Anionic Ring-Opening Polymerization of 4,4-Dimethyl-1,2-thiazetidin-3-one 1,1-Dioxide

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ABSTRACT: The ring-opening polymerization of the potassium salt of 4,4-dimethyl-1,2-thiazetidin-3-one 1,1-dioxide (DMTD) proceeded readily in polar aprotic solvents at room temperature in the presence of some initiators, leading to a poly(acylsulfonamide) with high molecular weight. The monomer DMTD also polymerized to the polymer in triethylamine or pyridine under similar conditions, after the corresponding organic quaternary salts of DMTD were formed *in situ*. The resulting poly(acylsulfonamide) was soluble in basic solvents like DMAC, and began to decompose at around 200°C, as determined by thermogravimetry.
    KEY WORDS   Anionic Ring-Opening Polymerization / 1,2-Thiazetidine-3-one 1,1-Dioxide / Poly(acylsulfonamide) / Solubility / Thermal Behavior /

It has been known for a long time that five- and six-membered cyclic imides have no ring-opening polymerizabilities under various conditions.[1] In our previous communication,[2] we demonstrated that 4,4-dimethyl-1, 2-thiazetidin-3-one 1,1-dioxide (DMTD), a kind of four-membered cyclic imide, underwent ring-opening polymerization in the form of its potassium salt, leading to a novel poly-(acylsulfonamide) with high molecular weight. The present paper is concerned with a detailed study of the polymerization of DMTD under various conditions and the properties of the resulting polymer.
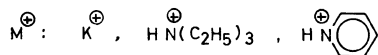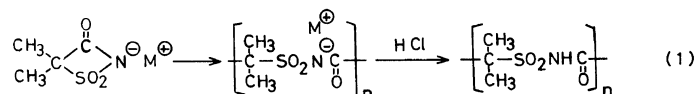
EXPERIMENTAL

Materials

4, 4-Dimethyl-1, 2-thiazetidin-3-one 1, 1-dioxide (DMTD), the potassium salt of DMTD (DMTD-K salt), and 4,4-dimethyl-2-phenyl-1,2-thiazetidin-3-one 1,1-dioxide (*N*-phenyl-DMTD) were synthesized according to the method reported previously.[2]

N, N-Dimethylacetamide (DMAC), *N*-methyl-2-pyrrolidone (NMP, supplied by Mitsubishi Chemical Industries Ltd.), hexamethylphosphoramide (HMPA), dimethyl sulfoxide(DMSO), and tetra-methylene sulfone (TMS), respectively, were purified by vacuum distillation and stored over 4 Å molecular sieves. Benzoyl chloride and other chemicals were obtained commercially and used as received.

Isolation of the Triethylammonium Salt of DMTD

A solution of 4.0 g (40 mmol) of triethylamine in 20 ml of diethyl ether was added to a solution of 5.0 g (34 mmol) of DMTD in 30 ml of the ether at room temperature. A white solid soon began to precipitate. The product was collected and dried *in vacuo*. The yield was 7.7 g (92%). This salt is very hygroscopic.

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IR (KBr) 1690 cm^{-1} ($\nu_{C=O}$) and 1240, 1150 cm^{-1} (ν_{SO_2}).

Anal. Calcd for C$_{10}$H$_{22}$N$_2$O$_3$S: C, 47.97%; H, 8.86%; N, 11.19%. Found: C, 47.8%; H, 8.6%; N, 11.2%.

Polymerization

Polymerization of DMTD-K Salt. To a solution of 0.467 g (2.5 mmol) of DMTD-K salt in 5 ml of TMS was added 15 mg (6 mol%) of acetic anhydride as an initiator, and the mixture was stirred at 20°C for 5 h. The solution went gradually into a hetero-geneous slurry as the polymerization proceeded. The polymer was isolated by precipitation with 200 ml of dilute hydrochloric acid. After thorough washing and drying, the resulting white fibrous polymer weighed 0.325 g (87%). The inherent viscosity of the polymer in DMAC was 3.37, measured at a con-centration of 0.5 g dl^{-1} at 30°C.

Polymerization of DMTD in the Presence of Triethylamine. To a solution of 0.26 g (2.5 mmol) of triethylamine in 5 ml of DMAC was added successively 0.373 g (2.5 mmol) of DMTD and 6 mg (1 mol%) of *N*-phenyl-DMTD, and the resulting solution was stirred at 20°C for 30 min. The viscous solution was worked up in the usual way. The polymer weighed 0.321 g (86%) and had an inherent viscosity of 7.89 in DMAC.

The polymer thus formed was identified as the poly(acylsulfonamide) by comparing its IR spectrum with that of the authentic polymer.[2]

RESULTS AND DISCUSSION

Polymerization

The ring-opening polymerization of DMTD-K salt was carried out in solution by using an appro-priate initiator at room temperature. The results are summarized in Table I. Polar aprotic solvents such as DMAC, NMP, HMPA, DMSO, and TMS were employed as the polymerization media. High mo-lecular weight polymers could be obtained in these solvents, despite the fact that the polymers separated out from the polymerization mixture as the reaction proceeded.

It is noteworthy that the addition of water to the polymerization mixture had no harmful influence on the molecular weight of the resulting polymer. In this regard this polymerization is quite different from the typical anionic ring-opening polymerization of the

Table I. Ring-opening polymerization of DMTD-K salt[a]

Solvent	Initiator		Polymer		
	Type[b]	Amount	Yield		η_{inh}[c]
		mol %	%		
DMAC	Ph-DMTD	1.0	91		4.63
NMP	Ph-DMTD	1.0	98		3.78
HMPA	Ph-DMTD	1.0	87		3.38
DMSO	Ph-DMTD	1.0	83		0.41
TMS	Ph-DMTD	1.0	97		4.95
TMS	Ph-DMTD[d]	1.0	97		4.70
TMS	BC	1.7	66		2.20
TMS	AA	6.0	87		3.37
TMS	BSC	6.1	63		3.07
TMS	DMTD	1.0	82		3.41

[a] Polymerization was carried out with 2.5 mmol of DMTD–K salt in 5 ml of the solvent at 20°C for 5 h.
[b] Ph-DMTD, *N*-phenyl-DMTD; BC, benzoyl chloride; AA, acetic anhydride; BSC, benzenesulfonyl chloride.
[c] Measured at a concentration of 0.5 g dl^{-1} in DMAC at 30°C.
[d] Water (0.1 ml) was added to the polymerization mixture.

usual lactams, in which the active lactam anion is inactivated on contact with a trace of water.[3,4]

It was pointed out in a previous paper[2] that the reaction product of DMTD-K salt with benzoyl chloride was not the expected *N*-benzoyl-DMTD, but the ring-opened polymer. Therefore, it is evident that benzoyl chloride first reacted with the DMTD-K salt, affording *N*-benzoyl-DMTD, which in turn initiated the ring-opening polymerization of the salt. Other acid derivatives, such as acetic anhydride and benzenesulfonyl chloride, which would form *in situ* reactive *N*-acyl-DMTDs by reacting with DMTD-K salt, were also employed successfully to initiate the polymerization. Moreover, *N*-phenyl-DMTD and DMTD itself were found to function as effective initiators.

Figure 1 shows the influence of the amount of *N*-phenyl-DMTD (initiator concentration) on the poly-merization. The inherent viscosity of the polymer markedly decreased with increasing amounts of the initiator, whereas the yield remained almost constant over a wide range of initiator concentration.

These results suggest that the ring-opening poly-merization proceeds through an anionic fast polyme-
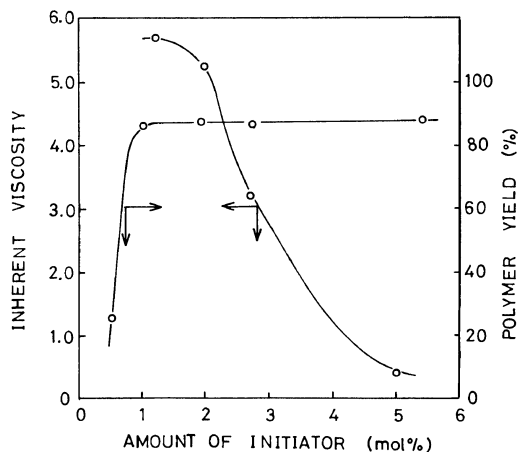
Figure 1. Effect of amount of the N-phenyl-DMTD initiator on yield and inherent viscosity of the polymer. Polymerization was carried out in TMS at 20°C for 30 min.

rization mechanism involving a comparatively slow initiation, which is followed by fast propagation, as proposed in a previous paper.[2]

It was found that DMTD underwent ring-opening polymerization in the presence of tertiary amines like triethylamine and pyridine through the *in situ* formation of organic quarternary ammonium salts of DMTD, which was independently isolable in the pure form (see experimental section). The polymerization proceeded readily at room temperature in polar aprotic solvents such as DMAC, NMP, and DMSO in a homogeneous solution throughout,

leading to high-molecular-weight polymers (Table II). The polymer obtained from organic quarternary salts of DMTD had somewhat higher inherent viscosity than that derived from DMTD-K salt.

Properties of Polymers

Table III shows the results of the qualitative solubility test of the poly(acylsulfonamide) and its salts. The parent polymer was soluble in basic solvents such as pyridine and DMAC, and showed swelling in aqueous sodium hydroxide, because of the acidic nature of the polymer backbone.

The dilute polymer solution in DMAC exhibited anomalous viscosity behavior when η_{sp}/c was plotted against c (concentration) (Figure 2). It is known that a polyelectrolyte solution is well expressed in the form of Fuoss' equation[5]

$$\eta_{sp}/c = \frac{A}{1 + B\sqrt{c}} + D$$

where A, B, and D are constants. A plot of c/η_{sp} against $\sqrt{c}$ was found to be linear in accordance with this relation, as shown in Figure 2. Therefore, the poly(acylsulfonamide) itself behaves as a polyelectrolyte in a basic solvent like DMAC.

Although the polymer–potassium salt did not completely dissolve in any organic solvents, the triethylamine salt was highly soluble in a wide range of solvents and even in water as a kind of anionic polyelectrolyte.

X-ray diffraction diagrams of the polymers were

Table II. Ring-opening polymerization of DMTD in the presence of tertiary amines[a]

Solvent	Tertiary amine	Polymerization time	Polymer	
		h	Yield %	η_{inh}[b]
Triethylamine	—	24	77	0.61
Pyridine	—	48	99	3.91
DMAC	Triethylamine	0.5	86	7.89
DMAC	Pyridine	2	85	2.34
NMP	Trietylamine	0.5	56	5.36
HMPA	Triethylamine	0.5	62	4.65
DMSO	Triethylamine	0.5	39	1.18

[a] Polymerization was carried out with 2.5 mmol of DMTD in 5 ml of the solvent in the presence of 2.5 mmol of the tertiary amine and 1 mol% of N-phenyl-DMTD at 20°C.

[b] Measured at a concentration of 0.5 g dl^{-1} in DMAC at 30°C.

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Table III. Solubility of poly(acylsulfonamide) and its salts

Solvent	Solubility[a]		
	Poly (acyl-sulfonamide)	Polymer–potassium salt	Polymer–triethylamine salt
Dimethylformamide	+	±	+ +
Dimethylacetamide	+ +	±	+ +
Dimethyl sulfoxide	+	±	+ +
Pyridine	+ +	±	+ +
m-Cresol	−	±	+ +
Methanol	−	−	+ +
Acetonitrile	−	−	+ +
Acetic acid	−	−	±
Acetone	−	−	±
Tetrahydrofuran	−	−	±
Water	−	+	+ +
Aqueous sodium hydroxide	±	±	±

[a] Solubility: (+ +) soluble at room temperature; (+) soluble on heating; (±) partially soluble or swelling; (−)insoluble.
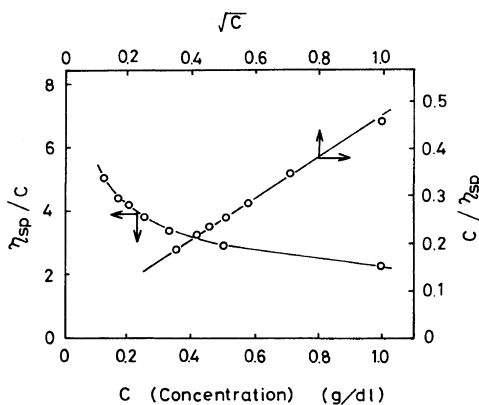

Figure 2. Viscosity behavior of the dilute solution of the poly(acylsulfonamide) in DMAC at 30°C.
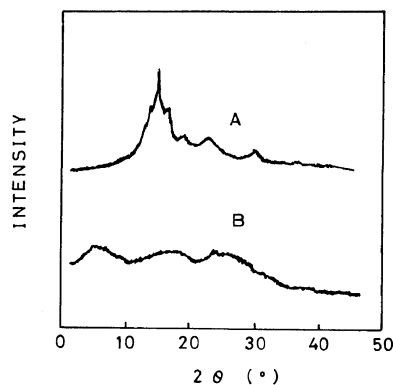

Figure 3. X-ray diffraction diagrams of polymers: (A) the poly(acylsulfonamide); (B) the polymer–potassium salt.

taken by the powder method with the use of nickel-filtered Cu-Kα radiation (Figure 3). The poly-(acylsulfonamide) was found to be crystalline and its potassium salt was amorphous. A polymer film cast from a concentrated DMAC solution was opaque and brittle, presumably owing to the highly crystalline nature of the poly(acylsulfonamide).

The thermal behavior of the polymers was evaluated by means of differential thermal analysis (DTA) and thermogravimetry (TG). These thermograms are shown in Figure 4. The poly-(acylsulfonamide) had an initial weight loss commencing at around 200°C, followed by rapid decom-position, whereas the potassium salt began to decompose at about 150°C and lost its weight rather gradually at higher temperatures. In addition, the DTA curves of the poly(acylsulfonamide) and its potassium salt exhibited an exothermic peak at around 220°C and 150°C, respectively, which was in good correlation with the initial weight-loss temperature observed in the TG curves. The ease of decomposition of the poly(acylsulfonamide) was probably due to thermal chain-scission of the polymer according to eq 2. This was supported by the appearance of an absorption at 2240 cm^{-1} (C≡N stretching band) and absorptions at 1220 and

Figure 4. DTA and TG thermograms of polymers; DTA in air at a heating rate of 10°C min⁻¹, and TG in nitrogen at a heating rate of 5°C min⁻¹; (A) the poly(acyl-sulfonamide); (B) the polymer–triethylamine salt; (C) the polymer–potassium salt.

$1040\,\mathrm{cm}^{-1}$ (SO_2 stretching bands of sulfonic acid) in the IR spectrum of the polymer after heat treatment at 200°C for 15 min under nitrogen.

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