Molecular characterization of sodium poly(acrylate) by an aqueous g.p.c./LS method

T. Kato, T. Tokuya*, T. Nozaki and A. Takahashi

Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan
(Received 24 March 1983; revised 9 May 1983)

The molecular characterization of a commercial sample of sodium poly(acrylate) (NaPA) has been carried out by a g.p.c./LS method in 0.3 N NaCl at 25°C. The sample is fractionated into eight fractions. The agreements between the weight-average molecular weights of the NaPA fractions determined by light scattering and those measured directly by the g.p.c./LS method are excellent. Universal calibration is established for both the standard poly(ethylene oxide) and the NaPA fractions. The degree of branching for the fractions with high molecular weights are estimated using the experimental results obtained by the g.p.c./LS method.

Keywords Sodium poly(acrylate); g.p.c./LS method; universal calibration; degree of branching

INTRODUCTION

The aqueous gel permeation chromatography (g.p.c.) has been applied extensively to the molecular characterizations of polyelectrolytes for the determination of molecular weight and molecular weight distribution[1-10]. As the chromatographic mechanism for elution from a g.p.c. column is complicated due to the electrostatic interactions, the size exclusion mechanism is not always dominant in the chromatographic separation for polyelectrolytes[8]. The specific properties of polyelectrolytes in g.p.c. measurements have been classified into four categories[6,9]: (1) The molecular sizes change markedly with the function of the molecular weight, the number of charged groups on a polymer chain, and the added-salt concentration in solution[11-13]. (2) Simple electrolytes as well as polyelectrolytes are excluded electrostatically from stationary gel matrices in water as eluent and also in an eluent of low salt concentrations[3,4,14,15]. This electrostatic exclusion is very effective in high-charged gel matrices[16]. (3) On flowing along the column, Donnan salt exclusion from the domain surrounding the polyelectrolyte chain in solution causes perturbation of the polyelectrolyte distribution between the mobile phase and the stationary gel phase[4,17]. The perturbation is responsible for the band-broadening effects. (4) The adsorption effect of polyelectrolytes on the gel matrices disturbs the size exclusion mechanism[9].

These effects depend initially on the type of eluent used. Therefore, the purpose of this study is to establish the optimum eluting conditions for g.p.c. measurements with high reliability. Normal g.p.c. separation of polyelectrolyte is examined using the universal calibration relation. After establishing the universal calibration, molecular characterization of a commercial sample of sodium poly(acrylate) is carried out by a g.p.c./LS method, a light-scattering detector combined with g.p.c.[18-21]. Then, the merit of the application of the g.p.c./LS method to polyelectrolytes is considered. The sample fractions with high molecular weights are branched polymers, resulting in high conversion to polymerization reactions of the commercial products. The degree of branching is estimated from the experimental results obtained by the g.p.c./LS method[21-23].

EXPERIMENTAL

Materials

The original sample of sodium poly(acrylate) (NaPA) used in this study, Aron A-20L, was purchased from Toa Gosei MFG. Co. The sample was purified three times by precipitation from an aqueous solution with methanol and was dissolved in 0.4 N NaOH aqueous solution at a concentration of 1 wt%. Using this NaPA solution, fractional precipitation was carried out at 25°C by stepwise addition of methanol–water mixtures in the presence of NaOH, as described previously[11,24]. Eight fractions were obtained and after desalting by precipitation, each fraction was freeze-dried and dried overnight *in vacuo* at room temperature.

A series of poly(ethylene oxide) (PEO) standards used were to obtain a calibration curve and to check the range of the retention volume for chromatographic separation. The molecular characteristics of PEO have been reported elsewhere[25]. Standard dextran (Pharmacia Fine Chemicals) was used as the reference material for determination of the g.p.c./LS instrumental constant. Water

* Present address: Shin-Etsu Chemical Co., Research and Development Laboratory, Nakakubiki-gun, Niigata 942, Japan

0032-3861/84/020218-07$03.00

was doubly distilled on an all-Pyrex distillation apparatus. All chemicals were of reagent grade.

Light scattering measurements

The weight-average molecular weights (M_w) of the NaPA fractions were measured by a Union Giken LS601A automatic light-scattering analyser. The 488 nm line of the vertically polarized argon-ion laser (NEC GLG 3000) was used as the light source. The scattered-light intensities were measured in an angular range from 10° to 150° at 10° intervals. Each NaPA fraction was dissolved in 0.3 and 1.0 N NaCl aqueous solutions as the solvent. The NaPA solutions for the measurements of light scattering and specific refractive index increment were dialized against the solvent for several days[12]. The optical purifications of both solution and solvent were carried out by filtration through a Millipore filter (0.45 nm pore size) directly into a light-scattering glass cell. The glass cell was placed in the centre of the thermostated toluene bath of the analyser. The bath was controlled to 25 ± 0.1°C. The specific refractive index increment $(dn/dc)_\mu$ was measured at 25°C by a C. N. Wood RF-600 differential refractometer using the 488 nm line of the argon-ion laser, where the subscript μ denotes that the chemical potential of the added-salt is constant both in the NaPA solution and in the solvent.

Viscosity

Intrinsic viscosities $[\eta]$ were measured in the different NaCl concentrations at 25°C on a capillary viscometer of the Ubbelohde suspended-level type. The viscosity measurements were also carried out in 1.5 N NaBr aqueous solution at 15°C, for the theta state for NaPA[11,13]. The kinetic energy correction and the shear-rate dependence were negligible.

Gel permeation chromatography

A Toyo Soda GPC instrument, specially designed for aqueous solution, was equipped with a TSK RI-8 differential refractometer (DRI) and a TSK HLC-CP8 model III microcomputer as a data processer. A column system for g.p.c. measurements in different NaCl concentrations comprised one TSK-GEL G3000PW column (7.5 mm i.d. × 600 mm) and two TSK-GEL G5500PW columns. The elution rate was 1.0 ml min^{-1} and the concentration of the sample solution injected was 0.5 mg ml^{-1}. The injection loop volume was 0.5 ml. The calibration curve obtained by the series of the PEO standards was almost a straight line for molecular weights of 2×10^3–1.3×10^6 g mol^{-1}[26]. The apparent molecular weights (M_{app}) of the NaPA fractions were estimated using the calibration curve of PEO. The exclusion limit of the column system was assumed to be $M_w \geqslant 3 \times 10^6$ g mol^{-1} for PEO.

For the g.p.c./light-scattering system (g.p.c./LS method), a TSK-LS-8 low-angle laser light-scattering pohotometer (LALLS) was added to the g.p.c. instrument as a molecular weight monitor. The vertically polarized 633 nm line of a He–Ne gas laser was used as the light source for LALLS. One TSK-GEL Toyoperl HW75SF column (7.5 mm i.d. × 300 mm) was added to the column system to improve the chromatographic resolution in the higher molecular weight range, $M_w \rangle 3 \times 10^6$ g mol^{-1}, for PEO. A filtrating apparatus with a Teflon Millipore filter (1.0 nm pore size) was attached to the column system just before LALLS. The eluent for the g.p.c./LS system was 0.3 N NaCl aqueous solution and the elution rate was 0.7 ml min^{-1}. The specific refractive index increment at 633 nm was also measured using the He–Ne gas laser.

As the polymer solution eluted from g.p.c. column is measured continuously by both DRI and LALLS, the recorder response of DRI ($H_{i,RI}$) and that of LALLS ($H_{i,LS}$) at a retention volume $V_{r,i}$ are given by:

$$H_{i,RI} = k_1 c_i \tag{1}$$

$$H_{i,LS} = k_2 K c_i M_i \tag{2}$$

where c_i is the polymer concentration eluted at $V_{r,i}$, M_i is the molecular weight of the polymer eluted, k_1 is the constant related to the specific refractive index increment of polymer samples, k_2 is the instrumental constant of LALLS, and K is the optical constant for the light-scattering system. The ratio of the recorder responses $(H_{i,LS}/H_{i,RI})$ is described by the following equations,

$$\frac{H_{i,LS}}{H_{i,RI}} = (k_2/k_1)KM_i = \psi M_i \tag{3}$$

$$\frac{\sum H_{i,LS}}{\sum H_{i,RI}} = \psi \frac{\sum c_i M_i}{\sum c_i} = \psi M_w \tag{4}$$

If the constant ψ is obtained from the experimental data of the standard samples, the weight-average molecular weights of the NaPA fractions may be estimated from the peak area ratio $(\sum H_{i,LS}/\sum H_{i,RI})$ of the g.p.c. chromatograms.

RESULTS AND DISCUSSION

Molecular characteristics for NaPA fractions

The values of $(dn/dc)_\mu$ for NaPA in 0.3 and 1.0 N NaCl aqueous solutions at 25°C were determined as 0.159 and 0.152 ml g^{-1} at 488 nm, respectively. The weight-average molecular weights determined by light-scattering measurements in 0.3 and 1.0 N NaCl solutions at 25°C are summarized in *Table 1*. The average values $(M_w)_{LS}$ listed in the fourth column are used as the molecular weights of samples in further discussions. Intrinsic viscosity data $[\eta]_0$ measured in 1.5 N NaBr aqueous solution at 15°C are shown. The data of NaPA–K with the narrow molecular weight distribution were kindly offered by Kitano *et al.*[27] *Figure 1* shows the double logarithmic plots of $[\eta]$ against $(M_w)_{LS}$ for NaPA in the different NaCl concentrations at 25°C and in 1.5 N NaBr solution at 15°C. The plots appear to level off towards molecular weights $(M_w)_{LS} \geqslant 6 \times 10^5$ g mol^{-1} for NaPA F5, except for the data of NaPA-K. The values of K_v as well as ν in the Mark-Houwink–Sakurada (MHS) viscosity equation, $[\eta] = K_v M^\nu$, calculated from the straight lines in *Figure 1* are summarized in *Table 2*. It is noteworthy that K_v obtained in 1.5 N NaBr solution at 15°C is slightly higher than the value reported previously[11] though the value of ν is 0.5. The discrepancy of the K_v values is attributed to the reliabilities of the molecular weights determined by the light-scattering technique. It is recommended that the new K_v values determined in this study are used in the MHS viscosity equation for NaPA at the theta state:

$$[\eta_0] = 14.5 \times 10^{-4} M^{0.5} \tag{5}$$

Table 1 Molecular characteristics for NaPA fractions

Sample	$M_w \times 10^{-6}$ (0.3N NaCl)	$M_w \times 10^{-6}$ (1.0N NaCl)	$(M_w)_{LS} \times 10^{-6}$	$(M_w)_{g.p.c./LS} \times 10^{-6}$	$[\eta]_0$	$\left(\frac{M_w}{M_n}\right)_{UCC}$
NaPA F1	3.27	3.37	3.32	–	2.02	2.51
NaPA F2	1.92	1.95	1.93	–	1.76	2.00
NaPA F3	1.30	1.10	1.20	1.19	1.40	1.69
NaPA F4	0.700	–	0.700	–	1.21	1.60
NaPA F5	0.619	0.580	0.600	0.56	1.11	1.59
NaPA F6	0.386	0.340	0.363	0.368	0.88	1.51
NaPA F7	0.210	0.203	0.207	0.195	0.71	1.34
NaPA F8	0.095	0.092	0.094	0.105	0.45	1.42
NaPA–K[a]	–	–	1.50	–	1.78	(1.1)

[a] The sample having a narrow molecular weight distribution reported by Kitano *et al.*[27]

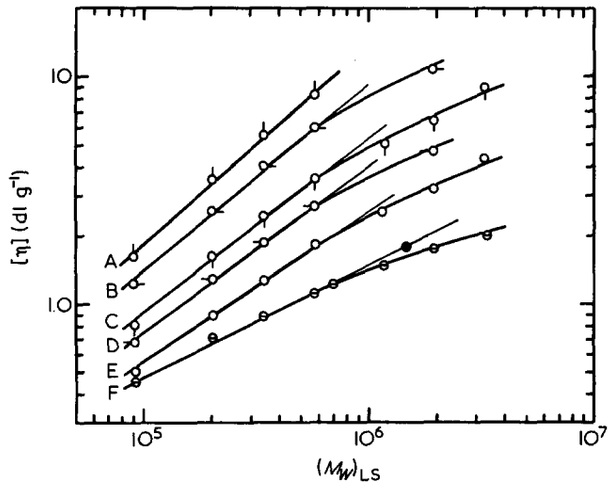

Figure 1 Double logarithmic plots of the intrinsic viscosity $[\eta]$ against $(M_w)_{LS}$ for the NaPA fractions in the different NaCl concentrations at 25°C and in 1.5 N NaBr solution at 15°C. Salt conc.: A, 0.05; B, 0.1; C, 0.3; D, 0.5; E, 1.0 N NaCl; and F, 1.5 N NaBr. ●, NaPA–K in 1.5 N NaBr

Table 2 Calculated values of K_V and ν in the different salt concentrations

C_s (mol l^{-1})	$K_V \times 10^4$	ν
	in NaCl aqueous solutions at 25°C	
0.05	0.735	0.88
0.1	1.46	0.80
0.3	1.69	0.75
0.5	1.86	0.72
1.0	4.15	0.63
	in 1.5 N NaBr solution at 15°C	
1.5	14.5	0.5

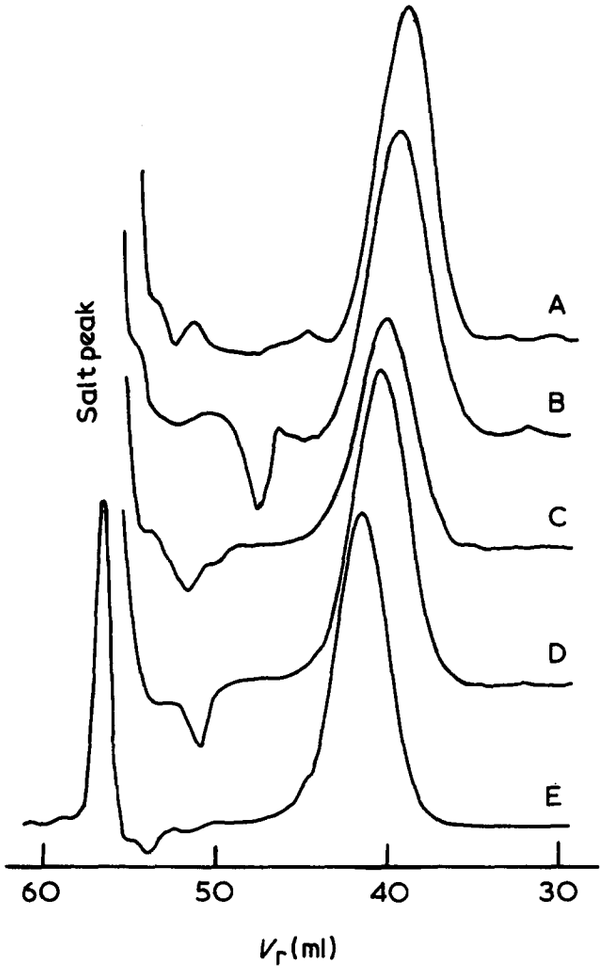

Figure 2 Chromatograms for NaPA F7 measured in the different NaCl concentrations. A, 0.05; B, 0.1; C, 0.3; D, 0.5; E, 1.0 N NaCl

Added-salt concentration dependence of chromatographic profile

Figure 2 shows the chromatograms of NaPA F7 measured by DRI in 0.05, 0.1, 0.3, 0.5, and 1.0 N NaCl aqueous solutions. As the molecular size of NaPA F7 in solution depends on the added-salt concentrations, the peak retention volume decreases with increasing salt concentration. Moreover, even though the electrostatic exclusion from gel phase is negligible in the low salt concentrations of 0.05 N NaCl, the tail of the chromatographic peak becomes uncertain owing to the perturbation of polyelectrolyte distribution between the mobile phase and the stationary gel phase, as a result of Donnan salt exclusion. Thus, the g.p.c. results measured in these lower salt concentrations appear to be ambiguous. *Table 3* shows examples of the salt concentration dependences on the apparent molecular weight $(M_w)_{app}$ and the molecular weight distribution index $(M_w/M_n)_{app}$. $(M_w)_{app}$ estimated using the calibration curve of the PEO decrease with increasing salt concentration of the eluent. The calculated $(M_w/M_n)_{app}$ values appear to be

constant in salt concentrations >0.3 N NaCl. It is concluded that the g.p.c. measurement for NaPA should be carried out in a high salt concentration e.g. 0.3 N NaCl, to determine the reliable value for the molecular weight distribution index.

Donnan salt exclusion

To improve the reliability of the g.p.c. measurements for polyelectrolytes, the perturbation of the polyelectrolyte distribution due to a Donnan salt exclusion should be reduced so that its effect is negligible in chromatograms. Thus, the chemical potential of the salt in the polymer solution injected should match that of the eluent. According to Lindstroem *et al.*[17] the quantity of a Donnan salt exclusion is related to the salt peak appearing in the total permeation limit of the g.p.c. column. *Figure 3* shows an example of the change in the salt peak when the NaPA solutions in the different salt concentrations were injected into the eluent of 0.303 N NaCl. The peak area (filled circle) and the peak height (open circle) of the salt peaks are plotted against the salt concentrations of the sample solutions in *Figure 4*. By interpolation, it is established experimentally that the salt concentration of 0.296 N NaCl may be the optimum concentration to eliminate the salt peak. It is noteworthy that, in this study, the gel cannot be considered as a semipermeable membrane for NaPA because of the finite polymer distribution of the gel.[17] However, this interpolation method is very useful for g.p.c. measurements for polyelectrolytes. It will always be necessary in practice to match the salt concentration to the polymer concentration injected into the g.p.c. column.

Table 3 Examples of g.p.c. results depending on the salt concentration of the eluent

	Salt concentration of eluent (NaCl)				
	0.05N	0.10N	0.30N	0.5N	1.0N
For NaPA F5					
$(M_w)_{app}/10^3$	105	108	85.0	71.0	63.0
$(M_w/M_n)_{app}$	–	1.65	1.60	1.59	1.59
For NaPA F7					
$(M_w)_{app}/10^3$	35.0	31.5	27.3	23.0	20.0
$(M_w/M_n)_{app}$	–	1.40	1.35	1.34	1.34

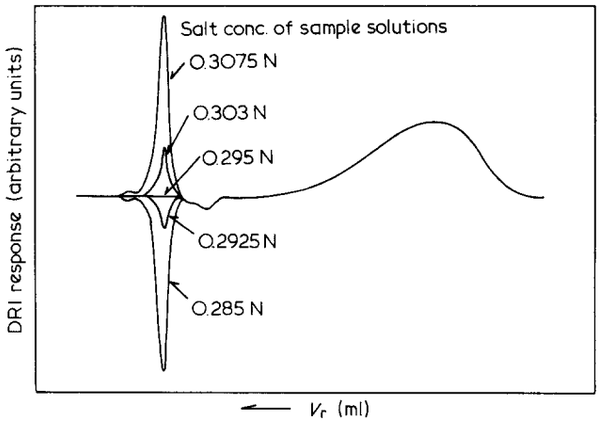

Figure 3 Example of the salt peak changes of chromatograms. The salt concentrations of sample solutions injected at the constant polymer concentration of 3 mg ml^{-1} are indicated in the Figure

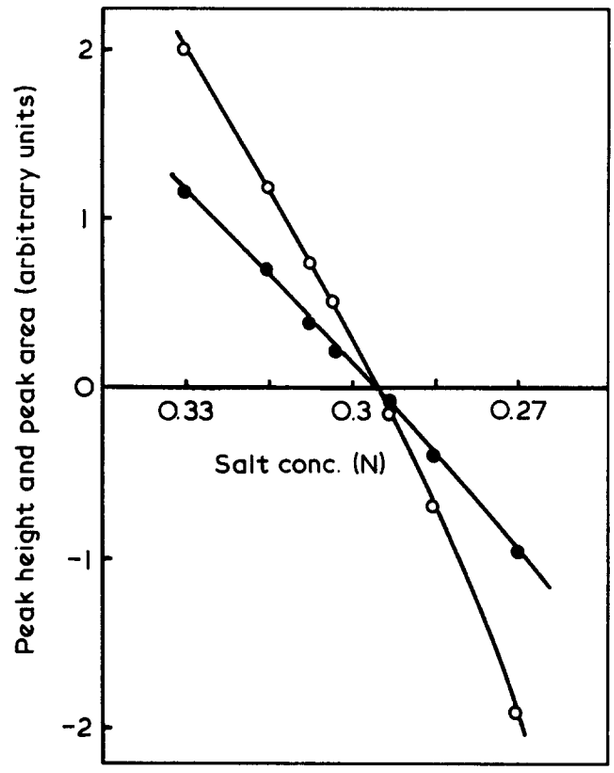

Figure 4 Plots of salt peaks excluded by a Donnan exclusion against the salt concentrations of sample solutions injected into g.p.c. column, eluent constant at 0.303 N NaCl. ○, Peak height; ●, peak area

G.p.c./LS method

Figure 5 shows examples of the chromatograms determined by DRI and LALLS for NaPA F3 and NaPA F7 in 0.3 N NaCl solution. The peak area of LALLS increases with the molecular weight of NaPA according to equation (2). The instrumental constant ψ is first estimated using the standard dextran and then corrected by the $(dn/dc)_\mu$ value for NaPA. The $(dn/dc)_\mu$ values for dextran and NaPA in 0.3 N NaCl solution at 25°C were as 0.139 and 0.147 ml g^{-1} at 633 nm, respectively. In the fifth column of Table 1 are listed the molecular weights $(M_w)_{g.p.c./LS}$ measured by the g.p.c./LS method. The agreement between $(M_w)_{LS}$ and $(M_w)_{g.p.c./LS}$ is excellent. As the chemical potential of the salt under the polymer peak agrees exactly with that of the eluent when eluting out the g.p.c. column, the weight-average molecular weights of NaPA can be determined without dialysis which is the advantage of using the g.p.c./LS method for polyelectrolytes.

Figure 6 shows the plots of $M_{g.p.c./LS}$ calculated from equation (3) against the retention volume V_r at appropriate intervals. The data of NaPA F3 correlate well with those of NaPA F7.

Universal calibration for NaPA

Figure 7 shows the plots of $\log [\eta]M$ against $V_{r,w}$ for the standard PEO and NaPA, where the product of $[\eta]$ and M is related to the hydrodynamic volume of polymer in solution according to Grubisic *et al.*[28] $V_{r,w}$ is the retention volume where M_w occurs. A single curve is obtained and the equation of the curve is approximated by:

$$\log [\eta]M = 16.2 - 0.2667 V_{r,w} \quad (6)$$

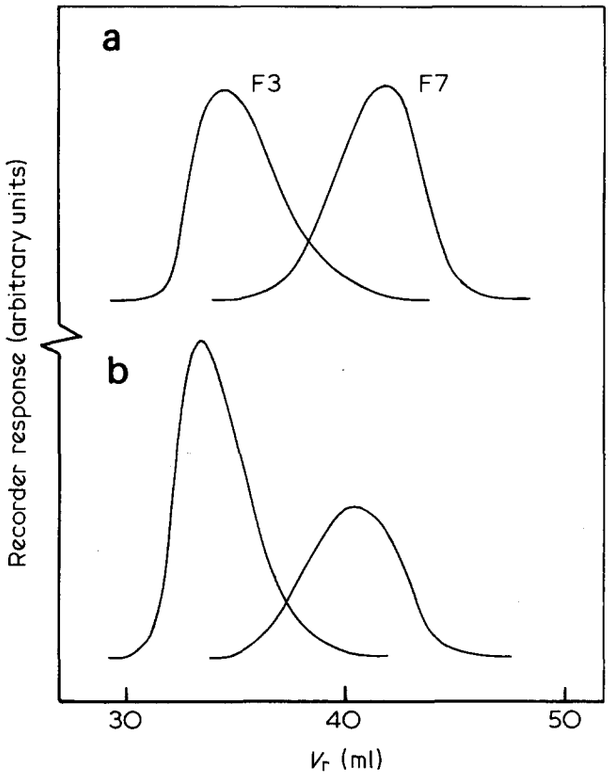

Figure 5 Examples of the chromatograms of the NaPA fractions measured by the g.p.c./LS method. Samples are shown in the Figure. (a) DRI; (b) LALLS

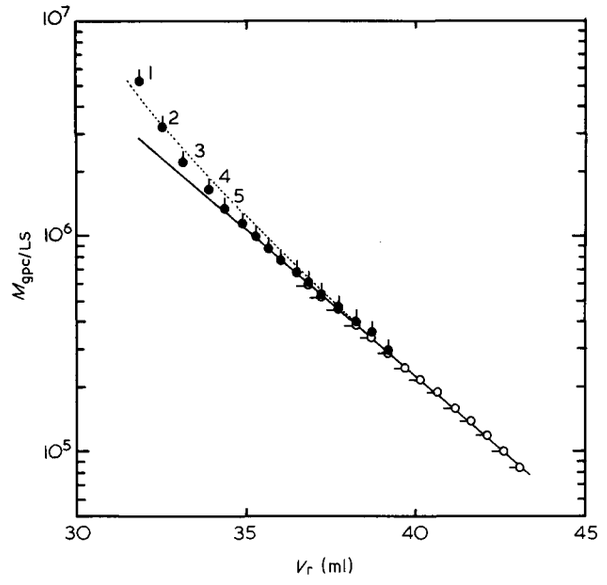

Figure 6 The plots of $M_{g.p.c./LS}$ against V_r for NaPA F3 (●) and NaPA F7 (○) measured by the g.p.c./LS method in 0.3 N NaCl at 25°C. The solid line is from equation (7) and the dotted line is calculated by the theoretical g_s of Zimm and Stockmayer for a randomly branched polymer of trifunctional branch points, assuming that λ is 1.67×10^{-6} mol g^{-1}

It is concluded here that the universal calibration is established for NaPA in 0.3 N NaCl aqueous solution except for the data of NaPA F1. The molecular weight distributions of the NaPA fractions may be determined directly from the chromatograms of NaPA in 0.3 N NaCl

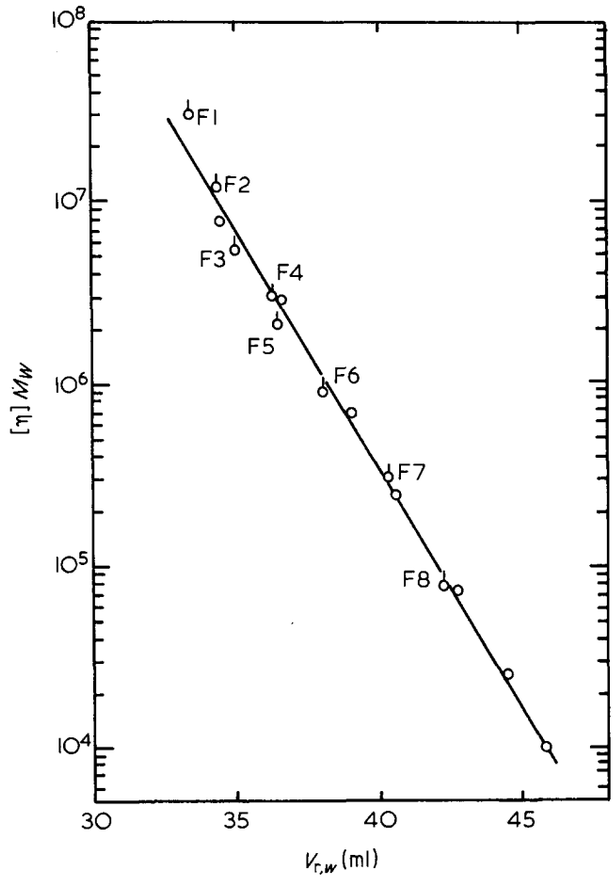

Figure 7 The plots of $\log[\eta]M_w$ against V_r for the standard PEO and the NaPA fractions in 0.3 N NaCl. The NaPA fractions are indicated in the Figure

using the universal calibration curve of equation (6). The molecular weight distribution indexes (M_w/M_n) thus obtained are listed in the last column of *Table 1*.

However, it is noteworthy that the experimental establishment of the universal calibration for polyelectrolytes appears very delicate and becomes complicated by electrostatic adsorption and exclusion effects between the mobile phase and the stationary gel phase. It has been reported previously[29] that the universal calibration does not hold for NaPA in the same experimental conditions. The disagreement between the results reported previously and the results here is due to the application history of the column system used in g.p.c. measurements. The old column system has been utilized in a wide variety of polyelectrolytes and eluents for a long time, many kinds of impurities, especially sulphonated aromatic substances, were adsorbed on the column matrices and many charged groups were accumulated. Thus, it is assumed that the interactions, e.g. electrostatic exclusion, were effective for polyelectrolytes even in 0.3 N NaCl aqueous eluent. The column system used in this study was fresh and no impurity is present on the surface. Therefore, if TSK-GEL PW-type is used for polyelectrolytes, suitable precautions are recommended for the desorption of impurity from the gel matrices, as reported by Kato and Hashimoto[9].

Substituting the MHS viscosity equation for NaPA in 0.3 N NaCl ($[\eta] = 1.69 \times 10^{-4}$ M$^{0.75}$) in equation (6) gives

the following calibration curve:

$$\log M = 11.41 - 0.1524 V_{r,w} \quad (7)$$

Equation (7) is shown as a solid line through the data of NaPA F3 and NaPA F7 in *Figure 6*. The agreement of the data points with equation (7) is good, except that the some data for NaPA F3 at low V_r deviate from a rectilinear relation between $\log M$ and V_r. The reason for this deviation is attributed to both the branching of the NaPA samples with higher molecular weight and the exclusion limit of the g.p.c. column system used. The retention volume of the exclusion limit (V_0) was estimated to be 29 ml using the fractions of the native dextran and the volume of the total permeation limit ($V_0 + V_i$) was estimated as 57.1 ml using the salt exclusion peak, where V_0 and V_i are the void volume of the column and the inner volume of the gel matrices, respectively. As the data were obtained at $V_r \gg V_0$, the effect of the exclusion limit may be negligible.

Estimation of the degree of branching

Taking into consideration the levelling off in the plots of $\log [\eta]$ against $\log M_w$, and the deviation of the data from the rectilinear calibration curve in *Figure 6*, it is concluded that the NaPA fractions with higher molecular weights have considerable branching on the polymer chain. The deviation of the point for NaPA F1 in *Figure 7* from the universal calibration may also be explained if the first fraction of NaPA is the highly branched sample, as described previously.[30]

The degree of branching may be estimated using a branching parameter (g_s) which is defined by the ratio of the unperturbed mean square radii of gyration of linear and branched polymers having the same molecular weight. The functional forms of g_s have been theoretically calculated for many branch shapes[31,32]. Moreover, the experimental branching parameter (g_η) is also defined by the ratio of intrinsic viscosity for linear and branched polymer with the same molecular weight as follows:

$$g_\eta = [\eta]_{b,M}/[\eta]_{l,M} \quad (8)$$

where the subscript l and b denote linear and branched polymers and the subscript M indicates the polymers having the same molecular weight M. The relation between g_s and g_η is:

$$g_s^a = g_\eta \quad (9)$$

where the value of a is from 1/2 to 3/2 depending on the theory used[31,33]. The following problems are encountered, however, on determining the degree of branching: (1) g.p.c. is carried out in good solvents. The parameter g_s is calculated only at the theta state and g_s in good solvents is not well understood; (2) the theoretical g_s does not agree with the experimental data even at the theta state.

Therefore, it is assumed tentatively that the NaPA sample is a randomly branched polymer of trifunctional branch points and a is 3/2 because the branched polymer also acts as nondraining coil even in good solvents, as discussed previously[30,34]. The g_s parameter for this model at the theta state has been derived by Zimm and Stockmayer[31] as the function of the weight average number of branch point per molecule (n_w) for a polydisperse system in the theta state. The ratio of n_w to the molecular weight is denoted as λ. Thus, assuming that the g_s parameter in the theta state may approximate the parameter in good solvents. The average degree of branching for the NaPA fractions is discussed using the g_η values estimated from the experimental data of g.p.c., as proposed by Dietz and Francis.[23]

On the basis of the universal calibration relation, the product of $[\eta]$ and M of branched and linear polymers eluted at the same retention volume is described as:

$$[\eta]_l M_l = [\eta]_b M_b \quad (10)$$

If the molecular weight of branching polymer M_b is the value of M in equation (8), $[\eta]_{b,M}$ may be estimated from equation (10) as:

$$[\eta]_{b,M} = ([\eta]_l M_l/M)_{V_r \text{ const.}} \quad (11)$$

Substituting equation (11) and the MHS viscosity equation, $[\eta] = K_v M^v$, for the linear NaPA in 0.3 N NaCl at 25°C into equation (8), the g_η parameter can be calculated from the ratio of the molecular weights of branched and linear polymers observed by the g.p.c./LS method at the constant retention volume as[23]:

$$g_\eta = (M_l/M_b)^{v+1} \quad (12)$$

Some data for NaPA F3 at low V_r deviate from equation (7) due to branching, these are the numbered points in *Figure 6*. The n_w values thus obtained by equation (12) are listed in *Table 4*. The dotted line in *Figure 6* is calculated by the theoretical g_s function of Zimm and Stockmayer assuming that λ is 1.67×10^{-6} mol g^{-1} as a constant. The ratio λ may be independent of the molecular weight of NaPA because the data for the numbered points fit the dotted line. If it is assumed that $a = 1/2$, the n_w values calculated become much larger than these values. For example, the n_w value of point no. 1 is estimated as 70 which is too large.

In conclusion, the universal calibration relation holds for both the NaPA fractions and the PEO standard in 0.3 N NaCl aqueous solution. The g.p.c./LS method is useful for determining both the molecular weight and the molecular weight distribution of polyelectrolytes without dialysis in a reasonably high added-salt concentration. The degree of branching for polyelectrolytes may be estimated in the same manner as that for the nonionic polymers by the method of Drott and Mendelson. However, the estimated values of n_w for the randomly-branched polymer are only apparent values.

ACKNOWLEDGEMENT

The authors wish to thank Professor I. Noda of Nagoya University for his help in measuring the intrinsic viscosity for NaPA–K.

Table 4 Numbers of Branches estimated by the g.p.c./LS method

Data no.	$M_b/10^6$	$M_l/10^6$	n_w ($a = 3/2$)[a]	n_w ($a = 1/2$)
1	5.3	2.9	7.0	70.0
2	3.3	2.3	4.0	20.0
3	2.4	1.75	2.6	15.5
4	1.65	1.50	0.6	2.3
5	1.35	1.30	0.2	0.8

[a] a is defined by $g_s^a = g_\eta$

REFERENCES

1 Spatorico, A. L. and Bayer, G. L. *J. Appl. Polym. Sci.* 1975, **19**, 2933
2 Dubin, P. L., Koontz, S. and Wright, K. L. *J. Polym. Sci., Polym. Chem. Ed.* 1977, **15**, 2047
3 Cooper, A. R. and Matzinger, D. P. *J. Appl. Polym. Sci.* 1979, **23**, 419
4 Domard, A., Rinaudo, M., and Rochas, C. *J. Polym. Sci., Polym. Phys. Ed.* 1979, **17**, 673
5 Brown, D. W. and Lowry, R. E. *J. Polym. Sci., Polym. Chem. Ed.* 1979, **17**, 1039
6 Rochas, C., Domard, A. and Rinaudo, M. *Eur. Polym. J.* 1980, **16**, 135
7 Siebourg, W., Lundberg, R. D. and Lenz, R. W. *Macromolecules* 1980, **13**, 1013
8 Rollings, J. E., Bose, A., Caruthers, J. M., Okos, M. R. and Tsao, G. T. *Am. Chem. Soc., Div. Polym. Chem. Polym. Prepr.* 1981, **22**, 294
9 Kato, Y. and Hashimoto, T. *J. Chromatogr.* 1982, **235**, 539
10 Higo, Y., Kato, Y., Itoh, M., Kozuka, N., Noda, I. and Nagasawa, M. *Polym. J.* 1982, **14**, 809
11 Takahashi, A. and Nagasawa, M. *J. Am. Chem. Soc.* 1964, **86**, 543
12 Takahashi, A., Kato T. and Nagasawa, M. *J. Phys. Chem.* 1967, **71**, 2001
13 Noda, I., Tsuge, T. and Nagasawa, M. *J. Phys. Chem.* 1970, **74**, 710
14 Neddermeyer, P. A. and Rogers, L. B. *Anal. Chem.* 1968, **40**, 755
15 Neddermeyer, P. A. and Rogers, L. B. *Anal. Chem.* 1969, **41**, 94
16 Kadokura, S., Miyamoto, T. and Inagaki, H. *Polym. J.* 1982, **12**, 933
17 Lindstroem, T., de Ruvo, A. and Soeremark, C. *J. Polym. Sci., Polym. Chem. Ed.* 1977, **15**, 2029
18 Ouano, A. C. and Kaye, W. *J. Polym. Sci. A* 1974, **12**, 1151
19 Ouano, A. C. *J. Chromatogr.* 1976, **118**, 303
20 Takagi, T. *J. Biochem.* 1981, **89**, 363
21 Kato, T., Kanda, A., Takahashi, A., Noda, I., Maki, S. and Nagasawa, M. *Polym. J.* 1979, **11**, 575
22 Drott, E. E. and Mendelson, R. A. *J. Polym. Sci. Part A-2*, 1970, **8**, 1361
23 Dietz, R. and Francis, A. *Polymer* 1979, **20**, 450
24 Takahashi, A. and Kagawa, I. *J. Chem. Soc. Japan, Ind. Chem. Section* 1961, **64**, 1637
25 Kato, T., Nakamura, K., Kawaguchi, M. and Takahashi, A. *Polym. J.* 1981, **13**, 1037
26 Kato, T., Okamoto, T., Tokuya, T. and Takahashi, A. *Biopolymers* 1982, **21**, 1623
27 Kitano, T., Taguchi, A., Noda, I. and Nagasawa, M. *Macromolecules* 1980, **13**, 57
28 Grubisic, Z., Rempp, P. and Benoit, H. *J. Polym. Sci. B* 1967, **5**, 753
29 Kato, T. and Takahashi, A. *Polym. Prepr. Japan* 1981, **30**, 1764
30 Kato, T., Itsubo, A., Yamamoto, Y., Fujimoto, T. and Nagasawa, M. *Polym. J.* 1975, **7**, 123
31 Zimm, B. H. and Stockmayer, W. H. *J. Chem. Phys.* 1949, **17**, 1301
32 Casassa, E. F. and Berry, G. C. *J. Polym. Sci., Part A-2* 1966, **4**, 881
33 Zimm, B. H. and Kilb, R. W. *J. Polym. Sci.* 1959, **37**, 19
34 Noda, I., Horikawa, T., Kato, T., Fujimoto, T. and Nagasawa, M. *Macromolecules* 1970, **3**, 795