

Condensation Polymers Containing Fluorine. II. Physical Characterization of Linear Polyesters from Hexafluoropentanediol*

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INTRODUCTION

In a previous paper,¹ methods of synthesizing linear polyesters from fluorine-containing diols were described, and a preliminary characterization of these polymers was included. A number of additional polyesters have now been prepared incorporating isophthalate and fumarate residues in addition to the adipate residue as previously reported in esterifications with 2,2,3,3,4,4-hexafluoropentanediol (HFPD). The main purposes of this paper are to describe the dependence of the intrinsic viscosity of hexafluoropentylene adipate (HFPA) on molecular weight, the dependence of the crystalline melting temperatures on polyester composition, the dependence of the glass transition temperatures on composition and on crosslinking, and the dependence of rate of crystallization on composition, crosslinking, and temperature.

EXPERIMENTAL

Preparation of Polyesters

The polyesters were prepared by reacting hexafluoropentanediol (HFPD) with stoichiometric quantities of a dibasic acid chloride or a mixture of dibasic acid chlorides. All the reagents were carefully purified either by repeated distillation or recrystallization. The adipyl chloride used was a colorless liquid with a b.p. of 52° at 0.1 mm. The HFPD² was recrystallized from benzene and had a m.p. of 77.5–78.5°. The isophthaloyl chloride had a m.p. of 44° after recrystallization from hexane or petroleum ether.

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The polymerization reactions consisted of mixing the reagents and solvent, *o*-dichlorobenzene (10–20% by weight), at room temperature, heating at 35–40° for 3–4 hours, then at 120–140° for another 3–4 hours, and finally at 200–220° for 3–4 hours. In the case of the adipate–isophthalate copolyesters, it was necessary to extend the final heating period to 10–12 hours, due to the difference in reactivity between the adipyl and isophthaloyl chlorides. A dry stream of nitrogen was started through the reaction flask when the temperature reached 80–100°. After completion of the reaction at 200–220°, the solvent was removed at this temperature by applying vacuum.

Preparation of Vulcanizates

The polyesters were compounded on a conventional rubber mill with water-cooled rollers for about 1 hr. The recipe consisted of 50 parts SRF black, 20 parts Purecal U, 19 parts DiCup 40-C, and 100 parts polyester, all by weight. Molding was carried out for 50–55 minutes at 160° and a pressure of 1250 p.s.i.

Molecular Weight

Molecular weights were determined for hexafluoropentylene adipate (HFPA) by the measurement of melt viscosity η employing a relation after Flory,³ established in the previous paper.¹ It was there reported that η of HFPA correlates with the weight-average chain length \bar{Z}_w according to the relation

$$\log \eta = -6.88 + (2050/T) + 0.153\bar{Z}_w^{1/2} \quad (1)$$

where T is the absolute temperature. The number-average molecular weight \bar{M}_n is calculated from \bar{Z}_w by means of the relation

$$\bar{M}_n = (161.1/13)(\bar{Z}_w + 6.5) \quad (2)$$

Equation (1) was established for values of \bar{M}_n up

to 7800¹; however, the relation is assumed to be valid here for calculating \bar{M}_n values up to 25,000.

Solution Viscosity

Solution viscosities were determined in chloroform at 30° in a suspended-level capillary viscometer (Cannon-Ubbelohde) having a solvent efflux time of 205 sec. The kinetic energy correction, applied to all efflux times, amounted to 0.1% of the efflux time for the solvent.

Dilatometry

Conventionally designed volume dilatometers were used. They contained a calibrated and graduated precision bore capillary tube 2 mm. in diameter. Due to the relatively low polyester viscosities, samples were prepared by heating the polymer under vacuum in a test tube in order to remove air. The test tube containing the sample was then inserted directly into the dilatometer tube after breaking the test tube off at the polymer meniscus. Dilatometer samples for vulcanized polyesters were cut from 0.025-in. molded sheets. The confining liquid, admitted under vacuum, was a silicone oil [General Electric Fluid SF-81 (40)]. It was necessary to remove traces of water from the oil by heating, and subsequently to keep the oil under anhydrous conditions, in order to prevent ice formation in the dilatometers at low temperatures. The change in the dilatometer capillary meniscus following final degassing never exceeded 1 mm. when the applied pressure was decreased from atmospheric pressure to 0.25 mm. Hg. Sample specific volumes were measured independently by hydrostatic weighing. The volumes of the dilatometer sample and the confining liquid were found by direct weighing. The sample weight varied from 6.5 to 10.6 g., the ratio of the weight of confining liquid to the weight of sample varying from 0.7 to 1.6.

The low temperature thermostat was a 1 gal. Dewar flask containing the usual components. A cold reservoir⁴ (a flask containing Dry Ice-acetone) was connected to it by means of an insulated copper rod 1¹/₈ in. in diameter. A Pyrex test tube 2 in. in diameter was inserted in the thermostat. This tube, containing the dilatometer, a stirrer, and a calibrated copper-constantan thermocouple, was filled to a level about 1 in. above the top of the thermostat, and served to minimize temperature fluctuations and permit observation of the capillary meniscus while the latter was totally immersed in

the thermostat liquid. Temperatures were recorded to within 0.02° by means of a Leeds and Northrup Precision Potentiometer (No. 8662).

In the determination of glass transitions, the temperature was changed at a rate of about 0.5°/min., readings being made at 5 to 10° intervals. At each temperature, maintained for 10 to 30 min. to insure equilibration, the maximum temperature fluctuation was about ±0.1°. A number of individual dilatometer-temperature readings were averaged to obtain the final level. In the determination of the isothermal rates of crystallization, dilatometer levels were recorded at 2-3 min. intervals. In all cases, dilatometer levels were corrected for the small divergences of the recorded temperature from the nominal temperature.

Melting Point Apparatus

Melting points were determined as the temperature at which the last traces of optical double refraction disappeared when a crystalline polyester sample was heated in an insulated hot stage. The samples, observed between crossed polaroids with a 60 power stereomicroscope, were heated from room temperature to their melting point over a period of about 1 to 2 hours.

RESULTS AND DISCUSSION

Description of Samples

Table I contains the dibasic acid composition, the intrinsic viscosity, the melt viscosity, and the molecular weight, calculated according to eqs. (1) and (2) (for the HFFPA samples), for a series of polyesters prepared from HFFPD.

Intrinsic Viscosity—Molecular Weight Relationship

The intrinsic viscosity $[\eta]$ and number average molecular weight \bar{M}_n data are included in Table I for the six HFFPA samples so examined. Huggins viscosity interaction constants fell in the range 0.37 ± 0.04 . Figure 1 is a plot of $[\eta]$ versus \bar{M}_n for this series. A linear relationship, represented by the equation

$$[\eta] = 3.20 \times 10^{-5} \bar{M}_n \quad (3)$$

is obtained. The observed linear relationship between $[\eta]$ and \bar{M}_n is characteristic of linear condensation polymers.⁵

TABLE I
Description of Samples

| Sample no. | $[\eta]$, 100 cm. ³ /g. | η , poise, at (°C.) | \bar{M}_n | Dibasic acid composition, mole-% | | |
|------------|--|-----------------------------|-------------|-------------------------------------|--------------|----------|
| | | | | Adipate | Isophthalate | Fumarate |
| G-1 | 0.182 | 50 (110) | 5,600 | 100 | — | — |
| G-3 | 0.279 | 480 (110) | 9,450 | 100 | — | — |
| 8856 | 0.418 | 2,540 (110) | 13,000 | 100 | — | — |
| 88 | 0.630 | 2,510 (205) | 19,100 | 100 | — | — |
| 50 | 0.641 | 4,120 (205) | 20,500 | 100 | — | — |
| 57 | 0.808 | 13,500 (215) | 24,600 | 100 | — | — |
| 131 | — | 2,990 (205) | 19,500 | 100 | — | — |
| 132 | 0.421 | 320 (201) | — | 80 | 20 | — |
| 75 | — | — | — | 75 | 25 | — |
| 140 | 0.22 | 38 (201) | — | 50 | 50 | — |
| 86 | — | 520 (205) | — | 48 | 50 | 2 |
| 124 | — | 326 (205) | — | 25 | 70 | 5 |
| G-4 | — | — | — | — | 100 | — |

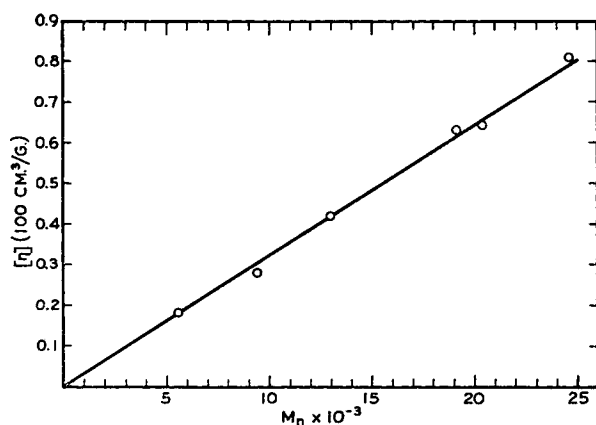


Fig. 1. Intrinsic viscosity versus number-average molecular weight for hexafluoropentylene adipate.

Melting Transitions

Table II includes the crystalline melting points T_m for a series of copolyesters covering the 0 to 100

mole-% isophthalate range. The values determined optically employed samples which had crystallized at room temperature. The double refraction of sample 8856 was notable in that it indicated large and perfectly formed spherulites over the range of 32–33°, which melted sharply at 34.5°. The patterns were notable in that 5 to 6 doubly-refractive areas radiated out from the center of each spherulite. Table II includes a dilatometrically determined T_m for sample 8856, following crystallization of the sample at 0° and subsequent melting over a 200-hr. period. Figure 2 includes a plot of this data, indicating a T_m of 34.5°, a value identical to that obtained by the optical method. For samples other than 8856, the T_m 's must be regarded as approximate since they were measured under nonequilibrium conditions; however, the data indicate a (nonlinear) increase in T_m with isophthalate content.

TABLE II
Melting and Glass Transition Temperatures

| Sample no. | Isophthalate, mole-% | T_g , °C. | Crystallinity | T_m , °C. | |
|------------|-------------------------|-------------|------------------------|---------------------|--------------|
| | | | | Optical | Dilatometric |
| 8856 | 0 | -58 | crystallized | 34.5 | 34.5 |
| 131 | 0 | -57 | crystallized | — | — |
| 131V | 0 | -51 | partially crystallized | — | — |
| 132 | 20 | -49 | amorphous | — | — |
| 132V | 20 | -44 | amorphous | — | — |
| 140 | 50 | -31 | amorphous | 47 | — |
| 75 | 25 | — | — | 48 | — |
| 86 | 50 | — | — | 49 | — |
| 124 | 70 | — | — | 67, 71 ^a | — |
| G-4 | 100 | — | — | 104 | — |

^a This single determination was made on a sample rendered birefringent by elongation.

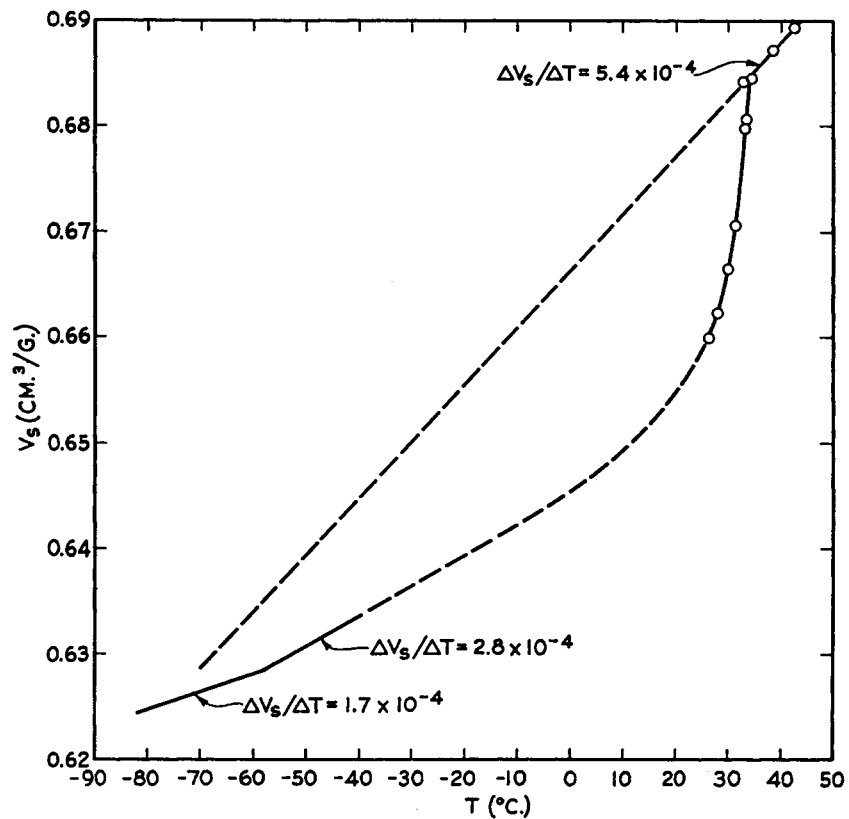


Fig. 2. Specific volume versus temperature for HFFA sample 8856.

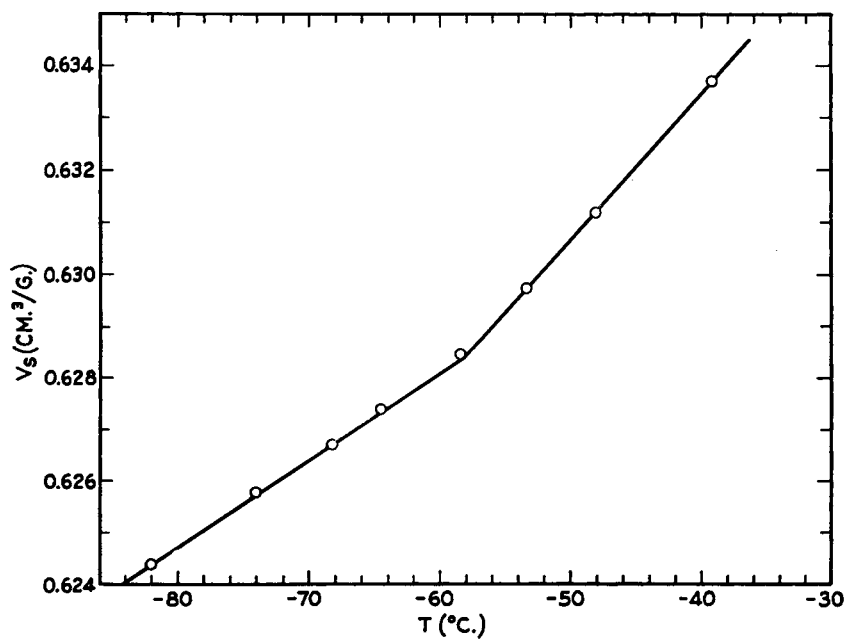


Fig. 3. Specific volume versus temperature for HFFA sample 8856 in region of T_g .

Glass Transitions

The glass transition temperatures T_g were determined dilatometrically. Figure 3 is a plot of specific volume V_s versus temperature for sample 8856. The data are accurately represented by two intersecting straight lines. These data are also included in Figure 2, which plots V_s versus temperature over the entire temperature range. The temperature coefficients of specific volume, $\Delta V_s/\Delta T$, are indicated in Figure 2. Due to the polyester's semicrystalline state, $\Delta V_s/\Delta T$ above T_g is smaller than it is for the liquid line above T_m . The additional T_g values were obtained directly from plots of dilatometer level versus temperature, where pairs of intersecting straight lines were accurately determined in each case. Such plots neglect the change in dilatometer volume with temperature in determining T_g , but this discrepancy does not effect the results. In every case, the measurements were made under conditions of both ascending and descending temperature. The T_g values obtained are listed in Table II, and include values for the vulcanizates of two of the polyesters, designated 131V and 132V. Whether the sample was allowed

to crystallize prior to the determination of T_g is also noted.

The data for samples 8856 and 131 indicate that -57° may be taken as the asymptotic limit of T_g with respect to \bar{M}_n for semicrystalline HFPA. The T_g 's observed for samples 131, 132, and 140 indicate that T_g increases as the copolyester isophthalate content increases from 0 to 20 to 50 mole-%, respectively, implying that the inclusion of isophthalate stiffens the polymer chain. A plot of T_g against isophthalate content yields a curve convex to the composition axis, a shape characteristic of vinyl addition copolymers.⁶ In certain cases, degree of crystallinity has been reported to affect T_g ,⁷ although this effect is not general^{7,8}; therefore, the T_g 's reported for those samples which were semicrystalline (8856, 131, and 131V) must not be assumed to be identical to the values which would be obtained for the amorphous polyesters. For samples 131 and 132, the vulcanizate T_g 's are 6° and 5° higher, respectively, than the values for the unvulcanized polyesters, illustrating the well-known effect of crosslinking on glass transition temperature.⁹

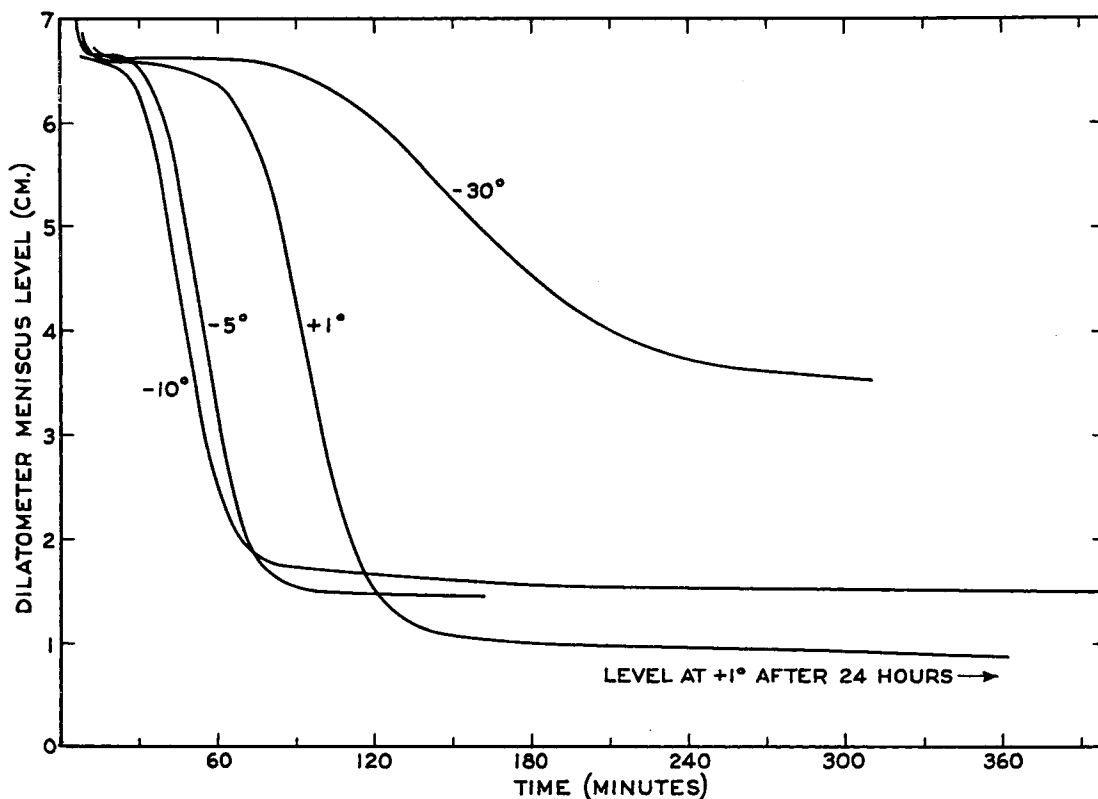


Fig. 4. Dilatometer meniscus level versus time for HFFA sample 8856 at each of four temperatures.

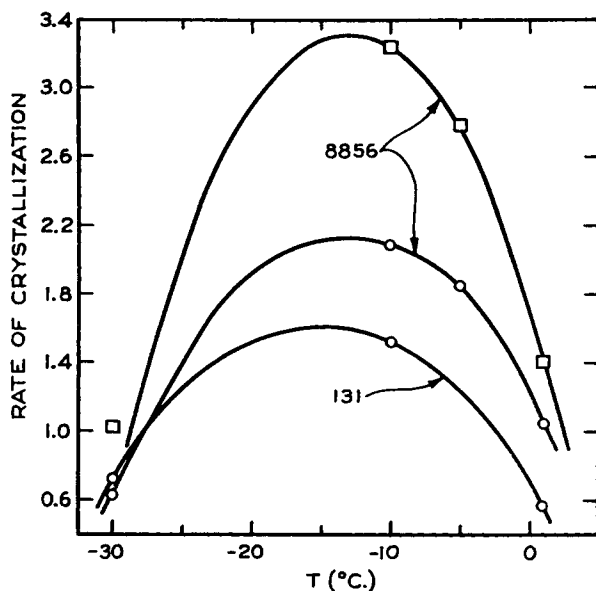


Fig. 5. Rate of crystallization versus temperature for HFFA samples 8856 and 131: (O) $t_{1/2}^{-1} \times 10^2$; (\square) $\tau_i^{-1} \times 10^2$.

imum rates of crystallization are estimated to occur at -13° and -15° , respectively. $(\Delta V_s / \Delta t)_m$ has also been plotted against temperature. The maximum in this curve is difficult to ascertain precisely, since it is broad, but it appears to occur at about -10° for sample 8856. The lower

molecular weight sample (8856) has a higher rate of crystallization over most of the temperature range examined; however, at -30° sample 131 crystallizes at a slightly higher rate, due presumably to an enhanced contribution of rate of nucleation to the overall kinetics at this temperature. The $t_{1/2}$ value obtained for 131V shows that the expected large decrease in the rate of crystallization occurs on introduction of crosslinks; however, the effect of the filler is not known. In addition, milling has been found to degrade HFFA to a limiting \bar{M}_n of about 15,000. The $t_{1/2}$ value for sample 132 demonstrates that the inclusion of 20 mole-% isophthalate in the copolyester greatly reduces the crystallization rate at -10° .

The crystallization curves may be analyzed employing eq. (4). n is determined by specifying the nucleation and growth processes, whereas α depends on the ultimate degree of crystallinity, the rate of formation of stable nuclei, and the growth rate of these nuclei. Mandelkern¹² has noted that α and n may be determined from experimental data by means of theoretical plots from eq. (4) for different values of n , of $(V_t - V_\infty)/(V_0 - V_\infty)$ versus $\log \tau^{1/n}$, where $\tau = \alpha t^n$. The experimental data are similarly plotted, using $\log t$ in place of $\log \tau^{1/n}$, where t is time. n and α are then obtainable by superimposing the experimental and theo-

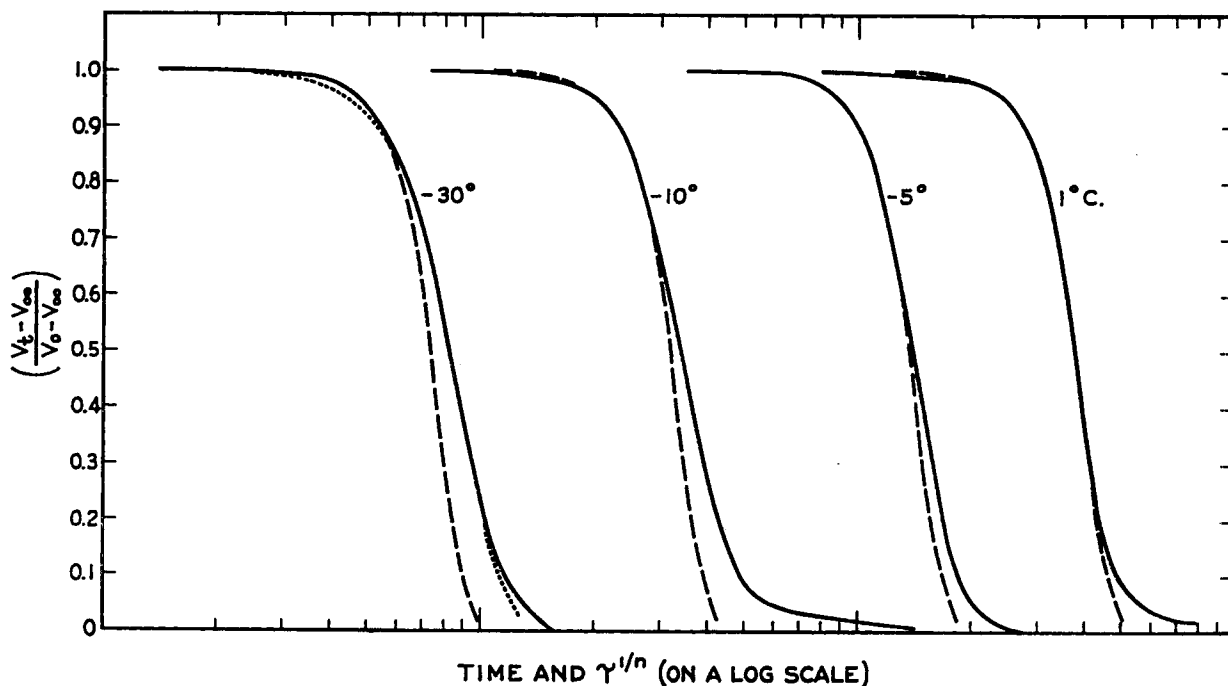


Fig. 6. Experimental and theoretical crystallization isotherms for HFFA sample 8856. $(V_t - V_\infty) / (V_0 - V_\infty)$ versus $\log t$ (—) and versus $\log \tau^{1/n}$ for $n = 6$ (- -) and for $n = 4$ (· · ·).

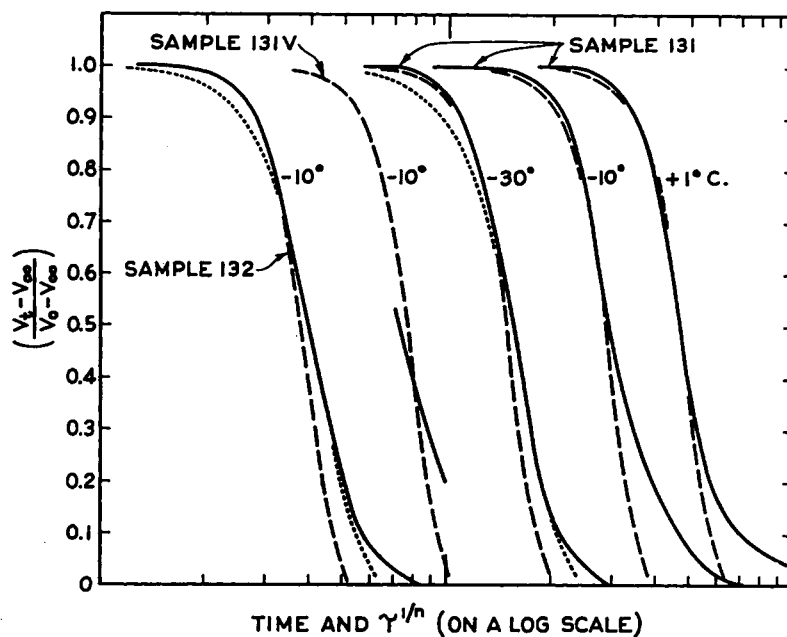


Fig. 7. Experimental and theoretical crystallization isotherms for HFGA samples 131 and 131V and for sample 132. $(V_t - V_\infty)/(V_0 - V_\infty)$ versus log time (—) and versus $\log \tau^{1/n}$ and for $n = 6$ (- -) and for $n = 4$ (· · ·).

retical plots and adjusting them horizontally to secure the best fit. Mandelkern et al.¹¹ have pointed out that the superimposibility of experimental isotherms recorded at different temperatures indicates invariance of the temperature coefficient throughout the course of crystallization and suggests that nucleation and growth occur concurrently.

The experimental isotherms, plotted as indicated above, are shown in Figures 6 and 7. The initial portions of each isotherm are best represented by eq. (4) with $n = 6$, and these theoretical isotherms are superimposed on all the experimental curves. In addition, some theoretical isotherms for $n = 4$ are included for purposes of comparison. At 1° , the two HFGA samples 8856 and 131 coincide with theory over a large extent of the crystallization process; as the isotherm temperature is lowered, departure from theory occurs over progressively larger portions of the crystallization process. Mandelkern¹² has suggested some reasons to account for the discrepancies which are generally observed beyond the initial stages of crystallization, noting that such discrepancies may be expected from the assumptions involved in the development of eq. (4). For both 8856 and 131, the ultimate degree of crystallinity decreases with decreasing temperature [see $(\Delta V_s)_e$, Table III], a general phenomenon attributed to an increase in rate of

nucleation at lower temperatures, resulting in smaller and less efficiently packed crystallites.¹⁶ It may be anticipated that complete superimposibility of the experimental isotherms will occur over the range between 1° and the melting point (34.5° for 8856) for each of these samples. The data for the vulcanizate of 131 at -10° (131V, Fig. 7), limited to the center portion of the isotherm, is precisely superimposable on the isotherm for the unvulcanized sample at -10° (131, Fig. 7).

It may be shown from eq. (4), for the crystallization of a given polymer obeying this relationship, that the quantity $(\Delta V_s/\Delta t)_{mt_{1/2}}/(\Delta V_s)_e$ and the corresponding quantity containing τ ; depend only on n and are independent of temperature. However, these quantities will decrease with temperature in the event that the experimental isotherms exhibit increasing divergence from eq. (4) as the temperature (and degree of crystallinity) is reduced. The decrease of these two quantities with temperature is shown by the data in Table III (columns 9 and 10) for HFGA. $(\Delta V_s/\Delta t)_{mt_{1/2}}/(\Delta V_s)_e$ has been calculated for 8856 at each temperature using the values of $(\Delta V_s/\Delta t)_{mt_{1/2}}$ obtained from the theoretical isotherms in Figure 6. As anticipated, the former quantity (column 11) is virtually independent of temperature; however, a slight maximum near the maximum rate of crystallization is indicated.

It has been reported that the isotherms for natural rubber are superposable over a range of temperatures in the region of the maximum rate of crystallization and, moreover, that the product of $(\Delta V_s/\Delta t)_m$ with either $t_{1/2}$ or τ_i is independent of temperature.^{16,17} In as much as complete superposability exists, this constancy of the above products is understandable, since the decrease in equilibrium degree of crystallinity is only 15%¹⁶ for rubber over the temperature range in question (1° to -30°). HFPA 8856 exhibits a 46% decrease in crystallinity over this temperature interval.

n has been found to be equal to 6, independent of temperature, molecular weight, and the inclusion of 20 mole-% isophthalate in the copolyester, over the initial stages of the crystallization process. It is apparently the highest value yet reported for a high polymer. The value of 6 cannot be explained by the mechanisms of nucleation and growth which have been assumed in the interpretation of crystallization kinetics. The values for n which have been predicted to be theoretically possible are in the range of 1 to 4^{11,12}; moreover, experimentally determined values for a variety of addition and condensation polymers, including polyesters, have been found to be in this latter range.¹⁸

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References

1. G. C. Schweiker and P. Robitschek, *J. Polymer Sci.*, **24**, 33 (1957).
2. E. T. McBee, W. Marzluff, and O. W. Pierce, *J. Am. Chem. Soc.*, **74**, 444 (1952).
3. P. J. Flory, *ibid.*, **62**, 1057 (1940).
4. R. M. Kell, D. G. McNulty, B. Bennett, P. B. Stickney, and R. G. Heiligmann, Final Report on "Experimental Study of the Melting and Glass Transitions of Elastomers," January 13, 1956, ASTIA No. 92651.
5. See, for instance: E. M. Frith and R. F. Tuckett, *Linear Polymers*, Longmans, Green, New York, 1951, p. 227.
6. See, for instance: L. A. Wood, *J. Polymer Sci.*, **28**, 319 (1958).
7. L. Mandelkern, G. M. Martin, and F. A. Quinn, Jr., *J. Research Natl. Bur. Standards*, **58**, 137 (1957).
8. See, for instance: R. F. Boyer and R. S. Spencer, in *Advances in Colloid Science*, Vol. II, Interscience, New York, 1946, p. 12.
9. *Ibid.*, p. 24.
10. M. Avrami, *J. Chem. Phys.*, **7**, 1103 (1939); *ibid.*, **8**, 212 (1940).
11. L. Mandelkern, F. A. Quinn, Jr., and P. J. Flory, *J. Appl. Phys.*, **25**, 830 (1954).
12. L. Mandelkern, *Chem. Rev.*, **56**, 903 (1956).

13. P. J. Flory and A. D. McIntyre, *J. Polymer Sci.*, **18**, 592 (1955).
14. W. H. Cobbs, Jr. and R. L. Burton, *ibid.*, **10**, 275 (1953).
15. L. A. Wood and N. Bekkedahl, *J. Appl. Phys.*, **17**, 362 (1946).
16. A. N. Gent, *J. Polymer Sci.*, **18**, 321 (1955).
17. E. W. Russell, *Trans. Faraday Soc.*, **47**, 539 (1951).
18. See, for instance: References 11, 12, 14, and 16; P. W. Allen, *Trans. Faraday Soc.*, **48**, 1178 (1952); L. B. Morgan, *Chem. and Ind. (London)*, **1951**, 796.

Synopsis

A number of fluorinated polyesters have been prepared by condensing hexafluoropentanediol with one or more dibasic acid chlorides, and melting and glass transition temperatures and rates of crystallization have been determined, largely by means of volume dilatometry. The relation between $[\eta]$ in chloroform at 30° and \bar{M}_n for hexafluoropentylene adipate (HFPA) was found to be $[\eta] = 3.20 \times 10^{-5} \bar{M}_n$. The melting point T_m was found to increase from 34.5° to 104° as the isophthalate content in a series of adipate copolyesters increased from 0 to 100 mole-%. The glass transition T_g increases from -57° to -31° as isophthalate content increases from 0 to 50 mole-%. T_g is raised about 6° by the crosslinking of the polyesters. Rates of crystallization were determined for two HFPA samples with \bar{M}_n 's of 13,000 and 19,500. Maxima in these rates occurred at about -13° and -15°, respectively. Respective $t_{1/2}$ values for (linear) HFPA, vulcanized HFPA, and a copolyester containing 20 mole-% isophthalate are 48, 1140, and 27,200 min., respectively, at -10°. All the crystallization isotherms conform to Avrami's equation, $(V_t - V_\infty)/(V_0 - V_\infty) = \exp\{-\alpha t^n\}$, for $n = 6$ over the initial stages of the process. At 1° both HFPA isotherms agree with the above equation over a large part of the process; however, as the isotherm temperature decreases, the equilibrium degree of crystallinity, as judged by the overall specific volume change, decreases and the isotherms diverge from Avrami's equation over progressively larger portions of the process. The product of the maximum rate of crystallization for each isotherm with either $t_{1/2}$ or τ_i , the "induction time," decreases with decreasing temperature, as would be expected in view of Avrami's equation. The value of 6 observed for n , a constant determined by the nucleation and growth mechanisms, is anomalous since only values of 1 to 4 are theoretically predictable. Values over the range of 1 to 4 have been observed experimentally by other workers for a variety of polymers.

Résumé

Plusieurs polyesters fluorés ont été préparés par condensation du hexafluoro-pentanediol avec un ou plusieurs chlorures d'acides dibasiques; leurs températures de fusion et de transition vitreuse et leurs vitesses de cristallisation ont été déterminées, surtout par dilatométrie. Le rapport existant entre $[\eta]$ dans le chloroforme à 30° et \bar{M}_n pour l'adipate de hexafluoropentylène (HFPA) était le suivant $[\eta] = 3.2 \times 10^{-5} \bar{M}_n$. Le point de fusion T_m croissait de 34.5 à 104° à mesure que la teneur en isophthalate croissait de 0 à 100 moles % dans la série des copolyesters adipiques. La température de transition vitreuse T_g croît de -57 à

-31° quand la teneur en isophthalate croît de 0 à 50 moles %. T_g augmente d'environ 6° par pontage du polyester. Les vitesses de cristallisation ont été déterminées pour deux échantillons HFPA de \bar{M}_n 13.000 et 19.500. Les maxima de vitesse se situent à environ -13 et -15° respectivement. Les valeurs $t_{1/2}$ pour le HFPA linéaire, HFPA vulcanisé et un copolyester contenant 20 moles % d'isophthalate étaient respectivement de 48, 1140 et 27.200 minutes à -10°C. Toutes les isothermes de cristallisation suivent l'équation d'Avrami, à savoir $(V_t - V_\infty)/(V_0 - V_\infty) = \exp\{-\alpha t^n\}$, où $n = 6$ pour les étapes initiales du processus. A 1° les deux isothermes HFPA concordent avec cette équation pour une grande partie du phénomène; toutefois quand la température de l'isotherme est abaissée, le degré de cristallinité à l'équilibre, tel qu'il est mesuré par une variation du volume spécifique global, décroît et les isothermes s'écartent de l'équation de Avrami sur des parties de plus en plus grandes du phénomène. Le produit du maximum de vitesse de cristallisation pour chaque isotherme par $t_{1/2}$ ou τ_i , temps d'induction, décroît avec une température décroissante, comme prévu sur la base de l'équation d'Avrami. La valeur de 6 observée pour n , constante dépendante des mécanismes de nucléation et de croissance, est anormale puisque seules des valeurs de 1 à 4 sont théoriquement prévisibles. Les valeurs de 1 à 4 ont été observées expérimentalement par d'autres chercheurs pour un grand nombre de polymères.

Zusammenfassung

Eine Anzahl von fluorierten Polyestern wurde durch Kondensation von Hexafluorpentandiol mit einem oder mehreren Säurechloriden zweibasischer Säuren dargestellt und die Schmelz- und Glasumwandlungstemperaturen sowie Kristallisationsgeschwindigkeiten grösstenteils mittels dilatometrischer Messungen bestimmt. Die Beziehung

zwischen $[\eta]$ in Chloroform bei 30°C und \bar{M}_n ist, wie gefunden wurde, für Hexafluorpentylendipat (HFPA) $[\eta] = 3,20 \times 10^{-5} \bar{M}_n$. Es wurde festgestellt, dass der Schmelzpunkt von 34,5 auf 104° ansteigt, wenn in einer Reihe von Adipinsäurecopolyestern der Isophthalatgehalt von 0 auf 100 Mol-% ansteigt. Die Glasumwandlung (T_g) nimmt beim Anstieg des Isophthalatgehaltes von 0 auf 50 Mol-% von -57 auf -31° zu. Durch Vernetzung der Polyester wird T_g um etwa 6° erhöht. Kristallisationsgeschwindigkeiten wurden für HFPA-Proben mit einem \bar{M}_n von 13000 und 19500 bestimmt. Diese Geschwindigkeiten zeigten Maxima bei etwa -13 und -15°. Die jeweiligen $t_{1/2}$ -Werte bei -10° betragen für (lineares) HFPA 48 min, für vulkanisiertes HFPA 1140 min und für einen Copolyester mit 20 Mol-% Isophthalat 27200 min. Alle Kristallisationsisothermen gehorchen in dem anfänglichen Teil des Vorganges der Gleichung von Avrami, $(V_t - V_\infty)/(V_0 - V_\infty) = \exp\{-\alpha t^n\}$, mit $n = 6$. Bei 1° stimmen beide HFPA-Isothermen mit der obigen Gleichung für einen grossen Teil des Prozesses überein; beim Absinken der Temperatur der Isotherme, nimmt jedoch, wie man aus der gesamten, spezifischen Volumsänderung erkennt, der Kristallinitätsgrad im Gleichgewicht ab und die Isothermen weichen von der Avrami-Gleichung über einen immer grösser werdenden Teil des Prozesses ab. Für jede Isotherme nimmt, wie man nach der Gleichung von Avrami erwarten kann, das Produkt aus der Maximalgeschwindigkeit der Kristallisation und $t_{1/2}$ oder τ_i , der "Induktionsdauer" mit fallender Temperatur ab. Der für n , eine Konstante, die durch den Keimbildungs- und Wachstumsmechanismus bestimmt ist, beobachtete Wert von 6, ist anomal, da nach der Theorie lediglich Werte zwischen 1 und 4 zu erwarten sind. Von anderen Autoren wurden bei einer Vielfalt von Polymeren Werte im Bereich von 1 bis 4 beobachtet.

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