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Studies on Glass

XIII. Glass Formation by a Hydrocarbon Polymer

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(Received October 14, 1935)

Polyisobutylene, with an average molecular weight of about 4900, is at room temperature a highly viscous liquid. When cooled, it has been found to form a glass, with the same transitions in thermal properties characteristic in the vitrification of substances of low molecular weight. The heat capacity of polyisobutylene has been measured from 118°K to 295°K. It increases by 32 percent between 192°K

and 202°K. The thermal expansion coefficient of polyisobutylene has been measured from 160°K to 300°K. It increases by 200 percent between 185°K and 205°K. The mean temperature of transition corresponds to a viscosity of about 10^{13} poises, in agreement with a rule observed generally for glass-forming materials. The factors on which the transition temperature depends are discussed.

INTRODUCTION

GLASSES have been described as amorphous solids, characterized by optical isotropy and by lack of symmetry or periodicity in the microscopic arrangement of structural elements. On the other hand, a very clear characterization of the vitreous state of matter from a macroscopic standpoint is given by thermal properties. When a glass is heated through the temperature range in which it softens to a viscous liquid, there is in nearly every case a rapid—almost discontinuous—increase in the heat capacity and thermal expansion coefficient, taking place in a small temperature interval. In contrast to the fusion of a crystalline solid there is no latent heat effect or sudden increase in volume. This type of phenomenon is termed by Ehrenfest¹ a “transition of the second order,” since discontinuities appear, not in the heat content and volume of the substance, but in the temperature derivatives of these quantities.

Transitions of this sort have been observed not only for silicate glasses² and various amorphous materials,³ but also for many simple organic compounds and for boron trioxide⁴ and elementary sulphur⁵ and selenium.⁵ In several cases (silicate glasses, boron trioxide, glucose,⁶

and glycerol⁷), the viscosity of the viscous liquid above the transition range of temperature has been studied. Extrapolation or continuation of measurements into the transition range indicates that, at the midpoint of the latter, the viscosity of the material is between 10^{13} and 10^{14} poises. This rule appears to hold irrespective of the nature of the material or of the mean temperature at which the transition takes place (510°K for boron trioxide; 185°K for glycerol).

All of the organic compounds previously studied are simple substances of low molecular weight, which can be undercooled without crystallization. As examples may be cited 3-methylhexane,⁸ ethyl alcohol,⁹ propylene glycol,⁹ lactic acid,⁸ and glucose.^{10, 11} The present study deals with a polymeric substance whose molecular size is of an entirely different order of magnitude. This substance, polyisobutylene, is an example of the linear or “chain-molecular” polymers which have been the subject of much investigation by Staudinger¹² and others.

Many organic polymers of very high molecular weight have been briefly described as “glassy” solids because of transparency and brittleness. It was anticipated that a lower polymer, being a viscous liquid at room temperature, would vitrify upon cooling and undergo the characteristic transition observed for simple organic compounds.

* Shell Research Fellow at Stanford University for the academic year 1934–35.

¹ Konink. Akad. Wetensch. Amsterdam **36**, 153 (1933).

² Jenckel, Zeits. f. anorg. allgem. Chemie **216**, 367 (1934).

³ Samsoen, Comptes rendus **181**, 354 (1925); **182**, 517 (1926).

⁴ Spaght and Parks, J. Phys. Chem. **38**, 103 (1934).

⁵ Mondain-Monval, Ann. chim. **3**, 5 (1935).

⁶ Parks, Barton, Spaght and Richardson, Physics **5**, 193 (1934).

⁷ Parks and Gilkey, J. Phys. Chem. **33**, 1428 (1929).

⁸ Parks, Thomas and Light, preceding article.

⁹ Parks and Huffman, J. Phys. Chem. **31**, 1842 (1927).

¹⁰ Parks and Thomas, J. Am. Chem. Soc. **56**, 1423 (1934).

¹¹ Parks, Huffman and Cattoir, J. Phys. Chem. **32**, 1366 (1928).

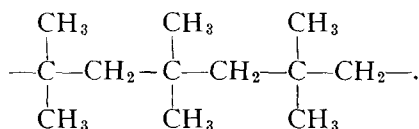
¹² Staudinger, *Die Hochpolymeren Organischen Verbindungen* (Julius Springer, Berlin, 1932).

This was amply confirmed in the present study on polyisobutylene, which is found to have a transition at a mean temperature of about 197°K. Data for the heat capacity and thermal expansion are here presented; the viscous properties of the material are described elsewhere.¹³

MATERIAL

The sample of polyisobutylene employed in this work was a mixture of polymers with a wide range of molecular weights. The average molecular weight, as determined by cryoscopic measurements in benzene solution, was about 4900.

The molecules of polyisobutylene, like those of other "linear" polymers, are generally supposed to be unbranched chains of great length. This hypothesis, while not at present susceptible to proof, is supported by the viscosity studies of Staudinger,¹² and (in the case of polystyrene and other polymers) by various physical measurements in dilute solution, such as diffusion¹⁴ and streaming double refraction.¹⁵ The most probable arrangement for the isobutylene units in polyisobutylene is:



If bond lengths and angles are the same as in normal paraffins, a molecular weight of 4900 corresponds to a length of about 220Å. Actually, more complicated arrangements may be involved, with side chains longer than the methyl groups.

The density of our sample, determined at three temperatures, is given in Table I. The refractive

TABLE I. Density of polyisobutylene.

Temperature (°C)	23.4	100.2	178.2
Density (g/cc)	0.9074	0.873	0.835

index at 27.1°C was $n_D = 1.50451$.

HEAT CAPACITY MEASUREMENTS

Method

Heat capacity measurements were carried out by a modification of the Nernst method of

¹³ Ferry and Parks, *Physics* **6**, 356 (1935).

¹⁴ Herzog and Kudar, *Zeits. f. physik. Chemie* **A167**, 343 (1934).

¹⁵ Signer and Gross, *Zeits. f. physik. Chemie* **A165**, 181 (1933).

aneroid calorimetry. The apparatus and procedure have been fully described elsewhere.^{16, 17} The absolute errors in the values reported are probably within less than 1 percent, except in the temperature interval of transition, where the thermal conductivity of the material is lower, and uncertainty in attainment of complete thermal equilibrium arises.

Results

In the first series of determinations, low temperatures were reached always by very slow cooling, to insure a well-annealed sample. The measurements involved occasional alternate heating and cooling, and overlapping series of values showed the results to be quite reproducible and unaffected by this thermal treatment, so long as the cooling was slow (crossing the transition region in about 24 hours). The results, expressed in terms of the 15° calorie per gram, and with all weights reduced to a vacuum basis, are given in Table II. These values are plotted against the absolute temperature in Fig. 1 as curve I. The heat capacity of the sample thus "annealed" by slow cooling increases by 32 percent within the temperature interval 192°K to 202°K (the "transition interval"). The rise in the curve is quite sharp, in spite of the wide range of molecular weights in the material.

A second series of determinations was made to show the effect of absence of annealing. The same sample was cooled rapidly, the transition interval being crossed in less than an hour. The heat capacity values for this unannealed sample are given in Table III, and are plotted as curve II in Fig. 1.

TABLE II. Specific heats in cal. per degree for polyisobutylene (annealed sample).

$T(^{\circ}\text{K})$	C_p	$T(^{\circ}\text{K})$	C_p	$T(^{\circ}\text{K})$	C_p
121.0	0.167	193.4	0.283	242.6	0.410
127.2	0.176	197.5	0.325	247.9	0.415
133.4	0.185	200.2	0.363	253.3	0.421
139.7	0.194	201.4	0.371	258.5	0.426
145.4	0.202	201.5	0.367	263.5	0.431
150.9	0.210	205.2	0.376	268.6	0.436
156.9	0.218	208.9	0.379	275.1	0.445
162.4	0.227	212.5	0.384	278.7	0.448
167.9	0.235	216.7	0.387	282.0	0.451
174.1	0.243	221.1	0.390	286.5	0.456
179.3	0.252	225.7	0.394	291.2	0.462
184.3	0.260	231.5	0.399	294.9	0.466
189.1	0.269	237.0	0.404		

¹⁶ Parks, *J. Am. Chem. Soc.* **47**, 338 (1925).

¹⁷ Parks and Kelley, *J. Phys. Chem.* **30**, 47 (1926).

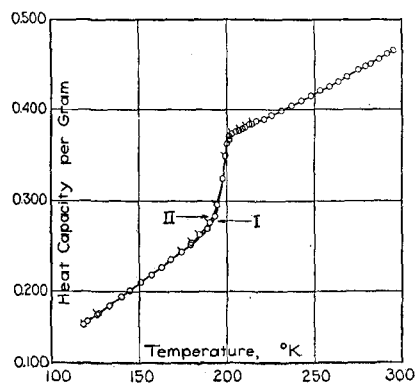


FIG. 1. The specific heat of polyisobutylene in calories per degree plotted against the absolute temperature. The plain circles (curve I) denote determinations made following slow cooling; the tailed circles (curve II), determinations made following rapid cooling.

TABLE III. *Specific heats in cal. per degree for polyisobutylene (unannealed sample).*

$T(^{\circ}\text{K})$	C_p	$T(^{\circ}\text{K})$	C_p	$T(^{\circ}\text{K})$	C_p
118.5	0.163	184.6	0.262	202.7	0.374
126.2	0.174	189.8	0.276	206.6	0.378
—	—	194.4	0.296	210.3	0.381
174.0	0.244	199.0	0.350	214.1	0.384
179.5	0.254				

The heat capacity rise is evidently slightly less sharp than in the case of the annealed sample. However, the values above and below the transition interval agree very closely in the two cases. Differences in thermal history apparently do not affect the heat capacity except at temperatures in and immediately below the transition region. This was also found to be true for propylene glycol,⁹ boron trioxide,¹⁸ and glucose¹⁰ glasses.

THERMAL EXPANSION MEASUREMENTS

Method and apparatus

Thermal expansion measurements were carried out in two types of dilatometers, constructed of Pyrex glass and of brass, respectively, with an aqueous solution of ethyl alcohol as a dilatometric fluid.

The Pyrex dilatometer design was essentially a large model of a liquid-in-glass thermometer. A cylindrical bulb 1.9 cm in diameter and 10.8 cm long was provided with a thermocouple well sealed in from the bottom, and an 80-cm capillary tube of suitable bore (2.4 mm or 1.7 mm) sealed

on the top. Introduction of the polyisobutylene was accomplished by cutting off the capillary to leave an aperture about 0.8 cm in diameter, filling with the polymer up to a point 3 cm below the break, and sealing the capillary back on.

The glass dilatometers were employed for measurements from room temperature down to 230°K. Below this point, the expansion coefficient of the polyisobutylene appeared to fall off steadily with decreasing temperature. This drop was attributed not to a real transition (which by analogy with the heat capacity results should appear only below 205°K), but to lack of internal mechanical equilibrium. The polyisobutylene, introduced at a temperature where it was moderately fluid (viscosity 10^5 poises), wetted the walls of the dilatometer and adhered firmly to them. When the temperature was lowered, the adherence to the walls prevented immediate contraction and uniform recession of the upper surface. Stresses were introduced, and these were relieved by viscous flow. Rough calculations based on a model of Poiseuille flow through a cylindrical tube¹⁹ indicated that, below 220°K, the time required for relief of these stresses would become longer than the times ordinarily taken for measurements. Thus the Pyrex dilatometers were inapplicable below 220°K.

The metal dilatometer obviated adherence of the polyisobutylene to the walls. It consisted of a cylinder and cap which, when assembled with a solder gasket, had the same external dimensions as the Pyrex bulb. It was provided also with a thermocouple well, and with a strong iron capillary tube which was continued by a calibrated Pyrex capillary attached at a joint sealed by litharge and glycerine cement. In the cylinder was placed a cylindrical basket of fine brass gauze, with a hole in the bottom to accommodate the thermocouple well. The basket was lined with filter paper to confine the polyisobutylene. This arrangement kept the material from contact with the rigid walls of the dilatometer, and the mechanical flexibility of the container permitted free contraction at low temperatures.

The dilatometric fluid was introduced into either type of dilatometer by evacuating the system and then, by means of a three-way

¹⁹ We are indebted to Professor F. Bloch for suggesting this model.

¹⁸ Thomas and Parks, J. Phys. Chem. **35**, 2091 (1931).

stopcock, allowing the freshly boiled-out liquid to flow over into it. Persistent bubbles were removed by introducing into the calibrated capillary a tube drawn out to a diameter of 0.8 mm and a length of a meter. This device also served in removing the dilatometric liquid, which was expelled by inverting the dilatometer and blowing air through the inner tube.

For temperature control, the dilatometer was surrounded by a cylindrical copper jacket, provided with a heating coil and copper-constantan thermocouple. A similar thermocouple measured the temperature in the well of the dilatometer; while a differential thermocouple, with one junction in the well and the other on the outside of the dilatometer, provided a control on radial temperature gradients. The thermoelectric forces of these thermocouples were measured with a White double potentiometer. The jacket was separated by an air gap from a brass can which was immersed in a cooling bath to attain and maintain low temperatures. Baths of ice, ice and alcohol, and alcohol and solid carbon dioxide were employed. For temperatures below the sublimation point of carbon dioxide, the outer can was provided with a coil of 3-mm copper tubing, through which liquid air was pumped,

the whole system being immersed in a bath of precooled alcohol. The apparatus is illustrated in Fig. 2.

Each series of expansion measurements was commenced at the bottom of the temperature range to be covered. Thermal equilibrium at any desired temperature was maintained by electrically heating the jacket sufficiently to compensate for the loss of heat from it to the outer can. Criteria for equilibrium were constancy of dilatometer temperature and absence of radial thermal gradients. The height of the liquid column in the capillary was read by a cathetometer. Determinations of corresponding temperatures and column heights were made at intervals of about 6°. The thermal expansion coefficient of volume was calculated over each such interval, and was assumed to represent the instantaneous value at the midpoint of the interval ($\alpha = (1/V)(dV/dT)$).

Thermal expansion of 92.5 percent aqueous ethyl alcohol

Ethyl alcohol fulfilled all the requirements for a dilatometric fluid over the appropriate temperature range. A sample from the ordinary laboratory supply was employed; the presence of water was an advantage, since it assured undercooling of the liquid below its melting-point (159°K). The density of the solution at 22.0°C was 0.8089 g/ml in vacuum, corresponding to a weight-concentration of 92.5 percent ethanol, according to the data of the *International Critical Tables*.

Since no expansion data for such a solution were available, measurements were first made for this alcohol with Pyrex dilatometers. The thermal expansion coefficients were calculated by the equation

$$\alpha_1 = \alpha_0 + (v_T/v_R)(A/V)(\Delta h/\Delta T), \quad (1)$$

where α_1 and α_0 are the expansion coefficients of the alcohol and Pyrex, respectively, v_T and v_R the specific volumes of the alcohol at the mean temperature of the dilatometer and at that of the capillary column, respectively, A the cross section area of the capillary, V the volume of that part of the dilatometer system whose temperature is controlled by the jacket, and Δh and ΔT the observed changes in height and temperature. The values for α_0 were calculated

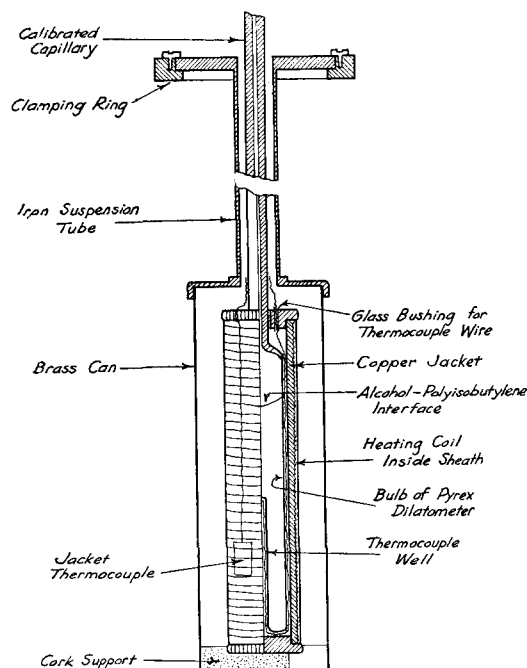


FIG. 2 Apparatus for measurement of thermal expansion.

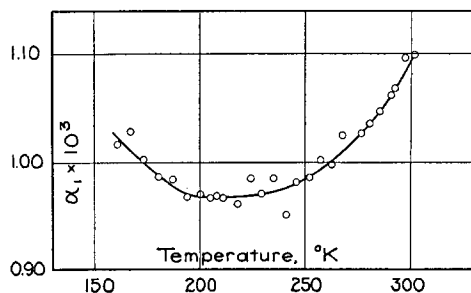


FIG. 3. The thermal expansion coefficient of 92.5 percent aqueous ethyl alcohol plotted against the absolute temperature.

from the data of Buffington and Latimer.²⁰ The values for v_T were calculated by rough numerical integration of α_1 , proceeding by successive approximations. The results for α_1 are plotted against the absolute temperature in Fig. 3. Above 0°C, these results are in very satisfactory agreement with values obtained by differencing density data from the *International Critical Tables*.

The expansion of the metal dilatometer was determined by calibration measurements with the same stock alcohol.

Thermal expansion of polyisobutylene

The expansion coefficients of polyisobutylene were calculated by the equation

$$\alpha_2 = 1/V_p \{ dV/dT - (V - V_p)\alpha_1 + (v_T/v_R)A(\Delta h/\Delta T) \}, \quad (2)$$

where V_p is the volume of the polyisobutylene at the mean temperature of the measurement. This was obtained by numerical integration of α_2 from room temperature (where the density of the polymer was known accurately) down, proceeding by successive approximations. The term dV/dT was given by the calibration for the metal dilatometer, or by $V\alpha_0$ for the Pyrex apparatus.

The results of six series of determinations are plotted in Fig. 4. The results from the metal dilatometer are more subject to fortuitous error, because the basket arrangement contained a much smaller sample of polymer than did the Pyrex bulb, and the contribution of the alcohol to the observed expansion was much greater. The absolute errors in the values above 230°K are believed to be within 4 percent.

²⁰ Buffington and Latimer, *J. Am. Chem. Soc.* **48**, 2305 (1926).

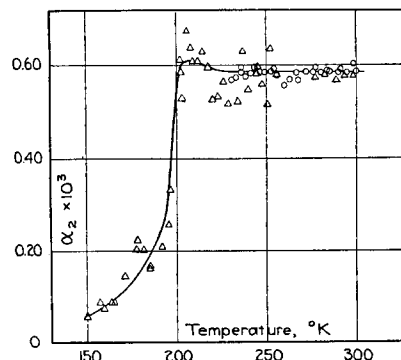


FIG. 4. The thermal expansion coefficient of polyisobutylene plotted against the absolute temperature. The triangles denote measurements with the metal dilatometer; the circles, measurements with Pyrex dilatometers.

The thermal expansion coefficient of polyisobutylene evidently increases by 200 percent within the temperature interval 185°K to 205°K.

It is of interest to note the complete similarity between these results and the expansion measurements of Bekkedahl²¹ on rubber hydrocarbon, a natural product obtained from latex.

DISCUSSION

The transitions in heat capacity and thermal expansion for polyisobutylene are entirely similar to those observed for simple organic glass-forming liquids and for boron trioxide, except that the magnitude of the increase in heat capacity is considerably less in the present case. Further, the viscosity-temperature curve of polyisobutylene,¹³ when extrapolated to 197°K (the midpoint of the transition interval), shows a viscosity of about 10^{13} poises, in agreement with the rule found generally for glass-forming systems.

The tendency toward vitrification as an alternative to crystallization has been discussed by Randall and others.²² If a liquid can be supercooled through its melting-point without crystallization starting, and the cooling is continued to a sufficiently low temperature, the material becomes so viscous that orientation of molecules into a crystal lattice is henceforth virtually impossible. Ease of supercooling is the deciding

²¹ Bekkedahl, *Bur. Standards J. Research* **13**, 411 (1934).

²² Randall, *The Diffraction of X-Rays and Electrons by Amorphous Solids, Liquids, and Gases* (Wiley and Sons, New York, 1934), pp. 182-184. See also Cline and Andrews, *J. Am. Chem. Soc.* **53**, 3671 (1931); and Zachariasen, *J. Am. Chem. Soc.* **54**, 3841 (1932).

factor; this probably arises from optical isomerism in many cases and from a variable association in the case of simple alcohols.⁸ In polyisobutylene, the steric hindrance of the long, clumsy chain molecules, and the variety of molecular species present, undoubtedly account for the failure to crystallize under any circumstances.

The temperature at which the transitions in heat capacity and thermal expansion occur seems in general to be connected with a viscosity of 10^{13} poises, and hence with a certain definite degree of intermolecular interaction. When glass-forming substances are arranged in the order of the mean temperatures of their transition regions, the series progresses regularly from nonpolar compounds through compounds of increasing dipole moment to a substance like boron trioxide, whose structure involves a network of valence bonds throughout. For equal dipole moments, the compounds fall in the order of increasing

molecular weights. Polyisobutylene, although virtually nonpolar, has a mean temperature of transition corresponding to rather polar compounds, falling between glycerol and lactic acid. This may be qualitatively explained on the basis of its huge molecular weight, which may be considered to overbalance the effect of the nature of the intermolecular forces. More specifically, we may consider the binding among the isobutylene units in the material. Binding between units in different macromolecules is of a purely van der Waals character, similar to the intermolecular interaction in nonpolar compounds. Units in the same macromolecule, however, are connected by chemical bonds—a type of binding more analogous to that in boron trioxide than to that in any other organic glass-forming material. The resultant of these two types of binding places the transition temperature of polyisobutylene somewhere between those of nonpolar heptanes (about 88°K) and boron trioxide (about 510°K).

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The Kinetics of the Oxidation of Gaseous Hydrocarbons

III. The Oxidation of Acetylene

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(Received October 7, 1935)

An investigation of the kinetics of the oxidation of gaseous acetylene has been made by the static method. The results show marked irregularities due to variations in the surface. The rate of the reaction is given by

$$-(d/dt)(C_2H_2) = K(C_2H_2)^{2.7}/(O_2)^{0.1}$$

when oxygen is in excess. In a packed bulb the order is diminished to about 1.4. Packing decreases the rate at high pressures and has little effect at low pressures. In an empty

vessel the CO/CO₂ ratio of the products is independent of the pressure. Packing decreases this ratio, and it further decreases rapidly with diminishing pressure. The apparent heat of activation of the reaction is about 35,000 calories. The addition of glyoxal to the reaction mixture causes no change in the rate of the reaction, while formaldehyde causes a marked retardation. The products of the reaction are discussed in the light of recent work on the oxidation and decomposition of glyoxal.

INTRODUCTION

THERE have been a number of previous investigations of the oxidation of acetylene. Bone and Andrew¹ interpreted their work by postulating the formation of the unstable dihydroxy compound C₂(OH)₂, which was assumed

to decompose directly into CO and HCHO. In a more recent investigation, Kistiakowsky and Lenher² found that the reaction was a chain process with the rate proportional to the square of the acetylene concentration, and a slight retardation by oxygen. The condensable products

¹ Bone and Andrew, J. Chem. Soc. **87**, 1232 (1905).

² Kistiakowsky and Lenher, J. Am. Chem. Soc. **52**, 3785 (1930).