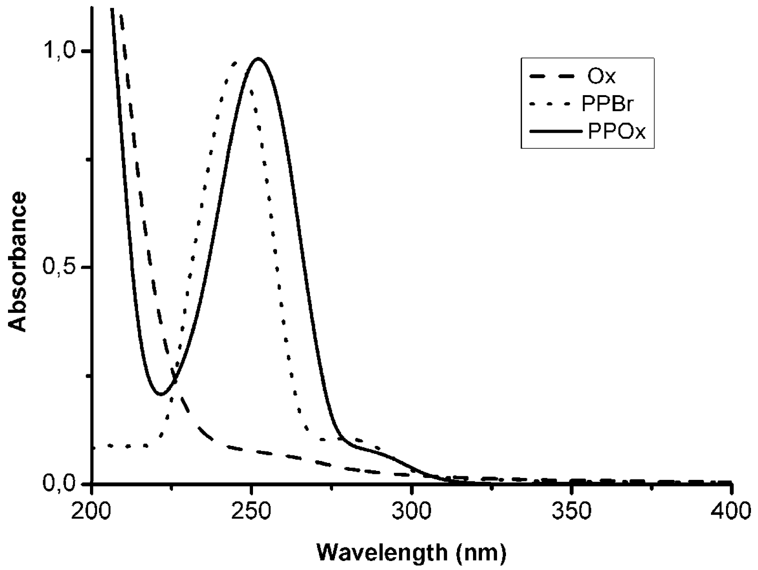
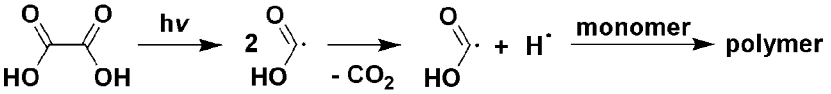


Figure 2. Absorption spectra of oxalic acid (Ox), phenacylpyridinium bromide (PPBr) and phenacylpyridinium oxalate (PPOx) (5×10^{-5} mol L^{-1}) in water.

The structure of the salt was confirmed by spectral analysis. In the ^{1}H-NMR spectrum of PPOx, characteristic methylene and aromatic peaks appeared at 5.6 and 7.4-8.0 ppm, respectively (Figure 1). The salt possesses characteristic spectra to the phenacyl moiety with two maxima at 244 and 282 nm. Notably, the counter anion exchange caused only a slight red-shift (6 nm) in the absorption spectrum. It can also be seen that oxalic acid, structural unit of the counter anion of PPOx, has a weak absorption at

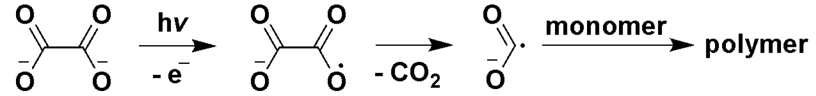
250-300 nm region. Oxalic acid is a well known photoactive acid that produces free radicals in the presence of light. It was reported earlier that oxalic acid can readily initiate photopolymerization of acrylamide (AAm) and related monomers in aqueous medium [32]. Photodecomposition of oxalic acid is believed to generate hydrogen and acid group bearing free radicals with the evolution of carbon dioxide. Both radical are then utilized in the initiation of vinyl polymerization (Scheme 2). The polymers thus formed were further reported to incorporate –COOH and -OH end groups in their chain ends [33].



(3)

Scheme 2. Photoinitiated free radical polymerization by using oxalic acid

Oxalate salts are also known to initiate free radical polymerization. Reaction starts by photoinduced electron transfer from oxalate ion to metal center or solvent. Monooxalate formation is primary step of the polymerization reaction.



(4)

Scheme 3. Photoinitiated free radical polymerization by oxalate salts

Attachment of structurally related oxalate anions to phenacylpyridinium ions would afford water solubility and enhancement of photoinitiation efficiency. Acrylamide (AAm), hydroxyl ethyl methacrylate (HEMA) and *N*-vinyl pyrrolidone (NVP) were used as monomers to test the efficiency of PPOx as photoinitiator for free radical polymerization in aqueous media. Typical results are given in Table 1. For comparison, polymerizations by using oxalic acid and precursor phenacylpyridinium bromide (PPBr) were also included.

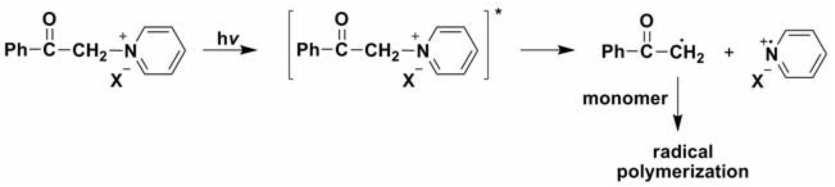
Table 1. Photopolymerization of different water-soluble monomers by using phenacylpyridinium oxalate and its components[a]

Run	Monomer	Initiator[b]	[M] (mol L^{-1})	Time (min)	Conversion (%)
1	AAm	PPOx	0,8	30	12
1		Ox	0,8	30	22
1		PPBr	0,8	30	4
2	HEMA	PPOx	2,1	30	35
2		Ox	2,1	30	12
2		PPBr	2,1	30	16
3	NVP	PPOx	4,7	60	16
3		Ox	4,7	60	17
3		PPBr	4,7	60	13

[a] at $\lambda > 300$ nm with a light intensity of 3 x 10^{-3} mW cm^{-2}, at room temperature, in water
[b] [I]: 12 x 10^{-3} mol L^{-1}
AAm; acrylamide, HEMA; 2-hydroxy ethyl methacrylate, NVP; *N*-vinyl pyrrolidone, PPOx; phenacylpyridinium oxalate, PPBr; phenacylpyridinium bromide, Ox; oxalic acid

As can be seen, the photoinitiation efficiency is significantly increased by changing the counter anion from bromide to oxalate. This behaviour can be attributed to the participation of both phenacylpyridinium and oxalate ions in radical generation processes.

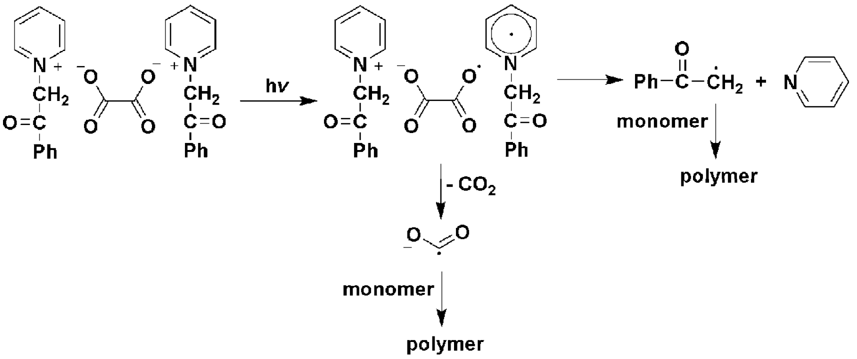
It is well known that the light-absorbing chromophore in phenacyl-type salts is the phenyl ketone group. Therefore, most of the primary reactions occur through the excitation of this group. Electronically excited PPOx may undergo homolytic cleavage resulting in the formation of free radicals capable of initiating polymerization of vinyl monomers (Scheme 3).



(5)

Scheme 4. Photoinitiated free radical polymerization by using phenacylonium salts

Additionally, electron transfer reaction within the photoexcited PPOx can also generate initiating free radicals. Pyridinium ion gives one electron to oxalate to produce pyrdinyl radical and oxalate radical anion. It is known that pyridinyl radicals are very short lived [34] and their back electron transfer reactions can be excluded. Decomposition of pyridinyl radicals to pyridine and phenacyl radicals according to reaction (5) appeared to be very probable.



(6)

(7)

Scheme 5. Photoinitiated free radical polymerization by using phenacylpyridinium oxalate

Oxalate anion radicals also yield initiating species by the evolution of carbon dioxide as described previously in equation 4.

It is interesting to note that the effect of monomer structure on the comparative initiation efficiency of PPOx and oxalic acid. PPOx seemed to be more efficient initiator for the polymerization of HEMA. This behavior may be explained in terms of hydrophilicity of both monomer and radicals produced from the initiators. The phenacyl radicals produced from PPOx are expected to be hydrophobic and reacts more readily with relatively hydrophobic monomer HEMA and less reactive towards hydrophilic monomer AAm.

In conclusion, although these results preliminary in nature they serve to indicate the efficiency and convenience of using phenacylpyridinium salt with oxalate counter anion as photoinitiator for free radical polymerization of appropriate monomers in aqueous media. Further studies are now in progress to develop other photoinitiators with better spectral sensitivity at longer wavelengths and still contain oxalate counter anions.

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