$E' \approx O(10^5)$ dyn/cm² [6] and $|\eta^*| \approx \eta' \approx O(10^{-2})$ (dyn sec)/cm² (P), where O denotes order of magnitude. The relations between the dynamic force f and dynamic deformation x as well as deformation rate $\dot{x}$ of spheres are

$$f = \pi R E^* x = \beta x$$

and

$$f = \pi R \eta^* \dot{x} = \gamma \dot{x}$$

respectively. Inserting these values of β and γ for $R = 2\ \mu$ in eq 6 provides a system which indeed will exhibit an underdamped oscillation. The quasifrequency of this oscillation is given by

$$\nu = \frac{\Omega}{2\pi} = \frac{1}{2\pi}\left(\frac{4\beta m - \gamma^2}{4m^2}\right)^{1/2} \approx 16{,}000 \text{ Hz}$$

If we choose E' and η' very reasonably to both be a factor of 2 larger, then the oscillation is still underdamped and the quasifrequency becomes $\nu = 7900$ Hz. Our calculation does not take the coupling between the viscoelastic balls into account; such coupling will lead to a spectrum of resonance frequencies all lower than the one calculated here. The model calculation thus shows that an audiofrequency resonance is a distinct possibility in heterogeneous gels.

The disappearance of the resonance in the case of the aged poly(vinyl alcohol) gel (lower part of Figure 2) is most likely a consequence of the known crystallization of this polymer. This changes the structure to a composite of small, hard balls suspended in a viscoelastic matrix.[5] A similar calculation but introducing the Stokes friction factor $\gamma = 6\pi\eta R'$ into eq 6 then leads to an overdamping regardless of the precise value chosen for the spring constant β and the mass m.

In the case of gelatin gels, the integrated Rayleigh scattering is *not* many times larger than that of the corresponding solution. Such solutions do not undergo a microphase separation upon gelation but form a loosely coupled network of polymer chains.[5] We have indeed not found an audiofrequency resonance in such gels, in accord with the known relaxational rather than oscillatory behavior of polymer strands in a diluent.

Our explanation of the observed resonance is, of course, only a qualitative one. The broadness, for example, is probably a reflection of the existence of an array of thermally excited modes. The essential feature is, however, brought out by our model: *strongly* coupled cooperative motions of structural elements in the gel lead to a reduced energy dissipation into the surroundings and therefore to underdamped oscillating fluctuations in the polarizability; isolated polymer molecules, or *loosely* coupled ones, will always be overdamped, thus giving rise to nonshifted Lorentzians, with or without diffusional character as the case may be.

Our findings seem worth pursuing because of the information they provide about the dynamics of inhomogeneous gel structures. Without homodyning, only the static aspects of gel structure are obtained from light-scattering measurements.

(6) J. D. Ferry, *J. Amer. Chem. Soc.*, **70**, 2244 (1948).

W. Prins*

Department of Chemistry, Syracuse University
Syracuse, New York 13210

L. Rimai, A. J. Chompff

Scientific Research Staff, Ford Motor Company
Dearborn, Michigan 48121

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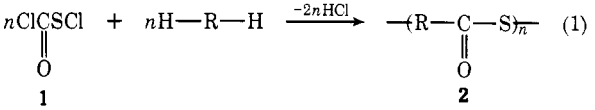
Sulfur-Containing Polymers. I. Polycondensation of Chlorocarbonylsulfenyl Chloride with Diamines

Chlorocarbonylsulfenyl chloride (**1**)[1] is a compound in which two different electrophilic functions of high reactivity are attached directly to each other. Both the chlorocarbonyl and the chlorosulfenyl groups of **1** are available for nucleophilic substitutions, *e.g.*, with amines, thiols, and alcohols.[2] One might expect, therefore, that a variety of novel polymers in which –C(O)–S– linkages are incorporated could be obtained by polycondensation of **1** with bifunctional nucleophiles. This expectation is realized by the use of diamines as the nucleophiles. The present communication describes the successful synthesis of previously unknown polycarbamoylsulfenamides from **1** and secondary aliphatic diamines.

1 was prepared by the hydrolysis of trichloromethanesulfenyl chloride. Polycondensation of **1** with diamines proceeds according to eq 1. The polymer formations were



(1)

carried out by interfacial polymerization and solution polymerization.

Preparation of Chlorocarbonylsulfenyl Chloride (1).[1] A mixture of 80 ml of concentrated sulfuric acid, 6.8 g (0.38 mol) of water, and 70.0 g (0.38 mol) of trichloromethanesulfenyl chloride was heated at 50° with vigorous stirring.

TABLE I
PREPARATION OF POLYCARBAMOYLSULFENAMIDES

Diamine	Method of polym[a]	Yield, %	Dec pt,[b] °C	η_{inh}	$\bar{M}_n$[c]
Piperazine	I	77	209	0.99[d]	
	S	100	210	0.76[d]	
trans-2,5-Dimethylpiperazine	I	94	230	1.52[e]	12,000
	S	79	238	0.46[e]	
1,3-Di-4-piperidylpropane	I	100	226	2.40[e]	
	S	91	226	1.13[e]	
N,N'-Dimethylhexamethylenediamine	I	88	204	0.74[e]	5,800
	S	96	196	0.20[e]	

[a] Method I, interfacial polymerization carried out in chloroform–water using sodium carbonate as acid acceptor. Method S, solution polymerization in chloroform using triethylamine as acid acceptor. [b] Determined by differential thermal analyses. [c] Obtained in chloroform solutions by a vapor pressure depression method. [d] Measured at 0.5 g/100 ml of *sym*-tetrachloroethane at 30°. [e] Measured at 0.5 g/100 ml of chloroform at 30°.

(1) W. Weiss, German Patent 1224720 (1964).
(2) G. Zumach and E. Kühle, *Angew. Chem., Int. Ed. Engl.*, **9**, 54 (1970).

TABLE II
POLYMER PROPERTIES

Polymer	Solubility: $CHCl_3$	Solubility: Cl_2CH-$CHCl_2$	Crystallinity	Elemental analysis, Calcd, %: C	H	N	S	Elemental analysis, Found, %: C	H	N	S
2a	P sol[a]	Sol	Highly crystalline	41.65	5.59	19.43	22.24	39.84[b]	5.57	18.59	22.46
2b	Sol	Sol	Amorphous	48.81	7.02	16.26	18.61	48.84	7.11	16.45	18.65
2c	Sol	Sol	Slightly crystalline	62.65	9.01	10.44	11.95	62.21	9.07	9.98	12.26
2d	Sol	Sol	Amorphous	53.43	8.97	13.85	15.85	51.82	8.91	13.60	16.33

[a] Partially soluble. [b] Ash content, 1.01%.

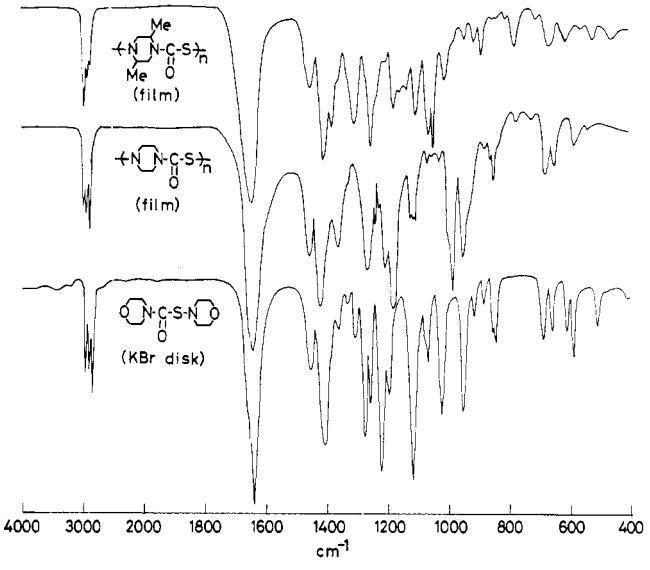


Figure 1. Infrared spectra of the polycarbamoylsulfenamides and the model compound.

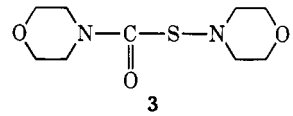
The reaction was followed by infrared spectra. After about 2 hr, the intense absorption bands at 795, 760, and 740 cm^{-1} characteristic of trichloromethanesulfenyl chloride disappeared. The organic layer was separated, and distillation gave 35.5 g (72%) of **1**, bp 97–99°.

Interfacial Polycondensation of 1 with *trans*-2,5-Dimethylpiperazine. A mixture of 3.9 g (0.038 mol) of *trans*-2,5-dimethylpiperazine, 8.2 g (0.077 mol) of sodium carbonate, 15 ml of chloroform, and 300 ml of cold water was stirred rapidly in a household blender. To this mixture was quickly added a solution of 5.0 g (0.038 mol) of **1** in 80 ml of chloroform and the resultant mixture was stirred for 5 min at high speed. The chloroform was removed on a rotary evaporator at room temperature. The mixture was then filtered and the solid washed several times with water to give, upon drying, 6.2 g (94%) of white polymer, η_{inh} 1.52 (in chloroform).

Solution Polycondensation of 1 with 1,3-Di-4-piperidylpropane. To a solution of 8.0 g (0.038 mol) of 1,3-di-4-piperidylpropane and 7.8 g (0.077 mol) of triethylamine in 200 ml of chloroform was added dropwise over a period of 10 min a solution of 5.0 g (0.038 mol) of **1** in 50 ml of chloroform, while the mixture was maintained below 20° by external cooling. After addition was completed stirring was continued for 20 min. The mixture was poured into excess methanol. The resultant white precipitate was filtered and washed with methanol. The yield was 9.3 g (91%), η_{inh} 1.13 (in chloroform).

Polymers were obtained in good yield irrespective of polymerization procedures; however, the interfacial method gave polymers with higher inherent viscosities (Table I). The inherent viscosities of the polymers were in the range 0.20–2.40, indicating that these polymers were of high molecular weight. The polymers obtained from piperazine, *trans*-2,5-dimethylpiperazine, and 1,3-di-4-piperidylpropane were white solids. The reaction with *N,N'*-dimethylhexamethylenediamine by the above procedures produced a resinous polymer.

The structures of the polymers were established from elemental analyses and infrared and nmr spectra. The results of elemental analyses of the polymers are listed in Table II. The infrared spectra of the polymers showed a characteristic carbonyl absorption at about 1650 cm^{-1} corresponding to a tertiary amide. In all polymers, there was a conspicuous absence of absorption bands corresponding to NH and carbonyl group of **1** (1790 cm^{-1}). Figure 1 shows the infrared spectra of **2a**, **2b**, and **3**, a model compound derived from **I** and morpholine.[3] The nmr spectrum of **2b** showed



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two doublets at δ 1.05 (J = 6.0 Hz) and 1.17 (J = 6.0 Hz) due to methyl protons in the ratio of 1:1. Similarly, the nmr spectrum of **2d** showed two singlets at δ 2.84 and 2.97 due to *N*-methyl protons in the ratio of 1:1. These findings are consistent with the postulated structure of the polymers.

In general, the polymers prepared here were soluble in chloroform, *sym*-tetrachloroethane, and *m*-cresol. They were insoluble in DMF, DMAc, DMSO, and HMPA. The only exceptions are that **2a** was partially soluble in chloroform and that **2d** dissolved in DMF and DMAc after prolonged stirring. Colorless, transparent films were readily obtained from most of the solid polymers with inherent viscosities of about 0.7 or above. All the polymers decomposed on heating without melting. The decomposition points in Table I were determined by differential thermal analyses. X-Ray diffraction studies have revealed that **2a** is highly crystalline, **2b** is amorphous, and **2c** is slightly crystalline. The polymers decomposed by uv irradiation with the liberation of carbonyl sulfide.

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(3) Mp 126–128° (from ether–petroleum ether) (lit.[2] mp 119°); mass spectrum (70 eV) *m/e* 232 M^+ (3), 114 (100), 86 (57), 42 (31). *Anal.* Calcd for $C_9H_{16}N_2O_3S$: S, 13.80. Found: S, 13.73.

Norio Kobayashi, Tamotsu Fujisawa*
Sagami Chemical Research Center
Ohnuma, Sagamihara-shi, Kanagawa, 229, Japan

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