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**ON THE STRUCTURE AND PROPERTIES OF VINYL POLYMERS AND THEIR MODELS. XIV.\*****GLASS TRANSITION TEMPERATURES IN THE SYSTEM POLY(VINYL CHLORIDE)-DILUENT\*\***

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The glass transition temperatures in the system poly(vinyl chloride)-diluent were determined by using the differential scanning calorimetry. 1- and 3-chloropentanes, 1,3- and 1,4-dichlorobutane and racemic 2,4-dichloropentane were used as diluents; the upper limit of the diluent concentrations was 25% by weight. The data were linearized in terms of Fox's equation. It has been found that the plastifying activities of the individual solvents are in good correlation with the thermal expansion coefficients at 30°C and with normal boiling points; on the other hand, the number of stable conformers (rotational isomers) has only a secondary effect, if any. These conclusions point out the decisive influence of the free volume.

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The ability of diluents to depress the glass transition temperature of polymers is very interesting both from the viewpoint of applications and for the verification of the theoretical concepts of glass transition. For practical purposes, it is desirable to extend the already existing procedures of predicting the plastifying activity of the compounds on the basis of the knowledge of the chemical structure, or of the accessible physical properties. An empirical correlation of the experimental data can be used for this purpose; the other way, which moreover offers a possibility to learn more about the nature of the glass transition, consists in a suitable choice of the systems under investigation and in a confrontation of the results with the predictions ensuing from the existing theories. At present, there are two basic theoretical views that are generally accepted. The free volume theory explains the glass transition as an extremely large, hindering of non-vibration modes of the molecular motion caused by a decrease in the free volume and a decay of rather large free spaces (holes) between the molecules<sup>1-5</sup>. The Gibbs-Di Marzio entropy theory brings the glass transition into connection with the second-order thermodynamic transition, whose cause lies in the disappearance of the configurational entropy, and consequently in the loss of the variability of the molecular order<sup>6-9</sup>. Each of both views leads to a correlation of the glass transition parameters with another group of properties of the compounds involved.

This paper is dealing with the effect caused by the addition of various chlorinated alkanes, that is, compounds resembling the polymer as much as possible, upon the

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glass transition temperature of poly(vinyl chloride). Attempts are made to correlate the experimentally determined plastifying activity with other properties of the compounds under investigation, so that it would be possible to decide which of the two theories mentioned above explains the nature of the glass transition with more adequacy.

### THEORETICAL

On the assumption that the glass transition takes place when the free volume decreases to its critical value and that the contributions of the individual components of the mixture to the free volume are additive, Kelley and Bueche<sup>10</sup> derived the equation

$$T = (\varphi_1 \Delta\alpha_1 T_1 + \varphi_2 \Delta\alpha_2 T_2) / (\varphi_1 \Delta\alpha_1 + \varphi_2 \Delta\alpha_2), \quad (1)$$

where  $T$ ,  $T_1$  and  $T_2$  are the glass transition temperatures of the mixture, softening agent and polymer respectively,  $\Delta\alpha_1$  and  $\Delta\alpha_2$  are differences between the thermal expansion coefficients in the liquid and in the glassy state respectively, and  $\varphi_1$  and  $\varphi_2$  are the respective volume fractions of the softening agent and polymer. If the glass transition temperature is measured over the usual concentration range of the softening agent (from zero to several tens per cent),  $T_1$  and  $\Delta\alpha_1$  have the character of mere adjustable parameters. Although  $T_1$  and  $\Delta\alpha_2/\Delta\alpha_1$  can be determined from a linearized plot, it is nevertheless better to prefer a one-parameter equation in the case of data with a major scatter. Such equation is represented by Fox's expression<sup>11</sup>

$$1/T = (w_1/T_1) + (w_2/T_2), \quad (2)$$

$w_1$ ,  $w_2$  being the weight fractions. As far as we know, this equation has not been derived in the literature. We shall therefore demonstrate how this equation can be obtained by using relationship (1). According to Simha and Boyer<sup>3</sup>, the product  $\Delta\alpha \cdot T$  for a polymer is about 1.25 to 1.35 times higher than that for a low-molecular weight liquid; the ratio of the density of the polymer  $\rho_2$  and of a similar monomeric compound  $\rho_1$  varies roughly within the same limits. We can therefore write an approximate relationship

$$\Delta\alpha_1 T_1 / \rho_1 = \Delta\alpha_2 T_2 / \rho_2, \quad (3)$$

which after substitution into (1) and rearrangement gives Eq. (2).

To discuss the plastifying activity from the viewpoint of the free-volume theory we regard as a suitable reference quantity either the characteristic temperature of the diluent  $T_1$  or the slope  $k = d(1/T)/dw_1$  given by

$$k = (1/T_1) - (1/T_2). \quad (4)$$

This derivative, in contrast with that obtained by differentiation with respect to the volume fraction  $\varphi_1$ , is not a function of the ratio  $\Delta\alpha_2/\Delta\alpha_1$ , if Eq. (3) is satisfied.

## EXPERIMENTAL

### Materials and Sample Preparation

Poly(vinyl chloride) — commercial, suspension type,  $\bar{M}_n = 34000$ ; fractions soluble in cold benzene  $\bar{M}_n = 8900$ . Chlorinated hydrocarbons were the same as in ref.<sup>12</sup>; of these, 2-chloro-2-methylbutane could not be employed, since it decomposed even at room temperature when brought into contact with the aluminium pan.

About 10 mg of a vacuum-dried polymer was pressed into a pellet and weighed in volatile sample pans of a DSC-1 calorimeter. The low-molecular weight component was added from a 10  $\mu$ l syringe and weighed after the pan was sealed. The samples were homogenized by a long-term heating above the glass-transition temperature (20–40 h to 70°C).

### Calorimetry

Heat capacity measurements were used in the glass transition determinations. The temperature of the point of intersection of the linear parts of the curve representing the course of heat capacity before and during the glass transition was taken as  $T_g$ . A Perkin-Elmer (USA) DSC-1 calorimeter used in the measurements yields a signal proportional to the heat capacity of the sample. The rate of increase in temperature used here (8°C/min) was the lowest admissible with respect to the sensitivity of the apparatus and to the weighed amount.  $T_g$  determined for check-up at a rate of temperature increase 16°C/min coincided within the limits of experimental error with  $T_g$  determined at a temperature increase 8°C/min. The samples were measured within a temperature range from 40°C below and 20°C above the glass transition. Owing to the dependence of the heat capacity of the polymer on the thermal history<sup>13</sup>, the sample was cooled each time at a rate 8°C/min. The reproducibility of the determination of  $T_g$  was about  $\pm 1^\circ\text{C}$ .

The density  $\rho$ , thermal expansion coefficient  $\alpha$ , boiling point  $T_b$  and heat of evaporation  $\Delta H_v$  were determined by a procedure described elsewhere<sup>12</sup>.

## RESULTS AND DISCUSSION

The results of measurements of the glass transition temperature of the original sample in the presence of diluents are given in Fig. 1. The measurement performed with the benzene-soluble fraction gave a similar dependence, but shifted to lower temperatures by several degrees; for instance, the glass transition temperature of the original sample in the dry state was  $T_2 = 80^\circ\text{C}$ , while for the soluble fraction we found  $T_2 = 71^\circ\text{C}$ .

The data were linearized by using Fox's Eq. (2); the plots of  $1/T$  against  $w_1$  were straight lines in all cases. The intercept on the  $y$ -axis corresponds to  $1/T_2$ . The slopes  $k$  and the values of  $T_1$  calculated from the slopes according to (4) are given in Table I for all systems investigated here; the initial slopes  $k'$  of the dependence of  $(1/T)$  on the mole fraction of the diluent ( $x_1$ ) have also been added:

$$k' = \lim_{x_1 \rightarrow 0} [\partial(1/T)/\partial x_1] = kM_1/M_2, \quad (5)$$

$M_1$ ,  $M_2$  are molecular weights; one mol of the monomer units is regarded as one mol of component 2.

Fox's equation can certainly be looked upon as an empirical relationship too, advantageous owing to its simplicity, whose parameter  $T_1$  can be taken as the starting point for a discussion which is also based on some theories other than that from which it has been determined. We believe that the applicability of the particular correlation equation (with adjustable parameters) for the experimental dependence of  $T_g$  on the diluent concentration cannot be considered an ar-

FIG. 1  
Glass Transition Temperature of the Original Poly(vinyl chloride) Sample Depending on the Weight Fraction of the Diluent

Curves: *a* 1-chloropentane ●, *b* 3-chloropentane ●, *c* 1,3-dichlorobutane ○, *d* 1,4-dichlorobutane ⊕, *e* 2,4-dichloropentane ⊗.

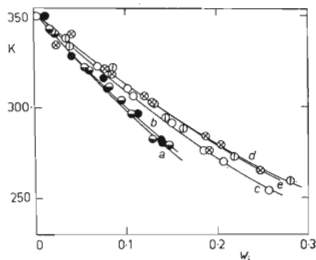


TABLE I

Parameters of the Plastifying Activity of 1-Chloropentane (*I*), 3-Chloropentane (*II*), 1,3-Dichlorobutane (*III*), 1,4-Dichlorobutane (*IV*), and 2,4-Dichloropentane (*V*) used as Diluents of Poly(vinyl chloride)

The first value of each parameter belongs to the original polymer, the second one to the benzene-soluble fraction of it.

Compounds	$T_1$ , K	$k \cdot 10^3$ , $K^{-1}$	$k' \cdot 10^3$ , $K^{-1}$
<i>I</i>	$126.1 \pm 0.5$	$5.09 \pm 0.03$	8.68
	$126.7 \pm 0.1$	$4.95 \pm 0.03$	8.44
<i>II</i>	$127.1 \pm 0.5$	$5.03 \pm 0.03$	8.58
	$129.4 \pm 0.5$	$4.82 \pm 0.03$	8.22
<i>III</i>	$142.7 \pm 0.5$	$4.17 \pm 0.03$	8.47
	$142.8 \pm 1.0$	$4.09 \pm 0.05$	8.31
<i>IV</i>	$151.8 \pm 0.6$	$3.75 \pm 0.03$	7.62
	$149.4 \pm 0.3$	$3.79 \pm 0.02$	7.70
<i>V</i>	$150.9 \pm 0.8$	$3.79 \pm 0.03$	8.55
	$150.0 \pm 0.8$	$3.75 \pm 0.04$	8.46

gument in favour of the original theory, since in the case of such a complex phenomenon the mathematical models leading from conception to equations may be very imperfect. It seems suitable to compare the effectivity of the individual diluents in connection with their physical properties and molecular structure.

If the plastifying activity of a compound is determined by its portion of the free volume, it should be possible to correlate the characteristic temperatures  $T_1$  with the quantities defining the portion of the free volume. If the theorem of the corresponding states is valid<sup>4</sup>, this portion is an unambiguous function of the reduced temperature  $\tilde{T}$  given by

$$\tilde{T} = ckT/q\epsilon^*, \quad (6)$$

where  $3c$  is the number of the external degrees of freedom of the thermal motion (*i.e.* such whose parameters are controlled by physical forces and not by chemical valences),  $k$  is Boltzmann's constant and the product  $q\epsilon^*$  is a measure of the intermolecular cohesion energy related to one mol. On the same assumptions, the product of the volume expansion and temperature is also an unambiguous function of  $\tilde{T}$ ; consequently, the thermal expansion coefficients of different compounds, if compared

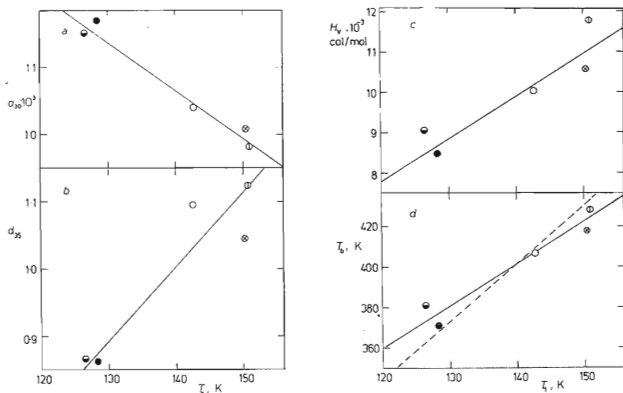


FIG. 2

Correlation of the Characteristic Temperature of the Diluent  $T_1$  with Its (a) Thermal Expansion Coefficient at 30°C, (b) Density at 35°C, (c) Heat of Evaporation at 35°C, (d) Normal Boiling Point (— — straight line  $T_b = a_1 T_1$ )

The  $T_1$  values represent the arithmetic mean value for both polymer samples. Assignment of points to the individual compounds — *cf.* legend to Fig. 1.

at the same temperature, should give an unambiguous correlation with the parameter  $T_1$ . On the other hand, the law of the corresponding states does not predict an unambiguous relationship between  $T_1$  and the density  $\rho$ , the heat of evaporation  $\Delta H_v$  and the cohesion energy density  $C_E$ , because these quantities are rather complex functions of the molecular parameters:

$$\rho = (M/rv^*) f_1(\tilde{T}), \quad \Delta H_v = qe^* f_2(\tilde{T}) + RT \quad (7, 8)$$

$$C_E = (qe^*rv^*) f_3(\tilde{T}) \quad (9)$$

the product  $rv^*$  characterizes the so-called hard core volume, *i.e.* the (molar) volume at  $T = 0$ .

It can be seen from Figs 2a–2c that the  $T_1$  values depart less from a linear dependence found by us in the case of  $\alpha$ , than in the case of density and the heat of evaporation. A plot of the cohesion energy density against  $T_1$ , not given here, leads to a distribution of points similar to the heat of evaporation, but their scatter is even larger. Our results suggest that different diluents are in the corresponding state at temperatures  $T_1$ . Since the normal boiling point  $T_b$  is also sometimes regarded as a corresponding state, there is a possibility of a correlation between  $T_1$  and  $T_b$ ; as can be seen in Fig. 2d, our data really fit well the relationship  $T_b = a_0 + a_1 T_1$ . Had the law of the corresponding states to hold rigorously, there should exist a direct proportionality between both temperature parameters, *i.e.*  $a_0 = 0$ ; a straight line which would fulfil this condition is represented in Fig. 2d by a broken line.

According to Gibbs-Di Marzio's theory<sup>9</sup>, the main factor determining  $k$  or  $T_1$  is the contribution of the diluent to the configurational entropy. This contribution consists of the translational, rotational and internal rotational motion. The number of the degrees of freedom of the former two types is proportional to the number of the molecules, and the contribution of a weight unit of the diluent to the translational and rotational entropy decreases with the molecular weight. The decrease of  $k$  with increasing molecular weight (*cf.* Table I) gives evidence that this is really so; a similar effect is of course predicted also by the free volume theory. It will therefore be of interest to evaluate the effect of the internal rotation after elimination of the two effects mentioned above. For this purpose, not  $k$  but  $k'$  given by Eq. (5) should be compared. The factor which determines the magnitude of  $k'$  should be represented by the number of stable conformers (or more exactly, the sum of Boltzmann's factors pertinent to all imaginable conformers). If it is borne in mind that the chlorine substituent at the unbranched end of the chain raises the number of stable conformers in a molecule, while the effect on the carbon atom inside the chain is an opposite one, it is evident that  $k'$  for 3-chloropentane ought to be considerably lower than for 1-chloropentane, and ought to increase for dichloro derivatives in the series 2,4-dichloropentane, 1,3-dichlorobutane, 1,4-dichlorobutane. Table I clearly

shows that this is not the case. It is not excluded, however, that the difference in the conformational entropy could serve as an explanation for the deviations of the individual points from the straight line in Figs 2a–2d.

The facts described here indicated that the effect of chlorinated alkanes used as softeners of poly(vinyl chloride) can be described on the basis of the free volume theory. For a rough empirical estimate, it can be of a certain importance that the value  $k'$  expressed in terms of the mol number is the same with the exception of one compound.

How delusive is the prospect of a generalization of these conclusions for other polymers will be evident from a forthcoming paper.

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