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Author(s)	Sugimura, Kazuki; Teramoto, Yoshikuni; Nishio, Yoshiyuki
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1 **Blend miscibility of cellulose propionate with poly(*N*-vinyl pyrrolidone-*co*-methyl**
2 **methacrylate)**

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5 Kazuki Sugimura, Yoshikuni Teramoto, Yoshiyuki Nishio*

6

7 Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto
8 University, Sakyo-ku, Kyoto 606-8502, Japan

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10 *Corresponding author. Tel.: +81 75 753 6250; fax: +81 75 753 6300.

11 *E-mail address:* ynishio@kais.kyoto-u.ac.jp (Y. Nishio).

12

13 **ABSTRACT**

14 The blend miscibility of cellulose propionate (CP) with poly(*N*-vinyl pyrrolidone-*co*-methyl
15 methacrylate) (P(VP-*co*-MMA)) was investigated. The degree of substitution (DS) of CP
16 used ranged from 1.6 to >2.9, and samples for the vinyl polymer component were prepared in
17 a full range of VP:MMA compositions. Through DSC analysis and solid-state ¹³C NMR and
18 FT-IR measurements, we revealed that CPs of DS < 2.7 were miscible with P(VP-*co*-MMA)s
19 of VP ≥ ~10 mol% on a scale within a few nanometers, in virtue of hydrogen-bonding
20 interactions between CP-hydroxyls and VP-carbonyls. When the DS of CP exceeded 2.7,
21 the miscibility was restricted to the polymer pairs using P(VP-*co*-MMA)s of VP = ca. 10–40
22 mol%; the scale of mixing in the blends concerned was somewhat larger (ca. 5–20 nm),
23 however. The appearance of such a “miscibility window” was interpretable as an effect of
24 intramolecular repulsion in the copolymer component. Results of DMA and birefringence
25 measurements indicated that the miscible blending of CP with the vinyl polymer invited
26 synergistic improvements in thermomechanical and optical properties of the respective
27 constituent polymers. Additionally, it was found that the VP:MMA composition range
28 corresponding to the miscibility window was expanded by modification of the CP component
29 into cellulose acetate propionate.

30

31 **Keywords:** Blend miscibility; Cellulose propionate; Poly(*N*-vinyl pyrrolidone-*co*-methyl
32 methacrylate); Scale of homogeneity; Synergistic effect

33

34 **1. Introduction**

35

36 Organic esters of cellulose (CEs) are industrially important materials utilized in various
37 fields including molded plastics, fibers, optical films, membranes, coatings, and so forth
38 (Edgar et al., 2001). For improvement in physical properties of CEs toward their further
39 applications, the blending with other polymers can be a significant method, and a number of
40 fundamental studies of CE blends have been carried out (Nishio, 2006). The authors' group
41 has thus far investigated the blend miscibility of CEs with two different types of polymers,
42 namely, biodegradable aliphatic polyesters such as poly(ϵ -caprolactone) (Higeshiro et al.,
43 2009; Kusumi et al., 2008; Nishio et al., 1997) and synthetic vinyl polymers (Miyashita et al.,
44 2002; Ohno et al., 2005; Ohno & Nishio, 2006; Ohno & Nishio, 2007a; Sugimura et al., 2013;
45 Yoshitake et al., 2013).

46 With regard to the CE/vinyl polymer blends, three separate systems of cellulose acetate
47 (CA), propionate (CP), and butyrate (CB), each blended with P(VP-*co*-VAc), were examined
48 mainly by differential scanning calorimetry (DSC); the counterpart P(VP-*co*-VAc) here
49 represents homo- and random co-polymers comprising *N*-vinyl pyrrolidone (VP) and/or vinyl
50 acetate (VAc) units. Figs. 1a–c survey the estimation results for the three systems, by
51 offering each miscibility map constructed as a function of the degree of ester substitution
52 (DS) of CE and the VP:VAc composition of P(VP-*co*-VAc) (Miyashita et al., 2002; Ohno &
53 Nishio, 2006; Sugimura et al., 2013). As can readily be seen by comparison of the three
54 maps, the region of miscible CE/P(VP-*co*-VAc) pairings was drastically changeable
55 depending on the carbon number of the acyl substituent of CE. Intriguingly, the CP system
56 provided the largest miscible region (see Fig. 1b). Such a specific improvement in the
57 miscibility with P(VP-*co*-VAc) of the CP blends was attributed to the structural affinity
58 favorable for a dipole-dipole antiparallel alignment between the propionyl side-group and the
59 VAc unit, as well as to the moderate length of the acyl substituent which generally works as a

60 steric hindrance to the hydrogen-bonding interactions associated with the residual hydroxyls
61 (Sugimura et al., 2013).

62 Another system of CA/VP-containing vinyl copolymer blends was also reported on the
63 miscibility and intermolecular interaction (Ohno & Nishio, 2007a), wherein methyl
64 methacrylate (MMA) was selected as the second constituent of the copolymer, because of the
65 distinguished optical property, weather resistance, and safety to living bodies of poly(methyl
66 methacrylate) (PMMA). Fig. 1d summarizes the result of miscibility estimation for the
67 CA/P(VP-*co*-MMA) blends. Regarding this system, an additional interest was focused on
68 the molecular orientation and optical anisotropy in uniaxially drawn films of the miscible
69 blends (Ohno & Nishio, 2007b); the birefringence development was widely controllable in
70 both the degree and polarity, by altering the DS of CA, the VP:MMA ratio in P(VP-*co*-MMA),
71 and the proportion of the mixing polymers. However, as mapped in Fig. 1d, the miscible
72 pairing of this system was realized in a region of lower DS of CA and higher VP fraction in
73 P(VP-*co*-MMA), and thus the blends were kind of a hydrophilic material.

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

86 and birefringence measurements, respectively.

87

88

89 **2. Experimental**

90

91 *2.1. Materials*

92

93 CP samples were synthesized from cotton cellulose with a viscosity average molecular
94 weight of 252,000 via a homogeneous reaction with acid chloride/base catalyst, in a
95 procedure similar to that used in previous studies (Kusumi et al., 2008; Nishio et al., 1997).
96 Two CAP samples were used; one was purchased from Eastman Chemical Co., and the other
97 was obtained by acetylation of a commercial CP (Scientific Polymer Products, Inc.) in the
98 same way as that adopted in a previous study (Aoki & Nishio, 2010). Codes “CP_x” and
99 “CA_yP_z” denote CP of propionyl DS = x and CAP of acetyl DS = y and propionyl DS = z ,
100 respectively. Table 1 summarizes data of molecular weight and glass transition temperature
101 (T_g) for all the CE samples used in this study. The vinyl polymers employed as a mixing
102 partner for the CPs and CAPs were poly(*N*-vinyl pyrrolidone) (PVP), PMMA, and
103 P(VP-*co*-MMA) copolymers, basically the same as those in the preceding paper (Ohno &
104 Nishio, 2007a). Data of characterization for all the vinyl polymers are also listed in Table 1.
105 As shown in the table, any of the P(VP-*co*-MMA) samples exhibited a single T_g and they
106 were all regarded as essentially random copolymer. Hereafter, a P(VP-*co*-MMA) sample of
107 VP:MMA = $m:n$ (in molar ratio) is encoded as P(VP _{m} -*co*-MMA _{n}).

108

109 *2.2. Preparation of blend samples*

110

111 Binary blend films of CP/vinyl polymer and CAP/vinyl polymer were prepared by

112 solution mixing and solvent evaporation in the same manner as that adopted in the preceding
113 works (Ohno & Nishio, 2007a; Sugimura et al., 2013). *N,N*-Dimethylformamide (DMF)
114 was selected as a common solvent and the film casting was carried out at 50 °C under reduced
115 pressure (<10 mmHg). The as-cast samples were further dried at 50 °C *in vacuo* for 3 days.

116

117 2.3. Measurements

118

119 DSC was carried out with a Seiko DSC 6200/EXSTAR 6000 apparatus. The
120 temperature readings were calibrated with an indium standard. The calorimetry
121 measurements were conducted on ca. 5-mg samples packed in an aluminum pan under a
122 nitrogen atmosphere. Each sample was first heated from ambient temperature (~25 °C) to
123 230 °C at a scanning rate of 20 °C min⁻¹, and then immediately quenched to -50 °C at a rate
124 of 80 °C min⁻¹. Following this, the second heating scan was run from -50 °C to 230 °C at a
125 rate of 20 °C min⁻¹ to record stable thermograms. For blend series of CA_{0.47}P_{2.48}, however,
126 the upper limit of temperature in the heating scan was programmed to be 260 °C, since a
127 melting endotherm was predicted to appear above 230 °C due to some extent of
128 crystallizability of the CAP. Thermograms presented in this paper were all obtained in the
129 second heating scan, and the *T_g* was taken as a temperature at the midpoint of a baseline shift
130 in heat flow characterizing the glass transition.

131 FT-IR spectra were measured on thinner film samples (<20 μm thick) by using a
132 Shimadzu IRPrestige-21 spectrometer. All the spectra were recorded at 20 °C in a
133 transmission mode over a wavenumber range 400–4000 cm⁻¹ with a resolution of 2 cm⁻¹ via
134 accumulation of 64 scans.

135 High-resolution solid-state NMR experiments were performed at 20 °C in a Varian NMR
136 system 400 MHz operated at a ¹³C frequency of 100.6 MHz. The magic-angle spinning rate
137 was 15.0 kHz. ¹³C CP/MAS spectra were measured with a contact time of 2 ms, and a 90 °

138 pulse width of 2.9 μs was employed. In the measurements of $T_{1\rho}^{\text{H}}$, a contact time of 0.2 ms
139 was used, and a proton spin-locking time τ ranged from 0.5 to 30 ms. 2048 scans were done
140 to obtain the ^{13}C CP/MAS spectra, while 4096 scans were accumulated for the relaxation time
141 measurements. Chemical shifts of ^{13}C spectra represented in ppm were referred to
142 tetramethylsilane by using the methine carbon resonance (29.47 ppm) of adamantane crystals
143 as an external reference standard. In order to minimize any possible effect due to the
144 thermal history and/or residual solvents, each sample was heat-treated at 250 $^{\circ}\text{C}$ *in vacuo* for
145 5 min just before the measurement.

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

152 Optical birefringence (Δn) of drawn CP/vinyl polymer samples was determined by using
153 an Olympus polarized optical microscope POS equipped with a Berek compensator, at room
154 temperature (20 $^{\circ}\text{C}$). Strips (20 \times 4 mm^2) cut from the as-cast films were uniaxially
155 stretched to the desired draw ratio at a temperature which was prescribed to be higher by 2 $^{\circ}\text{C}$
156 than T_g (as measured by DSC, mentioned above) of the blend sample used, in the same
157 procedure as that adopted in the previous work (Ohno & Nishio, 2007b). The percentage
158 elongation of the oriented samples was determined from the positions of ink marks on the
159 film.

160

161

162 **3. Results and discussion**

163

164 *3.1. Miscibility estimation by thermal analysis*

165

166 The miscibility state in the CP and CAP/vinyl polymer systems was estimated by T_g
167 determination in DSC. In general, if any blend sample of a given polymer/polymer pair
168 exhibits a single glass transition between the T_g s of the two component polymers and a
169 composition-dependent shift of the blend T_g is clearly observed, then the pair can be regarded
170 as a miscible one on the T_g -detection scale that is usually assumed to be less than a couple of
171 tens of nanometers (Nishio, 1994; Ultracki, 1990).

172

173 *3.1.1. Overview*

174 Fig. 2a displays a miscibility map for the CP/P(VP-*co*-MMA) system, constructed as a
175 function of DS of CP and VP fraction in P(VP-*co*-MMA). The data for a blend series of
176 CP/PVP homopolymer was quoted from a previous paper (Sugimura et al., 2013). In
177 perspective, polymer pairs composed of low-substituted CP and VP-rich P(VP-*co*-MMA)
178 were judged to be miscible. This suggests the contribution of a hydrogen-bonding
179 interaction between CP-hydroxyl and VP-carbonyl groups to the miscibility attainment. A
180 definite “miscibility window” emerged in a hydrophobic region satisfying propionyl DS > 2.7
181 and VP fraction = 9–40 mol%. As mapped in Fig. 2b, CAP/P(VP-*co*-MMA) blends using
182 partially acetylated CA_{0.16}P_{2.52} and CA_{0.47}P_{2.48} also imparted a miscibility window;
183 interestingly, the VP:MMA range forming the window became expanded, compared with that
184 for the corresponding CP/P(VP-*co*-MMA) blends using CP_{2.72} or CP_{2.93}. Actual
185 observations in the thermal analysis for the present CE blends are described below in detail.

186

187 *3.1.2. CP/PMMA blends*

188 Fig. 3a illustrates DSC thermograms measured for a blend series of CP_{1.59}/PMMA
189 homopolymer. As can be seen from the data, two independent glass transitions originating

190 from the two components were clearly detected for the blend samples of 20/80–80/20
191 compositions (in wt% ratio). Therefore, we can judge the CP_{1.59}/PMMA pair to be
192 immiscible. However, the T_g of the PMMA component was prone to slightly shift to higher
193 temperatures with an increase in the CP content, while the T_g of the CP component hardly
194 shifted from the original position.

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

202

203 3.1.3. CP/P(VP-co-MMA) blends

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

207 Any series of CP_{1.59}/P(VP-co-MMA) blends, prepared by using the copolymers of
208 VP:MMA = 9:91–76:24, provided a smooth variation of a single T_g which was situated
209 between the T_g values of the two unblended components (data not shown). Thus, it turned
210 out that CP_{1.59} formed a miscible monophasic system with P(VP-co-MMA)s of VP \geq 9 mol%.
211 Similar miscible behavior was confirmed in the use of CPs of DS = 1.71–2.62, as the thermal
212 data is exemplified for CP_{1.71}/P(VP_{0.22}-co-MMA_{0.78}) blends in Fig. 3b. We should note here
213 that the CPs of DS < 2.7 were miscible with P(VP-co-MMA)s of extremely low VP fractions
214 such as 10–30 mol%, because the same situation was never realized for the previous system
215 employing CA (see Fig. 1d).

216 Another noteworthy finding was that even high-substituted CPs of $DS > 2.7$ made a
217 miscible combination with MMA-rich P(VP-*co*-MMA)s having ca. 10–40 mol% VP residues,
218 despite the immiscibility of the CPs with PVP and PMMA homopolymers. Fig. 3c
219 exemplifies several DSC thermograms obtained for a polymer combination of
220 CP_{2.72}/P(VP_{0.32}-*co*-MMA_{0.68}); all the samples of 10/90–90/10 compositions gave a single T_g .
221 Thus, decidedly, the CP/P(VP-*co*-MMA) system exhibited a miscibility window. The advent
222 of such a window was unacceptable as to the CA/P(VP-*co*-MMA) system, but observed
223 previously for the CP/P(VP-*co*-VAc) and CB/P(VP-*co*-VAc) systems (see Figs. 1b and 1c)
224 (Sugimura et al, 2013; Ohno & Nishio, 2006). In these earlier studies, it was concluded that
225 a greater repulsion between the VP and VAc units in the random copolymer was mainly
226 contributory to the miscibility attainment; this was rationalized by assessment of
227 Krigbaum-Wall interaction parameters (μ) for the ingredient polymer pairs involving in the
228 CB/P(VP-*co*-VAc) system (Ohno & Nishio, 2007a). The intramolecular copolymer effect
229 may also be applicable to the present CP($DS > 2.7$)/P(VP-*co*-MMA) blends. The absence of
230 such a clear miscibility window in the map of the CA/P(VP-*co*-MMA) system (Fig. 1d) is due
231 to an inhibiting factor, i.e., the strong self-association ability of highly substituted CAs of DS
232 > 2.7 ; the CAs are rather easily crystallizable as cellulose triacetate II.

233 In comparison between the two maps (Figs. 1b and 2a) for the CP blends combined with
234 different copolymers, P(VP-*co*-VAc) and P(VP-*co*-MMA), obviously, the window region for
235 the CP/P(VP-*co*-MMA) system is narrower than that for the CP/P(VP-*co*-VAc) system.
236 Again, from estimation of the interaction parameters for the two units constituting the
237 respective copolymers concerned (Ohno & Nishio, 2007a), it has been derived that the
238 constituents VP and VAc in P(VP-*co*-VAc) strike an intense repellent character to each other,
239 while the VP and MMA units in P(VP-*co*-MMA) show a relatively weaker repulsive
240 interaction. Presumably, this deterioration of the intramolecular repulsive action in the
241 P(VP-*co*-MMA) copolymer is responsible for the appearance of the narrower window in the

242 CP/P(VP-*co*-MMA) map (Fig. 2a).

243

244 3.1.4. CAP/P(VP-*co*-MMA) blends

245 DSC thermograms obtained for a set of CA_{0.16}P_{2.52}/P(VP_{0.61-*co*}-MMA_{0.39}) blends are
246 displayed in Fig. 3d; we can see a single T_g shifting to lower temperatures along with an
247 increase in the P(VP_{0.61-*co*}-MMA_{0.39}) content. Such a miscible sign was observed for blend
248 series of this CAP with P(VP-*co*-MMA)s of VP = 13–76 mol%, but never done for the CAP
249 blends with PVP and PMMA homopolymers.

250 Fig. 3e shows a miscible evidence by DSC for a CA_{0.47}P_{2.48}/P(VP_{0.09-*co*}-MMA_{0.91})
251 combination using another CAP sample. Differing from the overall amorphous behavior of
252 CA_{0.16}P_{2.52}, the CA_{0.47}P_{2.48} sample exhibited an exothermic peak (180 °C) and an endothermic
253 peak (240 °C) after onset of the glass transition ($T_g = 132$ °C); the two peaks are ascribable to
254 a so-called cold-crystallization and subsequent melting of the formed crystal, respectively.
255 Such crystallizability was also noticed for CP_{2.93} of DS > 2.9, but the crystalline phase was
256 formed in somewhat slower crystallization kinetics. Despite of the crystalline habit common
257 to tri-esterified celluloses, as exemplified in Fig. 3e, the CA_{0.47}P_{2.48} blends with
258 P(VP_{0.09-*co*}-MMA_{0.91}) exhibited a definitely single composition-dependent T_g and then
259 produced a systematic depression in the melting point of the induced CAP crystal. This
260 coupled thermal behavior is typical of that of miscible blends composed of a pair of
261 crystallizable polymer/amorphous polymer (MacKnight et al., 1978). Similar DSC data
262 were obtained for additional six combinations of CA_{0.47}P_{2.48} with P(VP-*co*-MMA)s of VP =
263 13–50 mol%.

264 Fig. 2b summarizes the miscibility estimation for the CAP/P(VP-*co*-MMA) series using
265 CA_{0.16}P_{2.52} and CA_{0.47}P_{2.48}, as a function of VP fraction in P(VP-*co*-MMA); the corresponding
266 data for comparable CP/P(VP-*co*-MMA) blends using CP_{2.72} and CP_{2.93} are also shown there.
267 The two CAPs may be regarded as derivatives obtained from CPs of DS \approx 2.7 and 2.95,

268 respectively, by partial ester exchange for acetyl substitution. Plainly, both the
269 CAP/P(VP-*co*-MMA) series offer the miscibility window, as did the blend series using CPs of
270 $DS \geq \sim 2.7$; again, the intramolecular repulsion in the vinyl copolymer would be principally
271 responsible for the observation. However, the range of copolymer composition forming the
272 miscibility window is much wider in the CAP series, compared with that in the CP series of
273 the corresponding DS in total. This expansion of the window might be ascribed to an
274 additional repulsion effect originating in the CAP side. That is, the cellulose mixed ester
275 would also behave as a kind of copolymer dangling two different acyl side-groups along the
276 carbohydrate backbone. A similar deal of cellulose alkyl esters as copolymer has been made
277 in a few reports on their structural characteristics (Buchanan et al., 1996; Frazier & Glasser,
278 1995; Ohno & Nishio, 2006). Therefore, the CAP/P(VP-*co*-MMA) blends are actually taken
279 as a copolymer/copolymer system, where the miscibility should be affected by the duplicate,
280 intramolecular copolymer effect.

281

282 *3.2. Spectroscopic analysis of intermolecular interaction and mixing scale*

283

284 *3.2.1. FT-IR spectra*

285 Fig. 4 compiles FT-IR spectra obtained for blends of the miscible
286 CP_{1.71}/P(VP_{0.22}-*co*-MMA_{0.78}) pair, particularly focusing on two regions of (a) O-H and (b)
287 C=O stretching vibrations. Frequency shift and/or shape variation are clearly observed for
288 the specific IR bands as a result of the hydrogen-bonding formation between the residual
289 hydroxyls of the CP component and the VP-carbonyls of the copolymer. As shown in Fig.
290 4a, a band centering at 3482 cm⁻¹ (top data), which can be associated with a mixture of free
291 hydroxyls and intramolecularly hydrogen-bonded OH groups in the unblended CP, shifted to
292 lower wavenumber positions with increasing P(VP-*co*-MMA) content. Concomitantly,
293 another shoulder band became discernible on the side of further lower wavenumbers, as

294 indicated by a white arrow at $\sim 3300\text{ cm}^{-1}$ in Fig. 4a. This new band can be ascribed to the
295 stretching of intermolecularly hydrogen-bonded OH groups (Marchessault & Liang, 1960).

296 Concerning the frequency region of C=O groups (Fig. 4b), a 1683 cm^{-1} band assigned to
297 VP-carbonyl stretching vibration in the copolymer became asymmetric progressively as the
298 CP content increased in the binary blend system. Consequently, the absorption band was
299 dividable into two peaks, larger and smaller ones at $\sim 1685\text{ cm}^{-1}$ and $\sim 1660\text{ cm}^{-1}$, respectively
300 (see enlarged data in the range of $1650\text{--}1700\text{ cm}^{-1}$). These two IR signals for the VP unit of
301 the copolymer may be associated with the free carbonyl and hydrogen-bonded carbonyl
302 groups, respectively (Masson & Manley, 1991). The $\text{CP}_{1.71}/\text{P}(\text{VP}_{0.22}\text{-co-MMA}_{0.78})$ blends
303 provided an additional single band centering at $1730\text{--}1740\text{ cm}^{-1}$, but this band was virtually
304 made up of a prorated mixture of two carbonyl signals: a propionate C=O peak (1744 cm^{-1}) of
305 the CP component and an MMA C=O peak (1727 cm^{-1}) of the copolymer component.

306 The inter-component interaction based on the hydrogen bonding of $\text{OH}\cdots\text{O}=\text{C}$, just as
307 described above, was also ascertained not only for the blend series of $\text{CP}_{1.71}$ with VP-rich
308 $\text{P}(\text{VP-co-MMA})$ s including PVP, but also for other selected miscible pairs using CPs of $\text{DS} <$
309 2.7 . For contradistinction, it should be recalled that CA of $\text{DS} = 1.80$ never formed the same
310 kind of hydrogen-bonding interaction with $\text{P}(\text{VP}_{0.22}\text{-co-MMA}_{0.78})$ (Ohno & Nishio, 2007a)
311 and the polymer pair was immiscible (see Fig. 1d). This contrast to the observation for the
312 $\text{CP}_{1.71}/\text{P}(\text{VP}_{0.22}\text{-co-MMA}_{0.78})$ pair reflects the difference in self-association nature between CA
313 and CP, the former having the stronger ability.

314 When the copolymer $\text{P}(\text{VP}_{0.22}\text{-co-MMA}_{0.78})$ was blended with $\text{CP}_{2.89}$, however, there was
315 no indication of such an intermolecular hydrogen-bonding interaction in IR examinations
316 (data not shown). This result may be reasonable. With regard to the $\text{CP}(\text{DS} >$
317 $2.7)/\text{P}(\text{VP-co-MMA})$ pairs constituting the miscibility window in Fig. 2a, the blend
318 miscibility would be attained through the repulsion effect in the $\text{P}(\text{VP-co-MMA})$ side, not
319 driven by direct attraction based on that hydrogen bonding.

320

321 3.2.2. Homogeneity as estimated by solid-state ^{13}C NMR

322 As a useful relaxation technique in solid-state ^{13}C NMR, $T_{1\rho}^{\text{H}}$ measurements for specific
323 carbons in a multicomponent polymer system make it possible to estimate the mixing
324 homogeneity in a scale of ^1H spin-diffusion length that is usually within several nanometers
325 (Masson & Manley, 1991; Ohno et al., 2005; Zhang et al., 1992); the dimensional limit is
326 smaller than that (~ 20 nm) detectable by DSC thermal analysis. $T_{1\rho}^{\text{H}}$ values can be obtained
327 by fitting the decaying carbon resonance intensity to the following exponential equation:

$$328 \quad M(\tau) = M(0) \exp(-\tau/T_{1\rho}^{\text{H}}) \quad (1)$$

329 where $M(\tau)$ is the magnetization intensity observed as a function of the spin-locking time τ .
330 If two constituent polymers are homogeneously mixed on the scale over which ^1H
331 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
332 the respective components may be equalized to each other by the spin diffusion.

333 Using the above technique, we made a comparative assessment of the mixing scale for
334 the two miscible series of blends: $\text{CP}_{1.71}/\text{P}(\text{VP}_{0.22}\text{-co-MMA}_{0.78})$ and
335 $\text{CP}_{2.89}/\text{P}(\text{VP}_{0.22}\text{-co-MMA}_{0.78})$, the driving factor contributory to the respective miscibility
336 attainments being the intermolecular hydrogen-bonding interaction (for the former) or the
337 intramolecular repulsion effect in the copolymer (for the latter). Fig. 5 exemplifies ^{13}C
338 CP/MAS spectra obtained for $\text{CP}_{1.71}$, $\text{P}(\text{VP}_{0.22}\text{-co-MMA}_{0.78})$, and their 50/50 blend. The
339 peak assignments of the spectra are based on literature data for CP (Tezuka & Tsuchiya, 1995),
340 PVP (Zhang et al., 1992), and PMMA (Liu et al., 1994). The experiment of $T_{1\rho}^{\text{H}}$
341 quantifications was conducted through monitoring the following ^{13}C resonance signals with
342 better resolutions: C2/C3/C5 pyranose carbons (74 ppm) and propionyl carbons C8 (28 ppm)
343 and C9 (9.3 ppm) for the CP component, and $\text{C}_\alpha/\text{C}_\epsilon$ (52 ppm), $\text{C}_\beta/\text{C}_\zeta/\text{C}_\delta$ (45 ppm), and $\text{C}_\eta/\text{C}_\theta$
344 carbons (18 ppm) for the $\text{P}(\text{VP-co-MMA})$ component. Carbonyl carbons were not adoptable
345 for the quantification, because the corresponding peak (~ 173.5 ppm) of the CP component

346 merged into the other split signal of VP/MMA carbonyls (~174/177 ppm) of the copolymer.

347 Fig. 6 illustrate the decay behavior in intensity of the C2/C3/C5 and C_b/C_c/C_β peaks for
348 unblended CP (CP_{1.71} or CP_{2.89}) and P(VP_{0.22-co}-MMA_{0.78}), respectively, and also for their
349 50/50 blend imparting both resonance signals. The slope of each semi-logarithmic plot
350 corresponds to an inverse of $-T_{1\rho}^H$. The $T_{1\rho}^H$ data thus estimated for CP_{1.71}, CP_{2.89},
351 P(VP_{0.22-co}-MMA_{0.78}), and their miscible blends of CP/P(VP-co-MMA) = 75/25–25/75 are all
352 listed in Table 2.

353 As can be seen from Table 2 (upper part), $T_{1\rho}^H$ of the CP_{1.71} component, originally 20.0
354 ms as an average, rises systematically with an increase in the copolymer component, while
355 that of the P(VP_{0.22-co}-MMA_{0.78}) component (average value of 23.6 ms) diminishes
356 correspondingly with increasing CP_{1.71} content. Consequently, the two $T_{1\rho}^H$ values at every
357 blend composition are in good agreement with each other. Thus, it is reasonably deduced
358 that the two constituent polymers in the blends are intimately mixed within a range where the
359 mutual ¹H-spin diffusion is permitted over a period of the respective homogenized $T_{1\rho}^H$, e.g.,
360 ~22 ms for the 50/50 composition.

361 An effective path length L of the spin diffusion in a time $T_{1\rho}^H$ is given by the following
362 equation (McBrierty & Douglass, 1981):

$$363 \quad L \cong (6DT_{1\rho}^H)^{1/2} \quad (2)$$

364 where D is the spin-diffusion coefficient, usually taken to be $\sim 1.0 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ in organic
365 polymer materials (Assink, 1978; Masson & Manley, 1991; Radloff et al., 1996). By
366 adopting $T_{1\rho}^H$ data of 21–23 ms approximated for the CP_{1.71}/P(VP_{0.22-co}-MMA_{0.78}) blends of
367 75/25–25/75 compositions, the diffusion path length is calculated as $L = 3.5\text{--}3.7 \text{ nm}$.
368 Accordingly, it is confirmed that the relevant miscible series of hydrogen-bonding type is
369 virtually homogeneous in a scale of ca. 4 nm.

370 With regard to the CP_{2.89}/P(VP_{0.22-co}-MMA_{0.78}) series, on the contrary, $T_{1\rho}^H$ s of the two
371 components at every blend composition never became so close to each other (see Fig. 6b and

372 Table 2 (lower part)). This temporal disagreement implies that the relaxation processes of
373 the two polymers in the blends progressed independently without their cooperative spin
374 diffusion; thus the blends were found to be heterogeneous when viewed in a few nanometers
375 scale by $T_{1\rho}^H$ measurements. By the combined use of this result and the previous DSC data,
376 it can be judged that the scale of homogeneity in the CP_{2.89}/P(VP_{0.22-co}-MMA_{0.78}) blends
377 situated in the window region lies between approximately 5 and 20 nm.

378

379 3.3. Synergistic effects on properties of CP/P(VP-co-MMA) films

380

381 3.3.1. Mechanical properties estimated by DMA

382 Fig. 7a shows the temperature dependence of the dynamic storage modulus E' and loss
383 modulus E'' for CP_{2.18}/P(VP_{0.22-co}-MMA_{0.78}) blends of 75/25, 50/50, and 25/75 compositions,
384 together with the corresponding data for plain CP_{2.18} and P(VP_{0.22-co}-MMA_{0.78}). As
385 demonstrated clearly in the figure, the blend samples provided a single and sharp transition
386 signal, both in the E' drop and in the E'' peak, which shifted systematically with the
387 composition; this indicates a sign of good miscibility for the polymer pair. Similar behavior
388 was observed for other test series including CP_{2.18}/PVP and CP_{2.89}/P(VP_{0.22-co}-MMA_{0.78})
389 blends.

390 Fig. 7b collects the glass-state modulus E' (at 20 °C) versus composition plots for the
391 three series of CP_{2.18}/PVP, CP_{2.18}/P(VP_{0.22-co}-MMA_{0.78}), and CP_{2.89}/P(VP_{0.22-co}-MMA_{0.78});
392 however, the modulus data for the PVP homopolymer *per se* was not obtained because of a
393 brittle nature of the film. As can be seen from the plots in the figure, the modulus of any of
394 the blend films was usually higher than those of the respective unblended CP and vinyl
395 polymer samples. This result may be interpreted as a synergistic improvement in
396 thermomechanical property of the cellulosic and vinyl polymer materials by miscible
397 blending. Furthermore, we find by careful inspection that the rising level in the glassy

398 modulus of the CP blends varied with difference in the driving force for the miscibility
399 attainment; viz., the miscible blends of hydrogen-bonding type, referring to the CP_{2.18}/PVP
400 and CP_{2.18}/P(VP_{0.22-co}-MMA_{0.78}) series, exhibited a noticeable elevation in the modulus E' ,
401 whereas the CP_{2.89}/P(VP_{0.22-co}-MMA_{0.78}) series situated in the miscibility window showed a
402 comparatively smaller increase in the E' value.

403

404 3.3.2. Birefringence of CP/P(VP-co-MMA) films

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

$$410 \quad \Delta n = \{(3\langle \cos^2 \omega \rangle - 1) \Delta n^{\circ}\} / 2 \quad (3)$$

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

$$415 \quad \Delta n = v_1 \Delta n_1 + v_2 \Delta n_2 \quad (4)$$

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

418 Fig. 8 compiles results of the birefringence measurements conducted for drawn films of a
419 miscible CP_{2.09}/P(VP_{0.46-co}-MMA_{0.54}) series of hydrogen-bonding type. As is already
420 known (Ohno & Nishio, 2007b), vinyl polymers comprising VP and/or MMA units, including
421 the present P(VP_{0.46-co}-MMA_{0.54}), exhibit negative optical anisotropy ($\Delta n^{\circ}_{\text{VP-MMA}} < 0$) upon
422 stretching of their films. On the other hand, as seen in the figure, the CP of DS = 2.09

423 showed positive optical anisotropy ($\Delta n_{\text{CP}}^{\circ} > 0$) on stretching of the film, and the birefringence
424 increased sharply with the extent of elongation. The magnitude of Δn evaluated for this CP
425 was higher than that obtained previously for CA of DS = 2.18, when compared at a given
426 stage of elongation; this suggests that a flexible methylene-methyl sequence in the propionyl
427 side-group would be aligned parallel to the cellulose backbone, which contributes to the
428 increase of the parallel component of refractive index (n_{\parallel}).

429 The optical anisotropy of the oriented CP_{2.09}/P(VP_{0.46-co}-MMA_{0.54}) blends was seriously
430 affected in both the polarity and degree, by the compensation effect due to the positive and
431 negative contributions of the CP and copolymer components, respectively, to the overall
432 birefringence. When the CP content reached 50 wt%, the blend film assumed a character of
433 birefringence-free material, as shown in Fig. 8. That is, the 50/50 blend can behave like an
434 optically isotropic medium even though it should be mechanically anisotropic after
435 deformation. A copolymer-rich sample of CP_{2.09}/P(VP_{0.46-co}-MMA_{0.54}) = 30/70 always
436 provided negative birefringence, the absolute value of which was larger rather than that of the
437 unblended copolymer. This result suggests that the orientation of the vinyl copolymer
438 chains was enhanced in the presence of the CP component, possibly by virtue of the
439 inter-component interaction that can occur through hydrogen bonding between the carbonyl
440 and hydroxyl groups. The details of the actual molecular orientation behavior in these
441 drawn blends will be investigated in a subsequent paper.

442

443

444 **4. Conclusions**

445

446 Blend miscibility of CP with P(VP-co-MMA) was examined by DSC, and a data map
447 (Fig. 2a) was successfully constructed as a function of both the propionyl DS of CP and the
448 VP:MMA composition of P(VP-co-MMA). Compared to the previous system using CA (Fig.

449 1d), the miscible pairing region expanded to cover a considerably hydrophobic area of higher
450 DS and MMA-rich composition, with the advent of a miscibility window driven by repulsion
451 between the comonomer units constituting P(VP-*co*-MMA). However, the miscibility
452 window was evidently narrower relative to that observed formerly for the CP/P(VP-*co*-VAc)
453 system (Fig. 1b), reflecting that the intramolecular repulsion in P(VP-*co*-MMA) is weaker
454 than that in P(VP-*co*-VAc).

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

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

467 The miscibility characterization was also made for two CAP/P(VP-*co*-MMA) series
468 using propionyl-rich CAPs; both the series also offered a miscibility window (Fig. 2b). It is
469 astonishing that the range of copolymer composition forming the miscibility window was
470 much wider in the CAP series, compared with that in the CP series of the corresponding DS in
471 total. This expansion of the window would be ascribable to an additional repulsion effect
472 originating in the CAP side; the blends concerned are therefore taken as a
473 copolymer/copolymer system where the miscibility should be affected by the duplicated,
474 intramolecular copolymer effect.

475 From a practical point of view, the present results will be of great significance for
476 expanding the opportunities of material design based on the CE family. Further studies on
477 the miscibility and interactions are now in progress for other combinations of CAPs of various
478 acetyl/propionyl proportions with vinyl copolymers. Our insight will also be given into the
479 molecular orientation behavior in drawn blends made up of a miscible pair of CP or CAP and
480 P(VP-*co*-MMA), in relation to their birefringence characteristics as optical materials. These
481 are topics to be reported in a subsequent paper.

482

483

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485

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489

490

491 **References**

492

493 Aoki, D., & Nishio, Y. (2010). Phosphorylated cellulose propionate derivatives as
494 thermoplastic flame resistant/retardant materials: influence of regioselective
495 phosphorylation on their thermal degradation behaviour. *Cellulose*, *17*, 963–976.

496 Assink, R. A. (1978). Nuclear spin diffusion between polyurethane microphases.
497 *Macromolecules*, *11*, 1233–1237.

498 Buchanan, C. M., Dorschel, D., Gardner, R. M., Komarek, R. J., Matosky, A. J., White, A. W.,
499 & Wood, M. D. (1996). The influence of degree of substitution on blend miscibility and
500 biodegradation of cellulose acetate blends. *Journal of Environmental Polymer*

501 *Degradation*, 4, 179–195.

502 Edgar, K. J., Buchanan, C. M., Debenham, J. S., Rundquist, P. A., Seiler, B. D., Shelton, M.
503 C., & Tindall, D. (2001). Advances in cellulose ester performance and application.
504 *Progress in Polymer Science*, 26, 1605–1688.

505 Frazier, C. E., & Glasser, W. G. (1995). Intermolecular effects in cellulose mixed benzyl
506 ethers blended with poly(ϵ -caprolactone). *Journal of Applied Polymer Science*, 58,
507 1063–1075.

508 Higeshiro, T., Teramoto, Y., & Nishio, Y. (2009). Poly(vinyl pyrrolidone-*co*-vinyl
509 acetate)-*graft*-poly(ϵ -caprolactone) as a compatibilizer for cellulose
510 acetate/poly(ϵ -caprolactone) blends. *Journal of Applied Polymer Science*, 113,
511 2945–2954.

512 Kusumi, R., Inoue, Y., Shirakawa, M., Miyashita, Y., & Nishio, Y. (2008). Cellulose alkyl
513 ester/poly(ϵ -caprolactone) blends: Characterization of miscibility and crystallization
514 behaviour. *Cellulose*, 15, 1–16.

515 Liu, Y., Huglin, M. B., & Davis, T. P. (1994). Preparation and characterization of some liner
516 copolymers as precursors to thermoplastic hydrogels. *European Polymer Journal*, 30,
517 457–463.

518 MacKnight, W. J., Karasz, F. E., & Fried, J. R. (1978). Solid state transition behavior of
519 blends. In D. R. Paul & S. Newman (Eds.), *Polymer blends*, vol 1. (pp. 185–242). New
520 York: Academic Press.

521 Marchessault, R. H., & Liang, C. Y. (1960). Infrared spectra of crystalline polysaccharides. III.
522 Marcerized cellulose. *Journal of Polymer Science*, 43, 71–84.

523 Masson, J. F., & Manley, R. S. (1991). Miscible blends of cellulose and
524 poly(vinylpyrrolidone). *Macromolecules*, 24, 6670–6679.

525 McBrierty, V. J., & Douglass, D. C. (1981). Recent advances in the NMR of solid polymers.
526 *Journal of Polymer Science Macromolecular Reviews*, 16, 295–366.

527 Miyashita, Y., Suzuki, T., & Nishio, Y. (2002). Miscibility of cellulose acetate with vinyl
528 polymers. *Cellulose*, 9, 215–223.

529 Nishio, Y. (1994). Hyperfine composites of cellulose with synthetic polymers. In Gilbert R. D.
530 (Ed.), *Cellulosic polymers, blends and composites* (pp. 95–113). Munich: Hanser.

531 Nishio, Y. (2006). Material functionalization of cellulose and related polysaccharides via
532 diverse microcompositions. *Advances in Polymer Science*, 205, 97–151.

533 Nishio, Y., Matsuda, K., Miyashita, Y., Kimura, N., & Suzuki, H. (1997). Blends of
534 poly(ϵ -caprolactone) with cellulose alkyl esters: effect of the alkyl side-chain length and
535 degree of substitution on miscibility. *Cellulose*, 4, 131–145.

536 Ohno, T., & Nishio, Y. (2006). Cellulose alkyl ester/vinyl polymer blends: effects of butyryl
537 substitution and intramolecular copolymer composition on the miscibility. *Cellulose*, 13,
538 245–259.

539 Ohno, T., & Nishio, Y. (2007a). Estimation of miscibility and interaction for cellulose acetate
540 and butyrate blends with *N*-vinylpyrrolidone copolymers. *Macromolecular Chemistry
541 and Physics*, 208, 622–634.

542 Ohno, T., & Nishio, Y. (2007b). Molecular orientation and optical anisotropy in drawn films
543 of miscible blends composed of cellulose acetate and poly(*N*-vinylpyrrolidone-*co*-methyl
544 methacrylate). *Macromolecules*, 40, 3468–3476.

545 Ohno, T., Yoshizawa, S., Miyashita, Y., & Nishio, Y. (2005). Interaction and scale of mixing
546 in cellulose acetate/poly(*N*-vinyl pyrrolidone-*co*-vinyl acetate) blends. *Cellulose*, 12,
547 281–291.

548 Radloff, D., Boeffel, C., & Spiess, H. W. (1996). Cellulose and cellulose/poly(vinyl alcohol)
549 blends. 2. Water organization revealed by solid-state NMR spectroscopy. *Macromolecules*,
550 29, 1528–1534.

551 Sugimura, K., Katano, S., Teramoto, Y., & Nishio, Y. (2013). Cellulose
552 propionate/poly(*N*-vinyl pyrrolidone-*co*-vinyl acetate) blends: dependence of the

553 miscibility on propionyl DS and copolymer composition. *Cellulose*, 20, 239–252.

554 Tezuka, Y., & Tsuchida, Y. (1995). Determination of substituent distribution in cellulose
555 acetate by means of a ¹³C NMR study on its propanoated derivative. *Carbohydrate*
556 *Research*, 273, 83–91.

557 Utracki, L. A. (1990). *Polymer alloys and blends: thermodynamics and rheology*. Munich:
558 Hanser.

559 Yoshitake, S., Suzuki, T., Miyashita, Y., Aoki, D., Teramoto, Y., & Nishio, Y. (2013).
560 Nanoincorporation of layered double hydroxides into a miscible blend system of cellulose
561 acetate with poly(acryloyl morpholine). *Carbohydrate Polymers*, 93, 331–338.

562 Zhang, X. Q., Takegoshi, K., & Hikichi, K. (1992). High-resolution solid-state C-13 nuclear
563 magnetic resonance study on poly(vinyl alcohol)/poly(vinylpyrrolidone) blends. *Polymer*,
564 33, 712–717.

565

1 **Figure Captions**

2

3 **Fig. 1.** Miscibility maps for four blend systems (a) CA/P(VP-*co*-VAc), (b)
4 CP/P(VP-*co*-VAc), (c) CB/P(VP-*co*-VAc), and (d) CA/P(VP-*co*-MMA), quoted from previous
5 papers (Miyashita et al., 2002 for (a); Sugimura et al., 2013 for (b); Ohno & Nishio, 2006 for
6 (c); Ohno & Nishio, 2007a for (d)) in a rearranged style retaining the essence.

7

8 **Fig. 2.** (a) Miscibility map for the blend system CP/P(VP-*co*-MMA), depicted as a function
9 of DS of CP and VP fraction in P(VP-*co*-MMA), and (b) miscibility estimation for
10 CAP/P(VP-*co*-MMA) blends using partially acetylated CA_{0.16}P_{2.52} and CA_{0.47}P_{2.48} as a
11 function of VP fraction in P(VP-*co*-MMA), in comparison with the corresponding
12 CP/P(VP-*co*-MMA) blends using CP_{2.72} and CP_{2.93}, respectively. Symbols indicate that a
13 given pair of CP or CAP/P(VP-*co*-MMA) is miscible (○) or immiscible (×).

14

15 **Fig. 3.** DSC thermograms obtained for (a) CP_{1.59}/PMMA, (b) CP_{1.71}/P(VP_{0.22-*co*}-MMA_{0.78}),
16 (c) CP_{2.72}/P(VP_{0.32-*co*}-MMA_{0.68}), (d) CA_{0.16}P_{2.52}/P(VP_{0.61-*co*}-MMA_{0.39}), and (e)
17 CA_{0.47}P_{2.48}/P(VP_{0.09-*co*}-MMA_{0.91}) blends. Arrows indicate a T_g position taken as the
18 midpoint of a baseline shift in heat flow.

19

20 **Fig. 4.** FT-IR spectra of CP_{1.71}, P(VP_{0.22-*co*}-MMA_{0.78}), and their blends in the frequency
21 regions of (a) O-H and (b) C=O stretching vibrations. Data in the ranges of 3100–3500 cm⁻¹
22 and 1650–1700 cm⁻¹ are also shown on an enlarged scale. Solid arrows indicate a peak-top
23 position in the respective specific absorption bands, and white arrows indicate a shoulder
24 band associated with hydrogen bonding (see text for discussion).

25

26 **Fig. 5.** Solid-state ¹³C CP/MAS NMR spectra for CP_{1.71}, P(VP_{0.22-*co*}-MMA_{0.78}), and their

27 50/50 blend.

28

29 **Fig. 6.** Semilogarithmic plots of the decay of ^{13}C resonance intensities as a function of
30 spin-locking time τ , 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,
31 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
32 for the peak intensity of C2/C3/C5 pyranose carbons of CP and that of $\text{C}_b/\text{C}_c/\text{C}_\beta$ carbons of
33 the copolymer (see Fig. 5).

34

35 **Fig. 7.** (a) Temperature dependence of the dynamic storage modulus E' and loss modulus E''
36 for $\text{CP}_{2.18}/\text{P}(\text{VP}_{0.22}\text{-co-MMA}_{0.78})$ blends, and (b) the glassy state E' value (measured at 20 °C)
37 vs. composition plots for three series of blends, $\text{CP}_{2.18}/\text{PVP}$, $\text{CP}_{2.18}/\text{P}(\text{VP}_{0.22}\text{-co-MMA}_{0.78})$, and
38 $\text{CP}_{2.89}/\text{P}(\text{VP}_{0.22}\text{-co-MMA}_{0.78})$.

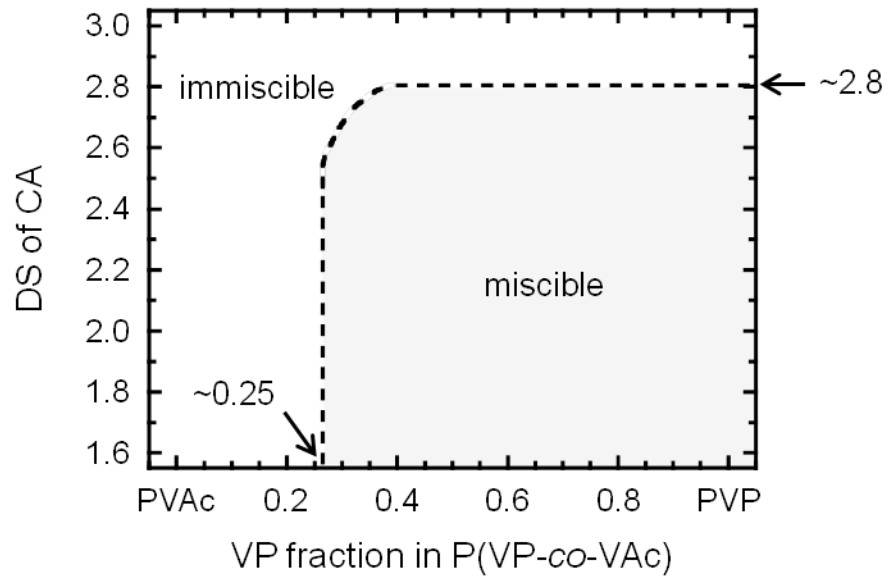
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40 **Fig. 8.** Plots of birefringence Δn vs. % elongation for drawn films of
41 $\text{CP}_{2.09}/\text{P}(\text{VP}_{0.46}\text{-co-MMA}_{0.54})$ blends.

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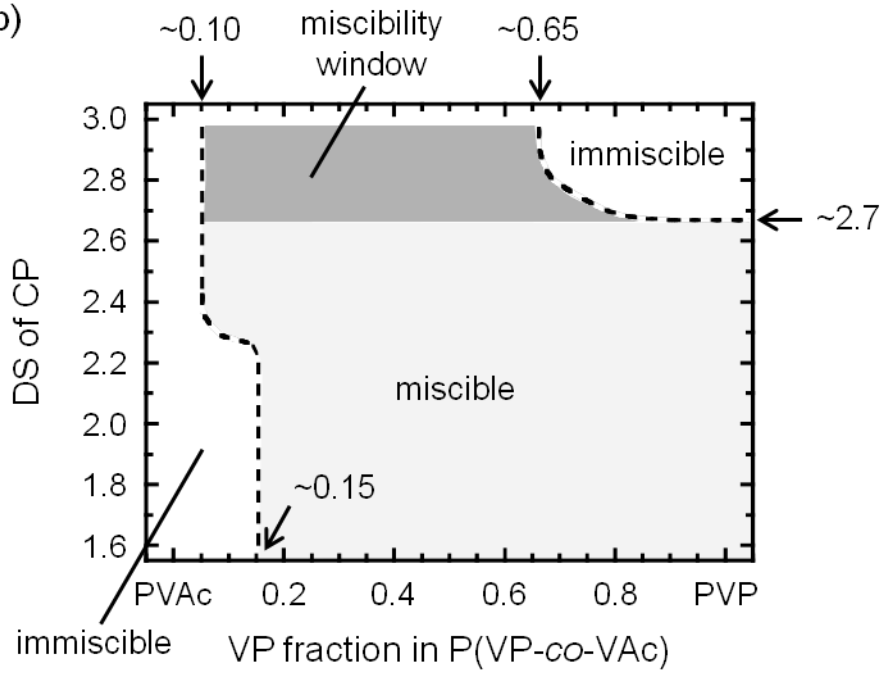
(a)



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(b)



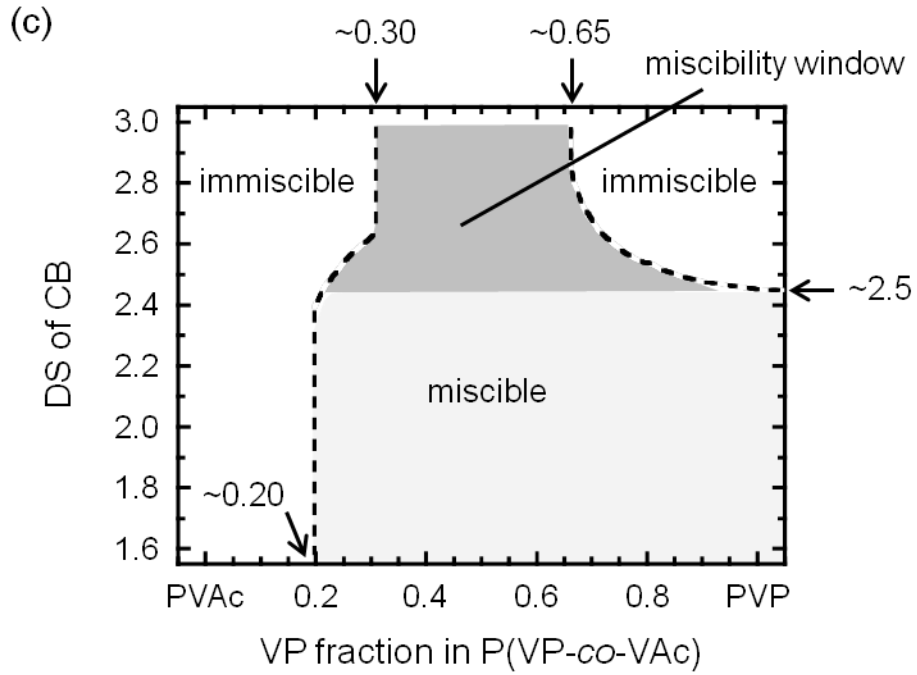
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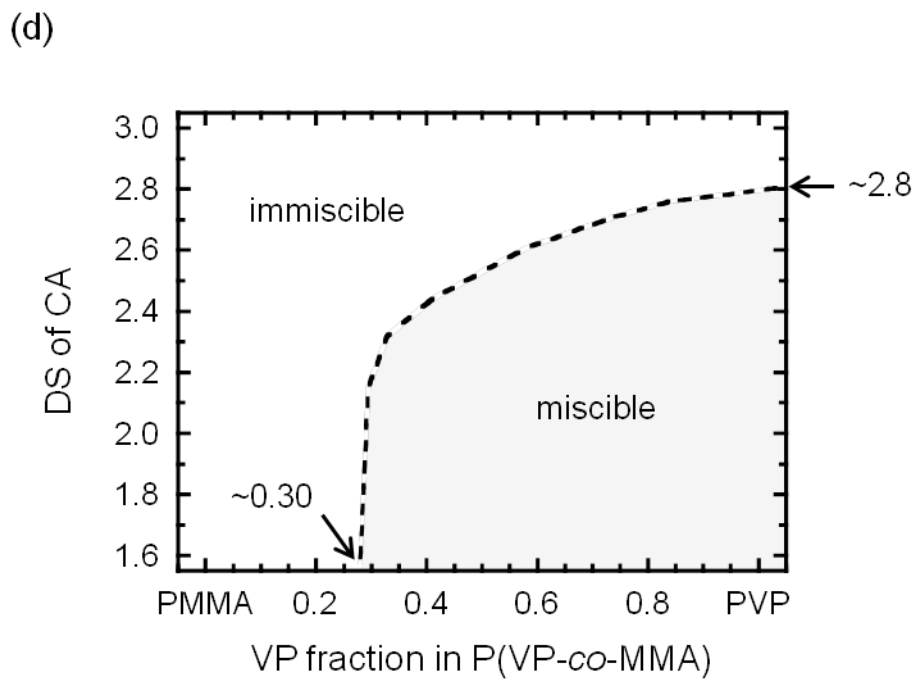
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<<Fig. 1.>>



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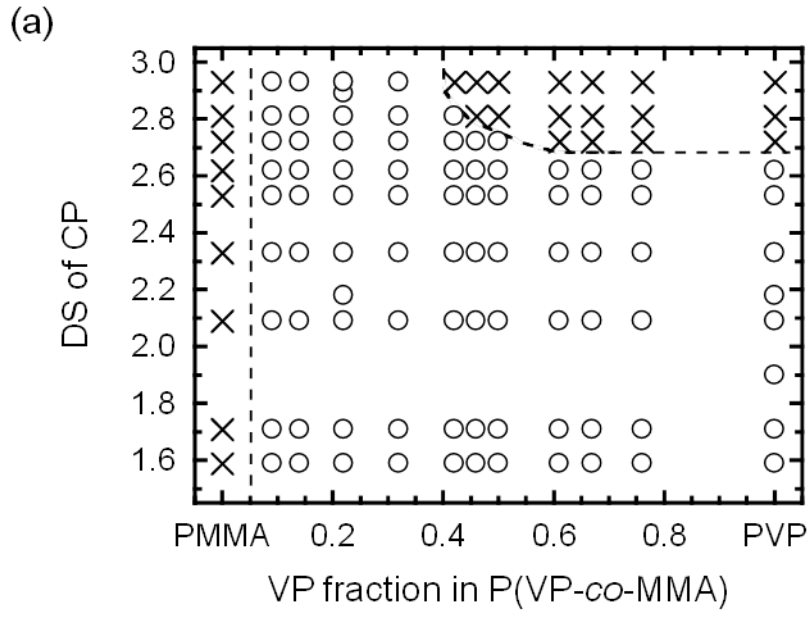
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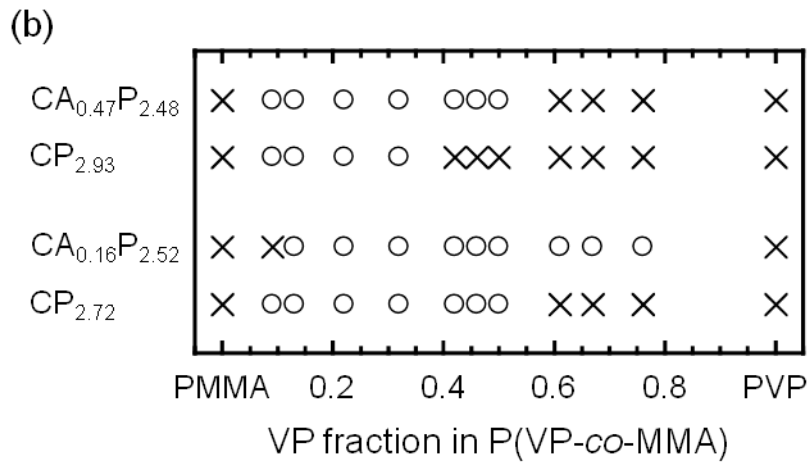
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<<Fig. 1. Continued.>>



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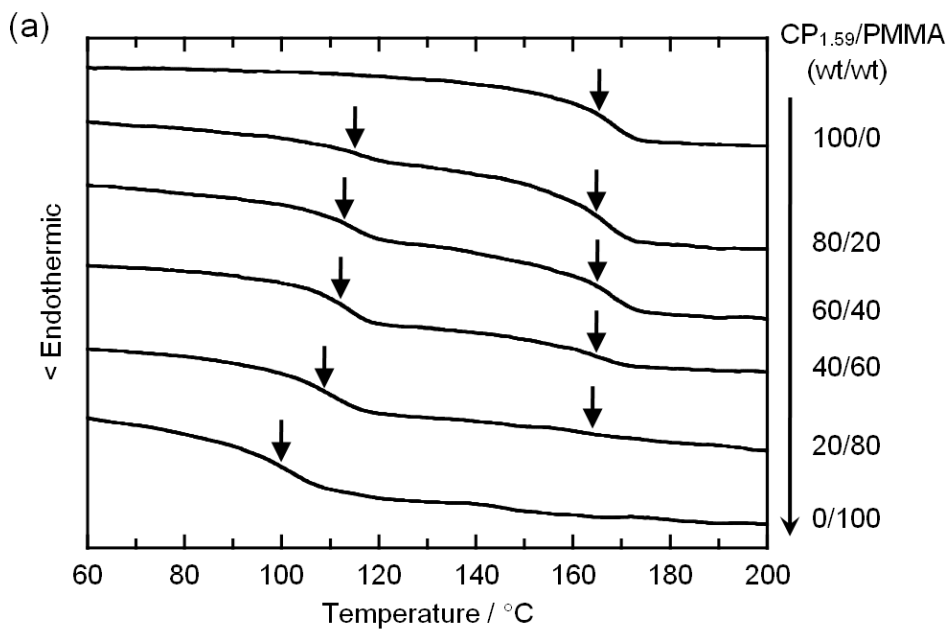
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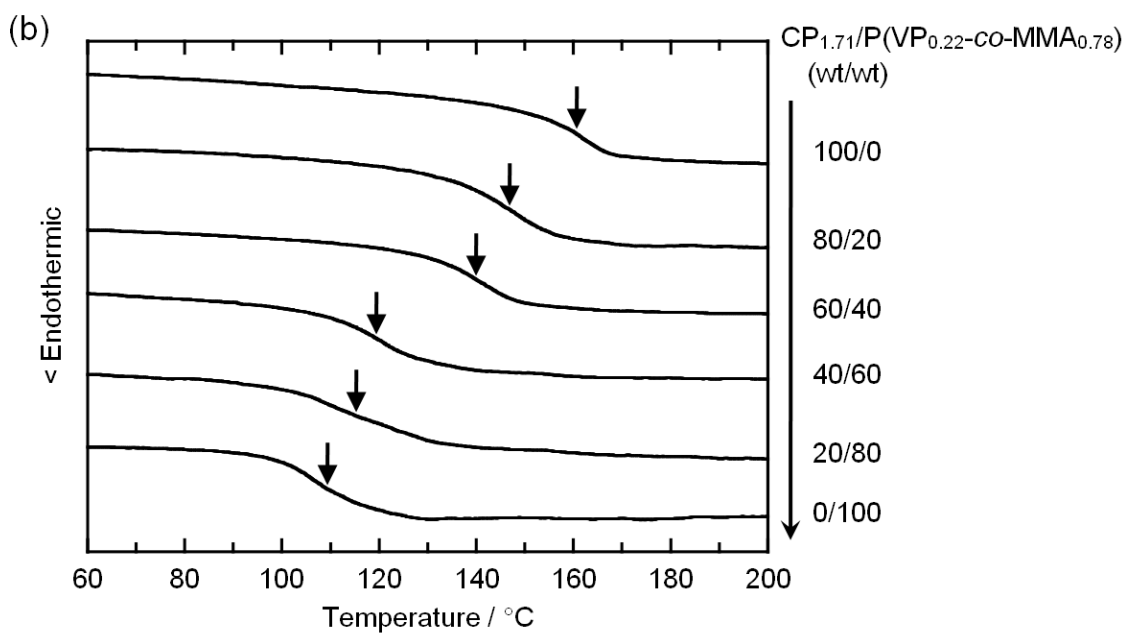
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<<Fig. 2.>>



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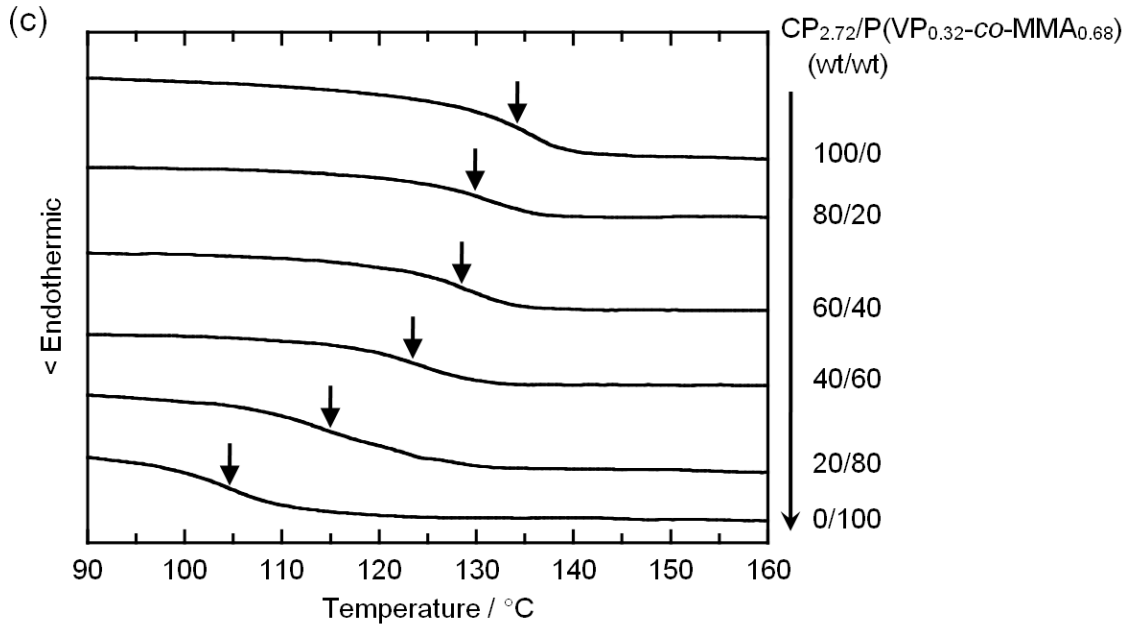
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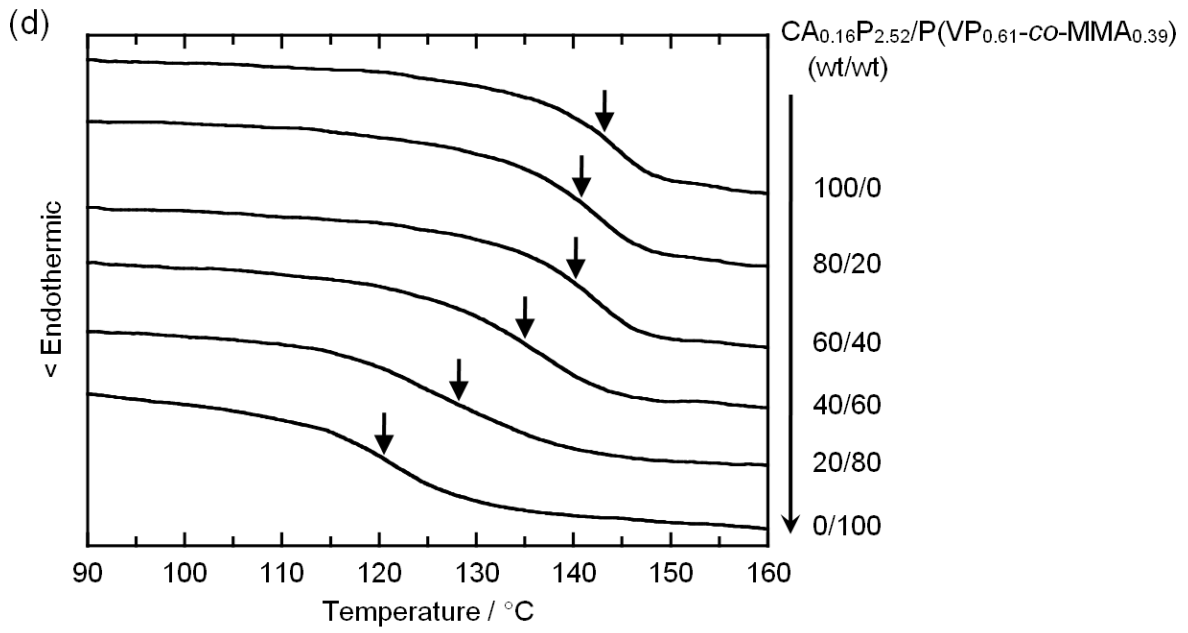
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<<Fig. 3.>>



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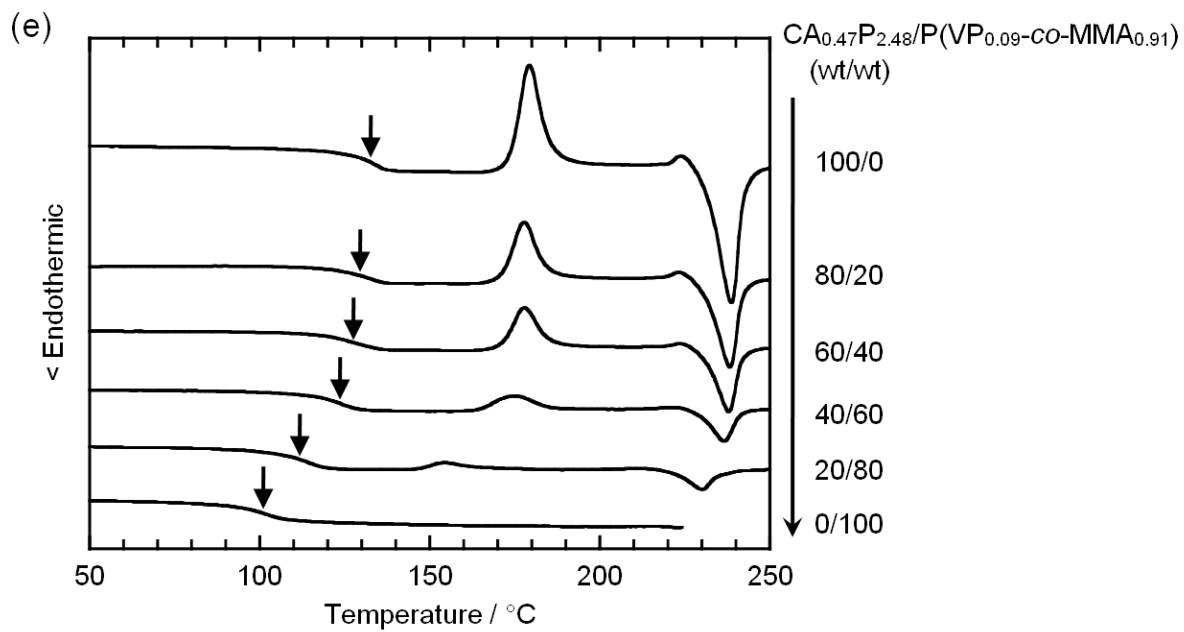


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<<Fig. 3. Continued.>>



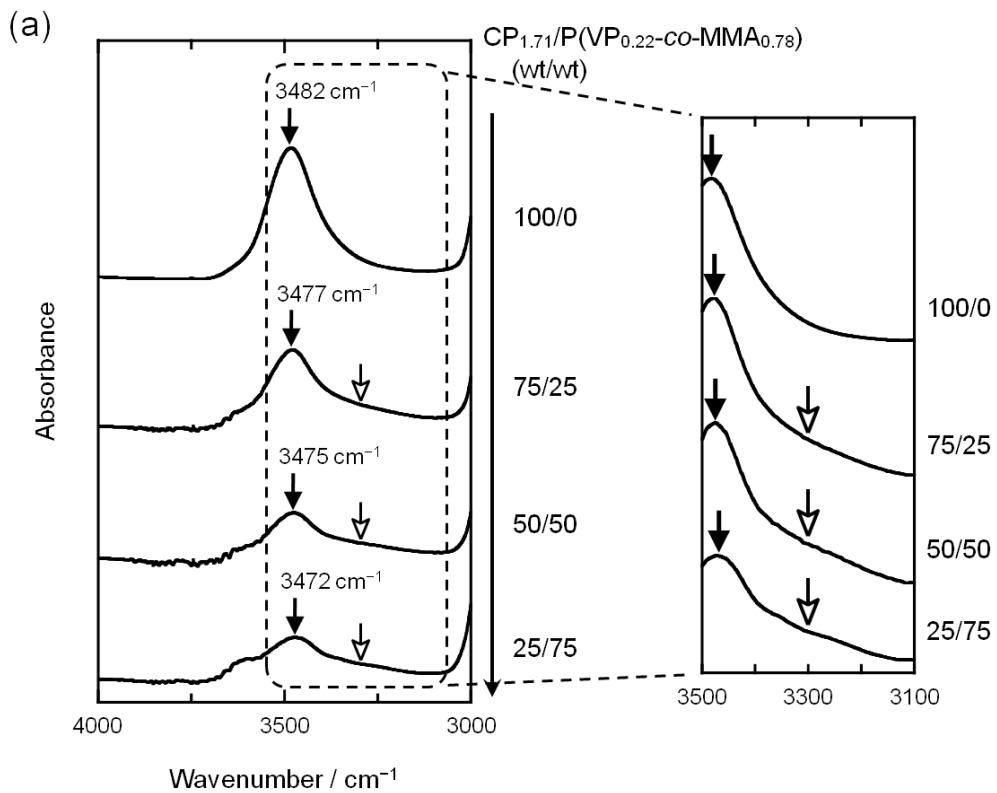
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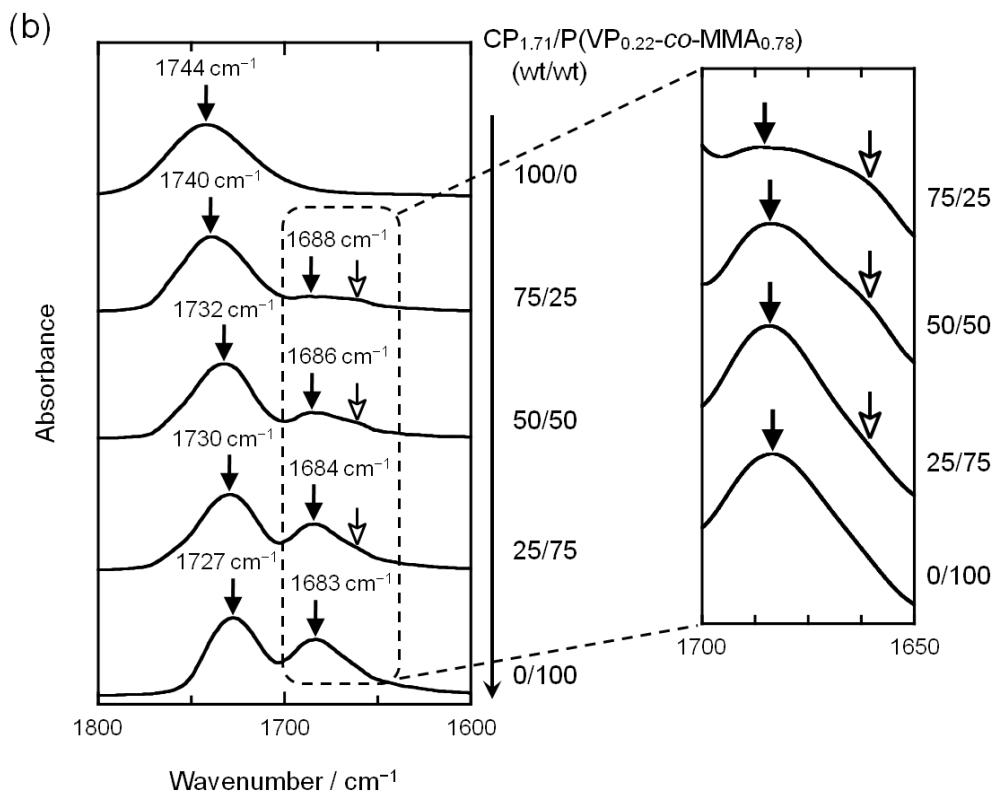
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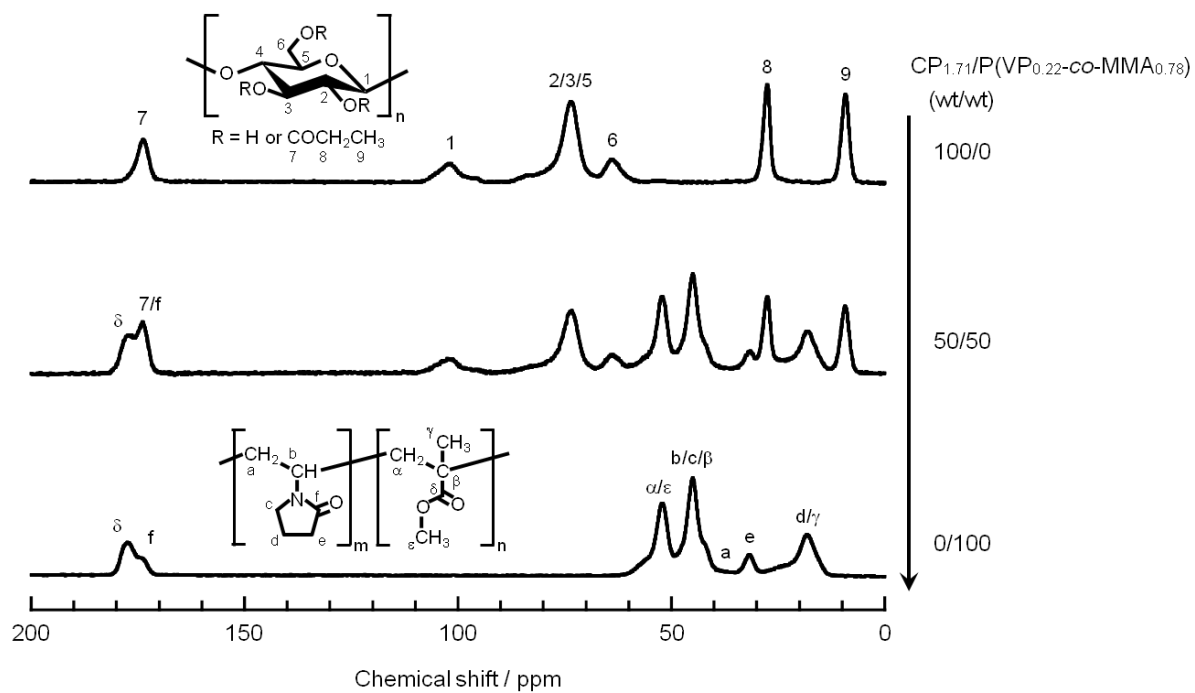


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<<Fig. 4.>>



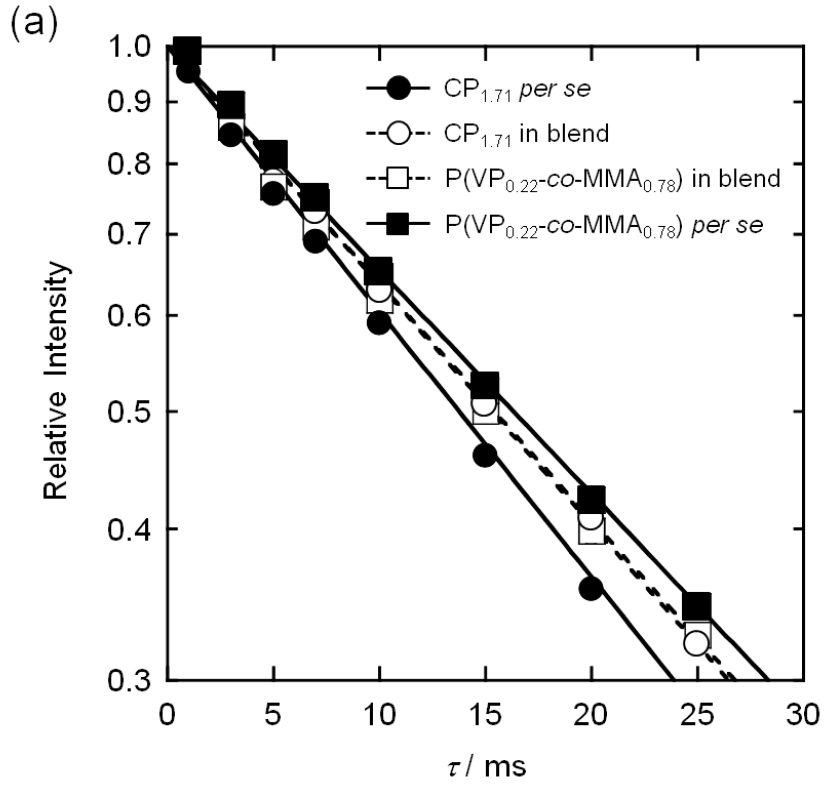
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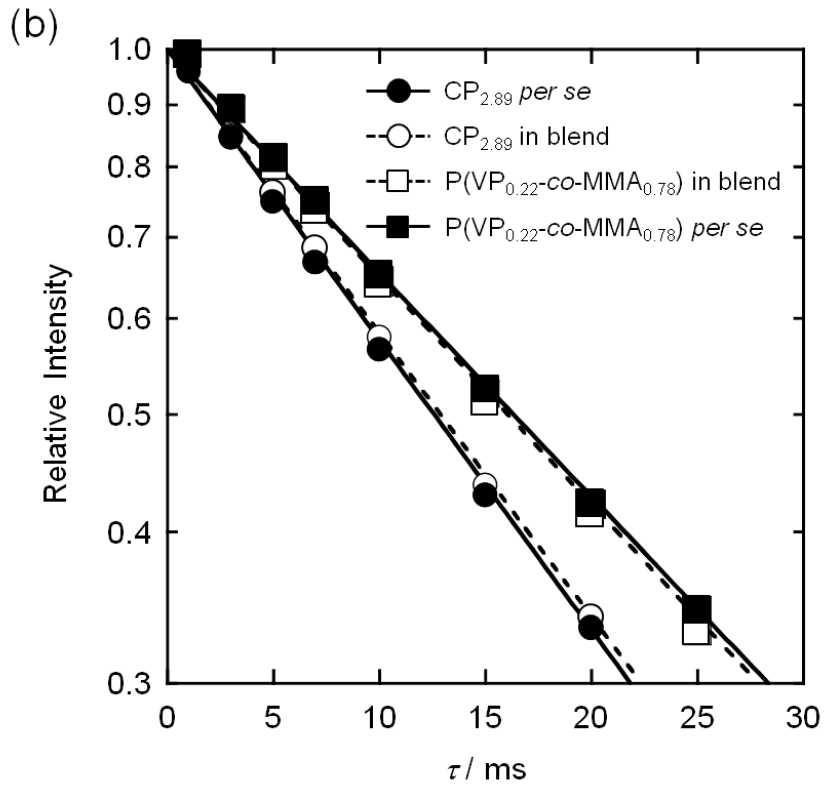
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<<Fig. 5.>>



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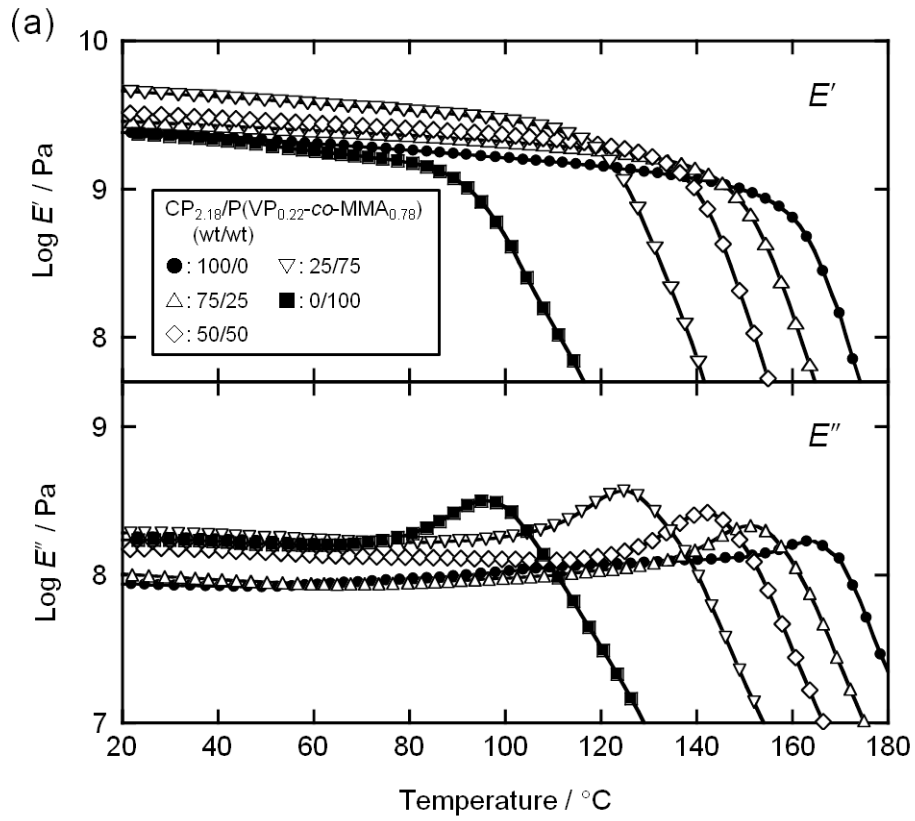


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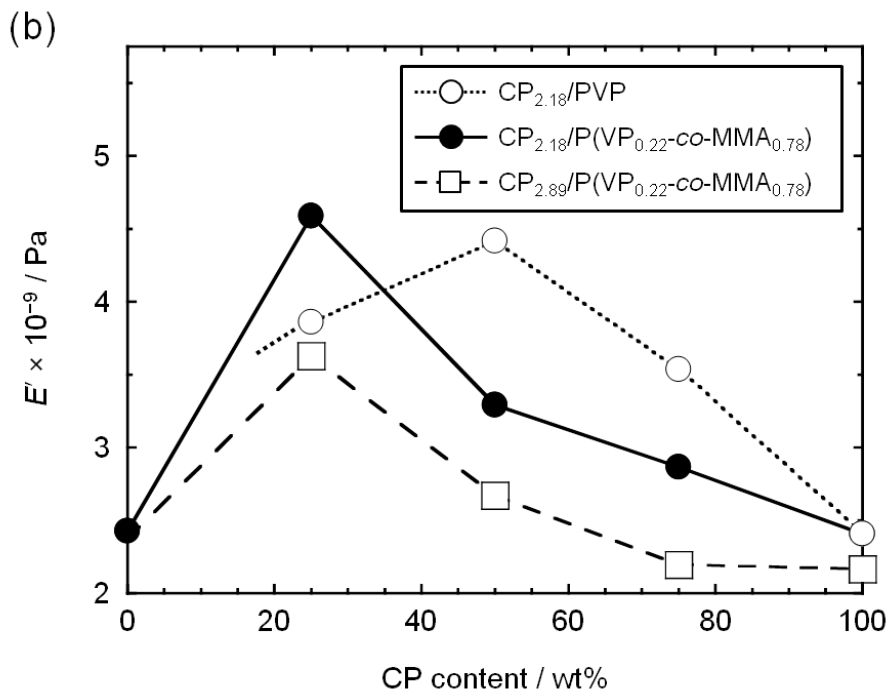
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<<Fig. 6.>>



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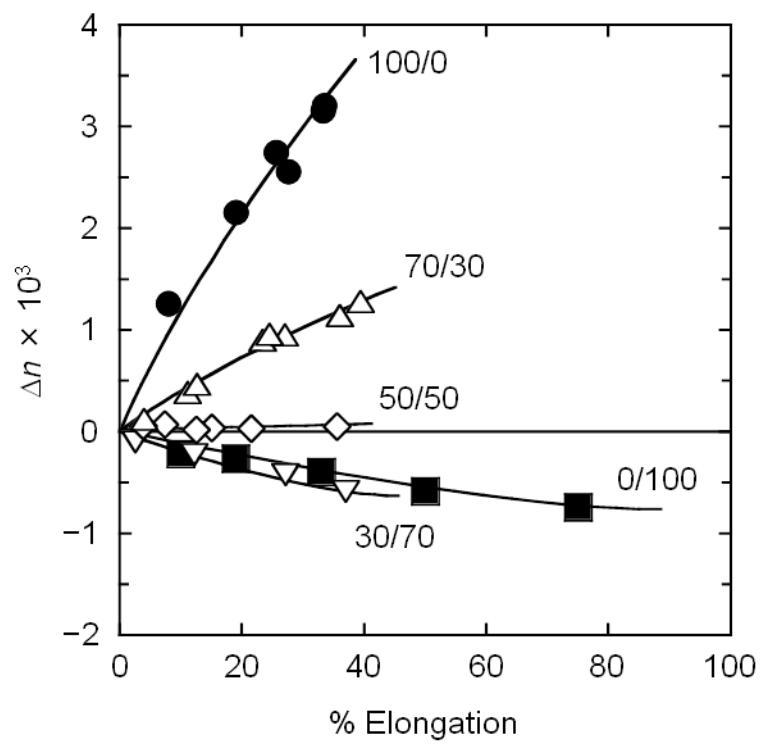
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<<Fig. 7.>>



<<Fig. 8.>>

1 **Table 1** Characterization of CP, CAP, and vinyl polymers used in the present study

Sample code ^a	M_w ^c	M_n ^c	M_w/M_n ^c	$T_g / ^\circ\text{C}$	Source
CP _{1.59}	1,230,000	585,000	2.10	165	Synthesized
CP _{1.71}	2,010,000	850,000	2.36	162	Synthesized
CP _{2.09}	1,190,000	571,000	2.08	160	Synthesized
CP _{2.18}	1,300,000	577,000	2.25	157	Synthesized
CP _{2.33}	844,000	258,000	3.27	155	Synthesized
CP _{2.53}	818,000	367,000	2.23	141	Synthesized
CP _{2.62}	979,000	359,000	2.73	138	Synthesized
CP _{2.72}	2,390,000	968,000	2.47	134	Synthesized
CP _{2.81}	1,990,000	837,000	2.38	128	Synthesized
CP _{2.89}	2,000,000	692,000	2.89	127	Synthesized
CP _{2.93}	1,250,000	525,000	2.38	124	Synthesized
CA _{0.16} P _{2.52}	258,000	73,400	3.51	143	Eastman Chemical Co.
CA _{0.47} P _{2.48}	240,000	98,500	2.44	132	Synthesized

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

^aThe DS values were determined by ¹H NMR.

^bThe VP contents were determined by FT-IR in a way described by Liu et al. (1994).

^cDetermined by gel permeation chromatography (mobile phase, tetrahydrofuran at 40 °C) with polystyrene standards.

^dDetermined by gel permeation chromatography (mobile phase, 10 mM L⁻¹ lithium bromide/DMF at 40 °C) with polystyrene standards.

^eNominal value.

^fSynthesized in our 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 a previous paper (Ohno & Nishio, 2007a).

- 2 **Table 2** $T_{1\rho}^H$ values obtained for two series of blends, CP_{1.71}/P(VP_{0.22-co}-MMA_{0.78}) and
 3 CP_{2.89}/P(VP_{0.22-co}-MMA_{0.78})

CP _{1.71} /P(VP _{0.22-co} -MMA _{0.78}) (wt/wt)	$T_{1\rho}^H$ / ms							
	CP _{1.71}				P(VP _{0.22-co} -MMA _{0.78})			
	C2/3/5	C8	C9	Ave.	α/ϵ	b/c/ β	d/ γ	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 _{2.89} /P(VP _{0.22-co} -MMA _{0.78}) (wt/wt)	$T_{1\rho}^H$ / ms							
	CP _{2.89}				P(VP _{0.22-co} -MMA _{0.78})			
	C2/3/5	C8	C9	Ave.	α/ϵ	b/c/ β	d/ γ	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