

**Anionic Polymerization of ϵ -Caprolactam. II.
Initiation by ϵ -Thiocaprolactone**

INTRODUCTION

The anionic polymerization of ϵ -caprolactam has been the subject of many investigations. Literally hundreds of initiators are cited in the literature.¹⁻⁵ The first paper in this series⁶ describes the use of a novel class of initiators, namely, the activated aromatic halides. This work stemmed from our long-standing interest in nucleophilic substitutions on 4,4'-dichlorodiphenyl sulfone. Another area of great interest to us is the chemistry of ϵ -caprolactone and its derivatives. It was previously reported⁷ that ϵ -caprolactone initiates the anionic polymerization of ϵ -caprolactam. Random copolymers of the two monomers were also described.⁸⁻¹² However, to our knowledge, no mention is made in the literature to the behavior of the thio analog (1) in these polymerizations:



EXPERIMENTAL

Test Tube Castings

To a clean, dry, 25 × 200-mm test tube held in a 150°C oil bath were added 56.5 ml (0.5 mole) of dry ϵ -caprolactam and 0.24 g (1×10^{-2} mole, 2 mole-%, 0.42 g of a 57 wt-% mineral oil dispersion) sodium hydride. A homogeneous solution of sodium ϵ -caprolactam in ϵ -caprolactam quickly formed. To this solution was added 0.65 ml (~ 0.005 mole, 1.0 mole-%) of thiocaprolactone. (The ϵ -thiocaprolactone was kindly supplied by Dr. P. E. Fritze, of this laboratory.) The polymerization started immediately and the system became so viscous that it did not flow after 3 min. Crystallization was evident after 4 min, and the solid polymer was removed from the bath after 5 min. When the cast polymer had cooled to room temperature, it was ground in a Wiley mill and extracted for 24 hr with boiling methanol. The extracted polymer had a reduced viscosity in *m*-cresol (0.1 wt-% at 25°C) of 1.97 dl/g and 5% extractables.

In a similar manner, castings were prepared directly in the form of test specimens which were then evaluated for their mechanical properties. Note that poly(ϵ -thiocaprolactone) could also be employed as the initiator¹³ and gave similar results.

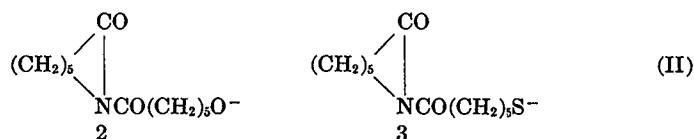
Polymerizations in a Laboratory Extruder

Several extrusion experiments were performed in a laboratory extruder as previously described.⁶

RESULTS AND DISCUSSION

One of the outstanding and completely unexpected features of the polymerization was the very rapid rate relative to the oxygen analog. For instance, in a typical polymerization employing 1.0 mole-% initiator and 2.0 mole-% catalyst at 150°C, the times for "no flow" and crystallization⁶ were 45 min and 3 to 4 min for the oxygen and sulfur compounds, respectively. A possible rationale for this behavior may be the relative

stability of the alkoxy and mercaptide anions (2 and 3). Both species are formed in the initiation step of the reaction:



If correct, one would hypothesize that greatly enhanced polymerization rates should be expected when the following initiator pairs are compared: thioester > ester; thio-carbonate > carbonate; thioanhydride > anhydride; etc. Further studies should establish the validity of these assumptions.

Except for its enhanced polymerization rate, ϵ -thiocaprolactone behaved similarly to other initiators such as *N*-acetyl- ϵ -caprolactam.¹⁴ The molecular weight of the polyamide was inversely proportional to the initiator concentration. The polymer was

TABLE I
Polymerization of ϵ -Caprolactam with ϵ -Thiocaprolactone Initiator^a

Run no.	Concentration, mole-%		Product rate, g/hr	Reduced viscosity ^b	% Extractables ^c
	Initiator	Catalyst NaH			
1	0.4	1.0	1,000	1.63	9.4
2	0.6	1.0	1,000	1.44	—
3	0.6	2.0	1,000	1.21	—
4	0.25	0.5	1,000	1.80	11
5	0.25	0.5	2,300	2.52	7.5
6	0.25	0.5	1,600	2.38	10.5
7	0.15	0.3	1,000	2.28	11.6
8	0.15	0.3	1,700	2.72	9
9	1	2	—	1.97	7.2
10	1	3	—	1.96	5.0

^a All runs but 9 and 10 were conducted by the extrusion technique.⁶ The latter runs were conducted for 5 min at 150°C.

^b 0.1 gram per 100 ml *m*-cresol at 25°C.

^c Determined by Soxhlet extraction (24 hr) of finely ground polymer with methanol.

TABLE II
Mechanical Properties of Anionically Prepared Nylon 6 Initiated by ϵ -Thiocaprolactone^a

Run no.	Tensile strength (dry), psi	Tensile modulus (dry), psi	Elongation, (dry), %	Izod impact, ft lb/in.
2	9,500	383,000	20	1.0
3	10,000	400,000	150	1.1
5	9,800	391,000	168	1.3
6	10,000	382,000	211	1.4
8	10,400	431,000	148	1.4
Cast ^b	10,300	441,000	32	0.9

^a Injection molded.

^b Cast for 5 min at 150°C.

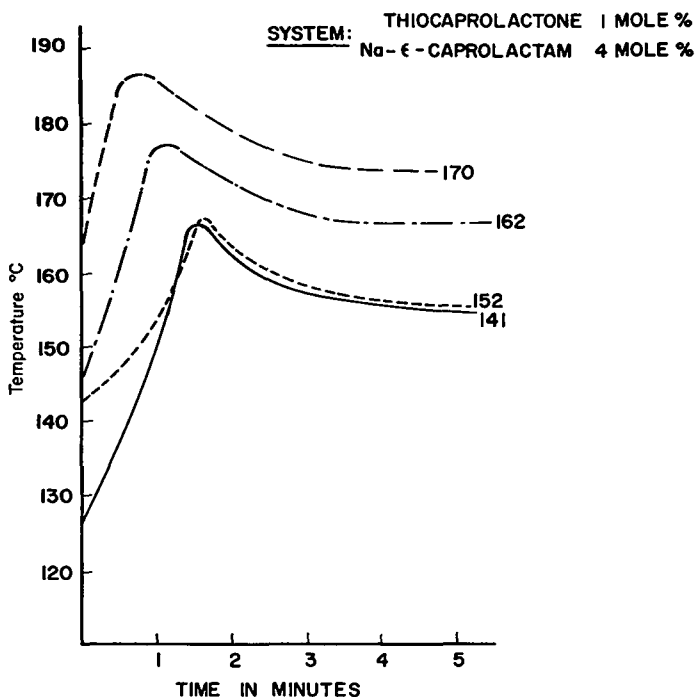


Fig. 1. Effect of polymerization temperature on peak exotherm time.

soluble and thermoplastic as expected from the monofunctional nature of the initiator. Polymerization data are summarized in Table I. A polymer which possessed a reduced viscosity of 1.70 dl/g (0.1% in *m*-cresol at 25°C) had a \bar{M}_w of 97,000 g/mole as determined by light scattering. The initiation by ϵ -thiocaprolactone was accompanied by a typical exotherm as shown in Figure 1. Polymerization was conducted both via casting conditions and in an extruder as described previously. Mechanical properties of the polymers prepared by casting and extrusion are shown in Table II.

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