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Characterization of Hydrogen Bonding in Cellulose–Synthetic Polymer Blend Systems with Regioselectively Substituted Methylcellulose

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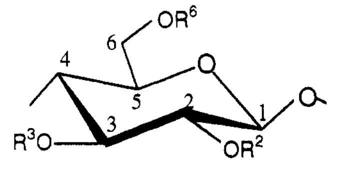
ABSTRACT: Specifically substituted *O*-methylcelluloses, 2,3-di-*O*-methylcellulose and 6-*O*-methylcellulose (parts B and C of Figure 1, respectively), were used as cellulosic components in blends with poly(ethylene oxide) (PEO) and poly(vinyl alcohol) (PVA). Since their hydroxyl groups (OH) form controlled intra- and intermolecular hydrogen bonds, the cellulose derivatives are useful as model compounds to investigate the effect of hydrogen bonding in cellulose–synthetic polymer blend systems. FTIR (Fourier transform infrared spectroscopy) spectra of the cellulosic–PEO blend films revealed that, while the primary hydroxyl groups at the C-6 position of cellulose interact strongly with ether oxygen in PEO, the secondary hydroxyl groups at the C-2 and C-3 positions show no evidence for polymer–polymer interactions. In the cellulosic–PVA blend films the FTIR analyses suggested that the secondary hydroxyl groups between the cellulose and the PVA were engaged in hydrogen bonds, and, in addition, a hydrogen bond between the anhydroglucose ring oxygen (O-5) of the cellulose and the hydroxyl groups of the PVA was formed. Thus, these results showed the specific regiochemistry of hydroxyl groups in cellulose and its importance to the study of the miscibility in cellulose–synthetic polymer blends.

Introduction

The difference in the regiochemistry and polarity of the three hydroxyl groups (OH) at the C-1, C-2, and C-3 positions of the cellulose ring (Figure 1A) is considered to be an important factor on the physical properties of cellulose such as solubility, crystallization, gel formation, liquid crystal formation, and resistance to enzymatic degradation. These properties, to a great extent, depend on the formation of the intra- and intermolecular hydrogen bonds by the three OH groups in cellulose. To date, extensive studies of hydrogen bonding have been done in crystalline cellulose.[1–7] However, research activity on the correlation between the regiochemical and polarity differences of the OH groups and the physical properties of cellulose has been limited by the difficulty of controlling the formation of the hydrogen bonds.

Recently, we (T.K. and D.G.G.) have developed methods to prepare *O*-alkylcellulose derivatives with a controlled distribution of substituents.[8–10] Of these derivatives, 2,3-di-*O*-methylcellulose[9] and 6-*O*-methylcellulose[10] (parts B and C of Figure 1, respectively) should be useful in correlating hydrogen-bond formation and physical properties. Thus, 2,3-di-*O*-methylcellulose, which has the primary OH groups at the C-6 position, can only form intermolecular hydrogen bonds, whereas 6-*O*-methylcellulose can form intramolecular hydrogen bonds (between OH at the C-3 and neighboring ring oxygen (O-5)) and can also form intermolecular hydrogen bonds.[4,6] Spectroscopic investigation of these derivatives should help to clarify the details of the hydrogen-bond formation of cellulose.

Here, we examine the specific OH regiochemistry for the hydrogen-bond formation on the miscibility of blends of cellulose with poly(ethylene oxide) and poly(vinyl alcohol) by Fourier transform infrared spectroscopy (FTIR). Because each regioselectively substituted cellulose model sample gives a narrow band in the OH region of the IR spectrum, the shift in frequency of this band indicates the presence of hydrogen bonding, and the position of the hydroxyls engaged in the hydrogen bond should be identified. Cellulose–synthetic polymer blends have been extensively studied. Nishio *et al.* reported that cellulose is miscible with several synthetic polymers including polyacrylonitrile,[11] poly(vinyl alcohol) (PVA),[12,13] poly(ϵ-caprolactone),[14] and poly(ethylene oxide) (PEO)[15,16] using wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and dynamic mechanical measurements. These studies were not an approach on the OH regiochemistry of the cellulose component as mentioned above. Our other concern is that PVA has OH groups in the side chain and PEO has ether bonds in the backbone structure. Since cellulose has two sites (hydroxyls and ring ether bonds) for the formation of hydrogen bonds in the side chain and skeleton, a pair of studies of the interaction between cellulose and PVA or PEO can not only clarify the polymer–polymer interaction in the blends but can also give a suggestion of the intra- and intermolecular hydrogen-bonding formation of cellulose molecules among themselves.



	R^2	R^3	R^6
(A)	H	H	H
(B)	CH_3	CH_3	H
(C)	H	H	CH_3

Figure 1. Chemical structures of (A) cellulose, (B) 2,3-di-*O*-methylcellulose, and (C) 6-*O*-methylcellulose.

Experimental Section

Materials. The cellulose samples, 2,3-di-*O*-methylcellulose (Figure 1B) and 6-*O*-methylcellulose (Figure 1C), were prepared

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by the methods reported previously.[9,10] Each polymer has a uniform structure. The weight-average molecular weight of both samples with approximately 2 × 10^4 on the basis of their GPC elution curves calibrated with polystyrene standards. The cellulose sample was a bleached sulfite pulp with a degree of polymerization of 935. Poly(ethylene oxide) was a Carbowax poly(ethylene glycol) sample with a nominal molecular weight of 20 000, purchased from Fisher Scientific. Poly(vinyl alcohol) (M_w 25 000; Fisher Scientific) was used after treatment in a 40% NaOH solution to remove residual acetyl groups. HPLC-grade, *N,N*-dimethylacetamide (DMAc; Aldrich Chemical Co., Inc.) was used without further purification.

Preparation of Samples. DMAc was used as the common solvent for all samples except for pure cellulose. Solution concentrations were 0.8 wt % for the cellulosic samples and 2 wt % for the synthetic polymer samples. All solutions were filtered and stored in a closed container.

Separately prepared solutions of the cellulosic and the synthetic polymers were mixed at room temperature in the desired proportions. The relative compositions of the two polymers in the mixed solutions were 80/20, 65/35, 50/50, and 30/70 by weight (cellulosic–synthetic polymers). After stirring for more than 3 days, the mixed solutions were used to prepare blend films by casting. One gram of each blended solution was poured into a flat-bottomed tray, left at room temperature, and heated up to 50 °C in air for 3 days. The DMAc solvent was evaporated to yield an as-cast film. It was further dried for 2 days under high vacuum at 50 °C to completely remove residual DMAc from the film and stored in a desiccator. Pure cellulose film was prepared by casting of a LiCl–DMAc cellulose solution[12] and subsequent washing and drying. The films were provided for measurements of FTIR. THe films prepared in the same way were heated up to 95 °C for cellulosic–PEO blends and to 230 °C for cellulosic–PVA blends, respectively, held at those temperatures for 7 min, and then quenched to 20 °C. The heat-treated films were also provided for FTIR measurements.

Measurements. Wide-angle X-ray diffraction patterns were recorded with a flat-film camera using nickel-filtered Cu Kα radiation produced by a Philips X-ray generator.

Fourier transform infrared (FTIR) spectra were obtained with a Nicolet 7199 FTIR spectrophotometer. The wavenumber range scanned was 4000–400 cm^{-1}; 64 scans of 2-cm^{-1} resolution were signal averaged and stored. Synthesized IR spectra were made by addition or subtraction of the two homopolymer spectra depending on the composition. The films used in this study were sufficiently thin to obey the Beer–Lambert law.[17]

Results and Discussion

1. Methylcellulose Samples as Models for Cellulose in Blends. There are three different hydroxyl groups in cellulose, and these groups take part in inter- and intramolecular hydrogen bonding. Thus, in general, cellulose displays a broad IR peak, due to a range of OH stretching vibrations (curve A in Figure 2). The 2,3-di-*O*-methylcellulose and 6-*O*-methylcellulose have fewer different hydroxyls, with diminished possibilities for hydrogen bonding, and as a result they both show narrow OH stretching vibration bands (curves B and C in Figure 2, respectively). The 6-*O*-methylcellulose absorption band is especially narrow and symmetric. One reason may be the formation of specific intramolecular hydrogen bonds between OH at the C-3 position and the neighboring ring oxygen (O-5) and between OH at the C-2 position and the ether oxygen of OCH_3 at the C-6 position.[18] On the other hand, the OH groups at the C-6 position in the 2,3-di-*O*-methylcellulose may form a range of intermolecular hydrogen bonds, giving a broader band. With these samples, shifts in the OH stretching frequency can be detected because of the narrow bands, and it is possible to investigate interactions of primary and secondary OH groups at the C-2, C-3, and C-6 positions.

The WAXD measurement of all homopolymers and their blend samples showed very diffused reflection patterns, indicating that they were predominantly amorphous,[11] as expected for celluloses regenerated in nonaqueous media.[19-22] In addition, heat-treated films showed the same IR spectra as those of as-cast films in the range of OH frequencies. Thus, morphological contributions of the samples should be negligible for interpretations of the following FTIR results.

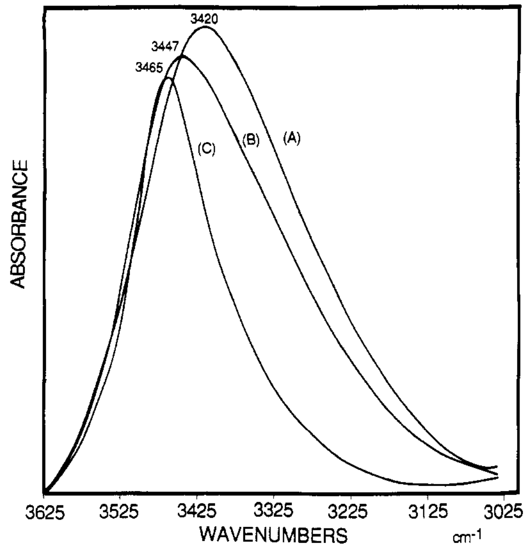


Figure 2. IR spectra of (A) a cellulose film, (B) a 2,3-di-*O*-methyl-cellulose film, and (C) a 6-*O*-methylcellulose film in the region of the OH stretching vibration.

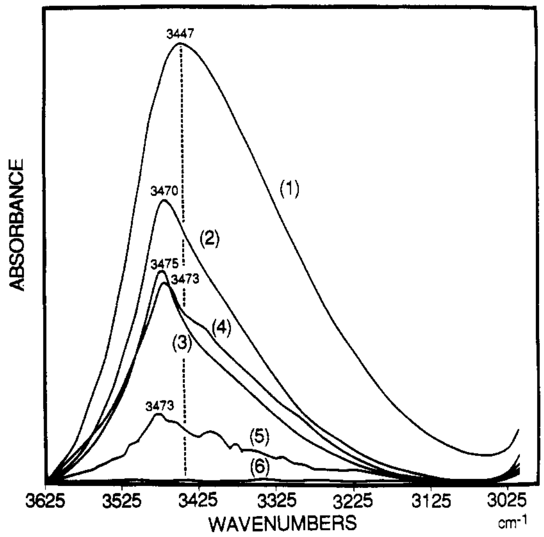


Figure 3. IR spectra of 2,3-di-*O*-methylcellulose–PEO blend films in the range of OH frequencies: (1) 100/0, (2) 80/20, (3) 65/35, (4) 50/50, (5) 30/70, (6) 0/100.

2. FTIR Characterization of Cellulosic–PEO Blends. The specific hydrogen-bonding interactions in the methylcellulose (cellulosic)–PEO blend system were examined by FTIR spectroscopy. The spectra of the film samples are shown in Figures 3–5.

(a) 2,3-Di-*O*-methylcellulose–PEO Blend. Figure 3 shows the OH bands for each blend sample. The intensity of the OH absorption bands increased with increasing cellulosic. The peak maxima of the blend samples shifted to higher wavenumbers by more than 20 cm^{-1} from the position of the OH absorption band of the 2,3-di-*O*-methylcellulose homopolymer. Because 2,3-di-*O*-methylcellulose has only a primary OH group at the C-6 position of the anhydroglucose unit and PEO has no significant OH absorption band, this shift must be due to the interaction occurring with the OH groups at the C-6 position of cellulose. The peak maxima for the blend samples did not change significantly with increasing PEO content, but the shape of the OH absorption bands differed

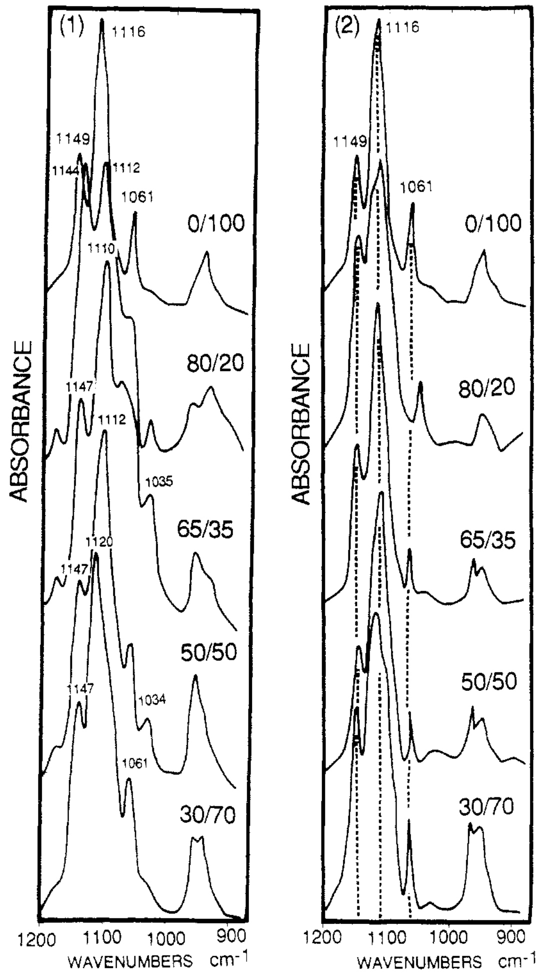


Figure 4. Change of the IR spectra of C–O–C frequencies in PEO synthesized by subtracting the spectrum of cellulose homopolymer samples: (1) 2,3-di-*O*-methylcellulose–PEO blend system; (2) 6-*O*-methylcellulose–PEO blend system.

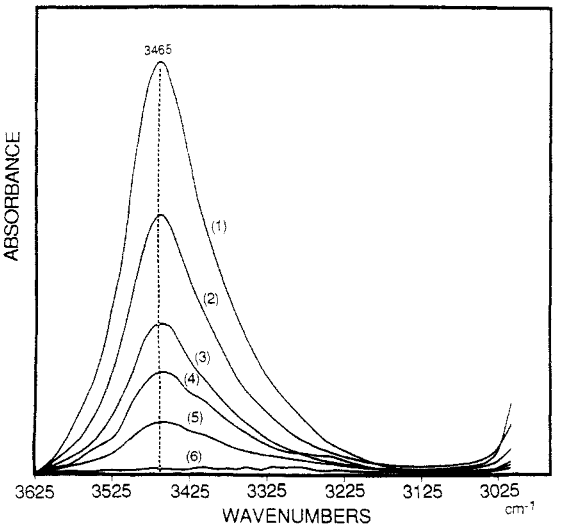
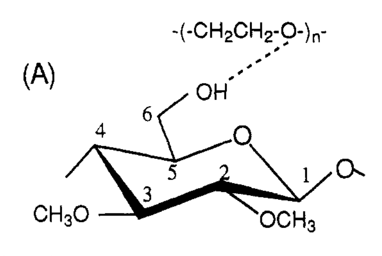
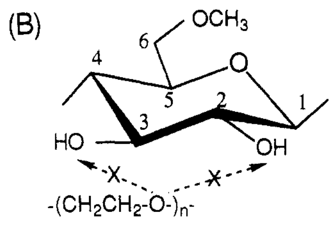


Figure 5. IR spectra of 6-*O*-methylcellulose–PEO blend films in the range of OH frequencies: (1) 100/0, (2) 80/20, (3) 65/35, (4) 50/50, (5) 30/70, (6) 0/100.

considerably (curves 2–5 in Figure 3). This suggests that a rearrangement of the hydrogen bonding occurred with a change of the composition. Figure 4, part 1, shows the change of the spectra of C–O–C frequencies in PEO, synthesized by subtracting the spectrum of 2,3-di-*O*-methylcellulose from that of blend film samples. The C–O–C stretching vibrations of all the blended films changed significantly from those of the PEO homopolymer, suggesting a perturbation of the PEO due to hydrogen bonding. Furthermore, with increasing the PEO content in the blends, the C–O–C bands changed markedly. This can be attributed to conformational changes in the PEO chain. These qualitative results indicate that the primary OH groups at the C-6 position of cellulose engage in a strong hydrogen-bonding interaction with the ether oxygen in the PEO skeleton as shown in Figure 6A.



2,3-di-*O*- methyl cellulose / Poly(ethylene oxide)



6-*O*- methyl cellulose / Poly(ethylene oxide)

Figure 6. Proposed hydrogen-bonding schemes for a cellulose–PEO blend system.

(b) 6-*O*-Methylcellulose–PEO Blend. Figure 5 shows that the peak maxima (3465 cm^{-1}) of the OH absorption bands of the blend samples did not shift with PEO content, and the peak shape of each blend did not change. There is, of course, a marked change in intensity. The difference spectra in Figure 4, part 2, also show that the C–O–C frequencies in the blends did not shift from that of the PEO homopolymer. Since this OH band absorption is only due to the OH groups at the C-2 and C-3 positions of cellulose, Figures 4, part 2, and 5 demonstrate an apparent absence of interaction between the OH groups in 6-*O*-methylcellulose and the ether oxygen in the PEO skeleton (Figure 6B).

3. FTIR Characterization of Cellulose–PVA Blends. The IR spectra of the blend films are shown in Figures 7–9. There are two functional groups for the hydrogen-bond formation in the anhydroglucose unit of cellulose: hydroxyls and ring oxygens (Figure 1A). Figures 7 and 8 show the comparison of the OH bands in the real spectra and the spectra synthesized by addition of the spectra of the two homopolymers. In Figure 9, we will discuss interactions between the ring oxygen in cellulose (as an electron donor) and the hydroxyl groups in PVA (as an electron acceptor), as discussed in the cellulose–PEO blend section.

(a) 2,3-Di-*O*-methylcellulose–PVA Blend. In curves 3–6 of Figure 7, the real spectra of OH frequencies differed very slightly from the synthesized ones with the change of the composition, suggesting that there is not significant hydrogen-bond formation between hydroxyls at the C-6 position of cellulosic and in the PVA. On the other hand, the variety of C–O bands and particularly the shift of peak top of the C–O bands in Figure 9, part 1, suggest that there is a particular hydrogen bond between OH groups in the PVA and oxygen in the cellulosic. In this case, there should be the shift of the OH groups in the PVA, but is was not clear in Figure 7. The shifted OH groups in the PVA may overlap with the hydroxyls of the cellulosic and apparently not be observed. Here, the interacting oxygen in the cellulosic could be either the ring oxygen

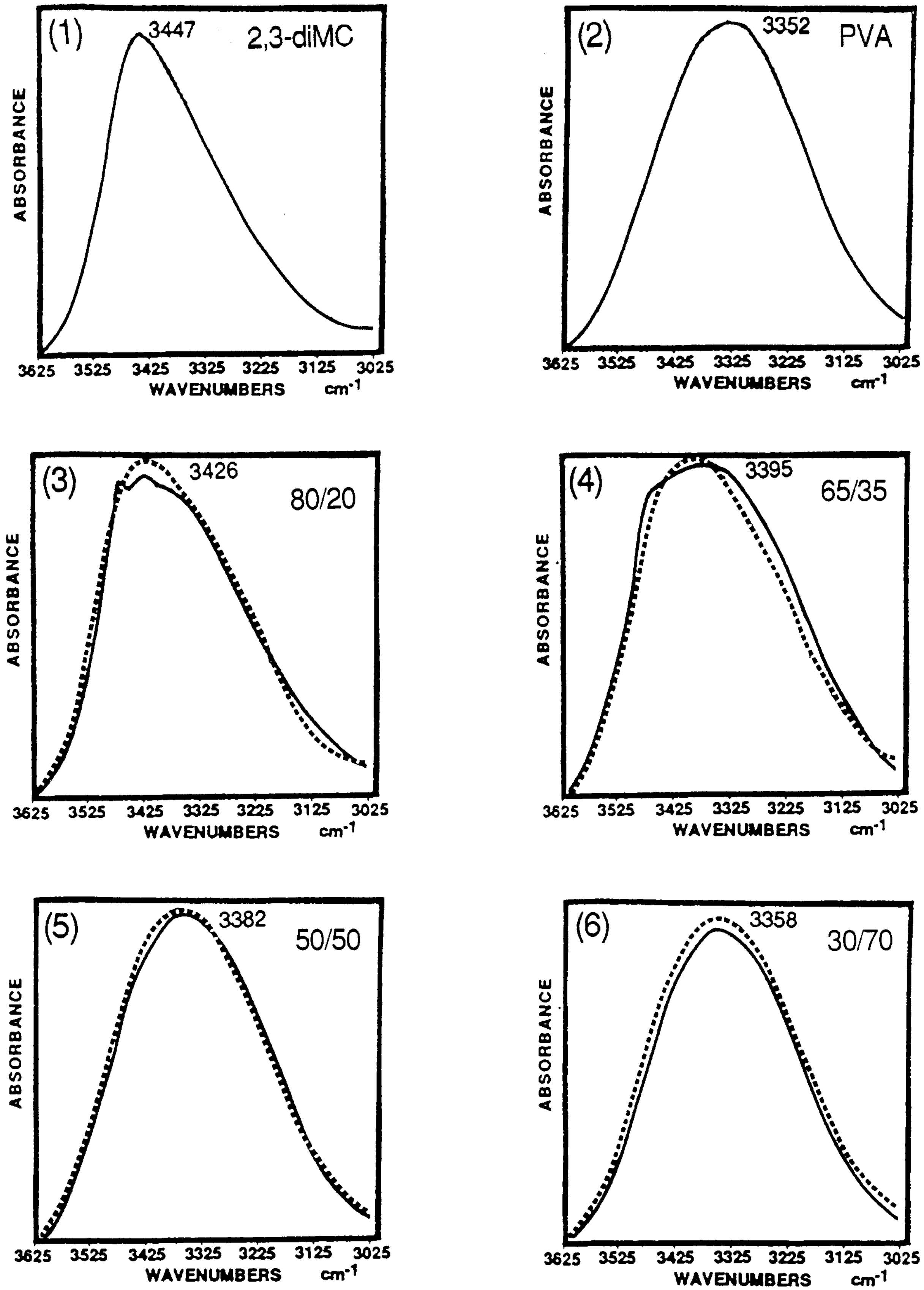


Figure 7. Comparison between the real spectra (solid line) and the spectra (dotted line) synthesized by addition of the spectra of two homopolymers in the 2,3-di-*O*-methylcellulose–PVA blends: (1) 100/0, (2) 0/100, (3) 80/20, (4) 65/35, (5) 50/50, (6) 30/70.

(O-5), the glucosidic linkage oxygen, or the methyl ether oxygen (OCH_3) (Figure 1B). To identify the oxygen, investigation of the 6-*O*-methylcellulose–PVA blend system was needed. Figure 9, part 2, of the 6-*O*-methylcellulose–PVA blend films, shows that C–O absorption does not change with the change of the composition. This suggests that the OH groups in the PVA did not interact with the oxygens in 6-*O*-methylcellulose: OCH_3 at the C-6 position, O-5, and glucosidic linkage oxygen. Of the three oxygens, the ring oxygen (O-5) is the only oxygen that can be affected stereochemically by the substitution of the OH groups at the C-6 position of the glucose unit. In other words, the ring oxygen can be the oxygen interacting with the OH groups of the PVA in the 2,3-di-*O*-methylcellulose–PVA blends, and the other two oxygens are intact. Interestingly, the OH groups in the

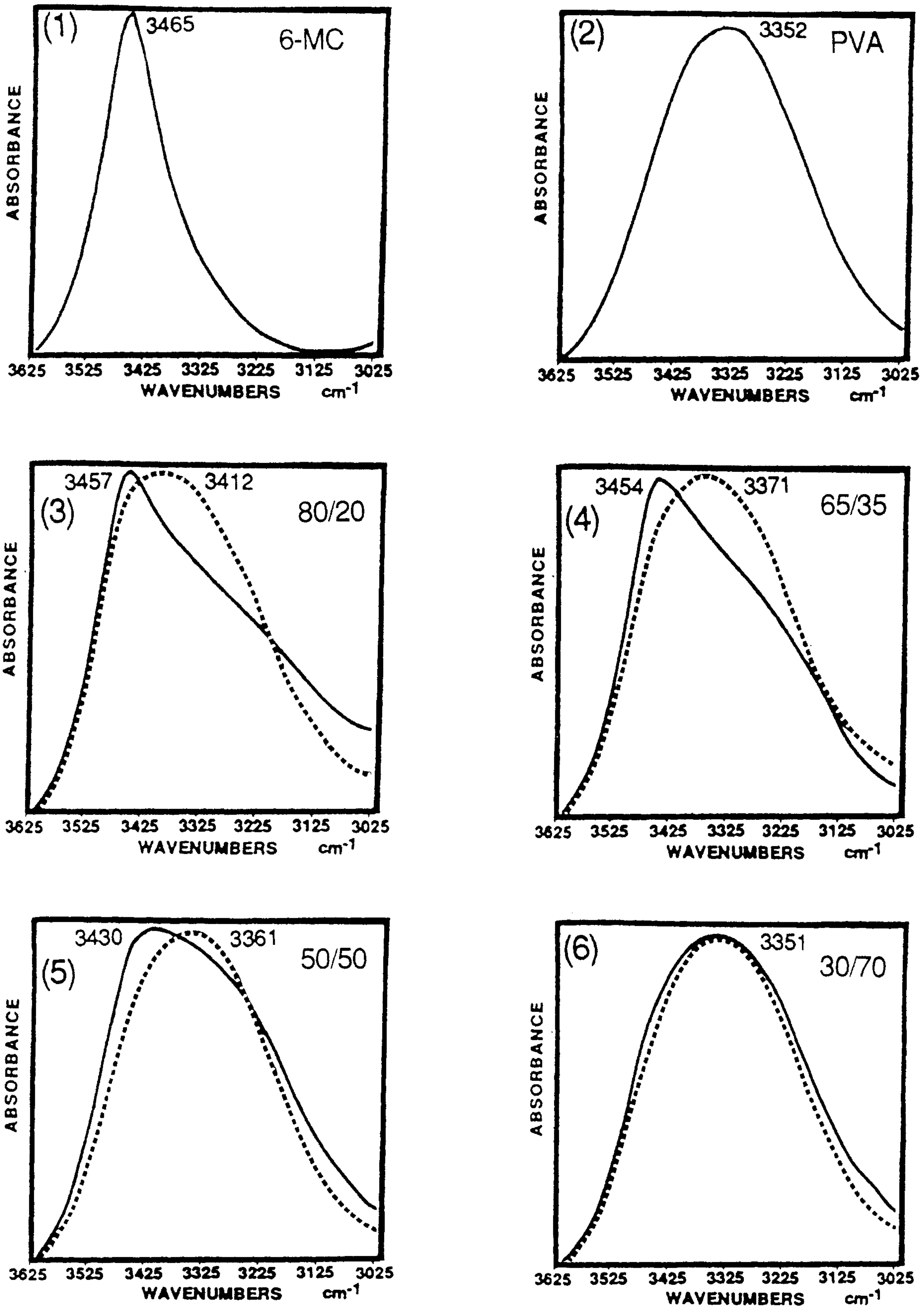


Figure 8. Comparison between the real (solid line) and the synthesized spectra (dotted line) in 6-*O*-methylcellulose–PVA blends: (1) 100/0, (2) 0/100, (3) 80/20, (4) 65/35, (5) 50/50, (6) 30/70.

PVA selectively engaged in a hydrogen bond with the ring oxygen, not with the hydroxyl groups at the C-6 position of cellulose (Figure 10).

(b) 6-*O*-Methylcellulose–PVA Blend. Notable differences between the real and the synthesized spectra appeared in the region of OH stretching vibrations of Figure 8 (traces 3–6), though there was no shift of C–O frequencies in Figure 9, part 2, as already described in the above section. This indicates that there is hydrogen bonding in the secondary hydroxyls at either the C-2 or the C-3 positions and at the side chain of PVA. According to Marchessault and Liang,[3,4,6] OH groups at the C-3 position in cellulose easily form an intermolecular hydrogen bond with the neighboring O-5, and in addition the polarity of OH groups at the C-2 position is higher. Thus, it is more feasible that the OH groups of the PVA should

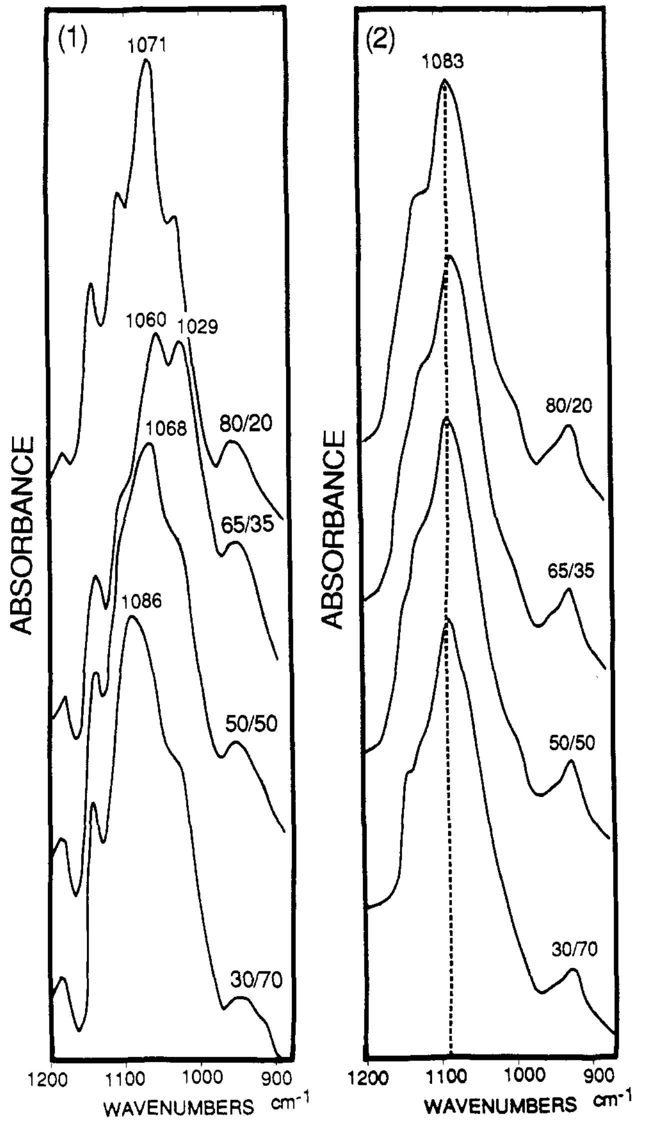


Figure 9. IR spectra of both (1) 2,3-di-*O*-methylcellulose–PVA and (2) 6-*O*-methylcellulose–PVA blend systems in the range of C–O frequencies.

interact with the OH groups at the C-2 position rather than that at the C-3 position of the cellulosic (Figure 10).

In the blends with a large content of the synthetic polymer components such as the composition of 30/70 and more, the absence of interchain interaction was observed for both 2,3-di-*O*- and 6-*O*-methylcellulose–PVA blend systems. The phenomenon can also occur in the cellulosics–PEO system. This appears to be due to microphase separation of the components.

Conclusions

IR examination of the blend films with regioselectively substituted *O*-methylcellulose, 2,3-di-*O*-methylcellulose, and 6-*O*-methylcellulose as cellulose model samples clarified the formation of hydrogen bonds in terms of the hydroxyl regiochemistry of cellulose. From the results, the hydrogen-bonding formations in pure cellulose–PEO or –PVA were estimated and the following conclusions 1–4 were drawn.

1. The flexible and primary OH groups at the C-6 position of the cellulosic engaged in a strong hydrogen bonding with the ether oxygen in the skeleton of PEO. However, the secondary OH groups at the C-2 and C-3 positions of the cellulosic did not form a significant interaction with the ether linkage oxygen of PEO. This suggests that, in pure cellulose–PEO blends, a hydrogen bond engaged at the C-6 position of the cellulose component should be more favorable than that at the C-2 and C-3 positions.

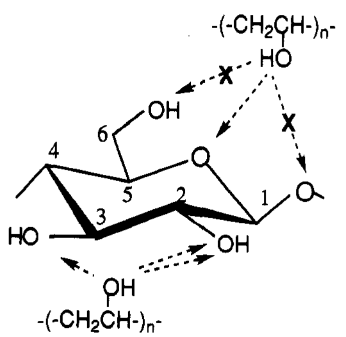


Figure 10. Proposed hydrogen-bonding scheme for the cellulose–PVA blend system.

2. In the pure cellulose–PVA blend system, there appears to be two types of hydrogen bonds: (i) hydrogen bonding between the OH groups at either the C-2 or the C-3 position of cellulose and the side-chain OH groups of PVA (this interaction is considered to form mainly at the C-2 position of cellulose); and (ii) hydrogen bonding between the ring oxygen (O-5) of cellulose and the OH groups in PVA (this interaction appeared to be stereohindered by the substitution of OH at the C-6 position).

3. These results showed that the formation of hydrogen bonds in cellulose–synthetic polymer blends depends on the specific regiochemistry of hydroxyl groups and glucose ring oxygen in the cellulose component.

4. On the basis of the above IR results with cellulose model compounds, cellulose was miscible with both crystalline synthetic polymers, PEO and PVA, at the molecular level as previously reported thermodynamically by Nishio and Manley.[12,13,15]

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