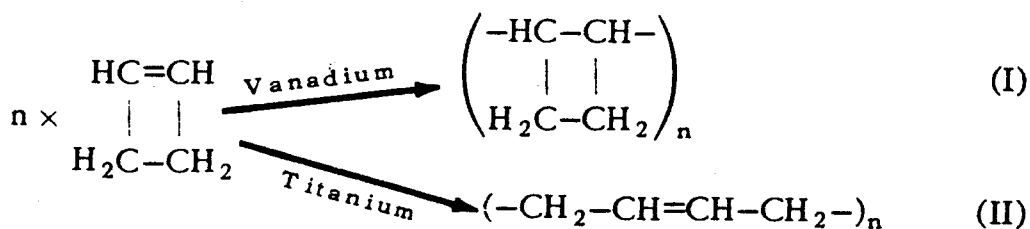


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COORDINATED POLYMERIZATION OF CYCLOBUTENE IN THE PRESENCE OF THE AQUEOUS RhCl_3 CATALYTIC SYSTEM

In two recent publications, (1,2), we have reported the stereospecific polymerization of cyclobutene to crystalline polymers in the presence of catalytic systems prepared from transition metal and organometallic compounds and acting through coordinated anionic mechanisms. Depending on the nature of the transition metal contained in the catalyst, the polymerization can proceed either by the opening of the double bond with formation of enchainment cyclobutane rings (I) or by cleavage of the ring and formation of a polymer having a 1,4-polybutadiene structure (II).



Depending on the catalyst composition and the reaction conditions, two crystalline polycyclobutylenamers-2 (I) having different stereoregularity could be obtained. Experimental evidences and analogies induced us to attribute provisionally to them the erythro di-isotactic and, the erythro di-syndiotactic structure, respectively.

We have now investigated the polymerization of cyclobutene in the presence of the aqueous RhCl_3 catalytic system, which was disclosed by Rinehart et al. (3) for the polymerization of butadiene to pure 1,4-trans-polybutadiene. Though this catalyst does not contain organometallic compounds, the polymerization of butadiene most likely involves at least a π -type of coordination between the metal and the olefinic group (4).

By operating under the conditions described by Rinehart (medium: water + sodium dodecylbenzene sulfonate, monomer/ RhCl_3 mol. ratio 200, reaction temperature $+50^\circ\text{C}$., reaction time 40 hr.), we obtained (conversion 10%) a crystalline polymer having the above indicated polycyclobutylamer-2 structure and high stereoregularity of the type we called erythro di-isotactic.

The polymerization of cyclobutene by ring cleavage (II) in the presence of the RhCl_3 system occurs, according to our observations, only as a side reaction (traces). This type of reaction predominates, on the contrary, in the polymerization of bicyclo-[2,2,1]-hept-2-ene (norbornene) in the presence of analogous "protic" solvent/ Ru^{3+} (or Os^{3+} , or Ir^{3+}) catalytic systems, as was recently shown by Michelotti (5).

As found in our previous experiences (2), cyclobutene can be polymerized only by catalysts acting through coordinated anionic mechanisms, but not by those acting through cationic, "classical" anionic, or radical mechanisms. Therefore, we are inclined to assume that the RhCl_3 catalytic system promotes the polymerization of cyclobutene through a mechanism involving coordination between monomer and rhodium.

Moreover, the stereoregularity observed in this polymerization suggests further analogies between the mechanism of the aqueous RhCl_3 catalytic system and that of those prepared from transition metal and organometallic compounds working in an anhydrous hydrocarbon medium. We are, in fact, inclined to hypothesize an anionic coordinated mechanism also for the RhCl_3 catalytic system. This should also be consistent with the accumulated evidences (6-10) that metals of the 8th group can form organometallic compounds of the π -allylic type, characterized by fairly high stability to compounds containing active hydrogen, like water or alcohols.

Also, in the polymerization of butadiene with soluble catalytic systems prepared from cobalt salts and organoaluminium compounds, which most likely proceeds through a coordinated anionic mechanism, the polymer chains should grow on a cobalt-carbon bond, which is presumably stabilized by the allylic structure of the end of the growing chain bound to the transition metal (11).

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