

The Glass Temperatures of Polyacrylonitrile and Acrylonitrile-Vinyl Acetate Copolymers

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INTRODUCTION

The value of the glass temperature of polyacrylonitrile is a matter of considerable uncertainty; values ranging from 52°C. to 180°C. have been reported by different investigators. Kolb and Izard¹ determined the specific volume of pure polyacrylonitrile as a function of temperature and found evidence for the occurrence of the glass transition at 87°C. Wiley and Brauer² determined the glass transitions of a series of butadiene-acrylonitrile copolymers, and by a linear extrapolation of the glass temperature-composition data obtained 52°C. as the glass-transition temperature of pure polyacrylonitrile. Gerke³ determined the glass temperatures for copolymers of butadiene and acrylonitrile and, extrapolating a plot of log glass temperature versus weight fraction acrylonitrile, obtained a glass temperature of 130°C. for pure polyacrylonitrile. He confirmed this value with measurements of two plasticized solutions of polyacrylonitrile in dimethylformamide. Krigbaum and Tokita⁴ found a glass-transition temperature of 104° for polyacrylonitrile by linear extrapolation of glass transition temperatures of solutions of polyacrylonitrile in dimethylformamide and in γ -butyrolactone.

Loshaek and Fox⁵ used an equation based on the assumed additivity of specific, occupied, and free volumes in copolymers to extrapolate data from the literature for butadiene-acrylonitrile copolymers. They thus arrived at a figure of 180°C. for the glass temperature of pure polyacrylonitrile. The present communication reports the results of an investigation of the glass temperatures of the vinyl acetate-acrylonitrile copolymer system over the whole range of composition.

EXPERIMENTAL

The copolymers and one of the polyacrylonitrile polymers used in this work were prepared by well-

known procedures at 50°C. in an aqueous emulsion system with persulfate-bisulfite initiator. Copolymer samples of over 10% vinyl acetate were polymerized to less than 15% conversion, while the remainder of the samples were allowed to attain 70-90% conversion. Even at 90% conversion, calculations indicate that the vinyl acetate monomer units would be randomly dispersed in copolymers with less than 10% vinyl acetate. Actual copolymer compositions were established by infrared analysis. The polymer was filtered, washed, dried in a vacuum oven at 50°C., and then pressed into discs about 1/2 in. in diameter and about 0.3 in. thick. These discs were formed under 20,000 psi in a vacuum mold at temperatures sufficiently high to give relatively clear samples visually free of bubbles and other defects. The temperature required varied from sample to sample and ranged from as low as 50 or 60°C. for the copolymers with high vinyl acetate content to as high as 160 or 170°C. for those containing a high percentage of acrylonitrile.

Measurements of the linear thermal coefficients of expansion were made in an apparatus which consists essentially of a movable vertical rod resting on the top of the sample. The movement of this rod, occasioned by the expansion of the sample, is sensed by a linear differential transformer and recorded continuously. The apparatus itself is sensitive, and reproducible, to 0.0001 in. During measurement the sample is immersed in a silicone oil bath, the temperature of which is controlled by appropriate heaters and control equipment. Those portions of the apparatus which are also immersed in the silicone oil bath, and therefore are subject to considerable temperature changes and gradients, are made of Invar metal in order to minimize the effects of thermal expansion of the apparatus itself. Heating and cooling rates were automatically maintained at approximately 1°C. per minute. The samples were weighed on an analytical balance

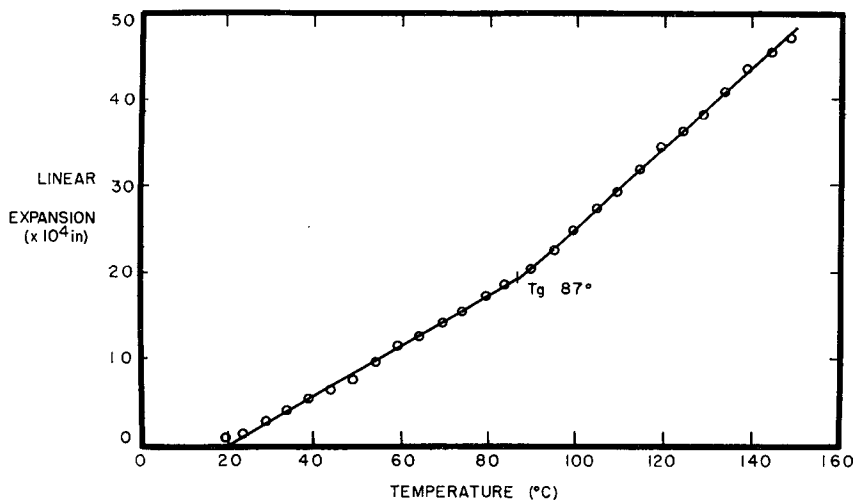


Fig. 1. Linear expansion of polyacrylonitrile.

before and after each run, and showed no evidence of change in weight. From this, from visual observations, and from the reproducibility achieved in successive determinations, it was judged that the samples were not penetrated by the silicone oil to any appreciable extent.

The results of a typical thermal expansion determination, in this case for pure polyacrylonitrile, are shown in Figure 1. The discontinuity in slope at 87°C. is clearly evident and is taken as the glass temperature, in agreement, incidentally, with Kolb and Izard.¹ In many cases measurements were taken on both the heating and cooling cycles, and in general the glass temperatures obtained from the heating and cooling curves agreed within about 1°C. It is judged from repeat runs that the glass temperatures obtained are reproducible to within 2–3°C.

RESULTS AND DISCUSSION

The data obtained for the glass temperatures are given in Table I, where the first column is the weight fraction of vinyl acetate and the second column gives the glass temperature T_g (°C.). The value for pure polyvinyl acetate was obtained from Kokes et al.⁶ who estimate it to be reliable to $\pm 2^\circ\text{C}$.

The assumption that the specific volume of a copolymer is an additive function of its components led Gordon and Taylor⁷ to propose the following equation relating the glass temperature of a copolymer to its composition and to the glass temperatures of its constituent homopolymers.

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (1)$$

In eq. (1), T_g is the glass temperature of the copolymer; T_{g1} and T_{g2} are the glass temperatures of components 1 and 2; w_1 and w_2 are the weight fractions of components 1 and 2; and k is an adjustable parameter which Gordon and Taylor identify with the ratio of the differences between

TABLE I
Glass Temperature for the Acrylonitrile-Vinyl Acetate Copolymer System as a Function of Composition

Weight fraction of VA (w_1)	Glass temperature, °C.
0	87
0	86
0	92 ^a
0	103 ^a
0.02	86
0.05	79
0.05	85
0.05	86
0.05	84
0.06	87
0.08	86
0.10	76
0.16	81
0.27	84
0.32	80
0.38	75
0.43	70
0.58	65
0.64	58
1.00	30 ^b

^a In this case another initiator was used instead of persulfate-bisulfite.

^b Data of Kokes, Long, and Hoard.⁶

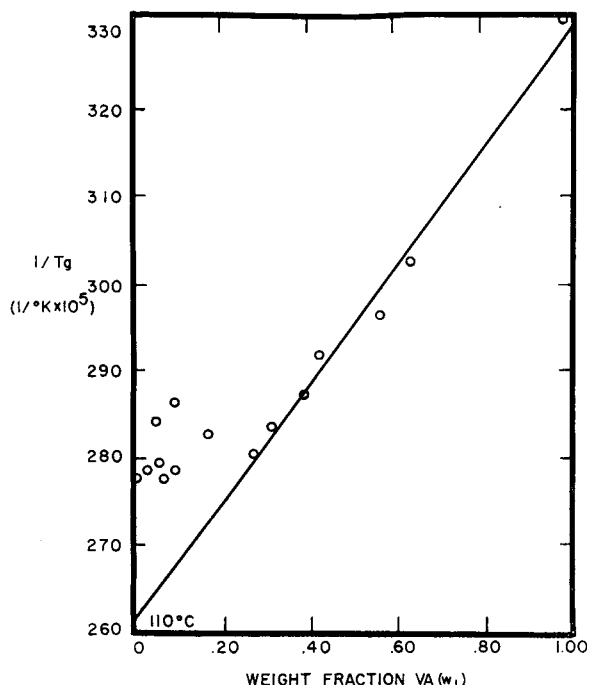


Fig. 2. Reciprocal of glass-transition temperature vs. composition of AN-VA copolymer.

the thermal expansion coefficients below and above the glass temperature.

Loshaek and Fox⁵ have re-examined the question of glass transitions of copolymers in the light of current views on the role the free volume plays in determining the glass temperature. They have derived, as a preferable relationship between the glass temperature of copolymers and their composition:

$$\frac{1}{T_g} = \frac{1}{w_1 + R w_2} \left[\frac{w_1}{T_{g_1}} + R \frac{w_2}{T_{g_2}} \right] \quad (2)$$

In eq. (2) those symbols used in eq. (1) have the same meaning, and the constant R is equal to kT_{g_2}/T_{g_1} , where k is the adjustable parameter of eq. (1). In the special case where $R = 1$, eq. (2) reduces to:

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \quad (3)$$

Mandelkern⁸ has given a slightly different derivation of eq. (2). In either case, the constant R incorporates the thermal expansion coefficient for the free volume, a quantity which is not readily related to experimentally measurable expansion coefficients. In view of this, Mandelkern feels that R is best left as an adjustable parameter.

It is observed experimentally that R is in the neighborhood of unity for most copolymer systems.^{5,8,9}

The data obtained in the present investigation have been analyzed in terms of both eq. (2) and eq. (3). The reciprocals of the glass temperatures are plotted against the weight fraction of vinyl acetate (eq. (3) in Figure 2). It is noted that for the composition range down to about 27 wt.-% vinyl acetate the experimental points give a reasonably good straight line, including the point for pure polyvinyl acetate. At lower vinyl acetate contents the glass temperature tends to level off in the neighborhood of 87°C., which is the experimental value for the glass temperature of pure polyacrylonitrile. The solid straight line in Figure 2 is the least-squares line through all the points for compositions with 27 wt.-% vinyl acetate or greater. If the glass-transition temperature of pure polyacrylonitrile were to be estimated by extrapolation of this line, the result would be 110°C.

It is also possible to obtain a reasonable fit to the data by use of eq. (2) or its equivalent, eq. (1), but in order to do so it is necessary to use the rather high value of $R = 2.7$ ($k = 2.3$). The glass temperatures are plotted directly against the weight fraction of vinyl acetate in Figure 3. The dotted line was obtained from eq. (2) with the use of the experimentally determined glass temperatures of the two homopolymers and a value of 2.7 for R . The solid line was obtained from eq. (3) ($R = 1$) and the least-squares line in Figure 2. It might be that a value of R slightly larger than unity would give a better fit to the points above 27% vinyl acetate than does eq. (3), but it was felt that the data are not sufficiently good to warrant such adjustment. If it is demanded that all values of glass temperature over the entire range of composition form a continuous curve, then clearly the dotted line is the proper one.

There is, however, strong reason to suspect this to be incorrect. This relationship, it must be remembered, was developed for an amorphous system, while polyacrylonitrile is known to be partially crystalline. It has also been observed that the last evidences of crystallinity in the x-ray patterns of these copolymers disappear only after the vinyl acetate content of the copolymers has been raised to greater than 20 to 25 wt.-%.¹⁰ The data on compositions of lower vinyl acetate content become suspect because of the complicating effects of crystallinity, and it is not expected that

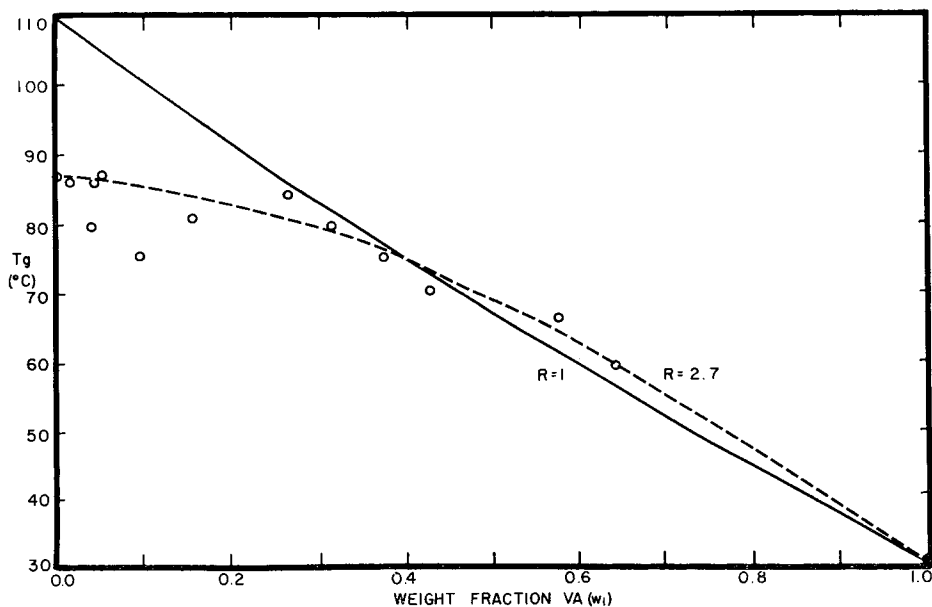


Fig. 3. Glass-transition temperature vs. composition of AN-VA copolymer.

the copolymer equation would be applicable in this region.^{5,8}

Nielsen¹¹ has shown by dynamic mechanical tests that the glass temperature of ethylene-vinyl acetate copolymers is almost constant for vinyl acetate concentrations up to 55 vol.-%. Also, x-ray studies showed crystallinity to disappear only at compositions of greater than 55 vol.-% vinyl acetate. He concludes that either the crystallites impose restrictions on the amorphous phase or, since the crystalline region contains only ethylene units, as indicated by x-ray data, the composition of the amorphous phase is not the same as the overall composition. Although there is no direct evidence at present to indicate which of these mechanisms is more important, the latter is felt to be the more nearly correct, since it predicts a more sudden leveling-off of the glass temperature.

The acrylonitrile-vinyl acetate copolymer system appears to be analogous to the ethylene-vinyl acetate system. If it is assumed that only acrylonitrile units are present in the crystalline phase, then as the percentage of acrylonitrile in the copolymer increases, more acrylonitrile units are incorporated into the crystalline phase, leaving the composition of the amorphous phase essentially constant. Consequently, the glass temperature should become a constant value once crystallinity develops, as is experimentally observed. Mandelkern et al.⁸ showed by dilatometric studies similar behavior for the chlorotrifluoroethylene-vinylidene

fluoride (CTF-VF) copolymer system. They found that in a copolymer with an 0.85 weight fraction of CTF the glass temperature changed from 20°C. to 7°C. as the state of the material changed from essentially amorphous to crystalline.

There still remains some question as to the glass transition temperature of polyacrylonitrile. Since this work was originally presented at the International Symposium of Macromolecular Chemistry at Wiesbaden, the figure of 87°C. for the glass transition of polyacrylonitrile has been rechecked experimentally several times. However, two samples made with a different catalyst system exhibited glass transitions of 92°C. and 103°C., respectively. There appear, therefore, to be real differences in the transition temperatures of different polyacrylonitrile polymers. X-ray patterns indicate that these two samples are less crystalline or have a different ordering of the chains than the sample with the transition at 87°C.¹⁰

Because of the complicating effect of crystallinity, the use of eq. (3) and the resulting estimate of 110°C. as the glass temperature of completely amorphous polyacrylonitrile is preferred. This is in good agreement with the results of Krigbaum and Tokita. It would seem that a much higher glass temperature would not be consistent with the data; on the other hand, the correct value could easily be somewhat lower than 110°C. and still be consistent with the present data. It is believed that much of the uncertainty about the glass

temperature of amorphous polyacrylonitrile as previously reported is due to the necessity of making long and uncertain extrapolations in order to avoid the complicating effects of crystallinity.

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Synopsis

The glass-transition temperatures T_g of various copolymers of acrylonitrile and vinyl acetate were measured by observing the linear expansion of molded discs. For vinyl acetate contents of 0 to 27 wt.-% the glass temperature is constant at 87°C. This value agrees with the results of Kolb and Izard for pure polyacrylonitrile. Fitting of the glass temperature-composition data above 27% vinyl acetate to the equation of Fox and Loshaek leads to an extrapolated value of 110°C. for completely amorphous polyacrylonitrile, which agrees with similar data of Krigbaum and Tokita. The difference between the two values can be explained in terms of the effects of crystallinity analogous to those discussed by Nielsen for ethylene-vinyl acetate copolymers. Moreover, experimental values of 92 and 103°C. were found for specially prepared samples of polyacrylonitrile. These samples were found to be less crystalline or to have a different ordering of the polymer chains as evidenced by x-ray data. It is concluded that the glass temperature of completely amorphous polyacrylonitrile can be no greater than 110°C. and that experimental values for semicrystalline polyacrylonitrile may range down to 87°C.

Résumé

Les températures de transition vitreuse de différents copolymères de l'acrylonitrile et de l'acétate de vinyle ont été mesurées par l'observation de la dilatation linéaire de disques moulés. Pour un pourcentage en poids d'acétate de vinyle variant de 0 à 27%, la température de transition reste constante et égale à 87°C. Pour le polyacrylonitrile cette valeur concorde avec les résultats de Kolb et Izard. En adaptant les résultats obtenus au moyen de la température de transition en fonction de la composition en acétate de vinyle au delà de 27%, à l'équation de Fox et Loshaek on obtient une valeur extrapolée de 110°C pour un polyacrylonitrile complètement amorphe, qui concorde avec les données de Krigbaum et Tokita. La différence entre les deux valeurs peuvent être expliquées par l'influence de la cristallinité, de façon analogue à la discussion de Nielsen sur les copolymères d'acétate de vinyle et d'éthylène. De plus, les valeurs expérimentales de 92° à 103°C. furent trouvées pour des échantillons de polyacrylonitrile préparé spécialement. Ces échantillons sont moins fortement cristallisés et ont un arrangement différent des chaînes de polymères comme le prouvent les R.X. Il faut donc conclure que la température de transition vitreuse du polyacrylonitrile complètement amorphe ne peut être plus élevée que 110°C. et que les valeurs expérimentales pour le polyacrylonitrile semi-cristallin doivent se situer plus bas jusqu'à 87°C.

Zusammenfassung

Die Glasumwandlungstemperatur (T_g) verschiedener Copolymerer von Acrylnitril und Vinylacetat wurde durch Messung der linearen Ausdehnung gepresster Scheibchen bestimmt. Bei einem Vinylacetatgehalt von 0 bis 27 Gewichtsprozent liegt die Glasktemperatur konstant bei 87°C. Für Polyacrylnitril stimmt dieser Wert mit den Ergebnissen von Kolb und Izard überein. Die Glasktemperaturdaten bei einer Zusammensetzung oberhalb 27% Vinylacetat ergeben, in die Gleichung von Fox und Loshaek eingesetzt, für völlig amorphes Polyacrylnitril einen extrapolierten Wert von 110°C., der mit ähnlichen Daten von Krigbaum und Tokita übereinstimmt. Der Unterschied zwischen den beiden Werten kann in Analogie zu Niensens Diskussion der Äthylen-Vinylacetatcopolymeren durch Kristallinitäts-einflüsse erklärt werden. Ausserdem wurden an speziell hergestellten Polyacrylnitrilproben experimentelle Werte von 92 und 103°C. gefunden. Diese Proben erwiesen sich nach den Röntgenergebnissen als weniger kristallin oder besaßen eine verschiedene Anordnung der Polymerketten. Man kommt zu dem Schluss, dass die Glasktemperatur eines völlig amorphen Polyacrylnitrils nicht höher als 110°C. sein kann und dass experimentelle Werte für semikristallines Polyacrylnitril bis zu 87°C. herunter liegen können.

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