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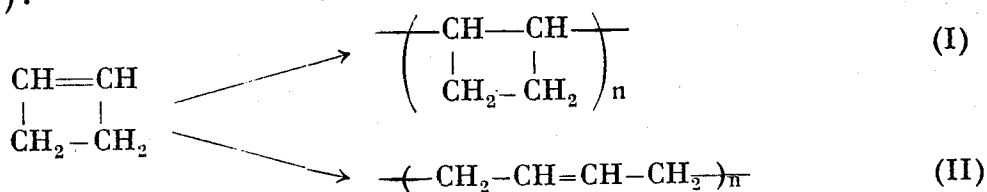
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The tendency of cyclo-olefins to polymerize by opening of the double bond decreases rapidly with increasing ring size. Thus, cyclopropene polymerizes spontaneously yielding high molecular weight polymers having polycyclopropane structure¹). Higher cyclo-olefins, like cyclopentene or cyclohexene, on the other hand, may be converted only to well defined cyclo-oligomers by the aid of acid catalysts²). No indications have been found about the polymerization of cyclobutene, which is unable to undergo spontaneous polymerization.

Catalysts acting through an anionic-coordinated mechanism do not homopolymerize cyclopentene and cyclohexene — not even to oligomers — probably owing to steric hindrance. However, using a comonomer which has a double bond free of substituents (ethylene) the effect of steric hindrance is reduced and a copolymerization can take place. In fact, we have recently obtained high molecular weight copolymers employing catalysts of the anionic-coordinated type³). In the case of cyclopentene we succeeded in preparing, under suitable conditions, crystalline cyclopentene-ethylene alternating copolymers with sterically ordered (erythro-isotactic) structure.

We have now observed that catalytic systems acting through an anionic-coordinated mechanism promote the polymerization of cyclobutene with a very good activity to high molecular weight homopolymers.

Depending on the nature of the catalyst, polymerization occurs by the opening of the double bond, yielding polymers, whose macromolecules consist of regularly enchainned cyclobutane rings (I) (polycyclobutylene-amer-2 according to the nomenclature of HUGGINS⁴), whereas in other cases polymerization takes place by opening of the ring, and the resulting polymers have the structure of 1,4-polybutadienes (II) (polybutenamer⁴):



Anionic-Coordinated Polymerization of Cyclobutene

More particularly, a catalyst prepared from VCl_4 and $Al(\text{hexyl})_3$ (1:2.5 molar ratio) in *n*-heptane yields quantitatively at -50°C . a crystalline high molecular weight polymer (Fig. 1, type 1) having a pure cyclobutyleneamer-2 structure.

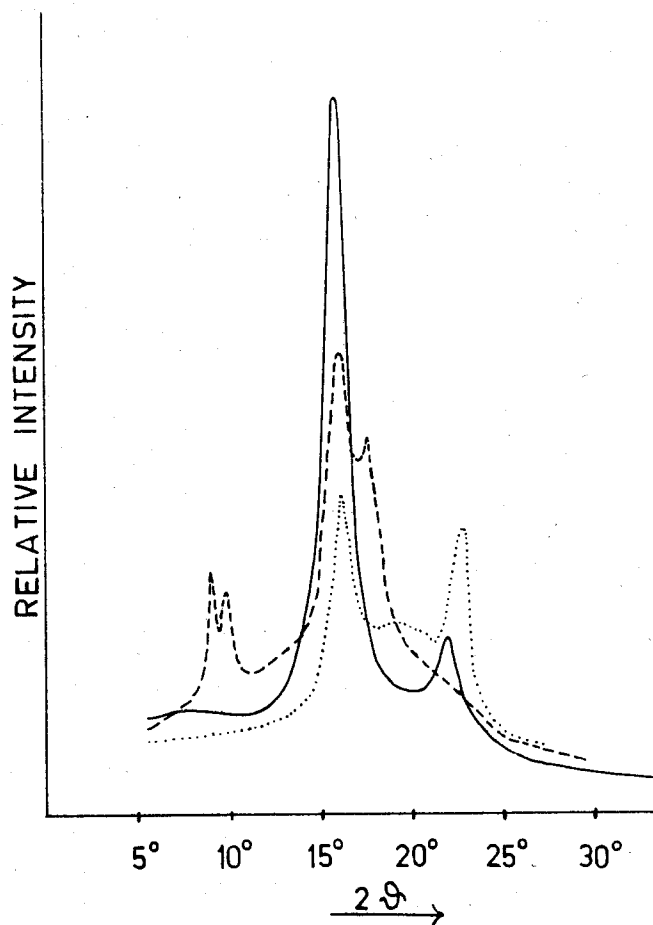


Fig. 1. GEIGER-counter registration of the X-ray spectrum ($\text{CuK}\alpha$ -radiations) of polymers of cyclobutene
(— type 1; ---- type 2; ····· type 3)

Similarly, a catalyst prepared from $V(\text{acetylacetonate})_3$ and $AlCl(\text{C}_2\text{H}_5)_2$ (1:5 molar ratio) in toluene yields quantitatively at -50°C . a crystalline high molecular weight polymer*) (Fig. 1, type 2), which also exhibits pure cyclobutyleneamer-2 structure.

The cyclobutyleneamer-2 structure of these two polymers is supported by the following observations resulting from the I.R. spectra of both polymers:

- absence of any type of absorption bands due to double bonds;
- absorption band at $6.97\ \mu$, characteristic for methylenic groups in ring position;

*) $[\eta]$ determined at 135°C . in tetralin is 0.2.

absorption band at 3.78μ , which we always observed in compounds having cyclic configurations.

Differences in position and intensity in the I.R. spectra of the two polymers with cyclobutylamer-2 structure only concern the absorption bands between 7 and 11μ , probably due to crystallinity.

This agrees with the somewhat different X-ray spectra of the two polymers, which cannot be attributed to different chemical structure. However, we have not yet succeeded in obtaining sufficient data for establishing whether this is due to differences of steric structure.

Furthermore, slight differences in the physical properties of the two types of polymers with cyclobutylamer-2 structure were observed: type 1 polycyclobutene is insoluble in all common organic solvents (b.p. up to 200°C .) and its density is 1.06. Type 2 polycyclobutene, on the other hand, is also insoluble in many low boiling solvents used by us, but is dissolved in some high boiling solvents, like tetralin or chlorobenzene; its density is 1.035. Both the types of polycyclobutenes show high melting temperatures.

On the contrary, by polymerization with some other catalysts, the opening of the cyclobutene ring and maintenance of the double bond have been observed:

A catalyst prepared from TiCl_4 and $\text{Al}(\text{C}_2\text{H}_5)_3$ (1:3 molar ratio) in *n*-heptane yields with high conversion at -50°C . a high molecular weight polymer, which is amorphous at room temperature, and whose I.R. spectrum exhibits substantially pure 1,4-polybutadiene structure (prevalingly *cis*-1,4 with a little quantity of *trans*-1,4 units). A weak band at 3.78μ indicates also the presence of a little quantity of macromolecules with cyclobutenamer-2 structure.

A catalyst prepared from $\delta\text{-TiCl}_3$ (solid solution of TiCl_3 with AlCl_3) and $\text{Al}(\text{C}_2\text{H}_5)_3$ (1:3 molar ratio) in *n*-heptane yields with high conversion at $+45^\circ\text{C}$. a crystalline high molecular weight polymer (Fig. 1, type 3), whose X-ray spectrum exhibits simultaneously crystallinity due to *trans*-1,4-polybutadiene and to polycyclobutylamer-2. The high degree of crystallinity would indicate a mixture of macromolecules of the two types of polymer rather than a copolymer. The I.R. spectrum indicates that the *trans*-1,4-butadiene units are accompanied by a little amount of *cis*-1,4-butadiene units and confirms the presence of polycyclobutenamer-2 units (weak band at 3.78μ).

The formation of two different enchainments of 1,4-butadienes (*cis* and *trans*) by titanium catalysts suggests that the opening of the cyclobutene ring, which has a *cis*-structure, takes place at the bond adjacent to the

double bond, because if the opening of the ring would take place at the bond opposite to the double bond, only butadiene units having cis-structure should be expected.

The possibility to carry out the polymerization of an unsaturated hydrocarbon distinctly into two different chemical polymerization ways by the substitution of titanium with vanadium in transition metal complexes, while operating under the same conditions, suggests different mechanisms for the co-ordinations of the olefin to the different catalytic complexes.

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