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Inclusion Compounds of Linear Polymers and Polymerization of Monomers Included in Perhydrotriphenylene

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Synopsis

The *trans-anti-trans-anti-trans* isomer of perhydrotriphenylene $C_{18}H_{30}$ forms crystalline inclusion compounds with linear macromolecules, such as polyethylene, 1,4-polybutadiene, and poly(oxyethylene glycol). The main results concerning the constitution, determined by x-ray diffraction and by differential thermal analysis, as well as the stability of these compounds, are reported here. Moreover, studies were made on the polymerization of various monomers included in PHTP by γ-rays radiation. In several cases, an inclusion compound of the polymer in PHTP is obtained from such a reaction. A high degree of stereoregularity has been observed for some of the polymers obtained (e.g., polydiolefins); the first reported example of an isotactic polymer obtained by γ-rays polymerization is due to the above method; it is the isotactic *trans*-poly-1,4-pentadiene.

The *trans-anti-trans-anti-trans*-isomer of perhydrotriphenylene (PHTP) (I)[1] has been recently synthesized at the Industrial Chemistry Department of the Polytechnic of Milan; this compound revealed a strong tendency to form inclusion compounds.[2]

Crystalline and very stable addition products have been obtained by using linear compounds as guest molecules, such as *n*-hydrocarbons, alcohols, ethers, mono- and dicarboxylic acids, even with a high molecular weight.

The crystalline inclusion compounds between PHTP and linear molecules belong to the hexagonal class, particularly to the $P6_3/m$ space group. The unit cell has the following constants: $a = b = 14.34 \pm 0.05$ A., $c = 4.78 \pm 0.02$ A. and contains two molecules of PHTP, placed on threefold crystallographic axes, separated by a $c/2$ distance along the c axis. X-ray data show that every PHTP molecule may be statistically replaced by its antipode, related by a mirror plane perpendicular to c. The projection of the molecules on the *ab* plane is shown in Figure 1. It can be easily seen that, although the two molecules are separated by normal Van der Waals distances, the unit cell contains approximately hexagonal empty spaces with an average diameter of about 5.5 A. Inside the crystal long

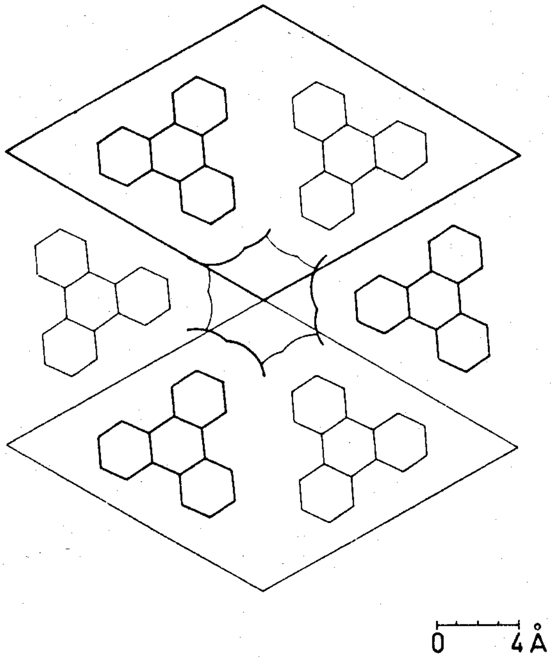

Fig. 1. Projection along the *c* axis of the crystal structure of hexagonal PHTP. Molecules at different levels have been represented by different line thicknesses. The external envelope of the Van der Waals radii has also been sketched, showing the minimum size of the canal.

channels are thus formed, which are filled up by included linear molecules, as in the case of urea–hydrocarbon compounds.[3] The melting temperature of these inclusion compounds is often above that of either component, which is rather unfrequent in the inclusion compounds known so far.

A peculiarity of PHTP is that it very easily forms inclusion compounds with linear macromolecular substances. This fact was already known for urea,[4] where, however, only poly(ethylene glycol) is known as a macromolecular guest molecule.

We succeeded in obtaining inclusion compounds between PHTP and several types of macromolecules, such as polyethylene, *cis* and *trans*-1,4 polybutadiene, polyisoprene, polydimethylbutadiene, poly(ethylene glycol), etc. In a series of papers presently in preparation, we deal with the general properties of several inclusion compounds with PHTP. In this paper we shall discuss the preparation and some properties of such compounds containing macromolecular substances. As for the preparation, we especially report a process for the obtainment of inclusion compounds with macromolecules, starting from PHTP and the monomer, by the effect of ionizing radiations.

Polymerization of Unsaturated Monomers Included in PHTP

The polymerization of crystal-included monomers has been known for a long time. We recall the research done by Clasen[5] and by Brown and White[6] on urea and thiourea. However, these studies only concerned the type of polymer formed, regardless of the nature of the inclusion compounds that might be possibly formed between the macromolecule and the host substance.

Our investigation, instead, concerns both topics. PHTP is easily soluble in many olefin monomers, and can be recrystallized from them. If the side dimensions of the guest molecule are consistent with the diameter of the canal, the monomer may be included into the crystal in amounts ranging from 4 to 10% by weight. The inclusion compound, or in other cases, the raw PHTP-monomer mixture, was subjected to the action of γ-rays emitted from a Co^{60} source.* The samples subjected to radiation were prepared so as to allow a uniform distribution of the radiations inside the samples.

With the use of a dry source, tests could be performed at −75°C. (solid CO_2 + acetone) by radiating samples held in a cooling bath. After completion of radiation, the vial content appeared as a finely powdered product (due to the disgregation of the crystals) or, in the cases of extensive polymerization, as a solid mass. The melting point of the crude product was often higher than that of pure PHTP (127–128°C.) and of the inclusion compounds with volatile low molecular weight compounds. This product has been partly examined as such, and partly subjected to extraction and sublimation to isolate the polymer. Its characterization was made by conventional methods.

The whole set of experiences done by us can be summarized as follows:

1. Some monomers polymerize when subjected to γ-ray radiation both in the presence and in the absence of PHTP. The polymer obtained is substantially identical in the two cases. This class comprises acrylic and methacrylic acids, methyl methacrylate, methyl acrylate, and acrylonitrile. The first four monomers yield amorphous polymers, while acrylonitrile yields a light yellow colored crystalline polymer, which is equal to that obtained by the conventional methods.

2. A series of diene monomers polymerizes in the presence of solid PHTP; the same monomers do not polymerize with an appreciable yield if they are subjected to radiation in the pure state, or if PHTP is present, but not as a crystalline phase. Examples of this class are: butadiene, isoprene, 2,3-dimethyl butadiene, *trans*-pentadiene-1,3.

IR and x-ray examinations reveal that butadiene and 2,3-dimethylbutadiene yield crystalline polymers with *trans*-1,4 structure, while isoprene yields an amorphous *trans*-1,4 polymer.

trans-Pentadiene, on the other hand, yields an isotactic *trans*-1,4 polymer, which is slightly crystalline by x-ray examination. Its IR spectrum is different from that obtained by Ivanov[1] by polymerization in urea in the region between 900 and 950 cm.$^{-1}$, and is identical with that of polypentadiene obtained by anionic coordinated polymerization in the presence of $Al(C_2H_5)_3 + VCl_3$ to which it was just attributed an isotactic *trans*-1,4 structure.[8]

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*Source of the G. Donegani Institute, Novara, Italy.

The pentadiene–PHTP system represents the first example of inclusion polymerization, in which an isotactic type regularity was induced.

As a general result it can be concluded that the polymerization of PHTP-included olefin and diolefin monomers differs in some extent from the urea and thiourea polymerization. For instance both butadiene and 2,3-dimethylbutadiene can be polymerized in PHTP, while the former can only be polymerized in urea and the latter in thiourea.

This fact points out a greater adaptability of the PHTP canals to the size of the included molecules; as further evidence, a powder x-ray examination performed on a PHTP–poly-2,3-dimethylbutadiene adduct has revealed the presence of a slightly different crystal structure from that usually observed with linear included molecules.

Thermal Analysis of Inclusion Compounds

As already pointed out, inclusion compounds in PHTP generally have higher melting points than pure PHTP. When linear macromolecules are included, the highest melting points are observed; the highest melting point so far obtained is 182°C. and corresponds to the addition products PHTP–polyethylene and PHTP–*trans*-1,4-polybutadiene.

These melting points were determined both by a polarizing microscope, which reveals a sharp dichroism, and by a differential microcalorimeter. Table I reports the values of some melting points, while some examples of curves are plotted in Figure 2. The behavior of the addition products obtained either by canal polymerization or by melting or crystallization is substantially identical.

TABLE I

Melting Points of PHTP–Macromolecule Inclusion Compounds

Polymer included	Method of preparation	Melting point, °C.
Polyethylene	A	182
Poly-*trans*-1,4-butadiene	A,B	182
Poly-*cis*-1,4-butadiene	A	158
Poly-*trans*-1,4-isoprene	B	170
Poly(*trans*-1,4-isotactic pentadiene)	B	175
Poly-*trans*-1,4(2,3-dimethyl)-butadiene	B	160
Poly(ethylene glycol) (Carbowax 4000)	A	144

A = PHTP + polymer. B = PHTP + monomer + γ rays.

When cooling is rapid, recrystallization after melting is rather difficult. This fact is proved both by the slopes of the calorimetric curves repeatedly obtained from the same sample and by the lower dichroism observed at the microscope.

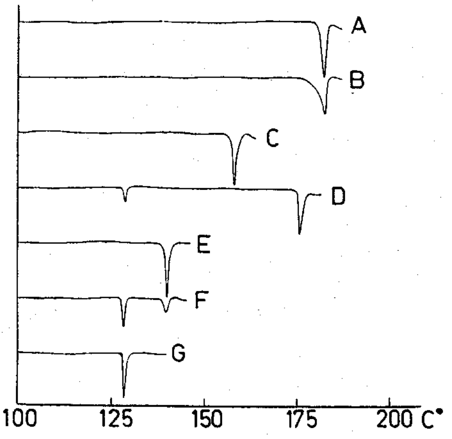

Fig. 2. Melting of inclusion compounds in PHTP, registered by a differential scanning calorimeter: (*A*) PHTP + polyethylene; (*B*) PHTP + polyethylene after rapid cooling; (*C*) PHTP + poly-*cis*-1,4-butadiene; (*D*) PHTP + poly-*trans*-1,4 isotactic pentadiene (obtained by inclusion polymerization): the peak at 127°C. corresponds to the PHTP in excess; (*E*) PHTP + Carbowax 4000; (*F*) PHTP after rapid cooling; (*G*) pure PHTP.

Annealing at temperatures near melting sometimes brings the samples to the initial conditions (polyethylene, *trans*-poly-1,4-butadiene). In the case of poly(oxyethylene glycol), a separation of the addition product and the appearance of an endothermal transition at about 128°C. (melting point of pure PHTP) have been observed. This fact shows that this inclusion product has a weak stability; this is also pointed out by the far lower melting point of this product in comparison with that of PHTP–hydrocarbon compounds, even with lower molecular weight (PHTP–Carbowax 4000, m.p. 144°C., PHTP + $n\mathrm{C}_{20}\mathrm{H}_{42}$, m.p. 153°C.).

X-Ray Analysis of Inclusion Compounds

X-ray single-crystal investigation of inclusion compounds between PHTP and macromolecules has been carried out with two polymers with relatively low molecular weights, i.e., a waxy heptane extract of polyethylene and a poly(ethylene glycol) with a nominal molecular weight of 4000 (Carbowax 4000). Single crystals were obtained by low crystallization from solutions in methyl ethyl ketone. The x-ray analysis revealed that both kinds of adducts are strictly isomorphous with those containing *n*-heptane.

Examination of the rotating crystal Weissenberg photographs, where the crystal was allowed to rotate around the hexagonal (*c*) axis, revealed the presence of diffuse streaks perpendicular to the *c* direction. They were attributed to the chain repetition along the macromolecules, the absence of the discrete spots being due to a noncrystallographic order among chains in neighboring canals. From the position of these diffuse streaks a measure of the chain repeat within ±1% has been derived in both cases, the corresponding values being 2.54 A. for polyethylene and 6.87 A. for polyoxyethylene. Consequently, we have deduced that the chain conformation

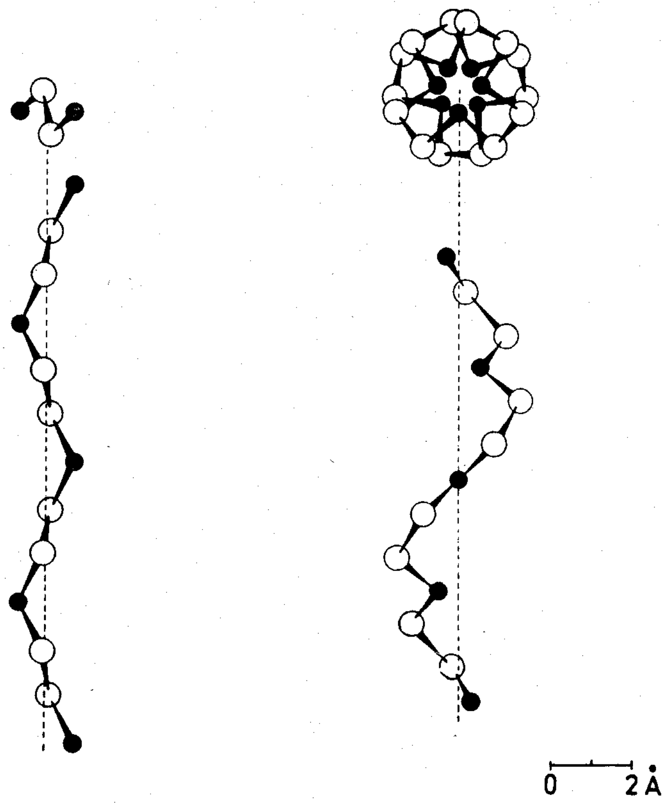

Fig. 3. End and side views of poly(ethylene glycol): (*a*) in a possible conformation when included in PHTP; (*b*) in the conformation proposed by Miyazawa et al.[10] for the pure crystalline state.

of included polyethylene is very close to the zig-zag planar conformation, as is the case for crystalline polyethylene. On the contrary, included polyoxyethylene assumes a much more elongated chain conformation than in the pure crystal state. In fact, from the above-reported repeat distance, and taking into account the size of the canals, the macromolecules must assume either a twofold helix conformation, or a glide plane conformation, two monomeric units being comprised in one chain repeat. The observed repeat distance, although significantly different from, is only slightly shorter than that expected for a completely zig-zag planar conformation (7.21 A.). Accordingly, we have assumed, as a most plausible hypothesis, that the actual chain model is characterized by a "*trans*" conformation on the (C—C) bond, introducing proper deviations from the "*trans*" conformation on the (C—O) bonds. This assumption is in agreement with the presence of nonstaggered conformations around the (C—O) bonds in several crystalline polymers.[9]

As an example, in Figure 3 a possible highly symmetrical chain model of included polyoxyethylene has been sketched. It is characterized by equal and opposite values of the (C—O) and (O—C) torsion angles (±141°) on every monomeric unit; the macromolecule possesses a twofold screw axis along the chain, and also inversion centers and mirror planes perpendicular to it. This model has suitable side dimensions in order to be included in the PHTP canals. For comparison, in the same figure the chain conformation of pure crystalline polyoxyethylene has been reported;[10] as it is apparent, in the latter case the macromolecules have a far more retracted shape, due to the *gauche* conformation (±65°) around the (C—C) bonds, while the (C—O) torsion angles have been assumed not to deviate very much from 180°.

As a final comment, the molecular conformation of POE included in PHTP seems also te be much more elongated than the conformation of the same polymer included in urea, according to the data reported by Tadokoro and co-workers.[11]

Experimental

Perhydrotriphenylene (PHTP) was prepared according to the method described in a previous paper.[1] It was crystallized by *n*-heptane and then maintained at 100°C. and at 2–5 mm. Hg for several hours until constant weight. Other samples were crystallized from methyl ethyl ketone.

Monomers were purified according to conventional methods and held *in vacuo* in the solid state for a long time.

The polymerization was carried out in 4-ml. glass vials containing PHTP (1 g.); the monomers were introduced in the vials by high vacuum technique and then the vials were sealed *in vacuo*. Some vials were heated until complete dissolution of PHTP and then cooled to room temperature in order to obtain the crystalline inclusion compound. Polymerizations were carried out at room temperature (25–30°C.) or at −75°C. in Dry Ice–acetone baths. The Co^{60} source used for radiations had a power of about 3300 c. and consisted of four mobile sources, allowing variable dose rate radiations. The absorbed dose was measured by an iron sulfate Frike dosimeter ($G_{Fe^{3+}} = 15.6$).

The samples radiated at room temperature were subjected to a dose rate equal to $5.5–7.5 \times 10^5$ rad/hr. corresponding to $9.6–13.1 \times 10^{15}$ e.v./g.-sec. and to a total dose of $1.1–1.5 \times 10^6$ rad. The samples radiated at −80°C. were subjected to a dose rate equal to $2.3–3.2 \times 10^5$ rad/hr., corresponding to $4.0–5.6 \times 10^{15}$ e.v./g.-sec. and to a total dose of $0.7–1.0 \times 10^6$ rad.

After radiation, the vials were cooled in liquid nitrogen, opened, and the nonpolymerized monomer was eliminated *in vacuo*.

Polymers were separated from PHTP by hot Kumagawa extractors, using selective solvents. Depending on the cases, we used methanol, acetone, or *n*-heptane. In some cases, the separation was performed by sublimation of PHTP at about 130°C. and at 0.1 mm. Hg.

Inclusion compounds between PHTP and linear macromolecules were obtained also by crystallization from solutions or by melting together the two components.

Melting points were determined by a Leitz hot plate polarizing microscope.

Thermal curves were obtained by a differential scanning calorimeter DSC 1 from Perkin Elmer, with a heating rate of 8 (or 16)°C./min.

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Résumé

L'isomère *trans-anti-trans-anti-trans* du perhydrotriphénylène $C_{18}H_{30}$ forme des dérivés d'inclusion cristallins avec des macromolécules linéaires telles que le polyéthylène, polybutadiène-1,4 et le polyoxyéthylèneglycol. Les principaux résultats concernant la constitution déterminée par la diffraction aux rayons-X er par analyse thermique différentielle, aussi bien que la stabilité de ces composés sont rapportés dans le présent travail. En outre, des études ont été faites sur la polymérisation des différents monomères inclus dans PHTP par radiation γ: dans de nombreux cas, un composé d'inclusion du polymère dans le PHTP est obtenu au départ d'une telle réaction. Un haut degré de stéréoregulairé a été observé pour certains des polymères obtenus (par exemple, les polydiolèfines); le premier exemple rapporté d'un polymère isotactique obtenu par polymérisation aux rayons-γ est dû à la méthode ci-dessus: le polypentadiène isotactique *trans*-1,4.

Zusammenfassung

Das *trans-anti-trans-anti-trans*-Isomere des Perhydrotriphenylens $C_{18}H_{30}$ bildet mit linearen Makromolekülen, wie Polyäthylen, 1,4-Polybutadien und Polyoxyäthylenglykol kristalline Einschlussverbindungen. Über die Hauptergebnisse bezüglich der durch Röntgenbeugung und Differentialthermoanalyse bestimmten Konstitution und der Stabilität dieser Verbindungen wird hier berichtet. Ausserdam wurden Versuche über die Polymerisation verschiedener, in PHTP eingeschlossener Monomerer durch γ-Strahlung ausgeführt; in mehreren Fällen wird durch diese Reaktion eine Einschlussverbindung des Polymeren in PHTP erhalten. Bei einigen der erhaltenen Polymeren (z.B. Polydiolefine) wurde ein hoher Grad an Stereoregularität beobachtet; das erste Beispiel eines durch γ-Strahlen-Polymerisation erhaltenen isotaktischen Polymeren, isotaktisches *trans*-Poly-1,4-pentadien, verdankt man dieser Methode.