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

Kanji Suyama, Kazuhiro Fuke, Masamitsu Shirai, and Masahiro Tsunooka

Department of Applied Chemistry, Osaka Prefecture University,
 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan, suyama@chem.osakafu-u.ac.jp

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 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 (lit:[12] 74.5–75 °C) and 231–234 °C (lit:[13] 234–235 °C), respectively. 1-Phenacyl-(1-azania-4-azabicyclo[2.2.2]octane) thiocyanate (PnDbSCN) was prepared as reported previously.[9]

N-Phenacyl-4-(*N,N*'-dimethylamino)-pyridinium bromide (PnDpBr) was obtained by mixing methanol solutions of phenacyl 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 =

Scheme 1. Photoreaction of a QAS having a thiocyanate anion.

3.08 (6H, d, NCH₃), 5.70 (2H, d, CH₂), 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*"-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). ¹H-NMR (CD₃CN): δ = 3.20 (6H, s, ArNCH₃), 3.45 (6H, s, S=C-N-CH₃), 5.86 (2H, s, CH₂), 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 (PnDpSCN) was obtained by a similar procedure to PnDpDt: colorless solid in 40.5 % yield: IR (KBr): 2040 (SCN), 1700 (C=O) cm⁻¹. ¹H-NMR (CD₃CN): δ = 3.22 (6H, s, CH₃), 5.74 (2H, s, CH₂), 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 PnSCN (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 μm. Base-treatment was carried out by putting films in an ammonia-saturated bottle for 30 min at room temperature. PGMA films were obtained

Fig. 1. UV spectral changes for PnSCN in PMMA on irradiation followed by base-treatment.

Scheme 2. Photoreaction of PnSCN in the presence of DABCO.

by spin-coating on silicone wafers from cyclohexanone / acetonitrile [5 / 2 (v/v)] solutions. Film thickness was ca. 0.5 μm, 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-6DQ low pressure mercury lamp (6 W) in air. Light intensity was 1.0 mW/cm² 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 (PnSCN) and an amine. Furthermore, because PnSCN 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 PnSCN were examined in polymer matrix.

Figure 1 shows UV spectral changes of PnSCN in PMMA films. On irradiation the absorbance in the region of 270 - 400 nm increased,

Fig. 2. IR spectral changes for PnSCN in PMMA on irradiation followed by base-treatment(---).

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 $2150 - 2005\text{ cm}^{-1}$ 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.

Fig. 3. UV spectral changes for PnDbSCN in PMMA on irradiation.

Fig. 4. SEC profiles of PGE/amine/POT mixtures after heating at $100\text{ }^{\circ}\text{C}$ for 1 h.

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 M_n 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 1. Physical properties of QAS.

Abbrev.	mp ($^{\circ}\text{C}$)	T_d^a ($^{\circ}\text{C}$)	$\lambda_{\text{max}}(\text{nm})^b$ (ϵ)	ϵ at 254 nm^b
PnDpDt	177.5-178	174	293 (11,900)	25,000
PnDpSCN	118-119	251	290 (30,900)	11,000

a) Measured by TGA.

b) In acetonitrile.

As listed in Table 1, T_d 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

Fig. 5. Thermal insolubilization of PGMA films containing (■) PnDbSCN and (●) PnDpSCN. GMA unit : QAS = 100 : 5 (mol/mol). Baking time: 3 min.

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 PnDpSCN 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. PnDpSCN from DMAP was newly prepared and confirmed its catalytic ability of crosslinking of PGMA films on irradiation followed by PEB.

REFERENCES

1. K. Dietliker, "Photoinitiators for Free Radical Cationic & Anionic Photopolymerization", 2nd. Ed., John Wiley & Sons, Chichester, England (1998) Chap. IV.
2. M. Shirai and M. Tsunooka, *Bull. Chem. Soc. Jpn.*, **71** (1998) 2483.
3. M. Shirai, K. Suyama, H. Okamura, and M. Tsunooka, *J. Photopolym. Sci. Technol.*, **15** (2002) 715.
4. J. E. Hanson, K. H. Jensen, N. Gargiulo, D. Motta, D. A. Pingor, A. E. Novembre, D. A.

Fig. 6. Photo-initiated thermal insolubilization of PGMA films in the presence of (□, ■) PnDbSCN and (○, ●) PnDpSCN. Open symbols : only irradiation, and closed symbols : irradiation followed by baking at 60 °C for 3 min.

Mixon, J. M. Kometani, and C. Knurek, in "Microelectronics Technology", ACS Symposium Series 614, American Chemical Society, Washington D. C. (1995) Chap. 9.

5. S. Hassoon, A. M. Sarker, A. Y. Polykarpov, M. A. J. Rodgers, and D. C. Neckers, *J. Phys. Chem.*, **100** (1996) 12386.
6. A. M. Sarker, A. Lungu, and D. C. Neckers, *Macromolecules*, **29** (1996) 8047.
7. A. M. Sarker, A. Mejiritski, B. R. Wheaton, and D. C. Neckers, *Macromolecules*, **30** (1997) 2268.
8. A. M. Sarker, Y. Kaneko, and D. C. Neckers, *Chem. Mater.*, **13** (2001) 3949.
9. H. Tachi and M. Tsunooka, *J. Polym. Sci. Part A: Polym. Chem.*, **39** (2001) 1329.
10. M. Tsunooka, H. Tachi, T. Yamamoto, and M. Shirai, "Advances in Photoinitiated Polymerization", ACS Symposium Series, American Chemical Society, Washington D. C. in press.
11. M. Tsunooka, Y. Kurokawa T. Yamamoto K. Suyama, and M. Shirai, *J. Photopolym. Sci. Technol.*, **15** (2002) 47.
12. M. Tsunooka, Y. Cha, and M. Tanaka, *Makromol. Chem., Rapid Commun.*, **2** (1981) 491.
13. M. Tsunooka, Y. Cha, and M. Tanaka, *J. Polym. Sci. Polym. Chem. Ed.*, **22** (1984) 739.