The dilute solution properties of maleic anhydride and maleic acid copolymers. II-unperturbed dimensions and persistence lengths of chains in solution

Toshio Shimizu
Department of Physics, Hamamatsu University School of Medicine, Hamamatsu, 431–31, *Japan*

(*Received* 10 *March* 1980; *revised* 23 *June* 1980)

The light-scattering, osmotic pressure and viscosity data reported in the preceding paper are used to estimate the characteristic ratios and the persistence lengths of poly(maleic anhydride-co-ethyl vinyl ether) (MAn) and poly(maleic acid-co-ethyl vinyl ether) (H–MA) in organic solvents and sodium salt of H–MA(Na–MA) in NaCl aqueous solutions. The characteristics ratios obtained by Stockmayer–Fixman's extrapolation method are as follows: 6.5 for MAn in organic solvents, 9.6 for H–MA in organic solvents, and 10.8 for Na–MA in NaCl aqueous solutions. The persistence lengths of these copolymers were also calculated by applying the wormlike chain model to viscosity data; ~9 Å for MAn in organic solvents and ~12 Å for H–MA in organic solvents. For Na–MA in NaCl aqueous solutions, the persistence lengths vary in proportion to the inverse root of the ionic strength C_s (i.e., $C_s^{-1/2}$). The persistence length in the absence of electrostatic interaction (i.e., $C_s \rightarrow \infty$) is about 10 Å which corresponds to the values of H–MA in organic solvents.

INTRODUCTION

In part I in this series of papers[1], the light-scattering, osmotic pressure, and viscosity data have been reported for poly(maleic anhydride-co-ethyl vinyl ether) (MAn) and poly(maleic acid-co-ethyl vinyl ether) (H–MA) in several organic solvents and the sodium salt of H–MA(Na–MA) in NaCl aqueous solutions. In this paper, we study the effects of (1) the presence of the maleic anhydride ring, (2) the short-range electrostatic interaction between a pair of adjoining carboxyl groups, and (3) the hydrophobic interaction among the alkyl ether side chains, on the polymer chain conformation and the chain flexibility. The data reported in part I in this series are used for the evaluations of the unperturbed dimensions and the persistence lengths to examine the local conformation of the polymer chain and the chain flexibility of three states of this copolymer: MAn, H–MA, and Na–MA.

The unperturbed dimensions are estimated with the Stockmayer–Fixman equation[2]. Among several methods, the Stockmayer–Fixman plot is the most convenient and appropriate for our data. Calculations of the persistence lengths of the present systems are performed by using the Yamakawa–Fujii method[3].

RESULTS AND DISCUSSION

Unperturbed dimensions

The coil dimensions may be calculated from the intrinsic viscosity by use of the Flory–Fox equation[4]

$$[\eta] = \Phi(L^2)^{3/2}/M \qquad (1)$$

or its equivalent for the unperturbed dimensions

$$K_0 = [\eta]_\theta/M^{1/2} = \Phi[(L^2)_0/M]^{3/2}, \qquad (2)$$

where (L^2) is the mean square end-to-end distance and subscripts 0 and θ mean the unperturbed state. In equations (1) and (2), Φ is the Flory viscosity constant and its value, originally thought to be constant at 2.1×10^{21} mol^{-1} (for $[\eta]$ in dl/g), is assumed to be[5] $\Phi = 2.6 \times 10^{21}$ nmol^{-1}. The measured viscosities reported in the Figures and Tables of ref 1 (part I of this series) may be extrapolated to obtain K_0 by the procedure according to the equation[6]

$$[\eta]/M^{1/2} = K_0 + 0.51\Phi B M^{1/2}. \qquad (3)$$

Here, B is related to the second virial coefficient.

The value K_0 is related to the characteristic ratio, C_∞, by

$$C_\infty = (K_0/\Phi)^{2/3} M_0/2l^2 \qquad (4)$$

where M_0 is a half value of the monomer molecular weight (i.e., 116 for Na–MA, 94 for H–MA, and 85 for MAn) and l is the bond length (i.e., 1.54 Å for a C–C bond)[7].

The plots of $[\eta]/M^{1/2}$ against $M^{1/2}$ are shown in *Figure 1*, according to equation (3) for MAn in organic solvents and for H–MA in organic solvents. In these plots the results in THF give a line with an almost zero negative slope confirming the near-ideal character of this solvent for H–MA. *Figure 2* shows similar plots for Na–MA in NaCl aqueous solutions with various concentrations of NaCl. A single common intercept is also observed in spite

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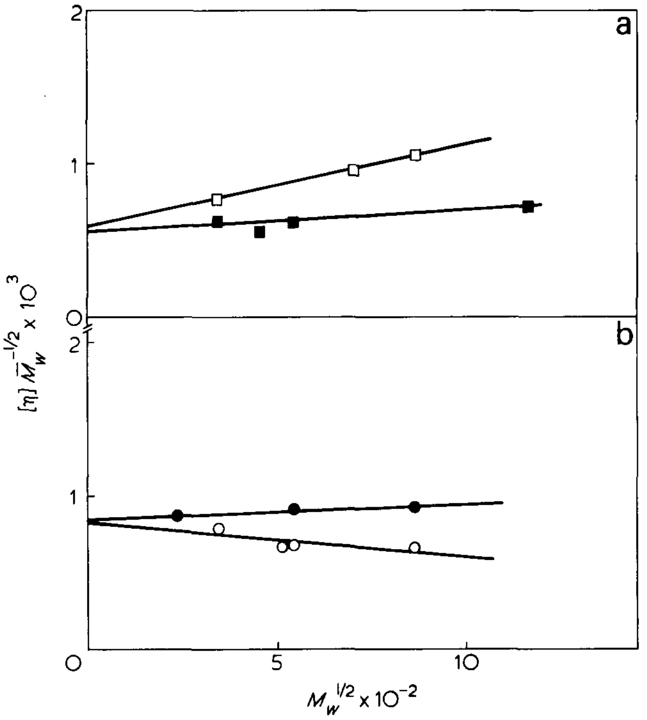

Figure 1 Stockmayer–Fixman plots for MAn (a) and H–MA (b): □, MAn in THF; ■, MAn in Acetone; ○, H–MA in THF; ●, H–MA in (90% Dioxane + 10% H_2O)

of the large values of ν (exponent in Mark–Houwink relation) at low ionic strengths.

The Stockmayer–Fixman plots are well satisfied for these three states (i.e., MAn, H-MA, and Na-MA), although the average molecular weights of which are largely different from one another, possibly due to degradation by hydrolysis. The intercepts obtained from *Figures 1* and *2*, and the corresponding values of C_∞ calculated according to equation (4) and using the value of M_0 for each state are listed in *Table 1*.

The characteristic ratio C_∞ for MAn is obtained to be 6.5 ± 0.5 at 25°C. This value is comparable to values for atactic vinyl polymers which are generally in the range of 5–10 (ref 8). The value of K_0 for MAn obtained in our study is 5.1×10^{-4}, lower than that of Matsuda *et al.* ($K_0=8.5\times10^{-4}$)[9]. The difference between our value and their reported one cannot be accounted for by the error (less than 20%) in the determination of the molecular weight of the copolymer and the measurements of the intrinsic viscosity. These rather small values obtained for MAn in organic solvents may be explained if the maleic anhydride groups, which hinder the internal rotation around the bond axis of the main chain, separate the distance between adjacent side chains and reduces the steric hindrance of the side chains to internal rotation in the main chain as argued by Endo *et al.*[10,11].

Alternatively, Barrales-Rienda and Pepper showed that the unperturbed chain dimension of polyacenaphthylene was remarkably small ($C_\infty=8.6$) in spite of the high degree of 'crowding' of chain[12]. They and Allegra *et al.*[13] argued that this could be accounted for by assuming that it is equally probable for the monomer residue to be incorporated into the chain by linkages of *cis* and *trans* to the five-membered ring. A similar argument seems available to explain the smaller values of MAn in organic solvents.

Though the characteristic ratios for H-MA and Na-MA show much larger values than for MAn, these values are also comparable to the values for vinyl polymers. The value of C_∞ for Na-MA is slightly larger than the value for H-MA, but both values are of the same order. Poly(acrylic acid) has a larger characteristic ratio in aqueous solutions ($C_\infty=11.3$ in 1.5N NaBr for Na-salt) than in organic solvents (e.g., 6.7 in dioxane)[14,15]. The opposite behaviour is observed for the characteristic ratio for poly(methacylic acid) (C_∞(aqueous) = 6; C_∞(organic) = 17)[16,17]. These phenomena result from the fact that poly(methacrylic acid) has hydrophobic groups, whereas poly(acrylic acid) has no hydrophobic side chain.

In the case of the present copolymer, the characteristic ratio in aqueous solutions exhibits a larger value than in organic media in spite of sufficiently large hydrophobic side chain. This is attributed to the high affinity of the oxygen atom in the ethyl ether side chain of this copolymer to water which may counteract the effect of the hydrophobic groups to the chain dimensions.

Persistence lengths

Yamakawa-Funjii's method.

The intrinsic viscosity $[\eta]$(dl/g) is written as follows[3]:

$$[\eta]=\Phi L_r^{3/2}/\lambda^3 M, \qquad (4)$$

where λ^{-1} is the Kuhn statistical length (i.e., $2q$ where q is the persistence length), M is the molecular weight of the polymer chain, and L_r is the reduced contour length which is written as,

$$L_r=\lambda L=\lambda M/M_L \qquad (5)$$

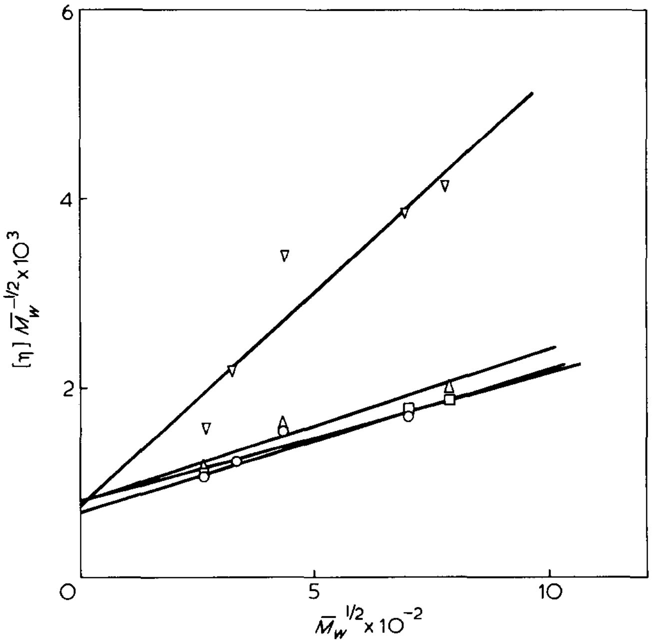

Figure 2 Stockmayer–Fixman plots for Na–MA in NaCl aqueous solutions: ▽, 0.18 M; △, 1.00 M; □, 2.00 M; ○, 4.00 M

Table 1 Characteristic ratios of MAn, H–MA and Na–MA

State	K_0	M_0	C_∞
MAn	5.7×10^{-4}	85	6.5
H–MA	8.7×10^{-4}	94	9.6
Na–MA	7.6×10^{-4}	116	10.8

with L the contour length and M_L the mass per unit chain length. Equation (4) is rewritten with the aid of equation (5) as follows:

$$[\eta]=\Phi(L_r,\ d_r)M^{1/2}/(\lambda M_L)^{3/2} \qquad (6)$$

where $\Phi(L_r, d_r)$ is the Flory viscosity constant which is a function of the reduced contour length L_r and the reduced hydrodynamic diameter $d_r(=\lambda d)$; d is the hydrodynamic diameter of polymer chain. Values of $\Phi(L_r, d_r)$ are summarized in ref 3.

The values of q were evaluated in order to obtain the best fit of viscosity data. In the cases of MAn or H–MA in organic solvents, the best fits were obtained by choosing a defined value of q for each condition. The values depending slightly on the molecular weight had to be chosen for the best fits in the case of Na–MA in NaCl aqueous solutions. The estimated values of the persistence length q and the other parameters are listed in *Table 2* and *Table 3*.

The values of the persistence length q for MAn in organic solvents are rather small (8–10) in spite of the local rigidity arising from the maleic anhydride ring. This means that the polymer chain of MAn behaves as a comparatively compact coil in the organic solvents. These smaller values may be interpreted in the same way as discussed on the small values of the characteristic ratio C_∞ of MAn in organic solvents in the previous section. The persistence lengths of H–MA in organic solvents and Na–MA in NaCl aqueous solutions are obviously larger than those of MAn in organic solvents; the polymer chains are more rodlike. The characteristic ratios for H–MA and Na–MA are larger than that of MAn. The values of q obtained for the present systems are the 'apparent' q because of the formalisms which omitted excluded volume effects in the above theories. Nevertheless, the persistence lengths derived in this manner reflect the flexibility of the present systems at least qualitatively.

Table 2 Persistence lengths and reduced hydrodynamic diameters of MAn and H–MA in organic solvents

State	Solvent	q (Å)	d_r
MAn*	Acetone	7.9	0.10
	THF	9.7	0.15
H–MA**	THF	10.2	0.10
	90% Dioxane + 10% H_2O	14.9	0.06

* M_L = 34 (g/Å)
** M_L = 37.6 (g/Å)

In the case of Na–MA in NaCl aqueous solutions, the persistence length varies slightly with the molecular weight and increases significantly with decreasing the ionic strength C_s: the polymer chain changes from coillike to rodlike with decreasing C_s. As shown in *Figure 3*, the persistence lengths of Na–MA vary in proportion to the inverse root of C_s (i.e., $C_s^{-1/2}$) in the range of C_s investigated in this study. Therefore, q is represented as follows:

$$q=q_0+q_{\mathrm{el}} \qquad (7)$$

where q_{el} is the electrostatic persistence length and is given by $q_{\mathrm{el}}=AC_s^{-1/2}$; A is a function of the molecular weight and the temperature, and q_0 is the persistence length in the absence of the electrostatic interaction (i.e., $C_s \to \infty$). The values of q_0 are given as intercepts in the q vs. $C_s^{-1/2}$ plots. A common intercept was found at (10 ± 1)Å. This value is in agreement with the values obtained for H–MA in the organic solvents. The values of q_{el} $(=q-q_0)$ are listed in parentheses in *Table 3*.

Thus, the electrostatic persistence length q_{el} is found to be proportional to $C_s^{-1/2}$ at least at high ionic strength.

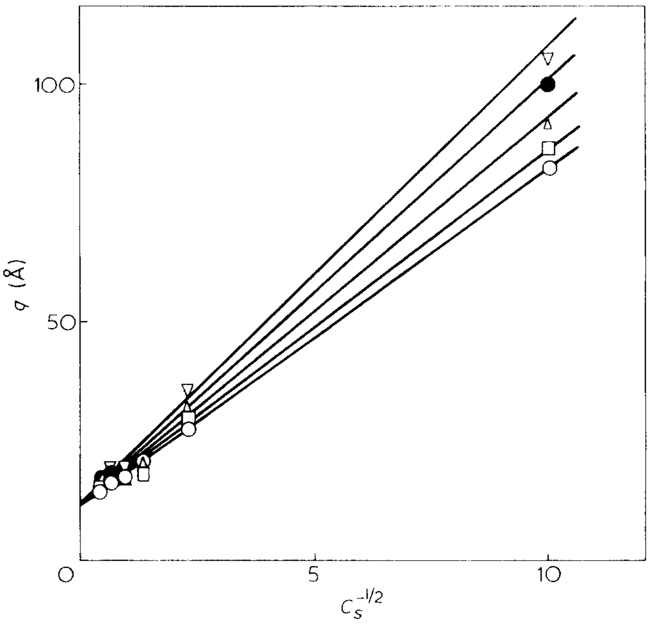

Figure 3 Persistence length vs. $C_s^{-1/2}$ for Na–MA in NaCl aqueous solutions: ▽, Fr. 1; ●, Fr. 3; △, Fr. 6; □, Fr. 10; ○, Fr. 12

Table 3 Persistence lengths of Na–MA at various concentration of NaCl

		q (and $q_{\mathrm{el}}=q-q_0$) (Å)				
C_s (M)	$C_s^{-1/2}$	Fr. 12 (M_w = 4.5 x 10^4)	Fr. 10 (M_w = 12.0 x 10^4)	Fr. 6 (M_w = 24.4 x 10^4)	Fr. 3 (M_w = 52.1 x 10^4)	Fr. 1 (M_w = 65.9 x 10^4)
0.01*	10.00	81.5 (71.1)	85.6 (75.2)	90.7 (80.3)	98.5 (88.1)	104.4 (94.0)
0.18**	2.36	27.2 (16.8)	29.4 (19.0)	30.9 (20.5)		35.5 (25.1)
0.50***	1.41		17.2 (6.8)	20.2 (9.8)	19.7 (9.3)	
1.00†	1.00	16.9 (6.5)		16.4 (6.0)		19.2 (8.8)
2.00†	0.71	16.3 (5.9)			17.8 (7.4)	18.2 (7.8)
4.00††	0.50	13.2 (2.8)	13.8 (3.4)	15.5 (5.1)	17.2 (6.8)	

* d_r = 0.03
** d_r = 0.06
*** d_r = 0.2
† d_r = 0.2 ~ 0.25
†† d_r = 0.25 ~ 0.35

This result contradicts the recent theoretical prediction of the proportionality of the electrostatic persistence length of a polyelectrolyte to the inverse of C_s (i.e., $C_s^{-1/2}$). However, the formalisms of these theories were derived for sufficiently low ionic strength[18,19,20]. Recent data on the flexibility of DNA molecules in aqueous salt solutions also suggest the linear relationships between the electrostatic persistence length and $C_s^{-1/2}$ (refs 21, 22, 23).

The q values for Na–MA in theta condition (i.e., $C_s \to \infty$) and in various NaCl concentrations correspond to the values derived for sodium polyacrylate (Na–PA) in aqueous solutions. For example, q values for Na–PA ($M_w = 5 \times 10^5$) is 145 Å in 0.01M NaBr and 12.5 Å in 1.5M NaBr (theta point)[15,16,24]. On the other hand, the smaller values of q have been obtained for the copolymer of ethylacrylate and sodium acrylate (Na–EA–A) ($M_w = 10^6$) which contains the hydrophobic side chains (ester groups): 27 Å in 0.01 M NaCl and 5.5 Å in 1.2 M NaCl (theta point)[24,25]. The similar values of q for Na–MA and Na–PA suggest that both polymers have comparable flexibility in aqueous solutions. On the basis of this result, the hydrophobic effects which cause the polymer coils to shrink are cancelled out by the high affinity of the oxygen atom in the ethyl ether side chain to water as described in the previous section.

ACKNOWLEDGEMENTS

The author thanks Dr. A. Minakata for stimulating discussions and for helpful criticisms of the manuscript.

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