Photo- and Thermochemical Behavior of Quaternary Ammonium Thiocyanates and Their Use as Crosslinkers

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Keywords: photobase generator, quaternary ammonium salt, thiocyanate anion, crosslink, epoxide, thiolate

INTRODUCTION

Photobase generators (PBGs) are attractive as a novel family of catalysts for polymerization and crosslinking of polymeric materials as well as photoacid generators.[1-3] Especially, PBGs which generate tertiary amines on irradiation are greatly expected to have highly catalyzing ability due to their strong basicity. Some quaternary ammonium salts (QASs) were proposed as candidates of the PBGs by Hanson et al.[4] and Neckers et al.[5-8].

We have also examined photochemical behavior of QASs having sulfur-containing anions and recently found that QASs having thiocyanate as a counter-anion showed higher stability than those having dithiocarbamates.[9,10] In the previous report, we proposed a mechanism of photochemical reaction of a QBS as illustrated in Scheme 1, however, the details are not clear.[11]

In this paper, we report further investigated results of photo- and thermochemical reaction of QASs having thiocyanate anions and the utilization of photo-products for polymerization and crosslinking of epoxy compounds. On the way of investigation, we found that 4-(N,N-dimethylamino)pyridine (DMAP) was a very effective amine for curing of epoxides, and QASs derived from DMAP were also investigated.

EXPERIMENTAL

Melting points were measured by a Yanako MT-3S micro melting point meter. IR, UV, and NMR spectral measurements were performed using Jasco FTIR410, Shimadzu 2400PC, and Jeol JNM-GX270 (270 MHz) spectrometers, respectively. Molecular weights were measured by size exclusion chromatography (SEC) with polystyrene standards and tetrahydrofuran (THF) eluent. Thermogravimetric analysis (TGA) was carried out by a Shimadzu TGA50 thermogravimetric analyzer with a heating rate of 10 K / min under N2.

Phenyl glycidyl ether (PGE) was distilled before use. DMAP and 1,4-diazabicyclo[2.2.2]-octane (DABCO) were used as received.

Both phenacetylthiocyanate (PnSCN) and 5-phenylloxazole-2-thione (POT) were prepared from phenacetyl 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 (lit:[12] 74.5-75 °C) and 231-234 °C (lit:[13] 234-235 °C), respectively. 1-Phenacetyl-(1-azania-4-azabicyclo[2.2.2]octane) thiocyanate (PnDbSCN) was prepared as reported previously.[9]

N-Phenacyl-4-(N',N'-dimethylamino)-pyridinium bromide (PnPBr) was obtained by mixing methanol solutions of phenacetyl bromide and DMAP in an ice 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). ¹H-NMR (D₂O): δ =
3.08 (6H, d, NCH$_3$), 5.70 (2H, d, CH$_2$), 6.78 (2H, d, 3- and 5-H in pyridine ring), 7.45-8.89 (7H, m, aromatic).

$N$-Phenacyl-4-($N'$,$N'$-dimethylamino)-pyridinium $N''$,$N''$-dimethylthiocarbamate (PnPdDi) was obtained by mixing methanol solutions of 2.0 g (6.2 mmol) of PnPdBr and 0.93 g (6.5 mmol) of sodium $N$,$N$-dimethylthiocarbamate followed by evaporation and recrystallization from ethanol; IR (KBr): 1705 (C=O), 975 cm$^{-1}$ (NC=S). $^1$H-NMR (CD$_3$CN): $\delta = 3.20$ (6H, s, ArNCH$_3$), 3.45 (6H, s, S=C-N-CH$_3$), 5.86 (2H, s, CH$_3$), 6.89 (2H, d, 3- and 5-H in pyridine ring), 7.58-8.00 (7H, m, aromatic).

$N$-Phenacyl-4-($N'$,$N'$-dimethylamino)-pyridinium thiocyanate (PnPdSCN) was obtained by a similar procedure to PnPdDi: colorless solid in 40.5 % yield; IR (KBr): 2040 (SCN), 1700 (C=O) cm$^{-1}$. $^1$H-NMR (CD$_3$CN): $\delta = 3.22$ (6H, s, CH$_3$), 5.74 (2H, s, CH$_3$), 6.91 (2H, d, 3- and 5-H in pyridine ring), 7.61-8.02 (7H, m, aromatic).

Number average molecular weights ($M_N$) of poly(glycidyl methacrylate) (PGMA) and poly(methyl methacrylate) (PMMA) were 138,000 and 107,000, respectively.

PMMA and a QAS or PnPSCN (15 mol%) against MMA unit) were dissolved in a mixture of THF : ethanol = 6 : 1 (v/v), and the resulting solution was cast into a Petri dish followed by slow evaporation. Thickness of the films was ca. 50 $\mu$m. Base-treatment was carried out by putting films in an ammonia-saturated bottle for 30 min at room temperature. PGMA films were obtained by spin-coating on silicone wafers from cyclohexanone / acetonitrile [5 / 2 (v/v)] solutions. Film thickness was ca. 0.5 $\mu$m, measured by a Nanometrics Nanospec / AFT M3000.

Thermal polymerization of PGE was carried out in a Pyrex tube at 100 °C for 60 min. The ratio of PGE : amine : POT was 100 : 5 : 5 (mol/mol). After heating during a given time, the mixture was diluted by THF and the molecular weights were measured by SEC.

UV-irradiation was performed using an UShio ULO-6D0 low pressure mercury lamp (6 W) in air. Light intensity was 1.0 mW/cm$^2$ at 254 nm, which was measured by an Orc UV-M02 illuminometer. Films were post-exposure baked (PEB) on a Koike HM-15G Hotplate.

Insoluble fraction of PGMA films was obtained from ratios of thickness before and after soaking the films in THF for 1 min.

**RESULTS AND DISCUSSION**

As observed for QAS having dithiocarbamates,[9] QASs having thiocyanate anions are expected to form phenacyl thiocyanate (PnPSCN) and an amine. Furthermore, because PnPSCN is known to be transformed into POT in the presence of amines,[13] the formation of POT / amine complex is expected as is shown in Scheme 2. Here, UV and IR spectral change of PnPSCN were examined in polymer matrix.

Figure 1 shows UV spectral changes of PnPSCN in PMMA films. On irradiation the absorbance in the region of 270 - 400 nm increased,
and a peak appeared at 312 nm after base-treatment. This result can be explained by the photo-isomerization of PnSCN into phenacyl isothiocyanate (PnNCS) followed by transformation to POT by base-treatment.

IR spectral changes in Fig. 2 support the above mechanism. A peak at 2160 cm⁻¹ due to thiocyanate groups in PnSCN decreased along with the appearance of broad peak at 2150 – 2005 cm⁻¹ due to isothiocyanate groups. By base-treatment, the latter peak decreased.

UV spectral changes of PnDbSCN in PMMA are shown in Fig. 3. A shoulder at 310 nm was observed, suggesting the formation of POT.

The effect of POT and amine on the thermal polymerization of PGE was investigated. The polymerization of PGE strongly depended on the kind of amine. DMAP was the most effective for the polymerization as shown in Fig. 4, and its molecular weight at peak top was 1200. DABCO was also effective. Although polymerization did not proceed by POT only and there was no effect of POT on the polymerization of DABCO / PGE systems, DMAP / POT / PGE system afforded higher Mₙ of polymer than DABCO / PGE system.

These results promoted us to prepare QASs derived from DMAP. The synthesis of PnDpBr, PnDpDt, and PnDpSCN were successful via conventional synthetic method. Unfortunately, the behavior of PnDpDt in polymer matrix could not be examined owing to extremely low solubility.

<table>
<thead>
<tr>
<th>Abbrev.</th>
<th>mp (°C)</th>
<th>Tₘ (°C)</th>
<th>λₘₐₓ (nm)</th>
<th>ε at 254 nm</th>
</tr>
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<tbody>
<tr>
<td>PnDpDt</td>
<td>177.5-178</td>
<td>174</td>
<td>293 (11,900)</td>
<td>25,000</td>
</tr>
<tr>
<td>PnDpSCN</td>
<td>118-119</td>
<td>251</td>
<td>290 (30,900)</td>
<td>11,000</td>
</tr>
</tbody>
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a) Measured by TGA.
b) In acetonitrile.

As listed in Table 1, Tₘ of PnDpSCN was higher than corresponding QAS of dithiocarbamate, PnDpDt. Furthermore, UV spectra of PnDpSCN in solvents showed little change even after 24 h. However, the stability of PnDpSCN was low, and
insolubilization occurred above 60 °C as shown in Fig. 5. This reason is unknown at present.

The photoreactions of QASs were also applied to the photo-initiated thermal crosslinking of PGMA films. Figure 6 shows insoluble fraction of PGMA films containing QASs on irradiation followed by heating at 60 °C. It is apparent that both PnDbSCN and PnPdSCN worked as photo-initiated thermal crosslinkers for PGMA films.

In conclusion, the formation of POT / DABCO complex was estimated on irradiation of PnDbSCN by IR and UV spectral analyses. Through the thermal polymerization of PGE using amines and POT, DABCO and DMAP showed excellent effect. PnPdSCN from DMAP was newly prepared and confirmed its catalytic ability of crosslinking of PGMA films on irradiation followed by PEB.

REFERENCES