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Monolithic glass formation by chemical polymerization

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Historically, glasses have been formed by solidification of oxide melts from elevated temperatures. Recently it has been demonstrated that monolithic oxide glasses can be formed by chemical polymerization at low temperatures. By the use of this technique, high-temperature reactions such as crystallization, phase separation, etc., which restrict glass formation in certain systems and regions, can be largely avoided. Thus, the technique not only permits investigation of glass structure from a fundamentally different point of view, but also allows the formation of new glasses which can not be formed by thermal means.

In this work, the nature of inorganic network formation by chemical polymerization is described. The method of preparing polymerizable active species in a soluble state and general considerations that must be observed to prevent incoherent self-condensation of glass-forming species during hydrolysis and polymerization are discussed. Certain characteristic properties of materials formed by chemical polymerization are also included.

1. Introduction

Although the random network theory of glass structure has been widely accepted since Zachariasen's [1] and Warren's [2] works, oxide glasses were not viewed as polymers until recently. First, unlike the formation of organic polymers, melting does not allow control over the polymerization process. Secondly, the molecular weight of oxide glasses is not only difficult to measure, but in most cases is meaningless as a characterization parameter due to the highly cross-linked nature of the structure. Recent developments indicate, however, that the oxide network can be formed by polymerization reactions near room temperatures [3–5]. This allows the glass technologist to exercise significant control over the nature and extent of polymerization, which is similar to organic network formation.

This advance in glass formation largely owes its success to the use of metal–organic compounds, particularly metal alkoxides, and to well-contrived utilization of their particular properties. These compounds do not occur naturally but can be synthesized readily [6–9]. Alkoxides of most of the glass-forming species, Si, B, Al, etc., are commercially available at relatively low cost. Soluble intermediate species capable of polymerizing into an oxide network can be formed from these alkoxides, as will be described. Various monolithic glasses can be prepared by reaction of these species chemically rather than by melting.

2. Experimental procedures and results

2.1. Formation of polymerizing species

Metal-alkoxides, in general, hydrolyse quite vigorously when brought into contact with water, forming oxides and hydroxides. The resulting materials are particulate and essentially useless for further polymerization reactions. Whether the oxide or the hydroxide forms during the hydrolysis depends primarily on the nature of the metal-alkoxides. Aluminum alkoxides, $Al(OR)_3$, for example, initially form the monohydroxide which tends to later convert to the trihydroxide [10].

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$$Al(OR)_3 + 2H_2O \rightarrow AlO(OH) + 3R(OH) \quad (1)$$

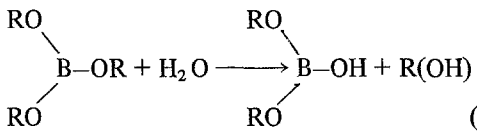
$$AlO(OH) + H_2O \rightarrow Al(OH)_3 \quad (2)$$

The reaction of boron alkoxides with water results in the formation of boron oxide:

$$2B(OR)_3 + 3H_2O \rightarrow B_2O_3 + 6R(OH) \quad (3)$$

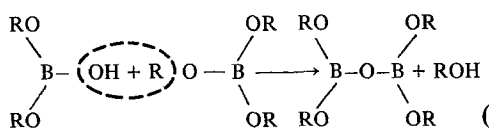
A third type of hydrolysis reaction, exhibited by silicon alkoxides, forms neither oxide nor hydroxide upon completion, even in excess water. Instead a soluble complex where "OH" or "OR" groups coexist in significant numbers is formed.

Completion of the hydrolysis reaction, resulting in the formation of hydroxide or oxide as represented by Reactions 1, 2 or 3, makes further polymerization impossible. The partially hydrolysed silanol complex, on the other hand, is suitable for network formation by chemical polymerization. In this work, it has been found that the reactions of alkoxides represented by Reactions 1, 2, and 3 can be manipulated to form active polymerizable species in soluble form similar to the silanol complexes. For example, when boron alkoxide is exposed to water, a series of transient species, $B(OR)_2(OH)$, $B(OR)(OH)_2$, $B(OH)_3$, representing various degrees of hydrolysis should form initially; e.g.,



(4)

The relative concentration of each species will depend on: first, the availability of water, and second, the dilution of the system. By diluting the alkoxides and the water with alcohol before mixing, one can control the type and extent of initial hydrolysis in these reactions. These initial species immediately undergo a series of condensation reactions, forming large numbers of secondary species where bridging oxygens occur:



(5)

The formation of the initial transient species and their condensation to form polymer chains can be represented by general equations:

$$B(OR)_3 + mH_2O \rightarrow B(OR)_x(OH)_y + yR(OH) \quad (6)$$

$$B(OR)_x(OH)_y \rightarrow BO_z(OR)_{x_1}(OH)_{y_1} + (x - x_1)R(OH) \quad (7)$$

where $z = [3 - (x_1 + y_1)]/2$.

In this system "OR" and "OH" groups cannot coexist in significant numbers; they react with each other, forming bridging oxygen and releasing alcohol until one of the groups is totally eliminated. If the species contain enough hydroxyl groups (if $y > x$ in Reaction 6), polymerization continues until all "OR" groups are removed from the network, and condensation of boric oxide occurs. If there are not enough hydroxyl groups to remove all the "OR" groups, (if $x > y$ in Reaction 6), then the polymer complex contains "OR" groups in the structure. When this occurs the complex remains soluble in alcohol and available for polymerization with other glass constituents. A schematic representation of the formation of condensed B_2O_3 and soluble and polymerizable species from boron alkoxide is shown in Fig. 1.

The hydrolysis product of aluminum alkoxides can also be kept in clear suspension or solution; this requires a highly diluted system. One of the best ways to introduce alumina into a glass struc-

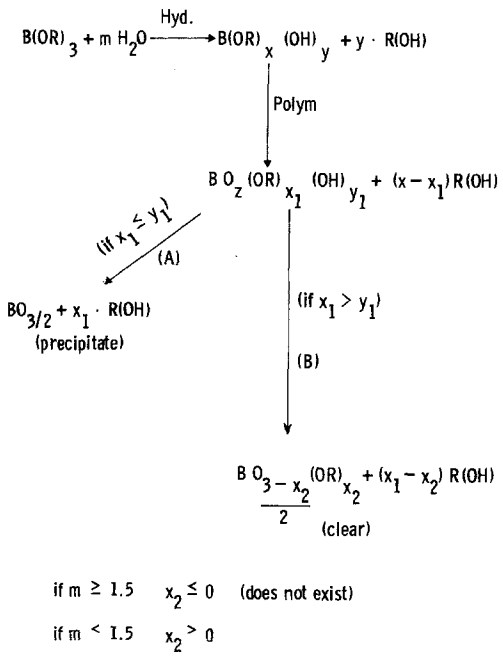


Figure 1 Formation of boron oxide (A); and a clear solution containing polymerizing species (B) by the hydrolysis of boron alkoxides.

ture is to prepare a clear aqueous solution of aluminum monohydroxide [11]. Gels of this solution retain their monolithic nature and yield transparent Al_2O_3 [12, 13]. The aqueous solution itself can be used to hydrolyse other alkoxides; some chemical bond formation occurs upon the reaction of alkyl groups with the hydroxyl groups of the aluminum.

The preferred way of introducing aluminum into a glass network is by direct reaction with the partially hydrolysed bonds of other alkoxides, e.g.:

$$\begin{array}{l} OR \\ \backslash \\ Al{-}OR \\ / \\ OR \end{array} + HO{-}\begin{array}{c} OR \\ | \\ Si{-}O{-} \\ | \\ OR \end{array} \longrightarrow \begin{array}{l} OR \\ \backslash \\ AL{-}O{-} \\ / \\ OR \end{array}\begin{array}{c} OR \\ | \\ Si{-}O{-} \\ | \\ OR \end{array} + R(OH) \qquad (8)$$

This scheme may be used in a very general way. For instance, when silica constitutes more than half of the structure, all other glass constituents can simply be introduced as alkoxides and reacted with the hydroxyl bonds of the silanol.

Silicon alkoxides, even in excess water, do not completely hydrolyse to an "OR"-free complex, e.g., $SiO_{(4-x)/2}(OH)_x$. Unlike the boron hydrolysis, "OR" and "OH" radicals can coexist in substantial numbers in the hydrolysed product:

$$Si(OR)_4 + H_2O \rightarrow SiO_{(4-x-y)/2}(OH)_x(OR)_y + R(OH) \qquad (9)$$

Again, the above reaction is a simplified form of a series of reactions involving polymerization of "OH" and "OR" radicals and forming bridging oxygens similar to those represented in Equations 6 and 7. In contrast to those reactions, hydrolysis does not go to completion, where either "OR" or "OH" radicals are completely exhausted. Instead, an equilibrium between these radicals and the mother liquor is reached. As the number of bridging oxygens increases in the hydrolysis product, $SiO_{(4-x-y)/2}(OH)_x(OR)_y$, the equivalent SiO_2 concentration also increases.

For an unhydrolysed tetraethylorthosilicate $Si(OC_2H_5)_4$, for example, the SiO_2 content is a little less than 28% by weight. If this material were to be hydrolysed without forming any bridging oxygen, that is, to $Si(OH)_x(OR)_y$, the silica content would vary from 25% for $x = 0$ to a little more than 62% for $y = 0$. However, with the presence of bridging oxygen, the polymer may contain as much as 85 to 90% SiO_2. This is shown

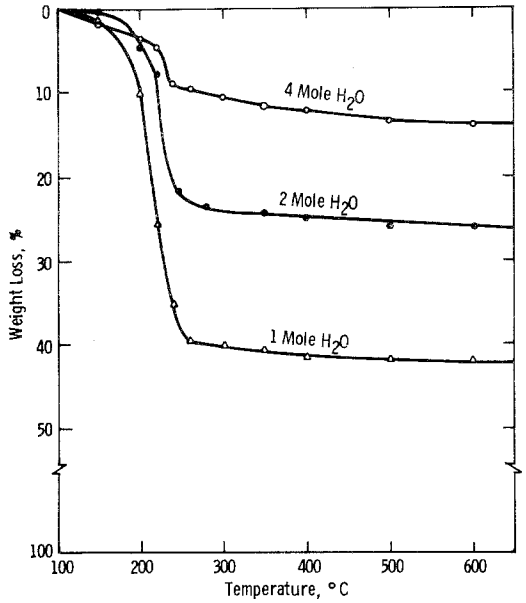


Figure 2 Variation of oxide content during heat treatment of silanol gels obtained by the hydrolysis of $Si(OC_2H_5)_4$ with different amounts of water.

in Fig. 2, where $Si(OC_2H_5)_4$ was hydrolysed in ethyl alcohol with 1, 2 and 4 moles of water per mole of alkoxide. Ethoxysilanols were then aged for several days and gelled by holding the samples slightly over 100° C for 48 h. These gels were thermally decomposed to SiO_2 by heating up to 600° C. Fig. 2 shows the weight loss of the gels during this degradation. The loss varied from slightly less than 15% for the 4-mole hydrolysed sample to more than 40% for the 1-mole hydrolysed sample. The SiO_2 content of the system with and without bridging oxygen as a function of the amount of hydrolysis water is shown in Fig. 3.

Fig. 2 also gives an indication of the kinetics of

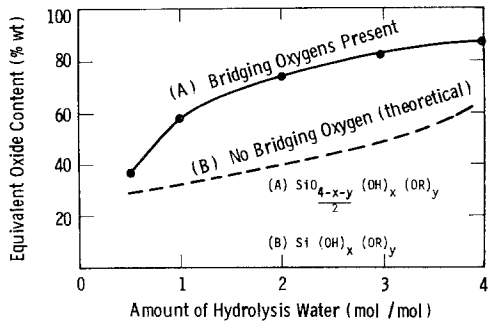


Figure 3 The formation of bridging oxygen is reflected in an increased oxide content of silanol gels hydrolysed with increasing amounts of water.

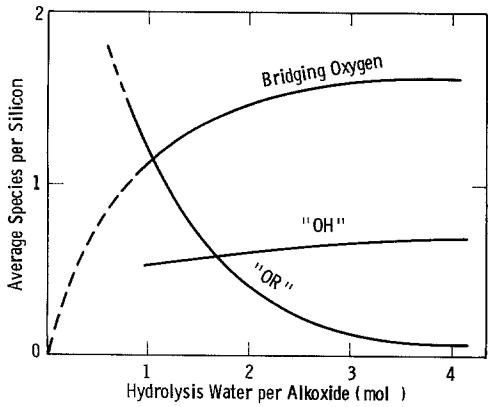


Figure 4 Average number of "bridging oxygen", "OR" and "OH" groups per silicon in silanol gels as a function of the amount of hydrolysis water.

"OR" and "OH" liberation in these materials upon heating. The sudden weight loss which occurs at around 200° C is related to "OR" liberation. The gradual and smaller weight loss related to "OH" liberation occurs throughout the heat treatment. The "OR"-related loss, as expected, is higher for the gels formed with less water. "OH" loss, on the other hand, varies less drastically with the amount of hydrolysing water. Calculations show that the average "OR" concentration drops significantly up to 3 moles of water and then levels off at the low value of 0.1 per mole of silicon. The "OH" concentration, however, is less affected throughout (see Fig. 4).

2.2. Formation of multicomponent glasses

Once the active polymerizing species are formed in a liquid state, various glass compositions can readily be prepared by chemically reacting these species [3]. One must start from an alkoxide which is slow to hydrolyse and polymerize. In most glass-forming systems, this happens to be silicon alkoxide, whose rate of reaction is much slower than, for example, alkoxides of B, Al, Ti, Zr, Na, etc.

The slowest hydrolysing alkoxide is first rendered to an active polymerizing species as described, while the fast hydrolysing alkoxide is kept in the original form so that self-polymerization cannot occur. If this rule is not observed, inhomogeneities will result. For example, if one were to initially form a self-polymerizing species from a fast hydrolysing alkoxide and try to react this with a slow hydrolysing alkoxide, the polymerization of the former with itself would take place faster than its reaction with the latter, and inhomogeneity would result. However, if the slow hydrolysing alkoxide is partially hydrolysed first, then reacted with the unaltered fast hydrolysing alkoxide, dissimilar constituents tend to become neighbours, i.e., $-M_1-O-M_2-$ rather than $-M_1-O-M_1-$. Thus greater homogeneity is attained.

The product of these reactions generally remains liquid due to the absence of sufficient hydroxyls to cause complete polymerization. After all glass constituents are similarly introduced and chemical bonds are formed, excess water should be added to remove the remaining "OR" groups without fear of segregation. This procedure generally causes the solution to polymerize to a clear gel.

The hydrolysis of alkoxide mixtures can also provide insight into the mechanism of reactions taking place. For example, Fig. 5 shows the regions of clear solution and precipitation formation when a mixture of various ratios of $Si(OC_2H_5)_4/B(OCH_3)_3$ were hydrolysed with

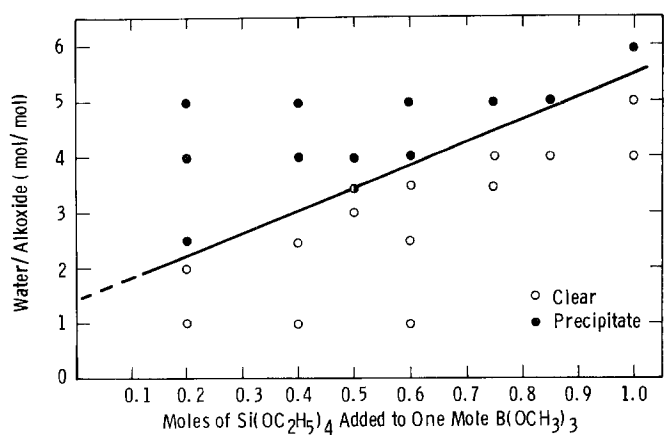


Figure 5 Regions of precipitate and clear solution formation in the alkoxide mixture $Si(OC_2H_5)_4/B(OCH_3)_3$ as a function of water content.

different amounts of water. The line separating clear solutions from those condensed can be represented by

$$M_{H_2O} = AM_1 + BM_2 \quad (10)$$

where M_{H_2O}, M_1, and M_2 are moles of water, boron and silicon alkoxides, respectively. With M_1 fixed at 1 mole, the y intercept and slope of the line in Fig. 5 yield values of $A = 1.5$ and $B = 4$. This means that 1.5 moles of H_2O are required to condense 1 mole of boron alkoxide, and about 4 more moles of water are needed per mole of silicon alkoxide added. These numbers imply the nature of the hydrolysis products. For example, the hydrolysis product of boron alkoxide is essentially oxide rather than hydroxide, requiring 1.5 mole of water per mole of alkoxide:

$$B(OR)_3 + 1.5\ H_2O \rightarrow \tfrac{1}{2}\ B_2O_3 + 3ROH. \quad (11)$$

This is consistent with earlier discussions.

2.3. Heat treatment and resultant oxide glasses

Once the polymerization is performed the gel must be dried and heat-treated. If it is desired that the gel remain monolithic, the initial drying stages are very critical, and drying must be done gradually, preferably at room temperature. After the liquid component is removed, the gel must be heat-treated to drive off the hydroxyls and remaining organics. By 400 to 500° C one obtains glass samples which are clear, non-particulate and essentially free of organics (Fig. 6).

Electron microscopy shows that the gel formed by this method consists of regions whose boundaries delineate the extent of localized polymerization. As heat-treated and organic radicals are removed, very uniform open channels begin to form. The distribution of channel diameters for a particular sample exhibits very little dispersion, varying only a few ångstroms from a mode diameter. This mode diameter falls somewhere between 20 and 100 Å, depending on the composition. At this stage, 50% or more of the sample volume may be occupied by channels. As the temperature is increased the pores are eliminated, and a dense glass or crystalline material results (see Fig. 7). Most of the glasses formed by this method will sinter to dense bodies well below their classical sintering temperature.

There are two main problems which might occur during heat treatment. One is entrapment of the pores. This is generally caused by rapid heating where the surface pores close before the internal pores are eliminated. Further heating raises the trapped gas pressure and causes bloating of pores when the temperature is high enough to permit it. The second problem is carbon formation, which is more complex in nature. It may occur as a result of insufficient oxygen, sealing off pores before the organic radicals have had a chance to burn off and escape, or thermochemical conditions. A silicon-based glass may turn black around 400° C. However, if this glass is kept at between 450 and 500° C, where temperatures are high enough to burn carbonaceous matter yet too low to seal off the pores, a gradual clearing will take place and the sample will eventually clear completely.

Another type of carbon formation may result from the thermochemical nature of the reaction taking place. This one is rather interesting and, in certain cases, can be used advantageously. For example, silanol gels produced from hydrolysis of ethyl silicate, if held at a temperature between 165 and 200° C for an extended period of time, undergo certain chemical changes so that subse-

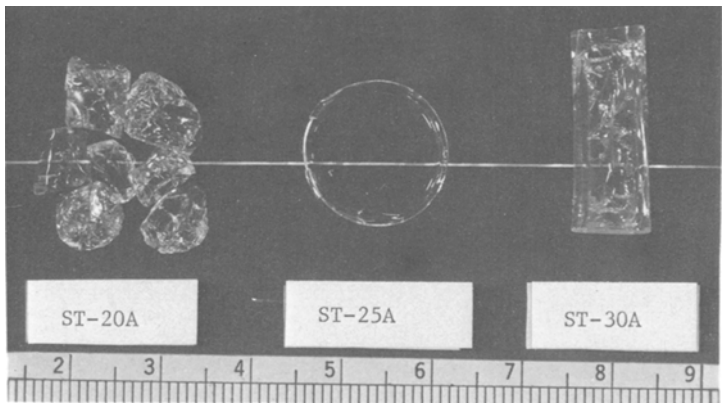


Figure 6 Glass samples formed by chemical polymerization without melting (heat treated to 500° C).

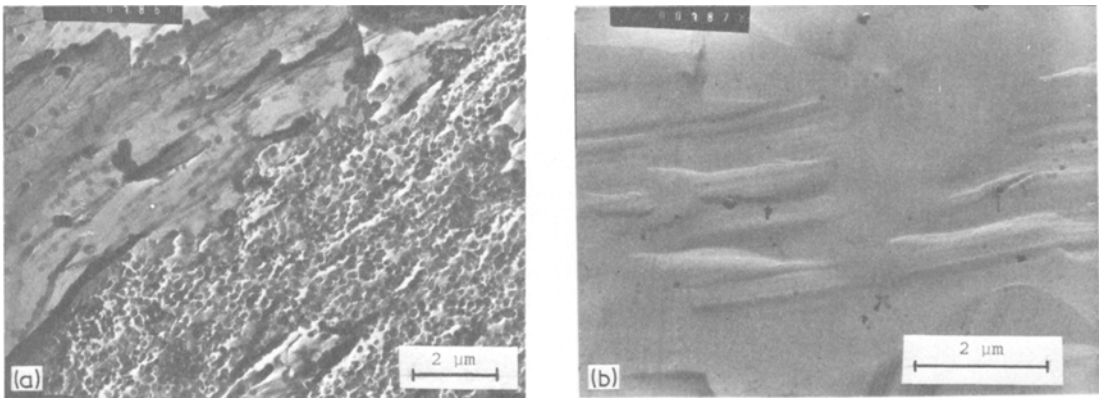


Figure 7 Fractured surface electron micrographs of a potassium silicate glass: (a) at 500° C, showing porosity; (b) at 1000° C, no porosity.

quent heat treatment at elevated temperatures causes carbon formation. Carbon formation can be prevented by passing through the critical temperature range rapidly.

For example, in Fig. 8 a gel was prepared by hydrolysis of $Si(OC_2H_5)_4$ with 2 moles of H_2O and placed in a boat equipped with thermocouples. This boat was then placed in a gradient furnace, which allowed the sample to receive heat treatment at temperatures varying from 100° C to 240° C along its length for 24 h. This heat treatment produced no carbon formation, and the sample remained white. The boat was then taken from the gradient furnace and placed into another furnace, where the entire sample was heated to 600° C. As is seen in Fig. 8, only those parts which had been previously subjected to heat treatment between 165 and 200° C showed carbon formation.

3. Conclusions

An oxide glass network can be formed by polymerization of certain species prepared from metal–organic compounds at or near room temperature. It is proposed that the formation of soluble polymerizing species from alkoxides requires the presence of both "OR" and "OH" groups in the structure. These groups normally coexist in the hydrolysis product of silicon alkoxides in significant numbers, allowing silanols to remain soluble in alcohol and be suitable for polymerization.

In the case of fast hydrolysing alkoxides, such as those of boron, aluminum, zirconium, etc., the hydrolysation reaction goes to completion by virtual elimination of "OR" groups thus forming insoluble oxide and hydroxides which precipitate out of the solution. It has been shown, however, that it is possible to form polymerizing species from these alkoxides also. This requires taking certain steps during the hydrolysis process which result in the retention of a certain amount of "OR" groups in the structure. When this is done, the hydrolysis product is soluble in alcohol and contains polymerizing species which can be used to form an oxide network. The oxide network thus formed requires a heat treatment to about 500° C to drive off the residual organics. When necessary, precautions are taken during drying and heat treatment so that the structure remains monolithic.

The glass network formed by this method is initially porous. The pores are in the form of open channels whose diameter is extremely uniform,

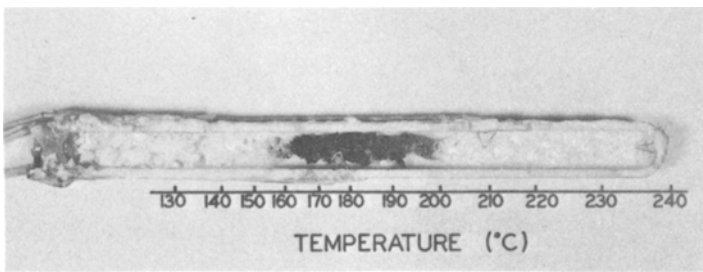


Figure 8 Carbon formation in silica. Only the part of the material subjected to heat treatment at between 160 and 200° C forms carbon upon heating to high temperatures.

remaining within several ångstroms of a mean value. This value varies with the individual system but is generally less than 100 Å. Pores can often be eliminated by a heat treatment at temperatures considerably lower than those required by the corresponding compositions prepared by classical methods. Densification to a carbon-free body requires that the surface pores are not sealed off by heat treatment before organic residues have had a chance to burn off and internal pores must be eliminated gradually.

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