

The poly (cyclic olefin) is expected to show higher heat-resistance, mechanical strength and modulus than those of conventional polyolefin materials because the molecular motion of its polymer chain is restricted by a cyclic group. In addition, poly(cyclic olefin) can be used as an optical material with low birefringence as it does not have any polar groups. However, the bulkiness of the cyclic olefin monomer is so high that effective catalysts have so far been limited.

Recently, we have succeeded in developing nickel-based catalysts having ultra-high activity for 1,3-cyclohexadiene polymerization (**Fig. 1**). For example, bis (allylnickel bromide) (ANiBr;1) combined with methylaluminoxane (MAO) catalyzed the 1, 3-cyclohexadiene polymerization within 10 minutes at room temperature in toluene to give the polymer in 80% yield. Furthermore, in cyclohexane or *o*-dichlorobenzene, the polymerization was completed within just 1 minute and the yield was almost quantitative. On the other hand, the Zr or Ti complex produced the polymer in only 10-30% yield even after 100 hours. Although the anionic initiator is effective for the 1, 3-cyclohexadiene polymerization, several hours are needed for the reaction to be completed at 40°C. The reasons why the ANiBr/MAO catalyst had higher activity than the other catalysts are as follows.

- 1) It has the same allyl nickel structure as the polymerization growing species.
- 2) It forms cationic species *in situ* by adding MAO.
- 3) It has sufficient reaction space for the sterically demanding monomer.
- 4) It has high solubility in various organic solvents.

Interestingly, it was found that the nickel catalysts have very high regioselectivity. Based on the ^1H , ^{13}C and two-dimensional NMR spectra, the 1,4-polymerization unit is perfectly dominant along the main chain synthesized by these nickel catalysts. As a result, the polymer had high crystallinity which was not obtained when using the anionic polymerization catalyst (**Fig. 2**). The melting point of the 1,3-cyclohexadiene homopolymer is about 320°C. By changing the ligand structure of the nickel catalysts (**Fig. 1**) or by copolymerizing with 1,3-butadiene, the melting point can be controlled from 250 to 300°C. Besides the nickel-based complexes, other late transition metal catalysts development is now in progress.

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References

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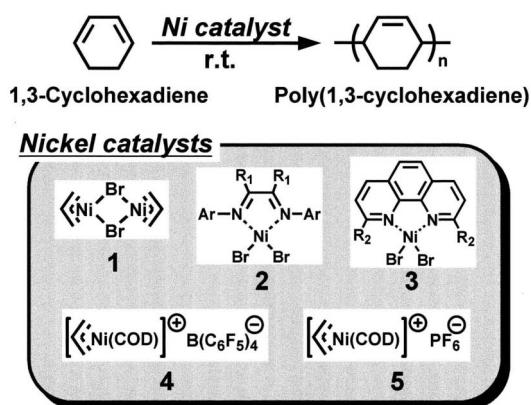


Fig. 1 Regiospecific polymerization of 1,3-cyclohexadiene using highly active nickel-based catalysts. Complexes 1-3 were activated by methylaluminoxane (MAO). ($\text{R}_1=\text{H}$, Me, Acenaphthene; $\text{Ar}=2,6$ -diisopropylphenyl; $\text{R}_2=\text{H}$, Ph; COD=1,5-cyclooctadiene)

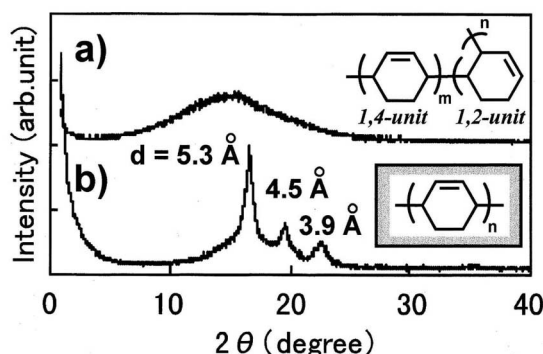


Fig. 2 X-ray diffraction spectra of poly(1,3-cyclohexadiene); synthesized a) by anionic polymerization, b) by nickel catalyzed polymerization. (1,4-unit dominant)