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Photoinitiated Cationic Polymerization of Cyclohexene Oxide by Using Phenacyl Benzoylpyridinium Salts

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Photoinitiated cationic polymerization reactions are widely used on an industrial scale for a number of different applications such as surface coatings, microelectronics, microlithography, and adhesives. Obviously, the growth of such an industry is dependent on the development of new photoinitiators fulfilling requirements for specific applications, e.g., wavelength selectivity, solubility, etc.

One type of commercially important and well-studied cationic photoinitiators are onium salts, namely iodonium[1] and sulfonium[1,2] salts. Alkoxy pyridinium[3,4] salts have also been developed as alternative cationic photoinitiators. However, all three types of salts appear to have poor spectral response at high wavelengths. To extend to their spectral sensitivity, onium salts are used in combination with various additives. Several pathways involving electron-transfer reactions either with photoexcited sensitizer,[5−8] the electron donor compounds in the excited charge-transfer complexes[9,10] or with free radicals[11−14] have been described. However, for industrial radiation curing applications, the use of one component photoinitiators having long wavelength absorption characteristics may still be advantageous because of the additional problems introduced by the co-initiator associated with solubility, compatibility, migration, and cost. Dialkylphenacyl sulfonium salts[15] are typical examples of one-component initiators that undergo reversible photolysis at relatively high wavelengths generating an ylide and a strong protonic acid. We have also developed structurally similar phenacyl anilinium salts as photoinitiators for cationic polymerization. In contrast to the corresponding sulfonium salts they undergo irreversible photolysis upon irradiation.[16,17] Since these salts did not provide the desired wavelength shift, it seemed approparíate to prepare phenacyl type salts from the precursors with an extended absorptivity.

In this study, phenacyl benzoylpyridinium salts were synthesized and their photoinitiation activity in cationic polymerization of cyclohexene oxide (CHO) was investigated. There is a considerable difference between the initiation mechanism of phenacyl benzoylpyridinium salts and its sulfonium analogues.

Structurally different phenacyl benzoylpyridinium (PBP) salts (Chart 1) were synthesized via a two-step reaction procedure. First, quaternization of nitrogen of benzolypyridine took place. The precipitation of insoluble bromide PBP salts in acetonitrile strongly shifts the equilibrium reaction forward. Second, ion exchange was performed by the addition of KPF_6 or $NaSbF_6$. Addition of these nonnucleophilic ions makes the soluble bromide PBP salts insoluble in water. For this reason, the desired final product is isolated from the aqueous medium by a simple filtration.

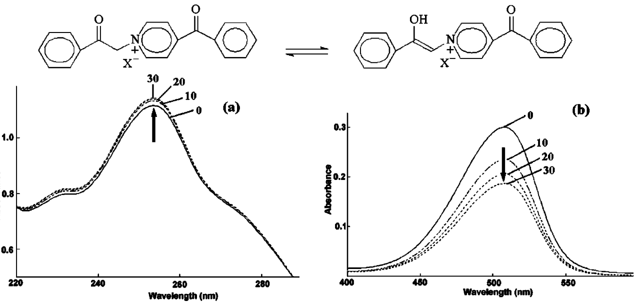
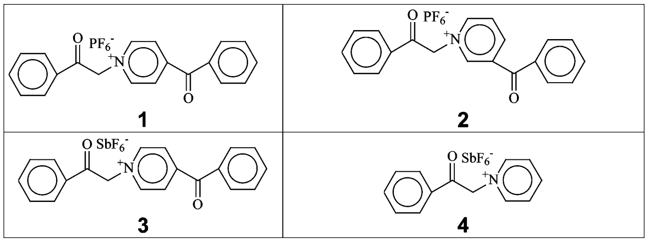


Figure 1. Typical UV spectral changes of salt **1** (see Chart 1) on irradiation at λ > 507 nm under nitrogen in CH_3CN, [**1**] = 2.4×10^{-5} M. UV spectra were taken every 10 min.

Chart 1



PBP salts are stable, light-sensitive compounds, colorless in solid form but colorful in common organic solvents such as acetonitrile, dimethyl sulfoxide (DMSO), acetone. PBP salts differ in the UV spectra from other types of phenacyl salts. All PBP salts possess the n−π* absorption with a maximum at about 300 nm, characteristic of acetophenone derivatives. PBP photoinitiators exhibit an absorption in the visible region.

The absorption of visible light by PBP salts may vary from 442 to 507 nm. In fact, this absorption is temporary and corresponds to the enol form of the salt. Depending on the concentration of PBP salts, the solution becomes colored by a short mixing with pipet and turns colorless after a while. As the concentration of PBP salt increases, the time needed for the disappearance of the color also increases. This implies that a reversible keto−enol tautamerization process (Figure 1) is facilitated with a little energy.

The next question concerns whether either or both forms undergo decomposition on irradiation to generate reactive species and consequently initiate the polymerization. Obviously, photodecomposition of the enol form would be particularly useful for visible light photoinitiation. For this purpose, first UV spectral changes of PBP salts on irradiation were investigated. As shown in Figure 1b, upon irradiation, the absorption at the visible region which belongs to the enol form rapidly diminishes while the absorption at shorter wavelength corresponding to the keto form increases (Figure 1a). Visually, the color of the solution drastically changed from pink to colorless, and it implied that the keto or enol form can be easily observed by the changing color.

Provided this assumption is fully correct, only the keto form should be capable of initiating cationic polymerization. Indeed, upon irradiation of the solutions containing any of the PBP salts and CHO as the cationically polymerizable monomer in UV range, polymerizations took place. In addition, no polymerization proceeded when irradiations were performed at the wavelength range where the enol forms absorb the light. Table 1 lists the polymerization results of CHO by using the various PBP salts

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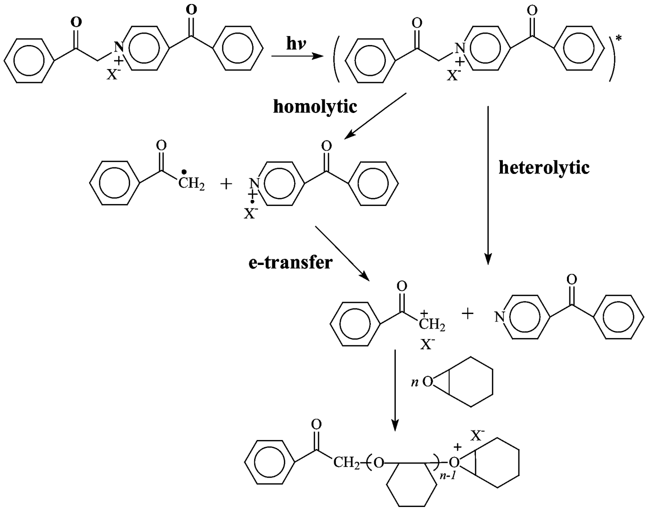
Table 1. Photopolymerization of Cyclohexene Oxide (9.88 mol L^{-1}) Using Various Salts at Room Temperature, Where [Salt] = 5 × 10^{-3} mol L^{-1} and Irradiation Time = 60 min

	irradition wavelength								
	250 nm			300 nm			350 nm		
salt[a]	convn (%)	$M_n{}^b \times 10^{-3}$	$M_w/M_n{}^b$	convn (%)	$M_n \times 10^{-3}$	$M_w/M_n{}^b$	convn (%)	$M_n \times 10^{-3}$	$M_w/M_n{}^b$
1	17	6.0	1.9	16	6.4	1.9	33	6.8	1.8
2	35	4.5	1.8	35	4.5	1.8	36	4.6	1.9
3	65	6.7	2.0	80	6.2	1.9	81	5.7	1.9
4	66	8.7	1.8	63	4.3	1.6	69	10.4	1.8

[a] Phenacyl benzoylpyridinium salts (see Chart 1). [b] Estimated by gel-permeation chromatography (tetrahydrofuran) based on polystyrene standard samples: M_n, number-average molecular weight; M_w, weight-average molecular weight.

Scheme 1. Photoinitiated Cationic Polymerization of Cyclohexene Oxide Using Phenacyl Benzoylpyridinium Salt



at different wavelengths in the UV region. The results indicate the effect of the position of precursor benzoyl group and counteranion on the rate of polymerization. The high reactivity of the salt at 4 position with $SbF_6{}^-$ counteranion. This behavior may be due to the more favored delocalization of the aromatic ring and nucleophilicity of the counteranions of the corresponding salts. Notably, pyridinium salt also initiates the polymerization of CHO, and high yields are attained.

Cationic photopolymerization mechanism of CHO is summarized in Scheme 1. The initiation mechanism suggests that electrically excited keto form of salt may undergo heterolytic cleavage, producing phenacylium cations. Alternatively, the reaction mechanism also offers homolytic cleavage, following electron transfer that yields the same species.

In summary, phenacyl benzoylpyridinium salts served as efficient photoinitiators for cationic polymerization of CHO. In addition, these salts exhibit keto−enol tautomerization and the form of the salt can be checked simply by the color changing from enol form (pink) to keto form (colorless). The initiation step involves the decay of the excited state of the keto form of the salt with both heterolytic and homolytic cleavages of carbon−nitrogen bond. Thus, phenacylium cations formed directly or subsequent intermolecular electron transfer, respectively, initiates the polymerization. Further detailed investigations and applications for organic reactions are now in progress.

Experimental Part. Materials. 2-Bromoacetophenone (Acros), 4-benzoylpyridine (Acros), 3-benzoylpyridine (Acros), petroleum ether (J. T. Baker), acetonitrile (J. T. Baker), sodium hexafluoroantimonate (Acros), and potassium hexafluorophosphate (Aldrich) were used as received.

Analysis. UV−visible spectra were recorded on a UV-1601 Shimadzu spectrophotometer. ^{1}H NMR spectrum was recorded on a Bruker 250 MHz spectrometer with DMSO-d_8 as the solvent and tetramethylsilane as the internal standard. Differential scanning calorimetry (DSC) as performed on a Perkin-Elmer DSC6 with a heating rate of 10 °C·min^{-1} under nitrogen flow. Molecular weights were determined using a gel permeation chromatography (GPC) instrument equipped with a Waters Styragel column (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 0.3 mL·min^{-1} and a Waters 410 Differential refractometer detector.

Synthesis of *N*-Phenacyl-4-benzoylpyridinium Hexafluorophosphate (1). Into a 25 mL round-bottom flask equipped with a magnetic stirrer were placed 1.5 × 10^{-5} mol of bromoacetophenone, 1.5 × 10^{-5} mol of 4-benzoylpyridine, and 10 mL of acetonitrile. The reaction mixture was stirred and held at room temperature for 9 h. White solid particles were obtained at the end. Then, acetonitrile was evaporated and the residue was dissolved in water. The aqueous solution was washed with petroleum ether. Finally, 1.5 × 10^{-5} mol of potassium hexafluorophosphate was added to the aqueous part in one portion. White precipitates were obtained (yield 22.2%); mp 208 °C (DSC). Anal. Calcd for $(C_{20}H_{16}NO_2PF_6)_n$ (447.32)$_n$: C 53.7; H, 3.6; N, 3.1. Found: C, 51.9; H, 3.3; N, 3.9. ^{1}H NMR (CD_3CN): $\delta = 6.39$ (s, 2H, $^+NCH_2$), 7.5−8.5 (m, 10H, C_6H_5; m, 4H, C_5H_4N). UV: λ_{max}/nm = 252, 507.

Synthesis of *N*-Phenacyl-3-benzoylpyridinium Hexafluorophosphate (2). The title compound was synthesized by the reaction of bromoacetophenone and 3-benzoylpyridine in a manner similar to **1** (yield 67.5%); mp 180 °C (DSC). Anal. Calcd for $(C_{20}H_{16}NO_2PF_6)_n$ (447.32)$_n$: C, 53.7; H, 3.6; N, 3.1. Found: C, 53.7; H, 3.6; N, 2.7. ^{1}H NMR (CD_3CN): $\delta = 6.26$ (s, 2H, $^+NCH_2$), 7.5−8.5 (m, 10H, C_6H_5; m, 4H, C_5H_4N). UV: λ_{max}/nm = 252, 442.

Synthesis of *N*-Phenacyl-4-benzoylpyridinium Hexafluoroantimonate (3). The title compound was synthesized by the reaction of bromoacetophenone, 4-benzoylpyridine, and sodium hexafluoroantimonate in a manner similar to **1** (yield 75%); mp 204 °C (DSC). Anal. Calcd for $(C_{20}H_{16}NO_2SbF_6)_n$ (538.14)$_n$: C, 44.6; H, 3.0; N, 2.6. Found: C, 44.1; H, 2.9; N, 3.6. ^{1}H NMR (CD_3CN): $\delta = 6.28$ (s, 2H, $^+NCH_2$), 7.5−8.5 (m, 10H, C_6H_5; m, 4H, C_5H_4N). UV: λ_{max}/nm = 253, 507.

Synthesis of *N*-Phenacylpyridinium Hexafluoroantimonate (4). The title compound was synthesized by the reaction of bromoacetophenone, pyridine, and sodium hexafluoroantimonate in a manner similar to **1** (yield 59%); mp 195 °C (DSC). Anal. Calcd for $(C_{13}H_{12}NOSbF_6)_n$ (433.99)$_n$: C, 35.9; H, 2.8; N, 3.2. Found: C, 33.8; H, 2.8; N, 2.6. ^{1}H NMR (CD_3CN): $\delta = 6.18$ (s, 2H, $^+NCH_2$), 7.5−8.5 (m, 10H, C_6H_5). UV: λ_{max}/nm = 248, 438.

Photopolymerization. Typical procedure. First, a bulk mixture of **1** (5.00 × 10^{-3} mol L^{-1}) and cyclohexene oxide (9.88 mol L^{-1}) 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 $\lambda = 250$ nm. At the end of irradiation for 1 h, polymers were precipitated in 10-fold excess methanol and dried in a vacuum. All the other polymerization using different benzoylpyridinium salts were performed under identical conditions except that the Pyrex tubes and lamps emitting nominally at $\lambda = 300$ and 350 nm were used. Conversions for all samples were determined gravimetrically.

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Supporting Information Available: Figure showing UV spectra of phenacyl benzoylpyridinium salts in acetonitrile. This material is available free of charge via the Internet at http://pubs.acs.org.

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