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Alternating Copolymerization of Chloroprene with Acrylonitrile by R_nAlCl_{3-n} (n = 1, 1.5, 2)-Vanadium Compound Systems

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ABSTRACT

Chloroprene and acrylonitrile were copolymerized by alkylaluminum halides with the formation of a 1:1 copolymer. The copolymer obtained was insoluble in organic solvents and the catalytic activity was not very high. The catalytic activity of alkylaluminum halides combined with small amounts of various vanadium compounds was markedly enhanced. It was found that different feed ratios of chloroprene and acrylonitrile resulted in the formation of a 1:1 copolymer soluble in organic solvents when copolymerization was stopped while both monomer remained in the polymerization system.

NMR and ir spectra of the copolymer suggested that the chloroprene unit of the copolymer had a 1,4-cis configuration. On decomposition of the ozonide of the prepared copolymer, no succinic acid was detected through analysis by thin layer chromatography. These results showed that the copolymer did not contain chloroprene diad.

INTRODUCTION

The alternating copolymerization of polar vinyl monomers, such as acrylonitrile or methyl methacrylate complexed with ethylaluminum dichloride and donor monomer styrene or butadiene, has been achieved by several authors [1-3]. It was reported that the alternating copolymer of butadiene-acrylonitrile had better tensile strength properties than nitrile rubber and the repulsion modulus compared with nitrile rubber [4]. The authors were interested in the probability of the alternating copolymerization of chloroprene-acrylonitrile by a complexing catalyst system.

Chloroprene and acrylonitrile were copolymerized by alkylaluminum halides alone, especially ethylaluminum dichloride, and the chloroprene content of the copolymer was approximately 50 mole % irrespective of different feed ratios of the two monomers, but the degree of alternation was not determined because of its low solubility in organic solvents. The preparation of a soluble elastic alternating copolymer was carried out by R_nAlCl_{3-n}-vanadium compound systems similar to the alternating copolymerization of butadiene with acrylonitrile [2, 5].

The most effective catalyst system was ethylaluminum dichloride and vanadyl chloride. Ir and NMR spectra of the copolymer suggested that the microstructure of the chloroprene unit of the copolymer was mainly 1,4-cis. It was characteristic that the usual radical chloroprene homopolymer was shown to have a 1,4-trans structure. Moreover, in the alternating copolymerization of butadiene or isoprene with acrylonitrile, the structures of the diene unit were of the 1,4-trans configuration.

In order to investigate the structure of the alternating copolymer, ozonolysis of the copolymer was carried out and the acid products in the reaction were analyzed by thin layer chromatography.

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).

Vanadium compounds were reagent grade and were used without further purification.

Monomers

Chloroprene, obtained from Toyo Soda Co., was distilled before use, bp 59°C (760 Torr).

Acrylonitrile was refluxed under calcium hydride and was distilled before use, bp 76°C (760 Torr).

Solvents

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

Copolymerization

Polymerization was carried out by the following method. A dry glass ampoule was evacuated and flushed with dry nitrogen gas and dipped in a -78°C bath. Toluene, acrylonitrile, ethylaluminum dichloride dissolved in n-hexane, vanadyl chloride dissolved in n-hexane, and chloroprene were added in this order by means of a hypodermic syringe. The ampoule was sealed and dipped in a thermostat at constant temperature. After a given time a small amount of methanol was added to the reaction mixture, and copolymer was obtained by pouring into a large excess of boiling water.

The elastic polymer was coagulated, then purified by reprecipitation from chloroform solution into methanol contained a small amount of N-phenyl-β-naphthylamine, and then dried in vacuo and weighed.

The copolymer obtained was not stable in air, and gel-polymer formation was observed after the polymer stood in air for a week, so it was kept in an ampoule evacuated and flushed with nitrogen and was used on analysis. The monomer ratio in the copolymer was calculated from the chlorine content determined by the combustion flask method.

Radical copolymerization was carried out in the presence of benzoyl peroxide in an oxygen-excluded glass ampoule at 60°C for 12 hr.

The copolymer was purified by the same method as described above and was analyzed by elemental analysis.

Polymer Characterization

NMR spectra were recorded on a 100 MHz high resolution NMR spectrometer Model Jeol JNM-4H-100. The deutero-chloroform solution containing tetramethylsilane as the internal standard was sealed in a Pyrex tube of 5 mm diameter. It was measured at 60°C.

Ir measurements of the copolymer were made with a Hitachi Co. Model EPI-S2 ir spectrometer as film.

The intrinsic viscosity of the polymer product was measured in a dimethylformamide solution at 30°C by means of an Ubbelohde-type viscometer.

Diels-Alder Adducts of Chloroprene and Acrylonitrile

The preparation of the Diels-Alder adducts of chloroprene-acrylonitrile followed the Inukai method [6]. To a suspension of 4.0 g of aluminum trichloride and 8.0 g of acrylonitrile in 150 ml of benzene warmed at 60°C, 27 g of chloroprene was added dropwise. The mixture was stirred at 60°C for 1.5 hr. The polymer was separated from the reaction mixture and that part of the solution was washed with 10% aqueous hydrochloric acid and water and then dried over anhydrous sodium sulfate overnight. Solvent benzene was distilled out and the adduct was recrystallized by methanol three times with a yield of 2.1 g, mp 52~53°C.

Elemental analysis of the reaction product was as follows. Calculated for C_7H_8NCl: C, 59.36; H, 5.65; N, 9.89; Cl, 25.08. Found: C, 58.93; H, 5.70; N, 9.85; Cl, 25.6.

The adduct gave only one peak by gas chromatography with a 2-m column of tricresylphosphate at 120°C and with a 4-m column of apiezone grease at 160°C.

Ozonolysis of Copolymers and the Diels-Alder Adduct

A solution of 1 g copolymer obtained in 200 ml chloroform was cooled at 5°C in a 500-ml round-bottomed flask equipped with a mechanical agitator, thermometer, reflux condensor, 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. Then 10 ml of 30% hydrogen peroxide was added to the mixture, followed by refluxing for 3 hr at 60°C. After cooling, the chloroform layer was dried up and was added to the aqueous layer. The aqueous layer was refluxed for another 2 hr at 100°C with complete decomposition of the ozonide. The aqueous solution was concentrated and dried under reduced pressure at 60°C. A total yield of 1.1 g viscous product was obtained and separated by thin layer chromatography.

A plate of thin layer (20 × 20 cm) was prepared with activated silica gel as a 0.25-mm thick support. The product was developed in a solvent of benzene, methanol, and acetic acid (70:20:8 vol%).

The spots corresponding to acid products were detected by treatment with bromphenol blue as the color-producing reagent.

RESULTS AND DISCUSSION

In radical copolymerization of chloroprene with acrylonitrile, monomer reactivity between the two monomers is so different that the composition of the copolymer obtained is usually rich in chloroprene.

On the other hand, the reactivity of acrylonitrile is enhanced by organoaluminum halides complexed with nitrile group on account of its electron-withdrawing property. The result of copolymerization of chloroprene with acrylonitrile catalyzed by ethylaluminum dichloride is shown in Table 1. As may be seen from Table 1, the composition of the copolymer prepared with ethylaluminum dichloride is independent of the initial monomer feed ratio, and the monomer reactivity ratios of both two monomers will obviously be close to zero. The result shows that equimolar copolymer could be prepared by an alkylaluminum halide alone, but the copolymer is not dissolved in organic solvents and so a cocatalyst is needed to prevent gel formation.

The copolymer is produced more efficiently by the alkylaluminum halide-vanadium compound system, similar to the alternating copolymerization of butadiene with acrylonitrile [3]. The result of the copolymerization by alkylaluminum halides combined with various vanadium compounds is shown in Table 2. Vanadium compounds soluble in the reaction mixture are very effective, and vanadyl

TABLE 1. Copolymerization of Chloroprene and Acrylonitrile with Ethylaluminum Dichloride at Various Feed Ratios[a]

Run no.	Chloroprene in feed (mole %)	Cl (%)	Chloroprene in copolymer (mole %)	Conversion (mole %)
1	10	24.2	48	6.1
2	20	23.9	47	8.5
3	50	25.5	51	20.1
4	80	26.7	54	11.1
5	90	25.8	52	14.6

[a] Polymerization conditions: Total monomer (chloroprene and acrylonitrile), 50 mmole; $EtAlCl_2$, 4 mmole; toluene, 5 ml; 20°C, 2 hr.

chloride is the most effective cocatalyst. When two components of the catalyst system are mixed with chloroprene in the absence of acrylonitrile, chloroprene reacts vigorously with them, even at -78°C, and polymerization does not occur successfully. High catalytic activity is noted when the alkylaluminum halide and vanadium compound are reacted in the presence of acrylonitrile monomer. The polymer obtained is soluble in acetone, chloroform, tetrahydrofuran, and dimethylformamide.

The composition curves in the copolymerization with ethylaluminum dichloride-vanadyl chloride system and benzoyl peroxide are shown in Fig. 1.

It is shown that different feed ratios of chloroprene and acrylonitrile resulted in the formation of 1:1 copolymer during the early stage of polymerization by the ethylaluminum dichloride-vanadyl chloride system. When the polymerization was carried out for 30 hr, the composition curve obtained was of the nonequimolar type, as shown in Fig. 1.

In this case the polymerization proceeded even after either monomer was completely consumed, so the composition of the copolymer obtained was rich in either monomer. When the

TABLE 2. Copolymerization of Chloroprene and Acrylonitrile with Et_nAlCl_{3-n}-Vanadium Compound Systems

Run No.	Catalyst	Mmole	Polymerization time (hr)	Conversion (wt%)	Gel (%)	CP (mole %)	[η]
6	$Et_2AlCl/VOCl_3$	1.0/0.1	24	65		53	0.34
7	$Et_{1.5}AlCl_{1.5}/VOCl_3$	1.0/0.1	24	55		52	0.38
8	$EtAlCl_2/VOCl_3$	1.0/0.1	24	77	13	53	0.62
9	$EtAlCl_2/VO(acac)_2$	1.0/0.1	24	20	30	52	0.46
10	$EtAlCl_2/V(acac)_3$	1.0/0.1	24	6	50	52	0.48

[a] Polymerization conditions: Chloroprene, 25 mmole; acrylonitrile, 25 mmole; toluene, 5 ml. The polymerization temperature was 0°C.

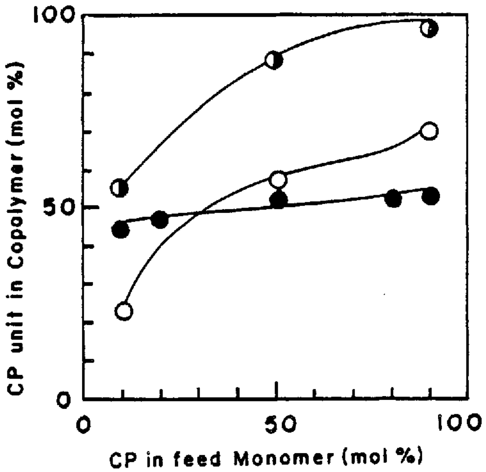

FIG. 1. Copolymerization curve of chloroprene-acrylonitrile under different conditions: with 1 mole % BPO, 60°C, 6 hr (◑) with $EtAlCl_2$-$VOCl_3$ (Al/V 10:1 mole ratio, Al 1 mole %) 0°C, 30 min (●), and.0°C, 30 hr (○).

polymerization in a feed ratio rich in either monomer was continued in order to attain higher conversion, the copolymer obtained came contained a part insoluble in organic solvents.

But there is little difference in chloroprene content between the soluble and insoluble fractions, which suggests that prepared copolymer is not a mixture of alternating copolymer and homopolymers.

The intrinsic viscosity of the copolymer did not increase but remained constant from an early copolymerization stage.

The NMR spectrum of a copolymer prepared with ethylaluminum dichloride-vanadyl chloride is shown for comparison in Fig. 2 with that of a radical copolymer having a equimolar composition and also of the Diels-Alder adduct of chloroprene and acrylonitrile. NMR spectra of trans- and cis-chloroprene homopolymer are also shown in this figure [7]. The absorption of methine proton of trans- and cis-polychloroprene appeared in the field at 5.35 and 5.51 ppm, respectively. In the absorption for the alternating copolymer of chloroprene and acrylonitrile, the signal seems to appear in the low field at 5.7 ppm on account of electron-withdrawing effect of nitrile group in the alternating unit of the copolymer, which is consistent

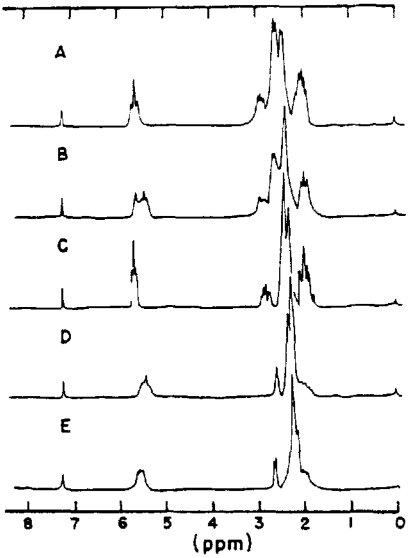

FIG. 2. NMR spectra of the copolymer A, $EtAlCl_2$-$VOCl_3$ CP 52 mole %; B, radical copolymer CP 51 mole %; C, Diels-Alder adduct; D, trans-polychloroprene; and E, cis-polychloroprene.

with the fact that the absorption of the methine proton of Diels-Alder adduct appears at 5.73 ppm.

These results indicate that copolymer structure consists of a chloroprene-acrylonitrile diad. On the other hand, the methine peak in the radical copolymer splits into two signals, a little broader, at 5.65 and 5.45 ppm. This might be due to the random structure of the copolymer.

The high field absorption centered at 2.90 ppm could be ascribed to the methine proton of the acrylonitrile unit. The signals became stronger with an increase in acrylonitrile content of the radical copolymer.

The two absorptions appearing at 2.45 and 2.55 ppm could be ascribed to the methylene protons of the chloroprene unit, and these two signals of the alternating copolymer are nearly equal.

A phenomenon similar to this is observed in the signals of methylene protons of the Diels-Alder adduct. The uppermost field absorptions centered at 1.75 ppm could be ascribed to the methylene protons of the acrylonitrile unit.

There are two possible configurations in the repeating unit of the alternating copolymer. An attempt to determine whether configuration of the alternating copolymer corresponds to head-to-tail or head-to-head was carried out by the comparison of the NMR spectra of Diels-Alder adducts produced by two methods, that is, one was carried out by using no catalyst and the other by using aluminum trichloride complexed with acrylonitrile. There was no difference in NMR spectra between two adducts obtained by the above methods, and so it was unsuccessful in determining whether the configuration of the alternating copolymer is head-to-tail or head-to-head.

Ir spectra of the each copolymer are shown in Fig. 3. Compared with the characteristic bands in the trans-polychloroprene, those of the cis-polychloroprene appear at 847, 1200, 1653, 3025, and 3282 cm^{-1}, respectively [7]. The bands of the alternating copolymer show strong similarity of those of the above-mentioned cis-polychloroprene.

These results suggest that the alternating copolymer prepared by ethylaluminum dichloride-vanadyl chloride is of cis-configuration in the chloroprene unit. On the other hand, the structure of the radical copolymer is similar to trans-polychloroprene.

In order to investigate the sequence distribution of the radical copolymer and the alternating copolymer, ozonolysis was carried out on each copolymer and the Diels-Alder adduct. It is known that ordinary trans-polychloroprene yields about 90% succinic acid on ozonolysis [8].

In the ozonization of the Diels-Alder adducts of chloroprene-acrylonitrile, the nitrile group also reacted with ozone, so we were unsuccessful in obtaining a model dicarboxylic acid corresponding to the chloroprene-acrylonitrile diad. Unknown acid products, which might perhaps be a mixture of di- and tricarboxylic acids, were detected by thin layer chromatography in the decomposition products of the ozonide. In the case of the ozonization of alternating copolymer, no succinic acid was detected.

On the other hand, a fair amount of succinic acid was detected in the radical-initiated equimolar copolymer. The acid was separated and identified by ir and NMR. These results show that copolymer prepared by ethylaluminum dichloride-vanadyl chloride could not contain chloroprene diad in the polymer backbone.

It is remarkable that the structure of the copolymer obtained was of the 1,4-cis configuration, for the alternation copolymer of butadiene or isoprene with acrylonitrile has a 1,4-trans structure.

It might be assumed that in the course of a complex formation

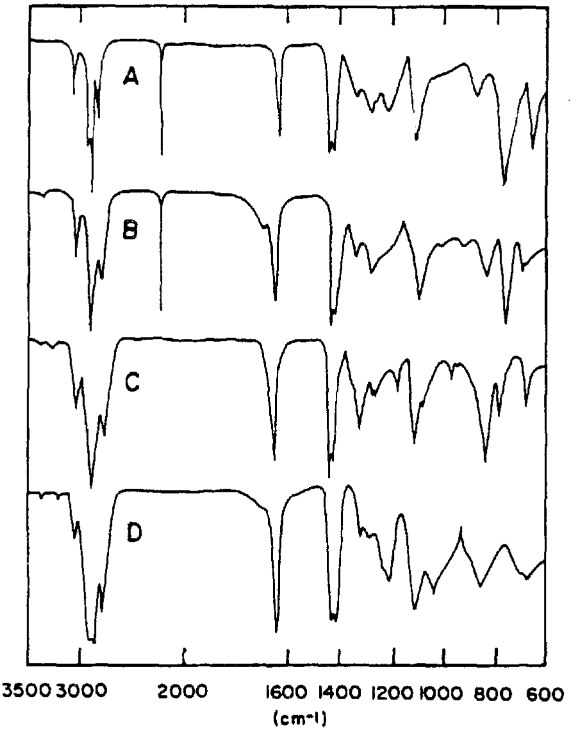

FIG. 3. IR spectra of A, chloroprene-acrylonitrile copolymer by $EtAlCl_2$-$VOCl_3$ CP 52 mole %; B, radical copolymer CP 45 mole %; C, trans-polychloroprene; and D, cis-polychloroprene.

of CP-AN-Al, the main catalyst ethylaluminum dichloride would interact with the chlorine atom of the chloroprene monomer and that the Al-Cl interaction would be favorable for the formation of a 1,4-cis structure.

ADDITIONAL REMARKS

While we were writing this paper, a short communication about the alternating copolymerization of chloroprene with acrylonitrile was published [9]. (Our work was presented at 17th Meeting of the Society of Polymer Science, Japan, at Kobe, July 10, 1971.)

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