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Desolvation Effects in the Esterolysis Catalyzed by Imidazole-Containing Polymers

Hiromi Kitano, Zong-Hua Sun,† and Norio Ise*

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.
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ABSTRACT: Catalytic effects of poly(acrylic acid-*co*-*N*-acryloylhistamine) (His-AA) or a terpolymer of acrylic acid, *N*-acryloylhistamine, and *N*-acryloyl-*n*-hexylamine (C_6-His-AA) on the hydrolyses of *p*-nitrophenyl acetate (PNPA) or *N*-carbobenzoxy-L-phenylalanine *p*-nitrophenyl ester (Z-Phe-ONP) are examined at various temperatures and pressures. In the hydrolysis of PNPA, all catalysts accelerate the reaction linearly with their concentration, whereas in the hydrolysis of Z-Phe-ONP catalyzed by C_6-His-AA, a saturation phenomenon is observed because of a complexation process like enzyme catalysis due to the hydrophobic interaction between the substrate and the catalyst. By double-reciprocal plots, both the reaction rate and dissociation constant of the substrate–catalyst complex are determined. Comparison of thermodynamic parameters such as $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta V^{\ddagger}$, ΔH, ΔS, and ΔV of these polymeric reaction systems with those of imidazole-catalyzed ones shows an increase in $\Delta V^{\ddagger}$ and a decrease in $\Delta S^{\ddagger}$, which suggest the important role of the desolvation effect and the restricted conformation effect of the ionic polymer catalyst, respectively.

Introduction

Polyelectrolytes have been paid keen attention as effective catalysts like enzymes.[1,2] Among the many factors that contribute to enzyme catalyses, solvation and/or desolvation effects of substrate and/or transition state have been pointed out to be quite important.[3,4] In various kinds of polyelectrolyte-catalyzed reactions such as cyanoethylation of an amino acid,[5] induced aquation of metal-ion complexes,[6] and alkaline hydrolyses of phenyl esters,[7] we have also pointed out the importance of the solvation–desolvation effect.[8] The polyelectrolytes we examined are so-called "domain catalysts", which carry out catalyses by providing reaction sites in the vicinity of their molecules with the help of hydrophobic and/or electrostatic interactions between substrates and catalysts. However, there have been very few studies concerning the solvation–desolvation effect in the catalyses by polyelectrolytes that have catalytically active sites in their molecules.[9]

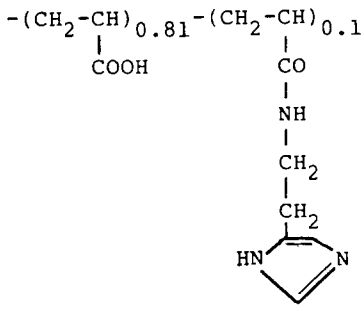
In this paper, we examine desolvation effects in the ester hydrolysis catalyzed by imidazole-containing polymers, the catalytic activities of which have been extensively studied by many researchers.[1,2]

Experimental Section

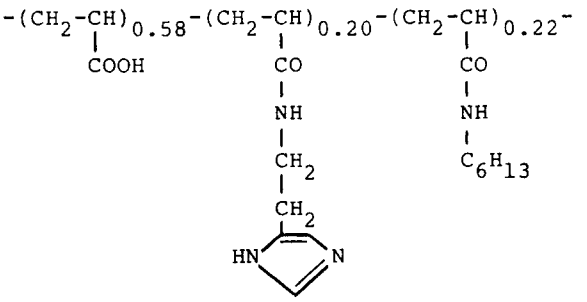
Materials. *p*-Nitrophenyl acetate (PNPA) (Tokyo Kasei Co., Tokyo) is recrystallized twice from chloroform. *N*-Carbobenzoxy-L-phenylalanine *p*-nitrophenyl ester (Z-Phe-ONP) from Sigma is used without further purification. A water-soluble carbodiimide, 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide hydrochloride (EDC), is obtained from Nakarai Chemicals, Kyoto, Japan. Poly(acrylic acid) solution (25%, 8000–12 000 cP at 30 °C, Wako Pure Chemicals, Osaka, Japan) is dialyzed for a week against water, which is purified by deionization and distillation. The other reagents are commercially available and are used without further purification.

Chart I
Chemical Structures of Catalysts

His-AA



C_6-His-AA



Polymer Catalysts. His-AA. To 40 mL of poly(acrylic acid) solution (0.23 equiv·L^{-1}) are added 2.0 g (10.4 mmol) of EDC and 0.20 g (1.8 mmol) of histamine, and the pH of the solution is kept at 4.5 for 1 h at room temperature.[10] The mixed solution is continuously stirred for 2 days. Then the pH of the solution is raised to 12 by addition of 1 N NaOH solution in order to hydrolyze the acylated imidazole ring of histamine,[11] and the solution

† Present address: Chengdu Institute of Organic Chemistry, Chinese Academy of Science, Chengdu, China.

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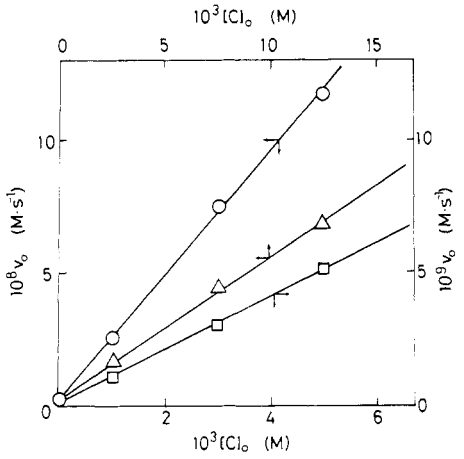

Figure 1. Catalytic effects of imidazole-containing compounds on the hydrolysis of PNPA at 25 °C (pH 8.2 Tris-HCl, [PNPA] = 50 μM): (○) imidazole; (□) His-AA; (△) C_6-His-AA.

is ultrafiltrated with a Visking dialyzing tube (8/32) located in a suction bottle. After 1 day, the solution, reduced in volume about 30 times, is diluted with distilled water. The ultrafiltration–dilution process is repeated several times until catalytic activity from the filtrate disappears.

C_6-His-AA. To 20 mL of poly(acrylic acid) solution (0.46 equiv·L^{-1}) are added 0.56 mL (4.2 mmol) of *n*-hexylamine and 2.36 g (12.3 mmol) of EDC at room temperature. The pH of the solution is kept at 4.5 for 1 h at room temperature, and the resulting copolymer (C_6-AA) is purified by repeated ultrafiltration and dilution. To 50 mL of C_6-AA (1.8 wt %) are added 0.50 g (4.5 mmol) of histamine and 1.0 g (5.2 mmol) of EDC using the conditions described for the His-AA case. This reaction gives the terpolymer C_6-His-AA. From both conductometric titrations and elemental analyses, the chemical structures of these polymers are determined and shown in Chart I.

Kinetic Measurements. The hydrolyses of the phenyl esters are followed by the increase in product absorbance at 400 nm using a high-sensitivity spectrophotometer (SM-401, Union Engineering, Hirakata, Osaka, Japan). The reactions at high pressures are followed by using a Union high-pressure spectrophotometer with a Drickamer-type reaction cell with sapphire windows.[6] The reaction cells of these photometers are thermostated at 25 ± 0.1 °C with a Neslab RTE-8 water bath. The reactions are carried out in 0.05 M Tris-HCl buffer because of its insensitivity to high pressures.[12]

Results and Discussion

The hydrolysis of PNPA is accelerated linearly with the concentration of added catalysts (Figure 1). From the slopes of these linear relationships, we can obtain the second-order rate constants of the polymer-catalyzed reaction (k_{cat}) using eq 1

$$v_0 = k_{cat}[C]_0[S]_0 + v_{sp} \quad (1)$$

where v_0, $[C]_0$, $[S]_0$, and v_{sp} are the observed initial reaction rate, initial concentration of imidazole residues in polymer catalyst, initial substrate concentration, and spontaneous reaction rate, respectively. The obtained k_{cat} values for the hydrolysis of PNPA are 0.47, 0.022, and 0.11 M^{-1} s^{-1} for imidazole, His-AA, and C_6-His-AA, respectively. The hydrophobic environment of C_6-His-AA can enhance the reactivity of its imidazole ring in comparison with His-AA as discussed later.

In the hydrolysis of Z-Phe-ONP, both imidazole and His-AA accelerate the reaction linearly, whereas the acceleration effect of C_6-His-AA shows a saturation phenomenon similar to that of enzyme catalyses (Figure 2). We can observe similar phenomena at various temperatures (Figure 3a) and pressures (Figure 4a). These phenomena can be attributed to the hydrophobic interaction

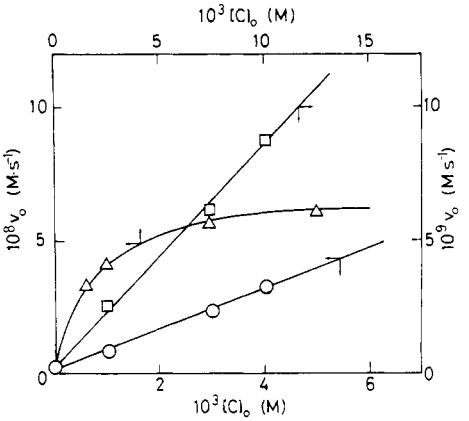

Figure 2. Catalytic effects of imidazole-containing compounds on the hydrolysis of Z-Phe-ONP at 25 °C (pH 8.2 Tris-HCl, [Z-Phe-ONP] = 13.4 μM): (○) imidazole; (□) His-AA; (△) C_6-His-AA.

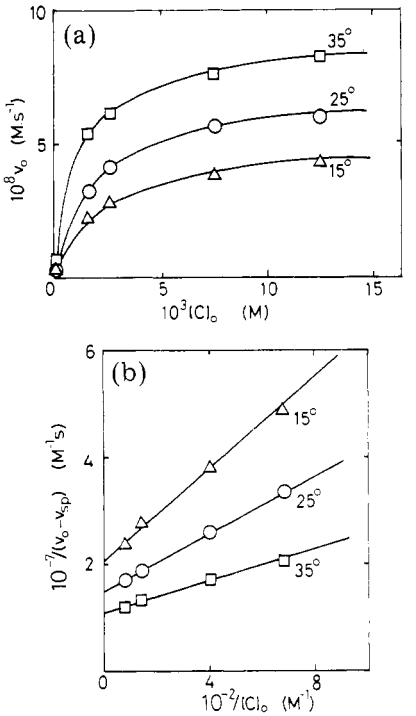

Figure 3. (a) Temperature effects on the hydrolysis of Z-Phe-ONP catalyzed by C_6-His-AA (pH 8.2 Tris-HCl, [Z-Phe-ONP] = 13.4 μM). (b) Double-reciprocal plots of (a).

between the substrate and the *n*-hexyl group of the catalyst.

We assume the following scheme in this reaction system

$$\begin{array}{ccccccc} C + S & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & CS & \xrightarrow{k_2} & CS' & \xrightarrow{k_3} & C + P_2 \\ k_{sp}\downarrow & & & & + & & \\ P & & & & P_1 & & \end{array}$$

where C, S, P, CS, CS′, P_1, and P_2 are the catalyst, substrate, product (P_1 + P_2), substrate–catalyst complex, acylated catalyst, and *p*-nitrophenol and acid part of the substrate, respectively. Under the conditions $[C]_0 >> [S]_0$ and $k_2 \gg k_3$, the observed reaction rate v_0 ($=k_{obsd}[S]_0$) is related to other parameters by eq 2

$$\frac{1}{v_0 - v_{sp}} = \frac{1}{[S]_0(k_2 - k_{sp})} + \frac{1}{[S]_0(k_2 - k_{sp})}\frac{K}{[C]_0} \quad (2)$$

where $K = k_{-1}/k_1$ and $k_{sp} = v_{sp}/[S]_0$. By double-reciprocal plots of $(v_0 - v_{sp})^{-1}$ vs. $[C]_0^{-1}$, we can obtain both the dissociation constant (K) and the reaction rate constant (k_2) of the substrate–catalyst complex of this reaction system.

Table I
Thermodynamic Parameters for the Catalytic Esterolyses[a]

substrate	catalyst	$\Delta G^{\ddagger}$, kcal·mol^{-1}	$\Delta H^{\ddagger}$, kcal·mol^{-1}	$\Delta S^{\ddagger}$, cal·mol^{-1}·deg^{-1}	$\Delta V^{\ddagger}$, mL·mol^{-1}
PNPA	imidazole[b]	17.9 ± 0.2	6.5 ± 0.2	−38 ± 1	−21 ± 2
	His-AA[b]	19.7	6.9	−43	−20
	C_6-His-AA[b]	18.7	6.7	−40	−21
Z-Phe-ONP	imidazole[b]	17.9	7.9	−33	−20
	His-AA[b]	18.5	6.4	−40	−13
	C_6-His-AA[c]	20.5	5.8	−49	−13 (−12[d])
substrate	catalyst	ΔG, kcal·mol^{-1}	ΔH, kcal·mol^{-1}	ΔS, cal·mol^{-1}·deg^{-1}	ΔV, mL·mol^{-1}
Z-Phe-ONP	C_6-His-AA[c]	−3.7 ± 0.2	3.4 ± 0.2	24 ± 1	1 ± 2

[a] pH 8.2 Tris-HCl buffer, 1% (v/v) CH_3CN-H_2O, at 25 °C. [b] Bimolecular process (for k_{cat}). [c] Intracomplex process. [d] For k_2/K.

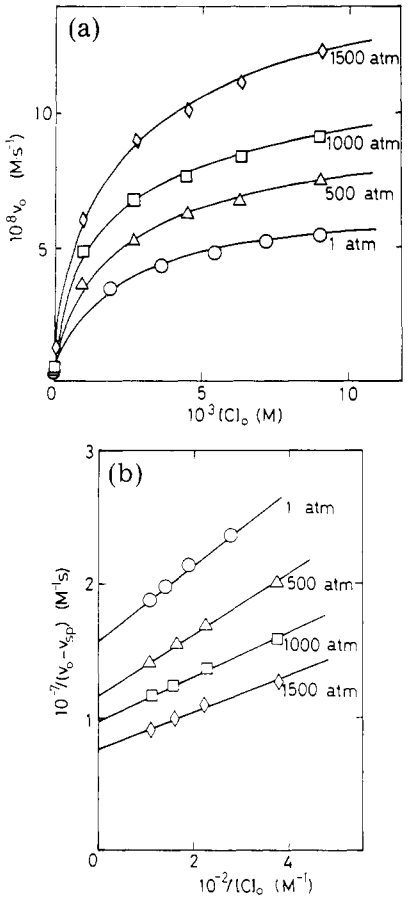

Figure 4. (a) Pressure effects on the hydrolysis of Z-Phe-ONP catalyzed by C_6-His-AA at 25 °C (pH 8.2 Tris-HCl, [Z-Phe-ONP] = 13.4 μM). (b) Double-reciprocal plots of (a).

The obtained k_2 and K values for the Z-Phe-ONP–C_6-His-AA system are 5.0×10^{-3} s^{-1} and 1.8 mM, respectively at 25 °C.

From double-reciprocal plots of this reaction system at various temperatures (Figure 3b) and pressures (Figure 4b), we can evaluate the thermodynamic parameters of this intracomplex catalytic process. The $\Delta V^{\ddagger}$ and ΔV values are estimated by using eq 3 and 4.[13] The pressure-dependence plots are shown in Figure 5. The obtained parameters are compiled in Table I together with those for the bimolecular systems. $\Delta V^{\ddagger}$'s for the bimolecular systems are evaluated with eq 3 using k_{cat}.

$$\Delta V^{\ddagger} = -RT\frac{\mathrm{d} \ln k_2}{\mathrm{d}P} \quad (3)$$

$$\Delta V = -RT\frac{\mathrm{d} \ln K}{\mathrm{d}P} \quad (4)$$

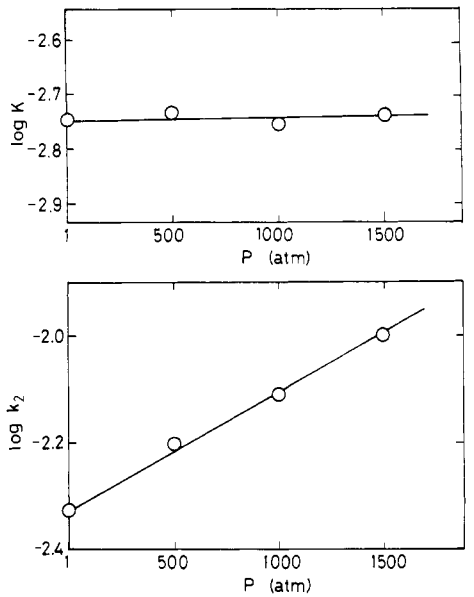

Figure 5. Pressure effects on K and k_2 values in the hydrolysis of Z-Phe-ONP catalyzed by C_6-His-AA at 25 °C.

All $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ values in Table I are negative, partly because of the increase in polarity in the activated complex (electrostriction)[14] and partly because the activated complex involves bonding between two previously discrete molecular species.[15]

In the hydrolysis of PNPA, the thermodynamic parameters for the polymer catalysts show quite similar tendencies to those for imidazole. Overberger et al.,[16] Kunitake et al.,[17] and we[18] previously reported that imidazole-containing polymer catalysts had smaller $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values than imidazole because of the high degree of order in the polymeric activated complex. In all the polymer catalysts ever examined, however, only the imidazole group is involved as an ionic active site (poly(4(5)-vinylimidazole),[16] poly(*N*-(5-benzimidazolyl)acrylamide-*co*-vinylpyrrolidone),[17] poly(*N*-(5-benzimidazolyl)acrylamide-*co*-*N*-(*p*-hydroxyphenyl)acrylamide),[17] and poly(*N*-methacryloylhistamine-*co*-acrylamide)).[18] These catalysts are considered to form extremely polarized (in other words, highly hydrated) activated complexes with PNPA, which resulted in largely negative $\Delta S^{\ddagger}$ values.

In contrast to these systems, His-AA and C_6-His-AA examined here have a large portion of acrylic acid residues. As pointed out by Overberger and Maki,[19] both imidazole and carboxyl groups in the polymer catalyst are supposed to act cooperatively in the hydrolysis of PNPA. Since acrylic acid residues of the catalysts are initially hydrated (the hydration number of the carboxylate group of poly-

acrylate ion was previously reported to be 3.4 per mole by us[20]), the increase in hydration cannot be so large in the course of activation. Thus $\Delta S^{\ddagger}$ values of His-AA and C_6-His-AA are only slightly more negative, and $\Delta V^{\ddagger}$ values are comparable to those of imidazole. A similar tendency is observed in the hydrolysis of PNPA catalyzed by imidazole-containing and carboxylic acid containing polymer latices.[18]

In the hydrolysis of Z-Phe-ONP, a much more hydrophobic substrate than PNPA, the situation is quite different. $\Delta S^{\ddagger}$'s of the polymer systems are more negative and $\Delta V^{\ddagger}$'s are less negative than those of the imidazole-catalyzed reaction. Similar tendencies were also observed in the polymer latex catalyzed alkaline fading reaction of triphenylmethane dyes and attributed to the difference in the interaction of the catalyst with the reactant and the activated complex.[20]

The decrease in $\Delta S^{\ddagger}$ values observed here is due to the oriented and restricted conformation of the activated complex. Z-Phe-ONP might be incorporated into the polymer domain deeper than PNPA because of a stronger hydrophobic interaction between the substrate and catalyst (for the Z-Phe-ONP-His-AA system, it is not strong enough to form the Michaelis-type complex that was formed in the Z-Phe-ONP–C_6-His-AA system). Considering that the degree of freedom of Z-Phe-ONP near the catalyst is more strongly restricted than that of PNPA, the more negative $\Delta S^{\ddagger}$ value for Z-Phe-ONP is understandable.

The increase in $\Delta V^{\ddagger}$ values might be due to the desolvation effect in the polymer catalysis. In the hydrolysis of Z-Phe-ONP, the substrate approaches the polymer domain, and hydrophobically hydrating water around the substrate is destabilized by the increase in polarity of the activated complex, and in addition, a great amount of water hydrating the carboxyl groups is destabilized by the bulky activated complex. This effect is also very important in the intracomplex catalysis (Z-Phe-ONP–C_6-His-AA system). The $\Delta V^{\ddagger}$ value for this system (−13 mL·mol^{-1}) is comparable to that of the polymeric bimolecular catalysis.

Taniguchi et al. reported that the $\Delta V^{\ddagger}$ values for the polymer-catalyzed ester hydrolysis were smaller than that of the imidazole-catalyzed one and attributed this to rupture of the hydrophobic interaction.[22] The polymer catalyst they used was a copolymer of 1-vinyl-2-methylimidazole and 1-vinylpyrrolidone (MI-VP). The polymer catalysts we examined here have both imidazole and carboxyl groups and resemble enzymes that have esterase actvities greater than that of the catalyst of Taniguchi et al. $\Delta V^{\ddagger}$ of PNPA hydrolysis catalyzed by α-chymotrypsin was reported to be −6 mL·mol^{-1} [23] and was quite a bit less negative than that by imidazole (−16 mL·mol^{-1},[22] −21 mL·mol^{-1} (this work)). $\Delta S^{\ddagger}$ of PNPA hydrolysis catalyzed by α-chymotrypsin was reported to be −11.9 cal·mol^{-1}·deg^{-1} [24] and −25.5 cal·mol^{-1}·deg^{-1} [25] and much less negative than that by imidazole (−38 cal·mol^{-1}·deg^{-1}).

The obtained ΔV for K (1 mL·mol^{-1}) for the Z-Phe-ONP–C_6-His-AA system is less negative than that for the 3-nitro-4-(butyryloxy)benzoic acid–MI-VP system (−8.4 mL·mol^{-1}) obtained by Taniguchi et al.[22] This result might also reflect the desolvation effect of the substrate and the polymer catalyst by their association: The substrate is surrounded by hydrophobically hydrating water and the catalyst by the electrically hydrating (electrostricted) water before the association. Hydrophobically hydrating water around the substrate is destabilized by the polar environment in the polymer domain, and electrostricted water in the vicinity of the imidazole residues is destabilized by the access of the bulky and hydrophobic substrate. ΔV for trypsin catalysis (+7 mL·mol^{-1}, Bz-Arg-NH_2) was reported to be larger than that for chymotrypsin catalysis (0 mL·mol^{-1}, indole) because of the liberation of electrostricted water in the former case[26] and is consistent with our result.

It should be mentioned here that the k_2/K value of C_6-His-AA (2.8 M^{-1} s^{-1}) is more than 6 times larger than the k_{cat} value of imidazole (0.44). Considering that k_{cat} of His-AA (0.17) is smaller than that of imidazole, the hydrophobic environment might promote the reactivity of catalytic groups similar to the hydrolysis of PNPA; in other words, the desolvation effect might participate in the catalysis. These results are consistent with the fact that the desolvation mechanism in enzyme catalysis is extremely important.[27] Enzyme activates its ionic catalytic groups in the hydrophobic portions of active sites.[28,29] For example, the Asp-102 carboxylate of chymotrypsin is buried in a nonpolar region near the catalytically important imidazole ring.[30] Cohen et al. also suggested that chymotrypsin catalysis by desolvation of the substrate in the neighborhood of hydrophobic residues of the enzyme molecule amounted to a factor of 10^3 or so in the reaction rates.[3].

From the results obtained here, it is concluded that multifunctional polymer catalysts that contain a large number of ionic groups carry out catalyses with the help of desolvation.

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Registry No. *p*-Nitrophenyl acetate, 830-03-5; *N*-carbobenzoxy-L-phenylalanine *p*-nitrophenyl ester, 2578-84-9.

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Phase Behavior in Copolymer Blends: Poly(2,6-dimethyl-1,4-phenylene oxide) and Halogen-Substituted Styrene Copolymers

Gerrit ten Brinke,* Frank E. Karasz, and William J. MacKnight

Materials Research Laboratory, Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003. *Received February 16, 1983*

ABSTRACT: A recently introduced mean field theory of phase behavior in polymer/copolymer systems is extended to random copolymer/copolymer systems. Miscibility in these systems does not require any specific interaction but rather a "repulsion" between the different covalently bonded monomers of the copolymers. Conversely, immiscibility may occur in systems with specific interaction due to an "attraction" between the different covalently bonded monomers of the copolymers. Using the mean field approach, we discuss in detail the phase behavior in polymer/copolymer systems. The requirements for the occurrence of a symmetric or an asymmetric (im)miscibility window in a temperature–copolymer composition diagram are derived. Using this treatment, we calculate all the segmental interaction parameters for blends of poly(2,6-dimethyl-1,4-phenylene oxide) with poly(*o*-chlorostyrene-*co*-*p*-chlorostyrene), poly(*o*-fluorostyrene-*co*-*p*-fluorostyrene), poly(styrene-*co*-*o*-chlorostyrene), poly(styrene-*co*-*p*-chlorostyrene), poly(styrene-*co*-*o*-fluorostyrene), and poly(styrene-*co*-*p*-fluorostyrene). The absence of miscibility in blends of poly(2,6-dimethyl-1,4-phenylene oxide) with any poly(*o*-bromostyrene-*co*-*p*-bromostyrene) copolymer is explained.

Introduction

It is well-known that high molar mass polymers are, in general, only miscible if there is a favorable specific interaction between them. According to the more recent theories of polymer mixing such as the equation of state[1,2] and the lattice–fluid theory,[3] the Gibbs free energy of mixing contains three different contributions: the combinatorial entropy of mixing, the exchange interaction, and a so-called free volume term. Although, as elaborated in particular by Koningsveld and co-workers,[4,5] this is in many respects too simple a picture, it clearly explains why specific interactions are a prerequisite for the miscibility of polymers. In this case the combinatorial entropy of mixing in negligible whereas the free volume contribution is positive and hence unfavorable for mixing.

There are, nevertheless, an increasing number of exceptions to this rule, but they all have one thing in common: at least one of the components is a random copolymer. An example in which both components are copolymers is given by poly(butadiene-*co*-styrene) and poly(vinyl chloride-*co*-vinyl acetate).[6] These are known to be miscible for a particular range of the copolymer compositions. However, none of the binary combinations of the homopolymers polybutadiene, polystyrene, poly(vinyl chloride), and poly(vinyl acetate) are miscible, an indication in effect of the absence of any specific interactions between them. Other examples that will be considered in some detail in this paper include poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with poly(*o*-chlorostyrene-*co*-*p*-chlorostyrene) (poly(*o*ClS-*co*-*p*ClS))[7,8] or with poly(*o*-fluorostyrene-*co*-*p*-fluorostyrene) (poly(*o*FS-*co*-*p*FS).[9,29]

In these systems miscibility if found for a certain range of copolymer compositions, but for a given system only up to a certain temperature at which phase separation occurs. The phase behavior in these binary mixtures is therefore of the LCST (lower critical solution temperature) type. In the temperature–copolymer composition plane a miscibility window is obtained, delineating the locus of the LCST's. A comparison between the windows for the PPO/poly(*o*ClS-*co*-*p*ClS) and for the PPO/poly(*o*FS-*co*-*p*FS) systems shows that their location is different. Whereas the maximum in the miscibility window for the first system occurs approximately at the center of the copolymer composition axis, for the second system it is shifted to the *o*-fluorostyrene-rich side of the diagram. We also note that a miscibility window is not observed in the PPO/poly(*o*-bromostyrene-*co*-*p*-bromostyrene) (poly(*o*-BrS-*co*-*p*-BrS)) system.[10]

Kambour et al.[11] recently formulated a Flory–Huggins type of theory for mixtures of homopolymers and random copolymers. They argued that such a system can be miscible, for a suitable choice of the copolymer composition, without the presence of any specific interaction because of a so-called "repulsion" between the two different monomers comprising the copolymer. In the first section we will introduce this theory in a slightly extended form applicable for blends of two different copolymers. Paul and Barlow[35] also developed a similar model for miscibility of copolymers in blends.

Using this theory, we will address a number of questions. First, some general arguments are given for the occurrence of exclusively LCST-type phase behavior in these kind of systems. Although the arguments are similar to the ones usually presented in discussions of blends of homopolymers, some differences appear because of the possible absence of any specific interaction in the systems under consideration. Next, it will be shown that the presence

* Present address: Department of Polymer Chemistry, State University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands.

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