Stereospecific Ring Cleavage Homopolymerization of Cycloolefins and Structural Examination of the Resulting Homologous Series of Linear Crystalline trans Polyalkenamers

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Herrn Kollegen W. KERN mit den besten Wünschen zum 60. Geburtstag gewidmet

SUMMARY:

Unsubstituted cycloolefins can be polymerized *via* ring cleavage to high molecular weight, linear, unsaturated polyalkenamers having the structure $(-CH=CH-(CH_2)_n-)_p$ using catalyst systems prepared from tungsten or molybdenum salts and organo-aluminum compounds. The polymerization of cyclobutene to polybutenamer (1,4 poly-butadiene) and of cyclopentene to polypentenamer is known. In the present paper the polymerizations of cyclohexene, cycloheptene, *cis* cyclooctene, and *cis/trans* cyclododecene are investigated in the presence of the same catalyst systems. While cyclohexene, due to the high stability of its ring, does not yield high molecular weight products, the other higher cycloolefins could be polymerized with good conversions to pure linear polyalkenamers.

The resulting linear polyalkenamers are built up of head-to-tail linked monomeric units containing mainly *trans* double bonds. The chemical and the pronounced steric regularity cause the crystallizability of these polymers.

The investigation of the crystal structure shows that the polymers, in which the methylene sequence n is an odd number, crystallize in orthorhombic unit cells, similar to those of the normal modification of polyethylene and of the *n*-alkanes. The *trans* polyalkenamers, in which the methylene sequence n is an even number, on the contrary, crystallize in monoclinic and in triclinic unit cells. *Trans* polyalkenamers having an odd methylene sequence are well distinguished from those with an even methylene sequence also in the completely different conformation of the polymer chains in the crystal.

Interesting correlations could be observed on the *trans* polyalkenamers. The melting temperatures depend on the length of the structural unit.

ZUSAMMENFASSUNG:

Unsubstituierte Cycloolefine können mit Katalysatoren aus Wolfram- oder Molybdän-salzen und aluminiumorganischen Verbindungen unter Ringspaltung zu hochmolekularen, linearen, ungesättigten Polyalkenameren der Formel $(-CH=CH-(CH_2)_n-)_p$ polymeri-sieren. Nachdem früher die Polymerisation des Cyclobutens zu Polybutenamer (1,4-Poly-

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butadien) und des Cyclopentens zu Polypentenamer beschrieben wurde, wird hier die Polymerisation von Cyclohexen, Cyclohepten, *cis*-Cycloocten und *cis/trans*-Cyclododecen in Gegenwart derselben Katalysatorsysteme untersucht. Während das sehr beständige Cyclohexen keine hochmolekularen Produkte gibt, konnten die anderen höheren Cycloolefine mit guten Ausbeuten zu reinen linearen Polyalkenameren polymerisiert werden.

Die erhaltenen, linearen Polyalkenameren bestehen aus kopf-schwanz-verknüpften Monomereinheiten und besitzen vornehmlich *trans*-Doppelbindungen. Die chemische und die weitgehende sterische Strukturregelmäßigkeit äußern sich auch in der Kristallisierbarkeit dieser Polymeren.

Die Untersuchung der Kristallstruktur zeigt, daß die Polymeren mit einer ungeradzahligen Methylensequenz n in rhombischen Elementarzellen kristallisieren, ähnlich der normalen Modifikation des Polyäthylens und der *n*-Alkane. Die *trans*-Polyalkenameren mit einer geradzahligen Methylensequenz n kristallisieren dagegen in monoklinen und triklinen Elementarzellen. *Trans*-Polyalkenamere mit ungerader Methylensequenz unterscheiden sich von denen mit gerader Methylensequenz auch in der vollständig verschiedenen Konformation der Polymerenketten im Kristallgitter.

Interessante Gesetzmäßigkeiten zeigen die Schmelztemperaturen der *trans*-Polyalkenameren in Abhängigkeit von der Länge der Struktureinheit.

In some recent publications we reported the polymerization of cyclobutene[1-3] and cyclopentene[4] to linear unsaturated high polymers having the structure of polyalkenamers[*]. This type of polymerization occurs *via* ring cleavage of the cycloolefin according to scheme (1):

$$p \; HC = CH \atop (CH_2)_n \;\; \rightarrow \;\; (-CH=CH-(CH_2)_n-)_p \tag{1}$$
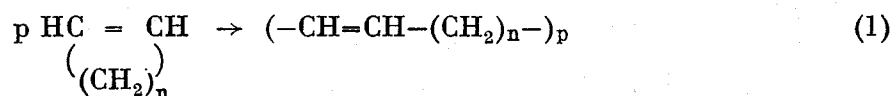
Thus, cyclobutene could be converted to polymers having the structure of 1,4 polybutadienes (polybutenamers) and cyclopentene to polypentenamers.

The fact that some catalysts of the basic, acidic or radical types appeared practically ineffective, while some other systems based on transition metals strongly promoted such polymerizations, induced us to attribute to these polymerizations an anionic co-ordination mechanism. In fact, positive results were obtained both with catalyst systems prepared from tungsten, molybdenum, and titanium salts and organometallic compounds and (in the case of cyclobutene) also with the ruthenium trichloride/protic solvent system. The catalytic activity as well as the stereospecificity of these systems vary remarkably with the transition metal

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[*] We adopt the official IUPAC nomenclature[5].

and with the particular cycloolefin. Table 1 summarizes the main results previously obtained by us.

These results indicate that the possibility to convert cycloolefins to polyalkenamers is thermodynamically influenced by the different ring tension of the various cycloolefins, and by the type of co-ordination established between the catalyst and the cycloolefin. In this paper we extend our investigations to the higher terms of the homologous series of cycloolefins, the ring tension of which is much lower than that of cyclobutene and even than that of cyclopentene.

Table 1. Characteristic results previously obtained in the ring cleavage polymerization of cyclobutene and cyclopentene

Cycloolefin	Catalyst system	% Structural units contained in the polymer		
		Alkenamer $(-CH=CH-(CH_2)_n-)$		Cycloalkylene $(-CH-CH-)$ $\quad\quad(\quad\quad)$ $\quad\quad(CH_2)_n$
		trans	cis	
Cyclobutene	$TiCl_4/Al(C_2H_5)_3$[a]	65	30	5
	$WCl_6/Al(C_2H_5)_3$[a]	40	30	30
	$MoCl_5/Al(C_2H_5)_3$[a]	30	30	40
	$RuCl_3/H_2O$[c]	50	50	0
	$RuCl_3/C_2H_5OH$[d]	100	0	0
Cyclopentene	$TiCl_4/Al(C_2H_5)_3$[b]	97	3	0
	$WCl_6/Al(C_2H_5)_3$[b]	90	10	0
	$MoCl_5/Al(C_2H_5)_3$[b]	1	99	0
	$RuCl_3/C_2H_5OH$[d]	no polymerization occurs		

[a] At $-20\,°C$. in toluene; [b] at $-30\,°C$. in the absence of diluent; [c] at $+50\,°C$.; [d] at $+20\,°C$.

Results of the Polymerizations

The following cycloolefins were examined: cyclohexene, cycloheptene, cis cyclooctene, and a 1:2 mixture of cis and trans cyclododecene. All these cycloolefins possess an internal double bond of the cis type, apart from the fraction of trans isomer contained in cyclododecene.

In fact, only the cis isomer is known for the lower cycloolefins going from cyclopropene to cycloheptene. In the case of larger rings, starting from cyclooctene, both cis and trans isomers are known, but with increasing ring size the relative thermodynamic stability of the trans isomer generally increases, while that of the cis isomer simultaneously decreases.

Considering that the cycloolefins studied here exhibit closer analogy, from a thermodynamic point of view, to cyclopentene than to cyclobutene, we employed for our investigations those catalysts, which had furnished the best results for the former monomer, *i.e.*, the three following catalyst systems based on 6th group metal halides:

$$WCl_6/Al(C_2H_5)_3; \quad WCl_6/Al(C_2H_5)_2Cl; \quad MoCl_5/Al(alkyl)_3$$
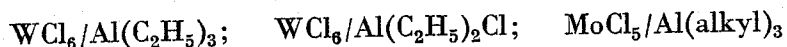
Some of the most significant data obtained from these polymerization runs are summarized in Table 2. We wish to point out some of the most remarkable results:

The only cycloolefin (among those examined), that did not yield high polymers with the aid of the above mentioned catalysts, is cyclohexene.

On the contrary, all other cycloolefins examined could be polymerized to linear polyalkenamers according to Eq. (1). By adopting suitable conditions (temperature, catalyst nature, and composition) it was possible to obtain linear polyalkenamers from cycloheptene, cyclooctene, and cyclododecene with good conversions (50 % and higher), analogously to what previously[4] observed for cyclopentene. However, the polymerization conditions being the same, the polymerization rate and the polymer conversion generally decrease considerably with increasing ring size. This observation points out the importance of the thermodynamic factor due to the ring tension. In the polymerization of the vinyl monomers, the disappearance of one double bond and the simultaneous formation of one new single bond per monomeric unit strongly favours the polymerization from an energetic point of view. On the contrary, in the formation of linear polyalkenamers from cycloolefins, every cleavage of one single bond in the ring is balanced by the formation of one new single bond in the polymer chain. The main energy contribution, which favours the ring cleavage polymerization of cycloolefins, is therefore the gain of the ring tension energy. This is considerable in cyclobutene, low in cyclopentene, even lower in cycloheptene, in *cis* cyclooctene, and in *cis* cyclododecene, and virtually null in cyclohexene.

In cyclohexene the conformation of the carbon atoms bound to each other by a single bond is completely staggered. Such a conformation is as stable as that existing in the corresponding linear unsaturated chain. It follows that in cyclohexene no thermodynamic factor favours the ring cleavage to polyhexenamer. However, another thermodynamic factor, which could favour the ring cleavage of the cycloolefins to polyalkenamers, should be mentioned. It is the transformation of a *cis* double bond of the

Table 2. Polymerization of higher cycloolefins in the presence of catalysts based on tungsten or molybdenum salts

Cycloolefin	Catalyst system [a]	Moles monomer / Moles W or Mo	Conditions [b] (hrs./°C.) (hrs./°C.)	Conversion (%)	X-rays examination	$[\eta]$ dl./g. [c]	% Structural units contained in the crude polymer [d] Alkenamer $(-CH{=}CH{-}(CH_2)_n{-})$ trans	cis	Cycloalkylene $(-HC{-}CH{-})(CH_2)_n$
Cyclohexene	$WCl_6/Al(C_2H_5)_2Cl$	25	3/−30 + 48/20	6	no high mol.-weight polymers are obtained				0
Cycloheptene	$WCl_6/Al(C_2H_5)_2Cl$	40	3/−30 + 63/20	18	crystalline	0.3	94	6	0
Cycloheptene	$WCl_6/Al(C_2H_5)_2Cl$	500	5/−30 + 60/20	7	crystalline	1.05	91	9	0
Cycloheptene	$WCl_6/Al(C_2H_5)_3$	40	5/−30 + 13/20	3	crystalline	0.4	85	15	0
Cycloheptene	$MoCl_5/Al(C_2H_5)_3$	40	3/−30 + 3/20		crystalline	n.d.[f]	93	7	0
cis Cyclooctene	$WCl_6/Al(C_2H_5)_3$	300	3/−30 + 14/20	23	crystalline	2.4	85	15	0
cis Cyclooctene	$WCl_6/Al(C_2H_5)_3$	300	1/−20 + 69/30	60	slightly crystalline	n.d.[f]	75	25	0
cis/trans Cyclo-dodecene (1:2) [e]	$WCl_6/Al(C_2H_5)_2Cl$	500	23/−40	5	crystalline	n.d.[f]	80	20	0
cis/trans Cyclo-dodecene (1:2)	$WCl_6/Al(C_2H_5)_2Cl$	500	5/−25 + 16/20	34	crystalline	2.15	94	6	0

[a] Molar ratio $Al(C_2H_5)_2Cl/WCl_6 = 5$; $Al(C_2H_5)_3/WCl_6 = 2.5$; $Al(alk)_3/MoCl_5 = 2.5$. [b] In the absence of a diluting medium, if not otherwise indicated. The low temperature period is immediately followed by a higher temp. period. [c] In toluene at 30 °C., except poly-dodecenamer measured in tetralin at 100 °C. [d] I.R. measurement of the structural units: molar absorptivity of cis double bonds $\varepsilon_{7,12}$ $(CCl_4) = 11$; 8; 8 [moles^{-1}·cm^{-1}·l.] (for dodecenamer, octenamer, heptenamer respectively); trans double bonds $\varepsilon_{10,35}$ $(CS_2) = 133$; 135; 152; respectively. [e] In the presence of 25% of toluene as diluent. [f] Not determined.

cycloolefin into a *trans* double bond in the linear polymer chain. In practice, the energy gain due to such a transformation is rather low and evidently results insufficient to determine the polymerization *via* ring opening of cyclohexene.

The polymers obtained from cycloheptene, cyclooctene, and cyclododecene in the presence of the above catalysts do not contain cycloalkylene units, *i.e.*, structural units originated by the opening of the double bond. They can therefore be defined pure polyalkenamers, in which the recurring units are all of the type indicated by Eq. (1). This fully agrees with what is already observed[4] for cyclopentene.

In the here described linear polyalkenamers the monomeric units are linked together in the normal head-to-tail arrangement. In the case of the *trans* polypentenamer obtained from cyclopentene we could already demonstrate[4] the existence of this type of linkage both by chemical methods (*e.g.*, by ozonization and examination of the degradation products) and by the crystal structure determination and IR analysis. Now the last two methods have been employed for the determination of the type of enchainment of the monomeric units, recurring in the present polyalkenamers. The head-to-tail linkage, when it results from a ring cleavage in defined position, is in fact characterized by the existence of a constant length of the methylene sequence between two subsequent double bonds: five in the case of polyheptenamer, six in that of polyoctenamer, and ten in that of polydodecenamer. The length of the methylene sequence in the case of head-to-head tail-to-tail linkages, on the contrary, depends on the site where the ring opens. In the case of cycloheptene, *e.g.*, three single bonds can in theory be opened. In the resulting three types of head-to-head tail-to-tail polymers one must expect an alternation of methylene sequences of two different lengths. The methylene sequences in these three regular polyheptenamers should therefore be: 0 and 10, or 2 and 8, or 4 and 6.

All these three cases of regular head-to-head tail-to-tail polyheptenamers, as well as the corresponding polyoctenamers and polydodecenamers, could be excluded on the basis of the crystal structure examination, but also owing to the absence of certain absorption bands in the IR spectra. The head-to-tail arrangement is, on the contrary, in all the polyalkenamers here described the only consistent with the results of the two methods.

With regard to the stereospecificity of these polymerizations there is not such a marked analogy with the results obtained in the polymeriza-

tion of cyclopentene. We remind that the catalysts $WCl_6/Al(C_2H_5)_2Cl$ and $WCl_6/Al(C_2H_5)_3$ polymerize cyclopentene essentially to *trans* polypentenamer, while the system $MoCl_5/Al(C_2H_5)_3$ promotes the formation of pure *cis* polypentenamer. In the case of cycloheptene, cyclooctene, and cyclododecene the molybdenum-containing system is much less active than that containing tungsten. However, both catalysts promote the formation of polyalkenamers, in which the double bonds are essentially or prevailingly of the *trans* type. Only by adopting particular experimental conditions we could obtain also from these higher cycloolefins polyalkenamers, in which the double bonds are prevailingly of the *cis* type. We shall deal with these particular techniques in another paper, since we wish to devote this publication to the *trans* polyalkenamers. In any case, we observe that the tendency to form essentially *trans* tactic polyalkenamers is much more specific for the higher cycloolefins than for cyclopentene. A possible explanation of this fact may be based on the lower energy level of a crystalline aliphatic chain containing *trans* double bonds compared with that of an amorphous aliphatic chain containing *cis* unsaturations. *Cis* polyalkenamers melt in fact at very low temperatures.

Double bonds of the vinyl type are virtually absent in the high molecular weight polyalkenamers, while they are present in the low molecular weight polyalkenamers in so low an amount that one can consider them to be endgroups. This indicates that no structural unit corresponding to the recurring units of 1,2 polybutadiene are present in our polyalkenamers, and this is a strong evidence for the perfect linearity of these polymers.

At the same time, the presence of vinyl endgroups constitutes a further evidence for our hypothesis[1, 3, 4] that the site of the opening of the cycloolefin ring in this type of polymerization is the single bond adjacent to the double bond.

The polymerization of cyclododecene to polydodecenamer is of particular interest, since this is the only examined cycloolefin in which the normally recurring *cis* isomer is accompanied by a fraction of the *trans* isomer. In this case we observed that the two isomers copolymerize yielding the same type of monomer unit.

Physical Properties and Crystal Structure of the trans Polyalkenamers

The possibility to polymerize cycloolefins to linear *trans* polyalkenamers makes now available a series of stereoregular linear polyhydrocarbons, in which the structural units constitute a homologous series. The homo-

logy of this polymer series does not derive from the different length of the side group, as, *e.g.*, in many series of polymers derived from vinyl monomers or from conjugated diolefins, but from the different length of the methylene sequence of each structural unit along the main chain. In the general formula of polyalkenamers, the length of the methylene sequence n of each structural unit, that is the number of methylene groups between two subsequent HC=CH double bonds, directly depends on the size of the starting cycloolefin.

The term in which n = 4 (polyhexenamer) is not obtainable by the same route, since cyclohexene, as seen above, cannot be polymerized by ring cleavage. However, polyhexenamer can be obtained, according to Natta et al.[6], by stereospecific alternating copolymerization of butadiene with ethylene, according to Eq. (2):

$$p\ CH_2{=}CH{-}CH{=}CH_2 + p\ CH_2{=}CH_2\ \rightarrow\ (-CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH_2{-})_p \quad (2)$$
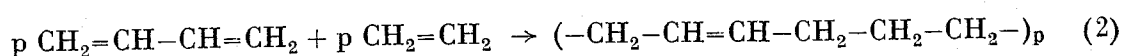
Since also the polymer obtained according to Eq. (2) essentially has double bonds of the *trans* type, we have now available the series of *trans* polyalkenamers listed in Table 3.

All linear polyalkenamers, obtained from cycloolefins and having a *trans* double bond content higher than 75 % of the total amount of double

Table 3. *Trans* polyalkenamers and methods for their preparation

Trans polyalkenamer	Length of methylene sequence n according to $(-CH{=}CH{-}(CH_2)_n{-})_p$	Method of preparation
Polyacetylene	0	polymerization of acetylene
Polypropenamer	1	still unknown
1,4 Polybutadiene	2	polymerization of butadiene
Polypentenamer	3	ring cleavage polymerization of cyclopentene
Polyhexenamer	4	alternating butadiene-ethylene copolymerization
Polyheptenamer	5	ring cleavage polymerization of cycloheptene
Polyoctenamer	6	ring cleavage polymerization of *cis* cyclooctene
Polydodecenamer	10	ring cleavage polymerization of *cis/trans* cyclododecene
Polyethylene	∞	polymerization of ethylene

bonds, are crystalline by X-ray examination. When their *trans* double bonds reach or exceed 85 %, they are highly crystalline and furnish excellent fibre spectra, rich in sharp reflections, which allow the determination of the identity period and of the crystal structure. The *trans* tactic polyalkenamers from cycloolefins having a number n > 4 of methylene groups between two subsequent double bonds give also well defined powder spectra. *Trans* polypentenamer (n = 3), on the contrary, behaves at room temperature as an elastomer: it is generally amorphous, but it crystallizes either when stretched (even at room temperature) or cooled below −20 °C. Fig. 1 reports the powder spectra of the various *trans* polyalkenamers here discussed and those of the polymers which can be considered to belong to the homologous series: the alternating *trans* tactic butadiene-ethylene copolymer (*trans* polyhexenamer), *trans*-1,4 polybutadiene, and polyethylene (orthorhombic modification).

When considering the physical properties and the crystal structure of the homologous series of *trans* polyalkenamers, we must bear in mind an important feature: the molecular weights of all these polymers are comprised in a field in which there is no significant variation of the physical and structural properties in the solid state in dependence on the molecular weight. All the differences in the above properties between the single terms of the series are virtually due to the different length of the structural unit of the polymer chains, *i.e.*, to the number n of methylene groups between two subsequent double bonds.

A first systematic difference distinguishes the polymers in which the methylene sequence n is even from those in which n is odd. This differentiation clearly results when comparing the identity periods of the various polymers (Table 4). In fact, the polymer terms, in which n is even, always contain only one structural unit in the identity period, while the terms, in which n is odd, always contain two of them. This is valid independently of the modification, in which the polymers crystallize.

The differences between the two series of *trans* polyalkenamers also concerns the space packing of the chains in the crystal lattice. In previous publications[4,7] we had already reported that *trans* polypentenamer crystallizes in an orthorhombic unit cell, which is very similar to that of the usually stable modification of polyethylene[8]. Now an analogous crystal structure has been found by us for another odd *trans* polyalkenamer: *trans* polyheptenamer (n = 5) also crystallizes in an orthorhombic unit cell having the same *a* and *b* constants as polyethylene. Also the space packing of the chains of *trans* polyheptenamer is quite similar to that known from *trans* polypentenamer and from polyethylene.
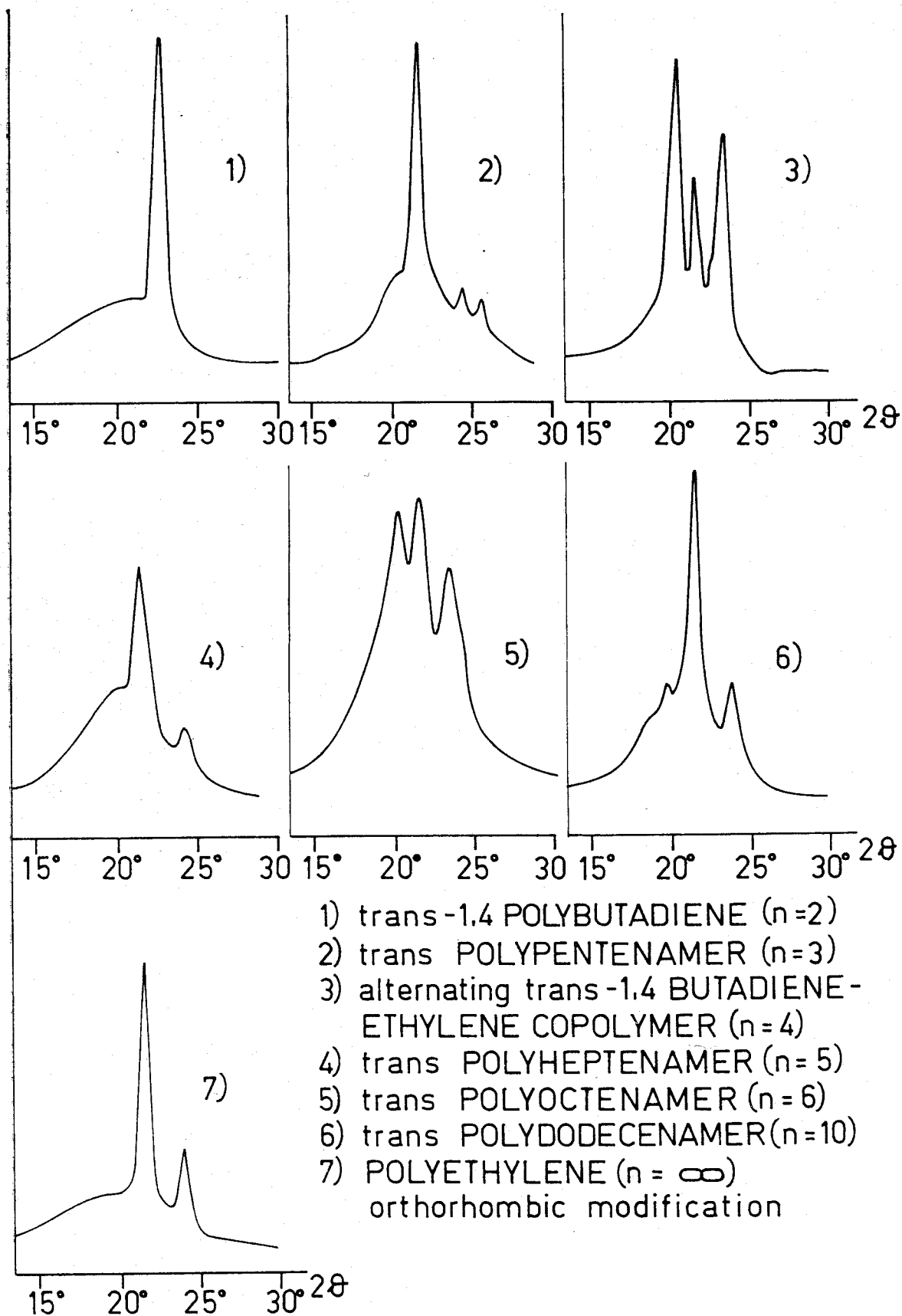
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1) trans -1.4 POLYBUTADIENE (n =2)
2) trans POLYPENTENAMER (n=3)
3) alternating trans -1.4 BUTADIENE -
   ETHYLENE COPOLYMER (n = 4)
4) trans POLYHEPTENAMER (n= 5)
5) trans POLYOCTENAMER (n = 6)
6) trans POLYDODECENAMER(n =10)
7) POLYETHYLENE (n = ∞)
   orthorhombic modification

Fig. 1. X-ray powder spectra of a series of *trans* polyalkenamers corresponding to the general formula $(-CH=CH-(CH_2)_n-)_p$ and of the orthorhombic modification of polyethylene (CuK$_\alpha$ radiation, GEIGER-counter recorded at room temperature except *trans* polypentenamer which was recorded at $-50\,°C$.)

Table 4. Crystallographic identity periods of *trans* polyalkenamers of the homologous series $(-CH=CH-(CH_2)_n-)_p$

Trans polyalkenamer	Methylene sequence n	Crystallographic identity period (Å)	Structural units contained in the identity period
1,4 Polybutadiene	2	4.85	1
Polypentenamer modification I .... (orthorhombic)	3	11.9	2
Polyhexenamer[a) modification III modification IV (monoclinic)	4	n.d.[b) n.d.	n.d. n.d.
Polyheptenamer modification I .... (orthorhombic)	5	17.1	2
Polyoctenamer modification III modification IV (monoclinic)	6	9.85 9.85	1 1
Polydodecenamer modification III modification IV (monoclinic)	10	14.85 14.85	1 1
Polyethylene orthorhombic modification .... monoclinic or triclinic modific.	∞	2.534 2.53	2[c) 2[c)

a) Alternating butadiene-ethylene copolymer.
b) n.d., not determined.
c) We consider structural unit the CH_2 group.

Moreover, the conformation of the polymer chains in the crystals is exactly the same in both odd *trans* polyalkenamers studied so far. Both *trans* polypentenamer and *trans* polyheptenamer chains in the orthorhombic lattice are characterized by a twofold screw axis parallel to the chain axis, by a symmetry center on each double bond, and by a mirror plane perpendicular to the twofold screw axis $(S(2/1)m$ symmetry[*)]). This crystalline form of the odd *trans* polyalkenamers will be denoted by "modification I", though it is the only so far observed with certainty in the odd series. However, another chain conformation of odd *trans* polyalkenamers is predictable. It is characterized by a glide plane parallel to the *c* axis, by a symmetry center on each double bond, and by a twofold axis normal to the glide plane $(t\,i\,c$ symmetry[*)]). Although we never

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*) According to the classification proposed by CORRADINI[9)].

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could isolate with certainty such a crystalline modification, some IR absorption bands in especially treated *trans* polyheptenamers possibly indicate its existence. This predictable modification will be called "modification II".

Also the *trans* polyalkenamers having an even number of methylene groups between two subsequent double bonds constitute, with regard to their crystal structure, a series with common properties, which markedly differ from those of the odd series. The crystallographic properties of the even series are more complex than those of the odd series, because all polymer terms so far examined (polyhexenamer, polyoctenamer, polydodecenamer) are polymorphous. We now recognize for all three polymers two main crystalline modifications, both containing only one structural unit in the identity periods, which are equal in length.

Only one type of chain conformation can be foreseen for the series of even *trans* polyalkenamers, in contrast to what already stated for the odd series. The only symmetry element of these chains is a symmetry center (*t i* symmetry [*]). Hence, the differences between the various crystalline modifications of the even series only concern the crystal symmetry and the packing of the chains.

One of the two main crystalline modifications of the even series is characterized by two main reflections, appearing in the powder spectra (CuK$_\alpha$ radiation) at 2ϑ angles of about 20° and 23.5°. This crystalline form will be denoted by "modification III" (in order to avoid confusions, the denominations "modification I" and "modification II" will be reserved for the crystalline forms of the odd *trans* polyalkenamers). It can be clearly observed in the powder spectra of *trans* polyhexenamer [**], of *trans* polyoctenamer, and, though less markedly, in that of *trans* polydodecenamer (Fig. 1). Modification III is most likely triclinic. It is usually prevailing in the lower terms of the series (polyhexenamer, polyoctenamer), while it is usually present in small quantity in the higher term of the series by us examined (polydodecenamer). However, modification III can be obtained virtually in the pure state also in the case of *trans* polydodecenamer by crystallization from benzene solution followed by stretching of the resulting film in the presence of residual benzene. The well oriented fibre spectrum of modification III of trans polydodecenamer is given in Fig. 2.

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[*] According to the classification proposed by CORRADINI[9].
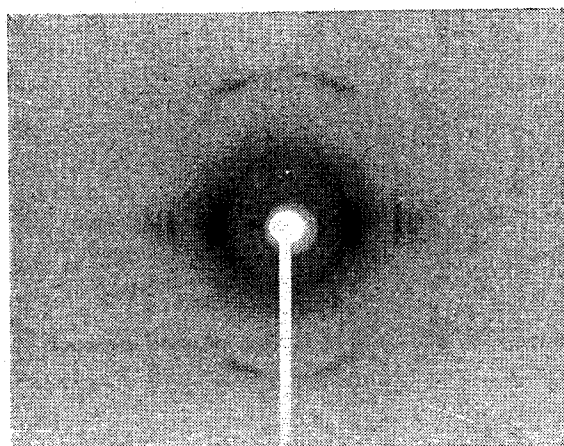
[**] Prepared according to [6].

Fig. 2. Fibre spectrum of modification III of *trans* polydodecenamer (CuK$_\alpha$ radiation)

The other main crystalline modification, which is present in all examined terms of even *trans* polyalkenamers, will be called "modification IV". It is characterized by a main reflection, appearing in the powder spectra (CuK$_\alpha$ radiation) at a 2ϑ angle of about 21.5° (Fig. 1). Modification IV normally prevails in the *trans* polydodecenamer and can be obtained virtually in the pure state in well oriented fibre spectra (Fig. 3). The unit cell of this modification is monoclinic. Also *trans* polyoctenamer could be obtained in the pure state in the crystal modification IV, by crystallization from benzene solution and stretching of the resulting film
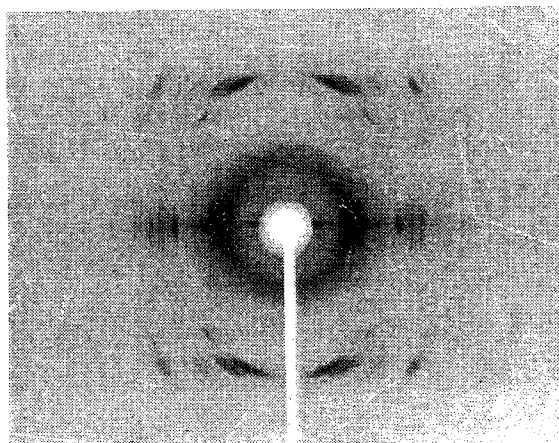

Fig. 3. Fibre spectrum of modification IV (monoclinic) of *trans* polydodecenamer (CuK$_\alpha$ radiation)

in the presence of residual benzene. On the contrary, by stretching of a molded film, crystal modification III of *trans* polyoctenamer is obtained. The crystalline modification IV of the even *trans* polyalkenamers has revealed close similarities with the modification I of the odd series both from a crystallographic point of view and with regard to certain physical properties, with which we shall deal below.

Besides the just mentioned two main modifications of even *trans* polyalkenamers, further more unstable crystalline modifications exist. In the fibre spectra of some especially treated *trans* polyoctenamers we could clearly recognize one of these modifications. Its structure, however, was as yet not elucidated. Further examinations are in progress in our laboratories on the crystal structure of the various *trans* polyalkenamers here discussed and on some other terms of the series so far unknown, and will be published later in more detail.

Trans-1,4 polybutadiene and *trans* polyacetylene, which can be considered part of the series of *trans* polyalkenamers, do not show a marked analogy, from the crystallographic point of view, with the other terms. Only the number of structural units contained in the identity period (Table 4) of *trans* polybutadiene is in agreement with the other terms.

The stereoregularity of the chains of the *trans* polyalkenamers also appears when comparing the IR spectra of the polymers in the crystalline and in the melted state. This comparison reveals a series of absorption bands due to the crystallinity of the chains in characteristic positions of the spectra of all examined *trans* polyalkenamers as well as in that of the crystalline alternating *trans* tactic 1,4 butadiene-ethylene copolymer. The most characteristic of these bands appears at 9.35 μ. A detailed study on these "crystallinity" bands is in progress and will be published in a near future.

Interesting results could also be drawn from the comparison of the melting temperatures of the various *trans* polyalkenamers. The X-ray method of the disappearance of the last reflection due to the crystallinity of a given modification was generally used, except in the case of *trans* polypentenamer, where the dilatometric technique was employed (Table 5).

The experimental values were plotted in a diagram (Fig. 4), in which the ordinate indicates the melting temperature and the abscissa the reciprocal value of the length of the structural unit[*]. A straight line results for all *trans* polyalkenamers, in which the methylene sequence $n \geqslant 3$ ($N \geqslant 5$). The values corresponding to the melting temperatures of *trans*-1,4 polybutadiene[10] (145 °C.) and of *trans* polyacetylene[11] (decomposes at high temperature before melting) are completely outside of this straight line. The different behaviour of these two polymers, which

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[*] In the 1/N value, reported in abscissa, N represents in the case of *trans* polyalkenamers the number of methylene groups of a sequence plus 2 ($N = n + 2$), in order to take into account the two carbon atoms of the double bond of the structural unit. In the case of *n*-alkanes and its derivatives N = total number of C-atoms of the molecules.

Table 5. Melting temperatures of the various crystalline modifications of *trans* polyalkenamers

Trans polyalkenamer[a]	Crystalline modification	Melting temp.[b] (°C.)
Polybutenamer (1,4- Polybutadiene)	?	145
Polypentenamer	I, orthorhombic	23
Polyhexenamer	III	61
(alternating butadiene-ethylene copolymer) .	IV, monoclinic	41
Polyheptenamer	I, orthorhombic	51
Polyoctenamer............................	III	67
	IV, monoclinic	62
Polydodecenamer	III	?
	IV, monoclinic	80

a) The melting temperatures of polypentenamer, polyheptenamer, polyoctenamer, and polydodecenamer refer to polymers containing from 6 to 10% *cis* double bonds as sterical impurity; that of polyhexenamer refers to a polymer containing a small excess of ethylene units, with respect to the 1,4 butadiene units, as chemical impurity.

b) Determination of the melting temperatures by X-ray method, except for polypentenamer, for which the dilatometric method was used.

is consistent with what above stated with regard to their crystal structure, is most likely due to the small distance between two subsequent double bonds, which allows their mutual influence. In the case of polyacetylene the methylene sequence is absent and the double bonds become conjugated, resulting in completely different properties, as indicated, *e.g.*, by its semiconductivity. It is, on this regard, not infrequent that the first terms of a homologous series exhibit properties, which are distinctly different from those of the other terms.

By extrapolating the straight line of Fig. 4 to the $N = \infty$ value, corresponding to polyethylene, one finds that the ordinate is cut at a point corresponding to a melting temperature of about 123 °C. This value seems reasonable if one considers that the investigated polyalkenamers contain a small amount of irregularities, which most likely lower the melting temperatures. In fact, the *trans* polyalkenamers derived from cycloolefins contain some percent of *cis* double bonds, and the *trans* polyhexenamer (alternating 1,4 butadiene-ethylene copolymer) a small excess of monomeric units derived from ethylene. One can therefore predict that a curve, refering to chemically and sterically pure linear *trans* polyalkenamers may be shifted some degrees higher and may cut the ordinate at a point, corresponding to a real linear polyethylene (about 130 °C.).
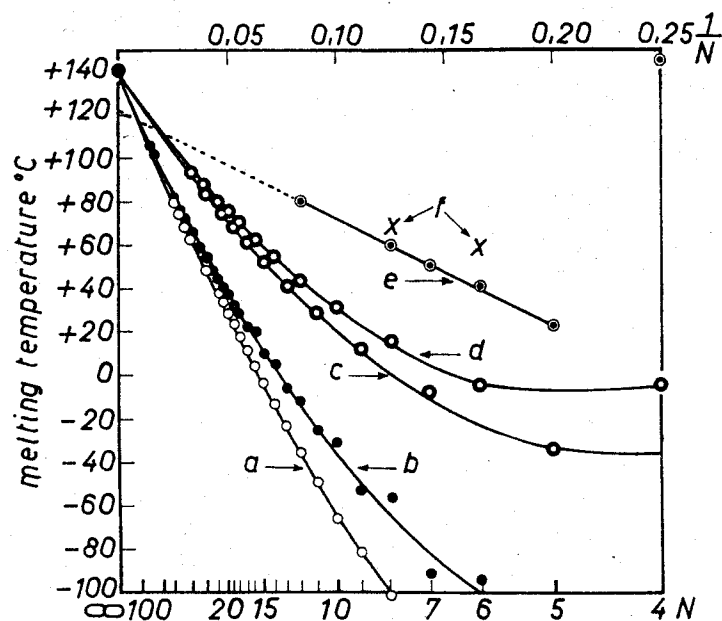
Fig. 4. Variation of the melting temperatures in function of the reciprocal value of the chain length, or respectively of the length of the structural unit, in some homologous series of aliphatic compounds and in the series of trans polyalkenamers

a = α-n-alkenes; b = n-alkanes; c = odd fatty acids; d = even fatty acids; e = odd and even trans polyalkenamers (modifications I and IV, respectively); f = even trans polyalkenamers (modification III). N = total number of carbon atoms of the chain or of the structural unit of the trans polyalkenamers

The slope of the m.p. vs. $1/N$ curve for trans polyalkenamers confirms the above statement that the melting temperatures of the trans polyalkenamers only depend on the length of the structural unit, provided that the molecular weights of the various terms can be considered the same and consequently without influence on the physical properties in the solid state.

Another factor must be taken into account when evaluating the curve relative to trans polyalkenamers. The melting temperatures reported in said curve refer to two different crystalline modifications. The melting points of the odd trans polyalkenamers and of polyethylene are those of polymers having analogous orthorhombic unit cells (modification I), whereas those of the even terms of the series correspond to polymers having analogous monoclinic unit cells (modification IV). It is surprising that two series of compounds, having different crystal symmetry, behave in such an analogous manner, but it confirms what already stated, that the structures of modifications I and IV are very similar both with regard to the packing of the macromolecules and from an energetic point of view, even if the symmetries of the unit cells and of the molecules are different. The energy level and the type of packing of the even trans poly-

alkenamers in the modification III, on the contrary, are very different from those of modifications I and IV. This observation is now confirmed by the distinctly different melting temperatures of these polymers when they crystallize in modification III (Table 5).

Comparsion of the Physical Properties of the Series of Crystalline Trans Polyalkenamers with those of Homologous Series of Linear Organic Molecules

It may be of interest to compare some physical properties of the crystalline *trans* polyalkenamers with those of other linear compounds, the limiting term of which ($N = \infty$) can also be considered to be polyethylene. The *trans* polyalkenamers can be compared, e.g., with the series of polyethers $(-O-CH_2)_n-)_p$. Also in this series the first two terms markedly differ from the other terms. Polyformaldehyde, having a methylene sequence $n = 1$, has a very high melting temperature ($\sim190\,^{\circ}C$.), while the next higher terms melt in the proximity of room temperature. Moreover, the chain conformation of polyformaldehyde in its stable modification[12-14] is that of a 9_5 (or 29_{16}) helix, and polyethylene oxide[15,16], which is the next higher term, has a 7_2 helix. The higher terms, like polyoxycyclobutane ($n = 3$) and polytetrahydrofurane ($n = 4$), on the contrary, were reported[15,16] to have the planar zigzag structure of polyethylene.

Significant analogies can be observed comparing the series of *trans* polyalkenamers with those of low molecular weight compounds, like n-alkanes and their derivatives, having the same number of carbon atoms as the structural units of the corresponding *trans* polyalkenamers. This comparison appears interesting in particular with reference to certain physical properties, like the crystal structure and the melting temperature.

Like in the case of *trans* polyalkenamers, also in that of n-alkanes, significantly different crystal structures distinguish the odd from the even terms. The odd n-alkanes crystallize in orthorhombic unit cells[17], which are very similar to those of the odd *trans* polyalkenamers and to that of the normally stable modification of polyethylene. On the contrary, the even n-alkanes crystallize in quite different monoclinic or triclinic unit cells[17]. It may be recalled that also polyethylene can exist in some less stable modifications, which seem interpretable on the basis of triclinic or respectively monoclinic unit cells[18-20]. Another close relationship can therefore be stated between even *trans* polyalkenamers, even

n-alkanes, and the less stable modifications of polyethylene. This analogy concerns the symmetry of the unit cell as well as the type of space packing of the molecules. It is not unlikely that such an analogy can be established with regard both to modification III (probably triclinic) and to modification IV (monoclinic) of the even *trans* polyalkenamers.

The different crystal structure of odd and even n-alkanes is the reason for the systematic differences in the melting temperatures of these compounds. The plot of the melting points *vs.* 1/N, which is given in Fig. 4 for *trans* polyalkenamers, n-alkanes, n-alkenes, and fatty acids, is represented by smooth curves having a common convergence point (melting point convergence law of Timmermans[21]). In general, two curves can be plotted: one for the even and one for the odd terms of the same series. The former curve generally runs higher than the latter. The melting temperatures of the even and those of the odd terms therefore generally constitute two different series. In the case of α-n-alkenes, and also in that of n-alkanes, the two curves are very close together, so that they can be represented by one single curve. The convergence point of all curves is situated at about 142 °C. and should correspond to an ideal, 100 percent crystallized polyethylene. This perfect convergence must be attributed to the fact that the curves (except that of the *trans* polyalkenamers) are referred to completely crystallized compounds. The observation, that the curve referring to the *trans* polyalkenamers does not cut the ordinate at the same point is justified by the nonideality of this curve, due mainly to the presence of steric or chemical impurities, which lowers the melting temperatures, but also to the impossibility of a complete crystallization, characteristic of all polymers.

A further analogy between the series of *trans* polyalkenamers and that of the low molecular linear compounds consists in the higher melting temperatures of the even series of, *e.g.*, the n-alkanes when compared with those of the odd series. The same phenomenon is observed in the series of *trans* polyalkenamers if one considers the highest melting form of the even series, *i.e.*, modification III (Table 5).

In our opinion, a thorough study on the structure of the various crystalline modifications of *trans* polyalkenamers should allow to extend our knowledge also on the various modifications of polyethylene and on the variation in conformation, which accompanies the chain folding in single crystals of this polymer.

Experimental

Cycloolefins

The cycloolefins were purified by fractionation in a TODD column on metallic sodium. Purity was greater than 99%; in the case of cycloheptene it was 98%. Cyclopentene and cyclohexene were supplied by Fluka A.G., Buchs (Switzerland); cycloheptene was prepared from cycloheptanol by dehydratation with β-naphthyl sulphonic acid according to RUZICKA[22]; cis cyclooctene was supplied by Light & Co., Colnbrook (England) and cyclododecene by Columbian Carbon Co., Princeton (U.S.A.).

WCl_6 and $MoCl_5$

Pure WCl_6 was prepared from a commercial product of Schuchardt, Munich (Germany) by treatment with CCl_4 at 280 °C., according to MICHAEL and MURPHY[23]. The very pure $MoCl_5$ is a commercial product of Schuchardt Comp.

Organometallic compounds

$Al(C_2H_5)_2Cl$ was used with 95% purity and $Al(C_2H_5)_3$ with purity of 85%. Both were supplied from Soc. Montecatini, Petrolchemical Division, Ferrara (Italy).

Preparation of linear trans polyalkenamers

The preparation of the crystalline trans polyheptenamer, as an example of the series, is here described. A three-necked flask, equipped with mechanical stirrer, nitrogen inlet tube, and tube for the introduction of reagents, was placed in dry nitrogen atmosphere. 86 mmoles of cycloheptene (10 ml.) and 0.172 mmoles of powdered WCl_6 were introduced. After cooling to −30 °C., 0.86 mmoles of $Al(C_2H_5)_2Cl$ were added. The reaction mixture was stirred for 5 hrs. at −30 °C. and then for 60 hrs. at +20 °C. The reaction was quenched by addition of an excess of methanol containing hydrochloric acid. The white polymer, which precipitated, was separated, dried under reduced pressure, redissolved in benzene containing phenyl-β-naphthylamine, and reprecipitated by pooring the solution in an excess of methanol. It was filtered and dried under reduced pressure at room temperature. 1.5 g. (18% conversion) of white solid fibrous crystalline trans polyheptenamer were obtained.

For the polymerization of higher cycloolefins, it is advisable to adopt a somewhat higher temperature (30−40 °C.) during the second polymerization period and to start the polymerization at a temperature just above the melting temperature of the monomer.

Solubility of crystalline trans polyalkenamers

Crystalline trans polyheptenamer and trans polyoctenamer are soluble at room temperature in benzene, toluene, chlorobenzene, CCl_4, and cyclohexane. They are insoluble or slightly soluble in n-heptane, dioxane, diethyl ether, tetrahydrofuran, anisol, acetone, and methylethyl ketone. Crystalline trans polydodecenamer is virtually insoluble, at room temperature, in the quoted solvents. However, it becomes soluble in the first class of solvents quoted above at higher temperatures (~50−60 °C.).

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