

Cellulose/Chitin Films Blended in NaOH/Urea Aqueous Solution

Hua Zheng,¹ Jinping Zhou,² Yumin Du,¹ Lina Zhang²

¹Department of Environmental Science, Wuhan University, Wuhan 430072, China

²Department of Chemistry, Wuhan University, Wuhan 430072, China

Received 1 August 2001; accepted 28 January 2002

ABSTRACT: Regenerated cellulose/chitin blend films (RCCH) were satisfactorily prepared in 6 wt % NaOH/4 wt % urea aqueous solution by coagulating with 5 wt % CaCl₂ aqueous solution then treating with 1 wt % HCl. The structure, miscibility, and mechanical properties of the RCCH films were investigated by infrared, scanning electron microscopy, ultraviolet spectroscopies, X-ray diffraction, tensile test, and differential scanning analysis. The results indicated that the blends were miscible when the content of chitin was lower than 40 wt %. Moreover, the RCCH blend film achieved the maximum tensile strength in both dry and wet states of 89.1 and 43.7 MPa, respectively, indicating that the tensile strength and water resistivity of the RCCH film

containing 10–20 wt % chitin was slightly higher than that of the RC film unblended with chitin. Structural analysis indicated that strong interaction occurred between cellulose and chitin molecules caused by intermolecular hydrogen bonding. Compared to the mechanical properties of chitin film, those of the blend films containing 10–50 wt % chitin were significantly improved. This work provided a novel way to obtain directly chitin material blended in the aqueous solution. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1679–1683, 2002

Key words: cellulose; chitin; blend films; miscibility; mechanical properties

INTRODUCTION

Cellulose, of which nearly 200 billion tons are reproduced worldwide each year, is biodegradable, nontoxic, biocompatible, hydrophilic, and chiral. Therefore, making use of cellulose to produce various products not only can protect the environment from pollution but also can save limited oil resources because of its biodegradability and potential to substitute for some petrochemicals.¹ However, cellulose has not reached its potential application in many areas because of its infusibility and insolubility. For many decades, commercial viscose fibers and cellophane have been manufactured from cellulose xanthate, although the process is marked by problems of discharge of toxic gases and substances. Nowadays, the research and development of novel solvents of cellulose and functional materials based on cellulose have attracted much attention. Recently, a novel solvent of cellulose, 6 wt % NaOH/4 wt % urea aqueous solution,^{2,3} has been found, and the regenerated cellulose films and its

blends have been prepared successfully from both cotton linters with viscosity-average molecular weight (M_{η}) of 8×10^4 and from *Bemliese* with M_{η} of 11.2×10^4 .^{4,5}

Chitin, a (1→4)-linked *N*-acetamido-2-deoxy- β -D-glucan, is the second most abundant organic resource in nature,⁶ and has good biocompatibility,^{7,8} biodegradability,⁸ and various biofunctionalities including antithromoboyenic, homeostatic, immunity enhancing, and wound healing.^{9,10} A chitin fiber was prepared by spinning a solution of chitin, and the fiber has been commercialized as absorbable surgical suture having a wound-healing function. Therefore, many attempts have been made to produce new biofunctional materials from chitin and chitosan such as films, fibers, nonwoven fabric, sponge, and gel forms.^{10,11} Blending is an important process for developing industrial application of polymeric materials.¹² Blending cellulose with other polymers is a simple and effective way to prepare functional polymeric composites, such as blend fibers of cellulose and chitin in 14% NaOH aqueous¹³ and blend films of cellulose and chitin in LiCl-*N,N*-dimethylformamide solution.¹⁴

In the present study we attempt to use NaOH/urea aqueous solution as a common solvent of chitin and cellulose to prepare cellulose/chitin blend films. The structure, miscibility, and properties of the blend films were studied by infrared (IR), ultraviolet spectroscopies (UV), X-ray diffraction, scanning electron micros-

Correspondence to: Y. Du (duyumin@whu.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 29977014 and 59933070.

Contract grant sponsor: China Capital Group Co., Shanghai, China.

copy (SEM), differential scanning analysis (DSC), and tensile test.

EXPERIMENTAL

Materials

Bemliese, a bemcot nonwoven cloth made from cotton linters in curprammonium, was a gift of Asahi Chemical Industry Co. (Japan) and its viscosity-average molecular weight (M_η) was determined to be 1.12×10^5 by viscometry in cadoxen at 25°C according to $[\eta] = 3.85 \times 10^{-2} M_w^{0.76}$ (mL/g).¹⁵

A commercial chitin from crab shell was provided by Zhejiang Yuhan Ocean Biochemistry Co. (China) and its degree of acetylation (DA) was calculated to be 92.5% from the nitrogen content by the following equation¹⁶:

$$DA = 1 - [(W_C/W_N - 5.14)/1.72] \times 100\% \quad (1)$$

where W_C/W_N is the ratio of carbon to nitrogen.

The intrinsic viscosity ($[\eta]$) of the chitin sample was measured in *N,N*-dimethylacetamide (DMAc) containing 5 wt % LiCl at $25 \pm 0.1^\circ\text{C}$ by using a Ubbelohde viscometer, and the M_η was calculated to be 13.1×10^5 according to the Mark-Houwink equation¹⁷:

$$[\eta] = 2.4 \times 10^{-2} M_\eta^{0.69} \text{ (mL/g)} \quad (2)$$

Preparation of films

A cellulose solution in 6 wt % NaOH/4 wt % urea aqueous solution was prepared according to a previous method.^{2,3} A 40-g sample of *Bemliese* was scissored into small pieces, then dispersed in 6 wt % NaOH/4 wt % urea aqueous solution and stirred for 5 min to obtain a slurry. The cellulose slurry was stored in a refrigerator (-5°C) for about 24 h; the frozen solid was then thawed and stirred vigorously at room temperature. The resulting solution was subjected to filtration and degasification. A clear cellulose solution (I) with a concentration of approximately 3.5 wt % was obtained. A chitin solution in 10 wt % NaOH aqueous solution was prepared according to Hirano's method.¹³ Chitin (40 g) was immersed in 154 mL 46 wt % NaOH in an ice bath for about 6 h, after which ice pieces were added. After stirring and freezing at -5°C for 24 h, the frozen solid was thawed and stirred extensively at room temperature, and the resulting chitin solution (II), with a concentration of 3.5 wt %, was used to prepare films.

A mixture of I and II was further mixed and stirred, then filtered and degassed at $10\text{--}15^\circ\text{C}$. The mixed solution was cast onto a glass plate to give a thickness of 0.5 mm, then immediately immersed into 5 wt % CaCl_2 aqueous solution to coagulate for 30 min; it was

then subsequently treated with 1 wt % HCl aqueous solution for 5 min. The transparent membranes obtained were washed by running water and distilled water, and then dried in air. By changing the weight content of chitin, the blend films were coded as RCCH-1, RCCH-2, RCCH-3, RCCH-4, and RCCH-5 for 10, 20, 30, 40, and 50% of chitin, respectively. The pure cellulose and chitin films were prepared the same way and coded as RC and CH, respectively.

Characterization of films

IR spectra of the RC, CH, and RCCH blend films were recorded with a Nicolet 170SX FTIR spectrometer (Nicolet Instruments, Madison, WI). The test specimens were prepared by the KBr-disk method.

X-ray diffraction was measured with an X-ray diffractometer (D/MAX-1200, Rigaku Denki, Japan). X-ray diffraction patterns with Cu-K_α radiation at 40 kV and 50 mA were recorded in the range of $2\theta = 6\text{--}40^\circ$. The degree of crystallinity (χ_c) was calculated according to the usual method¹⁸:

$$\chi_c = A_c / (A_a + A_c) \times 100\%$$

where A_c is the area of the crystal region and A_a is the area of the amorphous region.

Vacuum-dried samples (10 mg) were weighed accurately in an aluminum pan and sealed hermetically. DSC of the films was measured by using a DSC-2C thermal analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT) with a heating rate of $10^\circ\text{C}/\text{min}$, from 50 to 800°C under nitrogen atmosphere.

Scanning electron micrographs (SEM) were taken with an S-570 SEM (Hitachi Co., Tokyo, Japan). The wet films were frozen in liquid nitrogen, snapped immediately, and then vacuum-dried. The fracture section, sputtered with gold, was observed and photographed. The light transmittance (T_r) of the films (thickness 35 μm at the wavelength range, 200–800 nm) were measured by using a UV-160A spectroscope (Shimadzu Co., Kyoto, Japan).

The tensile strength (σ_b) and breaking elongation (ε_b) of the films in both dry and wet states were measured on a universal testing machine (CMT8502, Shenzhen SANS Test Machine Co., China) according to ISO 6239-1986(E) at a speed of 10 mm/min. The wet films were measured immediately after soaking in water for 12 h. Water resistance (R) of the films was estimated by

$$R = \sigma_b \text{ (wet)} / \sigma_b \text{ (dry)} \quad (3)$$

where σ_b (wet) and σ_b (dry) are the tensile strength of the films in the wet and the dry state, respectively.

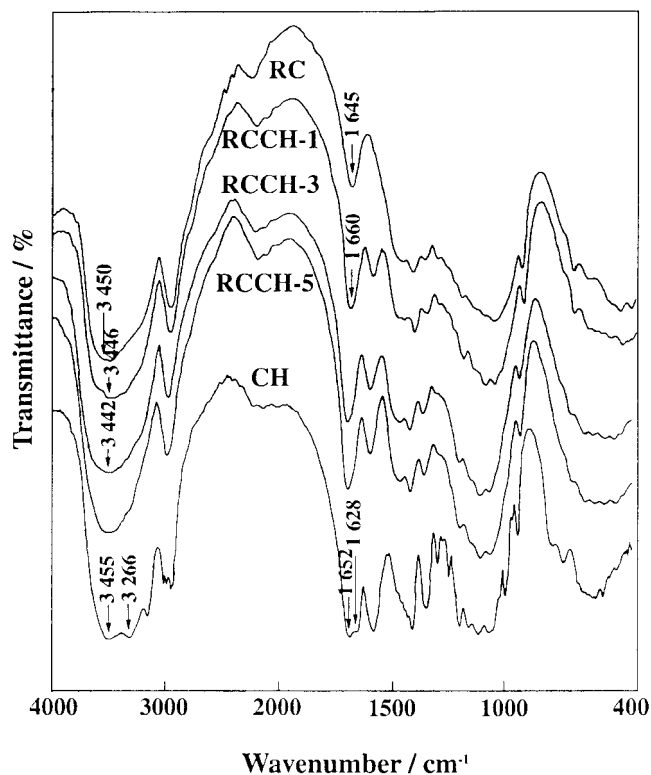


Figure 1 FTIR spectra of the films CH, RC, RCCH-1, RCCH-3, and RCCH-5.

RESULTS AND DISCUSSION

Miscibility of blend films

Usually, the miscibility in polymer blends was caused by specific interactions, and the presence of the interactions including hydrogen bonding, ion-ion pairing, and so forth favors the enthalpy for mixing and allows the components to mix completely.¹⁹ The hydrogen bond and the fraction of hydrogen-bonded groups can be directly investigated from IR spectroscopy.²⁰ Figure 1 shows the IR spectra of RC, CH, and the RCCH blend films. In the CH film, the peaks at 1652, 1555,

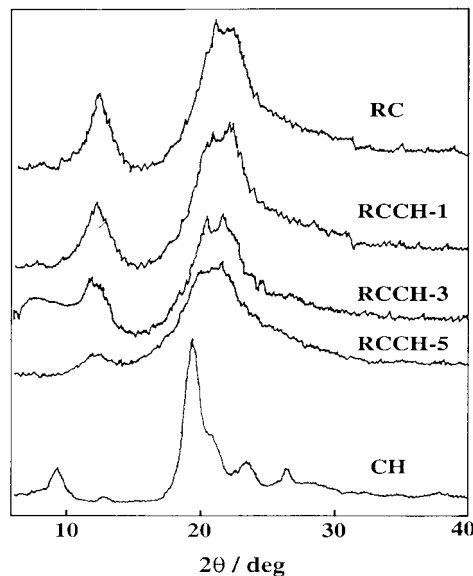


Figure 2 X-ray diffraction patterns of the films CH, RC, RCCH-1, RCCH-3, and RCCH-5.

and 1310 cm^{-1} were assigned, respectively, to amides I, II, and III; the broad bands at 3266 and 3455 cm^{-1} were attributed to the N—H and O—H stretching vibration bands of chitin, respectively. Compared to the CH and RC films, amide I of chitin for the blend films shifted to a higher frequency and the O—H stretching vibration was broadened and shifted to a lower frequency, suggesting that part of the hydrogen bonding $\text{C}=\text{O}\cdots\text{H}-\text{N}$ in chitin was broken and new hydrogen bonding between O—H in cellulose and N—H in chitin formed. This suggests a certain level of miscibility for the blend films.

X-ray diffraction patterns of the films are shown in Figure 2. The CH film has five diffraction peaks at $2\theta = 9.3, 12.3, 19.1, 23,$ and 26° , which is in agreement with the literature.²¹ RC film displayed typical cellulose II crystalline form and the peaks at $2\theta = 12, 20,$ and 21° correspond to the (110), (110), and (200)

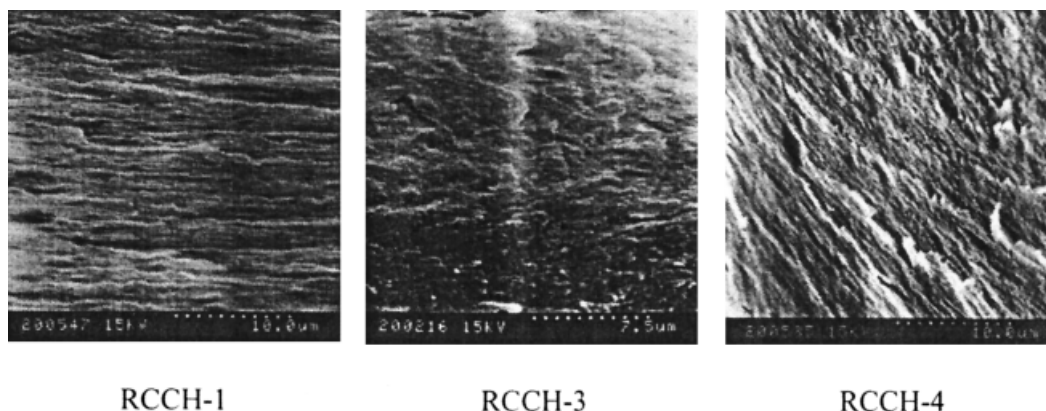


Figure 3 SEM of the cross section of films RCCH-1, RCCH-3, and RCCH-4.

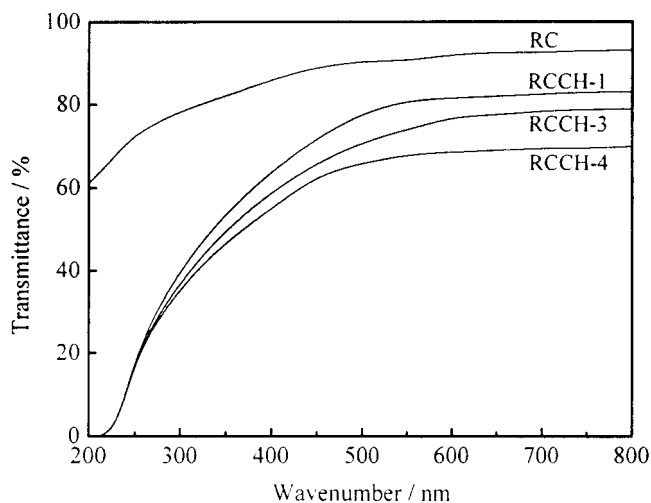


Figure 4 Optical transmittance of the films RC, RCCH-1, RCCH-3, and RCCH-4.

planes.²² The peaks at $2\theta = 9.3, 23,$ and 26° for chitin disappeared in the blend films, and the peak intensities of the (110) and (110) planes for cellulose decreased, whereas that of the (200) plane increased with increasing chitin content. The degree of crystallinity (χ_c) for the films is in the order of $RC < RCCH-1 < RCCH-2 < RCCH-3 < RCCH-4 < RCCH-5$. It is clear that the degree of crystallinity of the blend films decreased with an increase of cellulose content, suggesting that the original crystal structure of chitin and cellulose was broken as a result of the strong interaction between chitin and cellulose molecules.

Scanning electron micrographs (SEM) of the cross section for the films are shown in Figure 3. The cross sections of RCCH-1 and RCCH-3 display a homogeneous and dense structure, indicating that blend films RCCH-1 and RCCH-3 were miscible. However, RCCH-4 showed a certain microphase separation on the inner section.

Usually, the light transmittance (T_r) of the film is one of the methods by which to judge the miscibility of the blend films. If the blend is immiscible, the interface between two polymers will cause losses in light transmission because of the quality of light scattered and reflected, resulting in lower T_r values of the blends than that the pure polymer film. Figure 4 shows the T_r curves at the wavelength range of 200–800 nm of the films; the T_r values at 800 nm of the blends are listed in Table I. The blend films RCCH-1 and RCCH-2 showed better light transmittance over 80%, indicating that the RCCH blend membranes had a good miscibility. The miscibility of the blend films decreased with an increase of chitin content, which is in agreement with the results from SEM.

Thermal behavior of the films

DSC curves of the films CH, RCCH-1, RCCH-3, RCCH-4, and RC are shown in Figure 5. The exother-

TABLE I
The Physical and Mechanical Properties of Cellulose, Chitin, and Their Blend Films

Film number	T_r (%) 800 nm	σ_b (MPa) (dry/wet)	ε_b (%) (dry/wet)	R
RC	92	83.5/39.2	18.6/27.0	0.47
RCCH-1	82	89.1/43.7	14.1/23.1	0.49
RCCH-2	80	87.4/41.9	11.8/19.8	0.48
RCCH-3	78	72.1/27.5	7.2/15.1	0.38
RCCH-4	68	63.5/23.0	6.4/12.3	0.36
RCCH-5	61	50.4/18.1	5.8/11	0.36

mic peak appears at around 345 and 223°C of the RC and CH films because of the decomposition of glucopyranose rings for cellulose²³ and the decomposition of chitin, respectively. The decomposition temperature of cellulose and chitin in the blend films increased, indicating that a strong interaction exists between cellulose and chitin, which enhanced the thermostability of blend films.

Mechanical properties of the films

The effect of the chitin content on the tensile strength and breaking elongation of the blend films in both dry and wet states are described in Figures 6 and 7, re-

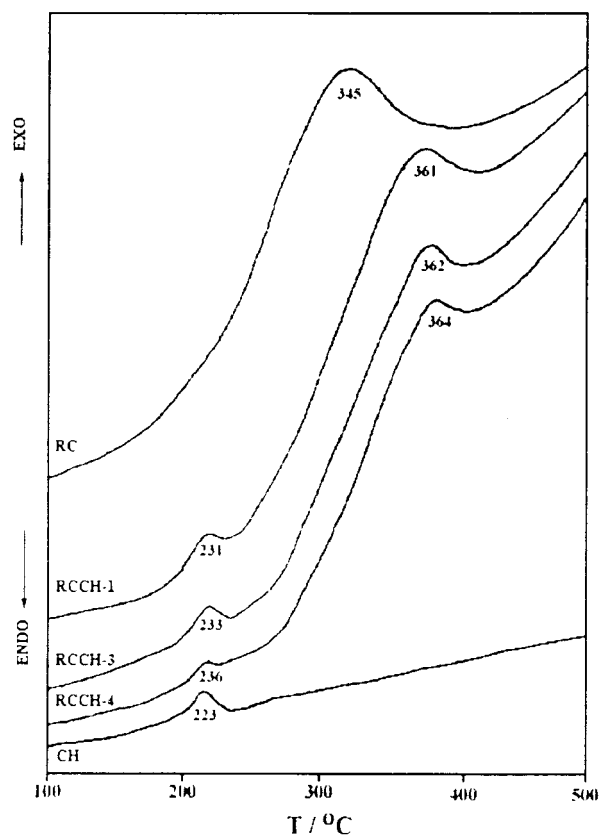


Figure 5 DSC curves of the films CH, RC, RCCH-1, RCCH-3, and RCCH-4.

spectively. The σ_b and ε_b values of the films are listed in Table I. The σ_b values of the blend films with chitin from 10 to 20% were higher than that of pure cellulose, and the maximum value for the RCCH1 film was 89.1 MPa in the dry state and 43.7 MPa in the wet state, respectively. The tensile strength of the blend films RCCH-1 and RCCH-2 was higher than that of RC film unblended with chitin. When the chitin content exceeded 30 wt %, tensile strength values of the blends drastically decreased, suggesting the immiscibility of the blend.

The breaking elongation and water resistance of the blend films decreased with an increase of chitin content. However, the water resistance of the blend films containing 10–20 wt % chitin was slightly higher than that of the RC film. It is worth noting that the mechanical properties of the blend films containing 10–50 wt % chitin were significantly improved, compared to chitin film, which is too brittle. Therefore, it provided a novel way of preparing cellulose/chitin blend films.

CONCLUSIONS

The regenerated cellulose/chitin blend films (RCCH) were directly prepared from cellulose and chitin in 6 wt % NaOH/4 wt % urea aqueous solution. Blend films RCCH-1, RCCH-2, and RCCH-3 displayed a homogeneous and dense structure. The RCCH blend films were miscible when the chitin content was lower than 40 wt % because of a strong hydrogen bonding between cellulose and chitin. The mechanical properties and thermostability of the blends were significantly improved, and the maximum tensile strength achieved in both dry and wet states was 89.1 and 43.7 MPa, respectively, when the chitin content was 10 wt %, thus providing a novel way to prepare cellulose/chitin blend films in the aqueous solution system.

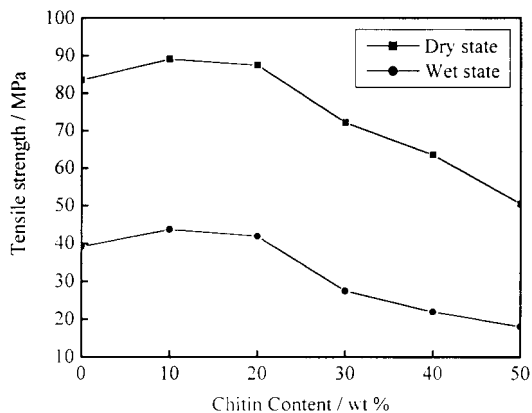


Figure 6 Effect of chitin content in blend films on tensile strength.

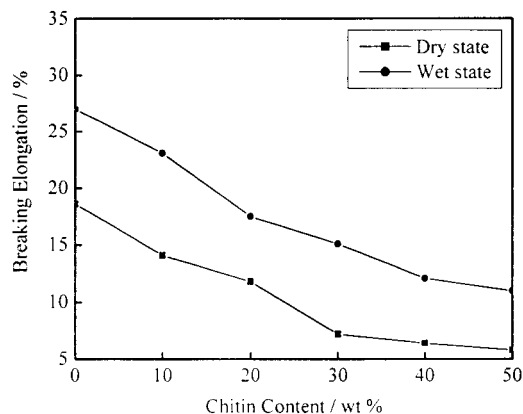


Figure 7 Effect of chitin content in blend films on breaking elongation.

The author gratefully acknowledge the financial support from China Capital Group Co. Ltd., Shanghai, China.

References

- Zhang, L.; Yang, G.; Liu, H. *Cellul Commun* 1999, 6, 89.
- Zhang, L.; Zhou, J.; Ruan, D. *Chin. Pat. Appl.* CN 00114485.5, 2000.
- Zhou, J.; Zhang, L. *Polym J* 2000, 32, 866.
- Zhou, J.; Zhang, L. *J Polym Sci Part B: Polym Phys* 2001, 39, 451.
- Zhang, L.; Ruan, D.; Zhou, J. *Ind Eng Chem Res* 2001, 40, 5923.
- Parisher, E.; Lombardi, D. *Chitin Source Book*; Wiley: New York, 1989.
- Hirano, S.; Seino, H.; Akiyama, Y.; Nonaka, I. In: *Progress in Biomedical Polymers*; Gebelein, C. G.; Dunn, R. L., Eds.; Plenum: New York, 1990; p 283.
- Shigemasa, Y.; Minami, S. *Chitin/Chitosan: A Handbook of Chitin and Chitosan*; Gihodo Publishing (Japan Soc.): Tokyo, 1995; p 178.
- Muzzarelli, R. A. A. *Cell Mol Life Sci* 1997, 53, 137.
- Hirao, S. *Biotechnol Annu Rev* 1996, 2, 237.
- Zheng, H.; Du, Y.; Yu, J.; Huang, R. *J Appl Polym Sci* 2001, 80, 2558.
- Lee, Y. M.; Kim, S. H.; Kim, S. J. *Polymer* 1996, 37, 5897.
- Hirano, S.; Midorikawa, T. *Biomaterials* 1998, 19, 293.
- Nishino, Y.; Manley, R. S. *Macromolecules* 1988, 21, 1270.
- Brow, W.; Wiskston, R. *Eur Polym J* 1965, 1, 1.
- Xu, J.; Stephen, P. M.; Richard, A. G. *Macromolecules* 1996, 29, 3436.
- Terbojevich, M.; Carraro, C.; Cosani, A.; Morsano, E. *Carbohydr Res* 1988, 180, 73.
- Klug, H. P.; Alexander, L. E. *X-ray Diffraction Procedure for Poly-crystalline and Amorphous Material*; Wiley-Interscience: New York, 1974.
- Jiang, M.; Li, M.; Xiang, M.; Zhou, H. *Adv Polym Sci* 1999, 146, 1221.
- Dong, J.; Ozaki, Y. *Macromolecules* 1997, 30, 286.
- Mo, X.; Wang, P.; Zhou, G.; Xu, Z. *Chem J Chin Univ* 1998, 19, 989.
- Purves, C. B. In: *Cellulose and Cellulose Derivatives, Part 1*; Spurlin, H. M.; Grafflin, M. W., Eds.; Interscience: New York, 1954; pp 29–98.
- Flaque, C.; Monteserrat, S. *J Appl Polym Sci* 1991, 42, 3205.