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Photochemical formation of ammonium/thiolate complexes from quaternary ammonium thiocyanates and its use in crosslinking of polymers

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Abstract

1-Phenacyl-(1-azania-4-azabicyclo[2.2.2]octane) thiocyanate (PnDbSCN) and *N*-phenacyl-4-(N',N'-dimethylamino)pyridinium thiocyanate (PnDpSCN) were prepared as novel photobase generators. These quaternary ammonium salts (QASs) have higher melting points and decomposition temperatures than corresponding QASs having dithiocarbamate anions. From ^{1}H NMR and UV spectral analyses, it was found that PnDbSCN turned to 1,4-diazabicyclo[2.2.2]octane (DABCO) and phenacylthiocyanate (PnSCN) on irradiation at 254 nm, and the resulting PnSCN was further transformed into 5-phenyloxazole-2-thione (POT) in the presence of DABCO to form ammonium/thiolate complexes. PnDpSCN also showed similar ^{1}H NMR spectral changes on irradiation. Poly(glycidyl methacrylate) (PGMA) films containing amines in the presence of POT crosslinked at lower temperature than those in the absence of POT, and PGMA films containing QASs became insoluble on irradiation followed by post-exposure baking.

Keywords: Quaternary ammonium salt; Photobase generator; Tertiary amine; Thiocyanate anion; Crosslinking

1. Introduction

Photobase generator (PBG) is attractive as a novel family of catalyst for polymerization or crosslinking of polymeric materials as well as photoacid generators [1]. However, there are not so many reports concerning PBGs. Although tertiary amines have higher activity as a base catalyst than primary and secondary amines, the example of PBGs that photochemically release tertiary amines is rare. Some quaternary ammonium salts (QASs) were proposed as photochemical precursors of the tertiary amines by Jensen and Hanson [2] and Neckers and co-workers [3–10].

We have already reported that QASs having dithiocarbamate anions were highly photoreactive PBGs and generated tertiary amines on irradiation as shown in Scheme 1 [11]. The amines worked as a catalyst of crosslinking of polymers and oligomers bearing epoxy groups. However, these QASs were unstable in solutions and films. Recently, we have found that QASs having thiocyanate anions showed higher stability than those having dithiocarbamates [12,13].

In this article, we report the photochemical reactions and thermal properties of QASs having thiocyanate anion along with theiability as crosslinking reagents of polymers bearing epoxy groups. Two QASs, 1-phenacyl-(1-azania-4-azabicyclo[2.2.2]octane) thiocyanate (PnDbSCN) and *N*-phenacyl-4-(N',N'-dimethylamino)pyridinium thiocyanate (PnDpSCN) were examined as photochemical precursors of strong bases such as 1,4-diazabicyclo[2.2.2]octane (DABCO) and *N*,*N*-dimethylaminopyridine (DMAP).

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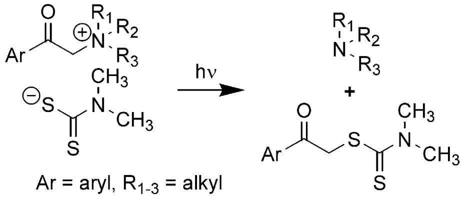

Scheme 1. Photoreaction of QASs having dithiocarbamate anions.

2. Experimental details

2.1. Apparatus

Melting points for QASs were obtained by using a Rigaku 8230B differential scanning calorimeter. Melting points for other compounds were measured by a Yanako MT-3S micro melting point meter and uncorrected. IR, UV, and NMR spectral measurements were performed using Jasco FTIR410, Shimadzu 2400PC, and Jeol JNM-GX270 (270 MHz) spectrometers, respectively. Molecular weights of polymers were determined by size exclusion chromatography (SEC) on equipment consisting of a Jasco PU-980 pump, a Jasco RI-930 detector, and a Shodex KF-806M column with polystyrene standards and tetrahydrofuran (THF) as an eluent. Thermogravimetric analysis (TGA) was carried out using a Shimadzu TGA50 thermogravimetric analyzer with a heating rate of 10 K/min under N_2. Onset temperatures from TGA curves were adopted as thermal decomposition temperature (T_d). Light intensity was measured by an Orc UV-M02 illuminometer. Film thickness was measured by a Nanometrics Nanospec/AFT M3000. Post-exposure bake (PEB) was carried out on a Koike HM-15G Hotplate.

2.2. Materials

DMAP and DABCO were obtained from Wako Chemical (Osaka, Japan).

Both phenacylthiocyanate (PnSCN) and 5-phenyloxazole-2-thione (POT) were prepared from phenacyl bromide and sodium thiocyanate at 0 °C in methanol and at 150 °C in *N*,*N*-dimethylformamide, respectively. After recrystallization, melting points of PnSCN and POT were 70.5–71.5 °C (literature [14], 74.5–75 °C) and 231–234 °C (literature [15], 234–235 °C), respectively. PnDbSCN was prepared as reported previously [11].

N-Phenacyl-4-(*N*′,*N*′-dimethylamino)pyridinium bromide (PnDpBr) was obtained by mixing methanol solutions of phenacyl bromide and DMAP in a ice-cold bath followed by evaporation and recrystallization from ethanol: yellowish powder in 87.4% yield. mp = 223–223.5 °C. IR (KBr): 1690 cm^{-1} (C=O). ^{1}H NMR (D_2O): $\delta = 3.08$ (6H, s, NCH_3), 5.70 (2H, d, $J = 5.1$ Hz, CH_2), 6.78 (2H, d, $J = 7.5$ Hz, 3- and 5-H in pyridine ring), 7.45–8.89 (7H, m, aromatic).

N-Phenacyl-4-(*N*′,*N*′-dimethylamino)pyridinium *N*″,*N*″-dimethyldithiocarbamate (PnDpDt) was obtained by mixing methanol solutions of 2.0 g (6.2 mmol) of PnDpBr and 0.93 g (6.5 mmol) of sodium *N*,*N*-dimethyldithiocarbamate followed by evaporation and recrystallization from ethanol: 1.03 g (45.8%) of yellow needles. IR (KBr): 1705 (C=O), 975 cm^{-1} (NC=S). ^{1}H NMR (CD_3CN): $\delta = 3.20$ (6H, s, $ArNCH_3$), 3.45 (6H, s, S=C–N–CH_3), 5.86 (2H, s, CH_2), 6.89 (2H, d, $J = 8.1$ Hz, 3- and 5-H in pyridine ring), 7.58–8.00 (7H, m, aromatic). Calcd. for $C_{18}H_{23}N_3OS_2$—C: 59.80, H: 6.41, N: 11.62; found C: 59.93, H: 6.40, N: 11.56.

N-Phenacyl-4-(*N*′,*N*′-dimethylamino)pyridinium thiocyanate (PnDpSCN) was obtained by a similar procedure to PnDpDt: colorless solid in 40.5% yield. IR (KBr): 2040 (SCN), 1700 (C=O) cm^{-1}. ^{1}H NMR (CD_3CN): $\delta = 3.22$ (6H, s, CH_3), 5.74 (2H, s, CH_2), 6.91 (2H, d, $J = 7.5$ Hz, 3- and 5-H in pyridine ring), 7.61–8.02 (7H, m, aromatic). ^{13}C-NMR (CD_3CN): $\delta = 40.73$, 63.54, 108.37, 118.29, 129.11, 130.10, 134.94, 135.54, 144.00, 157.56, 192.86. Calcd. for $C_{16}H_{17}N_3OS$—C: 64.19, H: 5.72, N: 14.04; found C: 64.23, H: 5.73, N: 13.98.

Poly(glycidyl methacrylate) (PGMA) and poly(methyl methacrylate) (PMMA) were prepared by radical polymerization using α,α′-azobisisobutylonitrile as an initiator. After reprecipitation, number average molecular weights of PGMA and PMMA were 138,000 and 107,000, respectively.

The stability of QASs in solution was monitored by UV spectral changes.

2.3. Equilibrium constant

Equilibrium constant of ammonium/POT complex formation (K) in the presence of excess amine is represented as Eq. (1),

$$K = \frac{[\mathrm{C}]}{([\mathrm{POT}] - [\mathrm{C}])([\mathrm{A}] - [\mathrm{C}])} \approx \frac{[\mathrm{C}]}{([\mathrm{POT}] - [\mathrm{C}])[\mathrm{A}]} \qquad (1)$$

where [C], [POT], and [A] are the concentrations of the complex, POT, and the amine, respectively. From Lambert–Beer equation,

$$\frac{A}{l} = \varepsilon'_{\mathrm{POT}}[\mathrm{POT}] = \varepsilon_{\mathrm{POT}}([\mathrm{POT}] - [\mathrm{C}]) + \varepsilon[\mathrm{C}] \qquad (2)$$

where $\varepsilon_{\mathrm{POT}}$ and ε are molar absorption coefficients of POT and the complex at 350 nm, respectively, l is 1 cm as path length of the cell, and A is the apparent absorbance of sample at 350 nm. $\varepsilon'_{\mathrm{POT}}$ is the apparent molar absorption coefficient of POT in the mixture. From Eqs. (1) and (2), $1/(\varepsilon'_{\mathrm{POT}} - \varepsilon_{\mathrm{POT}})$ can be related to 1/[A] in Eq. (3) as Ketelaar introduced previously [16],

$$\frac{1}{\varepsilon'_{\mathrm{POT}} - \varepsilon_{\mathrm{POT}}} = \frac{1}{K(\varepsilon - \varepsilon_{\mathrm{POT}})[\mathrm{A}]} + \frac{1}{\varepsilon - \varepsilon_{\mathrm{POT}}} \qquad (3)$$

2.4. Irradiation and crosslinking

UV spectral changes for QASs in solutions were measured in a tube bearing 1 cm × 1 cm quartz cuvette. Before