Infrared Spectra of Vinyl Chloride - Ethylene Copolymers

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The present authors have been carrying out a study of the copolymerization of vinyl chloride with ethylene by using various radical and Ziegler-Natta catalysts.[1-3] In view of the fact that there have been scarcely no studies of the infrared spectra of ethylene copolymers other than ethylene-propylene copolymers, it seems interesting to study the infrared spectra of vinyl chloride-ethylene copolymers. In this paper, the present authors wish to report the results of a qualitative investigation of the infrared spectra of vinyl chloride-ethylene copolymers obtained by the $Ti(O\text{-}n\text{-}Bu)_4$-$AlEtCl_2$-tetrahydrofuran (THF) catalyst system.

Experimental

The copolymer samples used in this study were prepared according to the methods described in a previous paper.[3] Samples containing more than 65 mol% vinyl chloride were obtained in a powdered form, and the infrared spectra of these samples were measured in the form of a KBr disk. Samples containing less than 65 mol% vinyl chloride were too viscous to be pressed into KBr disks; their spectra were measured by the capillary method.

A Japan-Spectroscopic Model DS-301 infrared spectrophotometer was used for the measurement.

Results and Discussion

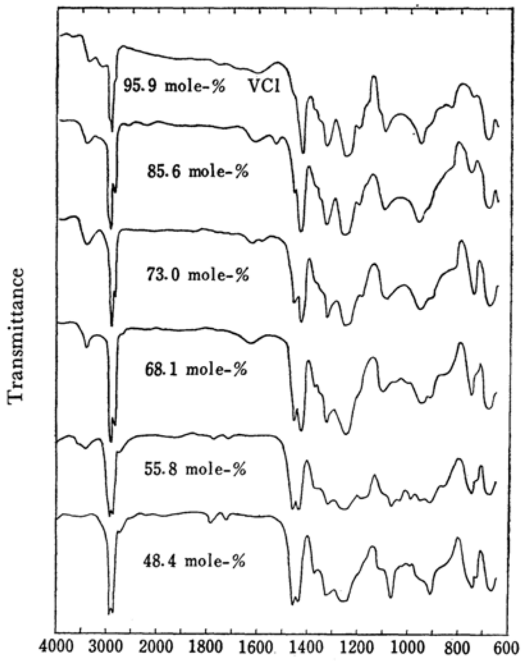

Fig. 1. Infrared spectra of vinyl chloride-ethylene copolymers.

Figure 1 shows the infrared spectra of several vinyl chloride - ethylene copolymers, together with the vinyl chloride contents. Table 1 lists the wave numbers of the infrared absorption peaks and shoulders as well as the tentative assignments.

General Features of the Infrared Spectrum. The CH_2-rocking mode generally appears in the region from 700 to 970 cm^{-1}; it will be discussed in some detail in the next section.

The CH_2-twisting mode of polyvinyl chloride

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[1] A. Misono, Y. Uchida and K. Yamada, This Bulletin, **39**, 2458 (1966).

[2] A. Misono, Y. Uchida and K. Yamada, *ibid.*, **39**, 1822 (1966).

[3] A. Misono, Y. Uchida and K. Yamada, *J. Polymer Sci.*, **B5**, 401 (1967).

TABLE 1. INFRARED ABSORPTION BANDS OF VINYL CHLORIDE-ETHYLENE COPOLYMERS

C-1	C-2	C-3	C-4	C-5	C-6	Assignment
(95.9)a)	(85.6)	(73.0)	(68.1)	(55.8)	(48.4)	
2967 s b)	2967 s					ν(CH)c)
2920 s	2920 s	2920 s	2920 s	2920 s	2920 s	$\nu_a(CH_2)$
2850w	2850m	2850m	2850m	2850 s	2850 s	$\nu_s(CH_2)$
1455sh	1455m	1455m	1455m	1455 s	1455 s	$\delta(CH_2)$
1424 s	1428 s	1430 s	1430 s	1430 s	1430 s	$\delta(CH_2)$
1375w	1375w	1375w	1375w	1375w	1375w	$w(CH_2)$
1350sh	1350sh	1350sh	1350sh			$w(CH_2)$
1330m	1330m	1330m	1323m	1320m	1320m	$\delta(CH)$
1250 s	1250 s	1250 s	1250 s	1250 s	1250 s	$\delta(CH)$
1195m	1195m	1195m	1195sh	1195sh		$\delta(CH)$
1095m	1100m	1105m	1106w	1105sh	1105sh	$\nu(CC)$
				1068m	1068m	$\nu(CC)$
967m	967m	967m	967m	967sh	967sh	$r(CH_2)$
925sh	920sh	915sh	912m	912m	913m	$t(CH_2)$
833w	833w	833sh	833sh			$r(CH_2)$
743sh	745w	745m	745m	745m	745m	$r(CH_2)$
			725sh	725sh	725w	$r(CH_2)$
685m	675m	675m	675m	675m	665m	$\nu(CCl)$

a) Vinyl chloride content expressed in mol%.
b) Relative intensity; s, strong; m, medium; w, weak; sh, shoulder.
c) ν, stretching; ν_a, antisym. stretching; ν_s, sym. stretching; δ, bending; w, wagging; r, rocking; t, twisting.

appears at 925 cm^{-1}.4) However, in the spectrum of the copolymer this band shifts to a lower frequency and increases in intensity as the vinyl chloride content of the copolymer decreases.

The C-C skeletal modes of polyvinyl chloride appear at 1095 cm^{-1}.4) This band rather quickly weakens as the vinyl chloride content of the copolymer decreases, and in the spectrum of the copolymer containing less than 50 mol% vinyl chloride the band becomes a very weak shoulder. On the other hand, in the spectrum of the copolymer containing less than 60 mol% vinyl chloride, a new band, one not observed in the spectrum of polyvinyl chloride, appears at 1070 cm^{-1}; it increases in intensity with the decreasing vinyl chloride content of the copolymer.

Polyvinyl chloride shows two bands due to the CH-bending modes at 1195 and 1250 cm^{-1}.4) As the vinyl chloride content of the copolymer decreases, the intensity of the band at 1195 cm^{-1} rapidly decreases; in the spectrum of the copolymer containing less than 50 mol% vinyl chloride, it completely disappears. On the contrary, the band at 1250 cm^{-1} still remains strong even if the vinyl chloride content of the copolymer becomes less than 50 mol%.

The CH_2-bending mode appears at 1428 cm^{-1} in the spectrum of polyvinyl chloride4) and at 1460 cm^{-1} in the spectrum of polyethylene.5) In the spectrum of the copolymer, a new band, one not observed in the spectrum of polyvinyl chloride, appears at 1455 cm^{-1}, whereas the band at 1428 cm^{-1} gradually weakens as the vinyl chloride content of the copolymer decreases. In the spectrum of the copolymer containing less than 50 mol% vinyl chloride, the intensity of the band at 1455 cm^{-1} is higher than that of the band at 1428 cm^{-1}.

In the spectrum of polyvinyl chloride, the CH-stretching modes appear at 2967, 2920, and 2849 cm^{-1}.4) Of these bands, the one at 2967 cm^{-1} disappears quickly as the vinyl chloride content of the copolymer decreases, and in the spectrum of the copolymer containing less than 70 mol% vinyl chloride, the band completely disappears. The band at 2849 cm^{-1} becomes stronger with the decrease in the vinyl chloride content of the copolymer.

The CH_2-Rocking Mode. The infrared spectral changes of the vinyl chloride-ethylene copolymers in the region of the CH_2-rocking mode will be discussed in some detail in order to elucidate the fine structures of the copolymers.

In the infrared spectra of the vinyl chloride-ethylene copolymers in this frequency region four peaks are observed, at 967, 833, 745, and 725 cm^{-1}; their intensities very with the composition change of the copolymer, as is shown in Fig. 2.

The peaks at 967 and 833 cm^{-1} appear in the spectra of the copolymer and of polyvinyl chloride.4)

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4) T. Shimanouchi and M. Tasumi, This Bulletin, **34**, 359 (1961).

5) S. Krimm, C. Y. Liang and G. B. B. M. Sutherland, *J. Chem. Phys.*, **25**, 549 (1956).

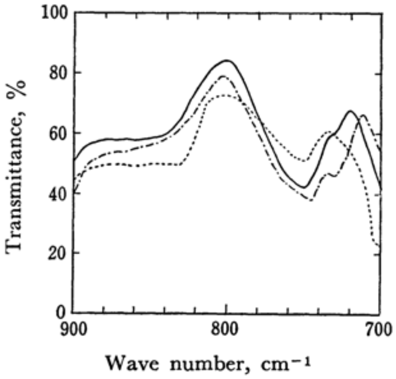

Fig. 2. Infrared spectra of the vinyl chloride-ethylene copolymers in the CH_2-rocking region.

---- 88.2 mol% VCl
—— 68.1 mol% VCl
-·-·- 48.4 mol% VCl

Hence, the peaks can be assigned to the $-(CH_2)_1-$ group in the copolymer with certainty.

The rocking mode of the $-(CH_2)_2-$ sequence has been shown to appear at 790—810 cm^{-1} by Murayama and Amagi in an infrared spectroscopic study of chlorinated polybutadienes.[6] However, the present authors have never been able to detect any absorption in this frequency region; hence, the $-(CH_2)_2-$ sequence does not exist in the copolymers investigated in this study.

The band at 745 cm^{-1} can be assigned to the $-(CH_2)_3-$ sequence on the basis of a comparison of it with the spectrum of 2, 6-dichloroheptane, which shows the CH_2-rocking modes at 752 and 743 cm^{-1}.

As for the $-(CH_2)_4-$ sequence, no assignment can be made because suitable model compounds have not yet been available. However, from the fact that the $-(CH_2)_2-$ sequence is absent, as has been described above, it seems reasonable to consider that the $-(CH_2)_4-$ sequence is also absent in the copolymer under investigation.

Polyethylene shows the CH_2-rocking mode at 720 cm^{-1}.[5] Nambu has reported that a chlorinated polyethylene containing about 20% chlorine, which corresponds to a vinyl chloride - ethylene copolymer containing about 20 mol% vinyl chloride, shows the CH_2-rocking mode at 715 cm^{-1}.[7] Accordingly, the CH_2-rocking modes of the $-(CH_2)_n-$ sequences in which n is five or more probably cannot be distinguished from that of polyethylene.

Since the $-(CH_2)_2-$ and $-(CH_2)_4-$ sequences arise from the head-to-head addition of the vinyl chloride units, the absence of such sequences, though the absence of the $-(CH_2)_4-$ sequence has been only speculative, demonstrates that, in the copolymers obtained by the $Ti(O\text{-}n\text{-}Bu)_4\text{-}AlEtCl_2$-THF catalyst system, a regular head-to-tail addition of the vinyl chloride units takes place.

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[6] N. Murayama and Y. Amagi, *J. Polymer Sci.*, **B4**, 119 (1966).

[7] K. Nambu, *J. Appl. Polymer Sci.*, **4**, 69 (1960).