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Optically Active Alternating Copolymer and Diels-Alder Adduct

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Summary

Asymmetric induction copolymerization and Diels-Alder reaction were investigated between acrylic monomer and olefin or diolefin with use of an optically active aluminum compound as the complexing agent. In the copolymerization, only benzofuran gave an optically active alternating copolymer, while butadiene and indene gave alternating copolymers but with no optical activity. $EtAlCl_2$-*l*-menthol was the most effective complexing agent. However, $EtAlCl_2$-*d*-neomenthol was ineffective.

On the other hand, Diels-Alder reaction was in general more easily stereocontrolled. For instance, both complexing agents were effective for the synthesis of optically active Diels-Alder adducts with butadiene or cyclopentadiene, perhaps due to the rigid cyclic structure in a transition state of the reaction.

Introduction

Until recently a large number of papers were published on the syntheses of optically active polymers by using prochiral monomers such as benzofuran (NATTA et al. 1961, HAYAKAWA et al. 1967), 2-methyl-4,5-dihydrofuran (KAMO et al. 1974), naphthofuran (BRESSAN et al. 1966), alkyl sorbate (NATTA et al. 1961, 1963) and 1,3-pentadiene (NATTA et al. 1961, 1963, FARINA et al. 1971). However, optically active copolymers from prochiral monomers are scarcely known. The authors reported the optically active alternating copolymer of acrylic monomers with benzofuran in the presence of the chiral aluminum compounds (KOBAYASHI et al. 1979).

In the Diels-Alder reaction, optically active addition products were produced from the optically active monomer such as di-(-)-menthyl fumarate with butadiene (KOROLEV et al. 1948, WALBORSKY et al. 1963), but not from a prochiral monomer. The optical yield was less than 3% but it was markedly increased to 76% in the presence of $AlCl_3$. An optically active Diels-Alder adduct may also be synthesized by a reaction of prochiral diene and dienophile in the presence of a chiral Lewis acid.

This paper deals with the synthesis of optically active alternating copolymers and Diels-Alder adducts from prochiral monomers with the aid of the chiral aluminum compounds.

Experimental

Reagents : Benzofuran(BF), indene(ID), butadiene(BD), cyclo-

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pentadiene(CPD), acrylonitrile(AN), methyl acrylate(MA), dimethyl fumarate, optically active alcohols and toluene were purified in the same manner as before (KOBAYASHI et al. 1979).

Aluminum compounds : 4-Menthoxybutylaluminum dichloride(MBAD) was prepared by adding ether solution (200 ml) of 4-menthoxybutylmagnesium chloride to an equimolar amount of $AlCl_3$ (36 g) dispersed in ether (200 ml) with stirring at room temperature. After the reaction for 3 days, $MgCl_2$ precipitated was filtered off and the ether solution was condensed to drying, and then hexane was added. The insoluble $MgCl_2$ was filtered off and finally a transparent oily product was obtained. The oily product could not be distilled even under highly reduced pressure by an oil diffusion pump. The oily product gave an equimolar amount of menthyl butyl ether and aluminum salt on hydrolysis, indicating the structure proposed below[II].
Menthylaluminum dichloride(MenAlCl_2) was prepared from menthylmagnesium chloride and $AlCl_3$. The method of preparation and isolation was almost same as that mentioned above. Alkoxyaluminum compounds were prepared in the same manner as before.

Copolymerization and Diels-Alder reaction : The copolymerization and Diels-Alder reaction were carried out in the same manner as before. Copolymers precipitated in methyl alcohol were purified repeatedly by a dissolution(DMF) and precipitation(MeOH) method. In the case of Diels-Alder reaction the reaction mixture was poured into a methyl alcohol-water mixture and then extracted with ether. The yield of 4-cyanocyclohexene was quantitatively analyzed and isolated by the GCG method by using a Silicon-DC-550 column and p-cymene as an internal standard. The product containing cyclopentadiene was analyzed by using a PEG 20M column and p-methylanisole as an internal standard. The retention time of the endo adduct was longer than that of the exo adduct, and the fractional GCG method was employed for the separation of both adducts.

The structures were determined by the ^{1}H-NMR and elementary analyses and the specific rotation measurement by a JASCO DIP-180 photometer.

Results and Discussion

Copolymerization of AN with BF : 3 or 4-alkoxyaluminum compounds are found to exist in a monomeric state (BAEHR et al. 1955). 4-Menthoxybutylaluminum dichloride also seems to exist in a monomeric state. A cyclic structure is formed by the coordination of ether oxygen onto the aluminum, because there is no ethyl ether remained by the NMR method. TABLE I summarizes the results of copolymerization of AN with BF. The AN-content in the copolymers decreases with increasing the amount of aluminum compound and a 1:1 copolymer could not be obtained because of the insufficient acid strength of MBAD as complexing agents. The [α] value of the copolymer is rather small. The coordination of AN onto aluminum compound may be disturbed by a strong donor oxygen of MBAD.

TABLE II shows the copolymerization results in the presence of various complexing agents. It is noticed that *d*-neomenthol [VII] scarcely induces the asymmetric induction copolymerization. This is perhaps due to the steric hindrance of the axial position of alkoxyaluminum group. Consequently, *d*-neomenthol is less

TABLE I. Copolymerization of AN with BF in toluene at 30°C for 24∿48 hr

complexing agent	[al]/[AN] molar ratio	yield,%	copolymer AN-content,%	$[\alpha]_D^{r.t.}$ a), degree
AIBN only	0	12.7	87.6	0
MBAD [II]	1.0	0.8	64.7	—
	0.67	0.8	74.1	—
MBAD [II] + AIBN	1.0	19.4	70.2	- 3.30 b)

[AN]/[BF]=1, [AIBN]/[II]=0.01 molar ratio, a) in DMF, b) [η]=0.38 in DMF at 25°C

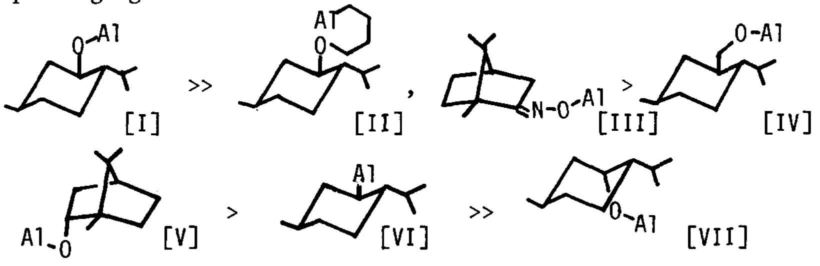
TABLE II. Copolymerization of AN with BF by various Lewis acids in toluene at 30°C for 16∿72 hr

complexing agent	copolymer yield %	AN-content %	$[\alpha]_D^{r.t.}$ a) degree	$[\eta]_{DMF}^{25°C}$ dl/g
$EtAlCl_2$-*l*-menthol[I]	22.8	57.6	-10.73	0.44
	25.9	58.4	-10.43	0.71
$EtAlCl_2$-*d*-neomenthol[VII] (65.7)	17.6	55.0	- 2.93	—
(73.9)	8.6	51.7	- 1.87	—
(93.1)	6.9	61.7	0	—
$MenAlCl_2$[VI]	43.4	51.5	- 0.63	—
$EtAlCl_2$-*l*-menthyl carbinol[IV]	59.4	51.6	- 2.81	—
$EtAlCl_2$-*l*-camphor oxime[III]	25.2	59.2	+ 3.07	0.12
$EtAlCl_2$-*l*-borneol[V]	13.8	63.4	- 1.67	0.20

[al]/[AN]=1, [AIBN]/[al]=0.01 molar ratio, a) in DMF. The number in the parenthesis means the content of *d*-neomenthol in the mixture of *l*-menthol and *d*-neomenthol.

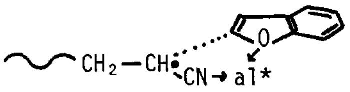
effective as a complexing agent. $MenAlCl_2$ gave alternating copolymer, although the [α] value of copolymer was very small. Accordingly, the best complexing agent is $menOAlCl_2$[I]. The growing chain end, for instance the terminal carbon having nitrile group, may be favorably controlled by the complexing agent of [I]. [IV] has a chiral center existing far from aluminum and [VI] near from aluminum. However, both complexing agents have a lower ability than [I] for the asymmetric induction copolymerization.

Consequently, the order of the asymmetric induction of the complexing agents is as follow:



Copolymerization of AN with ID or BD : ID having methylene instead of ether oxygen of BF was copolymerized with AN under a condition that $[menOAlCl_2]/[AN]=1$, $[AIBN]/[al]=0.01$ molar ratio in toluene at 30°C. The AN-content in the copolymers was 50.1 %. However, the copolymer did not show optical activity. Probably, the ether oxygen of BF may be an essential factor for the stereo-control of polymer chain by the coordination of oxygen onto aluminum.

In the case of AN-BD copolymerization the $menOAlCl_2$-$VOCl_3$ system did not show the polymerization activity at all. The $EtAlCl_2$-$VOCl_2(menO)$ and $menAlCl_2$-$VOCl_3$ system gave alternating copolymers having no optical activity.



Diels-Alder reaction of acrylic monomer with BD : TABLE III summarizes the reaction conditions and results. The polymer yield was negligibly small.

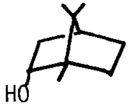
TABLE III. Diels-Alder reaction of AN with BD in toluene at 60°C

$[menOAlCl_2]/[AN]^{a)}$ molar ratio	[AN] mol/l	reaction time hr	yield %	$[\alpha]_D^{r.t.}$ degree$^{b)}$
1.0	0.82	15	73	+ 2.08
0.5	1.36	15	61	+ 2.08
0.2	2.31	15	55	+ 2.06
0.1	3.00	39	56	+ 2.16
0.05	3.00	39	43	+ 1.96
0.02	2.50	60	26	+ 2.05
0.01	2.50	60	19	+ 2.00
0	3.00	60	13	0

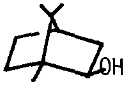
$[BD]/[AN]=2$ molar ratio, a) $EtAlCl_2$-*l*-menthol, b) in $CHCl_3$

The yield of 4-cyanocyclohexene is increased with increasing the amount of aluminum compound, while the [α] value remains constant, indicating the high reactivity of AN complexed with aluminum compound. At high temperature, for instance 100°C, the [α] value decreased to + 1.59 as it is in usual cases.

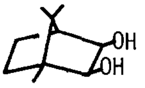
TABLE IV illustrates that $(menO)_2AlCl$ gives the adduct having relatively high [α] value, while the catalytic activity is low due to its weak acid strength. It is noteworthy that the Lewis acid $EtAlCl_2$-*d*-neomenthol is active for the synthesis of the optically active adduct but not for that of optically active copolymer. $EtAlCl_2$-*l*-isoborneol does not afford optically active adduct, but *l*-borneol does, suggesting that the endo alkoxyaluminum of 2-position is effective for the arrangement of the chiral field but not the exo alkoxyaluminum of 2-position.



l-borneol



l-isoborneol



l-bornane-2,3-diol

In the case of MA dienophile the [α] value of Diels-Alder

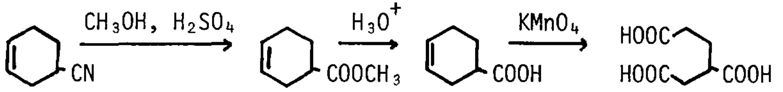
TABLE IV. Diels-Alder reaction of AN with BD in toluene at 60^{o}C

Lewis acid, C	[C]/[AN] molar ratio	reaction time, hr	yield %	$[\alpha]_D^{r.t.}$ degree$^{a)}$
Et_2AlCl-*l*-menthol (1:2)	0.1	24	7	+ 2.82
	0.02	24	6	+ 4.44$^{b)}$
Et_2AlCl-*l*-menthol (1:1)	0.5	54	26	+ 1.53
	0.1	54	56	+ 1.01
	0.02	54	45	+ 0.60
$EtAlCl_2$-*d*-neomenthol	0.1	498	58$^{c)}$	+ 2.74
$EtAlCl_2$-*l*-borneol	0.1	24	42	+ 0.45
$EtAlCl_2$-*l*-isoborneol	0.1	62	33	0
Et_2AlCl-*l*-bornane-2,3-diol	0.1	100	16	- 1.13

[BD]/[AN]=2 molar ratio, a) in $CHCl_3$, b) The optical yield was 6.2 %. c) at 0^{o}C. Purity of *d*-neomenthol was 86.6 %.

adduct decreased from + 2.37 to + 0.45 with decreasing the molar ratio of [menOAlCl$_2$]/[MA] from 0.5 to 0.01 in toluene at 0^{o}C. This tendency is probably due to the lower coordination ability of MA onto aluminum compound, because the reactivity of MA for Diels-Alder reaction is almost same as that of AN (SEGUCHI et al. 1975). In the case of dimethyl fumarate the [α] value of trans adduct was only - 0.63 in $CHCl_3$ at room temperature ([menOAlCl$_2$]/[diester]= 0.1, [BD]/[diester]=2 molar ratio in toluene at 60^{o}C).

The optical yield was determined as follows. In the course of these procedures, the configuration of α-carbon of AN unit was assumed to retain. The number in the parentheses means the [α] value of the compounds at room temperature.



(+ 2.07, $CHCl_3$) (+ 1.67,$CHCl_3$) (+ 1.47,EtOH) (+ 0.47,acetone)

The maximum rotation of butane-1,2,4-tricarboxylic acid was reported to be + 16.39 in acetone (FREUDENBERG et al. 1953). Thus, the optical purity of 4-cyanocyclohexene of [α]= + 2.07 was calculated to be 2.9 %. According to these procedures the maximum value of [α] of 4-cyanocyclohexene and 4-carbomethoxycyclohexene can be estimated to be + 71.4 and + 57.6 in $CHCl_3$ at room temperature, respectively.

Diels-Alder reaction of acrylic monomer with CPD : In the case of CPD the [α] value and the yield of endo adduct depend on the molar ratio of [menOAlCl$_2$]/[AN]. It may be due to the extremely high reactivity of CPD compared with BD even in the absence of Lewis acid catalyst, while polycyclopentadiene was produced as the by-products.

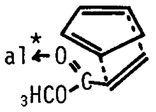
The [α] value of the exo adduct of MA with CPD could not measure because of low yield of exo adduct, except for the case c). It is reported (BERSON et al. 1961) that the endo and exo adduct have a maximum rotation value of - 141 and - 28.7 in ethanol at room temperature, respectively. It is noteworthy that the [α] value of endo adduct for AN-CPD is positive and that for MA-CPD

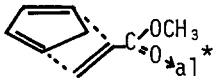
TABLE V. Diels-Alder reaction of AN or MA with CPD in toluene

$[menOAlCl_2]/[A]^{a)}$		reaction		yield	endo	$[\alpha]_D^{r.t.}$,	degree$^{b)}$
molar ratio		temp., °C	time, hr	%	%	endo	exo
A : AN	0.5	60	24	37	72.2	+ 6.39	- 0.57
	0.2	60	24	38	66.1	+ 5.00	- 0.32
	0.1	60	30	65	61.5	+ 3.82	- 0.07
	0	60	63	88	56.4	0	0
A : MA	0.2	0	75	—	—	- 5.66	—
	0.1	0	304	76	91.1	- 2.65	—
	0.1	30	48	87	91.7	- 4.02	+ 0.48$^{c)}$
	0	25	63	91	74.3	0	—

[CPD]/[A]=2 molar ratio, a) $EtAlCl_2$-*l*-menthol, b) in EtOH
c) see text.

negative. However, the absolute configuration of AN-CPD adduct is not known because of unstability of norbornene skeletal against the chemical modification of nitrile group to ester group. The optical yield of the endo and exo adduct (see TABLE V,c) was found to be 2.9 and 1.7 %, respectively. This difference may be ascribed to the fact that the transition state for the endo adduct may be more compact than that for the exo adduct. The former is favorable for the induction of chiral field on the adduct synthesis.





In conclusion, Diels-Alder reaction seems to be more easily stereocontrolled than copolymerization, perhaps due to the rigid cyclic structure in a transition state for the product of Diels-Alder reaction.

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