

Melting Points of Cellulose Nitrates

R. S. COLBORNE, *Bickley, Kent, England*

Synopsis

Fresh determinations and estimations of the melting temperatures of cellulose nitrates have been found to be much lower than previously reported and to be in line with those of other cellulose derivatives, varying from 200°C. for the dinitrate to 280°C. for a sample approaching the trinitrate in composition. The heat of fusion of at least 3000 cal./unit is also similar to values of other cellulose derivatives. The paper contains some observations on the applicability of Flory's theory of the effect of diluents on the crystalline melting temperature of polymers.

The structure requirements for polymers of high melting points have been discussed recently in several lectures, notably those by Mark¹ and Holliday,² and there is general agreement that, to have melting points much above about 360°C., polymer chains need a high degree of stiffness, which may be brought about by a "ladder" or "two-strand" structure or a closely coupled system of aromatic rings. Polymers with linear groups or non-aromatic rings joined together by oxygen links have a degree of flexibility and not exceptionally high melting points. An apparent exception to the general rule is an estimate made some years ago of "at least 1000°K." for cellulose trinitrate³ and of 890°K. for a cellulose nitrate of a lower degree of substitution,⁴ but there is nothing in the structure of the polymer to explain the anomaly, and of the cellulose derivatives whose properties are on record the triacetate has the highest melting point (300°C.). Cellobiose octanitrate, the nearest model compound for cellulose nitrate, melts at 140°C., but two forms of the octaacetate melt respectively at 222°C. (α) and at 192°C. (β).

The estimates referred to were based on long-range extrapolation of transition temperatures observed in mixtures of cellulose nitrate with a diluent; the extrapolation was an equation developed on a thermodynamic basis by Flory,⁵ in which the effect of diluents on the crystalline melting temperature of a polymer is expressed as

$$1/T_m - 1/T_m^0 = (RV_u/\Delta H_u V_1)(v_1 - \chi v_1^2) \quad (1)$$

where T_m = observed melting point, T_m^0 = melting point of undiluted polymer, ΔH_u = heat of fusion, V_u = molecular volume of repeating unit of polymer, V_1 = molecular volume of diluent, v_1 = volume fraction of diluent, and χ = interaction constant.

Although the formula is worked out from first principles, it involves certain assumptions, and Flory pointed out that it would not be accurate at great dilutions.

One feature of the formula is that the parameters V_u and V_1 are not independent of temperature, and neither is their ratio in most instances. Variations in the ratio V_u/V_1 are not important if only a small temperature range is concerned, but over several hundred degrees it may be substantial. Most liquids have coefficients of expansion of about 10^{-3} , but polymers are in the range of 10^{-4} . As an example, γ -butyrolactone has a coefficient of about 0.9×10^{-3} cm.²/g./°C., but cellulose nitrate is quoted as having one of 1.8×10^{-4} . Thus the ratio V_u/v_1 is 2.1 at 20°C., becoming 1.9 at 200°C. and 1.5 at 700°C.

Difficulties of extrapolation also occur when the volume fraction of diluent in a polymer mixture has to be estimated. Even if the coefficients of expansion of the components over the whole temperature range are known, it is not certain that volumes are additive, especially when the components are polar in nature.

The chief difficulty in applying the dilution formula, however, is evaluation of the interaction constant χ . The constant has been found to vary with concentration,⁶ but there are no means of calculating the extent of its variation. The effect of temperature on χ has been found to follow the equation⁷

$$\chi = \alpha + \beta/T \quad (2)$$

both on theoretical and practical grounds.

In all cases in which χ has been evaluated experimentally the parameter α has been found to account for a large proportion of the total. Recent work suggests that the effect of temperature on χ is even more complicated than expressed by eq. (2),⁸ but in any case there seems to be no justification for assuming, in the absence of experimental evidence, that the factor α can be ignored and χ be represented solely by the second term, i.e. that solely heat effects are concerned.

However, the effect of any errors in evaluating χ in eq. (1) is only substantial at high dilutions. For compatible polymer and diluents χ is usually in the range 0-0.5. It appears as the coefficient of v_1^2 in eq. (1), and the extent of its influence may be illustrated by the following table

v_1		$v_1 - \chi v_1^2$
0.2	≈	0.19 ± 0.01
0.4	≈	0.36 ± 0.04
0.6	≈	0.51 ± 0.09
0.8	≈	0.64 ± 0.16

At a volume fraction of diluent not more than 0.2 the probable error in neglecting χ is not more than 5% for a given polymer and several diluents;

therefore, the only variable to be considered (v_1 being constant and less than 0.2) is the molecular volume of the diluent (v_1), so that

$$1/T_m - 1/T_m^0 \approx 1/V_1 \quad (3)$$

A check with the published results shows that this relationship is approximately valid. The effect of diluents on the melting point of cellulose tributyrates⁹ has been recorded, and by interpolation the following results were obtained:

Diluent ($v_1 = 0.2$)	$V_1(1/T_m - 1/T_m^0) \times 10^3$
Tributyryl	38
Benzophenone	46
Ethyl laurate	40
Ethyl benzoate	44
Dimethyl phthalate	44

Experimental

Having regard to these considerations, it appears that in the extrapolation of transitions in dilute systems of cellulose nitrate the hypothetical crystalline melting point of the polymer might be liable to error, and it was decided to try to extend the range of published data to higher temperatures and concentrations.

The method used in the earlier investigations involved slow heating, and signs of decomposition limited the temperature to about 120°C. However, cellulose nitrate will resist decomposition up to about 200°C. for very short periods. It was found that the melting points of polymers could be determined with reasonable accuracy by means of the Kofler Heizbank, a chromium-plated metal bar heated at one end and giving a graduated temperature range down to less than 50°C. If a strip of film about 5 mils thick is laid on the bar and after a few seconds stripped from the cooler end, the film breaks and adheres at a definite point on the bar, from which point the temperature may be ascertained. Trials with a series of polymer films gave the following results:

	Temp., °C.
Polyethylene, low density	107
Polyethylene, high density	130
Polypropylene	160
Polycarbonate	230
Polyester (Melinex)	260
Poly(vinyl fluoride) (Tedlar)	268

The results are within a few degrees of the published crystalline melting points for the polymers but, since the films tested were commercial products that may have contained small amounts of additives, a slightly lower melting point was to be expected.

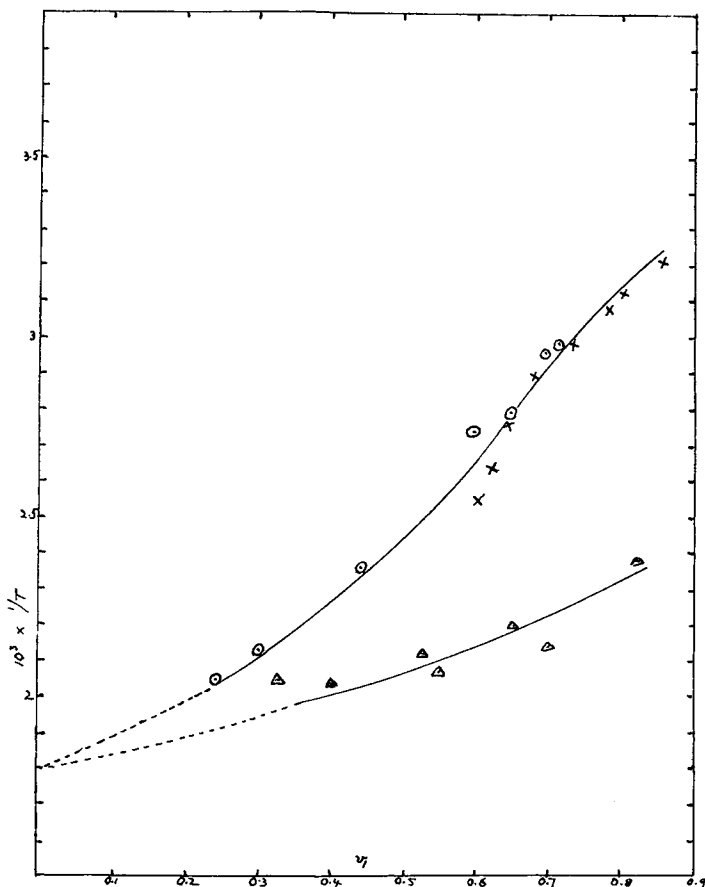


Fig. 1. Melting points of cellulose nitrate sample A, degree of substitution 2.83. Diluent: (Δ) dibutyl phthalate; (O) γ -butyrolactone; (\times) γ -butyrolactone.³

For this investigation three samples of cellulose nitrate were available. They were products of the nitration of cotton linters and were of high molecular weight:

<u>Sample</u>	<u>Degree of substitution</u>
A	2.83
B	2.23
C	2.0

Most of the films for test were made by dissolving the cellulose nitrate in acetone, together with appropriate amounts of liquid plasticizers of low volatility, and casting the solution on a glass plate. After evaporation of acetone the film was stripped and allowed to hang at room temperature for up to 24 hr., after which there was no more appreciable weight loss. It is known that a small amount of acetone, up to 1%, may be retained, and

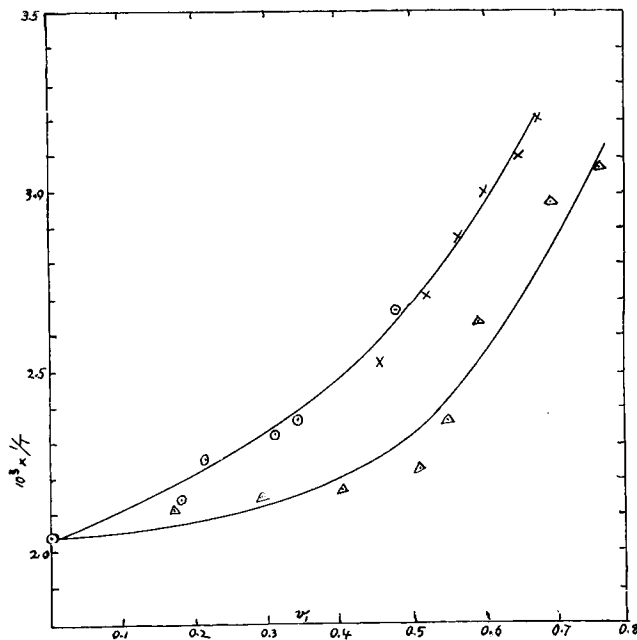


Fig. 2. Melting points of cellulose nitrate sample B, degree of substitution 2.23. Diluent: (O) γ -butyrolactone; (X) γ -butyrolactone;⁴ (Δ) dibutyl phthalate.

this would tend to lower the melting point, although it may be estimated that 1% acetone would, if still present on the film after heating, cause a lowering of not more than 5°C. Slight loss of high-boiling diluent would have the opposite tendency.

For mixtures of γ -butyrolactone an acetone solution containing a known amount of cellulose nitrate was cast in a 4-in. flat-bottom (Petrie) dish, and weighing was done at intervals. When a slow, constant rate of loss was reached, it was assumed that acetone was eliminated, and the residual film, the composition of which was known from the weight, was immediately tested on the Kofler bar as before.

The behavior of sample A is shown in Figure 1. As in the case of other cellulose derivatives, coherent films can be prepared with a high degree of dilution, covering a wide range of compositions. With dibutyl phthalate as diluent the least amount of diluent was about 0.25 weight fraction, at which the melting temperature was 210–216°C. A film with 0.74 weight fraction dibutyl phthalate melted at 162°C. Since sample A approximated in composition to the trinitrate, it was highly inflammable, and films caught spontaneously on fire after a few seconds of heating. It was possible to delay decomposition by covering the film with a microscope coverglass; this enabled the range of observations to be extended a short distance above 200°C. Moreover, at low dilution it was often possible to observe the point of fusion directly. A series with tri(chlorethyl) phosphate

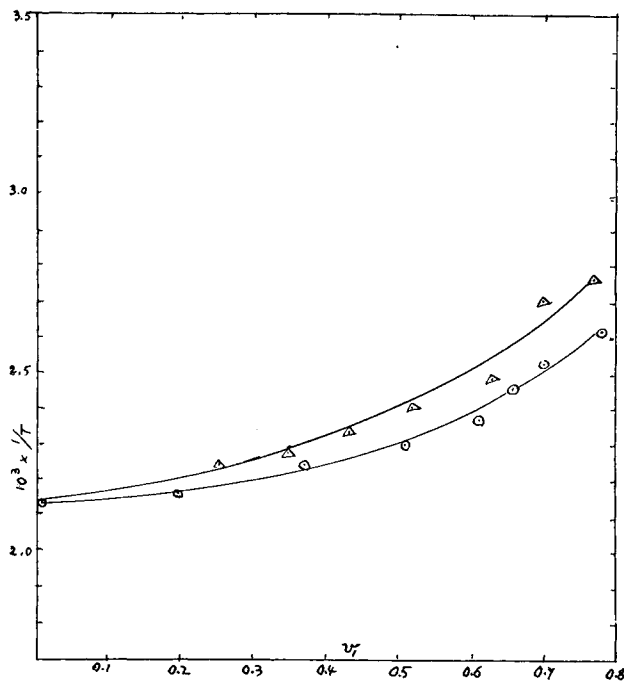


Fig. 3. Melting points of cellulose nitrate sample C, degree of substitution 2.0. Diluent: (O) dibutyl phthalate; (Δ) dilutyl phthalate.

gave similar results with somewhat lower melting temperatures for equivalent compositions.

The series with γ -butyrolactone covered the range of volume fractions from 0.25 to 0.75. Where the compositions overlap those in the earlier publication,³ reproduced for comparison, there is fair agreement. The lower limit of composition corresponded with a temperature of 210°C. At these temperatures the boiling point of γ -butyrolactone is reached, but diffusion from the film is not instantaneous, and a value for the melting point could be observed.

Although the melting point of the undiluted polymer could not be reached directly, it is clear from these results that it must be far lower than previously supposed. Extrapolation of the curves in Figure 1 over the comparatively short distance not reached experimentally gave a figure of about 280°C.

Sample B represents an industrial type of cellulose nitrate. Melting temperatures of mixtures with diethyl phthalate, dibutyl phthalate, and tritolylphosphate, besides γ -butyrolactone, were determined over a wide range of compositions; the results are shown in Figure 2.* In addition, Newman's results⁴ for a very similar type of cellulose nitrate with γ -

* For the sake of clarity results for series using diethyl phthalate and tritolylphosphate were omitted from Figure 2. They were very similar in appearance.

butyrolactone are reproduced, and it will be seen that they agree closely where they overlap, but there is a change of slope with lower proportions of diluent, leading to a value for the melting point of the undiluted polymer at 214°C.

An undiluted film from sample C was found to melt at 200°C. Its behavior on dilution with diethyl phthalate and with dibutyl phthalate is shown in Figure 3.

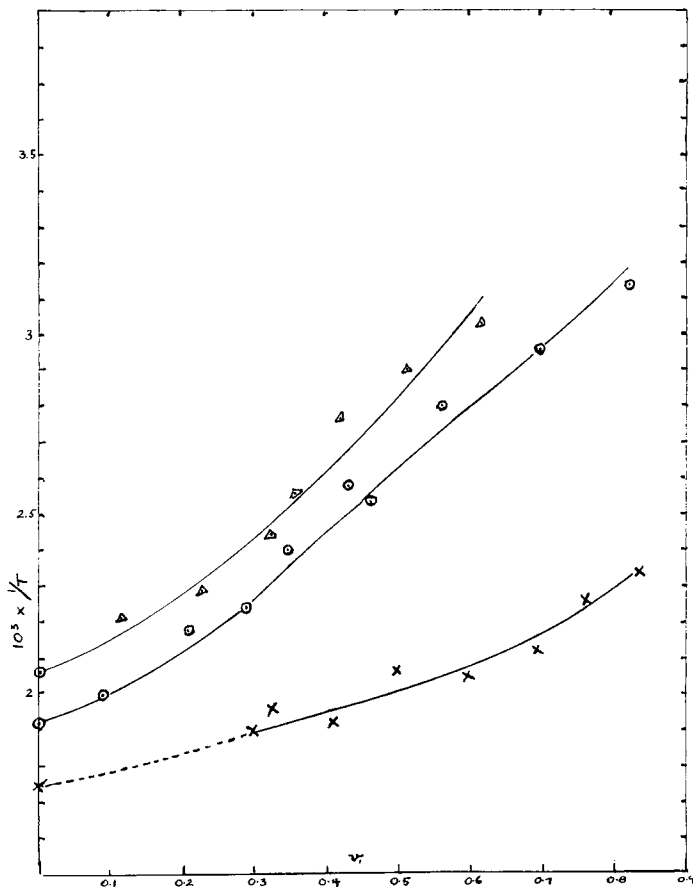


Fig. 4. Melting point: (O) cellulose acetate, degree of substitution 2.2, diluent tri(chlorethyl) phosphate; (X) cellulose triacetate, diluent tri(chloroethyl) phosphate; (Δ) cellulose propionate, diluent dimethyl phthalate.

For purposes of comparison similar tests were made with two types of cellulose acetate with tri(chlorethyl) phosphate. The results are shown in Figure 4. The diacetate was found to melt at 239°C., but the known melting point of triacetate (300°C.) is above the range of the instrument, and determinations were extended only to a volume fraction of diluent greater than 0.3, at which melting point was 251°C.

A further comparison was made with a sample of cellulose propionate (degree of substitution, 2.33), provided by British Celanese Ltd., which was found to melt at 213°C. (Fig. 4). Estimates of heat of fusion were made on the basis of eq. (1) from the slope of the plot of $1/T$ versus v_1 (at values of v_1 less than 0.2). The values obtained are subject to considerable error, but in any case the heats of fusion of cellulose nitrates are substantially higher than those recorded in earlier publications, and they agreed with the figures obtained for cellulose tributyrate and other cellulose esters.

TABLE I

Cellulose type	M.p., °C.	Diluent	ΔH_u , cal. ^a
Tributyrat ^e	207	Benzophenone	3000
Triacetate	300	Trichlorethylphosphate	3700
2.2 Acetate	239	Trichlorethylphosphate	2200
2.33 Propionate	213	Dimethylphthalate	2200
Nitrate A	ca. 280	γ -Butyrolactone	4800
		Bibutyl phthalate	2900
Nitrate B	240	γ -Butyrolactone	4800
		Dibutyl phthalate	4800
Nitrate C	200	Dibutyl phthalate	4500
		Diethyl phthalate	3500

^a ΔH_u is heat of fusion per mole of repeating unit.

Discussion

Cellulose nitrates have been shown not to be exceptional in their melting points, and this also removes another anomaly in the relationship to the glass transition temperature. Ueberreiter¹⁰ has recorded several values, apparently with different samples, but they are all around 50°C. and give a ratio to the melting temperature (°K.) of about 1.5, similar to that found for cellulose acetate and cellulose butyrate, as recorded by Boyer.¹¹

Only one other attempt to estimate the melting temperature of a polymer on the basis of eq. (1) has been noted.¹³ The authors applied the formula to systems of poly(vinyl chloride) and various diluents by determination of solution temperatures at extreme diluents. Although some correlation was found with known values of χ for such systems, the calculated value of the melting temperature of the polymer was lower than expected. Further work is needed to clear up this and other anomalies.

Using a similar method, Brooks and Lawrence¹² estimated a series of values for χ in mixtures of cellulose nitrate with alkoxy nitrates, but the values recorded appear to be out of scale.

The theory of the effect of diluents on the melting temperature of crystalline polymers as expressed in eq. (1) is a useful method of estimating the melting point of a thermally unstable polymer, providing that observation may be made with not more than 0.2 volume fraction of diluent; uncertainties in the evaluation of the interaction constant χ , however, tend

to make extrapolations from observations at higher dilutions liable to considerable error. One overall assumption is that one function can represent behavior of polymer diluent systems over the entire range of composition, but the possibility of a break in continuity cannot be excluded, and the data shown in Figures 1-4 could bear such an interpretation.

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