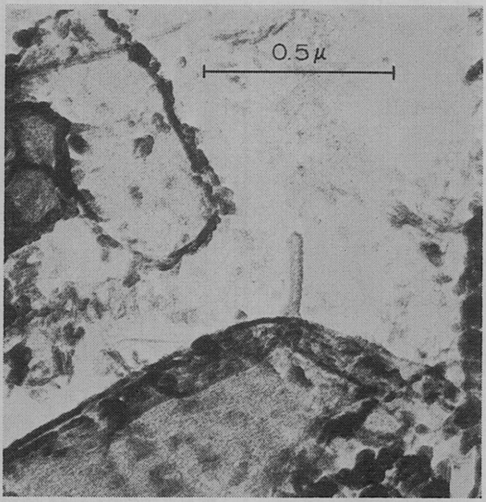

Figure 4. Electron micrograph of a single polypropylene fibril growing from lateral face of α-$TiCl_3$ crystal (carbon replica; Pt shadowed).

The rate of polymerization may be estimated from the size of the fibrils and the time of polymerization. In the calculation it is assumed that the fibrils have the density of isotactic polypropylene and that each fibril is attached to only one active site. The rate of polymerization is given by $R_p = k_p[C^*][M]$ where $[C^*]$ is the number of active sites and is taken as 1 mol and [M] is the concentration of monomer. The rate of polymerization was found to be $R_p = 2 \times 10^4$ mol sec^{-1} per mole of active sites of the monomer and the absolute rate constant was calculated to be $k_p = 2.5 \times 10^6$ l. mol^{-1} sec^{-1}. By comparison, Coover, *et al.*,[1] obtained $k_p = 48$ l. mol^{-1} sec^{-1} for the polymerization of propylene with α-$TiCl_3$–$AlEt_3$ catalyst in a slurry system. The discrepancy by a factor of 5×10^4 seems to be outside the usual limits for experimental error.

The first assumption which might be questioned is whether growth comes only from a single active site. This seems an attractive assumption, since all the globules are the same size and do not completely cover the available surface. If many sites were involved in the production of each globule one might expect a distribution of sizes and a more uniform surface coverage. The number of titanium atoms covered by the base of a globule or fibril is approximately 2000. It would seem that the maximum number of sites which could possibly be involved could not exceed this number, hence the minimum value for k_p must be about 1000 l. mol^{-1} sec^{-1}, or about 20 times the highest value reported previously for this catalyst system. A similar conclusion is reached if one assumes extended chain growth from a large number of sites at the base of the fibril. In this case the cross-sectional area of the polypropylene chain is 34.8 Å^2 and about 2000 would be accommodated in a fibril with a diameter of 300 Å.

Until the number of growth sites per fibril can be established unequivocally, the absolute value of k_p must remain in doubt, but it seems most likely that it lies between 1×10^3 and 3×10^6 l. mol^{-1} sec^{-1}. The lower values observed in slurry systems at higher conversions must surely be due to the fact that monomer must diffuse through a polymer film or a matrix of fibrils in order to reach the catalytic surface, and the rate is diffusion controlled under such conditions.

Certain other conclusions may be deduced from these data. If the area of an active site is that surrounding a single titanium atom this would be approximately 16 Å^2. With a propylene pressure of 143 mm, the rate of impact of propylene molecules on such a surface area can be calculated from the kinetic theory of gases to be 3.7×10^6 molecules per second. The fibrils grow at a rate of 2×10^4 molecules (of propylene) per second which is considerably slower and is obviously not controlled by the rate of gaseous diffusion to the uncovered surface of the catalyst. On the other hand, a simple calculation assuming Fick's law of diffusion and a diffusion coefficient of 10^{-6} cm^2 sec^{-1} for propylene through crystalline polypropylene suggests that if a single active site were at the center of the base of a fibril, the rate-controlling step could be the rate of diffusion of propylene through the polymer to the active site. Alternatively if the site is not occluded by the base of the fibril, a simple Langmuir treatment suggests that the rate-controlling step could be the rate of adsorption of monomer on a chlorine vacancy adjacent to a titanium atom in the crystal. The solution of these two possibilities must await the results of further research now in progress.

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Diels–Alder Polymers. Polyimides from a Biscyclopentadienone and Bismaleimides

The well-known 1,4-cycloaddition reaction of a 1,3-diene to a dienophile to form a six-membered adduct, commonly known as the Diels–Alder reaction, is one of the most useful synthetic organic reactions. Although this reaction usually provides a high yield of adduct, there are few reported syntheses of polymers which employ it as a step-growth reaction.[1] Most of these syntheses afford low molecular weight polymers due to the ease with which reverse reactions take place[2] and a high frequency of side reactions, such as chain-growth polymerization of the diene.[2,3] The rigid, ring-containing polymer which is formed may also precipitate from the reaction medium resulting in an early termination of the polymerization.[4]

Substituted cyclopentadienones are particularly interesting dienes, since their adduction to a dienophile is accompanied by the loss of carbon monoxide, and therefore the reverse reaction is prevented. Different substituents on the cyclopentadienone ring guide the course of the cycloaddition reaction. Certain tetrasubstituted cyclopentadienones with small substituents

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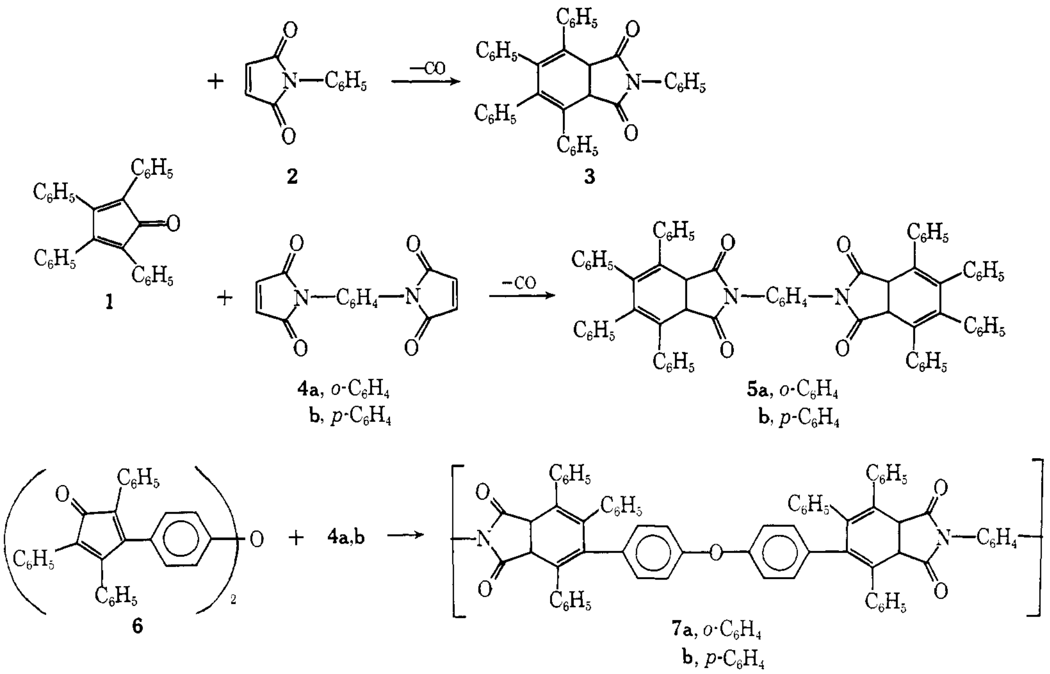
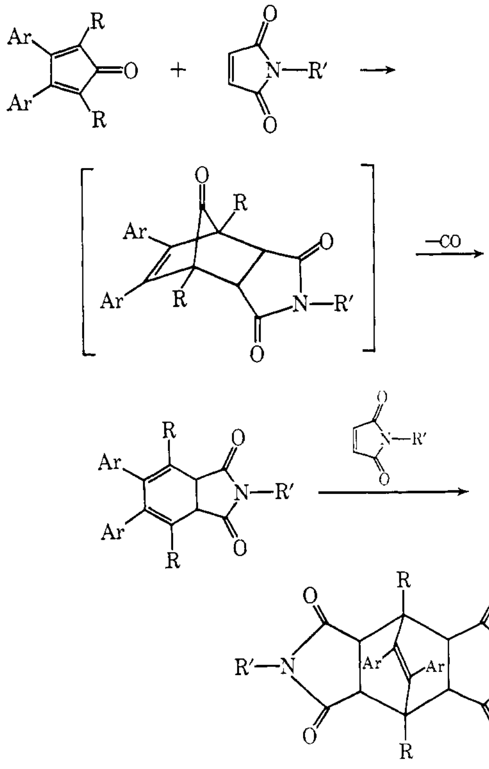
(1) J. K. Stille, *Fortschr. Hochpolym. Forsch.*, **3,** 48 (1961).
(2) J. K. Stille and L. Plummer, *J. Org. Chem.*, **26,** 4026 (1961).
(3) R. W. Upson, U. S. Patent 2,726,232 (Dec 6, 1955).
(4) W. J. Bailey, J. Economy, and M. E. Hermes, *J. Org. Chem.*, **27,** 3295 (1962).

SCHEME I



in the 2 and 5 positions undergo a double cycloaddition with reactive dienophiles at elevated temperatures, since the monoadduct affords a new diene after the loss of carbon monoxide.[5]

High molecular weight polymers have been obtained, in fact, from the reaction of appropriately substituted cyclopentadienones with bismaleimides,[6] where the reaction course is the one shown above with the 2:1 stoichiometry of maleimide moiety to cyclopentadienone. The reaction of biscyclopentadienones with diacetylenes has been carried out[7] to afford polyphenylenes. This polymerization exhibits a 1:1 stoichiometry, since forming the aromatic ring completes the reaction.



The reaction of a tetraaryl-substituted cyclopentadienone with a maleimide, however, stops at the dihydrophthalimide and the reaction also exhibits a 1:1 stoichiometry. Thus the reaction of tetraphenylcyclopentadienone[5] (**1**) with N-phenylmaleimide (**2**)[8] in refluxing α-chloronaphthalene (263°) for 1.5 hr or refluxing 1,2,4-trichlorobenzene (213°) for 18 hr provides a quantitative yield of imide **3**. Similarly, **1** reacts with N,N′-*o*- and -*p*-phenylenebismaleimide (**4a** and **b**) to afford the diimide model compounds, **5a** and **b**.

The analogous reactions of **4a** and **b** with 3,3′-(oxydi-*p*-phenylene)bis(2,4,5-triphenylcyclopentadienone) (**6**) afforded the corresponding polyimides (**7a** and **b**) in quantitative conversions (Scheme I). Polymer **7b**, obtained from the *p*-dimaleimide (**4b**), reaches an intrinsic viscosity of 1.01 in 4 hr in refluxing 1,2,4-trichlorobenzene, while **7a** attains an intrinsic viscosity of only 0.33 after 24 hr under the same conditions. Either there is considerable steric hindrance which slows down the polymerization reaction in the case of the *ortho* isomer, or the series of sharp kinks in the polymer chain limit the root-mean-square end-to-end distance and therefore affect the intrinsic viscosity considerably. Polymer **7** is soluble in dimethylformamide and forms clear, slightly yellow films. The polymer dehydrogenates slowly at elevated temperatures or more rapidly with chemical dehydrogenation reagents to form the totally aromatic polyimide.

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Received June 10, 1968

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(5) M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965).

(6) E. A. Kraiman, U. S. Patent 2,890,206 (June 9, 1959).

(7) H. Mukamal, F. W. Harris, and J. K. Stille, *J. Polym. Sci., Part A-1*, **5**, 2721 (1967).

(8) P. Kovacic and R. W. Hein, *J. Amer. Chem. Soc.*, **81**, 1187 (1959).