Phase separation and thermal degradation of poly(vinyl alcohol)/poly(methacrylic acid) and poly(vinyl alcohol)/poly(acrylic acid) systems by ^{13}C c.p./m.a.s. n.m.r.

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Phase separation and chemical structure changes occurring during thermal degradation are studied by high-resolution solid-state ^{13}C n.m.r. methods for poly(vinyl alcohol)/poly(methacrylic acid) (PVA/PMAA) = 1/1 complex and poly(vinyl alcohol)/poly(acrylic acid) (PVA/PAA) = 1/1 blend. ^{13}C cross-polarization/magic-angle spinning spectra and ^{1}H $T_{1\rho}$ are measured for samples subjected to various heat treatments. The results indicate that when the systems are heated to higher temperatures, phase separation occurs first because of the dissociation of intermolecular hydrogen bonding between the two different polymers. Further increases in temperature bring about thermal degradation. Degradation products of the complex and the blend are similar to those of the corresponding single-polymer systems. The thermal degradation temperatures for the complex and the blend are lower than for the single-polymer systems. This is ascribed to the loss of the crystalline phase of the PVA component and a lowering of glass transition temperatures of the PMAA and PAA components in the miscible system.

(Keywords: poly(vinyl alcohol); poly(methacrylic acid); poly(acrylic acid); polymer blends; polymer complexes; hydrogen bonding; phase separation; thermal degradation; high-resolution solid state ^{13}C n.m.r.)

INTRODUCTION

In recent papers, we reported solution and solid-state n.m.r. studies of poly(vinyl alcohol)/poly(methacrylic acid) (PVA/PMAA) complex and poly(vinyl alcohol)/poly(acrylic acid) (PVA/PAA) blends, i.e. hydrogen-bonding polymer systems[1,2]. The results showed that for the PVA/PMAA = 1/1 complex and PVA/PAA = 1/1 blend, component polymers are intimately mixed on a scale of 20–30 Å through the intermolecular hydrogen-bonding interaction. The crystalline phase of PVA disappears completely for both the PVA/PMAA = 1/1 complex and PVA/PAA = 1/1 blend. If we heat the complex and the blend, it is expected that phase separation occurs because of weakening of hydrogen bonding. We also expect thermal degradation of the systems at higher temperatures.

PVA, PMAA and PAA are all known to degrade when exposed to high temperatures. There have been reported two processes of thermal degradation of pure PVA[3,4]. The first process is principally dehydration, which begins at about 470 K and yields predominantly macromolecules with a polyene structure (*Scheme I*). The second process occurs at much higher temperatures. At that time the polyene structure is destroyed; carbon and hydrocarbons are produced. For pure PMAA and PAA[5–8], the initial process of thermal degradation involves the formation of six-membered cyclic anhydrides (*Schemes II* and *III-1*). Further heating of PAA results in removal of hydrogen from the backbone-chain (*Scheme III-2*). At much higher temperatures, substantial degradation occurs for both PMAA and PAA, yielding aromatic char with phenol functionalities and so on.

When PVA is complexed with PMAA or blended with PAA, the intermolecular interaction between the two different polymers influences the heat-resistant properties. To examine such influences, we applied solid-state high-resolution ^{13}C n.m.r. methods. Because the solid product formed during thermal degradation is usually insoluble in any solvent, fewer methods can be applied. C.p./m.a.s. spectra can be used for structural identification. The relaxation characteristics of each thermally degraded product can also be studied through well-resolved ^{13}C resonances[9,10].

In this paper, cross-polarization/magic-angle spinning (c.p./m.a.s.) spectra and ^{1}H $T_{1\rho}$ are measured for PVA, PMAA, PAA, PVA/PMAA = 1/1 complex and PVA/PAA = 1/1 blend which are heat-treated at temperatures ranging from 339 K to 583 K for a fixed period or at a fixed temperature for varying periods. For the study of thermal degradation of the systems, the main attention is focused on the initial process of degradation in which relatively stable polymers are produced (shown in the schemes). The results are discussed in term of phase separation and complexing and blending effects on the degradation.

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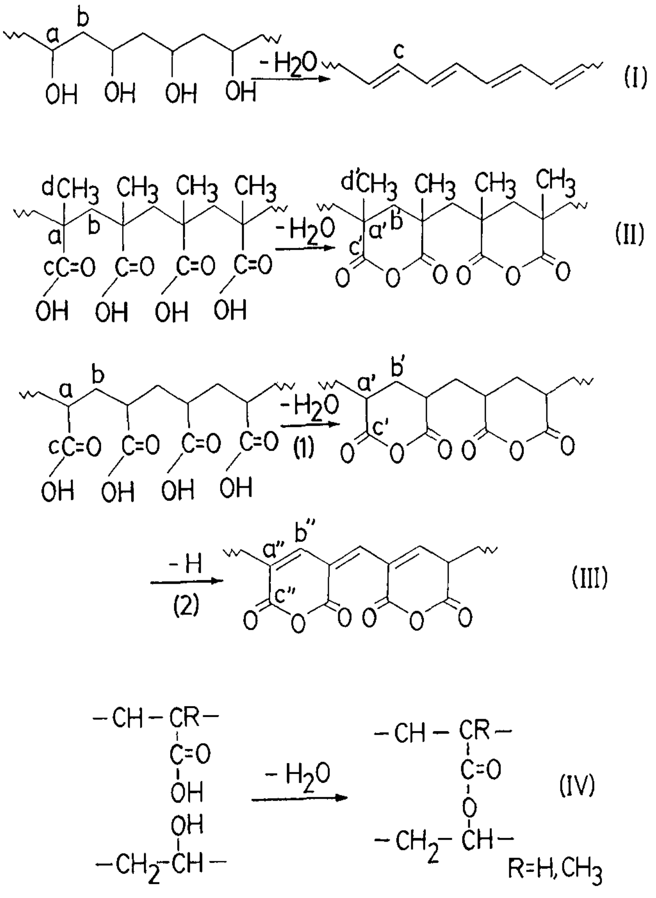

Scheme Thermal degradation equations of PVA (I), PMAA (II), PAA (III) and a possible reaction between PVA and PMAA or PAA (IV)

EXPERIMENTAL

Samples

The molecular weights of PVA, PMAA and PAA are 110000, 40000–70000 and 20000–40000, respectively.

The method of preparation of the PVA/PMAA complex and PVA/PAA blend has been described in detail in the previous paper[1]. PVA/PMAA samples were prepared by mixing 0.12 wt% aqueous solution of each polymer in monomer units of 1/1 at pH = 2. A powderish solid appeared immediately after mixing of the two solutions. The mixture was stirred for 1 day and allowed for stand for 20 h in order to precipitate the powder completely. The powder was filtered, washed and dried under reduced pressure at 323 K for 3 days. The PVA/PAA = 1/1 blend sample was prepared by mixing PVA and PAA in aqueous solution in 1/1 monomer units of the two polymers. A homogeneous mixed-solution was obtained. After stirring for 5 h, the solution was allowed to evaporate at room temperature for several days. A transparent film of PVA/PAA = 1/1 blend was obtained after further drying under reduced pressure at 323 K for 3 days.

The glass transition temperature (T_g) of the complex and the blend was measured by a Hitachi E101 differential scanning calorimeter at a scanning rate of 20 K min^{-1}. The PVA/PMAA = 1/1 complex and PVA/PAA = 1/1 blend show single T_g peaks at 413 K and 364 K, respectively.

PVA, PMAA, PAA, PVA/PMAA = 1/1 complex and PVA/PAA = 1/1 blend were heated in air at various temperatures for various periods. After heating, the samples were quenched into water at room temperature to freeze the structure of the samples.

N.m.r. experiments

N.m.r. experiments were carried out on a JEOL JNM-GX270 spectrometer operating at resonance frequencies of 270 and 67.8 MHz for ^{1}H and ^{13}C, respectively. High-resolution solid-state ^{13}C n.m.r. was performed by magic-angle sample spinning (m.a.s.) and high-power spin decoupling. To enhance the signal-to-noise ratio, the cross-polarization (c.p.) technique was applied. The ^{1}H decoupling frequency was chosen to be 3 ppm downfield from tetramethylsilane (TMS). A double-bearing aluminium oxide rotor was used. The setting of the magic angle was monitored by the ^{79}Br n.m.r. spectrum of KBr incorporated in the rotor[11]. The rate of magic-angle sample spinning was about 6 kHz and the contact time for c.p. was 1.2 ms. The radio-frequency field strength for both ^{1}H and ^{13}C was about 56 kHz. ^{1}H $T_{1\rho}$ measurement was performed by a method reported elsewhere[10]. The chemical shift of ^{13}C spectra is reported in ppm relative to t.m.s. by taking the methine carbon of solid adamantane (29.5 ppm) as an external reference.

RESULTS AND DISCUSSION

Phase separation

When the intermolecular hydrogen-bonding interaction between two different polymers in a blend is strong enough to override the effect of the free volume term which hinders intimate mixing[12], the blend can form a miscible system. This is the case for PVA/PMAA = 1/1 and PVA/PAA = 1/1 systems at lower temperatures. As temperature increases, the hydrogen-bonding interaction becomes weaker, while the effect of free volume becomes stronger. When the effect of free volume overcomes the hydrogen-bonding interaction, phase separation occurs.

Figures 1 and *2* show, respectively, c.p./m.a.s. ^{13}C n.m.r. spectra of PVA/PMAA = 1/1 complex and PVA/PAA = 1/1 blend subjected to various heat treatments. Assignments of spectra based on previous work[2] for PVA/PMAA and PVA/PAA samples without heat treatment are also shown. When the PVA/PMAA = 1/1 complex is heated at temperatures lower than 403 K, ^{13}C resonances of PMAA and PVA do not show any change in chemical shift (not shown here). When heated at 433 K for 1 h, the COOH peak at 182 ppm of the PMAA component in the complex without heat treatment shifts upfield and decreases in intensity. Furthermore, a new peak appears at 172 ppm. If heated for 3 h at the same temperature, the COOH peak shifts further upfield. Similar upfield shifts of the COOH peak of the PAA component were observed for the PVA/PAA = 1/1 blend subjected to heat treatment, as shown in *Figure 2*.

The chemical shift of the COOH carbon resonance is plotted against the heating temperature for PVA/PMAA = 1/1 complex and PVA/PAA = 1/1 blend in *Figure 3*. It is of interest to note that as the heating temperature approaches the glass transition temperature (364 K for PVA/PAA = 1/1 blend and 413 K for PVA/PMAA = 1/1 complex), the COOH peaks start to move upfield. It has been reported that the COOH carbon resonance shifts downfield when the COOH group is hydrogen bonded[13,14]. Since the polymer chain moves vigorously above the glass transition temperature,

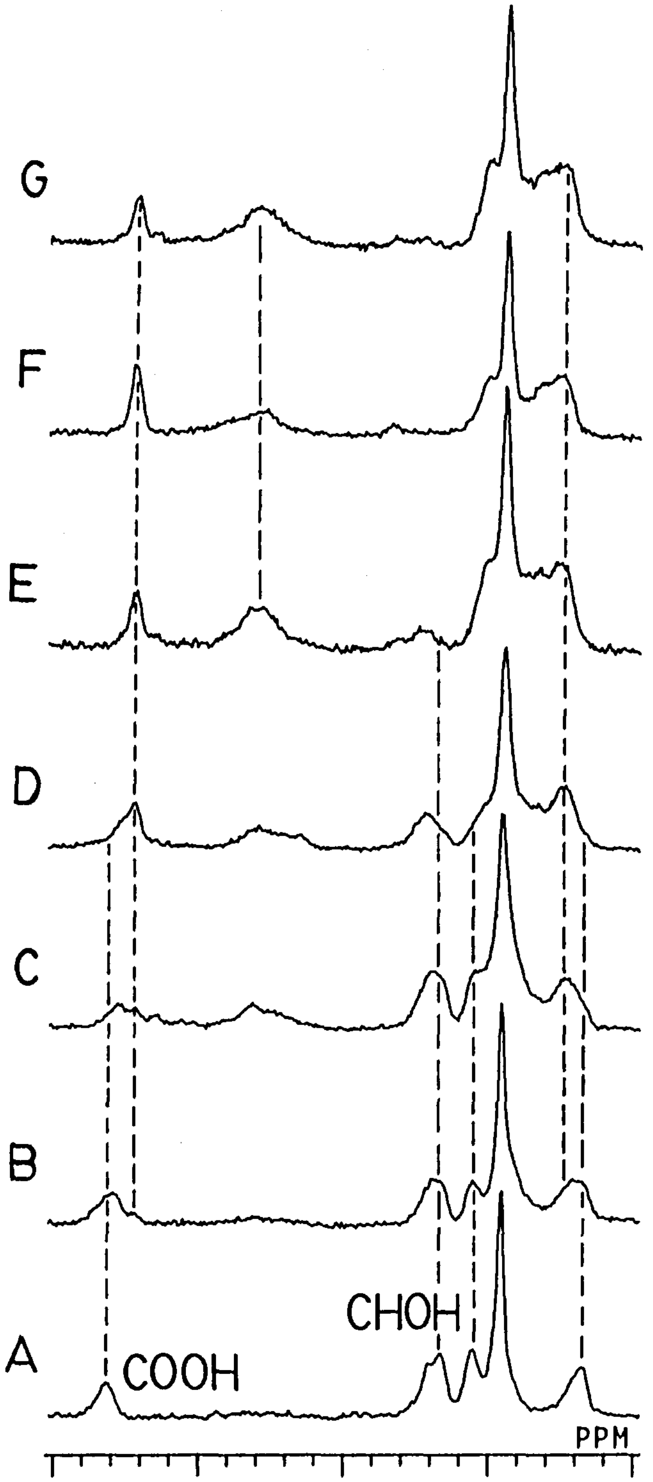

Figure 1 ^{13}C c.p./m.a.s. spectra of PVA/PMAA = 1/1 complex at various heating temperatures. (A) without heating; (B) heated at 433 K for 1 h; (C) heated at 453 K for 1 h; (D) heated at 488 K for 1 h; (E) heated at 523 K for 0.5 h; (F) heated at 523 K for 1 h; (G) heated at 583 K for 10 min

molecular motion would break hydrogen bonds. Thus, the hydrogen bonding interaction is reduced as the heating temperature increases, resulting in an upfield shift of the COOH carbon resonances.

Table 1 shows ^1H $T_{1\rho}$ values measured for each component of PVA/PMAA and PVA/PAA systems subjected to various heat treatments through well-resolved ^{13}C resonances. The ^1H $T_{1\rho}$ values are identical for the two polymer components in both PVA/PMAA and PVA/PAA systems heated at 433 K for 1 h. This suggests that the two polymers subjected to such heat treatment are still miscible in the same way as for non-heated systems[2]. If heated at 433 K for 3 h, the two polymer components have different ^1H $T_{1\rho}$ values. The $T_{1\rho}$ values of PMAA and PAA components approach, respectively, those of the corresponding pure polymers subjected to the same heat treatment. These results suggest that the phase separation occurs for PVA/PMAA = 1/1 and PVA/PAA = 1/1 blend when heated at 433 K for 3 h. $T_{1\rho}$ values of the PVA component in PVA/PMAA = 1/1 complex and PVA/PAA = 1/1 blend observed through the CHOH carbon resonance are almost the same, but differ from those of pure PVA. These results suggest that after the phase separation the phase structure of the PVA component remains the same for the complex and the blend, but differs from that of pure PVA.

The results of the chemical shift and ^1H $T_{1\rho}$ mentioned above lead us to conclude that phase separation occurs for both PVA/PMAA and PVA/PAA systems due to the dissociation of intermolecular hydrogen bonding above their glass transition temperatures.

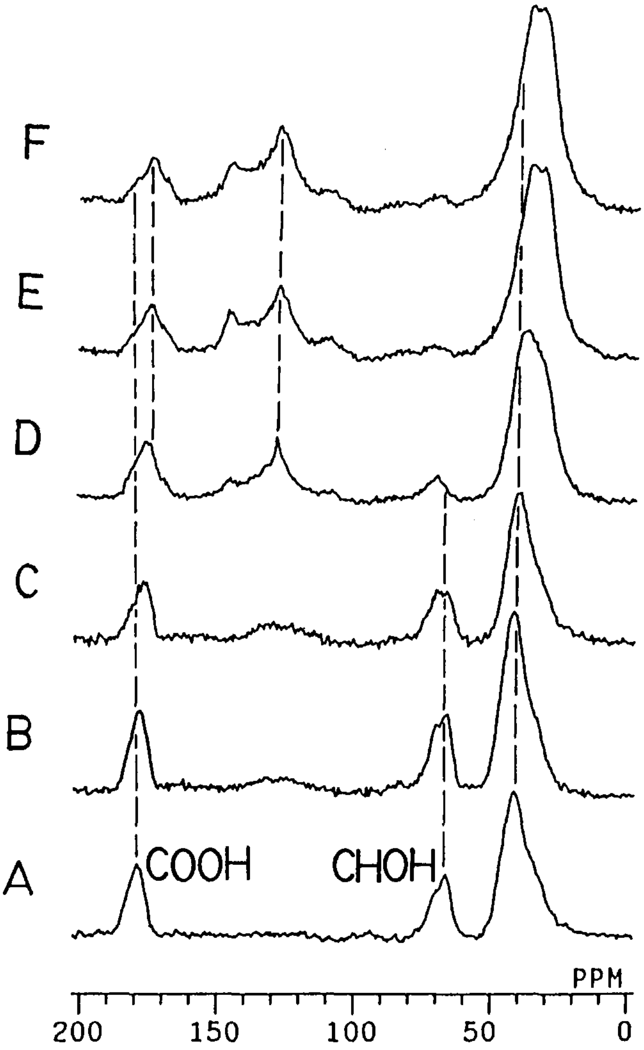

Figure 2 ^{13}C c.p./m.a.s. spectra of PVA/PAA = 1/1 blend heated at various temperatures. (A) without heating; (B) heated at 403 K for 1 h; (C) heated at 433 K for 1 h; (D) heated at 488 K for 1 h; (E) heated at 523 K for 1 h; (F) heated at 583 K for 10 min

Thermal degradation

The present results of heat treatment for single polymers of PMAA and PAA are similar to previous results[7]. *Figure 4* shows ^{13}C c.p./m.a.s. spectra of PMAA without heating (A) and with heating at 523 K for 1 h (B). Assignments shown in the figure are made on the basis of the previous work[7]. Symbols a, a′, b, b′, c, c′, d and d′ are referred to in *Scheme II*. When PMAA was heated at temperatures higher than 473 K, COOH carbon (resonance c) diminishes in intensity and a new peak appears at 172 ppm (c′). This suggests the formation of anhydride. After heating at 523 K for 1 h, the COOH peak totally disappears (*Figure 4*-B); the thermal degradation of *Scheme II* seems to be completed. Resonance c′ at 172 ppm is reasonably narrow, suggesting that the anhydride is rather homogeneous. All acid groups are transformed to cyclic anhydride. Other resonances of PMAA also show some changes corresponding to the formation of six-membered rings.

A similar change was observed for PAA as shown in *Figure 5*. Peak assignments a, a′, a″ and so on are referred to in *Scheme III*. After heating at 473 K for 1 h, COOH resonance c shifts upfield and decreases in intensity, while a new peak appears at 171 ppm (c′). Such a spectral change indicates the first process of thermal degradation shown in *Scheme III*. When heated at 523 K for 1 h, three new peaks at 147, 129 and 112 ppm appear, as shown in *Figure 5*-B; at this stage the second process of degradation occurs. The line width of the spectrum of *Figure 5*-B is broader than that of *Figure 4*-B. This implies that the degradation products of PAA have structural diversity as compared to those of PMAA; they are composed of a series of mixtures.

C.p./m.a.s. ^{13}C n.m.r. spectra of PVA subjected to various heat treatments are shown in *Figure 6*. Peak

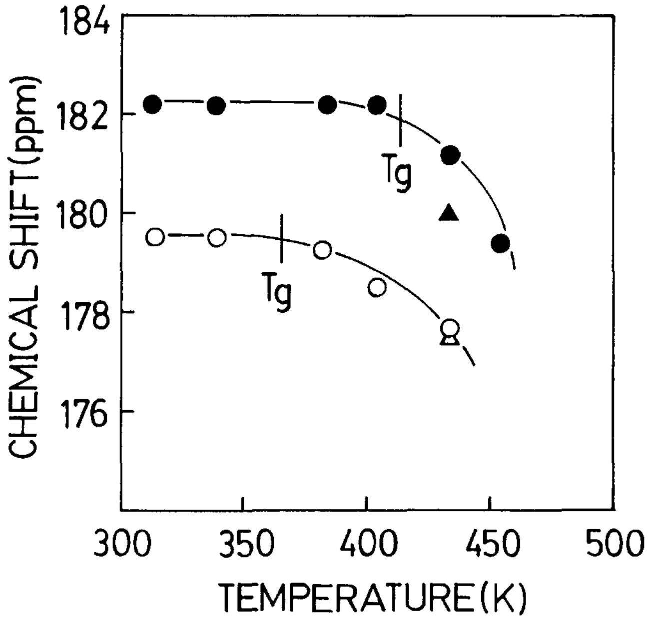

Figure 3 ^{13}C chemical shifts of COOH carbon resonances of PMAA (●) and PAA (○) components in PVA/PMAA and PVA/PAA systems heated for 1 h at various temperatures. The chemical shift positions in the two-polymer systems heated at 433 K for 3 h are also shown for PMAA (▲) and PAA (△) components

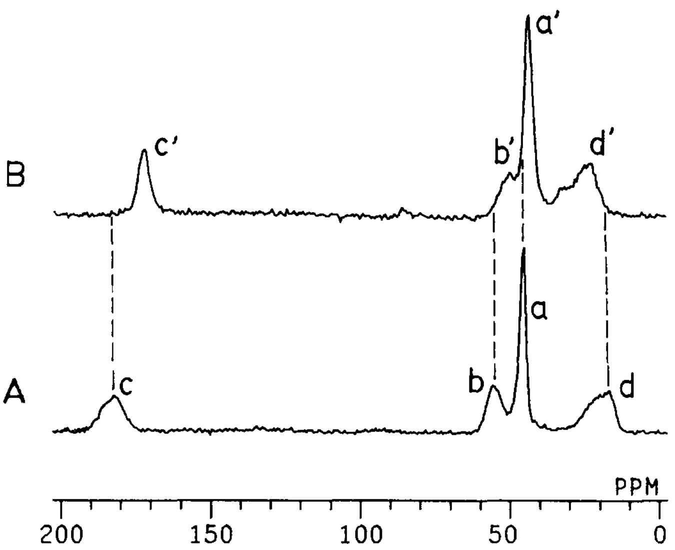

Figure 4 ^{13}C c.p./m.a.s. spectra of PMAA without heating (A) and PMAA heated at 523 K for 1 h (B)

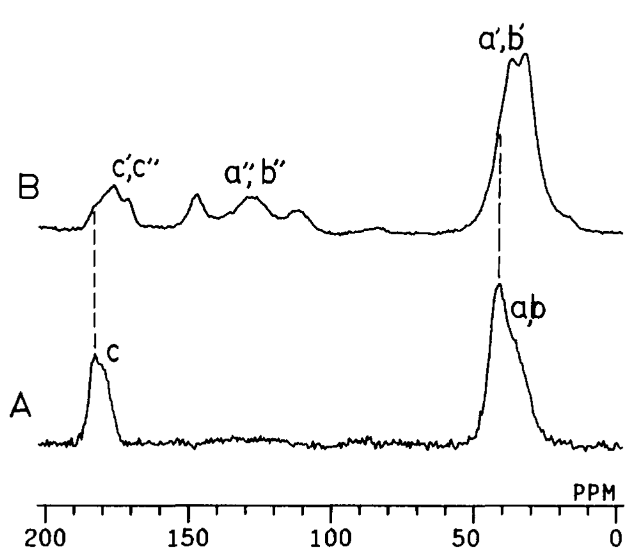

Figure 5 ^{13}C c.p./m.a.s. spectra of PAA without heating (A) and PAA heated at 523 K for 1 h (B)

Table 1 ^{1}H $T_{1\rho}$ values (ms) of PVA/PMAA and PVA/PAA systems with various heat treatments*

		PVA/PMAA complex			PVA/PAA = 1/1 blend		
	PMAA	PVA	PMAA	PVA	PVA	PAA	PAA
339 K, no heating	7.2	3.2	3.3	2.4/11	2.8	2.8	4.3
433 K/1 h	5.3	3.4	3.1	7.4	3.9	3.6	3.6
433 K/3 h	9.2	6.6	8.8	9.8	6.5	8.3	8.6

*The ^{1}H $T_{1\rho}$ values of PMAA and PAA components were measured through the COOH carbon signal. The ^{1}H $T_{1\rho}$ value of the PVA component was measured through the CHOH carbon signal

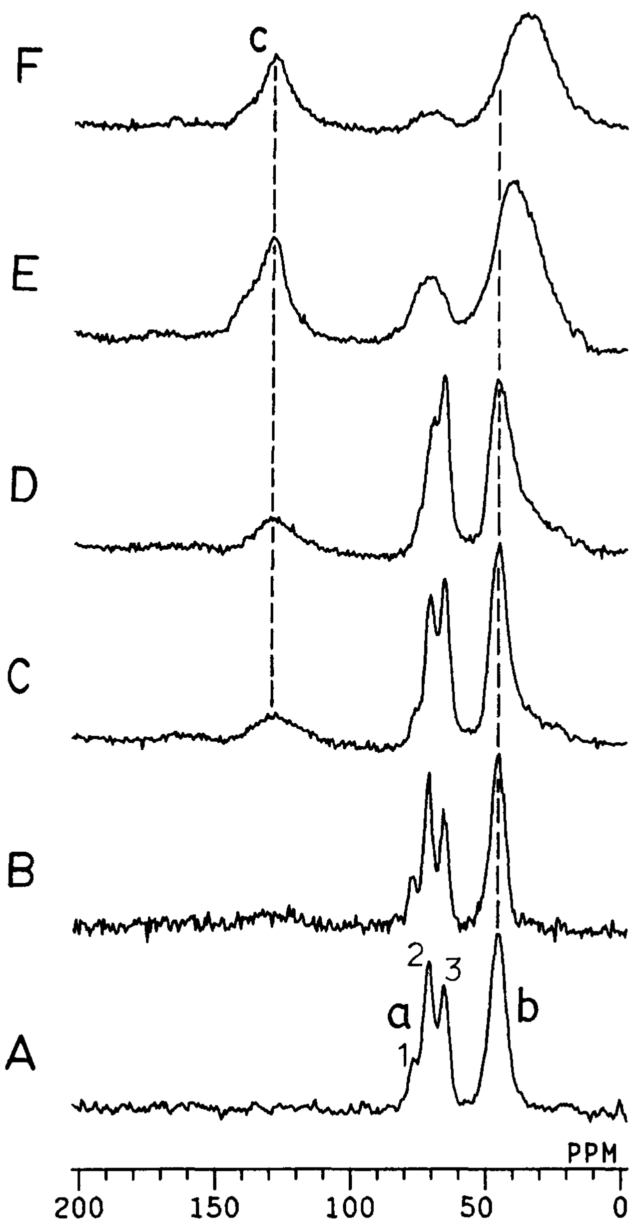

Figure 6 ^{13}C c.p./m.a.s. spectra of PVA heated at various temperatures. (A) without heating; (B) heated at 453 K for 1 h; (C) heated at 488 K for 1 h; (D) heated at 523 K for 0.5 h; (E) heated at 523 K for 1 h; (F) heated at 583 K for 10 min

assignments a, b and c are referred to in *Scheme I*. If heated for 1 h at temperatures lower than 453 K, no noticeable change is observed, except for narrower CHOH peaks and clearer three-peak characteristics. At this temperature no thermal degradation occurs. After heating at 488 K for 1 h, the spectrum shows two significant changes (*Figure 6*-C). One is that peaks 1 and 2 decrease in relative intensity, while peak 3 increases. The other is the appearance of a new peak at about 130 ppm (c). After heating at 523 K for 1 h (*Figure 6*-E), the three-peak characteristics of CHOH disappear completely; the whole CHOH resonance becomes a single broad peak at 70 ppm. The CH_2 peak (b) also becomes broader. Meanwhile, the new peak at 130 ppm increases noticeably in intensity. The CHOH peak almost disappears after heating at 583 K even for 10 min (*Figure 6*-F). The decrease in intensity of peaks 1 and 2 of the CHOH resonance of PVA at elevated temperatures is explained in terms of the dissociation of intramolecular hydrogen bonding of PVA[2]. Thermal degradation occurs at temperatures much higher than 480 K. The new peak at 130 ppm (c) can be attributed to polyene carbons (*Scheme I*) formed during thermal degradation.

Degradation products of the PVA/PMAA = 1/1 complex give resonances at the same chemical shift positions as those of PVA and PMAA subjected to similar heat treatment. The CHOH peak of the PVA component in the complex decreases in intensity with increasing temperature, whereas the intensity of the new peak at 130 ppm increases; the degradation of PVA and the formation of polyene structure (*Scheme I*) are suggested to occur. The peak of COOH carbon of the PMAA component in the complex not only shifts upfield, but also decreases in intensity accompanied by the appearance of a new peak at 172 ppm (*Figure 1*) as the temperature increases. Other carbon resonances of the PMAA component also change in a similar way as those of degraded pure PMAA. These results indicate that the amount of COOH groups is reduced and that anhydrides with a six-membered ring structure (*Scheme II*)[7] are formed as in the case of pure PMAA.

Similar results were obtained for the PVA/PAA = 1/1 blend (*Figure 2*). After heating at 488 K for 1 h (*Figure 2*-D), noticeable thermal degradation occurs for both PVA and PAA components, giving a spectrum as shown in *Figure 2*-D. The intensity of CHOH resonance of the PVA component decreases significantly, while the COOH carbon resonance of the PAA component changes similarly as that of pure PAA subjected to the same heat treatment. Meanwhile, three peaks at 147, 128 and 112 ppm were also observed. These peaks can be ascribed to degraded products of PAA (the same as peaks a″ and b″ shown in *Figure 5*-B) in *Scheme III-1* and those of PVA (the same as peak c shown in *Figure 6*-F) due to the formation of polyene (*Scheme I*). Since the peak at 130 ppm arises from both PVA and PAA components, the intensity is greater than those at 147 and 112 ppm.

The results of the ^{13}C c.p./m.a.s. spectra suggest that products of thermal degradation of PVA, PMAA and PAA components in the complex and the blend are similar to those of pure polymers subjected to similar heat treatments. The ^{1}H $T_{1\rho}$ values of PVA/PMAA = 1/1 and PVA/PAA = 1/1 systems heated at 523 K for 1 h are listed in *Table 2*.

The ^{1}H $T_{1\rho}$ values of pure PMAA heated at 523 K for 1 h observed through all carbon resonances have the same value, indicating the formation of a uniform polymer. However, for pure PVA and PAA, $T_{1\rho}$ values differ from one carbon resonance to another. The results of $T_{1\rho}$ as well as ^{13}C c.p./m.a.s. spectra suggest that degradation products of PVA and PAA are a series of mixtures. Thermal degradation of PVA is probably not complete at 523 K for 1 h; degradation products of PAA are mixtures of step 1 and step 2 (*Scheme III-1* and *2*). On the other hand, $T_{1\rho}$ values observed through peaks at 172, 44 and 25 ppm for pure PMAA and PMAA components in the PVA/PMAA complex are the same as each other. In addition, the $T_{1\rho}$ value that is observed through a peak at 130 ppm (a peak of degradation products of pure PVA) is also the same as the value observed through the corresponding peak of the PVA component in the complex. For the PVA/PAA = 1/1 blend heated at 523 K for 1 h, $T_{1\rho}$ values observed through peaks at 175 and 147 ppm of the PAA component

Table 2 ^{1}H $T_{1\rho}$ values (ms) of PVA/PMAA and PVA/PAA systems after heating at 523 K for 1 h

(Measured through the peak of)*	PMAA	PVA/PMAA = 1/1	PVA	PVA/PAA = 1/1	PAA
175 ppm				5.4	5.4
172 ppm	10.9	10.7			
147 ppm				7.1	7.1
130 ppm		7.1	7.2	6.6	
128 ppm					7.2
70 ppm			6.5		
44 ppm	11.0	10.7			
32–38 ppm			6.7	6.5	6.9
25 ppm	10.9	11.1			

*Refer to *Figure 9*

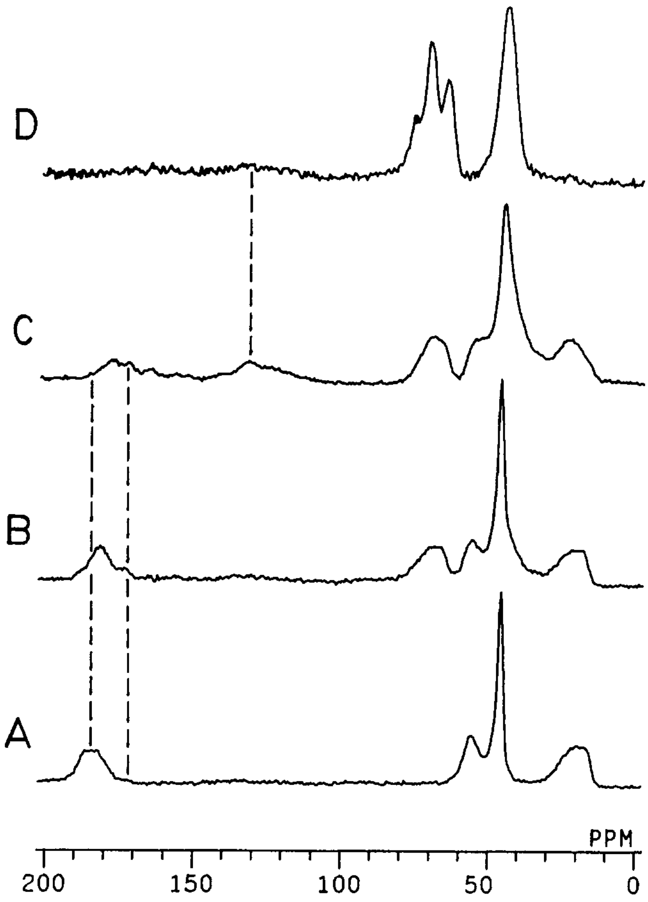

Figure 7 ^{13}C c.p./m.a.s. spectra of PMAA heated at 433 K for 1 h (A); PVA/PMAA = 1/1 complex heated at 433 K for 1 h (B); PVA/PMAA = 1/1 complex heated at 453 K for 1 h (C); PVA heated at 453 K for 1 h (D)

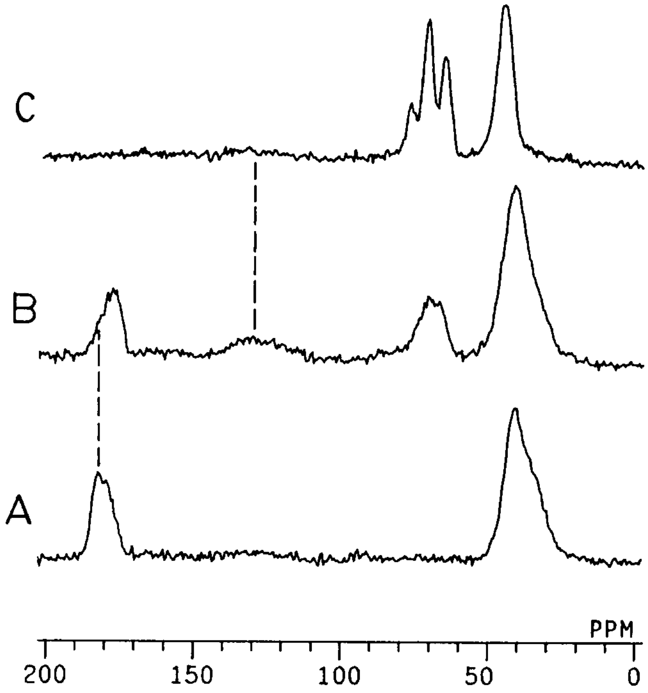

Figure 8 ^{13}C c.p./m.a.s. spectra of the samples heated at 433 K for 1 h. (A) PAA; (B) PVA/PAA = 1/1 blend; (C) PVA

are equal to those observed through corresponding peaks of pure PAA. These results indicate that thermal degradation products of the complex and the blend are the same as for the pure polymers, providing additional evidence to the conclusions of ^{13}C c.p./m.a.s. spectra results.

Although the products of thermal degradation of these systems are not much different from those of pure polymers, it is found that the complexing or the blending has a significant influence on the degradation. *Figure 7* shows ^{13}C c.p./m.a.s. spectra of pure PMAA and PVA/PMAA = 1/1 complex heated at 433 K for 1 h, and PVA/PMAA = 1/1 complex and pure PVA heated at 454 K for 1 h. After heating at 433 K for 1h, pure PMAA shows little degradation (*Figure 7*-A). The PVA/PMAA complex, however, gives an anhydride carbon peak at 172 ppm (*Figure 7*-B), indicating that the degradation of PMAA begins in the complex. Pure PVA shows almost no degradation (*Figure 7*-D) after heating at 453 K for 1 h, whereas the PVA component in the complex undergoes thermal degradation, as evidenced by the peak at 130 ppm (*Figure 7*-C) due to the polyene structure.

The results for the PVA/PAA = 1/1 blend are shown in *Figure 8*. When single polymers of PAA and PVA are heated at 433 K for 1 h, no spectral change is observed (*Figure 8*-A and C). For the blend heated even at the low temperature of 433 K for 1 h, however, there appears a new broad peak at 130 ppm (same as peak c shown in *Figure 6*-F), providing evidence for thermal degradation (*Figure 8*-B).

Figure 9 shows ^{13}C c.p./m.a.s. spectra of PAA, PVA/PAA = 1/1 blend, PVA, PVA/PMAA = 1/1 complex and PMAA heated at 523 K for 1 h. Under such conditions, the CHOH peak of the PVA component in

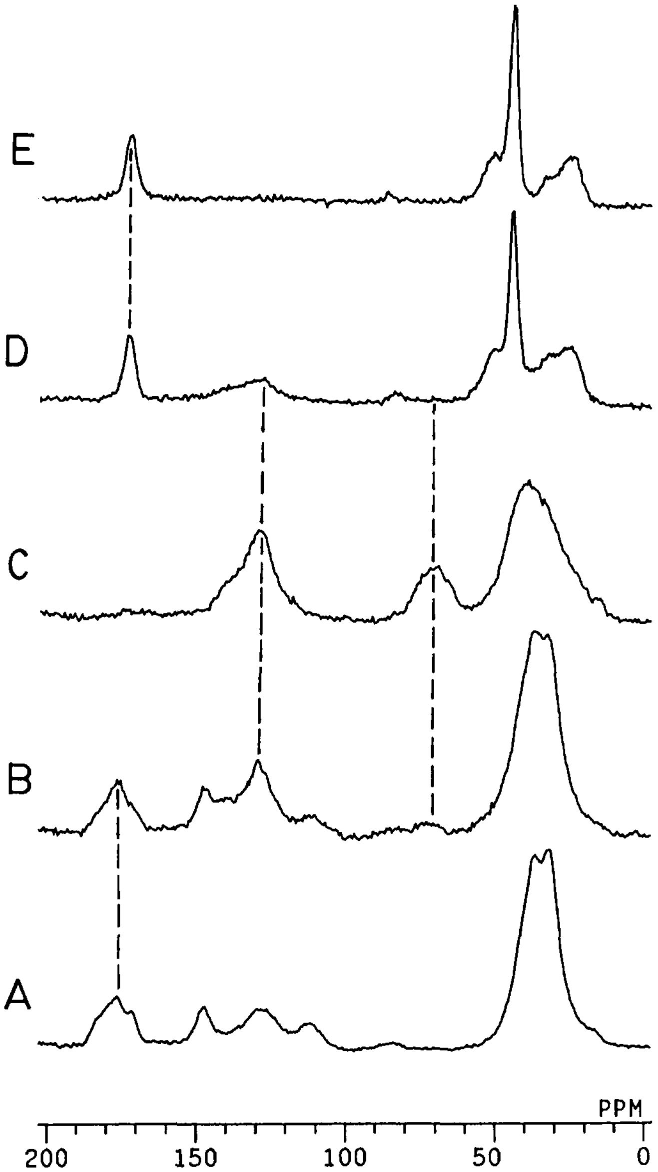

Figure 9 ^{13}C c.p./m.a.s. spectra of various samples heated at 523 K for 1 h. (A) PAA; (B) PVA/PAA = 1/1 blend; (C) PVA; (D) PVA/PMAA = 1/1 complex; (E) PMAA

the complex and the blend mostly disappeared (B and D), while the peak of pure PVA is still noticeable (C). These results indicate that the PVA/PMAA = 1/1 complex and PVA/PAA = 1/1 blend degrade at temperatures lower than for pure polymers.

Thermal degradation occurs by destroying intermolecular interactions and then breaking chemical bonds. The same polymer with lower crystallinity, therefore, has a lower degradation temperature than one with higher crystallinity. For amorphous polymers with the same chemical structure, the lower the glass transition temperature, the lower is the degradation temperature.

Pure PVA degrades at temperatures higher than 473 K[4], close to the melting point (503 K). When PVA forms a complex with PMAA or a blend with PAA, the crystalline phase of the PVA is destroyed[2]. Thermal degradation of the PVA component in the complex and the blend, therefore, occurs more easily; the temperature of degradation would be lower than for pure PVA. This is what we observed in this work.

The glass transition temperatures of PVA/PMAA = 1/1 complex and PVA/PAA = 1/1 blend measured in this work are about 413 K and 364 K, respectively, lower than those of pure PMAA (T_g = 501 K) and pure PAA (T_g = 379 K). It follows that the thermal degradation temperatures of the PMAA and PAA components also become lower due to the complexing or the blending effect observed in this work.

Since PVA is strongly associated with PMAA or PAA through intermolecular hydrogen bonding of COOH and OH groups[1,2], PVA is expected to react with PMAA or PAA to form a polyester (*Scheme IV*) at higher temperatures. However, we did not find any clear evidence for the formation of such a polyester. Phase separation and thermal degradation would hinder the occurrence of such reactions. It can be concluded that even though such a reaction may occur during heat treatment, the amount of polyester produced is small, or its products are easily degraded.

CONCLUSION

The dissociation of intermolecular hydrogen bonding between the two different polymers in PVA/PMAA = 1/1 complex and PVA/PAA = 1/1 blend brings about phase separation. Thermal degradation of the complex and the blend at more elevated temperatures yields degradation products similar to those of the single-polymer systems. The thermal degradation temperatures of the complex and the blend are lower than those of the single-polymer systems. The low degradation temperature of the PVA component in the complex and the blend is ascribed to the loss of crystalline phase in these systems. The lowering of degradation temperatures of PMAA and PAA components is ascribed to the lowering of the glass transition temperatures of the components in the miscible systems. In addition, the dissociation of hydrogen bonds may have certain effects towards lowering the thermal degradation temperature.

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REFERENCES

1 Zhang, X., Takegoshi, K. and Hikichi, K. *Polym. J.* 1991, **23**, 79
2 Zhang, X., Takegoshi, K. and Hikichi, K. *Polym. J.* 1991, **23**, 87
3 Gilbert, J. B., Kipling, J. J., McEnaney, B. and Sherwood, J. N. *Polymer* 1962, **3**, 1
4 Tsuchiya, Y. and Sumi, K. *J. Polym. Sci. A-1* 1969, **7**, 3151
5 McGaugh, M. C. and Kottle, S. *J. Polym. Sci. A-1* 1968, **6**, 1243
6 Eisenberg, A., Yokoyama, T. and Sambalido, E. *J. Polym. Sci. A*-1 1969, **7**, 1717
7 Fyfe, C. A. and McKinnon, M. S. *Macromolecules* 1986, **19**, 1909
8 Maurer, J. J., Eustace, D. J. and Ratcliffe, C. T. *Macromolecules* 1987, **20**, 196
9 Fyfe, C. A., McKinnon, M. S., Rudin, A. and Tchir, W. *Macromolecules* 1983, **16**, 1216
10 Axelson, D. E. and Russell, K. E. *Prog. Polym. Sci.* 1985, **11**, 221
11 Frye, J. S. and Maciel, G. E. *J. Magn. Reson.* 1982, **48**, 125
12 Patterson, D. and Robard, A. *Macromolecules* 1978, **11**, 690
13 VanderHart, D. L., Earl, W. L. and Garroway, A. N. *J. Magn. Reson.* 1981, **44**, 361
14 Grabelny, J., Rice, D. M., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1990, **23**, 2139