

Alternating Copolymerization of 1,3-Cyclooctadiene and Acrylic Monomers

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ABSTRACT: Three new kinds of alternating copolymers were successfully synthesized from 1,3-cyclooctadiene and acrylic monomers complexed with organoaluminum compounds. The copolymerization rate is as follows; acrylonitrile > methacrylonitrile > *cis*-crotonitrile. As an optimum condition giving the alternating copolymer, equimolar amounts of acrylonitrile, 1,3-cyclooctadiene, and EtAlCl₂ as a catalyst were used. The intrinsic viscosity of copolymers is from 0.40–0.60 dl/g. From their ¹H NMR and infrared spectra the preferential 1,4-addition and *cis*-structure of carbon–carbon double bond of cyclooctadiene unit were confirmed.

KEY WORDS Alternating Copolymer / 1,3-Cyclooctadiene / Acrylonitrile / Methacrylonitrile / Crotonitrile / Ethylaluminum Dichloride / ¹H NMR Spectrum / Infrared Spectrum / *cis*-1,4-Linkage / Reactivity /

The reactivity of the conjugated double bond of cyclic 1,3-diene compounds is dependent on ring size. Okamura, *et al.*,¹ have discussed the cationic polymerizability of cyclic diene monomers such as 1,3-cyclopentadiene (1,3-CPD), 1,3-cyclohexadiene (1,3-CHD), and 1,3-cyclooctadiene (1,3-COD) in relation to ring size. Yamaguchi, *et al.*, reported the remarkable difference in the alternating copolymerization of SO₂ and 1,3-CPD,² 1,3-CHD,³ or 1,3-COD.⁴ That is, SO₂ copolymerizes with the diene monomer at the 1,4-positions in the former two, whereas at the 1,2-positions in the latter. Moreover, 1,3-CPD,⁵ 1,3-CHD,⁶ and 1,3-cycloheptadiene⁷ are capable of giving the Diels–Alder adducts with maleic anhydride, while this cannot be done with 1,3-COD.⁸

According to the studies carried out so far, the authors have found that the alternating copolymers of linear 1,3-diene and acrylic monomer possess the 1,4-*trans* linkage.^{9–11} However, there is no available information for the alter-

nating copolymerization and the copolymer structure of cyclic 1,3-diene and acrylic monomer.

This report deals with the copolymerizations of 1,3-COD and acrylonitrile or its derivatives in the presence of Lewis acid.

EXPERIMENTAL

1,3-COD, acrylonitrile (AN), methacrylonitrile (MAN), and crotonitrile (CrN) were purified by distillation over calcium hydride before use. The two isomers of CrN were fractionated by distillation equipment having spinning bands and were identified by ¹H NMR spectra.

Ethylaluminum dichloride (EADC) and ethylaluminum sesquichloride (EASC) were used after vacuum distillation.

Copolymerization was carried out in a sealed glass tube under nitrogen atmosphere, and into which reagents such as solvent toluene, acrylic monomer and then an aluminum compound were introduced at –78°C in this order. After shaking the mixture at room temperature, 1,3-COD was finally added at –78°C. After copolymerization, the reaction mixture was poured into methanol containing hydrochloric acid.

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The copolymer yield was calculated based on the total monomer in the feed and the copolymer composition was determined by elemental analysis.

The intrinsic viscosity of the copolymers was determined in chloroform at 30°C. 100-MHz ¹H-NMR spectra of the copolymers were measured by a Varian HA-100 spectrometer in deuteriochloroform and their infrared spectra were measured in KBr tablets by Hitachi EPI-2 spectrometer.

RESULTS

Copolymerization of 1,3-COD and AN

1,3-COD polymerizes easily by conventional

cationic catalysts¹ but not by radical initiators. No copolymer of 1,3-COD and acrylic monomer has been known. Table I shows that 1,3-COD copolymerizes with AN complexed with a stoichiometric amount of EADC or EASC. When a large excess of 1,3-COD is used in the feed, the copolymerization system becomes heterogeneous, but the copolymerization is not retarded. The rate of copolymerization in the presence of EADC compared with that of benzofuran-AN copolymerization¹² is fast even without a radical initiator as a cocatalyst. Since the copolymer composition is consistently about 1:1, independent of the feed monomer ratio, and the radical polymerization of 1,3-COD is difficult, these equibinary copolymers are considered to be the

Table I. The copolymerization of 1,3-COD and AN in the presence of EADC or EASC in toluene at 30°C

1,3-COD, mol/l	AN		Catalyst		Polymn time, hr	Yield, %	Copolymer	
	mol/l,	feed mol%	mol/l				AN content, mol%	[η], ^a dl/g
0.54	1.52	73.9	EADC	1.46	16	5.9	50.7	0.45
0.94	1.52	61.9	"	"	"	5.4	49.5	0.63
1.54	1.52	49.7	"	"	"	5.5	48.6	0.63
3.08	1.52	33.0	"	"	"	3.8	48.1	0.56
4.62	1.52	24.8	"	"	"	4.5	49.9	0.68
0.54	1.52	73.9	EASC	1.47	46	7.0	50.3	0.27
0.94	1.52	61.9	"	"	"	6.7	50.2	0.37
1.54	1.52	49.7	"	"	"	6.0	50.5	0.44
3.08	1.52	33.0	"	"	"	4.9	49.5	0.63
4.62	1.52	24.8	"	"	"	5.3	48.8	0.55

^a In CHCl₃ at 30°C.

Table II. The copolymerization of 1,3-COD and MAN in the presence of EADC^a in toluene at 30°C

1,3-COD, mol/l	MAN		AIBN, mol/l	Polymn time, hr	Copolymer		
	mol/l,	feed mol%			Yield, %	MAN content, mol%	[η], ^b dl/g
0.74	1.49	66.9	0	72	0.8	55.3	—
1.47	1.49	50.3	0	72	0.8	51.9	—
2.95	1.49	33.6	0	72	0.9	48.6	—
0.74	1.49	66.9	0.0147	45	40.6	53.7	0.13
1.47	1.49	50.3	0.0147	19	34.9	53.4	0.23
2.95	1.49	33.6	0.0147	19	38.0	50.7	0.26
4.68	1.49	24.2	0.0147	19	29.7	50.1	0.26

^a EADC 1.46 mol/l.

^b In CHCl₃ at 30°C.

Table III. The copolymerization of 1,3-COD and CrN in toluene at 30°C

1,3-COD, mol/l	CrN ^a		Catalyst ^b	mol/l	Polymn time, hr	Copolymer		[η], ^c dl/g
	mol/l,	feed mol%				Yield, %	CrN content, mol%	
0.68	2.05	75.0	EADC	1.46	41	1.5	49.5	—
1.37	2.05	60.0	"	"	68	2.4	49.1	0.11
2.05	2.05	50.0	"	"	68	2.5	47.0	0.12
4.08	2.05	33.4	"	"	68	2.0	49.5	0.10
1.47	1.47	50.0	"	"	68	1.6	48.4	—
2.95	2.95	50.0	"	"	68	0.9	49.5	—
2.05	2.05	50.0	" ^d	"	169	0	—	—
0.68	2.05	75.0	EASC	1.47	118	1.5	50.4	—
1.37	2.05	60.0	"	"	"	1.4	50.3	0.06
2.05	2.05	50.0	"	"	"	1.2	50.0	0.06
4.08	2.05	33.4	"	"	"	1.0	49.0	0.09
1.47	1.47	50.0	"	"	"	0.5	48.8	—
2.05	2.05	50.0	" ^d	"	"	0	—	—

^a *cis/trans*=69.9/30.1.

^b AIBN is added by 1 mol% for EADC or EASC.

^c In CHCl₃ at 30°C.

^d Without AIBN.

alternating copolymers. The copolymers are fairly high-molecular-weight ones.

On the other hand, the free-radical copolymerization of 1,3-COD and AN by azobisisobutyronitrile (AIBN) at 60°C generally produces the AN-rich random copolymer. The monomer reactivity ratios, r_{AN} and $r_{1,3-COD}$ calculated by the Fineman—Ross method are found to be 2.2 and about zero, respectively.

Copolymerization of 1,3-COD and MAN

1,3-COD is also copolymerizable with MAN as shown in Table II. The rate is fairly slow without AIBN even in the presence of EADC but can be improved by the addition of 1-mol% AIBN for EADC. The copolymer composition is a little dependent on the monomer feed ratio through the equibinary copolymer is obtainable from 1,3-COD-excess monomer.

The monomer reactivity ratios, r_{MAN} and $r_{1,3-COD}$, in the free-radical copolymerization of 1,3-COD and MAN initiated by AIBN at 60°C are found to be 3.2 and approximately zero, respectively.

Copolymerization of 1,3-COD and CrN

The copolymerization of 1,3-COD and the α,β -disubstituted monomer, CrN (*cis/trans*=69.9/30.1 mixture) was attempted in the presence of

EADC or EASC as a complexing agent. Though no copolymer is obtained without AIBN, the equibinary one is prepared in the presence of 1-mol% AIBN for aluminum compounds independent of monomer feed ratio, probably corresponding to an alternating copolymer (Table III). EADC is also more effective than EASC in this system. The extremely slow rate of this reaction may be due to the steric hindrance of the β -substituent of CrN as well as a conventional radical polymerization.

The reactivity of *cis*-CrN and *trans*-CrN was investigated in detail using the fractionated pure

Table IV. The copolymerization^a of 1,3-COD and *cis*- or *trans*-CrN in toluene at 30°C for 72 hr

CrN, <i>cis/trans</i>	Copolymer		
	Yield, %	CrN content, mol%	[η], ^b dl/g
100/0	3.5	49.7	0.09
69.9/30.1	2.8	49.8	0.08
44.2/55.8	1.7	50.3	0.07
0.8/99.2	1.2	48.7	—

^a Feed conditions: 1,3-COD, 1.60 mol/l; CrN, 1.64 mol/l (50.5 mol% in feed); EADC, 1.46 mol/l; AIBN, 0.0147 mol/l.

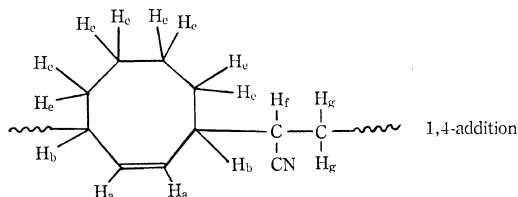
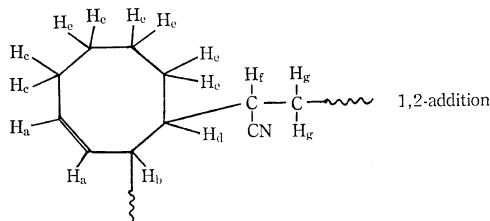
^b In CHCl₃ at 30°C.

cis or *trans* isomer of CrN. Table IV shows the comparison of the reactivities of both isomers with 1,3-COD. The determination of the *cis/trans* ratio of CrN was performed quantitatively by gas chromatography¹² and practically no isomerization of CrN monomer during copolymerization was confirmed by the determination of the *cis/trans* ratio of the residual CrN. According to these data, the *cis* isomer copolymerizes three times more rapidly than the *trans* isomer, while the reactivity of *cis*-CrN is more than ten times larger than that of the *trans*-CrN in the system of benzofuran—CrN copolymerization.¹²

¹H NMR Spectroscopy of the Alternating Copolymers of 1,3-COD and Acrylic Monomers

100-MHz ¹H-NMR spectra of three types of copolymers of 1,3-COD and acrylic monomers were measured in CDCl₃ and are illustrated in Figures 1, 2, and 3. The two modes of reaction are possible for the addition of the acrylic monomers to the conjugated diene. They are the 1,2- and 1,4-additions which should be distinguished by the ¹H NMR spectra of the polymers. For instance, the alternating copolymer obtained by the 1,2-addition should have one allylic methine (H_b), two allylic methylenes (H_c), one usual methine (H_d) and six methylene protons (H_e) on the cyclic unit and that by 1,4-addition 2H_b+8H_e. The equibinary copolymer obtained in this work shows a simple and clear spectrum pattern composed of three peaks (Figure 1) where the peak at δ_A 5.46 in the lowest magnetic field is assigned to the olefin protons (H_a) and the

major signal at δ_C 1.66 in the highest field to the methylene (H_e) and (H_g). From comparison with the spectra of the copolymers of butadiene or vinyl chloride and AN¹¹⁻¹³ the geminal proton (H_f) with nitrile is considered to appear in the lower field than δ_C and perhaps is contained in the signal at δ_B 2.70. In fact, the peak at δ_B 2.70 can be divided into two peaks at δ 2.8 and 2.6. The former is assigned to the H_f proton.



Though the allylic methylene signal is known to be observed at about δ 2.2 like cyclooctene,^{1,14} There is only minor peak of 3% with respect to the total intensity at δ 2. Moreover, the area ratio of δ_A : δ_B : δ_C is 1.0 : 1.5 : 5.0. Consequently, it is suggested quantitatively that the 1,4-addition occurs exclusively in the 1,3-COD—AN alternating copolymerization and the peak δ_B is assigned to (2H_b+H_f), because the area ratio

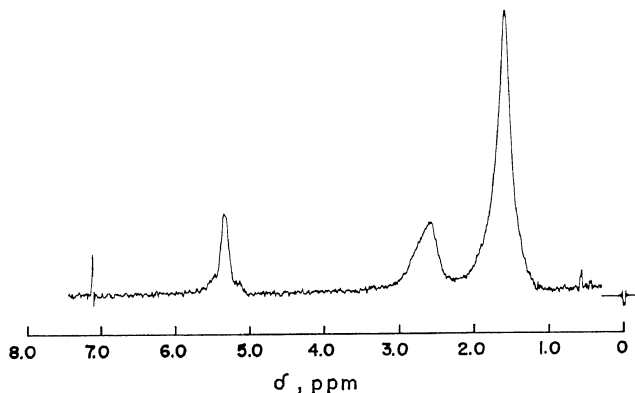


Figure 1. ¹H NMR spectrum of the alternating copolymer of 1,3-COD and acrylonitrile measured at 55°C.

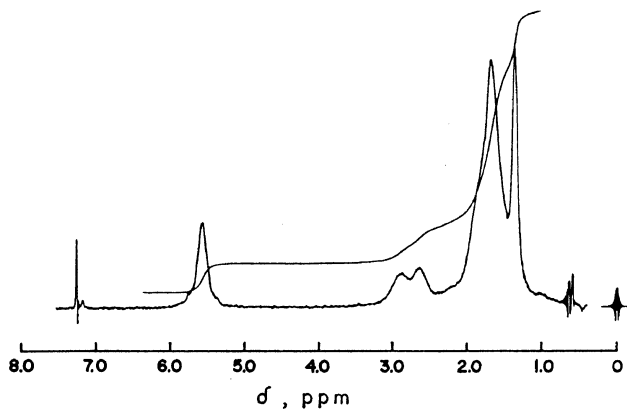


Figure 2. ^1H NMR spectrum of the alternating copolymer of 1,3-COD and methacrylonitrile measured at 31.5°C .

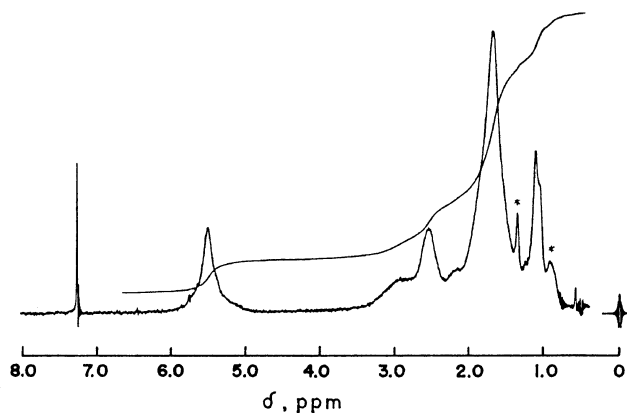


Figure 3. ^1H NMR spectrum of the alternating copolymer of 1,3-COD and crotononitrile measured at 31.5°C : *, assignment is unknown.

of $\delta_A : \delta_B : \delta_C$ must be 1.0 : 2.5 : 4.0, if the 1,2-addition occurs preferentially and the peak δ_B is assumed to be due to $(\text{H}_b + 2\text{H}_c + \text{H}_d + \text{H}_f)$.

The alternating copolymer of 1,3-COD and MAN also shows a simple and interesting spectrum (Figure 2), where the peak at δ_D 5.57 is assigned to the olefin protons, the peak at δ_F 1.67 to the methylene and δ_G 1.35 to the methyl protons, respectively. In this chart, the allylic methylene signal at about δ 2.2 was hardly observed. The two peaks at δ_E 2.90 and $\delta_{E'}$ 2.64 may be ascribed to the two allylic methines, separated because of their nonequivalence. As the area ratio of $\delta_D : \delta_E : \delta_{E'} : \delta_F : \delta_G = 2.0 : 1.0 : 1.0 : 10 : 3$, this system is considered to be subject to the 1,4-addition copolymerization.

The ^1H NMR spectrum of the alternating

copolymers of 1,3-COD and CrN is very complicated and shows the same pattern in spite of *cis* or *trans* configuration of the CrN monomer used. In Figure 3 the peaks at δ 5.51, 1.68, and 1.10 may be assigned to the olefin, methylene, and methyl protons, respectively, and the signals corresponding to the four protons are detected between δ 3.3 and 2.2 from the integrated curve, though this assignment is obscure owing to the coexistence of at least four kinds of methine. The allylic methylene signal at about δ 2.2 is also not remarkable in this spectrum. Consequently, the 1,4-addition copolymerization also seems to occur predominantly in this system.

Infrared Spectra of the Alternating Copolymers of 1,3-COD and Acrylic Monomers

The infrared spectra of these copolymers were

determined in KBr tablets using powder samples, where the peak of the nitrile is observed at 2270 cm^{-1} and that of the carbon—carbon double bond at $1640\text{--}1650\text{ cm}^{-1}$.

The configuration of the carbon-carbon double bond of various diene polymers is usually distinguished by using the bands owing to the out-of-plane deformation vibration of olefin protons as a key band.^{15,16} In this case, no peak resulting from the *trans*-1,4-configuration exists between $920\text{--}980\text{ cm}^{-1}$ in the copolymers. On the other hand, a strong peak appears at 730 cm^{-1} , and thus in the copolymers of 1,3-COD the double bond of the cyclooctene unit is considered to have the *cis* configuration. This structure is due to a 1,4-addition, but not to a 1,2-addition from the ^1H NMR spectra.

The infrared spectra of the alternating copolymers of the 1,3-COD with *cis*- or *trans*-CrN coincide perfectly with each other.

DISCUSSION

The new alternating copolymers were successfully synthesized from the 1,3-COD and acrylic monomers complexed with an equimolar amount of strong Lewis acids. Particularly, the copolymerization of 1,3-COD and AN is very rapid even without AIBN. When MAN is used instead of AN, the rate falls somewhat. Moreover, in the 1,3-COD—CrN system no copolymer is obtained without AIBN. This low copolymerizability of the latter is owing perhaps to the steric hindrance of the β -substituent of CrN. Besides, *cis*-CrN is more reactive than the *trans*-isomer. Previously, the authors found that *cis*-CrN is also more reactive than *trans*-CrN in the alternating copolymerization of benzofuran and CrN.¹² On the other hand, in an anionic polymerization of CrN the *trans* isomer has the same or a larger reactivity than the *cis* isomer.¹⁷ The molecular weight of the alternating copolymer decreases with a decrease in the apparent rate of copolymerization as follows; $\text{AN} > \text{MAN} > \text{CrN}$. The tendency may coincide with the order of steric hindrance of acrylic monomers.

The spectrometric analyses gave the informations for the characterization of these 1,3-COD—acrylic monomer alternating copolymers. Particularly, ^1H NMR spectra of these copolymers

were unexpectedly simple and it was clearly proved that the 1,4-addition copolymerization but not the 1,2-addition one occurs exclusively.

Yamaguchi, *et al.*,⁴ concluded that 1,3-COD copolymerizes alternately with SO_2 by the 1,2-addition from ^1H NMR spectra, though 1,3-CPD² and 1,3-CHD³ do this by the 1,4-addition, since the angle between the two double bonds of 1,3-COD is larger than that of the 1,3-CPD or 1,3-CHD in relation to ring strain^{18–20} which reduces its conjugate character and increases the olefinic character. This may be compatible with the fact that 1,3-COD cannot produce Diels—Alder adduct with maleic anhydride⁸ while 1,3-CPD,⁵ 1,3-CHD⁶, and 1,3-cycloheptadiene⁷ can do so.

However, 1,3-COD acts as a conjugated diene monomer in the copolymerization with complexed acrylic monomers as mentioned before. 1,3-COD may behave as either a conjugated diene compound or olefin according to the kind of reaction.

In order to know the reactivity of cyclic monoolefin and cyclic diolefin having eight carbon atoms, the copolymerization of *cis*-cyclooctene and AN was tried as a model reaction under the following conditions: AN 1.52 mol/l, cyclooctene 1.46 mol/l, EADC 1.46 mol/l, AIBN 0.015 mol/l in toluene at 30°C for 140 hr. An equibinary copolymer was obtained in very low yield (1.1%), but not without AIBN. Moreover, no copolymer was obtained using CrN as an acceptor even in the presence of AIBN. Thus, the reactivity of cyclooctene is remarkably inferior to that of 1,3-COD, indicating the conjugation of the two double bonds of 1,3-COD.

According to Yamashita, *et al.*,²¹ the *cis*-1,4 content in the butadiene homopolymer is 16.4%, and similarly in the butadiene—AN copolymer obtained by AIBN this is 18.9% while the butadiene—maleic anhydride copolymer has a *cis*-1,4 content as high as 73.7% perhaps owing to the strong cisoid interaction between the monomers. In the alternating copolymer of the diene monomers such as butadiene¹⁰ and *cis*- or *trans*-1,3-pentadiene²² with acrylic monomers complexed with Lewis acid, the microstructure of the diene unit is all *trans*-1,4. On the other hand, the cyclooctene unit of the copolymers of

1,3-COD and acrylic monomers is all *cis* form though the *trans*-cyclooctene unit is possibly present as well as the *cis* one.

The relative stabilities of *cis* and *trans* olefins can be estimated from their heats of hydrogenation. According to Turner and Meador²³ the heat of hydrogenation of cyclooctene, $-\Delta H$, is 23.0 and 32.2 kcal·mol⁻¹ with the *cis* and *trans* isomer, respectively. The empirical energy of *cis*-cyclooctene is 4.9 and that of the *trans* isomer is estimated to be 14.1 kcal·mol⁻¹ based on the strain energy in cyclooctane of 9.3 kcal mol⁻¹.²⁴ Thus, *cis*-cyclooctene is more stable than *trans* one. Consequently, the configuration of the diene unit formed in these alternating copolymers is considered to be dependent on the stability of the resulting *cis*-cyclooctene unit.

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