The dilute solution properties of maleic anhydride and maleic acid copolymers: 1. Light scattering, osmotic pressure and viscosity measurements

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(*Received* 14 *February* 1980*; revised* 21 *April* 1980)

Dilute solution behaviour of poly(maleic anhydride-co-ethyl vinyl ether) and poly(maleic acid-co-ethyl vinyl ether) has been investigated by light scattering, osmotic pressure, and viscosity measurements. The molecular weights ($\bar{M}_w$ and $\bar{M}_n$), the second virial coefficients A_2, and the intrinsic viscosities $[\eta]$ have been determined for three states of this copolymer: anhydride-form, H-form, and Na-salt independently. The constants in the Mark–Houwink relations were obtained for the above three states under different solvent conditions. The molecular weight of the anhydride-form is found to be higher than that of the acid-form or the Na-salt, suggesting the degradation in a process of hydrolysis. The second virial coefficient A_2 as well as the Mark–Houwink relation indicates that the anhydride-form and H-form behave as flexible polymer chains in good solvents. However, the polymer coil of Na-salt is highly expanded even at saturated NaCl concentration.

INTRODUCTION

Many reports have recently been published on the polyelectrolyte behaviours of alternating copolymers of maleic acid in aqueous solutions. In aqueous solutions, several characteristic properties have been observed: pH-induced conformational transition[1-7], two-step dissociation process of dicarboxylate groups[8-10], and binding of counterions[11-16] etc... These properties of the maleic acid copolymers are attributed to two factors: (1) hydrophobic interaction of non-polar side chains, and (2) short-range electrostatic interaction of a pair of adjacent nearest-neighbour carboxylate groups shown in *Figure* 1.

Viscosity of maleic acid copolymer solutions indicates the most remarkable behaviour. The specific viscosity usually exhibits a maximum at the half-neutralization point, decreasing appreciably with further increase of degree of neutralization by bases, irrespective of the size of hydrophobic side chain[2,5]. This phenomenon seems to be caused by the effects of the local charge density and the short-range electrostatic interaction of a pair of the adjacent carboxyl groups. The viscosities of the solution of maleic acid copolymers may reflect changes of the local conformation of the maleic anhydride ring or the pair of adjoining carboxyl groups in a polymer chain. Investigations are made into the influences of the maleic anhydride ring or the pair of adjoining carboxyl groups on the viscometric behaviour of solutions of the copolymer.

Although several data on the viscometric behaviour of the maleic acid copolymers have appeared in the literature[17,18], systematic studies are rather limited on the intrinsic viscosity $[\eta]$ and second virial coefficient A_2 of these copolymers covering a wide range of molecular weight. In this study, the measurements of light scattering, osmotic pressure and viscosity were carried out for alternating copolymers of maleic anhydride and ethyl vinyl ether (MAn) and alternating copolymers of maleic acid and ethyl vinyl ether. One of the most important reasons for choosing ethyl vinyl ether as the co-monomer is that the aqueous solutions of this copolymer do not precipitate easily with an addition of small salts. The molecular weights, the second virial coefficients, and the

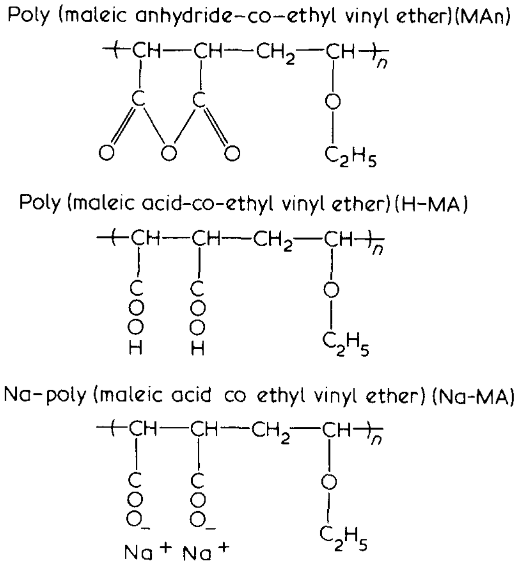

Figure 1 Chemical structure of MAn, H–MA, and Na–MA

0032–3861/80/1427–06$02.00

Table 1 List of solvents and non-solvents

Solvent	Non-solvent
Acetone	*n*-decane
Methyl ethyl ketone	*n*-octane
Tetrahydrofuran	iso-octane
Acetophenone	*n*-hexane
Ethyl acetate	Cyclohexane
Methanol	Ethyl ether
Ethanol	Benzene
	Dioxane
	Chloroform

intrinsic viscosities were obtained from these experiments for three states of this copolymer: anhydride-form(MAn), H-form(H-MA), and Na-salt(Na–MA).

EXPERIMENTAL

Preparation of polymers

Commercial maleic anhydride (Nagoya Katayama Chem. Co.) was recrystallized from chloroform (Katayama) and dried in a vacuum desiccator. Commercial reagent-grade ethyl vinyl ether (Katayama) was used without further purification. Polymerization was carried out in benzene solution with α,α'-azobis-isobutyronitrile as initiator under nitrogen atmosphere at 60°C for 5 h. The copolymer precipitated was separated with glass filter to remove benzene and free monomers. Then, the copolymer was purified by repeating precipitation from a tetrahydrofuran (THF) solution to large amounts of ethyl ether three times, dried in vacuum at room temperature, and was obtained as a white fine powder. The conversion was 34.7 wt%. The composition of the copolymer was determined by using an infrared spectrum measurement and a potentiometric titration method. The content of maleic anhydride obtained by the potentiometric titration was 50 ± 2 mol%.

To find appropriate solvent–precipitant systems for phase separation of this copolymer, combinations of seven kinds of solvents and nine kinds of non-solvents were tested in the temperature range between 0 and 50°C, which are listed in *Table* 1. Among them, two combinations were chosen; acetone–*n*–decane and acetone–cyclohexane. The former case is preferable, because a fairly transparent liquid–liquid phase separation takes place with decreasing temperature, whereas in the latter case the temperature dependence of the precipitation is very weak. A report by Ferry *et al.*[19] on the fractionation of this copolymer in the mixture of methyl ethyl ketone and cyclohexane was found to be inappropriate, because this copolymer precipitated as a solid phase with increasing temperature.

The phase separation in the former case was carried out by dissolving 70 g of the copolymer in 2500 ml of acetone. By stirring the solution, *n*-decane was added slowly until the solution became turbid. The amount of *n*-decane was 900 ml. The solution was kept at 45°C for 1 h, and then stirring was stopped and the solution was cooled very slowly overnight to 15°C to obtain a clear phase separation. The dense phase was sucked up gradually with a capillary and dissolved with tetrahydrofuran prior to the purification by successive precipitations with ethyl ether. To obtain the next fraction the remaining solution was stirred under reduced pressure until an appreciable change in turbidity was observed. This change is due to removal of acetone from the solution because of the large difference in boiling points of acetone and *n*-decane. By repeating the same procedure described above, the second fraction was obtained. In this manner 13 fractions were obtained.

Contamination of the hydrolysed fraction of the maleic anhydride ring was checked by infrared absorption of films cast from the acetone solution on a KBr plate. The strong absorption at 1780 cm^{-1} due to stretching of the carbonyl group of the anhydride and very weak band at 1720 cm^{-1}, due to that of the maleic acid, indicated the small possibility of the hydrolysis for all cases. This suggests that the fractionation process was made successfully according to the difference in the molecular weight, otherwise the first few fractions might contain the hydrolysed components irrespective of the molecular weight.

Preparation of solutions

Hydrolysis of MAn was performed by stirring the copolymer in 0.5N NaOH for half a day at room temperature. The solution was dialysed against deionized distilled water for three days. After filtration through G3 glass filter, the solution was deionized with a mixed-bed ion excahnge column in the H^+-form, and subsequently freeze-dried. Details of the procedure are reported elsewhere[16,20]. An original salt solution of Na–MA was obtained by dissolving the polyacid into NaCl aqueous solution of given concentration and adding the calculated amount of NaOH solution in a volumetric flask. The original solution was dialysed against a solvent to reach the Donnan membrane equilibrium with the solvent before all measurements. The dilutions were made by adding the same solvent.

Light scattering measurements

Measurements were made on a Chromatix Low Angle Light Scattering Photometer KMX-6 at room temperature (25°C). The light source was unpolarized 2mW He–Ne laser of 632.8 nm. Measurements were made at 4.96°. The instrument was calibrated using toluene and yielded a value for the Rayleigh ratio (at 22°C) of $R_{4.96} = 14.06 \times 10^{-6}\ \mathrm{cm}^{-1}$ in agreement with recent values[24,25]. As the secondary standard, the molecular weight of a monodisperse ($\bar{M}_w/\bar{M}_n < 1.10$) polystyrene (Pressure Chem. Co.) in toluene was determined. The molecular weight obtained agreed within 2% with the value of 390 000 reported by the Pressure Chem. Co.

Solutions and solvents were filtered by a Millipore filter FGLP having pore size 0.2 μm, and measurements were performed on the streaming solutions. No fluoresence contributed to the intensity of scattered light, but the band interference filter was inserted in front of the photomultiplier. Depolarization of the solution was found to be negligible.

Refractive index increments were measured at 25 ± 0.01°C with a Brice–Phoenix type differential refractometer with laser light of wave length 632.8 nm. The apparatus was calibrated by using aqueous solutions of KCl and NaCl as standard. In this study, the refractive index increments were measured for the unfractionated sample.

Osmotic pressure measurements

Osmotic pressure measurements were made with a Knauer High-Speed Membrane Osmometer. The os-

Table 2 Values of refractive index increment d*n*/d*c* and refractive index n_0 of solvents at 25°C

System	d*n*/d*c* (ml/g)	n_0
MAn in THF	0.0883	1.406
H–MA in THF	0.0908	1.406
Na–MA in 0.18M NaCl	0.1803	1.320

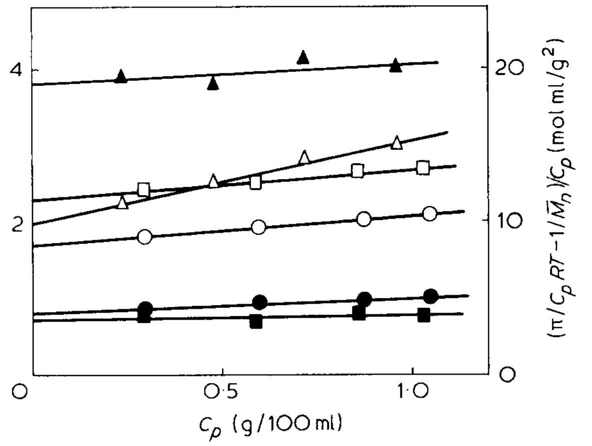

Figure 2 Plots of $(\pi/C_p)^{1/2}$ (open symbols) and $(\pi/C_pRT - 1/\bar{M}_n)/C_p$ (filled symbols) vs. C_p at 30.0°C: (○, ●) MAn in THF; (□, ■) H–MA in THF; (△, ▲) Na–MA in 0.18M NaCl. Plots of $(\pi/C_pRT - 1/\bar{M}_n)/C_p$ vs. C_p are according to the Casassa–Stockmayer procedure

motic pressure was recorded by a Hitachi Recorder 056. The measurements were made at 30.00±0.01°C.

Membranes used were regenerated cellulose membranes type SM11536 and a denser one type SM11539 of the Membranfilter-gesellschaft Sartorius–Werke A–G., Göttingen. Because the membranes SM11536 were permeable to the smallest molecular weight fraction, the membranes SM11539 were used for this sample. Before use, membranes were first equilibrated with solvents for 24 h, then placed in the osmometer cell, and flushed with solvents for 24 h. After calibration, the osmotic pressure was first measured on the solution with highest concentration, and the membrane used was immersed in the same solution for 24 h. Then the osmometer cell was rinsed carefully with solvent several times.

Measurements of the osmotic pressure were made in the usual way starting with the lowest concentration. The osmotic pressures were measured three times for each concentration, and then the cell was flushed with the solvents to restore the osmotic pressure of the solvents to zero-level. In practice, we were able to obtain the zero-level after measurements of the solutions with accuracy within 0.02 cm. That is to say, when the osmotic pressure of the solvents did not return to zero-level within that accuracy, the values of the osmotic pressure obtained were not adopted, and the measurements were made again for the same solution. This procedure was employed in all measurements to obtain really reliable osmotic pressures.

Viscosity

Solution viscosities were measured in THF and other solvents, using an Ubbelohde-type viscometer of flow time 84.4, 109.2 and 167.5 s at 30°C for acetone, THF and pure water respectively. Kinetic-energy corrections could be neglected in all cases. Measurements were carried out at 30±0.03°C in a water bath. Solutions and solvents were filtered through ultrafine glass-filter before use. Intrinsic viscosity [η] was determined from a common intercept extrapolated graphically to zero polymer concentration in the Huggins plot and Kraemer plot. Experimental uncertainty in [η] determined was estimated to be 3%.

RESULTS AND DISCUSSION

Refractive index increments

The values of refractive index increment d*n*/d*c* at 632.8 nm were obtained for the anhydride-form(MAn) and the H-form(H–MA) in THF solution, and the Na-salt(Na–MA) in 0.18M NaCl aqueous solution. These values as well as the values of the refractive index of solvents (n_0) are summarized in *Table* 2. The values of n_0 at 632.8 nm of THF was calculated from Hartmann's equation[21] and that of 0.18M NaCl aqueous solution was calculated from Sellmeier's formula[26] on the basis of literature values[21].

Molecular weights and second virial coefficients

Osmotic pressure data were treated by the square-root method; $(\pi/C_p)^{1/2}$ was plotted against C_p, where π is the osmotic pressure and C_p is the concentration of polymer solution. The number-averaged molecular weights $\bar{M}_n$ were calculated from the intercepts in this plot. The second virial coefficients A_2^{OP} was obtained from the intercept in the Casassa–Stockmayer plot[27].

In *Figure* 2, the results of the osmotic pressure are given for Na–MA in 0.18M NaCl aqueous solution, H–MA and MAn in THF at 30°C. In *Figure* 3, results of the light-scattering measurements are given for three states of the copolymer: MAn, H–MA, and Na–MA. Here, R_θ is the Rayleigh ratio at scattering angle θ and K is the optical constant. The weight-averaged molecular weights $\bar{M}_w$ were obtained from the intercept of this plot, and the second virial coefficients A_2^{LS} were evaluated from the slopes of the plots of (KC_p/R_θ) against polymer concentration C_p.

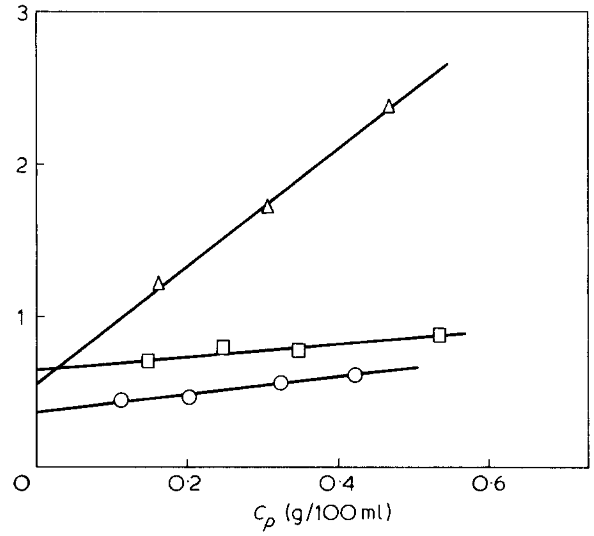

Figure 3 Plots of (KC_p/R_θ) vs. C_p at 25°C: (○) MAn in THF; (□) H–MA in THF; (△) Na–MA in 0.18M NaCl

Table 3 summarizes the data obtained in this manner for the weight-averaged molecular weights $\bar{M}_w$, the number-averaged molecular weights $\bar{M}_n$, the polydispersity indices $\bar{M}_w/\bar{M}_n$ and the second virial coefficients A_2 of the unfractionated sample in the forms of MAn, H–MA, and Na–MA.

These results show that the anhydride copolymer degradates considerably in a process of dissolution into the aqueous solutions. The molecular weights of H–MA and Na–MA are equal in value within the experimental error when the difference of molecular weight per monomer unit between two states (i.e. $M^{H}=188$, $M^{Na}=232$) is taken into account. Consequently, we cannot employ the values of molecular weight of anhydride-form to obtain the molecular weights of H–MA or Na–MA. We must determine the molecular weights of H–MA or Na–MA independently, when we study the solution properties of H–MA or Na–MA.

Table 3 Light-scattering, osmotic-pressure, viscosity data for an unfractionated sample

	MAn in THF	H–MA in THF	Na–MA in 0.18M NaCl
$\bar{M}_w \times 10^{-4}$	28.1	15.3	18.1
$\bar{M}_n \times 10^{-4}$	10.1	5.50	6.43
$A_2^{LS\dagger} \times 10^4$ at 25°C	2.81	2.03	19.1
$A_2^{OP\dagger} \times 10^4$ at 30.0°C	4.06	3.60	19.0
$\bar{M}_w/\bar{M}_n$	2.77	2.78	2.81

† mol.ml/g^2

In several previous studies about molecular-weight-dependent properties of maleic acid copolymers in aqueous solutions, the molecular weights determined in the anhydride-form in organic solvents have been adopted instead of those determined in a state of H–MA or Na–MA. Those values of the molecular weights are inadequate for the investigation of aqueous solution properties of maleic acid copolymers. In the cases of the copolymers with larger hydrophobic side chains (e.g. copolymer of maleic acid and butyl vinyl ether, copolymer of maleic acid and styrene etc.), particularly, the effects of degradation seem to be very serious[2].

The reason for the considerable degradation is unknown. Contaminations of unexpected labile bonds during the polymerization may cause such a reduction of molecular weight[22]. Another possibility is that the maleic anhydride group seems quite labile to the hydrolysis. Further investigation is needed to clarify the mechanism of the degradation.

In this study, the molecular weights in the state of Na-salt in 0.18M NaCl aqueous solution were determined independently of the molecular weights of anhydride-form. By using the values for Na–MA, values of molecular weight of H–MA were evaluated considering the difference of molecular weight per monomer unit between two states.

Same measurements as for the unfractionated sample were performed for the fractionated samples. The molecular weights, $\bar{M}_w$ and $\bar{M}_n$, polydispersity indices $\bar{M}_w/\bar{M}_n$, and the second virial coefficients A_2 obtained from the light scattering measurements for the fractionated samples of MAn in THF are shown in *Table* 4. In *Table* 5, the

Table 4 Light-scattering, osmotic-pressure, and viscosity data for MAn in organic solvents

Fr. No.	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$A_2^{LS} \times 10^4$ in THF at 25°C†	[η] (dl/g) at 30.0°C in THF	[η] (dl/g) at 30.0°C in Acetone
3	132	25.2	5.24	2.83		0.842
4	65.1	18.6	3.50	2.19	0.910	
6	47.0	11.4	4.12	3.07	0.679	
7	28.3	11.8	2.40	3.10		0.336
8	20.9	8.98	2.33	3.42		0.257
9	15.8	7.94	1.99	3.56		
10	12.2	6.54	1.87	4.06	0.392	0.215
11	9.51	5.07	1.88	4.68		
13	1.93	1.33	1.45			

† mol.ml/g^2

Table 5 Light-scattering, osmotic-pressure, and viscosity data for Na–MA in NaCl aqueous solutions

Fr. No.	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$A_2^{LS} \times 10^4$ at 25°C in 0.18M NaCl†	[η] (dl/g) at 30.0°C 0.01M	0.18M	0.50M	1.00M	2.00M	4.00M
1	65.9	20.4	3.23	7.9	12.44	3.26		1.58	1.45	
2	55.1	18.2	3.03	12.1	11.89	3.06				
3	52.1	16.4	3.18	12.3	11.74	2.68	1.44		1.25	1.18
4	38.9	18.5	2.10	11.4						
5	35.9	18.1	1.98	11.7						
6	24.4	9.06	2.69	14.3	5.00	1.47	0.982	0.710		0.683
7	19.4	7.64	2.54	13.9						
8	17.4	7.72	2.25	15.2		1.10				
9	12.5	7.47	1.67	17.3						
10	12.0	5.53	2.17	17.2	2.33	0.710	0.490			0.401
11	10.3	5.38	1.91	16.0						
12	4.54	3.32	1.37	13.6	1.26	0.420		0.301	0.290	0.283
13		2.29		29.4						

† mol.ml/g^2

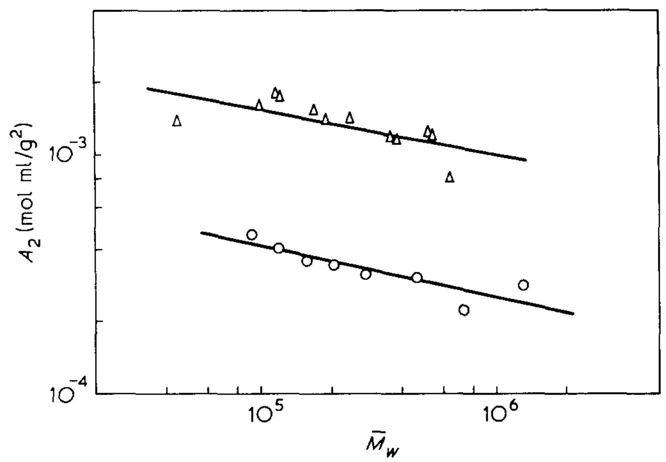

Figure 4 Double logarithmic plots of A_2 vs. $\bar{M}_w$ at 25°C: (○) MAn in THF; (△) Na–MA in 0.18M NaCl

Table 6 Viscosity data for H–MA at 30.0°C

Fr. No.	$\bar{M}_w \times 10^{-4}$	[η] (dl/g) in THF	[η] (dl/g) in (10% H_2O + 90% dioxane)†
1	53.4	0.718	
2	44.7		1.20
4	31.5	0.567	0.790
5	29.1	0.469	0.624
7	15.7	0.365	0.499
10	9.72	0.275	0.343
12	3.68		0.206
unfractionated sample	14.7	0.340	

† Addition of small amounts of H_2O is for a complete dissolution of the specimen

values of the same parameters of Na–MA determined in 0.18M NaCl aqueous solution are summarized.

Plots of log A_2 *versus* log $\bar{M}_w$ are given in *Figure* 4 for MAn in THF solution and Na–MA in 0.18M NaCl aqueous solution. The second virial coefficient A_2 *of* MAn in THF solution and that of Na-MA in 0.18M NaCl aqueous solution at 25°C are represented as follows:

$$A_2 = 5.05 \times 10^{-3}\ \bar{M}_w^{\ -0.217}\ (\text{mol}\cdot\text{ml/g}^2)\quad \text{for MAn} \tag{1}$$

$$A_2 = 1.38 \times 10^{-2} \bar{M}_w^{\ -0.190}\ (\text{mol}\cdot\text{ml/g}^2)\quad \text{for Na–MA} \tag{2}$$

The values of the exponent are comparable to values ($-0.1 \sim -0.3$) obtained for flexible polymers in good solvents.

Tables 4 and 5 indicate that the polymer sample was fractionated successfully in the order of the molecular weight by our successive precipitation procedure. The polydispersity indices, however, are fairly large as shown in the 4-th columns of *Tables* 4 and 5. Namely, each polymer fraction, especially that of high molecular weight, is rather polydisperse in spite of the fractionation. Contamination of molecules with high content of hydrolysed carboxyl groups may be responsible for the polydispersity. Removal of such components prior to the fractionation seems difficult in the present solvent-non-solvent system (acetone–*n*-decane). A search is expected for appropriate solvent–non-solvent systems. The degradation during the measurement of the osmotic pressure seems to be quite small, in spite of a fairly long time of a single measurement of the osmotic pressure.

Viscosity

Tables 4 and 5 collect the values of intrinsic viscosity [η] for MAn in organic solvents and Na–MA in NaCl aqueous solutions. The values of intrinsic viscosity and the molecular weights which were derived from the molecular weights of Na–MA, of several polymer fractions of H–MA are given in *Table* 6.

In *Figures* 5 and 6, the logarithmic plots of intrinsic viscosity for the various forms of this copolymer are shown as a function of molecular weight which is

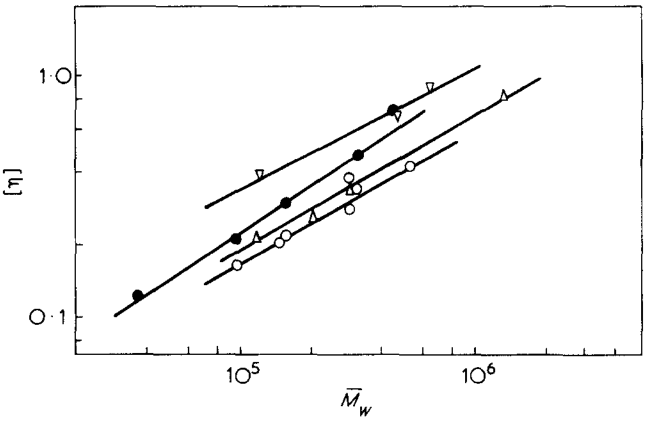

Figure 5 Double logarithmic plots of [η] vs. $\bar{M}_w$ at 30.0°C: (▽) MAn in THF; (△) MAn in Acetone; (○) H–MA in THF; (●) H–MA in (10% H_2O + 90% Dioxane)

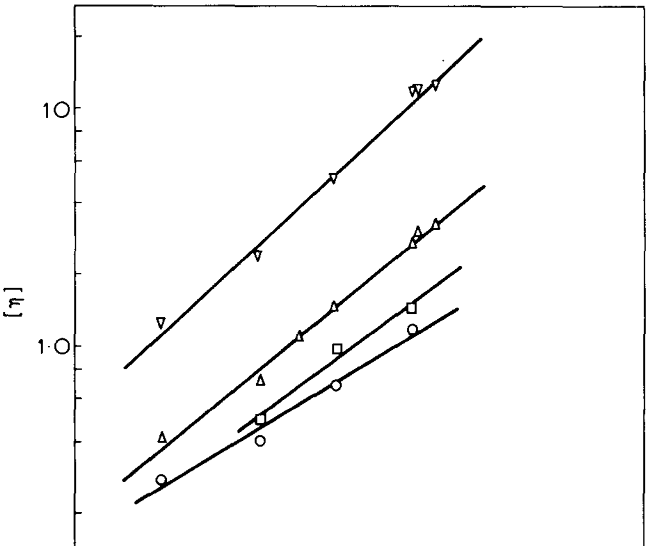

Figure 6 Double logarithmic plots of [η] vs. $\bar{M}_w$ for Na–MA in NaCl solutions at 30.0°C: (▽) 0.01M; (△) 0.18M; (□) 0.50M; (○) 4.00M

Table 7 Constants for the Mark–Houwink relation: $[\eta] = K \cdot \bar{M}_w^{\nu}$ (dl/g)

System	Solvent	Temp.	$K \times 10^5$	ν
MAn	THF	30.0°C	2.053	0.448†
	Acetone		2.220	0.582
H–MA	THF	30.0°C	4.148	0.565
	90% Dioxane +10% H_2O		1.838	0.661
Na–MA	0.01M NaCl	30.0°C	0.5922	0.919
	0.18M NaCl		0.6793	0.805
	0.50M NaCl		0.9996	0.732
	1.00M NaCl		4.242	0.608
	2.00M NaCl		4.683	0.599
	4.00M NaCl		4.491	0.593

† This value is not so reliable due to insufficient data

determined by light-scattering measurements. The straight lines drawn through the data points were estimated from persistence length calculations to be discussed in a subsequent paper[23]. In *Table* 7, are summarized the Mark–Houwink coefficients K and ν, as defined by:

$$[\eta] = K \cdot \bar{M}_w^{\nu}, \qquad (3)$$

determined from these straight lines.

It is noteworthy that values of exponent ν are very large in the cases of Na–MA in NaCl aqueous solutions. The large values for the exponent ν in 4.00M NaCl solution suggests that the polymer coil is far from its unperturbed state even at saturated NaCl concentration. The high expansion and remarkable toleration to the salt of this copolymer are likely to be attributable to the hydration of the pair of nearest-neighbour carboxyl groups and of the oxygen atom of alkyl ether side chain[15].

ACKNOWLEDGEMENT

The authors wish to thank Dr. H. Ohnuma, Osaka University, and Professor N. Imai, Nagoya University, for many illuminating discussions and much useful advice. The authors are also indebted to Professor S. Ikeda, Nagoya University, who made a Chromatix Low Angle Light Scattering Photometer KMX-6 available to us.

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