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Photoinitiated Cationic Ring-Opening Polymerization of Monothiocarbonate

Nihan Yonet,[†] Yusuf Yagci,*,[†] Bungo Ochiai,[‡] and Takeshi Endo[‡]

Department of Chemistry, Istanbul Technical University, Maslak, Istanbul 80626, Turkey, and Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

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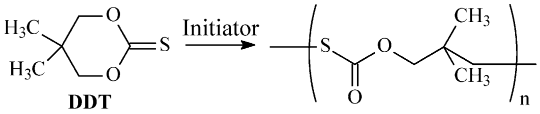
Cyclic carbonates[1] are an interesting class of monomers that undergo cationic and anionic ring-opening polymerization accompanied by volume expansion due to the difference in strength of intermolecular interaction between monomers and polymers.[2] Recently, six-membered cyclic thiocarbonates such as 5,5-dimethyl-1,3-dioxane-2-thione have been introduced as the structurally related monomers to yield the corresponding polymonothiocarbonates by controlled cationic polymerization[3] (Scheme 1).

Scheme 1



Initiator : Et_3OBF_4, TfOMe, TfOH, BF_3OEt_2

Kricheldorf et al.[4] previously reported that cationic ring-opening polymerization of the unsubstituted monomer, 1,3-dioxane-2-thione, also affords a polymonothiocarbonate. However, the polymers obtained in the latter case were insoluble in common organic solvents, and therefore, the polymerization mechanism and the polymer structure were not evaluated.

At present, there is growing interest in photoinitiated cationic polymerization of many industrially important monomers due to their wide range commercial applications.[5,6] Many cationic photoinitiators are known, and their photochemistry[7] has been studied in detail. Among them, onium-type photoinitiators such as iodonium,[8] sulfonium,[9] and alkoxypyridinium[10] salts occupy an important place due to their thermal stability, solubility in most of cationically polymerizable monomers, and efficiency in generating reactive species upon photolysis. Moreover, they can be photochemically activated in a broad wavelength range with the aid of various sensitizers and free radical photoinitiators.[11−15]

This paper describes photoinitiated cationic ring-opening polymerization of a six-membered monothiocarbonate, 5,5-dimethyl-1,3-dioxane-2-thione (DDT), by using onium salts. As will be shown below, both direct and indirect photoactivation of onium salts are studied.

The cationic polymerization of the monothiocabonate, DDT, was carried out with diphenyliodonium, triphenylsulfonium, and *N*-ethoxy-2-methylpyridinium salts as photoinitiators in CH_2Cl_2 under a dry nitrogen atmosphere, as summarized in Table 1.

Table 1. Photoinitiated Polymerization[a] of 5,5-Dimethyl-1,3-dioxane-2-thione (DDT) by Using Onium Salts in CH_2Cl_2 at Room Temperature

run	onium salt	conv (%)	M_n[c]	M_w/M_n[c]
1	Ph_2I^+	82.5	16 900	1.68
2[b]	Ph_2I^+	79.6	12 500	1.65
3	Ph_3S^+	92.6	15 000	1.67
4	EMP^+	~1		

[a] [DDT] = 1 mol L^{-1}; [onium salt] = 2×10^{-2} mol L^{-1}; λ = 300 nm, irradiation time = 2.5 h. [b] Polymerization was carried out in the presence of air. [c] Determined by GPC using polystyrene standards.

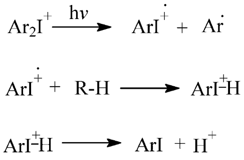
Table 2. Photoinitiated Cationic Ring-Opening Polymerization[a] of 5,5-Dimethyl-1,3-dioxane-2-thione (DDT) by Using $Ph_2I^+PF_6^-$ in CH_2Cl_2 at Room Temperature

run	$[DDT]/[Ph_2I^+]$	conv (%)	M_n[b]	M_w/M_n[b]
5	10	58	6 400	2.34
6	20	86	10 200	1.68
7	30	79	12 700	1.77
8	40	85	15 000	1.77
9	50	82	16 900	1.68
10	60	77	17 800	1.63

[a] [DDT] = 1 mol L^{-1}; λ = 300 nm; irradiation time = 2.5 h. [b] Determined by GPC using polystyrene standards.

Both iodonium and sulfonium salts are quite effective as photoinitiators upon irradiation at λ = 300 nm where they absorb light.[16] The higher reactivity of the sulfonium salts may be attributed to the compatibility of the salt with the monomer since both possess sulfur atom in their structure. The polymerization times are much shorter than those performed with conventional cationic initiators such as triethyloxonium salts and triflic initiators. Expectedly, oxygen has no inhibitory effect on the polymerization, and similar yield and molecular weight were obtained in the presence of air under identical experimental conditions. Moreover, the photoinitiated polymerizations were conducted at room temperature. This is an obvious advantage over the thermal polymerization performed moderately elevated temperatures. However, the molecular weight distributions of the polymers obtained by photochemical means are broader and in the range of 1.7 (see Tables 1 and 2). This is expected since in photopolymerization initiating species are generated continuously; growing polymer chains with large differences in chain lengths are present at the same time.[17] Therefore, polymers usually have broad molecular weight distributions. Upon photolysis, onium salt type initiators undergo irreversible photofragmentation to produce cation radicals and eventually Brønsted acids capable of initiating cationic polymerization as presented on the example of diphenyliodonium salt[18] (Scheme 2).

Scheme 2



R-H = Solvent or monomer
Counter anion is omitted

[†] Istanbul Technical University.
[‡] Yamagata University.

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Scheme 3

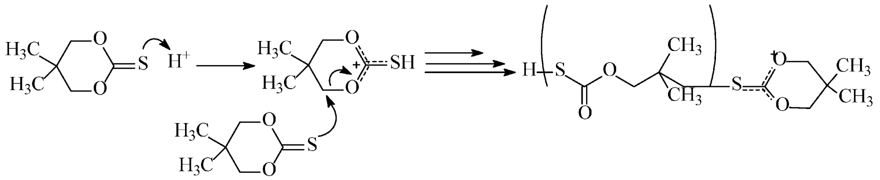


Table 3. Free Radical Promoted Cationic Polymerization[a] of 5,5-Dimethyl-1,3-dioxane-2-thione (DDT) by Using 2,2′-Dimethoxy-2-phenylacetophenone (DMPA) in the Presence of Onium Salts in CH_2Cl_2 at Room Temperature

run	onium salts[b]	$E_{1/2}^{\mathrm{red}}$ (V SCE)	conv (%)	M_n[b]	M_w/M_n[b]
11	Ph_2I^+	−0.2[23]	60.8	11 600	1.16
12	EMP^+	−0.7[24]	42.7	10 500	1.31
13	Ph_3S^+	−1.2[25]			

[a] [DDT] = 1 mol L^{-1}; [onium salt] = 2 × 10^{-2} mol L^{-1}; [DMPA] = 2 × 10^{-2} mol L^{-1}; λ = 350 nm, irradiation time = 2.5 h. [b] Determined by GPC using polystyrene standards.

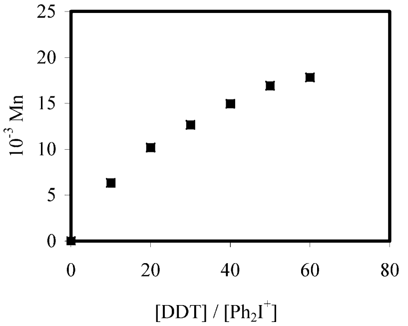
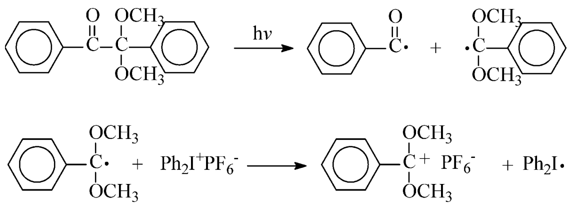


Figure 1. Relationship between M_n and the ratio of [DDT]/[Ph_2I^+]. Conditions: monomer, 0.25 mmol; solvent, 0.25 mL of CH_2Cl_2, under exposure of 300 nm wavelength for 2.5 h.

Scheme 4



The structure of the polymers was examined by ^{1}H NMR. The spectrum of the polymer exhibited three singlet at 0.98, 2.91, and 3.99 ppm, which were assignable to the methyl group and the α- and γ-methylenes with respect to the thiocarbonate sulfur atom. These results indicate that the photoinitiated ring-opening polymerization was accompanied by isomerization of the thiocarbonyl group into the carbonyl group (Scheme 3). This observation was further supported by a carbonyl absorption peak at 1712 cm^{-1} in the IR spectrum of the polymer.

In this connection, it should be pointed out that thermal polymerization using conventional cationic initiators[3] yielded polymers with the same structures. The M_n's of the polymers increased as the feed ratio of [**1**]/[Ph_2I^+] increased (Figure 1). However, in all cases the molecular weight distributions were rather broad than those obtained by conventional thermal cationic initiators[3] (M_w/M_n = 1.63−2.34) (see Table 2).

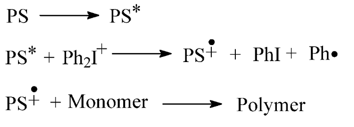
As stated in the Introduction section, photodecomposition of onium salts can be induced with the aid of many light-sensitive compounds.[19] Among them, the use of free radical initiators is a fairly flexible way and allows to extend the spectral sensitivity of the cationic initiating system to the absorbency of the free radical initiators. Suitable radical sources with wide range absorption characteristics are available and successfully employed in free radical promoted cationic polymerization. The crucial requirement in such systems is that photochemically generated radicals should be electron donating in order to facilitate successful oxidation to the initiating cations. For our purpose, we have deliberately selected 2,2-dimethoxy-2-phenylacetophenone as the free radical source since it undergoes α-cleavage with high quantum efficiency[20] and produces strong electron-donating dimethoxybenzyl radicals which are readily oxidizable to the corresponding cations[21] (Scheme 4).

Table 4. Photosensitized Polymerization[a] of 5,5-Dimethyl-1,3-dioxane-2-thione (DDT) by Using Onium Salts in CH_2Cl_2 at Room Temperature

run	photosensitizer	conv (%)	M_n[c]	M_w/M_n[c]
14	perylene	87.6	10 800	1.25
15	anthracene	71.8	13 600	1.29

[a] [DDT] = 1 mol L^{-1}; [onium salt] = 2 × 10^{-2} mol L^{-1}; [sensitizer] = 2 × 10^{-2} mol L^{-1}; λ = 350 nm, irradiation time = 2.5 h. [b] Determined by GPC using polystyrene standards.

Scheme 5



PS = Perylene or Anthracene
Counter anion is omitted

The efficiency of onium salts as oxidizing agents is related to their electron affinity.[22] The higher the oxidation power of the onium salt, the higher (more positive) is the reduction potential $E_{1/2}^{\mathrm{red}}(\mathrm{On}^+)$. As can be seen from Table 3, the iodonium salt is the most powerful oxidation agent which contributes to the higher conversion of monothiocarbonate. Triphenylsulfonium salt does not participate in such an electron-transfer process due to unfavorable redox potential. In this case cationic polymerization does not proceed. The intermadiate behavior of the pyridinium salt is also related to its redox potential.

Photosensitization with the aid of various sensitizers absorbing light at longer wavelengths, i.e., $\lambda > 350$ nm, can also help to extend the applicability of onium salts as photoinitiator.[26] For this purpose, the reactions of diphenyliodonium ions with excited states of perylene and anthracene were examined. In the ground state, these compounds absorb light between 350 and 400 nm. Long wavelength irradiation, i.e., λ = 350 nm, is employed, which permits the selection of absorption by the photosensitizer, but not by the iodonium salt. Typical results are presented in Table 4. It should be pointed out that both sensitizers are ineffective for initiating cationic polymerizations in the absence of the iodonium salt. Notably, both compounds act as sensitizers.

Detailed studies based on the flash photolysis experiments and calculation of free energy changes (ΔG) suggest that the sensitizing action of perylene and anthracene accomplished by electron transfer between the excited-state photosensitizer and onium ions resulting in the formation of the radical cation of the sensitizer according to the reactions are presented in Scheme 5:

It was shown that sensitizer radical cations react directly with monomers and initiate the polymerization.[14] In all cases, polymers with the isomerized structures were formed regardless of the initiation method employed.

In summary, we have shown that the photoiniated polymerization of monothiocarbonate can be achieved by using onium salt type photoinitiators. Both direct and indirect methods utilizing either free radical sources or photosensitizers were shown to be efficient in the photoinitiation process. Structural investigations revealed that polymerization was accompanied by isomerization as was observed with the conventional cationic initiators.

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Supporting Information Available: Experimental description of polymerization of 5,5-dimethyl-1,3-dioxane-2-thione (DDT), ^{1}H NMR and FTIR spectra of 5,5-dimethyl-1,3-dioxane-2-thione, and the polymer obtained by photoinitiated ring-opening polymerization (Table 1, run 1). This material is available free of charge via the Internet at http://pubs.acs.org.

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