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Dissociation Behavior of an Alternating Copolymer of Isobutylene and Maleic Acid by Potentiometric Titration and Intrinsic Viscosity

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ABSTRACT: The potentiometric titration and the intrinsic viscosity of the alternating copolymer of isobutylene and maleic acid were measured to study its dissociation behavior under various conditions. The results of the potentiometric titration show that the carboxyl groups in the copolymer appear to dissociate in two steps without any abnormal behavior due to the hydrophobic effect of the two methyl groups in the isobutylene units over the entire range of the degree of dissociation. The intrinsic viscosity of this copolymer has a clear maximum nearly at a half of the degree of dissociation and a linear relationship to the reciprocal square root of the concentration of the added salt. The dissociation behavior of this alternating copolymer is discussed in terms of the short-range and the long-range electrostatic interaction of the dissociation groups by the use of a linear Ising model. It is found that the model calculation is in better agreement with the experimental results if either a lower dielectric constant or hydrogen bonding between the nearest-neighbor carboxylic groups is assumed.

Introduction

The solution properties of the alternating copolymers of maleic acid with the hydrophobic monomers such as alkyl vinyl ethers or styrene have been studied in great detail by Strauss et al.[1] and Sugai et al.[2] Their primary concerns were in most cases the interrelation between the hydrophilic and the hydrophobic effects on various kinds of solution properties of such copolymers. Some exhibit clear evidence of a conformational transition from a compact globule to an extended coil upon increase of the degree of dissociation, α, of the carboxyl group in the maleic acid units. According to the results obtained by Dubin and Strauss[3] on the alternating copolymers of maleic acid with alkyl vinyl ethers, such a conformational transition seems to become clearer as the number of the carbons in the alkyl substituent becomes larger; for example, the alternating copolymer of maleic acid with octyl vinyl ether has a clear conformational transition whereas that with ethyl vinyl ether does not.[4] Similar phenomena are also observed in a certain poly(carboxylic acid) having hydrophobic substituents such as poly(methacrylic acid), PMeA,[5] which carries a methyl group at the α-position of COOH. However, such a conformational transition of poly(carboxylic acid) homopolymers seems to be caused by a very subtle change in the conditions, since the homologous polyacid, poly(crotonic acid), PCA, having a methyl group at the β-position, does show little sign of such a conformational transition.[6] These observations may suggest that besides the size of the hydrophobic group its arrangement in a polymer chain may be an important factor for such a conformational transition.

From another point of view it is also interesting to elucidate why the dissociation of the carboxyl groups in the alternating copolymers of maleic acid appears in two steps, since these copolymers must have the same linear charge densities as those of the common vinylic poly(carboxylic

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acids) such as poly(acrylic acid), PAA, if the charges are regarded to be smeared uniformly over a whole chain. It is also closely related to the subject of the effect the variation of the local charge distribution may have on the dissociation of the polyelectrolytes. The dissociation behavior of these alternating copolymers of maleic acid has been in general discussed as poly(dicarboxylic acids) with two successive intrinsic dissociation constants, one being more acidic than the other. If the dissociation process can be divided clearly into two parts at $\alpha = 0.5$, for example, the first dissociation process with a larger dissociation constant was assigned to the region of $\alpha < 0.5$ and the second with a smaller one to that of $\alpha > 0.5$. Thus the dissociation behavior at each region could be analyzed in terms of the rod model[7-9] with the smeared charges, which was successfully applied to the dissociation of PAA and PMeA by Nagasawa et al.[10,11] In some cases α is assumed even to range from 0 to 2 for convenience.[3,12]

On the other hand Minakata et al.[13,14] recently proposed another approach to analyze the dissociation behavior of these maleic acid copolymers. According to them, the apparent two-step dissociation should result from the unequal intercharge distances along a chain so that it can be interpreted on the basis of a linear Ising model with the short-range electrostatic interaction for the calculation of the activities of the carboxyl groups in the dissociated and the undissociated states, respectively, in addition to the long-range electrostatic potential. In their calculation the charges on a polyacid are not to be smeared but to be arranged at discrete positions in a polymer chain. Thus their method seems to be suitable for the analysis of dissociation behavior of the polyelectrolytes with lower densities of the dissociation groups such as hyaluronic acid reported by Cleland.[15]

We have reported the dissociation behavior of poly(maleic acid), PMA, and its stereoisomer, poly(fumaric acid), PFA, both of which have exactly twice as high charge densities as PAA.[16,17] It is found that they also appear to dissociate in two steps and that the two-step dissociation of PMA is clearer than that of PFA although they have the same structural formula –[CH(COOH)CH(COOH)]–. Moreover, the analysis reveals that the smeared charge model with a cylindrical symmetry is inapplicable to their dissociation behavior even at $\alpha < 0.5$ where their charge densities should be the same as those of the common vinylic polyacids. This is an unexpected conclusion because the smeared-charge rodlike model has been considered to be better for PMA and PFA than for the vinylic polyacids owing to their higher charge densities, probably in addition to the stiffer character of their chains, although such a model is not expected to describe the two-step dissociation. Taking into account the unequal distances between the neighboring carboxyl groups in the discrete model as done by Minakata et al.,[13,14] their characteristic dissociation behavior may be interpreted qualitatively on the assumption of their configurations reasonably expected from their preparation methods,[18] which have not been determined yet.

The purpose of this paper is to present the details of the dissociation behavior of the alternating copolymer of isobutylene and maleic acid, abbreviated here as PIM, measured by potentiometric titration and intrinsic viscosity, to analyze them on the basis of both the model with the smeared and with the discrete charge, respectively, and to discuss the characteristic dissociation behavior of the copolymer from the viewpoint of the electrostatic interaction as well as the hydrophobic interaction. Then these results are compared with the dissociation behavior of the other polyacids such as poly(carboxylic acids) or the alternating copolymers of maleic acid. It should be noted here that the chemical composition of PIM is the same as those of PMeA and PCA, although the two methyl and the two carboxyl groups in PIM are situated closer to each other, respectively, as represented by $-[CH_2C(CH_3)_2CH(COOH)CH(COOH)]-$.

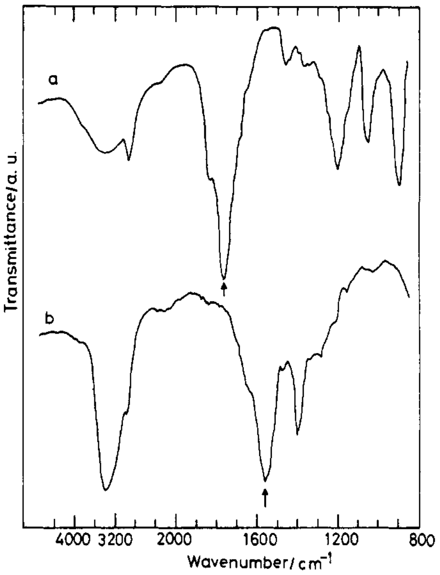

Figure 1. IR spectra of (a) an alternating copolymer of isobutylene and maleic anhydride and (b) the sodium salt of PIM. The absorbance depicted by arrows are explained in the text.

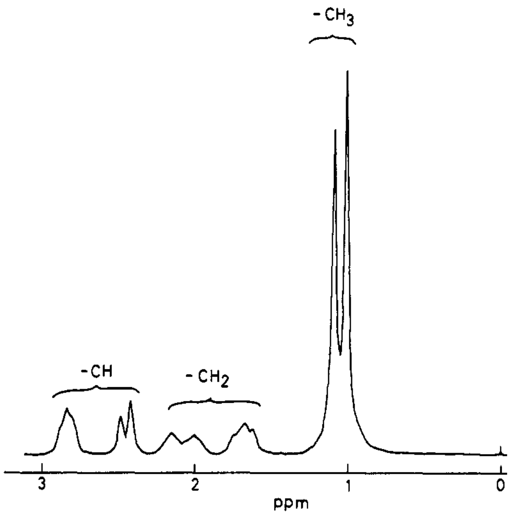

Figure 2. ^{1}H NMR spectrum, 270 MHz, of PIM in D_2O.

Experimental Section

Materials. The sample PIM used here was prepared by alkali hydrolysis of the corresponding alternating copolymer of isobutylene and maleic anhydride, supplied from Kuraray Co., commercially available as "ISOBAN-10", whose nominal molecular weight is $(1.5–1.6) \times 10^5$. The hydrolysis was carried out by keeping the anhydride polymer in 0.8 N NaOH solution at 60 °C under stirring in the Ar atmosphere for 4 h. The solution mixture after hydrolysis was dialyzed against water repeatedly and then passed through a mixed bed of ion-exchange resins to convert COONa into COOH in PIM.

The conversion of anhydride into carboxylate was confirmed qualitatively by IR spectra of the polymer before and after hydrolysis as shown in Figure 1 measured with a JASCO infrared spectrophotometer type A-3. From these IR spectra, it is observed that after hydrolysis the strong absorbance at 3300 cm^{-1} characteristic for the stretching vibration of the carboxylate appears and the absorbance of the carbonyl shifts from 1760 to 1560 cm^{-1}.

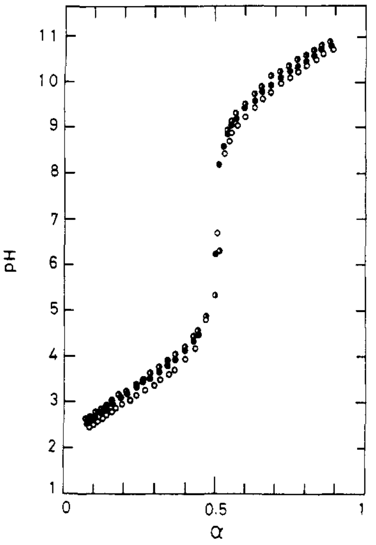

Figure 3. Normalized titration curves of PIM in NaCl solutions at C_s = 0.010 (◑), 0.050 (●), and 0.100 N (○).

Moreover the chemical composition of PIM was determined by a 270-MHz FT-NMR spectrometer of JEOL type GX-270 after hydrolysis. ^{1}H NMR spectrum of PIM in D_2O is shown in Figure 2 where the ratio of the area under the peak of CH_2 in the isobutylene unit to that of CH in the maleic acid unit is 1.04, in good agreement with the expected value. Therefore it is concluded that the sample PIM used here has the almost completely alternating sequences of isobutylene and maleic acid.

The solutions of PIM were prepared by passing them again through a mixed bed of ion-exchange resins and adding the required amount of the salt to them just before measurements. The concentrations of PIM, C_p, were usually 0.02–0.03 N for titration and the initial Cp's for viscometry were 2.5–0.5 g/dL depending on α and the concentration of added salt, C_s, ranged from 0.01 to 0.5 N. Most of the measurements were done by the use of NaOH as a titrant and NaCl as an added salt. In order to examine the effect of the type of counterion on the titration behavior, Li^+ and K^+ were also used for Na^+.

Potentiometric Titration and Viscometry. The potentiometric titration was carried out with a digital pH meter Model 225 of Iwaki Glass Co. with a glass electrode IW051 at room temperature, maintained nearly constant around 25 °C. The end point of the titration was determined after correcting for the activity of a proton by the blank titration since it was not clear enough to show a point of inflection in the titration curve. The details of the procedures in the titration experiments were reported previously.[16,17]

The intrinsic viscosity [η] was determined at 25.0 °C by a modified type of Ubbelohde dilution viscometer at different C_s's and α's in the same way as described previously.[17] The shear-rate dependence of [η] was found to be negligible even under the most viscous conditions.

Results

Some examples of normalized potentiometric titration curves of PIM at different C_s's in NaCl solutions are shown in Figure 3 as the plot of pH against α, from which PIM appears to dissociate in two steps in the same way as PMA[17] or the other alternating copolymers of maleic acid.[1,2] In addition, it is noted that at lower α there is neither precipitation in the PIM solution nor abnormal behavior in the titration curves and that even at higher α the PIM solution does not become turbid in contrast to PMA which causes precipitation in the region of higher α as reported previously.[17]

In general the apparent dissociation constant K_a defined by

$$pK_a = pH + \log [(1 - \alpha)/\alpha] \qquad (1)$$

is used to analyze the titration behavior of polyelectrolytes.

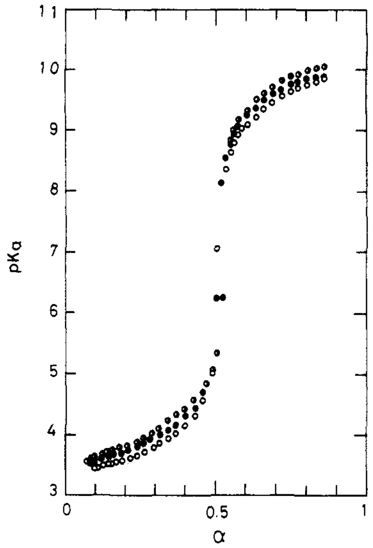

Figure 4. Plot of the pK_a of PIM against α at different C_s's. The symbols are the same as in Figure 3.

It is not constant but usually increases with α due to the electrostatic interaction between a proton dissociating and the ionized groups carried by a polyelectrolyte chain. Therefore pK_a can be expressed by the sum of two terms as

$$pK_a = pK_0 + (0.4343/RT)(dG_{el}/d\alpha) \qquad (2)$$

where pK_0 is the intrinsic dissociation constant independent of α, G_{el} is the electrostatic free energy of dissociation of a mol of proton which is a function of α, R, the gas constant, and T, the absolute temperature. Figure 4 is replotted according to eq 2 for the same results as in Figure 3. The apparent two-step dissociation is clear in this figure as well as in Figure 3. The plot of pK_a vs α for PIM is found not to show any sign of abnormal behavior in contrast to those of the hydrophobic polyacids such as PMeA[5] or the alternating copolymer of maleic acid with styrene,[2] both of which show characteristic inversed S-shape curves at α < 0.5 due to the conformational transition of these polymer chains caused by interrelation of the hydrophobic and the electrostatic interactions. In Figure 4 the point of inflection of pK_a in the middle of neutralization may as well be regarded as a α = 0.5, within the experimental errors arising mainly from the ambiguity of the end point in the titration.

The application of eq 2 in Figure 4 gives the intrinsic dissociation constant pK_0 of PIM to be 3.31 ± 0.05, almost independent of C_s and the type of the cation, as summarized in Table I, where the data for the other polyacids and the low molecular weight organic acids with the similar molecular structures are also cited from the literatures for comparison. The value of pK_0 of PIM seems to be slightly smaller than that of PMA or PFA,[17] and much smaller than that of PMeA or PCA.[6] By comparison with the data including the low molecular weight organic acids,[19] it can be concluded that the existence of the hydrophobic methyl groups near the COOH groups does not affect the value of pK_0 so much, but the neighboring COOH as a hydrophilic group lowers pK_0 of COOH in question to a great extent.

The electrostatic term of pK_a, ΔpK, can be separated as

$$\Delta pK = pK_a - pK_0 = (0.4343/RT)(dG_{el}/d\alpha) \qquad (3)$$

The typical plot of ΔpK at C_s = 0.100 N NaCl is shown in Figure 5, where for comparison the data of the other

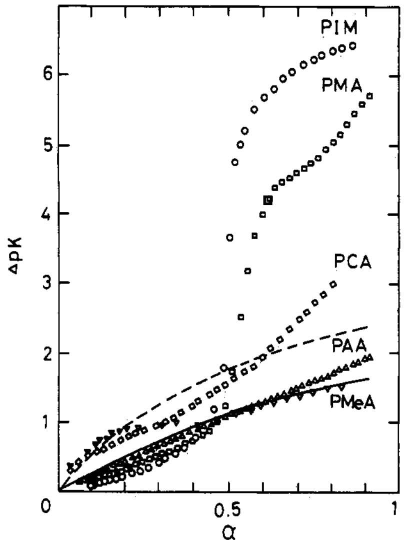

Figure 5. Plot of ΔpK vs α at $C_s = 0.100$ N NaCl for PIM (○), PAA (△),[17] PMeA (▽),[6] PCA (◇),[6] and PMA (□),[17] respectively. The solid line for PIM, PAA, PMeA, and PCA and the broken line for PMA are the curves calculated from a rod model with the smeared charges. The parameters used for calculation are shown in the text, except for PMA whose linear charge density is twice as high as that of the other polyacids.

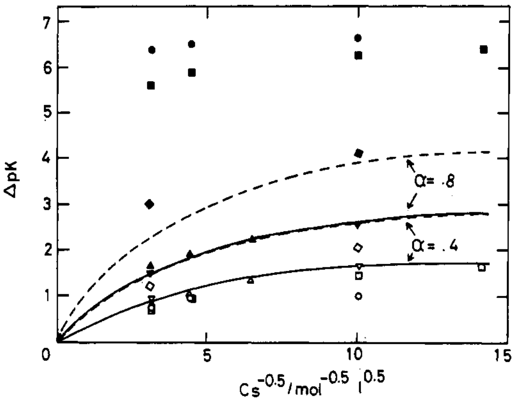

Figure 6. Dependence of ΔpK upon C_s at $\alpha = 0.4$ (open symbols) and at $\alpha = 0.8$ (filled symbols). The symbols and the lines are the same as in Figure 5.

polyacids are also reproduced from the literatures cited. It is found that among the polyacids shown here PIM is the least dependent upon the electrostatic interaction at lower α, has the most remarkable jump of ΔpK around $\alpha = 0.5$, and then is the most strongly affected by the electrostatic interaction at higher α. The dependence of ΔpK upon C_s is also shown in Figure 6 where all the data points were obtained by interpolation in similar plots to those in Figure 5.

Figure 7 shows the titration curves for Li^+ and K^+ as counterions in comparison with that for Na^+ in the salt solutions of the corresponding alkali metal chlorides at $C_s = 0.100$ N. There seems to be little difference in pK_a among them at $\alpha < 0.5$ but at $\alpha > 0.5$ the difference seems to be enlarged. By more precise examination, the value of pK_a is found to be slightly larger as the cation size increases over the whole region of α. This tendency is the same as that of PAA reported by Gregor et al.[20] but at lower α the tendency may be different from that of PMA,[17,21] which, in contrast, is slightly smaller at lower α as the cation size increases while the tendency at higher α is the same as that of PIM or PAA. The complicated dependence of pK_a upon the type of the cation has been interpreted partly by its accessibility to a polyion and partly by its hydration state.[20,21]

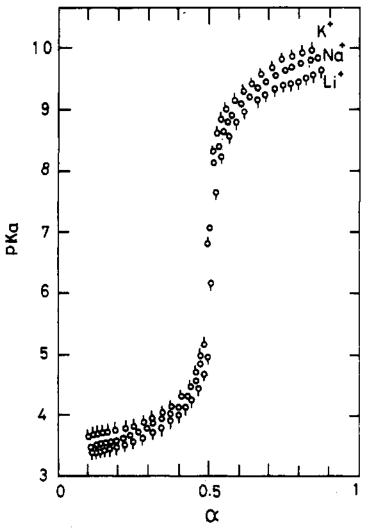

Figure 7. Plot of pK_a vs. α with Li^+ (♀), Na^+ (○), K^+ (ȯ) as counterion in the corresponding alkali-metal chloride solution at $C_s = 0.100$ N.

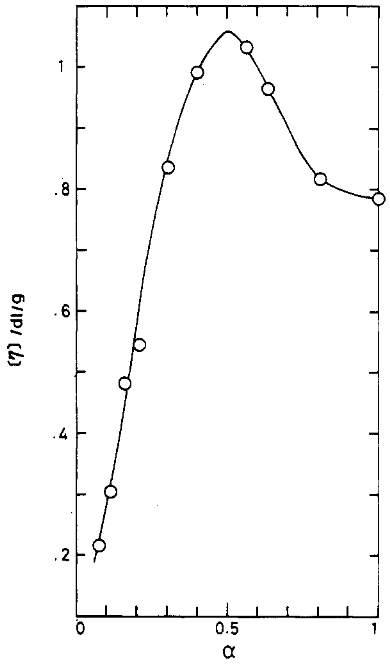

Figure 8. Dependence of $[\eta]$ of PIM upon α at $C_s = 0.100$ N NaCl.

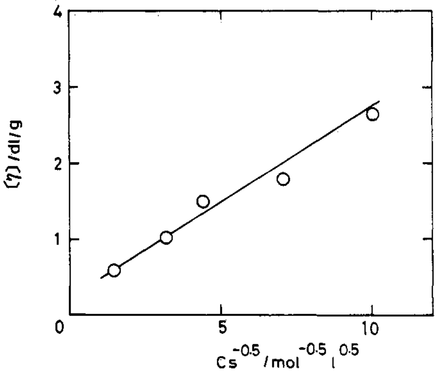

Figure 9. Dependence of $[\eta]$ of PIM upon C_s at $\alpha = 0.57$ in NaCl solution.

Figures 8 and 9 are the results of viscometry as the plot of $[\eta]$ vs. α and that of $[\eta]$ vs. $C_s^{-1/2}$, respectively. At constants C_s in Figure 8, $[\eta]$ increases with α up to $\alpha = 0.5$, attains a maximum nearly at $\alpha = 0.5$, and beyond it decreases noticeably. This behavior of $[\eta]$ during the course

Table I
Intrinsic Dissociation Constant

acid	cation	C_s/N	pK_0	pK_{0_1}	pK_{0_2}	ref
PIM	Na$^+$	0.100	3.25	2.95	9.2	
		0.050	3.31	2.98	9.3	
		0.010	3.35	3.03	9.3	
	Li$^+$	0.100	3.25	2.95	9.1	
	K$^+$	0.100	3.37	3.05	9.3	
		av	3.31 ± 0.05	3.00 ± 0.05	9.2 ± 0.1	this work
			3.02[a]	2.72	8.83	23
PEM[b]			3.95[a]	3.65	6.40	23
PPM[c]			3.70[a]	3.40	7.40	23
PMA			3.50	3.20	7.9	17
PFA			3.50	3.20	6.2	17
PAA			4.13			17
PMeA			4.8[d]			6
PCA			4.7[d]			6
propionic acid			4.87			19
n-butyric acid			4.82			19
isobutyric acid			4.85			19
malonic acid			3.16[a]	2.86	5.70	19
succinic acid			4.51[a]	4.21	5.64	19

[a] Estimated from pK_{0_1} in the reference cited. [b] Alternating copolymer of maleic acid with ethylene. [c] Alternating copolymer of maleic acid with propylene. [d] Extrapolated value to $\alpha = 0$ in Figure 2A of ref 6.

of dissociation is quite similar to that of PFA[17] except the fact that the PIM solution does not become turbid over the entire region of α while in the solution of PFA or PMA the precipitation of the polymer occurs even at higher α.[17] The dependence of $[\eta]$ upon C_s at $\alpha = 0.57$ shown in Figure 9 indicates that a linear relationship between $[\eta]$ and $C_s^{-1/2}$ holds within the experimental conditions in the same way as that of PAA reported by Noda et al.[22]

Discussion

From the present experimental results of both the potentiometric titration and the intrinsic viscosity it is concluded that the hydrophobic effect of the two methyl groups adjacent to one of the carboxyl groups in PIM is not so remarkable as to cause any conformational transition of a polymer chain since such an inversed-S-shaped curve was not detected in the plot of pK_a or that of $[\eta]$, against α, respectively, even at the region of low α as often found in the other hydrophobic polyacids. This conclusion may be also supported by the following findings: the solubility of PIM at low α in NaCl solution is high enough to keep the solution homogeneous without any aggregates and the addition of a small amount of methanol, known as a breaker of the hydrophobic bonding, to the 0.100 N NaCl solution of PIM does affect to a small degree the titration curve. Probably it will be able to be determined more directly by the other spectroscopic measurements that there exists no hydrophobic effect of the methyl groups of PIM. Thus the absence of the hydrophobic interaction in PIM suggests, together with the results of the other poly(carboxylic acids) in the literatures, that the apparent hydrophobicity of the methyl group situated at the β-position of COOH in PIM or PCA is too weak to cause any abnormal phenomena at lower α in contrast to the methyl group at the α-position in PMeA which is known to be hydrophobic enough to bring about a definite conformational transition from a compact globule to an extended coil.[5] The reason is not clear but it may be possibly that the methyl groups in the former are interposed by the hydrophilic COOH groups on both sides which prevent them from stacking up enough to form a stable compact globule at lower α in comparison with the latter.

It is noteworthy to refer to the dependence of the pK_a of PIM on the type of cations at $\alpha > 0.5$, shown in Figure 7, which is found to be quite different from that of PMA reported in the previous papers.[17,21] While the pK_a of PIM in the present study has only a slight dependence on the type of cations, the latter depends much more strongly on it where the difference in pK_a of PMA, for example, between Li$^+$ and K$^+$ at the same C_s as in Figure 7 amounts to more than 2 pH units at $\alpha = 0.9$,[17] which is sure to be one of the largest among the differences in pK_a of polyelectrolytes with different alkali cations ever observed. This difference between the behavior of PIM and that of PMA may give another clue to the occurrence of such dependence of pK_a. Taking into account both their local and overall charge densities, it is concluded that the dependence of pK_a on the type of cations becomes much greater as the overall charge density of the polyacid becomes higher. This is closely related to the fact that the larger cations such as K$^+$ have less access to the polyelectrolyte chain whose ionization groups are more densely arranged. In addition, it is probable that the variation in the states of hydration of the polyelectrolytes by the neutralization with alkali metal ions should also affect the dissociation process to a greater extent if the overall charge density on the polyelectrolyte is higher. These presumptions are in accordance with the conventional interpretation of such observations from the viewpoints of the effect of the cation.[20,21]

The potentiometric titration of vinylic poly(carboxylic acids) such as PAA or PMeA[10,11] especially at higher α have been successfully interpreted by a rod model with smeared charges whose electrostatic surface potential can be calculated by direct solution of the Poisson–Boltzmann equation with the aid of a computer.[7-9] The comparison of the experimental results of the potentiometric titration of PIM with the calculated values based on the rod model by Kotin et al.[7] is given in Figures 5 and 6 together with those of the other polyacids, where the diameter and the line charge density at $\alpha = 1$ along an axis of the rod are 0.55 nm and 3.98 nm^{-1}, respectively, which are the same as for PAA, PMeA, and PCA. In these figures, it is found that at $\alpha < 0.5$ the experimental data of PIM are below the calculated ones in the same way as those of PMA and PFA reported previously[17] whereas those of PCA and PMeA deviate above the calculated lines and those of PAA are nearly on the lines. Moreover, at $\alpha > 0.5$ the experimental data of PIM are far above the calculated curve, which is in good agreement with those of PAA and PMeA. It is concluded, therefore, that the calculation based on

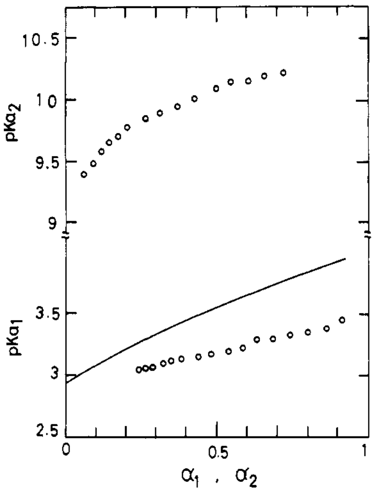

Figure 10. pK_{a_1} and pK_{a_2} of PIM at $C_s = 0.100$ N NaCl. The solid line is calculated from a rod model with the smeared charges. The parameters used are the same as in Figure 5.

a rod model with the smeared charges is not in agreement with the dissociation behavior of PIM at all. We will discuss briefly the dissociation behavior of PIM at lower α in the latter part of the present paper again.

In Figure 5 ΔpK of PIM is lowest at $\alpha < 0.5$ and highest at $\alpha > 0.5$. This means that at the earlier stage of the dissociation, the COOH groups in PIM are the easiest to dissociate under the least electrostatic interaction from the COO^- already dissociated, while at higher α the dissociation of COOH seems to be the most suppressed by the strong electrostatic effect of the existing COO^- groups. The reason for the remarkable inversion in ΔpK is not clear but may be attributed to the definite pairing of the COOH groups in the same maleic acid unit, presumably in addition to the existence of the two hydrophobic methyl groups adjacent to one of the COOH groups in PIM.

It may be natural to question whether the carboxyl groups should be regarded as the same kind or not, just like the rod model discussed above. Dubin et al.[3] and later Ohno et al.[12] derived elaborate equations to describe the dissociation of the alternating copolymers of maleic acid, on the assumption that they are dibasic polyacids which have two different intrinsic dissociation constants, K_{0_1}, and K_{0_2}. Alternatively, as mentioned in the Introduction, if K_{0_1} is much larger than K_{0_2}, then it is possible to separate the dissociation process into two parts at an inflection point, $\alpha = 0.5$ in Figure 3. Then we can redefine the degree of dissociation, α_i, and the apparent dissociation constant, K_{a_i} at each region, respectively (i = 1 or 2). The plots of pK_{a_i} vs α_i are shown in Figure 10. The values of pK_{0_i}, estimated by extrapolation at $\alpha_i = 0$, are also shown in Table I. It is noted that the value of pK_{0_1} should be smaller by log 2 than that of the corresponding pK_0 by definition.[17] The value of pK_{0_1} of PIM estimated here is a little larger than that of the corresponding pK_0 by definition,[17] reported by Bianchi et al.[23] while pK_{0_2} in the present study is smaller than their value as shown in Table I. However, in Figure 3 of ref 23 where the plot of pK_{0_i} vs. number of carbon atoms in the olefin unit is shown, only the data points of PIM deviate slightly from the line representing the tendency of the data of the alternating copolymers of maleic acid with various olefins. If the value of pK_{0_1} determined in the present study is put on the plot instead of their data, all the data seems to be just on the same line. Judging from such tendency, the values determined here seem more reasonable.

In Figure 10 there is still a large deviation of pK_{a_1} downward from the calculated curve by a rod model with the smeared charges in the same way as in Figure 5. Although the reason is not clear, a slower increase in pK_a or pK_{a_1} of PIM at lower α seems to be common to the polyacids having maleic acid units like PMA as pointed out previously.[17] Thus it could be ascribed to the existence of the carboxyl group in the nearest-neighbor carbon in the main chain, the effect of which may presumably be transduced either by the stronger dipole–charge interaction or by the possible formation of a hydrogen bond.

The distribution of the COOH groups along the main chain of PIM is not so uniform as in PMeA or PCA since the two COOH groups in the same unit of maleic acid are closer to each other than those in the different units. It is easily presumed that the interaction between the nearest-neighbor COOH groups should be much stronger. Thus in order to elucidate the characteristic dissociation behavior of PIM, it is necessary to introduce explicitly the electrostatic short-range interaction in the model which has essentially discrete rather than uniform charge distribution in such a rod model with the smeared charges as examined above. We adopt here the method of the Ising model which was applied to the analysis of the potentiometric titration of the alternating copolymer of maleic acid with ethyl vinyl ether.[13] In the present study we take into account the interaction up to the second nearest neighbor as the short-range interaction. The grand partition function, Ξ, of PIM which has N units of maleic acid is[13]

$$\Xi = a_0^{2N}\mathbf{E}(\mathbf{M}\mathbf{M}')^{N-1}\mathbf{M}\mathbf{A} \qquad (4)$$

where a_0 is the activity of the undissociated COOH. The vectors, **E**, **A**, and the matrixes, **M**, **M**′, are defined by

$$\mathbf{E} = (1 \quad 1 \quad 1 \quad 1) \qquad \mathbf{A} = (1 \quad 1 \quad a \quad a)^{\mathrm{T}} \qquad (5)$$

and

$$\mathbf{M} = \begin{bmatrix} 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ a & va & 0 & 0 \\ 0 & 0 & ua & uva \end{bmatrix} \qquad \mathbf{M}' = \begin{bmatrix} 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ a & v'a & 0 & 0 \\ 0 & 0 & u'a & u'v'a \end{bmatrix} \qquad (6)$$

respectively, where the superscript T means a transposed vector or a matrix, a is the ratio of the activity of the dissociated COO^- to a_0, u, v, u', and v' are the statistical weights of the electrostatic interactions assumed to be

$$u = \exp[-e^2/(DkTR_{2i-1,2i})]$$

$$v = \exp[-e^2/(DkTR_{2i-1,2i+1})]$$

$$u' = \exp[-e^2/(DkTR_{2i,2i+1})]$$

$$v' = \exp[-e^2/(DkTR_{2i,2i+2})] \qquad (7)$$

e is the elementary charge, D is the dielectric constant, k is the Boltzmann constant, and $R_{i,j}$ is the distance between the ith and the jth carboxyl groups from an end of the PIM chain. The degree of dissociation, α, can be derived by the common procedure of statistical mechanics as

$$\alpha = (1/2)(\mathrm{d}\log\lambda_1/\mathrm{d}\log a) \qquad (8)$$

since Ξ is approximately equal to λ_1^N for sufficiently large N where λ_1 is the largest eigenvalue of the matrix product **MM**′. The contribution of the interaction to ΔpK is divided, for convenience, into two terms as follows:

$$\Delta pK = \Delta pK_{\mathrm{short}} + \Delta pK_{\mathrm{long}} \qquad (9)$$

where the term $\Delta pK_{\mathrm{short}}$ due to the short-range interaction, up to the second nearest neighbor, in the present study is

$$\Delta pK_{\mathrm{short}} = \log a + \log[(1-\alpha)/\alpha] \qquad (10)$$

$$\mathbf{M} = \begin{bmatrix} h & h & h & h & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & h & h & h & h & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 \\ ha & ha & hva & hva & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & a & a & va & va & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & ua & ua & uva & uva \end{bmatrix}$$

$$\mathbf{M}' = \begin{bmatrix} 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & a & 0 & 0 & 0 & a & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & v'a & 0 & 0 & 0 & v'a & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & a & 0 & 0 & 0 & a & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & v'a & 0 & 0 & 0 & v'a & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & u'a & 0 & 0 & 0 & u'a & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & u'a & 0 & 0 & 0 & u'a \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & u'v'a & 0 & 0 & 0 & u'v'a \end{bmatrix}^{\rm T} \quad (14)$$

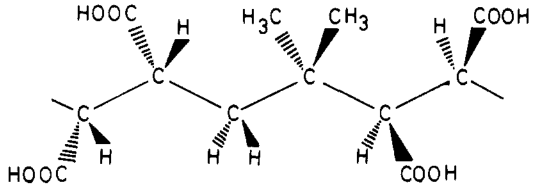

Figure 11. Schematic configuration of COOH along a PIM chain.

and $\Delta pK_{\rm long}$ due to the longer range interaction beyond it is

$$\Delta pK_{\rm long} = (0.4343/kT)\sum_{i,j}\alpha(e^2/DR_{i,j})\exp(-\kappa R_{i,j}) \quad (11)$$

where the summation is done over the possible pairs of i and j not counted in $\Delta pK_{\rm short}$ in eq 10. The following two assumptions are included implicitly in eq 11; the uniform dissociation of COOH and the Debye–Hückel potential with the Debye length κ^{-1}.

For calculation of the parameters u, v, u', and v' in eq 7, it is necessary to determine the distances between the carboxyl groups. We assume that a main chain of PIM has the extended trans zigzag conformation and that the COOH groups in the same maleic acid unit are as close to each other as possible but in the different units are separated as far as possible and that a proton of COOH or a charge of COO$^-$ is situated in the middle between two oxygen atoms. The schematic arrangements of the dissociation groups are depicted in Figure 11. From the following molecular parameters,

$$\text{C–C, 0.154 nm; C–O, 0.130 nm; } \angle\text{C–C–C, } 109°; \quad \angle\text{O–C–O, } 122°; \angle\text{O–C–C, } 119° \quad (12)$$

the distances between the carboxyl groups are

$$R_{2i-1,2i} = 0.351 \text{ nm} \qquad R_{2i-1,2i+1} = R_{2i,2i+2} = 0.607 \text{ nm} \qquad R_{2i,2i+1} = 0.604 \text{ nm} \quad (13)$$

The value of λ_1 at a given a is determined by a computer with a power method and then the derivative in eq 8 is calculated by the ratio of an increment of λ_1 to the increase by 10^{-4}% in a to determine α. Moreover, in order to calculate the long-range interaction by eq 11, we must also know the exact distribution of the distances between the carboxyl groups. However, since the segment distribution of such a flexible polyelectrolyte chain with the electrostatic excluded volume effect is not yet known exactly but probably is a complicated function of α,[22] the conformation of a chain is assumed to be fixed in the same arrangement as in Figure 11 over a whole chain at every step of the dissociation. Thus the evaluation of eq 11 by the direct summation over the rodlike conformation was carried out without averaging until the relative increase in $\Delta pK_{\rm long}$ becomes less than 1% by addition of the next term. This approximation seems to be crude but might be supported partly by the findings by Muroga et al.[24] that the local conformation of a polyelectrolyte chain changes little during the course of neutralization from the measurements of small-angle X-ray scattering. The assumption of the uniform dissociation in eq 11 is also not true but the effect of nonuniform dissociation does not so seriously affect the results of the calculation of $\Delta pK_{\rm long}$.

Taking the value of D as the same as in the bulk medium at 25 °C, 78, ΔpK thus calculated is shown by a broken line in Figure 12 together with $\Delta pK_{\rm short}$ and $\Delta pK_{\rm long}$ by dotted lines. From this figure it is clear that the essential contribution to the characteristic dissociation of PIM is the term $\Delta pK_{\rm short}$ as expected, although the magnitude of $\Delta pK_{\rm long}$ is still as large as that of $\Delta pK_{\rm short}$. However, the agreement of the calculation with the observed values is not satisfactory. Strictly speaking we are concerned with the short-range interaction between the carboxyl groups so close to each other that the dielectric constant D involved in eq 6 may be different from that in the bulk but we do not have any knowledge about the exact value of D at the molecular level. Therefore we tentatively select D as 15 only in the parameter u in eq 7, the statistical weight due to the shortest interaction between a proton and COO$^-$ in the same unit of maleic acid, and the other values of D in eq 7 and 11 are assumed as the same value as in the bulk. The recalculated values are shown in Figure 12 by a solid line. Comparing this with the broken line in the same figure, the agreement of the calculation with the experimental results is found to be improved to a great extent by introducing the lower dielectric constant only in the vicinity of the carboxyl group.

Another factor we must consider is the possible formation of a hydrogen bond between a pair of carboxylic groups in the same unit of maleic acid.[21] In fact there is some evidence for it in the ultraviolet and the infrared spectra of the PIM solution[25] in contrast to those of PAA in which it was confirmed by Leyte et al.[26] that there is no hydrogen bonding over the whole range of α. Therefore if we introduce the possibility of hydrogen bonding between COOH and COOH and between COOH and COO$^-$ in the same unit of maleic acid,[27] the matrixes **M** and **M′** in eq 6 are transformed to eq 14, and the vectors **E** and **A** are consequently transformed to

$$\mathbf{E} = (1 \;\; 1 \;\; 1 \;\; 1 \;\; 1 \;\; 1 \;\; 1)$$

$$\mathbf{A} = (1 \;\; 1 \;\; 1 \;\; 1 \;\; 1 \;\; 1 \;\; 1 \;\; 1 \;\; a \;\; a \;\; a \;\; a \;\; a \;\; a \;\; a \;\; a)^{\rm T} \quad (15)$$

The states corresponding to the row and the column of matrix **M** in eq 14 are

$$\mathbf{S}_{\rm r} = \begin{bmatrix} \text{H} & \text{H} & 0 & 0 & -\text{H} & - & - \\ | & | & | & | & | & | & | \\ \text{H} & -\text{H} & 0 & - & \text{H} & 0 & - \end{bmatrix} \quad (16)$$

$$\mathbf{S}_c = \begin{bmatrix} H & H & H & H & 0 & 0 & 0 & 0 & -H & -H & -H & -H & - & - & - & - \\ | & | & | & | & | & | & | & | & | & | & | & | & | & | & | & | \\ H & 0 & -H & - & H & 0 & -H & - & H & 0 & -H & - & H & 0 & -H & - \end{bmatrix}^T \qquad (17)$$

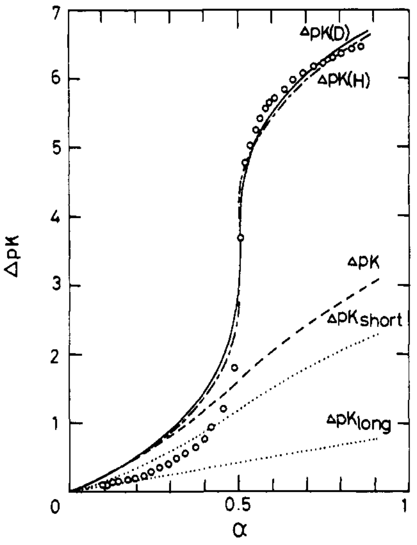

Figure 12. Comparison of calculation based on Ising model with the same experimental ΔpK (○) of PIM as in Figure 5. Lines are calculated by models, ΔpK without hydrogen bond at $D = 78$ (broken line), ΔpK(D) without hydrogen bond at $D = 15$ in the nearest neighbors (solid line), and ΔpK(H) with hydrogen bond between the nearest neighbors at $D = 78$ (chain line), respectively. Dotted lines are ΔpK_{short} and ΔpK_{long} for model calculation without a hydrogen bond at $D = 78$ with ΔpK represented by a broken line.

for the carboxyl groups in the same unit and as in eq 17 for those in the adjacent units. In $\mathbf{S}_r$ and $\mathbf{S}_c$, H, –H, 0, and – represent the hydrogen bonded, the hydrogen bonded and charged, the noncharged, and the charged states, respectively. Strictly speaking there should be some difference in the states of the hydrogen bonds between the uncharged–uncharged groups and the charged–uncharged groups, but in the present study as a first approximation all the parameters, h's in eq 14, the statistical weight due to the hydrogen bonding, are assumed as the same and defined by

$$h = \exp(-H/RT) \qquad (18)$$

where H is the apparent energy of hydrogen bonding per mole. To compare with the experimental results, the curves calculated on the model with the hydrogen bonding are shown by a chain line in Figure 12, where H is adjusted to be –21 kJ/mol. It is found that the effect of the hydrogen bonding also enables the model calculation to agree better with the experimental data although the value of H adopted here seems much larger than expected. In conclusion, if either the lower dielectric constant than that in the bulk or the possibility of the formation of a hydrogen bond is assumed only in the shortest interaction between a pair of carboxyl groups in the same unit of maleic acid, the calculation based on the linear Ising model can interpret satisfactorily the results of the potentiometric titration of PIM. In practice it is probable for both effects to overlap on the dissociation behavior of PIM. From precise examination, there still exists some deviation of the calculated curves at $\alpha < 0.5$ from the experimental data, which should arise from the crude approximations adopted in the present model; the errors involved at lower α may be presumably due to the statistical weights for the electrostatic interaction in eq 7 and 11, the nonaveraging procedure of the distribution of the dissociation group, and the assumption of both the uniform dissociation and the extended zigzag conformation of a PIM chain in eq 11.

The electrostatic long-range interaction which plays a dominant role in $[\eta]$ of a flexible polyelectrolyte chain is to be regarded as the electrostatic excluded volume effect at least at $C_s > 0.01$ N.[22] However, we did not have yet any explicit functional form of $[\eta]$ in terms of α but may reasonably consider that the function is to increase $[\eta]$ monotonously with increasing α. Then we have no definite reason why $[\eta]$ of PIM in Figure 8 has such a maximum nearly at $\alpha = 0.5$ despite no possibility of any conformational transition at such high α. The close relation of $[\eta]$ to the dimension of a polyelectrolyte chain, according to the Flory–Fox equation,[28] leads to the conclusion that the dimension of a PIM chain expands up to $\alpha = 0.5$ primarily by the electrostatic repulsion in the same way as PAA and contracts unexpectedly above it. The reason for contraction of a PIM chain has not yet been found but seems to be closely related to the stronger interaction between a polyion having locally higher charge densities and counterions around it, probably in addition to the effect of hydrogen bonding. Such peculiar dependence of $[\eta]$ on α is found commonly in the other maleic acid polymers such as PMA and PFA[17] or the alternating copolymer of maleic acid with styrene.[2] On the other hand, the linear dependence of $[\eta]$ on $C_s^{-1/2}$ as shown in Figure 9 is found often in polyelectrolyte solutions and can be derived form the empirical equation found by Noda et al.[22] for PAA, which is valid only for a flexible polyelectrolyte chain having rather low molecular weight as is the case in the present study.

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Phase Separation in Ternary Systems Solvent–Polymer 1–Polymer 2. 2. General Conditions for Multiple Critical Points

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ABSTRACT: Homogeneous and heterogeneous double critical points play an important role in the phase behavior of ternary systems. Criteria for these points have been derived in three ways: by two conceptually clear well-established methods (Korteweg's based on partial derivatives of free energy of mixing and Tompa's based on the shape of the critical line) and by a novel approach resting on double roots of the modified cloud-point function. Consistency of all three results proves the validity of the new approach, thus opening the way to generalizing it to critical points of higher multiplicity (a triple critical point condition is given as an example) and to systems with more than three components where the established methods fail. The present approach also improves our understanding of the phenomenon: it reveals the fundamental difference in the origin of multiplicity between the two kinds of double critical points.

1. Introduction

Most often the notion of a liquid–liquid phase equilibrium is associated with its simplest form, namely, a two-phase equilibrium that exists in a single region of the composition space of the given system. The crucial role played here by (single) critical points (CP's) is well-known. Particularly in multicomponent systems, however, the situation may be more complex: For instance, at some temperatures the two-phase equilibrium may exist in two or more distinct composition regions, separated from each other by a one-phase stable region. One can also encounter regions with multiphase equilibria (involving more than two conjugated phases). In such cases the source of this "anomalous" phase behavior can be traced to multiple CP's existing under some conditions somewhere in the system.

Mathematically speaking, multiple CP's arise as multiple roots of the set of equations defining the critical conditions. Physically, this is reflected in isothermal diagrams (e.g., in binodals) by two or more separate CP's approaching each other upon perturbation of the system variables and eventually merging into one multiple CP. Since each of the single CP's composing a given multiple CP can be either *stable or unstable* relative to the decomposition into infinitesimally close phases, one can distinguish multiple CP's of various kinds, each associated with a different type of phase behavior. For instance, the double CP's naturally fall into two categories, namely *homogeneous and heterogeneous*, depending on whether the two merging CP's are of the same type or not. This classification was proposed almost 100 years ago by Korteweg,[1] who had been studying plait points on deforming surfaces and formulated criteria for both categories in terms of partial derivatives of the surface.

Korteweg's reflections found their physical interpretation in the thermodynamics of ternary systems. Stable homogeneous double CP's (HODCP's) were located in some regular systems[2] as points of coalescence of two two-phase regions into a single one or points of disappearance of a loop-shaped two-phase region from the system. Thus, their existence is associated with the *change in the number* of distinct two-phase regions due to a change in temperature. On the other hand, the heterogeneous double CP's (HEDCP's) were found to play a crucial role in the mechanism of three-phase separation in quasi-binary ternary systems consisting of a solvent and of two fractions of the same polymer with widely differing molecular weights.[3] Consequently, they seem to be associated with the formation (or vanishing) of new regions with a *higher number of phases* than originally present. In contrast to HODCP's, the HEDCP's are not thermodynamically stable, being located on the boundary between metastable and unstable regions.

The triple CP existing in some ternary systems can be viewed as an overlap of two HEDCP's or of three single critical points (one unstable sandwiched between two stable ones). Although experimentally this case is somewhat illusive since for a quasi-binary ternary system it demands a unique chain-length ratio and a unique polymer composition, it is not unimportant: it marks the onset of systems with HEDCP's, hence, with three-phase separations. For instance, in the limiting case of $r_1 \rightarrow \infty$, the triple CP appears for the chain-length ratio $r_2/r_1 \cong 10$, and any system with the ratio higher than that will have an experimentally observable three-phase region.[3-5]

The question of multiple CP's in ternary systems has been examined in detail in both extreme simple cases: in *regular* solutions (yielding exclusively HODCP's[2]) where the nonideal behavior is strictly due to the difference in interactions between the three components and in *quasi-binary* solutions (producing exclusively HEDCP's[3,4]) where the only "ternary" factor is the difference in chain lengths between the two polymeric components. Our objective here will be to extend these considerations to the general case where both of the above features are present, i.e., to a "true" ternary system consisting of a solvent and of two chemically different polymers with different chain lengths. Obviously such a system could have either one (or both) of the double-CP types. Another objective is to develop a new way of identifying multiple CP's since the established methods rely heavily on geometrical interpretation, simple and appropriate for ternary systems but failing if the number of components becomes large. A

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