Polymer Bulletin 32, 77–81 (1994)

Polymer Bulletin

Gelation of cellulose whose hydroxyl groups are specifically substituted by the fluorescent groups

Hideyuki Itagaki[1,*], Ikunori Takahashi[1], Minako Natsume[1], and Tetsuo Kondo[2,*]

[1]Department of Chemistry, Faculty of Education, Shizuoka University, 836 Ohya, Shizuoka 422, Japan
[2]Forestry and Forest Products Research Institute, Tsukuba, Ibaraki 305, Japan

Summary

The hydroxyl groups of cellulose molecules were specifically substituted by fluorescent probe groups and their fluorescence behavior was studied with the change in the concentration of the THF solution. The results show that the fluorescent probes yield microscopic information on aggregation and that the hydroxyl groups at the 6-position of the cellulose repeating unit play an important role in this gelation process.

Introduction

The characteristic features of cellulose molecules such as the rigidity of the chain and the insolubility in many solvents are attributed to three hydroxyl groups (2-, 3- and 6-position) in an anhydroglucose unit of cellulose forming both inter- and intra-molecular hydrogen bonds. The substitution of the hydroxyl groups by functional groups is known to induce gelation (1) or liquid crystallization (2-4), where the intermolecular hydrogen bonds may play an important role. Thus we aimed at clarifying the function of each hydroxyl group of cellulose in the aggregated states such as gel.

We have already succeeded to study on the gelation process of isotactic polystyrene in decalin by means of fluorescent probe method (5), because the luminescent probe techniques can be effective tools to investigate microstructures and motions of polymer molecules especially because of its having the advantage of high sensitivity (6-8). As for cellulosic materials, Winnik et al. introduced fluorescent probes such as pyrenyl group to hydroxypropylcellulose and monitored their emission behavior in relation to polymer aggregation (9-13). Although their trial should be valued high, there are some problems in their samples: i.e., (i) a pyrenyl moiety is so bulky that its hydrophobic interaction with another pyrenyl group could be an important factor for the polymer-polymer association in water, (ii) the pyrenyl group of Winnik et al.'s samples is far from the cellulose main chain (12 atoms spaced between the pyrenyl group and the anhydroglucose unit), and (iii) the fluorescence probes are randomly introduced to the cellulose polymer.

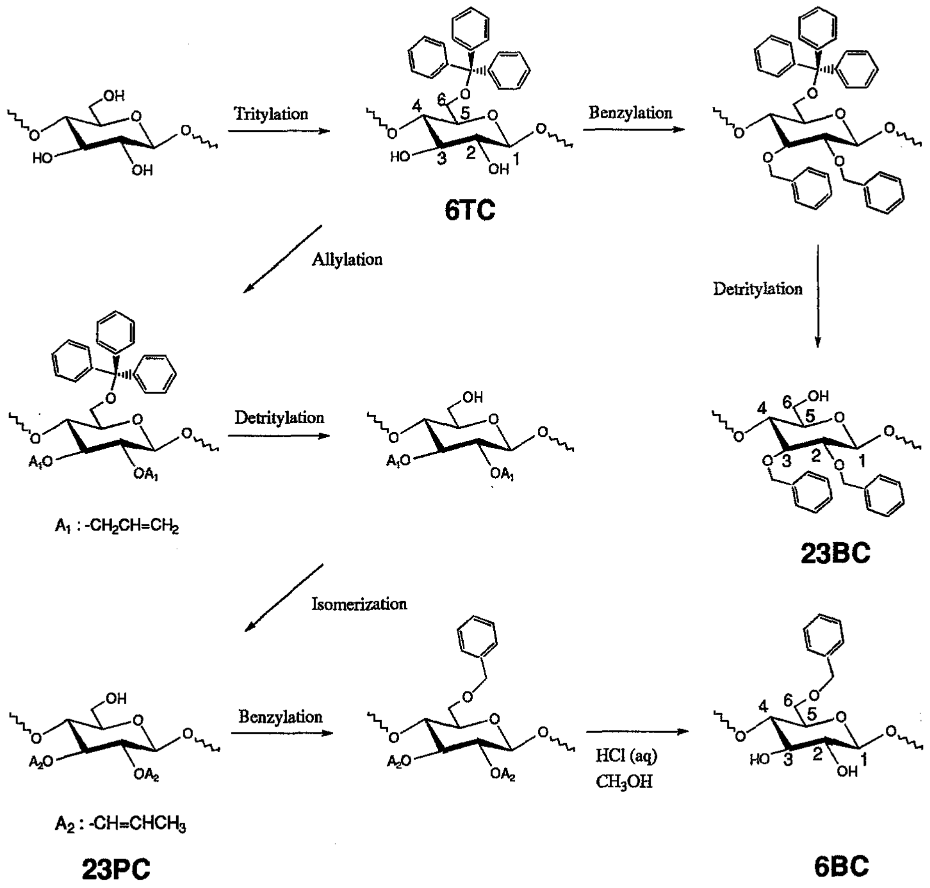
In order to get more microscopic information on the aggregated state formed by the hydrogen bonds in cellulose molecules, we chose one of the smallest fluorescent probes, that is benzyl group, and prepared cellulose samples whose hydroxyl groups are regioselectively substituted by them. Since the fluorescence probes are situated in the vicinity of the anhydroglucose unit, we anticipate that their fluorescence will be influenced by the polymer-polymer association and that they will give information on the function of each hydroxyl group of cellulose having different polarity to form a hydrogen bond. With the specifically fluorescent-labeled cellulose, we report their fluorescence behavior accompanying the gelation process in the present paper.

Experimental

Materials The cellulose samples whose hydroxyl groups are specifically substituted by benzyl group were prepared following to the procedure employed to synthesize 6-O-alkylcelluloses and 2,3-di-O-alkylcelluloses (Scheme 1). The detail of the preparative method is as follows.

---

[*] Corresponding authors



Scheme 1

Procedures for the preparation of cellulose samples used for the fluorescence measurements

6-O-(triphenylmethyl)cellulose (6TC) The synthesis of 6TC has been reported already (14,15); it was prepared from the completely deacetylated cellulose with triphenylmethyl chloride in dry pyridine. The yield of the product was 95% of the theoretical, and the degree of substitution (DS) by triphenylmethyl groups was 1.07 by ^{1}H-nmr measurements.

2,3-di-O-benzylcellulose (23BC) 2,3-Di-O-(benzyl)-6-O-(triphenyl-methyl)cellulose was first prepared by the benzylation of 6TC(1.0 g) after the procedure of Kageyama et al. (16) with 5.9 ml of benzyl chloride and 1.98 g of sodium hydroxide in 60 ml of dimethyl sulfoxide. Following isolation and purification with 95 % aq. methanol, this polymer (2.0 g) was then treated with HCl gas in 60 ml of CH_2Cl_2 for 3 min at 0°C to remove triphenylmethyl groups. The reaction mixture was poured into 150 ml of acetone and the product was isolated by centrifugation, washed with acetone, and dried under vacuum at 65°C. The triphenylmethyl groups was completely removed, checked by ^{13}C-nmr and FT-IR. DS by benzyl groups of the product was more than 1.9 (1.9-2.0).

6-O-benzylcellulose (6BC) 6BC was synthesized by way of 2,3-Di-O-(1-propenyl)-cellulose (23PC) whose preparation method was already described elsewhere (17). The benzylation of 23PC (2.0g) was carried out by the dropwise addition of benzyl chloride (9.9

ml) into 90 ml of the dimethyl sulfoxide solution of 23PC with 3.3 g of powered sodium hydroxide dispersed. The solution was kept under N_2 atmosphere for 4 h at 70°C. The reaction mixture was poured into 95 % aq. methanol. The yields of products were ~95% after the isolation and purification. Then 1-propenyl groups of 2.5 g of the benzylated 23PC was removed by the hydrolysis with 150 ml of 1M HCl in aqueous methanol at room temperature for 8 h. The product was isolated by pouring the mixture into cooled water, filtered, and washed thoroughly with distilled water. The final product was dried under vacuum at 65°C and characterized by FT-IR and nmr measurements. DS by the benzyl substituent of the product was 1.0.

Fluorescence Measurements Fluorescence spectra and fluorescence excitation spectra were measured on a Hitachi F-3000 spectrofluorometer. The emission signal was digitized and transferred into an NEC personal computer system. All the measurements were performed for the aerated solutions of THF, which was purchased from Wako Co. (spectrograde) and was used without further purification. Fluorescence measurements for the aerated THF solution of 23BC, 6BC and 6TC were carried out in a quartz cell with an optical path length of 1 mm. A cell was set at 45° to the exciting beam. Excitation wavelength was chosen to be 259 nm. The sample temperature was controlled by an Oxford DN1704 cryostat with a ITC-4 digital temperature controller. Temperature regulation is easily better than ± 0.1 K.

Results and Discussion

In order to examine whether the gelation process takes place or not, concentrated THF solutions of 23BC, 6BC, and 6TC were quenched below 0°C after making transparent solutions above 40°C. The gelation occurs only in THF solutions of 23BC whose concentration is higher than 1%, while even 3% solutions of 6BC and 6TC are kept to be in solution form. Since the concentration of 3% is close to the solubility limitation, it is concluded that the solutions of 6BC and 6TC do not form gel while the 23BC solution forms gel. The above results suggest that the intermolecular relationship of benzyl modified cellulose molecules requires the hydrogen bond engaged in the 6-position hydroxyl group, and that the 2- and 3-position hydroxyl groups of 6BC and 6TC do not play an important role to make their aggregation.

Next we tried to get microscopic information by means of fluorescence measurements. Figure 1 shows the fluorescence spectra of 23BC in both gel and solution forms

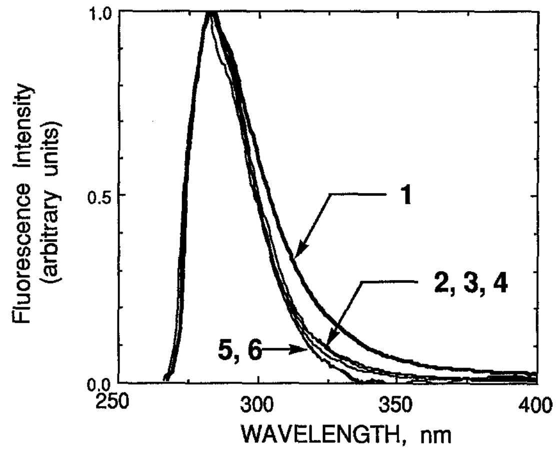


Figure 1 Fluorescence spectra of benzyl group of 23BC and 6BC in THF (excitation wavelength is 259 nm); (1) 3% 23BC at 273 K (gel form), (2) dilute solution of 23BC at 273 K, (3) 3% 23BC at 313 K (solution form), (4) dilute solution of 23BC at 313 K, (5) 3% 6BC at room temperature, and (6) dilute solution of 6BC at room temperature.

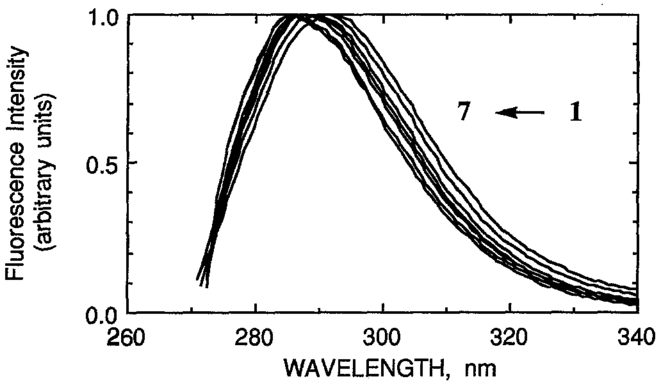


Figure 2 Concentration dependence of fluorescence spectra of triphenylmethanol in aerated THF at room temperature; the peak wavelength is 292 nm for 1.5M solution (1), 291 nm for 1.0M, 288 nm for 0.51M and 0.25M, 287 nm for 0.13M, 286 nm for 0.015M and 0.0076M (7).

together with those of 6BC in dilute and concentrated THF solutions. The fluorescence spectra of benzyl group of 6BC are precisely identical with each other no matter what the concentration is, demonstrating that it is isolated from other benzyl groups even at high concentration of 6BC as 3% (5 and 6 in Figure 1). However, the fluorescence spectrum of 23BC in THF at 273K (1 in Figure 1), which is in gel form, shows that the structureless fluorescence band appears in the longer wavelength region compared to the other spectra. Since its fluorescence excitation spectrum agrees well with the absorption spectrum, this fluorescence in the longer wavelength region is assigned to excimer emission. The fluorescence spectrum of dilute solution of 23BC (2 in Figure 1) compared to the spectra of 6BC suggests that the formation of intramolecular excimer in 23BC system is possible but that its emission intensity is quite low. Thus most excimer observed in 23BC gel (spectrum 1 in Figure 1), which was prepared by quenching the solution down to -80°C, is concluded to be formed intermolecularly. On the other hand, no intermolecular excimer is observed in concentrated solution (3%) of 23BC (see 3 and 4 in Figure 1) at higher temperatures where it appears to be in solution form, indicating that the hydrogen bond engaged in the 6-position hydroxyl group cannot be fixed stably at this high temperature and that there is no aggregation of cellulose molecules. In conclusion, Figure 1 suggests that the aggregation can be monitored by observing the formation of intermolecular benzyl excimer.

Although 6TC never forms gel at high concentration as 3%, we examined the fluorescence behavior of 6TC solutions with various concentrations, because the fluorescence of triphenylmethyl group can be a probe for microscopic concentration. Figure 2 shows that the fluorescence spectra of triphenylmethanol (TPM), a monomer model compound of 6TC, are dependent on the concentration; the emission peak shifts to longer wavelengths with an increase in concentration. Figure 3 shows that the fluorescence spectra of 6TC consist of only monomeric fluorescence at any concentrations and agree precisely with one another. If there is any significant interunit interaction among triphenylmethyl groups of 6TC caused by a hydrogen bond, the increase in microscopic concentration should induce the red-shift of its emission peak as well as the case of 6TC bulk film (peak wavelength, 295 nm). The 6TC concentration of 3% (wt/wt) is not more than 0.1M as triphenylmethyl moiety and the emission peak of 0.1M solution of TPM is not shifted so much relative to that of the dilute solution as shown in Figure 2. Thus we can conclude that 6TC molecules are uniformly soluble in 3% THF solution.

In summary the present results clearly show that the fluorescent probes give important information on aggregation and that the hydrogen bond engaged in the hydroxyl groups at the 6 position of the repeating unit of cellulose plays an important role in gelation process. Since we have established the effectiveness of our cellulose samples, we plan to

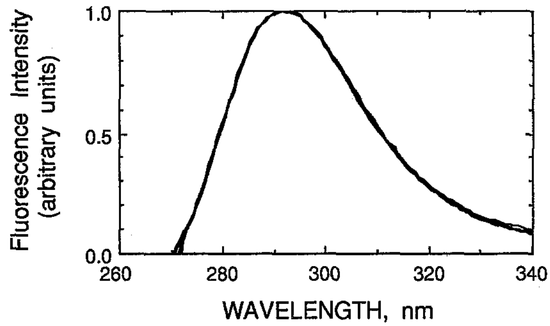


Figure 3 Concentration dependence of fluorescence spectra of 6TC in THF at room temperature; concentrations are 2.6, 0.52, 0.052, and 0.026 %(wt/wt).

clarify the gelation process of 23BC by monitoring the temperature and time dependence of the excimer formation efficiency in the near future.

References

(1) Clark A H, Ross-Murphy S B (1987) Adv Polym Sci 83: 129
(2) Gray D G (1983) J Appl Polym Sci Appl Polym Symp 37: 179
(3) Gray D G (1985) Faraday Discuss Chem. Soc 79: 257
(4) Yamagishi T, Fukuda T, Miyamoto T, Watanabe J (1988) Polym Bull 20:373
(5) Itagaki H, Takahashi I (1993) Chem Phys Lett 205: 446
(6) Winnik M A Ed. Photophysical and Photochemical Tools in Polymer Science (Conformation, Dynamics, Morphology); NATO ASI Series, Reidel, Dordrecht, 1986
(7) Hoyle C E, Torkelson J M Eds. Photophysics of Polymer Systems; ACS Symp. Series; American Chemical Society; Washington, DC, 1987
(8) Itagaki H, Horie K, Mita I (1990) Prog Polym Sci 15: 361
(9) Winnik F M, Winnik M A, Tazuke S, Ober C K (1987) Macromolecules 20: 38
(10) Winnik F M (1987) Macromolecules 20: 2745
(11) Yamazaki I, Winnik F M, Winnik M A, Tazuke S (1987) J Phys Chem 91: 4213
(12) Winnik F M (1989) Macromolecules 22: 734
(13) Winnik F M, Tamai N, Yonezawa J, Nishimura Y, Yamazaki I (1992) J Phys Chem 96: 1967
(14) Hearon W M, Hiatt G D, Fordyce C R (1943) J Am Chem Soc 65: 2449
(15) Kondo T, Gray D G (1991) Carbohydr Res 220: 173
(16) Kageyama K, Isogai A, Iiyama K, Nakano J (1985) Mokuzai Gakkaishi 31: 274; Chem Abstr 103: 23925g (1985)
(17) Kondo T (1993) Carbohydr Res 238: 231

Accepted November 17, 1993 S