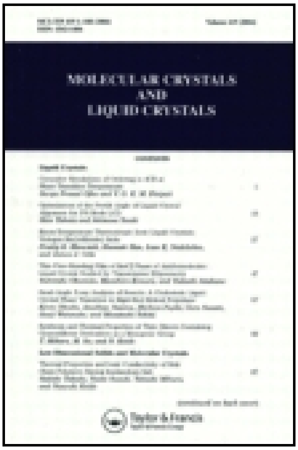

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Stability and Reactivity of Inclusion Compounds

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STABILITY AND REACTIVITY OF INCLUSION COMPOUNDS

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Abstract The general aspects of polymerization of diene monomers included in the crystal lattice of suitable hosts are discussed. Particular attention has been devoted to the behavior of adducts formed by perhydrotriphenylene. Study of the phase diagrams revealed a strict correlation between stability and reactivity in the solid state. Some recent results, concerning inclusion copolymerization and production of polymers with unusual steric structure (e.g., hemitactic polypropylene), are reported.

The performance of chemical reactions inside inclusion compounds, under well defined geometric restraints, is a possibility which has recently attracted much attention. In particular the use of channel-like inclusion compounds makes it possible to investigate reactions in a monodimensional space.

Addition polymerization is a typical example of reactions occurring under such conditions: it produces, in fact, linear macromolecules which fit very well into the space available inside the crystal structure, and proceeds according to a chain mechanism which amplifies (by a factor of 10^2- 10^4) the effect of the initiation step of the reaction (which is, as a rule, induced from outside). By-products such as H_2O or CO_2, whose presence would be a severe obstacle to the solid-state reaction, are not formed during polymerization. Furthermore, the polymeric nature of the product makes host-guest separation very easy because of their differing solubilities and/or volatilities.

Inclusion polymerization, which is often also known as channel, or canal, or tunnel polymerization, has been reviewed many times in recent years[1-4]. This paper reviews some general principles regarding structure, stability and reactivity of inclusion compounds, and goes on to discuss the most recent findings obtained in our laboratory with regard to the synthesis of polymers with defined structure.

GENERAL FEATURES OF INCLUSION POLYMERIZATION

Since its discovery by Clasen[5], inclusion polymerization has been studied from many points of view. Particular attention has been focused on the nature of hosts and monomers, on finding suitable initiators, on the study of active species and of polymerization mechanism, on determining polymer structures and the efficiency of control by the crystal lattice, on the nature and extent of asymmetric induction observed in the presence of chiral hosts, on finding better operating conditions and on determining the limit conditions of polymerization.

Generally speaking, the attention of the various groups engaged in this field of research have tended to focus on a given host crystal. This is due to the specific problems arising with each specific host. Brown[6], White[6,7] and Chatani[8,9] have studied urea and thiourea as hosts, whilst our own group dealt with perhydrotriphenylene (PHTP), Takemoto and Miyata with deoxycholic acid (DCA) and apocholic acid (ACA)[3,10], Wegner[11] and Allcock[12] tris(o-phenylendioxy)-cyclophosphazene (TPP).

Table 1 shows the hosts most studied to date. This article will mainly discuss polymerization in PHTP, a saturated tetracyclic hydrocarbon of formula $C_{18}H_{30}$ which has been found to be an ideal matrix for this type of study.

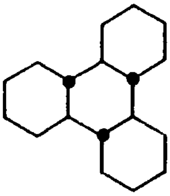
When performed in suitable conditions inclusion polymerization can be considered to be a living radical polymerization. High-energy radiation (γ or X) is used as an initiating agent, the function of which is to generate radicals in the host and in the monomers.

Polymerization in PHTP can be performed by two different techniques because of the ease with which inclusion compounds are formed, even by simple exposure to the guest vapors. In the first of these techniques the PHTP-monomer

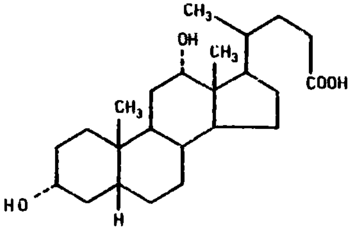
TABLE 1 Hosts for inclusion polymerization

Urea $H_2N\text{-}CO\text{-}NH_2$

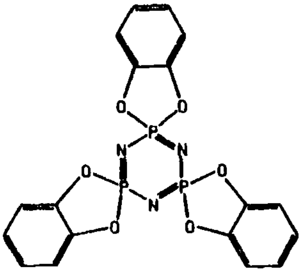
Thiourea $H_2N\text{-}CS\text{-}NH_2$



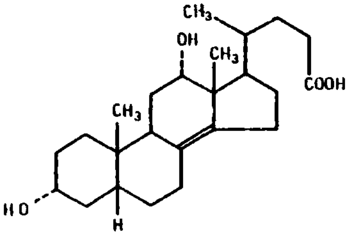
Perhydrotriphenylene
PHTP



Deoxycholic acid DCA



Tris(o-phenylendioxy)-
cyclophosphazene TPP



Apocholic acid ACA

inclusion compound is irradiated directly, whilst in the other technique pure PHTP is irradiated and stable radicals are trapped in the crystal lattice. Subsequently the monomer is added by high-vacuum techniques, and polymerization can be conducted under strictly controlled conditions. The possibility of obtaining block copolymers such as butadiene-isoprene is proof of the living nature of inclusion polymerization in pre-irradiated PHTP. These copolymers are synthesized in a two-stage process, by adding, one at a time, two different monomers to the same sample of preirradiated PHTP^{13}.

Inclusion polymerization of diene monomers in PHTP gives rise to polymers with a high degree of order^{14}: all the polymers examined have a rigorously 1,4-trans structure, and, with the sole important exception of polyisoprene, they present only head-to-tail sequences. Many of them - polybutadiene, polypentadiene, poly-2,3-dimethylbutadiene, poly-2-methylpentadiene - are crystalline and, structure of the monomer unit permitting, isotactic.

When optically active PHTP is used as the matrix, measurable optical activity is found in the isotactic polymers. This asymmetric synthesis, first performed in 1967[15], was the first example of asymmetric solid-state synthesis. Recently we succeded in demonstrating that asymmetric induction is not due to the presence of chiral radicals, but solely to the chirality of the crystal lattice[16]. Thus the process can be described as a through-space and not as a through-bond asymmetric induction.

Another important property of polymers obtained by inclusion polymerization is their particular morphology. When the host-polymer adduct (which is almost always the end product of inclusion polymerization) is decomposed under particular conditions, the polymer presents an extended-chain macroconformation instead of the usual folded-chain lamellar morphology. This feature, which is revealed by the unusual thermal behavior and by SAXS experiments, was observed by White[7] and Chatani[8] in urea and by ourselves in PHTP[17].

The hosts listed in Table 1 differ in selectivity, degree of constitutional and stereochemical control and asymmetric induction power. For example, urea and thiourea are highly selective with respect to monomer dimensions because of the rigidity of their structure, held together by hydrogen bonds. PHTP has the highest power of steric control, whilst DCA and ACA are preferable for chirality.

PHASE DIAGRAMS AND INCLUSION POLYMERIZATION

Inclusion polymerizations in urea are performed at low temperature (-70 to -40°C) because of the instability of most urea-monomer adducts at room temperature. In the case of PHTP polymerization takes place equally well at low or room temperature[18]. Positive results have recently been obtained even in runs at 90°C. The dramatic difference between the two examples can be explained by the difference in the corresponding phase diagrams. It may at once be pointed out that the difference between the two cases is

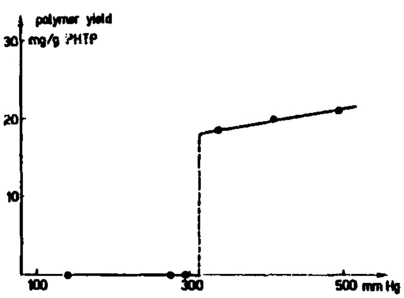


FIGURE 1. Yield-pressure diagram at 30°C.

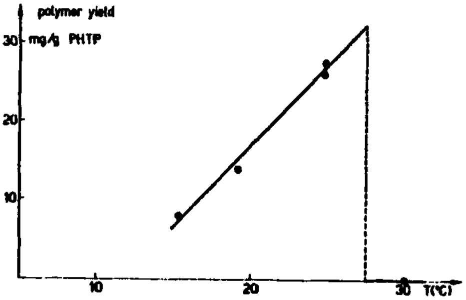


FIGURE 2. Yield-temperature diagram at 300 mm Hg.

not, or not only, due to the crystal structure of the two adducts, but rather to a set of relatioships involving at one and the same time the nature and stability of the inclusion compound, of the pure host, and above all the nature of the liquid phase formed by host and guest.

Sharp variations in polymerization yield with small variations in temperature and in monomer pressure had long since been observed[19]. In a series of experiments conducted with trans-pentadiene and pre-irradiated PHTP at constant temperature and increasing pressure, the polymerization yield was found to rise abruptly (at pressure values around 300 mm Hg) from zero to a finite value (Figure 1). In the same way in a series of experiments carried out at constant monomer pressure, polymer yield rose with increasing temperature until a critical value was reached, above which the yield dropped abruptly to zero (Figure 2). The point at which this discontinuity in behavior occurs, is on the decomposition curve of the PHTP - monomer inclusion compound.

To enlighten this phenomenon a wide study was performed on P-T-x phase diagrams of binary systems containing PHTP and guest[20]. As an example the P-T projection of the P-T-x phase diagram of the PHTP-heptane system is given in Figure 3a. The S-E curve represents the vapor (or decomposition) pressure of the inclusion compound or of solid mixtures of inclusion compound and PHTP; the B-E curve represents the vapor pressure of saturated solutions in equilibrium with pure crystalline PHTP; the R-M-C-E curve shows the vapor

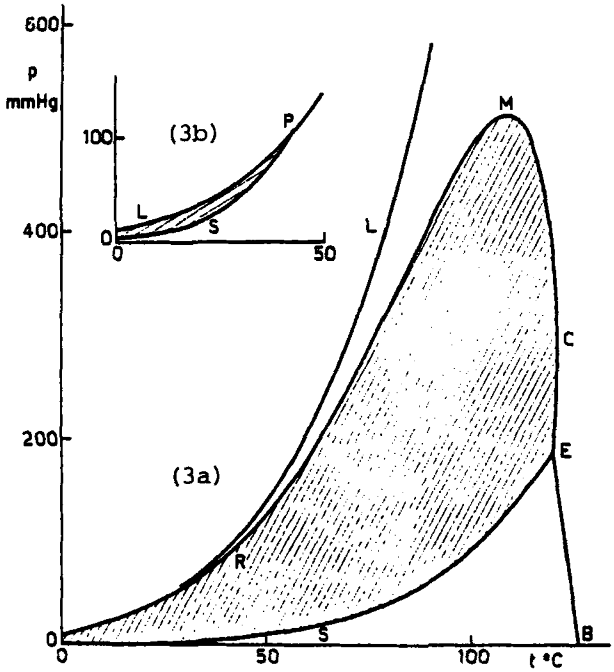


FIGURE 3. Comparison between the stability ranges of PHTP-heptane (3a) and urea-heptane (3b) adducts.

pressure of the saturated solution in equilibrium with crystalline inclusion compound. The most important point in the diagram is the quadruple or eutectic point E, in which four phases exist (vapor, liquid, inclusion compound, PHTP). This point is invariant from a thermodynamic point of view. Its position, in addition to the decomposition enthalpy of the inclusion compound (ΔH_V), determines the vapor pressure of the adduct at each temperature. In turn, the position of E depends on the melting temperature and enthalpy of pure PHTP, on the melting temperature and enthalpy and on the stoichiometry of the inclusion compound, as also on the degree of non-ideality of the liquid phase. With regard to this last factor, it is of interest to observe that when a host-guest miscibility gap occurs in the liquid phase (i.e., when the repulsion energy between the two components is over 2RT), point E shifts toward high pressures and low temperatures, thus reducing the range of stability of the adduct. When the miscibility gap is absolute, point E is to be found on curve L (vapor pressure of pure liquid guest) as can be seen in Figure 3b showing the phase diagram of the urea-heptane adduct[21]. From this diagram, derived from data by Schlenk[22], the maximum temperature for existence of the adduct is 42°C, about 80 K lower than that observed for the PHTP-heptane adduct, despite the fact that ΔH_V is very similar in both cases.

The structural and thermodynamic information now available clearly indicates that the range of temperature and pressure in which polymerization takes place coincides with the range of stability of the inclusion compound with the monomer. A knowledge of the phase diagram provides a quantitative basis for a comparison between the various hosts available for the polymerization of any given monomer.

INCLUSION COPOLYMERIZATION

In recent years inclusion copolymerization has aroused growing interest. From the point of view of macromolecular chemistry attention centers on the scope of the process with regard to possible pairs of monomers that can be used with a given host, and the distinguishing features of inclusion copolymerization compared with "free" copolymerization. From the solid-state point of view the question can be considered from another angle: what kind of information is to be obtained as regards the structure and reactivity of inclusion compounds. In this paper we shall attempt to view the question from the latter point of view.

In general terms, if a given host is put into contact with two different compounds each capable of acting as a guest, two events may take place: the formation of a mixture of two different inclusion compounds, (host + guest_1) and (host + guest_2); or the formation of a mixed inclusion compound (host + guest_1 + guest_2) in which the two guests are arranged in a more or less random fashion within each channel. Such an inclusion compound may be considered as a monodimensional mixed crystal. In the first case, following polymerization a mixture of the two homopolymers, in the second case a copolymer would be found, having composition identical to or different from that of the mixture of monomers used for the preparation of the inclusion compound. If we suppose that each stage of propagation is more rapid than exchange between the included monomer and the free monomer - which is a reasonable hypothesis for the monomers we used - the sequence of monomer units in the copolymer corresponds to that existing in the channel before the reaction. Copolymerization can thus be considered to be a non-conventional method for the structural investigation of inclusion compounds containing two different guests[23].

Our studies of inclusion copolymerization have so far covered 11 pairs of monomers chosen from the following: butadiene, isoprene, trans-1,3-pentadiene, 2,3-dimethylbutadiene, trans-2-methylpentadiene, 4-methylpentadiene[24]. Initially, to reduce possible difficulties arising from different forms and dimensions of the guests, we examined

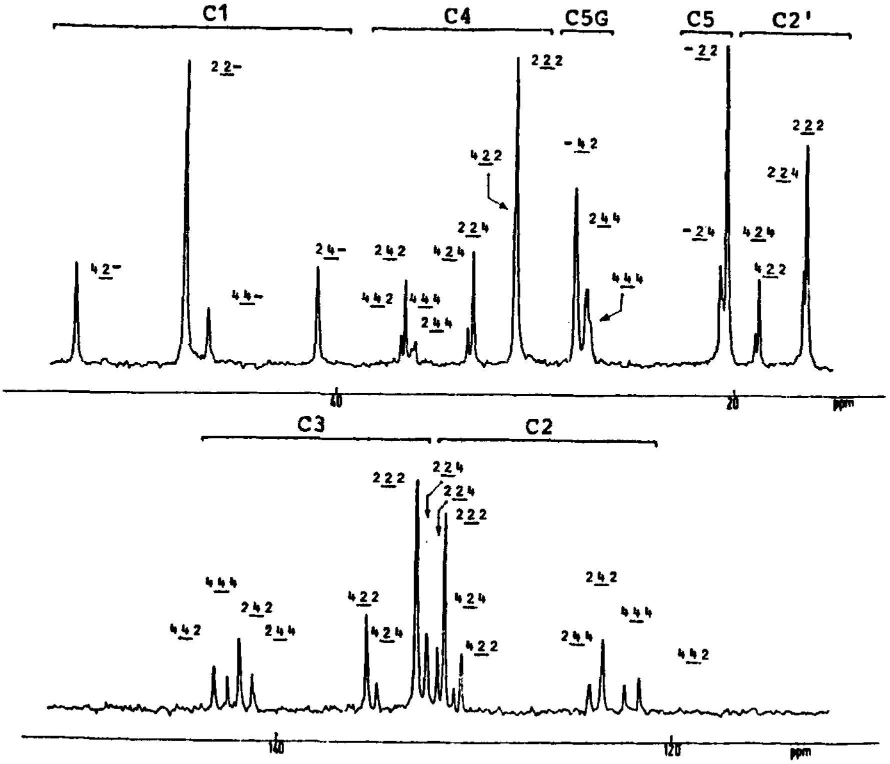


FIGURE 4. 25.2 MHz ^{13}C-NMR spectrum of 2-methylpentadiene - 4-methylpentadiene copolymer.

the reactivity of two isomorphous monomers: trans-2-methylpentadiene and 4-methylpentadiene. The use of ^{13}C-NMR spectroscopy is a particularly suitable method whereby to examine the microstructure of copolymers: a mixture of the two homopolymers should give rise to a spectrum containing 11 peaks, much simpler than that effectively obtained (Figure 4)[25]. The presence of at least 36 peaks of which 16 in the unsaturated carbon region, clearly indicates the presence of two monomer units in random succession. The spectrum is to be interpreted at the level of triads of monomer units, having a 1,4-trans head-to-tail structure. In Figure 4 the indication 224 shows that the signal is attributed to a carbon of the monomer unit deriving from the 2-methylpentadiene, preceded and followed by a 2-methylpentadiene and a 4-methylpentadiene unit respectively. The notation -24 indicates that the signals of the triads 224 and 424 coincide. The intensity of the signals makes it possible to determine the frequency of each sequence and hence to determine the rules of probability governing the constitution of the copolymer. In the case under examination the arrangement of the monomer units follows a Bernoulli distribution: in other words the inclusion copolymerization behaves like an ideal copolymerization. According to the above hypothesis of a slow exchange of monomers, this finding means that selective interactions between the two monomers have no important rôle in the formation of the ternary inclusion compound.

Copolymerization in PHTP is a more general process than might be imagined; in fact, all the monomer pairs examined have produced random copolymers in which the monomer units all have 1,4-trans structure. The process of copolymerization is not forbidden by the differing bulkiness of the monomers, as is shown by the two pairs butadiene - 2,3-dimethylbutadiene and butadiene - 2-methylpentadiene. In these cases too, we find a nearly bernoullian distribution of monomer units.

As a result the principle of monomer isomorphism is no longer a necessary condition for inclusion copolymerization. At the same time interesting possibilities are opened up for the use of this reaction in solid state synthesis.

HEMITACTIC POLYPROPYLENE

The synthesis of tailor-made polymers is one of the most interesting aims of recent macromolecular chemical research. In the same framework of ideas, inclusion polymerization in PHTP may also make important contributions related to its high degree of steric control.

As already mentioned, the poly-2-methylpentadiene produced in PHTP has a 1,4-trans isotactic structure (Figure 5). Mild reduction with diimmide converts it to a saturated polymer whose constitution corresponds to that of head-to-tail polypropylene. The polypropylene thus obtained has a steric structure differing from any other sample produced earlier[26]. It is in fact formed by an alternation of tertiary atoms of definite configuration with tertiary atoms of random configuration: the former (numbered 1,3,5,etc. in Figure 5) derive from the corresponding tertiary atoms present in the original polymer, whilst the configuration of the latter group (labelled 2,4,6,etc.) is determined at the moment of hydrogenation, which is a reaction of low specificity. It follows that if we express the structure of polypropylene

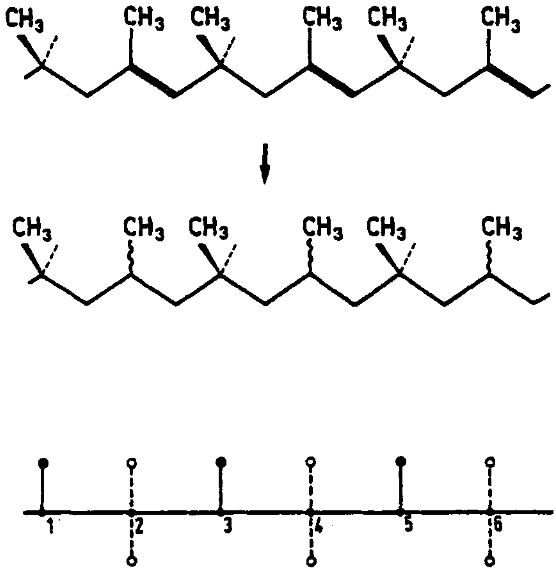


FIGURE 5. Synthesis and structure of hemitactic polypropylene

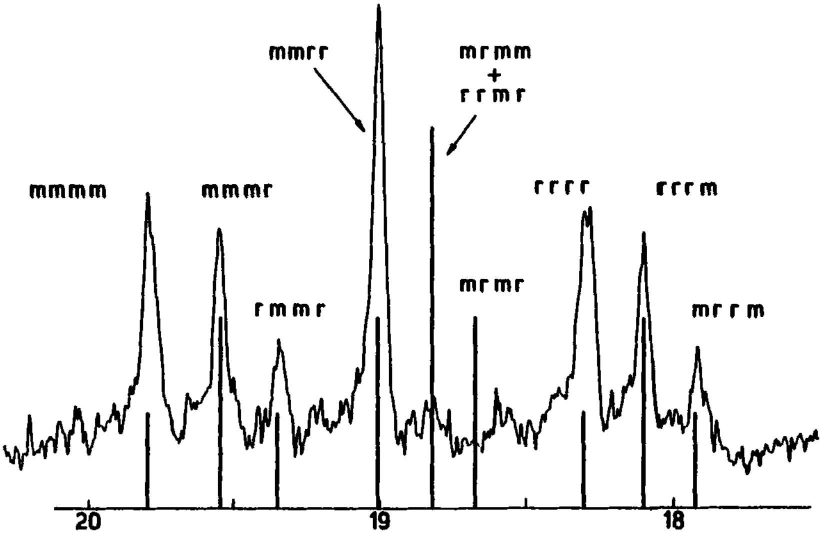


FIGURE 6. 25.2 MHz ^{13}C-NMR spectrum of hemitactic polypropylene recorded at 140°C.

in terms of steric diads m and r (having, respectively, two substituents on the same side of the chain or on opposite sides), no isolated m or r diads may exist (e.g. mrm), nor either any uneven sequences of m or r diads (such as rmmmr). For this polymer we have chosen the term <u>hemitactic polypropylene</u> in view of the fact that only one atom out of two has a definite configuration.

The ^{13}C-NMR spectrum agrees perfectly with the above predictions. Figure 6 shows the experimental spectrum in comparison with the line spectrum of an atactic sample in the region of the methyl resonance. The absence of the pentads mrmr, mrmm and rrmr is evident. Furthermore the intensity ratios between the various pentads agree very well with those computed (3:2:1:4:0:0:3:2:1). Further confirmation was obtained at the hexad level in the methylene region.

Once its structure has been ascertained hemitactic polypropylene can be utilized to obtain a better structural definition of polypropylene of any origin. As an example, we describe an application in the field of NMR analysis.

The spectrum of hemitactic polypropylene becomes simpler (in comparison with that of an atactic sample) as the resolution of the spectrometer increases, because the selection rules described above become more severe when long stereosequences are considered. If there are only three prohibited pentads out of ten, at the heptad level these amount to 22 out of 36. As a matter of fact, the spectrum recorded at room temperature at 50.3 MHz is sensitive to heptads, and it is possible to evidentiate even signals linked to certain particular nonads[27].

From this point of view hemitactic polypropylene represents the highest level of structural resolution yet observed in the study of the configurational sequences of synthetic polymers.

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