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**Phenomena of Isomorphism and Polymorphism in
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SUMMARY:

The properties of butadiene—pentadiene copolymers in which all butadiene and pentadiene units are trans-1,4, are briefly reported. These copolymers, independently of their composition, are crystalline and their melting temperatures are intermediate between those of trans-1,4 homopolymers of butadiene and pentadiene. These properties are attributable to the isomorphism between the trans-1,4 pentadiene units and the units of the high temperature stable modification of trans-1,4 polybutadiene.

In order to emphasize the influence of the isomorphism phenomena of monomeric units on the properties of the macromolecules, the properties of butadiene-pentadiene copolymers, in which the butadiene units are trans-1,4 and the pentadiene units are partly 1,2, are also reported.

ZUSAMMENFASSUNG:

Die Eigenschaften von Butadien/Pentadien-Copolymeren, in denen alle Butadien- und Pentadieneinheiten in trans-1,4-Stellung vorliegen, werden kurz abgehandelt. Diese Copolymeren sind, unabhängig von ihrer grundmolaren Zusammensetzung, kristallin. Ihre Schmelzpunkte liegen jeweils zwischen denjenigen der beiden Homopolymeren. Diese Eigenschaften sind auf die Isomorphie zwischen den trans-1,4-Pentadienbausteinen und den Grundbausteinen der bei hoher Temperatur beständigen Modifikation von trans-1,4-Polybutadien zurückzuführen. Um diesen Einfluß der Isomorphie zwischen Monomereinheiten auf die Eigenschaften von Butadien/Pentadien-Copolymeren zu verdeutlichen, wird auch über Copolymere berichtet, bei denen die Butadienbausteine in trans-1,4- und die Pentadienbausteine teilweise in 1,2-Stellung verknüpft sind.

In the course of a study on the copolymerisation of 1,3-butadiene with 1,3-pentadiene with the aid of stereospecific catalysts, two different types of copolymers were obtained; one type having both butadiene and pentadiene units with trans-1,4 enchainment and the other having butadiene units with trans-1,4 and pentadiene units some with trans-1,4 and some with 1,2 enchainment.

In this communication we report briefly the properties of these copolymers. Their study is of some interest because it permits to emphasize both an interesting phenomenon of isomorphism among monomeric units (in the meaning given to this phenomenon in a preceding paper¹⁾), and also the influence exerted by this type of isomorphism on the properties of the macromolecules.

The case of the copolymers examined here is made more interesting and complex because *trans*-1,4-polybutadiene can exist, as it is known²⁾, in two polymorphous modifications: one stable at low temperature (I) and the other one stable at higher temperature (II), with a 1st order transition (T_t) at about 75 °C. The two modifications have different identity periods (~ 4.85 Å for modification I, ~ 4.65 Å for modification II) and different equatorial encumbrment for each chain (which appears greater in the case of modification II); consequently they behave in a different way with regard to the effects of the introduction of *trans*-1,4-pentadiene units in the chain.

Copolymers having all units with trans-1,4 enchainment

The copolymers of this type were obtained using the heterogeneous $\text{Al}(\text{C}_2\text{H}_5)_3\text{-VCl}_3$ catalyst; both *trans* and *cis* isomer of 1,3-pentadiene can be used as comonomer. These copolymers are crystalline for the whole range of compositions examined by us (about 20 to 100 % butadiene); within this range, they exhibit a final melting temperature (T_m) intermediate between those of the *trans*-1,4 crystalline homopolymers of butadiene and of pentadiene³⁾, as shown in Table I.

Table I. Melting temperature of *trans*-1,4-butadiene-pentadiene copolymers *)

Copolymer composition (C ₄ mole-%)	T _m (°C.)
100	145
86	130
63	128
46	107
33	99
23	97
0	95

*) An accurate determination of the melting temperatures *vs.* composition curve was made difficult by the fact that the copolymers, which are crystalline, and therefore only slightly soluble, could hardly be separated into homogeneous fractions.

These properties indicate that trans-1,4-pentadiene units may be considered as isomorphous with the trans-1,4-butadiene units of the modification II.

What has been observed here represents as far as we know, the first case of isomorphism among monomeric units derived from diolefinic monomers; analogous isomorphism phenomena have been observed up to now only in the case of isotactic copolymers of some vinyl monomers¹⁾.

The crystallinity shown by trans-1,4-butadiene-pentadiene copolymers at room temperature varies depending on their composition. Copolymers rich in butadiene (approximately more than 85 %) exhibit the type of crystallinity present in modification I of trans-1,4-polybutadiene (Fig. 1, a). It has been observed that by increasing the pentadiene content, the type of crystallinity present in modification II begins to appear (Fig. 1, b); then this prevails, and finally, for those copolymers having about 40 to 60 mole-% of pentadiene, it remains the only type of crystallinity (Fig. 1, c). By further increasing the pentadiene content, the copolymers still show, at X-ray examination, the crystallinity of modification II; however, in the I.R. spectrum, the bands typical of trans-1,4 isotactic poly-pentadiene were observed. In those copolymers exhibiting the type of crystallinity of modification I or of modification II a slight increase of the equatorial encumbrance for each chain has been observed, with respect to the trans-1,4-polybutadiene, due to the presence of the methyl groups of

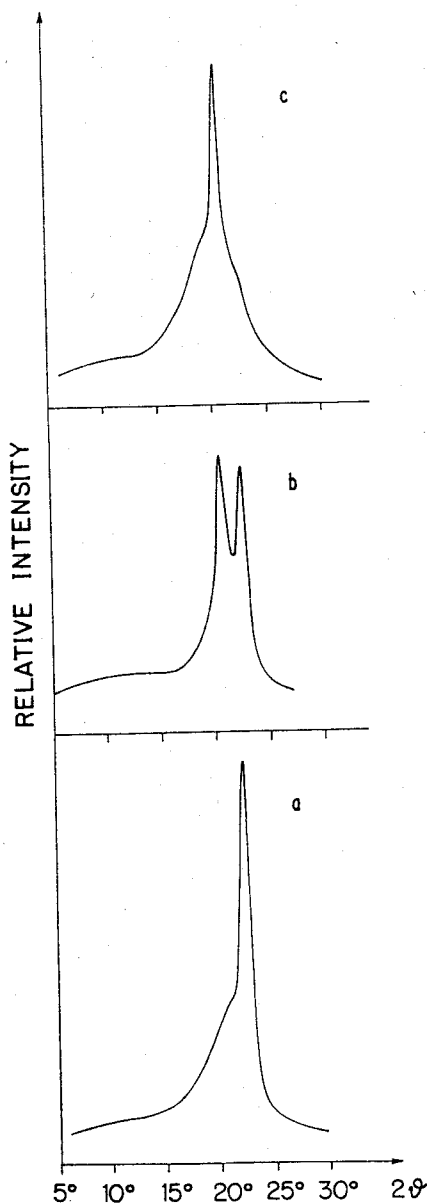


Fig. 1. X-ray powder spectra ($\text{CuK}\alpha$), registered by a GEIGER counter, of copolymer having the following composition (C_5 mole-%)
 a) 13.5; crystallinity of mod. I of trans-1,4-polybutadiene,
 b) 22.6; crystallinity of mod. I and mod. II of trans-1,4-polybutadiene,
 c) 53.8; crystallinity of mod. II of trans-1,4-polybutadiene

the pentadiene units. Such increase can be deduced from the slight shift in the position of the peaks in the X-ray spectra of the copolymers.

The fact that copolymers rich in butadiene show, at room temperature, the crystallinity of modification I, and those with a lower butadiene content show the crystallinity of modification II, is due to the fall in T_t by the introduction of trans-1,4-pentadiene units. Beyond a certain concentration of pentadiene units T_t is lower than $\sim 18^\circ\text{C}$., and, therefore, at room temperature, the crystallinity of modification II appears.

The fall in T_t may be interpreted by assuming that trans-1,4-pentadiene units are either not isomorphous, or only slightly isomorphous, with butadiene units of modification I, contrary to what occurs in modification II, which is characterized by a greater equatorial encumbrance for each chain.

Copolymers containing pentadiene units with 1,2 enchainment

The copolymers of this type, in which the butadiene units are all trans-1,4, while the pentadiene units are partly trans-1,4 and partly 1,2, were obtained using a homogeneous catalyst prepared from $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ and vanadium triacetylacetonate; only the *trans* isomer of 1,3-pentadiene can be copolymerized with this catalyst. In these copolymers, with the increase in the pentadiene content, a rapid decrease of the melting temperature occurs, whereas a less noticeable decrease of the 1st order transition temperature is observed.

Table II shows the variation of T_t and T_m of the copolymers with the composition. The properties of this second type of copolymers depend on the fact that the 1,2-pentadiene units, due to their bulky side group, are

Table II. Variation of T_t and T_m in butadiene-pentadiene copolymers obtained with the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl-V}(\text{Ac})_3$ *) soluble catalyst

Copolymer composition (C_5 mole-%)	T_t ($^\circ\text{C}$.)	T_m ($^\circ\text{C}$.)
0	75	145
13	47	81
14	42	74
16	37	54
19	27	46
23	—	21

*) $\text{V}(\text{Ac})_3$ = vanadium triacetylacetonate.

not isomorphous or not completely isomorphous with the butadiene units of modification II (and therefore, even more so, of modification I). It can be assumed that, in these copolymers, T_m ensues from two different contributions, one due to *trans*-1,4-, the other to 1,2-pentadiene units. By the effect of the former (isomorphous with the butadiene units of the modification II) T_m should decrease, in a first approximation, almost linearly *vs.* the composition, to a value ranging from 95 to 145 °C.; by the effect of the latter, it should decrease further in a fairly higher degree, according to the FLORY formula.

It is surprising, in this second type of copolymers, that small amount of pentadiene units determine a considerable ΔT_m . Copolymers with 5 mole-% of pentadiene have T_m at about 122 °C. This fact is a proof of a low enthalpy of fusion of modification II of *trans*-1,4-polybutadiene.

Relative measurements, performed by differential thermal analysis⁴), have shown that in *trans*-1,4-polybutadiene the enthalpy of transformation (ΔH_t) is higher than that of fusion (ΔH_m). Hence the low value of ΔH_m (which can be deduced from the rapid decrease of T_m in the copolymers) can be explained by taking into account that the entropy difference between the modification I and the molten polymer is mostly absorbed during the transformation from modification I to modification II. Such a transformation, as will be explained in another communication, corresponds essentially to an alteration of the regular conformation of the polymer chain.

Experimental

We report an example of preparation of each type of copolymer. A more detailed and complete description of their preparation as well as of their properties will be reported in a forthcoming paper.

a) In a 100-ml. glass container are introduced (N_2 atmosphere): anhydrous benzene 70 ml.; $Al(C_2H_5)_2Cl$ 0.3 ml.; 1,3-butadiene (PHILLIPS, 99% pure) 19 g.; 1,3-pentadiene (*trans*-isomer) 0.65 g.; vanadium triacetylacetonate 0.006 g. The reaction vessel is kept at -10 °C. by immersion in a cooling bath. After 50 min. the polymerization is stopped with CH_3OH and the polymer coagulated. It was obtained 0.7 g. of copolymer, crystalline at X-rays (mod. I) showing the following characteristics: pentadiene (moles-%) 13.8; T_t 42 °C., T_m 74 °C. (determined dilatometrically and by X-ray); $[\eta]$ 2 (100 ml./g.).

Varying the butadiene/pentadiene feed ratio, copolymers of every composition can be obtained. If the conversion is kept low, the copolymers are homogeneous in composition and need not to be fractionated.

b) In a three-neck flask (250 ml. capacity) equipped with a stirrer, are introduced (N_2): anhydrous benzene 100 ml.; $Al(C_2H_5)_3$ 2.2 ml.; 1,3-pentadiene (*trans*-isomer) 20.7 g.; butadiene (PHILLIPS, 99% pure) 2 g.; VCl_3 1 g. The polymerization is carried out at 20 °C. for 1 hr., then the reaction is stopped with CH_3OH and the copolymer is repeatedly and

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thoroughly washed with CH₃OH. 2 g. of copolymer are obtained which are then extracted with the series of solvents: diethyl ether, *n*-hexane, *n*-heptane. The extracts show the following characteristics:

ether extract: pentadiene (mole-%) 77; T_m 97°C. (polarizing microscope);
[η] 0.8 (100 ml./g.).

n-hexane extract: pentadiene (mole-%) 36; T_m 125°C. (polarizing microscope); [η] 1.5 (100 ml./g.).

n-heptane extract: pentadiene (mole-%) 9,h; T_m 137° C (polarizing microscope)

In those runs carried out at a very low concentration of butadiene, this latter is added dropwise (as concentrated solution in benzene) during the course of polymerization, in such a way as to keep its concentration in the polymerization medium as constant as possible.

Analyses of copolymers were made by I.R. considering the intensity of the methyl group band at 7.25–7.30 μ for the determination of the pentadiene, and the band at 7.38 μ for the determination of the butadiene. The I.R. method of analysis was checked by radiochemical method, in copolymers prepared with pentadiene labeled with C¹⁴.

Intrinsic viscosities were determined in toluene at 30°C.

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