ratio of weight to number average[10] is close to 2. Then from the relation $\overline{M}_n = 13,000\ [\eta]^a$ established for whole polymer, the molecular weight of a fraction is $26,000\ [\eta]^a$.

In the fractional distribution plots of π *vs.* x (Fig. 3), curves are drawn for random distribution for p' values of 0.9900 and 0.9925. The points are taken directly from the data of Table IV calculated from experiment; $x = 26,000\ [\eta]^a/113$ and since in effect an area is involved and the coördinate is taken by equal increments, $\pi = \Delta\%\cdot10^{-2}/\Delta x$ or $\Delta\%\cdot10^{-2}/23$ for all points except the first. It is evident that random distribution prevails within the limitations within which p' can be known.

Molecular weights discussed throughout this paper are based entirely on functional end-group measurements and they need to be checked by an independent measurement such as osmotic pressure on samples reasonably homogeneous. Attempts at measurements of the required precision have so far been defeated for lack of a suitable solvent–membrane combination but further work is under way. Another point that should be mentioned is that end-groups do not measure molecular weight of abnormal nylon samples. For example, holding molten polymer many hours in sealed tubes results in the disappearance of carboxyl from the polymer and a large increase in amine with no corresponding rational relation to viscosity properties.

Acknowledgments.—The writer is indebted to Miss Gertrude Bemiller of the analytical staff of the Nylon Research Section of the Rayon Department of this Company for most of the test work on the samples and to Mrs. Josephine Pechan of the Chemical Department for assistance in the experimental work. The writer has also profited by similar work on nylon by Mr. C. L. Arcus of the Imperial Chemical Industries, Ltd. of Great Britain.

Summary

Polyhexamethyleneadipamide has been fractionated into 46 cuts in a phenol–water two-liquid-phase system at 70°. The molecular weight distribution has been found to follow that predicted by the Flory equation based on the premise that in bifunctional reactions to form linear polymers, the activity of a functional group is independent of the length of polymer chain to which it is attached.

WILMINGTON, DELAWARE RECEIVED JUNE 21, 1946

[10] The effect of the material of lowest molecular weight on the $\overline{M}_w/\overline{M}_n$ ratio needs some emphasis. It may be noted from the fifth and sixth columns of Table IV that the first two figures contribute a large fraction to the sum of the dividends and practically nothing to the sum of the products. It is estimated that if the 5% of the polymer contributing all below 0.15 were removed, the $\overline{M}_w/\overline{M}_n$ ratio would drop to 1.5 and the osmotic molecular weight increase from 11,000 to 16,000, while a measured $[\eta]$ would only increase from 0.90 to 0.93.

[CONTRIBUTION FROM THE DEPARTAMENTO DE QUIMICA DA FACULDADE DE FILOSOFIA, CIÊNCIAS E LETRAS, UNIVERSIDADE DE SÃO PAULO, BRAZIL]

Mixed Crystals of Sulfoxides, Sulfones, Selenoxides and Selenones

BY HEINRICH RHEINBOLDT AND ERNESTO GIESBRECHT

In a previous paper[1] it was shown that symmetrically substituted sulfoxides give continuous series of mixed crystals with the corresponding sulfones. Furthermore, we have shown that selenoxides and selenones behave in a similar way, and that sulfoxides give mixed crystals in all proportions with selenoxides.[2] From these results it was concluded that we may attribute the same configuration to sulfoxides and selenoxides as to the corresponding sulfones and selenones, and that the selenoxides must have a tetrahedral configuration similar to that of the sulfoxides.

The relationship among these compounds goes so far that continuous series of mixed crystals are also formed by sulfoxides with selenones and by selenoxides with sulfones. Sulfones and selenones are completely isomorphous. This is proved here by the study of the solid–liquid phase diagrams of the four binary systems reported in Table I–IV and Figs. 1–4, all of which were found to form continuous mixed crystals.

Experimental

The study of the solid–liquid phase diagrams of the four binary systems was undertaken with the "thaw-melting method" as described in a previous paper.[1] In the tables "Th. p." means thawing point. All percentages indicated are by weight.

Binary Systems

1. Diphenyl Sulfoxide[3] and Diphenyl Selenone[3]

TABLE I

Selenone, %	Th. p., °C.	M. p., °C.	Selenone, %	Th. p., °C.	M. p., °C.
0.0	70.1	71.0	45.2	68.4	102.1
9.4	60.2	67.3	53.2	73.7	111.4
13.5	59.2	65.1	62.6	81.0	122.0
20.0	58.5	65.3	76.5	96.3	135.5
23.2	59.0	71.2	89.3	116.2	147.1
29.6	61.2	80.3	100.0	153.8	154.9
36.0	63.8	89.5			

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(1) H. Rheinboldt and E. Giesbrecht, THIS JOURNAL, **68**, 973 (1946).

(2) H. Rheinboldt and E. Giesbrecht, *ibid.*, **68**, 2671 (1946).

(3) On the preparation and purification of these compounds see ref. (2).

Continuous mixed crystal series of type III with minimum at 59° and 18% of diphenyl selenone.

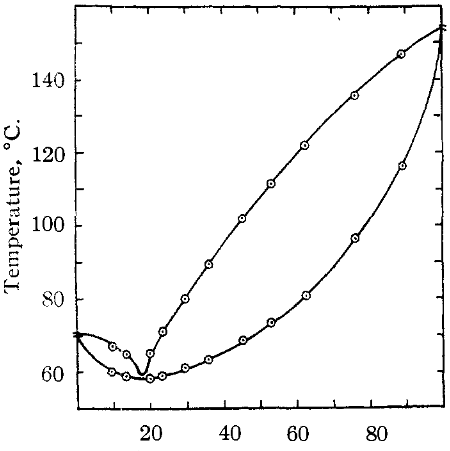

Fig. 1.—Binary system of diphenyl sulfoxide and diphenylselenone.

2. Dibenzyl Selenoxide and Dibenzyl Sulfone

Dibenzyl selenoxide, formerly prepared solely by hydrolysis of dibenzylselenium dibromide,[4] was obtained with excellent yield by oxidation of the selenide dissolved in acetone with hydrogen peroxide. To a solution of 5 g. of the selenide in 15 cc. of pure acetone, cooled to 0°, was added slowly and under stirring 2.2 g. of 30% hydrogen peroxide, thus avoiding an increase in the temperature. The flask was kept at 0° for half an hour, with occasional stirring, and then kept for two hours at 18–20°. When the solution was again cooled to 0°, part of the selenoxide formed was "precipitated." The filtered solution was concentrated under vacuum at room temperature and the residue obtained added to the precipitate. The material was dried for two hours at 15 mm. A yellowish product was obtained melting at 129.5–131°; yield 5.2 g., 98%. This substance, five times crystallized from dry benzene and dried under vacuum over calcium chloride, melts at 134.8°; after two more crystallizations from benzene and drying under vacuum over phosphorus pentoxide, the substance had a constant melting point of 135.5°; small colorless plates, somewhat brilliant, and very soluble in methanol, ethanol, acetone, chloroform; slightly soluble in benzene and petroleum ether. It dissolves in boiling water, with a slight decomposition (m. p. 133.7–134.8° after recovery) and a perceptible odor of benzaldehyde. Heated under 2 mm. at 120° the substance decomposes completely with separation of selenium and formation of benzaldehyde. Exposed to light for a few days the substance acquires a yellow, and then a brown color. Oxidation of the selenide cannot be done in glacial acetic acid on account of decomposition when adding hydrogen peroxide, even at 0°.

TABLE II

Sulfone, %	Th. p., ° C.	M. p., ° C.	Sulfone, %	Th. p., ° C.	M. p., ° C.
0.0	134.8	135.5	27.4	133.1	138.5
6.2	133.5	135.1	34.7	133.8	140.6
8.0	132.7	134.9	58.3	138.5	146.2
11.5	132.2	133.8	70.9	142.0	148.5
17.2	132.4	134.5	89.2	147.4	151.0
22.3	132.6	136.2	100.0	151.1	151.9

All mixtures of components of this system were prepared by close trituration. Continuous mixed crystal series of type III with minimum at 132° and 14% of dibenzyl sulfone.

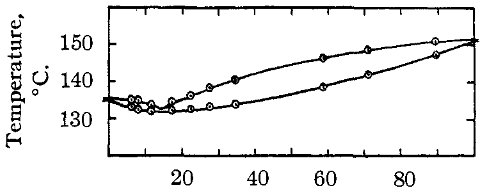

Fig. 2.—Binary system of dibenzyl selenoxide and dibenzyl sulfone.

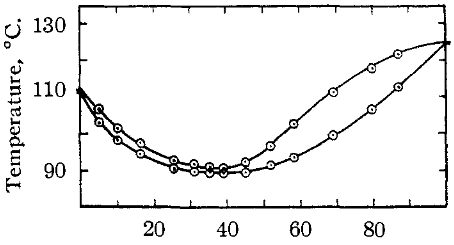

Fig. 3.—Binary system of diphenyl selenoxide and diphenyl sulfone.

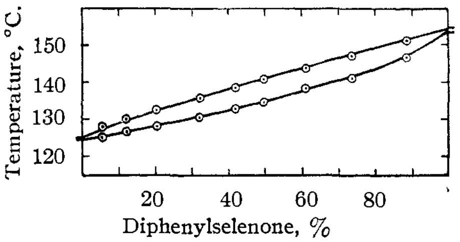

Fig. 4.—Binary system of diphenyl sulfone and diphenylselenone.

3. Diphenyl Selenoxide[3] and Diphenyl Sulfone

TABLE III

Sulfone, %	Th. p., ° C.	M. p., ° C.	Sulfone, %	Th. p., ° C.	M. p., ° C.
0.0	111.7	112.8	45.3	89.7	92.0
5.1	103.2	106.9	52.2	91.3	96.3
10.2	98.0	101.5	58.5	93.5	102.5
16.2	94.6	97.4	69.3	99.1	111.0
25.6	90.5	92.8	79.9	106.5	117.8
31.0	89.9	91.3	87.1	112.7	121.4
35.4	89.6	90.8	100.0	124.3	125.0
39.0	89.3	90.4			

Continuous mixed crystal series of type III with minimum at *ca.* 90° and 39% of diphenyl sulfone.

4. Diphenyl Sulfone and Diphenyl Selenone[3]

TABLE IV

Selenone, %	Th. p., ° C.	M. p., ° C.	Selenone, %	Th. p., ° C.	M. p., ° C.
0.0	124.3	125.0	49.5	134.4	140.8
5.5	125.2	128.0	60.9	137.3	143.9
12.2	126.5	130.0	73.5	141.1	147.1
20.3	128.0	132.4	88.7	146.7	151.1
32.1	130.5	135.7	100.0	153.8	154.9
41.8	132.6	138.6			

Continuous series of mixed crystals of type I.

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[4] W. Strecker and A. Willing, *Ber.*, **48**, 204 (1915), and ref. (2).

Summary

It is shown by the study of the solid–liquid phase diagrams that diphenyl sulfoxide and selenone, dibenzyl selenoxide and sulfone, diphenyl selenoxide and sulfone form continuous mixed crystal series of the minimum type (type III).

Diphenyl sulfone and selenone give a mixed crystal series of the ascendant type (type I).

SÃO PAULO, BRAZIL RECEIVED OCTOBER 25, 1946

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Sorption of Water Vapor by High Polymers

BY SHERMAN E. SMITH[1]

The remarkable extent to which the properties of textile fibers, protective films, and many plastics are modified by the sorption of water vapor has long maintained an interest in the subject.[2,3,4,5] The sorption of water by cellulose has received detailed consideration from Urquhart,[6] Peirce,[7] Assaf, Haas and Purves[8] and others.[9] In general, the more detailed discussions assume either special structural features for the cellulose or special types of association between cellulose and water. The necessity of such assumptions is questionable, since isotherms of virtually identical (usually sigmoid) form are obtained from many other systems in which such special considerations are out of the question. Such a relatively unorganized subject as sulfuric acid, for example, gives the sigmoid moisture-sorption isotherm characteristic of many high polymeric substances.

Several lines of evidence point clearly to a distinction between two principal classes of sorbed water: (1) that which is in some way bound on the inner or outer surface of the solid adsorbent by forces in excess of the normal forces responsible for condensation of water to the liquid state and (2) that which is normally condensed within the gel. The distinction is particularly noteworthy in the case of water sorbed by a somewhat polar sorbent. It is permissible, on statistical grounds, to divide the regain,[10] α, into two fractions, thus

$$\alpha = \alpha_b + \alpha_c \qquad (1)$$

Here α_c is specifically defined as that portion of the regain which is condensed with a normal heat of condensation, while α_b comprises that fraction which is bound by excessive forces. Peirce[7] and Filby and Maass[11] refer to these portions of the regain as separate (though contiguous) phases. It is to be expected that these fractions will depend on the relative vapor pressure in quite different ways. While α_b may be expected to reach a virtual maximum at a vapor pressure well short of saturation, α_c must increase progressively toward the saturation vapor pressure. The isotherm for α_b will be concave, and that for α_c convex, toward the axis of relative vapor pressures. The summation of the isotherms for the two fractions results in the sigmoid isotherm typical of high polymer sorption.

The interpretation of any conventional sorption isotherm depends on the assumption that m, of the x/m ratio, is a mass of sorbent presenting a definite and invariant surface. The same consideration is implicit in the use of the regain, α, which is equivalent to x when m is one gram. With sorption, however, high polymers usually undergo either limited or unlimited swelling, which must inevitably result in an increase in the number of sorptive points exposed within the structure. The assumption of such an increase in the effective surface has been employed by Urquhart,[6] and more concretely by Filby and Maass,[11] to explain the phenomenon of sorption hysteresis in cellulose. Here, precisely arises the principal difficulty in rationalizing the sorption isotherms for substances capable of gross swelling, for the regain is dependent not only on the relative vapor pressure, but also on the progressive effect of sorption on the structure of the swelling gel. The problem may be simplified by considering first the case of a hypothetical, non-swelling gel.

The Sorption of Water Vapor by a Non-swelling Gel.—The dependence of α_b on the relative vapor pressure may be expected to follow approximately the formulation of the Langmuir adsorption isotherm. Especially when the sorbent and sorbate are polar, α_b should achieve its maximum value at a vapor pressure well short of saturation. Even so non-polar a sorbate as nitrogen vapor approaches completion of the first or bound layer at $p/p_0 = 0.1$.[12] In a non-swelling gel, therefore, some characteristic relative vapor pressure, p_b/p_0, well short of saturation, will be

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[1] Present address: University of New Mexico, Albuquerque, N. M.

[2] F. T. Peirce, *J. Text. Inst.*, **15**, T501 (1924).

[3] A. C. Walker, *Textile Research*, **7**, 229, 289 (1937).

[4] G. H. Argue and O. Maass, *Can. J. Research*, **13B**, 156 (1935).

[5] K. C. Brown, J. C. Mann and F. T. Peirce, *J. Text. Inst.*, **21**, T186 (1930).

[6] A. R. Urquhart, *ibid.*, **20**, T125 (1929).

[7] F. T. Peirce, *ibid.*, **20**, T133 (1929).

[8] A. G. Assaf, R. H. Haas and C. B. Purves, THIS JOURNAL, **66**, 66 (1944).

[9] See Stamm, "Colloid Chemistry of Cellulosic Materials," U. S. Dept. Agric. Misc. Publ., No. 240, 1936.

[10] The regain is the weight ratio of sorbate to dry sorbent.

[11] E. Filby and O. Maass, *Can. J. Research*, **7**, 162 (1932).

[12] S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).