ON THE STRUCTURE AND PROPERTIES OF VINYL POLYMERS AND THEIR MODELS. XV.*

GLASS TRANSITION TEMPERATURES IN THE SYSTEM POLYSTYRENE–DILUENT**

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The plastifying activity of diluents in polystyrene was determined. Monomeric diluents (*i.e.* benzene, its alkyl derivatives and cyclohexane) and dimers, *i.e.* biphenyl, dibenzyl, 2,2'- and 3,3'-ditolyl, *trans*-stilbene, 1,3-diphenylbutane, 2,4-diphenylpentane and dicyclohexyl were used in the measurements. No connection with the properties defining the free volume was found, but a distinct effect of the number of stable conformers on the plastifying activity was observed. These findings indicate that the decisive role in the softening of polystyrene is played by the conformational entropy according to Gibbs–DiMarzio's conception.

The preceding paper reported the dependence of the glass transition temperature of poly(vinyl chloride) on the concentration of diluents (low-molecular weight polymer models), from which it follows that the position of the glass transition in the systems under investigation is determined by the magnitude of the free volume. In order to elucidate whether we have here a phenomenon characteristic also of other polymers, we investigated polystyrene and used both monomeric and dimeric models as diluents, *i.e.* compounds containing one or two six-membered rings per molecule.

EXPERIMENTAL

Materials. Polystyrene, by radical polymerization, fraction with $\overline{M}_n$ 130 000. Benzene, anal. purity grade, and toluene, chemically pure (Lachema, Brno), were purified by a standard procedure[1] and distilled with sodium on a packed column (40 TP). Ethylbenzene and isopropylbenzene, chemically pure (Lachema, Brno), were purified by refluxing with Raney nickel for 10 h, then distilled with sodium on a column. Cyclohexane, spectral purity grade, was distilled with sodium on a column. Biphenyl, zone melted (Lachema, Brno), was used without further purification, similarly to *trans*-stilbene (*puriss.*, Fluka). Dibenzyl (pract., Fluka) was vacuum redistilled on a column. The middle fraction was collected. Tert-butylbenzene, 1,3-diphenylbutane, 2,4-di-

Table I

Physical Constants of the Compounds

I Benzene, II toluene, III ethylbenzene, IV isopropylbenzene, V tert-butylbenzene, VI cyclohexane, VII biphenyl, VIII dibenzyl, IX trans-stilbene, X 3,3'-ditolyl, XI 2,2'-ditolyl, XII 1,3-diphenylbutane, XIII 2,4-diphenylpentane, XIV dicyclohexyl.

Compound	Purity %	ϱ^{25}		n_D^{25}		M.p. °C		B.p. °C	
		measured	lit[a]	measured	lit[a]	measured	lit[a]	measured	lit[a]
I	99·85	0·87362	0·87368[7]	—	1·49790[7]	—	5·50[8]	80·0	80·08[8]
II	99·54	0·86226	0·86226[7]	1·4940	1·49405[7]	—	−95·01[8]	110·5	110·623[7]
III	99·92	0·86261	0·86264[20]	1·4930	1·49320[20]	—	−94·95[9]	136·3	136·25[8]
IV	99·55	—	0·85748[7]	1·4882	1·48874[7]	—	−96·02[8]	152·1	152·39[7]
V	99·75	—	0·86240[10]	1·4906	1·49024[10]	—	−58·09[10]	—	169·12[10]
VI	99·85	0·77410	0·77389[7]	1·4237	1·42354[7]	—	6·554[9]	80·7	80·738[7]
VII	99·99	—	1·1750[11]	—	1·5870[11]	69·0	68·95[12]	256	256·1[13]
VIII	99·90	—	—	—	—	51·0	51·16[3]	288	280·5[3,b]
IX	—	0·99423	0·9989[14,c]	1·5919	1·5930[14]	124·0	124·2[11]	314	—
X	99·92	0·98853	0·98698[16]	1·5721	1·5720[17]	—	5–7[15]	289	286[15,d]
XI	99·31	0·96687	0·96982[3,e]	1·5524[e]	1·5323[3,e]	—	18·3[17]	260	258[15]
XII	99·90	0·99794	—	1·5524[e]? 1·5420	1·5464[4,e]	—	—	—	291[18], 302·5[3]
XIII	96·00	—	—	1·5420	—	—	−42[4]	—	152–4[4,f]
XIV	99·89	0·88257	0·88249[12]	1·4768	1·47768[12]	4	3·63[12]	241	239·04[12]

[a] References given as superscripts; [b] with decomposition; [c] 16°C; [d] 716 Torr; [e] 20°C; [f] 10 Torr.

phenylpentane, 2,2'- and 3,3'-ditolyl and dicyclohexyl were synthesized[2-5]. The physical constants of the compounds used are given in Table I along with the literary data.

Procedure. The glass transition temperature was determined from the thermal dependence of the heat capacity, recorded with a Perkin-Elmer, USA, DSC-1 microcalorimeter, using a procedure described earlier[6]. The solutions were homogenized by heating to 110°C for several days in volatile sample pans. The densities ϱ and thermal expansion coefficients α were determined at 25, 35, and 45°C in 15 ml two-capillary pycnometers, with a reproducibility better than $3 \cdot 10^{-5}$. The heats of melting ΔH_m were determined with a Perkin-Elmer DSC-1 calorimeter after calibration to the heat of melting of indium with an error of c. 2%. The heats of evaporation ΔH_v of low-molecular weight solvents were determined from the temperature dependence of the vapour pressure after Polák[19]. ΔH_v of dimers were determined by a direct calorimetric measurement[20]. The boiling points of the monomers were calculated from Antoine's equation; the boiling points of the dimers were determined with an accuracy of ±2°C by using a DSC-1 calorimeter.

RESULTS AND DISCUSSION

The dependences of the glass transition temperature on the weight fraction of the diluent were qualitatively similar to those obtained for poly(vinyl chloride)[6]. Linearization according to Fox's equation was carried out again; the characteristic temperatures T_1 and slopes k and k' thus obtained (Eqs (2), (4), and (5) from the preceding paper) are given in Table II. It is interesting to compare our values of T_1 with the glass transition temperatures of monomeric liquids determined viscometrically by Carpenter and coworkers[24] (for toluene T_g 113 K, for ethylbenzene 111 K, for isopropylbenzene 125 K and for tert-butylbenzene 142 K). The order of compounds according to increasing T_g is the same as according to T_1, and the average difference $T_1 - T_g$ is comparatively small (20 K), bearing in mind that our measurements were made in the range from $w_1 = 0$ to $w_1 = 0.25-0.40$, and that T_g of dry polystyrene (our value 376 K) lies by more than 250 K further. (We do not attempt to compare our results with those by Jenckel and Heusch[25] with benzene and toluene as diluents; T_g 85·5°C measured by them for dry polystyrene arouse suspicion that their polymer was not free from the monomer).

At the beginning of the discussion it should be noted that the diluents investigated here differ more from each other by their composition and topology of their molecules than it was the case with the small and comparatively homogeneous group of the chlorinated derivatives investigated in the preceding paper[6]. It would therefore be extremely optimistic to expect that the whole assembly will give a simple and unambiguous correlation of T_1 with some physical property. However, a comparison can be made within rather narrow groups of greatly similar compounds.

If we attempt to compare monomeric liquids, we can see that in the benzene — toluene — ethylbenzene series the thermal expansion coefficients α at 30°C decrease; the same holds for the heat of evaporation, if it is related to one gram or 1 cm³. The free volume theory suggests that the plastifying activity should decrease too, but what happens is just the opposite. If we notice other values of T_g found by Carpenter and coworkers[24] (propylbenzene 122 K, butylbenzene 125 K, sec-butylbenzene 127 K, pentylbenzene 128 K), we shall obtain a similar picture: although T_g increases with increasing number of aliphatic carbon atoms, the increase is much slower than would correspond to the increase in molecular weight and to the loss

in the translational and rotational entropy per mass unit connected therewith. Obviously, the increasing number of possible rotational conformers plays its role here; this is also indicated by the fact that the compounds with branched substituents have a somewhat higher T_g than the corresponding n-alkylbenzenes. Therefore, all the data of this group of compounds satisfy Gibbs–DiMarzio's conception (for the pair benzene–toluene, the different molecular symmetry reflected in differences in the rotational entropy should be borne in mind). A special discussion is due to tert-butyl-benzene: The high degree of symmetry of the substituent has as the consequence that the energy hindrances to its rotation around the bond to the benzene ring are probably very small[26]; however, this free rotation does not contribute to the conformational entropy, since owing to the almost spherical shape of the group the motion does not raise the number of possibilities for an arrangement of the polymer segments in the closest surroundings of the molecule. The behaviour rather reminds us of biphenyl than of alkylbenzenes, and the molar plastifying activities of tert-butylbenzene

TABLE II

Plastifying Activity, Thermal Expansion Coefficients and Heats of Phase Transformations of the Compounds

Compounds *I—XIV* cf. Table I.

Compound	T_1 K	$k \cdot 10^3$ K^{-1}	$k' \cdot 10^3$ K^{-1}	$\alpha_{30} \cdot 10^3$	ΔH_v, 25°C cal/mol	ΔH_m cal/mol
I	145.8 ± 1.8	4.20 ± 0.07	3·150	1.223^{21}	$8\ 090^{22}$	—
II	137.5 ± 1.0	4.61 ± 0.05	4·079	1.082^a	$9\ 079^{23}$	—
III	134.6 ± 0.8	4.77 ± 0.03	4·863	1.0298^{22}	$10\ 190^{22}$	—
IV	140.0 ± 0.3	4.48 ± 0.005	5·171	—	—	—
V	157.5 ± 0.5	3.70 ± 0.006	4·769	—	—	—
VI	158.5 ± 1.0	3.65 ± 0.03	2·950	1.242^a	$7\ 895^{23}$	—
VII	170.2 ± 2.5	3.22 ± 0.07	4·768	—	$15\ 670^{20}$	$4\ 510^a$ $4\ 450^{11}$
VIII	147.6 ± 0.8	4.11 ± 0.03	7·193	—	$15\ 670^{20}$	$5\ 480^a$ $1\ 300^3$ $5\ 590^{11}$
IX	193.2 ± 1.5	2.51 ± 0.02	4·344	—	—	$6\ 760^a$
X	168.0 ± 3.5	3.28 ± 0.13	5·741	0.738^a	$17\ 370^{20}$	—
XI	177.5 ± 1.5	2.98 ± 0.11	5·216	0.806^a	$16\ 120^{20}$	$3\ 850^a$
XII	170.2 ± 0.8	3.21 ± 0.02	6·482	0.769^a 0.768^{22}	$18\ 230^{20}$	—
XIII	184.0 ± 1.5	2.77 ± 0.02	5·967	0.740^a	—	—
XIV	175.5 ± 2.0	3.045 ± 0.05	4·862	0.810^a	$14\ 470^{20}$	$3\ 680^a$

[a] Our measurement.

and biphenyl are indeed the same. Our results agree well also with the results ensuing from Table II in a survey by Shen and Eisenberg[27] where T_g are summarized for dry polymers whose side groups end with butyl groups: the glass transition temperature increases if we pass from the n-butyl group *via* the sec-butyl group to the tert-butyl group. The high T_1 found for cyclohexane seems so far unexplainable.

It is interesting, for dimeric diluents, to compare three pairs of similar compounds: *1)* Of the dimers investigated, dibenzyl has the lowest and stilbene has the highest T_1. The primary cause of such diametrical difference certainly consists in the double bond of the stilbene molecule; however, this bond can act as a factor which reduces not only the number of the possible conformers, but also the free volume, as is indicated by a higher boiling point of stilbene. *2)* Also the higher plastifying effect of 1,3-di-phenylbutane compared to 2,4-diphenylpentane can be assigned both to a higher number of conformers and to a larger free volume of the former compound (*cf.* thermal expansions). *3)* A comparison of thermal expansions, boiling points and heats of evaporation of both ditolyls investigated leads to a conclusion that a higher T_1 should be expected for the 3,3′-isomer; the actual finding is however quite opposite, and can be explained by the loss of the possibility of the internal rotation due to the substitution at positions 2,2′. We can see that also the results obtained with the dimers rather suggest an effect of the conformational entropy than the free volume effect. If, however, an attempt is made to compare compounds whose molecular structures
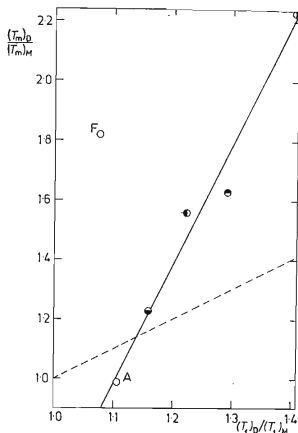

FIG. 1

Ratio of Melting Temperatures of Dimers $(T_m)_M$ and Monomers $(T_m)_D$ Depending on the Ratio of the Glass Transition Temperatures $(T_1)_D/(T_1)_M$

○ Dicyclohexyl/cyclohexane, ◔ biphenyl/benzene, ◑ 2,2′-ditolyl/toluene, ◐ 3,3′-dito-lyl/toluene, ◖ *trans*-stilbene/toluene, ⊗ di-benzyl/toluene. Broken line corresponds to the law of the corresponding states being rigorously valid.

are slightly more different, no reasonable relationship with either of both theories can be arrived at. For example, it is very difficult to comprehend the exceptionally high plastifying activity of dibenzyl, if *e.g.* 1,3-diphenylbutane has substantially more stable conformers. Obviously some other factors are involved here; one of them can be an interaction of the diluent with the polymer.

Since attempts to correlate quantitatively the plastifying activity of the whole assembly of dimers with other physical properties did not lead to the goal, we tried to relate the properties of the dimers (D) to those of the corresponding monomers (M). A certain success was achieved in the case of the ratio of the melting temperatures $(T_m)_D : (T_m)_M$ plotted in Fig. 1 against the ratio $(T_1)_D : (T_1)_M$. We can see that of the six pairs under consideration, only the dibenzyl–toluene pair escapes correlation. Of course, dibenzyl differs from the other five dimers by the flexibility of the groups incorporated between both rings. The position of the melting points is determined, on the one hand, by the energy consumed for the formation of the free volume during melting, and on the other, by the number of the degrees of freedom of thermal motion released by melting. Since our conclusions do not show the effect of the free volume as a decisive one for plastification, the successful correlation in Fig. 1 is an indirect confirmation of the effect of the conformational entropy.

Our results obtained with polystyrene systems bear out other theoretical views than do our data on poly(vinyl chloride). However, Gibbs–DiMarzio's theory and the free-volume conception are not set irreconcilably against each other. Adam and Gibbs[28] have shown that thermodynamic views of the configurational entropy allow to arrive at the same conclusion about the dependence of viscosity on temperature in the vicinity of T_g as the kinetic conception of the role played by the free volume. We should like to stress that Gibbs–DiMarzio's theory admits a dependence of the configurational entropy not only on the conformational variability of the molecule, but also on the number of holes, and thus also on the free volume. It is true that calculation based on this theory leads to a conclusion that the latter of both effects plays a very insignificant role, but this can be due to the imperfection of the lattice model used. On the other hand, the free volume theories (Cohen and Turnbull[29,30]) are imperfect in that they take the frequency of the elementary jumps depending only on the number (or size distribution) of the holes. For more complex molecules the probability of jumps will certainly also depend on the energy difference of the conformers before and after the jump, as well as on the cooperativity of the jump. The glass transition is apparently a result of rather a great number of effects, each of which plays its part in different systems to a different extent. This finding has been adequately expressed by Shen and Eisenberg[27] who characterize the glass-transition as a "many-faced" one; in connection with the investigation of this phenomenon they recall the story about three blind men, each of whom assigned to the elephant a different simple geometrical shape according to what part of elephant's body he was feeling about.

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