(*i.e.*, H_V-4 and V_V-4), nor was there a fiber component in the photograph. Apparently, the grafted PVA functions as a plasticizer which enables the collagen backbones to respond more readily to deformation and yet, at the same time, suppresses the packing of molecules into fibrils.

It was observed that swelling of relaxed collagen film with dilute saline solution brought out the V_V-2 pattern even without stretching. This is in agreement with X-ray results. It is found[24] that the X-ray pattern (both low angle and high angle) shows disorientation when collagen fiber is dry and that the orientation improves markedly when the fiber is wetted. This has been interpreted to mean that there has been a stabilization of the helical structure. The polar kinks, which have slightly larger diameters than the nonpolar regions, are straightened out in the wet state. Our result indicates further that wetting also reduces density fluctuation, implying alignment of rods under strain-free condition.

There is a general trend of increasing scattering intensity with the increase of temperature. The thickening of sample may be responsible for this change. Heating also has a slight orientation effect, as evidenced by the appearance of a faint V_V-2 pattern. As the sample was heated past 145°, there was no significant and sudden alteration of SALS pattern. Therefore, the crystalline melting point reported by some workers[8,9] for collagen–ethylene glycol must be a characteristic of that particular system. SALS disappears completely only when the actual flow temperature is reached.

In conclusion, this work has demonstrated that SALS is a powerful technique to study the morphology of collagen at both the protofibril and fibril levels and of their changes as induced by deformation, swelling, and heating. The results indicate that longitudinal as well as lateral alignment of collagen molecules can be revealed by the light-scattering patterns.

Acknowledgment. The authors are deeply appreciative to Professor R. S. Stein for his continuing interest in this work and for making the SALS apparatus available to us. This program is supported by the Public Health Service, National Institutes of Health Grant No. AM 14779.

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Stereospecific and Asymmetric Inclusion Polymerization. III. Polymerization of Substituted Butadienes Included in Racemic Perhydrotriphenylene[1]

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Received May 10, 1972

ABSTRACT: *trans*-2-Methyl-1,3-pentadiene, *trans*-3-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, *cis,cis*- and *cis,trans*-2,4-hexadienes were polymerized by irradiation of their perhydrotriphenylene inclusion compounds. Polymers have head-to-tail trans 1,4 structures and in some cases show crystallinity and stereoregularity. *trans,trans*-2,4-Hexadiene and 2,5-dimethyl-2,4-hexadiene do not polymerize under the same conditions. By an analysis of the stoichiometry of the adducts, we attributed the behavior of said monomers to intermolecular steric factors, related to the different length of the included molecules and to the geometric constraints existing inside the channels. In the case of polymerizable monomers, the distance between unsaturated atoms of two successive molecules is shorter than 5.5 Å. This value represents the critical reaction distance for this type of polymerization and is considerably higher than that found in other cases.

The leading interest of our research presently concerns the inclusion polymerization of dienic monomers in the presence of the equatorial isomer of perhydrotriphenylene (PHTP) as host component. In the last years we published several papers on the synthesis[2–6] and the structural features[7–9] of perhydrotriphenylene and gave some preliminary information on the radiation polymerization of several PHTP-included monomers.[10–12] In more recent papers, we described the stereospecific polymerization of *cis*- and *trans*-pentadiene[13] and studied the effect of both pressure and temperature on such polymerization.[1] In their turn, Allegra and Colombo, of this Institute, accomplished an X-ray analysis of the structure of a monocrystal of the PHTP–butadiene inclusion compound during polymerization.[14]

In this paper, we describe the results obtained using, as monomers, several substituted butadienes containing methyl groups in position 1, 2, 3, and/or 4. The aims of this research

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TABLE I
DIENE MONOMERS USED IN THE STUDY OF PHTP-INCLUSION POLYMERIZATION

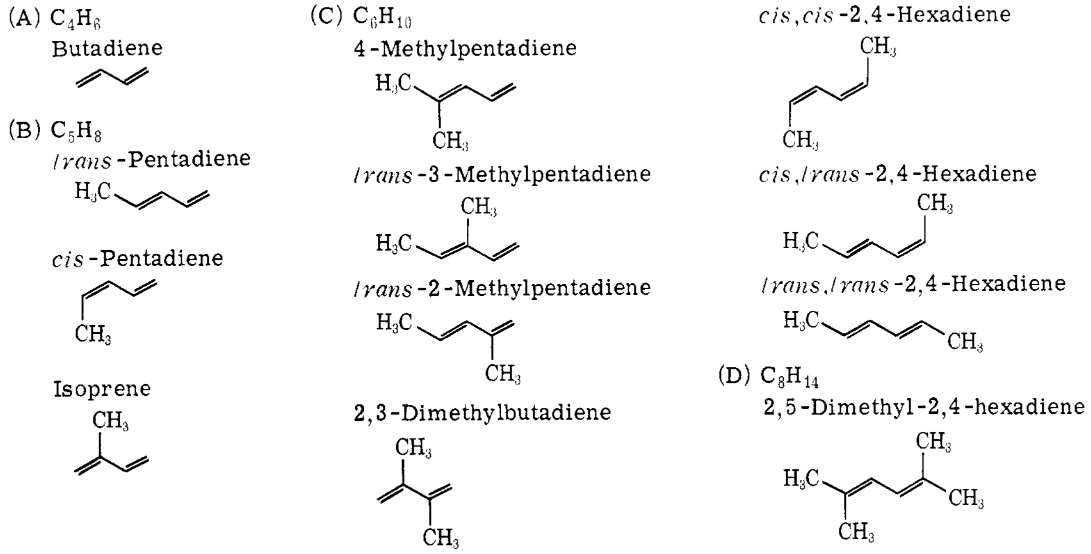

TABLE II
SOME DATA ON THE DIENE INCLUSION POLYMERIZATION

Monomer	Base unit	Intrinsic viscosity, dl/g	Mp, °C, of inclusion compound PHTP-polymer	Polymer properties
4-Methylpentadiene	$-CHCH{=}CHC(CH_3)_2-$	0.4–0.6	149–150°	Highly viscous oil; soluble in $CHCl_3$, CCl_4, toluene, etc.; insoluble in MeOH, acetone; slightly crystalline after vulcanization, identity period 4.8 Å
3-Methylpentadiene	$-CH_2CH{=}C(CH_3)CH(CH_3)-$	0.3–0.4	143–145	Viscous oil; soluble in $CHCl_3$, CCl_4. toluene, etc.; insoluble in MeOH, acetone
2-Methylpentadiene	$-CH_2C(CH_3){=}CHCH(CH_3)-$	Nd	158–160	Crystalline, identity period 4.8 Å; mp 181°; soluble in hot C_4Cl_6; insoluble in $CHCl_3$, toluene, MeOH, acetone, etc.
cis,cis-2,4-Hexadiene	$-CH(CH_3)CH{=}CHCH(CH_3)-$	0.65	Nd	Crystalline, mp 83°; soluble in $CHCl_3$, toluene, etc.; insoluble in MeOH, acetone
cis,trans-2,4-Hexadiene	$-CH(CH_3)CH{=}CHCH(CH_3)-$	0.25–0.35	128–133	Crystalline, mp 83°; soluble in $CHCl_3$, CCl_4, toluene, heptane; partially soluble in pentane and hexane; insoluble in MeOH, acetone

are on one side, the definition of the scope of this method of polymerization in relation to the constitution of the monomer and, on the other side, the production of new polymers. Some of the monomers studied have never been polymerized until now; as to other monomers, inclusion polymerization gave macromolecular structures differing from those obtainable by chemically induced polymerization, both radical and ionic.

Experimental Section

The monomers studied (see Table I) were pure grade commercial products and were used without further purification. 3-Methyl-1,3-pentadiene was synthesized according to Fisher and Chittinden[15] and purified by fractional distillation (trans isomer, 93%). Perhydrotriphenylene was obtained according to ref 3. Polymerizations were carried out as previously reported.[3] Ir spectra were recorded on Perkin-Elmer 221 and 457 spectrophotometers. Nmr spectra were run on a Varian HA 100 using TMS or HMDS as internal standards. The chemical shifts are given in δ units. Melting points were determined on a hot-stage microscope and are uncorrected. X-Ray data on nonoriented samples of polymers were obtained by a Norelco powder diffractometer equipped with a proportional counter and a pulse-height selector; Cu Kα radiation was used. Fiber diagrams of stretched polymer samples were obtained by using a cylindrical camera and photographic techniques. Intrinsic viscosities were determined in toluene at 30° using a Desreux-Bischoff viscosimeter. Ozonolysis was performed as previously described.[13] The oxidation products were examined without crystallization, in order to avoid any fractionation.

Polymer Characterization. In addition to the properties shown in Table II, we report some spectral and ozonolysis data.

Poly(4-methylpentadiene). Spectral data are: ir(film) 1382 (s), 1362 (s), 1330 (w), 1295 (vw), 1183 (m), 1050 (w), 971 (s), 915 (w) cm^{-1}; nmr(CCl_4) δ 5.30 (m, 2, $-CH{=}CH-$), 1.9 (d, 2, $-CH_2-$), 0.98 (s, 6, $-C(CH_3)_2-$). Polymer ozonolysis gives as the only product α,α-dimethylsuccinic acid, by comparison of nmr spectra.

Poly(3-methylpentadiene). Spectral data are: ir(film) 1670 (m), 1450 (s), 1390 (s), 1375 (s), 1360 (s), 1320 (m), 1260 (w), 1170 (w), 1090 (s), 1050 (s), 1020 (m), 970 (w), 915 (m), 895 (s), 880 (s), 845 (m),

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[15] H. L. Fisher, F. D. Chittinden, *Ind. Eng. Chem.*, **22**, 869 (1930).

810 (m) $\mathrm{cm^{-1}}$; nmr($\mathrm{CCl_4}$) δ 5.27 (m, 1, $-\mathrm{CH}{=}$), 2.18 (m, 3, $\mathrm{CH_2}$ and $-\mathrm{C}H(\mathrm{CH_3})-$), 1.09 (d, 3, $-\mathrm{CH}(\mathrm{C}H_3)-$). Ozonolysis gives β-methyllevulinic acid having the following nmr spectrum: δ 3.16 (m, 1, CH), 2.69 (t, 2, $\mathrm{CH_2}$), 2.32 (s, 3, $\mathrm{COCH_3}$), 1.24 (d, 3, $-\mathrm{CH}(\mathrm{C}H_3)-$). The amount of succinic acid was lower than 3%.

Poly(2-methylpentadiene). Spectral data are: ir(KBr pellet) 1381 (s), 1370 (s), 1319 (w), 1300 (w), 1262 (w), 1215 (w), 1181 (m), 1070 (sh), 1015 (w), 990 (m), 939 (m), 895 (w), 878 (s), 840 (w), 802 (s), 605 (m) $\mathrm{cm^{-1}}$; nmr ($\mathrm{C_4Cl_6}$ at 100°; chemical shifts were measured from HMDS as an internal reference and converted to δ values by adding 0.11 ppm) δ 4.91 (s, 1, $-\mathrm{CH}{=}\mathrm{C}$), 2.51 (m, 1, $-\mathrm{C}H(\mathrm{CH_3})-$), 1.91 (m, 2, $-\mathrm{CH_2}-$), 1.61 (s, 3, $=\mathrm{C}(\mathrm{CH_3})-$), 0.91 (d, 3, $-\mathrm{CH}(\mathrm{C}H_3)-$). Ozonolysis gives as the only product α-methyllevulinic acid having the following nmr spectrum: δ 2.81 (m, 3, $-\mathrm{CH}\text{-}\mathrm{CH_2}-$), 2.16 (s, 3, $\mathrm{COCH_3}$), 1.16 (d, 3, $-\mathrm{CH}(\mathrm{C}H_3)-$).

Polyhexadienes. The crude polymers obtained either from *cis,cis-* or from *cis,trans*-2,4-hexadiene present almost identical spectroscopic characteristics: ir(film) 1375 (s), 1348 (w), 1299 (w), 1290 (w), 1278 (w), 1261 (vw), 1240 (vw), 1180 (w), 1168 (w), 1115 (w), 1043 (m), 1012 (w), 963 (s), 905 (m) $\mathrm{cm^{-1}}$; nmr($\mathrm{CDCl_3}$) δ 5.23 (m, 1, $=\mathrm{CH}-$), 2.04 (m, 1, $-\mathrm{C}H(\mathrm{CH_3})-$), 0.92 (d, 3, $-\mathrm{CH}(\mathrm{C}H_3)-$). Ozonolysis yields a mixture of *rac-* and *meso*-α,α'-dimethylsuccinic acids, identified by comparison of the spectra. Nmr analysis of these acids was carried out, after decoupling from $\mathrm{CH_3}$, at δ 2.83 for the meso compound and at δ 2.72 for the racemic one. The ratio between the two acids is about 1:1.

The crude polymer obtained from *cis,trans*-2,4-hexadiene was fractionated by extraction with boiling pentane, hexane, and heptane: ir of the pentane fraction (film) 1370 (s), 1345 (sh), 1299 (w), 1290 (w), 1261 (vw), 1240 (vw), 1180 (w), 1115 (vw), 1043 (m), 1012 (w), 963 (s), 900 (m) $\mathrm{cm^{-1}}$ (ozonolysis of this fraction gives a mixture containing about 85% *rac-* and 15% of the *meso*-dimethylsuccinic acid); ir of the heptane fraction (film) 1370 (s), 1348 (w), 1278 (w), 1168 (w), 1115 (w), 1040 (m), 1012 (w), 972 (s), 962 (s), 905 (m) $\mathrm{cm^{-1}}$ (ozonolysis of this fraction gives a mixture of *rac-* and *meso*-dimethylsuccinic acids in a ratio of about 1:1.

Results and Discussion

The dienic monomers investigated so far are listed in Table I. In addition to butadiene, it includes three methylbutadienes, seven out of nine dimethylbutadienes, and a tetramethylbutadiene. All these monomers are included in PHTP and, except for 2,4-*trans,trans*-hexadiene and 2,5-dimethyl-2,4-hexadiene, they polymerize when their crystalline adducts undergo γ-ray irradiation. As already observed,[10] the reaction product is a PHTP–polymer inclusion compound.

Here we just consider the polymers of which we did not describe the structure before. The reader is referred to previous papers for the polymers obtained from butadiene,[10,11] *cis*-pentadiene,[13] *trans*-pentadiene,[10,13] isoprene,[10] and 2,3-dimethylbutadiene.[10]

As a general characteristic, the examined polymers have an essentially head-to-tail trans 1,4 structure. By ozonolysis, they were converted in high yield into the expected bicarboxylic or ketocarboxylic acids; the products corresponding to head-to-head addition were absent, or present in very small amounts.

The stereochemistry of the chain double bond may easily be determined by ir in poly(4-methylpentadiene) and polyhexadienes, owing to the characteristic out-of-plane vibrations of trans hydrogens, at 960–980 $\mathrm{cm^{-1}}$. The value of the identity period determined by X-rays (4.8 Å) indicates also for poly(2-methylpentadiene) a trans configuration. Only for poly(3-methylpentadiene), there is no corresponding experimental evidence.

Some polymers are partially crystalline by X-ray analysis. In addition to the already described polybutadiene, polypentadiene, and poly(2,3-dimethylbutadiene), we mention poly(2-methylpentadiene) and polyhexadienes obtained either from the cis,cis or from the cis,trans isomer. Also poly(4-methylpentadiene), when slightly vulcanized and examined under stretching, shows a low crystallinity, which allows us to determine an identity period of 4.8 Å. The polymer has no structural alternatives (isosyndio); hence this value just indicates a conformational regularity in the stretched state. As suggested by the value of the identity period, the conformation is similar to that of *trans*-1,4-polybutadiene, in spite of the higher bulkiness of the monomeric unit and of the existence of a methyl group in the plane of the double bond or very close to it.

With regard to poly(2-methylpentadiene), a fiber was obtained from a copolymer containing small amounts of monomeric units derived from 4-methylpentadiene.[16] Its identity period is 4.8 Å; this value supports a trans 1,4 isotactic structure. However, owing to the few reflections of the spectrum, a detailed structural analysis was not possible.

The resolution of the structure of polyhexadienes appeared more complex. The polymers obtained from the cis,cis and cis,trans monomers show ir and nmr spectra that are very similar to each other and to those obtained by Murahashi, Kamachi, and Wakabayashi by coordinate polymerization of the trans,trans isomer.[17] The product being more largely available, we focused our attention on the polymer obtained from the cis,trans monomer. Spectroscopic evidence proves the trans 1,4 structure, but several facts suggest that the product consists of an intra- or intermolecular mixture of different monomeric units. For example, the doublet of methyl in the nmr spectrum is not well resolved, thus indicating the existence of nonequivalent methyl groups. Moreover, almost equimolecular amounts of *meso-* and *rac*-dimethylsuccinic acids are obtained by ozonolysis.

When the crude polymer is subjected to boiling pentane extraction, a soluble fraction is obtained (about 30% of the total), which yields much better resolved ir and nmr spectra. In particular, the ir spectrum shows the disappearance of some weak bands between 1100 and 1350 $\mathrm{cm^{-1}}$. In the nmr spectrum, the methyl doublet is much better defined; moreover, by double decoupling from the methyl and ethylenic protons, the multiplet centered at δ 2.04 (due to saturated tertiary hydrogen) is converted into a singlet placed at δ 2.07. The same experiment done on the crude polymer reveals the presence of two signals at δ 2.07 and at 1.94, with an intensity ratio of about 2:1. (The signal at δ 1.94 is also observed in the pentane extract, but its intensity is far lower than that of the signal at δ 2.07.) We may therefore conclude that the steric structure is substantially homogeneous in the pentane extract.

Among the ozonolysis products, the *rac*-α,α'-dimethylsuccinic acid is dominant. This proves the threo configuration of the polymer.

The pentane extract of polyhexadiene is highly crystalline

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(16) This copolymer was obtained for the first time by chance, by polymerization of an initially pure 2-methylpentadiene sample, left several months at room temperature. The higher polymer solubility, the lower melting point (170 instead of 181°), and the differences found in both ir (which clearly shows the absorption at 975 $\mathrm{cm^{-1}}$ of the unsaturated trans hydrogens) and nmr spectra (indicating the presence of two types of methyls bound to saturated carbon atoms, one giving a doublet, the other a singlet) were observed both by polymerizing mixtures spontaneously formed and mixtures prepared from the two pure monomers. Formation of 4-methylpentadiene from 2-methylpentadiene is interpreted as a 1–5 sigmatropic hydrogen shift, according to the scheme $\mathrm{CH_2{=}C(CH_3){-}CH{=}CH{-}CH_3 \rightarrow CH_3{-}C(CH_3){=}CH{-}CH{=}CH_2}$.

(17) S. Murahashi, M. Kamachi, and N. Wakabayashi, *J. Polym. Sci., Part B*, 7, 135 (1969).

TABLE III
POLYMERIZATION RATE OF 1,4-SUBSTITUTED BUTADIENES

		4 substituents			
	Cis	H	CH_3	H	CH_3
	Trans	H	H	CH_3	CH_3
1 substituents Cis	Trans				
		++	+		
H	H	+++	+++	+++	+++
CH_3	H		++	+	Nd
H	CH_3			–	Nd
CH_3	CH_3				–

TABLE IV
STOICHIOMETRY, REPEAT AND INTERATOMIC DISTANCES OF PHTP–DIENE INCLUSION COMPOUNDS

Guest compounds	Molar ratio PHTP/guest	Repeat distance, Å	C_4–C_1', Å
Butadiene (X-ray)[a]	2	4.78	3.5
Butadiene[b]	1.95 ± 0.05	4.65 ± 0.1	Nd
cis-Pentadiene	3.39	8.10	4.9
trans-Pentadiene	3.64	8.70	5.1
4-Methylpentadiene	3.66	8.75	5.1
trans-3-Methylpentadiene	3.42	8.20	4.8
trans-2-Methylpentadiene	3.69	8.80	5.3
cis,trans-2,4-Hexadiene	3.76	9.00	5.4
trans,trans-2,4-Hexadiene[c]	4.14	9.90	6.3
2,5-Dimethyl-2,4-hexadiene[c]	4.05	9.70	6.1

[a] Reference 14. [b] This work. [c] These monomers do not polymerize after irradiation of their inclusion compound.

and melts at 83°; however, the molecular weight being low, and since it is difficult to obtain stretched fibers, we could not determine the type of repetition of the subsequent monomer units, *i.e.*, whether the polymer is isotactic or syndiotactic. Murahashi, Kamachi, and Wakabayashi[17] proposed an isotactic structure for the already mentioned polymer obtained from the trans,trans isomer. We do not have experimental data supporting this hypothesis which, however, seems very likely. On the other hand, we emphasize that our polymer is threo and not erythro.

The polyhexadiene fraction extracted by boiling hexane (30% of the total) consists of a mixture of macromolecules containing erythro and threo monomeric units, with predominance of the latter, and is very similar to the pentane extract.

The residue from the hexane extraction, which is completely soluble in boiling heptane and in aromatic and halogenated solvents, even in the cold, is partially crystalline; however, its X-ray powder spectrum is completely different from the previous ones. Furthermore, it does not show any transition at about 80°. Its ir spectrum—compared with that of the pentane fraction—shows significant differences, in particular in the region between 1100 and 1350 cm^{-1}, as indicated in the Experimental Section. By ozonolysis it was found that the polymer consists of nearly equal amounts of erythro and threo monomeric units.

The crude polymer obtained from *cis,cis*-hexadiene shows disappearance of dichroism at 83°; as revealed by ir and nmr analyses, its composition is intermediate between those of the hexane extract and of the hexane residue of the polymer obtained from *cis,trans*-hexadiene examined above.

Among all of the examined polymers, poly(3-methylpentadiene) is the least defined from the structural point of view; on the basis of the ozonolysis results, however, we may state that its structure is predominantly head to tail.

Steric Requirements for Inclusion Polymerization. Table III reports a qualitative evaluation of the relative rate of polymerization of several 1- or 1,4-substituted butadienes.

If butadiene is assumed as the reference molecule, the introduction of a terminal methyl in the cis position decreases the polymerization yield to a much lower extent than the introduction of a methyl into the trans position. To illustrate this effect, we can compare *cis*-pentadiene with *trans*-pentadiene, or *cis,cis*-hexadiene with *cis,trans*-hexadiene and with *trans,trans*-hexadiene, and also *trans*-pentadiene with 4-methylpentadiene that, under the same conditions, give an almost equal yield of polymer.

Among the examined dienes, only *trans,trans*-2,4-hexadiene and 2,5-dimethyl-2,4-hexadiene do not polymerize. The reason for such behavior must not be looked for in an intrinsic low reactivity of these compounds. In fact, both *trans,trans*-2,4-hexadiene[17] and 2,5-dimethylhexadiene[18] polymerize in the presence of coordination catalysts. Our results may only be explained by examining the causes that are specifically connected with the PHTP–monomer system. For example, the presence of two trans substituents in each molecule hinders two consecutive monomers from approaching each other to within the critical reaction distance. This may also explain the absence of a considerable number of head-to-head sequences in the polymerization of *trans*-pentadiene, of *trans*-2-methylpentadiene, of *trans*-3-methylpentadiene, and of 4-methylpentadiene. (In the case of *cis,trans*-2,4-hexadiene, head-to-head irregularity gives rise only to steric irregularity, which is experimentally observed, although it may also be attributed to other causes.)

An alternative explanation, which however is valid only for 2,5-dimethylhexadiene, might be the excessive bulkiness of the molecule and hence the impossibility of inclusion. As a matter of fact, we demonstrated in a previous paper[1] that monomer inclusion in PHTP is a preliminary condition for polymerization.

In order to solve this problem and to obtain further data on the monomer arrangement inside the channels, we carried out a systematic study on the stoichiometry of the PHTP–diene inclusion compounds, by the previously described equilibration technique at controlled temperature and pressure.[1] The data are shown in Table IV. In addition to the molar ratio, we report the repeat distance of the guest molecules, with the assumption that PHTP molecules are arranged perpendicularly to the axis of the channel with an identity period of 4.78 Å, and that a channel exists every two stacks of PHTP molecules. These assumptions were verified for all PHTP inclusion compounds examined so far by X-rays.[8]

All monomers used for this investigation, including those that do not polymerize, yield stable inclusion compounds under the irradiation conditions. Except for butadiene,[14] the values of the identity period either coincide or are very close to those of the highest extension of the guest molecules, determined by the conventional values of bond distances, valence angles, and van der Waals radii, as well as by supposing that dienes have a planar anti or transoid conformation (Figure 1). The last condition is experimentally supported by the presence of only trans unsaturation in all polymers examined. Small variations with respect to the largest dimensions may be explained by a slight shift and inclination of the

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(18) G. Audisio, to be published.

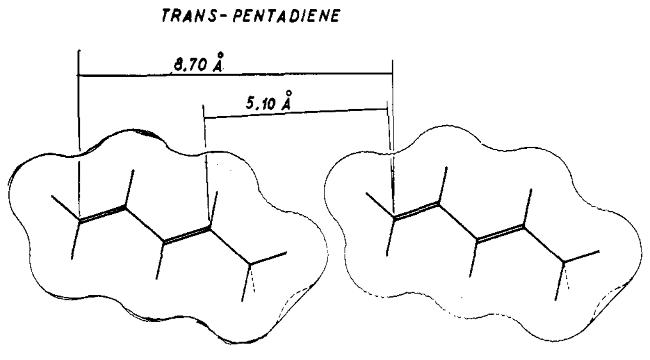

Figure 1. Molecular shape, relative disposition, and interatomic distances of two *trans*-pentadiene molecules inside the channel.

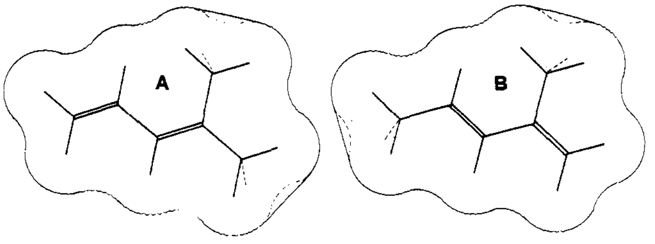

Figure 2. Molecular shape of 4-methylpentadiene (A) and *trans*-2-methylpentadiene (B).

molecules with respect to the channel axis, so that the side bulkiness is minimized and the contacts with PHTP molecules are less severe.

Some useful information may be obtained by an accurate examination of molecular shape. For example, the external shapes of 4-methylpentadiene and of *trans*-2-methylpentadiene are very similar (Figure 2); as a consequence, one may easily take the place of the other inside the channels. This fact could explain the formation of a copolymer between such monomers, as previously described.

More generally, the analysis of interatomic distances allows the distinction between two classes of dienes, one able and one unable to polymerize. With the assumption that included molecules follow one another, by simple translation, and that in such a way side bulkiness is minimized, it is possible to calculate the distance between the last unsaturated carbon atom of a monomer (*e.g.*, C_4) and the first atom of unsaturated carbon of the subsequent monomer (*e.g.*, C_1'). The distance C_4–C_1' varied between 4.9 and 6.3 Å (see Table IV), but for all polymerizable dienes it is lower than 5.5 Å, and only for the two nonpolymerized dienes it is significantly above this value. In this way a quantitative interpretation is attained of the previously quoted effect of the trans substituents.

This conclusion agrees only in part with Schmidt's statements[19] on the solid-state reactivity of a series of unsaturated organic compounds. Considerable differences exist both in the distances between reactive atoms and in the orientation of π orbitals.

Our observations concerning the C_4–C'_1 distance and the relative disposition of the monomers are especially valuable for classification and prediction, but are not intended as a description of the molecular geometry during polymerization. This would require the detailed knowledge of the shape of the chain and of the disposition of PHTP molecules at the border surface between the adducts PHTP–monomer and PHTP–polymer.

In a brilliant paper, Colombo and Allegra[14] described the structures of both reagents and products in the single-crystal reaction PHTP–butadiene → PHTP–polybutadiene; however, this kind of analysis cannot give sufficient elements for the description of the transition state. Although the geometry of this state is affected by some disorder, due to the variation of dimensions and symmetry of the unit cell, it is reasonable to think that the essential data of such geometry largely depend on the parameters determined above, *i.e.*, on the shape and dimensions of the guest molecule.

The high degree of regularity of this polymerization may be explained by the accidental coincidence between the identity period of trans 1,4-polydienes and the length of the *c* axis of the unit cell of the PHTP inclusion compounds (both values approach 4.8 Å). Consequently, the steric situation occurring at a certain polymerization step also occurs in the subsequent step. Were this true, the approach of the monomer to the growing chain should be the same for the whole chain, or at least for a large portion of it. The identity of the transition state is first of all reflected in the head-to-tail arrangement, but it might be decisive also for the steric regularity that, in all cases determined, is isotactic (*i.e.*, it involves a simple translation with a repeat period of one monomeric unit).

A geometric description of the stereochemical path is possible for the polymerization of *cis,trans*-2,4-hexadiene. By assuming the threo diiso trans tactic structure, the polymerization occurs by a constant steric attack and trans addition, provided that the mechanism is referred to the monomer in the anti conformation (in agreement with the description of the polymerization of dienes given by Farina and Peraldo[20]). The three parameters quoted here—anti conformation of the monomer, trans addition, and constant steric attack—are perfectly consistent with what is described above, concerning the geometric constraints existing inside the channels.

In conclusion, we may state that inclusion polymerization of diene monomers, although limited to some extent by the molecular geometry of the monomers, is a very versatile method for the preparation of ordered polymeric structures; in some cases it is even more effective and selective than the best known processes of stereospecific polymerization.

Acknowledgments. This work was supported by a grant of Consiglio Nazionale delle Ricerche, Italy. We wish to thank Dr. L. Zetta for recording the nmr spectra and Dr. G. Vicario of Donegani Institute of Research of Montecatini Edison S.p.A., Novara, for his assistance in the use of the ^{60}Co γ-ray source.

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