

The Ring-Opening Polymerization of Sultones. VII. Thermodynamic Parameters of 3-Hydroxy-1-propane Sulfonic Acid Sultone for Ring-Opening Polymerization

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ABSTRACT: The thermodynamic parameters of the ring-opening polymerization of 3-hydroxy-1-propane sulfonic acid sultone were studied.

When quinoline was used as an initiator, the polymerization proceeded through a macrozwitterion mechanism, and an equilibrium between monomer and polymer was observed.

On the basis of the concentration of monomer in the equilibrium system, the heat and the entropy of polymerization were obtained from the relationship of Dainton and Ivin.

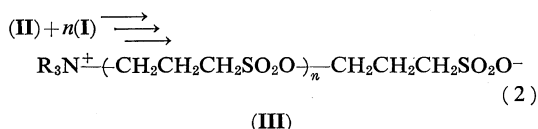
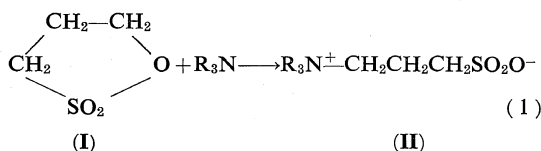
$$\ln [M]_e = \frac{1}{T} \frac{\Delta H_p}{R} - \frac{\Delta S_p^\circ}{R}$$

$$\Delta H_p = -5.5 \text{ kcal/mol}, \quad \Delta S_p^\circ = -19.1 \text{ cal/deg mol}$$

KEY WORDS Thermodynamic Parameter / Sultone / Macrozwitterion / Equilibrium Monomer Concentration / Heat of Polymerization / Entropy of Polymerization /

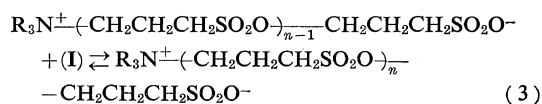
The ring-opening polymerization of sultones, cyclic sulfonic acid esters, has been reported.¹ A five-membered sultone, 3-hydroxy-1-propane sulfonic acid sultone (PS) (I), could be polymerized, but a six-membered sultone, 4-hydroxy-1-butane sulfonic acid sultone (BS), could not be polymerized.²

The polymerization of PS was assumed to be initiated by zwitterion (II), which was formed by the addition of PS with tertiary amine as a initiator (eq 1); then an anionic living polymerization through macrozwitterion (III) was presumed (eq 2).³



The ring-opening reaction of PS is known to proceed via an S_N2 reaction between the sulfonate anion of the propagating species and the monomer, in conformity with the alkyl-oxygen cleavage.

Equilibrium between monomer and polymer was observed in this polymerization (eq 3).



In the present study, the thermodynamic parameters of polymerization of PS were determined from the measurement of the heat of ring-opening polymerization ($-\Delta H_p$) and the entropy change (ΔS_p°) from the residual monomer concentration in the equilibrium system.

RESULTS AND DISCUSSION

The bulk polymerization of PS was carried

Ring-Opening Polymerization of Sultone. VII.

out at several temperatures using quinoline as an initiator. The monomer—polymer equilibrium in the PS polymerization at various temperatures was established within 3 to 48 hr of polymerization. The results are shown in Table I.

Table I. Equilibrium monomer concentrations for ring-opening polymerization of 3-hydroxy-1-propane sulfonic acid sultone^a

Temp, °C	Conversion, %	mp, °C	η_{sp}/C^b	Equilibrium monomer concentration $[M]_e$, mol/l
70	59.0	112—117	0.10	4.58
80	47.5	111—113	0.08	5.82
90	34.0	108—112	0.07	7.26
95	26.0	97—104		8.07
100	22.0	105—110	0.07	8.53
110	14.0	97—104		9.44

^a Polymerization was carried out with quinoline without solvent. PS 1.45 g; Quinoline, 0.075 g.

^b $C=0.5$ g/100-ml DMSO at 30°C.

The concentrations of monomer at equilibrium were calculated from the difference between the original monomer and the obtained polymer. The monomer concentrations ($[M]_e$) at equilibri-

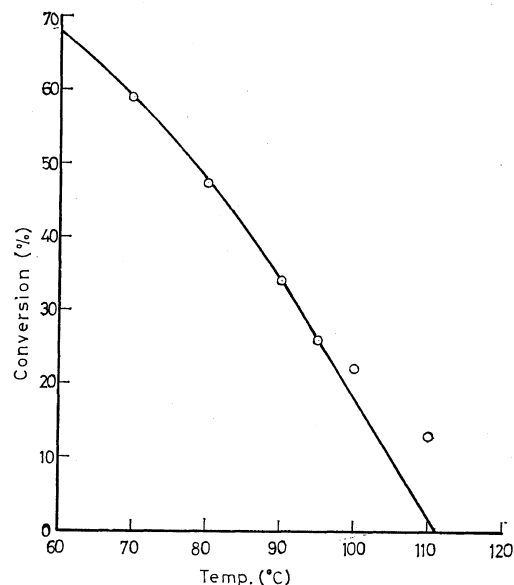


Figure 1. Polymer amount in polymerization at varying temperature.

um are given in Table I., and the conversion to polymer at equilibrium vs. temperature are plotted in Figure 1.

A value of the ceiling temperature for in bulk polymerization of PS, $T_c=110\pm 5^\circ\text{C}$, was derived from the curve in Figure 1. However, a slight amount of polymer was obtained at the ceiling temperature.

Figure 2 shows the NMR spectrum of the polymer formed with quinoline initiator at 80°C. The NMR peak at τ 5.1(a), 6.9(c), and 7.4(b) is assigned to the quinoline ion group at the end of the polymer chain, which is derived from quinoline in the initiation of polymerization.

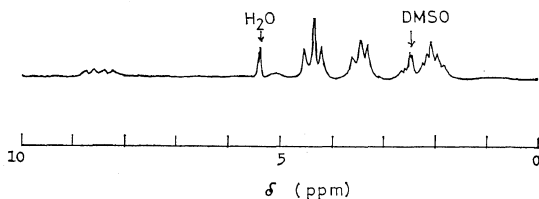
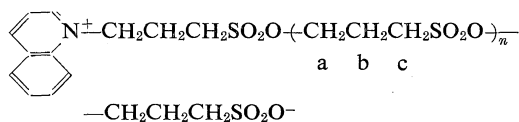


Figure 2. The NMR spectrum of polymer formed at 80°C. (DMSO_{d-6})

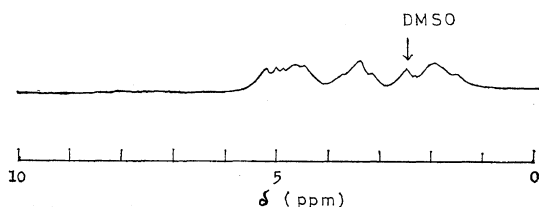


Figure 3. The NMR spectrum of polymer formed at 110°C. (DMSO_{d-6})

Figure 3 shows the NMR spectrum of the polymer formed by quinoline initiator at 110°C. A striking difference between the polymer formed at 110°C and the polymer formed at 80°C is the absence of the NMR peak due to quinoline protons at the end of polymer chain. The NMR peaks of methylene due to PS units in polymer chain were broad compared with those of Figure 2. Thus, it was difficult to believe

EXPERIMENTAL

The monomer PS was a commercial reagent, which was dried by sodium sulfate and purified by the repeated distillation under nitrogen atmosphere. bp 129.5–131.0°C/8.5–9 mmHg. (mp 34–35°C); NMR (CDCl₃) δ 2.65 (*m*, 2 H, —CH₂—), 3.23 (*t*, 2 H, —CH₂SO₂—), 4.48 (*t*, 2 H, —CH₂O—). The catalyst, quinoline, was purified by distillation over sodium hydroxide under dry nitrogen, bp 119°C/23 mmHg.

Polymerization were carried out in a sealed tube. PS was placed into a glass tube and was dried under high vacuum. Then the glass tube was filled up by dry nitrogen gas. To this solution quinoline was added with a microsyring as the initiator. After the glass tube was sealed, the glass tube was left in the thermostat for the required time.

After polymerization, the reaction mixture was poured into excess methanol, and the precipitated polymer was separated by filtration, washed with methanol, and weighed. The residual monomer was recovered by the evaporation of methanol from the filtrate; the production of other compounds was negligible.

The monomer concentration was calculated from the density of PS, which was determined

at each temperatures with a pycnometer; the results are shown in Table III.

Table III. Density of 3-hydroxy-1-propane sulfonic acid sultone

Temp, °C	60	80	100	120
d_4^{25}	1.372	1.355	1.335	1.317

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