Glassy State Transitions of Poly-(Chlorotrifluoroethylene), Poly-(Vinylidene Fluoride), and Their Copolymers [1]

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The glass transition temperatures, T_g, of poly-(chlorotrifluoroethylene), poly-(vinylidene fluoride), and copolymers prepared from these two comonomers were determined using dilatometric and interferometric methods. The glass temperature of poly-(chlorotrifluoroethylene) was found to be at 45° C, an upper limit for the glass temperature of poly-(vinylidene fluoride) was set at −35° C, and the glass temperatures for the copolymers were between the values for the two homopolymers.

These results are found to substantiate the recent theoretical deductions of Fox and Loshaek relating the glass temperature of a copolymer to its composition, and indicate that the glass temperature of a copolymer is a monotonic function of its composition. The effect of crystallization of a copolymer on the location of its glass temperature is illustrated and the various contradictory results of this effect that have been reported are discussed.

1. Introduction

It is well recognized [1] [2] that the glass transformation temperature, T_g, of a polymer is an important constant that characterizes the material. This temperature can serve as a convenient reference point in delineating the physical and mechanical properties of polymeric systems. For completely amorphous polymers rubberlike behavior will be observed above the glass temperature, whereas below this temperature the polymer will become hard and inelastic, and will embrittle very easily. Although many polymers are capable of undergoing crystallization they rarely attain complete crystallinity, and the amorphous or liquid-like regions of such systems can also undergo vitrification. The effect of vitrification on the physical properties of polymers of this type cannot be as clearly described as in the case of the completely amorphous polymers. The glass temperature in polymeric systems can be located by the abrupt changes that occur in its physical and mechanical properties as the temperature is varied, as well as by apparent changes that occur in certain thermodynamic quantities such as the volume-temperature coefficient or specific heat [2].

The elucidation of principles to explain the variation of the glass temperature with the chemical nature of the repeating unit of the polymer is one of the major objectives of physicochemical research in this field. Another objective of importance is the quantitative description of the way in which T_g of a given polymer will vary with molecular weight, with dilution by monomeric liquids, by copolymerization, or by branching. Efforts in attaining the latter objective have been in part successful by use of free volume concepts to describe the liquid state [3, 4, 5]. On the other hand, no well-defined theories exist at present that explain the dependence of T_g on the chemical nature of the repeating unit.

Discussions of this problem in terms of the configuration of the polymer chain [6, 7, 8] and the interaction energies between chains [6, 7] have been made. The development of such principles would, of course, be extremely helpful in the search for polymers having specific properties in a given temperature interval. As an aid in achieving this goal it is important to have available the values of T_g for polymers of widely differing chemical natures. Although such information is already available for a large variety of polymers [3, 4, 5, 6, 7, 9], reliable information for T_g of the relatively newer fluorine-containing polymers is either lacking or obscure.

The more common polymers of this type, poly-(tetrafluoroethylene), poly-(chlorotrifluoroethylene), and poly-(vinylidene fluoride), usually occur in the partially crystalline state, a fact that in itself makes the determination of T_g more difficult. An additional complication that occurs in the study of polymers of this type is the fact that rotational disordering may occur in the crystalline state. Such a transition has already been observed for poly-(tetrafluoroethylene) [10, 11] and is also suspected to occur in poly-(chlorotrifluoroethylene) [12]. A transition of this type will make difficult the unambiguous determination of T_g as these transitions also manifest themselves by changes in both the mechanical and thermodynamic properties of the polymer.

The complications that can occur in the determination of T_g are clearly indicated in the case of poly-(chlorotrifluoroethylene). Attempts to determine the glass temperature of this polymer have been made by many investigators [6, 7, 13, 14] using various techniques, and values ranging from −120° to +50° C have been assigned. Recently, Tobolsky and McLaughlin [15], by assuming that T_g for this polymer occurs approximately at room temperature, were able to explain their measurements of stress-relaxation as a function of temperature. The wide divergence in values of T_g that have been reported for this polymer is rather unusual and is undoubtedly due to the effect of crystallinity. It would thus appear highly desirable that an effort be made to

[2] Figures in brackets indicate the literature references at the end of this paper.

obtain a reliable value of T_g for this polymer. To accomplish this methods must be devised by which the amount of crystallinity is substantially reduced so that the crystalline portions do not obscure the experimental observations.

In the case of poly-(chlorotrifluoroethylene) the reduction in the degree of crystallinity can be accomplished by at least two methods. As Kaufman [16] has previously indicated, by an appropriate thermal treatment the amount of crystallinity in the homopolymer can be substantially reduced and the homopolymer can thus be studied in this state. Another method that can be used is to study the glass temperatures of suitable copolymers over a wide range of compositions. Copolymerization inevitably reduces the amount of crystallinity, and T_g for the homopolymers can be deduced by appropriate theoretical considerations [17].

The present paper describes dilatometric and interferometric experiments that lead to the determination of T_g of poly-(chlorotrifluoroethylene), poly-(vinylidene fluoride), and copolymers prepared from these two comonomers. By using an appropriate thermal treatment prior to the initiation of observations an unambiguous determination of the glass temperature of poly-(chlorotrifluoroethylene) can be made. The value assigned is substantiated by the studies on the copolymers, and these studies also lead to the assignment of an approximate value of T_g for poly-(vinylidene fluoride). No suitable thermal treatment could be devised to reduce the amount of crystallinity for this latter polymer so that studies of the homopolymer itself are not too conclusive.

2. Experimental Procedure

2.1. Materials

The samples of poly-(chlorotrifluoroethylene) and the copolymers of chlorotrifluoroethylene and vinylidene fluoride were kindly supplied to us by the M. W. Kellogg Co., who also determined the copolymer compositions by chemical analyses. Vinylidene fluoride was polymerized in a sealed tube under the influence of gamma-ray irradiation.[3] The polymers were molded at elevated temperatures into rectangular sheets about 3 mm thick. Exploratory dilatometric measurements indicated the presence of volatile material in all the polymers so that prior to the initiation of the length-temperature of volume-temperature measurements the samples were heated in a vacuum at 110° C for about 24 hours.

2.2. Procedures

The volume-temperature measurements were made with volume dilatometers, using mercury as a confining fluid. The dilatometers that were used and the experimental procedures have already been described [18, 19]. The length-temperature measurements were made using the automatic recording

[3] The authors are indebted to J. D. Michaelsen and D. W. Brown of NBS for the preparation of this polymer.

interferometer developed by Work [20]. The absolute densities of the samples were obtained by the method of hydrostatic weighing [21], using water as the flotation liquid.

3. Discussion and Results

3.1. Homopolymers

Volume-temperature and length-temperature measurements were made on the molded specimens of poly-(chlorotrifluoroethylene), using dilatometric and interferometric methods. Prior to the initiation of these studies, the samples to be investigated were wrapped in gold foil, heated for 30 minutes in a nitrogen atmosphere at 275° C, and quickly transferred to an ice-water mixture. The X-ray diffraction patterns of specimens that are treated in this manner indicate that the amount of crystallinity is substantially decreased. However, a small but well-defined peak still persists at a Bragg spacing of 5.5 A, which is the major spacing characteristic of this polymer [16]. Reproducible dilatometric results are obtained when the samples are conditioned in this manner and, if the temperature of observation does not exceed 110° C, no further crystallization occurs.

The dilatometric measurements extended over the temperature interval from $-30°$ to $+110°$ C, and in this range the observations were reproducible and independent of whether they were made on a heating or cooling cycle. Above 110° C the volume-temperature relations were no longer reproducible due to crystallization and decomposition. The dilatometric results for poly-(chlorotrifluoroethylene) in this reproducible temperature range are plotted in figure 1. The data are well represented by two straight lines that intersect at $+45°$ C and indicate a glass temperature at this point. The volume-temperature coefficient below this temperature is 1×10^{-4} cm^3 g^{-1} °C^{-1}, which is a value char-
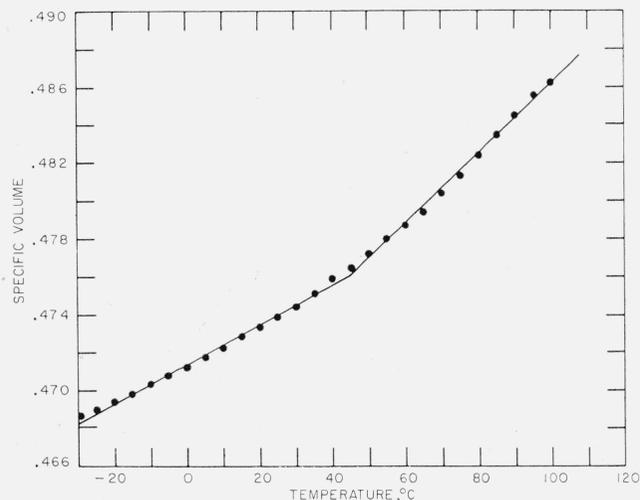
FIGURE 1. *Specific volume-temperature plot for poly-(chlorotrifluoroethylene).*

acteristic of the glassy state, whereas above this temperature this quantity is 2×10^{-4} cm^3 g^{-1} °C^{-1}. This latter coefficient is less than the value of 3.47×10^{-4} that has been recently reported [22] for the liquid polymer above its melting temperature. The differences in the value of the two liquid-like expansion coefficients may be due to the contribution of the crystalline regions to the volume-temperature coefficient above T_g. The possibility also exists that the liquidus is not linear from the melting temperature, about 220° C, to the glass temperature. The location of T_g at 45° C by these dilatometric measurements gives credence to the assumption made by Tobolsky and McLaughlin [15] in their interpretation of the temperature dependence of the mechanical properties of this polymer. This value also agrees with that which has been attributed to Reding [7]. If the amount of crystallinity of this polymer had not been substantially reduced, then the volume-temperature plot would be a gradually curving one in this temperature interval, and T_g would not have been detected by these methods.

Length-temperature measurements, encompassing a temperature range from $-180°$ to $+100°$ C, were also made on this polymer, using interferometric methods. A liquid-to-glass transformation at $+45°$ C is also indicated by this technique of measurement. The length-temperature coefficient is linear from the glass temperature to $-60°$ C, but as the temperature is decreased further, this coefficient also gradually decreases in a manner typical of materials in the glassy state [23]. When the polymer is initially heated in the interferometer its thickness increases by about 1 percent in going from the glassy to the liquid state. This change in thickness is irreversible during subsequent cooling and heating cycles, and no increase in volume is observed at a corresponding temperature by the dilatometric measurements. Because these samples were compression molded, this effect could be caused by the fact that strains induced in the system by the molding process are relieved by the increase in segmental mobility above the glass temperature. Similar results have been reported for the relief of strains in inorganic glasses as they transform to the liquid state [24].

The X-ray diffraction pattern for poly-(vinylidene fluoride) indicates that it is highly crystalline at room temperature. When this polymer is heated in a dilatometer in an effort to determine its melting temperature, excessive decomposition starts to occur at about 160° C, which is well below its melting temperature. This phenomenon precludes the determination or estimation of the melting temperature of this polymer, and as a result, in contrast to the situation for poly-(chlorotrifluoroethylene), no adequate thermal treatment could be devised to reduce substantially the crystallinity content. Thus, by necessity, the length-temperature and volume-temperature measurements had to be made on the highly crystalline polymer, which, as has been previously indicated, is very undesirable for the determination of T_g.

Length-temperature measurements were made in the range $-185°$ to $+30°$ C. Reliable dilatometric data, however, could only be obtained in the temperature interval $-30°$ to $+110°$ C. The results of the interferometric measurements are given in figure 2, where the expansion is plotted as a function of temperature. There is a definite linear portion to this plot that extends from $-35°$ to $+30°$ C and corresponds to a volume-temperature coefficient of 2.1×10^{-4} cm^3 g^{-1} °C^{-1}, a value that is corroborated by the dilatometric data. This value seems to be typical of the volume-temperature coefficient above T_g for this class of semicrystalline polymers. The gradual curvature of the plot in figure 2 below $-35°$ C makes difficult the accurate determination of a glass temperature solely from these data. As measurements of the temperature dependence of the mechanical properties of this polymer have not been reported, we can deduce only that $-35°$ C appears to be an upper limit for its glass temperature. As we shall see in the subsequent discussion, this value of T_g is consistent with the T_g's determined for the copolymers.
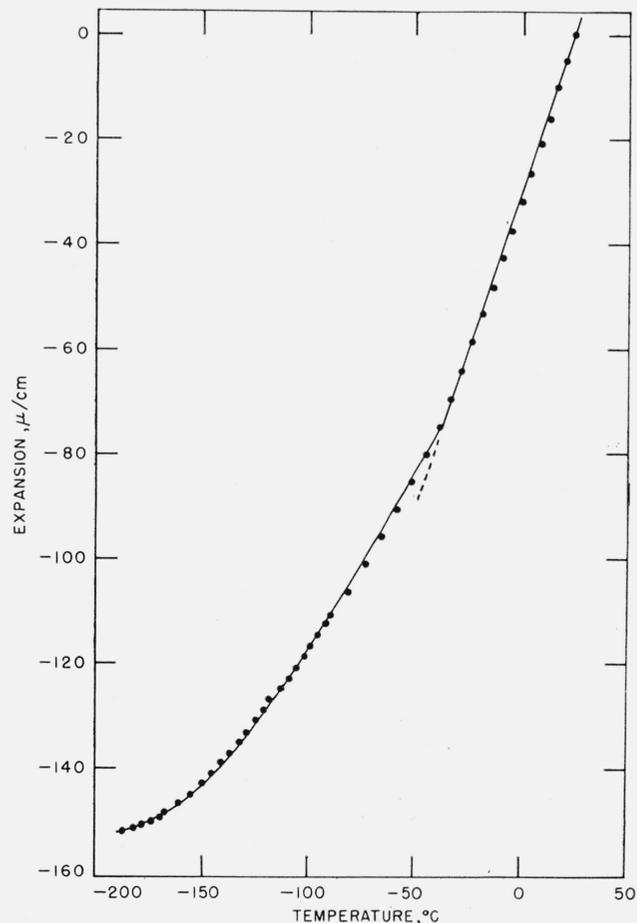

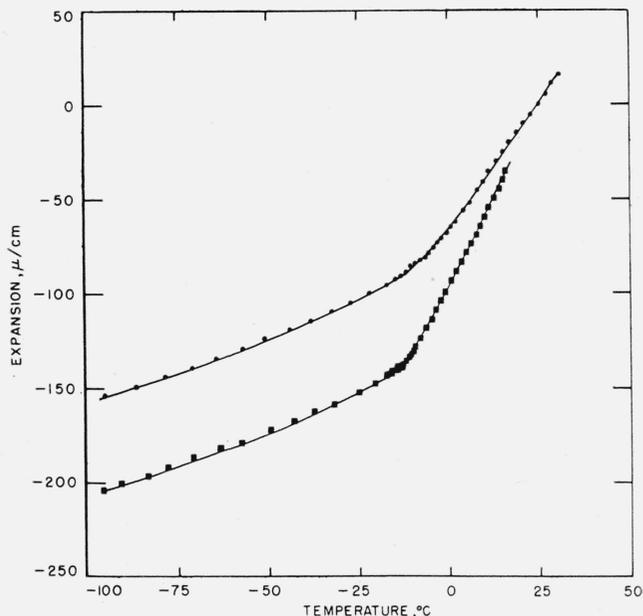FIGURE 2. *Expansion-temperature plot for poly-(vinylidene fluoride).*

FIGURE 3. *Expansion-temperature plot for copolymers of chlorotrifluoroethylene and vinylidene fluoride.*

Upper curve for copolymer having composition $w_1=0.60$. Lower curve for copolymer having composition $w_1=0.46$.

3.2. Copolymers

The glass temperatures of a series of copolymers prepared from chlorotrifluoroethylene and vinylidene fluoride were determined, again using both dilatometric and interferometric techniques. The composition of the copolymers studied ranged from 0.44 to 0.85 for the weight fraction, w_1, of the chlorotrifluoroethylene component. A typical plot of the expansion as a function of temperature for the copolymers containing 46 and 60 percent of chlorotrifluoroethylene, respectively, is given in figure 3, whereas curve B of figure 6 is a plot of the specific volume as a function of temperature of the copolymers whose composition is given by $w_1=0.85$. The glass temperatures of all the copolymers studied are summarized in table 1.

TABLE 1. *Glass temperatures of copolymers of chlorotrifluoroethylene and vinylidene fluoride of various compositions* [a]

w_1	T_g
	° C
0.85	+20
.64	−2
.60	−8
.46	−15
.43₅	−20

[a] w_1 = weight fraction of chlorotrifluoroethylene.

The crystallization behavior of the copolymers in the temperature interval of interest depends on composition, so that care must be exercised in the interpretation of the data in table 1 because it might be expected that T_g for a copolymer will depend on the amount of crystallization. The copolymers contain-

ing about 60 percent of chlorotrifluoroethylene do not crystallize. Thus T_g for copolymers of this composition could be unambiguously determined, and the value given in table 1 is for the amorphous polymers. Copolymers of this composition have a glass temperature slightly below 0° C and hence have little utility as elastomers below this temperature.

The copolymer having a composition specified by $w_1=0.85$, though crystallizable, could be quenched and maintained amorphous through the glass-transformation range. The value of T_g given in table 1 is that for the amorphous polymer. The effect of crystallization on T_g for this copolymer is discussed in a subsequent section. The values of T_g given for the polymers containing the higher amounts of vinylidene fluoride are for the polymers in the semicrystalline state because they could neither be melted nor adequately quenched. The glass temperatures for the copolymers range from +20° to −20° C and are in qualitative agreement with the value determined for poly-(chlorotrifluoroethylene) and the upper limit that has been estimated for poly-(vinylidene fluoride).

From theoretical considerations, Fox and Loshaek [17] have developed quantitative relations between the glass temperatures of a copolymer of specified composition and the glass temperature of each of the homopolymers derived from the respective comonomers. The free-volume concepts, which have been successful in predicting the dependence of glass temperature on molecular weight [3] and the effect of crosslinking [4], have been extended by these investigators to copolymer systems. A brief outline of their considerations is given in the following paragraphs, and their theoretical results are applied to the experimental data reported here.

At a reference temperature in the liquid state the specific volume of a polymer is considered to be composed of two parts, the occupied volume and the free volume. The occupied volume represents a closely packed liquid structure. For simplicity in the subsequent analyses, it is assumed that the specific volume and occupied volume of a copolymer are additive functions of each of its components. Thus for the specific volume, $\overline{V}$, of the copolymer, we write

$$\overline{V}=w_1\overline{v}_1+w_2\overline{v}_2, \qquad (1)$$

where $\overline{v}_1$ and $\overline{v}_2$ are the specific volumes of the two corresponding homopolymers, and w_1 and w_2 are the respective weight fractions of the two components. The dependence of the occupied volume on copolymer composition can be expressed in a manner similar to eq (1), and as a consequence the free volume of the copolymer becomes an additive function of composition.

Various criteria for glass formation can be considered. However, Williams, Landel, and Ferry [25] have concluded from an analysis of the temperature dependence of the viscosity-temperature coefficient of a variety of glass forming liquids that glass formation occurs when the ratio of the free volume to specific volume reaches a critical and constant value

independent of the nature of the liquid. We thus assume that at T_g for each of the homopolymers and of the copolymers the ratio of the free volume to specific volume is a constant designated as k; according to Williams, Landel, and Ferry [25], k is equal to 0.025.

Utilizing these assumptions, the result is obtained that [4]

$$1/T_g = [1/(w_1 + Rw_2)][w_1/T_{g_1} + w_2/T_{g_2}], \qquad (2)$$

where

$$R = [(\alpha_{L_2} - \alpha_2^* - k\alpha_{L_2})/(\alpha_{L_1} - \alpha_1^* - k\alpha_{L_1})][T_{g_2}/T_{g_1}]. \qquad (3)$$

In eq (2), T_g is the glass temperature of the copolymer of composition w_1, T_{g_1} and T_{g_2} are the glass temperatures of the respective homopolymers, and the α_L's represent their volume-temperature coefficients in the liquid state and the α^*'s the corresponding coefficient for their occupied volumes. Equation (2) is similar in form to an equation previously derived by Gordon and Taylor [26]. Because it is difficult to express α^* in terms of any of the measured volume-temperature coefficients, R is best considered an arbitrary parameter in eq (2). For the special case where $R=1$, eq (2) reduces to the simple relation that

$$1/T_g = w_1/T_{g_1} + w_2/T_{g_2}. \qquad (4)$$

Because T_g for poly-(vinylidene fluoride) has only been estimated, the best way of comparing the experimental results of this paper with the conclusions of eq (2) would be to calculate theoretical curves for different values of R and T_g for this polymer. In figure 4 the experimental results are represented by the solid circles and the theoretical curves, which best fit the data, are also given. In this plot curves A and B represent the simplest case where $R=1$ and T_g for poly-(vinylidene fluoride) has the values $-50°$ C and $-60°$ C, respectively. For curve C, $R=1.5$ and $T_g=-40°$ C, whereas curve D represents the situation where $R=1.2$ and $T_g=-50°$ C. No reasonable theoretical curves could be drawn when the glass temperature of poly-(vinylidene fluoride) was assigned a value greater than $-40°$ C. From the representation in figure 4 we can conclude that the results for the chlorotrifluoroethylene-vinylidene fluoride copolymer system are quantitatively consistent with the theoretical considerations of Fox and Loshaek [17]. However, due to the facts that values for T_g are not available for copolymers containing less than 45 percent trifluorochloroethylene and that there is uncertainty in the value of T_g for poly-(vinylidene fluoride), these data alone could not serve as a substantiation of eq (2).

Experimental verification of eq (2) was obtained by Fox and Loshaek [17], who determined T_g of a

FIGURE 4. *Theoretical curves of glass temperature against composition.*

Solid circles represent experimental results.

series of copolymers that were derived from a variety of comonomers and covered a wide composition range. Excellent agreement was found between the experimental observations and eq (2), whereas the value of the parameter R required to fit the data did not vary appreciably from unity for the different series of copolymers studied. These results substantiate eq (2) and indicate that T_g for a copolymer is a monotonic function of its composition, so that maxima or minima in the T_g-composition curve would not be expected. Thus, in an attempt to prepare copolymers having low glass temperature, comonomers should be selected whose homopolymers also have low glass temperatures.

3.3. Effect of Crystallization on Glass Transformation Temperature

Polymers in general do not crystallize completely, so that the amorphous or liquid-like regions, which may in some instances constitute more than half the volume of the polymer, are still capable of undergoing glass transformation. The random introduction of noncrystallizing copolymeric units into a homopolymer chain that can crystallize will reduce further the final amount of crystallinity that can be attained. It is of interest to know whether the glass temperature is affected by the amount of crystalli-

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[4] The above derivation of eq (2) and the subsequent definition of R differ slightly from that originally given by Fox and Loshaek [17]. However, the differences are minor and imperceptible when applied to experimental data.
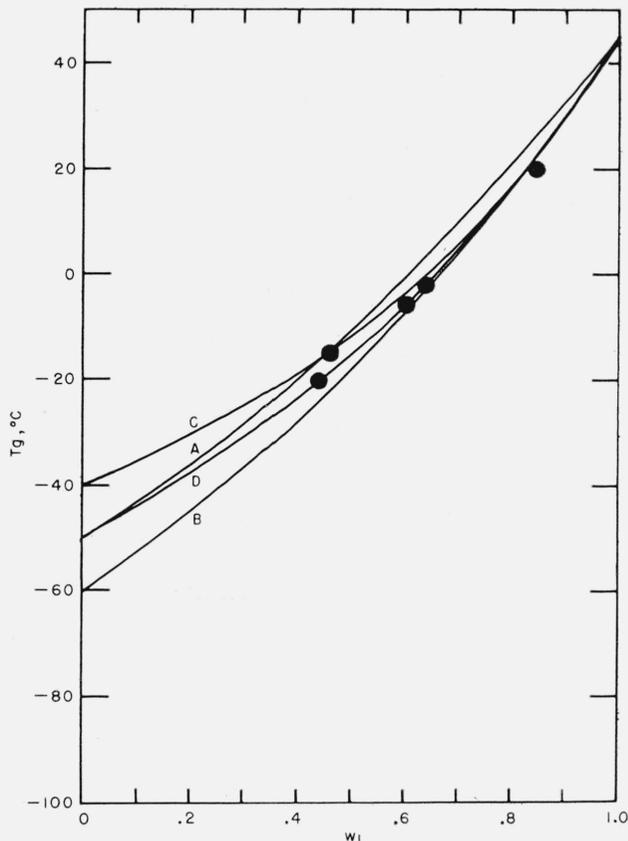
zation when the crystallization is induced solely by cooling without the application of any external stress. Contradictory experimental evidence exists as to whether there are any effects of this type in homopolymers and no definitive results appear to have been reported for copolymers.

Because the composition of the amorphous regions of a homopolymer does not change with crystallization one might expect that the glass temperature would also remain invariant. The results obtained by Bekkedahl [9] support this premise because, for natural rubber, T_g remained constant at $-70°$ C irrespective of whether the polymer was partially crystalline or completely amorphous. However, the results obtained by Kolb and Izard [27] and by Woods [28] for poly-(ethylene terephthalate), presumably a homopolymer, are in contradiction to those obtained for natural rubber. These investigators found from volume-temperature measurements that the glass temperature of poly-(ethylene terephthalate) increases by about 20 deg after crystallization ensues. A similar effect of the change in T_g with the amount of crystallinity, using dynamical mechanical methods, was also observed by Woods. Thus the experimental evidence for the effect of crystallization on the glass temperature of a homopolymer is at present contradictory and would appear to be specific for a given polymer.

If we consider a random copolymer composed of A and B units and if only the A units participate in the crystallization, then the amorphous regions of the copolymer will have a greater concentration of B units than the total composition. Because only the amorphous regions participate in the glass transformation we might expect the glass transformation of the copolymer to shift in the direction characteristic of the component that does not crystallize as the crystallization process progresses.

The situation just described can be realized for the copolymers of chlorotrifluoroethylene and vinylidene fluoride having the composition of $w_1 = 0.85$. If this copolymer is heated above its melting point and quickly quenched to $0°$ C, only a small amount of crystallinity develops. This is illustrated by the X-ray diffraction pattern for the copolymer treated in this manner given by curve B of figure 5, where an almost completely amorphous pattern is obtained. The volume-temperature curve for this copolymer is given in curve B of figure 6, and, as has already been mentioned, a glass temperature at $+20°$ C is indicated.

When this polymer is heated above $35°$ C more rapid crystallization ensues and the X-ray diffraction pattern A of figure 5 is obtained. The Bragg spacings in this pattern indicate that only the chlorotrifluoroethylene units are crystallizing, and hence the amorphous regions must contain a greater concentration of vinylidene fluoride units than the nominal composition. The volume-temperature curve corresponding to the more crystalline copolymer is given by curve A of figure 6. The specific volume for this copolymer is, of course, less than that for the amorphous polymer and the glass temperature
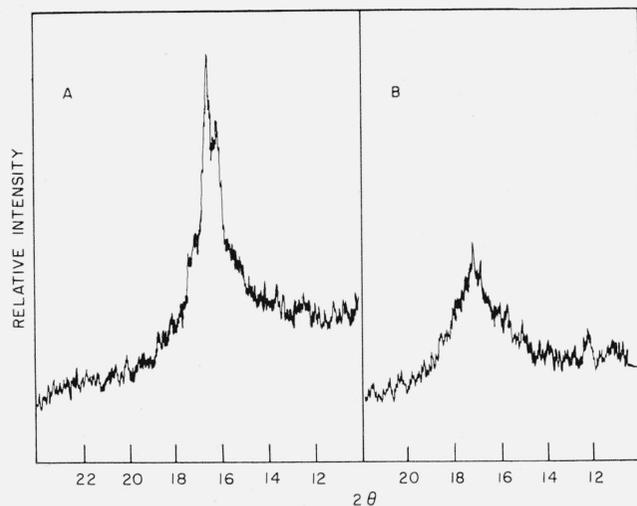

FIGURE 5. A, X-ray diffraction pattern of crystalline copolymer having composition $w_1 = 0.85$. B, Same copolymer after thermal treatment to reduce amount of crystallinity.
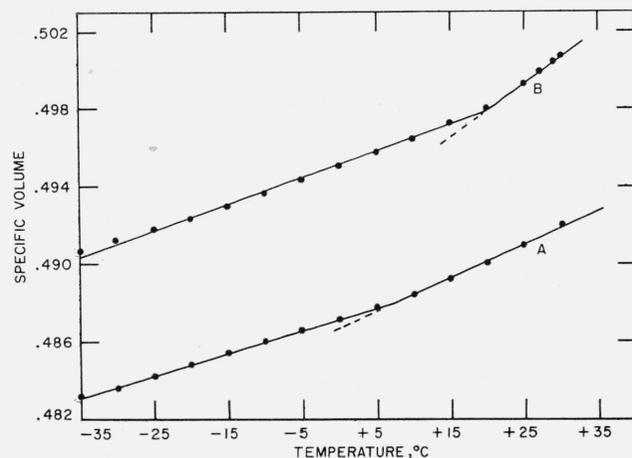

FIGURE 6. Volume-temperature plots of copolymer having composition corresponding to $w_1 = 0.85$.

Curve A, highly crystalline material; curve B, crystallinity substantially reduced.

occurs at $+7°$ C. These results are a clear indication that the crystallization of one type of unit in a random copolymer results in a shift in the glass temperature in the direction of higher compositions of the noncrystallizing component. Coincident with the development of crystallinity the volume-temperature coefficient above the glass temperature decreased from 3.0×10^{-4} cm^3 g^{-1} °C^{-1} for the amorphous polymer to 1.8×10^{-4} cm^3 g^{-1} °C^{-1} for the partially crystalline polymer. In their study of Saran, a copolymer of vinylidene chloride and vinyl chloride, Boyer and Spencer [29] found that as the fraction of the polymer that was crystalline varied from 0.187 to 0.67 the glass temperature remained constant. However, in this study the nature of the crystallizing units was not described and the possibility of cocrystallization exists. It is evident that

with the contradictory evidence now available more systematic studies of the effect of crystallization on $\dot{T}_g$ must be undertaken both for homopolymers and copolymers, though the results reported here indicate that crystallization will cause a shift in the value of T_g.

4. References

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