tension measurements give the same modulus. At the same time, we can observe that there is a direct relationship between the value of C_2 in extension and the value of the elastic modulus in compression. As a matter of fact, a zero value for C_2 in extension[6] gives in compression an elastic modulus invariable with the swelling, as is shown in Table I and Figure 1; on the other hand, in the conventional vulcanizates a decrease of C_2 with swelling in extension takes place with a strong decrease of the compression modulus.[3,4] In Figure 2 the relative modulus decreases are reported for two conventional vulcanizates and two of our vulcanizates. As shown, for conventional networks the decrease is of the order of 50–60%, while for solution vulcanizates the values are in the range ±10%.

The results demonstrate, therefore, that natural rubber vulcanized in the swollen state behaves as an ideal network, obeying eq 1. In this case, the C_1 coefficient of the Mooney–Rivlin equation in compression can be identified with the theoretical modulus of eq 1. It is independent of the strain conditions, extension or compression, and of the swelling degree.

Many suggestions can be made to interpret this result. First of all, according to what we have previously reported,[5] it is possible to say that our vulcanizates have a low percentage of physical entanglements in comparison with a conventional vulcanizate. A second hypothesis regards the last works of Prins,[7–9] in which the nonideality of the rubber networks is correlated with a certain degree of supramolecular organization in the amorphous material (bundles). As a matter of fact, vulcanization "stops" the topology of the polymer at the moment in which it takes place, and in our case it stops the topology of a polymer diluted by the solvent. Solvent removal allows an approach of the cross-link points, with a consequent supercoiling of the network chains. It is less probable, therefore, that parallel segments of adjacent chains can interact with bundle formation, owing to the supercoiled state of the network chains. Experimental studies are now in progress to verify this latter hypothesis.

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(6) This result has been previously reported.[5]

(7) R. Blokland and W. Prins, *J. Polym. Sci., Part A-2*, **7**, 1595 (1969).

(8) K. Dušek and W. Prins, *Advan. Polym. Sci.*, **6**, 1 (1969).

(9) M. Ilavsky and W. Prins, *Macromolecules*, **3**, 415 (1970).

Communications to the Editor

An Audiofrequency Resonance in the Quasielastic Light Scattering of Polymer Gels

We have observed a broad resonance in the frequency spectrum of the light scattered quasielastically by two dilute polymer gels. The resonance occurs at a few kilohertz and has been traced to underdamped, oscillatory behavior of viscoelastic, microscopic heterogeneities in the structural makeup of the gels.

Figure 1 shows the frequency distribution of the scattered light of a 1% aqueous solution of agarose (an alternating copolymer of 3,6-anhydro-α-L-galactopyranose and β-D-galactopyranose) at 70° as well as that of the gel obtained by cooling the solution to a temperature below the gel point at 42°. Figure 2 shows the results for a 5% poly(vinyl alcohol) gel in a mixture of water and ethylene glycol obtained by quenching the solution from 80 to 5° and subsequently measuring at room temperature. In this case, the maximum disappears upon aging of the gel.

The measurements were performed in a homodyning light-scattering spectrometer[1] consisting basically of a He–Ne laser (Spectraphysics Model 124), a thermostated rectangular glass cell of 2-mm optical path, and a wave analyzer (General Radio Model 1800 A) connected to a photomultiplier with a 10- or 33-K load resistor. The wave analyzer output was squared and accumulated in the memory of a multichannel analyzer (Technical Measurements, CAT 1000) for about 10 min, representing about eight sweeps through a preselected, motor-driven frequency range. The squaring assures that the power spectrum of the photocurrent is stored in the memory of the multichannel analyzer.[2] By utilizing an arbitrary static scatterer in the position of the sample cell, it was ascertained that the response to shot noise was flat over the entire frequency range covered in our measurements.

The rectangular sample cell and its thermostated jacket allowed measurements to be taken at external scattering angles, θ_e, varying from 10 to 50°. By inserting a Polaroid in the scattered beam, it was established that the frequency-shifted scattering was not depolarized. The same was true for the integrated Rayleigh scattering of the gels which was measured in an absolute light-scattering photometer without a homodyning arrangement. We are thus dealing with isotropic, quasielastic scattering, for which we can write the Rayleigh ratio, $R(\mathbf{K}, \omega)$, as follows

$$R(\mathbf{K}, \omega) = (16\pi^4/\lambda_0^4)\langle\eta^2\rangle \int_V d\mathbf{r} \int_{-\infty}^{+\infty} \gamma(\mathbf{r}, \tau) e^{i\mathbf{K}\mathbf{r}} e^{-i\omega\tau} d\tau \qquad (1)$$

Here λ_0 is the wavelength of the incident radiation *in vacuo* (λ_0 632.8 nm); $\langle\eta^2\rangle$ is the mean-square polarizability fluctuation of a volume element, characterized by a time–space correlation function $\gamma(\mathbf{r}, \tau)$, defined in such a way that $\gamma(\mathbf{r}, \tau) = \gamma(\mathbf{r}, -\tau)$; $\mathbf{K}$ is the scattering vector[2,3] which equals $(4\pi/\lambda) \cdot \sin \theta/2$, where λ is the wavelength and θ the scattering angle in the sample; and ω is the circular frequency *minus* that of the incident radiation. Upon performing the integration over the scattering volume, V, the power spectrum of the scattered light will be given by

$$R(\mathbf{K}, \omega) = (16\pi^4/\lambda_0^4)\langle\eta^2\rangle \int_{-\infty}^{+\infty} \Gamma(\mathbf{K}, \tau) e^{-i\omega\tau} d\tau \qquad (2)$$

where $\Gamma(\mathbf{K}, \tau) = \Gamma(\mathbf{K}, -\tau)$ is a time-correlation function.

The homodyning spectrometer measures the power spectrum of the photocurrent autocorrelation $\langle i(t)i(t + \tau)\rangle$. Since $i(t)$ is proportional to the scattered light intensity, *i.e.*, to the square of the scattered field, the power spectrum of the photocurrent, $S_i(\mathbf{K}, \omega)$, is proportional to the Fourier transform of the square of $\Gamma(\mathbf{K}, \tau)$[1]

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(1) L. Rimai, J. T. Hickmott, Jr., T. Cole, and E. B. Carew, *Biophys. J.*, **10**, 20 (1970).

(2) N. C. Ford and G. B. Benedek, *Phys. Rev. Lett.*, **15**, 649 (1965).

(3) S. B. Dubin, J. H. Lunacek, and G. B. Benedek, *Proc. Nat. Acad. Sci. U. S.*, **57**, 1164 (1967).

$$S_i(\mathbf{K},\omega) \propto \int_{-\infty}^{+\infty} \Gamma^2(\mathbf{K},\tau)e^{-i\omega\tau}d\tau \qquad (3)$$

The appearance of a maximum in our experimental results suggests that the form of the function $\Gamma(\mathbf{K}, \tau)$ should be that of an *underdamped* oscillation in time

$$\Gamma(\mathbf{K}, \tau) = \Gamma(\mathbf{K})e^{-\alpha\tau} \cos \Omega\tau \qquad (4)$$

For the purpose of this communication, it is sufficient to write only one underdamped oscillatory function, although it is realized that a better description would be given by an array of such functions, some more heavily weighted than others. Upon squaring eq 4, inserting the result in eq 3, and performing the integration, the resulting power spectrum of the photocurrent is given by

$$S_i(\mathbf{K}, \omega) \propto \Gamma^2(\mathbf{K}) \times \left[\frac{\alpha}{4\alpha^2 + (\omega - 2\Omega)^2} + \frac{\alpha}{4\alpha^2 + (\omega + 2\Omega)^2} + \frac{\alpha}{4\alpha^2 + \omega^2}\right] \qquad (5)$$

The last term represents a Lorentzian centered at the origin; the second term, one centered at a negative frequency. Both contribute monotonically decreasing components to the power spectrum. It is the first term that describes the observed maximum and reflects the underdamped oscillatory behavior of the time fluctuations in the local polarizability. The first two terms always appear simultaneously in the spectrum of a real correlation function that contains an oscillatory modulation.

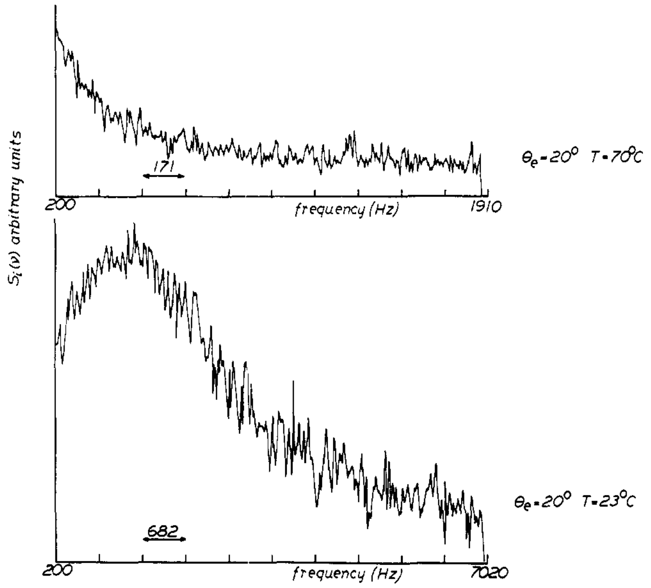

Figure 1. Frequency distribution of the light scattered by a 1% agarose solution (70°) and gel (23°): 1% agarose in water; accumulated frequency sweeps of 50-Hz bandwidth, 1 min/sweep.

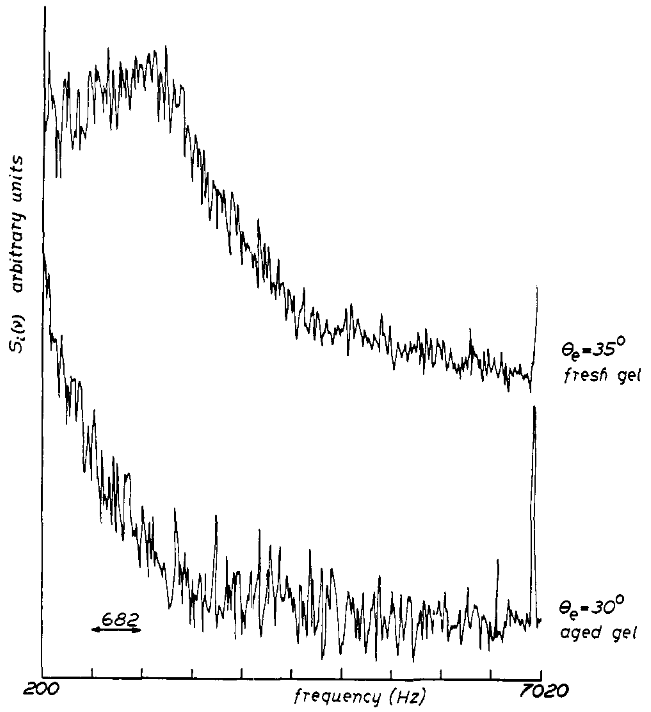

Figure 2. Frequency distribution of the light scattered by a 5% poly(vinyl alcohol) gel, before and after aging: 5% poly(vinyl alcohol) in 50% water–45% ethylene glycol; accumulated frequency sweeps of 50-Hz bandwidth, 1 min/sweep.

In polymer solutions of not too high molecular weight, one normally detects a single nonshifted Lorentzian of half-width $2\alpha = 2D\mathbf{K}^2$, where D is the translational diffusion coefficient.[4] In the course of this work we indeed observed such a single Lorentzian with diffusional characteristics for the 5% poly(vinyl alcohol) solution prior to gelling ($D = 9.4 \times 10^{-7}$ cm²/sec). In the case of agarose, a 0.1% solution at 70° exhibited two nonshifted Lorentzians, both of diffusional character (*i.e.*, proportional to $\mathbf{K}^2$) indicating that some aggregation of the primary polymer molecules occurs. The third Lorentzian which should be present in principle because of $\Gamma^2(\mathbf{K}, \tau) = \Gamma_1^2(\mathbf{K})e^{-2\alpha_1\tau} + \Gamma_1(\mathbf{K})\Gamma_2(\mathbf{K})e^{-(\alpha_1+\alpha_2)\tau}.$ $\Gamma_2^2(\mathbf{K})e^{-2\alpha_2\tau}$ could not be detected (calculated diffusion constants from α_1 and $\alpha_1 + \alpha_2$ are $D_1 = 1.57 \times 10^{-7}$ and $D_1 + D_2 = 1.71 \times 10^{-6}$ cm²/sec). The values of the diffusion constants, quoted above, are all reasonable considering that the molecular weights of the polymers are around 100,000. The 1% agarose solution at 70°, however, exhibited two nonshifted Lorentzians (of which the higher frequency one is shown in the upper part of Figure 1), which were *independent* of $\mathbf{K}^2$ in the angular range covered. Apparently, intermolecular coupling already occurred at this temperature and concentration, leading to a more complex decay of polarizability fluctuations than prescribed by translational diffusion.

A qualitative explanation of the observed resonance is based on the independent observation that the integrated Rayleigh scattering of both gels is many times larger than that of the corresponding solutions. The angular dependence of the scattering[5] indicates that regions of the order of 4 μ in diameter have been formed as a result of microphase separation during gelation. Considering these regions as soft, viscoelastic balls which are deforming each other under thermal excitation, we have to show that such motions are underdamped.

The highest frequency mode will be given by the solution of

$$m\ddot{x} + \beta x + \gamma\dot{x} = 0 \qquad (6)$$

provided $\gamma^2 - 4\beta m < 0$.

The mass m of a soft ball of a 1 or 5% aqueous polymer gel will be approximately $(4\pi/3)R^3 = 3.4 \times 10^{-11}$ g, if the radius R is 2 μ. The spring constant β and the frictional constant γ are obtained from typical values of the dynamic Young's modulus $E^* = E' + iE''$ and the dynamic viscosity $\eta^* = \eta' - i\eta''$. For dilute gels at audiofrequencies $|E^*| \approx$

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(4) T. F. Reed and J. E. Frederick, *Macromolecules*, **4**, 72 (1971).

(5) E. Pines, Ph.D. Thesis, Syracuse University, 1972; see also E. Pines and W. Prins, Abstracts, Rayleigh Centennial Symposium, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

$E' \approx O(10^8)$ dyn/cm^2 [6] and $|\eta^*| \approx \eta' \approx O(10^{-2})$ (dyn sec)/cm^2 (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).

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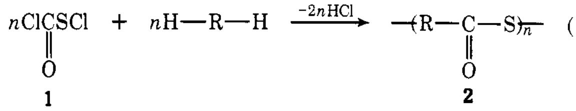
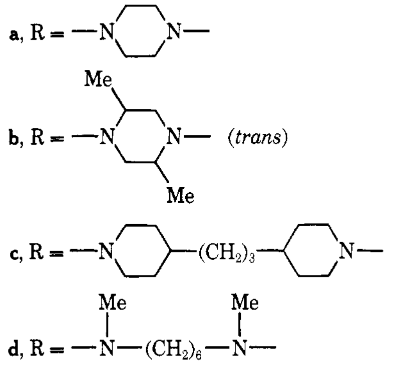
Sulfur-Containing Polymers. I. Polycondensation of Chlorocarbonylsulfenyl Chloride with Diamines

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 carried out by interfacial polymerization and solution polymerization.



$$n\underset{\underset{\textstyle \mathbf{1}}{\textstyle O}}{\mathrm{ClCSCl}} + n\mathrm{H{-}R{-}H} \xrightarrow{-2n\mathrm{HCl}} \lbrack\mathrm{R}{-}\underset{\underset{\textstyle \mathbf{2}}{\textstyle O}}{\overset{}{\mathrm{C}}}{-}\mathrm{S}\rbrack_n \quad (1)$$



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°.

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(1) W. Weiss, German Patent 1224720 (1964).

(2) G. Zumach and E. Kühle, *Angew. Chem., Int. Ed. Engl.*, **9**, 54 (1970).