

# Miscible Chitosan/Tertiary Amide Polymer Blends

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**ABSTRACT:** The miscibility of five chitosan/tertiary amide polymer blend systems was studied. Based on the optical transparency of the blend and the existence of a single glass transition temperature, chitosan was found to be miscible with poly(*N*-vinyl-2-pyrrolidone), poly(*N*-methyl-*N*-vinylacetamide), poly(*N,N*-dimethylacrylamide), poly(2-methyl-2-oxazoline), and poly(2-ethyl-2-oxazoline). Fourier transform infrared spectroscopy showed the existence of hydrogen-bonding interactions between chitosan and the tertiary amide polymers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1785–1790, 2000

**Key words:** chitosan; tertiary amide polymers; miscibility

## INTRODUCTION

Polymer blending offers a convenient means to prepare materials with a wide range of properties. Through a suitable choice of a pair of polymers, polymer blends can often be tailor-made to have specific and desirable properties. Blends of natural and synthetic polymers for biomedical applications are often called bioartificial polymeric materials.<sup>1</sup> In general, polymers are immiscible with each other in the absence of specific interactions. The miscibility of a polymer blend is commonly ascertained by measurement of its glass transition temperature ( $T_g$ ). A miscible polymer blend shows a composition-dependent  $T_g$ , while an immiscible blend shows two  $T_g$ 's corresponding to those of the component polymers. For applications where mechanical integrity is required, miscible single-phase polymer blends are desirable. For some applications such as toughening of plastics, two-phase immiscible blends are required.

Chitin is the second most abundant natural biopolymer, next only to cellulose.<sup>2</sup> Chitosan is

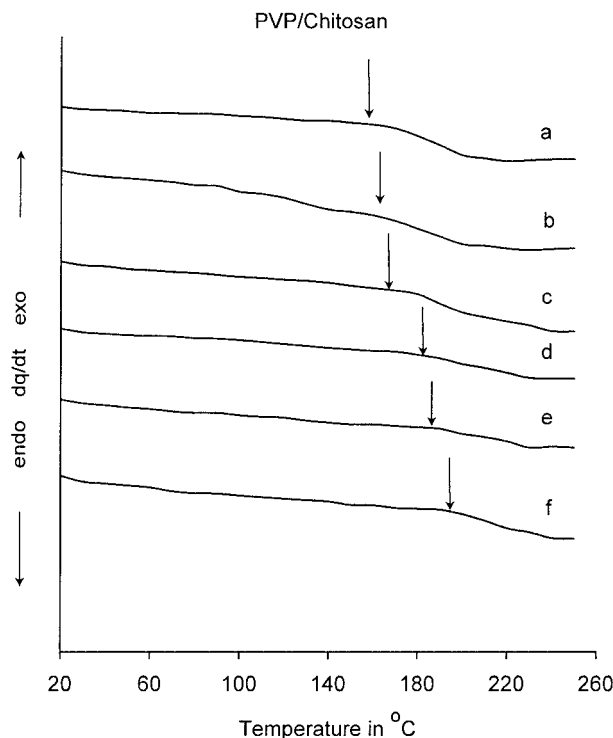
the deacetylated product of chitin, normally with a degree of deacetylation greater than 50%. Blends of chitosan with cellulose,<sup>3,4</sup> polyamides,<sup>5,6</sup> poly(vinyl alcohol) (PVA),<sup>7–9</sup> and poly(ethylene oxide)<sup>10</sup> have been studied. Chitosan/cellulose blends are transparent and the two polymers mix intimately as shown by scanning electron microscopy.<sup>4</sup> Chitosan is partially miscible with polyamide-4, but immiscible with polyamide-6.<sup>5</sup> Chitosan/PVA blends are homogeneous and have tensile strength greater than the sum of the component values.<sup>7</sup>

Poly(*N*-vinyl-2-pyrrolidone) (PVP), a tertiary amide polymer, is miscible with hydroxyl-containing polymers such as poly(*p*-vinylphenol) (PVPh),<sup>11</sup> PVA,<sup>12,13</sup> poly(hydroxyether of bisphenol-A),<sup>14–16</sup> and poly(2-hydroxypropyl methacrylate).<sup>17</sup> The amide carbonyl groups of PVP are capable of interacting with hydroxyl groups via hydrogen-bonding interactions, leading to miscibility. It is therefore likely that PVP may also interact with the hydroxyl and amino groups of chitosan to achieve miscibility. Qurashi et al.<sup>18,19</sup> used chitosan/PVP blends as membranes for dialysis. They reported that the membranes were transparent and there was no separation of PVP at any temperature based on differential scan-

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**Figure 1** DSC curves of chitosan/PVP blends containing (a) 0, (b) 10, (c) 25, (d) 50, (e) 75, and (f) 90 wt % of chitosan.

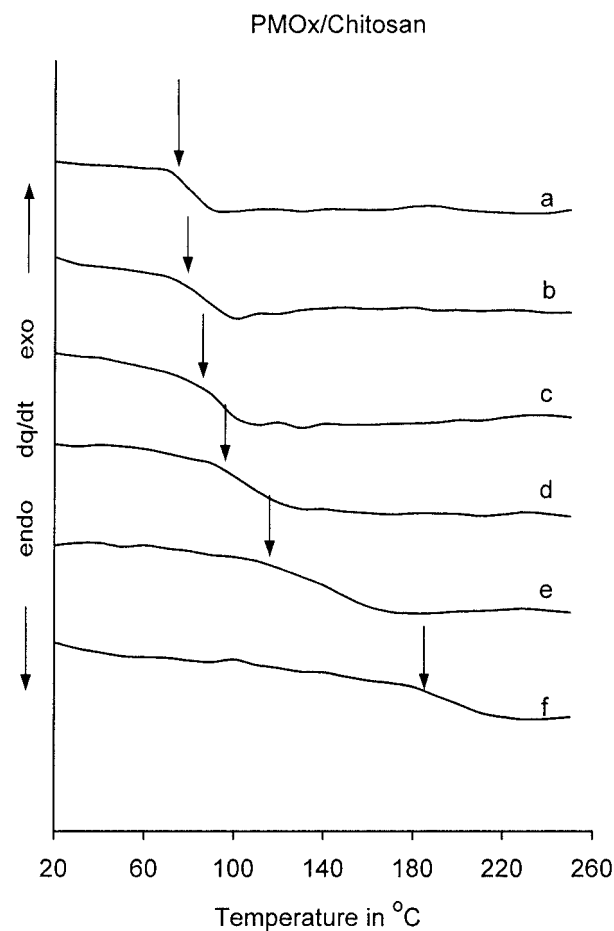
ning calorimetric (DSC) measurements. However, the miscibility of chitosan/PVP blends was not ascertained because all the blends as well as PVP did not show distinct glass transitions. Furthermore, they reported a decomposition temperature of 149°C for PVP. Their results are rather surprising because PVP is known to show a distinct  $T_g$  of about 170°C.<sup>11-17,20</sup> PVP is hygroscopic and its  $T_g$  value is sensitive to residual moisture in the sample.<sup>20</sup> As a result, an incompletely dried PVP and its blends show anomalous DSC curves and  $T_g$  values. The chitosan/PVP blend samples prepared by Qurashi et al.<sup>18</sup> were dried in air, presumably at room temperature. Such a drying process might not be able to produce completely dried samples.

We reexamined the miscibility of chitosan/PVP blends and the results are presented in this article. In addition, we also report the miscibility of chitosan with four other tertiary amide polymers, namely, poly(*N*-methyl-*N*-vinylacetamide) (PMVAc), poly(*N,N*-dimethylacrylamide) (PDMA), poly(2-methyl-2-oxazoline) (PMOx), and poly(2-ethyl-2-oxazoline) (PEOx). The four tertiary

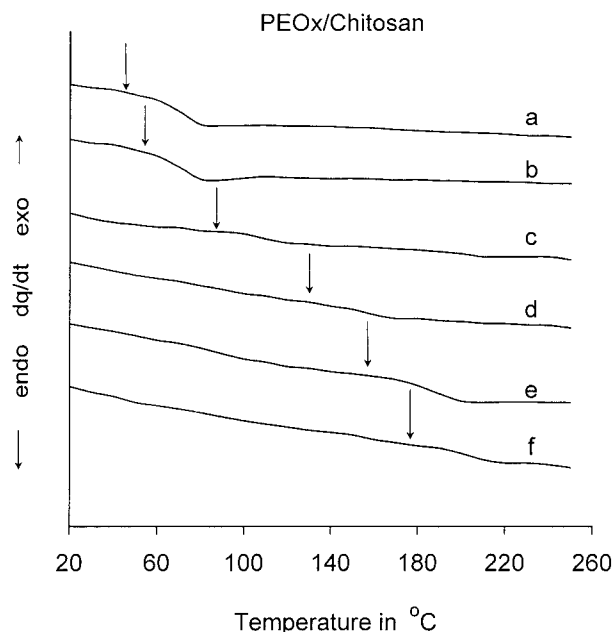
amide polymers are also miscible with hydroxyl-containing polymers.<sup>16,17,21-29</sup> It is of interest to note that Cao et al.<sup>30,31</sup> recently reported that chitosan acetate salt is miscible with PVP. The blends were clear and interactions between the two polymers were evidenced from an infrared spectroscopic study.

## EXPERIMENTAL

Chitosan with a reported degree of deacetylation of 76%<sup>9</sup> was purchased from the Tokyo Chemical Industry Co. (Tokyo, Japan). PVP and PEOx were purchased from the Aldrich Chemical Co. (Milwaukee, WI). PMVAc, PDMA, and PMOx were prepared in our laboratory as described previously.<sup>17,21-23</sup> The weight-average molecular



**Figure 2** DSC curves of chitosan/PMOx blends containing (a) 0, (b) 10, (c) 25, (d) 50, (e) 75, and (f) 90 wt % of PMOx.



**Figure 3** DSC curves of chitosan/PEOx blends containing (a) 0, (b) 10, (c) 25, (d) 50, (e) 75, and (f) 90 wt % of chitosan.

weights of PVP, PMVAc, PDMA, PEOx, and PMOx are 40, 3.7, 19.6, 61.2, and 18.5 kg/mol, respectively; their  $T_g$  values are 166, 136, 118, 56, and 65°C, respectively.

Various chitosan/tertiary amide polymer blends were prepared by solution casting from 90% formic acid. Initial dissolution of the polymers was done on a hot plate at about 80°C. The solvent was then allowed to evaporate slowly at room temperature, followed by further drying *in vacuo* at 90°C for 2 weeks. All the blends were stored in a desiccator to prevent moisture absorption.

The  $T_g$ 's of various samples were determined with a DuPont 910 differential scanning calorimeter using a heating rate of 20°C/min in a nitrogen atmosphere. Each sample was scanned several times between 20 and 250°C to check the reproducibility of the  $T_g$  values. The initial onset of the change of the slope of the DSC curve was taken as the  $T_g$ .

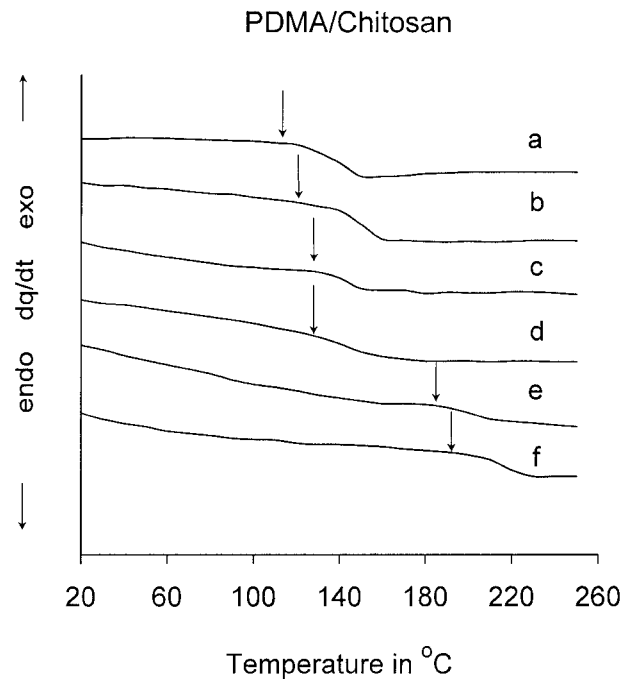
Samples for Fourier transform infrared (FTIR) spectroscopic characterization were prepared by grinding the dry blends with KBr and compressing the mixtures to form disks. The KBr disks were dried *in vacuo* at 90°C for 3 days. Infrared spectra were acquired with a Bio-Rad FTS165 FTIR spectrophotometer. Thirty-two scans were

signal-averaged at a resolution of 2 cm<sup>-1</sup>. To eliminate moisture absorption during the measurements, spectra were recorded at 105°C using an SPECAC high-temperature cell equipped with an automatic temperature controller which was mounted on the spectrophotometer. The optical appearance of the blends was examined using an Olympus BH2-UMA optical microscope with a magnification of 50×.

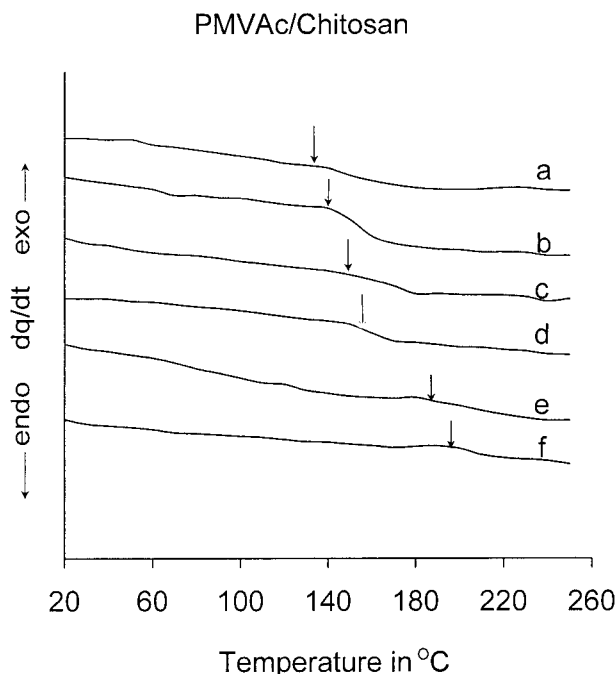
## RESULTS AND DISCUSSION

All the binary chitosan/tertiary polymer blends were transparent as examined by optical microscopy. Optical clarity is a good indication but not absolute proof of miscibility. An immiscible blend may be transparent if the two component polymers have identical refractive indices.

The existence of a single  $T_g$  in a polymer blend is the most commonly used criterion for miscibility. However, we had difficulty detecting with certainty the  $T_g$  of chitosan by DSC. Other researchers also encountered a similar difficulty in determining the  $T_g$  of chitosan.<sup>6,9,32</sup> Since all the tertiary amide polymers show distinct  $T_g$ 's, the



**Figure 4** DSC curves of chitosan/PDMA blends containing (a) 0, (b) 10, (c) 25, (d) 50, (e) 75, and (f) 90 wt % chitosan.



**Figure 5** DSC curves of chitosan/PMVAc blends containing (a) 0, (b) 10, (c) 25, (d) 50, (e) 75, and (f) 90 wt % of chitosan.

inability to detect the  $T_g$  of chitosan is not really a problem in order to ascertain the miscibility of the blends. If the chitosan/tertiary amide polymer blend is miscible, the  $T_g$  value of the blend will shift away from that of the tertiary amide polymer with increasing chitosan content in the blend. Conversely, if the chitosan/tertiary amide polymer blend is immiscible, the  $T_g$  value of the blend will remain unchanged as to that of the tertiary amide polymer.

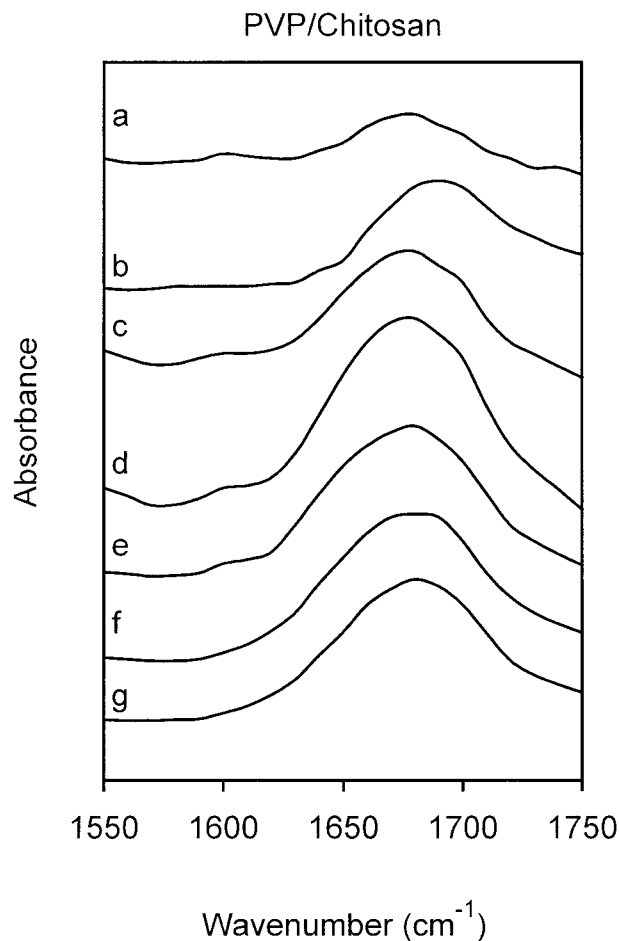
Figures 1–5 show the DSC curves of the five binary blend systems. In all cases, each blend showed a single glass transition and its value shifted away from that of the tertiary amide polymer with increasing chitosan content. Thus, the optical clarity and the existence of a single glass transition of the blend show that chitosan is miscible with all the five tertiary amide polymers.

The formation of a miscible polymer blend requires the presence of specific interactions between the two polymers. Tertiary amide polymers are able to form hydrogen-bonding interactions with hydroxyl-containing polymers through their amide carbonyl groups. Such interactions are evidenced by FTIR studies as manifested by a low-frequency shift of the carbonyl band.<sup>26–28</sup> However, when the hydrogen-bonding interaction is sufficiently strong, a new hydrogen-bonded car-

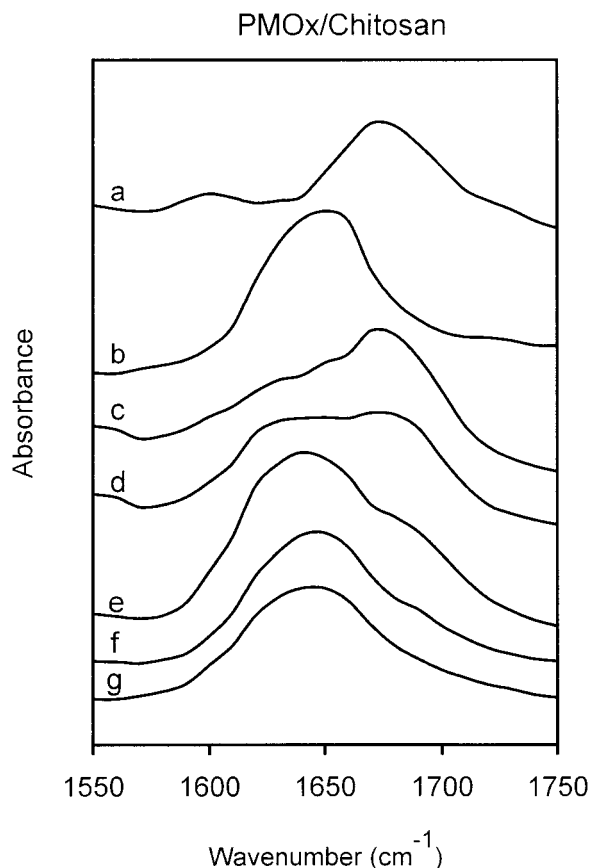
bonyl band located at a lower frequency develops.<sup>24,25,33</sup>

The hydroxyl and the amino groups of chitosan are capable of interacting with the amide carbonyl groups of the tertiary amide polymers. However, the O—H and N—H stretching bands of chitosan overlap in the 3000–3600  $\text{cm}^{-1}$  region. It is therefore difficult to observe the changes of these bands upon blending. Nevertheless, evidence of hydrogen-bonding interactions can be found from the change of the amide carbonyl band.

Figure 6 shows the FTIR spectra in the carbonyl region recorded at 105°C of the chitosan/PVP blends. The spectrum of chitosan shows a strong absorption band at 1676  $\text{cm}^{-1}$  (amide I) and a weak band at 1599  $\text{cm}^{-1}$  (amine deformation). The asymmetrical bending band of  $\text{NH}_3^+$  may also contribute to the 1599  $\text{cm}^{-1}$  band since the chitosan sample was cast from formic acid.



**Figure 6** FTIR spectra in the carbonyl region of (a) chitosan, (b) PVP, and chitosan/PVP blends containing (c) 90, (d) 75, (e) 50, (f) 25, and (g) 10 wt % of chitosan.



**Figure 7** FTIR spectra in the carbonyl region of (a) chitosan, (b) PMOx, and chitosan/PMOx blends containing (c) 90, (d) 75, (e) 50, (f) 25, and (g) 10 wt % of chitosan.

The amide carbonyl band of PVP absorbs at  $1690\text{ cm}^{-1}$ , which is quite close to the carbonyl band of chitosan. As a result, each of the chitosan/PVP blends shows a single carbonyl band. Nevertheless, the maximum of the carbonyl band shifts gradually with the blend composition, indicating the presence of interactions between the two polymers.

The amide carbonyl bands of the other four tertiary amide polymers are located at lower frequencies as compared to that of PVP. Figure 7 shows the FTIR spectra of the chitosan/PMOx blends. The amide carbonyl band of PMOx absorbs at  $1647\text{ cm}^{-1}$ , and the band shifts gradually to a lower frequency with increasing chitosan content in the blend. For example, the carbonyl band of PMOx shifted to  $1636\text{ cm}^{-1}$  for a blend containing 50 wt % of chitosan. The low-frequency shift of the amide carbonyl band of PMOx clearly shows that the carbonyl groups of PMOx are interacting with chitosan, leading to miscibility. The FTIR spectra of the other three blend systems also show

gradual shifts of the carbonyl bands of PEOx, PMVAc, and PDMA; the spectra are not shown here.

In conclusion, chitosan is miscible with PVP, PMOx, PEOx, PDMA, and PMVAc based on the optical transparency of the blends and the existence of a composition-dependent  $T_g$  in each blend. Evidence of hydrogen-bonding interactions in various blends is exemplified by the shift of the amide carbonyl band of the tertiary amide polymer.

## REFERENCES

1. Lazzeri, L. *Trends Polym Sci* 1996, 4, 249.
2. Peter, M. G. *J Macromol Sci Pure Appl Chem A* 1995, 32, 629.
3. Hasegawa, A.; Isogai, A.; Onabe, F.; Usuda, M.; Atalla, R. H. *J Appl Polym Sci* 1992, 45, 1873.
4. Isogai, A.; Atalla, R. H. *Carbohydr Polym* 1992, 19, 25.
5. Ratto, J. A.; Chen, C. C.; Blumstein, R. B. *J Appl Polym Sci* 1996, 59, 1451.
6. Ko, M. J.; Jo, W. H.; Kim, H. C.; Lee, S. C. *Polym J* 1997, 29, 997.
7. Miya, M.; Iwamoto, R.; Mima, S. *J Polym Sci Polym Phys Ed* 1984, 22, 1149.
8. Kim, J. H.; Kim, J. K.; Lee, Y. M.; Kim, K. Y. *J Appl Polym Sci* 1992, 44, 1823.
9. Kim, J. H.; Kim, J. K.; Lee, Y. M.; Kim, K. Y. *J Appl Polym Sci* 1992, 45, 1711.
10. Wang, W.; Roberts, G. A. F. *Adv Chitin Sci* 1997, 2, 561.
11. Moskala, E. J.; Varnell, D. F.; Coleman, M. M. *Polymer* 1985, 26, 228.
12. Peng, Z. H.; Nguyen, Q. T.; Neel, J. *Makromol Chem* 1989, 190, 437.
13. Peng, Z. H.; Nguyen, Q. T.; Neel, J. *Makromol Chem* 1990, 191, 185.
14. Eguiazabal, J. I.; Iruin, J. J.; Cortazar, M.; Guzman, G. M. *Makromol Chem* 1984, 185, 1761.
15. de Ilarduya, A. M.; Iruin, J. J.; Fernandez-Berridi, M. J. *Macromolecules* 1995, 28, 3707.
16. Dai, J.; Goh, S. H.; Lee, S. Y.; Siow, K. S. *Polymer* 1996, 37, 3259.
17. Dai, J.; Goh, S. H.; Lee, S. Y.; Siow, K. S. *J Appl Polym Sci* 1994, 53, 837.
18. Qurashi, M. T.; Blair, H. S.; Allen, S. J. *J Appl Polym Sci* 1992, 46, 255.
19. Qurashi, M. T.; Blair, H. S.; Allen, S. J. *J Appl Polym Sci* 1992, 46, 263.
20. Turner, D. T.; Schwartz, A. *Polymer* 1985, 26, 757.
21. Dai, J.; Goh, S. H.; Lee, S. Y.; Siow, K. S. *Polymer* 1993, 34, 4314.

22. Dai, J.; Goh, S. H.; Lee, S. Y.; Siow, K. S. *Polymer* 1994, 35, 2174.
23. Dai, J.; Goh, S. H.; Lee, S. Y.; Siow, K. S. *J Polym Res* 1995, 2, 209.
24. Meaurio, E.; Cesteros, L. C.; Katime, I. *Macromolecules* 1997, 30, 4567.
25. Meaurio, E.; Velada, J. L.; Cesteros, L. C.; Katime, I. *Macromolecules* 1996, 29, 4598.
26. Parada, L. G.; Cesteros, L. C.; Meaurio, E.; Katime, I. *Polymer* 1997, 39, 1019.
27. Parada, L. G.; Cesteros, L. C.; Meaurio, E.; Katime, I. *Macromol Chem Phys* 1997, 198, 2505.
28. Parada, L. G.; Meaurio, E.; Cesteros, L. C.; Katime, I. *Macromol Chem Phys* 1996, 199, 1597.
29. Wang, L. F.; Pearce, E. M.; Kwei, T. K. *J Polym Sci Part B Polym Phys* 1991, 29, 619.
30. Cao, S.; Shi, Y.; Chen, G. *Polym Bull* 1998, 41, 553.
31. Cao, S.; Shi, Y.; Chen, G. *J Appl Polym Sci* 1999, 74, 1452.
32. Guan, Y.; Liu, X.; Fu, Q.; Li, Z.; Yao, K. *Carbohydr Polym* 1998, 36, 61.
33. Lichkus, A. M.; Painter, P. C.; Coleman, M. M. *Macromolecules* 1988, 21, 2636.