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Cationic Ring-Opening Polymerization Behavior of Six-Membered Cyclic Sulfite

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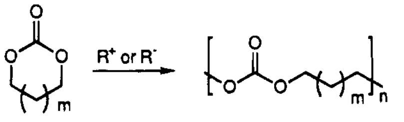
ABSTRACT: Cationic ring-opening polymerization behavior of six-membered cyclic sulfite (**1**) was examined. **1** was prepared by the reaction of 1,3-propanediol with $SOCl_2$ in 80% yield. Cationic ring-opening polymerization of **1** was carried out in the presence of cationic initiators such as benzyl bromide (BnBr), $BF_3{\cdot}OEt_2$, trifluoromethanesulfonic acid (TfOH), and methyl trifluoromethanesulfonate (TfOMe) in bulk to afford a polymer consisting of sulfite and ether moieties. The content of the poly(ether) unit was estimated to be 30−90%. The relative rate of polymerization by the initiators was estimated to be TfOH:TfOMe:$BF_3{\cdot}OEt_2$ = 3.5:2.5:1.0. Judging from the time−conversion curves and time−poly(ether) production curves, the elimination of sulfur dioxide in the propagating end of the polymer was confirmed to depend on the character of the counteranion.

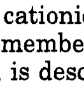
Introduction

Recently, we have reported that six-membered cyclic carbonates can undergo considerable expansion in volume during polymerization[1] (Scheme 1) as the recent most important finding in the field of expandable monomers. The origin of this volume expansion can be discussed from a viewpoint of the differences in the respective intermolecular interactions between the monomer and polymer, on the basis of the various physical data of cyclic carbonates and acyclic carbonates as polymer model compounds.[1d] Cyclic carbonates such as propylene carbonate have higher boiling points and larger dielectric constants, dipole moments, and densities than acyclic carbonates such as diethyl carbonate. These data may suggest that the volume expansion comes from the larger free volume of linear polycarbonate due to its smaller intermolecular interaction than that of the corresponding monomer cyclic carbonate. The larger the difference of the dipole moments between monomer and polymer is, the larger the volume expansion is.[2]

In the course of our research on the polymerization of cyclic carbonates, we have designed a new candidate for expanding monomers, cyclic sulfite, an analogue of cyclic carbonate. Since cyclic sulfite has been reported to have a large dipole moment,[3] it may show volume expansion on polymerization similarly to cyclic carbonate. In this paper, the cationic ring-opening polymerization behavior of six-membered cyclic sulfite, 1,3,2-dioxathiane 2-oxide (**1**), is described.

Scheme 1





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Experimental Section

Materials. Chloroform was refluxed over P_2O_5 and distilled. 1,3-Propanediol and *N,N*-dimethylformamide (DMF) were distilled under reduced pressure. Thionyl chloride was used as received. Pyridine was dried over KOH and distilled. Benzyl bromide (BnBr) and methyl trifluoromethanesulfonate (TfOMe) were dried over P_2O_5 for several hours and distilled under reduced pressure. $BF_3{\cdot}OEt_2$ and trifluoromethanesulfonic acid (TfOH) were distilled under reduced pressure before use.

Measurement. ^1H and ^{13}C NMR spectra were recorded (90 MHz for ^1H and 22.5 MHz for ^{13}C NMR) on a JEOL JNM-EX90 spectrometer, using tetramethylsilane (TMS) as an internal standard in deuteriochloroform ($CDCl_3$) or hexadeuteriodimethyl sulfoxide (DMSO-d_6) at 27 °C. FT-IR spectra were obtained with a JASCO FT/IR-3 spectrometer. The mass spectrum was measured on a Hitachi M-80 spectrometer. Molecular weights ($\bar{M}_n$ and $\bar{M}_w$: number- and weight-average molecular weights) and the distribution ($\bar{M}_w/\bar{M}_n$) were estimated by gel permeation chromatography (GPC) on a Toyo Soda HPLC CCP & 8000 system with a data processor, equipped with a refractive index detector and three polystyrene gel columns (Toyo Soda TSK gels G2500H, G4000H, and G5000H) using tetrahydrofuran as an eluent, with a flow rate 1.0 mL/min by polystyrene calibration at 30 °C. Densities of **1** and poly(**1**) were measured by the density gradient tube method at 25 °C using lithium bromide solution as a density gradient liquid.

Synthesis of 1,3,2-Dioxathiane 2-Oxide (1). Monomer **1** was prepared from thionyl chloride and 1,3-propanediol according to the reported method.[3c,4] A solution of thionyl chloride (18.0 g, 151 mmol) in chloroform (200 mL) was added dropwise at 0 °C into 1,3-propanediol (10.0 g, 131 mmol) in chloroform (200 mL) in the presence of DMF (11.0 g, 151 mmol) as a catalyst. The reaction mixture was stirred under reflux for 5 h and distilled under reduced pressure to afford **1** as a colorless liquid in 80% yield. Bp: 34−35 °C/2.8 mmHg (lit.[3c] 66−67 °C/14 mmHg). ^1H NMR ($CDCl_3$), δ: 1.50−1.85 (m, 1 H, $C{-}CH_2{-}C$, equatorial), 2.18−2.83 (m, 1 H, $C{-}CH_2{-}C$, axial), 3.70−4.10 (m, 2 H, $C{-}CH_2{-}O$, equatorial), 4.68−5.20 (m, 2 H, $C{-}CH_2{-}C$, axial). ^{13}C NMR ($CDCl_3$), δ: 28.0, 57.5. IR (KBr): 1204 cm^{-1} (axial $\nu_{S=O}$ bond). MS (*m/z*): 122 (M^+).

Cationic Polymerization of 1. Typical Procedure. $BF_3{\cdot}OEt_2$ (29.1 mg, 0.205 mmol) was introduced into a glass tube containing **1** (500 mg, 4.10 mmol) under a nitrogen atmosphere. After the reaction mixture was kept at 120 °C for 3 days under stirring, the reaction mixture was diluted

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Table 1. Cationic Ring-Opening Polymerization of Six-Membered Cyclic Sulfite (1)

run	initiator [amt (mol %)]	temp (°C)	time (days)	conversion[a] (%)	content of unit **3**[a] (%)	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[b]
1	BnBr (20)	60	17	40	46	850 (1.21)
2	BnBr (20)	120	17	77	62	840 (1.26)
3	BF_3·OEt_2 (5)	60	3	27	29	970 (1.22)
4	BF_3·OEt_2 (5)	60	5	31	47	960 (1.21)
5	BF_3·OEt_2 (5)	120	3	69	61	1220 (1.28)
6	BF_3·OEt_2 (10)	60	5	47	48	790 (1.20)
7	BF_3·OEt_2 (5)	25	30	26	27	680 (1.17)
8	TfOH (1)	60	3	26	52	1190 (1.36)
9	TfOH (5)	60	1	55	73	1340 (1.22)
10	TfOH (5)	60	3	86	84	2150 (1.35)
11	TfOH (5)	60	5	96	89	2220 (1.36)
12	TfOMe (5)	60	1	38	74	1330 (1.26)
13	TfOMe (5)	60	3	69	81	1580 (1.30)
14	TfOMe (5)	60	5	89	87	1740 (1.31)

[a] Determined by 1H NMR (solvent, CDCl3; 90 MHz). [b] Estimated by GPC (PSt standards; eluent, THF).

with methylene dichloride. After the polymerization was quenched by the addition of pyridine (10.0 mg, 0.147 mmol), the polymerization mixture was washed with 10% $NaHCO_3$ aqueous solution to transform the pyridinium salt of the polymer end to a hydroxyl group. The conversion of **1** was determined by the integration ratio of the signals of the α-methylene protons of **1** (3.70–4.10 and 4.68–5.20 ppm) and poly(**1**) (3.20–4.41 ppm) in the ^1H NMR spectrum of the crude polymerization mixture. The polymer was isolated as a pale brown transparent viscous liquid by preparative HPLC (Japan Analytical Industry LC908, equipped with polystyrene gel columns (JAIGEL H1 and H2), using chloroform as an eluent).

Synthesis of Model Polymer (Polycondensation). A three-necked flask was fitted with two dropping funnels. In one of the dropping funnels was placed a mixture of 1,3-propanediol (1.00 g, 13.1 mmol) and DMF (1.96 g, 26.8 mmol). To the other funnel was added thionyl chloride (1.60 g, 13.4 mmol). The two solutions in dropping funnels were added dropwise into the flask simultaneously at −25 °C, and the reaction mixture was stirred at −25 °C for 72 h. The unreacted thionyl chloride was distilled off under reduced pressure. Poly(propylene sulfite) was isolated by preparative HPLC in 50% yield as a brown transparent viscous liquid ($\bar{M}_n$: 700).

Results and Discussion

Monomer Synthesis. Six-membered cyclic sulfite **1** was prepared by the reaction of 1,3-propanediol with $SOCl_2$ in 80% yield. **1** was confirmed to have an axial S=O bond since the $\nu_{S=O}$ absorption in the IR spectrum was observed at 1204 cm^{-1}.[3c,4] Since no change of the signals in the ^1H NMR spectrum of **1** was observed from room temperature to 100 °C in DMSO-d_6, the S=O bond lay in an axial conformation. The strong preference for an axial S=O bond would result from a dipolar interaction analogous to the anomeric effect.[3c,5]

Cationic Polymerization. Cationic polymerization of **1** was carried out at 25, 60 or 120 °C in the presence of BnBr, BF_3·OEt_2, TfOH, and TfOMe in bulk. Separation of the polymerization mixture by preparative HPLC without quenching afforded only low molecular weight compounds because some kinds of reactions such as main chain fission of the polymer by the attack of cationic species might proceed. The conversion of **1** could not be determind by quenching with aqueous ammonia since **1** was easily hydrolyzed. Therefore, the reaction mixture was quenched with pyridine. Results of the cationic polymerization of **1** are summarized in Table 1. In all cases, the polymerization mixture changed from colorless to pale brown within 0.5–1 h.

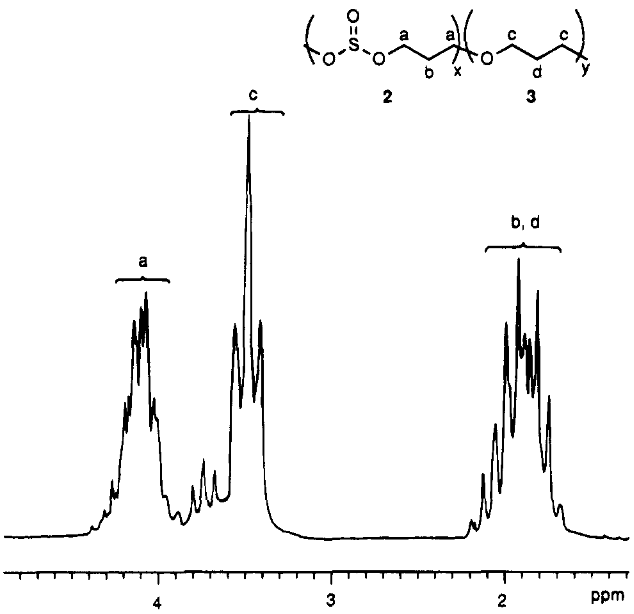


Figure 1. ^1H NMR spectrum (solvent $CDCl_3$) of poly(**1**) (run 5 in Table 1).

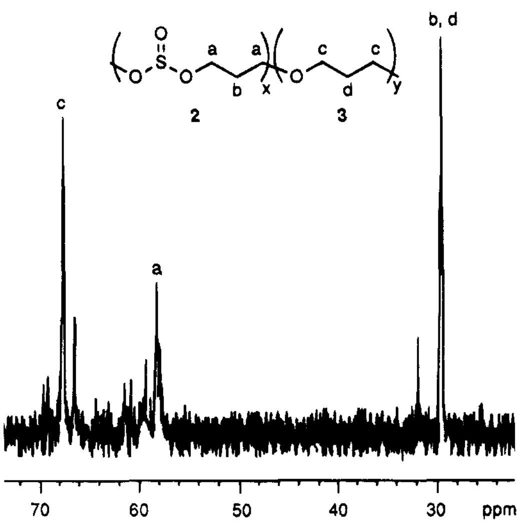


Figure 2. ^{13}C NMR spectrum (solvent $CDCl_3$) of poly(**1**) (run 5 in Table 1).

The $\bar{M}_n$ of the obtained polymer was 700–2200. The structure of the obtained polymer was examined by the ^1H and ^{13}C NMR and IR spectra. The ^1H and ^{13}C NMR spectra of the polymer are shown in Figures 1 and 2, respectively. To confirm the assignment of the ^1H and ^{13}C NMR spectra of the polymer obtained by the cationic polymerization of **1**, polycondensation of $SOCl_2$ with 1,3-propanediol was carried out under bulk conditions to obtain the model polymer. A low molecular weight polymer ($\bar{M}_n$ 700, determined by GPC) besides **1** was obtained. The molecular weight of the polymer was also calculated to be 720 from the integration ratio of the methylene protons adjacent to the sulfite and polymer end hydroxyl groups. The ^1H and ^{13}C NMR spectra of the polymer obtained by the polycondensation are shown in Figures 3 and 4, respectively. In the ^1H NMR spectrum of poly(**1**) (Figure 1), signals at 3.85–4.41 and 1.60–2.26 ppm assignable to the methylene protons α and β based on the sulfite moiety were observed, respectively. A signal at 3.30–3.63 ppm assignable to the methylene protons adjacent to the oxygen of the poly(ether) unit formed by the elimination of sulfur dioxide was observed. Since the polymerization was

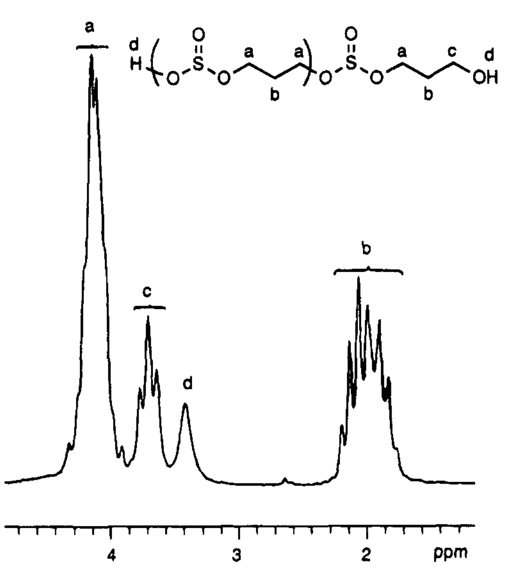


Figure 3. ^{1}H NMR spectrum (solvent $CDCl_3$) of polysulfite **2** obtained by polycondensation.

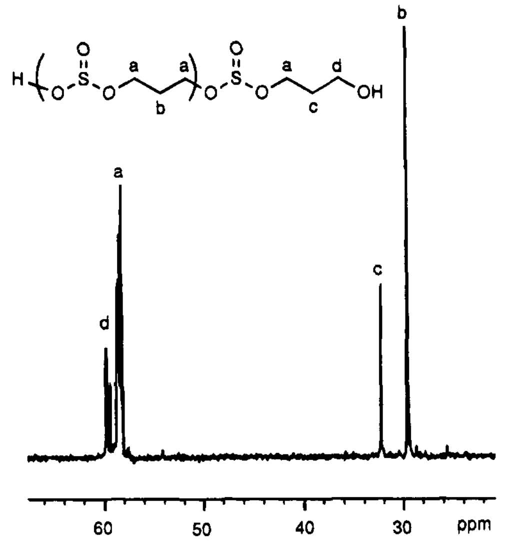
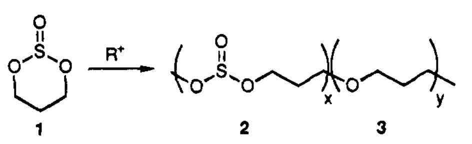


Figure 4. ^{13}C NMR spectrum (solvent $CDCl_3$) of polysulfite **2** obtained by polycondensation.

Scheme 2



quenched by the addition of pyridine, and the polymerization mixture was washed with 10% $NaHCO_3$ aqueous solution to transform the pyridinium salt of the polymer end to a hydroxyl group, the signal at 3.63–3.85 ppm might be assignable to methylene protons adjacent to the hydroxyl group of the polymer end. In the ^{13}C NMR spectrum of the polymer (Figure 2), two signals at 58.2 and 29.4 ppm assignable to the methylene carbons α and β to the sulfite moiety were observed, respectively. Signals at 67.6 and 29.4 ppm assignable to the methylene carbons α and β to the poly(ether) unit were also observed. In the IR spectrum of the polymer (run 5 in Table 1), absorptions at 1205 and 1117 cm^{-1} derived from $\nu_{S=O}$ of the sulfite moiety and ν_{C-O} of ether moiety were observed, respectively. Therefore, the obtained polymer was determined to consist of poly(sulfite) (**2**) and poly(ether) (**3**) units (Scheme 2).

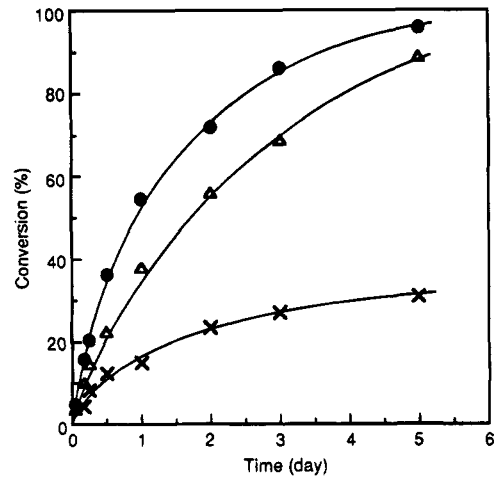


Figure 5. Time–conversion curves on cationic ring-opening polymerization of **1** at 60 °C in bulk. Initiator (1 mol %): (●) TfOH; (△) TfOMe; (×) BF_3·OEt_2 .

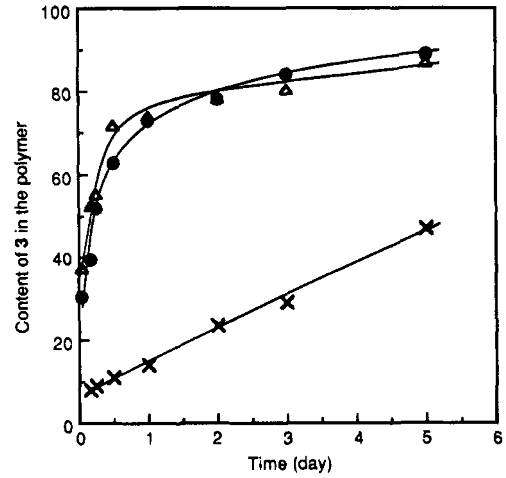


Figure 6. Time–poly (ether) production unit curves of cationic ring-opening polymerization of **1** at 60 °C in bulk. Initiator (1 mol %): (●) TfOH; (△) TfOMe; (×) BF_3·OEt_2.

The content of the ether unit (**3**) formed by the elimination of sulfur dioxide was estimated to be 30–90%. The glass transition temperature of the polymer (run 11 in Table 1) was −78 °C, and the 5% weight loss temperature under a nitrogen atmosphere was 228 °C.

Time–conversion curves of the cationic polymerization of **1** with TfOH, TfOMe, and BF_3·OEt_2 and time–content of unit **3** in the polymer curves are shown in Figures 5 and 6, respectively. The relative ratio of the observed rate of polymerization was estimated to be TfOH:TfOMe:BF_3·OEt_2 = 3.5:2.5:1.0. This order reflected the activity of those of cationic initiators.[6] The content of unit **3** in the polymer increased as the polymerization time increased. In the polymerizations initiated by TfOH and TfOMe, the elimination of sulfur dioxide rapidly proceeded at the initial stage.

The plausible polymerization and desulfoxylation mechanisms of the cationic polymerization of **1** are shown in Figure 7. The propagating end of the polymer might be in equilibrium between ionic structure **4** and covalent bond structure **5**, which should depend on the character of the counteranion. The equilibrium lies toward **4** when electrophilicity of the counteranion is small. Although the time–conversion curves between the polymerizations with TfOH and TfOMe were different, time–poly(ether) unit curves were nearly the same. In the case of BnBr as a cationic initiator, the

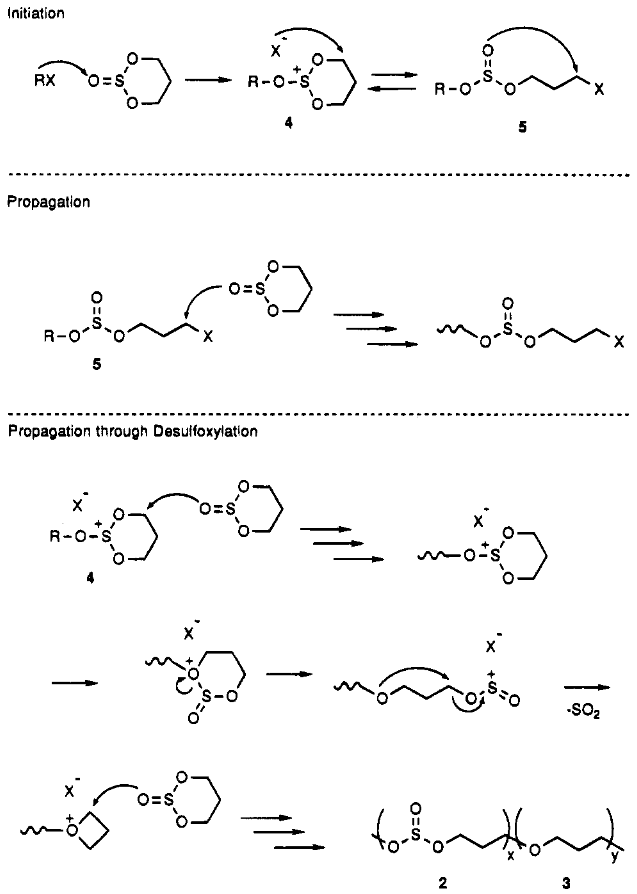


Figure 7. Possible polymerization mechanism of **1**.

elimination of sulfur dioxide was relatively smaller (runs 1 and 2 in Table 1). Therefore, in the polymerizations with TfOH and TfOMe, the equilibrium lay toward **4** and desulfoxylation occurred violently, while in the cases of BF$_3$·OEt$_2$ and BnBr, the equilibrium lay toward **5** since the electrophilicity of the counteranions was larger and the contents of desulfoxylated units were small. Namely, the desulfoxylation during the cationic polymerization of six-membered cyclic sulfite might depend on the character of the counteranion.

The volume change during the polymerization of **1** was evaluated from the densities of **1** and the polymer measured by the density gradient tube method. The density of **1** was 1.310, which was as large as those of cyclic carbonates, as expected.[1b,d] The density of the polymer obtained in run 11 in Table 1 was 1.098. Considering the elimination of sulfur dioxide from the polymer, the volume shrinkage of **1** on the polymerization was calculated to be 36.4%.[7]

Conclusion

The cationic polymerization behavior of six-membered cyclic sulfite, 1,3,2-dioxathiane 2-oxide (**1**), was examined. The following results could be demonstrated: (1) **1** underwent cationic polymerization in the presence of cationic initiators such as TfOH, TfOMe, and BF$_3$·OEt$_2$ in bulk to afford a polymer with $\bar{M}_n$ 700–2200. (2) The relative ratio of the polymerization rate was TfOH:TfOMe:BF$_3$·OEt$_2$ = 3.5:2.5:1.0. (3) The structure of the polymer consisted of a poly(sulfite) unit (**2**) obtained by the ring-opening polymerization and a poly(ether) unit (**3**) formed by the ring-opening polymerization accompanied by the elimination of sulfur dioxide. (4) The degree of elimination of sulfur dioxide was larger in the polymerization initiated by TfOH and TfOMe than in that by BF$_3$·OEt$_2$. (5) The elimination of sulfur dioxide in the propagating end of the polymer might depend on the character of the counteranion.

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(7) The volume change on polymerization in run 11 in Table 1 was calculated as follows:

$$\begin{aligned}\text{volume change (\%)} &= (V_p - V_m)/V_m \times 100\\ &= \{(\text{content}_2 \times \text{FW}_2 + \text{content}_3 \times \text{FW}_3)/\\ &\qquad \text{FW}_2(W/D_p) - W/D_m\}/(W/D_m) \times 100\\ &= \{(0.11 \times 122 + 0.89 \times 58)/(122 \times 1.098) -\\ &\qquad (1/1.310)\}/(1/1.310) \times 100 = -36.4\end{aligned}$$

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