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Crystallization Kinetic Studies of Vinylidene Chloride-Alkyl Acrylate Copolymers by Torsional Measurements*

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By following the changes in torsional modulus as a function of time, the effect of the length of an alkyl side chain on the rate of crystallization was determined

An investigation of the kinetics of isothermal crystallization of three copolymers of vinylidene chloride containing 10 mole % alkyl acrylate, namely octadecyl, octyl and butyl acrylate, was made by following the change in torsional modulus as a function of time (1). The main objective of this study was to determine the effect of alkyl side chain length on the rate of crystallization.

Preparation of Samples

The preparation of the copolymers of vinylidene chloride used for this study has been recently reported (2). Test specimens for torsional measurements 10 cm × .75 cm × .15 cm were obtained by molding the powder at 120°C. under 20 tons' pressure for about 5 minutes without the use of stabilizer. Molded specimens were straw colored, indicating little or no decomposition. To obtain amorphous specimens, the molded copolymers were conditioned in the temperature range 155° to 170°C. for 5 minutes. This is well above the temperature at which the crystallites of the copolymers are known to melt. The specimens were subsequently quenched in alcohol at −70°C. and maintained at this temperature until torsional measurements were made. Rates of crystallization were obtained by following the increase in torsional modulus at constant temperature, using a torsion wire apparatus (3). A constant temperature bath regulated to within ± 0.5°C. was used. Alcohol was used as the immersion medium below 25°C., water to 60°C., and air above 60°C.

Crystallization Kinetics

Plots of modulus versus time for three crystallization temperatures are depicted in *Figure 1,* the lower curves, for the copolymer containing 10 mole % octadecyl acrylate. The initial portion of the curves has been omitted since there is a 100-fold increase in modulus which was detected by the sensitivity of this method. The shape of each modulus-time curve is characteristic of a crystallization isotherm. Was the rate of torsional modulus change directly related to the amount of crystallinity which was developing in the specimen? Other investigations, Leitner (4) on rubber, and Dulmage (5) on polyethylene terephthalate, indicated that modulus and degree of crystallinity were not so related.

In order to establish whether a direct relationship between modulus and crystallinity existed for the copolymers investigated, the rates of crystallization in amorphous specimens were then studied by the conventional method of following the changes in density as a function of time. These measurements were carried out in a density gradient column held at constant tem-

*Presented at the 140th National Meeting of the American Chemical Society, Chicago, Illinois, September 3-8, 1961.
** Eastern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

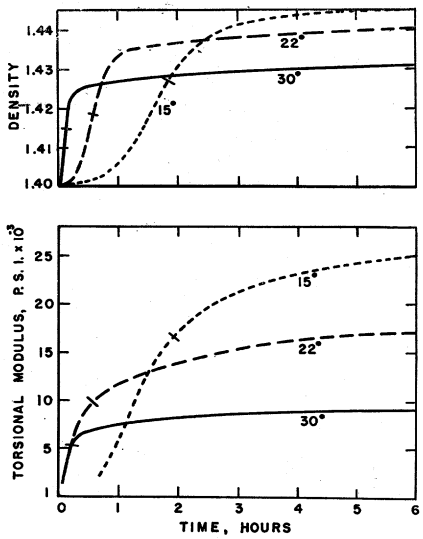

Figure 1. Crystallization isotherms at various temperatures obtained by torsional modulus and density gradient for a copolymer of vinylidene chloride containing 10 mole % octadecyl acrylate.

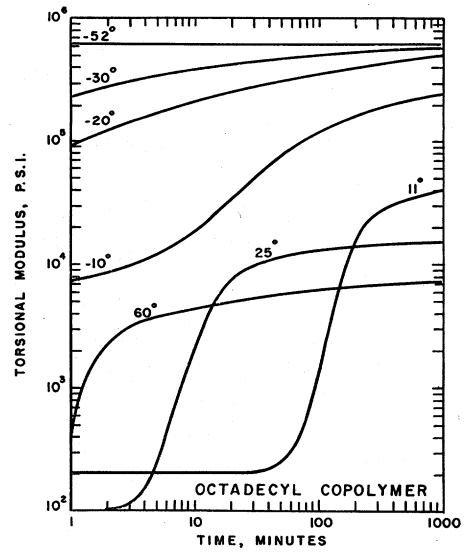

Figure 2. Selected crystallization isotherms of vinylidene chloride copolymer containing 10 mole % octadecyl acrylate.

perature. The corresponding density versus time isotherms for three temperatures are shown in *Figure 1*, the upper curves. The shape of the curves is similar to the torsional modulus curves. The time required to attain half of the maximum density was essentially the same as that required to reach half of the maximum modulus value. At 15°C., the observed half-time values were 112 minutes and 110 minutes for the density and modulus method, respectively; at 22°C., 36 and 35 minutes; and at 30°C., 8 and 11 minutes. Therefore, it was concluded that determination of crystallization rates by torsional modulus was justified here.

Rates of crystallization of the amorphous 10 mole % octadecyl copolymer were studied by following the rate of increase in torsional modulus for the temperature range −52°C. to 90°C. Shown in *Figure 2* are selected curves, of the rate of increase in torsional modulus at −52, −30, −20, −10, 11, 25, and 60°C. The initial modulus observed (at 1 minute) depends on the temperature employed. The lower the temperature the higher the initial modulus. At −52° the initial modulus is 6.2×10^5 p.s.i. while at 25° the modulus is 1.05×10^2 p.s.i. This probably reflects the mobility of polymer segments at the particular temperature employed.

Examination of the modulus-time data reveals that at −52° there is no change of modulus with time; the temperature is below the second order transition temperature of the system (−45°). As the temperature is increased at about −30° an increase in modulus with time is observed. The slope in the maximum change region of the isotherms increases with temperature. The overall shape of the isotherm is not too apparent until a temperature of −10° is attained when it is definitely sigmoidal and remains the same for all higher tempera-

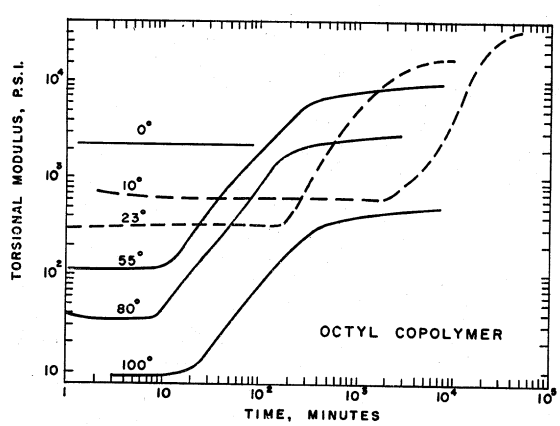

Figure 3. Selected crystallization isotherms of a vinylidene chloride copolymer containing 10 mole % octyl acrylate.

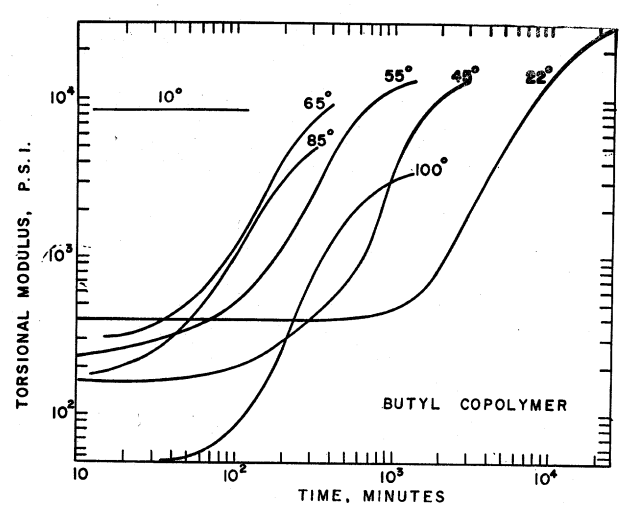

Figure 4. Selected crystallization isotherms of a vinylidene chloride copolymer containing 10 mole % butyl acrylate.

tures. In the temperature range 11° to 90° the slopes in the maximum change region of the isotherms are about the same. However, it should be noted that below −10° there is no apparent induction period. At about 5°C. an induction period was observed for the first time. It increases with increasing temperature and attains a maximum value at about 11° and subsequently decreases until a temperature of 30° is attained. Above 30° there is no indication of an induction period.

Similar crystallization rate studies were made on a 10 mole % octyl copolymer in the temperature range 0° to 100°. In *Figure 3* are shown the selected modulus-time curves of 0, 10, 23, 55, 80, and 100°C. for the octyl copolymer. The initial modulus as previously noted depends on the temperature employed. At 0° no crystallization was noted as indicated by constant modulus up to 6000 minutes, at which time measurements were discontinued. The curves are all sigmoidal; all show induction periods. In the temperature range 10° to 80° the isotherms obtained from the plotted data show a shift of the maximum slope region to shorter times with increased temperature. In the temperature range 80° to 100° this maximum slope region shifts to longer times with increased temperature.

Similar studies were made on the 10 mole % butyl copolymer for the temperature range 10° to 100°. Shown in *Figure 4* are the 10, 22, 45, 55, 65, 85, and 100°C. isotherms. The initial modulus is again dependent on the temperature employed. No crystallization was noted at 10° after 7 days at which time measurements were discontinued. Like the octyl copolymer, the curves are all sigmoidal. In the temperature range 22° to 65°, the isotherms show a shift of the maximum slope region to shorter times as the temperature increases. Above 65° to 100° the isotherms shift to longer times with increased temperature.

Analysis of the Isotherms

The kinetics of crystallization may be compared and analyzed by following the methods developed by Avrami (6) as calculated by the following expression:

$$\chi = e^{-Kt^n} \tag{1}$$

where K contains nucleation and growth constants and n has a value of 1, 2, 3 and 4 according to the nature of the nucleation and growth processes. χ is the fraction which has undergone crystallization and its value at any given time, t, can be calculated as follows:

$$\chi = \frac{D_t - D_o}{D_\infty - D_o} \tag{2}$$

where D_t is the density at that time, D_o is the initial density, and D_∞ the final density for that crystallization, or for this study.

$$\chi = \frac{E_t - E_o}{E_\infty - E_o} \tag{3}$$

where E is Young's modulus.

The number n can be obtained by matching theoretical plots of χ versus $\tau^{1/n}$, where $\tau = Kt^n$, with experimental plots of χ versus the log t, where t is time.

Seen in *Figure 5* are the superimposed data plots of χ versus log of time for the octadecyl copolymer. It is seen that superimposition of the 11° to 60° data for the octadecyl copolymer is good up to $\chi = .45$, but at increasing values the experimental data fall away from the theoretical curve (n = 3). This divergence from the theoretical has been designated by other researchers as secondary crystallization and the portion that fits the theoretical is known as the primary crystallization. In addition, above $\chi = .45$, the data obtained at the various temperatures diverge. The higher the temperature the greater the divergence. Below 11° the data could not be superimposed since the n values were changing and another type of rearrangement is probably responsible for the observed behavior. The n values in this region diminished to less than 1.

The superimposed octyl data of the 23° to 75° isotherms are shown in *Figure 6*. The observed points show good superposition up to $\chi = .50$ where they diverge both from the theoretical (n = 2) and from each other. The n value is not the same as that found

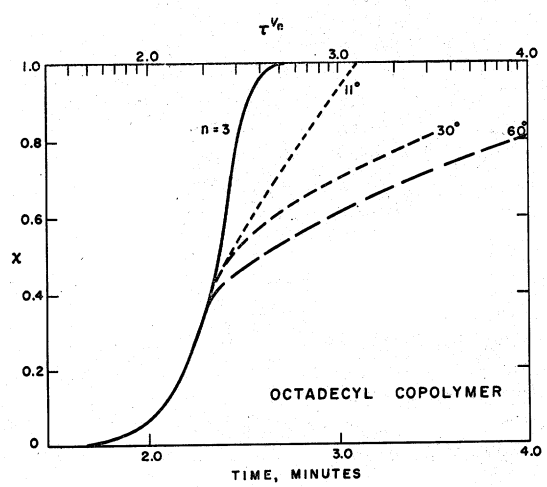

Figure 5. Superposition of experimental isotherms to the theoretical n = 3 for the copolymer of vinylidene chloride containing 10 mole % octadecyl acrylate.

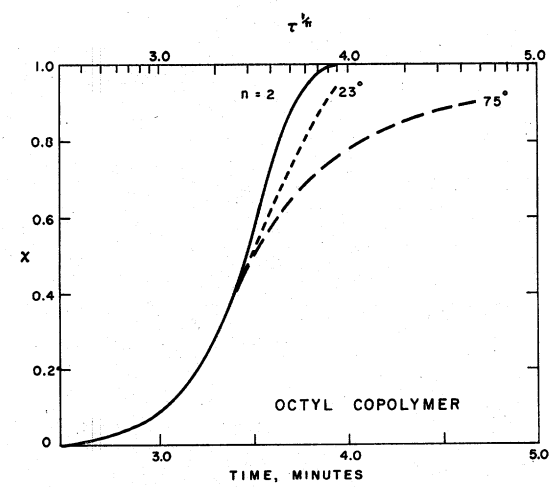

Figure 6. Superposition of experimental isotherms to the theoretical n = 2 for the copolymer of vinylidene chloride containing 10 mole % octyl acrylate.

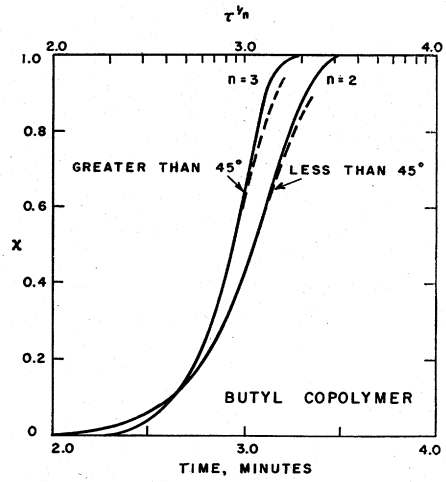

Figure 7. Superposition of experimental isotherms to the theoretical n = 2 and n = 3 for the copolymer of vinylidene chloride containing 10 mole % butyl acrylate.

for the octadecyl copolymer which was 3. Above χ = .50, the octyl plot shows much less divergence than the octadecyl copolymer, indicating that there is less secondary crystallization with a shorter alkyl side chain. At the temperature of 10° the n value was 3.

The superimposed isothermal data from 22° to 100°C. for the butyl copolymer are seen in *Figure 7*. Shown are two plots. The 45° to 100° isotherms fit the theoretical n = 3 and the 22° and 31° isotherms superimpose to n = 2. The data, unlike the octadecyl and octyl, show only slight deviation from the theoretical indicating that the short butyl side chain is less effected by secondary crystallization.

The growth constant K of the Avrami equation can be determined from the expression:

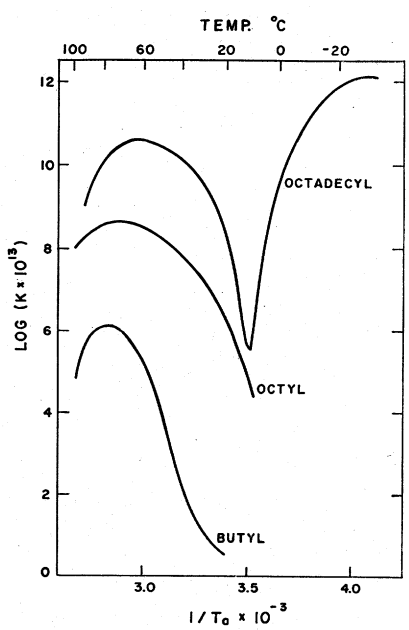

Figure 8. Variation of rate of crystallization with temperature.

$$K = (\ln 2)/(t_{1/2})^n$$

Figure 8 shows the plots of K versus temperature. The octadecyl acrylate copolymer shows a rapid increase in the K values from 90° to a maximum at about 60°. From 60° to about 35° the K values decrease at a slower rate followed by a rapid decrease to 10° where the minimum K value is noted. From 10° to −30° there is again a rapid increase in the K values. The K values for the octyl acrylate copolymer show a slow increase to a maximum at about 75° and then they slowly decrease to about 40° followed by a rapid decrease to 10°. The butyl acrylate copolymer shows rapidly increasing K values up to about 85° and then rapidly decreasing values. It is noted that in the temperature range 10° to 100° that the octadecyl copolymer shows the fastest growth rate and the butyl the slowest as evidenced by the displacement of the curves. In addition, below 10° the octadecyl curve exhibits a second segment not found for the other copolymers. There is ~~an~~ apparently another type of rearrangement occurring in this range.

Summary

Torsional modulus measurements were used to study the kinetics of crystallization of three copolymers of vinylidene chloride containing 10 mole % alkyl acrylate. The isotherms were found to be superimposable in the temperature range 11° to 60° for the octadecyl acrylate copolymer, 10° to 100° for the octyl acrylate copolymer, and 22° to 100° for the butyl acrylate copolymer. The geometrical growth and nucleation constant n of the Avrami equation was determined. The octadecyl acrylate copolymer had an n = 3 in the temperature range 11° to 90°. Below 11° the n value diminished to less than 1. The octyl acrylate copolymer had an n = 2 for the temperature range 23° to 100° and at 10°, n = 3. The value for the butyl acrylate copolymer in the temperature range 45° to 100° was n = 3, at 22° and 31°, n = 2. In addition, apparently the length of the alkyl side chain effects secondary crystallization as noted by the divergence of the observed from the theoretical data; at χ values greater than .45 the butyl copolymer shows essentially no divergence while the octyl and octadecyl copolymers show divergence. The amount of non-conformity varies with the temperature and increases with chain length. It was found that the rate of crystallization increased with increase in the length of the alkyl side chain, the octadecyl copolymer showing the fastest rate and the butyl copolymer showing the slowest in the same temperature range.

Literature References

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