

Alternating Copolymerization of Cyclopentene, Cyclohexene or Cyclopentadiene with Acrylonitrile

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ABSTRACT: The copolymerization of cyclopentene, cyclohexene or cyclopentadiene with acrylonitrile was investigated in the presence of ethylaluminum chloride as a complexing agent and a transition metal compound as a promotor. In the case of copolymerization of cyclopentene with acrylonitrile, an alternating copolymer was obtained in the presence of an equimolar amount of EtAlCl_2 contained in acrylonitrile. The addition of a transition metal compound enhanced the yield of the copolymer, but brought about no effect on the copolymer composition. A trace amount of $\text{Cr}(\text{acac})_3$ was the most effective promotor. Cyclohexene afforded an alternating copolymer in low yield in a nonpolar solvent such as heptane. On the other hand, cyclopentadiene hardly gave any alternating copolymer, but primarily a Diels–Alder adduct. It is noteworthy that cyclopentene or cyclohexene reacts with toluene as the solvent to produce alkylation products of a Friedel–Crafts type. The present monomer systems may prefer ionic species susceptible to side reactions rather than alternating copolymerization.

KEY WORDS Alternating Copolymerization / Friedel–Crafts Reaction / Ethylaluminum Chloride / Transition Metal Compound / Acrylonitrile / Cyclopentene / Cyclohexene / Cyclopentadiene / Tricyclopentyltoluene / Tricyclohexyltoluene /

Cycloolefins are known to be capable of polymerizing with ethylene. For example, Natta has discussed the anionic coordination polymerizability of cycloolefins such as cyclopentene or cyclohexene with ethylene in relation to steric factors.¹ According to one patent,² the copolymer of cyclopentene and acrylonitrile prepared in the presence of ethylaluminum sesquichloride has an alternating structure. In regard to cyclopentadiene, Yamaguchi³ reported an alternating copolymerization with SO_2 occurring at the 1,4-positions.

This report deals with alternating copolymerization, the catalytic activity of transition metal compounds, and certain simultaneous reactions other than the polymerization.

EXPERIMENTAL

Materials

Cyclopentene (CP), cyclohexene (CH), cyclopentadiene (CPD), and acrylonitrile (AN) were purified by distillation over calcium hydride before use. Ethylaluminum dichloride (EtAlCl_2), diethylaluminum chloride (Et_2AlCl), and triethylaluminum (Et_3Al) were used after vacuum distillation. Toluene, tetrachloroethane (TCE), and hexane were purified in the usual manner. Transition metal compounds of chemically pure grade were used without further purification. The transition metal compounds may possibly contain trace amounts of water.

Copolymerization

Copolymerization was carried out in a sealed

glass tube under a nitrogen atmosphere. Reagents including a transition metal compound, solvent, AN and an aluminum compound were introduced at -78°C in this order. After shaking the mixture at -78°C , cycloolefin or cycloolefin was added at -78°C . In many cases, the copolymerization proceeded heterogeneously, owing to the low solubility of transition metal compounds. After copolymerization, the reaction mixture was poured into methanol containing hydrochloric acid. The polymer precipitated was filtered and washed with methanol. The residual methanol solution was subjected to the analysis for side reactions. The copolymer yield was calculated on the basis of the total monomer in the feed.

Friedel-Crafts Reaction

Alkylation products of CH with toluene were isolated as follows. The residual methanol solution was evaporated. The residue was dissolved in ether, washed three times with water, and then dried. The oily matter obtained was fractionally distilled into two parts and the residue:

mixed cyclohexyltoluenes: bp $120-125^{\circ}\text{C}$ (20 mmHg), n_{D}^{20} 1.5250 (bp $92-93^{\circ}\text{C}$ (2 mmHg), n_{D}^{20} 1.5256),⁴ m/e 174 (M^+), 131, 83.

mixed dicyclohexyltoluenes: bp $160-165^{\circ}\text{C}$ (4 mmHg), n_{D}^{20} 1.5368 (bp $154-158^{\circ}\text{C}$ (1 mmHg), n_{D}^{20} 1.5366),⁴ m/e 256 (M^+), 226, 187, 173, 131, 83 (Found: C, 89.28%; H, 10.72%. Calcd: C, 89.06%; H, 10.94%).

The distillation residue was column chromatographed on a silica-gel with hexane- CCl_4 (1:1). The first fraction was recrystallized from ether-methanol (10:1) to give 2,4,5-tricyclohexyltoluene (C-1). The second fraction in the chromatography afforded isomers of tricyclohexyltoluene (C-2).

C-1 mp $137-138^{\circ}\text{C}$ (mp $135-136^{\circ}\text{C}$),⁵ m/e 338 (M^+), 295, 269, 255, 226, 187, 171, 131, 83 (Found: C, 88.77%; H, 11.23%. Calcd: C, 88.76%; H, 11.24%).

C-2 mp $128-132^{\circ}\text{C}$, m/e 338 (M^+), 269, 255, 187, 173, 131, 83 (Found: C, 88.63%; H, 11.37%. Calcd: C, 88.76%; H, 11.24%).

Similarly, in the copolymerization of CP with AN, alkylation products were isolated by working up the residual methanol solution as described above.

mixed cyclopentyltoluenes bp $117-122^{\circ}\text{C}$ (18 mmHg), n_{D}^{20} 1.5256 (bp 237.5°C (757 mmHg),

n_{D}^{20} 1.5287),⁶ m/e 160 (M^+), 117, 69.

mixed dicyclopentyltoluenes bp $150-154^{\circ}\text{C}$ (2 mmHg), n_{D}^{20} 1.5393 (bp $150-152^{\circ}\text{C}$ (2 mmHg), n_{D}^{20} 1.5391),⁶ m/e 228 (M^+) (Found: C, 89.24%; H, 10.76%. Calcd: C, 89.47%; H, 10.53%).

Chromatography of the distillation residue on the silica-gel with hexane- CCl_4 (1:1) afforded an oil, *i.e.*, mixed tricyclopentyltoluenes, m/e 296 (M^+) (Found: C, 89.52%; H, 10.48%. Calcd: C, 89.19%; H, 10.81%).

Measurement

The copolymer composition was evaluated by elemental analysis. The intrinsic viscosity of the copolymers was determined in dimethylformamide at $30 \pm 0.01^{\circ}\text{C}$. The 60 MHz ^1H NMR spectra of the copolymers were measured by a JNM-PMX60 spectrometer in CDCl_3 . The mass spectra were taken with a Hitachi RMU-7M mass spectrometer at 20 eV. The gel-permeation chromatographic measurement (GPC) was performed on a Toyosoda HLC-801A high speed liquid chromatograph, using a polystyrene-gel column (4 ft + precolumn): flow rate of THF 1.2 ml min^{-1} , press. 35 kg cm^{-2} . The gas chromatographic analyses (GCG) were made with a Yanagimoto GCG-550T gas chromatograph using a $1.5 \text{ m} \times 5 \text{ mm}$ column packed with Apiezon grease L on 10% chromosorb W-AW, at 185°C , with H_2 carrier gas at 3 kg cm^{-2} .

RESULTS AND DISCUSSION

Copolymerization of CP with AN

Table I shows that CP copolymerizes with AN complexed with a stoichiometric amount of EtAlCl_2 . However, Et_2AlCl and Et_3Al were virtually inactive. This order of activity agreed with the order of the acid strength of aluminum compounds. The copolymer composition was consistently 1:1, independent of the feed monomer ratio. These 1:1 copolymers are considered to be the alternating copolymers. The yield and the molecular weight of copolymers were not so high even after a long period of polymerization. This is in contrast to the fact that CP polymerizes easily by a conventional Ziegler or cationic catalyst⁷ and that the free radical copolymerization of CP with AN produces AN-rich random copolymers.⁸

In the copolymerization of AN with butadiene, an alternating copolymer was obtained using a

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Table I. Alternating copolymerization of CP with AN by ethylaluminum compounds at 0°C^a

AN	CP	AN/AN+CP	Al-comp.	Polymerization time	Polymer yield	AN content in polymer
mmol	mmol	mol%	mmol	h	%	mol%
20	20	50	Et ₃ Al 20	20	0	—
20	20	50	Et ₂ AlCl 20	20	Trace	—
10	30	25	EtAlCl ₂ 10	6	13.5	51.8
20	20	50	EtAlCl ₂ 20	6	10.9	50.3 ^b
30	10	75	EtAlCl ₂ 30	6	5.8	52.7

^a Polymerization condition: toluene, 5 ml.

^b $[\eta]_{\text{DMF}}^{30^\circ\text{C}} = 0.13 \text{ dl g}^{-1}$; $T_m = 101\text{--}110^\circ\text{C}$.

small amount of EtAlCl₂-VOCl₃,⁹ and VOCl₃ effected the regeneration of the organoaluminum halide.¹⁰ In the copolymerization of AN with vinyl chloride, VOCl₃ was also an effective promotor.¹¹ The various transition metal compounds used here are listed in Table II. In the presence of an equimolar amount of EtAlCl₂ with respect to AN, the alternating copolymerization proceeds more effectively with the addition of a small amount of the transition metal compound than without it.

Transition metal compounds such as Cr(acac)₃, CrCl₃, Ti(*n*-BuO)₄, VOCl₃, and VO(acac)₂ accelerate the polymerization effectively, but none of them have any influence on the copolymer composition. In general, the yield increased with the amount of the transition metal compound except for the case of Cr(acac)₃, although Cr(acac)₃ was the most effective promotor. On the other hand, metal halides such as CaCl₂, BeCl₂, MnCl₂, NiCl₂, CoCl₂, CuCl₂, ZnCl₂, and FeCl₃ failed to accelerate the polymerization.

The above results indicate that the alternating copolymerization of olefinic donor-acceptor monomers is also possible in the presence of an aluminum compound with a transition metal compound in a manner similar to the alternating copolymerization of 1,3-diene with acrylic monomers.⁹ However, in the case of olefinic donor-acceptor monomers, the amount of the aluminum compound could not be reduced even in the presence of a promotor. The reason for this may be the lower polymerizability of the intermediate ternary complex among olefinic donor-acceptor monomers and the aluminum compound compared to that of the diolefinic donor-olefinic acceptor and aluminum

Table II. Effect of metal compounds on the copolymerization of CP with AN at 0°C for 3 h^a

Metal comp.	Metal comp./Al mol%	Polymer yield %	AN content in polymer mol%	$[\eta]_{\text{DMF}}^{30^\circ\text{C}} \text{ dl g}^{-1}$
BCl ₃	10	19.0 ^b	50.4	0.13
	50	14.4 ^b	—	0.13
MgCl ₂	1	21.1	52.6	0.13
	10	22.2	—	—
HgCl ₂	10	33.9 ^b	51.8	0.13
PbCl ₂	10	37.4	—	0.13
CrCl ₃	0.1	17.5	50.1	0.12
	1	41.1	50.1	—
	10	57.8	50.2	0.13
Ca(acac) ₃	0.1	85.0	50.3	0.13
	1	74.6	51.2	0.12
	10	1.7	50.3	—
Ti(<i>n</i> -BuO) ₄	0.1	13.3	—	—
	1	13.5	52.3	—
	10	84.5	51.5	0.13
VO(acac) ₂	0.1	15.0 ^c	50.8	—
	1	23.2	52.2	0.13
	10	46.8	50.6	0.13
VOCl ₃	0.1	13.6	—	0.10
	1	24.0	51.2	0.13
	10	41.0	50.5	—

^a Polymerization conditions: AN, 20 mmol; CP, 20 mmol; EtAlCl₂/AN = 1.0 in molar ratio; toluene, 5 ml.

^b 20 h.

^c Used for NMR measurement.

compound.

The copolymers of CP and AN were white solids of low molecular weight with intrinsic viscosity

ranging from 0.12 to 0.14 dl g⁻¹. The copolymers were completely soluble in acetone, chloroform, acetonitrile and *N,N*-dimethylformamide but insoluble in hexane and benzene. The copolymers melted without decomposition between 110 and 135°C.

Copolymerization of CH with AN

CH is also copolymerizable with AN, and usually AN-rich copolymers are obtained as shown in Table III. Polymerization was fairly slow in the presence of EtAlCl₂ even in the presence of transition metal compounds. The low rate of copolymerization may be due to the steric hindrance of the cyclohexene

ring^{1,8} and the side reactions mentioned below. Table IV shows the copolymer composition to be remarkably influenced by the solvent used. The AN content in the copolymers obtained in toluene and tetrachloroethane was higher than 50%, regardless of the monomer composition. On the other hand, the copolymers prepared in heptane had nearly 50% of the AN units. However, the yield and molecular weight were also low.

The intrinsic viscosity of the copolymers was about 0.13 dl g⁻¹. The AN-rich copolymers were found to decompose at 173–190°C. On the other hand, the 1:1 copolymer melted without decomposition in the temperature range of 148–156°C and was soluble in acetone, chloroform and acetonitrile.

Table III. Copolymerization of CH with AN at 0°C for 4h^a

Transition metal comp.	Transition metal comp./Al	Polymer yield	AN-content in polymer
	mol%	%	mol%
None		2.1	88.6
Cr(acac) ₃	10	Trace	—
	1	Trace	—
CrCl ₃	10	7.6	73.6
Ti(OEt) ₃ Cl	10	12.1	86.2
VOCl ₃	10	18.3	88.7
VO(acac) ₂	10	1.6	84.3

^a Polymerization conditions: AN, 20 mmol; CH, 20 mmol; EtAlCl₂, 20 mmol; toluene, 5 ml.

Friedel-Crafts Reaction

In the reaction of CH with AN or CP with AN in toluene the Friedel-Crafts reaction was found to primarily occur as shown in Table V. The yield of the reaction products of CH-toluene was higher than that of CP-toluene. The catalyst composed of EtAlCl₂-VOCl₃ was the most active in the Friedel-Crafts reaction. Tri-substituted toluenes were the main products in the reaction of CH or CP and toluene even in the presence of AN, indicating the preferential reaction of cycloolefin toward a proton and the high reactivity of a cycloalkyl cation with toluene. A trace amount of water remaining in the reaction system may act as a proton source.

Table IV. Copolymerization of CH with AN by EtAlCl₂ in various solvents at 0°C for 4h

AN	CH	Solvent	EtAlCl ₂	Transition metal comp. ^a	Polymer yield	AN content in polymer
mmol	mmol	ml	mmol		%	mol%
10	30	Tol	5	None	0.5	91.1
20	20		5		1.2	88.7
30	10		5		1.6	79.6
10	30	TCE	5	VOCl ₃	4.4	61.7
20	20		5		4.9	56.6
30	10		5		6.3	64.0
10	30	Heptane	5	Cr(acac) ₃	0.2 ^b	52.5
20	20		5		1.1 ^b	51.5 ^c
30	10		5		0.5 ^b	53.0

^a Transition metal comp./EtAlCl₂ = 0.1 in molar ratio.

^b $[\eta]_{\text{DMF}}^{30^\circ\text{C}} = 0.13 \text{ dl g}^{-1}$.

^c Used for NMR measurement.

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Table V. Friedel–Crafts reaction of cycloolefin with toluene at 0°C for 3 h

AN	Cycloolefin	Toluene	EtAlCl ₂	Transition metal comp.		Polymer yield	Friedel–Crafts product			
							Yield ^a	A ^b	B ^b	C ^b
mmol	mmol	ml	mmol	mmol		%	mol%	mol%		
20	CH	20	5	20	None	2.1	20.0	40.9	20.8	38.3
20	CH	20	5	20	VOCl ₃	0.5	8.3	62.0	31.4	52.6
20	CH	20	5	20	Ti(<i>n</i> -BuO) ₄	0.5	3.5	35.0	38.5	53.1
0	CH	20	5	20	CrCl ₃	1.0	4.2	12.3	44.9	30.3
0	CH	20	5	20	VOCl ₃	0.05	—	43.0	28.9	57.9
20	CP	20	5	20	None	10.9	21.0	8.5	17.9	73.6
0	CP	20	5	20	VOCl ₃	0.05	—	33.0	13.2	63.8

^a The yield was calculated based on CH or CP in the feed.

^b Product distribution was determined by GPC analysis: A, cyclohexyltoluene or cyclopentyltoluene; B, dicyclohexyltoluene or dicyclopentyltoluene; C, tricyclohexyltoluene or tricyclopentyltoluene.

Table VI. Copolymerization of CPD with AN at 15°C for 3 h^a

AN	CPD	EtAlCl ₂	Polymer yield	AN content in polymer	Yield of Diels–Alder product ^b
mmol	mmol	mmol	%	mol%	mol%
10	30	2.5	7.0	29.0	47.7
20	20	5.0	5.9	60.0	29.0
30	10	7.5	4.3	77.0	23.2
10	30	5.0	7.1	24.2	31.5
20	20	10.0	7.0	46.5	27.0
30	10	15.0	4.5	53.3	36.2
10	30	7.5	6.6	33.1	42.6
20	20	15.0	7.1	40.2 ^c	26.7
30	10	22.5	5.5	49.2 ^d	32.0
10	30	9.0	6.3	8.0	38.7
20	20	18.0	18.9	21.0	18.4
30	10	27.0	3.8	25.0	29.8

^a Polymerization condition: toluene 6 ml.

^b The retention time of 2-cyanobicyclo[1.2.2]hept-5-ene, bp 95–97°C (20 mmHg) [bp 84–89°C (13 mmHg)],¹³ was the same as that of the authentic sample by GCG. The yield was calculated based on CPD in the feed.

^c Used for NMR measurement.

^d $[\eta]_{\text{DMF}}^{30^\circ\text{C}} = 0.65\text{--}0.81 \text{ dl g}^{-1}$; $T_m = 155\text{--}175^\circ\text{C}$ (brown colored).

Copolymerization of CPD with AN

The copolymerization of CPD with AN was attempted in the presence of EtAlCl₂ as a complexing agent, and the results are summarized in Table VI. The copolymer composition was considerably affected by the amount of EtAlCl₂ and the polymerization temperature, as in the copolymerization of benzofuran–AN.¹² With increasing or decreasing amount of EtAlCl₂, the AN-content deviated from

50%, even at the optimum temperature (15°C), and the use of an optimum amount of EtAlCl₂ (Al/AN=0.75 molar ratio) diminished the deviation of the AN content from 50%. The addition of VOCl₃ as a promotor to these systems was not effective. These facts may be due to the high reactivity of CPD toward cationic species. The 1:1 copolymer of CPD with AN was a white solid, high in molecular weight and soluble in *N,N*-dimethyl-

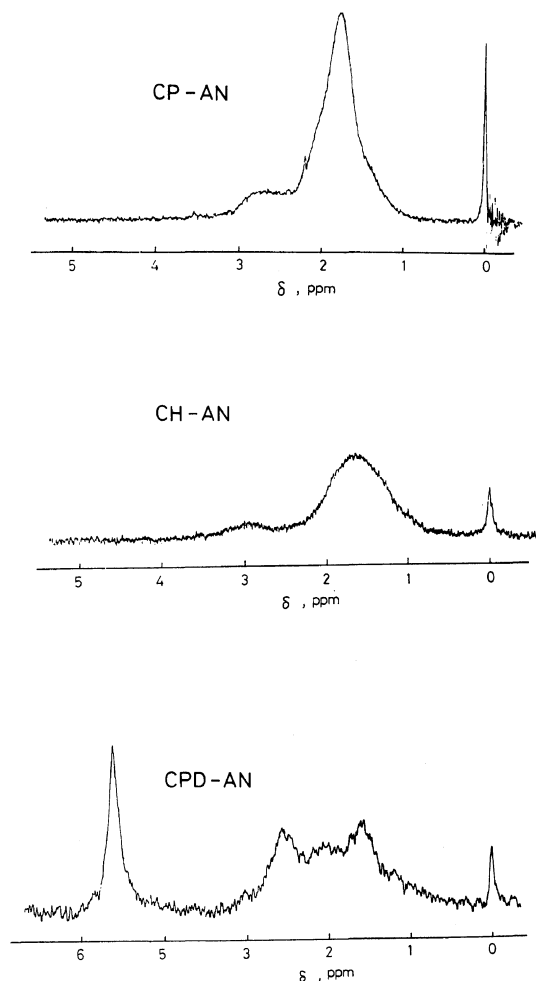


Figure 1. NMR spectra of copolymers at 36°C. AN content: CP-AN, 50.8%; CH-AN, 51.5%; CPD-AN, 42.0%.

formamide, acetone and chloroform. The intrinsic viscosity of the copolymers ranged from 0.65 to 0.81 dl g⁻¹ in DMF. However, the copolymers were easily oxidized by air and found to give polymers containing carbonyl groups from the absorption at 1655 cm⁻¹ in the infrared spectra.

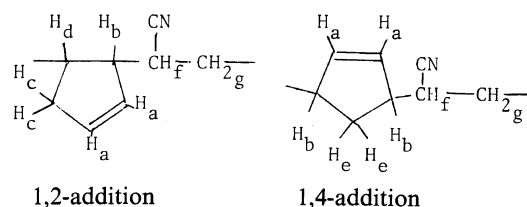
In the present system, the main reaction was a Diels-Alder reaction even at a low temperature (-30°C)¹³ because of the extremely high reactivity of CPD with AN complexed with a Lewis acid.

¹H NMR Spectra of Copolymers

60 MHz ¹H NMR spectra of copolymers of AN with CP, CH, or CPD were measured in CDCl₃ and

are illustrated in Figure 1. The AN-CP and AN-CH copolymers gave simple but broad spectrum patterns having two peaks. One peak at δ 2.8–3.0 was assigned to the proton attached to the α -carbon of the acrylonitrile unit and the other at δ 0.9–2.5, to the methylene protons, giving little information on the sequence distribution.

Two modes of the reaction are possible in the addition of AN to the 1,3-cyclopentadiene, *i.e.*, the 1,2- and 1,4-addition. The product in the 1,2-addition should have one allylic methine (H_b), one allylic methylene (2H_c), and one ordinary methine (H_d) on the cyclic unit and that in the 1,4-addition, two allylic methines (2H_b) and two methylene protons (2H_c). The ¹H NMR spectrum of the present copolymer of CPD and AN (AN content = 42%) is very complicated. The peak at δ 5.6 is assigned to the olefin proton (H_a) and the signal at δ 1.5 to the



methylene protons (H_e) and (H_f). The proton (H_f) neighboring the nitrile group is considered to appear in the lower field than H_b, H_c, or H_d, and is perhaps involved in the signal at δ 2.5–3.0. Although the allylic methylene (H_c) and the methine (H_d) signal of CPD-CPD dyad in the 1,2-addition polymer are known to appear at about δ 2.2,¹⁴ they were indistinguishable from the AN-CPD dyad.

The area ratio of S_A:S_B:S_C:S_D in the NMR chart, corresponding to the peaks at δ 0.7–1.8, δ 1.8–2.3, δ 2.3–3.2, and δ 5.2–6.0, respectively, is 2:2.6:1:2.4. In the alternating copolymer produced by the 1,4-addition or by the 1,2-addition, the area ratio should be 2(S_A):3(S_B):4(S_D) or 2(S_A):3(S_B):2(S_C):2(S_D), respectively.

In conclusion, it is suggested that both the 1,4-addition and 1,2-addition occur simultaneously in this system. This is at variance with the copolymerization of CPD-sulfur dioxide³ and 1,3-cyclooctadiene-acrylic monomer.¹⁵ A complexing agent may induce cationic species for the cationic polymerization of CPD resulting in an irregular opening of CPD unit together with the alternating copolymerization and the Diels-Alder reaction.

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