Synthesis and Characterization of Novel Azobezene-Modified Polymers: Azocellulose[†]

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Introduction

Polymers containing azobenzene chromophores have received much attention due to their potential use in various optical applications, such as optical information storage, optical switching, and nonlinear optics.[1−7] It is well-known that azobenzene chromophores exhibit photoinduced reversible trans−cis−trans isomerization cycles. These photoinduced conformational changes can significantly influence the bulk and surface properties of polymers containing azobenzene groups. It is reported that photoinduced surface relief gratings (SRG) could be directly formed on thin films of azobenzene-modified amorphous polymers at temperature below their glass-transition temperatures (T_g).[1−7] This phenomenon has been observed in various low molecular weight azobenzene polymers, such as epoxy polymers, polyacrylates, polyesters, conjugated polymers, polyazophenol, and others.[1−7] However, the investigation of SRGs on a high molecular weight azo polymer has not been reported.

Cellulose, the most abundant polymer found in nature, consists of anhydroglucose units linked together by β-1,4-glycosidic bonds. The glucose units alternate up and down along the polymer chain. Cellulose has a high T_g of ca. 230 °C due to bulky D-glucopyranose units and strong intra- and intermolecular hydrogen bonding.[8] In the polymer main chain, every D-glucopyranose unit contains three hydroxyl groups, one primary alcohol, and two secondary alcohols, which can be the potential sites to link azobenzene chromophores. These hydroxyl groups may have different reactivities due to their steric hindrances and the type of hydrogen bonding (intra- or intermolecular) formed in cellulose. In this paper, we report the synthesis of azocellulose polymers by linking 4-cyanophenylazophenol to ultrahigh molecular weight cellulose via Mitsunobu reaction.[9] These polymers with varying degree of substitution (DS) of azobenzene chromophores were characterized using FT-IR, UV−vis, and solid-state ^{13}C CP/MAS NMR spectroscopies.

Experimental Section

Materials. 4-Aminobenzonitrile, sodium nitrite, phenol, TPP (triphenylphosphine**)**, and DEAD (diethylazodicarboxylate) were obtained from Aldrich and used without further purification. Anhydrous *N*,*N*-dimethylformamide (DMF) was purchased from Fisher Scientific and kept over 3 Å molecular sieves and anhydrous magnesium sulfide. Cellulose (MW around 5.8×10^8) was also obtained from Aldrich and dried at 80 °C under vacuum for 12 h. 4-Cyanophenylazophenol dye was synthesized according to the literature procedures.[10]

Table 1. Azocellulose Polymers Obtained by Modification of Cellulose with 4-Cyanophenylazophenol

sample	cellulose (g)	TPP (g)	DEAD (mL)	dye (g)	DS
1	0.50	1.23	0.45	1.05	0.13
2	0.50	3.00	1.10	2.10	0.32
3	0.50	3.60	2.10	2.55	0.49
4	0.50	3.70	2.21	2.96	0.80
5	0.50	4.88	3.20	4.88	0.99

Synthesis of Model Compound 4-Cyano-4′-methoxyazobenzene. TPP (3.52 g, 13.4 mmol), methanol (10 mL) and DEAD (2.1 mL, 13.4 mmol) were added to the solution of 4-cyanophenylazophenol (1.00 g, 4.4 mmol) in 50 mL of anhydrous DMF in a 250 mL flask cooled in an ice bath. The mixture was stirred at room temperature for 2 days under nitrogen atmosphere and then added into the 200 mL 0.1 N sodium hydroxide solution. The precipitate was filtered, washed with water, and dried in a vacuum. A reddish orange crystalline product was obtained by passing through an active alumina column using toluene as eluent: yield 0.91 g (87%); mp 144 °C. ^{1}H NMR (DMSO-d_6): $\delta = 3.89$ (s, 3H), 7.17 (m, 2H), 7.97 (m, 4H), and 8.05 ppm (m, 2H). ^{13}C NMR (DMSO-d_6): $\delta = 55.71$, 112.46, 114.75, 118.41, 122.81, 125.20, 133.67, 146.07, 154.09, and 162.88 ppm.

Synthesis of Azocellulose Polymers. A typical synthesis procedure for azocellulose is described here for sample 3 in Table 1. DEAD (2.10 mL, 13.4 mmol) was added to the mixture of cellulose (0.50 g, 3.1 mmol glucopyanose units), 4-cyanophenylazophenol (2.55 g, 11.4 mmol), TPP (3.60 g), and 50 mL of anhydrous DMF in a 250 mL flask cooled in ice bath. The mixture was stirred for 1 week at room temperature under nitrogen atmosphere and then added into 150 mL of methanol. The precipitate was isolated by centrifuge. Any unreacted azophenol was removed by repeated dissolutions and precipitations with DMF and methanol. The precipitate was then washed with distilled water and freeze-dried to give azocellulose polymer power that showed orange color. The degree of substitution (DS) of polymer was determined on the basis of the molar extinction coefficient of the trans form of the model compound 4-cyano-4′-methoxyazobenzene ($\lambda_{max} = 361$ nm, $\epsilon_{max} = 2.13 \times 10^4$) in DMF solution. The DS for sample 3 is 0.49. Theoretically, the maximum DS would be 3 if all the hydroxyl groups were substituted by azobenzene chromophores on each glucose ring. A set of five samples was prepared with varying compositions and is shown in Table 1.

Characterization. ^{1}H and ^{13}C NMR spectra of azobenzene compounds were acquired on a Bruker ARX-500 MHz FT-NMR spectrometer in deuterated dimethyl sulfoxide (DMSO-d_6). Solid-state ^{13}C CP/MAS NMR spectra were obtained on a Bruker DRX 300 MHz NMR spectrometer operating at a frequency 75.46 MHz. The magic angle-spinning (MAS) rate for the 4 mm rotor was 10 kHz. Typical experimental parameters for collecting solid-state NMR data were as follows: 2K data size, 2 ms contact time, 31 250 Hz spectral width, and 32 ms acquisition time. 15 000 FIDs were co-added, and the data were weighed with an exponential function using a line broadening of 5 Hz prior to Fourier transformation (FT). The recycle time delay was 3 s. The proton $\pi/2$ pulse width was 3.6 μs. Infrared spectra were recorded on a Perkin-Elmer 1720 FT-IR spectrometer. The samples of cellulose and 4-cyanophenylazophenol were compacted into KBr pellets for recording FT-IR data. In the case of azocellulose polymers, a thin film was cast on KBr disks from a polymer solution in DMF. The UV−visible absorption spectra were recorded using a Perkin-Elmer Lambda 9 spectrophotometer. The thermal properties were investigated with a Du Pont thermal analyzer DSC 2910 under nitrogen atmosphere at a heating rate of 10 °C/min.

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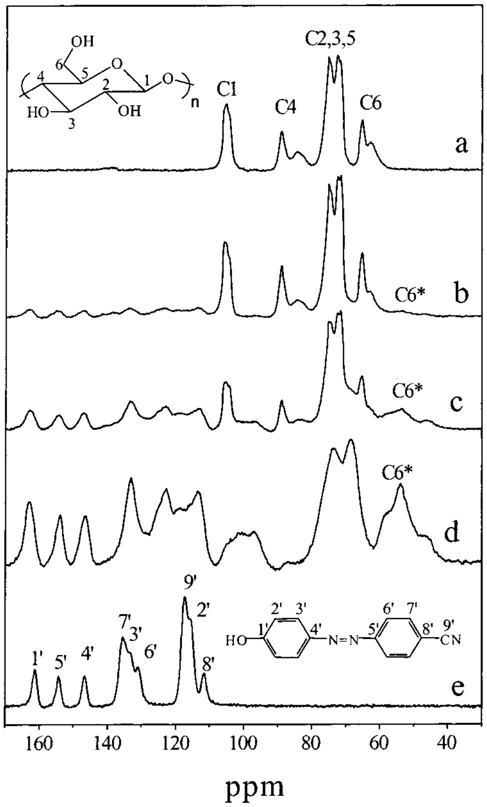


Figure 1. ^{13}C CP/MAS spectra of cellulose, 4-cyanophenylazophenol, and azocellulose polymers with different DS: (a) cellulose; (b) DS = 0.13; (c) DS = 0.49; (d) DS = 0.99; (e) 4-cyanophenylazophenol.

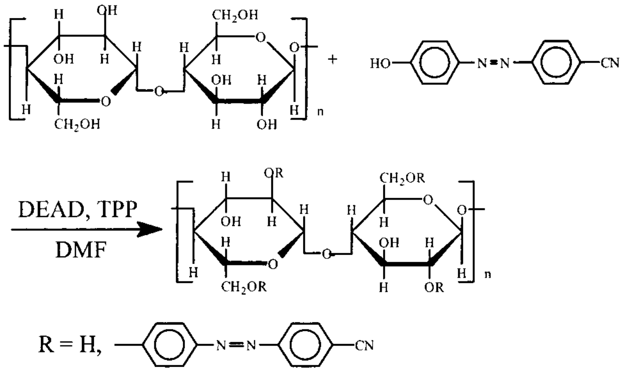
SRG Fabrication. SRGs were written on the azocellulose film cast on a glass substrate from the polymer solution containing mixed solvents of hexafluoro-2-propanol and trifluroacetic acid (80:20 by volume) using a simple interferometric setup [4] at 488 nm light with an intensity of 200 mW/cm^2 and an incidence angle of 14°. The polarization angle of the laser beam was set at 45° with respect to the orientation of the polarizers. The SRGs were investigated by atomic force microscopy (AFM).

Results and Discussions

Table 1 shows the experimental conditions for the synthesis of azobenzene-modified cellulose (azocellulose) polymers. The degree of substitution (DS) in these polymers was ranged from 0.13 to 0.99. Cellulose is not soluble in common solvent because of the strong intra- and intermolecular hydrogen bonding. However, azocellulose polymers can dissolve in DMF, especially for the polymer with high DS.

Figure 1 shows the ^{13}C CP/MAS NMR spectrum of cellulose (spectrum a), 4-cyanophenylazophenol (spectrum e) and azocellulose polymers with varying degree of substitutions (spectra b–d) as a result of Mitsunobu reaction (Scheme 1). The assignments of solid-state ^{13}C NMR resonance peaks for cellulose are based on the work of Atalla and Vanderhart.[11,12] The narrow resonance peak at 65.4 ppm is assigned to C6, the primary alcohol groups, in the crystalline domains. The resonance peaks for the ring carbons C2, C3, and C5 appear in the 70–80 ppm chemical shift range. The narrow resonance peak at 89.2 ppm is attributed to the C4 carbons in the crystalline domains. The broad upfield resonance peaks for C6 and C4 carbons (63.2 and 84.6 ppm) represent the amorphous region of the cellulose.

Scheme 1. Synthesis of Azocellulose Polymers by the Mitsunobu Reaction



The most downfield peak in spectrum a, at 105.5 ppm, is associated with C1, the anomeric carbon. A closer examination of this sharp resonance peak for C1 shows a weaker upfield shoulder suggesting the occurrence of nonequivalent glycosidic linkages. The ^{13}C CP/MAS spectrum of 4-cyanophenylazophenol and its resonance assignments are presented in spectrum e.

In the ^{13}C CP/MAS NMR spectrum b of azocellulose with DS of 0.13, a new peak (marked *) corresponding to C6* appears at 53.9 ppm. A closer examination of the amorphous peak of C6 indicates that it is a broad peak suggesting the coupling reaction predominantly occur in the amorphous region. Correspondingly, new peaks in the downfield region arising from azobenzene chromophores are weak compared with the resonance peaks of cellulose in the upfield region. As the DS increased from 0.13 to 0.99, the salient ^{13}C NMR spectral features are also changed. The weak peak at 53.9 ppm in spectrum b with DS of 0.13 becomes dominant in spectrum d with DS of 0.99. The C6 carbon resonance that appeared at 65.3 ppm is not observed mainly due to low concentration of unreacted C6 carbons in the polymer chains. The resonance at 89.2 ppm, which is attributed to the C4 carbons in the crystalline regions of the cellulose, decreases significantly from a sharp and strong peak in spectrum a to a weak and broad peak in spectrum d. This shows that the morphology of the azocellulose is predominately amorphous in the sample of spectrum d. As a result, the chemical shift of the crystalline carbon C4 resonance is moved to an upfield position of the amorphous carbon resonance of C4 and appears as a broad downfield shoulder to the resonance peaks of C2, C3, and C5 carbons of azocellulose (spectrum d). The strong and sharp resonance at 105.5 ppm, which is associated with the anomeric carbon C1, in spectrum a shifts to a broad upfield peak in spectrum d indicating the distribution of local environments of glycosidic bonds in the amorphous azocellulose. Correspondingly, the downfield peaks attributed to azobenzene chromophores in azocellulose also significantly increased with DS. The results of solid-state NMR analysis suggest that coupling reaction take place preferentially at the C6 carbon site. An upfield shift of 10 ppm for the C6 carbon resonance in spectra b–d in Figure 1 for azocellulose polymer is an indication of the Mitsunobu coupling at the primary alcohol site.

The FTIR spectra of cellulose (spectrum a), 4-cyanophenylazophenol (spectrum e), and azocellulose polymers (spectra b–d) are shown in Figure 2. The characteristic absorption band at 1242 cm^{-1} for the asymmetric C–O–C stretching of the azocellulose in

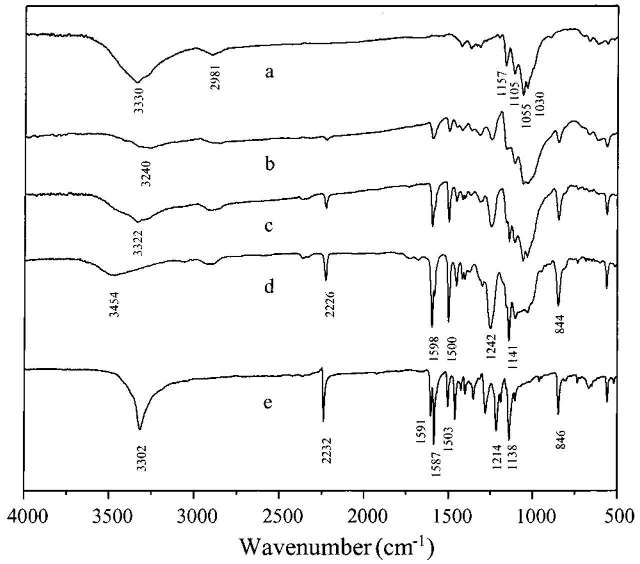


Figure 2. FTIR spectra of cellulose, 4-cyanophenylazophenol, and azocellulose polymers with different DS: (a) cellulose; (b) DS = 0.13; (c) DS = 0.49; (d) DS = 0.99; (e) 4-cyanophenylazophenol.

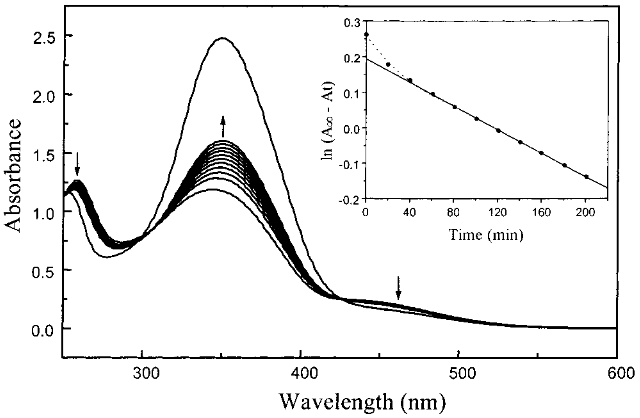


Figure 3. Thermal relaxation spectra of the film for azocellulose with a DS of 0.49. The spectra were recorded every 20 min right after the film was excited by UV light at 360 nm for 5 min. The top spectrum was recorded before photoexcitation. The inset is the plot of $\ln(A_\infty - A_t)$ as a function of time. A_∞ and A_t are the absorbances ($\lambda = 350$ nm) at infinite time (10 days) and at time *t*.

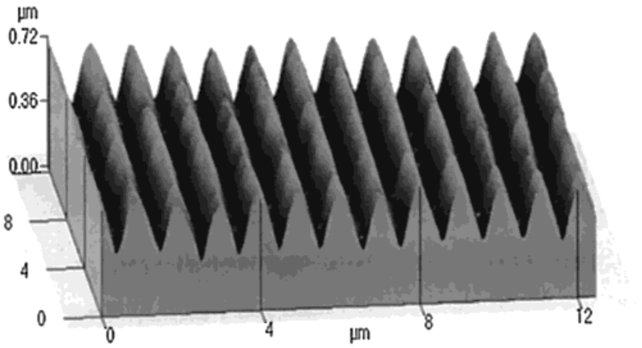


Figure 4. Three-dimensional view of the SRGs on the film of azocellulose with a DS of 0.80.

Table 2. Thermal Cis−Trans Relaxation Rate Constants

DS	0.13	0.32	0.49	0.80	0.99
$k \times 10^5\,(\mathrm{s}^{-1})$	3.12	4.98	2.77	4.13	3.80

spectra b−d increase as the DS changes from 0.13 to 0.99. Correspondingly, the vibration band of the chromophore that appeared at 1214 cm^{-1} for C−O stretching in spectrum e is absent in the spectra for azocellulose polymers. These two observation suggest that azobenzene chromophore is covalently linked to cellulose polymers. The characteristic absorption for azophenol chromophores at 2226 (C≡N stretching band), 1598 and 1500 (aromatic C=C stretching), 1141 (C−N stretching), and 844 cm^{-1} (out-of-plane C−H bending of 1,4-disubstituded benzene rings) also clearly indicate the attachment of azophenol chromophores to the cellulose.

It is known that the isomerization cycles of azobenzene chromophores are composed of trans−cis photoisomerization, cis−trans photoreconversion, and cis−trans thermal reconversion. The thermal reconversion process is significantly slower than the photoreconversion isomerization; thus, it is often the rate-determining step for a process, which involve repeated trans−cis−trans isomerization cycles.[13] Figure 3 show the spectra of the film for azocellulose with a DS of 0.49 after photoexciation with UV light at 360 nm for 5 min. The intense absorption at 350 nm due to the $\pi-\pi^*$ transition of the trans isomer increases, while the absorption maximum at 470 nm attributed to the $n-\pi^*$ transition of cis isomer[14] decreases in the thermal reconversion, or thermal relaxation, process. In the dark, the azobenzene chromophores in the polymer will undergo cis−trans isomerization, eventually returning back to their stable trans state.

If the relaxation processes that involve cis−trans isomerization are first order then a plot of $\ln(A_\infty - A_t)$ vs time should be linear with a slope of *k*, the rate constant of the thermal cis−trans isomerization. Here, A_∞ and A_t are the absorbencies at $\lambda = 350$ nm at equilibrium trans state and at time *t*, respectively. On irradiating the polymer films with UV light, the azobenzene chromophores recover back their original absorbance after a few days. Inset in Figure 3 shows a typical plot of $\ln(A_\infty - A_t)$ vs time obtained from a series of thermal relaxation spectra. The plot shows a linear behavior 40 min after the photoexcitation. The fast recovery component in the initial stage may be attributed to the relaxation of strained conformations of azobenzene chromophores that are trapped in the rigid glassy matrix.[13,14] Azocellulose polymers with varying DS also show similar features to that are presented in Figure 3. The rate constants for thermal relaxations of these polymers are shown in Table 2. These rate constants are of the same order (10^{-5} s^{-1}).

No glass trasition tempreatures were obtained for all the azocellulose polymers even when the temperature reached to decomposition stage (230 °C).

Figure 4 shows a typical 3-D view of SRGs on the thin film of azocellulose with a DS of 0.80. A modulation depth around 3000 Å with a grating space of 1 µm was observed.

Conclusions

Azobenzene-modified cellulose (azocellulose) polymers have been successfully synthesized through linking 4-cyanophenylazophenol to natural cellulose of ultrahigh molecular weight by the Mitsunobu reaction. These novel azocellulose polymers with varying degrees of substitution ranging from 0.13 to 0.99 were obtained by changing the molar ratios of reactants and were characterized by solid-state ^{13}C CP/MAS NMR and FT-IR spectroscopies. The analysis results suggest that the coupling reaction occur preferentially at the C6 carbon site indicating that the primary alcohol is the predominant reactive group among the three-hydroxyl groups present in the repeating unit of cellulose. The thermal cis−trans isomerization of azocellulose polymers exhibit two processes: (a) a fast process due to relaxation of azobenzene chromophores trapped in a strain conformation at temperatures below its glass transition temperature and (b) a slow process which follows a single exponential decay. Finally these polymers demonstrate for the first time that surface relief gratings can be inscribed on azo polymers with ultrahigh molecular weight.

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