Some Reactions of Pyrosulfuryl Fluoride[1]

MAX M. BOUDAKIAN,*[2a] GENE A. HYDE,[2b] AND SANTAD KONGPRICHA[2c]

Olin Corporation, Chemicals Division, New Haven, Connecticut 06504

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The reaction of pyrosulfuryl fluoride (1) with chloroethanol and phenol gave 2-chloroethyl fluorosulfate and phenyl fluorosulfate, respectively. Although benzene has been reported to be inert to 1 under ambient conditions, higher temperatures provided benzenesulfonyl fluoride in 51% yield. Treatment of benzoic acid with 1 gave a 7% yield of benzoyl fluoride. While published observations report exclusive formation of diethyl sulfate from diethyl ether and 1, reversal of the mode of addition furnished ethyl fluorosulfate in 64% yield. Bulk polymerization of tetrahydrofuran was effected by 1. Nonprotic anhydrides of halogenated oxy acids represent a new class of catalysts for the polymerization of cyclic ethers. Vinylidine fluoride and 1 react at 300° to give a complex mixture of products including sulfuryl fluoride, trifluoroethane sulfonyl fluoride, difluorovinyl sulfonyl fluoride, trifluoroethane, and difluoroethyl fluorosulfate. Autocondensation of acetone was effected by 1 to give water, mesityl oxide, and other condensation products.

Since its initial preparation in 1951,[3] relatively few reactions involving pyrosulfuryl fluoride, FSO_2OSO_2F (**1**), with organic substrates have been reported.[4] Heterolytic cleavage of **1** by secondary amines gave aminosulfuryl fluorides and fluorosulfate salts.[5,6] Lustig recently found that reactions of fluoro-organic anions with **1** provided fluoroalkyl fluorosulfate esters.[7] Fluorine-free sulfate esters were obtained by Sokol'skii from dialkyl ethers and **1**.[8] (Solvents such as benzene,[3] chloro- and chlorofluorohydrocarbons,[2] acetonitrile,[5,9] diethyl ether,[5,6] and nitro organics[7,9] are miscible with **1** under ambient conditions.)

Discussion

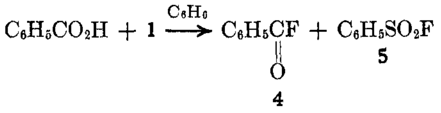
A brief study demonstrated that **1** reacts with a variety of substrates. Table I summarizes the reactions of **1** in comparison with those of the parent acid, fluorosulfuric acid.

Hayek and Koller[3] reported a violent reaction when ethanol and **1** were mixed at room temperature; no product(s) were identified. It was observed that **1** could effect fluorosulfation of 2-chloroethanol at 0° to give 2-chloroethyl fluorosulfate (**2**) in 40% yield.

$$\underset{}{ClCH_2CH_2OH} + \underset{\mathbf{1}}{FSO_2OSO_2F} \xrightarrow{0°} \underset{\mathbf{2}}{ClCH_2CH_2OSO_2F}$$

In a similar fashion, phenol was converted by **1** to phenyl fluorosulfate, $C_6H_5OSO_2F$ (**3**), in 23% yield.

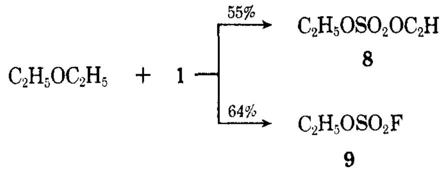
The reaction of **1** and benzoic acid in benzene solvent gave a mixture of benzoyl fluoride (**4**) and benzenesulfonyl fluoride (**5**). The formation of **5** from benzene was quite pronounced (51% yield) at elevated temperatures (170°, monel autoclave); the gas phase consisted of sulfuryl fluoride (**6**). (In contrast, Hayek observed that benzene and **1** were miscible under ambient conditions without any apparent reaction.[3]) Since Ruff and Lustig effected thermolysis of **1** at 150° (monel autoclave) to give sulfuryl fluoride (**6**) in 50% conversion,[10,11] the formation of **5** may be envisaged as fluorosulfonation by **6**. The inertness of toluene to sulfuryl fluoride (**6**) (benzoyl peroxide catalyst at reflux)[12] does not appear to support this interpretation.



$$C_6H_5CO_2H + 1 \xrightarrow{C_6H_6} \underset{\mathbf{4}}{C_6H_5\overset{}{C}(=O)F} + \underset{\mathbf{5}}{C_6H_5SO_2F}$$

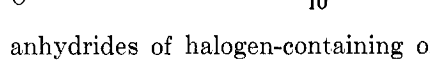
$$1 \longrightarrow \underset{\mathbf{6}}{SO_2F_2} + \underset{\mathbf{7}}{SO_3}$$

While diethyl ether can be employed as a solvent for ammonolysis reactions of **1** from −30 to +25°,[5,6] Sokol'skii[8] obtained a 55% yield of diethyl sulfate (**8**) upon the addition of **1** to refluxing diethyl ether; any ethyl fluorosulfate (**9**) formed immediately reacted with diethyl ether to give **8**. However, it was demonstrated in the present study that reversal of the mode of addition of reactants, *i.e.*, addition of diethyl ether to refluxing **1**, provided ethyl fluorosulfate (**9**) in 64% yield.



$$C_2H_5OC_2H_5 + 1 \begin{cases} \xrightarrow{55\%} \underset{\mathbf{8}}{C_2H_5OSO_2OC_2H_5} \\ \xrightarrow{64\%} \underset{\mathbf{9}}{C_2H_5OSO_2F} \end{cases}$$

Bulk polymerization of tetrahydrofuran was effected by **1** or pyrosulfuryl chloride fluoride to give 60–70% yields of poly(tetramethylene)ether glycol (**10**). Such nonprotic anhydrides of halogen-containing oxy acids represent a new class of catalysts for the polymerization of cyclic ethers. A related anhydride, pyrophosphoryl



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[1] Presented at the 158th National Meeting of the American Chemical Society, Division of Fluorine Chemistry, Sept 1969, New York, N. Y.

[2] (a) Olin Corp., Rochester, N. Y.; (b) Olin Corp., New Haven, Conn.; (c) Olin Corp., Joliet, Ill.

[3] (a) E. Hayek and W. Koller, *Monatsh. Chem.*, **82**, 942 (1951); (b) E. Hayek and A. Czaloun, *ibid.*, **87**, 790 (1956).

[4] Even long-known pyrosulfuryl halides have been ignored in such reactions: "Little attention has been paid to pyrosulfuryl chloride, although it has attractive possibilities as a reagent in organic chemistry." E. de B. Barnett and C. L. Wilson, "Inorganic Chemistry,' Longmans, Green and Co., London, 1953, p 434.

[5] (a) R. Appel and G. Eisenhauer, *Angew. Chem.*, **70**, 742 (1958); (b) *Z. Anorg. Allg. Chem.*, **310**, 90 (1961).

[6] S. Kongpricha, W. C. Preusse, and R. Schwarer, 148th National Meeting of the American Chemical Society, Division of Fluorine Chemistry, Chicago, Ill., Sept 1964, Abstracts, p 3K.

[7] M. Lustig, *Inorg. Chem.*, **9**, 104 (1970).

[8] G. A. Sokol'skii, *J. Gen. Chem. USSR*, **36**, 817 (1966).

[9] J. K. Ruff, *Inorg. Chem.*, **4**, 567 (1965).

[10] J. K. Ruff and M. Lustig, *ibid.*, **3**, 1422 (1964). Since treatment of **1** with cesium fluoride at 50° gave **6** and $CsSO_3F$, these authors suggested that the thermolysis of **1** at 150° in a "clean prefluorinated" monel bomb might have been initiated by metal fluorides present in the autoclave.

[11] In contrast, pyrolysis of **1** in a Hastelloy C-lined vessel to give **6** did not occur at a measurable rate at 200° (10 hr): E. L. Muetterties and D. D. Coffman, *J. Amer. Chem. Soc.*, **80**, 5914 (1958).

[12] H. J. Emeléus and J. F. Wood, *J. Chem. Soc.*, 2183 (1948).

TABLE I

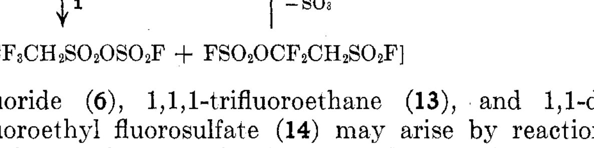
COMPARATIVE REACTIONS OF PYROSULFURYL FLUORIDE AND FLUOROSULFURIC ACID

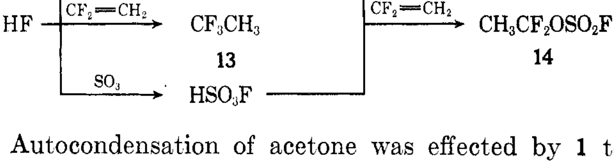
	$S_2O_5F_2$ (**1**)	HSO_3F
Alcohols	$ROSO_2F$ (40%)	$ROSO_2F$ (trace)[a]
Phenols	$C_6H_5OSO_2F$ (23%)	*p*-$HOC_6H_4SO_2F$ (58%)[b]
Benzoic acid	$C_6H_5\underset{\underset{O}{\|}}{C}F$ (7%)	No reaction[c]
Benzene	$C_6H_5SO_2F$ (51%)	$C_6H_5SO_3H$,[a,d] $C_6H_5SO_2F$,[b] $C_6H_5SO_2C_6H_5$[b,d]
Alkyl ether	$ROSO_2OR$ (55–62%)[e] $ROSO_2F$ (64%)	$ROSO_2F$ (30%)[a]
Tetrahydrofuran	$\text{-}\!\!\!+\!CH_2CH_2CH_2CH_2O\!+\!\!\!\text{-}_x$ (60–70%)	$\text{-}\!\!\!+\!CH_2CH_2CH_2CH_2O\!+\!\!\!\text{-}_x$[f]
Vinylidene fluoride	See text	$CH_3CF_2OSO_2F$[g]
Acetone	H_2O, mesityl oxide, other condensation products (red solution)	Red color test for HSO_3F[a]

[a] Reference 19. [b] Reference 26. [c] W. Baker, G. E. Coates, and F. Glockling, *J. Chem. Soc.*, 1376 (1951). [d] J. H. Simons, H. J. Passino, and S. Archer, *J. Amer. Chem. Soc.*, **63**, 608 (1941). [e] Reference 8. [f] H. Meerwein, D. Delfs, and H. Morschel, *Angew. Chem.*, **72**, 927 (1960). These investigators found that pyrosulfuric acid also polymerized tetrahydrofuran. [g] Reference 18.

tetrafluoride, $F_2P(O)O(O)PF_2$, was less effective as a polymerization catalyst; the yield of **10** was only 5%.

Vinylidene fluoride and **1** react at 300° to give <5% yield of **6** and **11**–**14**. One postulated sequence to **6**, **11**, and **12** involves pyrolysis of **1** to form **6** and **7**, subsequent addition of **6** to vinylidine fluoride to give 2,2,2-trifluoroethane sulfonyl fluoride **11**, and dehydrofluorination of the latter to provide difluorovinyl sulfonyl fluoride with the probable structure **12**.[13] However, we were unable to add **6** to vinylidene fluoride at 300–400° to give **11**.[14] An alternate route to **11** might involve addition of **1** to vinylidene fluoride, followed by expulsion of sulfur trioxide.[15,16] Sulfuryl fluoride (**6**), 1,1,1-trifluoroethane (**13**), and 1,1-difluoroethyl fluorosulfate (**14**) may arise by reactions similar to those previously reported: **6** and fluorosulfuric acid from hydrogen fluoride and **1**;[8] **13** from hydrogen fluoride and vinylidene fluoride;[17] and **14** from vinylidene fluoride and fluorosulfuric acid.[18]





Autocondensation of acetone was effected by **1** to give a dark red solution containing water, mesityl oxide, phorone, isophorone, and other condensation products. Meyer and Schramm's diagnostic test for fluorosulfuric acid involves addition of acetone to give a dark red solution of unknown composition.[19] The red color noted in the reaction of **1** and acetone may be due to fluorosulfuric acid arising by hydrolysis of **1** as a consequence of the above autocondensation.

Experimental Section

Chemicals.—Pyrosulfuryl fluoride (1) and pyrosulfuryl chloride fluoride were prepared from the reaction of fluorosulfuric acid and cyanuric chloride.[6,20] *Pyrosulfuryl fluoride has been reported to be toxic!*[3,11]

2-Chloroethyl Fluorosulfate (2).—**1** (36.4 g, 0.20 mol) was added slowly with stirring to 2-chloroethanol (16.1 g, 0.20 mol) kept at 0°. The reaction mixture was allowed to warm to 25° and then heated at 45–50° (2 hr). Volatiles were removed at 55° (1 mm); distillation of the latter provided 14 g of **2** (40% yield), bp 32° (2.6 mm).

Anal. Calcd for $C_2H_4ClSO_3F$: C, 14.77; H, 2.48; Cl, 21.81; F, 11.69. Found: C, 14.70; H, 2.48; Cl, 22.1; F, 11.9.

Phenyl Fluorosulfate (3).—Phenol (12.3 g, 0.13 mol) and **1** (23.8 g, 0.13 mol) were mixed at 10° and successively stirred at 25° (2 hr) and 53° (3 hr). Distillation provided 5.5 g of **3** (23.2% yield), bp 34–38° (2.7 mm), $n^{25.5}D$ 1.4688 (reported for **3**:[21] bp 180°; $n^{25.5}D$ 1.4628). Product identification (95% **3**, 5% phenol) was corroborated by comparison with the standard infrared spectrum of **3**,[21,22] by mass spectroscopy (*m/e* 65, 93, and 176), and by nmr (^{19}F singlet at −48.65 ppm). The distillation residue consisted of a nonvolatile [300° (0.05 mm)], fluorine-free (^{19}F nmr) solid; the infrared spectrum showed bands at 3.1 (OH), 5.9–6.3 (C=C), 6.5–7.2, 13–15 (phenyl), and 7.65, 8.65 μ (SO_2).

Reaction of 1 and Benzoic Acid in Benzene. A mixture of **1** (0.11 mol, 20.2 g), benzoic acid (0.074 mol, 9.1 g), and benzene (150 ml) was refluxed for 20 hr. After removal of benzene and unreacted **1**, 0.61 g (6.6% yield) of a liquid, bp <25° (4.5 mm), $n^{25}D$ 1.4980 (reported for **4**:[23] $n^{25}D$ 1.4988), was obtained. The product had the characteristic infrared spectrum of **4**,[24] along with the weak absorption indicative of **5**.[25] Further identification of **4** was obtained by nmr (^{19}F and ^1H) and mass spectroscopy (molecular weight ion peak at *m/e* 124). Unreacted benzoic acid (8.2 g, 90% recovery) was isolated by sublimation of the distillation residue. The sublimation residue (1.55 g) consisted of a fluorine-free (^{19}F nmr) liquid containing benzenesul-

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[13] M. M. Boudakian, G. A. Hyde, and E. H. Kober, U. S. Patent 3,492,348 (Jan 27, 1970).

[14] The addition of **6** to vinylidene fluoride could not be effected under ionic conditions (cesium fluoride/diglyme, 100–150°): S. Temple, Fourth International Fluorine Chemistry Symposium, Estes Park, Colo., July 1967, Paper No. 49.

[15] We thank Dr. D. D. DesMarteau of Northeastern University for this suggestion.

[16] The decomposition of methyl disulfuryl fluoride or perfluoroacetyl fluorosulfate to give methane sulfonyl fluoride and perfluoroacetyl fluoride, respectively, has been interpreted on the basis of sulfur trioxide expulsion: W. M. Johnson, H. A. Carter, and F. Aubke, *Inorg. Nucl. Chem. Lett.*, **5**, 719 (1969); D. D. DesMarteau and G. H. Cady, *Inorg. Chem.*, **5**, 169 (1966).

[17] C. B. Miller and L. B. Smith, U. S. Patent 2,669,590 (Feb 16, 1954).

[18] J. D. Calfee and P. A. Florio, U. S. Patent 2,628,972 (Feb 17, 1953).

[19] J. Meyer and G. Schramm, *Z. Anorg. Allg. Chem.*, **206**, 24 (1932).

[20] (a) R. F. Schwarer, S. Kongpricha, and W. C. Preusse, U. S. Patent 3,275,413 (Sept. 27, 1966); (b) *Inorg. Syn.*, **11**, 151 (1968).

[21] R. Cramer and D. D. Coffman, *J. Org. Chem.*, **26**, 4164 (1961).

[22] F. K. Butcher, J. Charlambous, M. J. Frazer, and W. Gerrard, *Spectrochim. Acta, Part A*, **23**, 2399 (1967).

[23] A. I. Mashentsev, *Zh. Obshch. Khim.*, **15**, 915 (1945); *Chem. Abstr.*, **40**, 6443 (1946).

[24] F. Seel and J. Langer, *Chem. Ber.*, **91**, 2553 (1958).

[25] N. S. Ham, A. N. Hambly, and R. H. Laby, *Aust. J. Chem.*, **13**, 443 (1960).

fonic acid and/or hydrate based on infrared and mass spectral analysis (molecular weight ion peak, *m/e* 158; peaks at *m/e* 48, 50, 64, 66, and 81 were suggestive of the $-SO_3H$ group).

Benzoic acid (0.5 mol, 61.1 g), **1** (0.4 mol, 76.8 g), and benzene (0.62 mol, 55 ml) were heated in a rocking 300-ml autoclave (monel) at 170° for 1.5 hr. The autoclave was cooled to 25° (100 psig); mass spectral analysis of the gaseous products showed only sulfuryl fluoride (**6**). Distillation did not give any unreacted **1**. The product, bp 107–110° (35 mm), consisted primarily of benzenesulfonyl fluoride (**5**) and small quantities of benzoyl fluoride (**4**) (ir). Redistillation provided 37 g of **5** (51% yield), bp 62–63° (3.5 mm), $n^{25}D$ 1.4894 (vpc 99.8%) [reported for **5**: bp 90–91° (14 mm);[26] $n^{18}D$ 1.4932;[26] $n^{20}D$ 1.4922[27]]. The product had the characteristic infrared spectrum of **5**;[25] mass spectral assay showed a molecular weight ion peak at *m/e* 160. Unreacted benzoic acid (>90% recovery) was isolated by sublimation of the distillation residue. The viscous sublimation residue (67.2 g) was not analyzed.

Ethyl Fluorosulfate (**9**).—Diethyl ether (18.5 g, 0.25 mol) was added dropwise to **1** (45.0 g, 0.25 mol) (initial temperature, 51°; final temperature, 95°). The reaction product was fractionally distilled to give 42 g of **9** (64% yield), bp 42°(51.5 mm) [reported[19] for **9**: bp 24° (12 mm)].

Anal. Calcd for $C_2H_5SO_3F$: C, 18.7; H, 3.9; S, 24.99; F, 14.8. Found: C, 19.11; H, 4.05; S, 24.99; F, 15.0.

Pyrosulfuryl Fluoride as Polymerization Catalyst.—Tetrahydrofuran was refluxed over sodium hydroxide pellets for 3 hr and distilled. The fraction, bp 66°, was stored over calcium hydride and redistilled under nitrogen prior to use.

A mixture of tetrahydrofuran (173.0 g, 2.39 mol) and **1** (2.89 g, 1.64 wt %) was stirred under a nitrogen atmosphere at 25°; within 2 hr, stirring had ceased. After 3.5 hr, 250 ml of water was added to the semisolid gel, the mixture was heated, and the aqueous layer was decanted. The opaque polymer was dissolved in 1.5 l. of hot tetrahydrofuran, the solution poured into 1 l. of water with stirring, and the precipitated polymer dried *in vacuo* to give 105 g of **10** (60.7% yield), mp 35–40°. The polymer had the characteristic infrared spectrum of polytetrahydrofuran.[28] Other properties of the polymer include intrinsic viscosity (30°), 0.50 (tetrahydrofuran), 0.52 (benzene); hydroxyl number, 10.0 mg KOH/g; number-average molecular weight, 8038 (benzene, 39°; vapor-pressure osmometer, Mechrolab, Inc., Model 302).

From tetrahydrofuran (149.7 g) and pyrosulfuryl chloride fluoride (1.41 g, 0.93 wt %) under a nitrogen atmosphere (25°, 20 hr), 101.2 g of polymer **10** (67% yield), mp 36–39°, was obtained.

From pyrophosphoryl tetrafluoride[29] (1.0 g, 0.95 wt %) and tetrahydrofuran (103 g) under nitrogen (25°, 22 hr), 5.1 g of **10** (5% yield), mp 30.2°, was obtained.

Reaction of 1 and Vinylidene Fluoride.—A mixture of **1** (21.8 g, 0.12 mol) and vinylidene fluoride (7.8 g, 0.12 mol, Matheson Co.) was heated in a 150-ml monel cylinder at different stages: 100° (1.5 hr), 200° (2 hr), and 300° (6 hr). During the first two stages, there was no evidence of reaction based on pressure change. At 300°, the pressure rose to 420 psig (1 hr) and gradually decreased to 310 psig.

The reactor was cooled to −94° and 6.9 g of volatiles collected [ir primarily SO_2F_2 (**6**), with trace quantities of vinylidene fluoride and CF_3CH_3 (**13**)]. The reactor was then warmed to 25° and 12.7 g of volatiles collected. The latter consisted of a fraction (wt 2.6 g) volatile at −23°; infrared and mass spectral analysis revealed the presence of **6** and **13**. Vpc trapping of the nonvolatile fraction (at −23°) provided unreacted 1 and the following compounds in decreasing order of magnitude (<5% yield).

$CF_2{=}CHSO_2F$ (12): mass spectral analysis, molecular weight ion peak at *m/e* 146; infrared spectrum showed bands at 3.2 (CH), 5.8 (C=C), 7.35 and 8.45 (SO_2F), and 12.5 μ (RR'C=CHR''); nmr (^1H) revealed the presence of a component containing a single proton.

$CF_3CH_2SO_2F$ (11): mass spectral analysis showed a molecular weight ion peak at *m/e* 166; both ir and nmr (^{19}F, ^1H) were consistent with structure **11**.

$CH_3CF_2OSO_2F$ (14): infrared spectrum showed bands at 6.75 and 7.95 (OSO_2F), 7.1, 8.8, and 10.5 μ (CF_2); mass spectral analysis indicated a fragmentation pattern suggestive of **14**; nmr (^1H) analysis was consistent with structure **14**.

The nonvolatile (at 25°) components (7.1 g) in the reactor consisted of a liquid and solid. The former was a complex mixture of high-boiling products which decomposed in the mass spectral hot inlet to give the following fragments: *m/e* 61 (CHSO), 67 (SOF), 83 (SO_2F), 97 (CH_2SO_2F or $C_2H_3F_2S$), and 147 ($C_2H_2SO_2F_3$). The solid had an infrared spectrum characteristic of polyvinylidene fluoride.

Attempted Reaction of Sulfuryl Fluoride (6) and Vinylidene Fluoride.—A mixture of **6** (3.8 g, 0.037 mol, Matheson Co.) and vinylidene fluoride (20.6 g, 0.32 mol) was heated in a 150-ml monel cylinder at 300–400° (5 hr). The pressure (810 psig) remained constant during this period. The reactor was cooled to −78° and volatiles removed (24.2 g, 99% of initial charge). Infrared and mass spectral analysis showed only starting materials.

Reaction of 1 and Acetone.—During an 0.5-hr period, acetone (26.8 g, 0.46 mol) was added to **1** (19.0 g, 0.46 mol) dissolved in 100 ml of benzene cooled to 5°. The solution was stirred 4 hr (5 to 25°); two dark red layers were formed. Distillation of the lower layer provided a fraction, bp 25° (2.5 mm), wt 2.1 g, consisting of water and a fluorine-free (^{19}F nmr) lower layer. Infrared analysis indicated that the latter consisted of mesityl oxide, as well as lesser amounts of isophorone, phorone, and unidentified components. Infrared analysis of the initial upper layer revealed the presence of unreacted starting materials and mesityl oxide.

Registry No.—**1**, 13036-75-4; **2**, 27669-92-7; **9**, 371-69-7; benzoic acid, 65-85-0; vinylidene fluoride, 75-38-7.

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[26] W. Steinkopf, K. Buchheim, K. Beythien, H. Dudek, J. Eisold, J. Gall, P. Jaeger, H. Reumuth, A. Semenoff, and A. Wemme, *J. Prakt. Chem.*, **117**, 1 (1927).

[27] W. Davis and J. H. Dick, *J. Chem. Soc.*, 2104 (1931).

[28] T. Saegusa, H. Imai, and J. Furakawa, *Makromol. Chem.*, **56**, 55 (1962).

[29] E. A. Robinson, *Can. J. Chem.*, **40**, 1725 (1962).