

Some Remarks on Amorphous and Atactic α -Olefin Polymers and Random Ethylene-Propylene Copolymers

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Synopsis

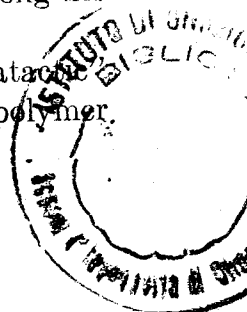
The necessity is pointed out to distinguish between an "amorphous" α -olefin polymer and an "atactic" α -olefin polymer. It is convenient to limit the term "atactic" only to those amorphous linear regularly head-to-tail polymers which possess the same chemical regularity as the corresponding tactic polymers, from which they differ only for the lack of steric regularity. A clear interpretation is given of the presence of bands at 1155 and 915 cm^{-1} in the IR spectra of isotactic and atactic polypropylenes. The presence of these bands is due to the $-\text{CH}_2-\text{CH}-$ monomeric unit, with a regular head



to-tail arrangement. The absence of these bands in the propylene polymers obtained with the aid of cationic-type catalysts depends on the presence of a very small content of monomeric units of this type. Finally the conclusion is drawn that the presence of the two above-mentioned bands in the IR spectrum of the ethylene-propylene copolymers does not indicate the presence of long propylene sequences of the isotactic type, and therefore the existence of a block copolymer, but only the presence of the monomeric unit mentioned above.

Tactic polymers of α -olefins were discovered more than ten years ago¹ and their nomenclature was defined in detail shortly thereafter.² However, there is still some confusion when it comes to defining actual polymers in terms of their steric structure. One reason for this is probably the fact that actual α -olefin polymers can be classified according to the definitions of tacticity which were established with reference to ideal macromolecules. Furthermore, the degree of tacticity of α -olefin polymers is not determined, in general, through actual, direct measurements of the number of steric inversions or permanences, but is derived indirectly through the measure of certain physical properties,² such as solubility and crystallinity. This indirect method is obviously only approximate and does not allow one to establish the actual number of steric inversions which may occur along the polymer chains.

A particular state of confusion seems to exist with regard to "atactic" and of "amorphous" α -olefin polymers. An ideal atactic α -olefin polymer.



can be defined² as a macromolecular compound in which monomer units of enantiomorphous steric configuration are distributed at random. In reality, for an α -olefin polymer to have the properties (solubility in certain organic solvents, lack of crystallinity) of an atactic polymer it will not be absolutely necessary that such a perfect random distribution exists; as shown by one of us² the presence of tactic blocks (stereoblocks) will not alter those properties, provided these blocks are sufficiently short (see also recent NMR studies of amorphous polypropylene³).

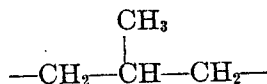
What we would like to stress particularly here is the need to draw a distinction between an "amorphous" α -olefin polymer in general and an "atactic" α -olefin polymer.

An α -olefin polymer can be amorphous (noncrystalline) not only because of irregular steric structure but also because of the presence in its macromolecules of irregularities and inversions in the enchainment of the monomer units, and also of monomer units which may be chemically different from each other, although derived from a single monomer.

In α -olefin polymers obtained through anionic coordinated polymerization no such chemical irregularities exist; amorphous α -olefin polymers thus obtained are amorphous only because of lack or insufficiency of steric regularity. They are linear, regular head-to-tail polymers, which possess the same chemical regularity as the corresponding tactic polymers, from which they differ only because of lack of steric regularity. (Steric regularity presupposes the existence of chemical regularity in the polymer macromolecules.) Therefore it is convenient to limit the term "atactic" only to such amorphous polymers. Some authors,^{4,5} however, have not taken this into account, and have recently considered as atactic polymers those which possess no chemical regularity at all.

This has led to an incorrect interpretation of certain bands of the infrared spectrum of polypropylene, and consequently to incorrect considerations on the structure of ethylene-propylene copolymers obtained through anionic coordinated polymerization. These authors,^{4,5} in fact, have noticed that propylene polymers obtained through cationic polymerization do not show in the infrared spectrum the bands at 1155 and 975 cm^{-1} which are always present in the infrared spectra of both crystalline and amorphous polypropylenes (ether extract or polymers in the molten state) obtained through anionic coordinated polymerization. The bands at 1155 and 975 cm^{-1} were attributed to isotactic polypropylene, and it was concluded^{4,5} that their presence in an ethylene-propylene copolymer was indicative of the presence of isotactic polypropylene sequences and therefore the existence of a block copolymer instead of a random copolymer. These conclusions are completely contrary to what can be derived from other experimental data, which we have accurately collected.

Bands at 1155 cm^{-1} and in the range 975-930 cm^{-1} are cited in the literature^{6,7} as characteristic of the group



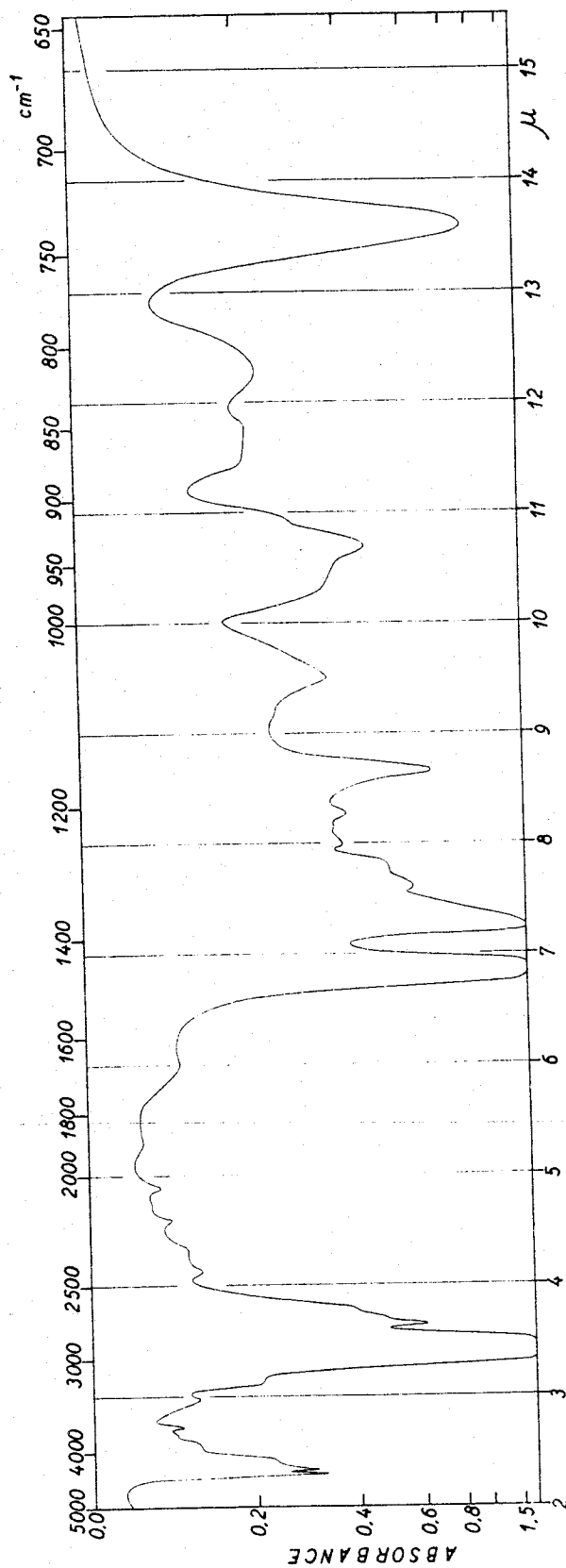


Fig. 1. Infrared spectrum of the ethylene-propylene alternating copolymer obtained by hydrogenation of polyisoprene.

TABLE I
Content of various monomeric units by infrared, %

Polymer	$\begin{array}{c} \text{CH}_3 \\ \\ \text{---CH---CH}_2\text{---} \\ \\ \text{CH}_3 \end{array}$ (1155 cm. ⁻¹)	$\begin{array}{c} \text{---CH}_2\text{---CH---CH---CH}_2\text{---} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	$\begin{array}{c} \text{---CH---} \\ \\ \text{CH}_2\text{---CH}_3 \end{array}$	$\begin{array}{c} \text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---} \\ \\ \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{---C---} \\ \\ \text{CH}_3 \end{array}$ (1378, 1245 cm. ⁻¹)	$\text{---(CH}_2\text{)}_n\text{---}$ for $n > 3$	(723 cm. ⁻¹)	
Polypropylenes obtained by fractionation of a crude polymer containing isotactic portions								
A. Boiling <i>n</i> -heptane-insoluble fraction: isotactic polypropylene	~100	(750, 1120 cm. ⁻¹)	(775 cm. ⁻¹)	(735 cm. ⁻¹)				
B. Boiling ethyl ether-insoluble, but boiling <i>n</i> -heptane-soluble fraction: isotactic stereoblock polypropylene	~98							
C. Boiling ethyl ether-soluble fraction atactic polypropylene	~95							

Polypropylenes obtained in the presence of catalysts acting through an anionic coordinated mechanism, able to polymerize propylene with syndiotactic enchainment¹⁵

- A. Crystalline syndiotactic polypropylene
 - B. Atactic polypropylene
- Polypropylenes obtained in the presence of catalytic systems acting with cationic mechanism

- A. Polypropylene obtained in the presence of the catalytic system $Al(C_2H_5)_2Cl_2 + TiCl_4$ (Al/Ti molar ratio = 1.5)¹⁰

- B. Polypropylene obtained in the presence of $AlCl_3$ ¹⁴

98-100%
~95

0-2
~5

Traces

~15

~20

~30

~10

~5

~10

~25

~30

~5

~5

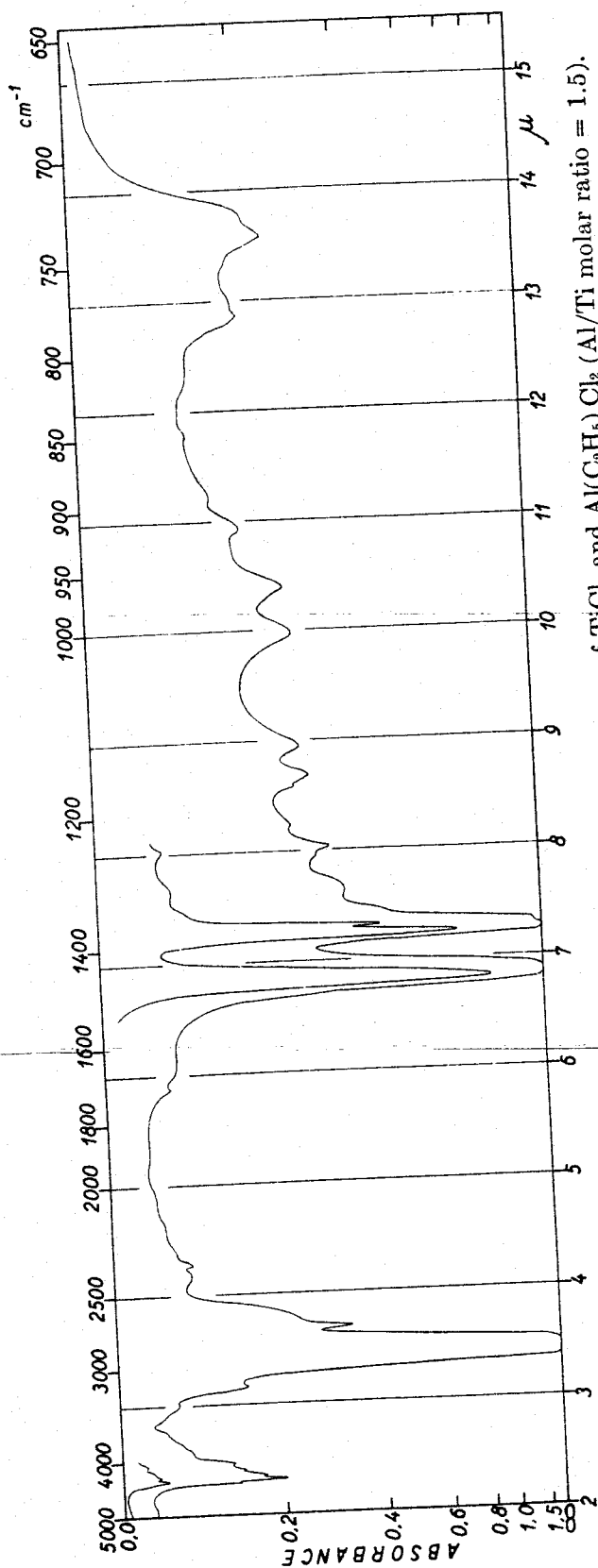
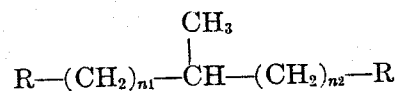


Fig. 2. Infrared spectrum of propylene polymer obtained in the presence of TiCl_4 and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ (Al/Ti molar ratio = 1.5).

The band at 1155 cm.^{-1} is in a very constant position, both for 3-methyl paraffins and 4-methyl paraffins and other substances containing the group



These include squalane (2,6,10,15,19,23-hexamethyltetracosane; API infrared spectrum no. 2290) and the polymer having the structure of the alternating ethylene-propylene copolymer obtainable by hydrogenation of 1,4-polyisoprene (Fig. 1).⁸ The position of this 1155 cm.^{-1} band is independent of the values of n_1 and n_2 , provided they are both equal to or higher than one. On the contrary, the position of the second band shifts in the range between 975 and 930 cm.^{-1} , depending on the values of n_1 and n_2 .

In 3-methyl paraffins and in such substances as 2,2,4-trimethylhexane and 3,3,5-trimethylpentane this band can be observed at about 965 cm.^{-1} , for 4-methyl paraffins it is seen at about 955 cm.^{-1} ; in squalane the band is at 930 cm.^{-1} , a position near that observed for the polymer, obtained by hydrogenation of polyisoprene (Fig. 1), having the structure of an alternating ethylene-propylene copolymer.

It is therefore evident that the shift of this band when observed in ethylene-propylene copolymers can give some indication of the distribution of propylene sequences in the copolymer. (Some experiments on this relationship presently being carried out appear quite promising.)

These bands, however, are not at all related to the isotacticity of polypropylene. (In fact, they are present also in the infrared spectrum of syndiotactic polypropylene.⁹) The fact that they are not practically present in propylene polymers obtained in the presence of cationic-type catalysts can be easily explained by the fact that the propylene units of these polymers do not have a regular head-to-tail enchainment and that such polymers contain many different units that, although derived from propylene, do not have the $-\text{CH}_2-\text{CH}(\text{CH}_3)-$ structure (Table I).

Figure 2 shows the spectrum of a propylene polymer obtained in the presence of a catalytic system formed by $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$ and TiCl_4 (Al/Ti ratio = 1.5) which, as is well known,^{10,11} is supposed to act through a cationic mechanism, due to the low Al/Ti ratio.

A band at 735 cm.^{-1} is noted which can be attributed to sequences of the $-(\text{CH}_2)_3-$ type, the concentration of which, on the basis of a comparison between the intensity of this band and of the band present in the spectrum of hydrogenated polyisoprene, can be calculated to be about 30%.

The band at 775 cm.^{-1} can be ascribed to structures of the $-\text{CH}(\text{CH}_2\text{CH}_3)-$ type. If the intensity of this band is compared with that present in the spectrum of polybutene-1, a concentration of about 20% can be calculated. The bands at 1120 and 750 cm.^{-1} can be attributed to structures of the $\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)-\text{CH}_2-$ type; by comparing the intensity of these bands with those present in the spectrum of an alternating ethylene-butene-2 copolymer,¹² a concentration of about 20% can

be calculated. From the bands at 1378 and 1245 cm.^{-1} the presence of about 10% of units of the $-\text{C}(\text{CH}_3)_2-$ type can be deduced.

These measures, although being only of an approximate character, lead to the conclusion that in the cationic type polymer under examination there are comparatively few propylene units of the $-\text{CH}(\text{CH}_3)-\text{CH}_2-$ type, having a regular head-to-tail enchainment.

By adopting a method of analysis used for ethylene-propylene copolymers¹³ based on the measurement of the band at 1155 cm.^{-1} , the presence of only 15% of these units can be deduced. We have obtained similar results also on examining a polymer obtained from propylene in the presence of AlCl_3 as catalyst (see Table I).^{4,14}

The results of the infrared examination of certain propylene polymers obtained through cationic polymerization are reported in Table I and compared with results for crystalline and amorphous polypropylenes obtained through anionic coordinated polymerization.

These considerations with respect to polypropylene can be applied also to ethylene-propylene copolymers. The presence of bands at 1155 cm.^{-1} and at about 970 cm.^{-1} does not indicate the presence of long sequences of isotactic propylene units, but only of propylene units of the $-\text{CH}(\text{CH}_3)-\text{CH}_2-$ type regularly enchainned with other propylene units or with ethylene units.

In the infrared spectra of copolymers obtained through anionic coordinated polymerization, bands are present at 1155 cm.^{-1} and in the range 970–930 cm.^{-1} . The intensity of these bands decreases with a decrease of the propylene content in the copolymer.

In copolymers which we have prepared using the catalytic system $\text{VCl}_4 + \text{SnPh}_4 + \text{AlBr}_3$ according to Phillips and Carrick,¹⁶ we have observed that these bands (comparatively weak) have an intensity corresponding to low propylene contents. But, in ethylene-propylene copolymers obtained with the aid of free radical catalysts¹⁷ these bands are not observed; this is because the number of $-\text{CH}(\text{CH}_3)-\text{CH}_2-$ groups in these copolymers is very small, much smaller in fact than the number that would result from the propylene content in the copolymers.

In ethylene-propylene copolymers obtained with the aid of catalysts formed by alkyl aluminum compounds and transition metal salts, the bands at 1155 and at about 970 cm.^{-1} should be considered as characteristic of the $-\text{CH}(\text{CH}_3)-\text{CH}_2-$ propylene units in random or block distribution. While variations in the propylene sequence distribution do not influence the position of the first band, they influence both position and form of the second band (Fig. 3).

As for the possibility of employing the band at 1155 cm.^{-1} to determine the propylene content in an ethylene-propylene copolymer, we have noted¹³ a relationship, not very far from linearity, between absorbance of the band at 1155 cm.^{-1} and contents $-\text{CH}(\text{CH}_3)-\text{CH}_2-$ propylene units.

The examination of different series of ethylene-propylene copolymers obtained by use of different anionic coordinated catalyst systems is now in

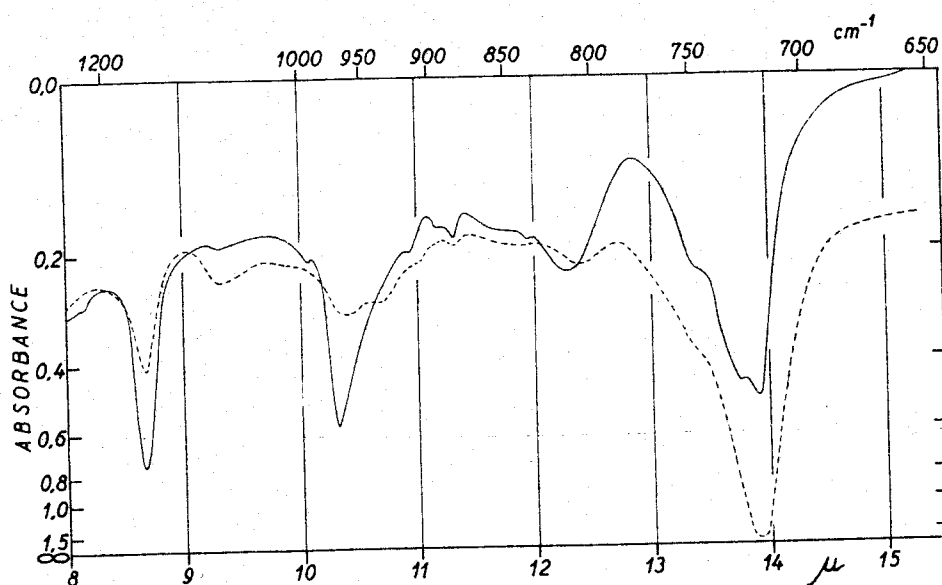


Fig. 3. Infrared spectra of ethylene-propylene copolymers having propylene sequences of different lengths. (—) long propylene sequences; (---) short propylene sequences.

progress, in order to establish whether and to what extent the absorbance of the band at 1155 cm.^{-1} is influenced by possible variations in the enchainment and distribution of the various monomer units.

We are also examining the absorbance of the bands used in other infrared methods of analysis of ethylene-propylene copolymers.¹⁸⁻²¹ We have noticed that the absorbance of the band at 1155 cm.^{-1} varies somewhat with the copolymerization catalyst used; however, the variations determined so far do not appear sufficient to prevent the possibility of using infrared methods of analysis based on this band.

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Résumé

Il est nécessaire de faire une distinction entre un polymère alpha-oléfinique "amorphe" et un polymère alpha-oléfinique "atactique". Le terme "atactique" doit s'appliquer uniquement aux polymères amorphes qui possèdent une régularité linéaire tête-à-queue et qui ont la même régularité chimique que les polymères tactiques correspondants dont ils diffèrent seulement par le manque de régularité stérique. On peut en avoir une interprétation claire par la présence de bandes à 1155 et 915 cm^{-1} dans le spectre infrarouge des polypropylènes isotactique et atactique. La présence de ces bandes est due à l'unité monomérique $-\text{CH}_2-\text{CH}-$ qui possède un arrangement régulier tête-à-queue.



L'absence de ces bandes dans les polymères de propylène obtenus au moyen de catalyseurs de type cationique dépend de la présence d'une très petite quantité d'unités monomériques de ce type. On peut conclure que la présence des deux bandes mentionnées ci-dessus dans le spectre infra-rouge des copolymères éthylène-propylène n'indiquent pas la présence de longues séquences de propylène du type isotactique, et par conséquent l'existence du copolymère à bloc, mais seulement la présence de l'unité monomérique mentionnée ci-dessus.

Zusammenfassung

Die Notwendigkeit, zwischen einem "amorphen" und einem "ataktischen" α -Olefinpolymeren zu unterscheiden, wird betont. Es ist angebracht, den Ausdruck "ataktisch" nur auf diejenigen amorphen, linearen, regelmässigen Kopf-Schwanzpolymeren zu beschränken, welche dieselbe chemische Regelmässigkeit wie die entsprechenden ataktischen Polymeren besitzen, von welchen sie sich nur durch den Mangel an sterischer Regelmässigkeit unterscheiden. Eine klare Zuordnung der Anwesenheit von Banden bei 1155 und 915 cm^{-1} im IR-Spektrum von isotaktischen und ataktischen Polypropylenen wird gegeben. Die Anwesenheit dieser Banden ist durch die $-\text{CH}_2-\text{CH}-$ mono-



merieinheit mit einer regelmässigen Kopf-Schwanzanordnung bedingt. Das Fehlen dieser Banden in Propylenpolymeren, die mit Hilfe kationischer Katalysatoren erhalten wurden, wird auf die Gegenwart einer nur sehr geringen Menge von Monomereinheiten dieses Typs zurückgeführt. Schliesslich kommt man zu dem Schluss, dass die Anwesenheit der oben erwähnten Banden im IR-Spektrum von Äthylen-Propylenkopolymeren nicht für das Vorhandensein langer Propylensequenzen vom isotaktischen Typ und daher auch nicht für die Existenz eines Blockcopolymeren spricht, sondern nur für die Anwesenheit der oben erwähnten Monomereinheit.

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