Phase changes

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Behavior of Polytetrafluoroethylene (Teflon) under High Pressures*

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The presence of polymorphic phase transitions, apparently unique among high polymers, enhances interest in polytetrafluoroethylene, while its potentialities for cryogenic applications make low temperature data particularly valuable. Compression measurements have been made on samples of Teflon at various temperatures between 75°K and 380°K and at pressures up to 21 000 atmos. The phase diagram found for the region above the ice point is in qualitative agreement with previously published results, with a possible additional transition appearing above room temperature at pressures of over 11 000 atmos. Time effects and a large pressure hysteresis make the transition parameters quite ambiguous, and the hysteresis becomes so broad at low temperatures that the phase diagram cannot be extended below the ice point. An apparent negative thermal expansion indicated by the isothermal compression measurements is shown to result from an incomplete high pressure transition. From an engineering standpoint, the measurements indicate that a Teflon gasket loaded to 3000 atmos at room temperature should maintain a seal at any lower temperature.

INTRODUCTION

POLYTETRAFLUOROETHYLENE (Teflon) possesses a high degree of crystallinity and displays several of the properties of the more usual crystalline solids, including polymorphic transitions and the maintenance of mechanical and electrical properties over a wide temperature range.

There are at least two polymorphic transitions. A room temperature first-order transition, involving a volume change of roughly 1%, has been the subject of extensive investigation.[1–4] Bridgman[5] and Weir[6] independently found a high pressure transition at room temperature, with a volume change of some 2.25%, and Weir has presented a phase diagram[7] and detailed compression data[8] for the region between the ice point and 80°C.

A second atmospheric pressure transition at 303°K was reported as a first-order transition by Quinn, Roberts, and Work.[3] This view was supported by the heat capacity measurements of Furukawa, McCoskey, and King.[9]

The rapid increase in yield strength with decreasing temperature below about 170°K,[10] together with internal friction and magnetic resonance measurements, indicate a glassy transition in the amorphous part of Teflon in this region.[11] "Melting" of the crystallites at

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[1] H. A. Rigby and C. W. Bunn, Nature **164**, 583 (1949).
[2] C. W. Bunn and E. R. Howells, Nature **174**, 549 (1954).
[3] Quinn, Roberts, and Work, J. Appl. Phys. **22**, 1085 (1951).
[4] P. Marx and M. Dole, J. Am. Chem. Soc. **77**, 4771 (1955).
[5] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 55 (1948).
[6] C. E. Weir, J. Research Natl. Bur. Standards **46**, 207 (1951).
[7] C. E. Weir, J. Research Natl. Bur. Standards **50**, 95 (1953).
[8] C. E. Weir, J. Research Natl. Bur. Standards **53**, 245 (1954).
[9] Furukawa, McCoskey, and King, J. Research Natl. Bur. Standards **49**, 273 (1952).
[10] C. A. Swenson, Rev. Sci. Instr. **25**, 834 (1954).
[11] N. G. McCrum, J. Polymer. Sci. **27**, 555 (1958).

about 600°K results in a completely amorphous material.

The present investigation was undertaken to extend existing compression data to higher pressures and lower temperatures in an effort to trace the high pressure transition† and to investigate the apparent negative thermal expansion at high pressure reported earlier.[10]

Measurements of compression were made at various temperatures between 75°K and 380°K, with pressures up to 21 000 atmos. The results qualitatively confirm Weir's phase diagram and indicate that the apparent negative expansion at high pressure below room temperature is probably due to an incomplete high pressure transition. They also show the practicality of Teflon as a gasket material in cryogenic engineering: the total room temperature compression in 3000 atmos is greater than the thermal expansion between 75°K and room temperature, so that a gasket loaded to 3000 atmos at room temperature should maintain a seal at any lower temperature.

The results cannot be considered to be better than semiquantitative in nature. The transitions are never sharp and exhibit considerable hysteresis. Even in terms of somewhat arbitrary criteria, transition parameters can be established only for temperatures above the ice point, and there is always considerable uncertainty in the volume changes. Because of the pressure hysteresis in the transitions and the large time effects often involved, precise compressibility data must be considered in terms of the entire history of the sample as well as possible variations in samples due to differences in the polymerization and original fabrication processes.

EXPERIMENTAL DETAILS

The material examined was a lightly pigmented du Pont Teflon which was originally supplied by the du Pont Corporation and used in the examination of the physical properties of polymers at very low temperatures.[10] It was analyzed by the du Pont Laboratories, through the courtesy of M. I. Bro, and found to be about 68% crystalline and to have a specific gravity, after a controlled heating and cooling cycle, (characterized by Bro as "similar to that described in ASTM D1457-56T,") of 2.25.[12]

The samples were machined cylinders. The first, sample *A*, was 0.250 in. in diam, approximately 0.20 in. long, and had a mass of 0.332 g. Sample *B* had twice the cross-sectional area, was about 0.25 in. long, and had a mass of 0.841 g. The larger volume sample provided a means for a more precise determination of transition pressures and a check on systematic errors. The samples lay for about a week at room temperature after machining, but were not otherwise annealed. No particular procedure was followed to relieve residual stresses between changes of temperature during the experimental runs other than allowing time for the new temperature to stabilize.

The method used in making the measurements was essentially the Bridgman piston displacement technique,[13] modified, as described in detail elsewhere,[14–16] to permit measurements over a large temperature range.

In brief, the procedure was to place the sample in a Carboloy (grade No. 55B) cylinder between close-fitting Carboloy (grade No. 779) pistons. Hardened beryllium copper compression rings were used to prevent extrusion of the sample. Force from a hydraulic ram was applied to the pistons through extension members which permitted control of the sample temperature while the ram remained at room temperature. A commercial dial indicator at room temperature, actuated by quartz rods connected to the Carboloy pistons, measured changes in length of only the sample and the pistons, thus eliminating from the measurements the large changes in the stress members of the press. Corrections for the expansion of the cylinder and the compression of the pistons are kept to a minimum by the use of Carboloy, which has a large elastic modulus, low thermal expansion, and very high compressive yield strength.

Calibration runs were made with samples of indium in the same lengths as the samples to be measured. The difference between the observed change in length and the change in length of the indium as computed from existing data[15,17] was taken as an all-inclusive press correction. The correction was linear except for the lowest pressures, and at room temperature amounted to some 21% of the total change in length observed. The slight curvature of the correction curve below 2000 atmos was considered negligible in comparison with the high initial compressibility of the Teflon.

The smallest divisions of the dial indicators used were 0.01 mm and 0.001 in. Tenths of divisions were estimated. Both instruments were calibrated with an accurate micrometer screw.

Two presses were used in the experiments. The smaller of these was the same press used in the investigation of the phase transition in solid mercury,[16] and was used with sample *B* to study the low pressure transition, up to pressures of about 5000 atmos.

All of the other data were taken with a larger press of similar design. The ten-ton ram in this press was capable of producing a pressure of about 27 000 atmos on a 0.25-in.-diam sample, but because flow of the Carboloy pistons became troublesome at a somewhat lower pressure, the experiments were carried only to

† Weir reported a decrease in ΔV with decreasing temperature for this transition, and previous unpublished results (C.A.S.) do not show a transition at temperatures below the ice point.

[12] M. I. Bro, E. I. du Pont de Nemours & Company (private communication).

[13] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 9 (1945)

[14] C. A. Swenson, Phys. Rev. **99**, 423 (1955).

[15] C. A. Swenson, Phys. Rev. **100**, 1607 (1955).

[16] C. A. Swenson, Phys. Rev. **111**, 82 (1958).

[17] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 1 (1945).

TABLE I. The mean transition pressures and estimated volume changes for the phase transitions in Teflon at various temperatures. The phase designations are those used by Weir.

I-II			II-III			I-III		
T °K	P atmos	ΔV cm³/g	T °K	P atmos	ΔV cm³/g	T °K	P atmos	ΔV cm³/g
293	1	0.0037	270	7300		348	4650	0.0132
301	650	0.0023	298	6275	0.0100	354	4900	0.0130
307.5	1050	0.0023	315	5550	0.0107	356	5475	0.0130
315	1650	0.0023	327	5100	0.0110	365	5600	0.0118
320	2000	0.0023	334	4850	0.0111	379	6050	0.0115
325	2450	0.0023	339	4675	0.0112			
330	3150	0.0023	342	4550	0.0112			
335	3450	0.0023						

21 000 atmos. Oil pressures in the hydraulic system were measured and kept constant by direct use of a floating-piston dead-weight gauge, sample pressures being computed from the ratio of ram piston to sample areas. As always, when using this technique, it was assumed that the sample was quite plastic so that the pressure was essentially hydrostatic.

Each press was enclosed in a cryostat similar to those previously described.[18] Although these cryostats were designed to maintain any desired temperature from 4°K to room temperature, it was found the range could be extended to about 380°K by using a simple on-off control on a small electric heater attached to the bottom of the press or to the inner wall of the cryostat. For these experiments, with liquid nitrogen used as a refrigerant below room temperature, a temperature range of 75°K to 380°K was available. Temperatures were measured with a copper-constantan thermocouple clamped to the side of the sample holder. Maximum deviation from the set temperature was less than 0.5°K.

RESULTS

The usual experimental run was an isothermal compression, dial gauge readings being taken for even increments of pressure on increasing, and then decreasing, pressures. A plot of the resulting data was made to obtain working curves of the type shown in Fig. 1. The true pressure for a given apparent length is taken to be the mean of the points on the increasing and decreasing pressure curves where the two curves are parallel, the hysteresis being due to friction in the sample and holder.[17] In the transition regions, application of the same correction for friction still leaves a pressure hysteresis, indicating an uncertainty in the volume-pressure relationship of the type Bridgman terms a "region of indifference." The 270°K and 315°K curves are both included in Fig. 1 to illustrate the expansion of the region of indifference with decreasing temperature.

Even where the "region of indifference" is small, the rounding of the curves and the change in slope with the change of phase make the definition of a transition

[18] C. A. Swenson and R. H. Stahl, Rev. Sci. Instr. **25**, 608 (1954).

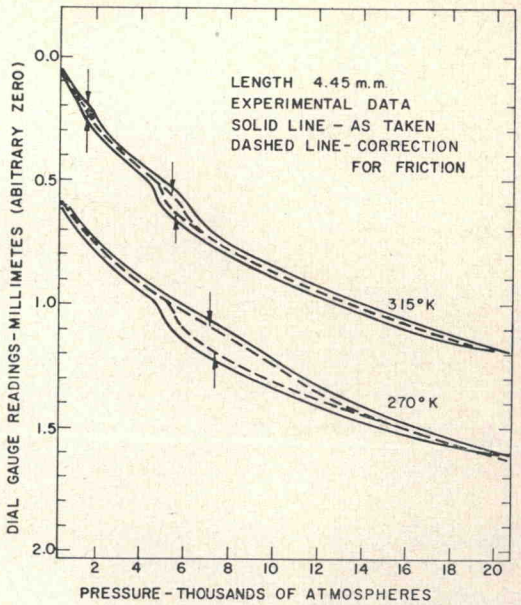

FIG. 1. Typical working curves obtained from Teflon sample A compression data, illustrating the expansion of the transition hysteresis with decreasing temperature. In the figure the word "correction" should read "corrected.

pressure quite difficult. The closest approach to a true equilibrium pressure would seem to be the mean of the pressures at which the increasing and decreasing pressure curves show the first sharp break (after correcting for friction). The points selected for 270° and 315°K are indicated on the figure by arrows. These points are quite well defined on the original curves, but much of the sharp change in slope has been lost in the reproduction.

The mean transition pressures as determined in this way are listed in Table I, along with the transition volume changes estimated by extrapolation of the isotherms to these pressures. Because of the changing slope above the transition, this is a rather doubtful procedure, but direct comparison of the curves shows the constancy of ΔV for the I-II transition above 293°K, and a slight increase of ΔV with temperature for the II-III transition. The volume change given for the I-II transition at atmospheric pressure was obtained from direct thermal expansion measurements (see the final section of this paper) by extrapolating the straight-line portions of the thermal expansion curve above and below the transition to 293°K. No adequate explanation of the smaller ΔV at higher pressures has been found. The values given for the I-III transition at the highest temperatures are quite uncertain, and the broad hysteresis at 270°K makes determination of the volume change at that temperature virtually impossible.

A phase diagram covering the corresponding region is shown in Fig. 2. The bars indicate the uncertainty due to the difference between the transition points on

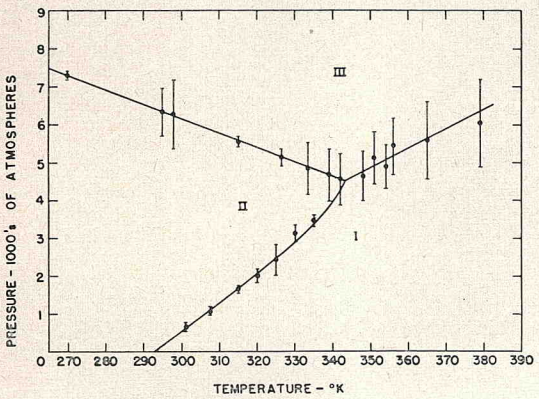

FIG. 2. Phase diagram for Teflon for the region above the ice point. The bars indicate the uncertainty in transition pressures due to the pressure hysteresis.

the increasing and decreasing pressure curves, and are not intended to reflect the sharpness of the transitions. Qualitatively, the diagram agrees with Weir's, but there is considerable difference in the slopes of the high-pressure transition lines. The differences are apparently due primarily to the different definition of transition pressure, all of Weir's data having been taken at decreasing pressure.

The location of the triple point at 343°K and 4500 atmos is in close agreement with Weir's results. Since it was impossible to separate the two transitions above 335°, the triple point was located by the intersection of the high-pressure lines. The transition volume changes computed from the measurements are thermodynamically consistent at the triple point with the diagram as shown.

In addition to those shown on the diagram, there is evidence of another transition above room temperature and at pressures near 11 000 atmos. The higher temperature isotherms show a probable volume discontinuity of the order of 0.3%, but the transition pressure is too uncertain to attempt to place it on the phase diagram.

The II-III transition becomes increasingly "sticky" with decreasing temperature, and below 270°K it is impossible to fix a transition pressure. Below about 240° the hysteresis loop extends over the full pressure range; that is, the transition is not complete even at the maximum pressure of 21 000 atmos. This results in an "apparent" negative thermal expansion at high pressures, clearly indicated by the isobars shown in Fig. 3.

As a check on this apparent negative thermal expansion coefficient, sample *A* was cooled to 78°K under a pressure of about 18 000 atmos. Dial gauge readings taken during cooling show a small but definite contraction. The plot of dial gauge readings *vs* pressure shows quite normal behavior on release of the pressure at 78°K, down to a pressure of 3000 atmos, where a rapid increase in expansion indicates the start of the III-II transition.

After release of the pressure, a compression run was made in the usual manner. The results agree closely with those obtained in the original run at this temperature. Unfortunately, there is no satisfactory way to evaluate the frictional effects in this experiment, so actual volumes cannot be computed, but a direct comparison of the two decreasing pressure curves indicates that cooling to 78°K under pressure results in a volume some 2% smaller than that resulting from compression to the same pressure at that temperature. This is the approximate magnitude of the volume change for the high pressure transition, which is of the same order as the apparent expansion indicated by the volume-pressure isotherms.

These results are considered quite conclusive evidence that there is not a true negative coefficient of thermal expansion at high pressure, but the smaller volume change resulting from compression at low temperature is due to an incomplete transition. The high density phase is not "frozen in" at 78°K, the transition taking place when the pressure is dropped below 3000 atmos. The shape of the curves suggests a similar transition, but with a much smaller volume change, after compression at the low temperature, indicating a probable mixture of phases at the maximum available pressure of 21 000 atmos.

The actual specific volumes shown in Fig. 3 are the result of some rather arbitrary adjustments in the initial volumes of the samples. Because of the "room temperature" transitions, it is not too surprising that the specific volumes computed from actual measurements on the samples did not agree; in fact, a room temperature volume becomes rather meaningless unless it is measured after some standardized thermal treatment. For this reason, the specific volumes were forced to agree at 315°K and 2600 atmos, well away from any transitions. This adjustment constituted a linear translation of the sample *A* volume curves and resulted in nearly perfect agreement between the two samples. Zero pressure volumes were computed from the standardized density as measured in the du Pont laboratories and separate thermal expansion measurements. Hence, the final computed volumes all result from extrapolation to zero pressure of the higher pressure values.

There is some additional uncertainty in the volumes indicated for the lower temperatures. Because of the rapid increase in the yield strength of Teflon with decreasing temperatures below 170°K,[10] the requirement that the sample be plastic is probably not met below that temperature. The error introduced should not be large, particularly at the higher pressures, and the general trend of the isobars is probably correct.

DISCUSSION

The complicated thermal behavior of Teflon is already evident from the many conflicting results and

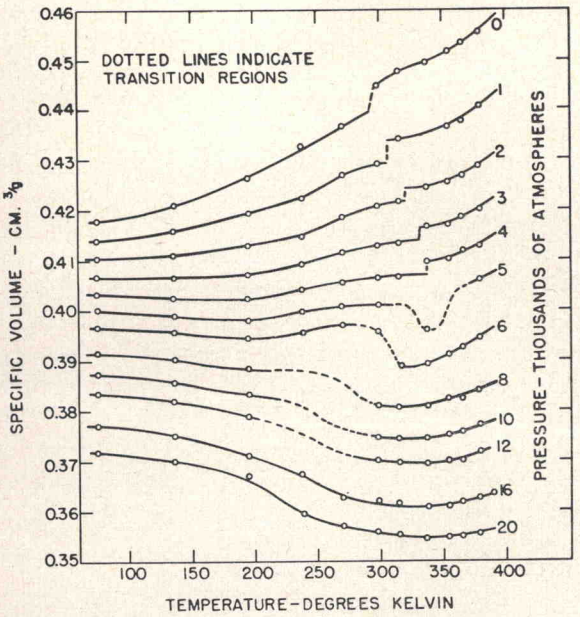

FIG. 3. Teflon volume-temperature isobars, computed from isothermal compression measurements. The apparent negative expansion at high pressures is believed to be due to an incomplete transition, so that the curves do not represent true equilibrium values for high pressures and low temperatures.

opinions appearing in the literature. The broad outline of the different phases seems quite well established, but the details and the nature of the transitions are still open to question.

A part of the confusion is no doubt due to differences in the samples used in various experiments. It is well known, and not surprising, that the properties of Teflon are strongly dependent on the degree of crystallinity, which can vary over a wide range. Crystallinity is determined by the molecular weight and the cooling rate from the "melting" temperature, and is apparently not altered by any process carried out below that temperature. However, the results of any experiment involving temperatures above about 300°C can be altered by changing the cooling rate from that temperature.

In addition to this influence of annealing on the degree of crystallinity, there are other strong time effects that make the transition parameters, in particular, even more ambiguous. Quinn, Roberts, and Work[3] noted the change in the width of the temperature hysteresis in the room temperature transitions with the rate of temperature change, and the very long time required for volume equilibrium to be reached after rapid cooling into the transition region. In calorimetric studies, Furukawa, McCoskey, and King[9] observed slow thermal drifts in this region. In the present pressure experiments, time effects were constantly noted; in the transition regions, the first sudden change in sample length with a change of pressure was followed by a slow creep. In order to limit the time involved in a run to a practical value, the usual procedure in such cases was to take dial gauge readings at one minute intervals. If no change could be observed in one minute, that reading was taken as the proper value and the pressure again changed. It is probable that the sharpness of the transitions would have been increased if a longer time were allowed for equilibrium to be established. Some indication of this was observed when the pressure was changed in smaller increments than usual. A longer time was then required for a given pressure change, and the transitions appeared somewhat sharper.

Noticeable creep of the dial gauge was not, in general, observed without some other evidence of a transition. However, there were a number of isolated instances of creep, with the resulting apparent length only a few microns off the smooth length *vs* pressure curve. It is reasonable to suppose that such time-dependent discontinuities in the compression are the result of transitions in small portions of the sample which did not change phase with the rest of it, either because of pressure differences (e.g., a "pocket" kept at lower pressure by the transition to a high density phase of the surrounding material) or because the transition was otherwise inhibited.

The dual structure of Teflon suggests a possible explanation of this and some other transition phenomena. The amorphous part of the material is apparently composed of those portions of the long, helical chain molecules common to two or more crystallites. X-ray studies of the room temperature transitions[2] show that the rearrangement consists of a partial uncoiling of the molecules, from 180° of twist per 13 (CF_2) groups to 180° of twist per 15 groups. Such a change must involve not only the crystallites, but the amorphous phase as well. One might picture a viscosity effect inhibiting the necessary rotation of the amorphous molecules, thus adding a strongly temperature- and pressure-dependent influence on the rate of transition.

The second "room temperature" transition has been a particularly confusing subject, and the data were carefully studied for any evidence of another first order transition at low pressures. No such evidence was found, although the low pressure experiments should have revealed a volume discontinuity of 0.2% (0.0008 cm^3/g) at any pressure over 300 atmos.

As a further check on this transition, the atmospheric pressure thermal expansion was measured from the ice point to 370°K. This was a simple linear expansion measurement on a rod 24.3 mm long, using the fused-quartz tube and dial indicator method.[19] Heating and cooling was at an average, but not constant, rate of 0.2 deg/hr, with a maximum of 0.6 deg/hr. As may be seen in Fig. 4, the only indication of a second transition to be found in the resulting data is an abrupt change in the slope of the expansion curve at 305°K, instead of the volume discontinuity reported by Quinn *et al.*[3] The smallest division on the dial indicator used for these

[19] Natl. Bur. Standards Circ. **No. 486**, 5 (1950).

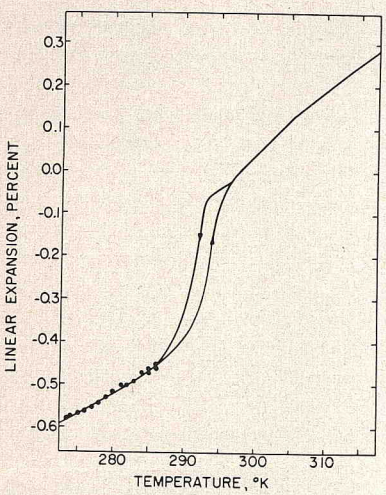

FIG. 4. Linear thermal expansion of Teflon in the transition region. Points are shown only for the lowest temperatures, where the maximum scatter occured. The expansion is expressed as percent of the measured length at 298°K. Measurements were made with an average, but not constant, temperature change of 0.2 deg/hr, with a maximum of 0.6 deg/hr.

measurements was 0.002 mm, and readings were estimated to $\frac{1}{10}$ division. The maximum scatter was less than 0.005 mm, so a discontinuity in length as small as 0.05% would have been easily detected. It is possible for Teflon to be anisotropic in the extruded form, a factor which would explain the difference between the values for ΔV_{I-II} as obtained from the pressure measurements and as calculated from the single linear thermal expansion measurements. Anisotropy could also possibly mask the second room temperature transition in the thermal expansion measurements, although not in the pressure measurements where it should have been seen.

It is apparent from zero pressure data that there is some modification of the structure of Teflon at about 300° to 305°K, but from the pressure results and other evidence in the literature there is some doubt that it is a true first-order transition. It seems more likely that this temperature marks the beginning of some type of dynamic disorder similar to that occuring in amorphous polymers at the transition point. This view is supported by the stress relaxation experiments of Nagamatsu, Yoshitomi, and Takemoto,[20] who found an activation energy peak at 298°K of the type which is characteristic of such second-order transitions, and by the x-ray studies, which indicate gradually increasing disorder above this temperature.

The effect of crystallinity on the transitions and x-ray studies at elevated pressures should provide interesting additional information about the complex behavior in this temperature region.

ACKNOWLEDGMENTS

The authors are indebted to E. I. du Pont de Nemours & Company for providing the sample, and they particularly wish to express their appreciation to Dr. M. I. Bro, who graciously provided the sample analysis and much of the available literature on the properties of Teflon.

[20] Nagamatsu, Yoshitomi, and Takemoto, J. Colloid Sci. **13**, 257 (1958).