

Viscoelastic and Photoelastic Properties of Polystyrene above Its Softening Temperature

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TABLE II. The comparison of the observed and the calculated fundamental frequencies of hexachloroethane.

Type	Calculated* (cm ⁻¹)	Raman observed	Type	Calculated* (cm ⁻¹)	Infra-red observed
A _{1g}	198	169	A _{2u}	382	—
	432	432		729	675
	1008	974			
E _g	218	224	E _u	134	—
	322	341		278	—
	889	853		744	769

*For the form of the potential function and the values of the force constants see reference 3.

The absorption spectra (8–16 μ) were observed in the solid state and in carbon tetrachloride solution. The experimental technique and the apparatus used were essentially the same as described in our previous paper.⁴ The result is shown in Table I. The band observed at 1008 cm⁻¹ is very weak and might be assigned to one of the combination tones.

The Raman spectra were remeasured in the solid state. In Table I the result is shown, which is in good agreement with that obtained by Hamilton and Cleveland.² The existence of a line at 169 cm⁻¹ reported by them was confirmed. It seems that there was found a line at 140 cm⁻¹ by Hg- ϵ excitation, but we are not sure if this is really a Raman line, because there is a weak mercury line practically at the same position. We can assign the line at 169 cm⁻¹ to a deformation vibration of the molecule and that at 140 cm⁻¹ to the lattice vibration, because the latter was not observed by Hamilton and Cleveland in the spectra of solutions.

The two infra-red active vibrations expected for the staggered form were detected by the present experiment (see Table II). The other three frequencies also active in the infra-red lie out of the observable region of our apparatus. If the molecular form were the eclipsed one, the frequency 769 cm⁻¹ of E_u observed in the infra-red spectra should also appear in the Raman effect. However, no Raman line was detected in this frequency region. We can, therefore, conclude in conformity with our previous result that the stable configuration of hexachloroethane is the staggered form D_{3d}. This conclusion had been established by our electron diffraction investigation.⁵

The calculated frequencies of the Raman active vibrations are in good agreement with the observed values (see Table II). This agreement shows that the Urey-Bradley field is an adequate potential function for the treatment of the normal vibration of such a molecule.

¹ S. Mizushima and Y. Morino, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* 29, 188 (1936).

² D. T. Hamilton and F. F. Cleveland, *J. Chem. Phys.* 12, 249 (1944).

³ T. Simanouti, *J. Chem. Phys.* 17, 734 (1949).

⁴ Simanouti, Turuta, and Mizushima, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* 42, 51 (1946).

⁵ Y. Morino and M. Iwasaki, *J. Chem. Phys.* 17, 216 (1949).

Viscoelastic and Photoelastic Properties of Polystyrene above Its Softening Temperature

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IN a study of creep, recovery after creep, stress relaxation, and optical anisotropy of polystyrene films above their softening temperature, we have obtained certain results which appear to be of significance in obtaining a better understanding of the mecha-

TABLE I. Creep of polystyrene at 110°C.

Time (sec.)	Elongation %	Birefringence A/mil	Stress lb./in. ²	Birefringence stress
0	0	0	24.4	—
40	22.1	-217	29.8	-7.28
75	33.3	-289	32.5	-8.90
130	46.5	-324	35.7	-9.08
190	57.2	-359	38.3	-9.38
275	69.3	-373	41.3	-9.02
375	83.9	-413	44.9	-9.22
480	99.5	-448	48.7	-9.22
590	116.4	-485	52.8	-9.18
700	132	-513	56.6	-9.08
820	154	-556	62.0	-8.97
940	173	-605	66.6	-9.08
1060	193	-634	71.5	-8.88

nism of viscoelastic deformations and of the molecular structure, not only of polystyrene, but also of so-called linear and amorphous linear high polymers in general.

Table I gives the strain and birefringence (A/mil) as a function of time at 110°C, when a constant weight is applied to a film* made from unfractionated polystyrene ($\eta=1.13$). As the cross section changes during the run, the stress per unit area varies also, and column 4 of Table I gives the actual values of stress calculated from the elongation using a Poisson's ratio of 0.5. Column 5 shows the ratio of the birefringence to stress which is constant except for the initial part of the run. It can also be seen that the ratio of birefringence to strain changes continuously. Similar experiments at other temperatures and with films made from fractionated polystyrene ($\eta=1.56$ ($\eta=0.59$)) and a film consisting of a mixture of fractionated polystyrene and a low molecular weight compound showed that this ratio is not only independent of stress, strain, and time but also does not depend on molecular weight within the investigated range and depends only very slightly on temperature.

Table II shows the stress and birefringence relaxation of a polystyrene film. Again the ratio of birefringence to stress is essentially independent of time and is the same as obtained from the "creep" experiment given in Table I. The significant feature of this experiment is the fact that this stretched film recovered almost completely when the external force was removed at any time during the relaxation process of stress and birefringence.

Finally, it was found that repeated stress and birefringence relaxation runs (cycling) on the same film had an effect on the shape and magnitude of the stress and birefringence relaxation curves; cycling always decreases the magnitude of the stress and leads to a more rapid initial stress decay. Similarly, it was found that repeated creep runs (in shear) did not yield identical curves but frequently gave higher initial compliances on consecutive runs.

In an attempt to find at least a qualitative interpretation of these results, we have come to the conclusion that the usual assumptions made to explain the viscoelastic behavior of linear high polymers¹—retarded elastic deformation and viscous flow—are not sufficient but that it becomes necessary to assume the existence of a semipermanent network structure.^{2,3} This structure

TABLE II. Stress and birefringence relaxation in polystyrene at 110°C (elongation = 95 percent).

Time (sec.)	Birefringence A/mil	Stress lb./in. ²	Birefringence stress
0	—	—	—
45	-738	>75	—
90	-573	62.5	-9.17
135	-516	56.0	-9.22
170	-476	50.8	-9.36
245	-426	46.8	-9.10
300	-410	44.3	-9.25
400	-369	40.2	-9.17
475	-361	39.1	-9.24
600	-343	36.5	-9.40
730	-311	33.9	-9.18
900	-295	33.9	-8.72
950	-287	32.6	-8.80

is most likely brought about by the intertwining of at least two or more chain segments belonging to the same or to different chain molecules and it is obvious that temperature and external forces have a pronounced effect on the average lifetime of these net points which are much less stable than the net points due to chemical crosslinking. Without the assumption of a semipermanent network, it does not seem possible to account for the fact (a) that the birefringence stress ratio remains constant and the deformation is almost completely recoverable at the same time, (b) that the birefringence and the stress can relax by a factor 2 to 3 without destroying the ability of the material to recover to its original length, (c) that "cycling" has an effect on the stress and birefringence relaxation and the initial creep compliance, and (d) that polystyrene exhibits anomalous flow characteristics² at temperatures much above its softening temperature. More experimental data and a more thorough discussion of some of the results given above, such as the initial change of the birefringence-stress ratio with time, the relationship of birefringence to orientation, etc., will be published in the near future.

* All films were prepared following a technique previously described; see Abstracts in Proceedings of the American Physical Society Meeting at New York, Phys. Rev. 75, 1279 (1949).

¹ T. Alfrey, Jr., *Mechanical Behavior of High Polymers* (Interscience Publishers, Inc., New York, 1948), pp. 93-228.

** Recently one of the authors suggested such a network structure on the basis of flow measurements on polystyrene at high temperature. (See J. Colloid Sci.)

³ R. Buchdahl, J. Colloid Sci. 3, 87 (1948).

On the Detection and Determination of Redundant Vibrational Coordinates*

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IN using valence-force coordinates (VFC) in a normal-coordinate treatment, one not infrequently finds it convenient, for symmetry reasons, to consider a redundant set; i.e., a set of coordinates which are not all independent. The neatest example is the set of six HCH angle deformations, $\Delta\alpha_{ij}$, in CH_4 ; these are of course connected by the redundancy condition

$$\sum_{i>j} \Delta\alpha_{ij} = 0. \quad (1)$$

Wilson¹ has discussed such redundant coordinates, the possible ways of treating them, and the consequent restrictions on the potential energy.

While one usually knows or easily finds out that a set of coordinates is redundant, it is not always so easy to find the redundancy condition analogous to (1).² The purpose of this note is to present a convenient way to do this, using Wilson's G matrix technique.¹ In our practice we need to find this redundancy, for we prefer to transform from our initial VFC to a set of symmetry coordinates one of which is precisely the redundancy; both the F and G matrices are so transformed. Then the G matrix has a row and column of zeros,¹ which may be neglected together with the corresponding row and column of the F matrix.

If the redundancy condition is initially not known, we may still set up symmetry coordinates, found from the VFC by elementary group theory.³ Moreover, the symmetry species containing the redundancy is easily found, either by noting which species has an extra coordinate, or (in case a needed coordinate has been inadvertently neglected and a redundant one unwittingly included) by observing that the G matrix factor for this species has a zero determinant.

Let S_k be the symmetry coordinates in which a redundancy lurks, so that $|G|=0$, where G is the inverse kinetic-energy matrix for the S_k . We seek to transform to the coordinates \bar{S}_n

such that \bar{S}_1 is the redundancy condition: $\bar{S}_1=0$. Let the transformation be orthogonal, so that

$$\bar{S}_n = \sum_k L_{nk} S_k, \quad (2)$$

$$\sum_n L_{nk} L_{nj} = \delta_{kj}. \quad (3)$$

Now if \bar{G} is the inverse kinetic-energy matrix for the \bar{S}_n , \bar{G} and G are related:

$$\bar{G}_{nm} = \sum_{jk} L_{nk} G_{kj} L_{mj}. \quad (4)$$

Moreover, since \bar{S}_1 is the redundancy,

$$\bar{G}_{1n} = \bar{G}_{n1} = 0, \quad \text{all } n. \quad (5)$$

Hence, taking $m=1$ in (4), multiplying through by L_{ni} , summing on n and using (3), we find

$$\sum_j G_{ij} L_{1j} = 0. \quad (6)$$

This tells us, then, how to find our redundancy condition $\bar{S}_1 = \sum_j L_{1j} S_j = 0$; if we regard our original G as the matrix of coefficients of a set of homogeneous linear equations, the transformation coefficients L_{1j} are just the "unknowns" whose ratios are determined. (Normalization completes the determination of the L_{1j} .) The remaining coefficients $L_{nk} (n \neq 1)$ may be written down as usual to make L orthogonal,⁴ and the resulting L used to transform both F and G .

If a species contains, say, s redundancies among n coordinates ($s > 1$), then the G matrix factor will be of order n but of rank $(n-s)$. The usual algebraic procedures⁵ for treating linear homogeneous equations will then give us the s sets of redundancy coefficients $L_{1j}, L_{2j}, \dots, L_{sj}$.

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** At Minnesota on leave from National University of Peking, China, 1947-48.

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¹ E. Bright Wilson, Jr., J. Chem. Phys. 9, 76 (1941).

² The reader complacent about geometry may write down the redundancy conditions among the six C-C distances and six C-C-C angles in cyclohexane.

³ E. P. Wigner, *Gruppentheorie* (Edwards Brothers, Inc., Ann Arbor, Michigan, 1944); p. 123.

⁴ *Inter alia*, reference 3, p. 31.

⁵ Bocher, *Higher Algebra* (The Macmillan Company, New York, 1907); Chapter IV.

The Methylene Radical

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IN a recent Letter to the Editor Laidler and Casey¹ discuss the methylene radical, CH_2 . They state that since the bond angle in the lowest state is about 140° , this state cannot be a triplet state. However, one may use hybrid orbitals for the two unshared electrons as well as for the two shared electron pairs.

Thus one may use the sp^3 hybrid orbitals² appropriate to AB_2C_2 for the covalent triplet structure. If Pauling's criterion³ of strength is employed and if the interaction energy⁴ of a shared electron pair equals that of an unshared electron, one would expect the tetrahedral structure (the structure with the H-C-H angle equal to $109^\circ 28'$) to be the most stable of the triplet structures.

The covalent singlet structure may be discussed as follows. Set up the functions appropriate to AB_2C , where A is the central atom, assuming the bonds lie in a plane. Thus

$$\psi_1 = a_1 s + b_1 p_x, \quad (1)$$

$$\psi_2 = a_2 s - b_2 p_x + c_2 p_y, \quad (2)$$

$$\psi_3 = a_3 s - b_3 p_x - c_3 p_y. \quad (3)$$

Here ψ_1 describes the orbital occupied by the unshared electron pair, and ψ_2 and ψ_3 describe the orbitals used in forming the bonds.