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The synthesis and thermotropic behaviour of an ethyl cellulose derivative containing azobenzene-based mesogenic moieties

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An ethyl cellulose derivative containing azobenzene-based mesogenic moieties was prepared by the reaction of 4-methoxyazobenzene-4'-oxyacetic acid and ethyl cellulose by esterification in the presence of *N,N'*-dicyclohexylcarbodiimide and 4-dimethylaminopyridine. Its chemical structure and liquid crystalline properties were characterized by FTIR, ¹H NMR, POM, DSC and WAXD. The degree of substitution of the cellulose backbone by the azobenzene-based mesogenic moieties is 0.9. The polymer is thermotropic and exhibits liquid crystalline behaviour over the temperature range 125–172°C.

1. Introduction

Since Werbowyi and Gray first reported in 1976 that hydropropyl cellulose displays liquid crystalline behaviour [1], the liquid crystalline properties of cellulose derivatives have aroused much interest in the field of liquid crystalline polymers. In the past two decades, a range of cellulose esters, such as, propionic, *n*-butyric, isobutyric and phthalic acid esters of hydroxypropyl cellulose have been prepared which show thermotropic liquid crystalline behaviour [2, 3]. Acetoxypropyl cellulose [4], hydroxyethyl cellulose acetate [5] and ethyl cellulose with an ethoxy content over 45 wt% have also been reported to exhibit thermotropic behaviour [6]. In all these investigations, flexible substituents have been introduced in to the cellulose side chains. To date few articles have reported examples in which bulky mesogenic moieties are grafted on to cellulose derivatives. Recently, Shaikn *et al.* reported the preparation and thermotropic behaviour of cholesterol-containing hydroxyethyl cellulose and polysaccharides [7, 8]. Terbojevich *et al.* reported the solution properties and mesophase formation of 4-phenylbenzoyl cellulose [9]. The synthesis and thermotropic behaviour of 4-methoxyphenyl-4'-oxyacetic acid benzoate grafted onto ethyl cellulose has also been reported [10]. Due to the semi-rigid main chain of cellulose derivatives, the chemical structure of

the mesogenic moiety containing cellulose derivatives is similar to the so-called combined liquid crystalline polymers [11, 12].

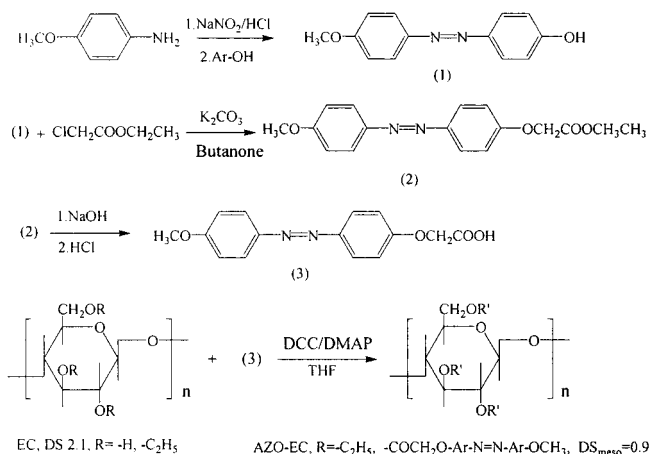
Recently, there has been much interest in azobenzene-containing liquid crystalline polymers because of their potential use in various optical applications, such as optical information storage, optical switching and nonlinear optics [13–16]. As far as we are aware, there are very few reports describing azobenzene chromophores grafted on to cellulose [17, 18], and furthermore there are almost no detailed studies of the thermotropic behaviour of cellulose derivatives containing azobenzene-based mesogenic moieties. In this work, a new ethyl cellulose derivative containing an azobenzene-based mesogenic moiety was synthesized. The residual hydroxy groups of the parent polymer ethyl cellulose, were completely esterified and the thermotropic behavior of the polymer characterized.

2. Experimental

2.1. Materials

Ethyl cellulose (EC, degree of substitution (DS) 2.1) was purchased from Luzhou Chemical Factory (Sichuan, PR China). Phenol, *p*-anisidine, and ethyl chloroacetate were analytical reagents (AR) obtained from Beijing Chemical Reagent Company (Beijing, PR China). *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were used as received (Arcos).

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Scheme 1. Synthetic route for the ethyl cellulose derivative containing azobenzene-based mesogenic moieties.

Tetrahydrofuran (THF) was distilled from sodium-benzophenone. Other solvents and reagents were AR grade and used without further purification.

2.2. Synthesis

The synthetic route used to prepare the ethyl cellulose derivative containing an azobenzene-based mesogenic moiety is shown in the Scheme.

2.2.1. 4-Hydroxy-4'-methoxyazobenzene (1)

This compound was prepared according to the method described by Stewart and Imrie [19]. Thus a solution of sodium nitrite (7.25 g, 0.105 mol) in distilled water (40 ml) was added slowly with vigorous stirring to a solution of *p*-anisidine (12.6 g, 0.102 mol) in 3M hydrochloric acid (125 ml) at 0°C; the resulting diazonium salt solution was then slowly added to a stirred solution of phenol (9.88 g, 0.105 mol) in 10% aqueous sodium hydroxide (100 ml) at 0°C. The dark brown suspension was acidified and the precipitate collected. The crude product was washed with copious amounts of water and recrystallized from ethanol/water (volume ratio 1/2); yield 16.4 g 72%, m.p. 138–139.6°C. FTIR (KBr, cm⁻¹): 3412(–OH), 1596, 1583, 1493(–Ar), 1232(Ar–O–CH₃), 843(–Ar). ¹H NMR (CDCl₃, ppm): 3.87 (s, –OCH₃, 3H), 6.88–7.01 (q, –Ar, 4H), 7.80–7.90(t, –Ar, 4H). MS: *m/z* = 228 (M⁺).

2.2.2. Ethyl (4-methoxyazobenzene-4'-oxy)acetate (2)

4-Hydroxy-4'-methoxyazobenzene (5.7 g, 25 mmol), ethyl chloroacetate (3.3 g, 27 mmol) and potassium carbonate (6.9 g, 50 mmol) were added to 100 ml 2-butanone. The mixture was heat at reflux with stirring for 12 h. It was then cooled to room temperature and poured into 500 ml ice-cold water, the resulting

precipitate was collected, recrystallized from ethanol and dried under vacuum; yield 6.1 g (78%), m.p. 110.6–112°C. FTIR (KBr, cm⁻¹): 1760 (–C=O), 1600, 1581, 1497 (–Ar), 1245 (Ar–O–CH₃), 846 (–Ar). ¹H NMR (CDCl₃, ppm): 1.30 (t, –CH₃, 3H), 3.88 (s, –OCH₃, 3H), 4.30 (q, –CH₂CH₃, 2H), 4.68 (s, –OCH₂–, 2H), 6.97–7.90 (m, –Ar, 8H). MS: *m/z* = 314 (M⁺).

2.2.3. 4-Methoxyazobenzene-4'-oxyacetic acid (3)

A mixture of ethyl (4-methoxyazobenzene-4'-oxy)acetate (4.7 g, 15 mmol), potassium hydroxide (2.24 g, 40 mmol), water (100 ml) and ethanol (20 ml) was heated under reflux with stirring for 24 h. The reaction mixture was poured into boiling water (1l) and the resulting solution filtered, the filtrate was acidified with concentrated hydrochloric acid allowed to cool. The resulting precipitate was collected, recrystallized from ethanol and dried under vacuum; yield 3.2 g (73%), m.p. 196.2–197.5°C with a little decomposition. FTIR (KBr, cm⁻¹): 2964 (–OH), 1703 (–C=O), 1599, 1579, 1496 (–Ar), 1236 (Ar–O–CH₃), 842 (–Ar). ¹H NMR (CDCl₃, ppm): 3.85 (s, –OCH₃, 3H), 4.80 (s, –OCH₂–, 2H), 7.07–7.87 (m, –Ar, 8H). MS: *m/z* = 286 (M⁺).

2.2.4. The ethyl cellulose derivative containing an azobenzene-based mesogenic moiety (AZO-EC)

1g Ethyl cellulose, 0.75g DMAP, 1.4 g 4-methoxyazobenzene-4'-oxyacetic acid and 40 ml THF were added to a 100 ml three-neck round bottom flask equipped with condenser and magnetic stirrer; a solution of 2.4 g DCC dissolved in 10 ml THF was then added slowly. The reaction was carried out at room temperature under the protection of N₂ for 16 h. The reaction mixture was then poured into an excess of methanol; the precipitate was dissolved in THF and reprecipitated from methanol. The air-dried product was Soxhlet-extracted with methanol and dried under vacuum at 50°C; yield 1.72 g (82%). The DS of the mesogenic unit was 0.90.

2.3. Characterization

The chemical structures of the intermediates and the final polymer were characterized by FTIR spectroscopy using a Bruker EQUINOX55 spectrometer and ¹H NMR spectroscopy using a Bruker 300 MHz spectrometer with tetramethylsilane as an internal standard. MS analysis was carried out with an AEI MS-50 mass spectrometer, using the electron ionization method (EI, 70 eV). The melting points (m.p) of intermediates were determined by polarizing optical microscopy (POM) (Olympus Model BH-2) equipped with a Mettler FP-5 hot stage at a heating rate of 1°C min⁻¹. The liquid crystalline texture of the polymer was also studied using

POM at a heating and cooling rate of $10^{\circ}\text{C min}^{-1}$. A differential scanning calorimeter (TA instruments DSC 2910) was used to measure the transition temperatures with a heating and cooling rate of $10^{\circ}\text{C min}^{-1}$. Wide angle X-ray diffraction was carried out using a WAXD spectrometer (Rigaku D/max-2400). The point-focused beam was monochromatized with a graphite crystal to isolate the CuK_{α} radiation (corresponding to a wavelength of 1.5418 \AA).

3. Results and discussion:

3.1. Synthesis

The esters of cellulose and its derivatives can be prepared by the acid-catalysed esterification of cellulose or its derivatives with acetic anhydride under relatively mild conditions [5, 20]. Reactivity, however, is decreased markedly and more drastic conditions are required on increasing the chain length of the carboxylic acid or if using an aromatic acid. The esterification can be carried out using acid chloride as the reagent and pyridine or triethylamine as catalyst [21, 22], but acid chlorides are more sensitive to moisture and thionyl chloride corrodes the equipment when it is removed from the acid chloride under reduced pressure. Esterification can be achieved also by activating the carboxylic acids using DCC and DMAP as catalysts [23–25]. It is convenient to prepare the ethyl cellulose derivative containing an azobenzene-based mesogenic moiety by the reaction of 4-methoxyazobenzene-4'-oxyacetic acid with ethyl cellulose using DCC and DMAP as catalysts.

The infrared spectra of AZO-EC and EC are shown in figure 1. Bands at 2972 and 2872 cm^{-1} are associated with the symmetric and asymmetric vibrations of $-\text{CH}_2$ groups on the EC and AZO-EC side chains. The band at about 1770 cm^{-1} in the spectrum of AZO-EC is indicative of the ester function. The very broad hydroxyl peak at $c: 3500\text{--}3400 \text{ cm}^{-1}$ in the spectrum of EC is

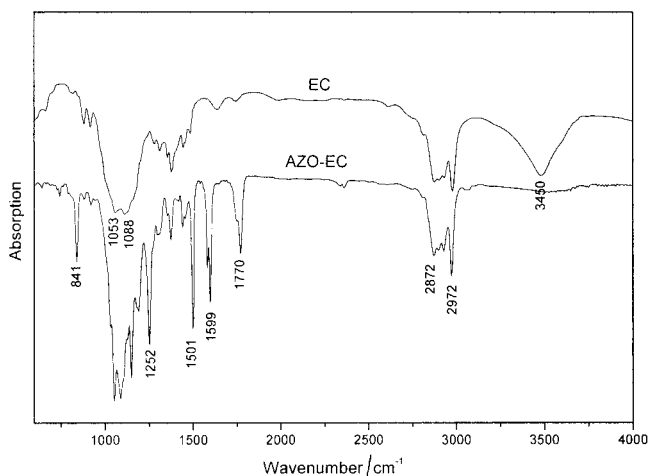


Figure 1. Infrared spectra of EC and AZO-EC.

almost absent in that of AZO-EC, suggesting complete esterification. The bands at 1600 and 1501 cm^{-1} in the AZO-EC spectrum are attributed to $\text{C}=\text{C}$ stretching in the aromatic rings. The peaks at 1252 , 1150 , and 841 cm^{-1} are associated with the ester $\text{C}-\text{O}-\text{C}$ and *para*-substitution of the aromatic ring.

The $^1\text{H NMR}$ spectrum of AZO-EC (CD_3Cl as solvent) is shown in figure 2. The peaks at 6.95 and 7.83 ppm correspond to the aromatic hydrogens in AZO-EC. The sharp peak at 3.83 ppm is attributed to the methoxy group hydrogens of the azobenzene mesogenic moiety. The DS of the mesogenic moiety can be calculated from the ratio of aromatic hydrogens to the other hydrogens in AZO-EC. The DS of the mesogenic moiety is calculated to be 0.90 .

3.2. Thermotropic behaviour

According to the literature [6], ethyl cellulose exhibits thermotropic behaviour only when its ethoxy content reaches $45 \text{ wt}\%$. However, in the present work, the ethyl cellulose, (i.e. the parent polymer of AZO-EC) still shows strong birefringence in the temperature range $150\text{--}180^{\circ}\text{C}$, although its ethoxy content is $42.8 \text{ wt}\%$. Therefore, it is a thermotropic liquid crystalline polymer. AZO-EC becomes soft and birefringence appears when it is heated to 125°C . Birefringence is observed when AZO-EC is heated to 130°C while the strongest birefringence is observed at 140°C . When the sample is heated to 169°C , the birefringence begins to disappear and has completely disappeared at 172°C ; this is indicative of a transition from the mesophase to the isotropic phase. Birefringence can also be observed during the subsequent cooling procedure at 150°C . During the second heating, birefringence is observed between 120 and 165°C and the transition temperature from the mesophase to the isotropic phase is 168°C . The difference in transition temperatures between the first and second heating runs may be attributed to differences in the thermal history of the sample.

A banded texture can be obtained by shearing the AZO-EC mesophase at about 160°C . Figure 3 shows a POM micrograph of the band texture for the AZO-EC film for a shearing direction parallel to the direction of the polarizer. The width of the bands is about $1 \mu\text{m}$. The formation of the band texture under an external field is considered to be characteristic behaviour of liquid crystalline polymers [26, 27]. Therefore, this confirms that AZO-EC is a thermotropic polymer which exhibits a mesophase in the temperature range $125\text{--}172^{\circ}\text{C}$.

The results of DSC experiments are in good agreement with the observations made by POM. In figure 4, curve 1 is the DSC trace of EC ($\text{DS}=2.1$).

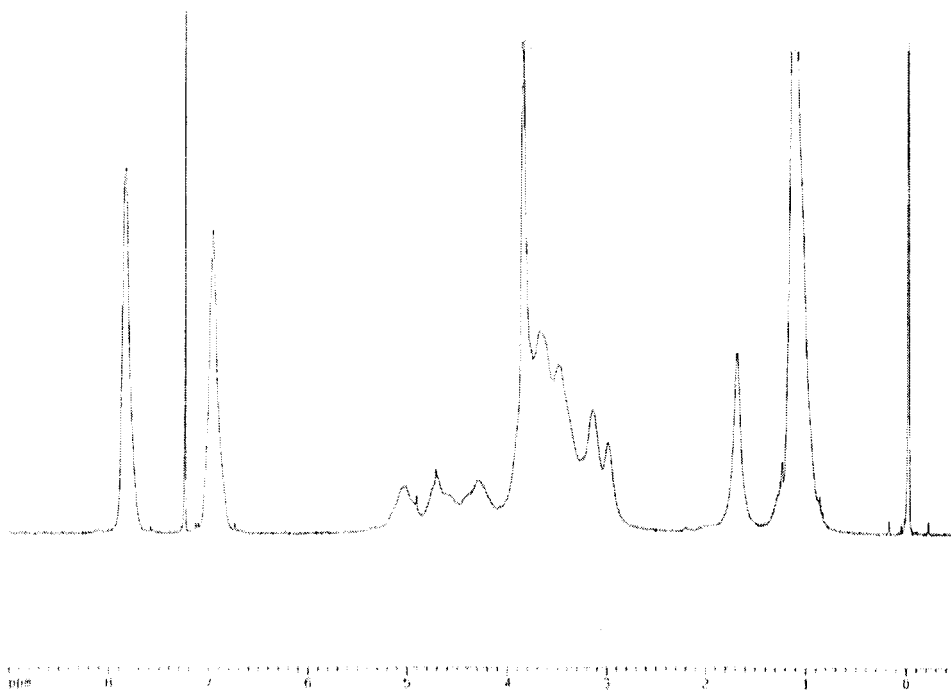


Figure 2. The ^1H NMR spectrum of AZO-EC.

There is a step in the baseline and an endothermic peak at 135°C and 178°C , respectively. The step corresponds to the glass transition and the endothermic peak at 178°C is attributed to the mesophase–isotropic phase transition. Curve 2 is the DSC trace of the first heating run of AZO-EC; a glass transition at 125°C and the mesophase–isotropic phase transition at 163°C are also observed. In the cooling run, the isotropic phase–mesophase transition begins at 155°C (curve 3). In the second heating run, after the thermal history of the sample has been removed, the glass transition occurs at 115°C and the mesophase–isotropic phase transition occurs at 162°C (curve 4).

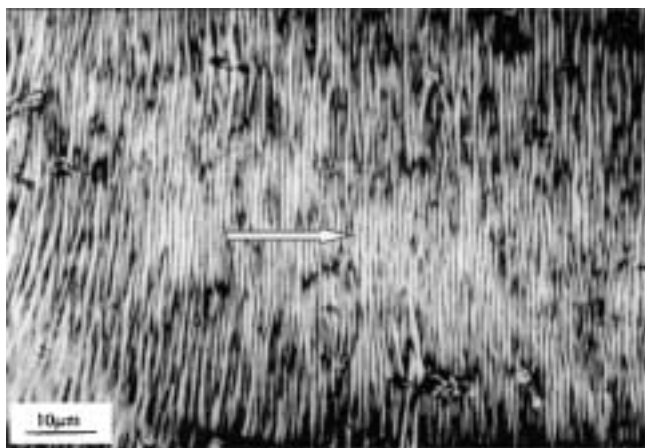


Figure 3. POM micrograph of the AZO-EC film sheared at 160°C , the arrow indicates the shearing direction.

The backbone of cellulose and its derivatives is a semi-rigid chain [28]. Thus structure of an ethyl cellulose derivative containing mesogenic moieties is similar to that of combined liquid crystalline polymers containing mesogenic units in both the main and side chains. The residual hydroxyl group on the main chain of ethyl cellulose is substituted by the bulky mesogenic units, which results in a decrease in intermolecular and

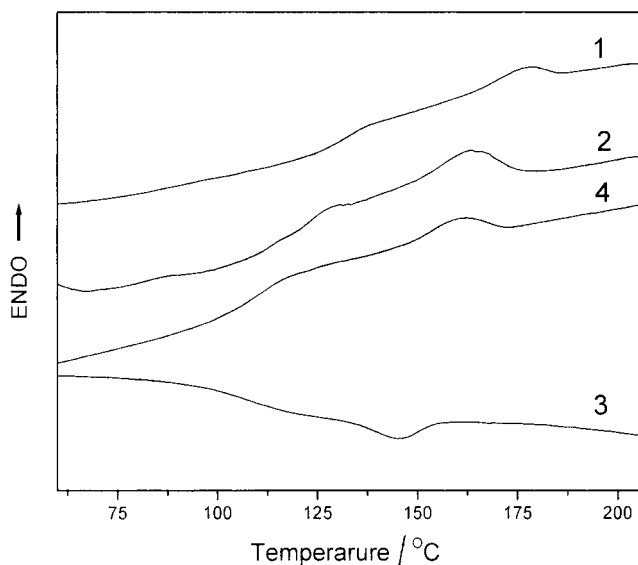


Figure 4. DSC curves. (1) EC, heating; (2) AZO-EC, first heating; (3) AZO-EC, cooling; (4) AZO-EC, second heating.

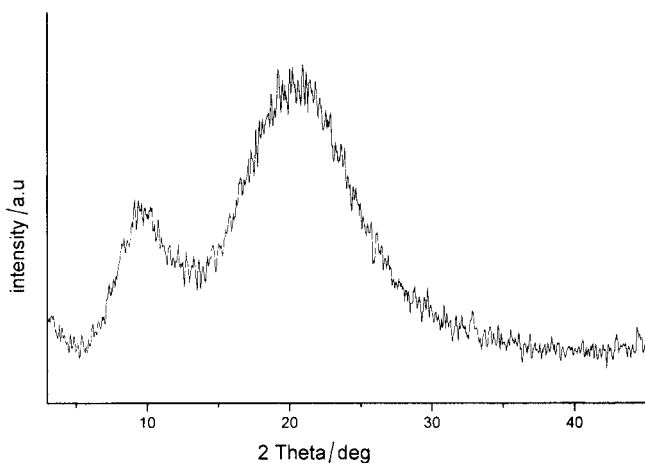


Figure 5. WAXD pattern of the AZO-EC film quenched from 160°C.

intramolecular hydrogen bonding. Therefore, the glass transition temperature and the mesophase–isotropic phase transition temperature of AZO-EC are lower than those of EC.

Figure 5 shows the WAXD pattern of the AZO-EC film quenched from the liquid crystalline state at 160°C. The two peaks at $2\theta = 9.54^\circ$ and 20.56° correspond to the inter-planar distance (9.26 Å) and the distance between cellulose chains (4.32 Å), respectively. These results are the same as those seen for hydroxyethyl cellulose acetate in the cholesteric liquid crystalline phase [5]. Therefore, the liquid crystalline phase of AZO-EC may be assigned as a cholesteric phase.

4. Conclusion

AZO-EC has been prepared by the reaction of 4-methoxyazobenzene-4'-oxyacetic acid and ethyl cellulose by esterification in the presence of *N,N'*-dicyclohexyl carbodiimide and 4-dimethylaminopyridine. AZO-EC shows a glass transition into the liquid crystalline state at 125°C upon heating, and to the isotropic melt at about 172°C. The transition from the isotropic melt to the liquid crystalline state begins at 155°C on cooling. A band texture is formed by AZO-EC on shearing at 160°C; the width of the bands is about 1 μm. The WAXD results suggest that AZO-EC shows a cholesteric phase.

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References

- [1] WERBOWYI, R. S., and GRAY, D. G., 1976, *Mol. Cryst. liq. Cryst.*, **34**, 97.
- [2] BHADANI, S. N., and GRAY, D. G., 1983, *Mol. Cryst. liq. Cryst.*, **99**, 29.
- [3] HOU, H., REUNING, A., WENDORFF, J. H., and GREINER, A., 2001, *Macromol. Biosci.*, **1**, 45.
- [4] TSEUNG, S., VANLENTE, A., and GRAY, D. G., 1981, *Macromolecules*, **14**, 715.
- [5] HUANG, Y., 1994, *J. appl. polym. Sci.*, **51**, 1974.
- [6] CHEN, J., HUANG, Y., YUAN, J., YAN, S., and YE, H., 1992, *J. appl. polym. Sci.*, **45**, 2153.
- [7] SHAIKN, V. A. E., MADAR, N. N., LONIKAR, S. V., RAJAN, C. R., and PONRATHNAM, S., 1998, *J. appl. polym. Sci.*, **70**, 195.
- [8] SHAIKN, V. A. E., MADAR, N. N., LONIKAR, S. V., RAJAN, C. R., and PONRATHNAM, S., 1999, *J. appl. polym. Sci.*, **72**, 763.
- [9] TERBOJEVICH, M., COSANI, A., FOCHER, B., GASTALDI, G., WU, W., MARSANO, E., and CONIO, G., 1999, *Cellulose*, **6**, 15.
- [10] WU, C., HUANG, Y., and CHEN, S., 2002, *Polym. Bull.*, **48**, 33.
- [11] CHA, S. W., JIN, J. I., KIM, D. C., and ZIN, W. C., 2001, *Macromolecules*, **34**, 5342.
- [12] CHEN, B. Q., KAMEYAMA, A., and NISHIKUBO, T., 1999, *Macromolecules*, **32**, 6485.
- [13] XIE, S., NATANSOHN, A., and ROCHON, P., 1993, *Chem. Mater.*, **5**, 416.
- [14] IKEDA, T., and TSUTSUMI, O., 1995, *Science*, **268**, 1873.
- [15] SAMINATHAN, M., RISHNA, C., PILLAI, S., and PAVITHRAN, C., 1993, *Macromolecules*, **26**, 7103.
- [16] SHANNON, P., GIBBONS, W., and SUN, S., 1994, *Nature*, **368**, 532.
- [17] MULLER, M., and ZENTEL, R., 2000, *Macromol. Chem. Phys.*, **201**, 2055.
- [18] YANG, S., JACOB, M., LI, L., CHOLLI, A., KUMAR, J., and TRIPATHY, S., 2001, *Macromolecules*, **34**, 9193.
- [19] STEWART, D., and IMRIE, C., 1996, *Polymer*, **37**, 3419.
- [20] HEINZE, T., and SHALLER, J., 2000, *Macro. Chem. Phys.*, **20**, 1214.
- [21] MARSANO, E., PAZ, L. D., TAMBUSCIO, E., and BIANCHI, E., 1998, *Polymer*, **39**, 4289.
- [22] PAWLOWSKI, W. P., SANKAR, S. S., GILBERT, R. D., and FORNES, R. E., 1987, *J. polym. Sci., polym. Chem. Ed.*, **25**, 3355.
- [23] HSIUE, G. H., SHA, Y. A., and JENG, R. J., 2001, *Macromol. Chem. Phys.*, **202**, 287.
- [24] SRAI, K., SHITARA, Y., and OHYAMA, T., 1996, *J. mater. Chem.*, **6**, 11.
- [25] REDL, F. X., KOTHE, O., BAUER, W., and DAUB, J., 2001, *Macromol. Chem. Phys.*, **201**, 2091.
- [26] CHEN, S., JIN, Y., and XU, M., 1987, *Polym. Commun.*, **28**, 208.
- [27] QIAN, R., and CHEN, S., 1992, *Makromol. Chem., macromol. Symp.*, **53**, 345.
- [28] GILBERT, R. D., and PATTON, P. A., 1983, *Prog. polym. Sci.*, **9**, 115.