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Melting Temperature and Polymer–Solvent Interaction: Polychlorotrifluoroethylene

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The melting temperatures of polychlorotrifluoroethylene–diluent mixtures have been measured. The results, when compared with the theory for the phenomenon, are shown to give consistent values for the heat of fusion and the solubility parameter of the polymer. The Flory–Huggins theory of polymer solutions was used to explain the results for higher diluent concentrations, where a two-phase system existed. The interaction parameters, μ, from this theory, have been assigned approximate values.

Introduction

The influence of solvents and plasticizers on the melting temperatures of semi-crystalline polymers is of considerable practical as well as theoretical importance. In the case of the polymer used in the present investigation the crystalline material is fairly brittle and crazes appreciably on bending. On the other hand, above the temperature at which the crystals melt it can be molded or formed into different shapes without breaking or crazing.

It has been shown by Flory[1] that the lowering of the crystal melting temperature by the addition of a diluent depends not only on the characteristics of the polymer and the concentration of the diluent but also on the polymer–diluent interaction. Therefore, by studying the crystal melting temperatures of mixtures of polymers and diluents one may obtain information about this interaction.

The present paper reports the results of experiments on the depression of the melting temperature in semi-crystalline polychlorotrifluoroethylene by four different liquids. The results are compared with what was to be expected on the basis of the theory for this phenomenon. The heat of fusion per gram of the crystalline polymer is obtained and the polymer–diluent interaction constants are compared with the solubility parameters of the diluents used.

Experimental

The polymer used was Kel-F-300 (hereafter referred to by the freon designation as poly-F-1113) prepared by the M. W. Kellog Co. of Jersey City, N. J. It has the empirical formula $(-CF_2CFCl-)_x$ where x is the degree of polymerization. The number average molecular weight of a similar sample of Kel-F-300 was determined by osmotic pressure measurements and found to be 100,000.[2] No attempt was made to fractionate the polymer.

The samples used for the melting measurements were of two kinds, the powder as received from the Kellog Co. and pressed sheets. The sheets, about 30 mils thick, were formed by heating the powder to 285° for 5 minutes and pressing in a hydraulic press for two minutes. Melting temperatures of the powder were identical with those of the sheets indicating that the degradation during the thermal treatment necessary to form the sheets was unimportant for the present purposes.

The powder or pieces of the sheet were weighed into small glass tubes and a measured volume of diluent added to each. The volume fractions of polymer were calculated using a density of 2.0 g./cc. for the polymer.[3] The sealed tubes were immersed in a silicone oil-bath and illuminated by light passing through a polaroid filter. They were observed with a telescope through another polaroid filter whose axis of polarization was set at 90° with respect to the first.

A definite temperature cycle was followed during the course of the experiments. The tubes were first heated above the crystal melting temperature and then cooled slowly until the samples were appreciably crystalline. Super cooling was noted in all cases. The temperature was then raised at the rate of 1° per minute or less until the crystals had melted.

There was some doubt as to whether an equilibrium mixture between polymer and diluent was obtained at the melting temperature. However, holding the samples at a temperature near the melting range for 24 hours and, in one case, for a week, produced no measurable change in the results. Likewise in the most dilute solutions stirring or shaking the sample tube had no effect on the results. It was concluded, therefore, that the mixtures were at equilibrium.

In all cases the crystals melted over a range instead of at one sharp melting point. According to theory[1] the proper temperature to measure for the present purposes is that at which the very last crystals melt. This temperature will obviously depend on the method of observation. The temperatures reported here are those at which the last visible crystal regions disappeared. Since the choice of this temperature depends somewhat on the observer there is a small uncertainty in the values. Repeated measurement on the same samples at different times places this uncertainty at about ± 2°. This precision seems sufficient for the present purposes.

The reciprocals of the melting temperatures, T_m, are given as a function of the volume fraction, v_1, of diluent in Table I. It can be seen that as v_1 increases $1/T_m$ increases and then finally levels off to an almost constant value.

TABLE I

MELTING TEMPERATURE OF POLY-F-1113–DILUENT MIXTURES

o-Chlorobenzotrifluoride		Mesitylene		Toluene		Cyclohexane	
v_1	$10^3/T_m$	v_1	$10^3/T_m$	v_1	$10^3/T_m$	v_1	$10^3/T_m$
0	2.08	0	2.08	0	2.08	0	2.08
.056	2.12	.062	2.13	.057	2.11	.063	2.10
.124	2.16	.106	2.15	.202	2.23	.100	2.12
.276	2.28	.223	2.24	.243	2.27	.255	2.22
.358	2.31	.357	2.32	.323	2.33	.274	2.24
.388	2.35	.374	2.33	.403	2.36	.318	2.28
.588	2.47	.661	2.45	.569	2.44	.386	2.32
.651	2.51	.732	2.45	.621	2.46	.487	2.37
.713	2.51	.772	2.45	.753	2.50	.562	2.39
.758	2.51	.792	2.45	.768	2.50	.611	2.40
.786	2.52	.952	2.44	.818	2.51	.677	2.39
.800	2.50	.980	2.46	.909	2.50	.687	2.40
.850	2.52			.980	2.50	.782	2.40
.900	2.53					.909	2.39
.951	2.51						

Discussion

The expression given by Flory[1] relating T_m and v_1 for higher molecular weight materials can be written

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = \frac{R}{h_\mu}\left[\frac{z}{z_s}v_1 - \beta v_1^2\right] \qquad (1)$$

where T_m° is the melting temperature of the pure polymer, z/z_s is the ratio of the molar volumes of

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[1] P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949); see also R. D. Evans, H. R. Mighton and P. J. Flory, THIS JOURNAL, **72**, 2018 (1950).

[2] H. S. Kaufman and M. S. Muthana, *J. Polymer Sci.*, **VI**, 251 (1951).

[3] The author is indebted to Dr. F. Price for making this value of the density of the amorphous polymer at the melting point available to him.

the statistical polymer repeating unit and the diluent, h_μ is the heat of fusion per mole of repeating unit, R is the gas constant, and β is the energy of mixing parameter equal to BV/RT_m. The molar volume of the repeating unit is given by V and B expresses the solvent–polymer interaction. In the simplest cases[4]

$$B = (\delta_p - \delta_0)^2 \qquad (2)$$

where δ_p and δ_0 are the solubility parameters of polymer and solvent. By making the proper substitutions Eq. (1) can be written in a more useful form as

$$1/T_m - 1/T_m^\circ = (R/\rho V_s h_f)v_1 - (B/\rho h_f)(v_1^2/T_m) \qquad (3)$$

where ρ is the polymer density, h_f is the heat of fusion per gram of crystalline polymer, and V_s is the molar volume of solvent. This equation predicts that a plot of $1/T_m$ *vs.* v_1 should increase linearly at first, showing some curvature for higher values of v_1 and, if B is large enough, go through a maximum.

The physical model on which the derivation of Eq. (1) was based assumed that the sample consisted of crystallites imbedded in amorphous polymer. As diluent was added the amorphous regions of the polymer were considered to be diluted and to conform to the previous theories of solutions of amorphous polymers.[5] Thus the free energy change on fusion of a crystallite was found to be dependent upon the amount of dilution of the amorphous phase. This treatment resulted in the above dependence of T_m on v_1.

If, however, the diluent is such a poor solvent that, in the temperature range under investigation, it is not completely miscible with the amorphous polymer there will be a region of maximum dilution. In this case if more solvent is added at the temperature at which the crystals have just disappeared a two-phase system comes into being, one concentrated and one dilute with respect to polymer. In such a case it is to be expected that the crystals imbedded in the amorphous phase will have melting points given by Eq. (1) up to a certain value of v_1. For higher v_1 values, since the dilution remains constant, the free energy of fusion does not change resulting in a constant value of T_m.

That such a phenomenon can occur can be easily demonstrated in another system. Richards[6] reports that, in his experiments with polyethylene, for low values of v_1 the crystal melting temperature and the solution temperature in nitrobenzene are identical. His results, given graphically, show the type of behavior expected from Eq. (1). He soon reaches a point, however, where, even though the crystals are melted he has to raise the temperature a large amount above T_m to get true solution. Since he reports only solution temperatures and discusses crystal melting temperatures vaguely for this concentration region it was thought to be worthwhile to measure T_m for a few points. Mixtures of polyethylene[7] and nitrobenzene having v_1 values of 0.772, 0.895 and 0.946 were prepared and measured in the same way as the samples of poly-F-1113. Within experimental error all melted at the same temperature where $1/T_m$ was 2.62–2.63 × 10^{-3}. This constancy of T_m is just what is to be expected on the basis of the above discussion. Fortunately in this system the refractive index difference between swollen polymer and solvent was large enough after the crystals had melted so that one could very easily see that it was a two-phase system. In general this was not the case with the experiments on poly-F-1113 although in the system with cyclohexane this diluted amorphous phase could be seen quite readily.

The data of Table I, up to, but not including, that where $1/T_m$ seems to level off have been analyzed in accordance with Eq. (3). This was done by plotting $(1/T_m - 1/T_m^\circ)/v_1$ *vs.* v_1/T_m and drawing the best straight line through the points. The intercept at $(v_1/T_m) = 0$ determines $(R/\rho V_s h_f)$ and the slope determines $B/\rho h_f$. From these two quantities B and h_f may be found.

A check on the consistency of the data or the validity of Eq. (1, 3) could be obtained by means of Eq. (2) if the solubility parameters of the solvents were known. Since good data are available for the calculation of δ_0 only at 298°K. these will be used. The values of δ_p calculated from B in this fashion would be strictly correct only if $(\partial\delta_p/\partial T) = (\partial\delta_0/\partial T)$. An examination of $\partial\delta/\partial T$ for other compounds shows that this is quite unlikely but that the error introduced by assuming it to be true is probably small. This step, then, affords a qualitative check on consistency. The values of the parameters obtained by this method are given in the first three columns of Table II.

TABLE II

Diluent	h_f (cal./g.)	δ_0	δ_p	μ
Toluene	10.5	8.9[4]	7.0	(0.59)
Mesitylene	9.5	8.8[4]	7.4	0.67
o-Chlorobenzotrifluoride	10.9	8.8[a]	7.2	0.66
Cyclohexane[b]	(11.5)	8.2[4]	(6.3)	(0.71)

[a] Solubility parameter estimated from Hildebrand's rule.[4] [b] The cyclohexane data are somewhat scattered for low values of v_1, presumably because of loss of solvent during the manipulation of the small sample tubes. Because of this the values given are only approximate.

The heats of fusion and the solubility parameters are remarkably constant when one considers the approximations made in the theory of the melting points and in that of the solubility parameters. An average heat of fusion of 10.3 cal./g. corresponds to 1.20 kcal./mole of monomer unit. This is to be compared with 1.57 kcal./mole of C_2H_4 units in the higher *n*-paraffins and in polyethylene. The heat of fusion per monomer unit is less in the case of poly-F-1113 and the melting point is much higher resulting in a smaller entropy of fusion. Such behavior might be expected from a polymer having rather bulky groups, compared to hydrogens, attached to the carbon atoms. This steric effect would, of course, result in a somewhat stiffer polymer chain.

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(4) J. H. Hildebrand and R. L. Scott, "The Solubility of Non-electrolytes," 3rd edition, Reinhold Publishing Corporation, New York, N. Y., 1950.

(5) M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941); P. J. Flory, *ibid.*, **9**, 660 (1941).

(6) R. B. Richards, *Trans. Faraday Soc.*, **41**, 127 (1945).

(7) The sample was labelled Polythene, #A-7983, produced by E. I. du Pont de Nemours and Co.

The possibility still exists of determining one other quantity from the data of Table I. The concentration, v_1, at which the amorphous polymer can swell no more is given by the Flory–Huggins[5] theory in terms of a parameter μ. The exact meaning of μ is still somewhat in doubt although it is known to consist of an entropy as well as an energy of interaction term. Approximate values of μ can be obtained by finding the concentration at which Eq. (1) gives a value of T_m equal to that found for the limiting value as v_1 is increased. The μ values obtained by means of the relation

$$-\mu = [\ln v_1 + (1 - v_1)]/(1 - v_1)^2$$

which is again the limiting expression for high molecular weights, are given in the last column of Table II.

There seems to be a correlation between μ and the solubility parameter of the solvent although the data in the case of toluene and cyclohexane do not permit a precise determination due to the already pronounced curvature of the $1/T_m$ *vs.* v_1 curves. Figures 1, 2 and 3 show the experimental data for *o*-chlorobenzotrifluoride, mesitylene and toluene. The solid line has been calculated from Eq. (1) using the parameters of Table II. The horizontal dotted line is drawn as the limiting value of $1/T_m$. It can readily be seen that the fit is within experimental error.

Thermodynamic investigations of dilute polymer solutions indicate that β may contain an entropy term in addition to the heat of mixing term used in the preceding analysis. The effects of this entropy contribution on the shapes of the lines drawn in Figs. 1–3 have been discussed in detail recently[8] and need not be repeated here. It is sufficient to point out that in these experiments, with quite similar diluent molecules, the data can be represented adequately with the simple form of Eq. (1–3).

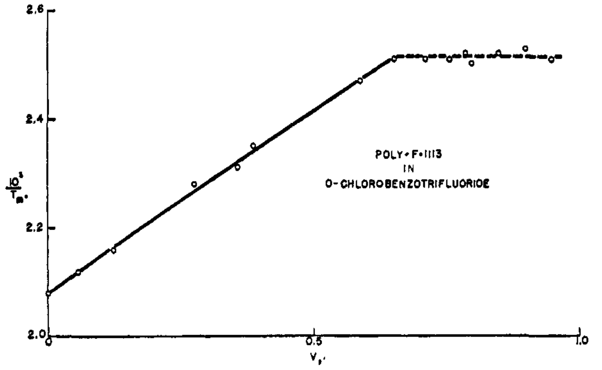

Fig. 1.—Reciprocal melting temperatures *vs.* volume fraction of *o*-chlorobenzotrifluoride.

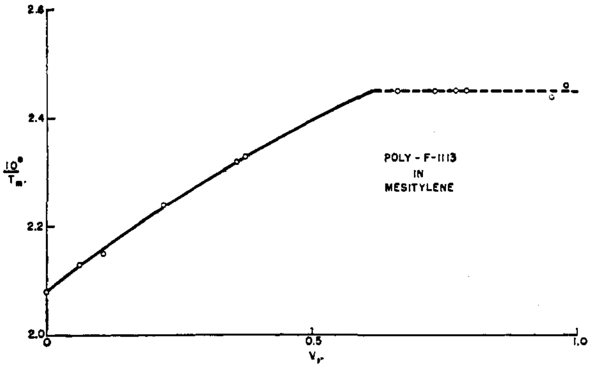

Fig. 2.—Reciprocal melting temperatures *vs.* volume fraction of mesitylene.

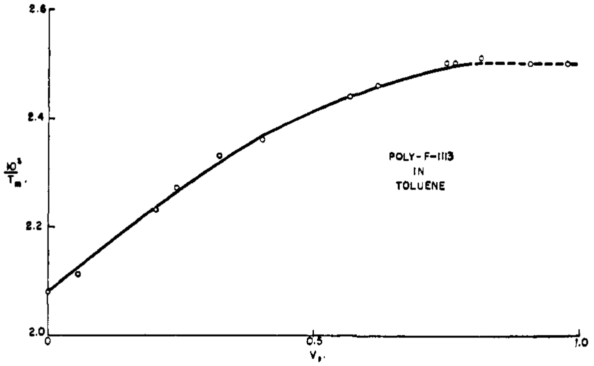

Fig. 3.—Reciprocal melting temperatures *vs.* volume fraction of toluene.

SCHENECTADY, N. Y. RECEIVED JUNE 22, 1951

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[8] P. J. Flory, L. Mandelkern and H. K. Hall, THIS JOURNAL, **73** 2532 (1951).