(Table I) and increases in size as the water volume increases. Thus the relative silane content in the products increases as the water volume increases. This increase presumably occurs *via* two routes—incorporation of silane as siloxane (SiOSi) units and as (a greater number of) SiOH end groups.

Siloxane units probably are the result of the following sequence of steps

$$\equiv\text{SiCl} \xrightarrow[-\text{HCl}]{\overset{\text{step 1}}{\text{H}_2\text{O}}} \equiv\text{SiOH} \xrightarrow[-\text{HCl}]{\overset{\text{step 2}}{\equiv\text{SiCl}}} \equiv\text{SiOSi}\equiv$$

Step 2 is believed to be slower than the desired reaction between SiCl and carboxylate ion. This is substantiated by the absence of detectable SiOSi units in reactions at low volumes of water even though the presence of SiOH is evidenced. In addition the interfacial synthesis of siloxanes from analogous systems produces chains generally about two to three units long compared with degrees of polymerization of 30 for the silicon polyester produced at low volumes of water. As is true with many interfacial systems the desired condensation step is probably in competition with other rapid steps and thus has a "tight reaction schedule" regarding polymer formation and growth. At higher volumes of water, hydrolysis is believed to become more important thus lowering the SiCl concentration. As water volume increases the reaction occurs to a greater degree *via* the slower step 2 than the desired pathway to polyester, possibly accounting for the decrease in molecular weight.

The yield trend is more difficult to explain. It is possible that a competing reaction for the silane is the formation of cyclic siloxanes. Such cyclic siloxanes are probably soluble in the organic phase (for instance 20) and thus are not collected as products. Linear siloxanes are insoluble in the reaction system and thus would be counted as yield. (The absence of detectable amounts of tetracyclic siloxanes is indicated by the absence of bands in the 1070–1090-cm^{-1} region.[18,20]) It is possible that the effect of increase in water volume enhances formation of linear siloxanes relative to (and at the expense of) cyclic siloxane formation, resulting in a greater yield of product at higher volumes of water. It is found for analogous systems under similar reaction conditions that yield of linear siloxane increases as aqueous volume increases. While the above may not be the answer, it offers a reasonable possibility. Differences in the ratio of adipate to water molecules and in diffusion rates of the adipate caused by changes in aqueous volume also may play a role in determining the product trend.

Hydrolysis is important in the interfacial synthesis of both the tin and silicon polyesters. It is not critical in tin polyester producing systems but is critical in silicon polyester synthesis. This is in keeping with the experimentally observed trend of group IV halide hydrolysis of Sn < Ge < Si.

Stereospecific and Asymmetric Inclusion Polymerization. II. The Effect of Pressure and Temperature on the Polymerization of *trans*-1,3-Pentadiene Included in Racemic Perhydrotriphenylene

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In a previous paper of this series,[2] we described two methods of polymerization of 1,3-pentadiene in the included state. The first consists of the irradiation of the monomer–perhydrotriphenylene (PHTP) inclusion compound, the second of the polymerization of the monomer in the presence of preirradiated pure PHTP. In the first case, by vapor pressure measurements, by differential thermal analysis, and by X-ray examination, we demonstrated that the starting material and the reaction product are the crystalline adducts of PHTP–pentadiene and PHTP–polypentadiene, respectively.

In the second case, we proposed a reaction scheme in which the inclusion of monomer into preirradiated PHTP precedes the polymerization. This scheme seems very likely since the polymerization rate is very low and the monomer was introduced into the reaction vial in the liquid state and in large excess.

In this paper we give decisive evidence supporting this scheme, which was obtained under more severe conditions, *i.e.*, by introducing the monomer in the gaseous state and in a controlled amount.

Experimental Section

Runs were carried out in small glass apparatus consisting of two vials separated by a break-seal (Figure 1). A weighed amount of monoclinic PHTP was placed in A and an excess of monomer was distilled in B. Both A and B were degassed and sealed under vacuum. PHTP was irradiated by a ^{60}Co source of 4000 Ci, with a dose rate of 0.6 Mrad/hr. If during irradiation the monomer was present in B, it was shielded by lead bricks; however, in most cases, the monomer was introduced into B after irradiation. The diaphragm was broken after placing A and B into thermostated baths ($t_A > t_B$); in this way, the temperature of the solid phase (t_A) and the monomer pressure ($p = f(t_B)$) were kept constant during the run. For absorption measurements, vessel B consisted of a calibrated tube having convenient dimensions to guarantee an accuracy of reading ±1% of the stoichiometric amount. The yield of polymerization was determined by weighing the polymer insoluble in boiling acetone, after complete extraction of PHTP. The preparation of PHTP and its characterization are reported in a previous paper.[3]

Results and Discussion

The rate of inclusion of gaseous *trans*-1,3-pentadiene in nonirradiated PHTP was measured at 30° and at pressures ranging between 141 and 460 Torr (t_B between 0 and 28°) (Figure 2). Below the decomposition pressure of the adduct (which at 30° equals 313 Torr), no absorption of pentadiene in PHTP takes place.

In the field of pressures between the decomposition pressure of the adduct and the vapor pressure of the saturated solution, the absorption of the guest component has a rate that depends on pressure and stops at an equilibrium value. Such a value coincides with that obtained by reaching equilibrium from the opposite side, *i.e.*, after distilling an excess of monomer from B to A.

From these experiments, we determined the stoichiometry of the adduct; it contains 76 mg of pentadiene/g of PHTP. To this value corresponds a repetition period of 8.7 Å per pentadiene molecule along the channel axis (for a comparison with other guest molecules, see other papers of ours[4,5]). When

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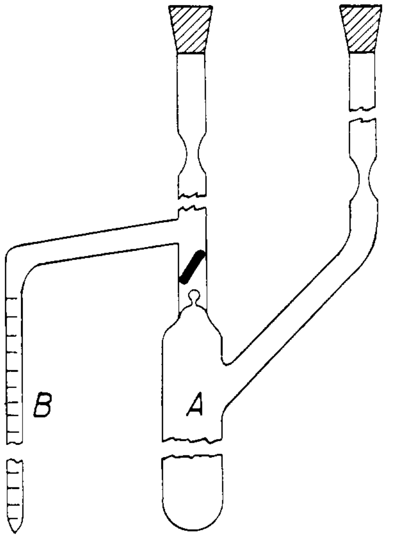

Figure 1. Vial for polymerizations in the presence of gaseous monomer.

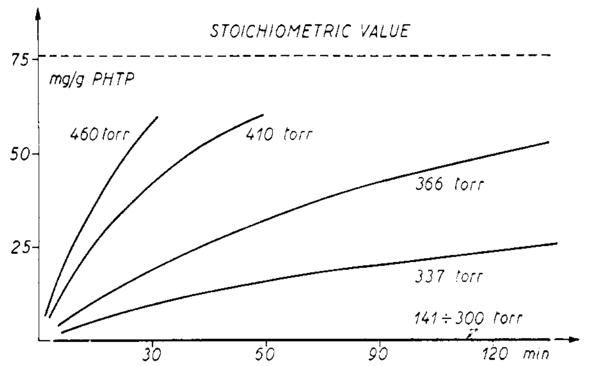

Figure 2. Absorption of *trans*-1,3-pentadiene in racemic nonirradiated PHTP; temperature of the crystal phase (t_A), 30°.

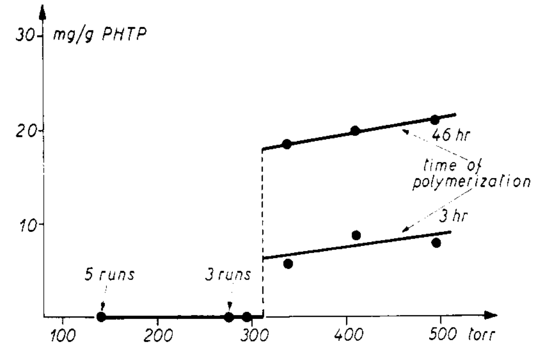

Figure 3. Dependence of the polymerization yield on monomer pressure; polymerization temperature (t_A), 30°.

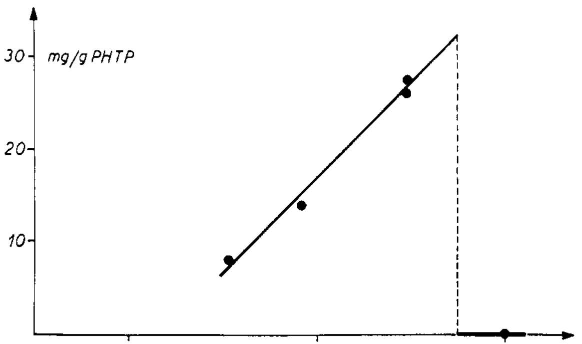

Figure 4. Dependence of the polymerization yield on temperature; monomer pressure, 275 Torr (t_B = 15.3°).

the pressure is higher than that of the saturated solution (*i.e.*, when $t_B \geqslant t_A$) an indefinite passage of the volatile component from B to A is observed.

The above data would supply decisive proof against our hypothesis only if the polymerization occurs at a pressure lower than that of decomposition of the adduct. However, our tests show that under such conditions the polymerization does not take place.

Figure 3 shows the dependence of the polymerization yield on pressure (t_B ranging between 15 and 30°), the radiation dose, time of aging of preirradiated PHTP, and polymerization temperature (t_A = 30°) being the same. Yield is practically null until pressure nears that of formation of the adduct; then by a slight variation of pressure, the yield suddenly reaches a considerable value and later increases more slowly with further increases of pressure. Under our conditions, the polymerization rate is far lower than that of inclusion (compare Figure 3 with Figure 2).

The variation of the polymerization yield with temperature at a constant pressure (t_B = 15°, t_A ranging from 15 to 30°) gives results perfectly consistent with the previous ones (Figure 4). The amount of polymer increases until the temperature of decomposition of the adduct (at the operating pressure), above which it suddenly falls to negligible values.

These data clearly show that the polymerization takes place only in the stability range of the crystalline adduct PHTP–pentadiene; when pressure falls below or temperature rises above the point of decomposition (respectively by operating at a given temperature or pressure) the inclusion compound disappears and the polymerization does not proceed. Therefore, also the polymerization in the presence of preirradiated PHTP must be considered as a true inclusion polymerization occurring in homogeneous phase inside the channels of the crystalline lattice.

In another set of runs, we wanted to check whether a heterogeneous mechanism, in which the inclusion compound formed at the very moment of polymerization, was possible under different experimental conditions, *e.g.*, in the presence of γ rays. Irradiation was therefore carried out in the presence of gaseous monomer at a pressure lower than that of decomposition: under such conditions, no polymerization took place. This is a further proof of the above reported conclusions.

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Increased Energy Deposition in a γ-Irradiated Polymer *via* a Metallic Microphase

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When a multiphase system is exposed to high-energy electromagnetic radiation, it is possible that a phase will receive a dose which differs from that which it would absorb when irradiated alone. An effect of this kind is expected to be greatest when the difference in electron density between the two phases is large and, therefore, it was sought by combining nickel and nylon (electron densities in the ratio 6) and expos-