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DETERMINATION OF THE COMPOSITION AND MOLECULAR-WEIGHT DISTRIBUTION OF A POLY(VINYL CHLORIDE–VINYL ACETATE) CO-POLYMER BY GEL-PERMEATION CHROMATOGRAPHY AND INFRARED SPECTROSCOPY

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SUMMARY

A combination of infrared (IR) analysis with gel-permeation chromatography (GPC) has permitted the determination of both the molecular-weight distribution and the composition of a vinyl chloride–vinyl acetate copolymer as a function of molecular weight. A sample of the copolymer was fractionated by repeated injection into an analytical scale GPC. Copolymer films made from the fractions were then subjected to IR analysis for the determination of the vinyl acetate content. The latter was high at low molecular weights and decreased with increasing molecular weight. Q factors for the copolymer at each increment of elution volume have been calculated from the Mark–Houwink equations for polyvinyl chloride ,polyvinyl acetate and polystyrene and from the vinyl acetate content of the copolymer. Molecular-weight averages of the copolymer have been calculated using a polystyrene calibration curve and the Q factors for the copolymer which are a function of elution volume and vinyl acetate content. The values calculated by this method are in good agreement with those measured by other workers.

INTRODUCTION

It is evident that the physical properties of copolymers are dependent on their composition and molecular weight. Several studies have been made of the determination of the copolymer composition as a function of molecular weight. In one study[1], fractional precipitation followed by IR analysis and viscosity measurement of the fractions was employed for a poly(vinyl chloride–vinyl acetate) copolymer [P(VC–VAc)] while another study[2] reported the use of gel-permeation chromatography (GPC) in combination with UV and differential refractive index (RI) detectors for a styrene–butadiene copolymer. The relationship between copolymer composition and molecular weight for a poly(styrene–vinyl stearate) copolymer has been investigated by preparative GPC and IR analysis of the fractions[3], and by the rapid stop-and-go GPC–IR technique[4].

Fractionation depends upon solubility parameters which are a function of both

composition and size, so that complete separations are not obtained. GPC should be useful in this context since its primary function is to separate polymer molecules of different size, independently of polymer composition. Several problems arise when the GPC technique is applied to P(VC–VAc) for the measurement of composition as a function of molecular weight. Vinyl chloride and vinyl acetate (VAc) are insensitive to a UV detector at *ca.* 254 nm where the usual solvent tetrahydrofuran (THF) has minimal absorbance. No adequate solvent has been found for an IR detector used in series with a RI detector. However, the dependence of the composition of P(VC–VAc) on molecular weight has been determined approximately[1], and a knowledge of the relationship between copolymer compositions and molecular weight would be very important for the precise measurement of molecular-weight averages by GPC.

In a recent paper by Janča and Kolínský[5], molecular weights and compositions of P(VC–VAc) copolymer fractions obtained by GPC and fractional precipitation were determined. In the range of VAc contents between 10 and 13%, a single Mark–Houwink equation for P(VC–VAc) was obtained, which can be used as a universal calibration method for the P(VC–VAc) copolymer. However, it is doubtful whether this equation is still effective outside of the given composition range.

The measurement of the composition of P(VC–VAc) as a function of molecular weight is described in this paper. P(VC–VAc) was fractionated with analytical GPC and large fractions were collected by repeated injection. Polymer films were made from the fractions by evaporating off the solvent, and the composition of the films was determined by IR analysis. A new and simple method for the calculation of molecular-weight averages of the entire copolymer, using a combination of universal calibration and the Q-factor method, is discussed.

EXPERIMENTAL

Apparatus

A Nihonbunko (JASCO) Trirotar high-performance liquid chromatograph with a differential refractometer detector (Waters Assoc., Model R-401) was used for GPC measurements. Two Shodex A 80M high-performance GPC columns (50 cm × 8 mm I.D.) packed with a mixture of polystyrene gels of nominal porosity 10^3, 10^4, 10^5 and 10^6 Å were used. A Nihonbunko Model IR-G IR spectrometer was used for the determination of the P(VC–VAc) copolymer composition. Ultrasonic treatment was carried out in a 150-W 26-kHz (nominal) laboratory ultrasonic cleaner (Kokusai Electric Co.).

Samples

P(VC–VAc) copolymer provided by Mitsui Chemical Co. (Tokyo, Japan) was used. The product was synthesized by suspension polymerization and contained 11.6 wt. % VAc. Several different copolymers having different VAc contents between 3 and 14 wt. % were used to calibrate the IR analysis. Poly(vinyl chloride) (PVC) samples used for the examination of molecular aggregation were PVC[1] obtained by suspension polymerization. Polystyrene standards for a calibration curve were obtained from Pressure Chemical Co. (Pittsburgh, Pa., U.S.A.), and poly(vinyl acetate) (PVAc) and PVC for the measurement of Q factors were purchased from ArRo Labs. (Joliet, Ill., U.S.A.).

GPC measurements

The solvent was THF, containing 0.025% butylated hydroxytoluene (BHT) as an antioxidant, at a flow-rate of 1.5 ml/min, and the temperature was ambient. A six-port injection valve permitted sample injections of constant volume by using a 0.25-ml loop. Sample concentrations were 0.05% (w/v) for the construction of a calibration curve and 0.1% (w/v) for the calculation of molecular-weight averages. PVC and P(VC–VAc) were ultrasonically treated at room temperature for 20 min after dissolving in THF. All the sample solutions were filtered through a Millipore PTFE membrane filter (1 μm) before injection into the gel permeation chromatograph.

VAc content of P(VC–VAc)

P(VC–VAc) copolymer containing 11.6 wt. % VAc (8.7 mol %) was dissolved in THF to give a 0.5% (w/v) solution, and then ultrasonically treated for 20 min. The volume injected into the gel permeation chromatograph was 0.5 ml and six fractions were collected over the elution range of the copolymer. The volume taken for fraction 1 was 2.0 ml, for each of fraction 2–5 was 1.5 ml and for fraction 6 was 2.5 ml (see Fig. 2). This fractionation was repeated ten times and the identical fractions from the individual injections were combined. The chromatogram was corrected for concentration effects[6].

Polymer films from the combined fractions were obtained by dropping the solutions on to a PTFE sheet and evaporating the solvent under a 250-W IR lamp. BHT added in the THF was extracted from the films by immersing them in methanol overnight. For the construction of the IR calibration curve, copolymer films of known VAc content were prepared from 10 ml of 0.1% solutions. The VAc contents in copolymer films were determined from the ratio of the intensity of the carbonyl absorbance at 1744 cm^{-1} to that of the methylene absorbance at 1425 cm^{-1} (ref. 7). The preparation of polymer films and the measurement of their composition were done in triplicate.

Molecular aggregation in PVC

Solutions of 0.1% (w/v) PVC in THF were prepared and exposed to ultrasonic irradiation for 3–40 min. Also, other PVC solutions in cyclohexanone were heated without the ultrasonic treatment at 130° for 5–60 min, and then, after cooling, a 0.5-ml portion was injected into the gel permeation chromatograph.

RESULTS AND DISCUSSION

VAc content of P(VC–VAc) fractions

The compositions of fractions of P(VC–VAc) as determined by IR analysis are summarized in Table I. The calibration curve for the determination of the VAc contents was expressed as

$$\text{VAc wt. } \% = 6.4 \ (D_{1744}/D_{1420}) \tag{1}$$

where D_{1744} and D_{1425} are the absorbances at 1744 cm^{-1} and 1425 cm^{-1}. This equation is valid for the copolymer in the range of 2–15 wt. % VAc.

The average weight percent of VAc for the whole copolymer as calculated from the VAc content and the weight percent of each fraction was 11.57. This is in agreement with the analysis of the unfractionated sample. The weight percent of

TABLE I

VINYL ACETATE CONTENT OF P(VC–VAc) FRACTIONS

Wt.% of VAc in unfractionated sample, 11.6. mol.% of VAc in unfractionated sample, 8.7. wt.% of VAc in the whole copolymer, calculated from each fraction, 11.57.

Fraction No.	VAc (wt. %)			Mean	VAc (mol %), mean	Weight per cent fraction
	Run					
	1	2	3			
1	5.9	6.3	6.9	6.4	4.7	7.1
2	10.0	10.0	10.6	10.2	7.6	24.4
3	11.3	11.0	11.9	11.4	8.6	31.8
4	14.0	12.4	13.1	13.2	10.0	22.6
5	14.5	14.2	14.0	14.2	10.7	10.3
6	14.6	15.0	14.2	14.6	11.1	3.8

each fraction was calculated from the area of the chromatogram (see Fig. 1). A correction was made for the difference in response factors between PVC and PVAc. A tendency for the VAc content to increase from the first fraction to the last, i.e., with decreasing molecular weight of the copolymer, can be observed (Table I). Similar results have been observed by Takeuchi and Mori[1] and Janča and Kolínský[5].

Determination of Q factors for PVC and PVAc

The measurement of polymer molecular-weight averages by GPC requires the construction of a calibration curve. A series of relatively monodisperse polystyrenes is generally used for the calibration of GPC systems. However, the calibration curve thus obtained cannot be applied directly to polymers other than polystyrene. The universal calibration method must be used in these cases[8]. In practive, knowing the Mark–Houwink equations for polystyrene and the polymer in question, the standard polystyrene curve can be transformed for the polymer in question.

A less accurate, but simpler procedure for the calculation of molecular-weight averages is to use the Q factor. This factor is obtained by dividing the molecular weight of the monomer unit by its extended chain length calculated from bond lengths and angles. Molecular-weight averages of the given polymer are obtained by calculating extended chain-length averages using a polystyrene calibration curve of log (extended chain length) *versus* elution volume. These values are then multiplied by the Q factor of the polymer. This procedure would be accurate if both the ratios of the extended chain length and the actual chain length in solution for polystyrene and the given polymer are the same or vary in the same proportion. Since the calculated Q factors of some polymers are usually inaccurate, it is preferable to first determine the Q factors experimentally in the same solvent at the same temperature, using fractions of the given polymer[9]. Although the use of Q factors for GPC molecular-weight calculations is not an accurate approach, it is still valuable for the calculation of copolymer molecular-weight averages because copolymer composition varies somewhat as a function of the copolymer molecular weight.

The curve of log M *versus* elution volume for a polymer B can be obtained from that for a polymer A using[10]

$$\log M_B = \frac{1}{1 + a_B} \cdot \log \frac{K_A \Phi_B}{K_B \Phi_A} + \frac{1 + a_A}{1 + a_B} \cdot \log M_A \qquad (2)$$
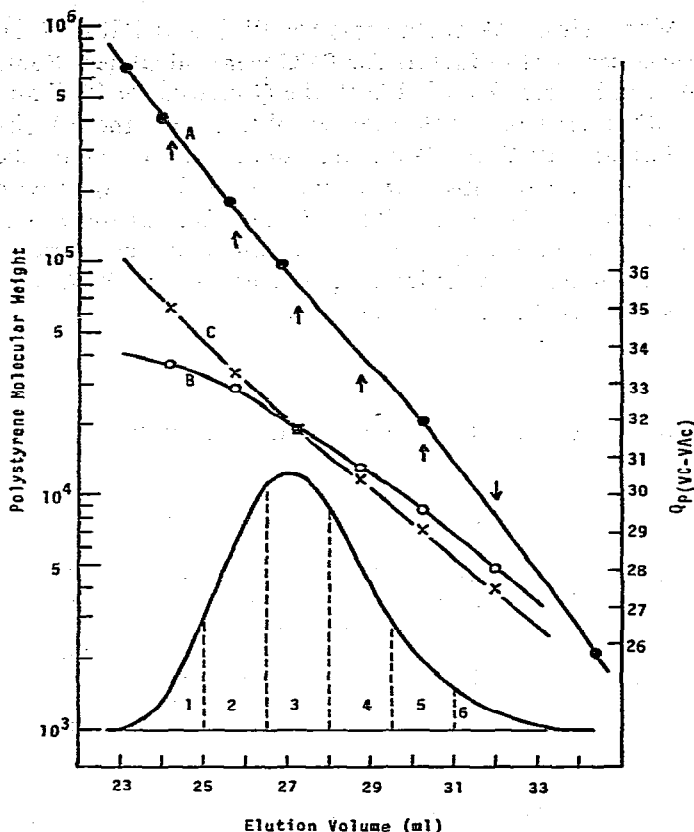
Fig. 1. Gel permeation chromatogram and Q factor for P(VC–VAc). A = polystyrene calibration curve; B = relation between Q factor and elution volume at different VAc contents; C = relation between Q factor and elution volume at constant VAc content.

where a and K refer to the Mark–Houwink coefficients for each polymer in the solvent used for GPC and at the experimental temperature; the Φ terms are obtained from

$$\Phi = \Phi_0(1 - 2.6\varepsilon + 2.86\varepsilon^2) \tag{3}$$

$$\varepsilon = (2a - 1)/3 \tag{4}$$

Φ_0 is a constant which cancels out. A refers to the standard polystyrene and B to the polymer in question. Taking polymer B as PVC or PVAc in eqn. 2, the molecular weights of PVC or PVAc molecules (M_{PVC}, M_{PVAc}) eluted at the same volume as a polystyrene molecule having molecular weight M_{PSt} can be calculated. Assuming that the Q factor of polystyrene is constant over the whole molecular-weight range and its value is 41.3, the Q factors of PVC and PVAc can be obtained from

$$Q_{PVC} = \frac{M_{PVC} \times 41.3}{M_{PSt}} \tag{5}$$

$$Q_{PVAc} = \frac{M_{PVAc} \times 41.3}{M_{PSt}} \tag{6}$$

Using several pairs of Mark–Houwink coefficients for PVC and PSt in THF at 25° from the literature, various series of Q factors for PVC were calculated. Some results are listed in Table II. As can be seen from Table II, the Q factors for PVC and PVAc increase or decrease with increasing molecular weight, unless the Mark–Houwink exponents of both PSt and PVC or PVAc are equal. According to the specifications for PVC provided by ArRo Labs., the Q factors for PVC vary with molecular weight and are 25.4 at molecular weight 2.5×10^4 and 28.0 at molecular weight 1.3×10^5, assuming the Q factors for PSt to be constant. (This assumption does not affect the values of calculated molecular-weight averages for PVC and PVAc, providing polystyrene is used as the primary standard.)

TABLE II

SEVERAL SERIES OF Q FACTORS FOR PVC (SERIES I–VI) AND PVAc (SERIES VII–IX)

Molecular weight of PSt (M_A)	Series								
	I	II	III	IV	V	VI	VII	VIII	IX
2100	27.3	27.7	25.2	29.7	27.1	23.9	36.5	41.1	42.4
20,400	25.8	29.1	25.2	27.5	25.4	27.0	41.6	50.8	48.3
97,200	24.8	30.0	25.2	26.1	24.2	29.4	45.6	58.8	52.8
180,000	24.4	30.4	25.2	25.5	23.8	30.5	47.3	62.3	54.7
411,000	23.9	30.9	25.2	24.8	23.2	31.9	49.6	67.3	57.3
670,000	23.6	31.2	25.2	24.4	22.8	32.7	51.0	70.4	58.9
1,800,000	23.0	31.8	25.2	23.6	22.2	34.5	54.0	77.3	62.4
PSt									
$K \times 10^4$	1.17	1.91	0.682	1.60	1.17	0.86	1.17	0.86	1.91
a	0.725	0.682	0.766	0.706	0.717	0.74	0.725	0.74	0.682
PVC (or PVAc)									
$K \times 10^4$	1.60	5.01	1.63	1.63	1.50	5.01	3.5	4.28	4.28
a	0.75	0.649	0.766	0.766	0.77	0.649	0.63	0.591	0.591
Ref.	11	12	13, 14	14	15	12, 16	11	16, 17	12, 17

Series II and VI in Table II were assumed to provide effective Q factors for PVC. Molecular-weight averages for standard PVC and PVAc were calculated using eqn. 2 and Mark–Houwink coefficients from series II, VI, VIII and IX in Table II. The results are shown in Table III. The Q factors in series VI and VIII are believed to be better than the other values, when compared to these values. Several other combinations of Mark–Houwink coefficients for PSt and PVC from ref. 18 were evaluated, but the results were not satisfactory. Substituting the coefficients from series VI and VIII into eqn. 2 yields the following equations from which the molecular weights of PVC and PVAc corresponding to that of PSt appearing at the same elution volume may be calculated

$$\log M_{PVC} = -0.4224 + 1.0552 \log M_{PSt} \tag{7}$$

$$\log M_{PVAc} = -0.3137 + 1.0937 \log M_{PSt} \tag{8}$$

TABLE III

MOLECULAR-WEIGHT AVERAGES FOR STANDARD PVC AND PVAc OBTAINED BY GPC

Standard values were obtained from ArRo Labs. $\bar{M}_w$ was obtained from light-scattering data using THF as solvent at 25°. $\bar{M}_n$ was obtained using membrane osmometry, with THF as solvent at 25°. Calculated Q factors are: 24.8 for PVC and 34.1 for PVAc.

Polymer	Standard value	Using calculated Q factor	Using series II and IX	Using series VI and VIII
PVC	$\bar{M}_w \times 10^{-4} = 13.2$	10.6	13.0 ± 0.2	12.8 ± 0.2
	$\bar{M}_n \times 10^{-4} = 5.40$	5.0	6.0 ± 0.2	5.7 ± 0.2
	$\bar{M}_w/\bar{M}_n = 2.44$	2.12	2.2	2.2
PVAc	$\bar{M}_w \times 10^{-4} = 33.1$	15.7	25.3 ± 0.2	29.5 ± 0.2
	$\bar{M}_n \times 10^{-4} = 8.30$	5.6	8.2 ± 0.4	8.8 ± 0.4
	$\bar{M}_w/\bar{M}_n = 3.99$	2.80	3.1	3.4

Q factors corresponding to these molecular weights are

$$Q_{PVC} = 15.62 \, M_{Pst}^{0.0552} \tag{9}$$

$$Q_{PVAc} = 20.06 \, M_{Pst}^{0.0937} \tag{10}$$

Calculation of molecular-weight averages of P(VC–VAc)

Systematic studies of the molecular-weight distribution of P(VC–VAc) by GPC and viscosity measurement were reported[5,19] and Mark–Houwink equations were proposed. GPC was used to fractionate P(VC–VAc). Number-average[19] and weight-average[5] molecular weights of fractions were determined in conjunction with their intrinsic viscosity. However, Chen and Blanchard[19] did not mention the variation of composition of the fractions and Janča and Kolínský[5] obtained an equation valid only for a limited VAc range. It is not practical to calculate molecular-weight averages for P(VC–VAc) copolymer using a universal calibration curve obtained with a single Mark–Houwink equation[5]. One must take into account not only the overall average composition but also heterogeneities in composition of the copolymer.

I propose an improved method for the calculation of molecular-weight averages of copolymers having heterogeneities in composition. This method can be applied to any copolymers if Mark–Houwink equations for the homopolymer components of the copolymer and for a standard polymer such as polystyrene in the solvent used in GPC and at the experimental temperature are known. Construction of a calibration curve for each homopolymer is not necessary. It is assumed that the chain length of P(VC–VAc) in solution is the sum of the VC and VAc parts of the copolymer. The chain length of both parts must be governed by the overall chain length of the copolymer. The Q factor for P(VC–VAc) at the given elution volume is then calculated using

$$Q_{P(VC-VAc)} = m_{PVC} \, Q_{PVC} + m_{PVAc} \, Q_{PVAc} \tag{11}$$

where m_{PVC} and m_{PVAc} are the molar fractions of VC and VAc in P(VC–VAc) and Q_{PVC} and Q_{PVAc} are the Q factors for PVC and PVAc at the same elution volume as that of P(VC–VAc) and are obtained from eqns. 9 and 10. The mol. % of VC in copolymer is the difference.

The Q factors of P(VC–VAc) are calculated as follows. (a) The chromatogram of P(VC–VAc) and a polystyrene calibration curve of molecular weight *versus* elution volume are plotted as in Fig. 1. The areas defined by the dashed lines represent each fraction. (b) The polystyrene molecular weight of each fraction is determined from the average elution volume of the fraction using the polystyrene calibration curve (Fig. 1, arrows). (c) Substituting these polystyrene molecular weights into eqns. 9 and 10 yields Q factors for PVC and PVAc at the average elution volume of each fraction of P(VC–VAc). (d) These Q factors and molar fractions in Table I are substituted into eqn. 11 and Q factors for P(VC–VAc) at each average elution volume are obtained. (e) Plotting the Q factors for P(VC–VAc) and the average elution volume and connecting each point yields a calibration curve giving the Q factor of P(VC–VAc) at the elution volumes. (f) The molecular weight of P(VC–VAc) at any elution volume can be obtained by multiplying the polystyrene extended chain length at the elution volume by $Q_{P(VC-VAc)}$. Molecular-weight averages for P(VC–VAc) are calculated by the usual procedure.

The calculated values of the molecular-weight average for P(VC–VAc) are shown in Table IV. For comparison, three other molecular-weight averages are listed. These were calculated from the molecular weights of polystyrene, from the Q factor ($= 25.6$) obtained from the molecular weight, bond length and angle of the monomer unit and from Q factors obtained assuming a constant VAc content.

TABLE IV

MOLECULAR-WEIGHT AVERAGES FOR P(VC–VAc) CALCULATED BY USING SEVERAL METHODS

Method	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
Method as in the text	7.87	3.66	2.2
Response correction	7.78	3.61	2.2
At constant VAc content	8.03	3.64	2.2
At $Q = 25.6$	6.31	3.10	2.0
As polystyrene	10.20	5.00	2.0
Using literature value*	8.40	4.03	2.1

* $[\eta] = 6.72 \times 10^{-4} M_w^{0.611}$ for P(VC–VAc) (ref. 5); $[\eta] = 0.86 \times 10^{-4} M_w^{0.74}$ for PSt (ref. 16).

When a differential refractometer is used as a detector, its response is proportional to the differential refractive index of the solute and the solvent and to the concentration of the solute. The specific refractive index increment ($\partial n/\partial c$) of PVC ($= 0.115$) is twice that of PVAc ($= 0.058$) (ref. 18). The system was calibrated by injecting various amounts of PVC and PVAc. The areas under the chromatograms were determined by graphical integration and used to calculate the response-factor ratio. The results were close to the above values. The chromatogram of P(VC–VAc) must be corrected by multiplying the response of the VAc unit by 2 using eqn. 12:

$$(H_{corr.})_i = (H_{uncorr.})_i \times (1 + W_{VAc,i}) \qquad (12)$$

where $(H_{corr.})_i$ is the corrected height of each increment of the elution volume in question, $(H_{uncorr.})_i$ is the uncorrected height of each increment of the elution volume and $W_{VAc,i}$ is the weight fraction of VAc content at the elution volume. Molecular-weight averages calculated from the corrected chromatogram are shown in Table IV.

The weight-average molecular weight of P(VC–VAc) determined using light scattering was 7.7×10^4 and is in good agreement with the experimental values in Table IV. The molecular-weight averages calculated assuming a constant VAc content and that calculated using the Mark–Houwink equation obtained by Janča and Kolínský[5] are slightly higher. Large differences were not observed between these values since the VAc content is not high. Fig. 2 shows a normalized molecular-weight distribution of P(VC–VAc) and the VAc composition as a function of molecular weight.
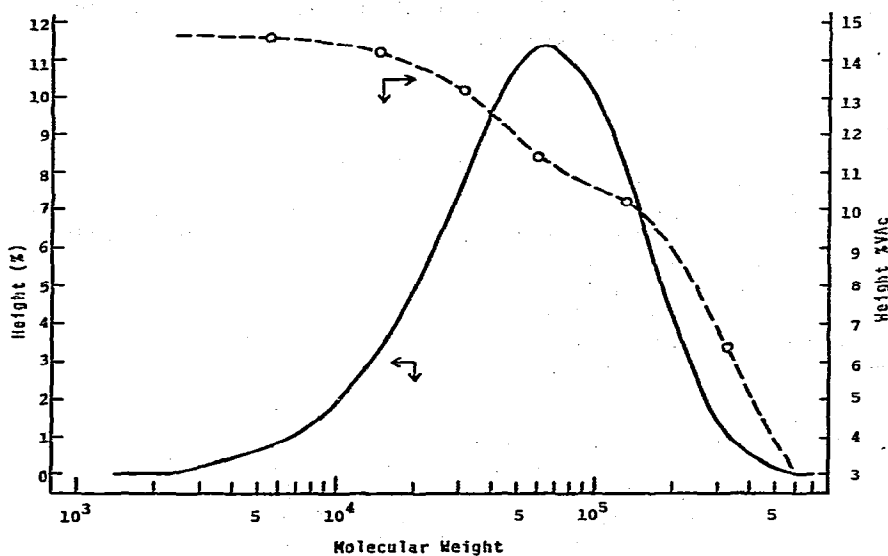

Fig. 2. The composition (– – –) and molecular-weight distribution (———) of P(VC–VAc).

The problem of molecular aggregation in PVC

The presence of molecular aggregates in PVC complicates the molecular-weight determinations. Several attempts have been made to eliminate the aggregates[12,20,21]. The dispersal of aggregates by ultrasonic treatment of a PVC solution in THF for periods as brief as 15 min has been reported[12]. Simultaneous degradation of the PVC molecules appeared to be prevented by the addition of a small amount of a non-ionic surfactant to the solutions. Heating PVC at 90° in THF for 2 h was also found to dissociate the aggregates[21].

In the present study the effects of ultrasonic and heat treatments were investigated. Molecular-weight averages were changed appreciably by these treatments (decreases by ca. 12–15%), but almost identical values were obtained after ultrasonic treatment for 5 min and heat treatment for 10 min. These experiments support the conclusion that dispersion of PVC molecules by these treatments is effective, and

that molecular degradation is essentially absent during these treatments. Similar results have been obtained when a non-ionic surfactant was added to the PVC solution. This implies that the non-ionic surfactant may not be necessary. Heating at a temperature of 95° was not effective in dispersing the aggregates even after heating for 60 min. Boiling of THF solutions had little dispersive effect.

After ultrasonic irradiation the high-molecular-weight tail disappeared, the entire chromatogram moved toward lower molecular weights and the height of the peak maximum increased. The low-molecular-weight portion was unchanged by ultrasonic treatment. Membrane filters of 1-μm pore diameter were blocked by an ultrasonically untreated THF solution of P(VC–VAc).

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