

Synthesis of chloroprene and α -cyanoethyl acrylate copolymer and its characterization

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(Received 5 August 1996; revised 11 November 1996)

The radical copolymerizations of chloroprene (CP) and α -cyanoethyl acrylate (CEA) were carried out in toluene at 45°C in moisture free atmosphere by use of dry nitrogen. Microstructures in the copolymers have been examined by ^1H and ^{13}C nuclear magnetic resonance and Fourier transform infra-red spectroscopy. They showed that the copolymer, whose composition ratio was nearly CP/CEA = 1/1 (mol), possessed predominantly-(CP-CEA)-repeating unit in which CP had the 1,4 unit. A reaction mechanism by way of Diels-Alder intermediate was discussed for this regular copolymerization. © 1997 Elsevier Science Ltd.

(Keyword: chloroprene; α -cyano acrylate; alternating copolymer)

INTRODUCTION

A large number of studies for polychloroprene had been performed and their contents were summarized by Johnson¹ in 1976. After that, several studies have been reported on chloroprene (CP) homopolymer²⁻⁸ and copolymers⁹. Since the CP monomer is more reactive than others, except for 2,3-dichloro-1,3-butadiene in free-radical polymerization, the kinds of useful comonomers are limited. For this reason, there have been few reports on CP copolymers.

In the case of the CP and sulfur dioxide system, Matsuda and Hara¹⁰ pointed out that the copolymerization had the possibility to rule out propagation of separate monomer and/or propagation processes involving a monomer charge-transfer complex¹⁰. Recently, Miyata and coworkers¹¹⁻¹³ resolved the detailed structure of CP-sulfur copolymer by ^1H nuclear magnetic resonance (n.m.r.). Ha *et al.*¹⁴ and Park *et al.*¹⁵ synthesized the copolymer of CP with methacrylate derivatives. Cho *et al.* performed the copolymerization of CP and maleic anhydride and investigated them by ^1H and ^{13}C n.m.r., who described that each monomer copolymerized in alternate manner¹⁶.

However, nobody has attempted to copolymerize CP and α -cyanoacrylate derivatives. In the present work, the radical solution copolymerization of CP and α -cyanoethyl acrylate (CEA) are carried out in dehydrated atmosphere because of avoiding anionic polymerization of the CEA monomer itself in the presence of moisture. Furthermore, the microstructures of the copolymers are determined by ^1H and ^{13}C n.m.r. and Fourier transform infra-red (FTi.r.), and the reaction mechanism is also discussed.

EXPERIMENTAL

Materials

CP monomer of 99.7% purity was supplied by Denki Kagaku Kogyo Co. Ltd. CEA monomer, which is produced by Koatsu Gas Kogyo Co. Ltd (commercial grade Cyanon S), was used without further purification. Its purity was 99.0%, and hydroquinone was used as an inhibitor. Toluene was special grade, which was bought from Wako Chemical Co., and its water content was reduced to less than 10 ppm by means of immersing molecular sieves 3A in it in a week before use for polymerization. An initiator for polymerization, 2,2'-azobis-2,4-dimethylvaleronitrile (ADV N), was purchased from Wako Pure Chemical Co., and used as received.

Copolymer synthesis

CP monomer, CEA monomer, toluene and a stainless steel bottle equipped with two valves, were placed in a gloved box which was maintained without moisture using dry nitrogen. After pouring each monomer and solvent into the bottle, both valves were tightly closed. Next, the bottle was connected to a 1-l glass autoclave dehydrated in advance, and then the reaction mixture, two monomers and the solvent, was introduced into the autoclave with pressurized nitrogen. The mixture was stirred and heated to 45 ± 0.5°C. Polymerization was begun by adding 10 wt% toluene solution of ADVN as an initiator and continued until the time when CEA monomer in the reaction mixture disappeared perfectly. Two copolymer samples, A and B in Table 1, were obtained by changing the mole ratios of CP and CEA in the feed. In a typical experiment, CP (41.5 g, 0.47 mol), CEA (58.1 g, 0.47 mol), toluene (300 g) and ADVN (3.0 g, 1.21 × 10⁻² mol) were used. Conversion of each monomer during the reaction was traced by gas chromatography on sampling at regular time intervals

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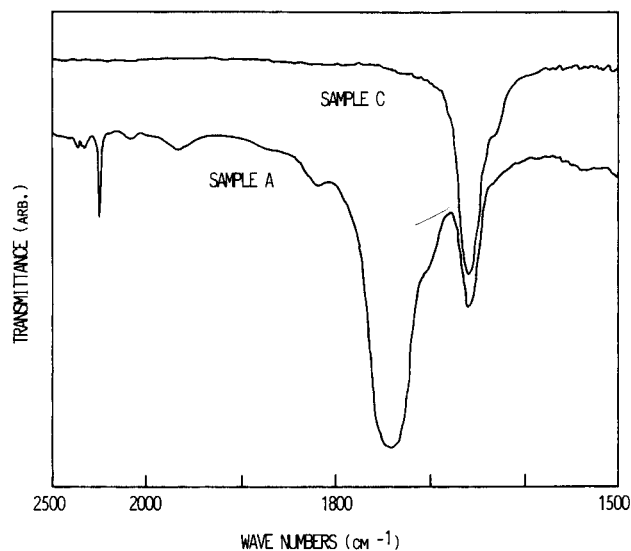


Figure 1 I.r. spectra of samples A and C

in nitrogen atmosphere. The obtained copolymer was purified by reprecipitation from benzene/methanol and then freeze-dried from benzene solution. It was stored at -60°C prior to various measurements.

Gel permeation chromatography

Molecular weights of the copolymers were measured at 35°C using a gel permeation chromatography (g.p.c.) system with a refractive detector (Shimadzu, RID-6A) and KF-80M (Shodex) columns. Tetrahydrofuran (THF) was used as an eluent. Low polydispersity polystyrene was employed as standards to draw a calibration curve. Average molecular weights, \overline{M}_w and \overline{M}_n , were calculated with g.p.c. data.

Fourier transform infra-red spectroscopy

FTi.r. spectra were recorded at 4 cm^{-1} resolution on a FTIR-8100M (Shimadzu) spectrometer. Films were cast from benzene solutions onto thallium bromide and thallium iodide compounds plates. The samples were dried up to remove benzene.

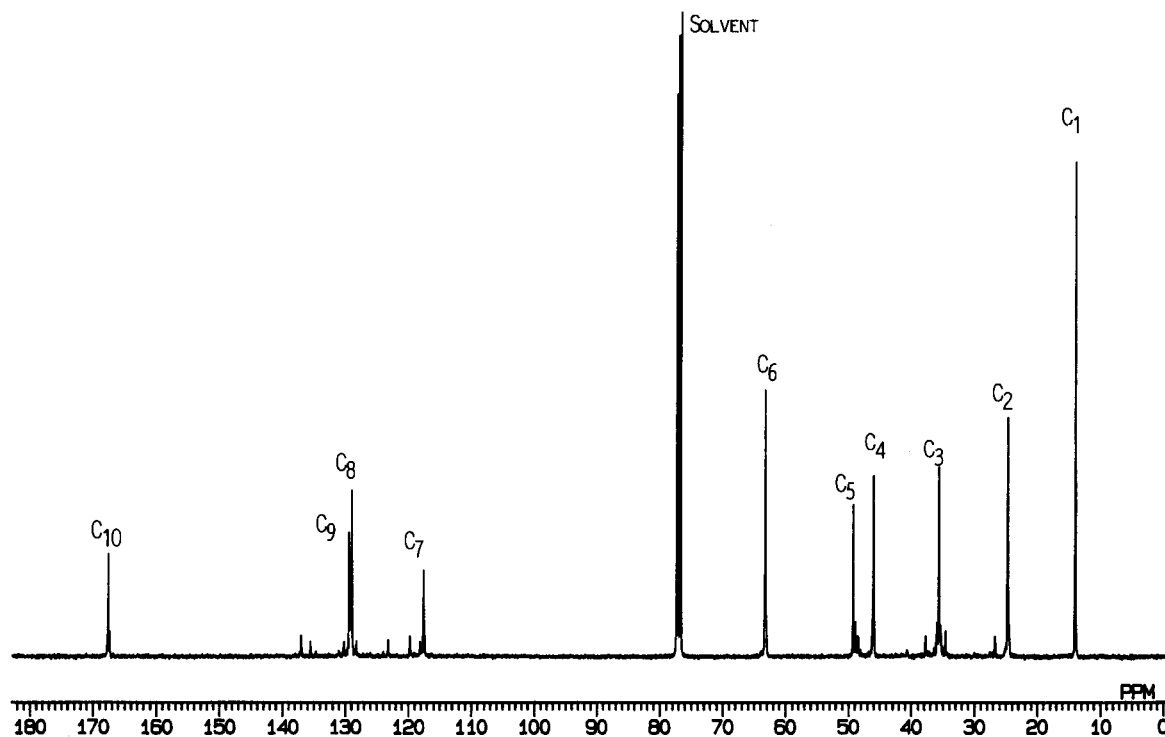


Figure 2 ^1H -decoupled ^{13}C n.m.r. spectrum of sample A

Table 1 Polymerization conditions, overall rates of polymerization, molecular weights and compositions of samples

Sample	Mol ratio in feed (CP/CEA)	Reaction time (h)	Overall rate of polymerization ^a ($R_p \times 10^5 \text{ mol l}^{-1} \text{ s}^{-1}$)	\overline{M}_n^b ($\times 10^{-4}$)	$\overline{M}_w/\overline{M}_n^b$	Mol ratio ^c in copolymer (CP/CEA)
A	1/1	2.5 ^d	69.4	12.0	1.9	1/1
B	9/1	1 ^d	34.9	9.3	1.8	2/1
C	CP only	52	1.4	1.8	2.1	CP homopolymer
D	1/1 ^e	2	—	No polymer formed		—

^a Data obtained by gas chromatography

^b Data obtained by g.p.c.

^c Data obtained by ^1H n.m.r.

^d Stopped when CEA monomer disappeared perfectly

^e No initiator was added

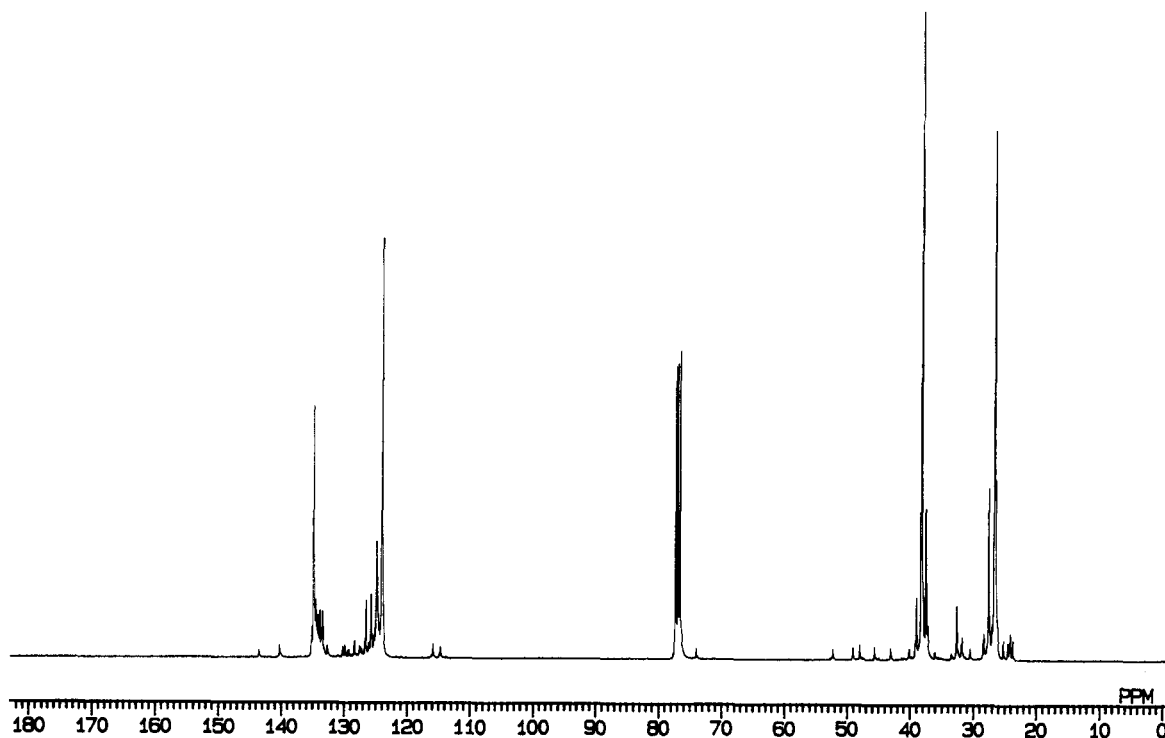


Figure 3 ^1H -decoupled ^{13}C n.m.r. spectrum of sample C

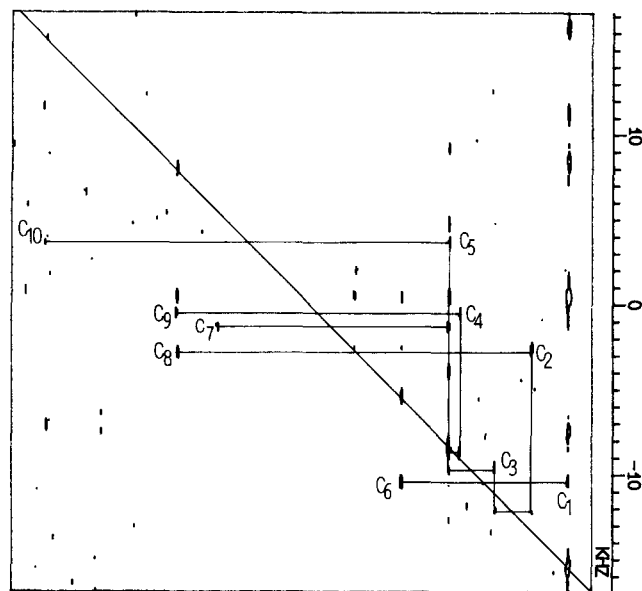
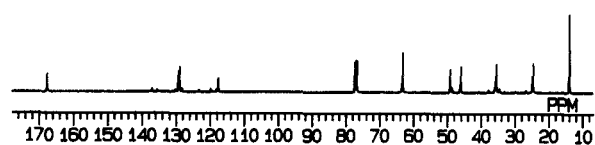


Figure 4 2D INADEQUATE spectrum of sample A

Nuclear magnetic resonance spectroscopy

^1H (400 MHz) and ^{13}C (100 MHz) n.m.r. spectra were recorded on 5 and 10 wt%, respectively, solutions of the copolymers in deuteriochloroform (CDCl_3) at 30°C using a Jeol JNM-GSX-400 spectrometer.

The typical recording conditions for ^1H n.m.r. spectra were 6 kHz spectral width, 5 s pulse repetition, $12.7\ \mu\text{s}$ 90° pulse width, 32 000 data points and 128

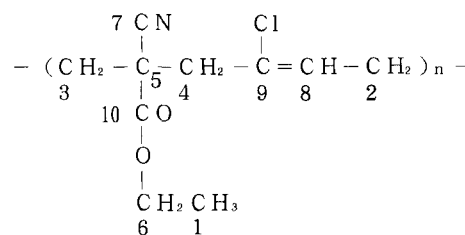


Figure 5 Chemical structure of sample A

accumulations. The recording conditions for ^1H -decoupled ^{13}C n.m.r. spectra were 24 kHz spectral width, 3 s pulse repetition, $20.0\ \mu\text{s}$ 90° pulse width, 32 000 data points and 20 000 accumulations. ^1H -off resonance decoupled ^{13}C n.m.r. spectra were recorded with conditions similar to those used for 1-dimensional spectra, except for 1.5 s pulse repetition and 40 000 accumulations. In addition, two-dimensional (2D) ^1H - ^1H correlation spectroscopy (COSY) and 2D ^{13}C incredible nature abundance double quantum experiment (INADEQUATE) spectra were also observed to assign the ^1H and ^{13}C spectra with Jeol software incorporated into the spectrometer on the pulse width described already. The value of J_{CC} was 50 Hz. The measurement was done on 30 wt% copolymer solution, in order to increase the sensitivity.

RESULTS AND DISCUSSION

Polymerization rate and molecular weights

Table 1 shows polymerization conditions and overall rate of polymerization R_p . From Table 1, it should be found that the R_p obtained by polymerization experiment in the existence of both CP and CEA monomers (experiments A and B) is over 25 times that of the CP

homopolymer (experiment C), i.e. the polymerization in CP and CEA system proceeds more rapidly than normal radical solution polymerization. Also, we observed that each consumption rate of CP and CEA was almost equal in the reaction. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of two copolymers and the CP homopolymer are also shown in *Table 1*. It is clear that the copolymers (A, B) have much higher molecular weights than has the CP homopolymer (C). These facts suggest that in CP and CEA system the chain propagation is very fast, i.e. the chain termination and the chain transfer with solvent are relatively slow. Furthermore, it is thought that the polymerization proceeded by radical initiation because a polymer was not at all formed in the absence of an initiator (experiment D). We will discuss this copolymerization mechanism later.

Fourier transform infra-red spectra

Figure 1 shows the spectra of samples A and C (CP homopolymer). In the spectrum of sample A two characteristic absorbing bands appear, at 2250 cm^{-1} due to $\text{C}\equiv\text{N}$ stretching vibration and at 1740 cm^{-1} due to $\text{C}=\text{O}$ stretching vibration. The strong absorbing band at 1662 cm^{-1} due to $\text{C}=\text{C}$ stretching vibration of

trans-1,4 units⁴ of the CP polymer are also observed in both of the spectra of samples A and C. The spectrum of sample A including the absorbing band representative of both CEA and CP is a proof that CEA copolymerizes significantly with CP. Incidentally, it is known that *cis*-1,4 units⁴ of CP polymer have an absorbing band at 1653 cm^{-1} . However, the absorbing band at 1653 cm^{-1} due to *cis*-1,4 units and that at 1662 cm^{-1} due to *trans*-1,4 units are not clearly discriminated in our i.r. measurements. We think that CP units in the copolymer (sample A) consist of a large number of *trans*-1,4 and a few *cis*-1,4 structures.

Nuclear magnetic resonance

Figure 2 and *Figure 3* show ^1H -decoupled ^{13}C n.m.r. spectra of samples A and C, respectively. Signals of sample A are different from that of CP homopolymer (sample C) in the chemical shift range of 10–170 ppm, and they are designated C_1 – C_{10} . ^1H off-resonances ^{13}C n.m.r. (o.f.r.) measurement is carried out in order to identify the carbon groups. The o.f.r. spectrum reveals that C_1 is methyl carbon, C_2 , C_3 , C_4 , C_6 are methylene, C_8 is methine and C_5 , C_7 , C_9 and C_{10} are quaternary.

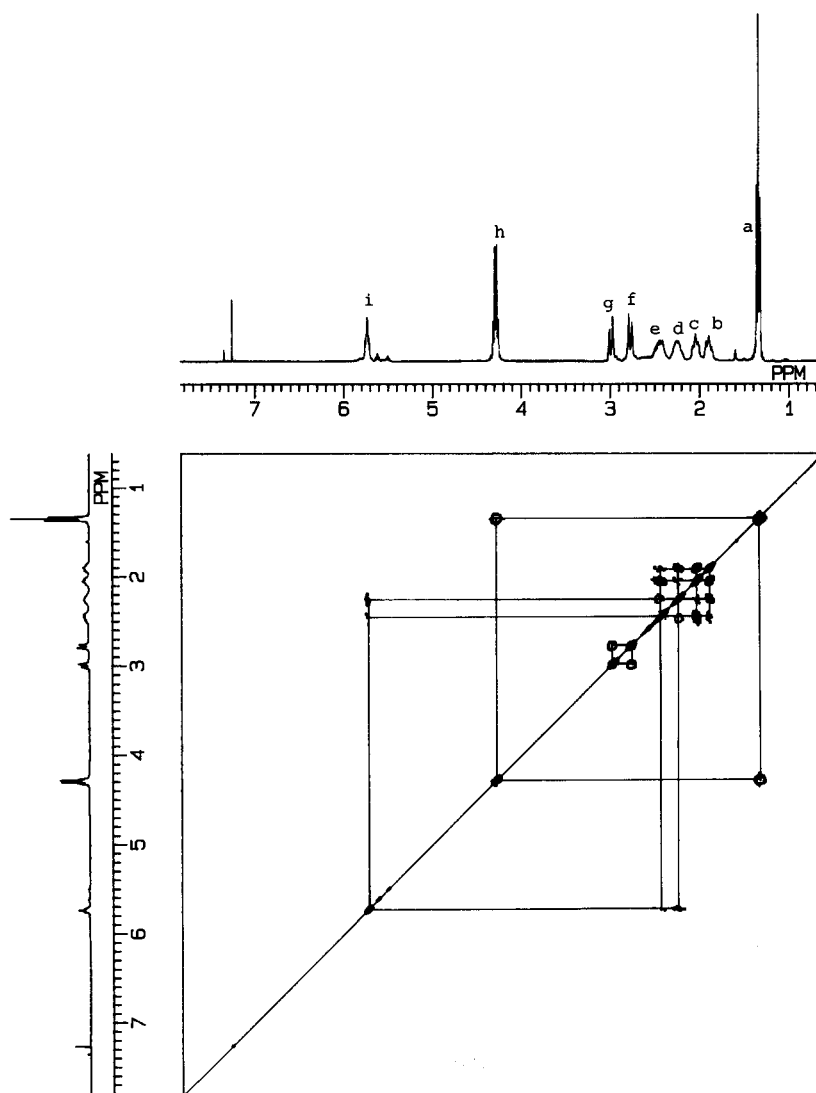


Figure 6 ^1H - ^{13}C COSY spectrum of sample A

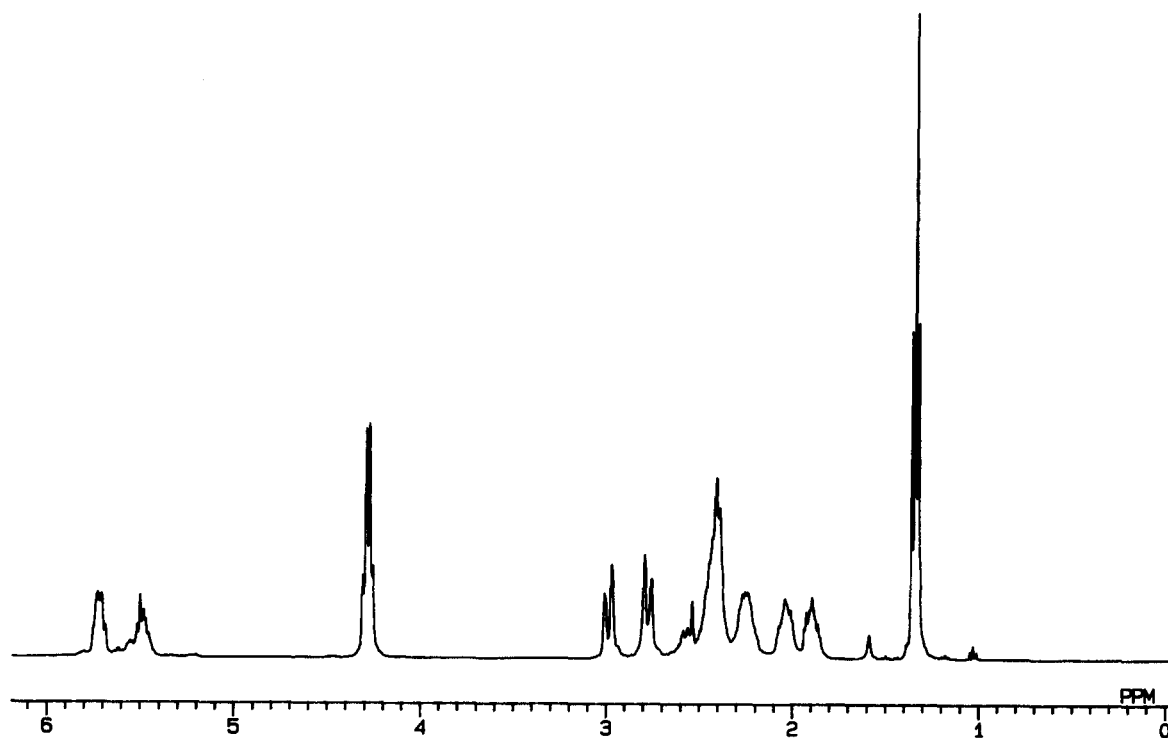


Figure 7 ^1H n.m.r. spectrum of sample B

Figure 4 shows the 2D INADEQUATE spectrum of sample A. Starting from the resonances of C_7 , which is a carbon in cyano group, ^{13}C - ^{13}C connectivities are traced out along the carbon skeleton. The following connectivities are found easily in Figure 4; C_7 - C_5 , C_5 - C_3 , C_5 - C_{10} are due to the CEA unit itself, C_1 - C_6 are due to the ethyl group of CEA, C_5 - C_4 are due to a chemical bond between CP and CEA units and C_4 - C_9 , C_2 - C_8 are due to the CP unit itself (refer to Figure 5, the chemical structure finally decided). A corresponding peak between C_8 and C_9 is not observed because chemical shift position is too close, but they are designated as $-\text{C}_8\text{H}=\text{C}_9\text{Cl}-$ in the CP unit, based upon each chemical shift position and atomic group. Therefore, it is concluded that sample A is an alternating copolymer which consists of $-(\text{CP-CEA})-$ repeating unit (see Figure 5). Of particular interest is that the copolymer is composed of the only repeating unit written in Figure 5. Also, the fact that CP in the repeating unit is a 1,4 structure agrees with the result of i.r. analysis described already. Considering that sample A is the alternating copolymer, the signals appearing in the ^1H n.m.r. spectrum are assigned with the ^1H - ^1H COSY spectrum. Figure 6 shows the ^1H - ^1H COSY spectrum. Signals f and g in Figure 6 are assigned to proton bonding to C_4 because they have no corresponding peak except for themselves. Signal i arises from the proton of C_8 , which has a double bond, and signals b and c are due to protons bonding to C_3 , because they have the corresponding peaks to signals d and e, respectively. Signal a is due to a proton bonding to C_1 and signal h is due to C_6 . On the basis of these assignments, the integral intensities of ^1H spectra are used to determine the composition ratio of CP and CEA. Each amount of CP and CEA in the copolymer can be calculated from signals g and f due to the methylene group of CP and signals b and c due to CEA.

Each integral intensity of CP and CEA is nearly equal, which also supports that sample A is the alternating copolymer.

Next, Figure 7 and Figure 8 show the ^1H spectra of samples B and C. From a comparison among the ^1H spectra of samples B, A (alternating copolymers) and C (CP homopolymer), it can be seen that the spectrum of B includes such signals as A and C. This suggests that copolymer B is a mixture of CP homopolymer and an alternating copolymer of CP and CEA.

Reaction mechanism

As seen from the results of n.m.r. analysis, the copolymer which we synthesized with equimolar amounts of CP and CEA possesses an extremely regular microstructure. Therefore, we shall now attempt to explain the copolymerization mechanism. It has been known, as the Diels-Alder reaction, that α -unsaturated carbonyl compounds undergo a quantitative reaction with conjugated dienes in the field of organic chemistry. On the other hand, a radical produced via a Diels-Alder intermediate or a charge-transfer complex was detected on an alternating copolymerization of styrene with maleic anhydride¹⁷. Then, we consider a reaction scheme by way of a Diels-Alder intermediate. The carbon bonded to chlorine atom in the CP monomer is somewhat rich in π electrons, and the carbon bonded to the cyano group in the CEA monomer is somewhat lacking. Therefore, it is supposed that at an initiation step (Step 1) such a reactivity of each carbon enables the CP and CEA monomers to form a six-membered ring intermediate (1) selectively in the transition state (see Figure 9). Another intermediate (2) likely forms in some cases. If a radical ($\text{R}\cdot$) generates from the decomposition of an initiator, it seems to be probable at first sight that the radical attacks either C_A or C_B . However, a radical formed by attack of C_B is expected to be more unstable than one formed by

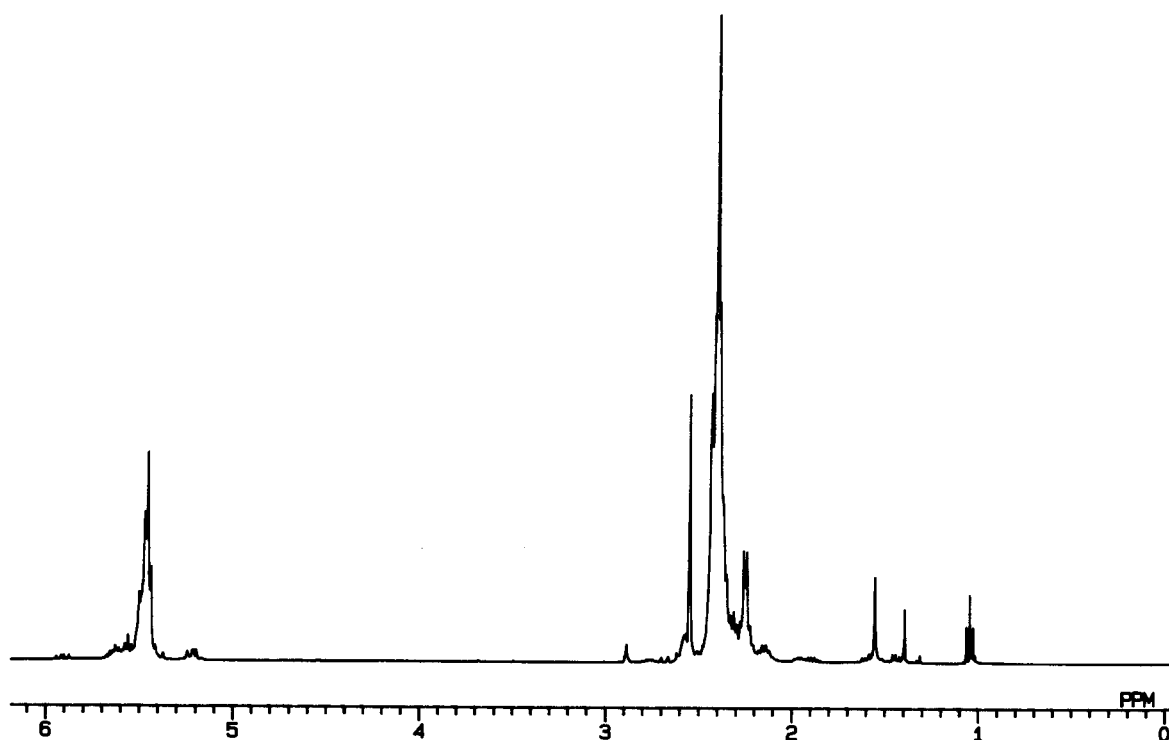


Figure 8 ^1H n.m.r. spectrum of sample C

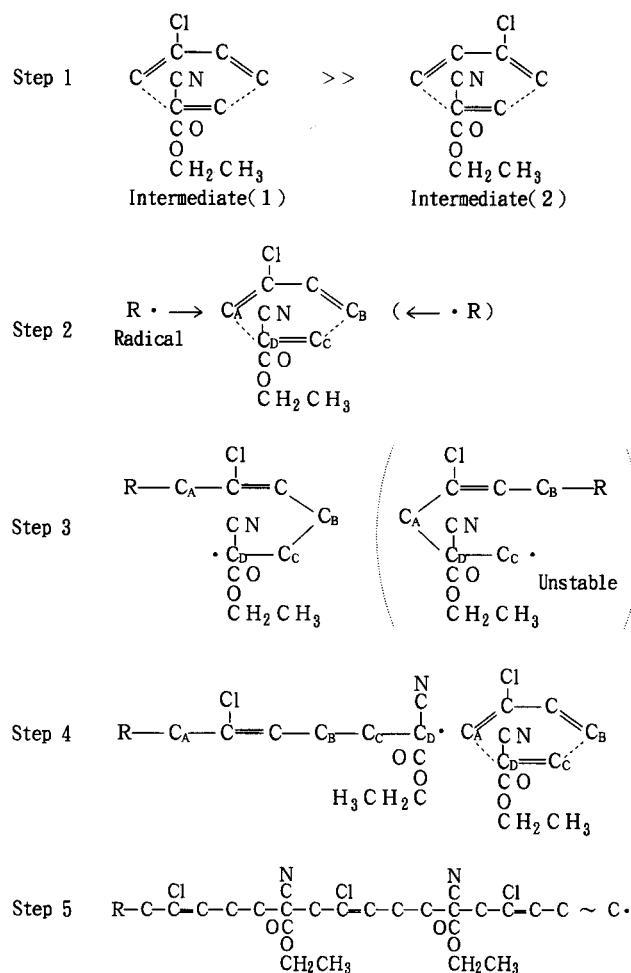


Figure 9 Copolymerization scheme of CP and CEA

attack of C_A , so that a route by attack of C_B does not participate in the copolymerization reaction (Steps 2–3). When an initial radical $\text{R}\cdot$ attacks C_A , C_B in the CP molecule and C_C in the CEA molecule form a covalent bond together, and the radical shifts toward C_D (Step 3). This radical also attacks another intermediate adjacent to itself (Step 4). Thus, repetition of Step 4 yields a chain radical (Step 5) and a CP-CEA alternating copolymer grows up. According to this scheme, it is possible to interpret the structure regularity of the copolymer A reasonably.

CONCLUSIONS

Copolymers of chloroprene (CP) and α -cyanoethyl acrylate (CEA) were synthesized in toluene in substantially moisture free atmosphere and examined by ^1H and ^{13}C n.m.r. and FTi.r. spectroscopy. The copolymers, synthesized on the condition equimolar with CP and CEA in feed, possessed the predominantly repeating unit of $-(\text{CP-CEA})-$ in which CP had the 1,4 unit. A reaction mechanism by way of Diels–Alder intermediate enables us to explain this regular copolymerization satisfactorily.

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