The Infrared Absorption Spectrum of the Vinyl Chloride - Vinyl Acetate Copolymer and Its Tacticity

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(Received June 9, 1965)

We have already reported a method for the infrared analysis of the vinyl chloride - vinyl acetate copolymer.[1] In that paper we suggested the possibility of discriminating between the copolymer and a mixture of the homopolymer of vinyl chloride and that of vinyl acetate (henceforth referred to as PVC and PVAc respectively); no difference in the frequencies of the absorption bands was observed, but the absorption intensities of some bands of the copolymer were markedly different from those of a mixture with the same composition. In this paper the infrared spectra in the 400—700 cm^{-1} range of the same samples will be measured. We will also study the relation between the vinyl acetate content of the copolymer and the tacticity of its vinyl chloride part. The crystallinity of the copolymer will also be discussed.

Experimental

The infrared spectra of the polymers were observed by means of a Nihon-Bunko double-beam infrared spectrophotometer, Model DS-402G. The samples of PVC, PVAc and the copolymers were the same as those used in a previous experiment.[1] The polymer films were obtained from the tetrahydrofuran solutions of the polymers by evaporating the solvent on mercury under reduced pressure.

Results and Discussion

The Infrared Absorption Spectra and Relative Absorption Intensities.—Shimanouchi et al.[2,3] have assigned the bands of PVC at 638 cm^{-1} and 615 cm^{-1} to the C–Cl stretching frequencies associated with the syndiotactic structure, an extended chain, and the band at 690 cm^{-1} to the isotactic structure, a three-fold helix. They have also concluded that the bands at 690 cm^{-1} and 615 cm^{-1} are due to the amorphous region of the polymer, and the band at 638 cm^{-1} to the crystalline region.

Three bands, at 690 cm^{-1}, 637 cm^{-1} and 615 cm^{-1}, were observed in the spectra of the copolymers and the mixtures. They were inferred to arise as follows: the 690 cm^{-1} band from the C–Cl vibration, and the 637 cm^{-1} band and the 615 cm^{-1} band from the vibrations of C–Cl and the acetyl group.[2,4] In Fig. 1 the ratios of the absorbance at 690 cm^{-1} to that at 637 cm^{-1}, of that at 637 cm^{-1} to that at 615 cm^{-1}, and of that at 690 cm^{-1} to that at 615 cm are plotted against the vinyl acetate content. It may be seen that there are great differences in the absorbance ratios between the copolymer and the mixture, the difference in the absorbance ratio of the 690 cm^{-1} and 637 cm^{-1} bands being the most noticeable.

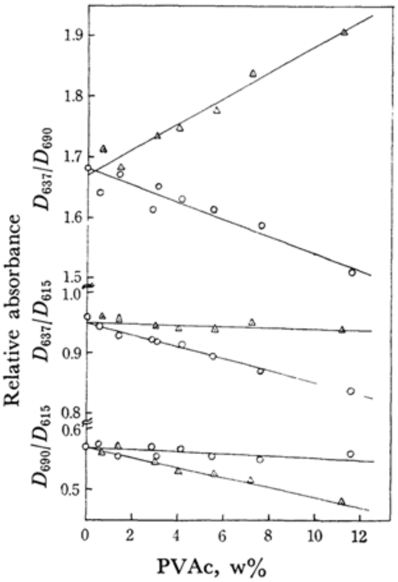

Fig. 1. Relative absorbances of the 690, 637 and 615 cm^{-1} bands.
○—○: Copoymers
△—△: Mixtures

The Tacticity of the Copolymer.—On the basis of the differences in absorbance ratio between the copolymer and the mixture, the tendency of the crystallinity and the tacticity of the copolymer to change with an increase in the vinyl acetate content of the copolymer was considered.

Figure 2 shows that the absorption intensity of the band at 690 cm^{-1} of the copolymers decreases less than that of the mixtures as the vinyl acetate content increases. If the intensity of the 690 cm^{-1}

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[1] T. Takeuchi and S. Mori, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **68**, 643 (1965).

[2] T. Shimanouchi, S. Tsuchiya and S. Mizushima, *Kobunshi*, **8**, 202 (1959).

[3] T. Shimanouchi, S. Tsuchiya and S. Mizushima, *J. Chem. Phys.*, **30**, 1365 (1959).

[4] H. W. Thompson and P. Torkington, *J. Chem. Soc.*, **1945**, 640.

band is not subjected to the influence of the copolymerization of PVAc, it might be possible to explain this result qualitatively in terms of the fact that the amorphous content of the isotactic region of the vinyl chloride part increases as the vinyl acetate content increases. As the bands at 637 cm^{-1} and 615 cm^{-1} were assigned to the bands due to the vibrations of both the acetyl group of PVAc and the C–Cl of PVC, it might not be appropriate to discuss the tacticity of the copolymer quantitatively. However, the relative absorbance of the 637 cm^{-1} band to the 615 cm^{-1} band of the copolymer was smaller than that of the mixture; this means that the absorption intensity at 637 cm^{-1} of the copolymer decreased, or that at 615 cm^{-1} increased, more than those of the mixture. If the influence of the copolymerization of PVAc is disregarded, it should be possible to explain these results by concluding that the crystalline content of the syndiotactic region of vinyl chloride decreases, or that the amorphous content of the syndiotactic region of the vinyl chloride part increases, as the copolymerization degree of vinyl acetate increases.

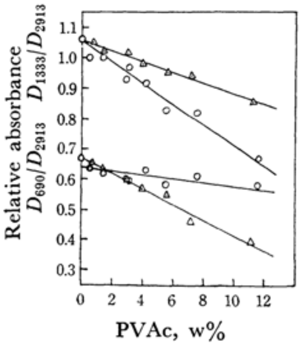

Fig. 2. Relative absorbances of 1333 and 690 cm^{-1} bands to the 2913 cm^{-1} band.1)

○—○: Copolymers △—△: Mixtures

The band at 1333 cm^{-1} of PVC was considered to be the crystalline band1); its absorbance of the copolymer decreased much more than that of the mixture as the vinyl acetate content increased (see Fig. 2). It was clear that the degree of crystallinity of the copolymer was smaller than that of a mixture of two homopolymers of the same composition. This fact was confirmed by the finding that the densities of the copolymers were smaller than those of the mixtures calculated from the densities of PVC and PVAc.

Grisenthwaite and Hunter5) have pointed out that the degree of crystallinity and the content of the syndiotactic region of the amorphous part of PVC increase as the polymerization temperature is lowered; basides, its isotactic region decreases. The results presented above lead to the following, differing conclusions: the degree of the crystallinity of the copolymer decreases as the vinyl acetate content increases, while the isotactic region of the amorphous vinyl chloride part increases.

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5) R. J. Grisenthwaite and R. F. Hunter, *Chem. & Ind.*, **1958**, 719.