中国科学院
纤维素化学开放研究实验室

Laboratory of Cellulose and
Lignocellulosics Chemistry (LCLC)
Academia Sinica

论文集

(1992—1993)

中国科学院广州化学研究所
Guangzhou Institute of Chemistry, Academia Sinica

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CELLULOSE CHEMISTRY AND TECHNOLOGY

MORPHOLOGICAL STUDY OF CYANOETHYL CELLULOSE-ORIENTED FILM

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Paper dedicated to Prof. HUA NING-XI's 65th birth anniversary

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The morphology and structure of the cyanoethyl cellulose-oriented film obtained from concentrated dimethyl acetamide solution was studied by polarized microscopy, small angle light scattering, X-ray diffraction, DSC and electron microscopy. It was found that the cyanoethyl cellulose could form the oriented film which had orientation degree casting from the oriented mesomorphic solution. The basic element of orientation was the fibril, whose orientation direction was found as correlated with the angle with the shear direction and the zigzag morphological structure in the oriented film. The orientation led to increasing thermal stability of the cyanoethyl cellulose.

INTRODUCTION

Since Werbowyj and Gray reported [1] that there were cholesteric phases in the concentrated aqueous solutions of hydroxypropyl cellulose, in 1976, the liquid crystals of cellulose and its derivates have gained considerable interest. Cellulose and its derivatives have heen found to form cholesteric liquid crystals, [2,3] because of their semi-rigid chains.

Polymer liquid crystals, when subjected to shear, exhibit a characteristic optical effect which appears as a band-like pattern of bright and dark bands, perpendicular to the shear direction.[4-17] This optical effect has been observed with main-chain polymer liquid crystals such as aromatic copolyester, polypeptides, polyisocyanates, aromatic polyamides and cellulose derivatives and it appears to be associated with the characteristic molecular organization and orientation induced during the shear process.

We have reported [18,19] that the cyanoethyl cellulose (CEC)/dimethyl acetamide (DMA) can form mesomorphic solutions above the critical concentration and, after it has been sheared, the mesomorphic solution shows the band-like texture in which the molecular chains orient themselves along the shear direction with the zigzag form. If the solvent is volatilized quickly enough under appropriate conditions, the CEC-oriented film can be formed. In this report, we discuss the morphology and structure

of the CEC oriented film. The investigations were carried out by polarized microscopy, small angle light scattering (SALS), X-ray diffraction, DSC and electron microscopy.

EXPERIMENTAL

The cyanoethyl cellulose (CEC) (DP = 300, DS = 2.5—3.0) was prepared by us. The dimethyl acetamide (DMA) was a CP reagent. The CEC was mixed with the DMA at room temperature. The solutions were seald up in tubes and laid over 12 hours at room temperature, after they were heated at 50° for 10 hours. The solutions were isotropic, at a concentration of 30—35 wt. % and anisotropic over this concentration value, at room temperature.

The 47.4 wt. % CEC/DMA mesomorphic solution was spread between two microscope slides, which were slipped with each other by shearing and the solution oriented. Then the sample was cooled, the solvent in the sample was volatilized quickly and the CEC-oriented film was obtained.

The textures of the film were observed with a polarized microscope (Leitz, ORTHOPLAN-POL).

The grating diffraction of the film was studied ba a small angle laser light scattering instrument (LS—1, Yingkou measuring and testing instrument factory, Liaoning, China).

An X-ray diffractometer (TUR—M62, Germany) was used to study the structure of the film and to measure the orientation degree of the film.

The observation of the morphological structure was carried out with a scanning electron microscope (S—430, Hitachi Ltd., Tokyo, Japan). The samples were etched by the saturated aquenous solution of $K_2Cr_2O_7$, for 1—3 minutes, before they were observed.

Thermal stability of the samples was studied by a differential scanning calorimeter (DSC—2C, Perkin-Elmer Ltd.) and the polarized microscope with a hot stage (Leitz Microscope Heating Stage 350).

RESULTS AND DISCESSION

The CEC—oriented film casting from the oriented mesomorphic solution shows the band-like texture under crossed polarizing light (Fig. 1). The direction of the bands is perpendicular to the shear direction and their width is about 1.5—3.0 μm. The intensity of depolarizing light transmission, which varies with the rotation angle between the shear direction and polar direction of the polarizer, is minimum when the shear direction is at an angle of 0° or 90° with the polar direction, and maximum when it is at an angle 45° with it (Fig. 2). According to the principle of depolarization applied to crossed polarizers, it is believed that the general orientation direction of the molecular chains coincide with the shear direction. On insertion of a first-order plate at 45° to crossed polarizers, the bands become blue and yellow. When the sample is rotated, with the crossed polarizers fixed, the bands are no longer equidistant. They move closer and closer, two by two and then merge at a certain rotation angle. The interference color is all yellow when the bands are laid across the first and third diametrically opposed quadrants of the cross and all blue when the bands are laid across the second and fourth ones.

The brightness and darkness of bands vary with the angle 0 between the shear direction and the polar direction of the polarizer. In Figure 1, when $\theta = 0$ there are very narrow dark bands between the bright bands, yet some bright bands become dark as the sample is rotated. When 0 is 20°, the birefringent texture appears alternative by as bright and dark bands with the same width. The orientation direction of the molecular

chains, at this time, is parallel to the polar direction in the dark bands but is at different angles with that in the bright bands. Therefore, in the CEC—oriented film, the orientation direction is at an angle of 20° to the shear direction. When θ is over 20°, the width of the dark bands be-

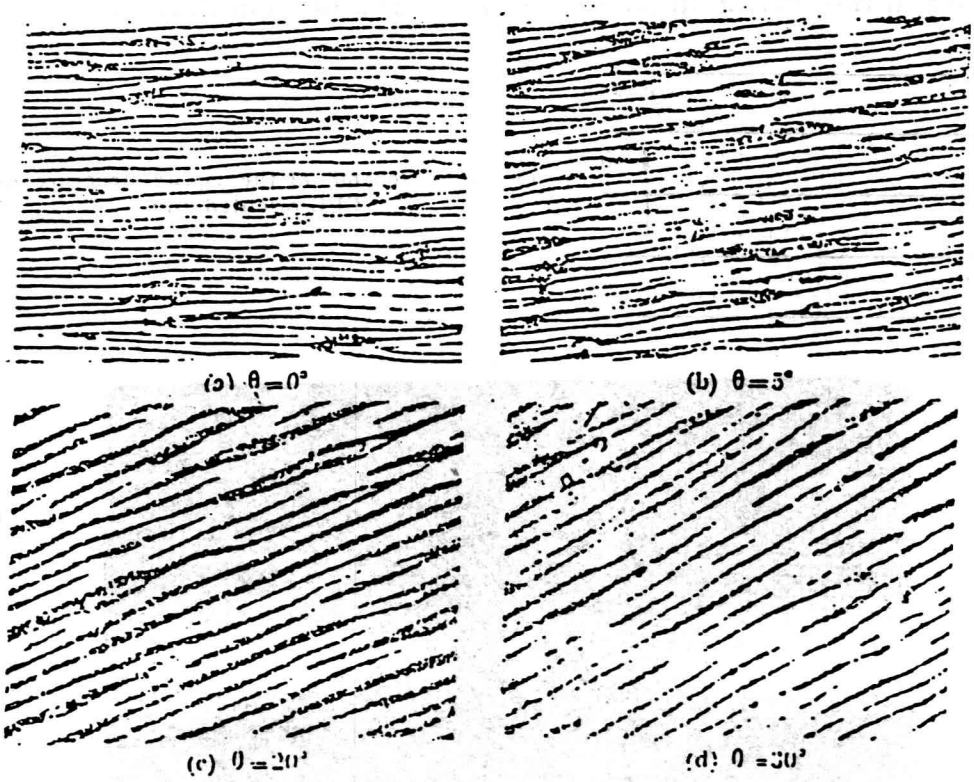

Fig. 1. — Textures of the CEC—oriented film. θ is the angle between the shear direction and polar direction, arrow shows the shear direction.

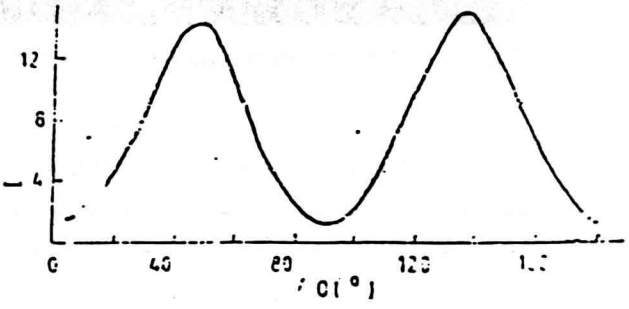

Fig. 2. — Dependence of depolarizing light transmission on the angle θ.

comes narrow again and finally the dark bands disappear. These results show that the molecular chains in the oriented film are oriented along the shear direction with a sawtoothed molecular pathway (Fig. 3).

Because of the sawtoothed structure, the oriented film shows the grating property in optics. The patterns of grating diffraction, H_v and V_v, in the SALS experiments have been observed when θ is 0°, 45° and 90° and the grating diffraction points are obtained (Fig. 4). The grating diffraction effect is very strong at H_v—0°, H_v—90° and V_v—45° but very weak at H_v—45°, V_v—0° and V_v—90°. In comparison with the theoretical calculating results (Table 1), it is clear that the orientation direction between neighbouring bands differs slightly and it plays an important role

in grating diffraction. At the same time, although it is small, the difference of the orientation degree in the oriented film exists and plays a minor role in grating diffraction.

The CEC—oriented mesomorphic solutions also show the band-like texture and the grating diffraction effect.[19] It is obvious that the CEC—ori-

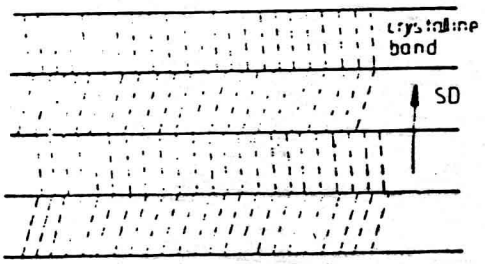

Fig. 3. Scheme of the zigzag structure of the CEC-oriented film.

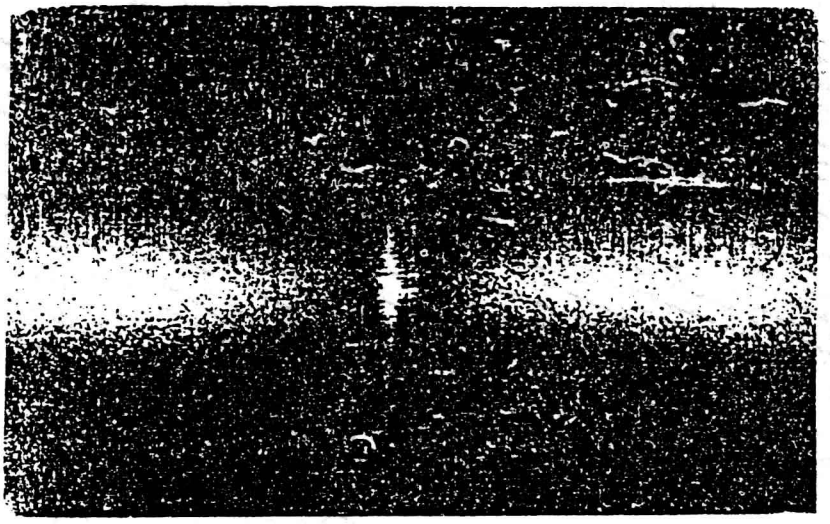

Fig. 4. — Grating diffraction (H_v 90°) of the CEC—oriented film.

TABLE 1

Dependence of grating diffraction effect on 0

		Grating diffraction effect		
		0°	45°	90°
Distribution of difference of the orientation direction in the bands	H_v	strong	nil	strong
	V_v	nil	strong	nil
Distribution of difference of the orientation degree in the bands	H_v	some	strong	some
	V_v	nil	strong	strong
Experimental results	H_v	strong	weak	strong
	V_v	weak	strong	some

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ented film maintains the structure of the oriented mesomorphic solutions, which can be further indicated by X-ray diffraction. Figure 5 presents a series of X-ray diffraction spectra of the CEC, in different states. The X-ray data of CEC in different states are listed in Table 2. The spectra

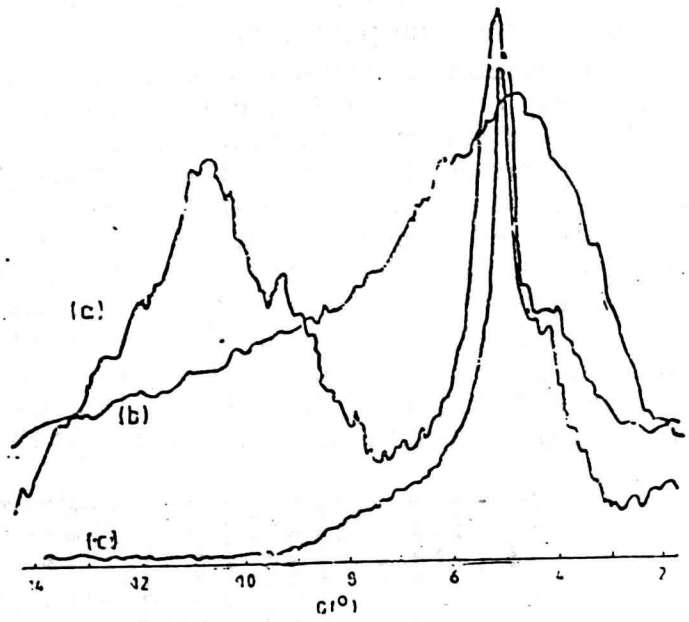

Fig. 5. —X-ray spectra, (a) CEC powder, (b) CEC/DMA mesomorphic solution, (c) CEC oriented film.

TABLE 2

X-ray diffraction data of the CEC samples

Sample	X-ray diffraction angle	Interplanar distance
CEC powder	θ=4.2°	10.52Å
	θ=4.6°	9.60Å
	θ=5.2°	8.50Å
	θ=10.7°	4.15Å
CEC—oriented film	θ=4.0°	d=11.04Å
	θ=4.3°	d=10.27Å
	θ=5.1°	d=8.67Å
CEC mesomorphic solution	θ=4.9°	d=9.02Å

of the mesomorphic solution and of the oriented film are different from that of the CEC powder. In the former spectra, there are no diffraction peaks when θ is about 11°. Therefore, the structure of the oriented film is different from that of the CEC powder, but similar to that of the meso-

morphic solution. Furthermore, the X-ray data shows that the interplanar distance is largest, middle and smallest in the mesomorphic solution, in the oriented film and in the powder, respectively. But the diffraction peak in the oriented film and the powder is sharper and stronger than that in the mesomorphic solution. These results indicate that the order degree of the molecular chains in the oriented film and the powder is higher than that in the mesomorphic solution.

The orientation degree of the oriented film, which has been measured by X-ray diffraction, is about 78 percent. It is clear that the orientation degree of the oriented film is high.

The oriented film shows the protruding band-like structure when observed by the scanning electron microscope after having been etched in the saturated aqueous solution of $K_2Cr_2O_7$. The width of the bands is about 2—3 μm and their direction is perpendicular to the shear direction (Fig. 6). This result confirms that there are parallel crystalline bands which are perpendicular to the shear direction in the oriented film. The fibrillar structures are also observed with a larger magnifying power (Fig. 7 a). The diameter of the fibrils is about 0.2 μm. This means that the basic element of orientation in the oriented film is the fibrils. In appropiate con-

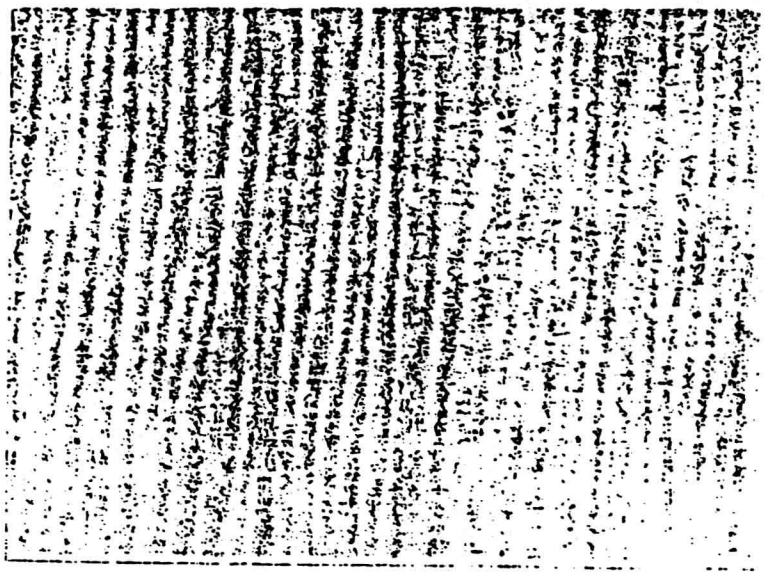

Fig. 6. — Electron micrograph of the CEC—oriented film, arrow shows the shear direction.

ditions, it can be seen that the patterns of the orientation for the fibrils in the shear direction is zigzag (Fig. 7 b). Therefore, the orientation directions between neighbouring bands is at an angle larger than 90°. The higher the shear rate is, the larger the angle is and the higher the orientation degree of the film is. Then, the results of the observation with polarized and electron microscopes and SALS are in agreement and suggest that the CEC—oriented film has a zigzag orientation texture.

The CEC—oriented film has a higher thermal stability than the CEC powder. The results of the DSC experiments show that the thermolysis

Cyanoethyl cellulose

temperature is about 455 K for the CEC powder and 535 K for the oriented film (Fig. 8). This means that the thermolysis temperature rises about 80 K after ther CEC has been oriented.

When the CEC-oriented film is heated in air at 5 — 10 K/min. and at the same time, observed by the polarized microscope, it can be found

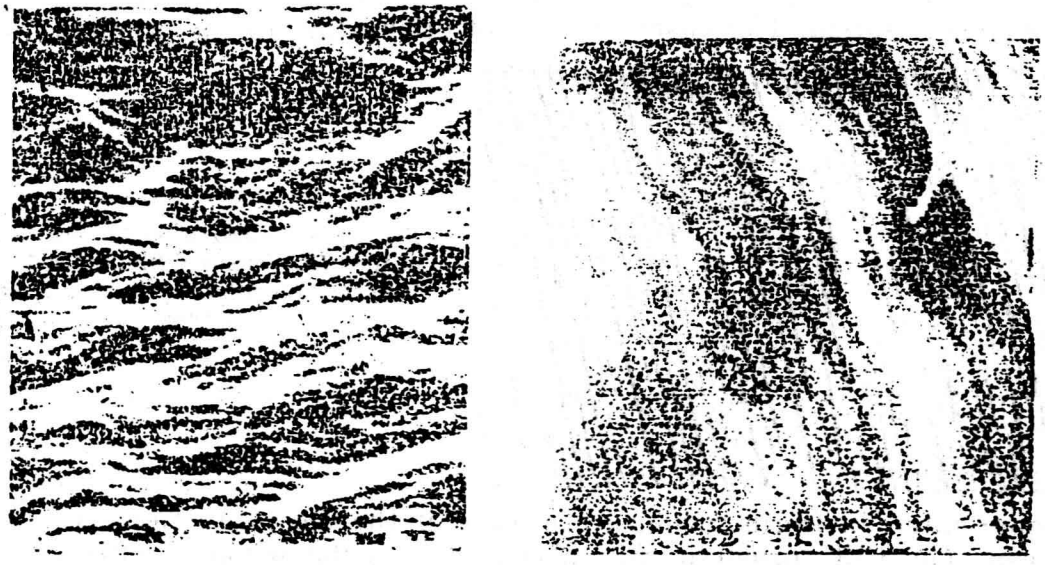

Fig. 7. Electron micrographs of the CEC-oriented film.

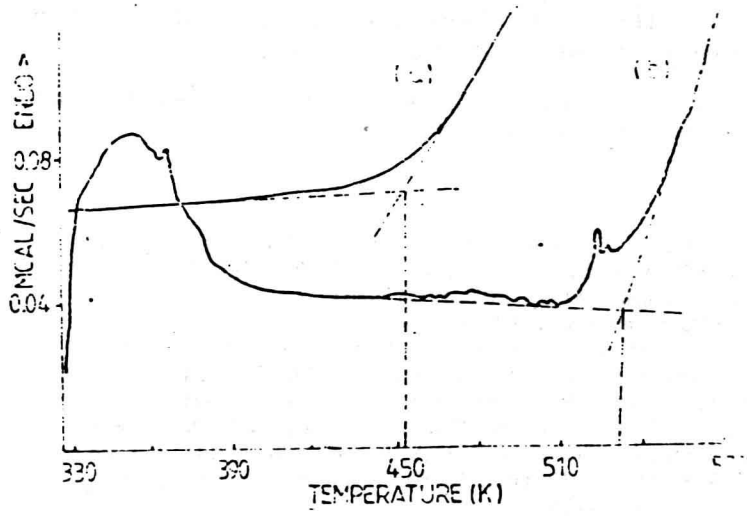

Fig. 8. — DSC spectra of (a) CEC powder and (b) CEC - oriented film.

that the orientation structure of the film is not destroyed by heat under 290°. Yet, when the temperature is over 290°, the film becomes slightly yellow, which means that decomposition begins. The film decomposes quickly when the temperature is about 300° and the orientation structure is destroyed. But, if the sample is cooled quickly, to room temperature, the band-like texture still exists in the parts of the film which have not

been decomposed (Fig. 9). Therefore, the orientation structure in the CEC-oriented film is very stable and cannot be destroyed before the decomposition of the CEC takes place.

CONCLUSIONS

The CEC — oriented film maintains the features of the oriented mesomorphic solution. The basic element of orientation in the oriented film is

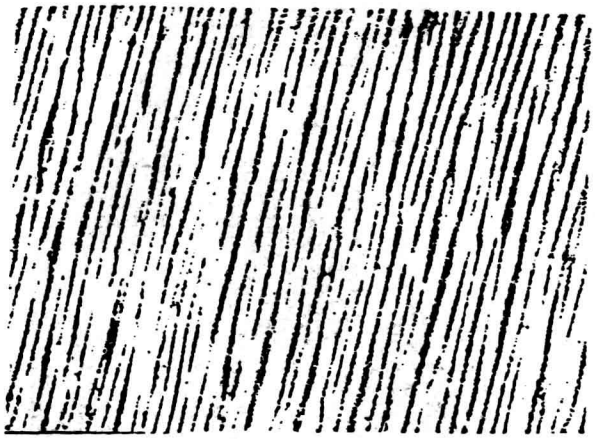

Fig. 9. — Polarized light micrograph of the CEC—oriented film cooled to room temperature, after having been heated at 300°.

represented by fibrils, which are oriented in the shear direction with zigzag form. The CEC-oriented film also shows the band-like texture and the grating diffration effect.

The thermal stability of the CEC increases greatly when it forms the oriented film and the orientation structure cannot be destroyed by heat, before the decomposition of the CEC occurs.

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SYNTHESIS OF CELLULOSE ACETATE CARBAMATE AND ITS MEMBRANE PROPERTIES

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ABSTRACT

The modification of cellulose acetate by toluene diisocyanate to form cellulose acetate carbamate (CAC) for improving its physical properties and microbial resistance was studied. The effects of reaction time and temperature, composition of reaction system, dosage of catalyst, and the kind of solvents used to isolate the product on the properties of the product CAC were investigated in detail. The membrane cast from CAC was tested in terms of salt rejection, water flux, resistance to hydrolyzation and microbial degradation. Results show that CAC is one of the excellent membrane materials with high salt rejection, good resistance to microbial degradation and hydrolyzation.

INTRODUCTION

Cellulose acetate (CA) is one of the most universally used materials for preparing RO membranes. It has many advantages, such as high permselectivity, high water flux, good resistance to chlorine, simple process of manufacture and low price. However, its chemical stability and resistance to microbial degradation are poor. This in turn shortens its service life, thereby limiting its applications.

Chemical modification of CA has become an important research field today. There have been many reports (refs. 1–9) both in China and abroad. For instance, diisocyanates have been used to react with parts of the residue hydroxyl groups of CA to form a polymer (CAC) with the structure of carbamates (refs. 10, 11), thereby increasing the tensile strength and stability against hydrolyzation and microbial degradation of membranes (refs. 12). There are also other application examples (ref. 13).

In the present paper the authors discuss in detail the reaction conditions of toluene diisocyanate (TDI) with CA, the effects of various parameters on the synthesis reaction and the properties of CAC cast membranes, and the determination of their RO properties and resistance to microbial degradation. In their experiments, IR spectroscopy, elementary analysis, X-ray diffraction and thermogravimetry techniques were used to probe the structure of CAC. The results showed that CAC is an excellent membrane material with high tensile strength, good resistance to hydrolyzation and to microbial decomposition.

EXPERIMENTAL

Reactants

CA with an acetyl content of 39.5%, which is commercially available from Shanghai Factory of Cellulose Acetate.

2,4-TDI (80/20) and acetone, both of technical-pure grade, from Taiyuan Chemical Plant. Iso-propanol, methanol and formamide, all analytically pure.

Synthesis of CAC

Dry CA 12.5 g was put into a flask equipped with a long vertical condenser and 100 ml acetone was added in. When the CA was completely dissolved at room temperature, the flask was put in a hot water bath and TDI and catalyst were added in, while stirring. After reaction the mixture was left to cool for a while and then it was precipitated with iso-propanol. The crude CA was washed with methanol, filtered and dried for the measurements followed.

Viscosity measurement

The CAC obtained was dissolved in the 1 : 1 mixed solvent of formamide and propylene oxide. Intrinsic viscosity was measured at 25 ± 0.5℃ using an Ubbelohde viscometer (ref.17).

Structural analysis

Nitrogen content was measured by the Kjeldahl method. The chemical structure was characterized with a PE-325 infrared spectrometer and analysed by X-ray diffraction technique (using a diffractometer of TU-M62).

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