

The Relation between the Alternating Copolymerization and the Diels—Alder Reaction

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ABSTRACT: The relation between the alternating copolymerization of butadiene with acrylonitrile and the Diels—Alder addition reaction was investigated. It was found that the acidity of the Lewis acids as complexing agents affects not only the former reaction but also the latter one, but the selectivity towards both reactions is little affected. On the other hand, the addition of the vanadyl compound as a cocatalyst or the irradiation of UV-light enhances the selectivity towards the alternating copolymerization preventing the formation of the Diels—Alder adduct. Experiments at varied temperatures show that the Diels—Alder reaction is a thermal reaction, whereas the alternating polymerization is enhanced by UV-irradiation with the low activation energy. However, the yields of the products in both reactions attain their maxima at a 1:1-monomer composition and at the same moderate acidity of the complexing agent such as aluminum halide. It is concluded that both reactions arise from the same intermediate such as the ternary complex and the difference may consist in the energy state of the intermediate. According to the Woodward—Hoffmann rule, the energy state of butadiene is normal for the Diels—Alder reaction, whereas it is triplet *transoid* for the alternating copolymerization.

KEY WORDS Alternating Copolymerization / Diels—Alder Reaction / Acrylonitrile—Methyl Methacrylate—Butadiene / Lewis Acid Catalyst / AIBN / UV-Irradiation / Vanadyl Chloride / Activation Energy / Reaction Mechanism /

In the alternating copolymerization of acrylic monomer with diolefin, an appreciable amount of Diels—Alder adduct was formed as a by-product when the reaction temperature was raised above room temperature. In the case with aluminum chloride(AlCl_3) as a complexing agent, the polymerization requires the much higher temperature because of its low activity, and as a result the much larger amount of Diels—Alder adduct is formed. The reaction between butadiene(BD) and acrylic compound accelerated by aluminum chloride at elevated temperature was already attempted by Inukai, *et al.*, and the main product was the Diels—

Alder adduct.¹

Gaylord, *et al.*,² pointed out that the Diels—Alder adduct was produced in greater amounts in the reaction with aluminum chloride than in the reaction with zinc chloride(ZnCl_2) and they ascribed the result to the difference of acidity of two Lewis acids; the former is more electron-attracting favoring the *cisoid* coordination of butadiene, whereas the latter is *transoid*, and as a result, the former affords the Diels—Alder adduct and the latter the alternating copolymer. However, as will be described later, Lewis acids affect markedly not only the Diels—Alder reaction but also the alternating copolymerization, and the effects run parallel to each other. An extensive study suggests that the essential factor for the selectivity towards the Diels—Alder addition and the alternating copolymerization is not the acidity of Lewis acids but the effect

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of UV-irradiation or that of vanadyl compounds as a cocatalyst.

EXPERIMENTAL

The reactions of butadiene and acrylic monomers were conducted according to the procedure reported previously.³ As metal halides and azobisisobutyronitrile, all commercial products of guaranteed grade were used. The reaction under UV-irradiation was conducted in a sealed test tube of hard glass. UV-light was supplied by a high pressure mercury lamp of 300 W, Model PIH 300, made by Eikosha Co.

The Diels—Alder adducts formed were quantitatively measured by a Yanaco GCG-500 T gas chromatograph using *p*-xylene as an internal standard (1.5-m length column packed with DOP, at 135°C, H₂ 30 ml/min) or by a Shimadzu Model GC-5A gas chromatograph using nitrobenzene as an internal standard (3-m length column packed with Chromosorb-W 60—80 mesh holding 25% of PEG-6000, at 180°C, under 100 ml/min helium stream) equipped with hydrogen flame detector and cooperating integration recorder.

Polymer compositions were calculated from C/N, C/O or C/N/O ratio obtained in the elemental analysis.

RESULT AND DISCUSSION

The reaction between acrylonitrile(AN) and butadiene(BD) was carried out at 0°C with use of ethylaluminum dichloride(EtAlCl₂) as a complexing agent and vanadyl chloride(VOCl₃) as a cocatalyst. The main product was an alternating copolymer but it was accompanied by an appreciable amount of Diels—Alder adduct. Figure 1 indicates that the Diels—Alder adduct is about 5% as much as the alternating copolymer, and at a 1:1-monomer composition the yields of products attain maxima both in the Diels—Alder adduct and the alternating copolymer. A similar tendency is obtained as shown in Figure 2. Here, the reaction was carried out with use of ethylaluminum dichloride alone.

These phenomena suggest that both the reactions may take place bimolecularly between two monomers or through a 1:1 complex. This is

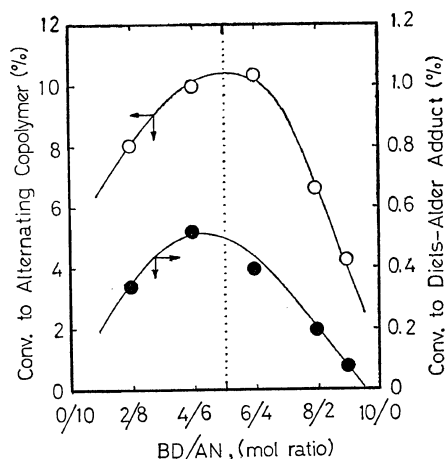


Figure 1. Effect of BD/AN ratio on the yield of reaction product: BD+AN, 532 mmol; EtAlCl₂, 2.66 mmol; VOCl₃, 0.13 mmol; reaction temp, 0°C, 20 hr.

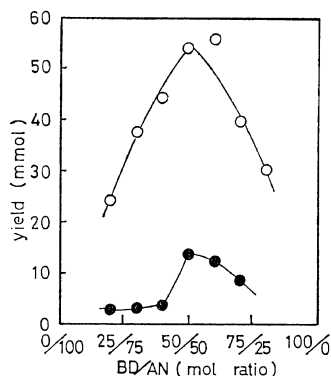
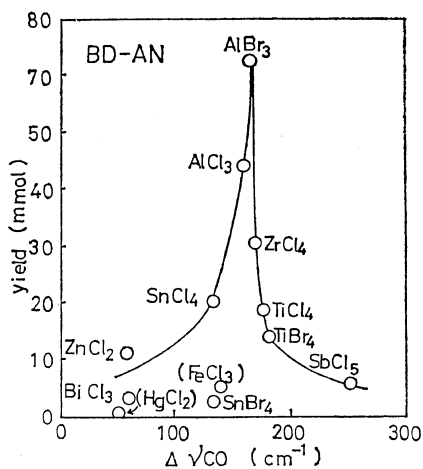


Figure 2. Effect of BD/AN ratio on the yield of reaction product: BD+AN, 400 mmol; EtAlCl₂, 10 mmol; toluene, 10 ml; *p*-xylene, 2 ml; ○, C#CC=Cc1ccc(C#N)cc1; ●, C#CC=Cc1ccc(C#N)cc1; reaction temp, 60°C, 3 hr; ●, C#CC=Cc1ccc(C#N)cc1; reaction temp, 0°C, 2.5 hr.

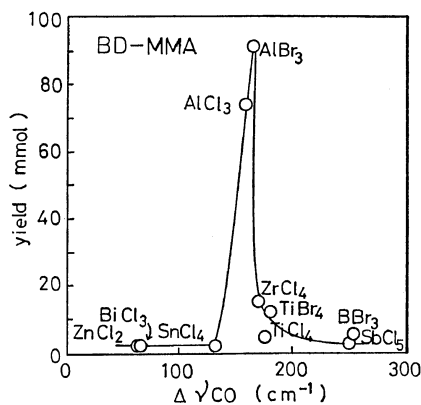
likely in the Diels—Alder reaction. On the contrary, in the copolymerization the reaction takes place not between two monomers except in the case of the polymerization of a 1:1-complexed monomer. In a simple copolymerization of butadiene and acrylonitrile—Lewis acid complex, the rate of alternating copolymerization R_p is expressed as follows;

$$R_p = \{k_{12}[M_1 \cdot][M_2] + k_{21}[M_2 \cdot][M]\}$$

Alternating Copolymerization



(a)



(b)

Figure 3. Effect of Lewis acidity on the yield of Diels—Alder adduct: AN, 100 mmol; MMA, 100 mmol; BD, 100 mmol; MX_n , 5 mmol; toluene, 10 ml, *p*-xylene, 1 ml; reaction temp, 50°C, 10 hr for AN—BD, 3 hr for MMA—BD.

where M_1 and M_2 are butadiene and acrylonitrile—Lewis acid complex, respectively, and $M_1\cdot$ and $M_2\cdot$ are the corresponding radicals, k_{12} and k_{21} being the rate constants. If the copolymerization attains the stationary condition

$$k_{12}[M_1\cdot][M_2] = k_{21}[M_2\cdot][M_1]$$

$$[M_1\cdot] + [M_2\cdot] = [R\cdot] = \text{const.},$$

it follows that

$$R_p = [R\cdot] \frac{k_{12}k_{21}[M_1][M_2]}{k_{21}[M_1] + k_{12}[M_2]}$$

This equation affords the maximum R_p at $[M_1]/$

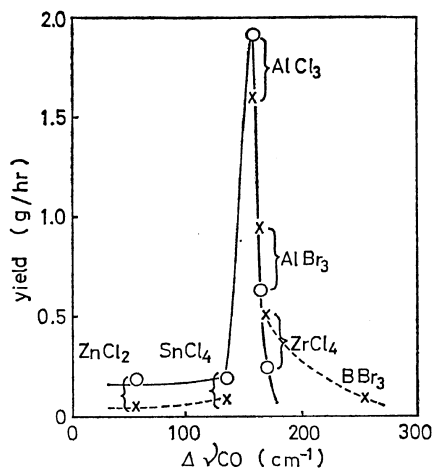


Figure 4. Effect of Lewis acidity on the yield of alternating copolymer: AN, 200 mmol; BD, 100 mmol; MX_n , 2 mmol; AIBN, 0.3 mmol; toluene, 10 ml; *p*-xylene, 1 ml; reaction temp, 50°C (○, AIBN) or 21°C (×, UV).

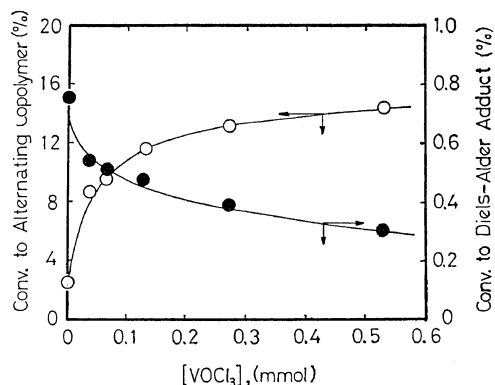
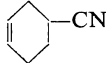


Figure 5. Effect of $VOCl_3$ on the yield of reaction product: AN, 266 mmol; BD, 266 mmol; $EtAlCl_2$, 2.66 mmol; reaction temp, 0°C, 33 hr.

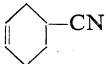
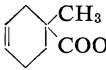
$[M_2]$ being $(k_{12}/k_{21})^{1/2}$ but not at $[M_1]/[M_2]$ being unity. Consequently the alternating copolymerization arises from a 1:1 complex intermediate such as Lewis acid—acrylic monomer—butadiene. As an intermediate complex for the alternating copolymerization, the ternary complex has already been proposed^{4,5} from kinetic study and NMR spectroscopic study of the reaction mixture.

The yields of the Diels—Alder adduct both between acrylonitrile and butadiene and between methyl methacrylate (MMA) and butadiene were

Table I. Effect of UV-irradiation on the yields of alternating copolymer and Diels—Alder adduct(a) BD—AN—AlCl₃ system^a

| Product | Yield, $\times 10^{-3}$ mmol/min unit | |
|---|---------------------------------------|------------------------|
| | Dark reaction | UV-irradiated reaction |
| Alt. copolymer ^b | 0 | 147.3 |
|  | 23.5 | 12.8 |

^a [BD], 266 mmol; [AN], 266 mmol; [AlCl₃], 2.66 mmol; 20°C, 40 min.^b $[-\text{CH}_2-\text{CH}(\text{CN})-\text{CH}=\text{CH}-\text{CH}_2-]_n$ unit.(b) BD—AN—MMA—AlCl₃ system^a

| Product | Yield, $\times 10^{-3}$ mmol/min unit | |
|---|---------------------------------------|------------------------|
| | Dark reaction | UV-irradiated reaction |
| Alt. copolymer ^b | | |
| (BD—AN) unit | 0 | 23.4 |
| (BD—MMA) unit | 0 | 27.5 |
| Diels—Alder adduct | | |
|  | 2.6 | 2.1 |
|  | 145.1 | 87.4 |

^a [BD], 266 mmol; [AN], 133 mmol; [MMA], 133 mmol; [AlCl₃], 2.66 mmol; 20°C, 280 min.^b $[-\text{CH}_2-\text{CH}(\text{CN})-\text{CH}=\text{CH}-\text{CH}_2-]_n$ or $[-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}=\text{CH}-\text{COOCH}_3-]_n$ unit.

investigated with use of various Lewis acids as complexing agents. As illustrated in Figure 3, the yields are demonstrated as a function of the acidity of the complexing agent.

The acidity of the Lewis acids was evaluated in terms of the magnitude of C=O shift of xanthone complexed with Lewis acid according to the method of Cook.⁶ The catalysts shown in parentheses were partly soluble in the reaction mixture. It is interesting that there is a maximum at a suitable acidity of Lewis acids. A similar effect is also found in the alternating copolymerization by Lewis acid under UV-irradiation or with AIBN as an initiator. As shown in Figure 4, the maxima exist in both cases at almost the same acidity. These relations

lead us to the conclusion that acidity of Lewis acid is an influential factor in the formation of the intermediate complexes for both reactions but not essential to the selectivity towards both reactions. The intermediate complex might be common to both reactions.

On the other hand, a characteristic effect of vanadyl chloride on the selectivity toward both reactions was found. Figure 5 indicates the variation of the selectivity with the amounts of the added vanadyl compound. The vanadyl chloride favors the formation of the alternating copolymer at the expense of the Diels—Alder product. Another factor influential on the selectivity was also found in UV-irradiation. The results of the reaction of acrylonitrile and butadiene and that of acrylonitrile, methyl methacrylate, and butadiene tercomponents in the presence of aluminum chloride with or without UV-irradiation are summarized in Table I. Aluminum chloride itself afforded no polymer in the dark and instead yielded the Diels—Alder products. But the irradiation of UV-light seems to change the product from the Diels—Alder adduct to the alternating copolymer. The effect is very similar to that of the addition of vanadyl chloride. The photo-reaction is favorable to the alternating copolymerization, whereas the thermal reaction is favorable to the Diels—Alder reaction.

In fact, the different activation energies of the Diels—Alder reaction and alternating copolymerization in the presence of ZnCl₂ are obtained from the Arrhenius' plots as illustrated in Figure 6. The *k*'s are the first-order rate constant of the reactions.

From these facts it is concluded that the Diels—Alder reaction and the alternating copolymerization arise from a common intermediate having a 1:1-composition of acrylic monomer and butadiene, and appreciable difference may exist in the activated states. The Diels—Alder reaction is a thermal reaction, whereas the alternating copolymerization is favored by the high energy reaction activated, for instance, by UV-irradiation or by the addition of vanadyl compounds as the catalyst component together with alkylaluminum halide.^{3,7,8} The energy states of both intermediates will be discussed in a further report concerning photopolymerization. The following is a tentative scheme for the

Table II. Photopolymerization of butadiene with acrylonitrile with use of $\text{AlCl}_3\text{--VOCl}_3$ catalyst^a (Effect of sensitizer and quencher)


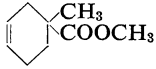
| VOCl_3 , mmol | Sensitizer or quencher | E_T^{11} kcal/mol | Reaction time, min | Polymer yield, % | $[\eta]^c$, dl/g | Gel content, % |
|------------------------|------------------------|---------------------|--------------------|------------------|-------------------|----------------|
| 0.106 | none | — | 120 ^b | trace | — | — |
| 0.106 | none | — | 120 | 11 | 1.45 | 0 |
| 0.106 | Xanthone | 74 | 120 | 26 | — | 15 |
| 0.106 | Naphthalene | 61 | 120 | 49 | 1.95 | 61 |
| 0.106 | Pyrene | 49 | 120 | 44 | 0.66 | 61 |
| 0 | none | — | 30 | 19 | — | 42 |
| 0 | Azulene | 31—39 | 160 | 0 | — | — |

^a [BD], 53 mmol; [AN], 304 mmol; $[\text{AlCl}_3]$, 2.12 mmol; [Sensitizer] or [Quencher], 1.06 mmol; reaction temp, 20°C.

^b Dark reaction.

^c Intrinsic viscosity of the soluble part in dimethyl formamide at 30°C.

Table III. Gas chromatogram of reaction mixture^a

| Reaction system (molar ratio) | Relative retention time, min | | | | | | |
|--|------------------------------|-----|------------------|-----|--|---|-----|
| | 0.5 | 1.1 | 1.7 | 2.9 | 5.1 | 5.6 | 7.8 |
| BD—MMA (9 : 7) | — | ○ | ○ | ○ | ○ | — | ○ |
| BD—AN (9 : 1) | ○ | — | ○ | ○ | ○ | ○ | — |
| BD | — | — | ○ | ○ | ○ | — | — |
| AN | ○ | — | — | — | — | — | — |
| BD—MMA— AlCl_3 (9 : 1 : 10^{-2}) | — | ○ | — | — | — | — | ○ |
| BD—AN— AlCl_3 (9 : 1 : 10^{-2}) | ○ | — | — | — | — | ○ | — |
| Tentative assignment | AN | MMA | Cyclodimer of BD | |  |  | |

^a Reaction conditions: room temp, 24 hr. Column conditions: Apiezone-L, 3 m, 150°C, He.

seems to inhibit the photopolymerization as shown in Table II.

These considerations are compatible with the requirement from the molecular symmetry. It is noticeable that the excited triplet state of butadiene is also favorable to the formation of cyclobutane derivatives in the reaction without a complexing agent.¹⁰ Table III indicates that the Diels—Alder adduct is mainly detectable gas-chromatographically from the reaction mixture of butadiene with acrylonitrile or methyl methacrylate in the presence of AlCl_3 under UV-irradiation, whereas both the Diels—Alder adduct and the cyclodimer of butadiene are obtained from the reaction mixture in the absence of AlCl_3 under UV-irradiation. The complexing agent may disturb the molecular symmetry for the formation of the cyclobutane ring and favors the alternating copolymerization.

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