

**Comparative Studies on  
Miscibility and Intermolecular Interaction for  
Cellulose Ester Blends with Vinyl Copolymers**

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## List of Abbreviations

|                       |                                                                    |
|-----------------------|--------------------------------------------------------------------|
| CA                    | Cellulose acetate                                                  |
| CAP                   | Cellulose acetate propionate                                       |
| CB                    | Cellulose butyrate                                                 |
| CE                    | Organic ester of cellulose                                         |
| CP                    | Cellulose propionate                                               |
| $\Delta n$            | Optical birefringence                                              |
| DMA                   | Dynamic mechanical analysis                                        |
| DMF                   | <i>N,N</i> -Dimethylformamide                                      |
| DS                    | Degree of substitution                                             |
| DSC                   | Differential scanning calorimetry                                  |
| $E'$                  | Dynamic storage modulus                                            |
| $E''$                 | Dynamic loss modulus                                               |
| $\mu$                 | Krigbaum-Wall interaction parameter                                |
| MMA                   | Methyl methacrylate                                                |
| $M_n$                 | Number-average molecular weight                                    |
| $M_w$                 | Weight-average molecular weight                                    |
| PMMA                  | Poly(methyl methacrylate)                                          |
| PVAc                  | Poly(vinyl acetate)                                                |
| PVP                   | Poly( <i>N</i> -vinyl pyrrolidone)                                 |
| P(VP- <i>co</i> -MMA) | Poly( <i>N</i> -vinyl pyrrolidone- <i>co</i> -methyl methacrylate) |
| P(VP- <i>co</i> -VAc) | Poly( <i>N</i> -vinyl pyrrolidone- <i>co</i> -vinyl acetate)       |
| $T_{1\rho}^H$         | Proton spin-lattice relaxation time                                |
| $T_g$                 | Glass transition temperature                                       |
| VAc                   | Vinyl acetate                                                      |
| VP                    | <i>N</i> -Vinyl pyrrolidone                                        |

# Chapter 1

## Background & Introduction

Organic esters of cellulose (CEs) have been commercially important polymers over nearly a century. Even though cellulose is poorly soluble in common solvents and thermally unmelted, the conversion to its esters affords secondary materials that are processible in various useful forms. Properties of the CEs can be varied over a certain range by controlling the type and number of ester substituents (acyl groups) in the chemical manufacturing process. There has been a great activity for CEs to develop specific applications such as coating, drug delivery (excipients), molded plastics including biodegradable ones, fibers, laminates, optical films, and membranes and other separation media.<sup>[1,2]</sup>

Among industrially established cellulosic products, cellulose acetate (CA) is particularly important and utilized for many industrial applications due to its desirable physical properties such as good optical clarity in film form, and a comparatively high modulus and adequate flexural and tensile strengths in fiber form.<sup>[2]</sup> Additionally, CAs with the degree of substitution (DS)  $\leq 2.5$  are inherently biodegradable under both aerobic and anaerobic conditions, although the degradation rate is largely dependent on the DS value.<sup>[1,2]</sup> In contrast to the above merits, CA alone cannot be molded so easily by thermal processing, because the glass transition temperature ( $T_g$ ) and melting point are fairly high, where significant thermal decomposition can take place. Therefore, in practice, a large amount of plasticizers such as phthalate compounds are usually mixed with CA for the thermal molding. The use of low molecular-weight plasticizers, however, can cause fume generation in the molding process due to their volatility or decomposition. In addition, bleeding-out of plasticizers from molded CA products can be pronounced in long-term uses. Consequently, it is of great significance to improve the original thermal property of CA by derivatization into a more tractable cellulosic polymer or by incorporation with other polymers at the molecular level.<sup>[3]</sup> Following such structural alterations, new functionalization as CA-based materials may also become possible, so as to be more usable in medical, pharmaceutical, and other bio-related fields as well as in a huge consumption type of commodities.

### ***Molecular Modification (Derivatization)***

The derivatization of CA is, plainly, a chemical modification of the molecular structure with another functional group. Traditional mixed esters, cellulose acetate propionate (CAP) and acetate butyrate (CAB), are still industrially produced to improve the solvent solubility and thermoplasticity of CA.<sup>[1,2]</sup> Concerning modern derivatizations of celluloses, there have been elaborate studies on various reaction techniques relating to (regioselective) C2/C3/C6 modifications,<sup>[4,5]</sup> those results would also be suggestive for improvement in property and/or function of conventional CEs. To take an example, silylation of CA was proven to improve the solubility in relatively non-polar organic solvents, thermal plasticity, and membrane-forming ability.<sup>[6]</sup> It was reported that free-standing membranes of the silylated derivatives exhibited higher gas permeability and good separation performance for CO<sub>2</sub>/N<sub>2</sub>, deservedly, the gas permeability becoming more improved with increasing silyl content in the modified CA. Another good example of functionalized CA is the synthesis of a series of derivatives (CA-MAs) having a cross-linkable mercapto group by esterification of CA with mercaptoacetic acid.<sup>[7]</sup> The CA-MA products show a sol-gel transition in solution and a shape memory-recovery behavior in film form through adequate redox treatments, due to the reversible, cross-linking association and dissociation between the introduced SH groups.

Recently, it has been demonstrated that the conventional propionylation or butyrylation of CA improves the optical property in film form such as orientation birefringence and its wavelength dependence (i.e., wavelength dispersion).<sup>[8]</sup> When CA films are drawn uniaxially, the acetyl group provides negative orientation birefringence, and its absolute value decreases with increasing wavelength of visible light, which is called “ordinary dispersion”. On the contrary, the propionyl and butyryl groups give positive orientation birefringence with ordinary but weak wavelength dispersion in drawn cellulose propionate (CP) and butyrate (CB) films, respectively. Using mixed esters of cellulose, CAP and CAB, interestingly, their drawn films can exhibit “extraordinary dispersion”; namely, the absolute value of the orientation birefringence increases with wavelength, although any of the acyl side-groups has an inherent character of imparting the ordinary dispersion behavior. The delicate control of birefringence and its wavelength dispersion for CE films will be a key technology in the field

of high-performance optical materials such as protective films of polarizer and retardation films for quarter- and half-wave plates.

Meanwhile, polymer blending and graft copolymerization are also important methods to improve the original physical properties including processibility of CA and related CEs, and to expand their availability. In both of the methods, the molecular-scale mixing with an appropriate second polymer component offers an opportunity to design new polymeric materials exhibiting wide-ranging and/or synergistic functions unattainable in gross mechanical mixtures as well as in single-component materials.

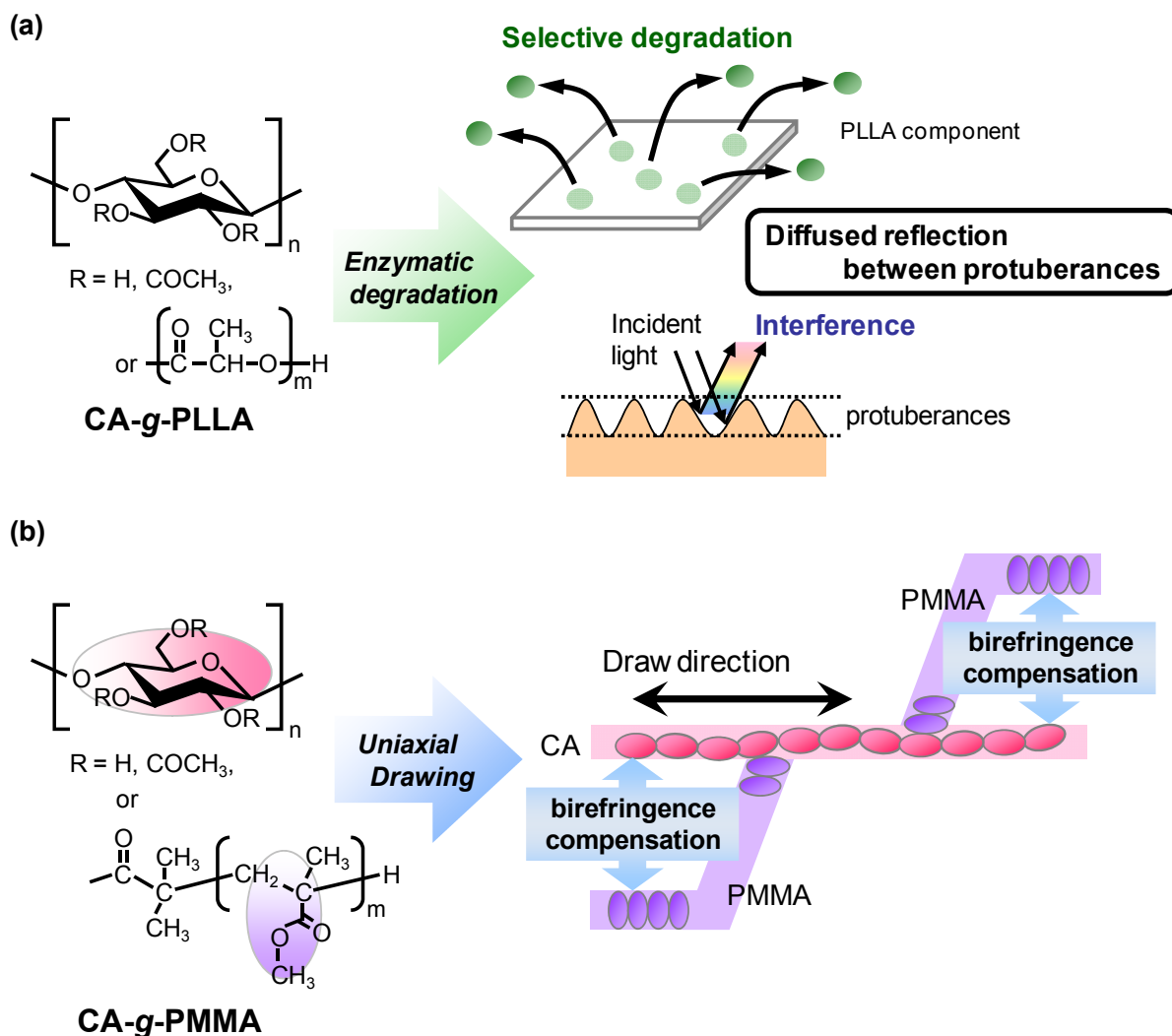
### ***Graft Copolymer***

Graft copolymerization of cellulosics is a traditional way to improve their original properties, and, practically, it has often been used for surface alteration of cotton and Rayon fibers and wooden products.<sup>[9,10]</sup> For modern material designs via graft copolymerization, it is important to obtain structurally well-defined copolymers by using high-selective catalysts for the initiation of graft reactions and also by establishing the effective purification procedure to remove some possible by-products.<sup>[3]</sup> A crucial molecular parameter is the molar substitution (MS) defined as an average number of introduced monomeric units of the grafted chains per anhydroglucose residue, which should be precisely determined by NMR etc.

Currently, an advanced use of the grafting technique is in the design of environmentally conformable and functionality-rich materials such as CA-*graft*-poly(hydroxyalkanoate) (CA-g-PHA) moldable in film or fiber form.<sup>[3]</sup> For example, a rigorous evaluation was made for various series of CE-g-PHAs to establish a general relationship between their molecular architecture and thermal transition behavior.<sup>[11,12]</sup> Incorporating grafts at  $MS \geq \sim 10$  ( $M_n \geq \sim 1000$ ) onto the CE trunk renders the attached PHA side-chain crystallizable. Therefore, in enzymatic hydrolysis of CE-g-PHA films, the degradation rate can be widely varied not only by altering the copolymer composition but also by controlling the phase structure involving the crystalline morphology.<sup>[13,14]</sup> Further, the *selective* enzymatic hydrolysis (typically for oxyalkanoyl units of the PHA component) transforms the initially smooth surface of the

respective films into a more undulated one with a number of fine protuberances, e.g., of several hundreds nanometers in height and a few micrometers in width. As regards a series of CA-g-poly(L-lactide) (PLLA), the film specimens often impart an iridescent color in the course of the partial degradation of PLLA side-chains, as illustrated in Figure 1-1a.<sup>[13]</sup> This effect is attributed to the interference of visible light due to diffused reflection between the microscopic protuberances formed on the surface of the films.

In perspective of the many-faceted applicability of cellulosic graft copolymers, attention should be paid to the respect that their practical properties as solid material would be varied depending on the state of polymer chain orientation therein. Inescapably, such orientation arises more or less in the manufacturing process of common polymers into dimensional products of film and filament or more bulky molding. Therefore, effort must be made for the multicomponent materials, too, to describe some relationship between their orientation behavior and particularly mechanical and/or optical properties.<sup>[15]</sup> Very recently, the molecular orientation and optical anisotropy induced by the stretching of CA-g-poly(methyl methacrylate) (PMMA) films have been discussed in connection with the copolymer compositions.<sup>[16]</sup> The copolymers were synthesized by atom transfer radical polymerization (ATRP) so that the molecular weight distribution of the PMMA side-chains was quite narrow. According to the report, the overall development of molecular orientation declines with an increase in degree of the MS of methyl methacrylate (MMA) unit in the graft part. In comparison of birefringence at a given stage of elongation of the copolymer films, the value of birefringence decreases rapidly with increasing MS, which eventually leads to the conversion from a positive birefringence for pristine CA (DS = 2.15) to a negative one for the composition containing >65 wt% PMMA that corresponds to the highest MS = 6.0 in the graft series used. This type of graft copolymer may deserve to be a high-functional material whose optical anisotropy is controllable delicately in terms of birefringence compensation (see Figure 1-1b) between the oriented trunk and graft chains.



**Figure 1-1.** Schematic representations of (a) surface modification of CA-g-PLLA film by selective enzymatic treatment, and (b) compensation of orientation birefringence in drawn CA-g-PMMA film. Polymer chains in part (b) are illustrated as a sequence of the polarizability ellipsoids of the constituent monomer units.

### Miscible Blending

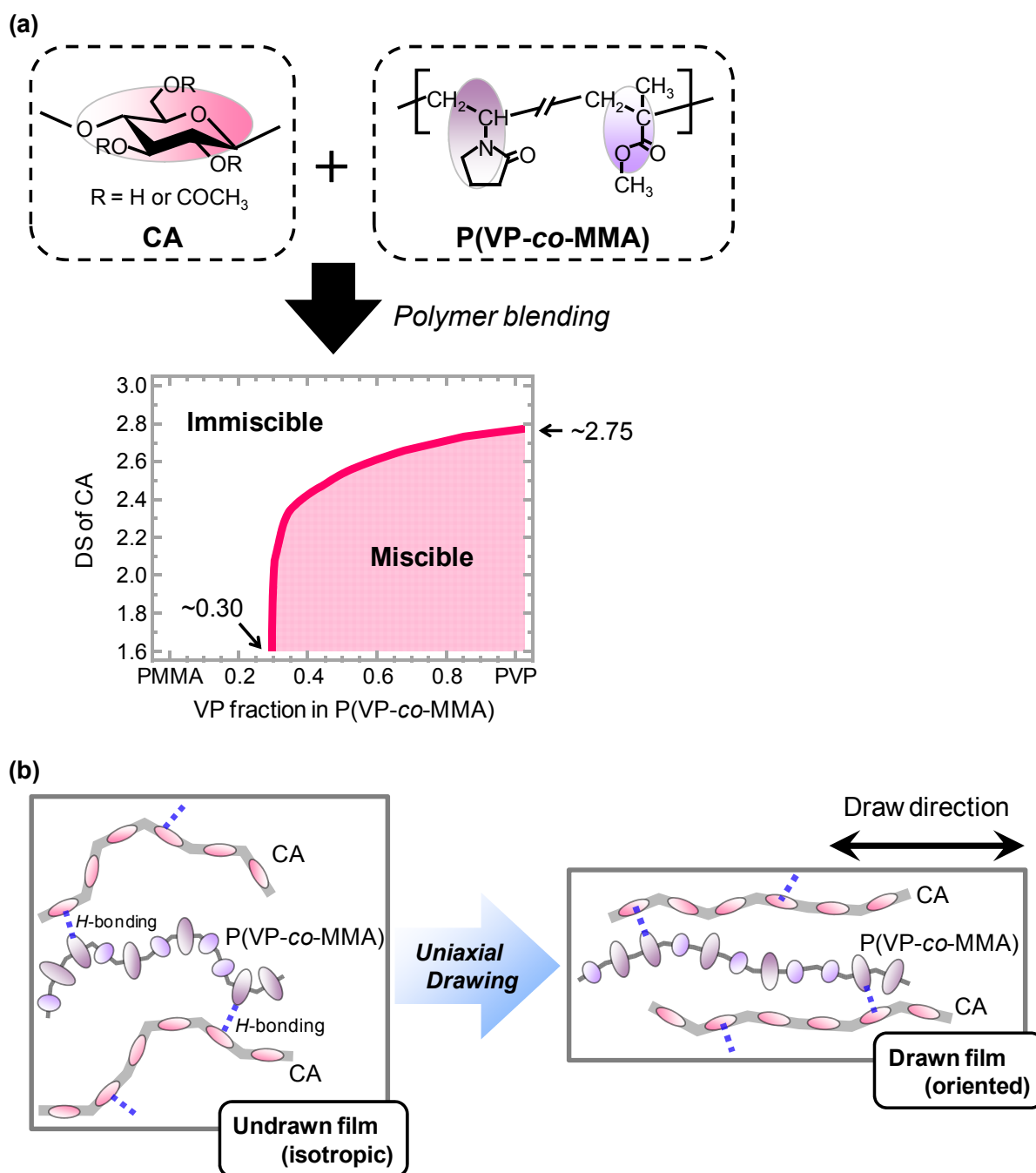
Miscible polymer blending is practically useful to manipulate the physical properties and functions of CEs, represented by CA, readily at the lowest cost possible.<sup>[1,3]</sup> Therefore, there have been a number of fundamental and practical blend studies of CEs; the counter components to CEs are categorized into mainly two sorts of polymers, biodegradable aliphatic polyesters such as poly(3-hydroxybutyrate) and poly( $\epsilon$ -caprolactone) (PCL),<sup>[1,3,17,18]</sup> and synthetic vinyl polymers.<sup>[3,8,19,20]</sup>

The employment of aliphatic polyesters including bacterially produced PHAs as the counterpart component for CEs may be of particular significance, because the resulting blend systems can be a biodegradation-controllable material of great promise.<sup>[1,3]</sup> Simultaneously, such incorporations would make it possible to overcome the thermal instability and mechanical brittleness of aliphatic polyesters, the defectiveness in property often leading to their limited applications. In this context, for example, the miscibility of PCL with various CEs was investigated as a function of the number  $N$  of carbons in the  $n$ -acyl substituent as well as of DS.<sup>[17]</sup> It was reported that CP ( $N = 3$ ), CB ( $N = 4$ ), and cellulose valerate (CV) ( $N = 5$ ) showed good miscibility with PCL in the amorphous mixing state. The miscibility was restricted to the polymer pairs using relatively high-substituted CE samples, i.e., CPs of  $DS \geq 2.45$ , CBs of  $DS \geq 1.85$ , and CVs of  $DS \geq 2.15$ . This result reasonably suggests that the possible factor for achieving the miscibility is not a specific interaction via hydrogen-bonding associated with residual hydroxyls of the CEs but a strong affinity in molecular structure between the components concerned; CB and CV have, most abundantly, the same structural unit as that of PCL (C-C-O-(CO)-C-C-C or C-O-(CO)-C-C-C-C), if the carbon atoms C-1 to C-6 in a glucopyranose unit are taken into account.

Meanwhile, poly( $N$ -vinyl pyrrolidone) (PVP) and its copolymers also can form miscible blends with CA and a few other CEs, in virtue of hydrogen-bonding formation between the residual hydroxyls of CE and the carbonyl groups of  $N$ -vinyl pyrrolidone (VP) units in the mixing system.<sup>[3,19]</sup> Ohno & Nishio reported the detailed characterization of miscibility for CA blends with a random copolymer comprising VP and MMA units, i.e., P(VP-*co*-MMA), through thermal analysis by differential scanning calorimetry (DSC).<sup>[19]</sup> Figure 1-2a displays a miscibility map for CA/P(VP-*co*-MMA) system, constructed as a function of DS of CA and VP:MMA composition of P(VP-*co*-MMA). CA can form completely homogeneous blends with P(VP-*co*-MMA) on a scale within a few nanometers, when the DS of CA is  $<2.75$  and the VP fraction in the copolymer is  $>30$  mol%. Regarding this system, an additional interest was focused on the molecular orientation and optical anisotropy in uniaxially drawn films of the miscible blends.<sup>[21]</sup> CAs of  $DS \leq 2.75$  exhibit positive optical anisotropy upon stretching of their films, whereas P(VP-*co*-MMA) copolymers show negative one (see the top of Figure 1-2a). Therefore, the birefringence development in the blends was widely controllable in both the degree and polarity, by altering the DS of CA, the VP:MMA ratio in

P(VP-*co*-MMA), and the proportion of the mixing polymers, due to cooperative orientation of the miscible two polymer components in the uniaxial drawing process (Figure 1-2b). With a certain specific blend composition, the drawn film can behave like an optically isotropic medium even though it should be mechanically anisotropic after deformation.

By the attainment of miscible blends of CA with amorphous vinyl polymers, like the above, the thermal (e.g.,  $T_g$ ), optical (e.g., orientation birefringence), and adsorption properties of CA can be improved, but the mechanical strength and heat resistance are often deteriorated. A remedy for such drawbacks in thermomechanical stability of the CA-based blends is the introduction of chemical cross-linkages, as has been applied to a miscible CA/poly(vinyl phenol) system.<sup>[22]</sup> Another effective method may be the use of layered clays (e.g., montmorillonite) as nano-filler.<sup>[23]</sup> For a miscible CA/poly(acryloyl morpholine) system, a successful reinforcement in thermomechanical property of the blend films was demonstrated by nanoincorporation of organophilic layered double hydroxides.<sup>[20]</sup>



**Figure 1-2.** (a) Chemical formulae of CA and P(VP-co-MMA) (*top*), and a miscibility map constructed for CA/P(VP-co-MMA) blends as a function of DS of CA and VP fraction in P(VP-co-MMA) (*bottom*); the data map was reproduced from ref 19. (b) Schematic representation of molecular orientation induced in a film of CA/P(VP-co-MMA) upon uniaxial drawing. In part (b) as well as in the *top* of part (a), polymer chains are illustrated in terms of a sequence of the polarizability ellipsoids of the constituent monomer units.

## Outline of this thesis

This thesis entitled “*Comparative Studies on Miscibility and Intermolecular Interaction for Cellulose Ester Blends with Vinyl Copolymers*” consists of five chapters. The main purpose of this thesis is to clarify an effect of alkyl side-chain length of the CE component on the miscibility and intercomponent interaction for binary blends of CE with VP-containing vinyl polymers. The result of this study will provide useful suggestion on the designing of high-functional multicomponent materials based on cellulose. The outline of this thesis is described below and also displayed schematically in Figure 1-3.

In Chapter 1, after introducing the current situation in scientific research of cellulose as promising functional polymers, the significance of further functionalization and utilization of CEs and a potential role of blending technique were emphasized. The outline of this thesis was also summarized briefly.

In Chapter 2, blend miscibility of cellulose propionate (CP) with synthetic copolymers comprising VP and vinyl acetate (VAc) units was examined, and a data map was constructed as a function of the DS of CP and the VP fraction in the copolymer component. Results of DSC and Fourier transform infrared (FT-IR) measurements indicated that the pairing of CP/P(VP-*co*-VAc) formed a miscible or immiscible blend system according to the balance in effectiveness of the following factors: 1) hydrogen bonding (*H*-bonding) between residual hydroxyls of CP and VP carbonyls of P(VP-*co*-VAc); 2) steric hindrance of propionyl side-groups to the interaction specified in 1); 3) intramolecular repulsion between the two units constituting the vinyl copolymer; and, additionally, 4) structural affinity between two segmental moieties involving the propionyl group and VAc unit, respectively. The factor 3 inducing intercomponent attraction is responsible for the appearance of a so-called “miscibility window” in the miscibility map, and the factor 4 substantially expands the miscible region whole, wider relative to those in the maps for the corresponding blend series based on CA and cellulose butyrate (CB). In further refined estimation by dynamic mechanical analysis (DMA) and quantification of the proton spin-lattice relaxation time in solid-state  $^{13}\text{C}$  NMR, it was found that the miscible blends of hydrogen-bonding type (using CPs of  $\text{DS} < 2.7$ ) were completely homogeneous on a scale within a few nanometers, whereas the polymer pairs situated in the window region (using CPs of  $\text{DS} > 2.7$ ) formed

blends exhibiting a somewhat larger size of heterogeneity (ca. 5–20 nm).

In Chapter 3, blend miscibility of CP with P(VP-*co*-MMA) was investigated. The DS of CP used ranged from 1.6 to >2.9, and samples for the vinyl polymer component were prepared in a full range of VP:MMA compositions. Through DSC analysis and solid-state  $^{13}\text{C}$  NMR and FT-IR measurements, it was revealed that CPs of  $\text{DS} < 2.7$  were miscible with P(VP-*co*-MMA)s of  $\text{VP} \geq \sim 10$  mol% on a scale within a few nanometers, in virtue of hydrogen-bonding interactions between CP-hydroxyls and VP-carbonyls. When the DS of CP exceeded 2.7, the miscibility was restricted to the polymer pairs using P(VP-*co*-MMA)s of  $\text{VP} = \text{ca. } 10\text{--}40$  mol%; the scale of mixing in the blends concerned was somewhat larger (ca. 5–20 nm), however. The appearance of such a “miscibility window” was interpretable as an effect of intramolecular repulsion in the copolymer component. Results of DMA and birefringence measurements indicated that the miscible blending of CP with the vinyl polymer invited synergistic improvements in thermomechanical and optical properties of the respective constituent polymers. Additionally, it was found that the VP:MMA composition range corresponding to the miscibility window was expanded by modification of the CP component into cellulose acetate propionate (CAP).

In Chapter 4, to interpret the expansion of the miscible markings for the CP/copolymer systems in comparison with the cases using CA and CB, Krigbaum-Wall interaction parameter ( $\mu$ ) was evaluated through solution viscometry for selective polymer pairs involved in the respective CE/copolymer blends. The results of  $\mu$  measurements were in good accordance with the previous miscibility estimations. The assessment of very small negative  $\mu$  values (i.e., extremely weak repulsion) for CP/poly(vinyl acetate) (PVAc) and CP/PMMA combinations and that of considerably larger negative  $\mu$  values for PVP/PVAc and PVP/PMMA combinations enabled us to give a rational explanation for the CP systems. The strongly repellent character of the two different monomer units constituting the copolymers permits accession of the CP component ( $\text{DS} > 2.65$ ) to them, which would be responsible for the advent of the miscibility window. Further expansion of the window observed when CAP was adopted instead of CP as the CE component was also well explained on the basis of a  $\mu$  data indicative of additional intramolecular repulsion in the CAP side.

In Chapter 5, major results obtained through this sequence of blend studies are summarized.

## Miscibility Characterization

Construction of “miscibility map”,  
as a function of DS of CE and VP fraction in vinyl copolymer

### CP/P(VP-co-VAc)

- Intermolecular *H*-bonding
- Intra-copolymer effect  
(*Miscibility window*)
- Structural affinity
- Scale of mixing

(Chapter 2)

### CAP/P(VP-co-MMA)

### CP/P(VP-co-MMA)

- Intermolecular *H*-bonding
- Intra-copolymer effect  
(*Miscibility window*)
- Structural affinity
- Scale of mixing

(Chapter 3)

### CA/P(VP-co-VAc)

### CB/P(VP-co-VAc)

### CA/P(VP-co-MMA)

## Synergistic improvement

- Thermomechanical property
- Optical birefringence

(Chapter 3)

## Estimation of Interaction Parameter

Quantification of  
“Krigbaum-Wall polymer-polymer interaction parameter”

- Side-chain length of CE
- Copolymer constituent

### CB/P(VP-co-MMA)

- Complementary mapping

(Chapter 4)

## High-functional Multicomponent Materials Based on Cellulosics

Figure 1-3. Schematic representation of the outline of this thesis.

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## Chapter 2

### Cellulose Propionate/Poly(*N*-vinyl pyrrolidone-*co*-vinyl acetate) Blends: Dependence of the Miscibility on Propionyl DS and Copolymer Composition

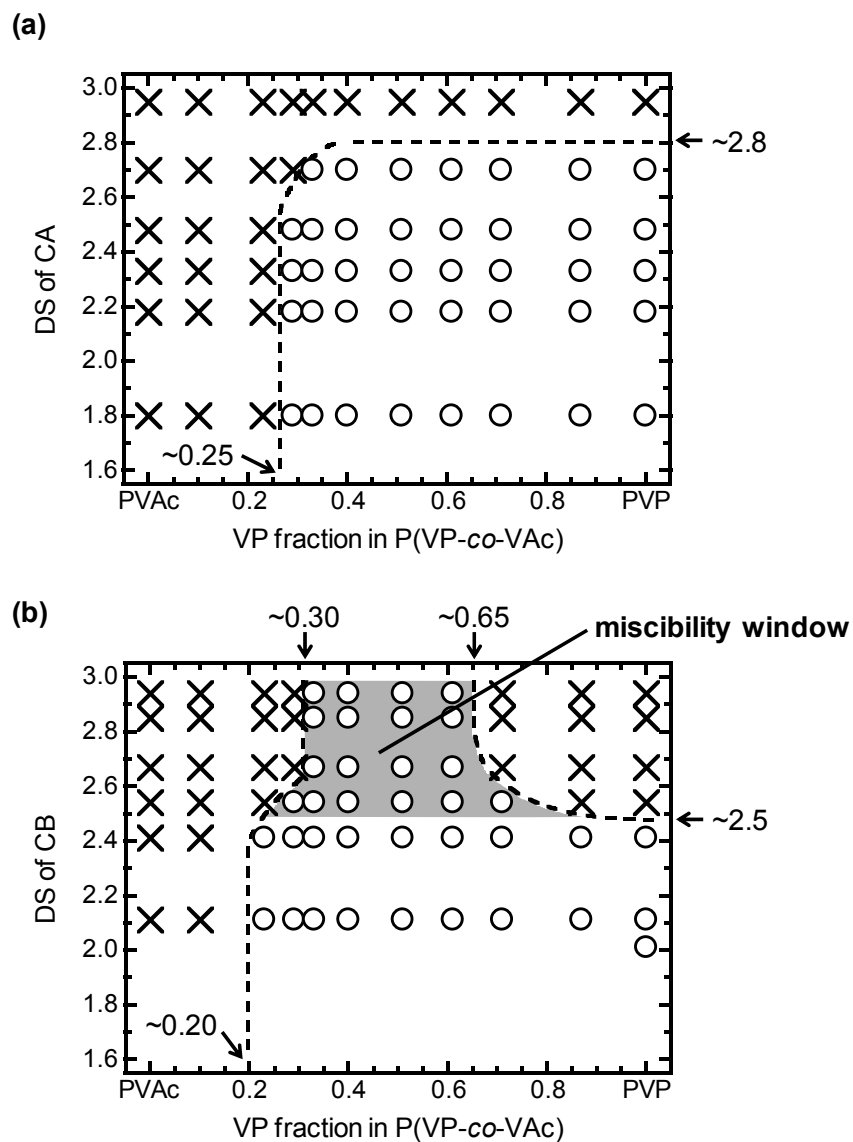
#### 2.1. Introduction

In Chapter 1, the author emphasized an importance of polymer/polymer blending for improvement in physical properties of cellulose esters (CEs) toward their further application. Against the background, characterization of miscibility and intermolecular interaction has been undertaken on the blends of industrially crucial CEs, cellulose acetate (CA) and butyrate (CB), with synthetic homo- and co-polymers comprising *N*-vinyl pyrrolidone (VP) and/or vinyl acetate (VAc) units, i.e., poly(*N*-vinyl pyrrolidone) (PVP), poly(vinyl acetate) (PVAc), poly(*N*-vinyl pyrrolidone-*co*-vinyl acetate) (P(VP-*co*-VAc)).<sup>[1-3]</sup> Through thermal analysis by differential scanning calorimetry (DSC), it was shown that the miscibility behavior of the CA or CB/vinyl polymer pairs (generically described as CE/P(VP-*co*-VAc)) was seriously affected by the degree of substitution (DS) and the ester side-chain length of the CE component, as well as by the VP fraction in the copolymer component. Two maps given in Figure 2-1 survey the estimation result.

In the CA/P(VP-*co*-VAc) system (Figure 2-1a), Fourier transform infrared (FT-IR) and solid-state <sup>13</sup>C CP/MAS NMR spectroscopy revealed that the blend miscibility was mainly governed by the hydrogen-bonding interactions between the residual hydroxyls of CA and the carbonyls of VP units in P(VP-*co*-VAc) and the miscible blends of this interaction type were homogeneous in a few nanometers scale.<sup>[1,2]</sup> In the CB/P(VP-*co*-VAc) system (Figure 2-1b), the hydrogen-bonding interaction was suppressed in frequency by steric hindrance of the bulky butyryl substituent, resulting in lowering of the critical DS required for attainment of the miscibility of CE with PVP and VP-rich copolymers (VP content > 65 mol%), as the critical values of 2.5 for CB and 2.8 for CA are designated in Figure 2-1. Furthermore, unlike the situation for the CA blends, highly substituted CBs of DS = 2.5–2.95 made a miscible pair with P(VP-*co*-VAc) copolymers containing ca. 30–65 mol% VP residues.<sup>[3]</sup> This unique copolymer composition range, generally termed a “miscibility window”, emerges as a result of indirect polymer-copolymer attraction driven by strong repulsion between the

VP and VAc constituents of the random copolymer. More concretely, since these two monomer species having mutually repellent characters were randomly combined in P(VP-*co*-VAc) by covalent bonding, the copolymers tended to form a miscible monophasic system with CB (DS > 2.5) so as to reduce the strong repulsion between the comonomers.<sup>[4]</sup> The absence of such a clear miscibility window in the map for the CA/P(VP-*co*-VAc) system may be interpreted as due to a strong self-association ability of highly substituted CAs of DS > ~2.8; the CAs rather crystallize in a cellulose triacetate II form.

As an extension of the above studies, attention was then directed to a similar miscibility map for cellulose propionate (CP)/P(VP-*co*-VAc) blends; the side-chain length of the CE component is just intermediate between the acetyl and butyryl substituents. Great interests are how far the miscible region spreads on the map constructed as a function of the DS and copolymer composition, and whether that kind of miscibility window emerges or not. Thereby, we will be able to make clearer the effects of the ester side-group and residual hydroxyls of CE on the blend miscibility and intermolecular interactions with the vinyl polymers concerned. In addition to conventional characterizations by DSC analysis and IR and NMR spectra, the homogeneity of miscible blends is evaluated in refinements of the mixing scale by complementary use of dynamic mechanical analysis (DMA) and proton spin-lattice relaxation time ( $T_{1\rho}^H$ ) measurements in solid-state  $^{13}\text{C}$  NMR spectroscopy.



**Figure 2-1.** Miscibility maps for two blend systems (a) CA/P(VP-co-VAc)<sup>[1]</sup> and (b) CB/P(VP-co-VAc)<sup>[3]</sup> depicted as a function of DS of CE and VP fraction of the copolymer with additional data. Symbols indicate that a given pair of CE/vinyl polymer is miscible (○) or immiscible (×).

## 2.2. Experimental Section

### 2.2.1. Materials

CP samples were synthesized from cotton cellulose with a viscosity average molecular weight of 252,000 via a homogeneous reaction with acid chloride/base catalyst, in a procedure similar to that used in previous studies.<sup>[5,6]</sup> Table 2-1 summarizes the characterization data including molecular weight and glass transition temperature ( $T_g$ ) for all the CP samples used in this study. The vinyl polymers employed as a mixing partner for the CPs were PVP, PVAc, and P(VP-*co*-VAc), basically the same as those in the preceding works.<sup>[1,3]</sup> Data of characterization for all the vinyl polymers are also listed in Table 2-1. As shown in the table, any of the P(VP-*co*-VAc) samples exhibited a single  $T_g$ , and the  $T_g$  versus copolymer composition relation was in good obedience to the Fox equation.<sup>[7]</sup> Thus the copolymers were all regarded as essentially random copolymer. Hereafter, a CP sample with DS =  $x$  is encoded as CP <sub>$x$</sub> , and a code P(VP <sub>$y$</sub> -*co*-VAc <sub>$z$</sub> ) denotes P(VP-*co*-VAc) copolymer of VP:VAc =  $y$ : $z$  (in molar ratio).

### 2.2.2. Preparation of Blend Samples

CP/vinyl polymer blends were prepared in film form from mixed polymer solutions by solvent evaporation, in the same manner as that adopted in the preceding works.<sup>[1,3]</sup> *N,N*-Dimethylformamide (DMF) was selected as a common solvent and the film casting was carried out at 50 °C under reduced pressure (<10 mmHg). The as-cast samples thus obtained were further dried at 50 °C *in vacuo* for 3 days.

For DMA measurements, the solution-cast samples were thermally molded into a flattened film ca. 0.1 mm thick by using a Toyo-Seiki hot-pressing apparatus. The hot-press molding was conducted at 230 °C with an applied pressure of 15 MPa for 30 s.

**Table 2-1.** Characterization of CP and synthetic vinyl polymers used in the present chapter

| Sample code <sup>a</sup>                       | $M_w^c$              | $M_n^c$ | $M_w/M_n^c$ | $T_g/^{\circ}\text{C}$ | Source                         |
|------------------------------------------------|----------------------|---------|-------------|------------------------|--------------------------------|
| CP <sub>1.71</sub>                             | 2,010,000            | 850,000 | 2.36        | 162                    | Synthesized                    |
| CP <sub>1.90</sub>                             | 1,860,000            | 824,000 | 2.26        | 161                    | Synthesized                    |
| CP <sub>2.18</sub>                             | 1,300,000            | 577,000 | 2.25        | 157                    | Synthesized                    |
| CP <sub>2.35</sub>                             | 2,210,000            | 925,000 | 2.39        | 153                    | Synthesized                    |
| CP <sub>2.54</sub>                             | 1,180,000            | 509,000 | 2.32        | 140                    | Synthesized                    |
| CP <sub>2.62</sub>                             | 979,000              | 359,000 | 2.73        | 138                    | Synthesized                    |
| CP <sub>2.72</sub>                             | 2,390,000            | 968,000 | 2.47        | 134                    | Synthesized                    |
| CP <sub>2.81</sub>                             | 1,990,000            | 837,000 | 2.38        | 128                    | Synthesized                    |
| CP <sub>2.89</sub>                             | 2,000,000            | 692,000 | 2.89        | 127                    | Synthesized                    |
| CP <sub>2.93</sub>                             | 1,250,000            | 525,000 | 2.38        | 124                    | Synthesized                    |
| Sample code <sup>b</sup>                       | $M_w^d$              | $M_n^d$ | $M_w/M_n^d$ | $T_g/^{\circ}\text{C}$ | Source                         |
| PVP                                            | 360,000 <sup>e</sup> | —       | —           | 177                    | Nacalai Tesque, Inc.           |
| P(VP <sub>0.87-co</sub> -VAc <sub>0.13</sub> ) | 56,500               | 28,000  | 2.02        | 124                    | Synthesized <sup>f</sup>       |
| P(VP <sub>0.73-co</sub> -VAc <sub>0.27</sub> ) | 52,100               | 25,000  | 2.08        | 111                    | Synthesized <sup>f</sup>       |
| P(VP <sub>0.62-co</sub> -VAc <sub>0.38</sub> ) | 51,600               | 24,400  | 2.11        | 101                    | Synthesized <sup>f</sup>       |
| P(VP <sub>0.52-co</sub> -VAc <sub>0.48</sub> ) | 28,000               | 5,120   | 5.47        | 89                     | Polyscience, Inc. <sup>g</sup> |
| P(VP <sub>0.40-co</sub> -VAc <sub>0.60</sub> ) | 51,100               | 20,700  | 2.47        | 76                     | Synthesized <sup>f</sup>       |
| P(VP <sub>0.33-co</sub> -VAc <sub>0.67</sub> ) | 23,300               | 3,800   | 6.12        | 72                     | Polyscience, Inc. <sup>g</sup> |
| P(VP <sub>0.23-co</sub> -VAc <sub>0.77</sub> ) | 59,400               | 26,100  | 2.27        | 55                     | Synthesized <sup>f</sup>       |
| P(VP <sub>0.10-co</sub> -VAc <sub>0.90</sub> ) | 46,500               | 27,700  | 1.68        | 45                     | Synthesized <sup>f</sup>       |
| PVAc                                           | 90,000 <sup>e</sup>  | —       | —           | 41                     | Polyscience, Inc.              |

<sup>a</sup> The DS values were determined by <sup>1</sup>H NMR.<sup>b</sup> The VP contents were determined by <sup>1</sup>H NMR.<sup>c</sup> Determined by gel permeation chromatography (mobile phase, tetrahydrofuran at 40 °C) with polystyrene standards.<sup>d</sup> Determined by gel permeation chromatography (mobile phase, 10 mM/L lithium bromide/DMF at 40 °C) with polystyrene standards.<sup>e</sup> Nominal value.<sup>f</sup> Synthesized in the author's laboratory by radical polymerization of two distilled monomers, VP (Aldrich Chemical Co.) and VAc (Nacalai Tesque, Inc.), in the same way as that described in ref 1.<sup>g</sup> Used after purification by dissolution in dichloromethane and reprecipitation into petroleum ether.

### 2.2.3. Measurements

DSC thermal analysis was carried out with a Seiko DSC 6200/EXSTAR 6000 apparatus. The temperature readings were calibrated with an indium standard. The calorimetry measurements were conducted on ca. 5-mg samples packed in an aluminum pan under a nitrogen atmosphere. Each sample was first heated from ambient temperature ( $\sim 25$  °C) to 230 °C at a scanning rate of 20 °C/min, and then immediately quenched to  $-50$  °C at a rate of 80 °C/min. Following this, the second heating scan was run from  $-50$  to 230 °C at a rate of 20 °C/min to record stable thermograms. Thermograms presented in this chapter were all obtained in the second heating scan and the  $T_g$  was taken as a temperature at the midpoint of a baseline shift in heat flow characterizing the glass transition.

FT-IR spectra were measured on thinner film samples ( $< 20$   $\mu\text{m}$  thick) by using a Shimadzu IRPrestige-21 spectrometer. All the spectra were recorded at 20 °C in a transmission method over a wavenumber range 400–4,000  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$  via accumulation of 64 scans.

DMA was conducted by using a Seiko DMS6100/EXSTAR6000 apparatus. Strips of rectangular shape ( $20 \times 5$   $\text{mm}^2$ ) cut from the molded films were used for measurements of the temperature dependence of the dynamic storage modulus ( $E'$ ) and loss modulus ( $E''$ ). The measuring conditions were as follows: temperature range,  $-150$  to 300 °C; scanning rate, 2 °C/min; oscillatory frequency, 10 Hz.

High-resolution solid-state NMR experiments were performed at 20 °C in a Varian NMR system 400 MHz operated at a  $^{13}\text{C}$  frequency of 100.6 MHz. The magic-angle spinning rate was 15.0 kHz.  $^{13}\text{C}$  CP/MAS spectra were measured with a contact time of 2 ms, and a 90 ° pulse width of 2.9  $\mu\text{s}$  was employed. In the measurements of  $T_{1\rho}^{\text{H}}$ , a contact time of 0.2 ms was used, and a proton spin-locking time  $\tau$  ranged from 0.5 to 30 ms. 2,048 scans were done to obtain the  $^{13}\text{C}$  CP/MAS spectra, while 4,096 scans were accumulated for the relaxation time measurements. Chemical shifts of  $^{13}\text{C}$  spectra represented in ppm were referred to tetramethylsilane by using the methine carbon resonance (29.47 ppm) of adamantane crystals as an external reference standard. In order to minimize any possible effect due to the thermal history and/or residual solvents, each sample was heat-treated at 250 °C *in vacuo* for 5 min just before the measurement.

## 2.3. Results and Discussion

### 2.3.1. Estimation of Miscibility and Intermolecular Interaction

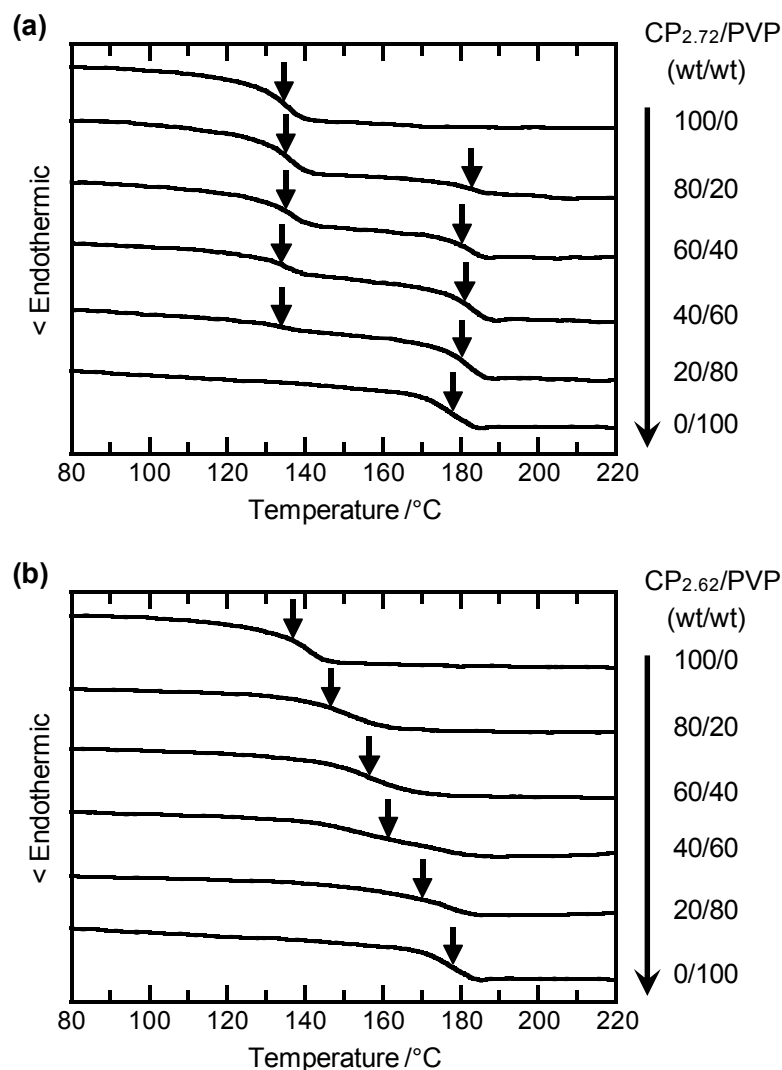
The miscibility state in the present CP/vinyl polymer system was estimated basically by  $T_g$  determination in DSC; generally, if any blend sample of a given polymer/polymer pair exhibits a single glass transition between the  $T_g$ s of the two component polymers and a composition-dependent shift of the blend  $T_g$  is clearly observed, then the pair can be regarded as a miscible one on the  $T_g$ -detection scale that is usually assumed to be less than a couple of tens of nanometers.<sup>[8,9]</sup> To examine the presence of intermolecular interactions, different blend compositions of selected CP/vinyl polymer pairs were subjected to FT-IR and CP/MAS NMR spectra measurements.

#### 2.3.1.1. CP/PVP Blends

When CPs of DS = 1.71–2.62 were used as a counter component to PVP, the solution-cast blend films prepared at 10/90–90/10 (wt/wt) compositions were all transparent in the visual inspection. By contrast, CP/PVP blends of propionyl DS = 2.72–2.93 formed a comparatively cloudy film at intermediate compositions of 40–70 wt% CP content.

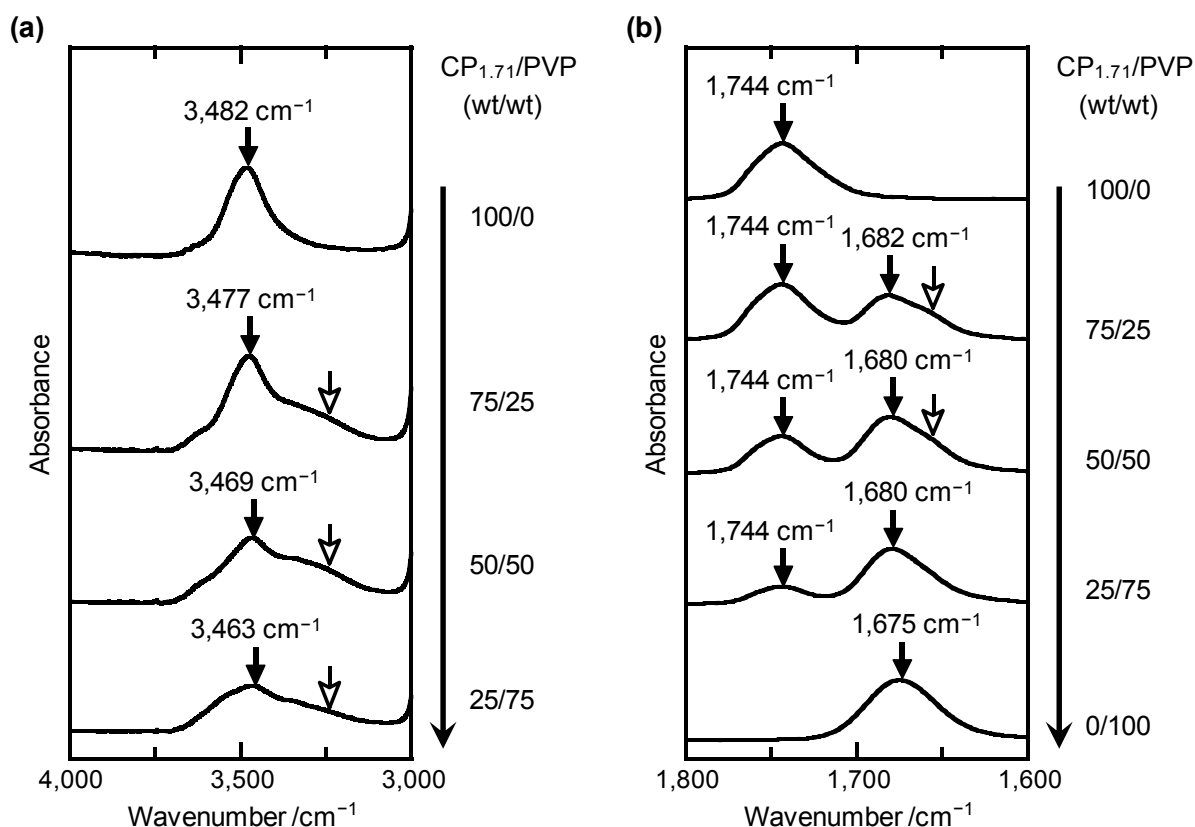
Figure 2-2a displays DSC thermograms obtained for CP<sub>2.72</sub>/PVP blends. From reading of the midpoint of the respective discontinuities in heat flow,  $T_g$  of CP<sub>2.72</sub> and that of PVP were evaluated as 134 °C and 177 °C, respectively. For the blend samples of 20/80–80/20 compositions, two independent glass transitions originating from the two components were clearly detected at almost the same positions as those observed for the unblended samples. This behavior of double  $T_g$ s was also noted for CP<sub>2.81</sub>/PVP and CP<sub>2.93</sub>/PVP blends. Thus, the CPs of DS > 2.7 are taken as immiscible with PVP.

Contrastively, the other six pairs of CP/PVP using propionyl DSs of <2.7 imparted a miscible sign. Figure 2-2b exemplifies DSC thermograms of CP<sub>2.62</sub>/PVP blends.  $T_g$  of CP<sub>2.62</sub> was determined to be 138 °C. The blends with PVP gave a single, composition-dependent  $T_g$  that shifted to higher temperatures along with an increase in the PVP content; thus it can be concluded that the CP forms a miscible monophasic system with PVP. This was also the case for the other CPs of DS = 1.71–2.54.



**Figure 2-2.** DSC thermograms obtained for (a) CP<sub>2.72</sub>/PVP and (b) CP<sub>2.62</sub>/PVP blends. Arrows indicate a  $T_g$  position taken as the midpoint of a baseline shift in heat flow.

Figure 2-3 compiles FT-IR spectra obtained for blends of the miscible CP<sub>1.71</sub>/PVP pair, on an enlarged scale for two regions of (a) O-H and (b) C=O stretching vibrations. As shown in Figure 2-3a, the unblended CP (top data) gave a band centering at 3,482 cm<sup>-1</sup>, which can be associated with a mixture of free hydroxyls and intramolecularly hydrogen-bonded OH groups. For the blends, it was observed that the band peak shifted to lower wavenumber positions with increasing PVP content, and, concomitantly, another absorption signal became more discernible as a shoulder on the side of further lower wavenumbers, as marked by a white arrow at ~3,300 cm<sup>-1</sup> in Figure 2-3a. This new band can be ascribed to the stretching of intermolecularly hydrogen-bonded OH groups.<sup>[10]</sup>



**Figure 2-3.** FT-IR spectra of CP<sub>1.71</sub>, PVP, and their blends in the frequency regions of (a) O-H and (b) C=O stretching vibrations. Solid arrows indicate a peak-top position in the respective specific absorption bands, and white arrows indicate a shoulder band associated with hydrogen bonding (see text for discussion).

Concerning the region of C=O stretching vibration (Figure 2-3b), a 1,744  $\text{cm}^{-1}$  band involved in the propionyl side-group of the CP component was almost unchanged in the peak location by the blending with PVP. However, a carbonyl signal of PVP, observed at 1,675  $\text{cm}^{-1}$  for the homopolymer, became asymmetric progressively as the CP content increased in the binary mixture; consequently, the absorption band was dividable into two peaks, a larger one at  $\sim 1,680 \text{ cm}^{-1}$  and a smaller one at  $\sim 1,660 \text{ cm}^{-1}$  (see data for CP-rich compositions in Figure 2-3b). These two split IR signals for the PVP component may be associated with the free carbonyl and hydrogen-bonded carbonyl groups, respectively.<sup>[11]</sup>

The above observations of the frequency shift and shape variation for the specific IR bands are evidently attributed to the hydrogen-bonding interaction between the residual hydroxyls of the CP component and the carbonyls of the PVP component. Conversely, this attractive interaction would contribute as a driving force to develop the good miscibility of

the CP/PVP blends, as did in the CA/PVP<sup>[1,2]</sup> and CB/PVP systems.<sup>[3]</sup> In a corroborating experiment, the immiscible CP/PVP blends using highly substituted CPs of DS = 2.81 and 2.93 exhibited no systematic variation of the corresponding bands in their FT-IR spectra.

By comprehensive comparison with the previous estimation shown in Figure 2-1, we notice that the upper limit in DS of CP miscible with PVP, which is ~2.7, is just intermediate between the corresponding ones, 2.8 and 2.5, for CA and CB, respectively. This is readily interpretable as due to the difference in effectiveness of the steric hindrance between the three ester side-groups which can inhibit the hydrogen-bonding interaction stated above, in consideration of the order of bulkiness for the acetyl, propionyl, and butyryl substituents.

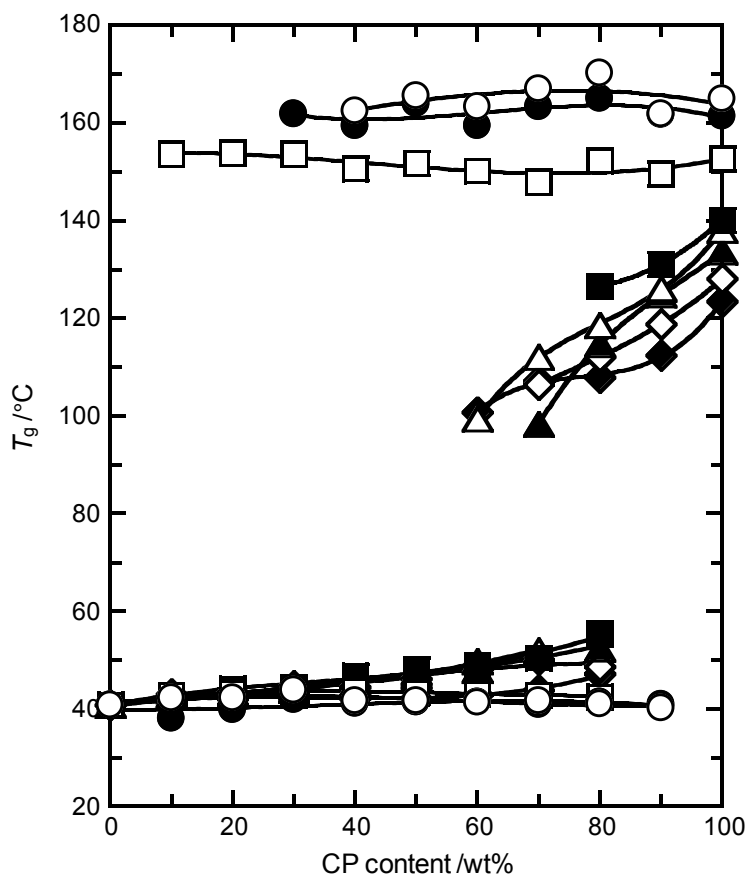
### 2.3.1.2. CP/PVAc Blends

As-cast films of CP/PVAc blends were mostly transparent to the naked eye (i.e., optically compatible) over the whole composition range. However, taking account of the refractive index 1.47–1.49 of CP, close to that of PVAc (1.4665),<sup>[12]</sup> it should be noted that the transparency of these films is not directly linked to the blend miscibility.

Figure 2-4 collects  $T_g$  versus composition plots for eight series of CP/PVAc blends (propionyl DS = 1.90–2.93). As can be seen from the plots, the three blend series using CPs of DS = 1.90, 2.18, and 2.35 were completely immiscible, because two  $T_g$  signals appeared without any noticeable shift from their original locations for the two components. Regarding the other blend series using CPs of DS > 2.5, however, an appreciable extent of  $T_g$  shift was detected for both of the two components at compositions of CP/PVAc = 60/40–90/10, indicating that a certain amount of the CP constituent was dissolved into the PVAc phase, and *vice versa*. Therefore, the CP(DS > 2.5)/PVAc pairs are judged to be partially miscible. Such partial miscibility was never definable to the CA/PVAc and CB/PVAc systems irrespective of DS of the CA or CB component; any blend of both systems provided two invariable  $T_g$ s independent of the mixing composition.

The finding of the partial miscibility (or better compatibility) for the pairs of highly propionylated CP/PVAc is quite significant in the present study, as embodied below for CP blends with the copolymer P(VP-*co*-VAc). A structural affinity between the propionyl side-group ( $\text{CH}_3\text{-CH}_2\text{-CO-O-C-}$ ) and the VAc unit ( $\text{-(CH}_2\text{-CH(O-CO-CH}_3\text{))}$ ) might be responsible to the advent of the partial miscibility; a similar effect has been pointed out in

former studies on CE/poly( $\varepsilon$ -caprolactone) blends.<sup>[5,6]</sup> The two structural unities containing a carbonyl moiety may be favorable for a relatively weak interaction of dipole-dipole anti-parallel alignment. The presence of such a weak interaction is also suggested in earlier papers dealing with a miscible system of PVAc with poly(methyl acrylate)  $(-\text{CH}_2-\text{CH}(\text{CO}-\text{O}-\text{CH}_3))_n-$ .<sup>[13,14]</sup>

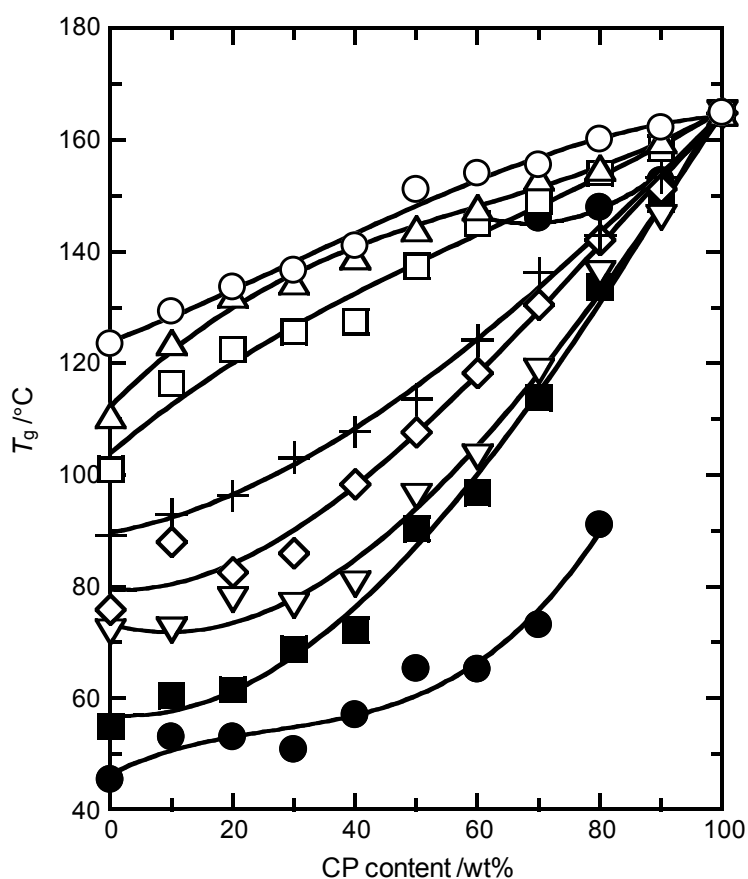


**Figure 2-4.**  $T_g$  versus composition plots for eight series of CP/PVAc blends. DS of CP: ○, 1.90; ●, 2.18; □, 2.35; ■, 2.54; △, 2.62; ▲, 2.72; ◇, 2.81; ◆, 2.93.

### 2.3.1.3. CP/P(VP-co-VAc) Blends

In visual appearance, as-cast films of CP blends with VP-VAc copolymers were homogeneous and transparent, except for films of several polymer pairs composed of CP of DS > 2.7 and P(VP-co-VAc) having more than 70 mol% VP residues.

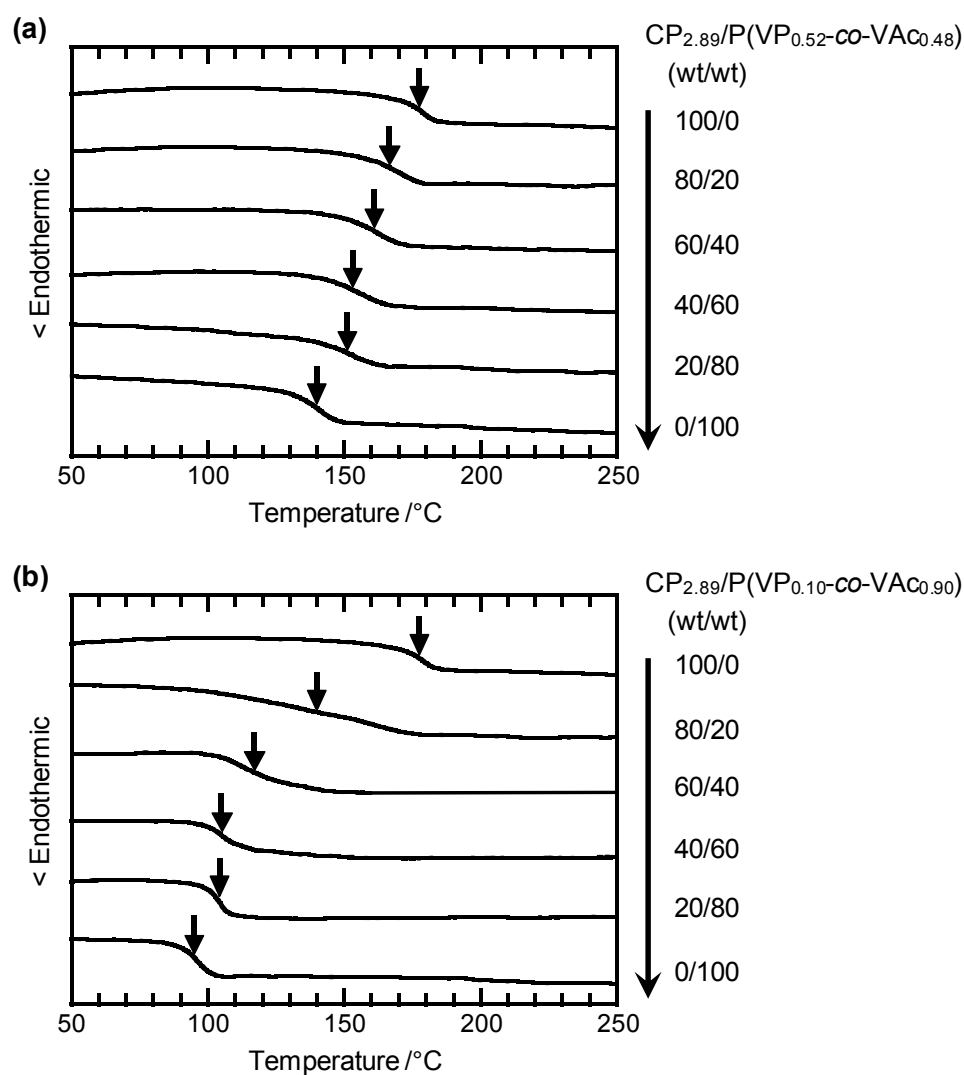
Figure 2-5 displays  $T_g$  variations with mixing composition for eight series of CP<sub>1.90</sub>/P(VP-*co*-VAc) blends, the VP fraction of the copolymer component ranging from 10 to 87 mol%. In the data plotting, when the VP fraction in P(VP-*co*-VAc) was  $\geq 23$  mol%, any blend series of CP<sub>1.90</sub>/P(VP-*co*-VAc) provided a smooth variation of a single  $T_g$  situated between the  $T_g$  values of the two unblended components. Thus, it turns out that CP<sub>1.90</sub> forms a miscible monophase with P(VP-*co*-VAc)s of VP > ~20 mol%. For selected blends of the miscible pairs, the presence of the hydrogen-bonding interaction between the CP-hydroxyl and VP-carbonyl groups was also ascertained by FT-IR measurements. With regard to a series of CP<sub>1.90</sub>/P(VP<sub>0.10</sub>-*co*-VAc<sub>0.90</sub>), a few samples of 60–80 wt% CP content gave two discrete  $T_g$ s, yet there occurred a noticeable extent of  $T_g$  shift over all the blend compositions, as can be seen from Figure 2-5. Therefore, exceptionally, this polymer pair is evaluated to be partially miscible.



**Figure 2-5.** Composition dependence of  $T_g$  for eight series of CP<sub>1.90</sub>/P(VP-*co*-VAc) blends. VP:VAc in P(VP-*co*-VAc): ●, 10:90; ■, 23:77; ▽, 33:67; ◇, 40:60; +, 52:48; □, 62:38; △, 73:27; ○, 87:13.

In the same way, CP<sub>2.18</sub> showed a similar miscibility behavior to that of CP<sub>1.90</sub>; viz., the CP was partially miscible with P(VP<sub>0.10</sub>-co-VAc<sub>0.90</sub>) and completely miscible with the other copolymers of VP:VAc = 23:77–87:13. Intriguingly, CP<sub>2.35</sub>, CP<sub>2.54</sub>, and CP<sub>2.62</sub> were all completely miscible even with P(VP<sub>0.10</sub>-co-VAc<sub>0.90</sub>) as well as with the others of VP > 20 mol%.

When the propionyl DS of the CP component reached 2.72 and more, the CPs were miscible with P(VP-co-VAc)s of ca. 10–65 mol% VP residues, despite their imperfect miscibility with PVAc and PVP homopolymers. Figure 2-6 exemplifies the miscible evidence in DSC for CP<sub>2.89</sub>/P(VP<sub>0.52</sub>-co-VAc<sub>0.48</sub>) and CP<sub>2.89</sub>/P(VP<sub>0.10</sub>-co-VAc<sub>0.90</sub>) combi-



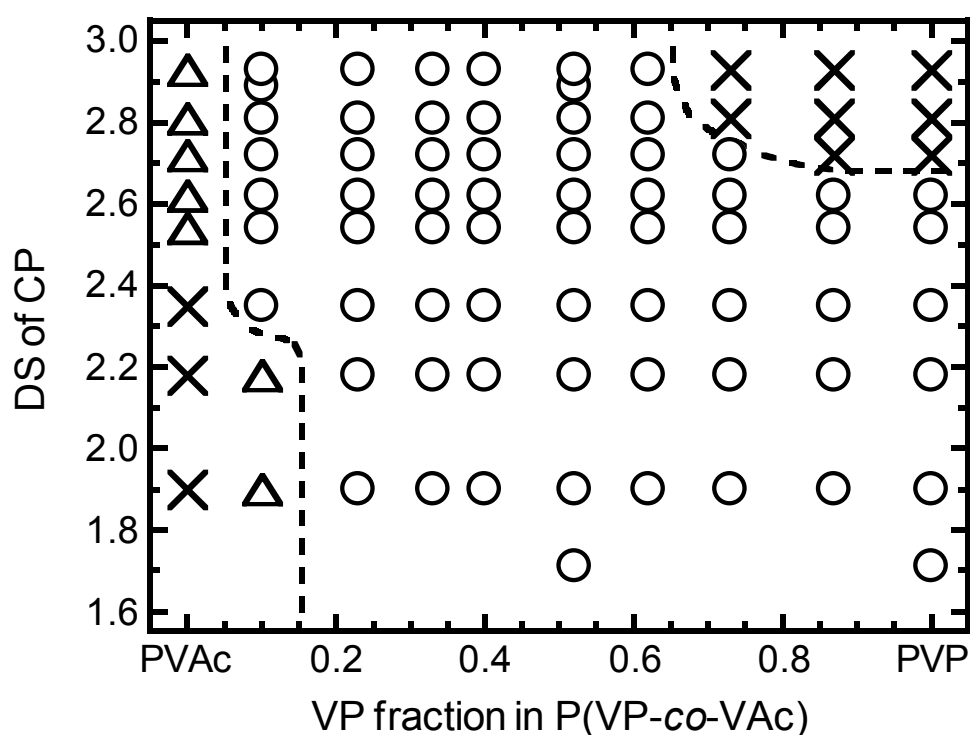
**Figure 2-6.** DSC thermograms obtained for (a) CP<sub>2.89</sub>/P(VP<sub>0.52</sub>-co-VAc<sub>0.48</sub>) and (b) CP<sub>2.89</sub>/P(VP<sub>0.10</sub>-co-VAc<sub>0.90</sub>) blends. Arrows indicate a  $T_g$  position.

nations. Accordingly, it follows that the CP/P(VP-*co*-VAc) system exhibited a definite miscibility window, as did the previous CB/P(VP-*co*-VAc) system (see Figure 2-1b). As for the miscibility window of the latter system, it was reasonably concluded that a greater repulsion between the VP and VAc units in the random copolymer was mainly contributory to the miscibility attainment; this was rationalized by assessment of the Krigbaum-Wall interaction parameters.<sup>[4]</sup> The intra-copolymer effect may also be applicable to the present CP(DS > 2.7)/P(VP-*co*-VAc) blends.

It should be stressed here that the CPs of DS > 2.7 were miscible with P(VP<sub>0.10</sub>-*co*-VAc<sub>0.90</sub>) abundant in VAc residues, as was the case for the ones of DS = 2.35–2.62. At the comonomer ratio of VP:VAc = 10:90, the intramolecular repulsion effect would decline to a considerable extent; instead, however, the interaction coming from the structural affinity between the ester side-group of CP and the VAc unit of the copolymer would be more prevailing. It can therefore be assumed that, as a result of favorable balance of the two effects, the high-substituted CPs were miscible with P(VP<sub>0.10</sub>-*co*-VAc<sub>0.90</sub>). To find a spectroscopic evidence of the latter interaction in which both CP- and VAc-carbonyls should be involved, FT-IR and solid-state <sup>13</sup>C CP/MAS NMR measurements were carried out for CP<sub>2.89</sub>/P(VP<sub>0.10</sub>-*co*-VAc<sub>0.90</sub>) and CP<sub>2.89</sub>/P(VP<sub>0.52</sub>-*co*-VAc<sub>0.48</sub>) blends. In the IR examination, however, the C=O stretching band of CP overlapped completely with the one of VAc. In the CP-MAS spectra measurements, the unblended copolymers gave a carbonyl resonance signal composed of two splitting peaks with their maximum at 171 ppm (for VAc unit) and 175 ppm (for VP unit); the splitting was relatively clear in a data for P(VP<sub>0.52</sub>-*co*-VAc<sub>0.48</sub>) (see Figure 2-9). Nevertheless, when the carbonyl carbon resonance of CP (173.5 ppm) merged with the split signal of the VP/VAc units, it was difficult to precisely estimate the respective three chemical shifts. Thus the structural affinity effect was undetectable for any of the blends; it appears to be substantially feeble, however.

On the basis of the thermal analysis data, a miscibility map for the CP/P(VP-*co*-VAc) system was successfully constructed, as shown in Figure 2-7. The diagram indicates that CPs of DS < 2.7, having a relatively higher amount of residual OH groups, are mostly miscible with the vinyl polymers of VP > ~20 mol%, primarily due to predominance of the hydrogen-bonding interaction. A miscibility window emerges in the region satisfying propionyl DS > 2.7 and VP fraction = 10–65 mol%, as a result of indirect intercomponent

attraction due to the stronger repulsion effect in the P(VP-*co*-VAc) component itself. To make a comparison of the map with the previous ones (Figure 2-1) for the corresponding blend systems of CA and CB, we find that the CP system produced the largest miscible region. As compared with the map for the CB blends, the DS boundary partitioning the miscibility states of CP/P(VP-*co*-VAc) (VP  $\geq$  65 mol%) pairs is driven up to  $\sim 2.7$  from the value  $\sim 2.5$  for the CB system. This elevation in DS may be ascribed to the modest effectiveness in steric hindrance of the propionyl group of medium size, relative to that of the more bulky butyryl group. Another factor expanding the miscible region in the map for the CP system is an intermolecular accessibility derived from the structural affinity of the propionyl side-group with the VAc unit; this effect may be applicable to the blending pairs of CPs of DS  $> \sim 2.3$  and P(VP-*co*-VAc)s of VP = ca. 10–20 mol%.



**Figure 2-7.** Miscibility map for CP/P(VP-*co*-VAc) blends, as a function of DS of CP and VP fraction in P(VP-*co*-VAc). The meanings of two symbols ○ and × are the same as defined in Figure 2-1. An additional symbol (△) indicates that a given pair of CP/P(VP-*co*-VAc) is partially miscible (dual  $T_g$ s approaching each other to an appreciable degree).

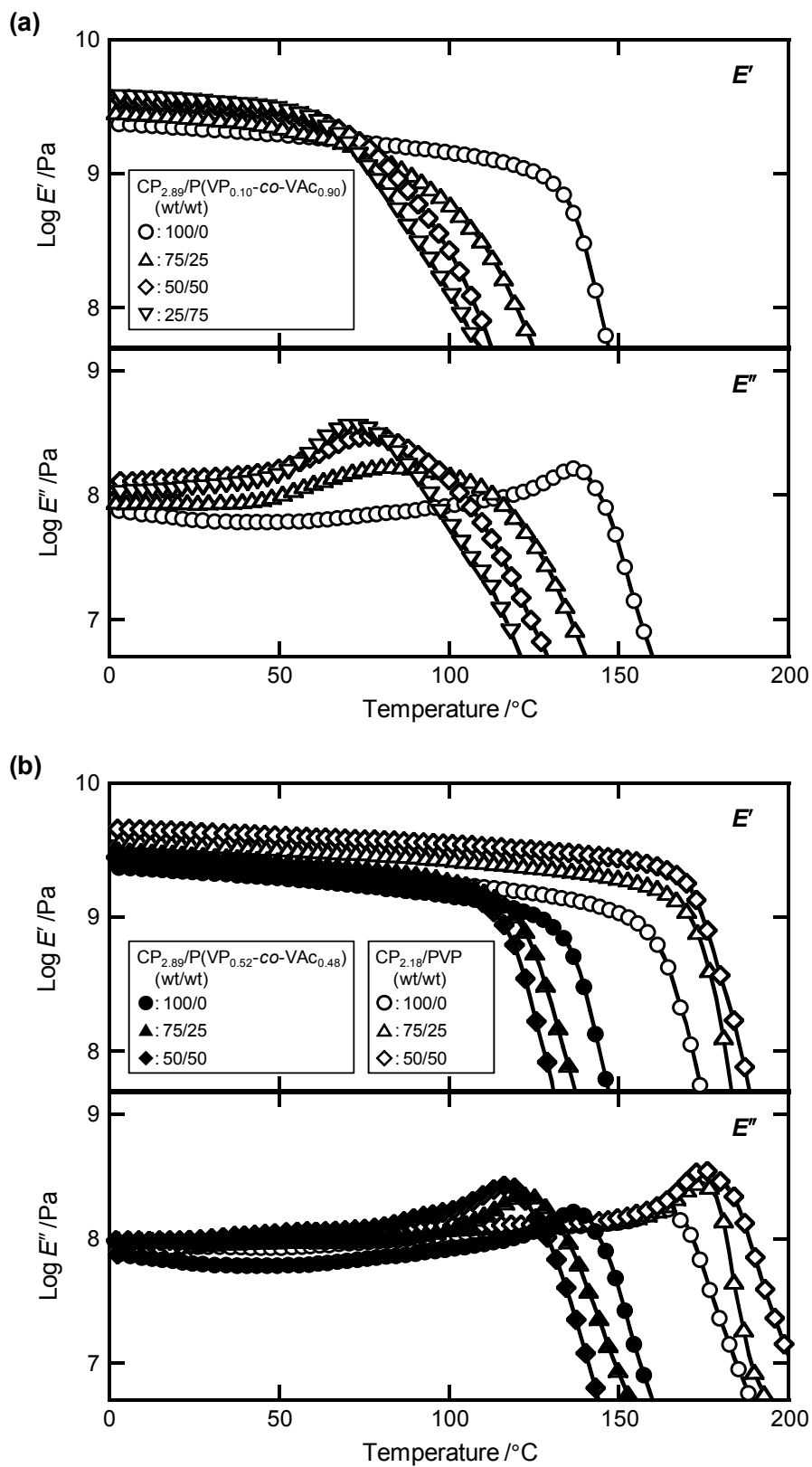
### 2.3.2. Insight into the Scale of Homogeneous Mixing

In the previous study on the CB/P(VP-*co*-VAc) system,<sup>[3]</sup> it was suggested that the degree of homogeneity for the combinations situated in the miscibility window was somewhat lower than that for the hydrogen-bonding type of miscible blends, reflecting a difference in absolute strength between the driving forces for the respective miscibility attainments. In this connection, we should remark that DSC thermograms for the 60/40–90/10 compositions of CP<sub>2.89</sub>/P(VP<sub>0.10</sub>-*co*-VAc<sub>0.90</sub>) blends exhibited a single, but relatively broader glass transition (see Figure 2-6b). A similar phenomenon was noted for other CP/P(VP-*co*-VAc) blends satisfying  $DS > 2.7$  for the CP and VP = 10–33 mol% for the copolymer. Such a broadening in temperature range of the glass transition may be interpretable as due to mixing of plural microdomains with subtly different fluctuations in polymer composition.<sup>[15]</sup> In relation to this assumption, further investigations were made into the homogeneity of mixing for the CP/P(VP-*co*-VAc) system by means of DMA and nuclear magnetic relaxation measurements.

#### 2.3.2.1. Thermal Transition Behavior Evaluated by DMA

As far as detection of  $T_g$  is concerned, DMA is more sensitive than calorimetric measurements in many cases of studies on multicomponent polymeric materials<sup>[9,16,17]</sup>. As a conventional matter, if DSC analysis is sensitive to heterogeneities with sizes of ca. 20–30 nm as an upper limit, DMA can detect a somewhat finer scale of heterogeneity, e.g., a domain size smaller than ~15 nm.<sup>[8,11,18]</sup>

Figure 2-8a shows the temperature dependence of the dynamic storage modulus  $E'$  and loss modulus  $E''$  for CP<sub>2.89</sub>/P(VP<sub>0.10</sub>-*co*-VAc<sub>0.90</sub>) blends of 25/75, 50/50, and 75/25 compositions, together with the corresponding data for plain CP<sub>2.89</sub>. As for the copolymer *per se*, the data was not obtained because of a brittle nature of the film. As demonstrated clearly in the figure, the unblended CP<sub>2.89</sub> sample showed a very sharp transition with an  $E''$  peak maximum at 137 °C; this temperature is somewhat higher than  $T_g$  (127 °C) determined by DSC, however. In contrast, the blend samples gave a much broader  $E''$  peak with a low onset point (~50 °C in common), and a more gradual  $E'$  falling as well, in the glass transition temperature region, this trend being particularly prominent in the data for the 75/25 and 50/50 compositions.



**Figure 2-8.** Temperature dependence of the dynamic storage modulus  $E'$  and loss modulus  $E''$  for (a) CP<sub>2.89</sub>/P(VP<sub>0.10</sub>-co-VAc<sub>0.90</sub>) and (b) CP<sub>2.18</sub>/PVP and CP<sub>2.89</sub>/P(VP<sub>0.52</sub>-co-VAc<sub>0.48</sub>) blends.

Figure 2-8b compiles DMA data of CP<sub>2.18</sub>/PVP and CP<sub>2.89</sub>/P(VP<sub>0.52-co</sub>-VAc<sub>0.48</sub>) blends, the illustration for each series being restricted to a few samples rich in CP content, there. Any of the two blend series provided a single and sharp transition signal, both in the  $E''$  peak and in the  $E'$  drop, which shifted systematically with polymer composition. From comparison with these data, the pair of CP<sub>2.89</sub>/P(VP<sub>0.10-co</sub>-VAc<sub>0.90</sub>) described on ahead is obviously inferior in the degree of miscibility to the other two, within a scale (~15 nm) detectable by DMA. Incidentally, it is interesting to find a homogeneity on the DMA scale for the CP<sub>2.89</sub> blends with P(VP<sub>0.52-co</sub>-VAc<sub>0.48</sub>) having equimolar amounts of VP and VAc units, although the blending pair is not of the hydrogen-bonding type such as the CP<sub>2.18</sub>/PVP one but situated in the miscibility window of that map (Figure 2-7).

#### 2.3.2.2. Homogeneity Estimated by Solid-state $^{13}\text{C}$ NMR Relaxation

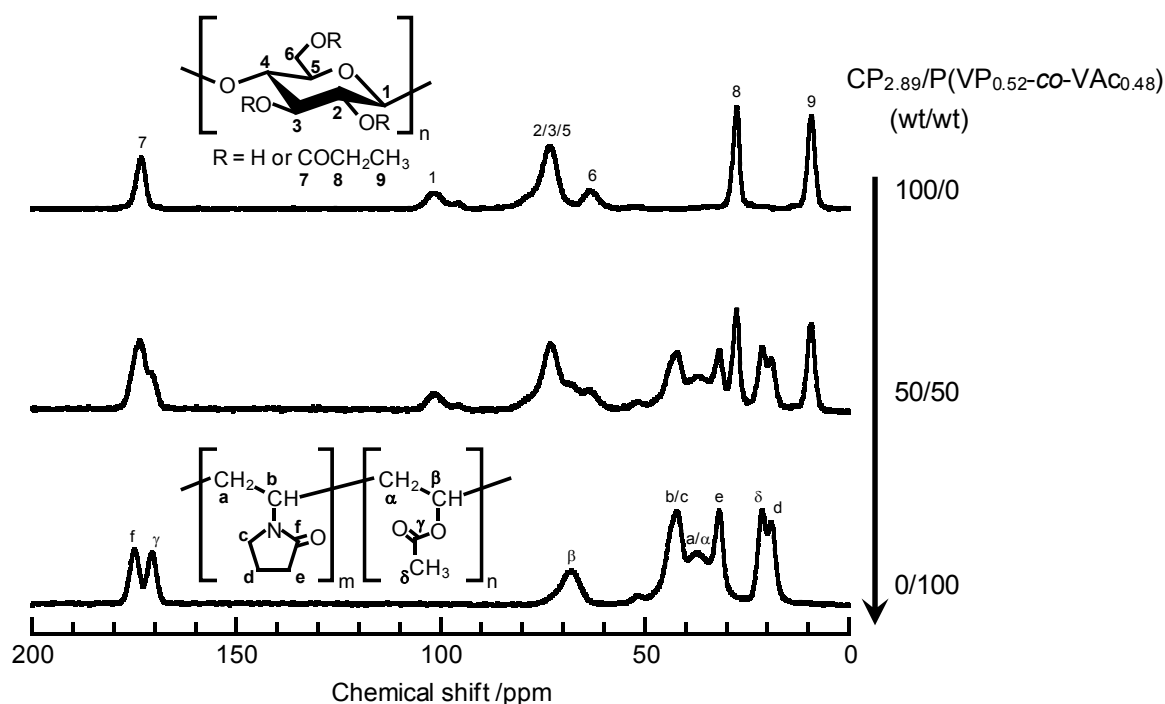
As a useful technique in solid-state  $^{13}\text{C}$  NMR,  $T_{1\rho}^{\text{H}}$  measurements for specific carbons in a multicomponent polymer system make it possible to estimate the mixing homogeneity in a scale of  $^1\text{H}$  spin-diffusion length that is usually within several nanometers.<sup>[2,11,19]</sup>  $T_{1\rho}^{\text{H}}$  values can be obtained by fitting the decaying carbon resonance intensity to the following exponential equation:

$$M(\tau) = M(0) \exp(-\tau/T_{1\rho}^{\text{H}}) \quad (2-1)$$

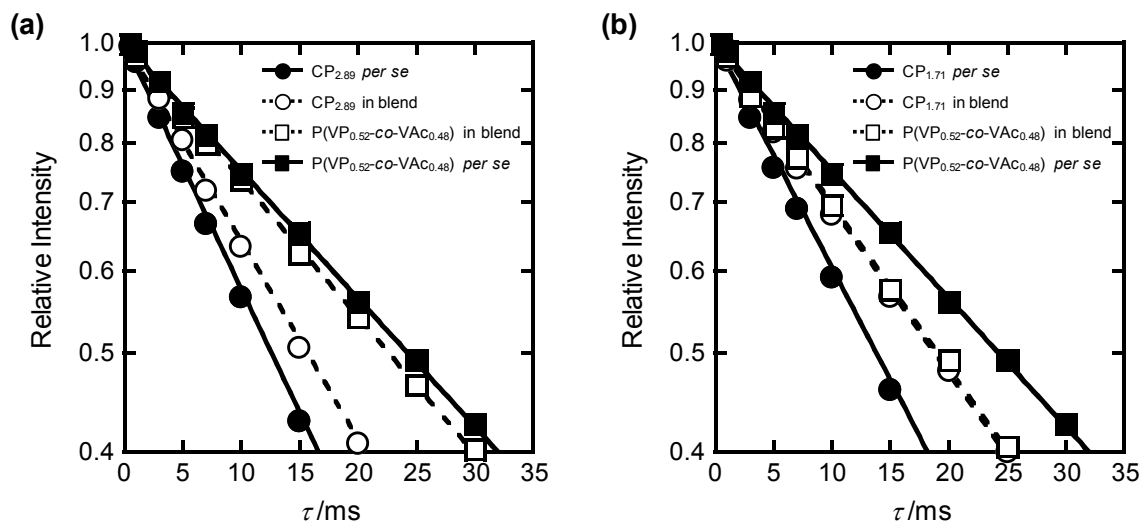
where  $M(\tau)$  is the magnetization intensity observed as a function of the spin-locking time  $\tau$ . In a general rule, if two constituent polymers are in a homogeneously mixed state on the scale over which  $^1\text{H}$  spin-diffusion can take place in a time  $T_{1\rho}^{\text{H}}$ , the  $T_{1\rho}^{\text{H}}$  values for different protons belonging to the respective components may be equalized to each other by the spin diffusion.

In terms of the NMR technique, a comparative assessment of the polymer-polymer mixing scale was made for three selected series of blends, CP<sub>2.89</sub>/P(VP<sub>0.52-co</sub>-VAc<sub>0.48</sub>), CP<sub>1.71</sub>/P(VP<sub>0.52-co</sub>-VAc<sub>0.48</sub>), and CP<sub>1.71</sub>/PVP. Figure 2-9 exemplifies  $^{13}\text{C}$  CP/MAS spectra obtained for CP<sub>2.89</sub>, P(VP<sub>0.52-co</sub>-VAc<sub>0.48</sub>), and their 50/50 blend. The peak assignments of the spectra are based on literature data for CP,<sup>[20]</sup> PVP,<sup>[19]</sup> and PVAc.<sup>[21]</sup> The experiment of  $T_{1\rho}^{\text{H}}$  quantifications was done through monitoring the following  $^{13}\text{C}$  resonance signals with better resolution: C2/C3/C5 pyranose carbons (74 ppm) and propionyl carbons C8 (28 ppm) and C9 (9.3 ppm) for the CP component, and C<sub>b</sub>/C<sub>c</sub> (42 ppm) and C<sub>δ</sub>/C<sub>d</sub> carbons (~20 ppm)

for the P(VP-*co*-VAc) component. Figure 2-10a illustrates the decay behavior in intensity of the C2/C3/C5 and C<sub>b</sub>/C<sub>c</sub> peaks for unblended CP<sub>2.89</sub> and P(VP<sub>0.52</sub>-*co*-VAc<sub>0.48</sub>), respectively, and for their 50/50 blend imparting both resonance signals as well. The slope of each semi-logarithmic plot corresponds to an inverse of  $T_{1\rho}^H$  as the time constant of the relaxation process. It was found from these plots that  $T_{1\rho}^H$  of CP<sub>2.89</sub> (18.5 ms) increased to 22.7 ms and that of P(VP<sub>0.52</sub>-*co*-VAc<sub>0.48</sub>) (35.4 ms) decreased to 33.1 ms by the 50/50 blending, but they never became so close to each other. Regarding the CP<sub>1.71</sub>/P(VP<sub>0.52</sub>-*co*-VAc<sub>0.48</sub>) pair (Figure 2-10b), on the contrary,  $T_{1\rho}^H$  values of the two components for the 50/50 blend coincided with each other just at the midpoint (27.9 ms) between the respective original values, 20.5 ms for CP<sub>1.71</sub> and 35.4 ms for the copolymer. A similar tendency of  $T_{1\rho}^H$  variations was observed in tracing of another set of the C8 or C9 signal of CP and the C<sub>δ</sub>/C<sub>d</sub> signal of P(VP-*co*-VAc).



**Figure 2-9.** Solid-state  $^{13}\text{C}$  CP/MAS NMR spectra for CP<sub>2.89</sub>, P(VP<sub>0.52</sub>-*co*-VAc<sub>0.48</sub>), and their 50/50 blend.



**Figure 2-10.** Semilogarithmic plots of the decay of  $^{13}\text{C}$  resonance intensities as a function of spin-locking time  $\tau$ , for solid films of (a)  $\text{CP}_{2.89}$ ,  $\text{P}(\text{VP}_{0.52}\text{-co-VAc}_{0.48})$ , and their 50/50 blend, and (b)  $\text{CP}_{1.71}$ ,  $\text{P}(\text{VP}_{0.52}\text{-co-VAc}_{0.48})$ , and their 50/50 blend. The monitoring was conducted for the peak intensity of C2/C3/C5 pyranose carbons of CP and that of  $\text{C}_b/\text{C}_c$  carbons of the copolymer (see Figure 2-9).

Table 2-2 lists all the  $T_{1\rho}^{\text{H}}$  data obtained for  $\text{CP}_{1.71}$ ,  $\text{CP}_{2.89}$ , PVP,  $\text{P}(\text{VP}_{0.52}\text{-co-VAc}_{0.48})$ , and their miscible blends of CP/vinyl polymer = 75/25–25/75. In the  $\text{CP}_{1.71}/\text{P}(\text{VP}_{0.52}\text{-co-VAc}_{0.48})$  series,  $T_{1\rho}^{\text{H}}$  of the  $\text{CP}_{1.71}$  component, originally 20.0 ms as an average, rises systematically with an increase in the copolymer content, while that of the  $\text{P}(\text{VP}_{0.52}\text{-co-VAc}_{0.48})$  component, originally 35.0 ms as an average, diminishes correspondingly with increasing  $\text{CP}_{1.71}$  content. In consequence, the two  $T_{1\rho}^{\text{H}}$ s at every blend composition are surely in good agreement with each other. Such a composition-dependent shift of the almost equalized  $T_{1\rho}^{\text{H}}$ s of two components is also observed for the  $\text{CP}_{1.71}/\text{PVP}$  blend series. Thus, it is reasonably deduced that the two constituent polymers in the two series of blends are intimately mixed within a range where the mutual  $^1\text{H}$ -spin diffusion is permitted over a period of the respective homogenized  $T_{1\rho}^{\text{H}}$ , e.g.,  $\sim 30.5$  ms for the 50/50 composition of  $\text{CP}_{1.71}/\text{PVP}$ .

**Table 2-2.**  $T_{1\rho}^H$  values obtained for three series of blends, CP<sub>2.89</sub>/P(VP<sub>0.52-co</sub>-VAc<sub>0.48</sub>), CP<sub>1.71</sub>/P(VP<sub>0.52-co</sub>-VAc<sub>0.48</sub>), and CP<sub>1.71</sub>/PVP

| CP <sub>2.89</sub> /P(VP <sub>0.52-co</sub> -VAc <sub>0.48</sub> )<br>(wt/wt) | $T_{1\rho}^H$ /ms  |      |      |      |                                                |             |      |
|-------------------------------------------------------------------------------|--------------------|------|------|------|------------------------------------------------|-------------|------|
|                                                                               | CP <sub>2.89</sub> |      |      |      | P(VP <sub>0.52-co</sub> -VAc <sub>0.48</sub> ) |             |      |
|                                                                               | C2/3/5             | C8   | C9   | Ave. | b/c                                            | $\delta$ /d | Ave. |
| 100/0                                                                         | 18.5               | 17.6 | 17.7 | 17.9 | —                                              | —           | —    |
| 75/25                                                                         | 20.3               | 18.8 | 18.0 | 19.0 | 32.9                                           | 29.7        | 31.3 |
| 50/50                                                                         | 22.7               | 20.5 | 19.2 | 20.8 | 33.1                                           | 30.9        | 32.0 |
| 25/75                                                                         | 25.3               | 22.6 | 21.2 | 23.0 | 34.7                                           | 33.8        | 34.3 |
| 0/100                                                                         | —                  | —    | —    | —    | 35.4                                           | 34.6        | 35.0 |

| CP <sub>1.71</sub> /P(VP <sub>0.52-co</sub> -VAc <sub>0.48</sub> )<br>(wt/wt) | $T_{1\rho}^H$ /ms  |      |      |      |                                                |             |      |
|-------------------------------------------------------------------------------|--------------------|------|------|------|------------------------------------------------|-------------|------|
|                                                                               | CP <sub>1.71</sub> |      |      |      | P(VP <sub>0.52-co</sub> -VAc <sub>0.48</sub> ) |             |      |
|                                                                               | C2/3/5             | C8   | C9   | Ave. | b/c                                            | $\delta$ /d | Ave. |
| 100/0                                                                         | 20.5               | 20.3 | 19.2 | 20.0 | —                                              | —           | —    |
| 75/25                                                                         | 24.3               | 23.0 | 21.6 | 23.0 | 24.5                                           | 24.1        | 24.3 |
| 50/50                                                                         | 27.8               | 26.8 | 24.5 | 26.4 | 27.9                                           | 26.9        | 27.4 |
| 25/75                                                                         | 33.0               | 29.7 | 27.8 | 30.2 | 33.7                                           | 30.9        | 32.3 |
| 0/100                                                                         | —                  | —    | —    | —    | 35.4                                           | 34.6        | 35.0 |

| CP <sub>1.71</sub> /PVP<br>(wt/wt) | $T_{1\rho}^H$ /ms  |      |      |      |      |      |      |
|------------------------------------|--------------------|------|------|------|------|------|------|
|                                    | CP <sub>1.71</sub> |      |      |      | PVP  |      |      |
|                                    | C2/3/5             | C8   | C9   | Ave. | b/c  | d    | Ave. |
| 100/0                              | 20.5               | 20.3 | 19.2 | 20.0 | —    | —    | —    |
| 75/25                              | 25.1               | 24.1 | 23.0 | 24.1 | 26.0 | 26.0 | 26.0 |
| 50/50                              | 30.9               | 30.1 | 30.8 | 30.6 | 30.6 | 29.5 | 30.1 |
| 25/75                              | 33.4               | 33.7 | 33.1 | 33.4 | 33.7 | 33.0 | 33.4 |
| 0/100                              | —                  | —    | —    | —    | 32.6 | 31.3 | 32.0 |

An effective path length  $L$  of the spin diffusion in a time  $T_{1\rho}^H$  is given by the following equation.<sup>[22]</sup>

$$L \cong (6DT_{1\rho}^H)^{1/2} \quad (2-2)$$

where  $D$  is the spin-diffusion coefficient, usually taken to be  $\sim 1.0 \times 10^{-12}$  cm<sup>2</sup>/s in organic polymer materials. By adopting  $T_{1\rho}^H$  data of 23–31 ms approximated for the CP<sub>1.71</sub>/P(VP<sub>0.52</sub>-*co*-VAc<sub>0.48</sub>) blends of 75/25–25/75 compositions, the diffusion path length is calculated as  $L = 3.7$ – $4.3$  nm. In a similar manner,  $L$  is determined to be 3.9–4.4 nm with  $T_{1\rho}^H = 25$ –33 ms for the corresponding CP<sub>1.71</sub>/PVP compositions. Accordingly, it is confirmed that any of these miscible blends using a low-substituted CP is virtually homogeneous in a scale of ca. 4 nm.

With regard to the CP<sub>2.89</sub>/P(VP<sub>0.52</sub>-*co*-VAc<sub>0.48</sub>) series, as evidenced in Table 2-2, there arises a serious disagreement between  $T_{1\rho}^H$ s of the two polymer components at every blend composition, although the mutual approach to a small extent is admitted. This larger temporal disagreement implies that the relaxation processes of the two polymers in the blends proceeded rather independently without their cooperative spin diffusion. By the combined use of this result and the previous DMA one, it can be concluded that the scale of homogeneity in the CP<sub>2.89</sub>/P(VP<sub>0.52</sub>-*co*-VAc<sub>0.48</sub>) blends lies between approximately 5 and 15 nm.

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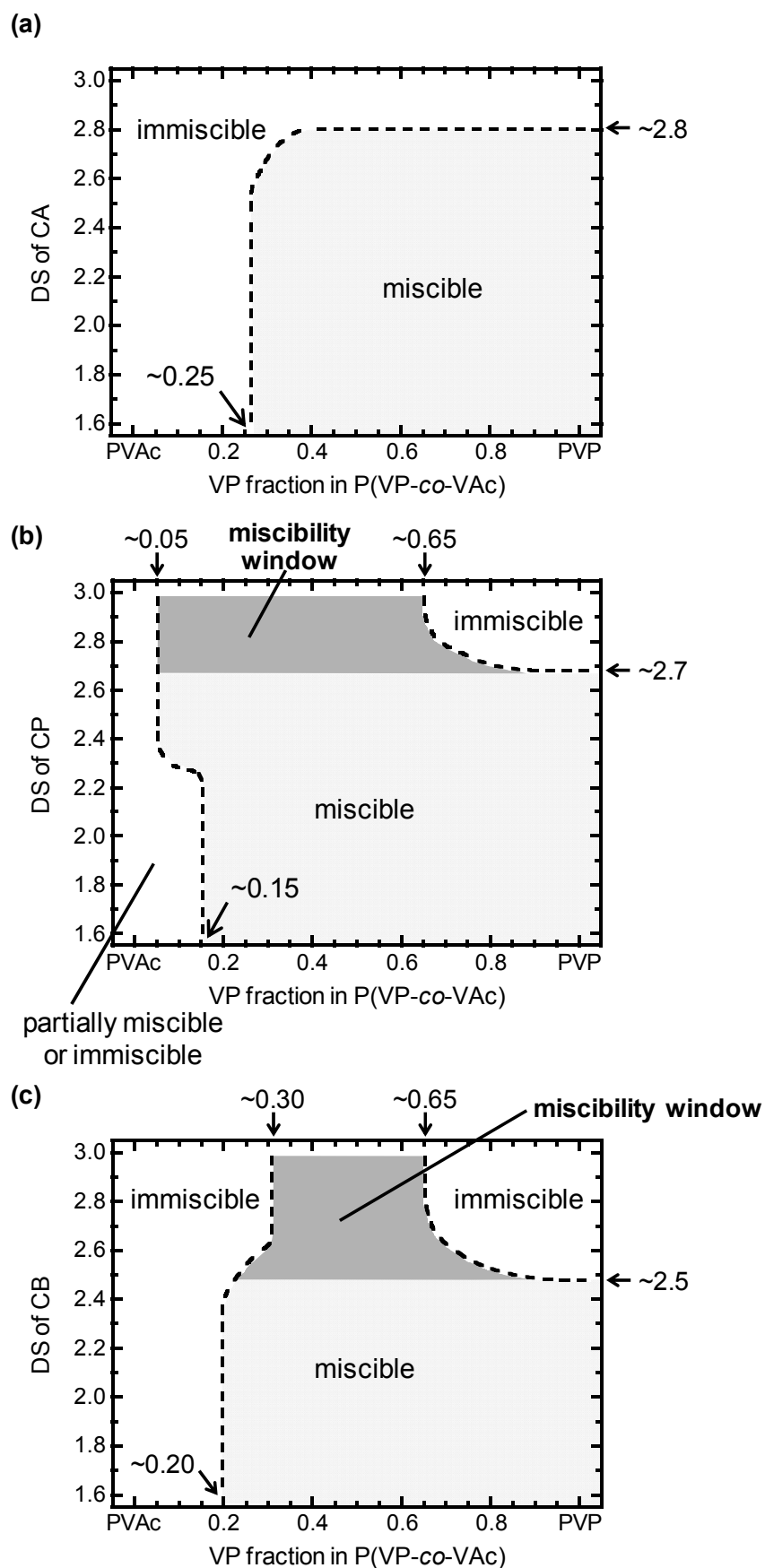
## Chapter 3

### Blend Miscibility of Cellulose Propionate with Poly(*N*-vinyl pyrrolidone-*co*-methyl methacrylate)

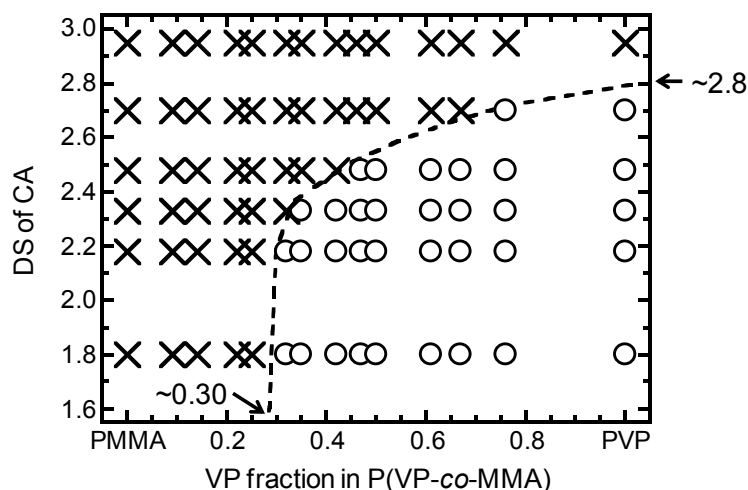
#### 3.1. Introduction

In Chapter 2 and related previous studies,<sup>[1,2]</sup> three separate systems of cellulose acetate (CA), propionate (CP), and butyrate (CB), each blended with P(VP-*co*-VAc), were examined mainly by differential scanning calorimetry (DSC); the counterpart P(VP-*co*-VAc) here represents homo- and random co-polymers comprising *N*-vinyl pyrrolidone (VP) and/or vinyl acetate (VAc) units. Figure 3-1 surveys the estimation results for the three systems, by offering each miscibility map constructed as a function of the degree of ester substitution (DS) of cellulose ester (CE) and the VP:VAc composition of P(VP-*co*-VAc). As can readily be seen by comparison of the three maps, the region of miscible CE/P(VP-*co*-VAc) pairings was drastically changeable depending on the carbon number of the acyl substituent of CE. Intriguingly, the CP system provided the largest miscible region (see Figure 3-1b). Such a specific improvement in the miscibility with P(VP-*co*-VAc) of the CP blends was attributed to the structural affinity favorable for a dipole-dipole antiparallel alignment between the propionyl side-group and the VAc unit, as well as to the moderate length of the acyl substituent which generally works as a steric hindrance to the hydrogen-bonding interactions associated with the residual hydroxyls.<sup>[3]</sup>

Another system of CA/VP-containing vinyl copolymer blends has also been reported on the miscibility and intermolecular interaction,<sup>[4]</sup> wherein methyl methacrylate (MMA) was selected as the second constituent of the copolymer, because of the distinguished optical property, weather resistance, and safety to living bodies of poly(methyl methacrylate) (PMMA). Figure 3-2 summarizes the result of miscibility estimation for the CA/P(VP-*co*-MMA) blends. Regarding this system, an additional interest was focused on the molecular orientation and optical anisotropy in uniaxially drawn films of the miscible blends;<sup>[5]</sup> the birefringence development was widely controllable in both the degree and polarity, by altering the DS of CA, the VP:MMA ratio in P(VP-*co*-MMA), and the proportion of the mixing polymers. However, as mapped in Figure 3-2, the miscible pairing of this system



**Figure 3-1.** Miscibility maps for three blend systems (a) CA/P(VP-co-VAc), (b) CP/P(VP-co-VAc), and (c) CB/P(VP-co-VAc), quoted from ref 1 for (a), Chapter 2 for (b), and ref 2 for (c), respectively, in a rearranged style retaining the essence.



**Figure 3-2.** Miscibility map for CA/P(VP-*co*-MMA), quoted from a previous study<sup>[4]</sup> with additional data. Symbols indicate that a given pair of CA/P(VP-*co*-MMA) is miscible (○) or immiscible (×).

was realized in a region of lower DS of CA and higher VP fraction in P(VP-*co*-MMA), and thus the blends were kind of a hydrophilic material.

As an extension of the blend studies stated above, next, attention should be directed to the miscibility characterizations of CP and cellulose acetate propionate (CAP) with P(VP-*co*-MMA), in expectation of a positive effect of the propionyl substitution which would expand the DS and VP:MMA ranges for miscible pairing of CE and P(VP-*co*-MMA), as has been observed for the CE/P(VP-*co*-VAc) system. The miscibility attainment even for hydrophobic combinations of high-substituted CP or CAP and MMA-rich copolymer may be of great significance, in view of the practical application to optical films and/or membranes. In the present chapter, the author inspected the main target system of CP/P(VP-*co*-MMA) blends on the miscibility, inter-component interactions, and scale of homogeneity, by DSC and Fourier transform infrared (FT-IR) and solid-state <sup>13</sup>C NMR spectroscopy. In addition to the basic characterizations, some mechanical and optical properties in film form of the CP/P(VP-*co*-MMA) blends were also investigated by dynamic mechanical analysis (DMA) and birefringence measurements, respectively.

## 3.2. Experimental Section

### 3.2.1. Materials

CP samples were synthesized from cotton cellulose with a viscosity average molecular weight of 252,000 via a homogeneous reaction with acid chloride/base catalyst, in a procedure similar to that used in previous studies.<sup>[6,7]</sup> Two CAP samples were used; one was purchased from Eastman Chemical Co., and the other was obtained by acetylation of a commercial CP (Scientific Polymer Products, Inc.) in the same way as that adopted in a previous study.<sup>[8]</sup> Codes “CP<sub>*x*</sub>” and “CA<sub>*y*</sub>P<sub>*z*</sub>” denote CP of propionyl DS = *x* and CAP of acetyl DS = *y* and propionyl DS = *z*, respectively. Table 3-1 summarizes data of molecular weight and glass transition temperature (*T*<sub>g</sub>) for all the CE samples used in this chapter.

**Table 3-1.** Characterization of CP and CAP used in the present chapter

| Sample code <sup>a</sup>             | <i>M</i> <sub>w</sub> <sup>b</sup> | <i>M</i> <sub>n</sub> <sup>b</sup> | <i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>b</sup> | <i>T</i> <sub>g</sub> /°C | Source               |
|--------------------------------------|------------------------------------|------------------------------------|------------------------------------------------------------|---------------------------|----------------------|
| CP <sub>1.59</sub>                   | 1,230,000                          | 585,000                            | 2.10                                                       | 165                       | Synthesized          |
| CP <sub>1.71</sub>                   | 2,010,000                          | 850,000                            | 2.36                                                       | 162                       | Synthesized          |
| CP <sub>2.09</sub>                   | 1,190,000                          | 571,000                            | 2.08                                                       | 160                       | Synthesized          |
| CP <sub>2.18</sub>                   | 1,300,000                          | 577,000                            | 2.25                                                       | 157                       | Synthesized          |
| CP <sub>2.33</sub>                   | 844,000                            | 258,000                            | 3.27                                                       | 155                       | Synthesized          |
| CP <sub>2.53</sub>                   | 818,000                            | 367,000                            | 2.23                                                       | 141                       | Synthesized          |
| CP <sub>2.62</sub>                   | 979,000                            | 359,000                            | 2.73                                                       | 138                       | Synthesized          |
| CP <sub>2.72</sub>                   | 2,390,000                          | 968,000                            | 2.47                                                       | 134                       | Synthesized          |
| CP <sub>2.81</sub>                   | 1,990,000                          | 837,000                            | 2.38                                                       | 128                       | Synthesized          |
| CP <sub>2.89</sub>                   | 2,000,000                          | 692,000                            | 2.89                                                       | 127                       | Synthesized          |
| CP <sub>2.93</sub>                   | 1,250,000                          | 525,000                            | 2.38                                                       | 124                       | Synthesized          |
| CA <sub>0.16</sub> P <sub>2.52</sub> | 258,000                            | 73,400                             | 3.51                                                       | 143                       | Eastman Chemical Co. |
| CA <sub>0.47</sub> P <sub>2.48</sub> | 240,000                            | 98,500                             | 2.44                                                       | 132                       | Synthesized          |

<sup>a</sup> The DS values were determined by <sup>1</sup>H NMR.

<sup>b</sup> Determined by gel permeation chromatography (mobile phase, tetrahydrofuran at 40 °C) with polystyrene standards.

**Table 3-2.** Characterization of vinyl polymers used in the present chapter

| Sample code <sup>a</sup>                       | $M_w$ <sup>b</sup>   | $M_n$ <sup>b</sup> | $M_w/M_n$ <sup>b</sup> | $T_g$ /°C | Source                   |
|------------------------------------------------|----------------------|--------------------|------------------------|-----------|--------------------------|
| PVP                                            | 360,000 <sup>c</sup> | —                  | —                      | 177       | Nacalai Tesque, Inc.     |
| P(VP <sub>0.76</sub> -co-MMA <sub>0.24</sub> ) | 78,700               | 31,400             | 2.51                   | 121       | Synthesized <sup>d</sup> |
| P(VP <sub>0.67</sub> -co-MMA <sub>0.33</sub> ) | 204,000              | 55,100             | 3.70                   | 134       | Synthesized <sup>d</sup> |
| P(VP <sub>0.61</sub> -co-MMA <sub>0.39</sub> ) | 193,000              | 52,700             | 3.66                   | 121       | Synthesized <sup>d</sup> |
| P(VP <sub>0.50</sub> -co-MMA <sub>0.50</sub> ) | 184,000              | 61,300             | 3.00                   | 119       | Synthesized <sup>d</sup> |
| P(VP <sub>0.46</sub> -co-MMA <sub>0.54</sub> ) | 257,000              | 91,100             | 2.82                   | 112       | Synthesized <sup>d</sup> |
| P(VP <sub>0.42</sub> -co-MMA <sub>0.58</sub> ) | 288,000              | 108,000            | 2.67                   | 117       | Synthesized <sup>d</sup> |
| P(VP <sub>0.32</sub> -co-MMA <sub>0.68</sub> ) | 97,300               | 37,800             | 2.57                   | 104       | Synthesized <sup>d</sup> |
| P(VP <sub>0.22</sub> -co-MMA <sub>0.78</sub> ) | 189,000              | 70,800             | 2.66                   | 111       | Synthesized <sup>d</sup> |
| P(VP <sub>0.13</sub> -co-MMA <sub>0.87</sub> ) | 91,800               | 44,100             | 2.08                   | 100       | Synthesized <sup>d</sup> |
| P(VP <sub>0.09</sub> -co-MMA <sub>0.91</sub> ) | 97,800               | 47,300             | 2.07                   | 101       | Synthesized <sup>d</sup> |
| PMMA                                           | 88,400               | 35,000             | 2.53                   | 100       | Aldrich Chemical Co.     |

<sup>a</sup> The VP contents were determined by FT-IR in a way described by Liu et al.<sup>[9]</sup>

<sup>b</sup> Determined by gel permeation chromatography (mobile phase, 10 mM/L lithium bromide/DMF at 40 °C) with polystyrene standards.

<sup>c</sup> Nominal value.

<sup>d</sup> Synthesized in the author's laboratory by radical polymerization of two distilled monomers, VP (Nacalai Tesque, Inc.) and MMA (Nacalai Tesque, Inc.), in the same way as that described in ref 4.

The vinyl polymers employed as a mixing partner for the CPs and CAPs were poly(*N*-vinyl pyrrolidone) (PVP), PMMA, and P(VP-*co*-MMA) copolymers, basically the same as those in the preceding work.<sup>[4]</sup> Data of characterization for all the vinyl polymers are listed in Table 3-2. As shown in the table, any of the P(VP-*co*-MMA) samples exhibited a single  $T_g$  and they were all regarded as essentially random copolymer. Hereafter, a P(VP-*co*-MMA) sample of VP:MMA =  $m:n$  (in molar ratio) is encoded as P(VP<sub>*m*</sub>-*co*-MMA<sub>*n*</sub>).

### 3.2.2. Preparation of Blend Samples

Binary blend films of CP/vinyl polymer and CAP/vinyl polymer were prepared by solution mixing and solvent evaporation in the same manner as that adopted in the preceding works.<sup>[3,4]</sup> *N,N*-Dimethylformamide (DMF) was selected as a common solvent and the film casting was carried out at 50 °C under reduced pressure (<10 mmHg). The as-cast samples were further dried at 50 °C *in vacuo* for 3 days.

### 3.2.3. Measurements

DSC was carried out with a Seiko DSC 6200/EXSTAR 6000 apparatus. The temperature readings were calibrated with an indium standard. The calorimetry measurements were conducted on ca. 5-mg samples packed in an aluminum pan under a nitrogen atmosphere. Each sample was first heated from ambient temperature (~25 °C) to 230 °C at a scanning rate of 20 °C/min, and then immediately quenched to -50 °C at a rate of 80 °C/min. Following this, the second heating scan was run from -50 to 230 °C at a rate of 20 °C/min to record stable thermograms. For blend series of CA<sub>0.47</sub>P<sub>2.48</sub>, however, the upper limit of temperature in the heating scan was programmed to be 260 °C, since a melting endotherm was predicted to appear above 230 °C due to some extent of crystallizability of the CAP. Thermograms presented in this chapter were all obtained in the second heating scan, and the  $T_g$  was taken as a temperature at the midpoint of a baseline shift in heat flow characterizing the glass transition.

FT-IR spectra were measured on thinner film samples (<20 µm thick) by using a Shimadzu IRPrestige-21 spectrometer. All the spectra were recorded at 20 °C in a transmission mode over a wavenumber range 400–4,000 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup> via accumulation of 64 scans.

High-resolution solid-state NMR experiments were performed at 20 °C in a Varian NMR system 400 MHz operated at a <sup>13</sup>C frequency of 100.6 MHz. The magic-angle spinning rate was 15.0 kHz. <sup>13</sup>C CP/MAS spectra were measured with a contact time of 2 ms, and a 90 ° pulse width of 2.9 µs was employed. In the measurements of proton spin-lattice relaxation time ( $T_{1\rho}^H$ ), a contact time of 0.2 ms was used, and a proton spin-locking time  $\tau$  ranged from 0.5 to 30 ms. 2,048 scans were done to obtain the <sup>13</sup>C CP/MAS spectra, while 4,096 scans

were accumulated for the relaxation time measurements. Chemical shifts of  $^{13}\text{C}$  spectra represented in ppm were referred to tetramethylsilane by using the methine carbon resonance (29.47 ppm) of adamantane crystals as an external reference standard. In order to minimize any possible effect due to the thermal history and/or residual solvents, each sample was heat-treated at 250 °C *in vacuo* for 5 min just before the measurement.

DMA was conducted by using a Seiko DMS6100/EXSTAR6000 apparatus for film specimens prepared by hot-press molding (230 °C, 15 MPa) of the solution-cast samples. Strips of rectangular shape (20 mm  $\times$  5 mm) cut from the molded films were used for measurements of the temperature dependence of the dynamic storage modulus ( $E'$ ) and loss modulus ( $E''$ ). The measuring conditions were as follows: temperature range, -150 to 300 °C; scanning rate, 2 °C/min; oscillatory frequency, 10 Hz.

Optical birefringence ( $\Delta n$ ) of drawn CP/vinyl polymer samples was determined by using an Olympus polarized optical microscope POS equipped with a Berek compensator, at room temperature (20 °C). Strips (20 mm  $\times$  4 mm) cut from the as-cast films were uniaxially stretched to the desired draw ratio at a temperature which was prescribed to be higher by 2 °C than  $T_g$  (as measured by DSC, mentioned above) of the blend sample used, in the same procedure as that adopted in the previous work.<sup>[5]</sup> The percentage elongation of the oriented samples was determined from the positions of ink marks on the film.

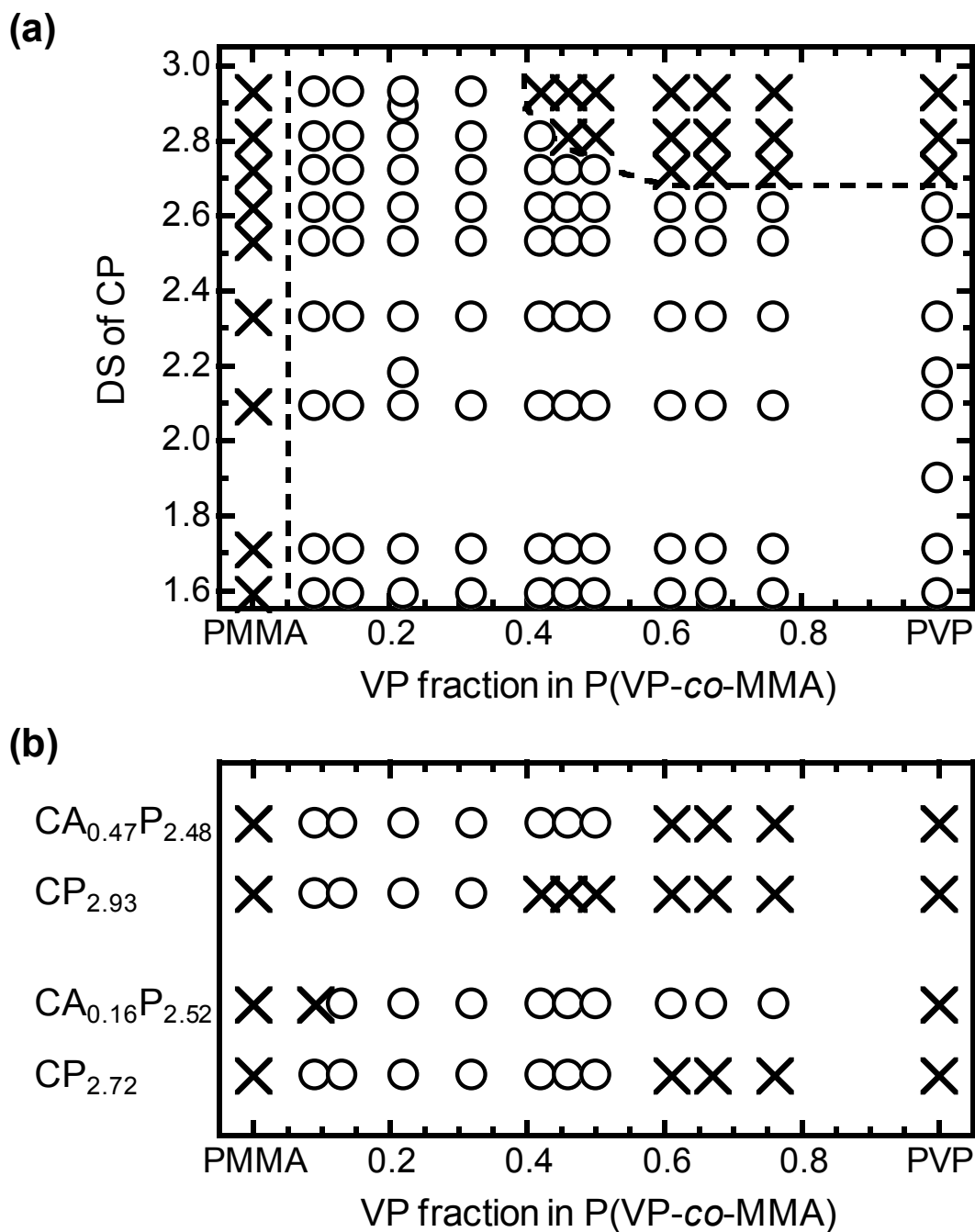
### 3.3. Results and Discussion

#### 3.3.1. Miscibility Estimation by Thermal Analysis

The miscibility state in the CP and CAP/vinyl polymer systems was estimated by  $T_g$  determination in DSC. In general, if any blend sample of a given polymer/polymer pair exhibits a single glass transition between the  $T_g$ s of the two component polymers and a composition-dependent shift of the blend  $T_g$  is clearly observed, then the pair can be regarded as a miscible one on the  $T_g$ -detection scale that is usually assumed to be less than a couple of tens of nanometers.<sup>[10,11]</sup>

##### 3.3.1.1. Overview

Figure 3-3a displays a miscibility map for the CP/P(VP-*co*-MMA) system, constructed as a function of DS of CP and VP fraction in P(VP-*co*-MMA). The data for a blend series of CP/PVP homopolymer were quoted from the preceding chapter.<sup>[3]</sup> In perspective, polymer pairs composed of low-substituted CP and VP-rich P(VP-*co*-MMA) were judged to be miscible. This suggests the contribution of a hydrogen-bonding interaction between CP-hydroxyl and VP-carbonyl groups to the miscibility attainment. A definite “miscibility window” emerged in a hydrophobic region satisfying propionyl DS > 2.7 and VP fraction = 9–40 mol%. As mapped in Figure 3-3b, CAP/P(VP-*co*-MMA) blends using partially acetylated CA<sub>0.16</sub>P<sub>2.52</sub> and CA<sub>0.47</sub>P<sub>2.48</sub> also imparted a miscibility window; interestingly, the VP:MMA range forming the window became expanded, compared with that for the corresponding CP/P(VP-*co*-MMA) blends using CP<sub>2.72</sub> or CP<sub>2.93</sub>. Actual observations in the thermal analysis for the present CE blends are described below in detail.



**Figure 3-3.** (a) Miscibility map for the blend system CP/P(VP-*co*-MMA), depicted as a function of DS of CP and VP fraction in P(VP-*co*-MMA), and (b) miscibility estimation for CAP/P(VP-*co*-MMA) blends using partially acetylated CA<sub>0.16</sub>P<sub>2.52</sub> and CA<sub>0.47</sub>P<sub>2.48</sub> as a function of VP fraction in P(VP-*co*-MMA), in comparison with the corresponding CP/P(VP-*co*-MMA) blends using CP<sub>2.72</sub> and CP<sub>2.93</sub>, respectively. Symbols indicate that a given pair of CP or CAP/P(VP-*co*-MMA) is miscible (○, single  $T_g$ ) or immiscible (×, dual  $T_g$ s).

### 3.3.1.2. CP/PMMA Blends

Figure 3-4a illustrates DSC thermograms measured for a blend series of CP<sub>1.59</sub>/PMMA homopolymer. As can be seen from the data, two independent glass transitions originating from the two components were clearly detected for the blend samples of 20/80–80/20 compositions (in wt% ratio). Therefore, the CP<sub>1.59</sub>/PMMA pair can be judged to be immiscible. However, the  $T_g$  of the PMMA component was prone to slightly shift to higher temperatures with an increase in the CP content, while the  $T_g$  of the CP component hardly shifted from the original position.

DSC measurements were also performed on the other eight series of CP/PMMA blends prepared by using CPs with different DS values ranging from 1.71 to 2.93. The data were all similar to that given in Figure 3-4a; the thermograms indicated the presence of double  $T_g$ s corresponding to those of the two constituent polymers, but habitually with some extent of elevation in the PMMA  $T_g$ . It is thus reasonably concluded that all the CP/PMMA blends are substantially immiscible irrespective of the DS of the CP used, even though a certain level of compatibility of PMMA with CP may be admitted.

### 3.3.1.3. CP/P(VP-co-MMA) Blends

In visual appearance, as-cast films of CP blends with VP-MMA copolymers were homogeneous and highly transparent, except for cloudy films of several polymer pairs composed of CP of DS > 2.7 and P(VP-co-MMA) having more than 50 mol% VP residues.

Any series of CP<sub>1.59</sub>/P(VP-co-MMA) blends, prepared by using the copolymers of VP:MMA = 9:91–76:24, provided a smooth variation of a single  $T_g$  which was situated between the  $T_g$  values of the two unblended components (data not shown). Thus, it turned out that CP<sub>1.59</sub> formed a miscible monophasic system with P(VP-co-MMA)s of VP ≥ 9 mol%. Similar miscible behavior was confirmed in the use of CPs of DS = 1.71–2.62, as the thermal data is exemplified for CP<sub>1.71</sub>/P(VP<sub>0.22</sub>-co-MMA<sub>0.78</sub>) blends in Figure 3-4b. It should be noted here that the CPs of DS < 2.7 were miscible with P(VP-co-MMA)s of extremely low VP fractions such as 10–30 mol%, because the same situation was never realized for the previous system employing CA (see Figure 3-2).

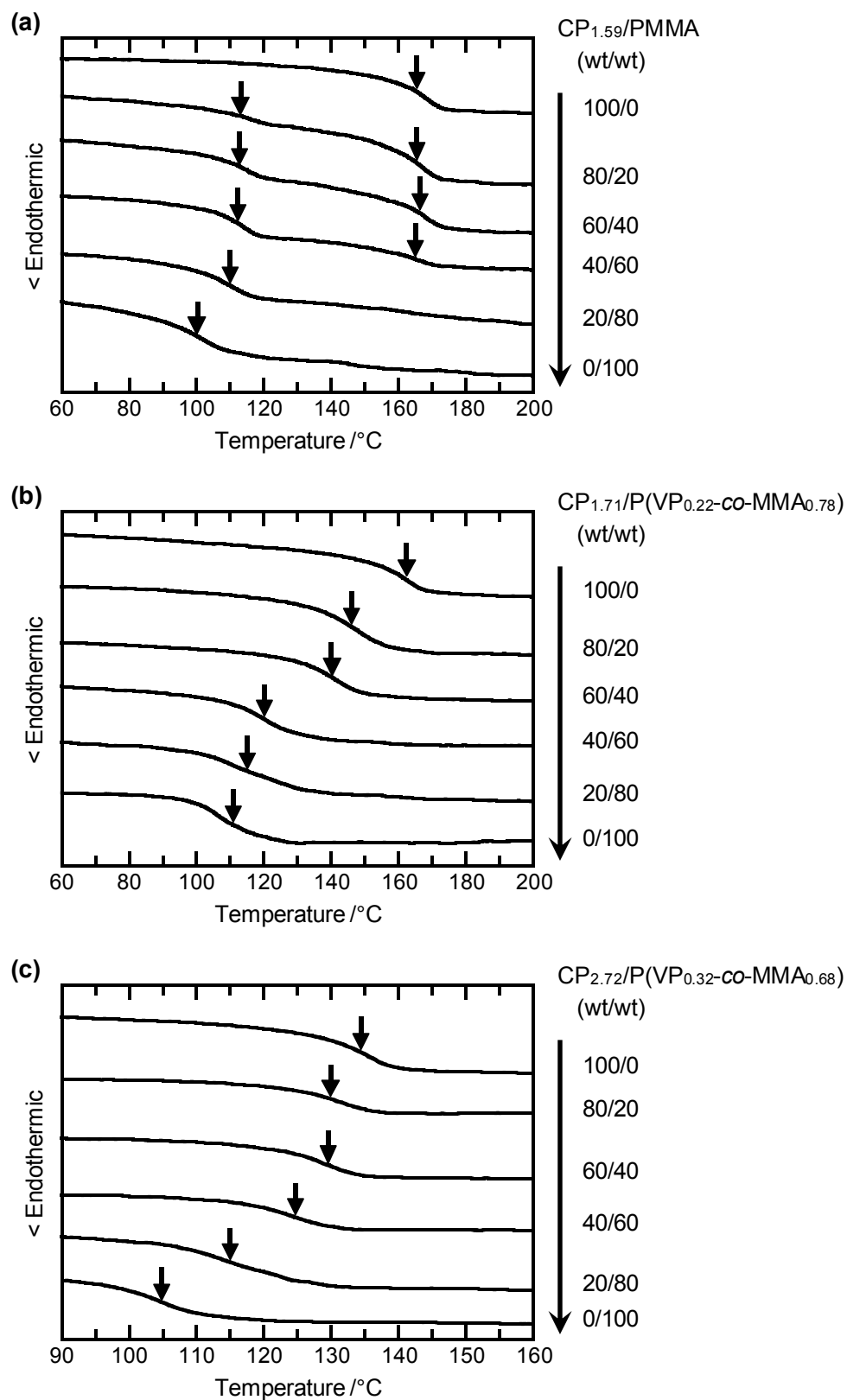
Another noteworthy finding was that even high-substituted CPs of DS > 2.7 made a miscible combination with MMA-rich P(VP-co-MMA)s having ca. 10–40 mol% VP residues,

despite the immiscibility of the CPs with PVP and PMMA homopolymers. Figure 3-4c exemplifies several DSC thermograms obtained for a polymer combination of CP<sub>2.72</sub>/P(VP<sub>0.32</sub>-*co*-MMA<sub>0.68</sub>); all the samples of 10/90–90/10 compositions gave a single  $T_g$ . Thus, decidedly, the CP/P(VP-*co*-MMA) system exhibited a miscibility window. The advent of such a window was unacceptable as to the CA/P(VP-*co*-MMA) system, but observed previously for the CP/P(VP-*co*-VAc) and CB/P(VP-*co*-VAc) systems (see Figures 3-1b and 3-1c).<sup>[2,3]</sup> In these earlier studies, it was concluded that a greater repulsion between the VP and VAc units in the random copolymer was mainly contributory to the miscibility attainment; this was rationalized by assessment of Krigbaum-Wall interaction parameters ( $\mu$ ) for the ingredient polymer pairs involving in the CB/P(VP-*co*-VAc) system.<sup>[4]</sup> The intra-copolymer effect may also be applicable to the present CP(DS > 2.7)/P(VP-*co*-MMA) blends. The absence of such a clear miscibility window in the map of the CA/P(VP-*co*-MMA) system (Figure 3-2) is due to an inhibiting factor, i.e., the strong self-association ability of highly substituted CAs of DS > 2.7; the CAs are rather easily crystallizable as cellulose triacetate II.

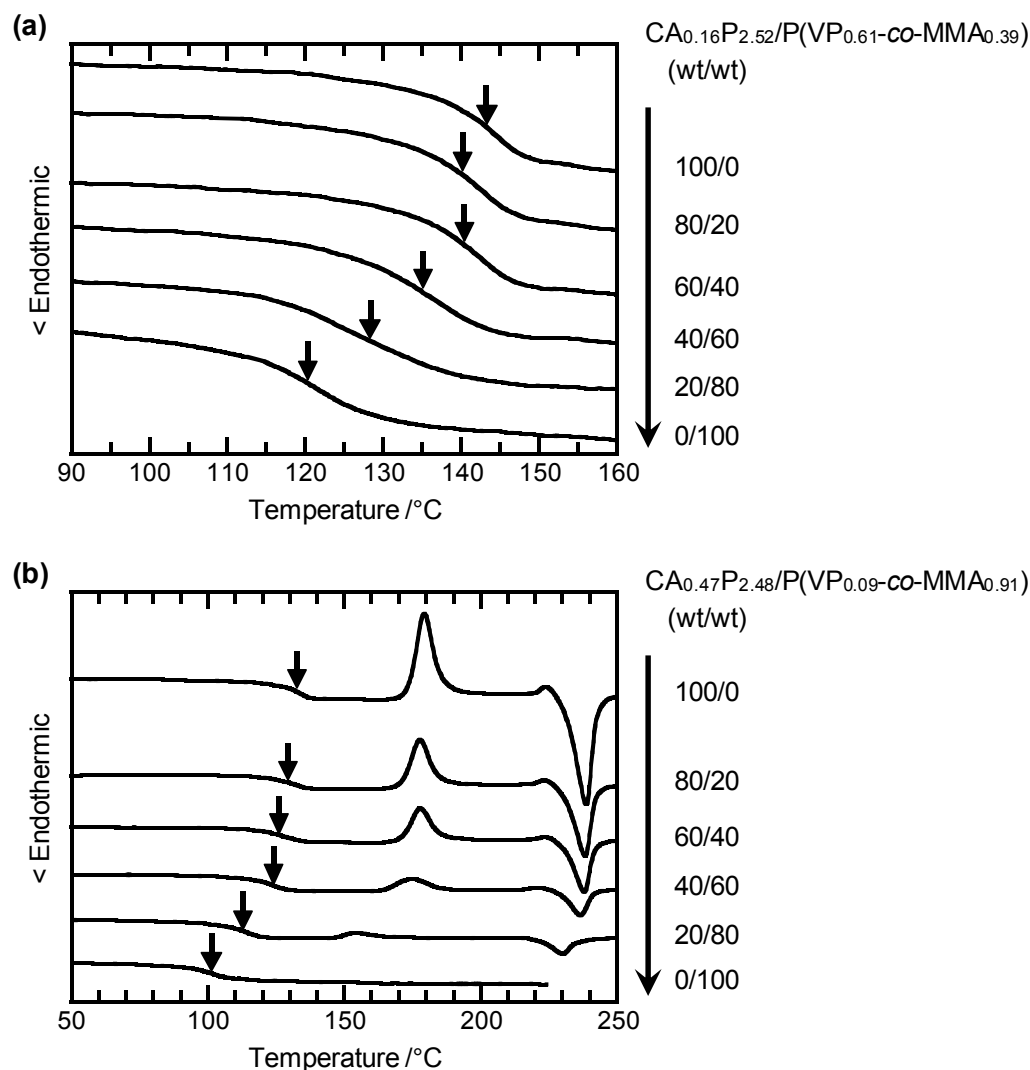
In comparison between the two maps (Figures 3-1b and 3-3a) for the CP blends combined with different copolymers, P(VP-*co*-VAc) and P(VP-*co*-MMA), obviously, the window region for the CP/P(VP-*co*-MMA) system is narrower than that for the CP/P(VP-*co*-VAc) system. Again, from estimation of the interaction parameters for the two units constituting the respective copolymers concerned,<sup>[4]</sup> it has been derived that the constituents VP and VAc in P(VP-*co*-VAc) strike an intense repellent character to each other, while the VP and MMA units in P(VP-*co*-MMA) show a relatively weaker repulsive interaction. Presumably, this deterioration of the intramolecular repulsive action in the P(VP-*co*-MMA) copolymer is responsible for the appearance of the narrower window in the CP/P(VP-*co*-MMA) map (Figure 3-3a).

#### 3.3.1.4. CAP/P(VP-*co*-MMA) Blends

DSC thermograms obtained for a set of CA<sub>0.16</sub>P<sub>2.52</sub>/P(VP<sub>0.61</sub>-*co*-MMA<sub>0.39</sub>) blends are displayed in Figure 3-5a; we can see a single  $T_g$  shifting to lower temperatures along with an increase in the P(VP<sub>0.61</sub>-*co*-MMA<sub>0.39</sub>) content. Such a miscible sign was observed for blend series of this CAP with P(VP-*co*-MMA)s of VP = 13–76 mol%, but never done for the CAP blends with PVP and PMMA homopolymers.



**Figure 3-4.** DSC thermograms obtained for (a) CP<sub>1.59</sub>/PMMA, (b) CP<sub>1.71</sub>/P(VP<sub>0.22</sub>-co-MMA<sub>0.78</sub>), and (c) CP<sub>2.72</sub>/P(VP<sub>0.32</sub>-co-MMA<sub>0.68</sub>) blends. Arrows indicate a  $T_g$  position taken as the midpoint of a baseline shift in heat flow.



**Figure 3-5.** DSC thermograms obtained for (a)  $\text{CA}_{0.16}\text{P}_{2.52}/\text{P}(\text{VP}_{0.61}\text{-co-MMA}_{0.39})$  and (b)  $\text{CA}_{0.47}\text{P}_{2.48}/\text{P}(\text{VP}_{0.09}\text{-co-MMA}_{0.91})$  blends. Arrows indicate a  $T_g$  position.

Figure 3-5b shows a miscible evidence by DSC for a  $\text{CA}_{0.47}\text{P}_{2.48}/\text{P}(\text{VP}_{0.09}\text{-co-MMA}_{0.91})$  combination using another CAP sample. Differing from the overall amorphous behavior of  $\text{CA}_{0.16}\text{P}_{2.52}$ , the  $\text{CA}_{0.47}\text{P}_{2.48}$  sample exhibited an exothermic peak (180 °C) and an endothermic peak (240 °C) after onset of the glass transition ( $T_g = 132$  °C); the two peaks are ascribable to a so-called cold-crystallization and subsequent melting of the formed crystal, respectively. Such crystallizability was also noticed for  $\text{CP}_{2.93}$  of  $\text{DS} > 2.9$ , but the crystalline phase was formed in somewhat slower crystallization kinetics. Despite of the crystalline habit common to tri-esterified celluloses, as exemplified in Figure 3-5b, the  $\text{CA}_{0.47}\text{P}_{2.48}$  blends with  $\text{P}(\text{VP}_{0.09}\text{-co-MMA}_{0.91})$  exhibited a definitely single composition-dependent  $T_g$  and then

produced a systematic depression in the melting point of the induced CAP crystal. This coupled thermal behavior is typical of that of miscible blends composed of a pair of crystallizable polymer/amorphous polymer.<sup>[12]</sup> Similar DSC data were obtained for additional six combinations of CA<sub>0.47</sub>P<sub>2.48</sub> with P(VP-*co*-MMA)s of VP = 13–50 mol%.

Figure 3-3b summarizes the miscibility estimation for the CAP/P(VP-*co*-MMA) series using CA<sub>0.16</sub>P<sub>2.52</sub> and CA<sub>0.47</sub>P<sub>2.48</sub>, as a function of VP fraction in P(VP-*co*-MMA); the corresponding data for comparable CP/P(VP-*co*-MMA) blends using CP<sub>2.72</sub> and CP<sub>2.93</sub> are also shown there. The two CAPs may be regarded as derivatives obtained from CPs of DS  $\approx$  2.7 and 2.95, respectively, by partial ester exchange for acetyl substitution. Plainly, both the CAP/P(VP-*co*-MMA) series offer the miscibility window, as did the blend series using CPs of DS  $\geq$   $\sim$ 2.7; again, the intramolecular repulsion in the vinyl copolymer would be principally responsible for the observation. However, the range of copolymer composition forming the miscibility window is much wider in the CAP series, compared with that in the CP series of the corresponding DS in total. This expansion of the window might be ascribed to an additional repulsion effect originating in the CAP side. That is, the cellulose mixed ester would also behave as a kind of copolymer dangling two different acyl side-groups along the carbohydrate backbone. A similar deal of cellulose alkyl esters as copolymer has been made in a few reports on their structural characteristics.<sup>[2,13,14]</sup> Therefore, the CAP/P(VP-*co*-MMA) blends are actually taken as a copolymer/copolymer system, where the miscibility should be affected by the duplicate, intra-copolymer effect.

### 3.3.2. Spectroscopic Analysis of Intermolecular Interaction and Mixing Scale

#### 3.3.2.1. FT-IR Spectra

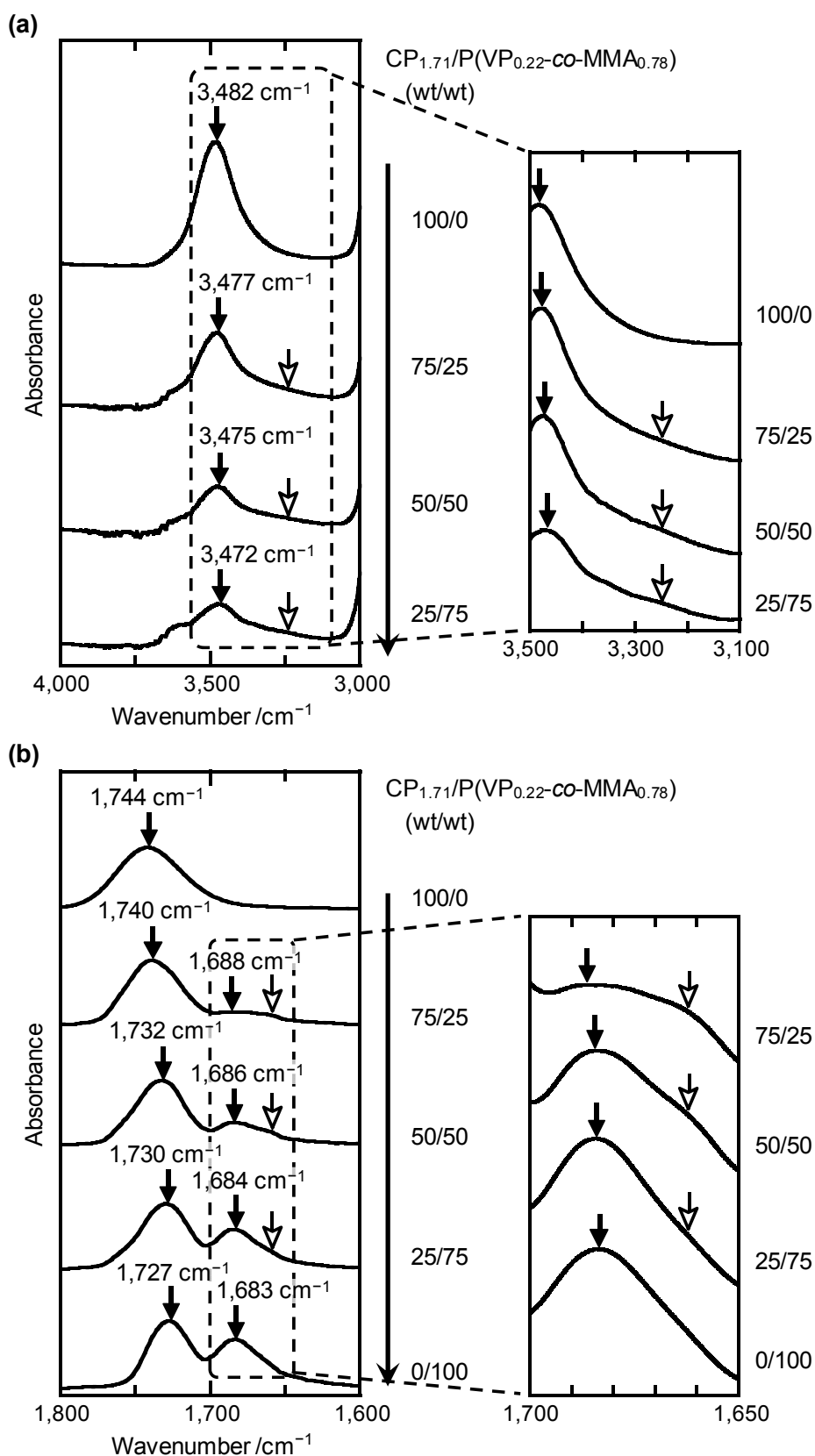
Figure 3-6 compiles FT-IR spectra obtained for blends of the miscible CP<sub>1.71</sub>/P(VP<sub>0.22</sub>-*co*-MMA<sub>0.78</sub>) pair, particularly focusing on two regions of (a) O-H and (b) C=O stretching vibrations. Frequency shift and/or shape variation are clearly observed for the specific IR bands as a result of the hydrogen-bonding formation between the residual hydroxyls of the CP component and the VP-carbonyls of the copolymer. As shown in Figure 3-6a, a band centering at 3,482 cm<sup>-1</sup> (top data), which can be associated with a mixture of free hydroxyls and intramolecularly hydrogen-bonded OH groups in the unblended CP, shifted to lower

wavenumber positions with increasing P(VP-*co*-MMA) content. Concomitantly, another shoulder band became discernible on the side of further lower wavenumbers, as indicated by a white arrow at  $\sim 3,300\text{ cm}^{-1}$  in Figure 3-6a. This new band can be ascribed to the stretching of intermolecularly hydrogen-bonded OH groups.<sup>[15]</sup>

Concerning the frequency region of C=O groups (Figure 3-6b), a  $1,683\text{ cm}^{-1}$  band assigned to VP-carbonyl stretching vibration in the copolymer became asymmetric progressively as the CP content increased in the binary blend system. Consequently, the absorption band was dividable into two peaks, larger and smaller ones at  $\sim 1,685\text{ cm}^{-1}$  and  $\sim 1,660\text{ cm}^{-1}$ , respectively (see enlarged data in the range of  $1,650\text{--}1,700\text{ cm}^{-1}$ ). These two IR signals for the VP unit of the copolymer may be associated with the free carbonyl and hydrogen-bonded carbonyl groups, respectively.<sup>[16]</sup> The CP<sub>1.71</sub>/P(VP<sub>0.22</sub>-*co*-MMA<sub>0.78</sub>) blends provided an additional single band centering at  $1,730\text{--}1,740\text{ cm}^{-1}$ , but this band was virtually made up of a prorated mixture of two carbonyl signals: a propionate C=O peak ( $1,744\text{ cm}^{-1}$ ) of the CP component and an MMA C=O peak ( $1,727\text{ cm}^{-1}$ ) of the copolymer component.

The inter-component interaction based on the hydrogen bonding of OH---O=C, just as described above, was also ascertained not only for the blend series of CP<sub>1.71</sub> with VP-rich P(VP-*co*-MMA)s including PVP, but also for other selected miscible pairs using CPs of DS < 2.7. For contradistinction, it should be recalled that CA of DS = 1.80 never formed the same kind of hydrogen-bonding interaction with P(VP<sub>0.22</sub>-*co*-MMA<sub>0.78</sub>)<sup>[4]</sup> and the polymer pair was immiscible (see Figure 3-2). This contrast to the observation for the CP<sub>1.71</sub>/P(VP<sub>0.22</sub>-*co*-MMA<sub>0.78</sub>) pair reflects the difference in self-association nature between CA and CP, the former having the stronger ability.

When the copolymer P(VP<sub>0.22</sub>-*co*-MMA<sub>0.78</sub>) was blended with CP<sub>2.89</sub>, however, there was no indication of such an intermolecular hydrogen-bonding interaction in IR examinations (data not shown). This result may be reasonable. With regard to the CP(DS > 2.7)/P(VP-*co*-MMA) pairs constituting the miscibility window in Figure 3-3a, the blend miscibility would be attained through the repulsion effect in the P(VP-*co*-MMA) side, not driven by direct attraction based on that hydrogen bonding.



**Figure 3-6.** FT-IR spectra of CP<sub>1.71</sub>, P(VP<sub>0.22</sub>-co-MMA<sub>0.78</sub>), and their blends in the frequency regions of (a) O-H and (b) C=O stretching vibrations. Data in the ranges of 3,100–3,500 cm<sup>-1</sup> and 1,650–1,700 cm<sup>-1</sup> are also shown on an enlarged scale. Solid arrows indicate a peak-top position in the respective specific absorption bands, and white arrows indicate a shoulder band associated with hydrogen bonding (see text for discussion).

### 3.3.2.2. Homogeneity as Estimated by Solid-state $^{13}\text{C}$ NMR

As a useful relaxation technique in solid-state  $^{13}\text{C}$  NMR,  $T_{1\rho}^{\text{H}}$  measurements for specific carbons in a multicomponent polymer system make it possible to estimate the mixing homogeneity in a scale of  $^1\text{H}$  spin-diffusion length that is usually within several nanometers;<sup>[16–18]</sup> the dimensional limit is smaller than that ( $\sim 20$  nm) detectable by DSC thermal analysis.  $T_{1\rho}^{\text{H}}$  values can be obtained by fitting the decaying carbon resonance intensity to the following exponential equation:

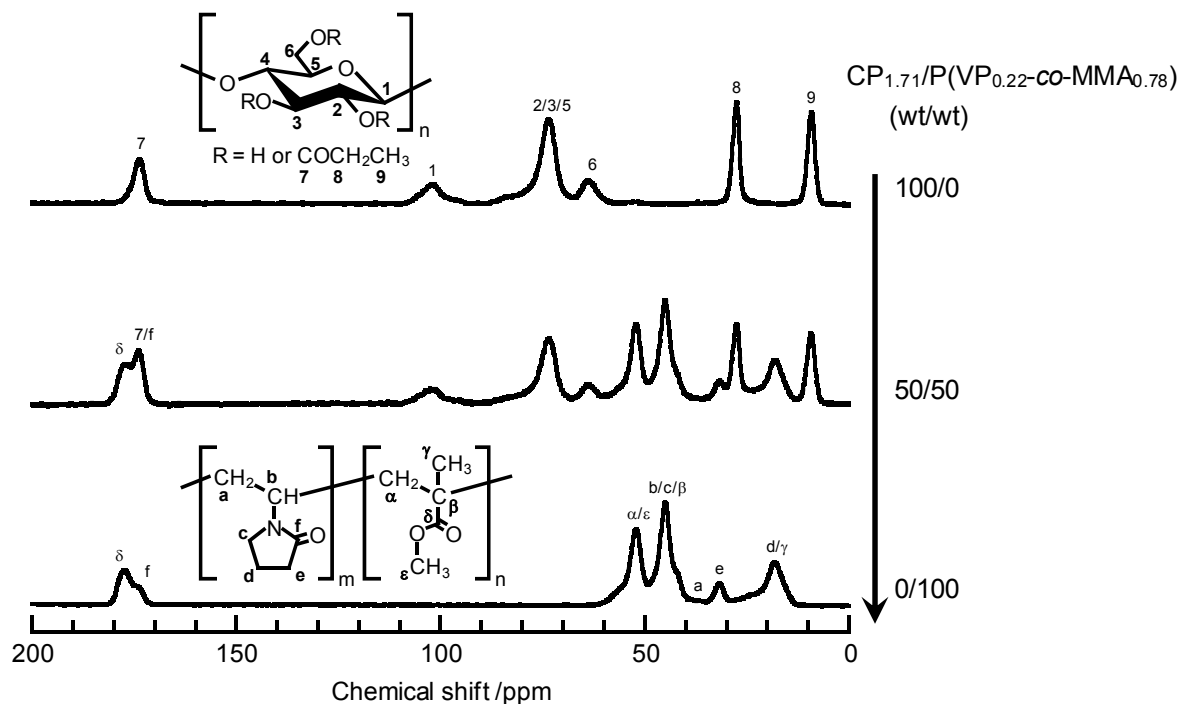
$$M(\tau) = M(0) \exp(-\tau/T_{1\rho}^{\text{H}}) \quad (3-1)$$

where  $M(\tau)$  is the magnetization intensity observed as a function of the spin-locking time  $\tau$ . If two constituent polymers are homogeneously mixed on the scale over which  $^1\text{H}$  spin-diffusion can take place in a time  $T_{1\rho}^{\text{H}}$ , the  $T_{1\rho}^{\text{H}}$  values for different protons belonging to the respective components may be equalized to each other by the spin diffusion.

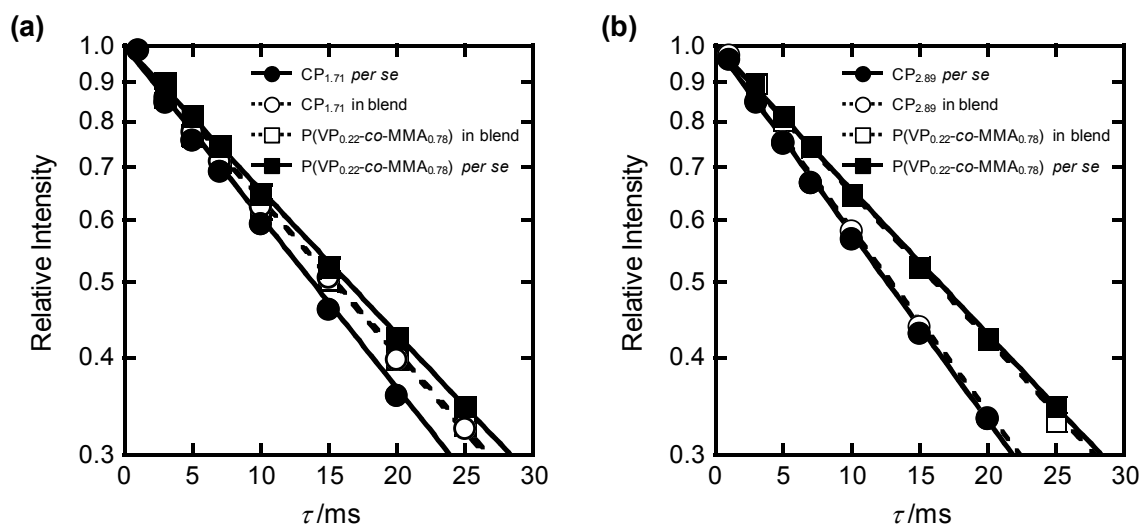
Using the above technique, a comparative assessment of the mixing scale was made for the two miscible series of blends: CP<sub>1.71</sub>/P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>) and CP<sub>2.89</sub>/P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>), the driving factor contributory to the respective miscibility attainments being the intermolecular hydrogen-bonding interaction (for the former) or the intramolecular repulsion effect in the copolymer (for the latter). Figure 3-7 exemplifies  $^{13}\text{C}$  CP/MAS spectra obtained for CP<sub>1.71</sub>, P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>), and their 50/50 blend. The peak assignments of the spectra are based on literature data for CP,<sup>[19]</sup> PVP,<sup>[17]</sup> and PMMA.<sup>[9]</sup> The experiment of  $T_{1\rho}^{\text{H}}$  quantifications was conducted through monitoring the following  $^{13}\text{C}$  resonance signals with better resolutions: C2/C3/C5 pyranose carbons (74 ppm) and propionyl carbons C8 (28 ppm) and C9 (9.3 ppm) for the CP component, and C $_{\alpha}$ /C $_{\varepsilon}$  (52 ppm), C $_{\beta}$ /C $_{\delta}$ /C $_{\beta}$  (45 ppm), and C $_{\delta}$ /C $_{\gamma}$  carbons (18 ppm) for the P(VP-co-MMA) component. Carbonyl carbons were not adoptable for the quantification, because the corresponding peak ( $\sim 173.5$  ppm) of the CP component merged into the other split signal of VP/MMA carbonyls ( $\sim 174/177$  ppm) of the copolymer.

Figure 3-8 illustrate the decay behavior in intensity of the C2/C3/C5 and C $_{\beta}$ /C $_{\delta}$ /C $_{\beta}$  peaks for unblended CP (CP<sub>1.71</sub> or CP<sub>2.89</sub>) and P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>), respectively, and also for their 50/50 blend imparting both resonance signals. The slope of each semi-logarithmic plot corresponds to an inverse of  $-T_{1\rho}^{\text{H}}$ . The  $T_{1\rho}^{\text{H}}$  data thus estimated for CP<sub>1.71</sub>, CP<sub>2.89</sub>, P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>), and their miscible blends of CP/P(VP-co-MMA) = 75/25–25/75 are all listed in

Table 3-3.



**Figure 3-7.** Solid-state  $^{13}\text{C}$  CP/MAS NMR spectra for  $\text{CP}_{1.71}$ ,  $\text{P}(\text{VP}_{0.22}\text{-co-MMA}_{0.78})$ , and their 50/50 blend.



**Figure 3-8.** Semilogarithmic plots of the decay of  $^{13}\text{C}$  resonance intensities as a function of spin-locking time  $\tau$ , for solid films of (a)  $\text{CP}_{1.71}$ ,  $\text{P}(\text{VP}_{0.22}\text{-co-MMA}_{0.78})$ , and their 50/50 blend, and (b)  $\text{CP}_{2.89}$ ,  $\text{P}(\text{VP}_{0.22}\text{-co-MMA}_{0.78})$ , and their 50/50 blend. The monitoring was conducted for the peak intensity of C2/C3/C5 pyranose carbons of CP and that of  $\text{C}_\beta/\text{C}_\alpha/\text{C}_\beta$  carbons of the copolymer (see Figure 3-7).

**Table 3-3.**  $T_{1\rho}^H$  values obtained for two series of blends, CP<sub>1.71</sub>/P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>) and CP<sub>2.89</sub>/P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>)

| CP <sub>1.71</sub> /P(VP <sub>0.22-co</sub> -MMA <sub>0.78</sub> )<br>(wt/wt) | $T_{1\rho}^H$ /ms  |      |      |      |                                                |              |             |      |
|-------------------------------------------------------------------------------|--------------------|------|------|------|------------------------------------------------|--------------|-------------|------|
|                                                                               | CP <sub>1.71</sub> |      |      |      | P(VP <sub>0.22-co</sub> -MMA <sub>0.78</sub> ) |              |             |      |
|                                                                               | C2/3/5             | C8   | C9   | Ave. | $\alpha/\varepsilon$                           | b/c/ $\beta$ | d/ $\gamma$ | Ave. |
| 100/0                                                                         | 20.5               | 20.3 | 19.2 | 20.0 | —                                              | —            | —           | —    |
| 75/25                                                                         | 21.2               | 21.6 | 20.5 | 21.1 | 21.2                                           | 21.5         | 21.2        | 21.3 |
| 50/50                                                                         | 22.2               | 22.8 | 21.7 | 22.2 | 22.1                                           | 22.1         | 22.4        | 22.2 |
| 25/75                                                                         | 23.1               | 22.9 | 22.9 | 23.0 | 22.9                                           | 23.0         | 22.8        | 22.9 |
| 0/100                                                                         | —                  | —    | —    | —    | 23.3                                           | 23.5         | 24.0        | 23.6 |

| CP <sub>2.89</sub> /P(VP <sub>0.22-co</sub> -MMA <sub>0.78</sub> )<br>(wt/wt) | $T_{1\rho}^H$ /ms  |      |      |      |                                                |              |             |      |
|-------------------------------------------------------------------------------|--------------------|------|------|------|------------------------------------------------|--------------|-------------|------|
|                                                                               | CP <sub>2.89</sub> |      |      |      | P(VP <sub>0.22-co</sub> -MMA <sub>0.78</sub> ) |              |             |      |
|                                                                               | C2/3/5             | C8   | C9   | Ave. | $\alpha/\varepsilon$                           | b/c/ $\beta$ | d/ $\gamma$ | Ave. |
| 100/0                                                                         | 18.5               | 17.6 | 17.7 | 17.9 | —                                              | —            | —           | —    |
| 75/25                                                                         | 18.9               | 19.5 | 18.7 | 19.0 | 22.7                                           | 23.5         | 23.2        | 23.1 |
| 50/50                                                                         | 18.8               | 18.5 | 19.2 | 18.8 | 23.3                                           | 23.4         | 23.1        | 23.3 |
| 25/75                                                                         | 18.9               | 18.6 | 18.8 | 18.8 | 23.1                                           | 22.6         | 23.7        | 23.1 |
| 0/100                                                                         | —                  | —    | —    | —    | 23.3                                           | 23.5         | 24.0        | 23.6 |

As can be seen from Table 3-3 (upper part),  $T_{1\rho}^H$  of the CP<sub>1.71</sub> component, originally 20.0 ms as an average, rises systematically with an increase in the copolymer component, while that of the P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>) component (average value of 23.6 ms) diminishes correspondingly with increasing CP<sub>1.71</sub> content. Consequently, the two  $T_{1\rho}^H$  values at every blend composition are in good agreement with each other. Thus, it is reasonably deduced that the two constituent polymers in the blends are intimately mixed within a range where the mutual <sup>1</sup>H-spin diffusion is permitted over a period of the respective homogenized  $T_{1\rho}^H$ , e.g., ~22 ms for the 50/50 composition.

An effective path length  $L$  of the spin diffusion in a time  $T_{1\rho}^H$  is given by the following equation:<sup>[20]</sup>

$$L \cong (6DT_{1\rho}^H)^{1/2} \quad (3-2)$$

where  $D$  is the spin-diffusion coefficient, usually taken to be  $\sim 1.0 \times 10^{-12}$  cm<sup>2</sup>/s in organic polymer materials.<sup>[16,21,22]</sup> By adopting  $T_{1\rho}^H$  data of 21–23 ms approximated for the CP<sub>1.71</sub>/P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>) blends of 75/25–25/75 compositions, the diffusion path length is calculated as  $L = 3.5\text{--}3.7$  nm. Accordingly, it is confirmed that the relevant miscible series of hydrogen-bonding type is virtually homogeneous in a scale of ca. 4 nm.

With regard to the CP<sub>2.89</sub>/P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>) series, on the contrary,  $T_{1\rho}^H$ s of the two components at every blend composition never became so close to each other (see Figure 3-8b and Table 3-3 (lower part)). This temporal disagreement implies that the relaxation processes of the two polymers in the blends progressed independently without their cooperative spin diffusion; thus the blends were found to be heterogeneous when viewed in a few nanometers scale by  $T_{1\rho}^H$  measurements. By the combined use of this result and the previous DSC data, it can be judged that the scale of homogeneity in the CP<sub>2.89</sub>/P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>) blends situated in the window region lies between approximately 5 and 20 nm.

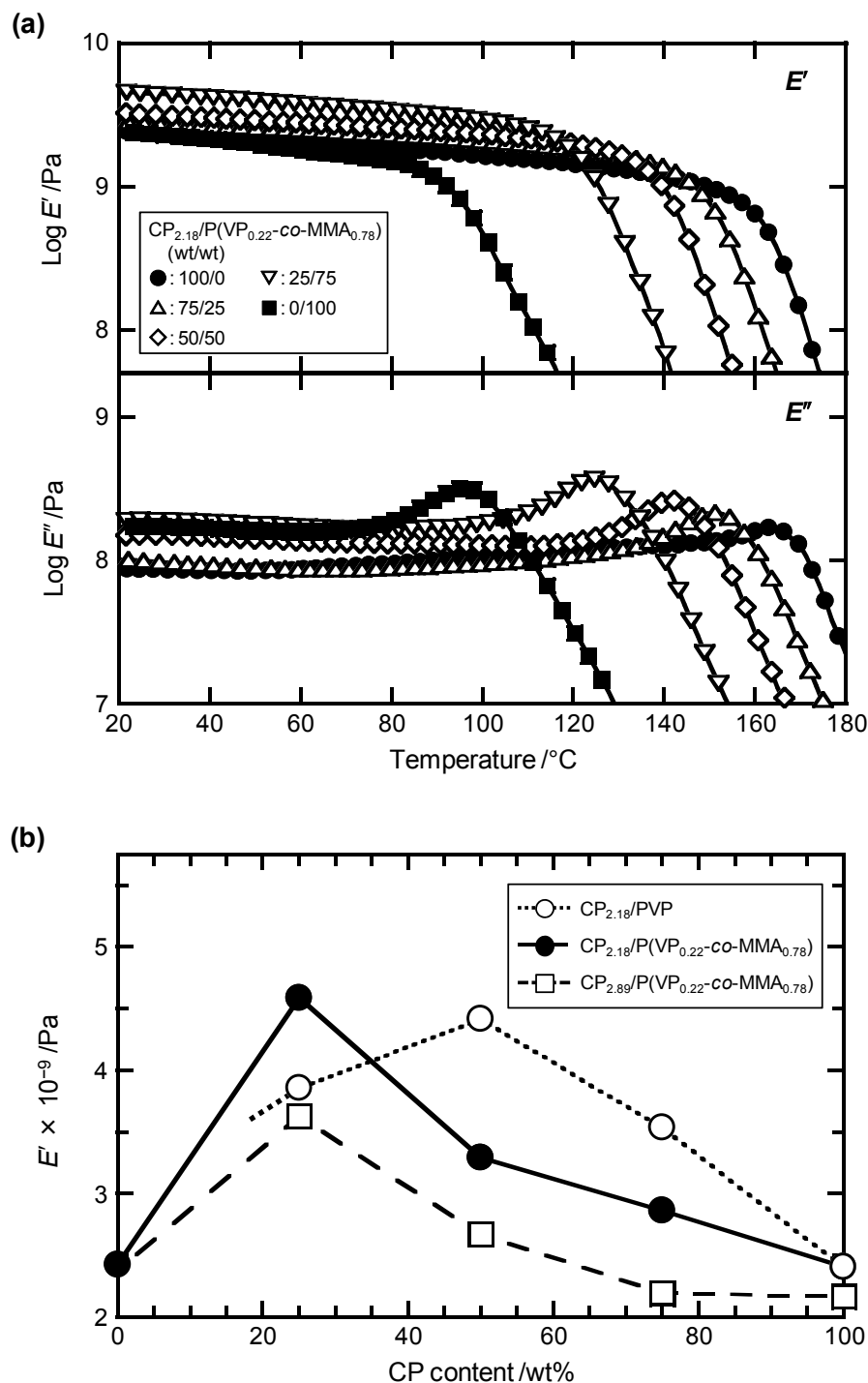
### 3.3.3. Synergistic Effects on Properties of CP/P(VP-co-MMA) Films

#### 3.3.3.1. Mechanical Properties Estimated by DMA

Figure 3-9a shows the temperature dependence of the dynamic storage modulus  $E'$  and loss modulus  $E''$  for CP<sub>2.18</sub>/P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>) blends of 75/25, 50/50, and 25/75 compositions, together with the corresponding data for plain CP<sub>2.18</sub> and P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>). As demonstrated clearly in the figure, the blend samples provided a single and sharp transition signal, both in the  $E'$  drop and in the  $E''$  peak, which shifted systematically with the composition; this indicates a sign of good miscibility for the polymer pair. Similar behavior was observed for other test series including CP<sub>2.18</sub>/PVP and CP<sub>2.89</sub>/P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>) blends.

Figure 3-9b collects the glass-state modulus  $E'$  (at 20 °C) vs. composition plots for the three series of CP<sub>2.18</sub>/PVP, CP<sub>2.18</sub>/P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>), and CP<sub>2.89</sub>/P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>); however, the modulus data for the PVP homopolymer *per se* was not obtained because of a brittle nature of the film. As can be seen from the plots in the figure, the modulus of any of the blend films was usually higher than those of the respective unblended CP and vinyl polymer samples. This result may be interpreted as a synergistic improvement in thermo-

mechanical property of the cellulosic and vinyl polymer materials by miscible blending. Furthermore, it is found by careful inspection that the rising level in the glassy modulus of



**Figure 3-9.** (a) Temperature dependence of the dynamic storage modulus  $E'$  and loss modulus  $E''$  for  $CP_{2.18}/P(VP_{0.22}\text{-}co\text{-}MMA_{0.78})$  blends, and (b) the glassy state  $E'$  value (measured at 20 °C) vs. composition plots for three series of blends,  $CP_{2.18}/PVP$ ,  $CP_{2.18}/P(VP_{0.22}\text{-}co\text{-}MMA_{0.78})$ , and  $CP_{2.89}/P(VP_{0.22}\text{-}co\text{-}MMA_{0.78})$ .

the CP blends varied with difference in the driving force for the miscibility attainment; viz., the miscible blends of hydrogen-bonding type, referring to the CP<sub>2.18</sub>/PVP and CP<sub>2.18</sub>/P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>) series, exhibited a noticeable elevation in the modulus  $E'$ , whereas the CP<sub>2.89</sub>/P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>) series situated in the miscibility window showed a comparatively smaller increase in the  $E'$  value.

### 3.3.3.2. Birefringence of CP/P(VP-co-MMA) Films

Optical birefringence derives from the orientation of polymer chains which have inherently the anisotropy of polarizability. In the simplest case of uniaxial stretching of amorphous homopolymers, the birefringence, defined as  $\Delta n = n_{\parallel} - n_{\perp}$  with a refractive index ( $n_{\parallel}$ ) parallel to the draw direction and that ( $n_{\perp}$ ) perpendicular to it, varies monotonically with the degree of orientation, according to the equation:

$$\Delta n = \frac{(3 \langle \cos^2 \omega \rangle - 1) \cdot \Delta n^0}{2} \quad (3-3)$$

where  $\Delta n^0$  is an intrinsic birefringence for the perfect uniaxial orientation of polymer chains, and  $\langle \cos^2 \omega \rangle$  is the second moment of orientation for an anisotropic segmental unit with a certain polarizability. In the case of the stretching of a blend composed of polymer 1 and polymer 2, the birefringence  $\Delta n$  of the deformed sample may be represented by

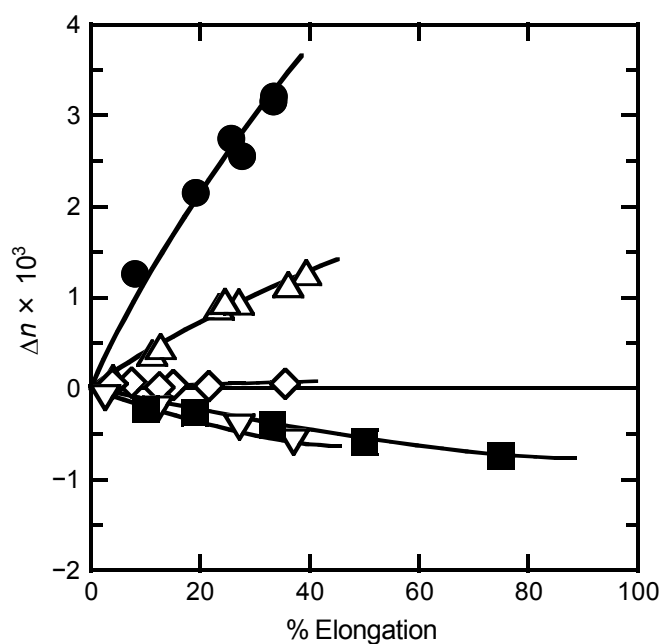
$$\Delta n = v_1 \Delta n_1 + v_2 \Delta n_2 \quad (3-4)$$

where  $v_i \Delta n_i$  ( $i = 1, 2$ ) indicates the contribution of an oriented polymer component  $i$  to the total birefringence and  $v_i$  denotes the volume fraction of that component.

Figure 3-10 compiles results of the birefringence measurements conducted for drawn films of a miscible CP<sub>2.09</sub>/P(VP<sub>0.46-co</sub>-MMA<sub>0.54</sub>) series of hydrogen-bonding type. As is already known,<sup>[5]</sup> vinyl polymers comprising VP and/or MMA units, including the present P(VP<sub>0.46-co</sub>-MMA<sub>0.54</sub>), exhibit negative optical anisotropy ( $\Delta n^0_{\text{VP-MMA}} < 0$ ) upon stretching of their films. On the other hand, as seen in the figure, the CP of DS = 2.09 showed positive optical anisotropy ( $\Delta n^0_{\text{CP}} > 0$ ) on stretching of the film, and the birefringence increased sharply with the extent of elongation. The magnitude of  $\Delta n$  evaluated for this CP was higher than that obtained previously for CA of DS = 2.18, when compared at a given stage of elongation; this suggests that a flexible methylene-methyl sequence in the propionyl side-group would be aligned parallel to the cellulose backbone, which contributes to the increase

of the parallel component of refractive index ( $n_{\parallel}$ ).

The optical anisotropy of the oriented CP<sub>2.09</sub>/P(VP<sub>0.46</sub>-*co*-MMA<sub>0.54</sub>) blends was seriously affected in both the polarity and degree, by the compensation effect due to the positive and negative contributions of the CP and copolymer components, respectively, to the overall birefringence. When the CP content reached 50 wt%, the blend film assumed a character of birefringence-free material, as shown in Figure 3-10. That is, the 50/50 blend can behave like an optically isotropic medium even though it should be mechanically anisotropic after deformation. A copolymer-rich sample of CP<sub>2.09</sub>/P(VP<sub>0.46</sub>-*co*-MMA<sub>0.54</sub>) = 30/70 always provided negative birefringence, the absolute value of which was larger rather than that of the unblended copolymer. This result suggests that the orientation of the vinyl copolymer chains was enhanced in the presence of the CP component, possibly by virtue of the inter-component interaction that can occur through hydrogen bonding between the carbonyl and hydroxyl groups.



**Figure 3-10.** Plots of birefringence  $\Delta n$  vs. % elongation for drawn films of CP<sub>2.09</sub>/P(VP<sub>0.46</sub>-*co*-MMA<sub>0.54</sub>) blends.

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## Chapter 4

### Insight into Miscibility Behavior of Cellulose Ester Blends with *N*-Vinyl Pyrrolidone Copolymers in Terms of Viscometric Interaction Parameters

#### 4.1. Introduction

In the preceding chapters,<sup>[1,2]</sup> the author discussed the miscibility and intermolecular interaction for binary blends of cellulose propionate (CP) with non-crystalline vinyl polymers, poly(*N*-vinyl pyrrolidone) (PVP) and its random copolymers; poly(*N*-vinyl pyrrolidone-*co*-vinyl acetate) (P(VP-*co*-VAc)) or poly(*N*-vinyl pyrrolidone-*co*-methyl methacrylate) (P(VP-*co*-MMA)) was selected as the copolymer component. On the basis of thermal analysis data obtained by differential scanning calorimetry (DSC), a miscibility map for the respective blend systems was constructed as a function of the degree of substitution (DS) of CP and the *N*-vinyl pyrrolidone (VP) fraction in the copolymer component. By comparison with the estimation results formerly obtained for cellulose acetate (CA) and butyrate (CB) systems,<sup>[3–5]</sup> it was revealed that the miscibility behavior of cellulose ester (CE)/VP-containing vinyl copolymer blends was seriously affected by a small difference in alkyl chain-length (carbon number) of the acyl substituent in the employed CE. Intriguingly, the CP/P(VP-*co*-VAc) system produced the largest miscible region among the three series of CE/P(VP-*co*-VAc) blends.<sup>[1]</sup> Similarly, the miscible pairing region for the CP/P(VP-*co*-MMA) system was much larger than that for the CA/P(VP-*co*-MMA) system, with spreading to the sides of higher DS of CP and lower VP fraction of P(VP-*co*-MMA) in the map.<sup>[2]</sup> However, the mapping for CB/P(VP-*co*-MMA) blends is not made (see later discussion).

Using supplementary data from Fourier transform infrared (FT-IR) and solid-state NMR measurements, it has been tentatively concluded that the CE/VP-containing copolymer combinations assume miscible or immiscible behavior according to the balance in effectiveness of the following four factors:<sup>[1,2]</sup> (1) hydrogen-bonding attraction between residual hydroxyls of CE and VP-carbonyl groups of the vinyl (co)polymer; (2) steric hindrance of bulky side-groups to the interaction specified in (1); (3) indirect attraction via intramolecular repulsion between the comonomer units in the copolymer; and (4) weak interaction due to

structural affinity (e.g., dipole-dipole antiparallel alignment) between the ester side-group of CE (such as  $\text{CH}_3\text{-CH}_2\text{-CO-O-C-}$ ) and the vinyl acetate (VAc) ( $\text{-(CH}_2\text{-CH(-O-CO-CH}_3\text{))}$ )- or methyl methacrylate (MMA) ( $\text{-(CH}_2\text{-(CH}_3\text{)C(-CO-O-CH}_3\text{))}$ )- unit. Unfortunately, however, the factors 3 and 4 could not be directly detected by the spectroscopic measurements.

To clarify the contributions of the copolymer effect and structural affinity to the miscibility attainment of the CE/vinyl polymer blends, another method besides thermal and spectroscopic techniques is necessary. In a previous work,<sup>[5]</sup> Ohno & Nishio preliminarily estimated the attractive or repulsive action between chain segments of the polymer ingredients participating in the three systems, CA/P(VP-*co*-VAc), CA/P(VP-*co*-MMA), and CB/P(VP-*co*-VAc), in terms of Krigbaum-Wall polymer-polymer interaction parameters ( $\Delta b$  and  $\mu$ ) determinable by dilute solution viscometry. Particularly  $\mu$  data gave a satisfactory account of the difference in the miscibility behavior between the three blend systems (see section 4.3.2). In this context, the present chapter covers complementary assessments of  $\mu$  parameters for various ingredient polymer pairs involved with the CP/P(VP-*co*-VAc) and CP/P(VP-*co*-MMA) systems. Through comprehensive comparison of the results with the  $\mu$  data formerly obtained for the CA and CB systems, some profound insights are provided into the positive effect of propionyl substitution leading to expansion of the miscible paring region in the maps of the CP systems. Additional attention is turned to miscibility behavior of CB/P(VP-*co*-MMA) and cellulose acetate propionate (CAP)/P(VP-*co*-MMA) blends.

## 4.2. Experimental Section

### 4.2.1. Materials

CA was kindly provided from Daicel Corporation, and CAP was purchased from Eastman Chemical Co. CP and CB samples were synthesized with acid chloride/base catalyst from cotton cellulose via a homogeneous reaction in the author's laboratory, as has been described in previous studies.<sup>[4,6,7]</sup> Table 4-1 summarizes the characterization data including molecular weight and glass transition temperature ( $T_g$ ) determined by DSC (see below) for all the CE samples used in this study. Codes "CE<sub>x</sub>" and "CA<sub>y</sub>P<sub>z</sub>" denote CE of ester DS =  $x$  and CAP of acetyl DS =  $y$  and propionyl DS =  $z$ , respectively.

The vinyl polymers employed as a mixing partner for the CEs were PVP, poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA), P(VP-*co*-VAc), and P(VP-*co*-MMA). Data of characterization for all the vinyl polymers are also listed in Table 4-1. As shown in the table, any of the copolymer samples exhibited a single  $T_g$ , and the  $T_g$ -copolymer composition relationships were in good obedience to a well-known Fox equation,<sup>[8]</sup> with a possible extent of scattering due to the difference in molecular weight; thus they were all regarded as essentially random copolymer. Hereafter, a P(VP-*co*-VAc) copolymer of VP:VAc =  $m:n$  (in molar ratio) is encoded as P(VP<sub>*m*</sub>-*co*-VAc<sub>*n*</sub>), and the same encoding rule is also applied for P(VP-*co*-MMA) samples.

### 4.2.2. Preparation of Blend Samples

Powder materials of CEs and vinyl polymers were individually dissolved in *N,N*-dimethylformamide (DMF) at room temperature (~25 °C), at a polymer concentration of 1.00 g/dL. Blend solutions for viscometric measurements were prepared by mixing equal amounts of two solutions of the component polymers. For DSC measurements, two solutions of the required pairing polymers were mixed at the desired weight proportions. The mixed polymer solutions were then poured into a Teflon<sup>®</sup> tray and film samples were made by evaporation of DMF at 50 °C under reduced pressure (< 10 mmHg). The as-cast films were further dried at 50 °C *in vacuo* for 3 days, before supplying to the thermal analysis.

**Table 4-1** Characterization of CEs and synthetic vinyl polymers used in the present chapter

| Sample code <sup>a</sup>             | $M_w$ <sup>d</sup> | $M_n$ <sup>d</sup> | $M_w/M_n$ <sup>d</sup> | $T_g$ /°C | Source               |
|--------------------------------------|--------------------|--------------------|------------------------|-----------|----------------------|
| CP <sub>2.72</sub>                   | 1,070,000          | 367,000            | 2.92                   | 134       | Synthesized          |
| CA <sub>0.16</sub> P <sub>2.52</sub> | 258,000            | 73,400             | 3.51                   | 143       | Eastman Chemical Co. |
| CA <sub>2.70</sub>                   | 237,000            | 73,000             | 3.25                   | 186       | Daicel Co.           |
| CB <sub>2.67</sub>                   | 998,000            | 285,000            | 3.50                   | 114       | Synthesized          |
| CB <sub>2.41</sub>                   | 952,000            | 218,000            | 4.37                   | 132       | Synthesized          |
| CB <sub>2.01</sub>                   | 651,000            | 294,000            | 2.21                   | 139       | Synthesized          |

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| Sample code                                                 | $M_w$ <sup>e</sup>  | $M_n$ <sup>e</sup> | $M_w/M_n$ <sup>e</sup> | $T_g$ /°C | Source                         |
|-------------------------------------------------------------|---------------------|--------------------|------------------------|-----------|--------------------------------|
| PVP                                                         | 24,500 <sup>f</sup> | —                  | —                      | 162       | Nacalai Tesque, Inc.           |
| PVAc                                                        | 90,000 <sup>f</sup> | —                  | —                      | 41        | Polyscience, Inc.              |
| P(VP <sub>0.52</sub> -co-VAc <sub>0.48</sub> ) <sup>b</sup> | 28,000              | 5,120              | 5.47                   | 89        | Polyscience, Inc. <sup>g</sup> |
| PMMA                                                        | 88,400              | 35,000             | 2.53                   | 100       | Aldrich Chemical Co.           |
| P(VP <sub>0.22</sub> -co-MMA <sub>0.78</sub> ) <sup>c</sup> | 189,000             | 70,800             | 2.66                   | 111       | Synthesized <sup>h</sup>       |
| P(VP <sub>0.50</sub> -co-MMA <sub>0.50</sub> ) <sup>c</sup> | 184,000             | 61,300             | 3.00                   | 119       | Synthesized <sup>h</sup>       |

<sup>a</sup> The DS values were determined by <sup>1</sup>H NMR.<sup>b</sup> The VP content was determined by <sup>1</sup>H NMR.<sup>c</sup> The VP contents were determined by FT-IR in a way described by Liu et al.<sup>[9]</sup><sup>d</sup> Determined by gel permeation chromatography (mobile phase, tetrahydrofuran at 40 °C) with polystyrene standards.<sup>e</sup> Determined by gel permeation chromatography (mobile phase, 10 mM/L lithium bromide/DMF at 40 °C) with polystyrene standards.<sup>f</sup> Nominal value.<sup>g</sup> Used after purification by dissolution in dichloromethane and reprecipitation into petroleum ether.<sup>h</sup> Synthesized in the author's laboratory by radical polymerization of two distilled monomers, VP (Nacalai Tesque, Inc.) and MMA (Nacalai Tesque, Inc.), in the same way as that described in ref 5.

### 4.2.3. Measurements

Viscosity measurements were performed for dilute polymer solutions in DMF with an Ubbelohde capillary viscometer, which was placed in a thermo-regulated water bath (30 °C). The temperature of the water bath was controlled within an accuracy range of  $\pm 0.1$  °C. The polymer concentration of the starting sample was adjusted to 1.00 g/dL, and dilutions of the solutions were made to yield at least 4 lower concentrations by adding appropriate doses of DMF. The measurements following the respective dilutions were done after elapsing of an equilibrium time of 15 min. The elution time of each solution from the set gauge of the viscometer was determined as the average of five readings.

DSC thermal analysis was carried out with a Seiko DSC 6200/EXSTAR 6000 apparatus. The temperature readings were calibrated with an indium standard. The calorimetry measurements were conducted on ca. 5-mg film samples packed in an aluminum pan under a nitrogen atmosphere. Each sample was first heated from ambient temperature ( $\sim 25$  °C) to  $\sim 220$  °C at a scanning rate of 20 °C/min, and then immediately quenched to  $-50$  °C at a rate of 80 °C/min. Following this, the second heating scan was run from  $-50$  to 230 °C at a rate of 20 °C/min to record stable thermograms. Thermograms presented in this chapter were all obtained in the second heating scan, and the  $T_g$  was taken as a temperature at the midpoint of a baseline shift in heat flow characterizing the glass transition.

### 4.3. Results and Discussion

#### 4.3.1. Quantification of Interaction Parameter

Following the preceding work,<sup>[5]</sup> a viscometric method developed by Krigbaum & Wall<sup>[10]</sup> and other groups<sup>[11,12]</sup> was applied to assess the attractive or repulsive interactivity between the CE-vinyl polymer constituents focused so far in this series of blend studies. The result was greatly useful to understand the difference in miscibility behavior between the blend systems, as embodied in a later discussion.

A viscometric interaction parameter,  $b$ , for a non-electrolyte dilute polymer solution is defined to fulfill a liner relationship given by the Huggins equation:<sup>[13]</sup>

$$\eta_{sp}/c = [\eta] + bc \quad (4-1)$$

where  $c$  is the solute concentration, and  $\eta_{sp}$  and  $[\eta]$  are the so-called specific and intrinsic viscosities, respectively. The  $b$  is assumed to reflect an interaction between chain molecules of the considered polymer and determined from a slope of the plot of  $\eta_{sp}/c$  vs.  $c$ . The parameter  $b$  is also related to the Huggins coefficient  $k$  by

$$b = k[\eta]^2 \quad (4-2)$$

The  $k$  value generally ranges from 0.3 (in good solvents) to ~0.7 (in the  $\Theta$  state).<sup>[14]</sup>

With regard to a blend solution of two different polymers in a common solvent, Equation (1) is applicable in a rewritten fashion:

$$(\eta_{sp})_m/c_m = [\eta]_m + b_m c_m \quad (4-3)$$

where the subscript m denotes “mixture”, and  $b_m$  is a comprehensive viscometric interaction parameter that reflects an overall interaction involving three possible combinations of polymer chains of the same species (1-1 and 2-2) or not (1-2).

In this viscometric treatment, the polymer-polymer miscibility is estimated by comparison between an experimentally obtained value and an ideally calculated one of  $b_m$ . The former value,  $b_m^{ex}$ , is determined from the plot of  $(\eta_{sp})_m/c_m$  vs.  $c_m$  for blend solutions of a given polymer pair. The latter ideal value,  $b_m^{id}$ , is calculated by the following equation.<sup>[10]</sup>

$$b_m^{id} = w_1^2 b_{11} + w_2^2 b_{22} + 2w_1 w_2 b_{12} \quad (4-4)$$

where  $w_i$  is the weight fraction of component  $i$  in the polymer mixture, and  $b_{ij}$  is an

interaction parameter between the molecular chain of polymer  $i$  and that of polymer  $j$ , and thereby a potential value of  $b_{12}$  may be given by

$$b_{12} = \sqrt{b_{11} \times b_{22}} \quad (4-5)$$

Here, a Krigbaum-Wall interaction parameter,  $\Delta b$ , is defined as

$$\Delta b = b_m^{\text{ex}} - b_m^{\text{id}} \quad (4-6)$$

If  $\Delta b$  is positive, the polymer 1 and polymer 2 are mutually attractive and therefore the pair is taken as miscible. Contrarily, if  $\Delta b$  is negative, the repulsive pair is considered to be immiscible. When there is a large difference between  $[\eta]$  values of both polymers ( $[\eta]_1$  and  $[\eta]_2$ ), the following alternative parameter  $\mu$  as a standard in non-dimensional unit may be more useful to predict the miscibility between the two components.<sup>[12]</sup>

$$\mu = \frac{\Delta b}{([\eta]_2 - [\eta]_1)^2} \quad (4-7)$$

The absolute value of  $\mu$ , i.e.,  $|\mu|$ , should represent the relative strength of attractive or repulsive interaction between the two component polymer molecules.

Table 4-2 summarizes data of  $[\eta]$  and  $b$  parameters ( $b_m^{\text{ex}}$  and  $b_m^{\text{id}}$ ) obtained by the viscometry for DMF solutions of CEs, vinyl polymers, and selected blending pairs of 50/50 composition, together with the polymer-polymer interaction parameters  $\Delta b$  and  $\mu$  determined for the blends. The values of  $[\eta]$  and  $b_m^{\text{ex}}$  were obtained directly from the reduced viscosity ( $\eta_{\text{sp}}/c$ ) versus concentration plots, and those of  $b_m^{\text{id}}$ ,  $\Delta b$ , and  $\mu$  were calculated by the relevant equations ((4-4), (4-6), and (4-7)) given above. For comprehensive purposes, some data were quoted from the previous study.<sup>[5]</sup> As can be seen in the table, the  $[\eta]$  values of the cellulose and those of the vinyl (co)polymers are fairly far apart, and hence the standardized parameter  $\mu$  is mainly used below for discussion on the interaction and miscibility between the blend constituents.

**Table 4-2** Data of intrinsic viscosity and interaction parameters estimated by viscometry for CEs, synthetic vinyl polymers, and their respective 50/50 blends

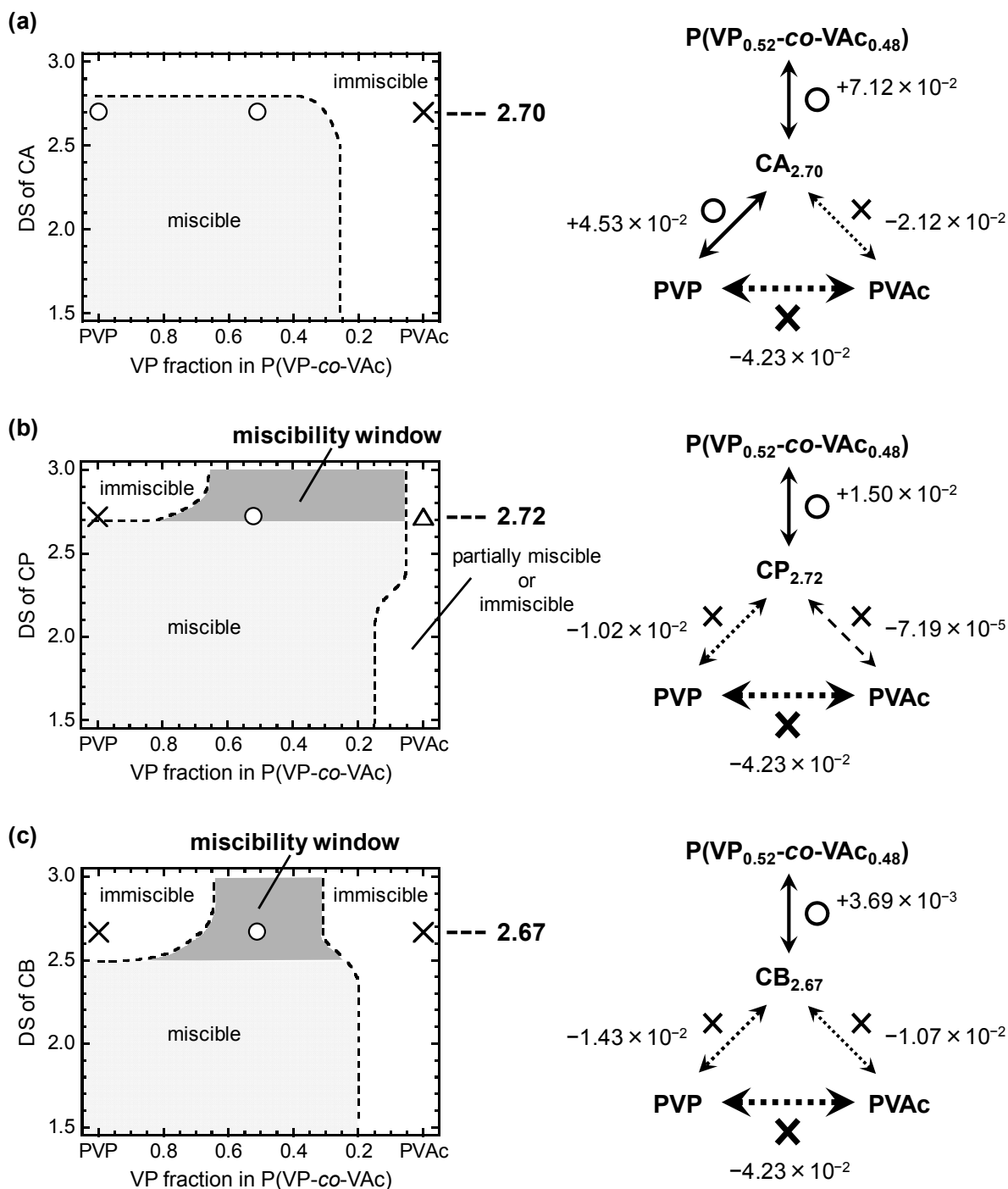
| Samples                                                                              | $[\eta] / \text{dL} \cdot \text{g}^{-1}$ | $b_m^{\text{ex}} / \text{dL}^2 \cdot \text{g}^{-2}$ | $b_m^{\text{id}} / \text{dL}^2 \cdot \text{g}^{-2}$ | $\Delta b / \text{dL}^2 \cdot \text{g}^{-2}$ | $\mu$                  |
|--------------------------------------------------------------------------------------|------------------------------------------|-----------------------------------------------------|-----------------------------------------------------|----------------------------------------------|------------------------|
| CP <sub>2.72</sub>                                                                   | 6.27                                     | $1.84 \times 10^1$                                  | —                                                   | —                                            | —                      |
| CA <sub>0.16</sub> P <sub>2.52</sub>                                                 | 1.85                                     | 1.84                                                | —                                                   | —                                            | —                      |
| CA <sub>2.70</sub> <sup>a</sup>                                                      | 2.28                                     | 1.86                                                | —                                                   | —                                            | —                      |
| CB <sub>2.67</sub> <sup>a</sup>                                                      | 5.61                                     | $1.13 \times 10^1$                                  | —                                                   | —                                            | —                      |
| PVP <sup>a</sup>                                                                     | $1.46 \times 10^{-1}$                    | $1.18 \times 10^{-2}$                               | —                                                   | —                                            | —                      |
| PVAc <sup>a</sup>                                                                    | $6.10 \times 10^{-1}$                    | $1.32 \times 10^{-1}$                               | —                                                   | —                                            | —                      |
| P(VP <sub>0.52-co</sub> -VAc <sub>0.48</sub> ) <sup>a</sup>                          | $1.67 \times 10^{-1}$                    | $1.21 \times 10^{-2}$                               | —                                                   | —                                            | —                      |
| PMMA <sup>a</sup>                                                                    | $2.92 \times 10^{-1}$                    | $3.01 \times 10^{-2}$                               | —                                                   | —                                            | —                      |
| P(VP <sub>0.22-co</sub> -MMA <sub>0.78</sub> )                                       | $3.64 \times 10^{-1}$                    | $3.45 \times 10^{-2}$                               | —                                                   | —                                            | —                      |
| P(VP <sub>0.50-co</sub> -MMA <sub>0.50</sub> ) <sup>a</sup>                          | $5.54 \times 10^{-1}$                    | $9.47 \times 10^{-2}$                               | —                                                   | —                                            | —                      |
| CP <sub>2.72</sub> /PVP                                                              | 3.77                                     | 4.46                                                | 4.85                                                | $-3.84 \times 10^{-1}$                       | $-1.02 \times 10^{-2}$ |
| CP <sub>2.72</sub> /PVAc                                                             | 3.42                                     | 5.42                                                | 5.42                                                | $-2.30 \times 10^{-3}$                       | $-7.19 \times 10^{-5}$ |
| CP <sub>2.72</sub> /P(VP <sub>0.52-co</sub> -VAc <sub>0.48</sub> )                   | 3.20                                     | 5.41                                                | 4.85                                                | $+5.59 \times 10^{-1}$                       | $+1.50 \times 10^{-2}$ |
| CP <sub>2.72</sub> /PMMA                                                             | 3.67                                     | 4.98                                                | 4.99                                                | $-1.15 \times 10^{-2}$                       | $-3.23 \times 10^{-4}$ |
| CP <sub>2.72</sub> /P(VP <sub>0.22-co</sub> -MMA <sub>0.78</sub> )                   | 3.09                                     | 5.17                                                | 5.02                                                | $+1.49 \times 10^{-1}$                       | $+4.27 \times 10^{-3}$ |
| CP <sub>2.72</sub> /P(VP <sub>0.50-co</sub> -MMA <sub>0.50</sub> )                   | 3.12                                     | 5.32                                                | 5.29                                                | $+3.05 \times 10^{-2}$                       | $+9.33 \times 10^{-4}$ |
| CA <sub>0.16</sub> P <sub>2.52</sub> /PVP                                            | $9.80 \times 10^{-1}$                    | $5.06 \times 10^{-1}$                               | $5.35 \times 10^{-1}$                               | $-2.91 \times 10^{-2}$                       | $-1.01 \times 10^{-2}$ |
| CA <sub>0.16</sub> P <sub>2.52</sub> /PMMA                                           | 1.07                                     | $5.83 \times 10^{-1}$                               | $5.84 \times 10^{-1}$                               | $-5.03 \times 10^{-4}$                       | $-2.08 \times 10^{-4}$ |
| CA <sub>0.16</sub> P <sub>2.52</sub> /P(VP <sub>0.50-co</sub> -MMA <sub>0.50</sub> ) | 1.13                                     | $7.01 \times 10^{-1}$                               | $6.91 \times 10^{-1}$                               | $+9.71 \times 10^{-3}$                       | $+5.79 \times 10^{-3}$ |
| CA <sub>2.70</sub> /PVP <sup>a</sup>                                                 | 1.38                                     | $7.50 \times 10^{-1}$                               | $5.43 \times 10^{-1}$                               | $+2.07 \times 10^{-1}$                       | $+4.53 \times 10^{-2}$ |
| CA <sub>2.70</sub> /PVAc <sup>a</sup>                                                | 1.47                                     | $6.87 \times 10^{-1}$                               | $7.47 \times 10^{-1}$                               | $-5.95 \times 10^{-2}$                       | $-2.12 \times 10^{-2}$ |
| CA <sub>2.70</sub> /P(VP <sub>0.52-co</sub> -VAc <sub>0.48</sub> ) <sup>a</sup>      | 1.61                                     | $8.63 \times 10^{-1}$                               | $5.44 \times 10^{-1}$                               | $+3.20 \times 10^{-1}$                       | $+7.12 \times 10^{-2}$ |
| CA <sub>2.70</sub> /PMMA <sup>a</sup>                                                | 1.28                                     | $5.85 \times 10^{-1}$                               | $5.92 \times 10^{-1}$                               | $-6.64 \times 10^{-3}$                       | $-1.67 \times 10^{-3}$ |
| CA <sub>2.70</sub> /P(VP <sub>0.50-co</sub> -MMA <sub>0.50</sub> ) <sup>a</sup>      | 1.40                                     | $6.78 \times 10^{-1}$                               | $6.99 \times 10^{-1}$                               | $-2.12 \times 10^{-2}$                       | $-7.06 \times 10^{-3}$ |
| CB <sub>2.67</sub> /PVP <sup>a</sup>                                                 | 2.97                                     | 2.59                                                | 3.01                                                | $-4.27 \times 10^{-1}$                       | $-1.43 \times 10^{-2}$ |
| CB <sub>2.67</sub> /PVAc <sup>a</sup>                                                | 3.14                                     | 3.20                                                | 3.47                                                | $-2.69 \times 10^{-1}$                       | $-1.07 \times 10^{-2}$ |
| CB <sub>2.67</sub> /P(VP <sub>0.52-co</sub> -VAc <sub>0.48</sub> ) <sup>a</sup>      | 2.82                                     | 3.13                                                | 3.02                                                | $+1.10 \times 10^{-1}$                       | $+3.69 \times 10^{-3}$ |
| CB <sub>2.67</sub> /PMMA <sup>a</sup>                                                | 3.04                                     | 3.13                                                | 3.13                                                | $-2.37 \times 10^{-3}$                       | $-8.35 \times 10^{-5}$ |
| CB <sub>2.67</sub> /P(VP <sub>0.22-co</sub> -MMA <sub>0.78</sub> )                   | 2.42                                     | 3.21                                                | 3.15                                                | $+5.84 \times 10^{-2}$                       | $+2.12 \times 10^{-3}$ |
| CB <sub>2.67</sub> /P(VP <sub>0.50-co</sub> -MMA <sub>0.50</sub> ) <sup>a</sup>      | 3.16                                     | 3.28                                                | 3.37                                                | $-8.67 \times 10^{-2}$                       | $-3.39 \times 10^{-3}$ |
| PVP/PVAc <sup>a</sup>                                                                | $3.90 \times 10^{-1}$                    | $4.66 \times 10^{-2}$                               | $5.57 \times 10^{-2}$                               | $-9.13 \times 10^{-3}$                       | $-4.23 \times 10^{-2}$ |
| PVP/PMMA                                                                             | $2.40 \times 10^{-1}$                    | $1.95 \times 10^{-2}$                               | $1.99 \times 10^{-2}$                               | $-4.02 \times 10^{-4}$                       | $-1.87 \times 10^{-2}$ |
| CA <sub>2.70</sub> /CP <sub>2.72</sub>                                               | 4.34                                     | 7.88                                                | 8.01                                                | $-1.29 \times 10^{-1}$                       | $-8.12 \times 10^{-3}$ |

<sup>a</sup> Data were quoted from ref 5.

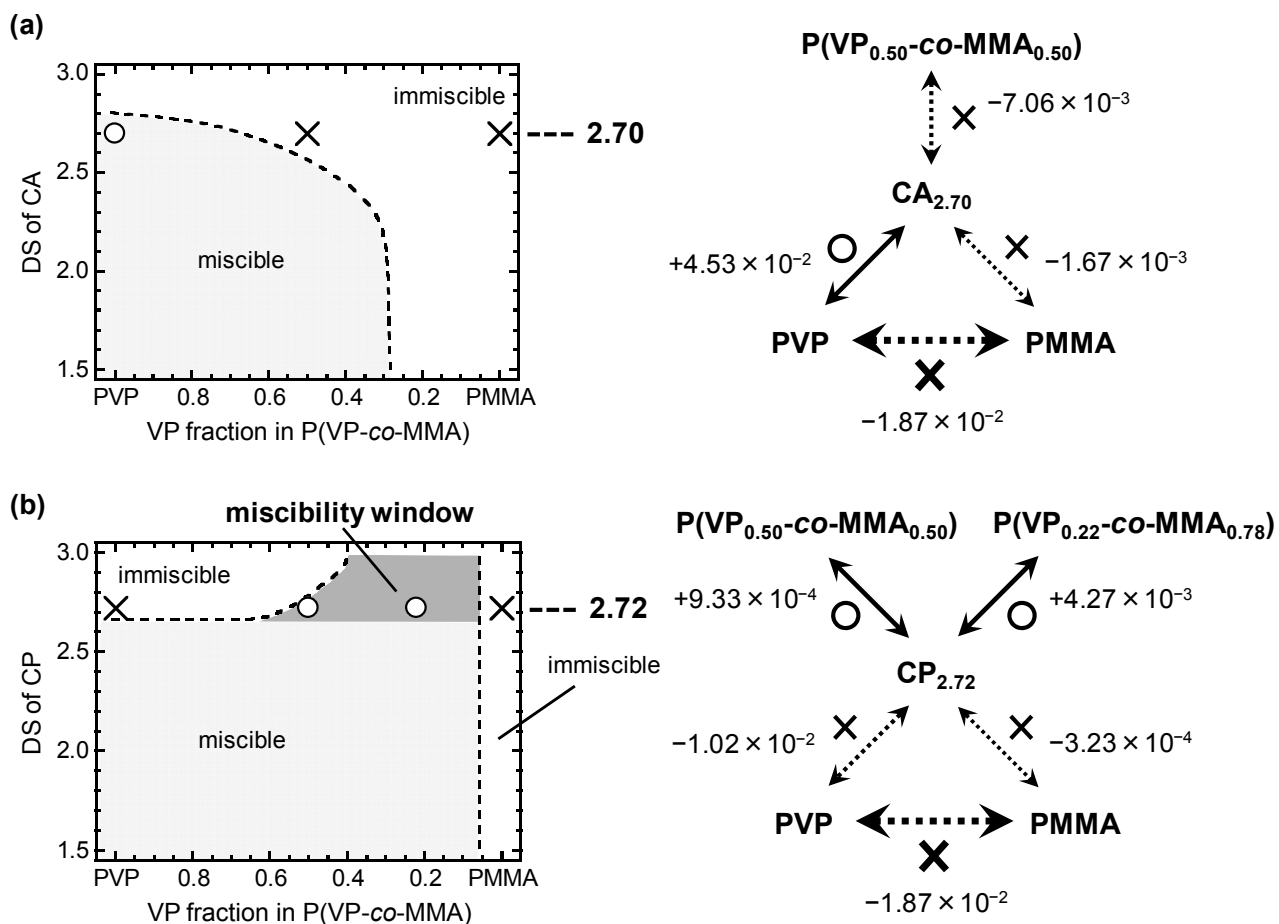
### 4.3.2. Overview of $\mu$ Records for CA and CB Blends

First, the author briefly reviews the preceding results of  $\mu$  assessment for CA/P(VP-*co*-VAc), CB/P(VP-*co*-VAc), and CA/P(VP-*co*-MMA) blends.<sup>[5]</sup> Figures 4-1a, 4-1c, and 4-2a summarize simplified miscibility maps of the three blend systems, with addition of the illustrations in terms of  $\mu$  data obtained for selected polymer combinations (DS of CEs,  $\sim 2.7$ ; VP:VAc or MMA of copolymers,  $\sim 0.5:0.5$ ) critical to the respective systems. The individual  $\mu$  evaluations were in consistency with the respective miscibility mappings based on DSC thermal analysis; viz., a positive  $\mu$  value was obtained for miscible pairs of cellulosic/synthetic polymers, while immiscible blends all provided a negative  $\mu$  value.

As exemplified for a highly butyrated CB/P(VP-*co*-VAc) series (Figure 4-1c, right), the  $\mu$  data concerned with the “three” constituting polymer ingredients made an order with respective to the degree of “immiscibility”: PVP/PVAc ( $-4.23 \times 10^{-2}$ ) > CB<sub>2.67</sub>/PVP ( $-1.43 \times 10^{-2}$ )  $\geq$  CB<sub>2.67</sub>/PVAc ( $-1.07 \times 10^{-2}$ ). The mutually repellent character of the PVP/PVAc pair is considerably stronger than the corresponding ones of the other pairs CB<sub>2.67</sub>/PVP and CB<sub>2.67</sub>/PVAc. Then it can be taken that the intramolecular repulsion inherent in the VP-VAc copolymer indirectly realized the miscible behavior of the CB<sub>2.67</sub>/P(VP<sub>0.52</sub>-*co*-VAc<sub>0.48</sub>) blend; this polymer pair is surely attractive to each other, giving a positive  $\mu$  value,  $+3.69 \times 10^{-3}$ . This reasoning would satisfy us about the appearance of the miscibility window (Figure 4-1c, left), as amplified in the following sections. On the other hand, such an explicit window never appeared in the map of the CA/P(VP-*co*-VAc) system (see Figures 4-1a and 4-2a), although there should have arisen the intra-copolymer effect improving the miscibility in the blends of relatively high-acetylated CAs. The absence of the window may be interpreted as due to an inhibiting factor, i.e., the strong self-association ability of highly substituted CAs of DS > 2.7; the CAs are rather easily crystallizable as cellulose triacetate II form. Differing from this, no crystallizing habit was detected even for a CB synthesized at DS = 2.94.<sup>[4]</sup> The lesser self-association nature of CB should be advantageous to that attractive interaction with the P(VP-*co*-VAc) component.



**Figure 4-1.** Miscibility maps (*left*) with additional illustrations using  $\mu$  data (*right*) for (a) CA/P(VP-*co*-VAc),<sup>[3]</sup> (b) CP/P(VP-*co*-VAc),<sup>[1]</sup> and (c) CB/P(VP-*co*-VAc) systems.<sup>[4]</sup> The miscibility maps are represented in a simplified style retaining the essence. Symbols indicate that a given pair of CE/vinyl polymer is miscible ( $\bigcirc$ , single  $T_g$ ), immiscible ( $\times$ , dual  $T_g$ s), or partially miscible ( $\triangle$ , dual  $T_g$ s approaching each other to an appreciable degree).



**Figure 4-2.** Miscibility maps (*left*) with additional illustrations using  $\mu$  data (*right*) for (a) CA/P(VP-*co*-MMA)<sup>[5]</sup> and (b) CP/P(VP-*co*-MMA) systems.<sup>[2]</sup> The miscibility maps are represented in a simplified style retaining the essence. The meanings of two symbols ○ and × are the same as used in Figure 4-1.

Meanwhile, another vinyl polymer combination of PVP and PMMA provided a  $\mu$  value of  $-1.87 \times 10^{-2}$ , from which the binary system is suggested to be immiscible. In fact, the blend samples showed a common behavior of essentially double  $T_g$ s in DSC measurements.<sup>[5]</sup> However, the  $|\mu|$  value for the PVP/PMMA pair is smaller than that ( $|\mu| = 4.23 \times 10^{-2}$ ) for the PVP/PVAc pair. Thus it is deduced that the constituents VP and MMA in P(VP-*co*-MMA) show a somewhat weaker repulsive interaction than the VP and VAc units in P(VP-*co*-VAc). Presumably, this deterioration of the latent copolymer effect is responsible for the observation of a narrower miscible region in the CA/P(VP-*co*-MMA) map (Figure 4-2a) relative to that in the CA/P(VP-*co*-VAc) map (Figure 4-1a).

### 4.3.3. Inspection of Miscibility Maps for CP Blends in $\mu$ Terms

#### 4.3.3.1. CP/P(VP-co-VAc) System

As shown in Figure 4-1b (right), a negative  $\mu$  value  $-1.02 \times 10^{-2}$  was obtained for the combination of CP<sub>2.72</sub> and PVP homopolymer, while  $\mu$  of the CP<sub>2.72</sub>/P(VP<sub>0.52</sub>-co-VAc<sub>0.48</sub>) pair was positive,  $+1.50 \times 10^{-2}$ . From these assessments, PVP and P(VP<sub>0.52</sub>-co-VAc<sub>0.48</sub>) are taken as immiscible and miscible, respectively, with the highly esterified CP. The judgment is actually in accordance with the result of miscibility estimation by thermal analysis for the blends (see Figure 4-1b, left). For another essential pair, CP<sub>2.72</sub>/PVAc, a negative  $\mu$  of  $-7.19 \times 10^{-5}$  was obtained, but the absolute value is much smaller than that for the CP<sub>2.72</sub>/PVP pair by more than two orders of magnitude. The former pair was previously marked to be partially miscible by observation of two  $T_g$ s approaching each other to an appreciable extent, and the low magnitude of  $\mu$  reflects such a “better compatibility” of highly substituted CP with PVAc homopolymer.

Despite no presence of strong intermolecular attraction between CP<sub>2.72</sub> and the two homopolymers (PVP and PVAc), the CP component was able to be miscible with the copolymer comprising VP and VAc units. This phenomenon is explicable as being due to the more intense repulsive action between the VP and VAc segments in the P(VP-co-VAc) copolymer component, as in the case of the CB/P(VP-co-VAc) system. We find for sure in Figure 4-1b (right) that the PVP/PVAc pair shows the largest negative  $\mu$  value ( $-4.23 \times 10^{-2}$ ) in the three polymer pairs participating in the CP<sub>2.72</sub>/P(VP-co-VAc) system. In general, when two monomer species repelling each other are randomly combined by covalent bonding, the resulting copolymer tends to intimately mix with the other polymer of less self-associating nature, so as to reduce the strong repulsion between the comonomer units.<sup>[15,16]</sup> This is the reason why the high-esterified CP and CB can be miscible with P(VP-co-VAc) in a restricted range of the copolymer composition, even though there is a scarcity of specific attractive force (i.e., proton donor-acceptor interaction) between the two mixing components.

As is obvious in Figure 4-1, the miscible region in the CP/P(VP-co-VAc) map is larger than the corresponding ones in the other maps of CA/P(VP-co-VAc) and CB/P(VP-co-VAc). In perspective comparison, the region involved in the CP system expands particularly to the side of VAc-rich compositions. This improvement virtually comes from the better com-

patibility of CP with PVAc supported above by the  $\mu$  data of  $-7.19 \times 10^{-5}$  for CP<sub>2.72</sub>/PVAc. This value in  $|\mu|$  is overwhelmingly small, compared with  $\mu = -2.12 \times 10^{-2}$  for CA<sub>2.70</sub>/PVAc (Figure 4-1a, right) and  $\mu = -1.07 \times 10^{-2}$  for CB<sub>2.67</sub>/PVAc (Figure 4-1c, right).

For three pairs of P(VP<sub>0.52-co</sub>-VAc<sub>0.48</sub>) with the CEs of DS  $\approx 2.7$ , we can rank them according to  $\mu$  data, as follows: CA<sub>2.70</sub>/P(VP<sub>0.52-co</sub>-VAc<sub>0.48</sub>) ( $+7.12 \times 10^{-2}$ ) > CP<sub>2.72</sub>/P(VP<sub>0.52-co</sub>-VAc<sub>0.48</sub>) ( $+1.50 \times 10^{-2}$ ) > CB<sub>2.67</sub>/P(VP<sub>0.52-co</sub>-VAc<sub>0.48</sub>) ( $+3.69 \times 10^{-3}$ ), all showing miscibility. The CA<sub>2.70</sub>/P(VP<sub>0.52-co</sub>-VAc<sub>0.48</sub>) pair exhibited the highest  $\mu$  value, which is attributable to the direct interaction based on the actually detected hydrogen bonding between CA-hydroxyl and VP-carbonyl groups,<sup>[3,17]</sup> however, the increase of  $\mu$  relative to that for CA<sub>2.70</sub>/PVP ( $+4.53 \times 10^{-2}$ ) suggests a secondary contribution of the intra-copolymer effect to the miscibility attainment. The hydrogen bonding effect seriously declines in the other two systems adopting propionyl and butyryl substitutions for the CE component. Consequently, the miscibility of CB<sub>2.67</sub> with P(VP<sub>0.52-co</sub>-VAc<sub>0.48</sub>) is realized only through the intra-copolymer repulsion as an indirect driving force. As to the CP<sub>2.72</sub>/P(VP<sub>0.52-co</sub>-VAc<sub>0.48</sub>) pair, besides the copolymer effect, a weak interaction due to structural affinity between the propionyl ester group and VAc unit also acts as a factor contributory to the miscibility attainment.

#### 4.3.3.2. CP/P(VP-co-MMA) System

Figure 4-2b (left) displays a simplified diagram of the miscibility mapping conducted for CP/P(VP-co-MMA) blends. In the right side of Figure 4-2b,  $\mu$  data are collected for four combinations of CP<sub>2.72</sub> with P(VP<sub>0.50-co</sub>-MMA<sub>0.50</sub>), P(VP<sub>0.22-co</sub>-MMA<sub>0.78</sub>), PVP, and PMMA, the values being  $+9.33 \times 10^{-4}$ ,  $+4.27 \times 10^{-3}$ ,  $-1.02 \times 10^{-2}$ , and  $-3.23 \times 10^{-4}$ , respectively. Judging from the positive or negative sign of  $\mu$ , the P(VP-co-MMA) copolymers are taken as potentially miscible with CP<sub>2.72</sub>, whereas both the homopolymers are not. These judgments entirely agree with the actual markings for the CP<sub>2.72</sub>/P(VP-co-MMA) series in the miscibility map. In addition, PVP/PMMA blends are immiscible and this polymer pair provides a larger negative  $\mu$  ( $-1.87 \times 10^{-2}$ ) than the CP<sub>2.72</sub>/PVP and CP<sub>2.72</sub>/PMMA pairs. The relationship in repulsion (immiscibility) between the three ingredient polymer pairs participating in the CP<sub>2.72</sub>/P(VP-co-MMA) series is basically similar to that found for the CP<sub>2.72</sub>/P(VP-co-VAc) series (see Figure 4-1b, right). Accordingly, it is reasonable to assume

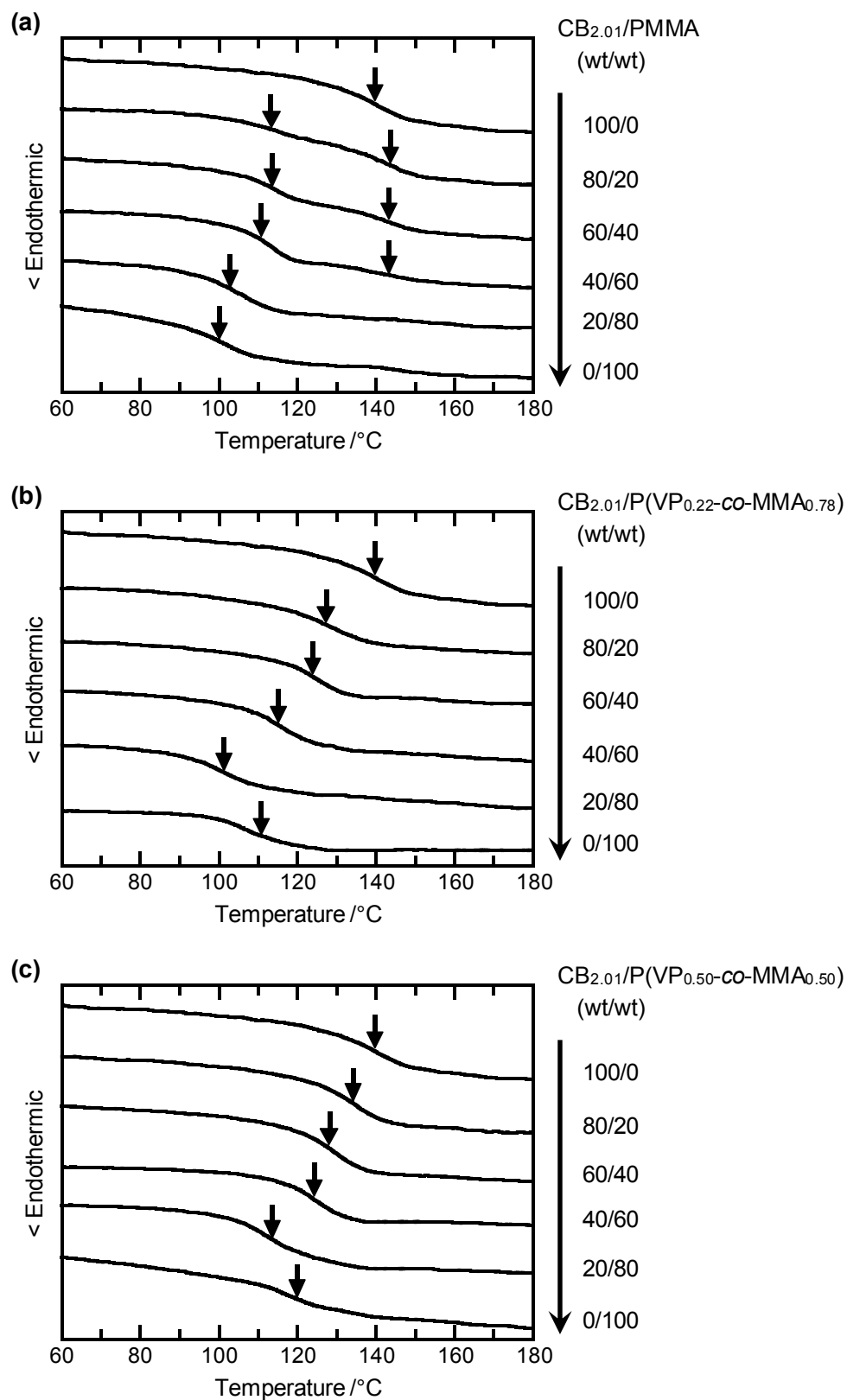
that the intramolecular repulsive effect of the VP-MMA copolymer gave rise to the miscibility window in the map for the CP/P(VP-*co*-MMA) system. However, the window region observed for this system is obviously narrower than that for the CP/P(VP-*co*-VAc) system (see Figure 4-1b, left). This narrowing of the window may be ascribed to the weaker repulsion in the VP-MMA copolymer relative to that in the VP-VAc copolymer ( $\mu = -4.23 \times 10^{-2}$ ), as has been applied to the comparative discussion of the two maps for the corresponding blends of CA. The location of the window in the side of MMA-rich compositions owes to the better affinity between CP and MMA segments, as supported by the lower order ( $10^{-4}$ ) of  $\mu$  obtained for the CP<sub>2.72</sub>/PMMA pair.

#### 4.3.4. Complementary Mapping for CB/P(VP-*co*-MMA) System by Application of $\mu$ Assessment

In the miscibility characterization of CE/vinyl copolymer blends, the total mapping for the CB/P(VP-*co*-MMA) system has not yet been accomplished by thermal analysis. A main reason is that  $T_g$ s (ca. 110–120 °C) of CBs of DS  $\approx$  2.5–2.9 are fairly close to those (ca. 100–115 °C) of P(VP-*co*-MMA)s of VP < 50 mol%. However, the following data were previously acquired for the system concerned: (i) CB and PVP homopolymer formed miscible blends of hydrogen-bonding type unless the butyryl DS exceeded  $\sim$ 2.5 (see Figure 4-1c);<sup>[4]</sup> (ii) a polymer pair of CB (DS = 2.94) with P(VP<sub>0.50</sub>-*co*-MMA<sub>0.50</sub>) was judged to be immiscible (double  $T_g$ s).<sup>[5]</sup>

To depict the miscibility map of the CB/P(VP-*co*-MMA) system more closely, the author newly examined the blend miscibility of relatively low-substituted CBs (DS < 2.5) with P(VP-*co*-MMA)s by DSC and also quantified  $\mu$  for additional pairs of CB (DS  $\geq$  2.6) with MMA-rich P(VP-*co*-MMA)s by viscometry. A major concern is whether the miscibility window emerges or not in the CB/P(VP-*co*-MMA) map.

Figure 4-3a illustrates DSC thermograms measured for blend samples of CB<sub>2.01</sub>/PMMA homopolymer. As can be seen from the data, two independent glass transitions originating from the two components were detected for the 40/60–80/20 compositions (in wt% ratio), signaling immiscibility of the CB<sub>2.01</sub>/PMMA pair. The same behavior of double  $T_g$ s was also observed for CB<sub>2.41</sub>/PMMA blends. In contrast, Figure 4-3b and 4-3c offer a typical



**Figure 4-3.** DSC thermograms obtained for blends of  $\text{CB}_{2.01}$  with (a) PMMA, (b)  $\text{P}(\text{VP}_{0.22}\text{-co-MMA}_{0.78})$ , and (c)  $\text{P}(\text{VP}_{0.50}\text{-co-MMA}_{0.50})$ . Arrows indicate a  $T_g$  position taken as the midpoint of a baseline shift in heat flow.

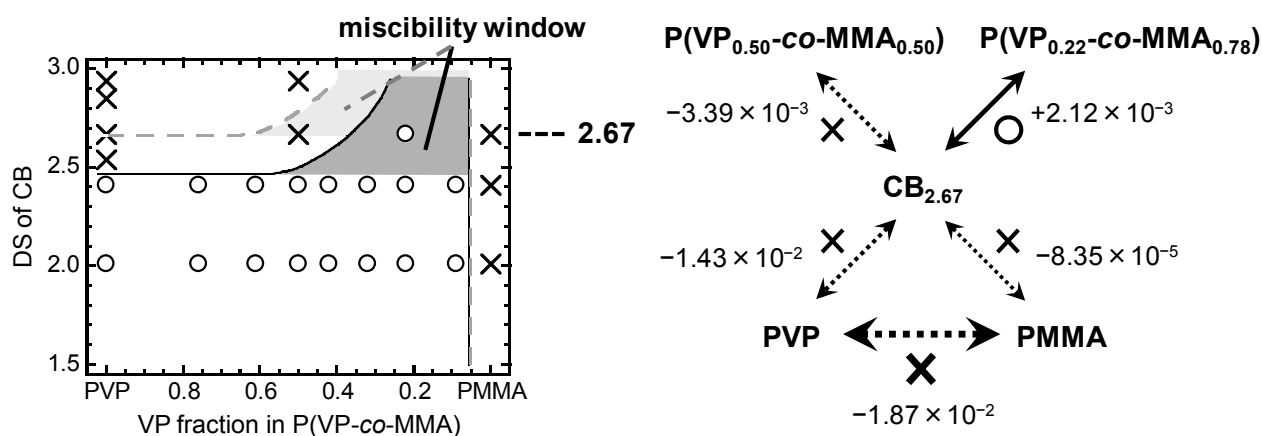
miscible evidence in DSC (i.e., composition-dependent single  $T_g$ ) for CB<sub>2.01</sub>/P(VP<sub>0.22</sub>-*co*-MMA<sub>0.78</sub>) and CB<sub>2.01</sub>/P(VP<sub>0.50</sub>-*co*-MMA<sub>0.50</sub>) blends, respectively. Similar miscible behavior was confirmed for other polymer combinations using CB<sub>2.41</sub> and/or P(VP-*co*-MMA)s of VP  $\geq$  9 mol% (MMA  $\leq$  91 mol%). Thus, it turns out that the lower limit in VP fraction of P(VP-*co*-MMA) that can be miscible with CB (DS  $< \sim 2.5$ ) is  $\sim 10$  mol%, which is almost the same limit as that found when CP was the CE component (see Figure 4-2b). In a reasoning similar to that applied to interpret the CP/P(VP-*co*-MMA) map, the miscibility of CB with P(VP-*co*-MMA)s so rich in MMA residues (e.g., MMA = 87 and 91 mol%) would be invited by a good compatibility between the butyl ester side-group and the MMA unit. This may be supported by  $\mu$  assessment of an extremely small negative value ( $-8.35 \times 10^{-5}$ ) for a polymer pair CB<sub>2.67</sub>/PMMA (see Table 4-2).

In the present viscometric  $\mu$  measurements, a definitely positive data such as  $\mu = +2.12 \times 10^{-3}$  was found for CB<sub>2.67</sub>/P(VP<sub>0.22</sub>-*co*-MMA<sub>0.78</sub>). This indicates that even CB of DS  $> 2.5$  is potentially miscible with the vinyl copolymer rich in MMA. Figure 4-4 (left) summarizes a miscibility map constructed for the total system of CB/P(VP-*co*-MMA) by the combined use of the DSC and  $\mu$ -assessment results. In the map, solid lines separate the miscible and immiscible regions connected with DS of CB and VP fraction of P(VP-*co*-MMA), to provide a miscibility window in the upper right portion. As illustrated in the right side in Figure 4-4,  $\mu$  parameters for three combinations of the ingredient polymers pertinent to the CB<sub>2.67</sub>/P(VP-*co*-MMA) series are all negative, but the PVP/PMMA pair gives the largest absolute value ( $1.87 \times 10^{-2}$ ). This situation again supports the contribution of the intra-molecular repulsion inherent in the P(VP-*co*-MMA) copolymer to the appearance of the miscibility window. However, the region is diminished to some extent, compared to the window in the CB/P(VP-*co*-VAc) map (Figure 4-1c), because the repulsion between VP and MMA units is weaker than that between VP and VAc units, as already mentioned above.

Here it should be further noted that CB<sub>2.67</sub> of DS  $\approx 2.7$  is estimated to be immiscible with P(VP<sub>0.50</sub>-*co*-MMA<sub>0.50</sub>) of VP:MMA = 50:50 from the  $\mu$  data of  $-3.39 \times 10^{-3}$ . In contrast, a comparable pair using CP, i.e., CP<sub>2.72</sub>/P(VP<sub>0.50</sub>-*co*-MMA<sub>0.50</sub>), was miscible, which was decisive from both  $T_g$  and  $\mu$  determinations (see Figure 4-2b). It follows, therefore, that the miscible pairing region (mainly associated with the window) in the CB/P(VP-*co*-MMA) map is a little narrower than that of the CP/P(VP-*co*-MMA) map. This comparison is made

clearer in Figure 4-4 (left), as guided by solid lines and broken ones inserted therein.

As indicated above, intimate mixing of two polymer components through the copolymer repulsion effect is unrealized on blending  $CB_{2.67}$  with  $P(VP_{0.50}\text{-}co\text{-}MMA_{0.50})$ . In interpretation of this, the following data should be recalled:  $\mu = -1.87 \times 10^{-2}$  for PVP/PMMA and  $-1.43 \times 10^{-2}$  for  $CB_{2.67}$ /PVP (see Figure 4-4, right), the two values being close to each other. In the employment of the copolymer of VP = 50 mol%, probably, the relatively strong repulsion would still work between the CB component and the VP residue and inhibit the mutual approach of the two polymer components. Consequently, the intra-copolymer effect to attain miscible CB/P(VP-*co*-MMA) blends is active only at restricted copolymer compositions considerably rich in MMA. On the other hand, the repulsion between  $CP_{2.72}$  and PVP ( $\mu = -1.02 \times 10^{-2}$ ) is evidently weaker than that between PVP and PMMA (see Figure 4-2b, right), and the copolymer effect would be significant even at the composition of VP = 50 mol%, resulting in the miscible blending of the  $CP_{2.72}$ /P( $VP_{0.50}\text{-}co\text{-}MMA_{0.50}$ ) pair. In addition, a low frequency of intermolecular hydrogen-bondings might contribute to this miscibility attainment as a secondary effect. This inference took into consideration the DS boundary of  $\sim 2.7$  partitioning the mixing states of CP/P(VP-*co*-MMA) blends (VP  $\geq$  60 mol%) (Figure 4-2b, left).

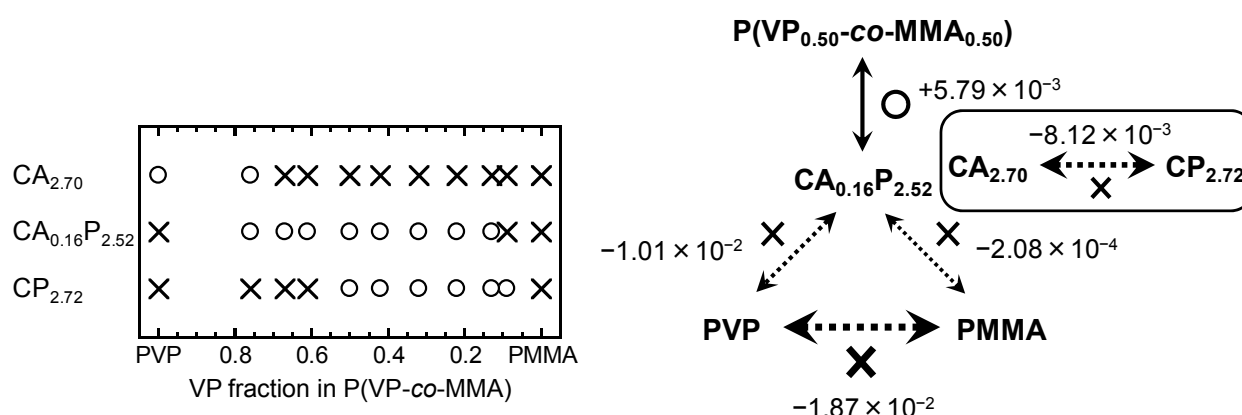


**Figure 4-4.** Miscibility map (*left*) and additional illustration (*right*) using  $\mu$  data for CB/P(VP-*co*-MMA) blends. The meanings of two symbols  $\bigcirc$  and  $\times$  are the same as used in Figure 4-1. Solid lines in the map represent a boundary partitioning the miscible and immiscible regions for the CB/P(VP-*co*-MMA) system, and, for comparison, the corresponding boundary for the CP/P(VP-*co*-MMA) system (Figure 4-2b) is drawn by broken lines.

### 4.3.5. Inspection of Estimation Results of Miscibility for CAP/P(VP-*co*-MMA) Blends in $\mu$ Terms

Finally, the author refers to miscibility behavior of CAP blends with P(VP-*co*-MMA). To make a comparison with the result for the CP<sub>2.72</sub>/P(VP-*co*-MMA) series, a partially acetylated cellulose propionate sample, CA<sub>0.16</sub>P<sub>2.52</sub> (acetyl DS = 0.16; propionyl DS = 2.52), was selected as the mixed ester component.

Figure 4-5 (left) collects the miscibility data<sup>[2]</sup> based on thermal analysis for the target CA<sub>0.16</sub>P<sub>2.52</sub>/P(VP-*co*-MMA) blends, together with the corresponding data in the uses of CP<sub>2.72</sub> and CA<sub>2.70</sub>. In the right side, an additional illustration is given in terms of  $\mu$  assessment. The combination of CA<sub>0.16</sub>P<sub>2.52</sub> and P(VP<sub>0.50</sub>-*co*-MMA<sub>0.50</sub>) imparted a positive  $\mu$  value of  $+5.79 \times 10^{-3}$ , while negative  $\mu$  data of  $-1.01 \times 10^{-2}$  and  $-2.08 \times 10^{-4}$  were assigned to CA<sub>0.16</sub>P<sub>2.52</sub>/PVP and CA<sub>0.16</sub>P<sub>2.52</sub>/PMMA pairs, respectively. Therefore, the P(VP<sub>0.50</sub>-*co*-MMA<sub>0.50</sub>) copolymer is potentially miscible with the mixed ester CA<sub>0.16</sub>P<sub>2.52</sub>, whereas both the homopolymers are not. These judgments are consistent with the results of miscibility estimation by DSC for the respective blends, also supporting that the CA<sub>0.16</sub>P<sub>2.52</sub>/P(VP-*co*-MMA) series offers a miscibility window, as did the blend series using CP<sub>2.72</sub>. Furthermore, the immiscible polymer pair of PVP/PMMA provides a larger negative  $\mu$  ( $-1.87 \times 10^{-2}$ ) than the other immiscible pairs of CA<sub>0.16</sub>P<sub>2.52</sub>/PVP and CA<sub>0.16</sub>P<sub>2.52</sub>/PMMA. From this triangular relationship, the intramolecular repulsive effect of the VP-MMA



**Figure 4-5.** Mapping of miscibility data<sup>[2]</sup> (left) and additional illustration in  $\mu$  terms (right) for CA<sub>0.16</sub>P<sub>2.52</sub>/P(VP-*co*-MMA) blends. For comparison, miscibility data for the corresponding blends using CA<sub>2.70</sub> and CP<sub>2.72</sub> are also mapped in the left figure. The meanings of two symbols O and X are the same as used in Figure 4-1.

copolymer may be regarded as being responsible for the emergence of the miscibility window in the map for the CAP/P(VP-*co*-MMA) blends.

However, it is astonishing that the VP:MMA range involved in the window became more expanded in the CA<sub>0.16</sub>P<sub>2.52</sub>/P(VP-*co*-MMA) series, when compared with the situation in the CP<sub>2.72</sub>/P(VP-*co*-MMA) series. In order to explain this expansion, attention was directed to another intramolecular repulsive interaction that might have arisen in the mixed ester component *per se*. Thereupon, a cellulose ester pair CA<sub>2.70</sub>/CP<sub>2.72</sub> was explored by thermal analysis and viscometry for evaluations of the miscibility and interaction parameter; the residual hydroxyl contents of the ester derivatives are equalized to that of CA<sub>0.16</sub>P<sub>2.52</sub>. DSC measurements confirmed that CA<sub>2.70</sub>/CP<sub>2.72</sub> blends exhibited dual  $T_g$  signals corresponding to those of the two constituents at any blending proportion. The Krigbaum-Wall interaction parameter of this polymer pair was estimated to be negative, as  $\mu = -8.12 \times 10^{-3}$  (see Figure 4-5, right), in conformity with the immiscible behavior of the blends. The absolute value of this  $\mu$  is appreciably large, although it is below  $|\mu| = 1.87 \times 10^{-2}$  for the PVP/PMMA pair. The present result suggests that a relatively strong repulsive interactivity can work between the two cellulosic ester components.

In view of the above context, it is deduced that the cellulose mixed ester would also behave as a kind of copolymer dangling two different ester groups along the carbohydrate backbone; thus, the CAP/P(VP-*co*-MMA) blends are taken as a copolymer/copolymer system where the miscibility should be affected by the duplicated, intra-copolymer effect. The expansion of the window in the mapping of the CA<sub>0.16</sub>P<sub>2.52</sub>/P(VP-*co*-MMA) blends can be ascribed to such an additional repulsion effect originating in the CAP side.

## Reference and Notes

- [1] See Chapter 2 in this thesis.
- [2] See Chapter 3 in this thesis.
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## Chapter 5

### Summary & Conclusions

A sequence of studies in the present thesis was directed towards the characterization of miscibility and intercomponent interaction on binary blends of cellulose alkyl esters (CEs) with synthetic vinyl copolymers containing an *N*-vinyl pyrrolidone (VP) unit, with a goal of further improvement in physical properties (e.g., optical property) of the celluloses. Cellulose propionate (CP) was selected as the main target derivative, and an effect of alkyl chain length (carbon number) of the acyl substituent in the employed CE was closely inspected. The major results are listed below:

The miscibility state in the CE/VP-containing vinyl polymer system is determined by the balance in effectiveness of the following four factors.

1. Direct attraction based on *hydrogen-bonding* between the residual hydroxyls of the CE component and the carbonyl groups of VP units in the vinyl polymer component is the primary determinant for the blend miscibility (Chapter 2 and 3).
2. *Steric hindrance* of comparatively bulky substituent (propionyl or butyryl side group), leading to suppression of the above interaction in frequency, causes a lowering of the degree of miscibility in the blends (Chapter 2 and 3).
3. Indirect interaction driven by a stronger repulsion between the two monomeric units constituting the copolymer (including mixed esters of cellulose), i.e., *the intra-copolymer effect*, is secondly contributory to the miscibility attainment, resulting in the advent of a so-called “*miscibility window*” in data maps (Chapter 2, 3, and 4).
4. Weak intermolecular accessibility derived from *structural affinity* (e.g., dipole-dipole antiparallel alignment) between two segmental moieties involving the ester side-group of CE (such as  $\text{CH}_3\text{-CH}_2\text{-CO-O-C-}$ ) and vinyl acetate (VAc) ( $\text{-(CH}_2\text{-CH(-O-CO-CH}_3\text{))-}$ ) or methyl methacrylate (MMA) ( $\text{-(CH}_2\text{-(CH}_3\text{)C(-CO-O-CH}_3\text{))-}$ ) unit of the copolymer also acts as a driving factor contributory to the miscibility attainment (Chapter 2, 3, and 4).

In addition, miscible blends of the hydrogen-bonding type are completely homogeneous on a scale within a few nanometers, whereas the polymer pairs situated in the miscibility window are homogeneous in a somewhat larger scale of heterogeneity (ca. 5–20 nm) (Chapter 2 and 3). This reflects a difference in absolute strength between the driving forces for the respective miscibility attainments.

Through comprehensive comparison of the data obtained for cellulose acetate (CA) and butyrate (CB) systems, it is revealed that the CP system provided the largest miscible region, possibly due to the moderate length of the acyl substituent, appropriate to the attractive interactions between the blend components as described above. The thermal and optical properties of CP are also improved noticeably by the miscible blending with the copolymers (Chapter 2 and 3).

The results of the studies collected in the individual chapters are summarized as follows.

## **Chapter 2.**

Miscibility characterization was performed on blends of CP with synthetic vinyl polymers containing VP and/or VAc units, i.e., PVP, PVAc, and P(VP-*co*-VAc) random copolymers. On the basis of thermal analysis data obtained by differential scanning calorimetry (DSC), a miscibility map (Figure 2-7) was successfully constructed as a function of both the degree of substitution (DS) of CP and the VP:VAc composition of P(VP-*co*-VAc). Fourier transform infrared (FT-IR) spectroscopy was also utilized to detect a hydrogen-bonding type of intermolecular interaction contributory to the miscibility attainment. As denoted in that map, polymer pairs of CP/P(VP-*co*-VAc) satisfying  $DS < 2.7$  for the CP component and  $VP > 20$  mol% for the vinyl polymer component were miscible. This miscibility is given rise to, more or less, by virtue of the hydrogen bonding between CP-hydroxyls and VP-carbonyls, and hence the effectiveness should be greater when the propionyl DS is lower and the VP fraction is higher. The upper limit of  $DS = 2.7$  required for the miscibility was intermediate between the corresponding ones, acetyl  $DS = 2.8$  and butyryl  $DS = 2.5$ , for the comparable systems employing CA and CB. This observation can be explained as being due to the difference in bulkiness between the three sorts of acyl

substituents, each exerting an effect of steric hindrance to decline the hydrogen-bonding interaction.

CPs of  $DS > 2.7$  exhibited miscibility with P(VP-*co*-VAc)s of VP = 10–65 mol%, despite their imperfect miscibility with both PVP and PVAc homopolymers; this resulted in advent of a definite “miscibility window” in the map, as has been experienced formerly in the study of CB/P(VP-*co*-VAc) blends. The behavior may be interpreted to be occasioned principally by intramolecular repulsion between the comonomer units in P(VP-*co*-VAc). In addition, another effect, the structural affinity between the propionyl side-group and the VAc unit, contributes to the miscibility realized for blends of highly propionylated CPs ( $DS > 2.3$ ) with VAc-rich copolymers (VP:VAc = 10:90–33:67). Eventually, the miscible pairing region extended more widely in the map for the CP/P(VP-*co*-VAc) system, compared with the situations in the corresponding blend systems using CA and CB. It is astonishing afresh to find that only one difference in carbon number of the acyl substitution drastically changed the miscibility behavior of CEs with a given synthetic copolymer.

However, caution should be exercised to the scale of homogeneity in the CP/P(VP-*co*-VAc) blends being estimated to form a miscible monophasic. As a result of further investigation by dynamic mechanical analysis (DMA) and proton spin-lattice relaxation time quantifications in solid-state  $^{13}\text{C}$  NMR, we had awareness of the following respects: The miscible blends of hydrogen-bonding type are completely homogeneous on a scale of a few nanometers ( $\leq 4$  nm), whereas the blend series situated in the miscibility window are homogeneous with a possible microdomain size between ca. 5 and 15 nm. In the latter assessment, CP blends with P(VP-*co*-VAc)s extremely rich in VAc (e.g., VP:VAc = 10:90) are excepted from the relevant group, their miscibility being invited by a rather weak interaction due to the structural affinity effect. The blends of exception can contain heterogeneous domains of ca. 15–20 nm sizes as a tentative estimate.

### Chapter 3.

Blend miscibility of CP with poly(*N*-vinyl pyrrolidone-*co*-methyl methacrylate) (P(VP-*co*-MMA)) was examined by DSC, and a data map (Figure 3-3a) was successfully constructed as a function of both the propionyl DS of CP and the VP:MMA composition of

P(VP-*co*-MMA). Compared to the previous system using CA, the miscible pairing region expanded to cover a considerably hydrophobic area of higher DS and MMA-rich composition, with the advent of a miscibility window driven by repulsion between the comonomer units constituting P(VP-*co*-MMA). However, the miscibility window was evidently narrower relative to that observed for the CP/P(VP-*co*-VAc) system, reflecting that the intramolecular repulsion in P(VP-*co*-MMA) is weaker than that in P(VP-*co*-VAc).

From spectroscopic measurements by FT-IR and solid-state NMR, it was found that miscible blends composed of CP of DS < 2.7 and P(VP-*co*-MMA) of VP > 10 mol% were substantially homogeneous on a scale within a few nanometers (e.g., ~4 nm), by virtue of the hydrogen-bonding formation between CP-hydroxyls and VP-carbonyls. On the other hand, miscible pairs using CPs of DS  $\geq$  2.7 and P(VP-*co*-MMA)s of VP = 10–40 mol%, situated in the window region, produced blends having a somewhat larger size of homogeneity (ca. 5–20 nm).

By DMA and birefringence measurements, we successfully demonstrated synergistic improvements in thermomechanical and optical properties in film form of the miscible CP/P(VP-*co*-MMA) blends. Particularly striking effects of the synergism were observed for the miscible blends of hydrogen-bonding type. With a certain specific polymer composition, the drawn blend can show a zero-birefringence character.

The miscibility characterization was also made for two cellulose acetate propionate (CAP)/P(VP-*co*-MMA) series using propionyl-rich CAPs; both the series also offered a miscibility window (Figure 3-3b). It is astonishing that the range of copolymer composition forming the miscibility window was much wider in the CAP series, compared with that in the CP series of the corresponding DS in total. This expansion of the window would be ascribable to an additional repulsion effect originating in the CAP side; the blends concerned are therefore taken as a copolymer/copolymer system where the miscibility should be affected by the duplicated, intra-copolymer effect.

## **Chapter 4.**

The blend miscibility of CP with VP-containing vinyl copolymers P(VP-*co*-VAc) and P(VP-*co*-MMA) is improved in respect of the miscible pairing number, compared with the

cases using CA and CB. This behavior was satisfactorily explained by comparing the attractive or repulsive interactivities between related polymer ingredients in terms of the Krigbaum-Wall interaction parameter  $\mu$  that was determined by solution viscometry. Especially, great contributions of both the intra-copolymer effect and the structural affinity effect to the miscibility attainment were made clear by the  $\mu$  assessments. The former effect is explicitly responsible for the miscibility window appearing in the maps constructed for the CP/vinyl copolymer systems, and this is also applicable to the maps for the CB systems. The comparatively narrower window observed when the counter component to CP or CB was P(VP-*co*-MMA) is interpretable as due to the lesser strength in repulsion of the VP-MMA copolymer relative to that of the VP-VAc copolymer. The structural affinity effect is concretely connected with a good compatibility of the propionyl group of CP with the VAc or MMA unit of the partner copolymer in the CP-based two systems, and, in the employment of CB, this effect is active between the butyryl and MMA moieties in the CB/P(VP-*co*-MMA) system only.

Such a useful  $\mu$  measurement was also applied to the inspection of miscibility mapping for CAP blends with P(VP-*co*-MMA). The observed expansion of the miscibility window relative to that for the comparable CP blends was explicable in terms of the  $\mu$  data, which indicated additional repulsion in the side of the cellulose mixed ester component; therefore, the CAP/P(VP-*co*-MMA) blends should be taken as a copolymer/copolymer system where the duplicated copolymer effect works.

On account of the results summarized above, the author is convinced of a considerable attainment of the initial purpose of this thesis.

From a practical standpoint, the clarification of the substituent effect on intercomponent interactions and the delicate characterization (and even prediction) of blend miscibility will be of great significance for designing multicomponent materials based on cellulosics. By applying the micro-compositional technique, magnificent synergetic improvements in the thermal and optical properties of the respective constituent polymers can be invited.

Finally, the author expects that the results of this thesis will be contributory to progress in the use of CE-based materials in a wide spectrum of industry.

## List of Publications

The contents of this thesis have been described in the following publications.

### Original Papers

1. Sugimura, K.; Katano, S.; Teramoto, Y.; Nishio, Y. Cellulose propionate/poly(*N*-vinyl pyrrolidone-*co*-vinyl acetate) blends: dependence of the miscibility on propionyl DS and copolymer composition. *Cellulose* **2013**, *20*, 239–252. **(Chapter 2)**
2. Sugimura, K.; Teramoto, Y.; Nishio, Y. Blend miscibility of cellulose propionate with poly(*N*-vinyl pyrrolidone-*co*-methyl methacrylate). *Carbohydr. Polym.* **2013**, *98*, 532–541. **(Chapter 3)**
3. Sugimura, K.; Teramoto, Y.; Nishio, Y. Insight into miscibility behavior of cellulose ester blends with *N*-vinyl pyrrolidone copolymers in terms of viscometric interaction parameters., to be submitted for publication. **(Chapter 4)**

### Commentary (Book chapter)

1. Sugimura, K.; Teramoto, Y.; Nishio, Y. Cellulose acetate. In *Encyclopedia of Polymeric Nanomaterials*; Kobayashi, S., Müllen, K., Eds.; Springer: Berlin/Heidelberg, in press; DOI: 10.1007/978-3-642-36199-9\_328-1. **(Chapter 1)**
2. Nishio, Y.; Sugimura, K.; Teramoto, Y. In *Development of Hierarchically and Dimensionally Desired Cellulose Functional Materials*; Kondo, T., Ed.; CMC: Tokyo, 2013; pp 69–78.

### International Conference

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