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DEPENDENCY OF "COMPRESSIBILITY OF MIXING UNIT" ON SHORT-RANGE INTERACTION IN VINYL ACETATE - METHYL ACRYLATE COPOLYMER SOLUTIONS

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The dilute solution properties of vinyl acetate - methyl acrylate random copolymers are investigated by the viscometric two-parameter theories in the statistical thermodynamics of homopolymer solution at zero frequency and by the measurement of adiabatic compressibility at 1 MHz. The short-range interaction parameter and "compressibility of mixing unit" for the copolymer are examined in relation with those of the parent homopolymers.

It is found that the "compressibility of mixing unit" of polymer depends on the short-range interaction independently of the long-range interaction.

"Compressibility of mixing unit", κ_2 , is defined by a following equation$^{1)}$

$$\kappa_2 = [\frac{1}{\kappa_1} \frac{\rho_2}{6^6 \rho_1} (8 - \frac{\bar{\kappa}_{20}}{\kappa_1} - \frac{\rho_2}{\rho_1})^6]^{-1} \tag{1}$$

where ρ, κ and $\bar{\kappa}_{20}$ are density, adiabatic compressibility and partial specific compressibility$^{2)}$ and subscripts 1 and 2 denote the quantities characteristic of solvent and solute (in this study, polymer), respectively. This equation is derived from Nomoto's relation$^{3)}$ of the molecular sound velocity$^{4)}$ in mixed liquids. Then, κ_2 is specified by the inter-segment potential energy in polymer solutions. The adiabatic compressibility is obtained by measurements of ultrasound velocity and density.

It has previously been reported that κ_2 is inherent to polymer species independently of solvent in homopolymer solutions.$^{5)}$ Present investigation is undertaken to see if the compressional response of polymer segments is related to the short-range interaction.

The viscometric two-parameter theories$^{6)}$ in the statistical thermodynamics are extended to vinyl acetate - methyl acrylate copolymer solutions. The short-range and the long-range interaction parameters, K_θ and B, are derived from the Stockmayer-Fixman equation

$$[\eta] / M^{0.5} = K_\theta + 0.51\Phi_0 B M^{0.5} \tag{2}$$

where $K_\theta = \Phi_0 (\bar{r}_0^2 / M)^{1.5}$;$\Phi_0 = 2.87 \times 10^{23}$;$\bar{r}_0^2$ is the unperturbed mean-square end to end distance; and M is the molecular weight of polymer. The short-range interaction parameters involve not only K_θ or $(\bar{r}_0^2 / M)^{0.5}$ but also the steric factor σ. The steric factor σ is a measure of hindrance to internal rotations about the skeletal links and is defined as

$$\sigma = (\bar{r}_0^2 / \bar{r}_{0f}^2)^{0.5} \qquad (3)$$

with $\bar{r}_{0f}^2$ being the mean-square end to end distance of a freely rotating chain.

Vinyl acetate and methyl acrylate are isomers. The vinyl acetate - methyl acrylate copolymer, which was prepared in acetone solution by using benzoyl peroxide as an initiator according to Sakurada-Yoshida's procedure,[7] was subsequently fractionated by use of acetone - water system at room temperature. Its sample code and monomer composition were F-VM and VAc-content = 60%, respectively. The determination of the monomer composition was done according to the procedure of Sakurada-Kawashima's electrochemical analysis.[8] The number-average molecular weights, $\bar{M}n$, of fractions of F-VM were obtained by the osmotic-pressure measurements which were made by using a Zimm-Mayerson osmometer. The osmotic-pressure data were analyzed according to the equation

$$(\pi / c)^{0.5} = (RT / \bar{M}n)^{0.5} [1 + (A_2\bar{M}n / 2)c] \qquad (4)$$

where π, c and A_2 are the osmotic pressure, the concentration of polymer solution and the second virial coefficient, respectively. Intrinsic viscosity measurements were made by using an Ubbelohde dilution viscometer in various solvents. Neither the kinetic-energy correction nor the non-Newtonian correction was found to be necessary.

The number-average molecular weights and intrinsic viscosities are given in Table 1. All measurements of intrinsic viscosity, osmotic pressure and adiabatic compressibility were made at 30 ± 0.01 °C.

Table 1. $\bar{M}n$ and $[\eta]$ of F-VM copolymer in various solvents at 30°C.

		$[\eta]$ (ml/g)				
Sample code	$\bar{M}n \times 10^{-4}$	acetone	ethyl acetate	benzene	toluene	DCE*
F-VM-1	58	126	127	169	76	204
F'-VM-2	52	117	107	124	68	-
F-VM-2	43	93	92	111	65	134
F-VM-3	31	82	80	86	52	119
F-VM-4	14	49	48	51	35	65

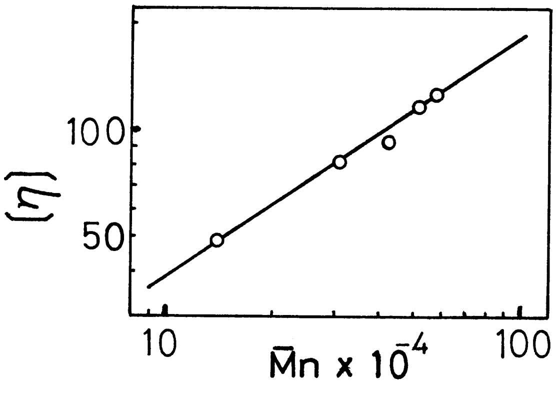
*DCE : 1,2 - dichloroethane

These results may be reproduced by

$$[\eta] \text{ (ml/g)} = 1.52 \times 10^{-2} \bar{M}n^{0.68} \text{ in acetone at 30°C.}$$

This Houwink-Mark-Sakurada relation between $[\eta]$ and $\bar{M}n$ in acetone is shown in Fig.1. As shown in Fig.2, plots of $[\eta]/\bar{M}n^{0.5}$ vs. $\bar{M}n^{0.5}$ in various solvents have the same intercepts on the ordinate, and therefore eq.(2) may be applied to VAc-MA copolymer solutions.

Fig.1. Intrinsic viscosity - molecular weight relationship for VAc-MA copolymers F-VM in acetone at 30°C.



An average value, $K_\theta = 9.1 \times 10^{-2}$, obtained in five solvents from the intercepts on the ordinate is listed in Table 2 with those of the parent homopolymers.

Table 2. K_θ- and σ- values and the composition of VAc-MA copolymer.

Sample code	MA - content (%)	$K_\theta \times 10^2$	σ
PMA[9]	100	9.5	2.08
F-VM	40	9.1	2.06
PVAc	0	8.8	2.04

On the other hand, the variation of κ_2 with the composition of VAc-MA copolymer is given in Table 3. The κ_2-values of the copolymers obtained in various solvents were constant within the range of measurement error.

Table 3. The variation of κ_2 with the composition of VAc-MA copolymer.

Sample code	MA - content (%)	$\kappa_2 \times 10^{12}$ (cm^2/dyne)
PMA	100	42
O-VM	60	44
F-VM	40	46
PVAc	0	49

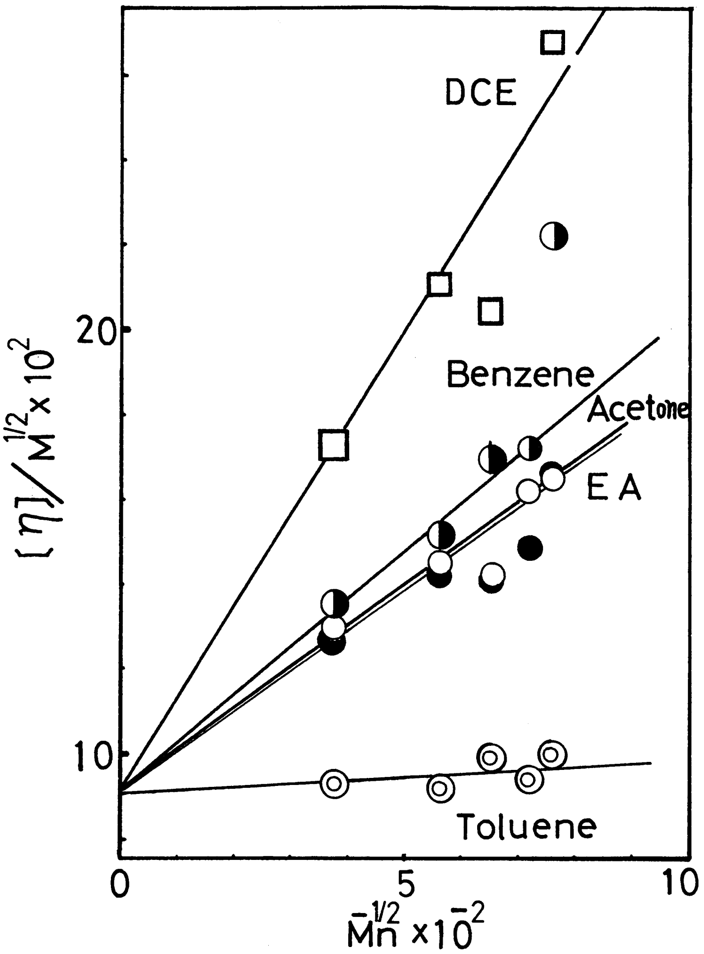


Fig. 2. Plots $[\eta]/\bar{M}_n^{0.5}$ vs. $\bar{M}_n^{0.5}$ for VAc-MA copolymer in 1,2-dichloroethane (□), benzene (◑), acetone (○), ethyl acetate (●), and toluene (◎) at 30°C.

From the results given in Tables 2 and 3, both κ_2 and σ vary linearly with the monomer composition of VAc-MA copolymer, and consequently, it is found that κ_2 has a linear relation to σ, as shown in Fig. 3.

These results suggest that the number of compressional segment pair has a linear relation to the fraction of methyl acrylate sequence.

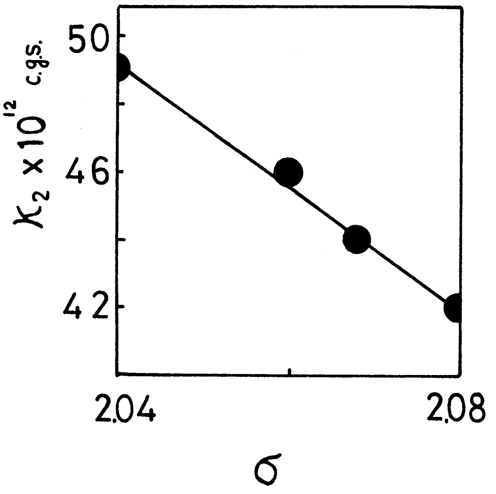


Fig.3. The variation of κ_2 with σ in VAc - MA copolymers and the parent homopolymers.

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