

아크릴로니트릴의 중합시 1,2-DACH의 첨가가 PAN의 입체규칙성에 미치는 영향에 관한 DFT 연구

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A Density Functional Study on the Addition Effect of 1,2-DACH on the Stereoregularity of PAN in the Polymerization of AN

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1. Introduction

Many researchers have made efforts to control the stereoregularity in radical polymerization of vinyl monomers because the physical and chemical properties of the polymer are significantly affected by the stereostructure.[1]-[4] In general, monomer design, reaction conditions(e.g. solvent, temperature, and monomer concentration), and additives can alter the stereochemistry of the radical polymerization of acrylic monomer. Yoshii et al. reported that highly stereoregular polyacrylonitrile(PAN) was polymerized from AN/urea canal complex under high energy irradiation at -78°C . [5] Also, isotactic PAN has been prepared by using Na-Y and N- β zeolite channels as a host.[6] But these methods were very complicated and difficult. So, our previous study focused on a simple method to control of stereostructure of PAN, which utilizes as an additive 1,2-diaminocyclohexane(DACH) with different configurations that has hydrogen-bonding interaction with nitrile group of acrylonitrile(AN). Although it was observed 4-5% of enhancement in the stereocontrol of PAN, it was not clearly understand how 1,2-DACH affects in the stereocontrol mechanism of PAN. In this work, it was thus aimed at elucidating the role of 1,2-DACH in stereocontrolling of PAN using computer simulation method that adopts density functional theory (DFT).

2. Simulation Methodology

Density functional theory calculations were performed to elucidate the effects of different configuration of 1,2-DACH(i.e. cis- and trans- configurations) on the stereocontrol of PAN. The geometries of reactants, transition states, and products were optimized, respectively, and energies of these states were calculated using Dmol3 with the GGA/BLYP method, respectively. Vibrational analysis was performed to determinate whether the calculated geometries are correct at the stationary point.[7]-[8] The calculations have been carried out on the *Materials Studio (Accelrys, U.S.A.)*.

3. Results and Discussion

In this calculations, behavior of tacticity on the polymerization of AN without free 1,2-DACH was also studies for the comparison data. Fig 1. shows the scheme of the reaction profile and structures of each state in the case of the addition of cis-1,2-DACH. And it was observed that syndio-product had lightly lower value of activation energy (6.41kcal/mol) than the iso-product had. Fig 2. shows the scheme of the reaction profile and structures in the case of the addition of trans-1,2-DACH. In this case, syndio-product had much lower value of activation energy (5.19kcal/mol) than the iso-product had. Though the calculation results, it was found that how two different configurations of 1,2-DACH influenced on tacticities of PAN, such as syndio- or iso-product.

4. Conclusions

Though the DFT simulation, it was found that 1,2-DACH of different configurations was an important factor controlling the stereoregularity of PAN. For example, in the 0.5 molar ratio of 1,2-DACH/AN, the stereoregularity of PAN was better controlled by cis-1,2-DACH than by trans-1,2-DACH, however, 1,2-DACH of both configurations energetically favored the formation of syndio-product.

5. References

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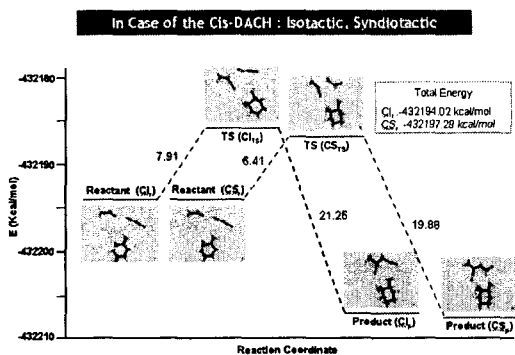


Fig 1. Scheme of the reaction profile in the case of cis-1,2-DACH : Molecular structures and energies of each state

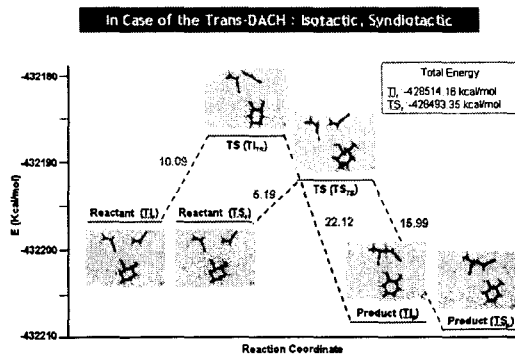


Fig 2. Scheme of the reaction profile in the case of trans-1,2-DACH : Molecular structures and energies of each state