

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Crystallization in High Polymers. VII. Heat of Fusion of Poly-(N,N'-sebacoylpiperazine) and its Interaction with Diluents¹

BY PAUL J. FLORY, LEO MANDELKERN AND HENRY K. HALL

Melting temperatures T_m of the polyamide poly-(N,N'-sebacoylpiperazine) and its mixtures with *m*-cresol, with *o*-nitrotoluene and with diphenyl ether, have been measured either dilatometrically or, at lower polymer concentrations, by visual observation. The observed dependence of T_m on composition agrees with the predictions of theory. Heats of fusion calculated from the melting temperature depressions by the three diluents are in good agreement, the average value being 6200 cal. per mole of repeating unit, or 25 cal. per g. of polymer. Van Laar heat of mixing parameters also are evaluated from the data for the three mixtures. The diphenyl ether-polyamide system separates into two phases at lower polymer concentrations; the observed consolute temperature leads to a value for the heat of mixing parameter which agrees satisfactorily with that calculated from the melting temperature data. The dependence of T_m on composition in several series of copolyamides in which N,N'-sebacoylpiperazine is the principal constituent yields about 5000 cal. per mole for the heat of fusion. The value obtained from the results with polymer-diluent mixtures is considered to be the more reliable, and the probable source of the discrepancy is discussed. Poly-(N,N'-sebacoylpiperazine) exhibits a well defined glassy state transition at 82°.

Introduction

The degree of crystallinity and the melting temperature of a polymer may be depressed by a copolymerized structural unit, by an increase in the concentration of end groups when the average chain length is diminished, or by a monomeric diluent incorporated with the polymer. The effects of these various extraneous constituents on the degree of crystallinity, and in particular on the melting temperature, have been treated theoretically from a statistical point of view.² Thus, in the case of a random copolymer comprised of repeating units A and B, the latter being incapable of entering the crystal lattice characteristic of the former, the "melting temperature" T_m at which the last traces of crystallinity disappear at equilibrium should be related to the "mole" fraction X_A of A units according to the equation

$$1/T_m - 1/T_m^0 = -(R/h_u) \ln X_A \quad (1)$$

where T_m^0 is the equilibrium melting temperature for the homo-polymer of high molecular weight in the absence of diluent, and h_u is the heat of fusion per repeating unit (A). For a polymer of limited chain length in which the number average degree of polymerization is x_n and the chain length distribution is the "most probable" one³

$$1/T_m - 1/T_m^0 = (R/h_u)(2/x_n) \quad (2)$$

For a polymer of high molecular weight containing a volume fraction v_1 of a diluent

$$1/T_m - 1/T_m^0 = (R/h_u)(z/z_s)[v_1 - \kappa_1 v_1^2] \quad (3)$$

where z/z_s is the ratio of the molar volumes of the polymer repeating unit and the diluent, and κ_1 is the heat of mixing parameter (which replaces μ_1 of earlier theories) given by

$$\kappa_1 = Bv_1/RT_m \quad (4)$$

where B is the Van Laar heat of mixing parameter and v_1 is the molar volume of the diluent.

Each of the above equations reduces at infinite dilution to

$$1/T_m - 1/T_m^0 = -(R/h_u) \ln y_2 = (R/h_u)(1 - y_2) \quad (5)$$

where y_2 is the mole fraction of the extraneous in-

redient: copolymerized units, chain ends (*two* per molecule), or diluent. Equation (5) may be deduced on the most general thermodynamic grounds from the assumption that the activity of the extraneous ingredient is proportional to its concentration⁴ at sufficiently low concentrations, through the use of the Gibbs-Duhem equation.

An investigation of the melting temperatures of copolyesters and copolyamides as functions of composition, of polyesters as functions of chain length and type of end group, and of mixtures of a polyester with several diluents was presented in a recent paper.⁵ Although the results of that investigation largely substantiated the relationships given above, certain discrepancies appeared. In particular, heats of fusion calculated according to equation (1) from melting temperatures of copolyesters were much lower than were those computed using equation (2) from the depression of T_m with decrease in x_n , or from the influence of diluents using equation (3). Only limited data were obtained pertaining to this latter method. In the present work the depression of the melting temperature of the polyamide poly-(N,N'-sebacoylpiperazine) by addition of diluents has been investigated in a more conclusive fashion. It appears that the parameter B , which specifically characterizes the solvent-polymer interaction, as well as the heat of fusion h_u of the polymer, may be evaluated from such measurements. Melting temperatures of copolymers of sebacoylpiperazine also have been measured, and an approximate value of h_u has been obtained from these data also.

Experimental

Materials.—Crude piperazine was purified by fractional distillation, first through a 5-plate column and then through a column of 20-plate efficiency. The center cut boiling at 150–152° was retained for use. Piperazinium salts of sebacic, pimelic and adipic acids were prepared as described

(4) It is easy to show that the activity of a copolymerized unit will be proportional to its concentration at infinite dilution only if these units are distributed through the polymer chains at random. Similarly, the activity of end groups will be proportional to their concentration only if the chain length distribution is the most probable one, which corresponds to random distribution of chain ends. For polymers of uniform chain length, for example, the dependence of T_m on chain length does not reduce to equation (4), as is shown by the previously published relationship (equation (29) of ref. (2)) derived statistically for this case.

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

(1) The work presented in this paper was carried out at Cornell University in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

(2) P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).

(3) P. J. Flory, *THIS JOURNAL*, **58**, 1877 (1936); **64**, 2205 (1942).

by Coffman, Berchet, Peterson and Spanagel⁶ by mixing methanol or 95% ethanol solutions of piperazine and of the recrystallized dibasic acid, equimolar quantities being used. Piperazinium isophthalate was prepared by adding the required amount of piperazine to a suspension of the sparingly soluble acid in 95% ethanol; the mixture was stirred overnight. Hexamethylenediammonium adipate was furnished by the Carothers Laboratory of the du Pont Company. Melting points of the salts are given below.

	M.p., °C.	
	Obsd.	Lit.
Piperazinium sebacate	167	167-168 ⁷
Piperazinium pimelate	153.5	155 ⁷
Piperazinium adipate	248	247 ^{7,a}
Piperazinium isophthalate	245	
Hexamethylenediammonium adipate	170	170 ⁶

^a Rapid heating.

The solvents used as diluents in the melting point studies, namely, *m*-cresol, diphenyl ether and *o*-nitrotoluene, were purified by distillation.

Preparation of Polymers.—The polyamides and copolyamides were prepared essentially as previously described^{6,8} by heating 5 to 10 g. of piperazinium sebacate, or an appropriate mixture with another of the salts, at 217° for several hours in a 15 mm. glass tube sealed at the lower end and equipped with a head permitting application of vacuum or the introduction of inert gas through a tube which could be extended below the surface of the molten mixture. A slow stream of oxygen-free nitrogen was bubbled continuously through the polymerizing mixture. Toward the completion of the polymerization, residual moisture and other volatile products were removed by evacuation; bubbles in the melt were removed by alternately evacuating and admitting nitrogen several times. Melt viscosities were measured using methods previously described.⁸ After allowing the sample to cool, the tube was broken and all adhering pieces of glass were removed from the solid polymer. A bubble-free section of the polymer was selected for transfer to the dilatometer chamber made from glass tubing of slightly larger inner diameter than that of the sample. In the preparation of the copolyamides the weighed salts were intimately mixed before melting in order to assure the same composition throughout the specimen.

Dilatometry.—The micro-melting point method previously employed,⁶ involving the determination of the temperature at which a small specimen ceases to depolarize transmitted light (as observed between crossed Polaroids, or Nicol prisms, using a low power microscope equipped with a suitable hot stage), proved to be insufficiently reproducible when applied to the polymers under investigation here. Even after careful annealing, different specimens from the same sample gave results differing by several degrees. No definite melting temperatures for most of the copolyamides could be obtained by this method. Consequently, the far more laborious determination of the volume-temperature curve was resorted to, the temperature being raised by small increments at intervals of several hours.

A dilatometric method similar to that described by Bekkedahl⁹ was used for the measurement of volume as a function of temperature.¹⁰ The accurately weighed sample (see above) was placed in the dilatometer bulb. A glass plug was inserted on top of the sample in most of the experiments before sealing the dilatometer in order to reduce the amount of mercury required, and thus to improve accuracy of the measurements.⁹ After sealing the dilatometer bulb, it was evacuated (<0.005 mm.) for several hours and then filled with mercury under vacuum. The quantity of mercury in the dilatometer was established by weighing. The dilatometer was immersed in an oil, or melted wax ("Coto flake"), constant temperature bath regulated within ±0.1°. A modified thyatron relay of the type described by Sturte-

vant¹¹ assured constant operation of the bath over long periods of time, as was required for much of the work reported here. Measurements ordinarily were begun some 20° below the anticipated melting temperature, the temperature being raised by small increments at suitable intervals as described later. The 2 mm. "Tru-Bore" capillary of the dilatometer was graduated in mm., and the position of the mercury meniscus at each temperature was estimated to ±0.1 mm. with the aid of a magnifier.

For measurements on the pure polyamide and on mixtures with diluents, samples of 2 to 3 g. were used. Larger samples, 5 to 8 g., of the copolyamides were employed in order to accentuate the much smaller volume changes due to melting.

The specific volume of molten poly-(sebacylpiperazine) was determined using a pycnometer pipet^{6,10} having a capacity of 0.9545 ml. at 189°, as calculated from the volume at 25° and the expansion coefficient of the Pyrex pycnometer. The specific volume of the polymer was found to be 0.9263 ± 0.0007 g./ml. at 189°. Knowing the volume of the polymer sample at this temperature, the amount of mercury and the expansion coefficients of mercury and glass, the absolute specific volume of the polymer at each temperature could be calculated from the dilatometer scale reading. Precision of the specific volume measurements was within ±0.0002 g./ml.

For the purpose of converting dilatometer readings to specific volumes, the density of each copolyamide was assumed to be equal to that of the unmodified liquid polyamide (extrapolated) at a reference temperature a few degrees above T_m for the copolyamide. Any errors thus introduced in the absolute values of the specific volumes are of little consequence, inasmuch as we are primarily concerned with the location of melting temperatures from changes in volume with temperature.

In preparing polymer-diluent mixtures, several grams of accurately weighed polymer and approximately the desired quantity of diluent were placed in a small glass tube equipped with a stirrer. Tube and stirrer were weighed before introducing the components for the mixture. After flushing with nitrogen, the mixture was heated to 190° and stirred gently until homogeneity was assured. The stirrer was raised above the surface of the mixture and allowed to drain, after which the tube and contents were brought to room temperature. Diluent which had distilled to the wall of the tube above the sample and to the stirrer was removed, and the tube and contents including the stirrer were reweighed to determine the weight of the mixture and hence the proportion of diluent which it contained. The mixture was removed from the tube and a weighed sample was transferred to the dilatometer as described above.

Specific volumes of mixtures were computed, on the assumption of no volume change on mixing, from the interpolated densities of the diluents and the density of the polyamide using T_m of the mixture as the reference temperature. Densities of the liquids were taken from the "International Critical Tables." From the thus calculated volume of the sample at T_m , the dilatometer readings at all other temperatures were converted to specific volumes.

Determination of Melting Temperatures at Higher Diluent Concentrations.—The dilatometric method was not used at concentrations of diluent greater than 45 to 50% because of the fluidity of the mixture which would have seriously complicated the filling of the dilatometer. Instead, the weighed polymer and diluent were sealed in a small glass capsule which was immersed, axis vertical, in an oil thermostat-bath, and then shaken by the vertical reciprocating action of a stiff wire connecting the capsule to an eccentric drive on a stirring motor above the bath. From 1 to 2 g. of mixture was used. The polymer was completely dissolved by first shaking at a sufficiently elevated temperature, then cooled until crystalline polymer appeared. The temperature of the bath was thereafter raised at a rate of 1° in 5 min. while shaking the sample. T_m was taken as the temperature at which the easily observed intense turbidity of the white crystalline polymer disappeared. This extremely convenient method fails at higher concentrations where the mixture is excessively viscous.

Liquid-liquid phase separation in the system diphenyl

(6) D. D. Coffman, G. J. Berchet, W. R. Peterson and E. W. Spanagel, *J. Polymer Sci.*, **2**, 306 (1947).

(7) T. Leiser, H. Gehlen and M. Gehlen-Keller, *Ann.*, **556**, 114 (1944).

(8) P. J. Flory, *This Journal*, **62**, 1057 (1940); T. G. Fox, Jr., and P. J. Flory, *ibid.*, **70**, 2384 (1948).

(9) N. Bekkedahl, *J. Research Natl. Bur. Standards*, **43**, 145 (1949).

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

(11) J. M. Sturtevant, "Physical Methods of Organic Chemistry," Vol. I, edited by A. Weissberger, Interscience Publishers, Inc., New York, N. Y., 1945, p. 327.

ether-poly-(*N,N'*-sebacoylpiperazine) was observed with the identical experimental arrangement. The two liquid phases did not disperse in such a manner as to produce an easily recognized turbidity. On stopping the agitation, the separation of the system into two layers could be observed readily, however, when two phases were present.

Results and Discussion

Pure Poly-(*N,N'*-sebacoylpiperazine).—The specific volume of the pure polyamide is shown in Fig. 1 as a function of temperature from 30 to 200°. The polymer had a melt viscosity of 830

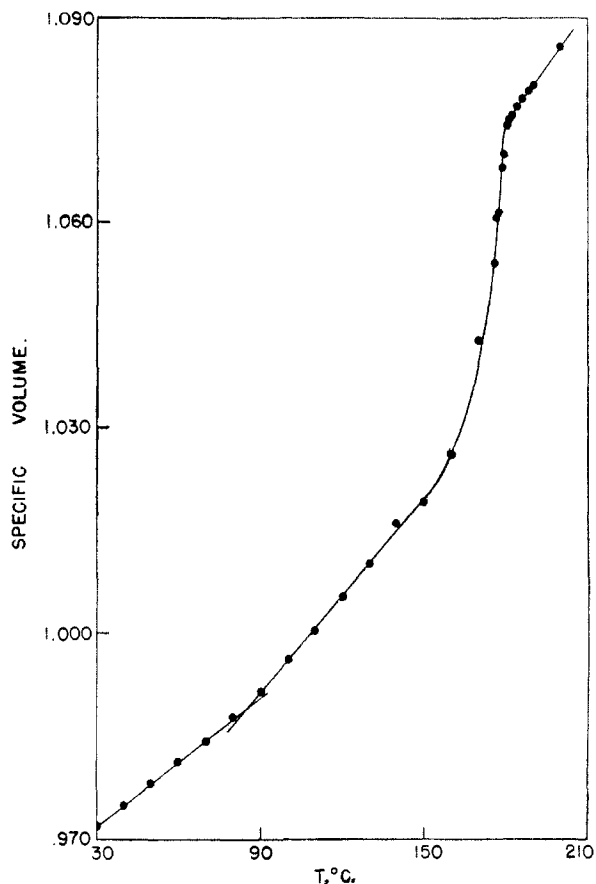


Fig. 1.—Specific volume vs. temperature for poly-(*N,N'*-sebacoylpiperazine).

poises at 190°; although the molecular weight was not determined, on the basis of the melt viscosity it is safe to presume that it was about 10,000 (number average) or perhaps somewhat more—enough to reduce the depression of T_m by the chain ends to no more than one or two degrees at most. The thermal history of the sample prior to the dilatometric measurements consisted merely in the gradual uncontrolled cooling of the melt at the time of preparation. The dilatometric measurements were run with ascending temperature. The volume reached a steady value within an hour or two at each temperature below 160°. From 160 to 175° the volume increased gradually for some time after each increase in temperature, and then decreased to a value which seemed constant after about three hours. Apparently, partial melting occurred in this range followed by recrystallization. Above 175° the temperature was changed by one-degree increments; the volume increased very

slowly toward an asymptotic value which seemed to be substantially attained after about 20 hr. at each temperature. It would appear that the melting process at constant temperature may proceed rather slowly and that it is by no means an instantaneous process, at temperatures just below T_m at any rate. There was no indication, however, that melting would have proceeded to completion on prolonged standing at any temperature below 180°. When the polyamide was brought from a temperature well below T_m to within a few degrees of T_m (e.g., to a temperature in the range from 175–180°), the sample melted completely and failed to recrystallize after many hours. It seems to be necessary to provide conditions such that less stable crystalline regions melt while more stable arrangements are formed without permitting total melting. If all crystallinity is destroyed in this process, the sample must be cooled substantially below T_m in order to initiate nucleation. At temperatures conducive to nucleation, imperfect crystalline arrangements are stable and these are again formed in preference to the higher melting, better ordered arrangements. This phenomenon has been observed previously in polyesters⁵ and doubtless is related to the peculiar melting behavior of rubber investigated by Bekkedahl and Wood.¹² In another experiment not reproduced here, the temperature was increased in half-degree increments above 175° and the sample was held at each temperature for six hours. The indicated melting temperature was 180–181°, in precise agreement with the results shown in Fig. 1.

In addition to the melting temperature (T_m) at 180–181°, the results in Fig. 1 show a well defined glassy state transition (second order transition¹⁰) at 82°. The slopes of the specific volume-temperature plot below and above the transition temperature T_g are 3.10×10^{-4} and 4.60×10^{-4} , respectively. Inasmuch as this transition presumably is confined to the amorphous portion of the polymer, the expansion coefficient for the liquid polymer above T_g doubtless is substantially greater than the above value and, in particular, the change at T_g in the expansion coefficient for the liquid must be larger than is indicated.

Polymer-Diluent Mixtures.—Typical volume-temperature plots for two polymer-diluent mixtures are shown in Fig. 2. The mixtures reached volume equilibrium more rapidly than the undiluted polymer. Usually an hour at each temperature was sufficient. After completion of the melting, the volume was sometimes measured as the temperature was decreased by successive increments to a point several degrees below T_m . Inasmuch as the mixture supercooled readily,¹³

(12) N. Bekkedahl and L. A. Wood, *J. Chem. Phys.*, **9**, 193 (1941); see also "Advances in Colloid Science," Vol. II, edited by H. Mark and G. S. Whitby, Interscience Publishers, Inc., New York, N. Y., 1946, Chapter 2 by L. A. Wood.

(13) The extent to which the solutions could be supercooled before crystallization set in appeared to be quite sharply defined. For example, a mixture containing 33% diphenyl ether failed to crystallize when held for as much as eight hours at a temperature 14° below T_m , but crystallization set in almost at once at 16° below T_m . Whether the sample was heated a fraction of a degree, or 60° above T_m prior to cooling did not alter by more than one degree the extent of supercooling at which crystallization commenced.

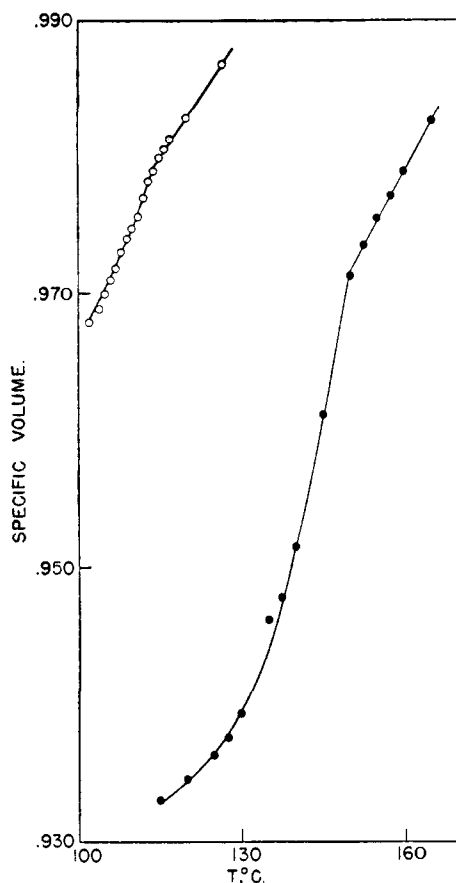


Fig. 2.—Specific volume vs. temperature for polymer-diluent mixtures: *m*-cresol, $v_1 = 0.302$ (O); diphenyl ether, $v_1 = 0.433$ (●).

the volume-temperature relationship for the mixture was readily established in this manner in the vicinity of T_m . The melting temperature was taken as the point of intersection of the line for the semicrystalline polymer, obtained with ascending temperature, with the volume-temperature line for the totally liquid sample. Melting temperatures for mixtures containing higher proportions of diluent were determined by visual observation while gradually warming the mixture in a sealed tube subjected to shaking, as described above.

Results of these experiments are summarized in Table I. The temperature interval in the vicinity T_m and the time during which the mixture was held at each temperature is given in the third column. In Fig. 3 the melting temperatures are plotted against the volume fraction $1 - v_1$ of polymer. Volume fractions in all cases are calculated from the specific volumes of the polymer and diluent at T_m for the mixture, assuming no volume change on mixing. Also included in Fig. 3 are four points (open circles) indicating compositions of the two liquid phases into which the diphenyl ether-polyamide system separates at low concentrations of polymer below a critical miscibility temperature of about 510°K. The presence of two phases at a given temperature was easily detected by observing the separation into two layers when shaking was interrupted.

TABLE I
MELTING TEMPERATURES OF POLYMER-DILUENT MIXTURES

Diluent and its volume fraction v_1	Method	Temp. measurements and time at each temp.	T_m , °C.	h_u cal./mole repeating unit	B cal./cc.
<i>m</i> -Cresol					
0.173	Dilatometric	1/2°/6 hr.	151 ± 0.5	6400	-12.5
.302	Dilatometric	1°/hr.	115 ± 0.5		
.473	Dilatometric	1°/hr.	73 ± 0.5		
Diphenyl Ether					
0.127	Dilatometric	1°/6 hr.	168 ± 0.5	5700	+ 3.7
.324	Dilatometric	1/2°/6 hr.	156 ± 0.5		
.433	Dilatometric	2°/hr.	151 ± 0.5		
.489	Visual	1°/5 min.	141 ± 0.5		
.675	Visual	1°/5 min.	140 ± 0.5		
.743	Visual	1°/5 min.	142 ± 1		
.881	Visual	1°/5 min.	140 ± 0.5		
.942	Visual	1°/5 min.	140 ± 1		
.981	Visual	1°/5 min.	140 ± 0.5		
<i>o</i> -Nitrotoluene					
0.234	Dilatometric	1°/hr.	156 ± 0.5	6350	+ 1.1
.493	Visual	1°/5 min.	127 ± 1		
.739	Visual	1°/5 min.	110 ± 1		
.948	Visual	1°/5 min.	99 ± 1		
.978	Visual	1°/5 min.	97 ± 1		
.991	Visual	1°/5 min.	94 ± 1		

According to theory (see equation (3)) the limiting slopes of T_m plotted against the "mole fraction" of diluent (*i.e.*, the ratio of moles of diluent to moles of diluent plus moles of repeating unit) should be the same for different solvents. In other words, the limiting slopes in Fig. 3 where T_m is plotted against $1 - v_1$ should be inversely proportional to the molar volume of the diluent. That this is true within experimental error is brought out more clearly by the method of plotting in Fig. 4 (*cf. seq.*). The curves shown in Fig. 3 for the different diluents diverge as the concentration of diluent is increased. For the best solvent,

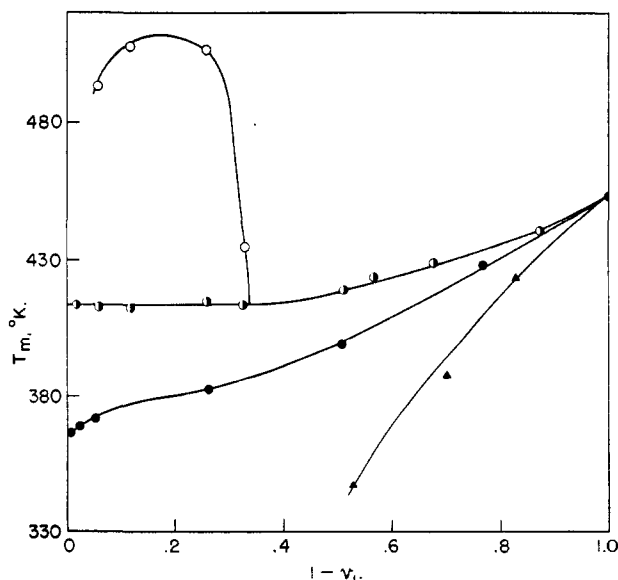


Fig. 3.—Melting temperature T_m vs. volume fraction of polymer $1 - v_1$ for various diluents: diphenyl ether (○); *o*-nitrotoluene (●); *m*-cresol (▲).

m-cresol, in which the polymer is quite soluble at room temperature, T_m decreases rapidly with

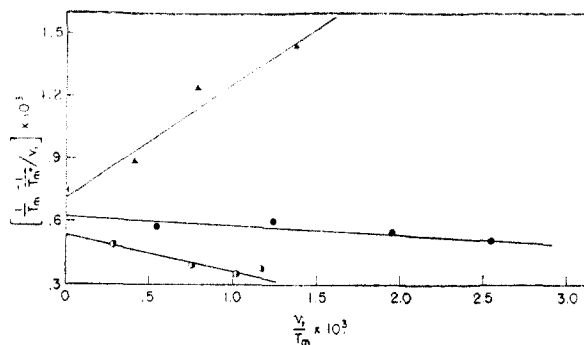


Fig. 4.— $(1/T_m - 1/T_m^0)/v_1$ vs. v_1/T_m for various diluents: diphenyl ether (○); *o*-nitrotoluene (◻); *m*-cresol (▲).

increase in v_1 ; the curve shows downward concavity. The curves for the poorer solvents show opposite curvature, for higher proportions of diluent at any rate. Melting temperatures for the poorest solvent, diphenyl ether, are above those for *o*-nitrotoluene at all concentrations.

The melting curve for the diphenyl ether-polyamide system appears to reach a critical point at $v_1 \cong 0.66$ and $T_m = 413\text{--}414^\circ\text{K}$. Two liquid phases and crystalline polymer co-exist at this point, and at lower concentrations of polymer T_m is independent ($\pm 1^\circ$) of the over-all composition, as is required by the phase rule. Similar behavior has been observed by Richards¹⁴ for mixtures of polyethylene with diluents. We shall return to a further discussion of the liquid-liquid equilibrium curve later.

The theory² on which equation (3) is based obviously is in error at very low polymer concentrations for it predicts a finite melting temperature at the lowest polymer concentrations. This would correspond to zero solubility of the crystalline polymer at any temperature T such that¹⁵

$$T \leq [(R/h_u)(z/z_s)(1 - \kappa_1) + 1/T_m^0]^{-1}$$

The error arises from the tacit assumption of a uniform distribution of polymer segments throughout the amorphous regions,² whereas in fact the polymer concentration will be enhanced in the vicinity of crystallites. This inaccuracy should become more serious the lower the polymer concentration and the lower the chain length. Results for *o*-nitrotoluene as diluent show that T_m appears to proceed toward a limit with decreasing concentration as required by equation (3), but at very low concentrations a rounding off is clearly evident.

For the purpose of making a quantitative comparison of the data with equation (3) it is convenient to substitute from equation (4) for κ_1 and to rearrange the resulting expression to

$$(1/T_m - 1/T_m^0)/v_1 = (R/h_u)(z/z_s)(1 - Bv_1v_1/RT_m) \quad (6)$$

This suggests the plots shown in Fig. 4. For both *o*-nitrotoluene (omitting points at polymer concentrations below $1 - v_1 = 0.052$) and for diphenyl ether (omitting points below the critical polymer concentration $1 - v_1 = 0.34$) these plots are linear

(14) R. B. Richards, *Trans. Faraday Soc.*, **42**, 10 (1946).

(15) We use here the limiting relationship for infinite chain length. The argument is not altered, however, if terms due to the finite length of the chain are included. See equation (28) of ref. (2).

within experimental error, in agreement with equations (3) and (6). Although the points for *m*-cresol scatter, they may be approximated by a straight line also. Values of the heats of fusion h_u calculated from the intercepts of these plots are given in the fifth column of Table I. They are in satisfactory agreement, the average being 6200 cal. per mole of structural units, or 25 cal. per g. of polymer. Values for the parameter B calculated according to equation (6) from the slopes and intercepts of the lines drawn in Fig. 4 are given in the last column of Table I.

The B 's evaluated in this manner may not be accurately representative of the heat of mixing, for the present experiments do not preclude the possibility that they arise in part from entropy contributions. Thermodynamic measurements^{16,17} on dilute polymer solutions point to the presence of an entropy term which depends on the square of the concentration. Thus the chemical potential of the solvent in polymer solutions may be written

$$\mu_1 - \mu_1^0 = RT \left\{ \ln v_1 + (1 - v_1)(1 - 1/x) + \left[\kappa_1 + \left(\frac{1}{2} - \psi_1 \right) \right] (1 - v_1)^2 \right\} \quad (7)$$

where x is the ratio of the volumes of the polymer and the solvent molecules, and ψ_1 characterizes the entropy of dilution at very low concentrations.^{17,18} The first two terms on the right of equation (7) represent the entropy of dilution according to the simple lattice theory.¹⁹ $R(1/2 - \psi_1)(1 - v_1)^2$ represents the additional entropy (according to the lattice theory $\psi_1 = 1/2$), and $RT\kappa_1(1 - v_1)^2$ represents the van Laar heat of dilution, with κ_1 retaining the definition of equation (4). It follows necessarily that the chemical potential of the polymer *unit* must, in the limit of infinite chain length ($x = \infty$), assume the form

$$\mu_2 - \mu_2^0 = -(RTz/z_s) \left\{ v_1 - \left[\kappa_1 + \left(\frac{1}{2} - \psi_1 \right) \right] v_1^2 \right\} \quad (8)$$

A review of the derivation of equation (3) shows that $\kappa_1 + (1/2 - \psi_1)$ should replace κ_1 in equation (3), if equation (8) is valid and if $\psi_1 \neq 1/2$. Hence, in place of Bv_1/R in equation (6), we should use $(Bv_1/R) + (1/2 - \psi_1)T_m$.

The above leads to the conclusion that the plots shown in Fig. 4 should be curved unless $\psi_1 = 1/2$. Such curvature as might be expected over the available temperature range, however, would be too small to be detected with certainty without the aid of far more precise measurements than are possible at present. In effect, the present method is scarcely capable of differentiating between a heat and an entropy term in v_1^2 in the expression for the chemical potential of the polymer unit. Hence, the values of B given in Table I may exceed the true Van Laar heat of mixing parameter by an amount equal to $RT(1/2 - \psi_1)/v_1$. Considera-

(16) M. J. Shick, P. M. Doty and B. H. Zimm, *THIS JOURNAL*, **72**, 530 (1950).

(17) T. G. Fox, Jr., and P. J. Flory, *ibid.*, **73**, 1909 (1951); **73**, 1915 (1951).

(18) P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950). We properly neglect here the influence of non-uniformity of distribution of polymer segments on the thermodynamic functions at very low concentrations.

(19) P. J. Flory, *ibid.*, **10**, 51 (1942).

tion of the values of ψ_1 computed from data on dilute polymer solutions^{16,17,20} suggests that the discrepancy probably does not exceed about one cal. per cc. Although the heat of mixing of *o*-nitrotoluene with the polyamide might conceivably be very nearly zero rather than slightly positive as indicated in Table I, the classification of solvents according to the slopes indicated by the data shown in Fig. 4 probably is not seriously altered by such corrections.

According to the lattice theory of polymer solutions,¹⁹ the critical temperature T_c for total miscibility (*i.e.*, the consolute temperature) for a system composed of homogeneous polymer and solvent is related to Bv_1 as

$$T_c = Bv_1 x / (1 + \sqrt{x})^2 \quad (9)$$

where x is the ratio of the molar volume of the polymer to that (v_1) of the solvent. An independent value for B may be calculated from x and T_c with the aid of this relationship. The results (open circles) shown in Fig. 3 for diphenyl ether indicate a critical temperature T_c for complete miscibility of about 510°K. The problem of phase separation for a heterogeneous polymer is complex,^{21,22} but it is evident that the critical temperature depends on a higher molecular weight average. However, the value of B is not very sensitive to x . Assuming a value of 25,000 for the effective molecular weight average, corresponding to $x \cong 150$, $B = 3.4$ cal. per cc., in good agreement with the value deduced from the melting temperature depression. It will be noted that the maximum in the liquid equilibrium curve occurs at a low polymer concentration, although not as low as the theoretically predicted value¹⁹ $1 - v_1$ (crit.) $\cong 1/x^{1/2}$.

Copolyamides.—Various copolyamides were prepared by treating mixtures of piperazinium sebacate with a piperazinium salt of another dibasic acid, or with hexamethylene diammonium sebacate. The mole fraction X_A of piperazinium sebacate was varied from 0.90 to 0.70. Typical dilatometric runs on two of the resulting copoly-

amides are shown in Fig. 5. The results are summarized in Table II, and in Fig. 6 they are plotted according to equation (1). The heat of fusion calculated from the slope of the line drawn through the points is 5000 cal. per mole of repeating units, which is appreciably smaller than the value of h_u deduced from the depression of T_m by diluents.

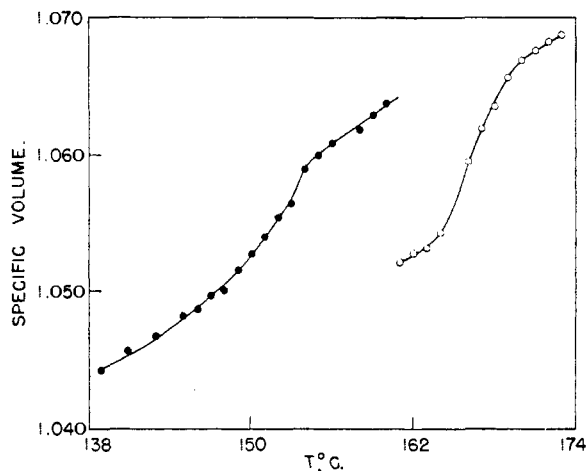


Fig. 5.—Specific volume vs. temperature for copolyamides containing the co-ingredient N,N'-sebacoylhexamethylenediamine: $X_A = 0.90$ (O); $X_A = 0.70$ (●).

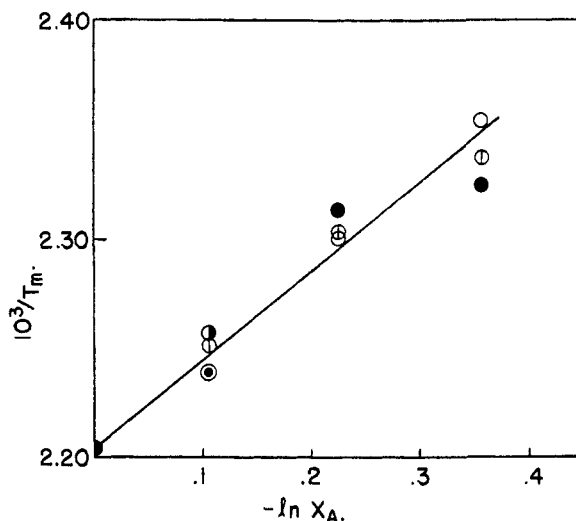


Fig. 6.— $1/T_m$ vs. $-\ln X_A$ for copolyamides where X_A is the mole fraction of N,N'-sebacoylpiperazine units. Co-ingredients: N,N'-isophthaloylpiperazine (O); N,N'-adipoylpiperazine (⊙); N,N'-pimeloylpiperazine (●); N,N'-sebacoylhexamethylenediamine (⊕).

According to theory the melting temperature required for the application of equation (1) must represent the temperature at which perfect crystallites made up of indefinitely long sequences of A units melt. In a random copolymer very long sequences are present in extremely small quantity. The observed T_m will be somewhat lower, for it represents the melting temperature for crystallites consisting of sequences of such length as to be present in sufficient abundance to be detected by the method used.² Considerations such as

TABLE II
MELTING TEMPERATURES OF COPOLYAMIDES

Co-ingredient	Melt vis- cosity at 190° poises	Mole frac- tion X_A of seba- coyl piper- azine units	Temp. incre- ments and time at each temp. °C. Hr.	T_m , °C.
N,N'-Isophthaloyl piperazine		0.9	1 1	174 ± 0.5
N,N'-Isophthaloyl piperazine	85	.8	1 1	163 ± 1
N,N'-Isophthaloyl piperazine	260	.7	1 1	152 ± 0.5
N,N'-Adipoyl piperazine	110	.9	1 4	170 ± 0.5
N,N'-Pimeloyl piperazine	250	.9	1 4	174 ± 0.5
N,N'-Pimeloyl piperazine	215	.8	1 1	159 ± 0.5
N,N'-Pimeloyl piperazine	70	.7	1 1	157 ± 0.5
N,N'-Sebacoyl hexamethylene diamine	25	.9	1 4	170 ± 1
N,N'-Sebacoyl hexamethylene diamine	60	.8	1 1	161 ± 0.5
N,N'-Sebacoyl hexamethylene diamine	50	.7	1 4	155 ± 0.5

(20) T. G. Fox, Jr., P. J. Flory and A. M. Bueche, *THIS JOURNAL*, **73**, 285 (1951).

(21) H. Tompa, *J. Chem. Phys.*, **17**, 1008 (1949).

(22) W. H. Stockmayer, *ibid.*, **17**, 588 (1949).

these may account for the sigmoid shape of the volume-temperature curves for copolymers. More important, they lead to the conclusion that the experimentally measured T_m will be low by an unspecified number of degrees. This error should be expected to increase as $1 - X_A$ is increased, hence a systematic error is introduced making the calculated h_u too small. The observed discrepancy between the heats of fusion evaluated by the two

methods may arise from this source. However, it is not as great as was observed on comparison of the heats of fusion calculated for linear polyesters⁵ on the basis of equations (1), (2) and (3), respectively. The T_m 's for the polyesters and copolyesters were determined by the less accurate light depolarization method, which may have increased the discrepancy.

ITHACA, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Two Stage Polymerizations. II. Preparation and Polymerization of Vinyl Ethers of Unsaturated Alcohols¹

BY GEORGE B. BUTLER AND JAMES L. NASH, JR.

Five new unsaturated ethers of ethylene glycol have been prepared and characterized. These compounds were prepared by reaction of the appropriate sodium alkenoxide with vinyl β -chloroethyl ether. It has been shown that those ethers containing two unsaturated radicals, only one of which is a vinyl radical, may be polymerized in presence of boron trifluoride at -70° to produce linear polymers containing residual unsaturation. These unsaturated polymers were cross-linked at elevated temperatures by peroxide catalysts to produce insoluble and infusible polymers. In addition, studies were made of the effect of several typical peroxide catalysts on several of these unsaturated ethers. In general, cross-linked polymers were obtained. Copolymerization of a typical ether of this type with a vinyl alkyl ether at -70° with BF_3 produced a linear polymer.

The first paper of this series² reported a study of the polymerization reactions of allyl ethers of allyl substituted phenols. It was shown that these ethers could be made to undergo a two-stage polymerization, the first stage resulting in the formation of unsaturated linear polymers as the result of polymerization of the allyloxy radical in presence of boron trifluoride, and the second stage resulting in the formation of cross-linked polymers by thermal polymerization of the allyl side chains.

The pronounced reactivity of vinyl ethers at low temperature in the presence of acid catalysts³⁻⁵ prompted us to prepare and study vinyl ethers of other unsaturated alcohols as compounds which may lend themselves to a stepwise polymerization in which only the vinyl radical polymerized under a given set of conditions. This should result in an unsaturated linear polymer, which may later be cross-linked under a different set of conditions. It has previously been shown⁶ that allyl ethers are copolymerized with other monomers in presence of peroxide catalysts at elevated temperatures. Those ethers containing two or more allyl groups serve as cross-linking agents for other monomers.^{7,8} It has also been shown that divinyl ethers result in cross-linked polymers when subjected to polymerization in presence of acid catalysts.³

All of the compounds prepared and studied contained the vinyloxy radical. In the absence

of other vinyloxy radicals, these compounds were found to produce only linear polymers at low temperatures in presence of boron trifluoride. These polymers were then subject to peroxide-catalyzed polymerization at elevated temperatures, resulting in cross-linked polymers. Polymerization of an ether which contained both the vinyloxy and furfuryloxy radicals resulted in a cross-linked polymer at -70° in presence of boron trifluoride. However, since the furfuryloxy radical is composed of both a vinyloxy and an allyloxy radical, this was not unexpected.

The potential usefulness of a compound capable of undergoing a two stage polymerization would be considerably enhanced if the degree of unsaturation in the first stage polymer could be varied over a wide range. Therefore, we considered it important to determine whether or not compounds of this type would copolymerize with a typical vinyl alkyl ether under similar conditions. Our experiments have shown that this can be done, resulting in a first stage polymer having a much lower degree of unsaturation than the homopolymer.

Although the chief purpose in preparation of these ethers was to determine whether or not the two-stage polymerization could be accomplished, studies were also made of the effect of several typical peroxide catalysts on several of these compounds. In general, reasonably large quantities of catalyst were required to initiate polymerization, but in most cases cross-linked polymers resulted. However, ethylene glycol vinyl furfuryl ether produced only linear polymers in presence of benzoyl peroxide.

Experimental

Materials.—Vinyl β -chloroethyl ether was obtained from Carbide and Carbon Chemical Corporation. The redistilled fraction boiling between $107-110^\circ$ was recovered for use. Furfuryl alcohol was obtained from Quaker Oats Company and the fraction distilling between $68-70^\circ$ (10

(1) Abstracted from a thesis presented by James L. Nash, Jr., to the Graduate School of the University of Florida in partial fulfillment of the requirements for the degree of Master of Science.

(2) Butler and Ingley, *THIS JOURNAL*, **73**, 1512 (1951).

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