

Isotactic *trans*-1,4 Polymers of 1,3-Pentadiene*

G. NATTA, L. PORRI, P. CORRADINI, G. ZANINI, and F. CIAMPELLI, *Istituto di Chimica Industriale del Politecnico, Milan, Italy*

Introduction

The polymers of 1,3-pentadiene having 1,4 enchainment are constituted of monomeric units that contain two sites of steric isomery, i.e., double bonds, which can be *cis* or *trans*, and the tertiary carbon atoms, which can be *d* or *l*. This gives rise to the possibility of several crystallizable stereoisomers of 1,4-polypentadienes, among which, for instance, are the *trans*-1,4 or *cis*-1,4 isotactic and the *trans*-1,4 or *cis*-1,4 syndiotactic polymers. Polypentadienes, which are all *trans*- or all *cis*-1,4, but which have a statistical disorder in the configuration of the tertiary carbon atoms, should be unable to crystallize, in analogy with what has been observed in the case of atactic polymers of α -olefins.

In this paper we report the synthesis† of crystalline polymers of 1,3-pentadiene having isotactic *trans*-1,4 structure and of polymers which are all *trans*-1,4 but which are amorphous, owing to a disorder in the configuration of the tertiary carbon atoms.

Various heterogeneous catalysts obtained from alkylaluminum compounds and titanium or vanadium chlorides can be employed for the synthesis of these polymers. The results reported in this paper concern only the $\text{Al}(\text{C}_2\text{H}_5)_3\text{-VCl}_3$ system, which appears to be highly stereospecific.

Infrared and x-ray investigations of the isotactic *trans*-1,4-polypentadiene have shown that this polymer may exist in two modifications, crystalline and paracrystalline, the latter being well ordered only in one direction. A characterization of the two modifications by x-ray and IR is also reported in this paper.

Experimental

Triethyl aluminum was 90–95% pure, the main impurity being $\text{Al}(\text{C}_2\text{H}_5)_2\text{-OC}_2\text{H}_5$. *n*-Heptane, used as *solvent*, was refluxed on Na–K alloy for about 24 hr., then distilled and stored under pure nitrogen. *Vanadium chloride* (VCl_3) was ground and thoroughly washed with anhydrous *n*-heptane.

* Note VI on the "Stereospecific Polymerization of Conjugated Diolefins." For Note V, see *Chim. e ind. (Milan)* **41**, 1163 (1959).

† The synthesis of these polymers was first disclosed in 1955, in an Italian patent.¹ Later on, preliminary information on this subject was given in short communications.²

Monomers were prepared by pyrolysis of 2,4-pentanediol diacetate.³ By fractionation of the crude pyrolyzate, a fraction (a) containing 90–95% of the *trans* isomer of pentadiene, and a fraction (b) rich in *cis* isomer were obtained. A chromatographic separation of fraction (a) (Perkin-Elmer Vapor fractometer, preparative column H) was performed in order to obtain the pure *trans* isomer; fraction (b) was treated with maleic anhydride³ and the *cis* isomer thus obtained was finally purified by gas chromatography.

The *polymerizations* were carried out in glass bottles of about 100 ml. capacity kept in agitation. In standard runs, 0.3 g. of VCl_3 was suspended in 15 ml. of *n*-heptane, then 0.6 ml. of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 4 ml. of monomer was added. All the polymerization runs were carried out at room temperature. The polymers were precipitated with methanol, then repeatedly and carefully washed with methanol and finally dried under vacuum at room temperature. In order to separate the amorphous fraction from the crystalline, the crude polymer was extracted with boiling ether, which extracted the amorphous polymers. In some runs, the amorphous ether-extracted polymers were then extracted with acetone in order to remove the low molecular weight oily products. All the operations were carried out under N_2 atmosphere.

Melting temperatures were determined with the aid of a polarizing microscope.

The *infrared spectra* of the polymers were obtained with Perkin-Elmer 21 and 221 spectrophotometers with prisms of CaF_2 and NaCl . The samples were examined: (a) as solutions in CCl_4 , or in the molten state (using an ordinary heating cell); (b) as films obtained either by hot-pressing or by deposition from solutions in CS_2 on NaCl windows. The films thus obtained are usually of the paracrystalline modification, and it is necessary to anneal them in order to obtain their transformation into the crystalline form.

For the *x-ray examination* of the polymers, a Norelco diffraction apparatus equipped with a Geiger counter was employed. The fiber spectra of the paracrystalline modification were obtained by cutting, from a thin sheet of polymer obtained by hot-pressing, a narrow strip that was subsequently cold-stretched. In order to obtain fiber spectra of the crystalline modification, a polymer sheet was first annealed by melting and slow cooling; from it, a fiber was cut, which was then very slowly stretched at a temperature as close as possible to the melting temperature.

Results

(a) Polymerization

Table I shows some results of polymerizations carried out at room temperature with the heterogeneous $\text{Al}(\text{C}_2\text{H}_5)_3$ – VCl_3 system. Either the pure *cis* or the pure *trans* isomer of pentadiene, or mixtures of the two isomers, were employed. The polymerization results may be summarized as follows:

TABLE I
Polymerization of 1,3-Pentadiene with the $\text{Al}(\text{C}_2\text{H}_5)_3\text{-VCl}_3$ system^a

1,3-Pentadiene <i>trans</i> isomer, %	Polym. period, hr.	Polymer, g.	Residue from ether extn., % ^b	Melting temp., °C.
100	14	1.23	87	95
"	15	1.5	83.5	95
"	17	1.4	88	—
"	70	2.4	85	95
"	72	2.4	85	—
77	14	1.44	69	92
75	14.30	0.68	66	92
50	14.30	0.64	65	90
50	15	0.95	58	89
50	16	0.87	64	90
28	14.30	0.67	69	89
25	16	1.47	64	91
0	16	0.95	94	95
0	76	1.6	92	95

^a Monomer 4 ml.; VCl_3 0.3 g.; Al/V molar ratio 2.5; heptane 15 ml.

^b About 95% soluble in boiling benzene; $[\eta]$ at 30°C. in toluene 1.3–1.5 100 cm.³/g.

(a) The pure *cis* or *trans* isomer gives crude polymerization products containing a low percentage of ether-extractable amorphous fraction. The residue of the ether extraction of the polymers obtained from each of the two isomers show identical x-ray and IR spectra and the same melting temperature (about 95°C.). Strong bands at 12.8, 11.54, 10.65, and 9.75 μ are present in the IR spectrum (Fig. 1) of the polymers in the solid state; these bands do not appear in the spectrum of polymers in the molten state or in solution. The x-ray spectrum of polymers obtained as residue of the ether extraction (without any further thermal treatment) corresponds to that of the paracrystalline modification.

(b) The crude polymers obtained from mixtures of *cis* and *trans* isomers contain a percentage of ether-extractable amorphous fraction higher than that of products obtained from the pure isomers. Such an ether fraction (examined after removing the oily low molecular polymers by acetone extraction) is essentially formed, as revealed by IR examination, by monomeric units that contain *trans* internal double bonds. This fact alone does not prove that the monomeric units are of the *trans*-1,4 type, because 3,4 units may also possibly show *trans* internal double bonds in the lateral chain. It must, however, be observed that the amorphous ether fraction shows the band that is characteristic of the methyl group at 7.29 μ , that is, at the same wavelength of isotactic *trans*-1,4-polypentadienes; in polypentadienes having 3,4 enchainment this band is slightly displaced, at about 7.26 μ (prisms of CaF_2).⁴ The position of the methyl band proves that monomeric units in the amorphous ether fraction are of the *trans*-1,4 type, at least for the most part.

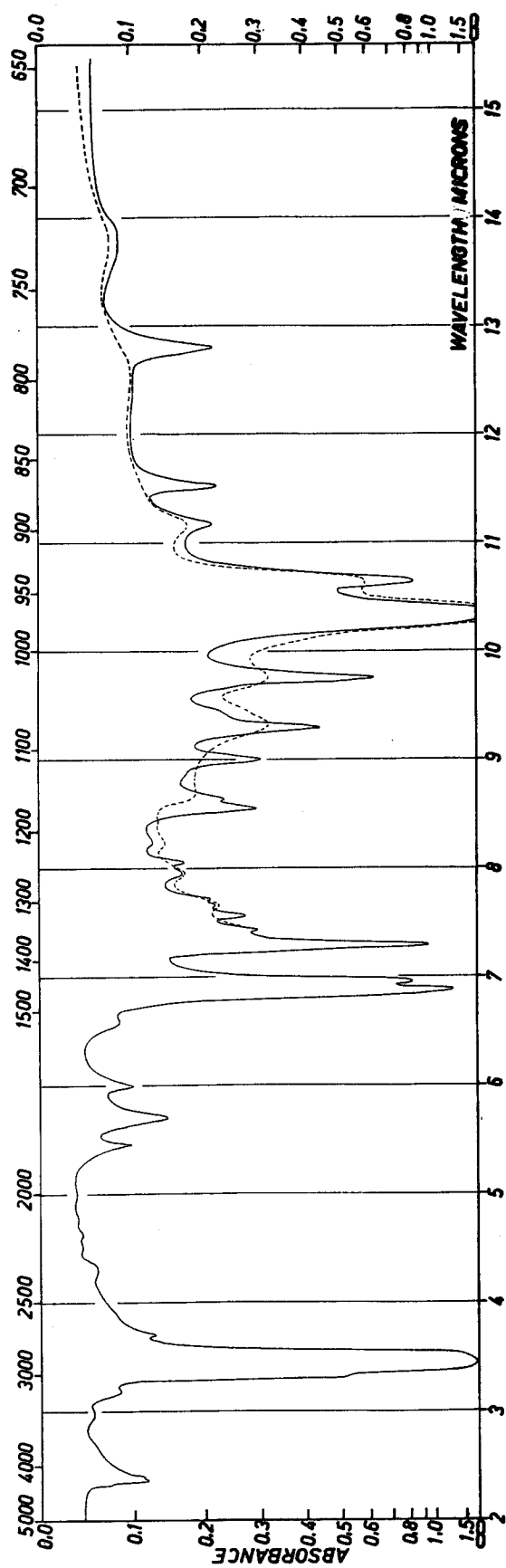


Fig. 1. IR spectra of the *trans*-1,4 isotactic polybutadiene (—) in the solid state, paracrystalline modification, and (---) in the molten state.

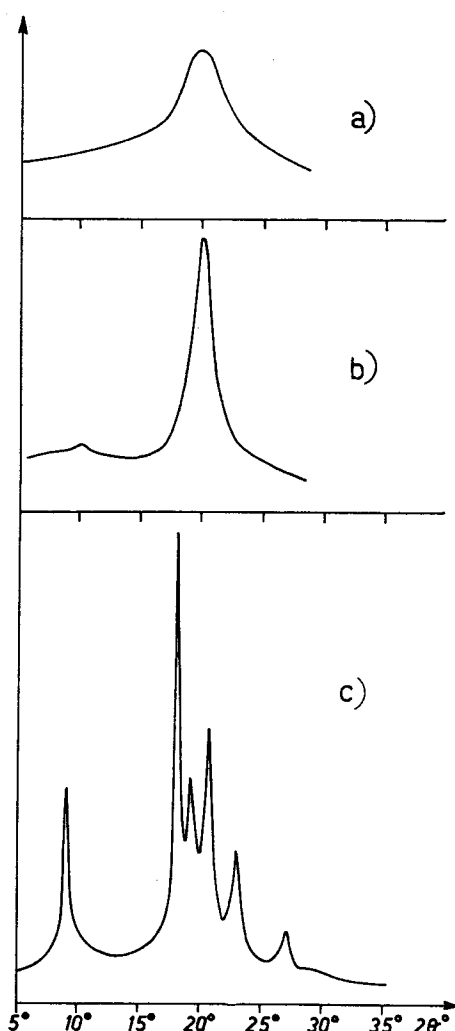


Fig. 2. X-ray spectra ($\text{CuK}\alpha$) of *trans*-1,4 polymers of 1,3-pentadiene: (a) atactic; (b) isotactic, paracrystalline modification; (c) isotactic, crystalline modification.

On the other hand, the monomeric units do not show, at least in a detectable way, head-to-tail inversions, which should be proved by the presence of a weak band (due to the $-\text{CH}_2-\text{CH}_2-$ group) in the region around $13.3\ \mu$. The absence of crystallinity observed by x-ray examination (Fig. 2a) of this fraction, which has substantially *trans*-1,4 enchainment, must therefore be attributed to a certain disorder in the configuration of the asymmetric carbon atoms. However, it does not seem that such a fraction should be considered as completely atactic, with respect to the configuration of the tertiary carbon atoms, since in the IR spectrum, in the solid state, one observes the presence of the characteristic, though very weak, bands at 12.80 , $11.54\ \mu$, etc. This seems to indicate the existence of short segments of stereo-ordered monomeric units.

(c) The ether-insoluble fraction of polymers obtained from isomer mixtures, shows, by x-ray, when examined without annealing, the same spectrum, corresponding to the paracrystalline modification of the product

obtained from pure isomers. However, the melting point of this fraction is generally below 95°C. Furthermore, in the IR spectrum of the solid polymer, the above-mentioned bands are less intense than those present in the spectrum of products obtained from the pure *cis* or *trans* isomer.

Since the polymer obtained using mixtures of *cis* and *trans* isomers has a *trans*-1,4 enchainment, as revealed by the position of the methyl group band, the lowering of the melting point as well as the lower intensity of the above-mentioned bands in the IR spectrum must be attributed to a lower degree of steric order, with regard to the configuration of the tertiary carbon atoms to which the methyl groups are linked.

(b) *Characterization of the Isotactic trans-1,4-polypentadiene*

The polymers directly obtained from the polymerization, under the experimental conditions followed by us, always result in the paracrystalline modification; this modification, as has already been mentioned, may be transformed into the crystalline by melting and very slow cooling (about 10 hr. from 100 to 50°C.). The crystalline modification may be transformed back to the paracrystalline by melting and fast cooling.

The paracrystalline and crystalline modifications show different densities, about 0.94 for the former and about 0.97 for the latter.

Figure 2 (b,c) shows the x-ray spectra registered with a Geiger counter, in the angular region from $2\theta = 5^\circ$ to $2\theta = 30^\circ$, of an isotactic *trans*-1,4-polypentadiene sample, in both the paracrystalline and the crystalline modifications. The spectrum of the paracrystalline modification shows a rather broad peak, the intensity maximum of which corresponds to a Bragg distance of 4.55 Å., whereas the spectrum of the crystalline modification is rich in sharp reflections, characteristic of a high degree of order. The fiber spectra of both modifications give an identity period of 4.8 Å. The mean distance among the chains may be evaluated from the presence of two very strong equatorial reflections at $d = 4.85$ Å. and $d = 4.35$ Å.* Considering that the experimental value of the density is 0.97 and that the identity period is 4.8 Å., any structure should be rejected for which it is necessary to set more than one monomeric unit in that period.¹ On the basis of x-ray data, therefore, we need not take into account possible syndio-3,4 and iso-3,4 enchainments, which also, by IR, could appear to be characterized by a *trans*-type internal double bond present in the side chain. With regard to the steric configuration of the $>\text{CH}-\text{CH}_3$ groups, it can only be isotactic, because the number of monomeric units contained in the identity period is 1.

The position of the methyl group with respect to the chain may be foreseen on the basis of the principle of the minimum of internal energy of an isolated chain.⁵

* All reflections of the fiber spectrum may be interpreted on the basis of a unit cell having the constants $a = 19.73 \pm 0.15$ Å., $b = 4.85 \pm 0.05$ Å., $c = 4.8 \pm 0.1$ Å.; $\alpha = \beta = \gamma = 90^\circ$; number of monomeric units per unit cell = 4.

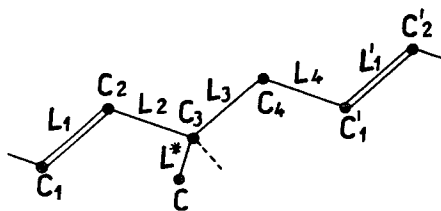


Fig. 3. Chain segment of *trans*-1,4 isotactic polypentadiene.

In Figure 3 a chain segment is shown of isotactic *trans*-1,4-polypentadiene arbitrarily stretched on a plane. The internal rotation angles characterizing it are three: the angle between L_1L_2 and L_2L_3 planes (σ_2), the angle between L_2L_3 and L_3L_4 planes (σ_3), and the angle between L_3L_4 and L_4L_1' planes (σ_4). The convention used to measure such angles has already been described.⁶

Owing to the analogy of the identity periods, and in agreement with the principle of the maximum displacement of the simple bonds, we shall assume as possible internal rotation angles characterizing the chain conformation of polypentadiene the same angles ascribed by us to the chain of *trans*-1,4-polybutadiene:

$$\begin{array}{lll} \sigma_2 = 120^\circ & \sigma_3 = 180^\circ & \sigma_4 = 240^\circ \\ \sigma_2 = 240^\circ & \sigma_3 = 180^\circ & \sigma_4 = 120^\circ \end{array}$$

In the case of polypentadiene it is necessary to introduce two further internal rotation angles, σ_2' between the L_1L_2 and L_2L^* planes, and σ_3' between the L_3L_4 and L^*L_3 planes (with $\sigma_2 - \sigma_2' = \sigma_3' - \sigma_3$). As the carbon atom C_3 is asymmetric, two isotactic enantiomorphous sequences are possible, one with $\sigma_2' = \sigma_2 + 120^\circ$, the other with $\sigma_2' = \sigma_2 - 120^\circ$.

In order to avoid that σ_2' equals 0° (*cis* conformation of the L^* bond with regard to L_1 , unfavored by the approach between C_1 and C atoms), we should have $\sigma_2 = 120^\circ$ when the absolute conformation of the C_3 atom is such that $\sigma_2' = \sigma_2 + 120^\circ$, and $\sigma_2 = 240^\circ$ when the absolute configuration of the C_3 atom is such that $\sigma_2' = \sigma_2 - 120^\circ$. From this we derive that right- and left-handed chains exist in this polymer, contrary to the isotactic polymers of vinyl monomers, C_3 being asymmetric; each chain or segment of chain is associated with one of the two absolute configurations of C_3 .

Whereas the x-ray spectra of the paracrystalline modification greatly differ from those of the crystalline, the IR spectra of the two modifications are very similar, revealing only a few slight shifts of frequencies and a few variations of intensity. The IR spectra of the two modifications (NaCl) are shown in Figure 4. Figure 5 shows some details of the spectra (CaF_2) from which the differences between the two modifications are more evident.

The fairly slight difference between the IR spectra of the two modifications indicates that the IR spectrum of the polymeric chain is not remarkably influenced by the interactions between neighboring macromolecules. The spectrum seems to be essentially determined by the regularity of the chain conformations, and since a regular conformation may be obtained

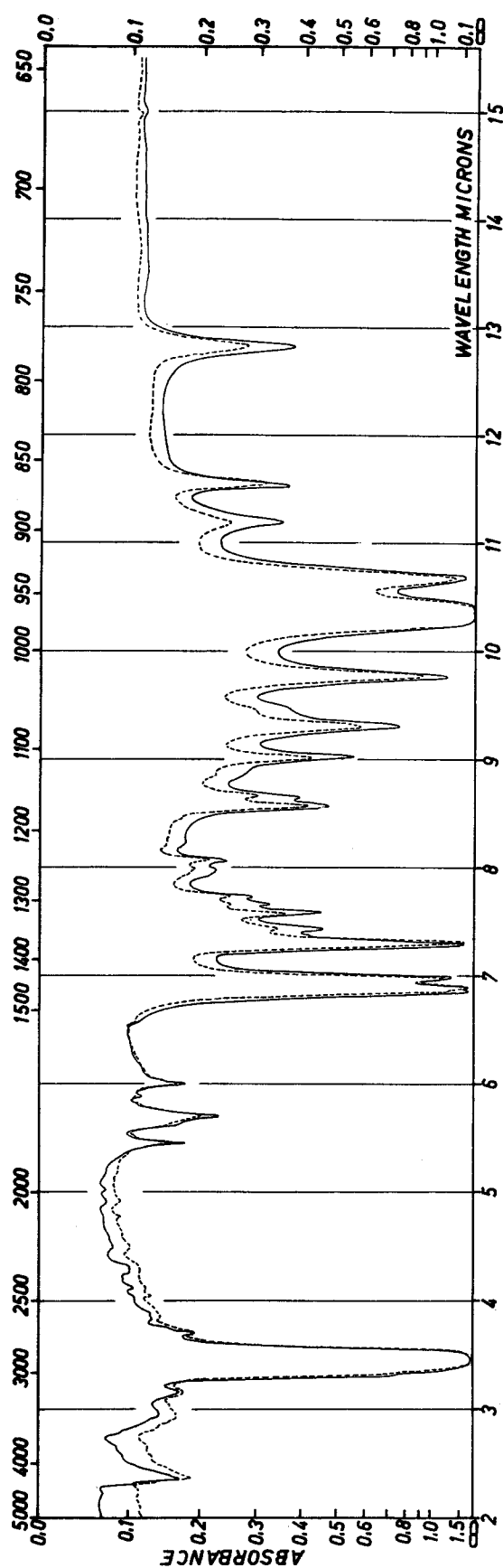


Fig. 4. IR spectra of *trans*-1,4 isotactic polypentadiene: (—) crystalline modification; (---) paracrystalline modification.

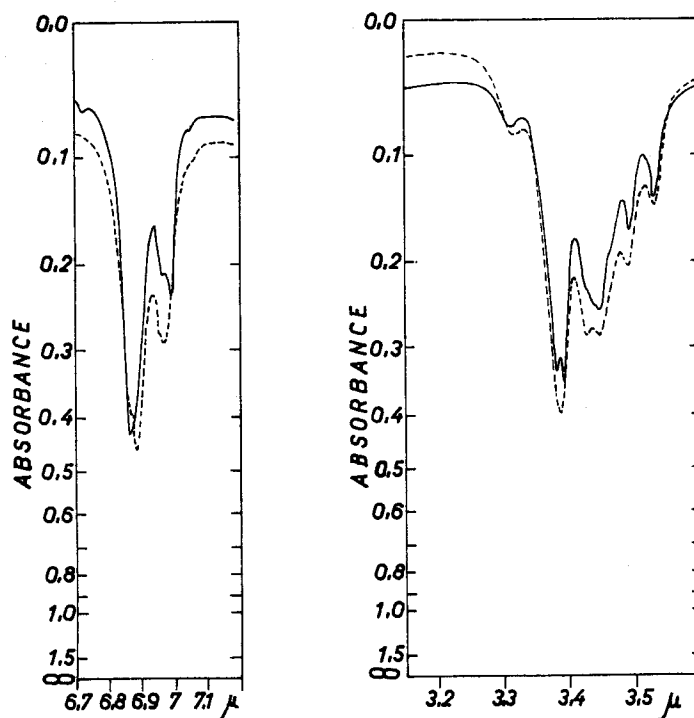


Fig. 5. Some details of the IR spectra of *trans*-1,4-polybutadiene in the crystalline (—) and paracrystalline (---) modification (CaF_2 optics).

even when a tridimensional ordered lattice does not exist, as in the paracrystalline modification, the IR spectrum is not greatly influenced by the degree of order existing in the directions perpendicular to the chain axes, in analogy with what has been observed for other crystalline polymers.⁷

Hence the intensities of the IR bands at 12.80, 11.50 μ , etc. cannot be a measure of the crystallinity, considered as order in the three dimensions. Since they depend on the regularity of the chain conformations they can, however, be regarded as a proof of their structure regularity, considered as a regular repetition of a stereo-ordered structural unit.

The ratio of the intensity of the band at 11.54 μ (which is one of the bands present only in the spectrum of the solid polymer) to the intensity of the band at 2.32 μ (which is a band independent of the physical state of the polymer) has been determined for the various polymers examined. Such a ratio, which is a measure of the relative intensity of the band, is much higher for the polymers obtained from the *cis* or *trans* isomer than for polymers obtained from mixtures of two isomers (on a conventional scale, 100 for polymers obtained from pure isomers, 68 for polymers obtained from 50:50 mixtures).

Analogous results can be obtained by taking into consideration the band at 12.80 μ instead of that at 11.54 μ .

Discussion

From the IR and x-ray examinations it is seen that the ether-insoluble polybutadienes obtained with the aid of the $\text{Al}(\text{C}_2\text{H}_5)_3\text{-VCl}_3$ heterogeneous

catalytic systems are stereo-ordered both with regard to the configuration of the double bonds (all of the *trans* type) and with regard to the configuration of the asymmetric carbon atoms (isotactic). Such polymers, according to the terminology proposed by one of us, may be called "ditactic."⁸

It seems to us that the isotactic type of regularity of the configuration of asymmetric carbon atoms must be attributed to the presence of an ordered heterogeneous catalytic surface, in analogy with what has been observed in the isotactic polymerization of α -olefins. Actually, when using soluble catalysts,⁹ we have not succeeded, at least up to now, in obtaining *trans*-1,4 stereo-ordered polymers from the two isomers of pentadiene.

We must consider it probable that the addition of the monomeric unit to the growing polymeric chain takes place by the same type of opening, using both the *cis* and the *trans* isomer. It follows that a stereo-ordered isotactic polymer will be obtained, starting from a pure isomer of pentadiene, only when the presentation of the monomer with regard to the active center is always the same. On the other hand, enantiomorphous monomeric units should be obtained when a molecule of *cis* isomer and one of *trans* isomer subsequently polymerize at the same active center. The presence of crystallinity, even if in a lower degree, in polymers obtained from a mixture of the two isomers, which contrasts with what takes place in statistical copolymerization, may be attributed to one or both of the following reasons: (a) Each active center acts in an elective way with regard to a type of isomer, which therefore reacts at that active center with a higher rate than the other isomer. (b) Considering a single growing chain, the reactivity of the two isomers depends on the structure of the last polymerized monomeric unit, so as to favor the sequence of monomeric units having the same configuration.

The fact that the lowering of the melting temperature of polymers obtained from mixtures of the two isomers is rather small in comparison with the decrease in intensity of the bands in the IR spectrum may be attributed to the fact that also in this case macromolecules containing fairly long isotactic sequences are present. The melting temperature may also be influenced by the fact that a partial isomorphism among enantiomorphous monomeric units is possible, so that a chain section can crystallize even if it contains a small percentage of very dispersed enantiomorphous monomeric units.

Pentadiene polymers having 1,4 enchainment are especially interesting because they possess asymmetric carbon atoms; such polymers, in fact, contain the $\text{=CH-CH(CH}_3\text{)-CH}_2\text{-}$ group, and the tertiary carbon atom is actually asymmetric, even if considered in its near surrounding. This differentiates the tertiary carbon atoms of these polymers from those of the isotactic polymers of α -olefins and other vinyl monomers. Therefore, it must be assumed that each ordered macromolecule having an isotactic structure or each sequence of isotactic monomeric units is optically active.

The absence of optical activity in the polymers obtained by us with the $\text{Al(C}_2\text{H}_5)_3\text{-VCl}_3$ system must be clearly attributed to the statistical equiva-

lence of the *d* and *l* sequences. It seems likely that macromolecules showing an optical activity of a different degree and of different sign, in racemic mixture, are present in the polymer together with macromolecules that are inactive by internal compensation (mesoforms).

A study of the polymerization of pentadiene using asymmetric initiators is now in progress in our laboratory, because of the results obtained in the synthesis of optically active polymers of *trans-trans* disubstituted 1,3-butadiene¹⁰ and other polytactic polymers.¹¹ In runs performed with optically active aluminum alkyl-VCl₃ catalyst, optically active high molecular weight *trans*-1,4 isotactic polypentadiene has already been obtained, thus demonstrating that the asymmetric synthesis of high polymers is possible also in the case of hydrocarbon monomers that do not contain preformed sites of optical asymmetry. The work in the field of the synthesis of optically active *trans*-1,4 isotactic polypentadiene will be the object of a forthcoming paper.

References

1. Natta, G., L. Porri, and G. Mazzanti, Ital. Pat. 536,631 (Mar. 12, 1955).
2. Natta, G., P. Corradini, and L. Porri, *Atti. accad. nazl. Lincei, Rend., Classe Sci. fis. mat. e nat.*, **20**, 728 (1956). Natta, G., L. Porri, P. Corradini, and D. Morero, *Chimica e Industria (Milan)*, **40**, 362 (1958). Natta, G., L. Porri, P. Corradini, G. Zanini, and F. Ciampelli, *Atti accad. nazl. Lincei, Rend., Classe Sci. fis. mat. e nat.*, in press.
3. Frank, R. L., et al., *J. Am. Chem. Soc.*, **69**, 2313 (1947).
4. Unpublished data from our laboratory.
5. Natta, G., and P. Corradini, *Nuovo Cimento, Suppl.*, **25**, 9 (1960).
6. Natta, G., P. Corradini, and I. W. Bassi, *Atti accad. nazl. Lincei, Rend.; Classe Sci. fis. mat. e nat.* **28**, 284 (1960).
7. Natta, G., *Makromol. Chem.*, **35**, 93 (1960).
8. Natta, G., and F. Danusso, *J. Polymer Sci.*, **34**, 3 (1959).
9. Unpublished results.
10. Natta, G., M. Farina, M. Donati, and M. Peraldo, *Chimica e Industria (Milan)*, **42**, 1363 (1960); *Makromol. Chem.*, in press.
11. Natta, G., M. Farina, M. Peraldo, and G. Bressan, *Makromol. Chem.*, **43**, 68 (1961).

Synopsis

Crystalline polymers of 1,3-pentadiene, which are composed of *trans*-1,4 units and show an isotactic configuration of the tertiary carbon atoms, have been obtained with the use of the heterogeneous Al(C₂H₅)₃-VCl₃ catalytic system. The *cis* or *trans* isomer of pentadiene yields polymers that are more stereoregular than those obtained from mixtures of the two isomers. Isotactic *trans*-1,4-polypentadiene may exist in two modifications: crystalline and paracrystalline (unidimensionally regular). The two modifications are characterized by different x-ray spectra and different densities. *trans*-1,4 Isotactic polypentadienes contain tertiary carbon atoms which are actually asymmetric. This permitted obtaining optically active polypentadienes by using polymerization catalysts prepared from optically active aluminum trialkyls.

Résumé

Des polymères cristallins de 1,3-pentadiène, composés d'unités 1,4-*trans* et présentant une configuration isotactique aux atomes de carbone tertiaire, ont été obtenus en

présence d'un système catalytique hétérogène à base de $\text{AlEt}_3\text{-VCl}_3$. L'isomère-*cis* ou *trans* du pentadiène fournit des polymères qui sont plus fortement stéréoréguliers que ceux obtenus au dépens de mélange des deux isomères. Le polypentadiène 1,4-*trans* peut exister sous deux variétés: cristalline et paracristalline (c.a.d. régulière en une seule dimension). Les deux modifications sont caractérisées par des spectres aux rayons-X différents et par des densités différentes. Les polypentadiènes 1,4-*trans* isotactiques contiennent des atomes de carbone tertiaire qui sont en fait asymétriques. Cela a permis d'obtenir des polypentadiènes optiquement actifs en utilisant des catalyseurs de polymérisation préparés au départ d'aluminium-trialcoyle optiquement actif.

Zusammenfassung

Bei Verwendung des heterogenen $\text{Al}(\text{C}_2\text{H}_5)_3\text{-VCl}_3$ -Katalysators wurden kristalline Polymere von 1,3-Pentadien erhalten, die aus *trans*-1,4-Einheiten zusammengesetzt sind und eine isotaktische Konfiguration des tertiären Kohlenstoffatoms zeigen. Das *cis*- oder *trans*-Isomere des Pentadiens ergibt Polymere mit grösserer sterischer Regelmässigkeit als Mischungen der beiden Isomeren. Isotaktisches *trans*-1,4-Polypentadien kann in zwei Modifikationen auftreten: kristallin und parakristallin (eindimensional regelmässig). Die beiden Modifikationen sind durch verschiedene Röntgenspektren und verschiedene Dichten charakterisiert. Isotaktische *trans*-1,4-Polypentadiene besitzen tertiäre Kohlenstoffatome, die tatsächlich asymmetrisch sind. Dies gestattet die Herstellung optisch aktiver Polypentadiene mit Polymerisationskatalysatoren, die aus optisch aktiven Aluminiumtrialkylen hergestellt wurden.

Received April 26, 1961