The Size of Silicone Molecules

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THE SILICONE POLYMERS, which are synthetic organosilicon resins, oils, and elastomers based on frameworks of alternate silicon and oxygen atoms, are well enough known by now so that their composition and their modes of preparation are fairly well understood. Very little is known, however, about the size and configuration of the large molecules that make up such silicone polymers, beyond the fact that such macromolecules have remarkably little attraction for each other. The question that gives rise to the present discussion is whether or not the methods of resinography might be applied to the problem, and what information might so be gained.

Resinography is the graphic study of resins, involving the use of the microscope and all of its adjuncts in techniques somewhat similar to those of metallography and mineralography. As applied to the study of fabricated plastics, for example, such study yields information about the kind and shape of fillers, the distribution of strengthening materials, and the degree of wetting of such included bodies by the binding resin (*5*). The particular technique of resinography that is of most value in the present instance, however, is the electron microscopy of fracture surfaces of synthetic high polymers (*6*). By fracturing a cooled solid specimen and then preparing a replica of the surface, the commensurate irregularities and discontinuities of the fracture surface may be shown by micrographing the replica at high magnification in the electron microscope.

To show the features most plainly, a particular kind of replica must be made. The fractured surface first is coated with a 5 percent aqueous solution of gelatin, which is stripped off after drying. Silica is evaporated onto the gelatin replica in a vacuum evaporator, and the gelatin is dissolved away from the silica by water, to leave a positive "print" of the surface in silica. In order to emphasize some surface features in elevation, it is possible to "shadow" the replica by depositing uranium by evaporation at a small angle, giving the same effect as one gets in observing hilly terrain in the light of a setting or a rising sun. The final replica then is electron-micrographed at magnifications up to 20,000. Selected micrographs are enlarged photographically as required by the fineness of detail in the micrograph and the distance of viewing the final picture.

The technique of embrittling a high polymer and preparing a replica of its fracture surface is generally similar to one of the methods employed in 1944 by Ladd in his electron-microscopical studies of colloidal carbon in vulcanized rubber (*2*). He cooled a block of tire tread stock in a bath of acetone-dry ice and cracked the block in two. A negative replica of the broken surface was made of softened De Khotinsky cement or polystyrene. This was stripped off when hard and a drop of 2 percent Formvar solution in ethylene dichloride was placed on the negative impression and allowed to harden. The cement or polystyrene was dissolved away, leaving the Formvar positive replica to be electron-micrographed. Ladd obtained poor definition of the carbon particles and experienced difficulty in interpreting the micrographs. Apparently he abandoned the method in favor of pressing out a thin film and vulcanizing it in this condition. Such a method, of course, requires uncured material to begin with and assumes the toleration of probable distortion of the morphology.

Rochow and Rowe (*6*) were more fortunate in using a water-dispersible material like gelatin because it was readily peeled from the fracture surface and yet wetted the surface sufficiently to form a good impression. They subsequently applied this technique to vulcanized tire tread stock[1] after taking the further precaution to immerse it in liquid nitrogen to be certain of obtaining a brittle fracture. Fig. 1 is an electron micrograph of a gelatin-silica bireplica of the carbon-reinforced, cured tire tread stock. The carbon particles are shown singly and in aggregates. The particles are shown in three manifestations: (1) as black disks representing carbon particles that were pulled from the fracture surface and remained with the final replica, (2) as elevated gray disks representing carbon particles that remained at or very near the replicated fracture surface and (3) as depressed gray disks representing carbon particles that went with the mate of the fracture surface. The gray matrix represents the cured, natural rubber polymer.

One probably sees no structure in the matrix as shown at this magnification, and by halftone reproduction. If, however, the micrograph is enlarged to 100,000 ×, the matrix may be perceived to be particu-

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[1] Material by courtesy of A. R. Davis, Research Laboratories, American Cyanamid Company, Stamford, Connecticut.

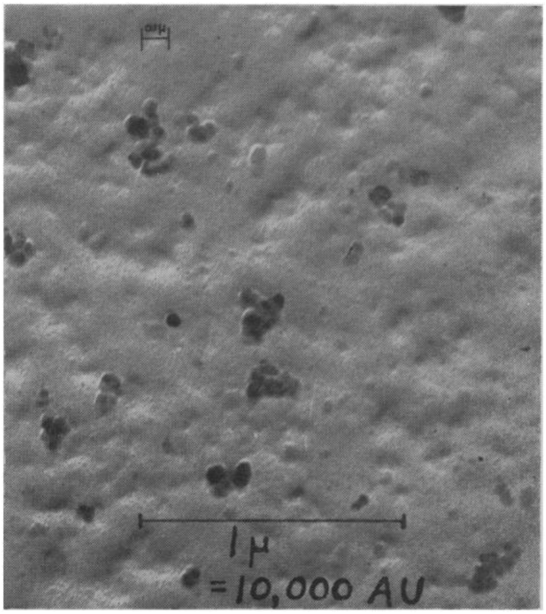

FIG. 1. Bireplica of fracture surface of black natural rubber. Positive print. Magnification 35,700 ×.

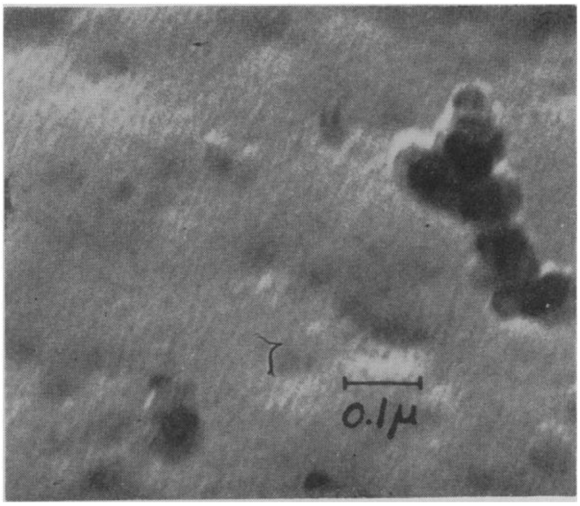

FIG. 2. "Close-up" of fracture surface of black natural rubber. Magnification 100,000 ×.

late, as shown in Fig. 2. The smallest particles shown in the picture are about 0.65 mm in diameter, those occurring most frequently being about 1.3 mm and most of the largest about 2.0 mm. Since the magnification is 100,000 ×, these diameters, expressed in angstroms, are 65,130 and 200, respectively.

It is a natural assumption that the discontinuities which appear on a fracture surface reflect weaknesses in the cohesion of the structural units of the solid, i.e., the substance fractures between the structural entities. In a single polymeric phase, such as the rubber elastomer shown in Fig. 2, the structural entities are assumed to be the macromolecules. Using the values just given for the diameters of typical particles, and the first of the methods of calculation given later in this discussion, the macromolecular weights of cured natural rubber are found to vary from 81,000 to 2,200,000, with most of them in the region of 650,000. Values determined on uncured ("soluble") natural rubber by older methods, such as measurement of viscosity or osmotic pressure of solutions, vary between 68,000 and 435,000 (*1*) and less and more. It appears, then, that the discrete particles are the macromolecules themselves. It is assumed that the rubber phase breaks by tearing apart such molecules rather than by splitting the molecules themselves. Expressed otherwise, the intermolecular (Van der Waals') forces are weaker than the chemical bonds which hold the macromolecule together, as would be expected and as indeed is inherent in the fundamental concept of molecules.

Application of this resinographic method of molecular size determination is of particular interest in silicones because of their peculiar properties. Silicones always are polymeric (as is silica itself), but the size of the molecules and the particular mechanism of their growth have been in doubt. It had been assumed in the early work that the processes leading to increase of molecular weight were interrupted by various agencies not always related to the purity of the intermediates, and this interruption was supposed to leave molecules of decidedly low molecular weight, at least by the standards of the chemistry of organic high polymers. Such a view gave an easy explanation for the low melting point of diphenyl silicone, the comparatively low tensile strength of silicone rubber as ordinarily made, and the low change of viscosity with temperature in silicone oils (*4*). These are manifestations of the easy motion of molecules relative to one another, and, of course, a small molecular size contributes greatly to such ease of motion. However, the low boiling point of dimethyl polysiloxanes of known molecular weight and configuration (and indeed the low boiling points of most organosilicon substances) should have hinted that such relative ease of molecular motion and detachment was not due to low molecular weight but rather to inher-

TABLE 1

MOLECULAR WEIGHT OF DIMETHYLSILOXANE ELASTOMER*

Fraction	Percent of polymer	Avg mol wt
A	17	2,800,000
B	14	1,500,000
C	18	610,000
D	27	290,000
E	15	much less than 290,000

* Taken from Scott (*9*).

ently low intermolecular attraction. Finally, when Scott (*9*) determined the molecular weights of five fractions of a representative silicone elastomer (Table 1), it was realized that the molecules of silicone rubber were indisputably large by ordinary standards—in fact, much larger than those reported for many common organic elastomers. The work of Wilcock (*11*) showed in turn that the flow properties of methyl silicone oils could be explained entirely in terms of low intermolecular forces, resulting in high molar volumes and a small energy requirement for motion of the characteristic unit of flow. It remained for Roth (*7*) to explain such low intermolecular attractions in terms of the exceedingly free motion of dimethylsiloxane units about the Si-O bond, such freedom being related in turn to the ionic character of such a bond.

It must be conceded, then, that the properties of silicone polymers are due to the unique combination of large molecules containing many points of relatively free motion, and that such properties therefore derive from the presence of siloxane bonds in the molecule rather than from the mere presence of silicon atoms. This has been demonstrated in very definite fashion by Sommer (*10*), who has shown a decided difference between polymers based on the Si-O-Si networks and those based on Si-CH_2-Si networks, despite the almost equivalent molecular weight.

When it was realized that the properties of silicone polymers were not due to limited molecular weight, and that some silicones might contain molecules of exceedingly large size, the actual size became of much interest. The only investigation of molecular weight until very recently was that of Scott, noted above. Scott dissolved a sample of dimethyl silicone elastomer in ethyl acetate and precipitated fractions of decreasing molecular weight by adding acetone progressively to the solution; he then determined the molecular weight by measuring the osmotic pressure of dilute solutions of the fractions by a dynamic method. Such a method naturally is limited to soluble polymers, and some question arises even then about whether molecules are brokenapart by the process of solvation. The method is closed to many silicone resins which are no longer soluble in organic solvents after they are fully cured, but it also is desirable to know the size of the molecules in such resins. Nevertheless, Scott's measurements provide an opportunity to compare the results of the resinographic investigation with those of the more conventional dynamic osmometer method.

The first sample of silicone polymer chosen for test was a molded sheet of white silicone "rubber,"[2] prepared from dimethyl silicone elastomer and titanium dioxide filler. A piece was cooled in liquid nitrogen and fractured. A silica replica was prepared by the method previously described, except that an 8 percent solution of polyvinyl alcohol was used instead of gelatin solution. Fig. 3 shows a micrograph of the replica. The white specks are particles of crystalline titanium dioxide filler, which also is represented by the elevations and depressions caused respectively by particles on or near the fracture surface and those remaining with the fracture-mate. Thus we have a method for portraying the actual distribution of particulate substances from pigment-sizes down to and including reinforcing agents such as carbon black and dehydrated silica gel.

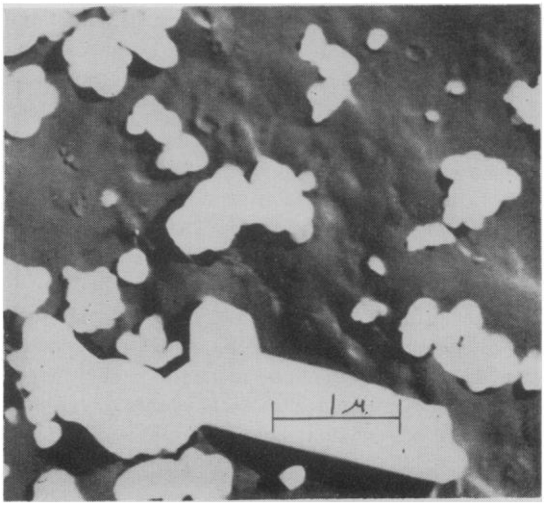

FIG. 3. Bireplica of fracture surface of white silicone rubber. Negative print of electron micrograph of polyvinyl + silica bireplica. Magnification 17,000 ×.

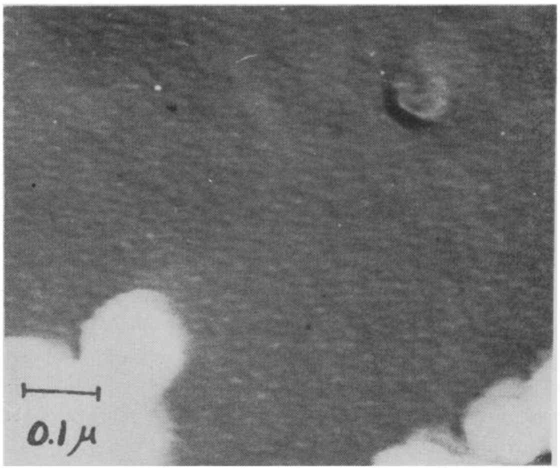

FIG. 4. "Close-up" of fracture surface of white silicone rubber. Magnification 100,000 ×.

The gray background in Fig. 3 is the silicone matrix. At this magnification the matrix presents a grainy ap-

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[2] Submitted by courtesy of the General Electric Company.

pearance, but no definite structure can be ascertained. At a magnification of 100,000 × (Fig. 4) the graininess is more distinct, and is seen to be due to a particulate structure. In the electron micrograph, one millimeter corresponds to 100 A in the original specimen, so that a direct measurement of the particle size becomes possible. The largest grains appear to be elliptical, and are about 0.93 mm by 3.7 mm. The smaller ones are more spherical, and are about 0.93 mm to 1.9 mm in diameter. Some still smaller grains may be seen, but measurement of them is difficult. For calculation, we may take a sphere of 1.0-mm diameter to be representative of many of the larger particles (but not the largest). One millimeter, as we have said, corresponds to 100 A in the original, and the volume of a sphere 100 A in diameter is $\frac{4}{3}\pi\ (50)^3$, or 524,000 A^3. We are justified only in calling it about 520,000 A^3.

We need now to translate this size into its more common terms of molecular weight, and one way of doing this is to determine the weight of a single macromolecule and multiply the weight (stated as the fraction of a gram) by Avogadro's number representing the number of molecules contained in one gram-molecular weight of a substance (6.02×10^{23} molecules). The specific gravity at the room temperature for the hard gum from which the white silicone rubber was compounded was measured to be 0.972. Thus the weight of one molecule of the particles with radius 50 A (5×10^{-7} cm) is: $520{,}000 \times 10^{-24}$ cm^3/molecule $\times$ 0.972 g/cm^3 $\times$ 6.02×10^{23} molecules/mol = 304,000 g/mol; and hence the macromolecular weight is 304,000.

A somewhat different method is to determine the volume of a single $(CH_3)_2SiO$ unit and divide this into 520,000 A^3 to find the number of such units in the macromolecule. The dimensions of such a dimethyl siloxane unit have been estimated by Norton (*3*) to be 3.0 by 7.0 A in surface area and 6.0 A deep, and hence the volume is 126 A^3 (Norton's estimate is based on molecular models which assume covalent radii, and probably involve some error in the Si-O bond distance, according to the more recent ideas of Roth (*7*). Dividing this into 520,000 A^3 gives 4120 such dimethylsiloxane units in the representative grain of Fig. 4, and since each dimethylsiloxane unit has a weight of 74.1 in atomic weight units, the molecular weight of our representative grain is 306,000, much the same as by the first method. By comparison with Scott's molecular weights in Table 1, it is seen that the structural units in the silicone matrix of Fig. 4 seem indeed to correspond to the real macromolecules.

Another estimate of the volume occupied by one $(CH_3)_2SiO$ unit may be made without recourse to models by utilizing the detailed and accurate crystallographic measurements reported by Roth and Harker (*8*) for octamethylspiropentasiloxane, $(CH_3)_8Si_5O_6$. This substance crystallizes in the space group D_{dh}^{19} (*I 4/amd*), with $a = 14.09$ A and $c = 10.18$ A. There are four monomeric units (of the composition given above) in each unit cell, and the calculated density is 1.18. From the parameters the volume of the unit cell is 2016 A^3; from the density and the atomic weights the volume is 2030 A^3. If we consider each monomeric molecule as being composed of four $(CH_3)_2SiO$ groups and one SiO_2 group, then we have in the unit cell sixteen $(CH_3)_2SiO$ and four SiO_2 groups. The volume of an SiO_2 group may be estimated as about 2.2 A^3 in the particular structure; alternatively, we could use the volume of a silicon tetrahedron in silicate minerals, which is about 1.5 A^3, for the volume is very small anyway in comparison with the organosilicon structures. Four SiO_2 groups therefore occupy about 6 A^3, leaving 2010 A^3 for the sixteen $(CH_3)_2SiO$ groups. This is equivalent to 126 A^3 per dimethylsiloxane unit, or exactly the same volume as Norton obtained, studying models.

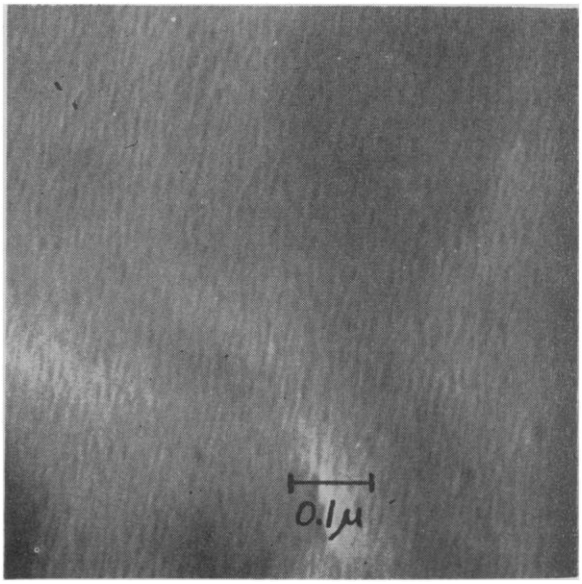

FIG. 5. Fracture surface of iron-red silicone rubber. Magnification 100,000 ×.

It follows that the previous conclusion is supported, i.e., a particle or discontinuity 1.0 mm in diameter in Fig. 4 corresponds to a piece of dimethylsiloxane polymer of molecular weight 300,000, and hence is probably a single large molecule of the polymer.

More refined measurements were made on Fig. 5, which is a negative electron micrograph of a polyvinyl alcohol plus silica bireplica of a sample[3] of "hard gum" silicone elastomer filled with a relatively

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[3] By courtesy of A. Kneitel, Chemical Department, General Electric Company, New York City.

coarse material, presumably iron oxide. The filler represents little area in the picture and the macromolecules are abundantly portrayed. The smallest ones are round with diameter of about 100 A and, calculated on the basis of specific gravity and Avogadro's number, their molecular weight is 310,000. Most of the particles in Fig. 5 are pictured elliptical: 100 A wide and 200 A long. Assuming 100 A for the third diameter, the macromolecular weight is 610,000, which value also lies in the range given by Scott and listed in Table 1. The largest particles have dimensions roughly 100 A by 800 A. Assuming the third dimension to be also 100 A, the macromolecular weight is 2,500,000, which is very close to Scott's maximum in Table 1.

It should be emphasized that measurements of the kind described herein require the highest resolution of which the RCA Model U electron microscope is capable, and further improvement in practical resolution is much to be desired. There may be many smaller molecules in Figs. 4 and 5, for example, than those which have been measured, and the shapes may appear to be rounded only because of their fuzzy outlines, which also render more precise measurements difficult. It is hoped that a new RCA accessory, the magnetic lens shield, placed around the path of electrons between the objective and projector lenses, will help produce much sharper outlines and consequently more precise measurements. Other improvements in technique will undoubtedly follow to refine the values to the extent that statistical descriptions and analyses may be obtained on the variations in sizes and shapes. Then significant differences will be manifested among chemical and physical variations in the preparation of silicones and all other families of high polymers.

The distinct advantages of the resinographic method of studying the molecular structure of high polymers are:

1. It *pictures* rather than *infers* the shapes and sizes of the macromolecules.
2. The measurements are direct, the calculations simple, and the assumptions minor.
3. The method applies to all high polymers if they can be rendered brittle for fracturing and will remain rigid until a replica of the fractured surface is made. That is, the method applies to soluble high polymers whose molecular weights can be confirmed by established methods and it also applies to insoluble and infusible high polymers whose molecular weights have heretofore been unknown.
4. The method appears to be applicable to commercial (filled) plastics of fabricated shapes. The high polymeric matrix shows between the very distinctive particles of filler and other included material and there are always plenty of macromolecules of the high polymer for examination. Thus samples of special formulation, purity, or shape are not required.
5. The fracture surface is not destroyed by replication. Thus it is available for further experimental treatment such as aging, curing, or other influences on molecular sizes and shapes.

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