Evidences from X-Ray Diffraction

There are serious limitations to use of x-ray diffraction for studying mesomorphic structure, for it is difficult to get enough information on a diffraction pattern, frequently only a first order of long-spacing being obtainable besides the diffuse "liquid" halo. However, on favorable film patterns or diffractometer charts it was possible to obtain 1st, 2nd and 4th orders for a lamellar neat structure. It was also possible to obtain spacings for middle in the ratio $1:\sqrt{3}:\sqrt{4}$ as Luzzati (11) has reported for other middle phases.

No diffraction data reliably attributable to the viscous isotropic phase were obtained. This phase may be identifiable with the "cubic" phase reported by Luzzati et al. (12), but the present author refrains from interpretation.

Experimental 1st order long spacings of neat and middle phases are reported in Table II.

Crystalline States

Efforts to explore the diffraction patterns of crystalline states were only preliminary partly due to prevalence of phase mixtures. Very likely different degrees of crystal hydration were involved. Results obtained are summarized in Table III.

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N-2-Mercaptoethyl Amides of Fatty Acids—A New Class of Derivatives[1]

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Abstract

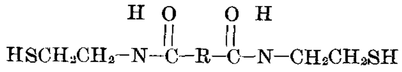
Twelve N-2-mercaptoethyl amides have been prepared by reacting 2-aminoethyl mercaptan with a carboxylic acid in refluxing xylene or toluene. All products were well-defined crystalline compounds except for the dimer acid derivatives. Addition of dithiol amides, prepared from dimer acids and 2-aminoethyl mercaptan, to diolefins gave a new class of potential protective coatings, a polyamide of a dimerized fatty acid with a β-thio linkage. Oxidation of the dithiols gave the corresponding disulfides, another new class of compounds, a polyamide with a β-disulfide structure. Film properties have been obtained with both classes of polymers. Air-dried films were soft and tacky, but baking the films improved hardness. Dry-to-touch times of less than 2 hr at 150C and good alkali resistance were obtained.

Introduction

The literature contains few references to N-2-mercaptoethyl amides (1–5,8,9,11,13,15,17,18). Most of them relate to biochemical studies, but references 2, 5 and 11 concern organic syntheses. In penicillin studies, N-(2-mercaptoethyl)2,2-dimethyl-3-phenyl-3-ketopropionamide was prepared from β-lactam (5). Kuh and Quadbeck (11) prepared N-2-mercaptoethyl acetamide and N-2-mercaptoethyl benzamide by reacting ethylene imine with thioacetic and thiobenzoic acids, respectively. Babichev and Shokol (2) reported on the reaction of 2-aminoethyl mercaptan with the anhydrides of succinic, glutaric and phthalic acids. They obtained the imide or amide depending upon the conditions of the reaction instead of the anticipated ω-(2-thiazoline) alkanoic acids.

We have prepared mercaptoethyl amides of mono- and dibasic acids and studied the addition of dimercaptans to nonconjugated terminal diolefins to give polymers that might serve as a new class of protective coatings. N,N′-Bis(2-mercaptoethyl)-amides were synthesized from 2-aminoethyl mercaptan and dibasic acids, and the reaction can be shown as follows:

$$HOOCRCOOH + H_2NCH_2CH_2SH \longrightarrow$$



$$HSCH_2CH_2-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-CH_2CH_2SH$$

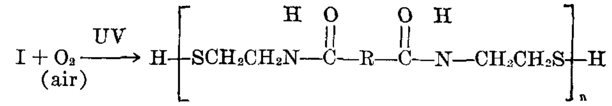
[I]

Biallyl and [I] were reacted in the presence of a persulfate catalyst. A free radical addition gave a new type of polyamide with a β-thio linkage [II] as shown in the following equation, where I is represented as HSR°SH:

$$HSR^{\circ}SH + (CH_2{=}CHCH_2)_2 \longrightarrow H\left[SR^{\circ}S(CH_2)_6\right]_n H$$

[II]

On oxidation, I gave a new type of polyamide with a β-disulfide structure.



$$I + \underset{\text{(air)}}{O_2} \xrightarrow{UV} H\left[SCH_2CH_2\overset{H}{N}-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-CH_2CH_2S\right]_n H$$

[III]

This paper describes the preparation of N-2-mercaptoethyl amides and some polymers obtained therefrom.

Experimental

N,N′-Bis(2-mercaptoethyl)-azelamide

2-Aminoethyl mercaptan was prepared from the hydrochloride (Eastman P8567) by the method of

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[2] No. Util. Res. and Dev. Div., ARS, USDA.

TABLE I

Analytical Data and Melting Points of N-2-Mercaptoethyl Amides

N-2-Mercaptoethyl amide	Sulfur, %		Nitrogen, %		M.P., C[a,b]
	Theory	Found	Theory	Found	
Lauramide	12.36	12.21	5.40	5.27	74–6(43–44)
Myristamide	11.15	11.20	4.87	4.80	80–2(54–55)
Palmamide	10.16	10.00	4.44	4.32	88–90(62–63)
Stearamide	9.33	9.51	4.08	4.06	122–4(69–70)
Arachidamide	8.63	8.67	3.77	3.74	94–6(75–76)
Behenamide	8.02	7.61	3.51	3.26	93–4(80)
Azelamide	20.92	19.63	9.14	8.68	140–2(106–107)
Oleamide	9.38	9.14	4.11	4.04	107–8[c](14)
Elaidamide	......	......	......	......	109–10(44–45)
Mixed oleamide and elaidamide	......	......	......	......	106–9(......)

[a] Fisher-Johns melting point apparatus.
[b] Melting point of parent acids in parentheses.
[c] Partially elaidinized to the elaidic derivative (see text).

Gabriel and Colman (6) and was sublimed into a tared 250-ml round-bottom flask. To 12.1 g (0.157 moles) of freshly sublimed 2-aminoethyl mercaptan was added 14.8 g (0.078 moles) of azelaic acid (Eastman 1421) and 125 ml toluene. The flask was connected to a Dean-Stark distilling receiver and bulb condenser and was refluxed for 17 hr. During this time, 3.2 cc (theory 2.8) of water collected in the Dean-Stark receiver. The toluene was distilled from the reaction mixture with the last traces being removed under reduced pressure (1 to 2 mm Hg). The crude product, 23.4 g (97.2%), melted at 103–108C. After three recrystallizations from ethanol and drying over P_2O_5 a pure N,N′-bis(2-mercaptoethyl)-azelamide was obtained. Elemental analyses for sulfur and nitrogen and melting points of the amides are listed in Table I.

N,N′-Bis(2-mercaptoethyl)-dimer Amide

Except for the recrystallization step, the N,N′-bis-(2-mercaptoethyl)-dimer amide was prepared from 83% dimer acid (Emery Empol 1018) in the same manner described for N,N′-bis(2-mercaptoethyl)-azelamide. After removal of the solvent, an oil remained that had a viscosity of 26,400 cp at 25C as determined with a Rotovisco Haake rotating viscometer: $n_D^{25} = 1.5098$. Infrared absorptions were noted at 3.05 μ, 3.9 μ and 6.1 μ (Fig. 1). Elemental analysis showed 8.17% sulfur and 3.46% nitrogen. Based on a neutral equivalent of 288 for the dimer acid used, the theory for sulfur and nitrogen is 9.24% and 4.03% respectively.

The dimer amide was also prepared from 95% dimer acid (Emery Empol 1014). This product had a viscosity of 22,400 cp at 25C and a refractive index of 1.5058 at 30C.

Polymers from N,N′-Bis(2-mercaptoethyl)-dimer Amide and Biallyl

N,N′-Bis(2-mercaptoethyl)-dimer amide and biallyl were emulsion polymerized by Marvel's method A (14). The emulsifying agent was a 1% solution of a neutral alkyl aryl sulfonate (Colgate Palmolive Mentor Beads LD) acidified to a pH of 3.0 with dilute sulfuric acid. The initiator-activator solution was prepared from ammonium persulfate, sodium bisulfite and cupric sulfate. Coagulation was accomplished with an aluminum potassium sulfate solution. Polymerizations were made with I prepared from Empol 1014 (95% dimer) and with Empol 1018 (83% dimer) (Table II). The polymer from the 95% dimer (I^d) and biallyl had a viscosity of 92,000 cp, and that from the 83% dimer (I^c) and biallyl had a viscosity of 141,000 cp. All viscosities were determined at 25C on a Rotovisco Haake rotating viscometer with a plate-cone attachment. The n_D^{25} of I^c is 1.5098 and the n_D^{30} of I^d is 1.5058.

TABLE II

Viscosity and Film Properties of N,N′-Bis(2-mercaptoethyl)-dimer Amides and Derivatives

Polymer	Viscosity cp	Dry-to-touch hr[a]	Film hardness[b]	
			Sward	Pencil
Dimer amide I[c]	26,400	3¼	2	3
Dimer amide I[d]	22,400	3¼	2	....
Biallyl-I[d]-copolymer	92,000	2½	2	4
Biallyl-I[c]-copolymer	141,000	2	2	5
III[d]	144,000	½	2	5
III[d]	660,000	1¼	2	5
III[d]	$>2 \times 10^6$	1¾	2	6

[a] 0.03% Fe, 0.03% Zr baked at 150C.
[b] Baked 20 min at 200C with drier.
[c] From Empol 1018.
[d] From Empol 1014.

UV Radiation of I^d

The apparatus used for this experiment is shown in Figure 2. Into the flask was weighed 27 g of I^d from Empol 1014 and 178 g of benzene. This solution was stirred magnetically while air was bubbled through the solution at a rate of approximately two bubbles per second. Sample was irradiated with a Nester Faust NF UV-300 combination UV source (2537 Å) consisting of a quartz coil, a protective quartz sleeve and an NF UV-400 power supply. Temperature was maintained at 60 ± 2C. Irradiation times were varied from 2 days to 1 week. After irradiation, solvent was removed and the viscosity of the residual polymers III varied from 144,000 cp for the 2-day exposure to a viscosity of greater than 2×10^6 cp for a week's exposure (Table II).

Film Preparation and Evaluation

Driers were added as 0.03% metal (naphthanates except for zirconium octoate) to the sample (50% solids in toluene) and films were drawn wet at 4 mils on black iron discs with a doctor blade. Sand trails and drying time data were determined at 150C by the method of Schwab, Teeter and Cowan (16).

Film Hardness

Film hardness was determined with a Sward Rocker and by the pencil method (7). These films were drawn at 4 mils wet thickness (50% solids in toluene) on 4½ in. x 6 in. x ¼ in. plate glass and baked 20 min at 200C.

Alkali Resistance

Approximately 0.2 ml of a 5% NaOH solution was

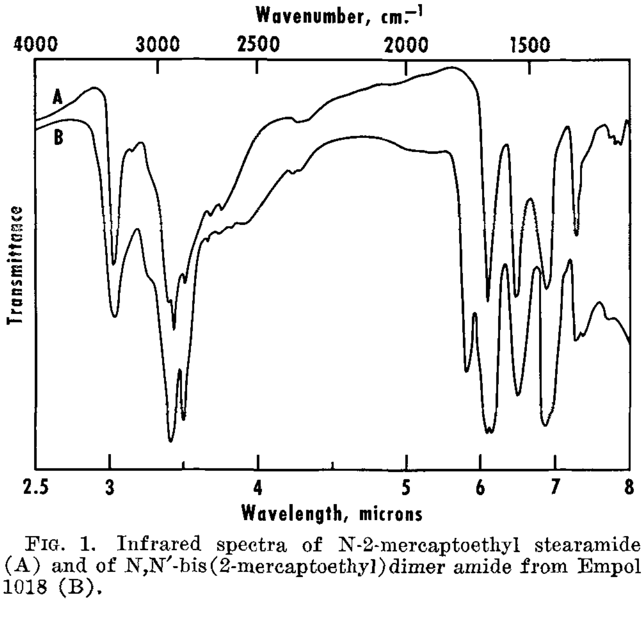

FIG. 1. Infrared spectra of N-2-mercaptoethyl stearamide (A) and of N,N′-bis(2-mercaptoethyl)dimer amide from Empol 1018 (B).

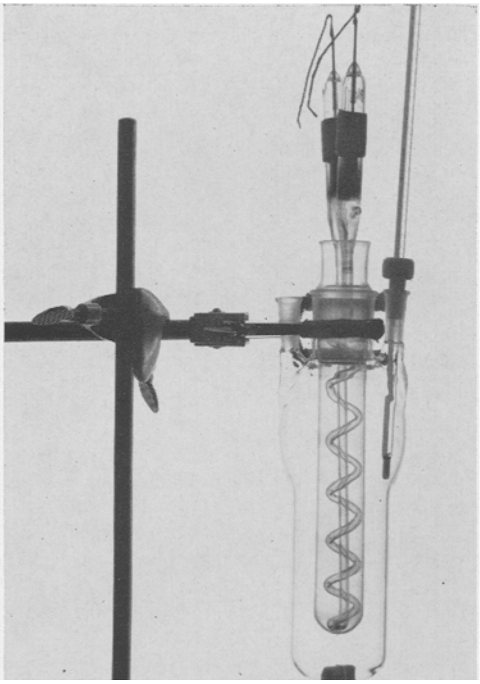

FIG. 2. Ultraviolet irradiation apparatus used in oxidation experiments.

placed in two different locations on the film and a watch glass (No. 1½) was inverted over each drop. The edge of the watch glass was sealed with wax to prevent evaporation. During the first 8 hr, observations were made hourly and at 24-hr intervals thereafter. Films were considered to have failed when they showed definite signs of solution.

Results and Discussion

Elemental analyses and melting points of the crystalline N-2-mercaptoamides are listed in Table I, along with the melting points of the parent acids. The N-2-mercaptoethyl amides melt above their corresponding acids. Infrared absorption data showed that the product from oleic acid was elaidinized; approximately two-thirds of the sample melting at 107–108C is elaidic. The elaidinization of methyl oleate by mercaptans is well known and has been studied by Kircher (10). He deduces that elaidinization is much faster than the addition of the sulfhydryl group to the double bond, and he explains the reaction as a reversible thiyl attack on one of the unsaturated carbon atoms.

The infrared analysis of N-2-mercaptoethyl stearamide (Fig. 1, Curve A) exhibited a characteristic band for NH (3.05 μ), SH (3.9 μ) and C=O (6.1 μ). Curve B is that of I^c from Empol 1018, a product difficult to purify. Similar absorptions are noted at 3.05, 3.9 and 6.1 μ as with N-2-mercaptoethyl stearamide, but the absorption at 6.1 μ is a doublet and probably results from impurities in dimer product. In addition, a carbonyl adsorption at 5.80 μ was present in B and strongly suggests a free acid in the polymer. A potentiometric titration confirmed the presence of 9.8% unreacted dimer acid. When an 8.13 mole excess of 2-aminoethyl mercaptan was added to crude product I^c and the mixture refluxed in toluene for an additional 48 hr, followed by solvent removal and stripping of unreacted amine, a potentiometric titration curve showed the presence of a 2.5% dimer acid. An acid content of this magnitude is not unexpected since Loening et al. (12) have shown that there is a sharp decrease in esterification rates of aliphatic acids with increasing chain branching. They attribute this decrease to a combination of steric and ponderal effects.

Baked films of I and certain derivatives therefrom are listed in Table II. Most polymers gave precipitates with lead and cobalt driers. A successful drier system was a combination of iron naphthenate and zirconium octoate at a concentration of 0.03% metal. Baked films prepared from the N,N′-bis(2-mercaptoethyl)-dimer amides were somewhat soft and have long dry-to-touch times.

The emulsion polymerizations of dimer amides [I] from Empols 1014 and 1018 with biallyl gave polymers with respective viscosities of 92,000 and 141,000 cp. The higher viscosity obtained from Empol 1018 (83% dimer) is anticipated since the trimer content (approximately 17%) would produce crosslinking and a more viscous polymer. Films of biallyl polymers from Empol 1014 and 1018, with or without driers, showed poor air drying. Baking at 150C gave dry-to-touch times of 2 and 2½ hr, respectively, for polymers of Empol 1018 and 1014. The higher trimer sample had the shorter drying time. These data, as well as Sward Rocker Hardness and the pencil test, are listed in Table II. The discrepancy noted between the pencil and Rocker hardness data is not surprising since the methods are measuring somewhat different properties. Pencil hardness values also show significant differences. Resistance to 5% aqueous alkali was outstanding; all films were unaffected after 2 weeks.

Oxidation by air in presence of ultraviolet irradiation of N,N′-bis(2-mercaptoethyl)-dimer amide of Empol 1014 (See III^d, Table II) gave viscous polymers; the viscosity of the polymers varied from 144,000 cp for 2 days' irradiation to a viscosity greater than 2×10^6 cp for 1 week of irradiation. Dry-to-touch times for these polymers increased as the viscosity of the unoxidized polymer increased. Hardness improved with increasing viscosity in these polymers. The dimer amide polymer with a viscosity of greater than 2×10^6 cp gave the hardest film. Alkali-resistance times were excellent for all films.

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