THERMODYNAMIC DATA ON TRANSTACTIC POLYBUTADIENE

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THE peculiar properties of the transtactic polymer of 1,3-butadiene, which had been synthesised with a very high steric purity (> 99 per cent) for the first time at this Institute in 1955,(1) as well as the properties of its copolymers with 1-methylbutadiene, which also shows a prevailingly trans-1,4 structure, led us to study the thermodynamic properties connected with its first order transitions.

As already described in previous papers of ours, transtactic polybutadiene shows a high melting temperature (145°C) and another first order transition at 76°C. The X-ray analysis on oriented fibres enabled us to establish that the crystals of modification I, which is stable at low temperature and has an identity period of 4.85 Å, are transformed into modification II, which has a different crystalline structure, and is stable at higher temperature, while their orientation is not modified. This transformation is accompanied by a contraction of the identity period along the **c** axis to 4.65 Å, with a simultaneous expansion of the equatorial dimensions, which causes a decrease of the crystal density.

Fig. 1 shows the chain conformation of polybutadiene (modification I), characterised by a regular succession (+120–120) of the internal rotation angles between the carbon atoms adjacent to the double bond. Modification II shows a main chain structure more disordered than that of modification I; this is probably due to a random distribution of the internal rotation angles (+120–120) of the main chain.

The chains of modification II have a larger equatorial bulkiness and are packed into crystals according to a hexagonal or pseudo-hexagonal arrangement. By the equatorial reflections observed, the distance between the chain axes is 4.95 Å; this, in spite of the contraction of the identity period, causes an increased volume by about 10 per cent with respect to modification I.

It has been impossible so far to determine the complete crystalline structure of modification II, due to the fact that crystals do not show a perfect three-dimensional order owing to the disordered structure of the main chain. Therefore the type of irregularity of the crystals is quite different from that observed, for instance, in the smectic modifications of certain polymers (e.g. polypropylene). In fact in the smectic modification each chain maintains its regular structure while the order of packing is lacking; on the contrary, modification II of transtactic polybutadiene shows a certain disorder in the main chain conformation of the macromolecules.

Thus an oriented fibre of modification I tends to shrink when heated above the transition temperature, with production of mechanical work, if some contrast to the shrinkage occurs. The variation of the transformation temperature vs. the mechanical stresses which the crystals are subjected to, will be determined by us in another paper, in spite of the difficulties met when trying to perform accurate measurements: they are caused by viscous flows that can hinder the obtainment of completely repetitive cycles.

In this paper we shall be concerned with the determination of the thermodynamic properties connected with the phase transformations in the absence of mechanical stresses.

The thermodynamic properties of transtatic polybutadiene were studied a few years ago by Mandelkern and coworkers.(2) They employed samples polymerised in emulsion and considered them as copolymers of trans-1,4 units forming the crystal lattice, with cis-1,4 and 1,2 units acting as impurities. Since these authors did not have a pure transtactic polymer at their disposal, interpretation of the melting temperature data in terms of enthalpy of fusion could not be definite. In fact, owing to experimental difficulties, the determination of the melting temperature of copolymers, and therefore of the melting enthalpy by copolymeric samples of various compositions, is markedly inaccurate.(3) Moreover doubts can exist about the distribution of steric impurities along the polymeric chain.

The progress attained in the stereospecific polymerisation during these last years has allowed the preparation of particularly high-steric-purity transtactic polybutadiene(4); thus it

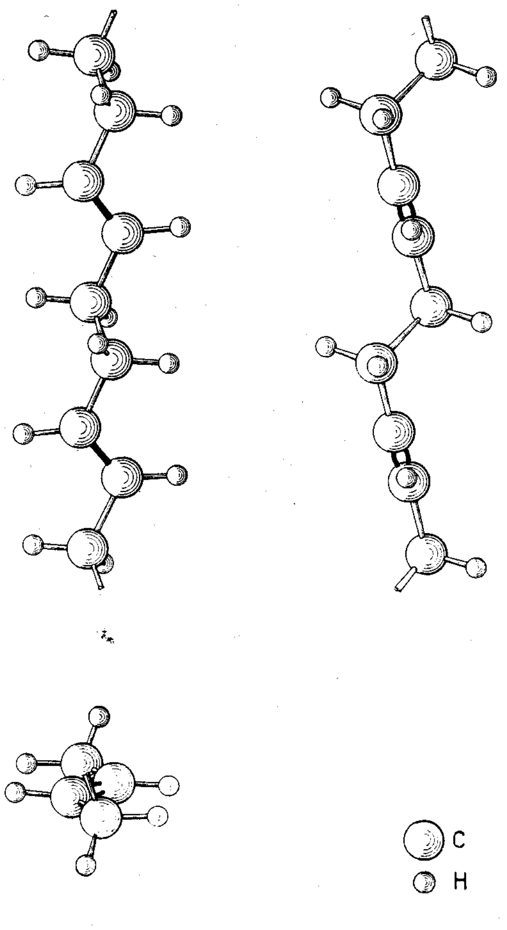

Fig. 1. left: Conformation of the chain modification I of transtactic polybutadiene

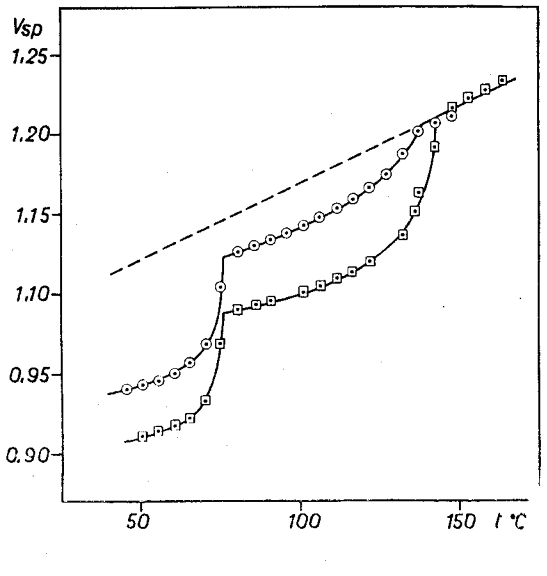

Fig. 2. right: Specific volume-temperature curves for two transtactic polybutadiene samples of different steric order (curves are not at equilibrium)

TABLE I

Melting temperature T_m (in °K) of transtactic polybutadiene mixtures with diluents at various fractions in volume (B mixtures in benzophenone; C=mixtures in α-chloronaphthalene)

Mixture	T_m	v_1
(a) polybutadiene-modification II		
B_1	$402{\cdot}_5$	0·100
B_2	$399{\cdot}_5$	0·155
B_3	395	0·204
B_4	395	0·220
B_5	$388{\cdot}_5$	0·307
B_6	383	0·410
B_7	$377{\cdot}_5$	0·508
B_8	380	0·513
B_9	$376{\cdot}_5$	0·611
C_1	369	0·391
C_2	$361{\cdot}_5$	0·489
C_3	354	0·589
pure polymer	414	0
(b) Polybutadiene-modification I		
C_4	346	0·853
C_5	$343{\cdot}_5$	0·898

was possible to determine the thermodynamic properties of the polymer with greater accuracy.

Fig. 2 shows the dilatometric properties of transtactic polybutadiene. The curves concern two polybutadienès with a different degree of steric order: beside the solid-liquid transition temperature, which for high-steric-purity samples attains 145°C., a transition exists at 76°C., which, as previously mentioned, by X-ray analysis and IR spectrography proves to be of the solid-solid type.(4,5)

The enthalpy of fusion of the crystalline modification stable above 76°C. was measured by the dilatometric technique.

For this purpose mixtures were prepared by using a finely-powdered polybutadiene as polymeric sample, and controlled amounts of diluents, benzophenone and α-chloronaphthalene, in glass vials: these mixtures were firstly placed under vacuum and kept in a -60° ÷ -70°C. bath ; then they were sealed and kept at 150°C. for several hours. The mixtures thus obtained were then put in mercury dilatometers and placed in a thermostatic bath, whose temperature was increased by 2.5°C. every 25 minutes. This high heating rate could lead to some inaccuracy in the final value of enthalpy, but made it possible for the polymer to avoid prolonged thermal treatments, which could essentially modify its structure.

The experimental results obtained are summarised in Table Ia.

Fig. 3 describes the same results plotted on the basis of the formula(6) :

$$\frac{1}{v_1}\left[\frac{1}{T_m}-\frac{1}{T_m^o}\right]=\frac{R}{\Delta H_u}\,\frac{V_u}{V_1}\left[1-\chi_1 T_m\frac{v_1}{T_m}\right] \qquad [1]$$

The densities of the diluents at various temperatures were determined for the calculation of V_1 and v_1 ; V_u was obtained by extrapolating the specific volumes of the pure molten polymer as shown in Fig. 2.

Table II and Fig. 3 summarise the final results.

The experimental dilatometric curves also show that the transition temperature of 76°C. of the pure polymer remains unaltered when varying the percentage of the diluents, as would obviously be expected from a transition of the solid-solid type.

The dilatometric method was also employed for the determination of both enthalpy and temperature of melting of the modification stable at room temperature, of transtactic polybutadiene.

Two mixtures of polybutadiene with α-chloronaphthalene were prepared for this purpose. Their percentages of diluent were high enough to enable the melting temperature to be lower than transition temperature: under these conditions the transition was relative to the modification I-liquid. The data concerning two of these mixtures are reported in Table Ib.

The decrease of melting temperature, due to the presence of α-chloronaphthalene of modification I is expressed by a relationship of the type [1] in which the term $\chi_1 T_m$, concerning the interaction transtactic polybutadiene-α--chloronaphthalene is known from Table II, while the ΔH_u and T^o_m parameters are unknown.

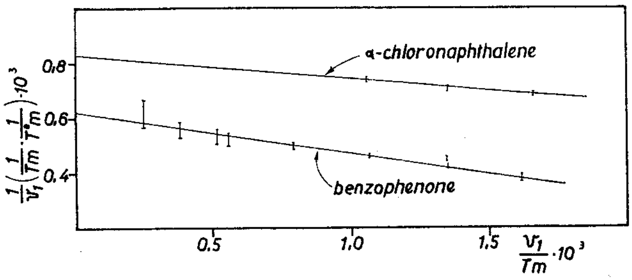

Fig. 3. Plotting according to (I) concerning the modification II in diluents: benzophenone and α-chloronaphthalene

TABLE II

Final data of enthalpy of fusion and of interaction with diluents of transtactic polybutadiene—modification II (ΔH_u in cal/monomeric unit; $\chi_1 T_m$ in °K)

Diluent	ΔH_u	$\chi_1 T_m$
benzophenone ...	1170	245
α-chloronaphthalene ...	1060	105
	average value 1100	

In addition the chemical potentials of the two crystalline modifications become equal at the solid-solid transition temperature T_t, and they can be still expressed in terms of their respective enthalpies and melting temperatures: thus it is supposed that the values of entropies and enthalpies of fusion of the two modifications keep constant within the limited range of temperatures examined. It is thus possible to evaluate the ΔH_u and T^o_m parameters concerning modification I; their values can be very inaccurate, and therefore are only indicative values.

Calculations lead the average value:

$$\Delta H_u^I = 2{,}400 \pm 1{,}000$$

which is about double that concerning modification II.

The melting temperature ranges from 90° to 130°C.; a higher probability seems to occur at about 100°C.

With regard to the entropies of fusion, modification II has $\Delta S_u = 2.7$ eu/mole ; this value is exceptionally low in comparison with the foreseeable value of about 4.5 ÷ 6. No reason exists why a particular stiffness should be attributed to the molecule of melted transtactic polybutadiene; it follows that a partial disorder of the polybutadiene crystals of modification II must be admitted. This was confirmed by X-rays(7) and I.R. analysis, which reveal that modification II appears in a incompletely ordered state.

The value of ΔS_u, however, is quite normal, if modification I is considered; for this the most probable value is 6.4 eu/mole, indicating that the crystals of transtactic polybutadiene already acquire some entropy from their solid-solid transition.

This fact should generally be important in reasoning about melting conformational entropy, when polymers showing stable polymorphic modifications are considered.

The low enthalpy of fusion of modification II of transtactic polybutadiene helps to explain the considerable decrease of melting temperature of samples having steric impurities in the polymeric chains, contrary to what happens for other linear macromolecules. This property is very important from a practical standpoint, because it allows one to obtain homopolymers and copolymers of butadiene (e.g. with 1-methylbutadiene) that are crystalline, but have a melting temperature lowered by 100°C. or more. Thus they get interesting elastomeric and excellent dynamic properties at room temperature, in spite of their high trans-1,4 unit content.

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