markably high compared to the rates with other reducing agents. Hydrazine, hydroxylamine, iodide, oxalate, sulfite and stannous ion react only very slowly, if at all, with Np(V) at room temperature. The observed rates of reduction with these reagents are probably mainly the rates of disproportionation of Np(V) to Np(IV) and Np(VI).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Melting and Glassy State Transitions in Cellulose Esters and their Mixtures with Diluents[1,2]

BY LEO MANDELKERN AND PAUL J. FLORY

Specific volume–temperature measurements carried out dilatometrically on cellulose triacetate, cellulose acetate containing 2.3 acetyl groups per glucose unit, cellulose tributyrate, and cellulose butyrate containing 2.6 butyryl groups per unit indicate two second order transitions in each case. For the triacetate these occur at 30 and 105° and for the tributyrate at 40 and 120°. The partial esters exhibit somewhat higher transitions than the corresponding triesters. The change in the expansion coefficient at the lower transition is unusually small, but unmistakable nevertheless. The upper transition is depressed much less by diluents than is the glassy transition of polystyrene. Melting temperatures T_m of mixtures of cellulose tributyrate with diluents have been determined from the volume change observed dilatometrically. Extrapolation of these measurements yields $T_m^0 = 206$–$207°$ for cellulose tributyrate. The depression of T_m depends on the volume fraction of diluent in the manner predicted by theory; results for six different diluents give 3000 ± 200 cal. for the heat of fusion per mole of repeating unit. Undiluted cellulose (2.6) butyrate melts at 178°, showing a surprisingly large volume change for a copolymeric material. This observation, and the small difference in T_m compared with the tributyrate as well, indicate cocrystallization of dibutyrate and tributyrate units. The entropy of fusion of cellulose tributyrate is compared with values for several synthetic chain polymers. Heats of mixing with amorphous cellulose tributyrate, also calculated from the dependence of T_m on diluent concentration, are zero within experimental error for three of the diluents (tributyrin, benzophenone and ethyl benzoate); for the others (hydroquinone monomethyl ether, dimethyl pththalate and ethyl laurate) they are positive.

Introduction

Melting and second order transition phenomena in cellulose derivatives have remained remarkably obscure in contrast to the importance attached to these phenomena in other polymers. Ueberreiter[3] measured the specific volumes of two cellulose acetates over rather limited temperature ranges with results which indicate a second order, or glassy state, transition at 49° in one case and at 56° in the other. Clash and Rynkiewicz[4] reported similar measurements on several plasticized cellulose esters of unspecified composition. Although crystallinity has been established by X-ray methods in a number of instances,[5,6] the temperature at which the last traces of crystallinity disappear at equilibrium, *i.e.*, the melting temperature T_m^0, has remained virtually unknown for any cellulose derivative. Part of this lack of information on melting temperatures may be attributed to the failure of conventional methods; the cellulose derivatives often melt above their thermal decomposition temperatures, and where this is not the case they "melt" to liquids so viscous that the physical change may not be evident by direct observation.

The dilatometric method has proved highly successful, though tedious, for the study of first order (melting) transition phenomena as well as for the detection of second order (glassy) transitions in polymers.[7,8] A recent statistical thermodynamic theory of crystallinity in polymers and their mixtures with diluents affords several methods for determining the heat of fusion of the crystalline polymer from melting temperature studies.[9] The preferred one of these involves measurement of the depression of T_m by diluents. According to the theory referred to

$$(1/T_m - 1/T_m^0) = (R/h_u(\mathrm{V}_2/\mathrm{V}_1)(v_1 - \kappa_1 v_1^2) \quad (1)$$

where T_m^0 is the absolute melting temperature of polymer (of high molecular weight) in the absence of diluent: h_u is the heat of fusion per mole of structural unit; V_2 and V_1 are the molar volumes of the polymer unit and of diluent molecules respectively; v_1 is the volume fraction of the diluent, and κ_1 is the energy of mixing parameter characteristic of a given polymer-diluent pair; κ_1 is equal to $B\mathrm{V}_1/RT$ where B represents the energy of mixing per cc. at infinite dilution. Thus, the depression of the melting point of the polymer by diluent should depend on the heat of fusion of the crystalline polymer, the molar volume of the diluent and its energy of interaction with the polymer. Equation (1) may be rearranged to the more convenient form

$$(1/T_m - 1/T_m^0)/v_1 = (R/h_u)(\mathrm{V}_2/\mathrm{V}_1)(1 - \kappa_1 v_1) \quad (2)$$

A plot of the function on the left, once T_m^0 has been established either directly or by extrapolation, against v_1/T_m permits determination of both h_u and κ_1 from the slope and intercept. Thus, both the heat of fusion of the polymer and the mixing parameter κ_1 may be deduced from measurements

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[1] The work reported in this paper comprises a part of a program of research on the physical structure and properties of cellulose derivatives supported by the Allegany Ballistics Laboratory, Cumberland, Maryland, an establishment owned by the United States Navy and operated by the Hercules Powder Company under Contract NOrd 10431.

[2] Presented before the Division of Polymer Chemistry at the 118th Meeting of the American Chemical Society, Chicago, Illinois, September, 1950.

[3] K. Ueberreiter, *Z. physik. Chem.*, **B48**, 197 (1941).

[4] R. F. Clash, Jr., and L. M. Rynkiewicz, *Ind. Eng. Chem.*, **36**, 279 (1944).

[5] W. O. Baker, C. S. Fuller and N. R. Pape, THIS JOURNAL, **64**, 776 (1942).

[6] K. Hess and C. Trogus, *Z. physik. Chem.*, **B15**, 157 (1932).

[7] L. A. Wood, "Advances in Colloid Science," Vol. II, Interscience Publishers, Inc., 1946, p. 63 ff.

[8] Paul J. Flory, Leo Mandelkern and Henry K. Hall, THIS JOURNAL, **73**, 2532 (1951).

[9] P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).

of T_m as a function of v_1. The heat of mixing parameter B may then be calculated from κ_1. This method has been demonstrated previously for mixtures of the polyamide, poly-(N,N′-sebacoylpiperazine), with several diluents.[8] It is to be noted that the above method yields the heat of fusion *per mole of crystalline polymer units;* direct calorimetric measurements generally are not suitable for this purpose owing to the presence of an unknown proportion of the polymer in the amorphous condition.

In the investigations reported in this paper, specific volumes of four cellulose esters, a tributyrate, a partial butyrate, a triacetate and a partial acetate, have been measured carefully over wide temperature ranges. Glass transitions have been observed in all cases. Binary mixtures of the tributyrate with each of six different diluents have been studied similarly, with particular emphasis on determination of the melting temperature and its dependence on concentration and the type of diluent. These measurements are interpreted according to equations (1) and (2).

Experimental

Materials.—A sample of cellulose tributyrate and one of a cellulose butyrate containing an average of 2.6 butyryl groups per anhydroglucose unit, henceforth referred to as cellulose (2.6)-butyrate, were made available to us by C. J. Malm of the Eastman Kodak Company.[10] Their intrinsic viscosities in acetone at 30° were 2.03 and 2.15, respectively. Two cellulose acetates were obtained from the Hercules Powder Company. Acetyl determinations according to the methods of Genung and Mallat[11] and of Malm, Genung, Williams and Pile[12] confirmed that one of these was the triester and the other a cellulose (2.3)-acetate. The intrinsic viscosity of the cellulose triacetate was 1.10 in chloroform at 25° and that for the (2.3)-acetate was 1.62 in acetone at the same temperature.

The diluents, tributyrin, benzophenone, dimethyl phthalate, ethyl laurate, ethyl benzoate and hydroquinone monomethyl ether (HQMME), obtained from the Eastman Kodak Co. ("white label" reagent grade) were dried before use.

Procedure.—Specific volumes were determined in conventional type dilatometers as described by Bekkedahl,[13] mercury being used as the confining fluid.[8,14] Samples weighing between 1.5 and 2.5 g., prepared in the manner described below, were placed in the dilatometer-bulb, after which the bulb was sealed with due care to prevent charring of the sample. Mercury was introduced into the dilatometer under vacuum (<0.005 mm.) and the amount of mercury in the dilatomer was determined by weighing. Since the dilatometer volume was not measured independently, absolute specific volumes were not obtainable solely from the dilatometric measurements. The results of Malm, Fordyce and Tanner[15] afforded absolute density values for the unplasticized polymers at suitable reference temperatures, on the basis of which dilatometric measurements at all other temperatures could be converted to absolute specific volumes. For the polymer–diluent mixtures absolute specific volumes were not computed. Instead, ratios of the specific volume to that of 30° were calculated from the dilatometric measurements. Absolute values of the densities are of little importance here inasmuch as the conclusions drawn from the data depend on relative volume changes only.

All the measurements above 0° were made in a constant-temperature oil-bath regulated to within ±0.1°. An ice-water mixture was used at 0°, and Dry Ice–acetone at −20°. The dilatometer capillaries were made of "True Bore" tubing 2 mm. in diameter. The height of the mercury column in the capillary was read to ±0.1 mm. giving a precision of ±0.0002 ml./g. in the specific volume of the sample. The height of the mercury in the capillary was measured at fixed temperatures in the temperature range of interest for the particular sample. Temperature sequences and the times for which the sample was held at each temperature will be discussed below.

For the computation of the volume fractions of the plasticized samples at various temperatures it is necessary to know the densities of the diluents and of the amorphous polymer as functions of temperature. The densities of the diluents were obtained from data in the literature where available; otherwise they were measured at two temperatures about 100° apart and assumed to vary linearly in between. The density of a mixture of cellulose tributyrate and ethyl laurate with $v_1 = 0.289$ was measured in a pipet pycnometer[16] at 189°, which is 26° above its melting temperature. Assuming the volume change on mixing to be zero, the density of amorphous cellulose tributyrate was computed at this temperature, and expressed as a function of temperature with the aid of dilatometric data on this sample above its melting temperature. This relationship was extrapolated below T_m for the interpretation of results on plasticized mixtures.

Sample Preparation.—Specimens for the dilatometers were prepared in either of two ways. Samples of the pure polymers and of mixtures of cellulose tributyrate with less than 25% of diluent were cast in the form of thick films. Mixtures of cellulose tributyrate containing higher proportions of diluent were molded in the form of cylindrical slugs.

Films of unplasticized polymer were prepared by casting solutions of the polymer on a mercury surface. The bulk of the solvent was removed by slow evaporation in a vacuum desiccator, after which the films were leached with water or methanol for a day, then dried to constant weight at about 120° in a vacuum oven. The cellulose (2.3)-acetate, the (2.6)-butyrate and the tributyrate were cast from acetone solution and leached in water; the cellulose triacetate was cast from methylene chloride, and methyl alcohol was the leaching agent. The concentration of the solution was adjusted so that film thicknesses of about 0.04 cm. were obtained. The cellulose triacetate, diacetate and dibutyrate were sufficiently flexible so that they could be coiled into rolls which were placed in the dilatometer. The cellulose tributyrate films were too brittle to be rolled, and therefore were cut into rectangular strips for insertion in the dilatometer bulb.

For the preparation of plasticized cellulose tributyrate films, a solution containing weighed amounts of polymer and diluent was cast onto a mercury surface, and the bulk of the casting solvent was removed as before. The film was leached for a day in a liquid miscible with the acetone but immiscible with the diluent. Thereafter it was allowed to remain overnight in a vacuum oven at about 50°. For the purpose of determining the composition of the samples, a small portion of the film was removed, weighed, treated for 24 hours with a leaching agent in which the diluent was miscible, then dried to constant weight in a vacuum oven.

Samples containing higher proportions of diluent were prepared by mixing as previously described[8] at 160 to 190°.

Results and Discussion

Glass Temperatures of Unplasticized Polymers.—Volumes of the cellulose triacetate, of the (2.3)-acetate and of the tributyrate were measured dilatometrically at suitable temperature intervals. Equilibrium was reached quickly at each temperature, and so long as the temperature never exceeded about 120° the volume was independent of the thermal history. After bringing the sample to a temperature above 120° for the first time,

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[10] We are also indebted to Dr. Malm for providing the analyses of the cellulose butyrates.

[11] L. B. Genung and R. Mallat, *Ind. Eng. Chem., Anal. Ed.*, **13**, 369 (1941).

[12] C. J. Malm, L. B. Genung, R. F. Williams, Jr., and M. A. Pile, *ibid.*, **16**, 502 (1944).

[13] N. Bekkedahl, *J. Research Natl. Bur. Standards*, **43**, 145 (1949).

[14] See also T. G. Fox, Jr., and P. J. Flory, *J. Applied Phys.*, **21**, 581 (1950).

[15] C. J. Malm, C. R. Fordyce and H. A. Tanner, *Ind. Eng. Chem.*, **34**, 430 (1942).

[16] P. J. Flory, THIS JOURNAL, **62**, 1057 (1940).

slightly smaller specific volumes were found at each lower temperature than had been observed previously; these values were maintained on subsequent cooling–heating cycles. The agreement between results for different specimens from the same polymer was good, deviations of the specific volumes being only about ±0.05%. Although the glass transitions are believed to be governed by kinetic factors, the time for volume relaxation usually is measurable only in the neighborhood of the transition temperature.[14] With the cellulose esters, however, volume equilibrium appears to be established as soon as thermal equilibrium is reached at all temperatures, both for heating and for cooling cycles, and no further changes were observed for periods up to 24 hours. Specific volumes obtained by averaging the results of the three or more dilatometric runs on separate samples after heating above 120° in each case are plotted in Figs. 1, 2 and 3. The data for each ester are best represented by three intersecting straight lines, indicating two transitions of the second order type. Although specific volumes measured during the initial heating up to 120° were displaced slightly above those shown in Fig. 1, 2 and 3, the temperatures at which the changes in slope occurred were the same within experimental error.

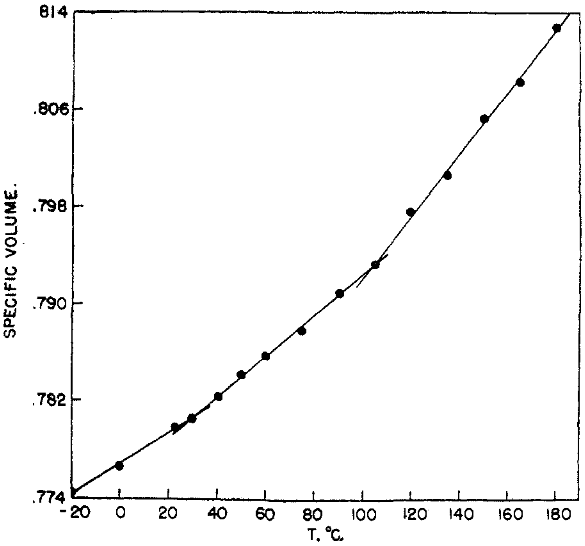

Fig. 1.—Specific volume–temperature curve for cellulose triacetate.

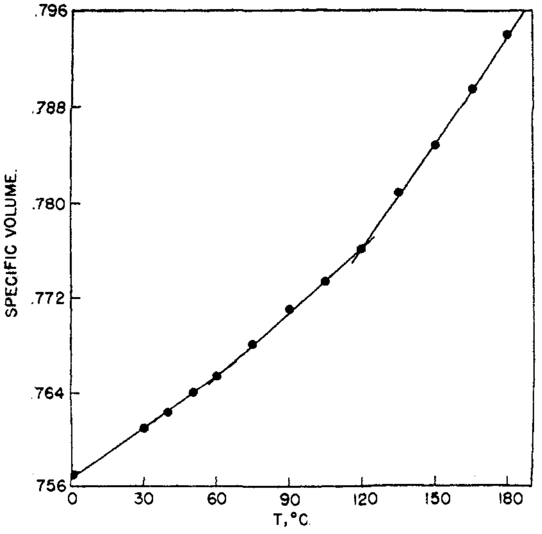

Fig. 2.—Specific volume–temperature curve for cellulose (2.3)-acetate.

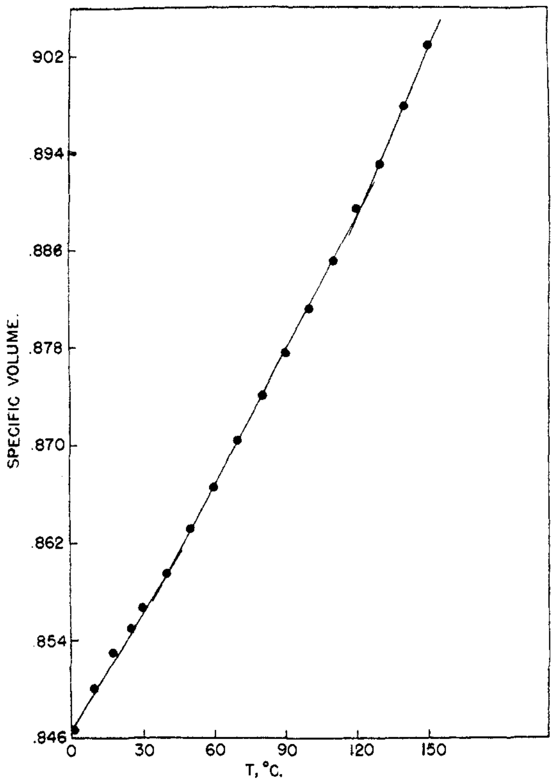

Fig. 3.—Specific volume–temperature curve for cellulose tributyrate.

A summary of the data obtained from these measurements is given in Table I. $T_g(1)$ and $T_g(2)$ represent, respectively, the temperatures of the lower and higher discontinuities in the slope of the specific volume–temperature plot; $(dv/dT)_1$ is the slope below $T_g(1)$; $(dv/dT)_2$ is the slope between $T_g(1)$ and $T_g(2)$ and $(dv/dT)_3$ is the slope above $T_g(2)$.

TABLE I

SECOND ORDER TRANSITION TEMPERATURES FOR CELLULOSE ESTERS

Cellulose ester	$T_g(1)$ °C.	$T_g(2)$ °C.	$(dv/dT)_1$, in ml./°C. × 10^4	$(dv/dT)_2$	$(dv/dT)_3$
Triacetate	30	105	1.25	1.70	2.60
(2.3)-acetate	60	120	1.45	1.75	2.95
Tributyrate	40	120	3.00	3.70	4.85
(2.6)-butyrate	65	125	3.25	4.30	7.10

The observation of two second order transitions appears to be without precedent, hence the evidence supporting their existence deserves careful scrutiny. The size of the points in Figs. 1–3 slightly exceeds the average deviation for an individual experiment. Since each point represents the average for three or more independent observations, it is extraordinarily unlikely that errors of random origin may have vitiated any one of them by an amount exceeding the diameter of the point. Although the change in slope at $T_g(1)$ is small, its reality can scarcely be questioned in the light of the data. Furthermore, a corresponding transition has been observed in every organic acid ester of cellulose we have investigated so far. This transition was found also by Ueberreiter[3] in cellulose acetates. His volume–temperature measurements did not extend above 70°; the data for each ester were represented by two straight lines intersecting at temperatures in agreement with the $T_g(1)$'s reported here.

The changes in slope (Table I) at the heretofore unreported transition $T_g(2)$ are larger, being comparable in magnitude with the slope changes observed at the second order transitions for other polymers. In drawing intersecting straight lines it is not meant to suggest that the changes in slope are abrupt at either of the transitions. The data indicate, however, that the major portion of the change in slope may extend over a range not exceeding 10° at either $T_g(1)$ or $T_g(2)$. Since these so-called second order transitions appear to be rate-controlled phenomena, rather than thermodynamic transitions, the question of their abruptness is not of foremost importance. While we prefer to postpone discussion of the significance of each of the observed transitions pending the outcome of further experiments, it appears possible that they represent "freezing in" temperatures for different types of motion.

Melting temperatures of the cellulose acetates and cellulose tributyrate are too high to be observed dilatometrically inasmuch as thermal decomposition becomes troublesome above about 180°. However, for the cellulose (2.6)-butyrate the dilatometric observations could be extended through the melting range and somewhat beyond with the results shown in Fig. 4. In the vicinity of the melting temperature, 178°, there is a large increase in the specific volume over a relatively narrow temperature range. The large volume change on melting indicates that the degree of crystallinity is relatively high in spite of the copolymeric character of the partially substituted polymer chains. This polymer also shows two second order transitions (Table I).

Increases either in polarity or in size of the structural unit tend to raise T_g. The more polar, partially substituted esters have higher transition temperatures than the corresponding triesters; the bulkier butyrate groups raise the transition temperatures above those for the corresponding acetates. Polymers which have stronger intermolecular forces would be expected to exhibit smaller expansion coefficients in the amorphous state. However, this prediction cannot be tested with the present data owing to lack of information on the degrees of crystallinity in the different esters. On the other hand, if it is assumed that the expansion coefficient affords a measure of the proportion of amorphous material, the data of Table I indicate that the triesters are more crystalline than the partially esterified derivatives, and that the acetates are more crystalline than the butyrates.

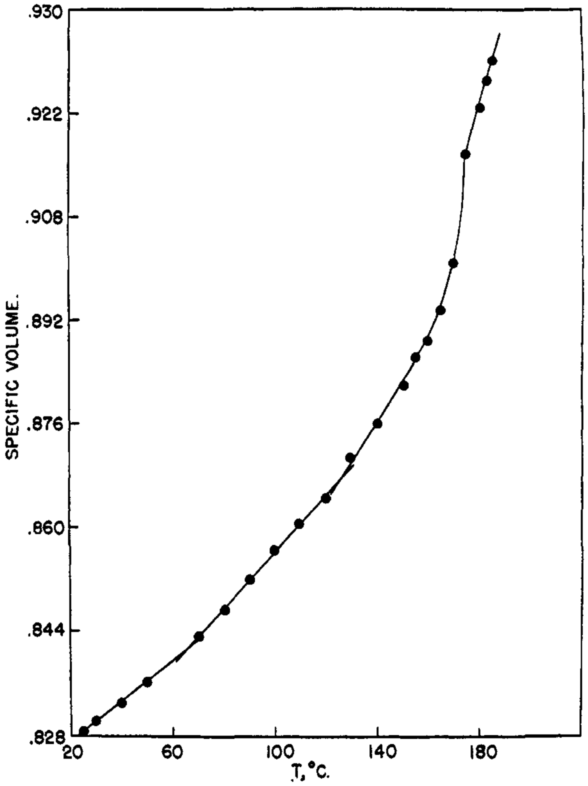

Fig. 4.—Specific volume–temperature curve for cellulose (2.6)-butyrate.

Depression of Glass Temperature of Cellulose Tributyrate by Diluents.—The influence of diluents on $T_g(2)$ for cellulose tributyrate was studied using ethyl benzoate, dimethyl phthalate, ethyl laurate and benzophenone. The results are given in Table II, and, for three of the diluents, they are shown in Fig. 5. The volume fractions given were computed for the temperature $T_g(2)$ in each case. The effects of the various diluents, with the possible exception of ethyl laurate, are similar. There is an initial steep non-linear depression followed by an approximately linear further depression over a large range in concentration. These results may be inter-

TABLE II

UPPER SECOND ORDER TRANSITION TEMPERATURES $T_g(2)$ FOR PLASTICIZED CELLULOSE TRIBUTYRATE

v_1	$T_g(2)$, °C.	v_1	$T_g(2)$, °C.
Ethyl laurate		Benzophenone	
0.287	90 ± 3	0.109	105 ± 2
.365	85 ± 1	.149	102 ± 1
.476	75 ± 1	.184	101 ± 1
.580	65 ± 1	.280	90 ± 2
.636	59 ± 3	.356	82 ± 1
		.441	75 ± 1
		.486	72 ± 1
		.563	61 ± 1
Ethyl benzoate		Dimethyl phthalate	
0.069	108 ± 1	0.095	98 ± 1
.079	104 ± 1	.139	93 ± 1
.266	89 ± 1	.151	93 ± 1
.407	75 ± 1	.163	88 ± 1
.515	68 ± 1	.294	79 ± 1
		.392	69 ± 1
		.512	54 ± 1

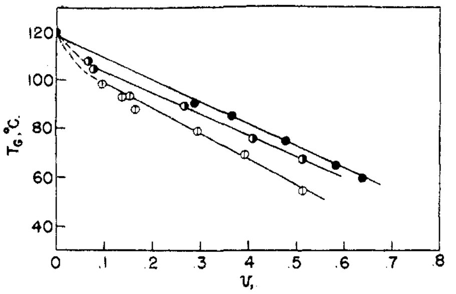

Fig. 5.—Dependence of the glass transition temperature T_g for cellulose tributyrate on diluent concentration: ethyl laurate (●), ethyl benzoate (◑), dimethyl phthalate (⦶).

preted qualitatively in terms of the semi-crystalline character of the polymer. Inasmuch as the diluent enters the amorphous regions only, its concentration there is greater than the average composition. The curves of Fig. 5 suggest that, except in the case of ethyl laurate, small amounts of diluent do not decrease appreciably the proportion of crystalline material (and conceivably might actually increase it if the degree of crystallinity is controlled by mobility rather than by equilibrium considerations), but that with addition of further amounts the crystalline regions tend to be "dissolved out." Hence, the actual concentration of diluent in the amorphous region increases rapidly at first, then more slowly as crystalline polymer is converted to the amorphous state with further increases in the proportion of diluent. The over-all depression of the transition temperature is small, being of the order of 50 to 60° for a volume fraction of diluent of 0.50. This is much less than has been noted for polystyrene by Fox[17] where T_g is depressed about 150° by the same amount of diluent. Ueberreiter[3] has found depressions of from 80–100° at $v_1 = 0.50$ for ethyl cellulose and nitrocellulose, but from the results given it is not clear whether they apply to $T_g(1)$ or to $T_g(2)$, assuming that two second order transition temperatures occur in these cellulose derivatives also.

Melting Temperatures of Plasticized Cellulose Tributyrate Samples.—Two typical sets of results of the dilatometric determination of the melting temperature are shown in Figs. 6 and 7. In the neighborhood of the melting points there is a change in volume, though relatively small, over a narrow temperature range. The melting temperature, taken as the temperature at which the last traces of crystallinity disappear, is 163° for the sample in Fig. 6, and 94° for that in Fig. 7. Volume equilibrium is attained almost simultaneously with thermal equilibrium, even through the melting range, and it is unnecessary to wait long times in the neighborhood of T_m for the volume to become constant. The volume temperature dependence is completely reversible with no evidence of supercooling. This is in contrast to the recent results for a polyester[18] and a polyamide,[8] for which premelting was observed, the volume changes on melting were much larger and supercooling was evident. The upper glass temperature $T_g(2)$ is lowered by the diluent from 120 to 90° in Fig. 6 and to 72° in Fig. 7.

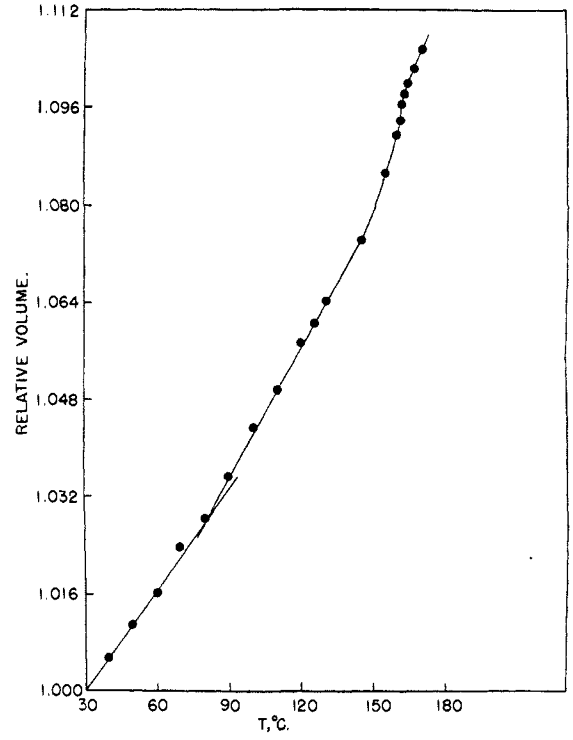

Fig. 6.—Relative volume-temperature curve for cellulose tributyrate–ethyl laurate mixture; $v_1 = 0.289$.

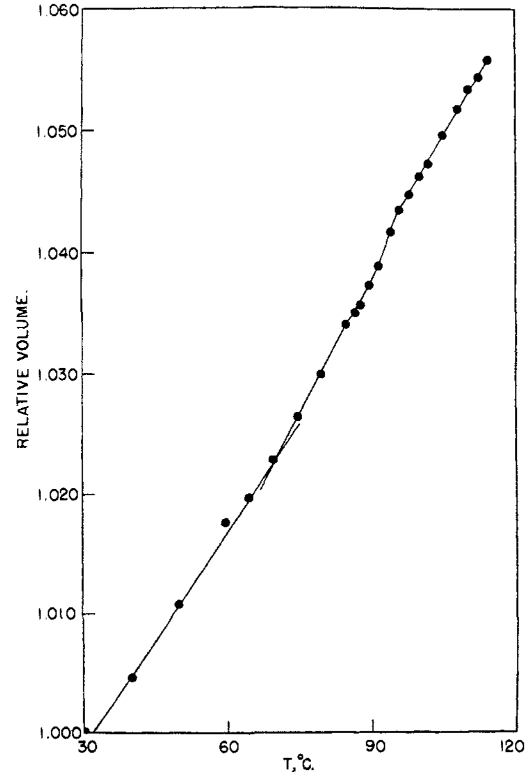

Fig. 7.—Relative volume-temperature curve for cellulose tributyrate-benzophenone mixture; $v_1 = 0.486$.

Extrapolation of the melting points for mixtures with a given diluent yields in each case 206–207°

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(17) T. G. Fox, Jr., unpublished data.

(18) R. D. Evans, H. R. Mighton and P. J. Flory, THIS JOURNAL, **72**, 2018 (1950).

for T_m°, the melting temperature of pure cellulose tributyrate.[19] This value was confirmed on thin film samples using a micro melting point apparatus, similar to that described previously.[18] As has been noted the melting temperature of the pure cellulose tributyrate could not be determined dilatometrically, as extensive decomposition took place.

In Table III there are listed the experimental results for the melting temperatures and the corresponding diluent compositions. The volume fractions used were computed at T_m of the particular sample, on the assumption that there was no volume change on mixing. Figure 8 is a plot of $1/T_m$ in $°K.^{-1}$ against the volume fraction for benzophenone, HQMME and ethyl laurate which were chosen as typical of the six diluents studied. According to equation (1) a plot of this type should be linear only if κ_1 is zero, *i.e.*, if there is no heat of mixing between polymer and diluent. This is the case for benzophenone, data for which are shown in Fig. 8, and also for tributyrin and ethyl benzoate. The heat of fusion, h_u, per structural unit of the polymer may be calculated according to Eq. (1) from the slope of the line in Fig. 8.

TABLE III

MELTING TEMPERATURES T_m OF PLASTICIZED CELLULOSE TRIBUTYRATE COMPOSITIONS

v_1	T_m, °C.	v_1	T_m, °C.
Ethyl laurate		Tributyrin	
0.289	163.5 ± 0.5	0.331	163 ± 0.5
.366	152 ± .5	.439	145 ± .5
.477	143.5 ± .5	.593	123.5 ± .5
.581	135.5 ± .5	.679	116 ± .5
.637	130.5 ± .5	.730	107 ± .5
Benzophenone		Ethyl benzoate	
0.109	178 ± 0.5	0.267	131.5 ± 0.5
.148	162 ± .5	.318	125 ± .5
.184	157 ± .5	.408	109 ± .5
.280	135 ± .5	.516	88 ± .5
.356	120 ± .5	.559	79 ± .5
.441	104 ± .5		
.486	94 ± .5		
.563	82.5 ± .5		
.663	65.5 ± .5		
HQMME		Dimethyl phthalate	
0.234	122.5 ± 0.5	0.169	159 ± 0.5
.295	106 ± .5	.300	131.5 ± .5
.388	87.5 ± .5	.397	105.5 ± .5
.490	79 ± .5	.518	98 ± .5

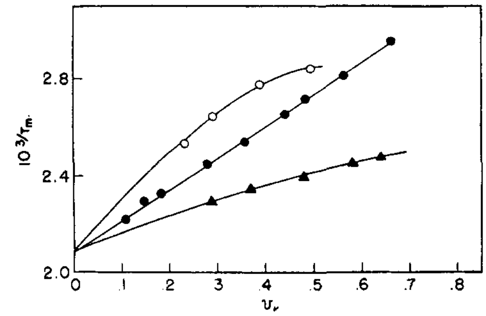

Fig. 8.—Dependence of the reciprocal melting temperature $1/T_m$ of cellulose tributyrate on the volume fraction of diluent: benzophenone (●), HQMME (○), ethyl laurate (▲).

According to equation (2) a plot of $(1/T_m - 1/T_m^\circ)/v_1$ against v_1/T_m should be linear. B is obtained from the slope and intercept of this plot, and h_u from the intercept. As is shown in Fig. 9, the results for HQMME, ethyl laurate and dimethyl phthalate may be represented by straight lines when plotted in this manner. Molar volumes of polymer and diluent used for the calculation of h_u and B were those at 207°, the melting point of the pure polymer. Table IV gives the results for the six diluents. The same value of h_u, 3000 cal./mole ± 200, is obtained from the depression of the melting point by the different diluents as required by theory.

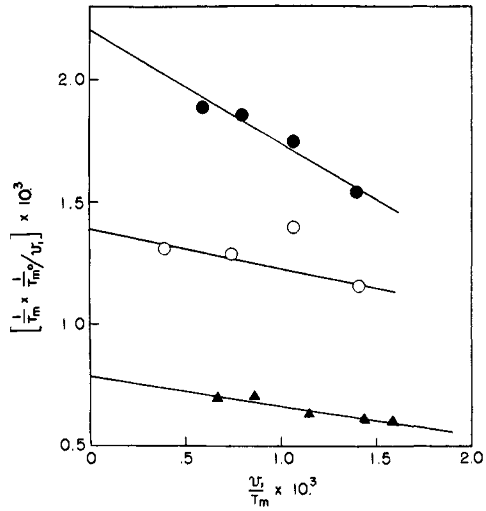

Fig. 9.—$(1/T_m - 1/T_m^\circ)/v_1$ against v_1/T_m for mixtures of cellulose tributyrate with various diluents: HQMME (●), dimethyl phthalate (○), ethyl laurate (▲).

TABLE IV

HEAT OF FUSION OF CELLULOSE TRIBUTYRATE AND INTERACTION CONSTANT WITH VARIOUS DILUENTS

Diluent	h_u, cal. mole^{-1}	B, cal. cc.$^{-1}$
Tributyrin	2800	0.0
Benzophenone	2900	.0
Hydroquinone monomethyl ether	2800	2.8
Dimethyl phthalate	2800	1.2
Ethyl benzoate	3200	0.0
Ethyl laurate	3100	1.0

For tributyrin, benzophenone and ethyl benzoate $B = 0$, while for the other diluents B is positive, which is indicative of poorer solvent power. The B's calculated in this manner may not be representative solely of a heat of mixing, for there is the possibility that they arise in part from entropy contributions.[20] Analysis of thermodynamic data on other polymer systems suggests that an entropy term in $v_1{}^2$ in addition to the heat term $\kappa_1 v_1{}^2$ may also be needed in equation (1). Hence the

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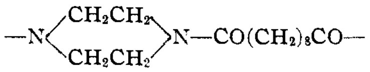
[19] The melting point of this polymer is difficult to determine in a conventional type capillary tube as sintering occurs at 190°. A similar phenomenon is observed in completely amorphous polystyrene at about 105°.

[20] See ref. 8 for a detailed discussion of this point.

TABLE V

ENTROPIES OF FUSION FOR VARIOUS POLYMERS

		Entropy of fusion	
Polymer	Repeating unit	E.u./mole of repeating unit	E.u./no. bonds permitting rotation
Polyethylene[21]	$-CH_2-$	2.0	2.0
Cellulose tributyrate	$C_{12}H_{28}O_8$	6.2	3.1
Poly-(decamethylene sebacate)[18]	$-O-(CH_2)_{10}-O-CO-(CH_2)_8CO-$	34.8	1.5
Poly-(N,N′-sebacoylpiperazine)[8]	 $-N\left\langle\begin{smallmatrix}CH_2CH_2\\CH_2CH_2\end{smallmatrix}\right\rangle N-CO(CH_2)_8CO-$	13.7	1.2

value obtained for B, regarded as a measure of the heat of mixing, might be too great by as much as one unit. Consideration of possible entropy contributions to the empirical κ_1 leads to the conclusion that the plots in Fig. 9 should in general be curved (even when $B = 0$). However, the anticipated deviations from linearity would be too small to be detected by the present experimental methods over the small temperature range studied. In any event, the empirical classification of solvents according to their B values remains valid.

For a random copolymer comprised of repeating units A and B, the latter being incapable of crystallizing with the former, the melting temperature has been shown[9] to be related to the "mole" fraction X_A of A units according to the equation

$$1/T_m - 1/T^0_m = -(R/h_u)\ln X_A \qquad (3)$$

where h_u is the heat of fusion per mole of repeating unit A. Assuming that the butyrate groups are distributed at random over all hydroxyl positions, the mole fraction (X_A) of tributyrate units should equal $(2.6/3.0)^3$. Substituting this estimate of X_A together with the previous value of h_u (3000 cal./mole) in equation (3) yields 148° for the predicted melting temperature. This is 30° below the observed melting point of 178°, which strongly suggests that the dibutyrate units are able to cocrystallize with the tributyrate units. The large volume change on melting that is observed provides further support for this conclusion.

The heat of fusion of cellulose tributyrate, 8 cal. per g., is much lower than values determined for other polymers. Raine, Richards and Ryder[21] give 56 cal./g. for polyethylene. Studies of the depression of the melting point of poly-(N,N′-sebacoyl-piperazine), by diluents yielded 25 cal. per g.,[8] while for the polyester decamethylene sebacate the value 36 cal. per g. is indicated.[18] Baker and Fuller[22] have studied cooling curves of a variety of crystalline polymers, and cellulose tributyrate proved to be the exception in that it showed no flat, or "halt," in the vicinity of the melting temperature. Since our results indicate that cellulose tributyrate crystallizes rather more rapidly than other polymers, Baker and Fuller's observation cannot be attributed to ease of supercooling caused by the alleged rigidity of the cellulose chain. It is readily accounted for, however, by the low heat of crystallization.

The entropies of fusion of cellulose tributyrate and several other polymers for which the required heats of fusion are available are compared in Table V. The entropies of fusion per repeating unit are widely variable, as might be expected from the enormous differences in the sizes and structures of the units. In quest of a better basis for comparison, the entropies per repeating unit were divided by the number of chain bonds about which free rotation is permitted. These values, given in the last column, are more nearly uniform being in the neighborhood of R calories per bond.[23] According to the lattice theory[24] the configurational entropy of fusion *per segment* should be $R \ln(\gamma - 1) \cong R$, where γ is the coördination number of the lattice.

The smaller values of the entropies per bond for decamethylene sebacate and for poly-(N,N′-sebacoylpiperazine) as compared with polyethylene may reflect a persistence of order in the liquid state caused by interactions between the polar groups. Or, it may be the result of randomness in the crystal. If the distance between planes containing the polar groups is less than would be required for full extension of the intervening polymethylene chains, these latter may be randomly spiraled to some extent.[25] The higher value for cellulose tributyrate probably arises from increased freedom of the butyrate substituents in the liquid state. Stiffness of the cellulose chain, *i.e.*, restrictions on rotation about the inter-unit C–O bonds, would lower the entropy of fusion per chain bond. The entropy of fusion affords no evidence for abnormal stiffness of this sort.

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[21] H. C. Raine, R. B. Richards and H. Ryder, *Trans. Faraday Soc.*, **41**, 56 (1945).

[22] W. O. Baker and C. S. Fuller, *Ind. Eng. Chem.*, **38**, 272 (1946).

[23] This observation recalls the communal entropy of melting of Eyring and co-workers; see J. Hirschfelder, D. Stevenson and H. Eyring, *J. Chem. Phys.*, **5**, 897 (1937). We prefer to consider this as coincidental rather than to suggest application to polymers of the hole theory of melting.

[24] P. J. Flory, *ibid.*, **10**, 51 (1942).

[25] In this connection, see W. O. Baker and C. S. Fuller, THIS JOURNAL, **64**, 2399 (1942).