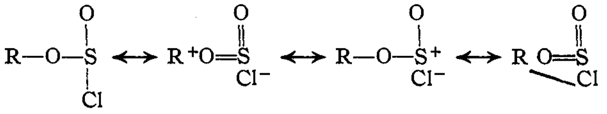
action is much slower in the latter solvent. While it is not possible to say that the reaction to give retention of configuration is absent in isoöctane, it is certainly much slower in this solvent than in dioxane. If the reaction does indeed go by the mechanism of Hughes and Ingold,[5] then the reduction in rate on changing to the less polar solvent (unless due to a specific solvent effect) implies that the transition state has a higher dipole moment than the normal chlorosulfite, and contributions to the transition state from structures II and III



$$\mathrm{R{-}O{-}\underset{\underset{Cl}{|}}{\overset{\overset{O}{|}}{S}} \longleftrightarrow R^{+}O{=}\overset{\overset{O}{\|}}{S}\ Cl^{-} \longleftrightarrow R{-}O{-}\overset{\overset{O}{|}}{S}{}^{+}\ Cl^{-} \longleftrightarrow R\ O{=}\overset{\overset{O}{\|}}{S}{-}Cl}$$

I II III IV

as well as I and IV should be considered. This view is consistent with the very rapid reaction of thionyl chloride with phenylcarbinols,[13] because of the further stabilization of structure II, and also with the apparent instability of chlorosulfites from tertiary alcohols, indicated by failures to obtain these compounds. We have not shown rigorously that the reaction is independent of impurities in the dioxane or isoöctane, but the careful purification of the dioxane coupled with reproducibility of rates using different batches indicates that the effect of impurities in this notoriously impure solvent is not large; the isoöctane was probably quite pure but our investigations were more limited than in dioxane, and we believe that the reproducibility of rates in this solvent may have been due partly to a reproducibility of experimental conditions, and may be influenced by factors such as surface or impurities.

In order to make sure that the reaction of *d*-2-octyl chlorosulfite in dioxane was not one of the anomalous second-order reactions previously noted, the disappearance of chlorosulfite was followed spectrophotometrically although the concentration was twenty to fifty times that used in the other kinetic runs. The similarity of rate constant as well as the observed first-order kinetics under these conditions confirms the unimolecular nature of the reaction in this solvent.

It can therefore be concluded that there is a first-order reaction of secondary alkyl chlorosulfites which goes with retention of configuration, but that this will occur only in favorable environments. In other environments inversion may predominate.

HOUSTON, TEXAS RECEIVED JULY 2, 1951

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

The Development of Crystallinity in Polychlorotrifluoroethylene

BY FRASER P. PRICE

Polychlorotrifluoroethylene on cooling from above its first-order transition point (205–210°) develops crystalline regions in the form of spherulites. The development of this crystallinity is accompanied by an increase in dielectric constant and loss, tensile strength, opacity and density. Spherulites appear only on cooling from above the melting point. Their growth rates are linear with time and depend on the growing temperature and the viscosity of the melt. Between 175–190° the number of spherulites does not increase with time and is determined by the highest temperature above the melting point to which the sheet was heated. Below 175° the number increases with time. These facts indicate heterogeneous nucleation above 175° and heterogeneous plus homogeneous nucleation below 175°. A sheet quenched to room temperature from above its melting point develops evidence of crystallinity only very slowly when heated to 150–190°. This is due to the very slow coalescing of microcrystalline regions to produce the gross effects of crystallinity. Density measurements have been made from 15–230° and thermal expansion coefficients calculated. It is proposed that spherulite growth is a consequence of the long chain structure of high polymers and that all crystallizable polymers will show this growth under the correct conditions.

Introduction

Crystalline regions in an amorphous polymer matrix are known to have profound effects on the mechanical, electrical and optical properties of the polymer mass.[1] This paper describes an investigation of the development of crystallinity in polychlorotrifluoroethylene and some of the effects of this crystallinity on the electrical, mechanical and thermodynamic properties of the polymer.

Microscopic study of a sheet of polychlorotrifluoroethylene cooling slowly from 250° reveals the growing spherulitic structures shown in Fig. 1. While similar type structures have been observed in polyethylene,[2] polyurethan[3] and polyamides,[4] it is believed that this is the first time that such well-defined structures in an organic high polymer have been observed and their behavior described.

Materials and Procedures

Polychlorotrifluoroethylene was obtained from the M. W. Kellogg Company under the trade name, KelF. Samples of two grades, KelF NST 300 (KelF Hi) and KelF NST 240 (KelF Lo), were used throughout this study. The former had a specific viscosity in a 1% solution at 140° in dichlorobenzyltrifluoride of 2.24, the latter had a specific viscosity under the same conditions of 0.86. The 15-mil sheets of polymer used in this investigation were obtained by pressing the white granular powder at 260° and 1000 p.s.i.

This polymer has a transition point analogous to a melting point, which it will henceforth be called, at about 210°. This is evidenced by a change from a bright to a completely dark field when observed between crossed Nicols under the microscope and by abrupt changes in electrical and thermodynamic properties.

The apparatus used to prepare samples for microscopic examination consisted of a tube oven, with its axis vertical, mounted over a silicone oil-bath. The oven temperature, T_1, constant to ±1°, was above the polymer melting point, while the bath temperature, T_2, was below the melting point and was held constant to ±0.2°. The polymer sheet,

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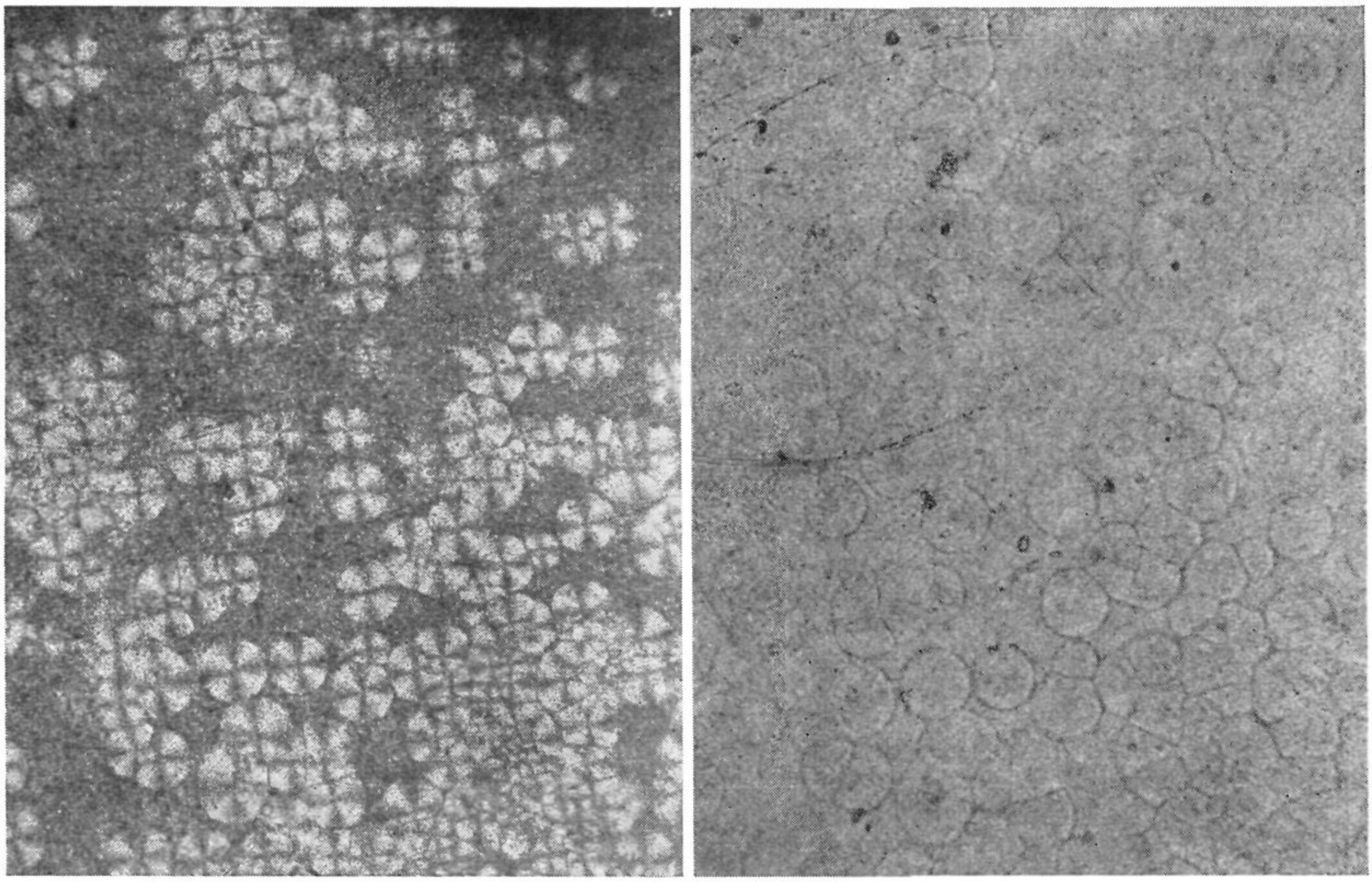
(1) T. Alfrey, Jr., "Mechanical Behavior of High Polymers," Interscience Publishers, Inc., New York, N. Y., 1948; R. E. Reinhardt, *Ind. Eng. Chem.*, **35**, 422 (1943).

(2) C. W. Bunn and T. C. Alcock, *Trans. Faraday Soc.*, **41**, 317 (1945).

(3) Von E. Jenckel and H. Wilsing, *Z. Elektrochem.*, **53**, 4 (1949).

(4) R. Gabler, *Naturwissenschaften*, **35**, 284 (1948).



(a) (b)

Fig. 1.—Spherulites in polychlorotrifluoroethylene: (a) with crossed Nicols; (b) without crossed Nicols; field 2.3 mm. × 1.7 mm.

a 1″ square mounted between $^1/_{32}$″ aluminum sheets, was suspended in the center of the oven for a predetermined length of time and then suddenly dropped through the open bottom of the oven into the oil-bath. Here it remained for a length of time sufficient to grow the spherulites to the desired size. They were then frozen in by suddenly quenching the sandwich in cold water. Both quenching operations required less than two seconds. In this manner it was possible to vary independently, T_2, time at T_2, T_1 and time at T_1. The sheets of polymer were then wiped clean of silicone oil and water before microscopic observation and measurement. The spherulites in five fields of the microscope were counted and with knowledge of the area of the field and the thickness of the sample, the number per cubic millimeter was computed. The average diameter of the spherulites was obtained by using a micrometer eyepiece and measuring fifty spherulites picked at random. In most cases the size distribution was extremely sharp. Only at 170° did the distribution become so broad as to cast doubt on the procedure of calculating the average diameter as $\Sigma n_i d_i/\Sigma n_i$, where n_i = number of spherulites of diameter, d_i, for only fifty particles.

Investigation of the tensile strength of this polymer was made on a conventional tensile machine with a jaw travel of about 0.1″ per minute. Dumbells of $^1/_4$″ width of neck and about 2″ length of neck were cut from sheets prepared in the manner indicated below.

The dielectric constant and loss at elevated temperatures were measured using a General Radio capacitance bridge. A 15-mil sheet of polymer was placed in a guarded cell in an oven whose temperature was regulated to ±2° and the electrical properties measured at various temperatures. Measurements were made with the temperature rising or falling at about 1°/min.

Time-lapse motion pictures of spherulite growth were taken with a 16-mm. Bell and Howell "Filmo" camera. A special hot stage was constructed of a piece of 10-mil platinum sheet about $^3/_8$″ wide in which a $^1/_{16}$″ hole was drilled. This was mounted on the microscope stage between crossed Nicols. The platinum strip was heated electrically and its temperature measured by a platinum-rhodium thermocouple welded to it. A 10-mil sheet of polymer was placed over the hole in this heater and heated and cooled as desired. Heating and cooling were very rapid. Motion pictures were taken under a variety of conditions at a speed of a frame per second with and without crossed Nicols.

Because this polymer loses small unweighable amounts of gas at elevated temperatures, a weighing-immersion method rather than a dilatometric one was chosen to measure densities. A modified analytical balance was mounted above a silicone oil thermostat containing a vessel in which the polymer specimens were hung. The thermostat temperature was controlled to ±0.1° and the immersion vessel had a long finger in its bottom containing silicone oil. The samples, stacks of $^1/_{16}$″ sheets about 1″ by $^1/_2$″ weighing approximately 15 g., were hung on small 10-mil tungsten wire stirrups above the silicone oil in the immersion vessel. Measurements were made by attaching the polymer to the balance with a 2-mil tungsten wire and weighing in the silicone oil, the density of which was determined at each temperature by weighing a quartz bob of known density in the oil. Measurements were made only after the samples had been at temperature for at least two hours.

For density measurements in the range of 15 to 55° conventional dilatometers of the sealed-off type[5] were used. In these dilatometers the polymer was in the form of stacks of $^1/_{16}$″ thick discs. Ethyl alcohol of determined volume coefficient of thermal expansion was used as a filling liquid.

The short investigation of crystallinity in this polymer that was carried out with X-rays was done with a Philips Geiger counter X-ray spectrometer. Copper Kα, nickel-filtered radiation was used. Rapid traces of scattered intensity *versus* angle were run so that these examinations were very cursory. However, it is believed that the results have sufficient precision to justify the qualitative conclusions drawn from them.

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(5) N. Bekkedahl, *J. Research Natl. Bur. Standards*, **42**, 145 (1949).

Results and Discussion

The structures shown in Fig. 1 are truly spheres for, in addition to their having the same vertical and horizontal dimensions, if they were flat discs some would appear as ellipses or rods. The photomicrographs show that the well-defined boundaries between crystalline and non-crystalline regions are discernible even with unpolarized light. The pictures also show that when two spherulites meet, the boundary between them remains. A sample which is completely filled with spherulites has the close-packed structure shown in the lower right-hand corner of Fig. 1a and 1b. This is the same pattern observed by other investigators and correctly attributed to spherulitic structure. The black cross in the center of each sphere in Fig. 1a results from its behaving like a group of close-packed anisotropic crystals all radiating from a common point and, therefore, there are four regions at or near extinction.

Spherulite Nucleation and Growth.—The effect of varying growing temperature, T_2, on number and size of spherulites in sheets held at 268–270° for 10 minutes before quenching is shown in Fig. 2.

The deviations of the number densities are large because measurements were made on different sheets and by counts of only five fields. However, there was no trend in number density with time. In the sheets containing the largest spherulites, overlapping was so extensive that counts could not be made. There is a definite trend toward fewer spherulites as the growth temperature is raised and at 195° none appear in one-half hour. No average is given for the 170° run because (a) the number density increased from 228/mm.^{3} at 1.5 min. to 499/mm.^{3} at 3.0 minutes, and (b) evidence presented below supports the conclusion that the spherulites are being born at later and later dates.

Measurements made on sheets of KelF Lo gave growth rates of 1.7, 2.7 and 12.4 μ/min. at 195, 190 and 185°, respectively. These rates are consistently higher at a given temperature than those shown in Fig. 2. The data presented immediately above and those in Fig. 2 show an increasing growth rate with decreasing temperature. However, below 150°, spherulites never appear and the samples remain isotropic. Hence somewhere between 170 and 150° the growth rate must fall to zero. The fact that the diameter depends linearly on time indicates that the growth process is not diffusion controlled for if it were the dependence should be on the square root of time.[6] The observed dependence on time implies a constant velocity of material transport per unit area across the spherulite boundary. This is typical of crystallization from melts where the rate is not diffusion controlled.

The low molecular weight polychlorotrifluoroethylene consistently shows higher growth rates than does the high molecular weight material. This is probably the result of a lower viscosity of the former with consequent greater mobility of the crystallizing molecules. This higher growth rate gives the impression of more spherulites per unit volume in the low molecular weight polymer. However, a particle count on a sheet heated 10 minutes at 269° and then held 1.5 minutes at 185° gave 224 particles/mm.^{3} Thus, the numbers of spherulites in both high and low molecular weight samples are practically identical.

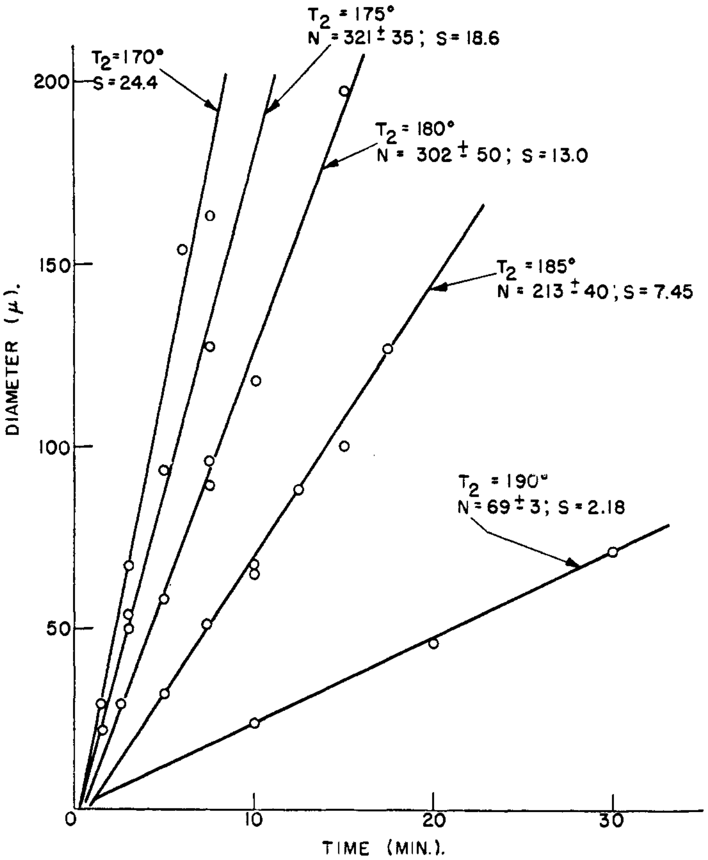

Fig. 2.—Spherulite growth in KelF Hi; 10 min. at T_1 = 270°; N = number density (mm.$^{-3}$); S = growth rate (μ × min.$^{-1}$).

At 175° and above, the number density of the spherulites is constant and the size distributions are extremely sharp. At 170° the number density becomes greater and the size distribution becomes much broader with increasing time. These facts indicate that at 175° and above, all the spherulites are born at the same time, while at 170° and presumably below, they are born at later and later times.

The effect of varying the upper temperature, T_1, was next investigated. Sheets were held for ten minutes at various upper temperatures and then quenched to 185° for five minutes. When T_1 was 274, 260 and 251°, the spherulite number densities were 209/mm.^{3}, 225/mm.^{3} and 712/mm.^{3}, respectively, while the corresponding diameters were 28.2, 26.2 and 26.1 μ. When T_1 was 240°, spherulites were too numerous to count. Thus, the growth rate is determined predominantly by the growth temperature, while T_1 determines the number den-

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(6) F. C. Frank, *Proc. Roy. Soc.*, **A201**, 586 (1950).

sity. The small increase in growth rate with increasing T_1 is probably due to degradation of the polymer.

The effect of increasing time at the upper temperature was studied by holding the sheets at 270° for varying times and quenching to 180° for 7.5 min. As the time at T_1 was increased from 10 to 20 min., the average spherulite diameter increased from 96.7 to 111.7 μ, while the number density did not change. Here again, the rate is controlled predominantly by T_2 but there is evidence of a secondary effect of degradation of the polymer by prolonged heating at T_1 producing larger growth rates.

Another piece of evidence germane to the problem of crystallization in polychlorotrifluoroethylene is the following: A sample was heated to 269° for 10 minutes and then slowly cooled to 220° and held for 1.5 hours. Upon quenching to 185° it was found that the number density of spherulites corresponded to that expected from a 269° quench. Thus, the number of spherulites is determined by the highest temperature to which the sample is heated provided that this temperature is above the melting point, and that the growing temperature is between 190–175°. This happens even though the sample might be held for prolonged lengths of time at a lower temperature, still above the melting point. This behavior is explicable on the basis of a theory of Turnbull[7] for thermal history sensitive nucleation in metallic melts.

The theory briefly is this: It assumes that the melt contains foreign impurities (heterogeneities) which have submicroscopic cracks and crevices in them. Below the melting point these cracks are filled with crystalline material. If the crystalline material wets the surface of the heterogeneity, a higher temperature than the bulk melting point is required to melt the crystals in the cracks. The height of this temperature above the melting point depends on the curvature and size of the cracks and the interfacial tension. Thus, as the temperature is raised, more and more of the crystals in the cracks are melted. Now, if the temperature is lowered but not to the melting point, the cracks in which the crystals have completely melted will not fill with crystals again, because to the molecules which come in contact with the crack wall it appears as a plane surface. Thus, cooling to slightly above the melting point does not reconstitute those crystalline regions which have been melted. Upon cooling below the melting point, if the bulk of the liquid will supercool, the points of nucleation are those cracks containing crystalline material which has not been melted by the highest temperature attained in the given experiment. If, as the theory implies, all the crystalline regions start on heterogeneities in the melt, then it would be expected that spherulites would appear time after time at the same points in the polymer mass. In order to check this, a time lapse motion picture was made of spherulites growing at 180° after quenching from 280°. After the sample was completely filled with spherulites, it was then melted by heating for five minutes at 280° and another motion picture taken after it had been quenched to 180° again. Transparent prints were made of single frames of the two motion pictures after about five minutes at 180°. These prints when superposed showed that out of the 19 spherulites in the second print, 18 appeared in exactly the same position in the first print. The extra one in the second print was well removed from the other spherulites. The fact that sensibly all the spherulites appeared in exactly the same position in the two cases shows conclusively that they were heterogeneously nucleated, and that they did not start as the result of random fluctuations of order at 180° or from incomplete destruction of order on melting. Thus, between 175 and 190° the spherulites are heterogeneously nucleated. The decreasing number of spherulites, as the growth temperature is raised, is probably due to some of the crystal-filled cracks being too small to function as nuclei above a certain temperature.

A short, rather cursory, investigation of these spherulites using the X-ray was next undertaken. It was found that quenching from above the melting point to room temperature produced samples which showed no marked peaks, only a broad amorphous band in the region of 10–20° scattering angle. Samples in which spherulites had been grown showed a group of sharp peaks around 16°. When the heights of these peaks were measured for various samples, it was found that they developed very much more rapidly than the volume of crystallinity indicated by the spherulite growth rates. Samples in which the spherulites constituted only 1% of the volume had peaks which were 90% as high as those of samples completely filled with spherulites. Further, since there was no observable difference in peak position between the two cases, the spacings in the crystalline regions in the two cases must have been the same. Therefore, there is an ordering process, detectable by X-rays, which develops much more rapidly than do the spherulites. The most probable reason that this rapid process is not easily detectable by the polarizing microscope is that the crystalline regions are randomly oriented and too small (*ca.* 500–1000 Å.) to scatter the polarized light appreciably. Close examination of the time-lapse motion pictures shows that, with crossed Nicols, near the start an over-all grayness develops suddenly from the completely dark background and that the spherulites appear much more slowly out of this generally gray field. Very probably the sudden appearance of this grayness corresponds to the development of the X-ray crystallinity. Tiny crystalline regions were postulated by Jenkel and Wilsing[3] to explain the results of thermal investigation of polyurethans.

In summary, then, the crystallization of polychlorotrifluoroethylene has the following characteristics: (1) As the melt is cooled below the melting point, very small randomly oriented regions of crystallinity develop rapidly.

(2) These small crystalline regions then transform into spherulites at a much slower rate. If the temperature is between 175 and 190° the spherulites are heterogeneously nucleated. At 170°, and presumably below, the spherulites are both heterogeneously and homogeneously nucleated. By the latter is

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(7) D. Turnbull, *J. Chem. Phys.*, **18**, 198 (1950).

meant that they can start in the bulk phase as the result of random fluctuations of order and do not require a heterogeneity for initiation. This is shown by the broadening of the size distribution and by the rapid increase in their number density at 170°.

(3) The growth rate is determined by the temperature and the viscosity of the melt from which the spherulites are growing. In the temperature range between 170° and the melting point the growth rate increases with decreasing temperature. However, since at 150° the rate has fallen to zero, there must be a maximum somewhere between.

(4) In the temperature range of 175–190° the number of spherulites is determined by the highest temperature above the melting point to which the polymer was heated. Below 170° more and more appear as time goes on.

The growth of spherulitic structures has been observed and described in selenium,[8] a polymeric substance. Similar structures have been observed in a variety of linear organic polymers[2,3,4] and it is known that graphite (a type of two-dimensional polymer) in cast iron will, under certain conditions, form spherulites. Even the low molecular weight substances which form spherulites[9] are materials which can form hydrogen-bonded chains. Therefore, it is profitable to speculate as to whether all crystallizable long chain polymers will produce spherulites under the proper conditions.

The hexagonal planes in graphite spherulites and the long chains in polyethylene[2] spherulites are normal to the radii. The hexagonal planes of the graphite may be considered the two dimensional analog of the linear polyethylene. In graphite the slowest direction of growth is normal to the hexagonal planes and hence this slow rate would be that observed for spherulite growth. It is reasonable to expect a similar situation in polyethylene and other polymers as the chains, lined up perpendicular to the face of a crystal, are already quite well aligned where they project from the crystal into the amorphous region. Thus less energy would be required to align these projecting segments than would be necessary to incorporate a new molecule into another crystal face. Since spherulites form only under conditions of considerable supercooling, the differences in growth rates from different crystal faces will be large. Thus when a number of crystallites start to grow out from some center (heterogeneity), if their direction of slow growth is radial, the spaces between these crystallites will fill in very rapidly and a sphere will be formed. The rapid tangential growth produces in the sphere the wedge-shaped regions clearly shown in the pictures of selenium spherulites.[8] Any crystallite which does not have the proper orientation with respect to the spherulite radius will grow into a very thin plate or needle and become unobservable.

If a polymer sample has a very wide molecular weight distribution, then some of its very low molecular weight material may not be able to crystallize. Thus, when the crystallites start to grow they may not be able to fill in the space between them to form spheres due to increased local concentration of the low molecular weight material. In this case a burr-like structure will be produced. This has been observed in a sample of polychlorotrifluoroethylene which had a wide molecular weight distribution as judged by a wide melting range. Similar structures ought to be observed in plasticized crystallizable polymers.

The simultaneous nucleation of a number of crystallites of the correct orientation from a single heterogeneity is easy to envision. However, since at 170° and below in polychlorotrifluoroethylene spherulites appear at later and later dates, there must be some process of homogeneous nucleation. The explanation of this process is found in the rapid development of the microcrystals shown by the X-ray. If a small temperature fluctuation starts some of these growing in a minute region then those which have their rapid growth direction normal to radii from some point will develop into spherulites. The others will grow very rapidly into very thin needles or plates and disappear.

Therefore, the conditions for spherulite growth are: (1) Formation of nuclei which are, or which can transform into, a number of crystalline regions radiating from a common center. (2) Growth conditions such that growth from at least one crystal face is much slower than from other faces. This may facilitate the transformation mentioned in 1 above.

Linear high polymers have properties which satisfy both conditions 1 and 2 above and, therefore, it is probable that all crystallizable polymers will transform into spherulite structures under proper conditions.

All the results presented above were obtained in sheets which had been quenched to the crystallization temperature from above their melting points. However, if a sample is quenched to room temperature from above its melting point and subsequently heated to 170–190°, no spherulites appear, and the sample remains unchanged in appearance. It still has the high transparency and relatively good flexibility it had before heating and the X-ray shows no sharpening of the group of 16° peaks. A very similar type of behavior has been observed in linear polyamides.[10] The only reasonable explanation of this state of affairs is that the quenching to room temperature produces an amorphous material in which on heating again extremely large numbers of nuclei appear. These nuclei are so numerous that the sample rapidly acquires very nearly the equilibrium amount of crystallinity, but the crystalline regions are so small that they cannot scatter much light nor be detected by the X-rays. Since the crystallites have a higher density than the amorphous matrix, when they form they must leave voids in the matrix for the density is less than that corresponding to equilibrium. These microcrystalline regions transform only very slowly by solution, and redeposition into larger blocks which can be detected by the X-ray.

Density Measurements.—Density measurements were made on the polymers used in the

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[8] G. Borelius, *et al.*, *Arkiv För Fysik*, **1**, 305 (1949).

[9] E. M. Chamot and C. W. Mason, Vol. I, "Handbook of Chemical Microscopy," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 335.

[10] C. S. Fuller, W. O. Baker and N. R. Pape, THIS JOURNAL, **62**, 3275 (1940).

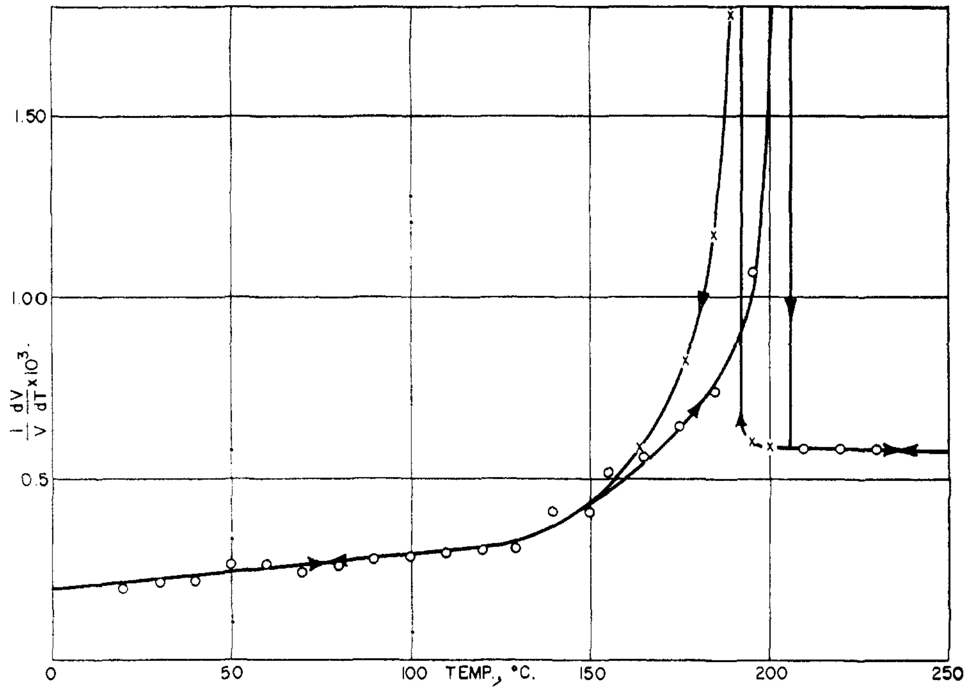

Fig. 3.—Coefficient of thermal expansion of polychlorotrifluoroethylene with rising and falling temperature.

preceding experiments in addition to some of intermediate molecular weight. The weighing technique was used in the range 40–230° and the dilatometer technique from 15–55°. While with any given sample the density at a given temperature could be reproduced to 0.05%, there was about a 1% spread between different samples of the same polymer measured at the same temperature after the same treatment. This was probably due to irreproducibility in pressing sheets. The differences among samples of various molecular weights were within this 1% spread and hence no significant effect of molecular weight on density was observed. In spite of this irreproducibility in absolute density, measurements made with temperature rising and falling showed strictly parallel curves for all the samples. Thus, the coefficient of thermal expansion was the same for all of these. A plot of this coefficient from 20 to 230° is shown in Fig. 3. It can be seen that below 150° the ascending and descending temperature curves superpose indicating that equilibrium has been attained although abnormal behavior is indicated by the curvature above 135°. Between 150 and 205° they do not coincide indicating non-attainment of equilibrium and above 205°, in the melted state, attainment of equilibrium is again very rapid. The hysteresis shown by the non-coincidence of melting and freezing points is also exhibited by the electrical properties described below. The departure from linearity above 135° on the ascending temperature curve indicates a type of premelting postulated by others.[11,12] As might be expected the coefficient of expansion behaves much like other derivative thermodynamic properties such as the heat capacity.[12]

In the region of 0 to 130° and 195 to 230° the coefficient of expansion for the solid and liquid forms, respectively, are linear in temperature and can be expressed by the equations

$$\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}T} = 1.96 \times 10^{-4} + 9.46 \times 10^{-7}T$$

For crystallized material (1)

$$\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}T} = 6.45 \times 10^{-4} - 2.9 \times 10^{-8}T$$

For liquid (2)

where V is the volume and T the temperature. Since the coefficient of expansion of the liquid is greater than that of the crystallized form and since the liquid is the less dense there must be a temperature at which the extrapolated density of the liquid is the same as that of the crystallized material. The average density of several samples of different molecular weights at 100° is 2.19 g./cc. and at 220°, 1.94 g./cc. With these figures and equations 1 and 2, it is possible to calculate that at 4° the density of the liquid should be equal to that of the crystals. In view of the length of the liquid extrapolation it probably would be better to say that this temperature of equal densities is somewhat below room temperature. This shows that differences in density at room temperature cannot be used as a measure of the extent of crystallinity in this polymer. Also, since only very rarely does the density of a liquid exceed that of its solid at the same temperature and since this polymer is flexible at room temperature, it is extremely probable that the second-order transition is slightly below room temperature.[13]

None of the optical or X-ray experiments performed on this polymer gave any marked indication that crystallization could occur in sheets quenched to room temperature from above the melting point,

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(11) P. J. Flory, *et al.*, *J. Chem. Phys.*, **17**, 223 (1949); THIS JOURNAL, **72**, 2018 (1950).

(12) H. C. Raine, R. B. Richards and H. Ryder, *Trans. Faraday Soc.*, **41**, 56 (1945).

(13) W. Kauzmann, *Chem. Revs.*, **43**, 219 (1948).

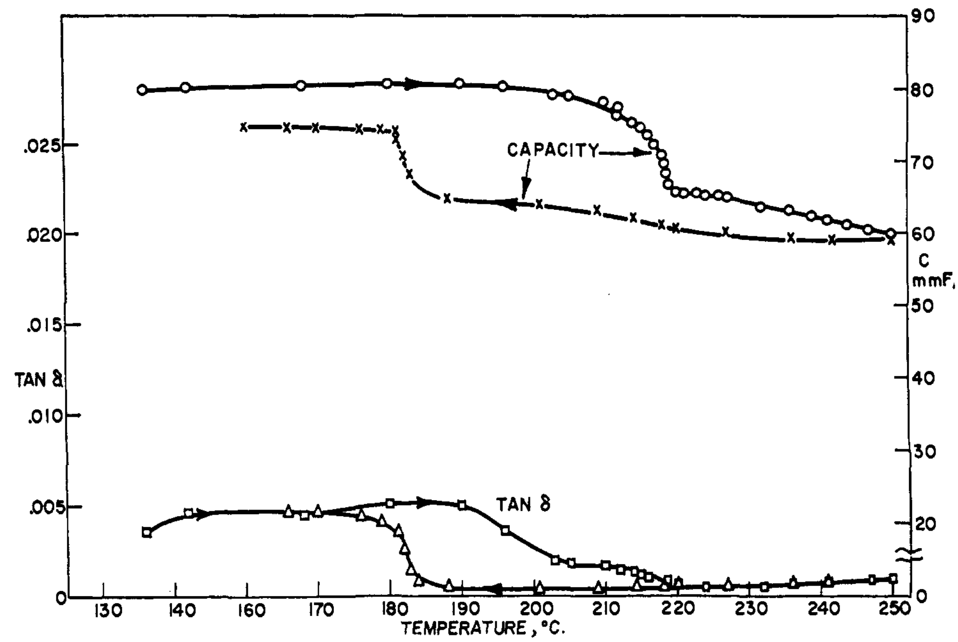

Fig. 4.—Dielectric constant and loss at 10 kc. in polychlorotrifluoroethylene with rising and falling temperature.

and then heated to between 150 and 190°. Density experiments demonstrated, however, that sheets quenched to room temperature when heated to 150 or 180° increased in density to the equilibrium value very slowly over a period of about 50 hours. Thus, whereas, on cooling slowly crystallinity develops at a rapid rate, when the temperature of an amorphous sheet is raised the process is very much slower.[10] This is probably due to the rapid growth of many microcrystalline regions which melt and recrystallize to give the maximum density. The solution is the slow rate-controlling step.

Influence of Crystallinity on Mechanical Properties.—A sheet of polychlorotrifluoroethylene quenched from above its melting point to room temperature is transparent and quite flexible and tough. It contains no spherulites and shows an amorphous pattern with X-rays. A sheet which contains many spherulites, however, is translucent, brittle and stronger under tension than the quenched sheet.

Long-elongation curves were obtained for the dumbbell specimens described above. The yield points for samples which had been treated in the indicated manner are presented in Table I.

TABLE I

YIELD POINTS OF SAMPLE UNDER TENSION

T_1 = 265–270°, 10 min. at T_1

Sample	Treatment after holding at T_1	Yield point (lb./in.^{2}) $\times 10^{-3}$
A	Quench to room temperature	2.9
B	Quench to 185°, hold 20 min., quench to room temperature	4.7
C	Quench to room temperature, heat 20 min. at 185°, quench to room temperature	3.1

The results show a marked increase in yield point with increased spherulite formation. Reheating the quenched sheet produced very little change. This is probably due to the presence of the many microcrystalline regions in the amorphous matrix. These would have a relatively small effect on the rheological properties of the matrix compared to the effect of the much larger spherulites.

There was one marked difference between Samples A and C. Sample C showed extensive crazing in the unnecked portion of the dumbbell. This was shown by neither A nor B. The craze marks were small surface cracks about 3 μ wide and 50 μ long all with the long axis perpendicular to the direction of stress. This produced an opalescence in the neck of C when viewed at certain angles with respect to the incident light.

Effect of Crystallinity on Dielectric Properties.—The capacity and loss at 10 kc. of a condenser filled with polychlorotrifluoroethylene as a function of rising and falling temperature are given in Fig. 4. The capacity is a direct measure of the dielectric constant.

The plots show that: (1) On heating, the dielectric constant drops to a fairly constant value between 200 and 210°, but on cooling the low temperature value is not attained until about 185°. The 19% difference in dielectric constant between these two temperatures is not due to a density change, which is only 8%. It must be due to an orientation of dipoles in the crystalline material. (2) The broad loss peak at about 190° observed on heating the crystallized sheet does not reappear on cooling until about 185°. This shows conclusively that this loss region is associated with spherulite formation. There is another much larger loss region below 100° at 10 kc. which is associated with the usual dipolar motion in the liquid phase.

The dielectric properties described show the same hysteresis as do the density and the appearance and disappearance of spherulites, and they all occur over the same temperature range. There can be no doubt that the profound changes in dielectric constant and loss are associated with the appearance or disappearance of crystallinity.

A much more comprehensive investigation of the electrical properties of the low molecular weight forms of these polymer has been carried out by other investigators in this Laboratory. Part of this has already been published,[14] and the reader is referred to this for a more detailed explanation of the electrical effects of the processes involved.

Acknowledgment.—The author wishes to express his grateful appreciation to the following: Mr. R. P. Carreker for tensile measurements, Mr. R. Cech for aid in taking motion pictures, Mr. S. I. Reynolds and Miss V. G. Thomas for the electrical measurements, and to Dr. A. M. Bueche for much helpful discussion during the course of the investigation.

SCHENECTADY, N. Y. RECEIVED APRIL 18, 1951

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[14] S. I. Reynolds, V. Thomas, R. M. Fuoss and A. H. Sharbaugh, THIS JOURNAL, **73**, 3714 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Evidence on the Elementary Reactions of Halogens Activated by Radiative Neutron Capture in Ethyl Halides and in Hydrocarbons[1]

BY SULAMITH GOLDHABER AND JOHN E. WILLARD

The organic yields (*i.e.*, fraction of nuclear events resulting in organic compound formation) of the radiative neutron capture reactions of the halogens in purified ethyl halides have been determined in the liquid and solid state, in the presence of scavengers for thermal atoms, and in hydrocarbon solvents. Among the important results are: (1) both the organic and inorganic yields of the bromide (and possibly also the iodide and chloride) are due in part to hot processes and in part to thermal processes; (2) the organic yields decrease in the order iodide, bromide, chloride; (3) the organic yields of the bromide and iodide increase with dilution with hexane; (4) the organic yields of dilute solutions of iodine or ethyl iodide appear to increase with increasing chain length of the hydrocarbon solvent from pentane to octane; (5) the organic yield of the iodide is the same in the solid phase as in the liquid phase whereas the yields of the bromide and chloride are much higher in the solid. The results have been interpreted in terms of the relative probability of nine possible competing types of elementary reactions. It is suggested that the *density* of radical production in the volume element where the tagged atom loses its energy may be a controlling factor in some cases and that the activation energy for thermal reaction with molecules of the medium may be so in other cases.

The purpose of this work was to obtain further evidence on the nature of the energy transfer processes and elementary reactions which lead to stable compounds of halogen atoms which have been activated by radiative neutron capture[2] in liquid and solid organic media.

Experimental

Purification of Reagents.—The ethyl halides and the hydrocarbons used in this work were obtained from the Eastman Chemical Co. and the Matheson Chemical Co. Impurities (presumably unsaturated compounds) present in the materials as received were found to influence seriously the results of the radiative neutron capture experiments. Except as noted below the reagents were therefore purified by prolonged vigorous mechanical stirring with successive portions of 100% sulfuric acid until no further coloration developed in the acid. After this treatment they were washed with sodium carbonate solution and with water, dried with Mallinckrodt Analytical Reagent anhydrous magnesium sulfate, and fractionally distilled through a 12" Vigreux column, a 65% middle cut being retained.

Ozonization was used as a second method of removing unsaturated compounds from ethyl bromide. Oxygen containing about 5% ozone was bubbled through the liquid for an hour and the latter was then washed with aqueous sulfite solution to hydrolyze ozonides and remove the products of the hydrolysis. Drying and fractional distillation was carried out in the same manner as following the sulfuric acid treatment.

The concentrated sulfuric acid wash of ethyl chloride was effected by bubbling the halide gas through a 22-inch column of the acid. In other experiments the ethyl chloride purification consisted of illumination in the presence of bromine at 0° with a 1000-watt lamp, washing, drying and distillation. In some cases phosphorus pentoxide was used for the drying. The ethyl iodide was illuminated with a 1000-watt lamp in the presence of dissolved iodine, washed, dried and fractionally distilled.

Neutron Irradiations.—All the liquid phase neutron irradiations were carried out at 0° (because of the low boiling points of some of the samples) with the organic liquid in the annular space between the two walls of a soft glass vessel shaped like a wide-mouthed dewar flask and provided at the top with tubes for filling and emptying. During irradiations the vessel was surrounded by 10 l. of ice and water and an Sb–Be photoneutron source was inserted in the center tube, which was filled with water. The source contained about 3 curies of Sb^{124} and gave about 6×10^6 neutrons per sec. The time of irradiation was usually less than an hour for chlorine and iodine activation (Cl^{38} and I^{128}) and about 5 hours for bromine activation (Br^{80} (4.4 hr.)). For irradiations at liquid air temperatures the organic liquid was contained in a quartz flask, immersed in liquid air in a dewar flask which was surrounded with water. The Sb–Be source was placed in the water close to the dewar.

Extraction and Counting.—Following neutron exposure the irradiated solutions were extracted with water 0.1 *M* in sodium sulfite and 0.1 *M* in sodium halide. Except in the case of ethyl chloride elemental halogen was added to the organic liquid before removal from the irradiation vessel since it was found that this removed activity which had been picked up by the walls. In all cases the walls were rinsed with fresh extracting solution. Several counts taken on extracting solution rinses and on rinses made with concentrated caustic solution indicated that loss to the walls introduced negligible error in the final results. All experiments with bromides and chlorides were done in dim red light to preclude photochemical reaction.

The methods of counting and calculating the results were similar to those described earlier[2] except for the ethyl chloride experiments when counting was done at 0° with a hydrogen or helium filled Geiger–Muller tube with external quenching circuit.

The sum of the measured counting rates of the aqueous and organic fractions obtainable with the Sb–Be source was of the order of 500 c./m. in the case of the ethyl chloride experiments, and the experiments with very dilute solutions of the halides in hydrocarbons. Much higher rates were obtainable with the pure ethyl bromide and ethyl iodide. The standard deviation of the counting measurements was about ±1% with the pure ethyl bromide and iodide and

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[1] Presented before the Division of Physical and Inorganic Chemistry at the April, 1951, Meeting of the American Chemical Society.

[2] For a description of such processes and references to related work see S. Goldhaber, R. S. H. Chiang and J. E. Willard, THIS JOURNAL, **73**, 2271 (1951).