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Copolymerization of Ketene Cyclic *N,O*-Acetals with Carbon Disulfide: Evidence for Formation of Zwitterionic Intermediates by Means of ^{1}H NMR Spectroscopy

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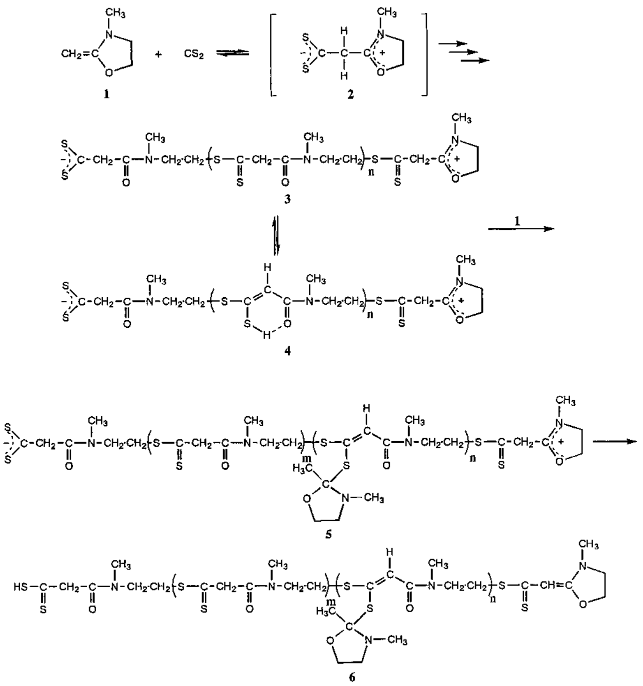
Introduction. Spontaneous polymerization of various pairs of electrophilic and nucleophilic monomers has been of particular interest in the field of polymer chemistry. When both monomers are olefins, that is, electron-poor and electron-rich olefins, tetramethylene intermediates formed by the reaction between the β-carbon atoms are postulated as the initiation species for spontaneous polymerization.[1] A zwitterionic tetramethylene initiates anionic or cationic homopolymerization of electron-poor or electron-rich olefins, respectively, while a biradical tetramethylene initiates 1:1 alternating copolymerization through a charge transfer mechanism. On the other hand, it has been reported that a zwitterionic intermediate is the key species responsible for producing 1:1 alternating copolymer when the nucleophilic monomers are heterocyclic compounds such as imino ethers etc.[2]

In the course of our study of polymerization of cyclic ketals having an exo-methylene group adjacent to the oxygen atom, we found that 4-methylene-1,3-dioxolane derivatives spontaneously copolymerize with maleic acid derivatives to afford 1:1 alternating copolymers via a charge transfer mechanism.[3] Furthermore, we have reported on the spontaneous reaction and copolymerization through a zwitterion mechanism for pairs of 2-methylene-1,3-dioxolane derivatives or ketene cyclic acetals, whose β-carbons are highly polarized and hence have extraordinarily high nucleophilicity owing to the mesomeric effect of the two conjugated oxygen atoms,[4] and heterocumulenes[5] such as phenyl isocyanate, phenyl isothiocyanate, and carbon disulfide.

It is anticipated that the β-carbon atoms of the carbon−carbon double bond of ketene *N,O*-acetals are more polarized and have far higher anionoid character compared with those of ketene *O,O*-acetals because the electron-donating property of the nitrogen atom is stronger than that of the oxygen atom. In this paper, we describe the copolymerization of ketene cyclic *N,O*-acetals with carbon disulfide and demonstrate the formation of a zwitterionic intermediate by means of ^{1}H NMR spectroscopy.

Results and Discussion. An orange-red color immediately developed with violent evolution of heat upon mixing 2-methylene-3-methyl-1,3-oxazolidine (**1**)[6] with carbon disulfide (CS_2) [feed ratio: $\mathbf{1}/CS_2 = 1/1$ (mol/mol)] in acetonitrile at room temperature. The polymerization temperature immediately rose until the mixture refluxed and then gradually decreased to room temperature. The red polymeric product was isolated in 79% yield as an *n*-hexane-insoluble viscous oil, whose mean molecular weight ($\bar{M}_n$) was estimated to be 1000. The product was soluble in chloroform, *N,N*-dimethylformamide, and acetone but insoluble in *n*-hexane, ether, and methanol. The IR spectrum of the copolymer showed the characteristic absorption of the amide carbonyl band at 1640 cm^{-1}, together with a strong absorption at 1570 cm^{-1} ascribed to the carbon−carbon double bond. The ^{1}H and ^{13}C NMR spectra of the copolymer were very complicated but clearly showed a singlet signal at 5.9 ppm due to the olefinic methine proton and a signal at 91.7 ppm assignable to the center carbon in the ortho ester structure. Elemental analysis of the copolymer indicated the $\mathbf{1}/CS_2$ composition was about 65:35. Taking into account these facts and the previously reported result of the copolymerization of ketene cyclic *O,O*-acetal and carbon disulfide,[5c] it is reasonable to presume a zwitterion (**2**) from **1** and CS_2 as a key intermediate as shown in Scheme 1. The reaction between two molecules of **2** with opening of the ring gives a dimeric zwitterion (**3**(n=0)), which reacts with **2** and/or each other to produce an oligomeric zwitterion (**3**(n>1)). By the successive combination reaction of **3**(n>1) with **2**, the oligomeric zwitterion grows a macrozwitterion (**3**), which tautomerizes to an enethiol form (**4**). The addition reaction of the residual monomer (**1**) to **4** takes place to give a macrozwitterion (**5**) pendant with the ortho ester structure. Finally, the termination reaction occurs by the transfer of a proton from the α-carbon of the oxazolinium cationic center to the dithiocarboxylate anion, resulting in a low molecular weight copolymer (**6**).

Scheme 1



It is reasonable to consider that a 1:1 alternating copolymer, consisting of ketene cyclic *N,O*-acetal and CS_2, with a high molecular weight should be obtained if neither the enethiol structure forms in the copolymer structure nor the proton transfer reaction takes place. In order to ascertain the above concept, we designed 2-isopropylidene-3-methyl-1,3-oxazolidine (**7**),[7] which has two methyl groups instead of two hydrogen atoms at the β-carbon atom of **1**.

Upon mixing **7** with CS_2, a vigorous exothermic reaction immediately took place with a developing dark

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Table 1. Copolymerization of Ketene Cyclic *N,O*-Acetal (7) with Carbon Disulfide

	reaction conditions				copolymer		
no.	ratio [CS_2/**7**]	solvent	temp (°C)	time (h)	yield (%)[a]	$\overline{M}_n \times 10^{-3}$ [b]	$\overline{M}_w/\overline{M}_n$ [b]
1	1.0	CH_3CN	ambient[c]	*d*	71	88	2.7
2	1.0	CH_2Cl_2	−15	48	90	9.5	1.8
3	5.0	neat	ambient[c]	*d*	99	300	6.5
4	5.0	neat	−50	1	99	260	2.0

[a] Insoluble in *n*-hexane. [b] Determined by GPC (eluent $CHCl_3$, based on polystyrene standards). [c] The reaction temperature instantaneously rose to ca. 80 °C. [d] Instantaneous.

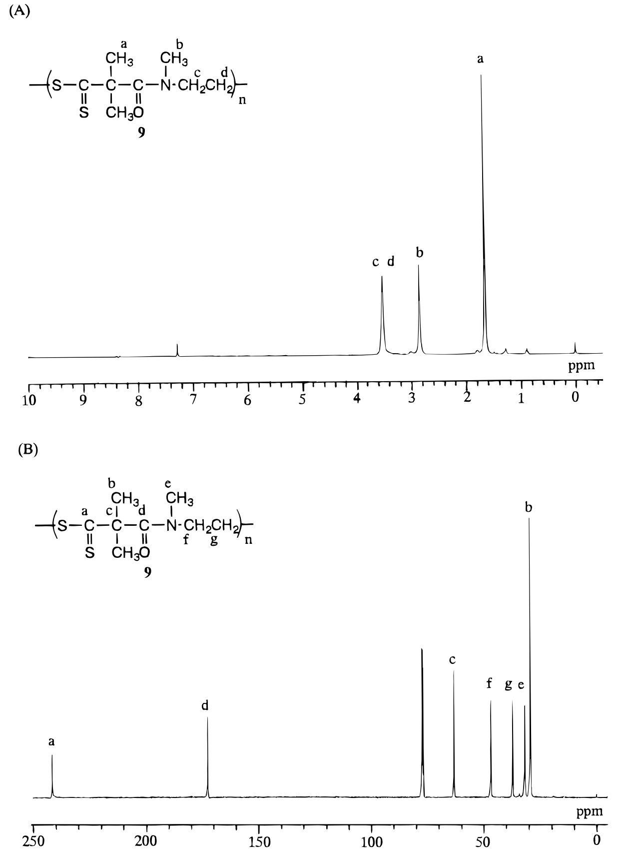


Figure 1. NMR spectra of copolymer (**9**): (A) ^1H, 400 MHz, $CDCl_3$; (B) ^{13}C, 100 MHz, $CDCl_3$.

red color to produce an orange red solid.[8] In order to prevent the abrupt reaction, the copolymerization was performed with cooling at −50 °C for 1 h.[9] Orange-yellow 1:1 alternating copolymers were isolated as *n*-hexane-insoluble powders. These results are summarized in Table 1. As expected, higher molecular weight 1:1 alternating copolymers were obtained by both solution and bulk copolymerization. IR spectra of the 1:1 alternating copolymers showed a strong thiocarbonyl absorption at 1080 cm^{-1} as well as an amide carbonyl band at 1650 cm^{-1}. As shown in Figure 1, the ^1H NMR spectra of the alternating copolymers showed signals at 1.65 (s, 6H, C**H**$_3$CC**H**$_3$), 2.85 (s, 3H, C**H**$_3$N), and 3.55 ppm (m, 4H, NC**H**$_2$C**H**$_2$S), and the ^{13}C NMR spectra showed characteristic signals due to the amide carbonyl carbon at 172.4 ppm (N**C**=O) and the thiocarbonyl carbon at 241.4 ppm (S**C**=S) as well as the absence of a signal around 100 ppm ascribed to the center carbon atom of the ortho ester structure. These spectral data indicate that the zwitterionic intermediate (**8**), formed by the reaction of **7** and carbon disulfide, continuously reacts with each other by the attack of dithiocarboxylate anion on the β-carbon atom to the oxazolinium center to afford a macrozwitterion (**9**), as shown in Scheme 2. The high molecular weight of the 1:1 alternating copolymers might be due to the quantitative formation of the zwitterionic intermediate (**8**) which does not have any transferable protons.

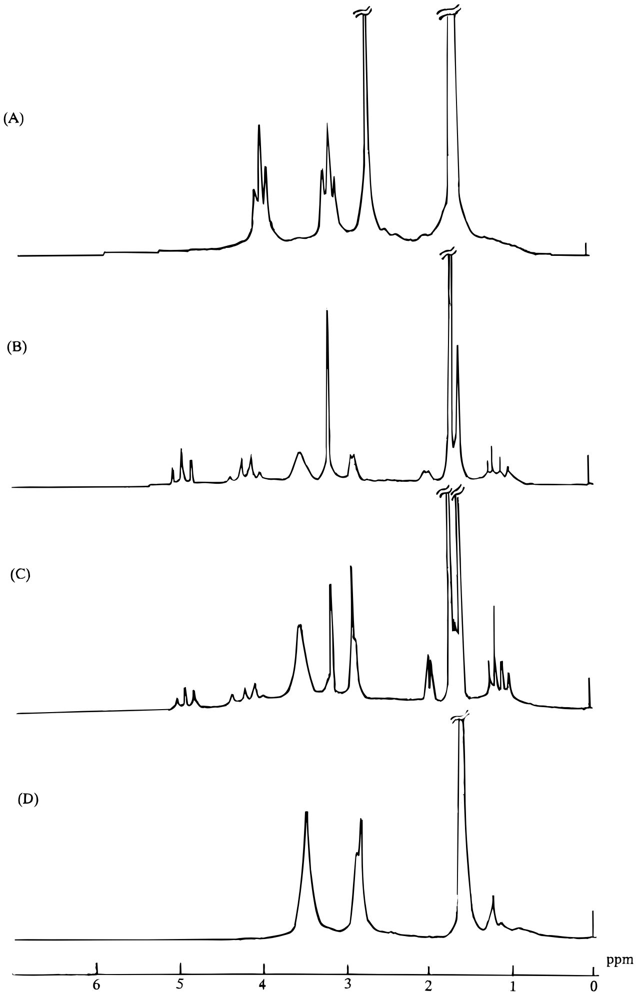
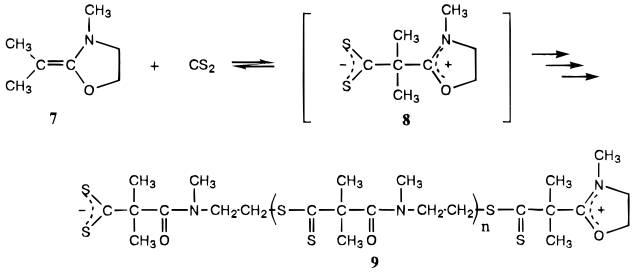


Figure 2. ^1H NMR spectra of the reaction mixture of **7** and CS_2 in CD_3CN: (A) **7**; (B) just after mixing at −30 °C; (C) 10 min at −30 °C; (D) 10 min after the temperature was raised to 25 °C.

Scheme 2



In order to confirm the formation of **8**, the reaction of **7** and carbon disulfide was carried out at −30 °C and followed by ^1H NMR spectroscopy. As shown in Figure 2, the signals at 2.7 (s, 3H, C**H**$_3$N), 3.1 (t, 2H, OCH_2C**H**$_2$N), and 4.0 ppm (t, 2H, OC**H**$_2$$CH_2N$), ascribed to the 1,3-oxazolidine structure, completely disappeared, and new signals at 3.1, 4.1, and 4.9 ppm assignable to the oxazolinium structure were observed when carbon disulfide was added to **7** (Figure 2B). These three signals gradually decreased with increasing of two new signals at 2.9 (s, 3H, C**H**$_3$N) and 3.6 ppm (s, 4H, NC**H**$_2$C**H**$_2$S), and completely disappeared when the reaction temperature was raised to 25 °C. These spectra evidently demonstrate that the copolymerization of **7** and CS$_2$ proceeds through a zwitterionic intermediate (**8**) to afford the 1:1 alternating copolymer with complete ring-opening (**9**).

In conclusion, spontaneous copolymerization of ketene cyclic *N*,*O*-acetals with carbon disulfide has been demonstrated. The copolymerization of 2-isopropylidene-3-methyl-1,3-oxazolidine (**7**) and carbon disulfide proceeded through a zwitterion mechanism with complete ring-opening to afford a 1:1 alternating copolymer (**9**) having a high molecular weight, as we expected. The present study may be the first example where zwitterionic intermediates can be observed in a 1:1 alternating copolymer system.

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(6) Bp 86−87 °C/95 Torr; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.65 (s, 3H), 2.73 (d, J = 2.9 Hz, 1H), 3.17 (d, J = 2.9 Hz, 1H), 3.22 (t, J = 6.8 Hz, 2H), 4.11 (t, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz) δ 34.1, 51.0, 51.5, 64.6, 162.7.

(7) Bp 89−90 °C/55 Torr; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.64 (s, 3H), 1.67 (s, 3H), 2.68 (s, 3H), 3.15 (t, J = 7.3 Hz, 2H), 3.98 (t, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz) δ 17.2, 17.7, 41.8, 53.9, 63.9, 81.9, 153.6.

(8) Carbon disulfide (3.0 g (39 mmol)) was placed in a polymerization tube equipped with a No-Air stopper. After 10 min of purging with a stream of argon at room temperature, 1.0 g (7.9 mmol) of **7** was added by a syringe. An exothermic reaction instantaneously took place, and the reaction temperature rose to ca. 80 °C. The reaction mixture gave rise to an orange-red solid. After the solid was dissolved by the addition of 5 mL of chloroform, the resulting solution was poured into *n*-hexane to precipitate the copolymer. The precipitated orange-yellow powders were collected and dried under reduced pressure, yielding 1.58 g (99%, entry no. 3 in Table 1). Anal. Calcd for $C_8H_{13}ONS_2$: C, 47.26; H, 6.44; N, 6.89; S, 31.54. Found: C, 46.76; H, 6.47; N, 6.75; S, 31.11.

(9) Carbon disulfide (3.0 g (39 mmol)) was placed in a polymerization tube equipped with a No-Air stopper. After 10 min of purging with a stream of argon at −50 °C, 1.0 g (7.9 mmol) of **7** was added by a syringe. The reaction mixture was maintained at the same temperature for 1 h. After the reaction mixture was dissolved by the addition of 5 mL of chloroform, the resulting solution was poured into *n*-hexane to precipitate the copolymer. The precipitated orange-yellow powders were collected and dried under reduced pressure, yielding 1.57 g (99%, entry no.4 in Table 1). Anal. Calcd for $C_8H_{13}ONS_2$: C, 47.26; H, 6.44; N, 6.89; S, 31.54. Found: C, 47.38; H, 6.45; N, 6.92; S, 31.61.

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