Cyclopentadiene과 ethylene의 Diels-Alder 반응

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Diels-Alder reaction of cyclopentadiene with ethylene

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INTRODUCTION

In recent years, there has been an increasing interest in polynorbornene and photoresist polymer. The former is important because it is one of the fundamental materials for the synthesis of low-galvanic polymers, while the latter is a useful material in the semiconductor industry. Cyclic olefin copolymer(COC) is another important material because its property can easily be varied and the availability of COC ranges from elastomers to High Performance Engineering Plastics including high transparent resins and photochemical polymers. Conventionally, COC's are prepared by copolymerization of cyclic monomers such as norbornene with olefinic comonomers, light alkenes or styrene [1].

In line with the growing interest for the polynorbornene, photoresist polymer, and COC, the synthesis of norbornene has drawn attention because norbornene is one of the most important precursor for these materials. Although it has been generally known that norbornene can be prepared by Diels-Alder reaction, there is little information available for the detailed reaction procedure [2].

In this regard, we have aimed here to investigate the norbornene synthesis via Diels-Alder reaction under various reaction conditions. In addition, a postulated mechanism is proposed on the basis of a kinetic study.

EXPERIMENTAL

Preparation of cyclopentadiene (CPD)

Norbornene(NBN) synthesis is carried out via Diels-Alder reaction with CPD as a diene and ethylene as a dienophile. Because unstable CPD exists as dicyclopentadiene(DCPD) at ambient temperature, the pyrolysis of DCPD is prerequisite to use CPD as a reactant.

Pyrolysis of DCPD was carried out in a 100-ml three-neck round bottom flask equipped with a funnel to drop DCPD and a condenser. 20ml of DCPD was dropped to heated silicon oil(190°C) and then the pyrolyzed materials were quenched by liquid nitrogen trap. The resulting mixtures obtained from the former pyrolysis step were evaporated at 50°C to prepare pure CPD. The corresponding CPD was stored in a deep-freezer at -70°C before use.

Thermal Reaction

The Diels-Alder reaction of CPD and ethylene was carried out in a semi-batch autoclave. 0.044mol of CPD, 0.022mol of cyclohexane(internal standard), and solvent(34ml) were added to the reactor and the reaction mixture heated to the desired temperature. After the reactor was pressurized with ethylene, the reaction was started. Samples were taken out periodically during the course of reaction and analyzed by GC on HP-1 column with an FID detector. The products were confirmed by comparison with authentic samples and using the method of GC-mass analysis.

We also performed the reaction with DCPD because an *in-situ* pyrolysis of DCPD is possible at high temperatures. This indicates that the cumbersome pyrolysis step can be avoided.

RESULTS AND DISCUSSION

Figure 1 shows the results of reactions with CPD and DCPD, respectively. At a temperature of 260°C, the reaction with DCPD was faster than that with CPD. This indicates that the high temperature accelerates the pyrolysis of DCPD. Moreover, CPD produced by the *in-situ* pyrolysis may be easily reacted with ethylene. This leads to the increase in the reaction rate.

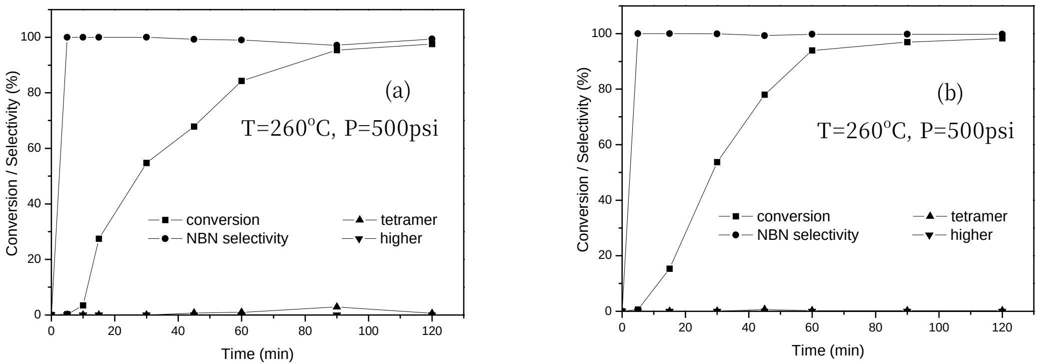


Fig. 1. Reaction results with two different reactants: (a) CPD as a reactant; (b) DCPD as a reactant.

Temperature effect

The effect of temperature on conversion and NBN selectivity was investigated under the reaction pressure of 500psi. In view of the reaction rate, it is natural that raising the reaction temperature may give rise to the enhancement of the reaction rate in the thermal reaction. As shown in Fig. 2, increasing temperature from 220°C to 260°C results in the increase of conversion. Above the reaction temperature of 260°C, however, conversion decreased. It is likely that the decrease of conversion is due to the reduced partial pressure of ethylene induced by the solvent evaporation at a higher temperature. The effect of temperature on NBN selectivity under the reaction pressure of 500psi is shown in Fig. 3. It was revealed that NBN selectivity decreased as the reaction temperature increased. The result of GC-mass analysis indicates that the reduced NBN selectivity at a higher temperature was caused by the formation of tetracyclopentadiene by the copolymerization of NBN with CPD.

Pressure effect

Figures 4 and 5 represent the effect of pressure on the reaction performance. It is clear that the increase of pressure is favorable to accelerate the reaction rate because the high pressure may increase the solubility of ethylene. Furthermore, it was found from Fig. 5 that the increase of pressure also results in the improvement of NBN selectivity. It is considered that the high pressure of ethylene keeps the ratio of ethylene to CPD high in the reaction mixture. Therefore, the reaction of ethylene with CPD takes place more readily than that of CPD with NBN, which leads to the formation of by-product such as tetracyclopentadiene.

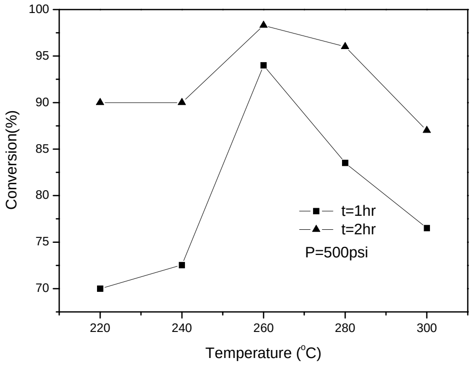


Fig. 2. Effect of temperature on conversion.

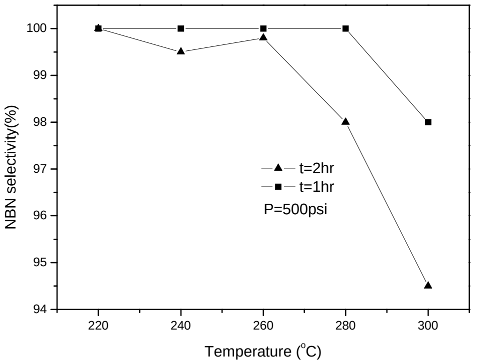


Fig. 3. Effect of temperature on NBN selectivity.

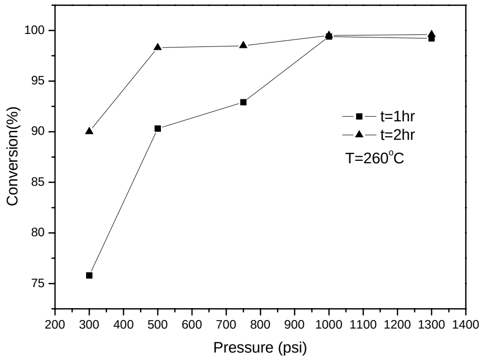


Fig. 4. Effect of pressure on conversion.

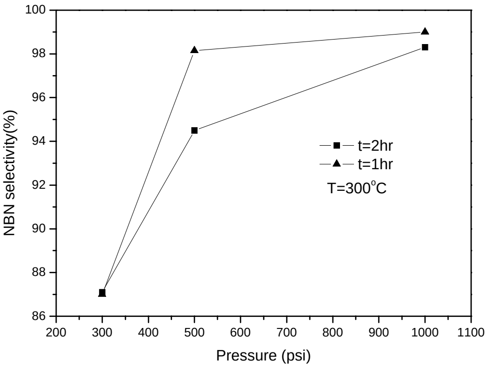
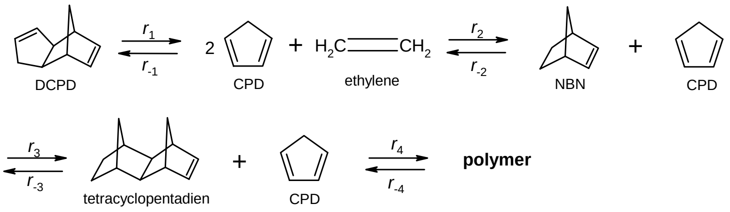


Fig. 5. Effect of pressure on NBN selectivity.

Reaction kinetics of NBN synthesis



Scheme 1

The general reaction scheme of the Diels-Alder reaction of CPD with ethylene is presented in Scheme 1. All of the reactions are equilibrium–limited, and the net rates of formation for individual components are as follows:

$$r_{\mathrm{DCPD}} = -r_1 + r_{-1}, \qquad r_{\mathrm{CPD}} = r_1 - r_{-1} - r_2 + r_{-2} - r_3 + r_{-3}, \qquad r_{\mathrm{NBN}} = r_2 - r_{-2} - r_3 + r_{-3},$$

$$r_{\mathrm{tetracyclopentadiene}} = r_3 - r_{-3} - r_4 + r_{-4}, \qquad r_{\mathrm{higher\ aggregator}} = r_4 - r_{-4}$$

where r_i denotes the reaction rate of the i-th reaction. Since there are many reactions and species involved, it may not be allowed to include all the parameters appearing in the expressions for the individual reaction rates. Therefore, it is necessary to simplify the rate expressions on the basis of the experimental and reported results. First ethylene dependence may be neglected because ethylene is continuously supplied in excess under the condition of constant pressure during the entire reaction course, and thus r_{-2} may be assumed negligibly small. We also exclude r_4 and r_{-4} because polymer was not detected under the present reaction conditions. Without sufficient information on the orders of reactions, we will assume that the reaction orders may be specified by the stoichiometric coefficients except for the case of r_2 [5,6]. As a result, we have

$$r_1=k_1[DCPD],\quad r_{-1}=k_{-1}[CPD]^2,\quad r_2=k_2[CPD]^{n_{21}},\quad r_3=k_3[NBN][CPD],\quad r_{-3}=k_{-3}[tetracyclopentadiene]$$

For the purpose of parameter estimation, the reaction was carried out with the initial DCPD concentration of 0.8M at 260°C and 500psi. The kinetic parameters were estimated with Polymath software [4] by minimizing the sum of squares of residuals between the experimental measurements and the results obtained by the above kinetic model. The minimization was performed by the Levenberg-Marquardt method.

The estimated parameter values are listed in Table 1 and the simulation results obtained by using the estimated parameter values are shown in Fig. 6 in comparison with the experimental results. Considering the simplifying assumptions discussed in the above, one may claim that the kinetic model with the estimated parameters can predict the experimental results reasonably well.

Table 1 Kinetic parameters estimated the Levenberg-Marquardt method

Parameter	k_1	k_{-1}	k_2	k_3	k_{-3}	n_{21}
Property	0.03743	0.00352	0.04858	0.04036	0.056	1.12727

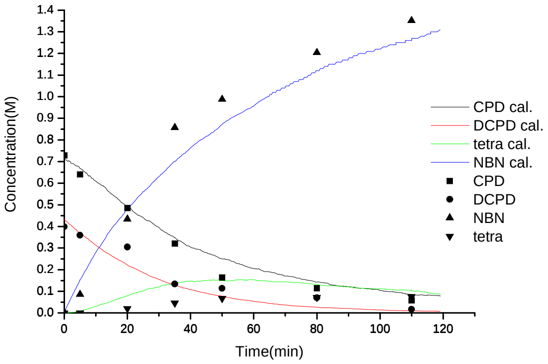


Fig. 6. Simulation result with the estimated parameter values.

CONCLUSIONS

NBN has been synthesized via Diels-Alder reaction. The best reaction performance was obtained when the reaction was carried out with DCPD as a reactant at 260°C and 1000psi. In addition, the kinetic model with the estimated parameters can predict the experimental results well.

ACKNOWLEDGMENTS

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