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Copolymerization of Vinyl Chloride and Ethylene Initiated by Trialkylboron-Peroxide Catalyst Systems

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Low-pressure copolymerization was carried out in a water-methanol mixture(1 : 1 by weight) at 0°C. It was found that, when hydroperoxides were used as cocatalysts, triethylboron and tri-*n*-butylboron were active as catalysts, while triphenylboron was inactive. As cocatalysts, hydroperoxides were more active than disubstituted peroxides. The highest catalytic activity was observed when the cocatalyst/catalyst molar ratio was 0.4. The initiating radical has been suggested to be the hydroxy radical, and the initiating mechanism has been discussed briefly. The yield and the reduced specific viscosity of the copolymer decrease rapidly with an increase in the ethylene content of the monomer mixture. The monomer reactivity ratios were: r_1(vinyl chloride)$=4.16$ and r_2(ethylene)$=0.05$. This indicates that the copolymerization reaction proceeds via a normal radical mechanism. The resulting copolymer shows characteristic absorption peaks at 750 cm^{-1} in the infrared spectrum and at 8.37 τ in the NMR spectrum.

Since Furukawa et al.[1] and Ashikari[2] found that alkyl derivatives of boron acted as powerful radical initiators for vinyl polymerization, many studies have been reported on the polymerization and copolymerization of various vinyl monomers. The copolymerization of vinyl chloride and ethylene at a high pressure has been studied in some detail by Burkhalt et al.[3] and Erussalimsky et al.[4] However, no details have been reported on the radical copolymerization of these monomers at a low pressure.

In the course of their studies of the copolymerization of vinyl chloride and ethylene, the present authors found that trialkylboron and hydroperoxides provided excellent catalyst systems which copolymerize these monomers to high-molecular-weight copolymers with a high ethylene content, even at low temperatures. In order to study this subject further, the authors carried out some experiments; they thus obtained the interesting results to be reported here.

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1) J. Furukawa, T. Tsuruta and S. Inoue, *J. Polymer Sci.*, **26**, 234 (1957).

2) N. Ashikari, ibid., **28**, 250, 641 (1958).

3) R. D. Burkhalt and N. L. Zutty, ibid., **A1**, 1137 (1963).

4) B. Erussalimsky, F. Suntoff and N. Tumarkin, *Makromol. Chem.*, **66**, 205 (1963).

Experimental

Materials.—Vinyl chloride supplied by the Chisso Co. was used without further purification; no impurity was detected in it by gas chromatography. Ethylene supplied by the Nihon Petroleum Co. was used without further purification; no impurity was detected in it by gas chromatography. Triethylboron was prepared from ethylmagnesium bromide and boron trifluoride according to the method of Brown[5] (b. p. 92—112°C). Tri-*n*-butylboron was prepared from *n*-butylmagnesium bromide and boron trifluoride according to the method of Johnsen et al.[6] (b. p. 116°C/21 mmHg). Triphenylboron was prepared from phenylmagnesium bromide and boron trifluoride according to the method of Krause et al.[7] The reaction mixture containing triphenylboron was extracted with benzene several times; then the benzene extract was concentrated and distilled (b.p. 154°C/3 mmHg). The peroxides were used without further purification, while methanol was purified by distillation. Ion-exchanged water was boiled prior to use.

Polymerization.—The reaction vessel was a stainless steel autoclave with a 300 ml. capacity and equipped with an electro-magnetic stirring device. Trialkylboron and peroxide were separately sealed into a glass ampule with a 1 ml. capacity attached to the stirring rod of the autoclave. A measured quantity of the reaction medium, a water-methanol mixture (1 : 1 by weight), was introduced into the autoclave, and the inner air was evacuated by a vaccum pump after the autoclave had been cooled to −30°C. Then a measured quantity of vinyl chloride was introduced into the autoclave from a glass pressure tube. When the temperature of the autoclave reached 0°C, ethylene was introduced from a storage tank and the reaction was started by breaking glass ampules containing catalytic components by means of ethylene pressure. Afterward, the reaction temperature was kept within 0±3°C. After a given time, the reaction was stopped by expelling the residual monomers as soon as possible. The resulting copolymer was filtered, washed repeatedly with water and methanol, and dried in vacuo at 50°C. The crude copolymer thus obtained was then precipitated by adding a tetrahydrofuran solution of the copolymer to methanol, filtered, dried in vacuo at 50°C, and subjected to the following analyses.

Analyses of the Copolymer.—The reduced specific viscosity of the copolymer was measured using 5 g./l. cyclohexanone solution at 30°C. The composition of the copolymer was calculated from the results of the elemental analyses of C, H and Cl. The infrared spectrum of the copolymer was masured with a Hitachi double-beam spectrometer, model EPI-S2 (potassium bromide disk). The NMR spectrum of the copolymer was measured with a Nihon Denshi high-resolution NMR spectrometer, model C-60, in a 10% solution of monochlorobenzene at 60°C, using tetramethylsilane as the internal standard.

Results and Discussion

The Effect of the Catalytic Composition.—Henceforth, alkylboron will be called the catalyst, and the other component, the cocatalyst, according to custom. In many studies using alkylboron as the catalyst, oxygen is used as the cocatalyst. However, considering the difficulty of accurately measuring of the oxygen amount, the authors decided to use organic or inorganic peroxides instead of oxygen.

The results of copolymerization with catalytic systems consisting of various catalysts and cocatalysts are summarized in Table I. It may clearly be seen that if either the catalyst or the cocatalyst is absent, copolymerization does not occur. When trialkylboron is used as the catalyst, the cocatalytic activities decrease in the following order:

t-butyl hydroperoxide ≫ cumene hydroperoxide > benzoyl peroxide > hydrogen peroxide, α, α'-azobisisobutyronitrile, di-*t*-butyl peroxide.

Hydroperoxides are more active than disubstituted peroxides when they are combined with trialkylboron. On the other hand, when *t*-butyl hydroperoxide is used as the cocatalyst, the activities of the catalyst are in the following order:

tri-*n*-butylboron ≈ triethylboron ≫ triphenylboron.

On the basis of the above results, the catalyst system consisting of tri-*n*-butylboron or triethylboron and *t*-butyl hydroperoxide was used in every copolymerization experiment to be reported on in this paper unless otherwise mentioned.

Figure 1 shows the influence of the cocatalyst/catalyst molar ratio on the yield and the reduced specific viscosity of the copolymer. The catalytic activity changes remarkably with the ratio, being highest at the ratio of 0.4. The ethylene content of the copolymer also becomes highest at the same ratio. These results are in agreement with those

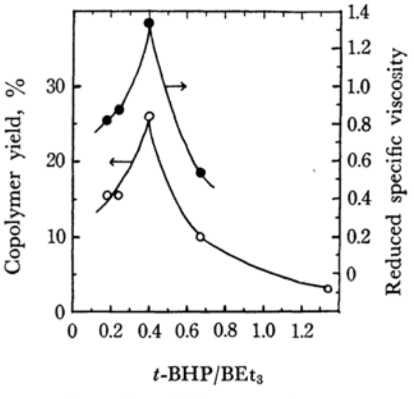

Fig. 1. Effect of *t*-BHP/BEt$_3$ molar ratio on yield and reduced specific viscosity of copolymer. experimental condition; vinyl chloride: 25.0 g., ethylene 14.8 l., *t*-BHP: 0.77 mmol., water: 93 g., methanol: 93 g., polyvinyl alcohol: 0.25 g., temperature: 0°C, time: 5 hr.

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[5] H. C. Brown, *J. Am. Chem. Soc.*, **67**, 374 (1945).

[6] J. R. Rohnson, H. R. Snyder and M. G. van Campen, ibid., **60**, 115 (1938).

[7] E. Krause and R. Nitshe, *Ber.*, **55**, 1261 (1922).

TABLE I. COPOLYMERIZATION RESULTS WITH VARIOUS CATALYST SYSTEMS

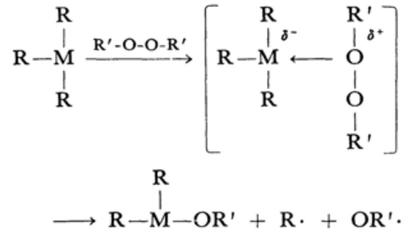
Catalyst	Amount mmol.	Cocatalyst	Amount mmol.	Conversion %	η_{sp}/C	VCl content mol.%
BEt_3	3.30	—	—	trace	—	—
BEt_3	—	*t*-BHP	0.85	0	—	—
BEt_3	1.92	*t*-BHP	0.77	28.6	1.026	80.58
BEt_3	1.90	CHP	1.26	9.82	0.786	82.82
BEt_3	1.87	BPO	1.25	5.31	0.406	93.81
BEt_3	1.83	H_2O_2	1.22	4.98	0.965	86.08
BEt_3	1.88	*t*-BPB	1.24	4.55	0.568	90.93
BEt_3	1.88	AIBN	1.25	4.11	0.366	94.93
BEt_3	1.92	di-*t*-BPO	1.28	4.12	0.496	91.07
BBu_3	2.13	*t*-BHP	0.85	30.1	1.076	84.55
BPh_3	1.90	*t*-BHP	0.76	0	—	—

Polymerization condition: vinyl chloride, 25.0 g. (0.40 mol.); ethylene, 14.8 l. (at 30°C, 0.60 mol.); polyvinyl alcohol, 0.25 g.; water, 93 g.; methanol, 93 g.; temperature, 0°C; time, 5 hr.

Abbreviations: BEt_3, triethylboron; BBu_3, tri-*n*-butylboron; BPh_3, triphenylboron; *t*-BHP, *t*-butyl hydroperoxide; CHP, cumene hydroperoxide; BPO, benzoyl peroxide; *t*-BPB, *t*-butyl perbenzoate; AIBN, α,α-azobisisobutyronitrile; di-*t*-BPO, di-*t*-butyl peroxide

found in vinyl chloride[8] and vinyl acetate[9] polymerizations carried out in the presence of the trialkylboron-oxygen catalyst system, in which the highest catalytic activity has been observed at the point where trialkylboron exists in about a three fold excess over oxygen.

Furukawa et al.[10] have supposed that the initiating mechanism of an organometallic compound-peroxide catalyst system in vinyl chloride polymerization would be as follows:



$$\begin{array}{c}\mathrm{R}\\ |\\ \mathrm{R{-}M}\\ |\\ \mathrm{R}\end{array} \xrightarrow{\mathrm{R'\text{-}O\text{-}O\text{-}R'}} \left[\begin{array}{ccc} & \mathrm{R} & \mathrm{R'}\\ & |\,\delta^- & |\,\delta^+\\ \mathrm{R}{-} & \mathrm{M} \longleftarrow & \mathrm{O}\\ & | & |\\ & \mathrm{R} & \mathrm{O}\\ & & |\\ & & \mathrm{R'}\end{array}\right]$$

$$\longrightarrow \mathrm{R{-}\overset{\overset{R}{|}}{M}{-}OR'} + \mathrm{R\cdot} + \mathrm{OR'\cdot}$$

where the metal may be either aluminum or boron. They have supposed that the resulting radicals might be able to initiate the vinyl polymerization, but no experimental support has been given.

The present authors could isolate a low-molecular-weight copolymer on solution polymerization in *n*-hexane using the triethylboron-cumene hydroperoxide catalyst system. The infrared spectrum of the resulting copolymer is shown in Fig. 2. Before the treatment with benzoyl chloride, the copolymer shows a stretching vibration of the hydroxy group at 3430 cm^{-1}, this vibration disappears when the copolymer is treated with benzoyl chloride, and a new stretching vibration absorption of the carbonyl group appears at 1700 cm^{-1}. The rest of the spectrum is the same as that of the high-molecular-weight copolymer to be shown later.

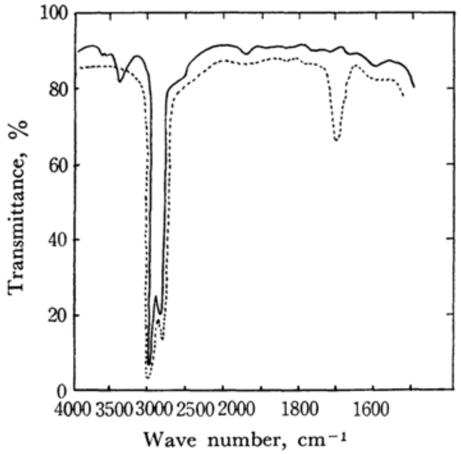


Fig. 2. Infrared spectra of low molecular weight copolymer.
Full line; untreated copolymer
Dotted line; after benzoylation

Hansen et al.,[11] after studying the reaction of triethylboron and oxygen in *n*-hexane, have suggested that an ethyl radical was formed during the reductive decomposition of a peroxide of triethylboron with an excess of triethylboron. In another report,[12] they have shown, from the results of kinetic studies of the polymerization of methylmethacrylate by the triethylboron-oxygen catalyst system, that the highest rate of polymerization was

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[8] G. Borsini and M. Cippolla, *J. Polymer Sci.*, **B2**, 291 (1964).

[9] F. Ide and Y. Takayama, *J. Soc. Chem. Japan, Ind. Chem. Sect. (Kyogyo Kagaku Zasshi)*, **63**, 529 (1960).

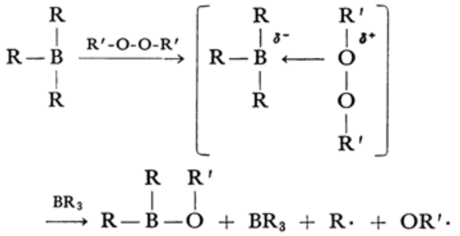
[10] J. Furukawa, T. Tsuruta and S. Shiotani, *J. Polymer Sci.*, **40**, 237 (1959).

[11] R. L. Hansen and R. R. Hamann, *J. Phys. Chem.*, **67**, 2868 (1963).

[12] R. L. Hansen, *J. Polymer Sci.*, **A2**, 4215 (1964).

obtained when the triethylboron concentration was twice the oxygen concentration. Also, Bawn et al.[13] and Welch[14] have reported similar findings concerning the initiation mechanism of the trialkylboron-oxygen catalyst system.

From the results of the present authors and those of the other authors cited above, it seems better to consider, also in the case of the trialkylboron-peroxide systems, the initiating radical as arising from such a mechanism in which the 1 : 1 complex of trialkylboron and peroxide is reduced by another molecule of trialkylboron rather than from Furukawa's mechanism. One probable mechanism may be as follows:



$$R_3B \xrightarrow{R'\text{-O-O-}R'} \left[R_3B^{\delta-} \longleftarrow O^{\delta+}(R')\text{—}O\text{—}R' \right] \xrightarrow{BR_3} R\text{—}B(R)\text{—}O\text{—}R' + BR_3 + R\cdot + OR'\cdot$$

Hydroperoxides might be able to coordinate to the boron atom of trialkylboron with less steric hindrance and might, hence, show a greater catalytic activity.

The Effects of the Monomer Composition.—The effects of the monomer composition on the yield and the reduced specific viscosity of the copolymer are shown in Fig 3. As the ethylene content in the monomer mixture increase, both the yield and the viscosity of the copolymer decrease rapidly, ethylene does not polymerize under the present experimetnal conditions.

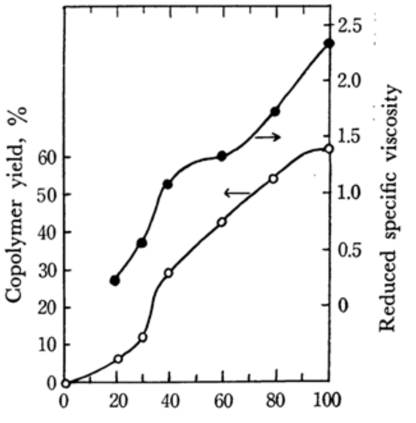


Fig. 3. Effect of monomer composition on yield and reduced specific viscosity of copolymer.
Experimental condition; vinyl chloride+ethylene: 1.0 mol., BBu_3: 2.18 mmol., *t*-BHP/BBu_3: 0.40, water: 93 g., methanol: 93 g., polyvinyl alcohol: 0.25 g., temperature: 0°C, time: 5 hr.

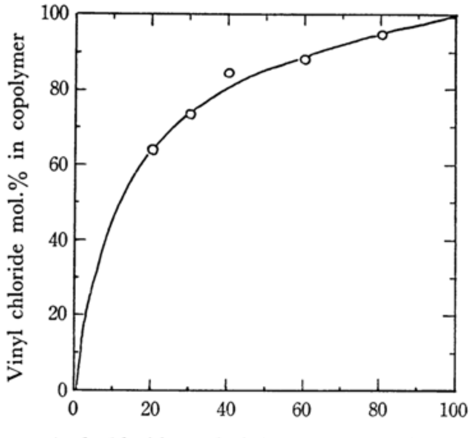


Fig. 4. Effect of monomer composition on copolymer composition.
Experimental condition; vinyl chloride+ethylene; 1 mol., BBu_3: 2.18 mmol., *t*-BHP/BBu: 0.40, water: 93 g., methanol: 93 g., polyvinyl alcohol: 0.25 g., temperature: 0°C, time: 5 hr.

The copolymer composition curve is shown in Fig. 4. The monomer reactivity ratios determined from the Finemann-Ross plot are r_1(vinyl chloride)$=4.16$ and r_2(ethylene)$=0.05$. These values almost equal those obtained by the authors using the *t*-butyl hydroperoxide - ascorbic acid catalyst system[15] ($r_1=4.70$, $r_2=0.08$). This indicates that the copolymerization reaction proceeds via a normal radical mechanism. The monomer reactivity ratios obtained by the authors are slightly different from those of Burkhalt et al.[1] ($r_1=3.60$, $r_2=0.24$) and Erussalimsky et al.[2] ($r_1=1.85$, $r_2=0.20$), which have been obtained from high-pressure copolymerization studies.

The Infrared and NMR Spectra of the Copolymer.—The infrared spectra of the copolymers containing 64.08 and 84.55 mol.% of vinyl chloride respectively are shown in Fig. 5. Most of the spectra show features intermediate between those of polyvinyl chloride and those of polyethylene, but a characteristic absorption absent in both homopolymers is observed at 750 cm^{-1}, the intensity of which absorption increases with an increase in the ethylne content of the copolymer.

Sheppard et al.[16] have studied the infrared spectra of polymethylene halides and found that the methylene rocking vibration absorption, which appeared at 720 cm^{-1} in polymethylene, shifted to a higher region, between 770 cm^{-1} and 790 cm^{-1}, in the case of trimethylene or pentamethylene

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[13] C. E. H. Bawn, D. Margerison and N. M. Richardson, *Proc. Chem. Soc.*, **1959**, 397.

[14] F. J. Welch, *J. Polymer Sci.*, **61**, 243 (1962).

[15] A. Misono et al., unpublished data.

[16] J. K. Brown and N. Sheppard, *Trans. Faraday Soc.*, **231(A)**, 555 (1952).

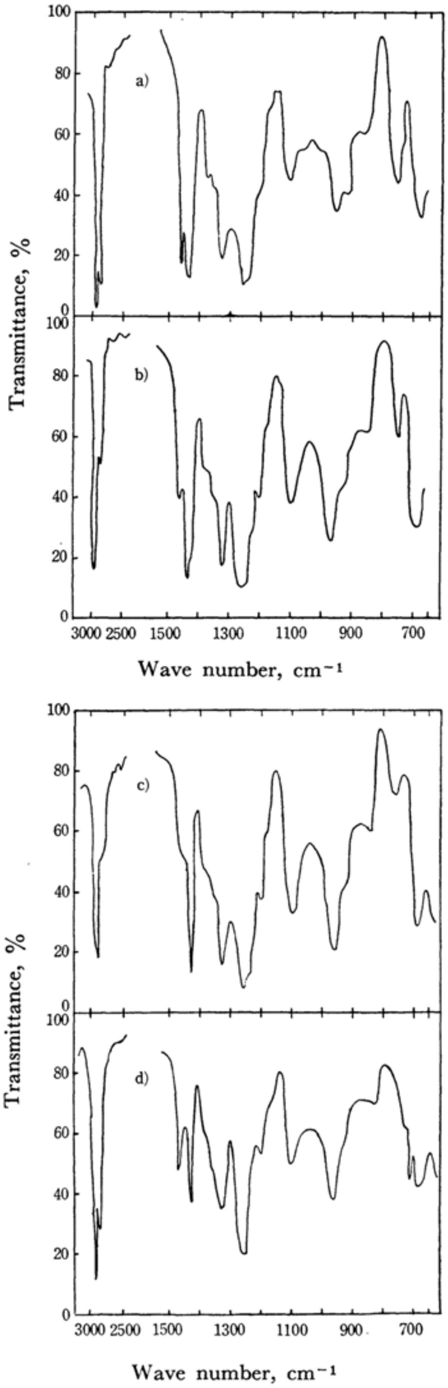

Fig. 5. Infrared spectra of copolymers and mixture of homopolymers.

a) Copolymer containing 64.08 mol.% of vinyl chloride

b) Copolymer containing 84.55 mol.% of vinyl chloride

c) Copolymer containing 94.69 mol.% of vinyl chloride

d) Mixture of polyvinyl chloride and poly ethylene (80: 20 molar ratio)

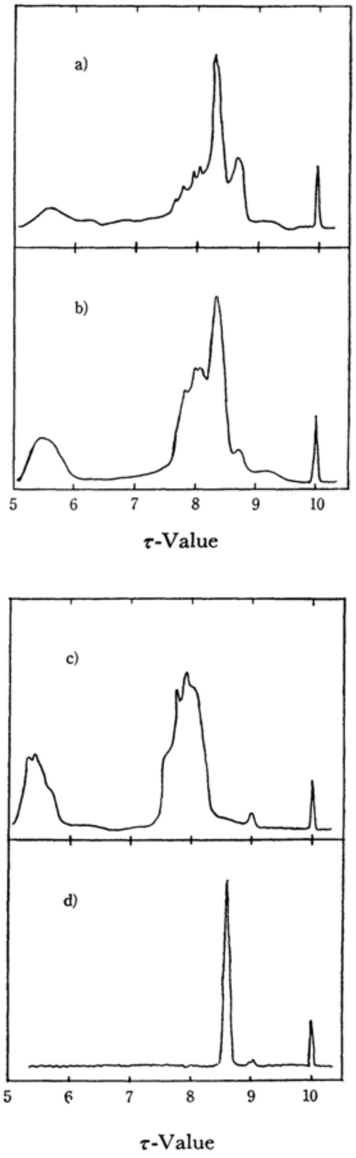

Fig. 6. NMR spectra of copolymers and homopolymers.

a) Copolymer containing 64.08 mol.% of vinyl chloride

b) Copolymer containing 84.55 mol.% of vinyl chloride

c) Polyvinyl chloride d) Polyethylene

chloride. From these observations, it seems reasonable to assign the absorption at 750 cm^{-1} observed in the copolymer to the following structure in the copolymer chain:

$$\text{-CHCl-CH}_2\text{-CH}_2\text{-CH}_2\text{-CHCl}$$

The NMR spectra of the copolymers containing 64.08 and 84.55 mol.% of vinyl chloride are shown in Fig. 6. The characteristic absorption is observed at 8.32 τ, whereas absorptions at 7.78

τ, 7.96 τ and 5.46 τ are also observed in polyvinyl chloride. Johnsen has made assignments of these absorptions in polyvinyl chloride.[17] An absorption at 8.68 τ is observed also in polyethylene. The characteristic absorption at 8.32 τ may be assigned to the following structure in the copolymer chain:

$$-\mathrm{CHCl}-\mathrm{CH_2}-\mathrm{CH_2}-$$

Summary

The copolymerization of vinyl chloride and ethylene has been carried out by the use of various trialkylbron-peroxide catalyst systems. A catalyst system consisting of triethylboron or tri-*n*-butylboron and *t*-butyl hydroperoxide showed the best activity. As for the molar ratio of the two catalyst components, the highest catalytic activity was observed when the *t*-butyl hydroperoxide/triethylboron molar ratio was 0.4. The initiating radical was supposed to be a hydroxy radical from the results of a study of the infrared spectra of a low-molecular-weight copolymer. The initiating radical might arise from the reductive degradation of a 1 : 1 complex of trialkylboron and peroxide with excess of trialkylboron. The yield and the reduced specific viscosity of the copolymer changed greatly with the composition of the monomer mixture; the richer the vinyl chloride content in the monomer mixture, the higher the yield and viscosity. The monomer reactivity ratios were determined to be r_1(vinyl chloride) : 4.16 and r_2-(ethylene) : 0.05. The infrared spectrum of the copolymer showed a characteristic absorption at 750 cm^{-1}, and also in the NMR spectrum at 8.32 τ. These characteristic absorptions might be assigned to a boundary structure in the copolymer chain as follows:

$$-\mathrm{CHCl}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-$$

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[17] U. Johnsen, *J. Polymer Sci.*, **54**, S6 (1961).