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Stereospecific and Asymmetric Inclusion Polymerization. I. Polymerization of *trans*- and *cis*-1,3-Pentadiene Included in Racemic Perhydrotriphenylene

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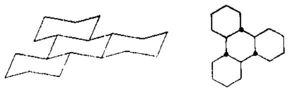
ABSTRACT: Some features of the radiation polymerization of *cis*- and *trans*-1,3-pentadiene included in racemic PHTP are described. Both monomers give a crystalline head-to-tail *trans*-1,4 polymer, to which an isotactic structure may be attributed. Under our experimental conditions, only the included monomer polymerizes; tests carried out with ^{14}C-labeled PHTP show that not all polymeric chains are bound to radicals derived from PHTP. At −75°, a highly stereoregular polymer is obtained only when operating with a monomer:PHTP ratio lower than that required for the formation of the inclusion compound. Remarkable phenomena of postpolymerization have been observed. This fact is the ground of a new method of inclusion polymerization, consisting in the irradiation of pure PHTP and subsequent introduction of the monomer. A linear dependence of the molecular weight on the polymerization yield has been observed in these conditions.

The polymerization of olefins and diolefins included in a crystalline matrix[2,3] has recently aroused some interest, owing to its considerable stereospecificity. For example, crystalline *trans*-1,4-polybutadiene and syndiotactic poly(vinyl chloride) were obtained by inclusion polymerization in urea.[3]

The discovery that the equatorial stereoisomer of perhydrotriphenylene (PHTP) (I) forms channellike inclusion compounds both with low molecular weight substances and with linear macromolecules[4] (Figure 1) led us to study the radiation polymerization of several monomers included in this new host component. A preliminary account of this research, as well as some aspects of the inclusion polymerization of butadiene, has already been published.[5,6]



I

We observed that the polymerization of various monomers in PHTP is highly stereoregular and gives rise in many instances to crystalline polymers. As a matter of fact, *trans*-1,3-pentadiene yields a polymer identical with that obtained by coordination polymerization, to which an isotactic *trans*-1,4 structure was attributed.[7] An even more important result was obtained by irradiating *trans*-1,3-pentadiene included in optically active PHTP; the polymer was optically active. This result represents the first asymmetric polymerization in the solid state.[8]

In this series of papers we will describe the research carried out on PHTP inclusion polymerization. Although several aspects of this polymerization have been considered, the final aim of our research was to explain the reasons of the steric control of this reaction. In this first paper, we discuss some thermodynamic features and refer to the results obtained under different experimental conditions, using racemic PHTP, both ^{14}C labeled and unlabeled. We also report the results obtained by polymerizing the monomer in the absence of radiations, using preirradiated PHTP.

Forthcoming papers will deal with the inclusion polymerization of other dienes and trienes and with the asymmetric induction occurring in the presence of optically active PHTP.

Additional details concerning the chemical behavior and resolution of PHTP,[9–11] as well as the structure of its inclusion compounds,[12,13] were reported in other papers.

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(2)(a) H. Clasen, *Z. Elektrochem.*, **60**, 982 (1956); (b) J. F. Brown and D. M. White, *J. Amer. Chem. Soc.*, **82**, 5671 (1960).

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(5) M. Farina, G. Natta, G. Allegra, and M. Löffelholz, *J. Polym. Sci., Part C*, **16**, 2517 (1967).

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(9) M. Farina and G. Audisio, *Tetrahedron Lett.*, 1285 (1967).

(10) M. Farina and G. Audisio, *Tetrahedron*, **26**, 1827 (1970).

(11) M. Farina and G. Audsio, *ibid.*, **26**, 1839 (1970).

(12) G. Allegra, M. Farina, A. Immirzi, A. Colombo, U. Rossi, R. Broggi, and G. Natta, *J. Chem. Soc. B*, 1020 (1967).

(13) G. Allegra, M. Farina, A. Colombo, G. Casagrande Tettamanti, U. Rossi, and G. Natta, *ibid.*, *B*, 1028 (1967).

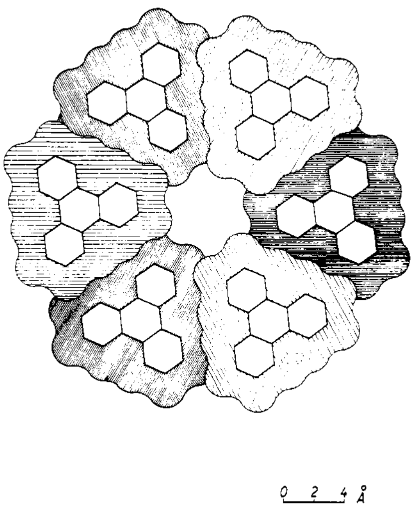

Figure 1. View of a hexagonal PHTP inclusion compound in the ab plane.

Thermodynamic and Structural Remarks

Preliminary research showed that conjugated dienes are the most convenient monomers for PHTP-inclusion polymerization.[5] Table I reports some of the monomers examined. In all cases a true inclusion polymerization takes place: at the same temperature and with the same radiations dose, pure monomers irradiated in the liquid state did not give any product insoluble in boiling methanol. Spectroscopic analysis shows only the presence of negligible amounts of isomerization and oligomerization products.

Notwithstanding the different size of the monomers used (*e.g.*, butadiene and 2,3-dimethylbutadiene), all the monomers and the corresponding polymers are included in PHTP as demonstrated by thermodynamic and structural data.

The thermodynamic study of PHTP-inclusion compounds will be reported in another paper;[14] here we just give some results concerning unsaturated guest components. From the ratio between the vapor pressure of the pure monomer and that of the PHTP-included monomer at the same temperature, the equilibrium constant of reaction 1 is directly obtained.

$$\text{PHTP(crystalline)} + \text{monomer(liquid)} \rightleftarrows \text{inclusion compound(crystalline)} \qquad (1)$$

When the adduct is not formed, the ratio between the vapor pressures of the monomer in the absence and in the presence of PHTP must be very close to 1, since the molar fraction of PHTP in saturated solutions at room temperature is very low (<0.03). The data reported in Table II show that all the examined monomers are stabilized by inclusion in PHTP.

Evidence for the existence of PHTP–polymer adducts is given by crystallographic studies and by thermal analysis. The adduct with *trans*-1,4-polybutadiene is isomorphous with that having low-molecular weight linear hydrocarbons; on the contrary, the reflections observed in the X-ray powder spectrum of adducts containing poly-2,3-dimethylbutadiene and polypentadiene do not correspond either to that of pure PHTP or to that of the adduct with polybutadiene and indicate the existence of inclusion compounds of a new type.[12] The product obtained after irradiation of the PHTP–pentadiene adduct melts at a temperature much higher than that of pure PHTP.[5] This is a typical behavior of PHTP inclusion compounds containing long chains of carbon atoms.[4,12,14] However, since no quantitative data are available on the stability of the PHTP–polymer inclusion compounds, we cannot say at present how much inclusion polymerization differs thermodynamically from the polymerization in bulk.

Table I

Included monomer	Structure of polymer
1,3-Butadiene	1,4-*trans*, crystalline
Isoprene	1,4-*trans*, amorphous
2,3-Dimethyl-1,3-butadiene	1,4-*trans*, crystalline
trans-1,3-Pentadiene	1,4-*trans*, isotactic, crystalline
cis-1,3-Pentadiene	1,4-*trans*, isotactic, crystalline

Table II
Equilibrium Constant of Reaction 1 at 24.7°

Monomer	P: vapor pressure of the inclusion compound (exptl), Torr	P_0: vapor pressure of the liquid monomer (calcd from lit. values), Torr	$K = P_0/P$
cis-1,3-Pentadiene	153	374.6[a]	2.45
trans-1,3-Pentadiene	255.5	405.8[a]	1.80
Isoprene	245.5	543.3[b]	2.20
2,3-Dimethyl-1,3-butadiene	66.7	149.0[c]	2.25

[a] F. D. Rossini, B. J. Mair, and A. J. Streiff, "Hydrocarbons from Petroleum," Reinhold Publishing Corp., New York, N. Y., 1953, p 205. [b] F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," Carnegie Press, Pittsburgh, Pa., 1953, p 361. [c] G. A. McD. Cummings and E. McLaughlin, *J. Chem. Soc.*, **49**, 1391 (1955).

When studying the reactivity of unsaturated compounds in the solid state, Schmidt found that addition reactions best occur when the atoms involved are superposed at a distance of 3.7–4.0 Å.[15] Such conditions take place in the PHTP–butadiene adducts, where, on the basis of preliminary structural data, the disposition sketched in Figure 2 exists.

At present, we cannot extend such conclusions to the case of pentadiene, in that the structure of the relative adduct is not known so far.

The polymer structure was determined by spectroscopic methods (ir and nmr), by comparison with polymers having a known structure, and by oxidative degradation. All polymers obtained by inclusion polymerization have *trans*-1,4 monomer units. This is a consequence of the steric restrictions inside the channels, which favor an *anti* conformation of the monomer during the addition. This fact also occurs

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(14) M. Farina, G. Audisio, and M. T. Gramegna, paper to be submitted.

(15) M. Lahay and G. M. J. Schmidt, *J. Chem. Soc. B*, 312 (1967).

for isoprene, although, as known, its stable conformation in the free state is *syn*.

Both *cis*- and *trans*-1,3-pentadienes yield the same polymer, as demonstrated by superposition of ir and nmr spectra. The presence of methylsuccinic acid as the major component and of a small amount of succinic acid (less than 5%) among the ozonolysis products as well as spectroscopic evidence indicate that polypentadiene essentially has a head-to-tail structure.

The chemical and steric regularity of the product may be determined in the ir spectrum by comparing the intensity of the band at 937 cm^{-1} with that of the band at 965 cm^{-1} and by the absence of absorptions at 910 cm^{-1}, in the typical region of vinyl unsaturations. The nmr spectrum shows three groups of signals, respectively, having relative areas 2:3:3 and situated at δ 5.40 (–CH=CH– *trans*), at 2.0–2.2 (saturated CH and CH$_2$), and at 1.0 (doublet, CH$_3$). The broadening of the bands and the appearance of additional signals between 1.2 and 1.8 in some samples indicate the presence of structural defects.

Polypentadiene melts at about 90° and has a very low degree of crystallinity which can be enhanced by slow cooling from the melt. Its behavior is thus analogous to that of the polymer obtained by coordination polymerization. Some questions concerning the structural interpretation by X-rays are still open. However, the formation of optically active polymers indicates the presence of fairly long isotactic sequences, since asymmetric induction generally requires a very high steric order. Moreover, the accurate examination of the band width in the nmr spectrum reveals that the products obtained by this method are even more stereoregular than those obtained by anionic coordinated polymerization.

Inclusion Polymerization of *cis*- and *trans*-1,3-Pentadiene

With respect to butadiene, the use of pentadiene offers some definite advantages in the study of inclusion polymerization. The solubility of polypentadiene in aromatic and halogenated solvents in the cold allows an easier characterization of the polymer without serious risks of cross-linking or degradation. Moreover, a more direct examination of the reaction stereochemistry is possible, because of the presence of two different centers of stereoisomerism (C=C double bond and asymmetric carbon atom) in each monomeric unit.

As already observed for butadiene,[6] only a semiquantitative approach to the PHTP-inclusion polymerization may be made, owing to the scarce reproducibility of the results. However, dispersion of data may be reduced by an accurate control of the purity of PHTP and of the experimental conditions.

The yield of polymerization of *trans*-pentadiene increases with the radiation dose and with the polymerization time. Although we generally operated with monomer in excess (about three times more than the amount required to form the inclusion compound), only the included monomer polymerizes; the highest value obtained experimentally reaches 119 mg of polymer/g of PHTP, against the value of 138 mg corresponding to the total filling of the channels. This value was calculated by admitting the identity period of polypentadiene in the channel equal to that of PHTP (4.78 Å). *cis*-Pentadiene polymerizes more rapidly than the *trans* isomer. In the runs at low conversion, the total dose and the polymerization time being the same, the yield of polymer obtained from the *cis* isomer is more than twice than that obtained from the *trans* one.

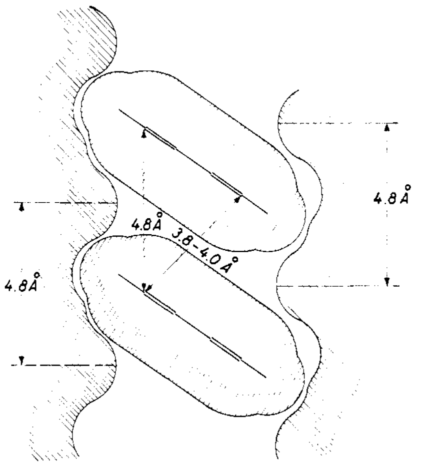


Figure 2. Schematic disposition of butadiene molecules inside the channel.

Unlike butadiene, we observed a remarkable postirradiation polymerization; Table III shows the results of runs carried out on the *trans* isomer at constant dose rate, and at variable times of irradiation and of polymerization. Postirradiation polymerization occurs more extensively at low radiation doses. Furthermore, the molecular weights slightly decrease both with the dose and with the polymerization time. A similar phenomenon had been observed by White[3] in the polymerization of urea-included butadiene.

Some runs in which irradiation and polymerization were carried out at −75° using the usual amount of monomer (300% excess) gave a product containing many structural defects. The ir and nmr spectra revealed the presence of 1,2 and 3,4 polymerized units, with side groups –CH=CHCH$_3$ and –CH=CH$_2$, respectively. The same effect was also found in the polymerization of butadiene, where the presence of 1,2 monomeric units is clearly observed.

However, when the polymerization is carried out with less monomer than that stoichiometrically required for the formation of the inclusion compound (*i.e.*, by irradiating a system in which the condensed phases are the pure crystalline PHTP and the inclusion

TABLE III
POLYMERIZATION OF *trans*-1,3-PENTADIENE INCLUDED IN PHTP[a]

Irradiation time, min	Radiation dose, Mrad	Time of polymerization after irradiation			
		3 min		24 hr	
		Yield	[η]	Yield	[η]
5	0.05	46.2	1.95	64.7	1.75
15	0.15	65.6	1.75	73.3	1.45
30	0.30	73.3	1.60	81.3	1.55
60	0.60	81.4	1.75	84.7	1.40

[a] Yields in milligrams of polymer per gram of PHTP; dose rate 0.6 Mrad/hr.

Table IV
Polymerization of *trans*-1,3-Pentadiene Included in ^{14}C-Labeled PHTP

Run	Method of polymerzn^a	M_n(osmometric)	M_n(radiochemical)	M_{osm}/M_{rad}
1 (first fraction)	A	69,000	143,000	0.48
1 (second fraction)	A	47,000	120,000	0.39
1 (third fraction)	A	32,000	82,000	0.39
2 (first fraction)	A	69,000	157,000	0.44
2 (second fraction)	A	52,000	120,000	0.43
2 (third fraction)	A	18,000	33,000	0.54
3 (crude polymer)	B	33,500	38,000	0.88
4 (crude polymer)	C	59,000	53,000	1.11

[a] A, irradiation of inclusion compound at room temperature; B, irradiation of inclusion compound at −75°; C, polymerization in the presence of preirradiated PHTP.

compound), the spectroscopic analysis reveals that the polymer does not contain structural defects and that its stereoregularity is higher than that obtained at room temperature.

Therefore, the seemingly lower degree of regularity of the polymers obtained at low temperature in the runs carried out under the usual conditions should be attributed to a radiation-induced polymerization outside the channels.

Polymerization into ^{14}C-Labeled PHTP

The presence of radicals trapped in inclusion compounds irradiated by X- or γ-rays was ascertained by Griffith by the esr method both in the case of urea[16a] and of PHTP.[16b] According to this author, radicals chiefly derive from the guest component; however, we obtained evidence for stable radicals also by irradiation of pure PHTP.[17] It was, therefore, very interesting to check whether the radicals derived from PHTP were chain initiators. This is of considerable importance in order to explain the asymmetric induction observed during these polymerizations.

For this purpose, we synthesized ^{14}C-labeled PHTP, starting from labeled benzene and 1,4-dichlorobutane. Dodecahydrotriphenylene was obtained as an intermediate product; it was hydrogenated under drastic conditions on Pd to perhydrotriphenylene.

The polymer obtained by using the labeled host component shows a measurable radioactivity, as a proof of the presence of radicals derived from PHTP. However, the radiochemical molecular weight is much higher than the osmometric one; as a consequence, only a part of macromolecules (about 30–50%) contains a labeled group (Table IV).

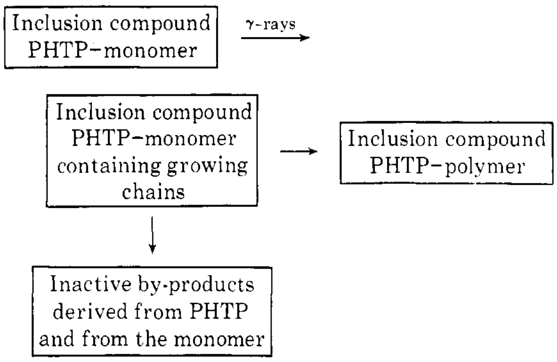
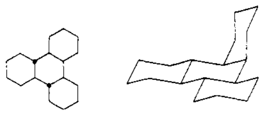


Figure 3. Scheme of polymerization of the inclusion compound PHTP–monomer.

If we exclude the presence of remarkable chain transfer phenomena (as it occurs in the postirradiation polymerization that will be described in the next section), the existence of two distinct initiation processes may be proposed; the first involves only molecules of the monomer, the second involves radicals derived from PHTP, according to the scheme shown in Figure 3. The ratio between these two processes is influenced by temperature and by other interdependent factors (*i.e.*, dose rate, the time of irradiation, and of polymerization).

Polymerization of Dienes Included in Preirradiated PHTP

PHTP radicals are responsible, at least in part, for the polymerization in the channels. This led us to attempt a new method of inclusion polymerization. Monoclinic pure PHTP (space group $P2_1/a$) was irradiated by γ-rays under vacuum. *trans*-1,3-Pentadiene was added in the liquid state by high-vacuum techniques after completing irradiation; under these conditions, a slow polymerization took place having the same or an even better stereoregularity than previously observed. We demonstrated that this is a true inclusion polymerization by irradiating other polycyclic hydrocarbons, similar to PHTP, but which are unable to give inclusion compounds, and precisely the *syn-trans-anti-trans-anti-cis* isomer of perhydrotriphenylene (II)[18] and the *trans-syn-trans-syn-trans* isomer of perhydronaphthacene (III).[19] With respect to PHTP,



II

III

these compounds have the same formula $C_{18}H_{30}$ (and therefore the same electronic density) and the same number of secondary and tertiary carbon atoms. However, only PHTP allows the postirradiation poly-

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(16) (a) O. H. Griffith and H. M. McConnell, *Proc. Nat. Acad. Sci. U. S.*, **48**, 1877 (1962); (b) O. H. Griffith, *ibid.*, **54**, 1296 (1965).

(17) Experiments carried out by Dr. G. R. Luckhurst, Varian, Zürich, whom we warmly thank.

(18) M. Farina, G. Audisio, and P. Bergomi Bianchi, *Chim. Ind.* (Milan), **50**, 446 (1968).

(19) M. Farina, G. Allegra, G. Logiudice, and U. Pedretti, *Tetrahedron Lett.*, 551 (1969).

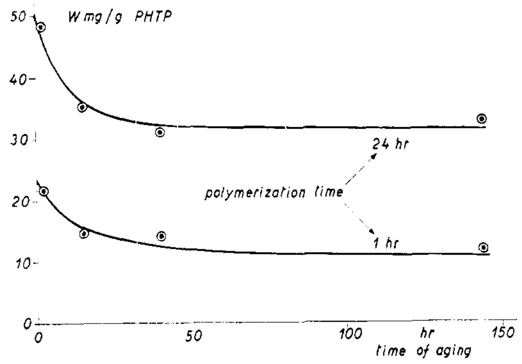

Figure 4. Dependence of polymer yield on the time of aging at different polymerization times.

merization of pentadiene and butadiene. In the presence of II, very small amounts of polymer were obtained, which probably arise from the impurities of I contained in the sample used; on the contrary, III is entirely inactive.

The dose being the same, the polymer yield depends on both the time of aging and of polymerization (Figure 4). The influence of the first factor, *i.e.*, of the time from the end of irradiation to the introduction of the monomer, vanishes rapidly; after an initial decrease, the yield is independent of aging. The decrease of the number of active centers is connected with the survival of only those radicals stable in the solid state, with spontaneous decomposition and/or transformation of the other radicals. With regard to this, we may point out that an intramolecular hydrogen abstraction and formation of Δ_1- and Δ_2-hexadecahydrotriphenylene was observed in the thermal decomposition of *t*-butyl perester of perhydrotriphenylene-2-carboxylic acid,[11] a reaction that occurs through a PHTP radical.

The polymerization in the presence of preirradiated PHTP also occurs with butadiene and with *cis*-pentadiene. The rate of polymerization of butadiene is several times higher than that of *cis*-pentadiene which, in its turn, is higher than that of *trans*-pentadiene. The polymerization process with these monomers is also highly stereoregular, as revealed by ir and nmr analyses.

An interesting characteristic of the polymerization of *trans*-pentadiene consists in the relationship between polymer yield and molecular weight. In a set of strictly controlled polymerizations, the dose and time of aging being the same, the intrinsic viscosity of the polymer increases with the polymerization yield according to

$$[\eta] = K_b W^b$$

(W is the polymer yield per gram of PHTP) (Figure 5). The value of b ranges between 0.67 and 0.69, and practically coincides with the value of exponent a in the analogous relationship between intrinsic viscosity and molecular weight

$$[\eta] = KM^a$$

In fact, the experimental value of a is close to 0.70.

By comparing the two equations and considering equal exponents, M is found to be directly proportional to W. This means that the number of chains is practically constant during polymerization and that marked phenomena of chain transfer do not exist.

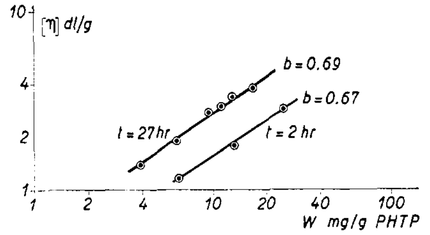

Figure 5. Polymerization of *trans*-1,3-pentadiene included in preirradiated PHTP. Relationship between intrinsic viscosity and polymer yield at different times of aging.

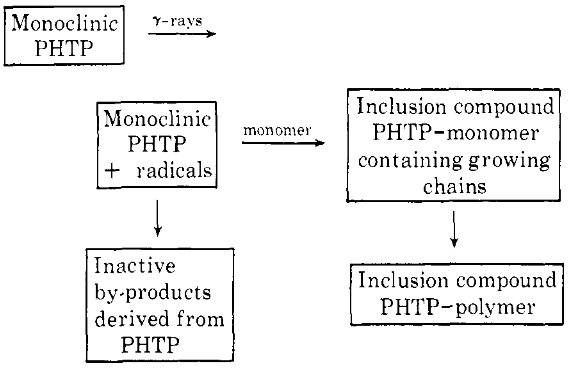

Figure 6. Scheme of polymerization in the presence of preirradiated PHTP.

These remarks are confirmed by the very high values of [η] (ranging from 2 to 4.5 dl/g, whereas in the direct radiation polymerization of the inclusion compounds it ranges between 1 and 2) and by tests carried out with ^{14}C-labeled PHTP, which show a substantial agreement between radiochemical and osmotic molecular weights (see Table IV).

Moreover, some qualitative information may be acquired from the analysis of the sedimentation patterns by ultracentrifugation: the polymers obtained from preirradiated PHTP have a narrower distribution of molecular weights than the polymers from the usual inclusion polymerization.

The general reaction scheme is shown in Figure 6. The differences observed between the inclusion polymerization using preirradiated PHTP and that obtained by direct irradiation of the adduct (Figure 3) are clearly connected with the different composition of the substance subjected to irradiation (pure PHTP in the first case, PHTP + monomer in the second) and with the different fate of the primary irradiation products. However, since the same phenomena of stereoregularity exist, the polymerization process is essentially the same. In both cases, the geometrical restrictions required for channel inclusion seem to determine the polymer structure.

Further conclusions on this point will be described when dealing with the polymerization of pentadiene in optically active PHTP.

Experimental Section

Analytical Methods. The infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. The nmr spectra were run on a Varian HA 100 spectrometer using

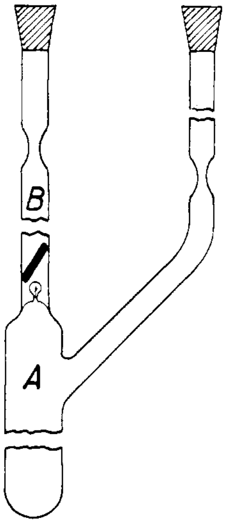

Figure 7. Vial for polymerization in the presence of preirradiated PHTP.

TMS as an internal standard. The chemical shifts are given in δ units. The ^{60}Co radiation source had a power of about 4000 Ci. The absorbed dose was measured by an iron sulfate Fricke dosimeter. Dose rates at room temperature were $5.4–7.0 \times 10^5$ rads/hr, at $-75°$, $2.2–2.9 \times 10^5$ rads/hr. Radioactivity of perhydrotriphenylene and of the polymers was determined by a Beckman CPM-100 or by a Packard 3020 instrument at liquid scintillation system. Intrinsic viscosity was determined in toluene at 30° and expressed as grams per deciliter. The number average molecular weight was determined by a Mechrolab 502 osmometer, in toluene at 30°. Sedimentation patterns were recorded in chloroform at 30° and 44,600 rpm by ultracentrifuge SPINCO Model E.

Materials. Perhydrotriphenylene was prepared according to the method already described in previous papers.[18] The procedure for obtaining a sample of perhydrotriphenylene ^{14}C labeled on the central ring is described. ^{14}C benzene (0.5 mCi), from The Radiochemical Center, Amersham, U. K., was diluted in a vacuum line with 2.6 g (33 mmol) of pure benzene and distilled into a flask containing $AlCl_3$ (3 g) and 1,4-dichlorobutane (26 g, 200 mmol). After removal from the vacuum line, the flask was magnetically stirred at room temperature for 1 week in dry atmosphere. The reaction was stopped by addition of methanol and dodecahydrotriphenylene was precipitated by addition of acetone, filtered, and crystallized from a benzene–acetone mixture, yield 3.55 g (45%). Dodecahydrotriphenylene (3 g) dissolved in *n*-heptane (100 ml) was hydrogenated at 300° and 100 atm in the presence of Pd/C for 1 week. Isomer I was isolated as an inclusion compound with *n*-heptane and crystallized twice from heptane. The reaction and crystallization solvent was again placed into the autoclave in hydrogenation conditions in order to convert part of the low-melting isomers into isomer I, which was recovered by crystallization; yield 2.0 g of pure isomer I; mp 127–128°; specific activity 58 nCi/mg.

cis- and *trans*-pentadienes (Fluka, Switzerland) were 99% pure (by glc) and were used without any treatment.

Polymerization Methods. Inclusion compounds were irradiated in glass vials, which, after filling with reagents, were degassed on the vacuum line ($<2 \times 10^{-5}$ Torr) in liquid nitrogen and sealed. At the end of the polymerization, perhydrotriphenylene was separated from the polymer by extraction with boiling acetone. The residual polymer was characterized according to usual methods.

Polymerizations in the presence of preirradiated perhydrotriphenylene were carried out in glass vials shown in Figure 7. Perhydrotriphenylene placed in A was irradiated under vacuum. After irradiation, the vial was connected to the vacuum line and the monomer distilled in B. The vial was selaed after degassing at 2×10^{-5} Torr in liquid nitrogen. After a fixed time, the diaphragm was broken and the monomer added to perhydrotriphenylene. The product was then processed as indicated above.

The polymer was fractionated by controlled precipitation with methanol at 30° from dilute solutions in $CHCl_3$.

Ozonolysis. Ozonolysis of polypentadiene was carried out by subjecting dilute solutions of polypentadiene in $CHCl_3$ to an ozone stream (0.45 mmol of O_3/min). The solution was maintained in an ice bath and the amount of O_3 used corresponded to five to six times the stoichiometric requirement. After removing $CHCl_3$ under reduced pressure and in the cold, distilled water was added; it was then refluxed for 2 hr in the presence of powdered Zn. It was filtered and refluxed in H_2O_2 at 3% for 4 hr, the excess of H_2O_2 was decomposed with traces of Pd/C; the solution was concentrated, filtered, and passed on Amberlite IR-120 (H) resin. After evaporation under reduced pressure and in the cold, methylsuccinic acid was obtained in 55% yield. The composition and purity of the crude product of ozonolysis was determined by nmr (in deuterated acetone) and by glc after silylation with bistrimethylsilylacetamide,[20] or after methylation with diazomethane.

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