POLYMERIZATION OF 1,3-PENTADIENE IN SOLUTION AND EMULSION, RESP. INITIATED BY COORDINATION CATALYSTS OF RHODIUM COMPLEXES TYPE

J.ZACHOVAL, J.KŘEPELKA and M.KLÍMOVÁ

Department of Macromolecular Chemistry,
Institute of Chemical Technology, Prague 6

The polymerization of 1,3-pentadiene pure stereoisomers as well as their mixture was carried out both in homogeneous nonpolar medium using rhodium tris(acetylacetonate)–diethylaluminium catalyst and in emulsion using tetrallyldirhodium chloride catalyst. The resulting low molecular polymers ($2 . 10^3 - 6 . 10^3$) possessed similar structure consisting of 20% of *trans*-1,2-isomers, 80% of *trans*-1,4 isomers and a small amount of cyclic structure ($\sim 3\%$). The microstructure of polymer is independent of the catalyst concentration and the type of catalytic system. The experimental data are interpreted on the basis of π-allyl mechanism of polymerization involving coordination of 3,4 double bond of the monomer prior to its attachement to the growing polymer chain.

A whole series of 1,3-pentadiene stereoregular polymers has been prepared during last years using Ziegler–Natta type coordination catalysts[1]. In these types of polymers the monomer units are bonded predominantly in 1,4 or 1,2 positions. If it is assumed that the internal double bond participates in the formation of polymer chain then the formation of three ditactic structures is to be expected. So far iso-*trans*-1,4-polypentadiene[2], iso-*cis*-1,4- polybutadiene[3], syndio-*cis*-1,4-polypentadiene[4] and syndio-*trans*-1,2-polypentadiene[5] have been prepared and characterized from a series of theoretically possible stereoregular poly-1,3-pentadienes. Besides stereoregular polymers also polymers with inexpressive participation of various types of bonds are formed when non-stereospecific catalysts are used. This depends on the polymerization technique used and on the catalytic system employed[1].

In this paper we wish to report on the polymerization of 1,3-pentadiene isomers catalysed both by rhodium tris(acetylacetonate)–diethylaluminium chloride in nonpolar homogeneous medium and by tetralkyldirhodium chloride in polar medium in emulsion. The purpose of these experiments was to compare both catalytic systems from the viewpoint of properties and microstructure of resulting polymers and character of the polymerization process. The choice of seemingly different polymerization techniques and catalytic systems was made on the basis of data about the polymerization of 1,4-butadiene[6-8], where both systems exhibit high stereospecifity ($\sim 100\%$ of *trans*-1,4-structure) giving low-molecular polymers.

EXPERIMENTAL

Chemicals. The mixture of 1,3-pentadiene isomers was isolated from a C_5 fraction which is a by-product of butadiene synthesis by the Lebedeff method. A mixture obtained by repeated extraction with water and rectification (b.p. 41·5—41·8°C) was 99·6% pure and contained 62·3% of *trans*- and 37·7% of *cis*-isomer. *trans*-1,3-Pentadiene was separated from the mixture of isomers in form of a sulfon whose thermal decomposition[9] gave back the monomer 98·7% pure (determined by glc). *cis*-1,3-Pentadiene (98%, b.p. 42·5) was isolated by rectification after the reaction of both isomers with maleic acid anhydride[10]. Benzene was purified by rectification after the removal of thiophene, then dried by 40 h refluxing over the sodium-potassium alloy. Diethylaluminium chloride was vacuum distilled (b.p. 70—71°C/Torr). Rhodium tris(acetylacetonate) was prepared by a modified method commonly used for synthesis of metal acetylacetonates[11]. A crude product was twice crystallized from ethanol–water (1 : 3) mixture. Tetrallyldirhodium chloride was prepared by the method due Powell[12] and purified by a double recrystallization from dichloromethane–methanol (2 : 1) mixture.

Polymerization. Solution polymerization was carried out in an all-glass apparatus[7] using a common technique. Emulsion polymerization was performed by a standard method in an apparatus described by Mikeš[13]. The initial composition of polymerization mixture was following: monomer 0·2 mol; water 40 mol; tetrallyldirhodium chloride 0·01 mol/l water phase; sodium laurylsulphonate 0·0024 mol. Polymerizations were stopped by transferring the polymerizing mixture from the reactor into a vessel containing excess of methanolic solution of N-phenyl-β-naphthylamine (0·5% w/v), the conversion of monomer to polymer was determined by weighing.

Characterization of polymers. Infrared spectra of 0·5% w/v solutions of polymers in tetrachloromethane were taken using a Perkin-Elmer 325 spectrometer. NMR spectra were measured on a Tesla PS 477 (60 MHz) instrument; the samples were dissolved in deuterated chloroform (5% w/v) using tetramethylsilane as an internal standard. The intensity ratio of bands at τ 9·15 and τ 8·43 was used to evaluate the content of *trans*-1,2 and *trans*-1,4 structures[14], being aware that this method is not quite correct; the doublet at τ 9·15 is relatively broad and it partially overlaps with the band at τ 8·97 corresponding to the methylene protons of 1,2 structures. Moreover the integral intensity of the τ 9·15 band increases in the presence of cyclic forms as a consequence of overlap of the band corresponding to cyclic forms ($\rangle$CH—CH_3) with the band due to *trans*-1,4 structure. The number molecular weight of polymers was determined osmometrically in the vapour phase in benzene using a Knauer instrument, squalane being used as a calibration standard. The concentration of double bonds in polymer was determined by iodometric titration[15].

RESULTS AND DISCUSSION

The polymerization of 1,3-pentadiene pure isomers as well as their mixture was carried out both in benzene solution using rhodium catalytic system Rh(Acac)₃–Al. $(C_2H_5)_2$Cl, and in emulsion system catalysed by tetrallyldirhodium dichloride. Both catalytic systems are able to initiate the polymerization of *trans*-1,3-pentadiene whereas in the case of *cis*-1,3-pentadiene monomer only oligomeric products were formed in a low yield. These were not characterized farther. When the molar ratio [Al]/[Rh] > 4 then the polymerization proceeds at a measurable rate; both the molecular weight and the polymer yield increase with the increasing [Al]/[Rh]

TABLE I

The Yield of Polymer (p_p), Oligomers (p_0), Cyclic Structures (C), Participation of 1,2 and 1,4 Structures, resp. ($C_{1,2}$, $C_{1,4}$) and the Molecular Weight of the Polymer During Polymerization of cis- and trans-1,3-Pentadiene and Isomer Mixture, resp.

Monomer Al/Rh[a]	T, °C t, h	P_p, % (p_0, %)	C_{NMR}, % C_{ref}, %[b]	$C_{1,2}$, % $C_{1,4}$, %	$\bar{M}_n$
		Homogeneous system			
Mixture 40/20	20 24	traces —	— —	— —	— —
Mixture 40/13	20 24	traces —	— —	— —	— —
Mixture 40/8	20 48	53·1 (11·6)	3·8 2·5	19·5 80·5	2 285 —
Mixture 40/5	20 24	36·6 (25·9)	2·8 —	20·0 80·0	2 390 —
Mixture 40/4	20 48	73·6 —	2·3 7·9	23·3 76·6	5 460 —
Mixture 40/10	60 24	traces (39·6)	— —	— —	— —
Mixture 80/10	20 48	75·1 (18·6)	5·1 6·2	20·5 79·5	3 090 —
trans- 40/8	20 48	76·5 —	2·6 4·5	21·2 78·8	2 470 —
trans- 40/5	20 48	55·5 (15·2)	4·1 5·0	23·0 77·0	6 030 —
trans- 40/10	60 24	traces (36·6)	— —	— —	— —
cis- 80/10	20 72	0 (10·2)	— —	— —	— —
		Emulsion system			
Mixture 60/10	60 24	55·1 (18·2)	1·9 1·1	18·1 81·9	1 710 —
trans- 0/10	60 24	78·1 (15·4)	3·6 3·5	21·3 78·7	2 680 —
cis 0/10	60 24	0 (18·1)	— —	— —	— —

[a] Concentration in mmol/l. [b] According to ref.[15].

ratio. If the mixture of isomers is polymerized under identical conditions then the degree of conversion and the molecular weight of a product are lower (Table I). All the polymers prepared were transparent, orange in colour, viscous, soluble in aromatic, halogenated solvents and boiling ether.

The exact determination of microstructure of polypentadienes is rather difficult if we take into account a whole number of possible types of stereoisomers together with the presence of cyclic structures present in a polymer prepared in the presence of ionic catalysts[15]. The infrared spectra of polymer prepared by means of both catalytic systems do not differ from one another as far as the number, intensity and position of absorption bands is concerned (Table II). The intense band at 965 cm^{-1} corresponds to the *trans*-disubstituted double bond which involves both 1, 2 (*I*) and 1, 4 (*II*) structure. The absence of *cis*-disubstituted double bonds signifies that in no case the isomerization leading to the formation of *cis* analogues of *I* or *II* occurs during polymerization. From this point of view the catalysts used here exhibit high stereospecificity.

TABLE II
Infrared Spectrum of Poly(1,3-pentadiene)

$\tilde{\nu}$, cm^{-1}	Assignment	$\tilde{\nu}$, cm^{-1}	Assignment	$\tilde{\nu}$, cm^{-1}	Assignment
965	$\gamma(CH{=}CH)^a$	1 453	$\delta_s(CH_3)$	2 920	$\nu_{as}(CH_2)$
1 370	$\sigma_{as}(CH_3)^b$	1 480	$\delta(CH_2)$	2 960	$\nu_{as}(CH_3)$
1 376	$\sigma_{as}(CH_3)^c$	1 660	$\nu(C{=}C)$	3 035	$\nu(CH{=}CH)$
1 436	$\sigma(CH_2)$	2 835	$\nu_s(CH_2)$	3 075	$\nu(CH{=}CH)$
		2 870	$\nu_s(CH_3)$		

^{a} *trans*-Substituted double bond. ^{b} In 1,4 structure. ^{c} In 1,2 structure.

TABLE III
Chemical Shifts τ in Poly(1,3-pentadiene)

Group	Observed		Published[15]	
	1,2-*trans*	1,4-*trans*	1,2-*trans*	1,4-*trans*
>CH—	8·13	8·13	8·10	8·00
—CH$_2$—	8·90	8·13	8·97	8·00
—CH$_2$=CH—	4·83	—	4·90	4·70
=CH—CH$_3$	8·43	—	8·45	—
>CH—CH$_3$	—	9·15	—	9·05

The presence of *I* and *II* is indicated by a doublet due to deformation asymmetrical vibration of a CH$_3$ group at 1370 cm^{-1} and 1376 cm^{-1}. The quantitative determination of both forms on the basis of molar absorbances of corresponding bands is, however, not accurate because of the presence of cyclic structures in the polymer. The absorption bands due to methyl groups are overlapping each other; also the methyl groups belonging to the cyclic structures absorb in the same frequency region. Because of a high cyclic structures concentration (3·8% determined on the basis of degree of unsaturation) and a poor resolution of methyl group bands, it was not possible to determine the ratio of *I* and *II* structures from infrared spectra. So far tactic *trans*-1,4-polypentadienes have not been prepared by means of homogeneous complex catalysts[1]. The interpretation of infrared spectra in the region 2700 cm^{-1} – 3200 cm^{-1} indicates that the spectra of our polymers are very similar to those of stereoregular isotactic *trans*-1,4-polypenta-
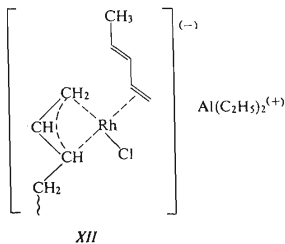

I

II

syn-
III

anti-
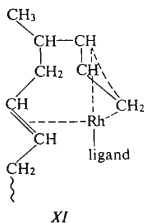*IV*

syn-
V

anti-
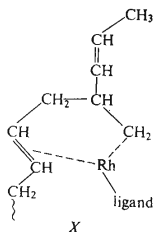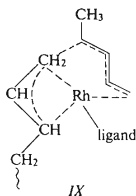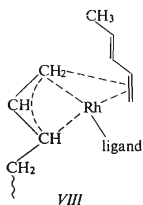*VI*

syn-
Va

anti-
VIa

VII
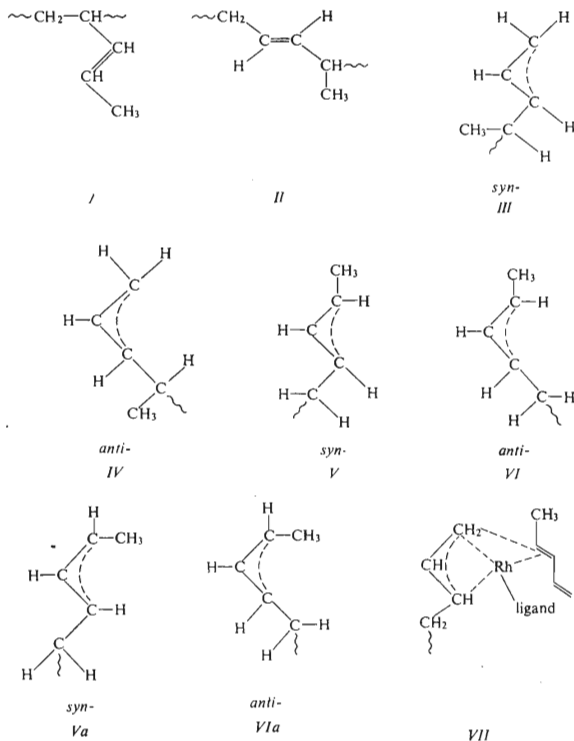
dienes. Relatively high content of 1,2-units in the polymer (20%), low degree of polymerization and the presence of cyclic structures substantially influence the ability of polymer to crystallize. The possible presence of short isotactic sequences cannot, however, be excluded on the basis of identity of infrared spectra alone.

NMR spectra of polymers obtained by both methods are identical and they contain, besides the bands corresponding to *trans*-1,4 structure *II*, also the bands due to the structure *I* (Table III). The presence of cyclic structures was proven by measuring the integral intensity ratio of parafinic and olefinic protons. This ratio was, in all the cases, greater than three; the cyclic structures content was calculated from the difference between measured and theoretical value. The data were then compared with those obtained from double bond determination (Table I). Neither polymerization conditions nor the catalyst influence substantially the microstructure of the polymer. This suggests that individual steps of the propagation reaction are the same for both catalytic systems employed.

The cyclic structure content in the polymer products is, in the case of homogeneous catalytic system, dependent on the ratio [Al]/[Rh] (Table I). Their formation could thus be connected with the cyclization reaction of the polymer initiated cationically by the excess of diethylaluminium chloride. The presence of cyclic structures in a polymer obtained by emulsion polymerization does not, however, exclude the possibility of direct participation of a transit metal in the cyclization.

The polymerization of dienes initiated by transition metal containing catalysts is usually interpreted on the basis of the π-allyl mechanism[1,16,17]. π-Allyl arrangement of a growing end of a polypentadiene chain can, during the solution polymerization of *trans*-1,3-pentadiene assume structures *III*, *IV*, *V* and *VI* (regardless the configuration of the asymmetrical centre). The absence of *cis*-1,2-structures indicates that no isomerization occurs during the polymerization and thus no structures *Va* and *VIa* are formed during the π-allyl arrangement. The absence of *cis*-1,4 structures suggests that the coordination of the monomer proceeds *via* one double bond; simultaneous coordination of both double bonds would be possible only in the case of *cis*-conformation of *trans*-1,3-pentadiene and it would give rise to the formation of the *anti*-structure of the π-allyl type — the condition generally necessary for *cis*-1,4-structures formation in the polymer[16,17]. The identical structure of polymers obtained both in polar and non-polar media signifies that the coordination conditions as well as π-allyl arrangement structures are the same for both polymerization types. The coordination of either internal or external double bond of 1,3-pentadiene cannot be excluded taking into account the electron density distribution in this molecule[18]. Homogeneous catalytic system (as well as the emulsion system) is not active for the polymerization of isoprene and 2,3-dimethylbutadiene, resp., in these cases a π-allyl arrangement would be formed which is not very stable. The stability of π-allyl structures generally decreases with increasing substitution[19]. This fact is in favour of the existence of structure *III*. The existence of structures *I* and *II* in the polymers could be accounted for either by different energy of activation requi-

red for the coordination of 3,4 and 1,2 double bonds (*VII*, *VIII*), resp., or by the possibility of transient cyclic structure formation *IX* subsequently coordinating in the position 3,4; the formation of a new π-allyl arrangement *IX* would also account for the presence of isotactic sequences in the polymer. The mechanism of polymerization *via IX* is more probable in view of the fact that *cis*-1,3-pentadiene cannot be polymerized by the catalysts used here. It is known that the reactivity of *cis*-1,3-pentadiene is generally lower as a consequence of sterical hindrances[1]. In the process of its coordination, similarly to *VIII* and *IX*, the methyl group in *cis*-coordinated monomer would cause strong steric screening in the process of transient complex formation. The mechanism of polymerization in emulsion could be interpreted analogously, admitting the formation of two π-allyl bonds on a Rh(III) centre; this would be in agreement with the data obtained for the polymerization of butadiene initiated by the same catalytic system[8].

The character of a ligand in coordinated π-allyl complex plays an important role during the polymerization of both butadiene and pentadiene. Strong electron donors of Lewis base type or triphenylphosphine inhibit completely the polymerization when present at the ratio[20] [Al]/ /[Ph₃P] = 1. An active catalyst is formed only when diethylaluminium chloride or rhodium chloride in combination with triethylaluminium[20] is used as an organometallic component. The condition necessary for the catalytically active complex is thus the formation of a halogenide

as a ligand. During the reaction of components of a homogeneous catalytic system a considerable change in the conductivity occurs at the ratio [Al]/[Rh] > 3; it is likely that the propagation occurs through an ion particle of type *XII* (ref.[21]).

The suggested interpretation of the polymerization mechanism of *trans*-1,3-penta-diene is based only on the products structure thus representing only a mechanistic approach to the problem. It is likely that the actual mechanism is substantially more complicated due to transfer and termination processes.

REFERENCES

1. Kennedy J. P., Törnquist E.: *Polymer Chemistry of Synthetic Elastomers.* Interscience, New York 1969.
2. Natta G., Porri L., Corradini P., Zannini G., Ciampelli F.: J. Polymer Sci. *51*, 463 (1961).
3. Natta G., Porri L., Stoppa G., Allegra G., Ciampelli F.: J. Polymer Sci. *1B*, 67 (1961).
4. Natta G., Porri L., Carbonaro A., Cimpelli F., Allegra G.: Makromol. Chem. *51*, 29 (1962).
5. Natta G., Porri L., Sovarzi G.: European Polymer J. *1*, 81 (1965).
6. Zachoval J., Veruovič B.: Polymer Letters *4*, 965 (1966).
7. Veruovič B., Zachoval J.: Chem. průmysl *16*, 344 (1966).
8. Zachoval J., Mikeš F., Křepelka J., Prouzová O., Přádová O.: European Polymer J. *8*, 397 (1972).
9. Craig D.: J. Am. Chem. Soc. *65*, 1010 (1943).
10. Frank R. L., Emmek R. D., Johnson R. S.: J. Am. Chem. Soc. *69*, 2313 (1957).
11. Dwyer F. P., Sargassen A. N.: J. Am. Chem. Soc. *75*, 984 (1952).
12. Powell J., Shaw B. L.: J. Chem. Soc. *A 1968*, 583.
13. Mikeš F.: *Thesis.* Institute of Chemical Technology, Prague 1968.
14. Ciampelli F., Lachi N. P., Venturi M. T., Porri L.: European Polymer J. *3*, 353 (1967).
15. Gallo S. G., Wiese H. K., Nelson J. F.: Ind. Eng. Chem. *40*, 1277 (1948).
16. Dolgoplosk B. A.: Vysokomolekularnyje Sojedinenija *13*, 325 (1971).
17. Kormer V. A., Babickij B. D.: International Symposium on Macromolecular Chemistry, Preprint 413, Prague 1965.
18. Julg A., Labarre J. F.: Compt. Rend. *252*, 4001 (1961).
19. Emerson G. F., Pettit E.: J. Am. Chem. Soc. *84*, 4591 (1962).
20. Křepelka J., Zachoval J.: Sborník Vysoké školy chemicko-technologické v Praze, in press.
21. Štrop P., Křepelka J., Zachoval J.: Sborník Vysoké školy chemicko-technologické v Praze, in press.