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Properties of Vinyl Chlorides-Ethylene Copolymers

Akira MISONO and Yasuzo UCHIDA

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo

and Kunikazu YAMADA

Research Institute, Sekisui Chemical Co., Shimamoto-cho, Mishima-gun, Osaka

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Properties of vinyl chloride-ethylene copolymers rich in vinyl chloride have been studied by means of infrared as well as NMR spectroscopy and dynamic mechanical testing. The infrared and NMR spectra of the copolymer indicate that crystallinity decreases with decreasing sequence length of the vinyl chloride segment. The copolymer containing more than 80 mol % vinyl chloride shows optical melting point, a plot of which *versus* logarithmic composition satisfies Flory's relationship. Temperature dispersion curve of elastic modulus E′ of the copolymer also indicates that the crystalline region of vinyl chloride segments disappears as the ethylene content increases. Glass transition temperature as determined by loss modulus E″ fits Gordon-Taylor's relationship well provided the coefficient *k* equals unity.

From the results of crystallographic,[1–3] mechanical[4–6] and thermal studies,[7] it is considered that polyvinyl chloride can be regarded as a semi-crystalline polymer, though its crystalline region is very small. On the other hand, Flory[8] has shown that the crystallinity of an original polymer decreases regularly depending on the amount of the comonomer incorporated. Many copolymer systems have been examined in relation to the melting point depression predicted by Flory.[9] Few vinyl chloride copolymers, however, have been studied in this respect probably because of their poor crystallinity. We reported the syntheses[10–12] and some aspects of structural problems[13,14] of vinyl chloride-ethylene copolymers. It has been suggested that the copolymer is more or less crystalline on the basis of our recent investigation. We wish to report on the results of a preliminary study on the properties of the copolymers.

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Experimental

Copolymer samples were prepared by using the catalyst system consisting of tri-*n*-butylboron and *t*-butyl hydroperoxide in a water-methanol mixture (1 : 1 by volume).[1] The composition of the copolymer was determined from the results of elementary analysis of C and Cl. The infrared spectrum of the copolymer was measured with a JASCO 201 infrared spectrometer by the KBr disk method. The NMR spectrum of the copolymer was measured by a Japan Electron Optics high resolution NMR spectrometer, model JNM-60, in a 10 wt/vol% monochlorobenzene solution of the copolymer at 60 MHz and 110°C using tetramethylsilane as internal standard. The melting point of the copolymer was measured by a Yanagimoto hotstage polarizing microscope. The dynamic viscoelasticity of the copolymer was measured by Toyo Measuring Instruments Vibron viscoelastometer, model DDV-II, at 11 Hz using a sheet of sample prepared by hot-pressing at 100°C for 5 min under a pressure of 70 kg/cm^2.

Results and Discussion

In the region 700 to 600 cm^{-1} of the infrared spectrum of polyvinyl chloride, four absorption bands were observed at 690, 635, 615 and 603 cm^{-1}.[2] They are denoted by α, β, γ and δ, respectively. The δ-band cannot be observed in the spectrum measured by the KBr disk method. The four bands were assigned to the C–Cl streching modes from comparison with the spectrum of polyvinyl bromide. β- and δ-bands were assigned to the crystalline bands.[2,3] In Fig. 1 are shown the infrared spectra of vinyl chloride-ethylene copolymers together with that of polyvinyl chloride, observed in the KBr region. The α-band observed in polyvinyl chloride shifts to somewhat lower frequency and its intensity decreases as the vinyl chloride content of the copolymer decreases. Intensity of β-band also decreases with decreasing vinyl chloride content and, completely disappears in the spectrum of the copolymers containing less than 60 mol% vinyl chloride. In

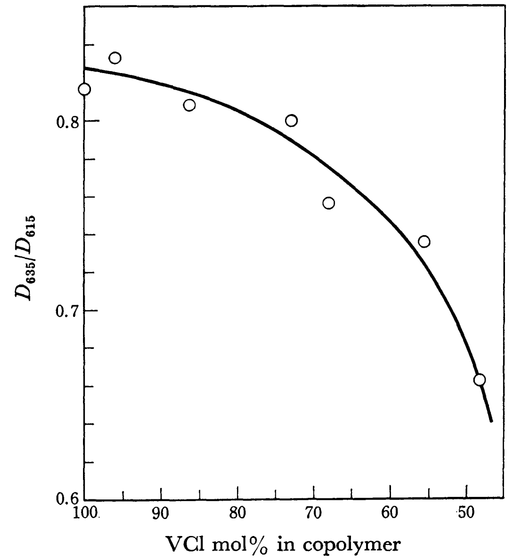

Fig. 2. D_{635}/D_{615} as a function of copolymer composition.

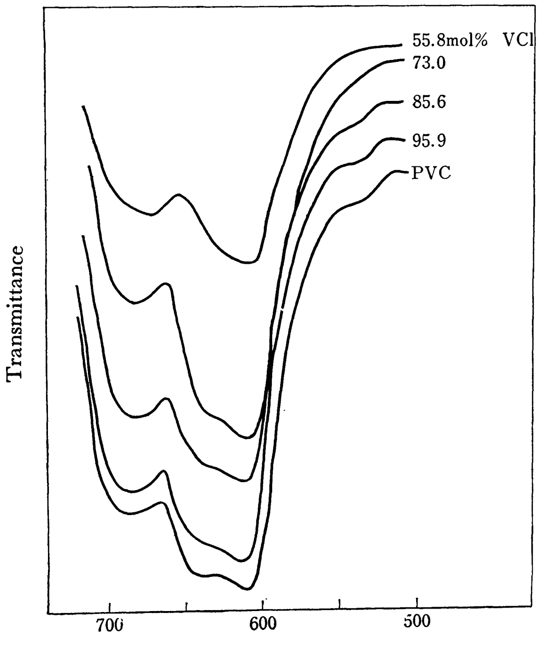

Fig. 1. Infrared spectra of polymers in KBr region.

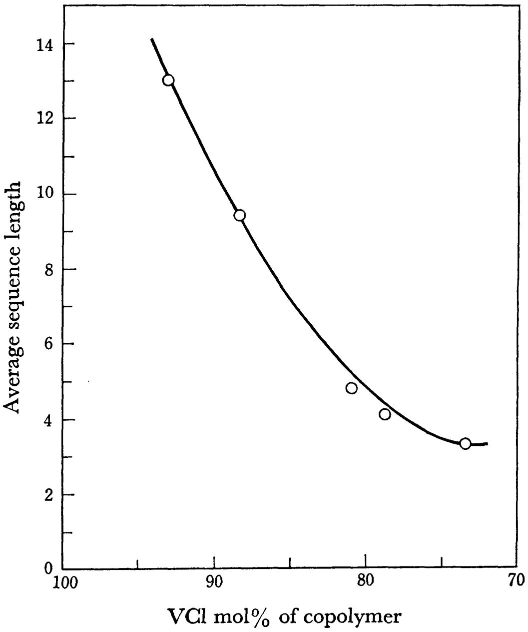

Fig. 3. Average sequence length of vinyl chloride unit of copolymer as a function of their composition.

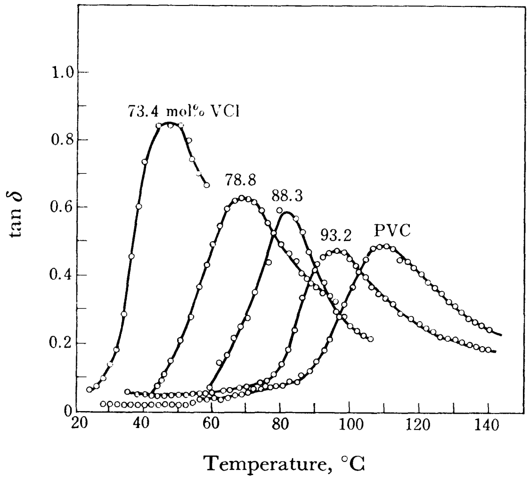

Fig. 4. Mechanical damping of polymers.

Fig. 2 the change in the ratio of optical densities of β- and γ-bands are shown. It may be seen that the crystallinity of the copolymer decreases with the decreasing vinyl chloride content. In Fig. 3 is shown the average sequence length of vinyl chloride units determined by NMR technique.[14] The decrease in the average sequence length of vinyl chloride units with the decreasing vinyl chloride content may be correlated with the decressing crystallinity observed in the infrared spectra.

The loss tangent curves of the copolymers are shown in Fig. 4. The temperature of the maximum loss tangent decreases linearly with the decreasing vinyl chloride content. This seems to correspond to the change in glass transition temperature according to the change in copolymer composition. Glass transition temperature of the copolymer will be discussed later on the basis of the temperature dependence of loss modulus E″. Decrease in the temperature of the maximum loss tangent with the decreasing vinyl chloride content seems to be analogous with what has been observed in plasticized polyvinyl chloride.[4] Increase in magnitude and decrease in half-height width of loss tangent with the increasing ethylene content, however, are in contrast with the increase in half-height width with the increasing amount of plasticizer in plasticized polyvinyl chloride.[4] The difference may reflect the mechanism of plasticizing functioning in each polymer. The plasticizer plasticizes polyvinyl chloride by decreasing the intermolecular interaction between chloride atoms located on each polymer chain, whereas the ethylene unit incorporated into the copolymer plasticizes the polymer by diminishing the number of chlorine atoms distributed along the polymer chain. We need to investigate the behavior of loss tangent in lower temperature regions, in order to see more closely the mechanism of plasticization. However, the viscoelastometer used in this study was not equipped with a low temperature bath, and no study was carried out.

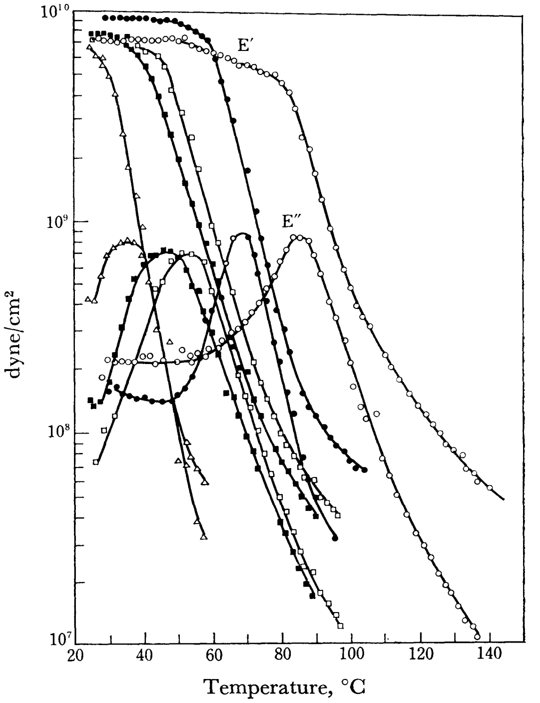

Fig. 5. Elastic and loss moduli of polymers.
○ PVC, ● 93.2 mol% VCl, □ 88.3 mol% VCl
■ 78.8 mol% VCl △ 73.4 mol% HCl

Dynamic elastic and loss moduli of the copolymers are shown in Fig. 5. The temperature where glass transition begins decreases with the increasing ethylene content of the copolymer and, the width of the transition region also decreases in the same manner. This is different from the behavior of plasticized polyvinyl chloride in which the width of transition region increases with the increasing amount of plasticizer.[4] The temperature dependence of elastic modulus of polyvinyl chloride has been studied, and the existence of the rubbery region continuing from the transition region has been elucidated in terms of microcrystallites occurring in vinyl chloride segments.[5,6] In our polymers, a part of such rubbery region is observed as a curvature of elastic modulus E′ continuing from the high temperature-end of the transition region. Such a curvature, however, disappears when the ethylene content exceeds about 10 mol%, where the average sequence length of vinyl chloride units is estimated as about 10. These results might indicate that more than about 10 monomer units of vinyl chloride are required appreciable crystallinity of the copolymer. Nambu[15] has concluded that as least 20 to 30 monomer units are necessary for the crystallization of vinyl chloride segments from the results

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[15] K. Nambu, *Kobunshi Kagaku*, **20,** 131 (1963).

of investigation on vinyl chloride-diethylfumarate copolymers, in which the bulky side group of the comonomer seems to render the vinyl chloride segment more difficult to crystallize than in vinyl chloride-ethylene copolymers.

It is established that the main dispersion of polyvinyl chloride, which is associated with glass transition, can be attributed to the motion of long segments of main chain. The peak temperature of loss modulus E″ varies monotonously according to the change in copolymer composition as shown in Fig. 6, and this relationship fits Gordon-Taylor's equation provided the coefficient k equals unity.[16]

$$c_2=(T_g-T_{g1})/\{k(T_{g2}-T_g)+(T_g-T_{g1})\}$$

where T_g, T_{g1} and T_{g2} are the glass transition temperatures of the copolymer, homopolymer 1 and homopolymer 2 respectively, c_2 the weight fraction of the comonomer 2 in the copolymer, and k is the ratio of the difference of expansion coefficients of the homopolymer 1 and 2 above and below the glass transition temperature. Glass transition temperatures thus determined are in good consistency with diatometrically observed ones.[17]

The copolymer containing more than about 80 mol% vinyl chloride shows appreciable birefringence under polarized light. The birefringence does not disappear on annealing the copolymer a little below melting point, hence cannot be due to internal strain of the sample. Birefringence was hardly observed in the copolymer containing less than 80 mol% vinyl chloride. The melting points of the copolymers are shown as a function of their composition in Fig. 6. Figure 7 shows a plot reciprocal melting point *versus* logarithmic compossition. This relationship can be expressed by Flory's equation[8]

$$1/T_m-1/T_m{}^0=-(R/\Delta H_u)\ln N$$

where T_m is the copolymer melting point, $T_m{}^0$ that of the crystallizable homopolymer, N the mole fraction of crystallizable units in the copolymer, and ΔH_u the heat of fusion per mole of repeating unit. The slope of the straight line gives about 3900 cal/mol as the heat of fusion, which is in good agreement with the reported value of 3040 cal/mol.[18]

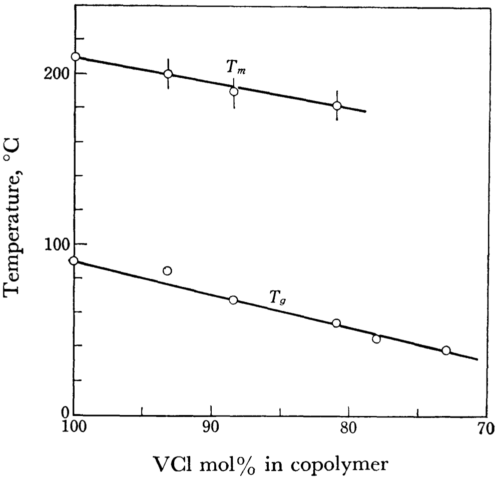

Fig. 6. Glass transition temperature and melting point of copolymers as a function of their composition.

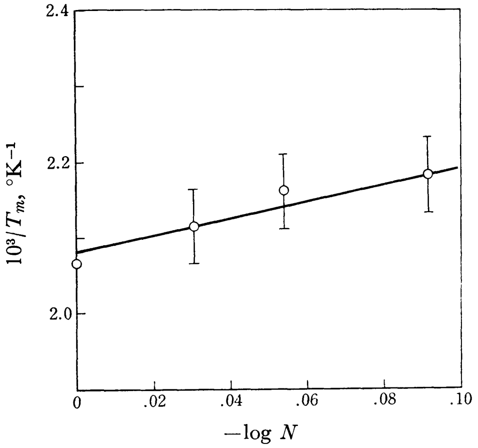

Fig. 7. Melting point depression of copolymer.

The results on the copolymer melting point, together with those on the infrared study and dynamic mechanical testing, prove that vinyl chloride-ethylene copolymers rich in vinyl chloride are more or less crystalline. From the linearity of Flory's plot the crystal structure of the original vinyl chloride segments does not seem to undergo change by copolymerization caused by the introduction of ethylene unit.

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