Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Copolymerization of Chloroprene with Methyl Methacrylate by the $Et_nAlCl_{3\cdot n}$ (n=1, 1.5, 2)-Vanadium Compound System

Akio Masaki[a]; Mitsuo Yasui[a]; Iwao Yamashit[a]
[a] Government Industrial Research Institute Osaka Midorigaoka, Ikeda, Osaka, Japan

To cite this Article Masaki, Akio , Yasui, Mitsuo and Yamashit, Iwao(1972) 'Copolymerization of Chloroprene with Methyl Methacrylate by the $Et_nAlCl_{3\cdot n}$ (n=1, 1.5, 2)-Vanadium Compound System', Journal of Macromolecular Science, Part A, 6: 7, 1285 — 1300

To link to this Article: DOI: 10.1080/10601327208056896

URL: http://dx.doi.org/10.1080/10601327208056896

J. MACROMOL. SCI.—CHEM., A6(7), pp. 1285-1300 (1972)

Copolymerization of Chloroprene with Methyl Methacrylate by the Et_nAlCl_{3-n} (n = 1, 1.5, 2)-Vanadium Compound System

AKIO MASAKI, MITSUO YASUI, and IWAO YAMASHITA

Government Industrial Research Institute Osaka
Midorigaoka Ikeda
Osaka, Japan

ABSTRACT

The copolymerization of chloroprene with methyl methacrylate was studied in the presence of Et_nAlCl_{3-n} (n = 1, 1.5, 2)-vanadium compounds. Monomer reactivity ratios in various catalyst concentrations were compared with that of a usual radical initiator. The apparent monomer reactivity ratio changed with the concentration of alkylaluminum halide.

In this polymerization, alternating copolymer could not be prepared by the ordinary catalyst concentration by which the alternating copolymerization of chloroprene with acrylonitrile was carried out. The addition of more than 10 mole % of the alkylaluminum halide based on two monomers was required to prepare the copolymer which had equimolar composition irrespective of the feed monomer ratio.

The configuration in the repeating unit of the copolymer was discussed by comparison with the NMR and IR spectra of the radical copolymer and the cyclic Diels-Alder adduct of chloroprene-methyl methacrylate. The high alternating tendency was clarified by ozonolysis of the copolymer which was prepared under the conditions which produced equimolar copolymer in various feed monomer ratios. The chloroprene

unit of the copolymer was present in the 1,4-trans structure in the copolymer prepared by the Et_nAlCl_{3-n}-vanadium compound system.

INTRODUCTION

Radical copolymerization of chloroprene with methyl methacrylate was studied to establish a reactivity series between dienes and polar vinyl monomers [1]. Recently the alternating copolymerization of polar vinyl monomers complexed with alkylaluminum halides by the addition of donor monomers has been achieved by several authors [2-5].

In order to apply the analogous synthetic method of alternating copolymers, the copolymerization of chloroprene with acrylonitrile was studied in a previous report [12]. It was found that the alternating copolymer was produced more efficiently than with butadiene-acrylonitrile copolymerization. IR and NMR spectra of the alternating copolymer of chloroprene and acrylonitrile suggested that the microstructure of chloroprene unit was mainly 1,4-cis. The result is remarkable, for the structure of diene unit in the alternating copolymer of butadiene or isoprene with acrylonitrile was claimed to be 1,4-trans [3, 6, 7]. In the present study the copolymerization of chloroprene with methyl methacrylate complexed with alkylaluminum halides and cocatalyzed by vanadium compounds was investigated. The catalytic activity was a little lower than that of chloroprene-acrylonitrile copolymerization. When the copolymerization was carried out in various feed ratios of the two monomers, the chloroprene content in the copolymer obtained changed with the monomer feed ratio. The apparent monomer reactivity ratio calculated by the Fineman-Ross method was different from that by radical initiator, and the reactivity of methyl methacrylate was enhanced [1]. In order to prepare an equimolar copolymer of chloroprene-methyl methacrylate irrespective of monomer feed ratio, the concentration of alkylaluminum halide required more than 10 mole % based on total feed monomers.

The configuration of the copolymer sequence was compared with that of the radical copolymer by NMR spectroscopy. Ozonolysis of the copolymer was carried out and the acid products of the reaction were analyzed by thin-layer chromatography. The polymer structure was investigated by using those results.

EXPERIMENTAL

Catalyst Components

Diethylaluminum chloride, obtained from Texas Alkyl Inc., was distilled under reduced pressure, bp 110°C (30 Torr).

Ethylaluminum dichloride and ethylaluminum sesquichloride were prepared from the reaction of aluminum trichloride and triethylaluminum; $EtAlCl_2$, bp 111°C (30 Torr), and $Et_{1.5}AlCl_{1.5}$, bp 113-115°C (48 Torr).

Monomers

Chloroprene, obtained from Toyosoda Co., was distilled before use, bp 59°C (760 Torr). Methyl methacrylate was purified as usual and distilled before use, bp 101°C (760 Torr).

Solvents

Solvents were of reagent grade and were purified by ordinary methods.

Copolymerization

The chloroprene-methyl methacrylate copolymerization procedure and the method of analyzing the copolymer obtained were described in a previous report on the alternating copolymerization of chloroprene with acrylonitrile [12]. The intrinsic viscosity of the product copolymer was measured in toluene solution at 30°C by means of an Ubbelohde-type viscometer.

Diels-Alder Adduct of Chloroprene and Methyl Methacrylate

The preparation of the Diels-Alder adduct of chloroprene and methyl methacrylate followed the Inukai method [8]. The reaction was carried out in both the presence and absence of aluminum trichloride as the complexing reagent. The reaction procedure in detail was described in the previous report [12]. The reaction mixture was distilled at 71-73°C/5 Torr in both cases. The distillate was composed of three components, which were observed as the main peak and two small peaks by gas chromatography with a 2-m column of tricresyl phosphate at 140°C. The main peak was separated by a Varian Aerograph Model 700 and was measured by NMR.

Ozonolysis of the Copolymer and Diels-Alder Adduct

A solution of 1 g copolymer in 200-300 ml chloroform was cooled to 5°C in a 500-ml round-bottomed flask equipped with a mechanical agitator, reflux condensor, thermometer, and a gas inlet tube. Water (100 ml) was added and the mixture was ozonized by using the output of a Japan Ozone Co. Model 0-10-3 ozone generator. Ozonization was continued for 4 hr at 5°C with an estimated O_3 output of 0.5-1.0 g/hr.

The viscous ozonide obtained was treated with 10 ml of 30% hydrogen peroxide and was boiled for 2 hr to insure complete oxidation. The aqueous solution was concentrated and dried under reduced pressure at 60°C. A total yield of 1.0-1.2 g viscous product was obtained and separated by thin-layer chromatography.

The thin-layer plate (20 × 20 cm) was prepared with activated silica gel as a support of 0.25 mm thickness. The ozonization product was developed in a solvent of benzene, dioxane, and acetic acid (80:50:16 vol %). The clear yellow spots corresponding to acid products were observed by treatment with bromophenol blue as the color-producing reagent.

RESULTS AND DISCUSSION

The results of the copolymerization of chloroprene with methyl methacrylate by radical initiator and ethylaluminum dichloride are shown in Tables 1 and 2. Monomer reactivity ratios calculated from the Fineman-Ross method are as follows: r(CP) = 4.32, r(MMA) = 0.07 with benzoyl peroxide, and r(CP) = 1.27, r(MMA) = 0.02 with $EtAlCl_2$.

It is noteworthy that the alternating copolymerization did not occur in the presence of $EtAlCl_2$, although the reactivity of methyl methacrylate was enhanced by $EtAlCl_2$. The result is shown by the composition curves of the copolymerization which was carried out in various monomer feed ratios (Fig. 1).

In the system the polymerization proceeds as homogeneous, and the copolymer obtained is soluble in organic solvents. As the catalytic activity of organoaluminum halide alone is rather low, the effect of acceleration of the polymerization rate was studied by the addition of various vanadium compounds [3]. The result is shown in Table 3. The vanadium compounds accelerate the polymerization rate and $VOCl_3$ is the most effective cocatalyst.

Essential differences in the polymer structures were not observed in the IR and NMR spectra of the copolymers obtained by various vanadium compounds. The composition curves in the copolymerization with various concentration of $EtAlCl_2$-$VOCl_3$ are shown in Fig. 2.

The apparent monomer reactivity ratio is influenced by the concentration of $EtAlCl_2$, and the values of r(CP) and r(MMA) calculated by the Fineman-Ross method are 0.84 and 0.02 with 1 mole % $EtAlCl_2$

TABLE 1. Radical Copolymerization of Chloroprene and Methyl Methacrylate[a]

Run No.	CP in feed (mole %)	Conversion (wt %)	Cl (%)	CP in copolymer (mole %)
1	5.0	4.7	7.7	21.1
2	10.0	18.2	17.3	46.2
3	20.0	22.2	22.4	58.8
4	50.0	37.6	32.1	83.0
5	80.0	39.2	36.2	91.4

[a] Polymerization conditions: Total monomer of chloroprene and methyl methacrylate 50 mmoles, benzoyl peroxide 2 mole % based on monomers, 60°C, 8 hr.

TABLE 2. Copolymerization between Chloroprene and Methyl Methacrylate with $EtAlCl_2$[a]

Run No.	CP in feed (mole %)	Conversion (wt %)	Cl (%)	CP in copolymer (mole %)
6	10.0	1.2	18.5	49.2
7	20.0	1.8	20.2	53.4
8	50.0	2.9	24.7	64.4
9	90.0	3.4	27.6	71.3

[a] Polymerization conditions: Total monomer of chloroprene and methyl methacrylate 50 mmoles, $EtAlCl_2$ 1 mmole, toluene 5 ml, 20°C, 12 hr.

TABLE 3. Copolymerization between Chloroprene and Methyl Methacrylate with Et_nAlCl_{3-n}-Vanadium Compound System[a]

Run No.	Catalyst	mmole	Polym. time (hr)	Conversion (wt %)	CP in copolym. (mole %)	[η]
10	$Et_2AlCl/VOCl_3$	1.0/0.1	3	8.6	68.3	0.22
11	$Et_{1.5}AlCl_{1.5}/VOCl_3$	1.0/0.1	3	7.7	69.8	0.27
13	$EtAlCl_2/VOCl_3$	1.0/0.1	3	10.5	60.4	0.35
14	$EtAlCl_2/VCl_4$	1.0/0.1	12	8.1	63.9	0.24
15	$EtAlCl_2/V(acac)_3$	1.0/0.1	12	0.8	71.3	0.58
16	$EtAlCl_2/VO(acac)_2$	1.0/0.1	12	16.4	67.3	0.43
17	$EtAlCl_2/VOCl_3$	1.0/0.1	12	20.4	61.0	0.36

[a] Polymerization conditions: Chloroprene 25 mmoles, methyl methacrylate 25 mmoles, toluene 5 ml, polymerization temperature 20°C.

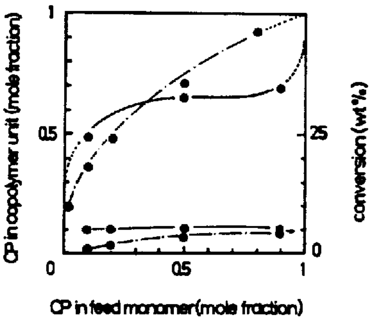

FIG. 1. Copolymerization curve of CP-MMA with BPO (filled circle) and with Et_2AlCl (open circle).

for total feed monomer, and 0.18 and 0.00 with 10 mole % $EtAlCl_2$, respectively.

The results show that the alternating polymerization tendency of the copolymerization of chloroprene with methyl methacrylate is lower than that of chloroprene with acrylonitrile as shown in Fig. 3.

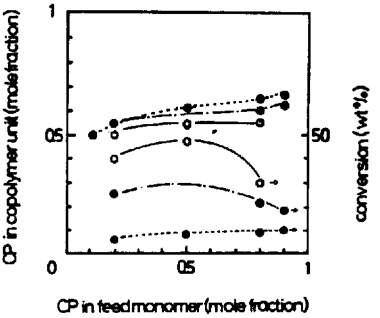

FIG. 2. Copolymerization curve of CP-MMA with various concentrations of $EtAlCl_2$-$VOCl_3$ system. Total monomer concentration 5.2 mole/l; Al/V, 10 (by mole); Al/monomer, 10 mole % (open circle); Al/monomer 5 mole % (filled circle): Al/monomer, 1 mole % (open circle with triangle).

In the copolymerization of chloroprene-acrylonitrile, the polymerization rate seems to be maximum when the monomer feed is 1:1. On the other hand, in chloroprene-methyl methacrylate copolymerization

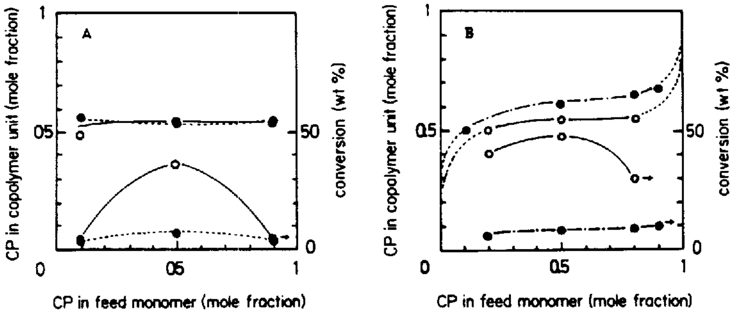

FIG. 3. Comparison of copolymerization curves of CP-AN and CP-MMA with $EtAlCl_2$-$VOCl_3$ system. A: Copolymerization curve of CP-AN, total monomer concentration 5.2 mole/l; Al/V, 10 (by mole); Al/monomer, 2 mole % (open circle); Al/monomer, 1 mole % (filled circle). B: Copolymerization curve of CP-MMA, total monomer concentration 5.2 mole/l; Al/V, 10 (by mole); Al/monomer, 10 mole % (open circle); Al/monomer, 2 mole % (filled circle).

the maximum rate is observed when the catalyst concentration is more than 10 mole % based on two monomers. This fact suggests that the equilibrium constant of the donor-acceptor complex in the chloroprene-methyl methacrylate copolymerization system is smaller than that in the chloroprene-acrylonitrile system [9].

The dependence of the conversion and intrinsic viscosity on time in the polymerization of chloroprene-methyl methacrylate with $EtAlCl_2$-$VOCl_3$ are shown in Fig. 4. The conversion increases linearly, but the intrinsic viscosity remains constant during the polymerization, which suggests that the polymerization does not proceed successively and the chain transfer reaction occurs in the early stages of polymerization.

Infrared spectra of copolymers prepared by radical initiator and $EtAlCl_2$-$VOCl_3$ are shown in Figure 5. For comparison with these copolymers, IR spectra of polychloroprene and polymethyl methacrylate are also shown. Some characteristic bands observed in the copolymer at 1730 cm^{-1} are assigned to the ester carbonyl group and at 1660 cm^{-1} are assigned to carbon-carbon double bond fundamental stretching of the chloroprene unit. The band which exists at 1480 cm^{-1} and is assigned to the methylene group in polymethyl methacrylate disappears and a new band appears at 1460 cm^{-1} in the copolymer. There is no remarkable difference between the radical copolymer and the copolymer prepared with $EtAlCl_2$-$VOCl_3$ when the chloroprene contents in the copolymers are equal.

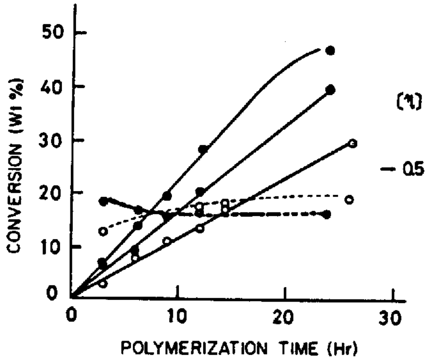

FIG. 4. Dependence of the conversion and intrinsic viscosity on time in the polymerization of CP-MMA with various concentrations of $VOCl_3$ in the catalyst of the $EtAlCl_2$-$VOCl_3$ system. CP = MMA = 2.6 mole/l. $EtAlCl_2$ = 0.1 mole/l. $VOCl_3$ = 5.2×10^{-3} mole/l (open circle), 10.4×10^{-3} mole/l (filled circle), 15.4×10^{-3} mole/l (open circle with triangle). Polymerization temperature 20°C.

The NMR spectra of the radical copolymers with different compositions are shown in Fig. 6. The absorptions of the radical-initiated copolymer can be assigned as follows: 5.5 ppm for methine proton of the chloroprene unit, 3.7 ppm for methoxy protons of the methyl methacrylate unit, 1.4-2.7 ppm for methylene protons of the copolymer, and 1.2 ppm for methyl protons of the methyl methacrylate unit. In the absorption of methylene protons of the copolymer, the relative intensity of the absorption at 2.4 ppm increases with the chloroprene content of the copolymer, which suggests that the absorption should be ascribed to the chloroprene-chloroprene diad in the copolymer. The high field absorptions at 0.9-1.2 ppm of methyl protons of the methyl methacrylate unit are split into three signals with an increase in the methyl methacrylate content of the copolymer.

This may be due to the increased block units of methyl methacrylate in the copolymer. The NMR spectra of the copolymer obtained with $EtAlCl_2$-$VOCl_3$ and Diels-Alder adduct of chloroprene-methyl methacrylate are shown in Fig. 7. The absorption of the chloroprene-chloroprene diad also clearly exists in the copolymer which was prepared in chlorprene rich in feed. It decreases as the composition of chloroprene and methyl methacrylate in the copolymer becomes closer to equimolar. However, the absorption exists even in the copolymer which is assumed to be of alternating structure, as shown in Fig. 7-C, and so the absorption may be overlapped with methylene protons of the

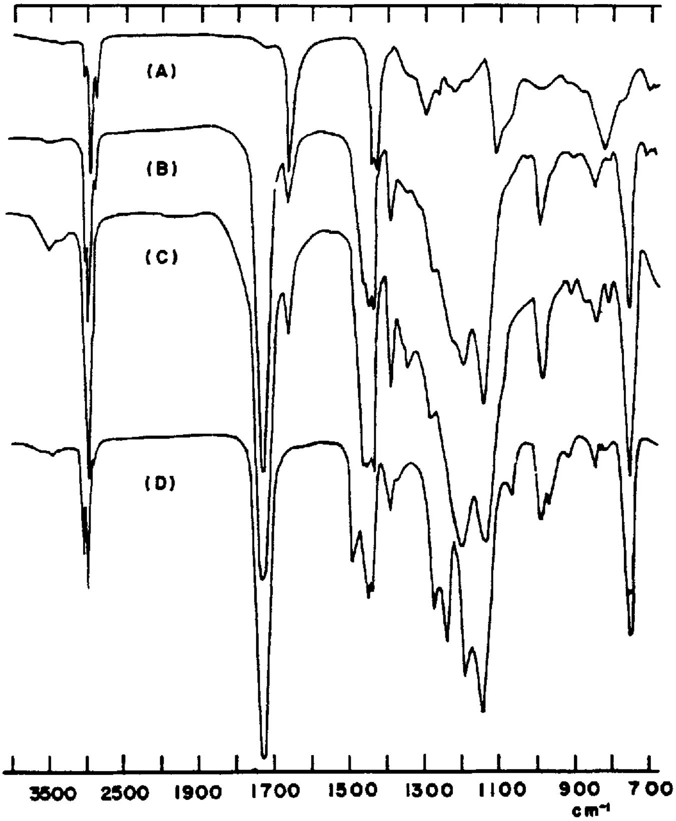

FIG. 5. Infrared spectra of CP-MMA copolymers with BPO and $EtAlCl_2$-$VOCl_3$. A: Poly-CP with BPO. B: Copolymer with BPO (CP, 47 mole %). C: Copolymer with $EtAlCl_2$-$VOCl_3$ (CP, 50 mole %). D: Poly-MMA with BPO.

chloroprene-methyl methacrylate diad. The absorption of methine proton of the Diels-Alder adduct appears at 5.2 ppm and that of the copolymers which are obtained both with benzoyl peroxide and $EtAlCl_2$-$VOCl_3$ appear to shift to the same upper field, 5.5 ppm. Since the structure of the Diels-Alder adduct seems to be of cis configuration and the absorption of the copolymer prepared by radical initiator is in the same position as that by $EtAlCl_2$-$VOCl_3$, it is suggested that the copolymer prepared with $EtAlCl_2$-$VOCl_3$ takes a 1,4-trans structure [7].

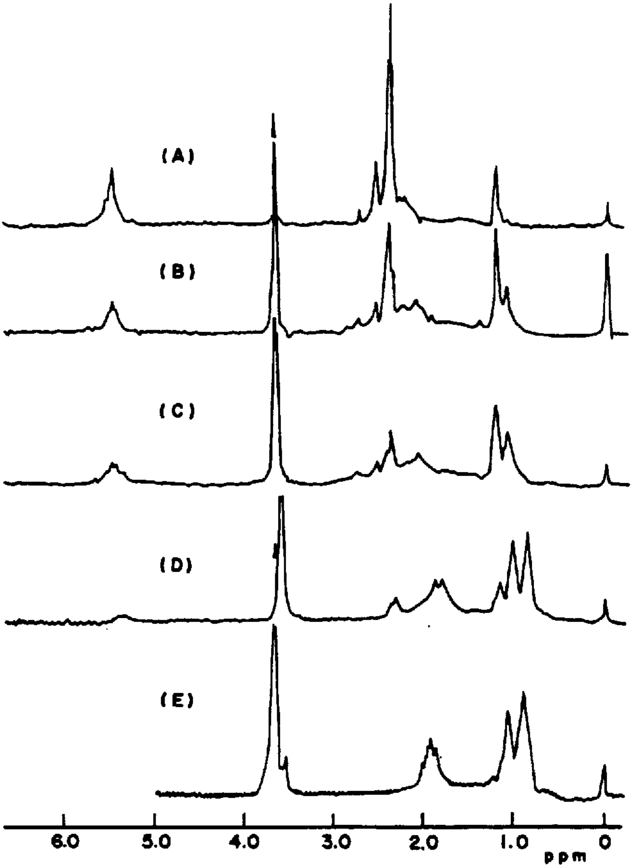

FIG. 6. NMR spectra of CP-MMA copolymers with BPO. A: CP in copolymer, 83.0 mole %. B: CP in copolymer, 58.8 mole %. C: CP in copolymer, 46.2 mole %. D: CP in copolymer, 21.1 mole %. E: Poly-MMA.

In order to investigate the difference in the sequence distribution between the radical copolymer and the copolymer prepared with $EtAlCl_2$-$VOCl_3$, ozonolysis was carried out and the decomposition products of ozonide were analyzed by thin-layer chromatography. It is known that succinic acid is produced by the ionization of chloroprene homopolymer quantitatively [10]. Methyl methacrylate

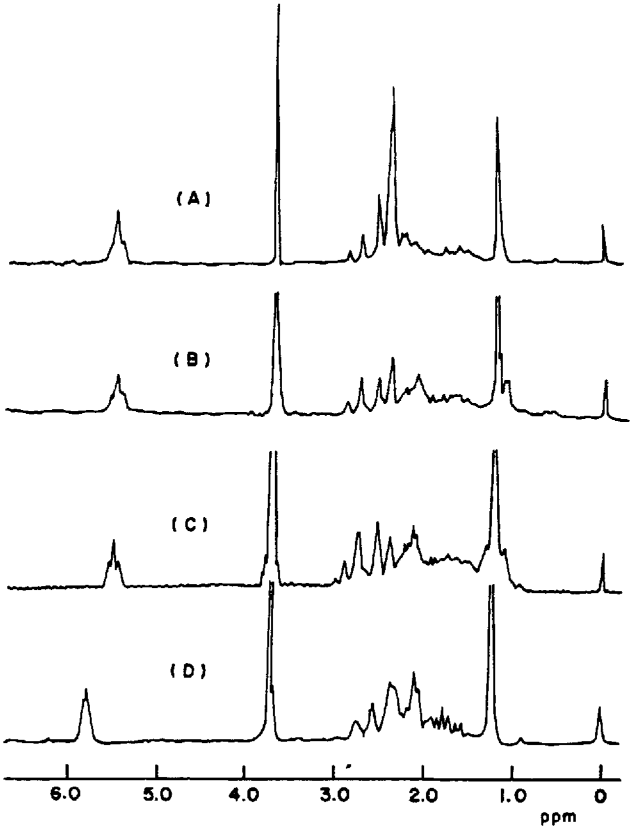

FIG. 7. NMR spectra of CP-MMA copolymers with $EtAlCl_2-VOCl_3$ and that of the Diels-Adler adduct of CP-MMA. A: Al/total monomer, 2 mole % (CP 70.5 mole %). B: Al/total monomer, 2 mole % (CP 50.3 mole %). C: Al/total monomer, 10 mole % (CP 49.7 mole %). D: Diels-Adler adduct.

homopolymer was not decomposed by ozone under our ozonization conditions, and the original polymer was recovered completely. In the case of the ozonization of the Diels-Alder adduct of chloroprene-methyl methacrylate, two separate spots have R_f values of 0.3 and 0.6 were detected by thin-layer chromatography. If the ozonization reaction proceeds as in theory, only one spot of dicarboxylic acid in the product of the decomposition of ozonide should be observed. But there is a probability that the ester group of the Diels-Alder adduct is hydroxylated in the process of ozonide decomposition. It was confirmed that one of these two spots at R_f 0.6 disappeared and transferred to the R_f 0.3 spot when the decomposition reaction was allowed to continue overnight in the presence of 5% hydrochloric acid. These two spots were therefore used as the standard for the chloroprene-methyl methacrylate diad structure of the copolymer. The results of the ozonization of the copolymer are shown in Fig. 8. In the ozonization reaction of the radical copolymer of chloroprene-methyl methacrylate content 1:1, a considerable amount of succinic acid was separated from the reaction products as crystal and identified by IR and NMR. This indicates that the structure of the copolymer is rich in chloroprene-chloroprene diad.

In the decomposition products of the copolymer prepared with $EtAlCl_2$-$VOCl_3$, succinic acid was also detected by thin-layer chromatography although the quantity of the acid was much smaller than that of the radical copolymer. The copolymer prepared with the usual catalytic concentration of $EtAlCl_2$-$VOCl_3$ contained chloroprene-chloroprene diad in the polymer unit, even when the apparent content of the two monomers was equimolar. On the other hand, the ozonization products of the copolymer prepared with 10 mole % $EtAlCl_2$ was in good agreement with that of the Diels-Alder adduct in the thin-layer chromatogram, as shown in Fig. 8. It is shown that the copolymer prepared by this catalyst concentration in different monomer feed ratios alternates regularly in the polymer structure.

In the case of the copolymerization of chloroprene-methyl methacrylate with $EtAlCl_2$-$VOCl_3$, the apparent reactivity ratio depends on the concentration of catalysts, and a considerable amount of $EtAlCl_2$ is required to cause alternating copolymerization.

It has been proposed that the alternating polymerization of polar vinyl monomers with butadiene would proceed in the course of a donor-acceptor complex with the alkylaluminum halide [11]. It is assumed that the active monomer is a complex of alkylaluminum chloride and both monomers. The copolymerization with $EtAlCl_2$-$VOCl_3$ suggests that a CP-MMA-Al ternary complex also exists, and the concentration of the complex influences the polymerization rate and the regularity of alternating copolymerization. It seems that the electron-donating ability of chloroprene is smaller than that of butadiene, and the lower concentration of the complex makes it difficult to obtain alternating copolymer.

It is reasonable to assume that the reactivity of the complex is not so different from that of noncomplexed chloroprene monomer.

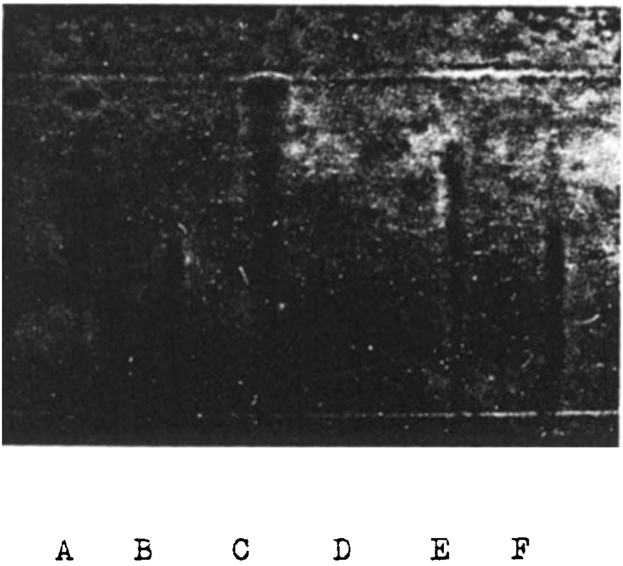

FIG. 8. Thin-layer chromatogram of ozonization products of copolymers and Diels-Alder adduct. A: Copolymer with $EtAlCl_2$-$VOCl_3$, Al/monomers 2 mole % (CP 50 mole %). B: Copolymer with $EtAlCl_2$-$VOCl_3$, Al/monomers, 10 mole % (CP 50 mole %). C: Chloroform-soluble fraction of copolymer with BPO (CP 47 mole %). D: Crystal part of copolymer with BPO, which has the same R_f value as succinic acid. E: Water-soluble fraction of copolymer with BPO (CP 47 mole %). F: Diels-Adler adduct of CP-MMA.

The difference of the microstructure between chloroprene-acrylonitrile copolymer and chloroprene-methyl methacrylate copolymer was remarkable, and further study of the copolymerization mechanism might be required to clarify the difference.

REFERENCES

[1] K. W. Doak and D. L. Dineen, J. Amer. Chem. Soc., 73, 1048 (1951).
[2] M. Hirooka, H. Yabuuchi, S. Morita, S. Kawasumi, and K. Nakaguchi, J. Polym. Sci., Part B, 5, 47 (1967).

[3] J. Furukawa, Y. Iseda, K. Haga, and N. Kataoka, J. Polym. Sci., Part A, 8, 1147 (1970).
[4] N. G. Gaylord and A. Takahashi, J. Polym. Sci., Part B, 6, 743 (1968).
[5] M. Taniguchi, A. Kawasaki, and J. Furukawa, J. Polym. Sci., Part B, 7, 411 (1969).
[6] N. G. Gaylord and A. Takahashi, J. Polym. Sci., Part B, 7, 443 (1969).
[7] E. Oikawa and K. Yamamoto, Polym. J. (Japan), 1, 669 (1970).
[8] T. Inukai and M. Kasai, J. Org. Chem., 30, 3567 (1965).
[9] S. Iwatsuki, Y. Tanaka, and Y. Yamashita, Kogyo Kagaku Zasshi, 67, 1467 (1964).
[10] C. A. Aufdermarsh, J. R. Pariser, and R. Pariser, J. Polym. Sci., Part A, 2, 4727 (1964).
[11] J. Furukawa, E. Kobayashi, Y. Iseda, and Y. Arai, Polym. J. (Japan), 1, 442 (1970).
[12] A. Masaki and I. Yamashita, J. Macromol. Sci.—Chem., A6, 439 (1972).

Received for publication May 7, 1972