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Sonderdruck aus

DIE MAKROMOLEKULARE CHEMIE

Band 66

1963

Seite 218–221

Kurzmitteilung

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by

G. NATTA and G. MORAGLIO

HÜTHIG & WEPF VERLAG · BASEL

From the Istituto di Chimica Industriale del Politecnico, Milano, and Centro Nazionale
Chimica delle Macromolecole, del C.N.R., Sez. 1, Milano, Italy

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Melting Enthalpy and Entropy of *Cis*tactic Polybutadiene

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(Eingegangen am 16. Mai 1963)

*Cis*tactic polybutadiene (polymer of 1,3-butadiene having 1,4 enchainment and all the monomeric units practically in *cis* configuration), which has lately acquired a considerable importance for its applications as synthetic elastomer, shows remarkable analogies with natural rubber and with the corresponding synthetic *cis*tactic polymer of isoprene.

Therefore, it is justified the ever increasing interest in the knowledge of the properties of *cis*tactic polybutadiene obtained by stereospecific catalyses¹. Now these can yield chemical and steric purities (measured as ratio of the number of *cis*-1,4-monomeric units to the total number of butadiene units) even above 98 %.

This paper describes measurements of the melting enthalpy and entropy performed for this type of polymer by the method of the lowering of melting temperature by diluents; in addition, information are also obtained on the enthalpic interaction parameters between the butadiene units with a *cis* configuration and the diluents used.

The polybutadiene sample employed was obtained by stereospecific polymerization at 0°C. with the aid of the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ and cobalt diacetylacetonate catalyst system, in the presence of a pentane-benzene mixture as solvent²).

Toluene and *n*-heptane were used as diluents: these were pure commercial products, purified, dehydrated and fractionated in a TODD column.

The melting temperatures of both pure polymer and of the mixtures were measured by dilatometric method adopting the equipments similar to those described in another paper³).

The temperature of the thermostatic bath was raised of about 1°C./hr., and the mercury levels of the dilatometers were registered by a cathetometer. This fairly high heating rate derives from the experimental difficulty to make the thermostatic baths operate at low temperatures for very long times. Greater experimental details are given in another paper⁴).

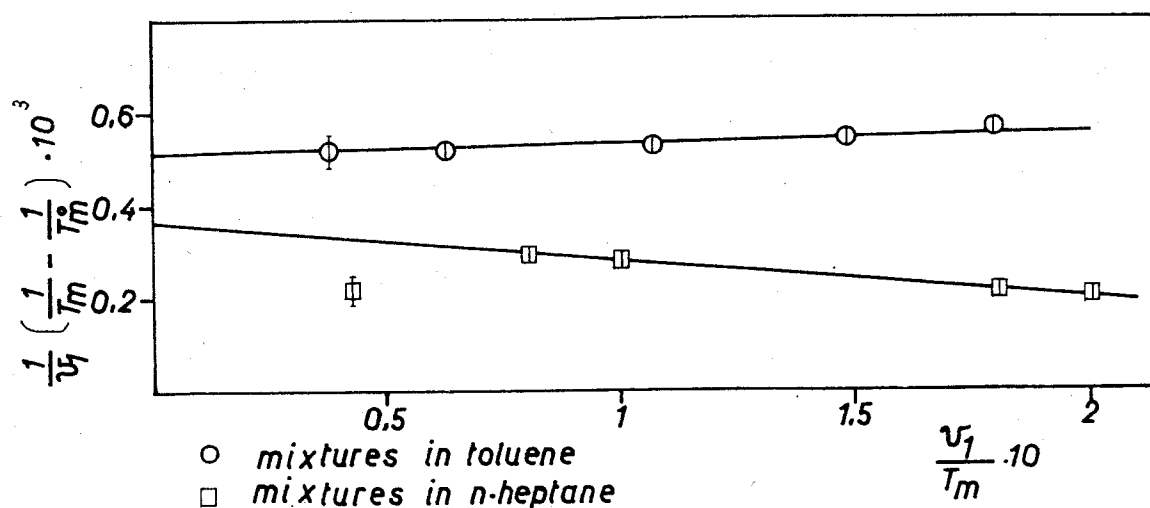
Melting Enthalpy and Entropy of *Cis*tactic Polybutadiene

Table 1. Melting temperature (in °K.) of mixtures of *cis*tactic polybutadiene with diluents at various fractions in volume (T = mixtures in toluene, E = mixtures in *n*-heptane)

Mixture	T _m	v ₁	Mixture	T _m	v ₁
T ₁	268	0.141	E ₁	271	0.158
T ₂	264 _{,5}	0.237	E ₂	267	0.302
T ₃	258	0.415	E ₃	265 _{,5}	0.378
T ₄	251 _{,5}	0.590	E ₄	262 _{,5}	0.689
T ₅	245 _{,5}	0.732	E ₅	262	0.765
polymer alone: T _m ⁰ = 273.5					

Table 1 reports the melting temperatures of various polymer-diluent mixtures and of the pure polymer. These data are plotted in the diagram of the following figure, according to the known FLORY formula⁵⁾:

$$\frac{1}{v_1} \left(\frac{1}{T_m} - \frac{1}{T_m^0} \right) = \frac{R}{\Delta H_u} \cdot \frac{V_u}{V_1} \cdot \left(1 - \chi_1 \cdot T_m \cdot \frac{v_1}{T_m} \right) \quad (1)$$



where ΔH_u is the melting enthalpy of the polymer, V_u and V_1 the molar volumes of the monomeric unit and of the diluent respectively, v_1 is the volume fraction of the solvent and χ_1 an interaction parameter molten polymer/diluent.

From intercepts for $\frac{v_1}{T_m} \rightarrow 0$ it results that ΔH_u is equal to 2,180 for mixtures in toluene and to 2,200 cal./structural unit for those in *n*-heptane. Therefore

$$\Delta H_u = 2,200 \pm 100 \text{ cal./structural unit}$$

and consequently, a variation of entropy of 8 u.e./structural unit on melting can be attributed to *cistactic* polybutadiene.

A certain interest lies on the evaluation of the interaction enthalpic parameter χ_1 of every employed solvent with *cis* butadiene units, as may be calculated from the diagrams of Fig. 1.

The diagram concerning toluene shows that χ_1 is practically nil: this means that the liquid *cistactic* polybutadiene-toluene mixtures are practically athermic. This is quite analogous to what occurs for natural rubber-toluene mixtures, the athermicity of which was demonstrated⁷⁾. The behaviour of the straight line concerning the mixtures with *n*-heptane of Fig. 1 also suggests that χ_1 has, in this case, a positive value; it can be thus concluded that the mixtures of *cistactic* polybutadiene in this solvent are endothermic. This fact is also analogous to the behaviour of natural rubber with respect to the homologous hydrocarbons of *n*-heptane, such as dodecane and tetradecane, for which positive values of χ_1 have been observed⁶⁾.

It is interesting to compare the melting enthalpies and entropies of the tactic polymers of butadiene and of isoprene with 1,4 enchainment (see Table 2).

Table 2. Thermodynamic data concerning the melting of polymers of butadiene and of isoprene with 1,4 enchainment

	T_m (°C.)	ΔH_u (cal.mole ⁻¹)	ΔS_u (cal. degree ⁻¹ mole ⁻¹)	Ref.
<i>cistactic</i> polybutadiene (98,5 ⁰ / ₀)	1	2,200	8	***)
<i>transtactic</i> polybutadiene	{ mod. I*)	100	2,400	8)
	{ mod. II	146	1,100	8)
Natural rubber	28	1,050	3.5	6)
Gutta percha**)	74	3,040	8.8	9)

*) Approximate data.

**) Data referred to the high-melting modification.

***) This paper.

In a previous paper⁸⁾ we had attributed the low melting entropy of *transtactic* polybutadiene, mod. II, to a disorder in the conformations of the chains, due to a statistical distribution of the internal rotation angles: this disorder explains the different value observed for the identity period along the chain axis of modification II with respect to modification I.

Table 2 also shows that ΔS_u of *cis*-1,4 polyisoprene is far lower than of *cistactic* polybutadiene. In this case, the difference cannot be attributed

to irregularity of the type observed for modification I of *trans*tactic polybutadiene; but we think that it should be attributed, at least in part, to a particular type of disorder of packing of the chains. This had already been observed by NYBURG¹⁰⁾, in the study of the crystalline structure of natural rubber, and interpreted by him as a disordered succession of chains having a different relative orientation of the methyl groups.

On the contrary, the study done by one of us on the structure of *cis*-tactic polybutadiene¹¹⁾ revealed a regular packing of the chains in the crystals, even if the type of lattice is analogous to that of *cis*-1,4 polyisoprene. The structure of this last polymer was also discussed in that paper, where it was also observed that the experimental X-ray diffraction intensities might be attributed to a particular disorder due to the statistical distribution of two types of layers of molecular thickness. This hypothesis allowed to eliminate the inconvenience of the too small VAN DER WAALS contacts ($< 3.2 \text{ \AA}$), which should occur in the NYBURG structure, according to which single molecules of different orientation in each layer in casual vicariance are admitted.

However, whatever is the interpretation given to the structure of *cis*tactic polyisoprene, the lack of a perfect order of packing of the macromolecules in the crystals is always observed, contrary to the corresponding polymer of butadiene; this could contribute to the rather low experimental value of ΔS_u for natural rubber in comparison with a calculated value of 4.5 to 6 u.e./structural unit. The high value of ΔS_u of *cis*tactic polybutadiene can be also explained on the basis of a high contribution to entropy by an increase in volume on melting.

In any case, quantitative and conclusive reasonings should be made considering the entropic conformational contribution, for the calculation of which all the necessary data are not yet available.

1) It.P. 566,940; G. NATTA, L. PORRI, and P. CORRADINI.

2) It.P. 597,770; G. NATTA, L. PORRI, and L. FIORE.

3) F. DANUSSO, G. MORAGLIO, W. GHIGLIA, L. MOTTA, and G. TALAMINI, *Chim. e Ind. [Milano]* **41** (1959) 748.

4) G. MORAGLIO, *Accad. Naz. Lincei*, in press.

5) P. J. FLORY, *J. chem. Physics* **17** (1949) 223.

6) D. E. ROBERTS and L. MANDELKERN, *J. Amer. chem. Soc.* **77** (1955) 781.

7) H. L. WAGNER and P. J. FLORY, *J. Amer. chem. Soc.* **74** (1952) 195.

8) G. NATTA and G. MORAGLIO, *Rubber Plastics Age* **44** (1963) 42.

9) L. MANDELKERN, F. A. QUINN, and D. E. ROBERTS, *J. Amer. chem. Soc.* **78** (1956) 926.

10) S. C. NYBURG, *Acta crystallogr. [Copenhagen]* **7** (1954) 385.

11) G. NATTA and P. CORRADINI, *Nuovo Cimento* **15** (1960) 111.