

Regioselective Substitution of 2-Isocyanatoethylmethacrylate Onto Cellulose

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ABSTRACT: Cellulose is a well-known versatile polymer that presents a wide range of material properties via the substitution and grafting reactions of its hydroxyl groups. Because of their commercial potential, combinations of cellulose and vinyl polymers have been examined with various grafting methods. In this study, the condensation reactions of regioselective and nonregioselective substitution with 2-isocyanatoethylmethacrylate were performed in a homogeneous solvent system of dimethyl acetamide/lithium chloride. The successful substitution was confirmed by Fourier transform infrared spectroscopy, ¹H-NMR, cross-polarization/magic angle spinning ¹³C-NMR, thermogravimetric analysis, and X-ray diffraction. The substituted celluloses showed excellent thermal stability and a different polymorph with a depressed cellulose–intrinsic polymorphic phase. The 2-isocyanatoethylmethacrylate side chain seemed to expand the intermolecular distance with enhanced chain mobility and trigger the formation of a novel crystalline polymorph with a dramatically improved thermal stability. This investigation provided us with a useful understanding of the modification of cellulose with spatial distribution control for advanced future applications requiring a combination of cellulose with vinyl polymers. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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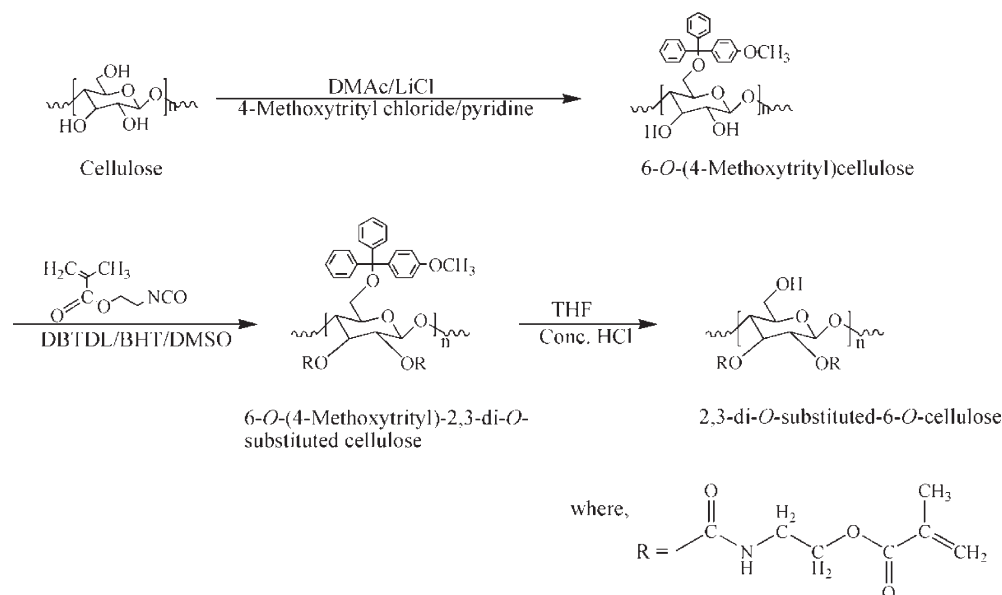
INTRODUCTION

Cellulose is the most abundantly available biomacromolecule; it consists of a linear β -(1-4)-glucan structure with three alcoholic groups per anhydroglucose unit (AGU) and a primary and two secondary alcohols functions with different reactivities. This biomacromolecule was investigated and developed as fibers and films of its derivatives, such as cellulose acetate, carboxymethyl-cellulose, and alkyl cellulose; these have mainly been modified by esterification and etherification. However, because of its unique structure, cellulose has broad potential in the design of more advanced polymeric materials, such as sensor matrices, recognition devices, selective membranes, organic–inorganic complex materials, and bioactive and biocompatible materials. To prepare these kinds of advanced materials, the functional groups of cellulose are modified to alter its properties.

Because the spatial distribution of substituents has a strong influence on ordered hydrogen bonding, intermolecular interactions, and crystal structures, the precise control of the distribution provides a useful tool for tailoring the physical and chemical properties of cellulose. Thus, it is necessary to establish a

preparation method of cellulose derivatives with controlled spatial distribution of substituted moieties within the AGU. The modification of the more reactive C-6 primary hydroxyl group in cellulose is especially convenient and useful.

Many regioselective substitution reactions have been reported for cellulose, including esterification,¹ etherification,¹ methylation,² bromination/azidation,³ and oxidation.⁴ The most effective preparation of regioselectively substituted cellulose derivatives has been carried out largely by the selective protection of the 6-O position with bulky protective groups, such as trityl,^{5,6} trimethylsilyl,⁷ and hexyl dimethylsilyl groups.⁸ Thus, the synthetic route requires two essential reaction steps that introduce and remove the protecting group (protecting and deprotecting). After the deprotecting step, the reactive OH groups are easily accessible for further modification, such as by acylation, silylation, esterification, etherification, halogenation, oxidation, and other subsequent functionalization for further reactions.⁵ These modifications of AGU provide a versatile route for the structural and property design of advanced cellulose-based materials.



Scheme 1. Regioselective substitution reaction of cellulose.

Combinations of celluloses and vinyl polymers have been intensively investigated because of their commercial importance. In previous studies, various free-radical polymerizations have been used for a range of cellulose graft copolymers based on vinyl and acrylic monomers. However, these methods have some drawbacks. Although the drawbacks vary with the type of monomer and grafting method, they typically include (1) possible chain scission, (2) a relatively low grafting yield, (3) very long grafted side chains, and (4) potentially large amounts of homopolymer formation and their associated removal difficulties.⁹

In this study, we aimed to achieve regioselective substitution of cellulose by a condensation reaction with methacrylate having reactive isocyanate functionality to obtain cellulose with carbon–carbon double bonds in a spatially well-controlled manner. The resulting polymers were expected to be useful for combinations of cellulose with any vinyl polymer. Copolymerization with various vinyl monomers, reactive processing including reactive injection molding or simple blending, can benefit from this regioselective substitution and the resulting substituted celluloses. In particular, we show that the modification could be carried out under homogeneous conditions. In this article, we report for the first time the effects of regioselective substitution of methacrylate monomer through a urethane linkage on the thermal and crystalline properties of cellulose.

EXPERIMENTAL

Materials

Cellulose was obtained from the deacetylation of cellulose acetate from Sigma-Aldrich (St. Louis, MO, molecular weight = 30,000, acetyl content = 39.8%). Lithium chloride (LiCl), butyl hydroxyl toluene (BHT), Dibutyltin dilaurate (DBTDL), anhydrous dimethyl acetamide (DMAc), and anhydrous pyridine were purchased from Sigma-Aldrich. Sodium hydroxide, methanol, *N,N*-dimethylformamide (DMF), and tetrahydrofuran (THF) were

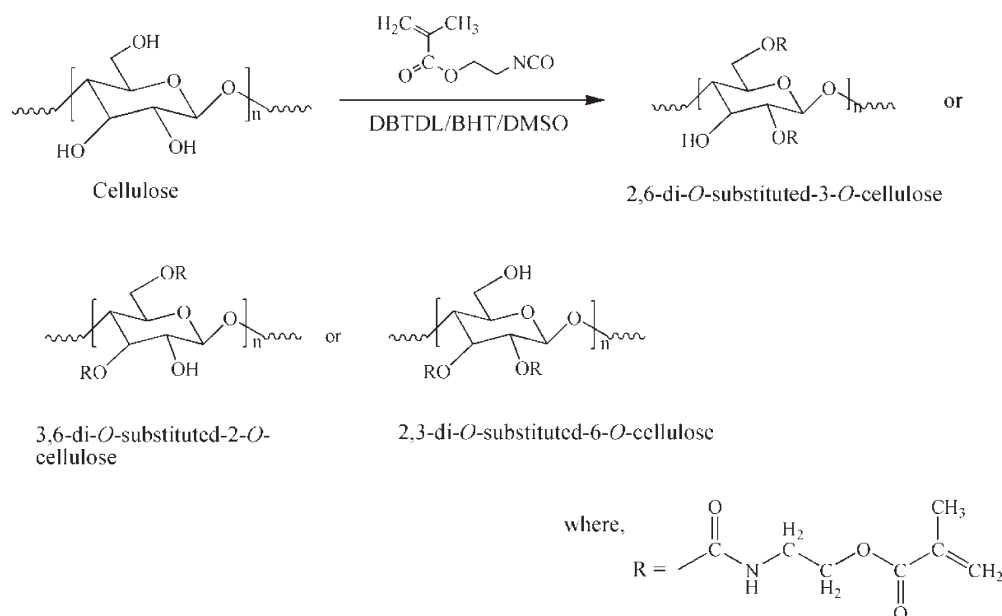
purchased from Samchun Chemical Co. (Seoul, South Korea). 2-Isocyanatoethylmethacrylate, and 4-methoxytrityl chlorides, were purchased from Tokyo Chemical Co. (Tokyo).

Protection of the Primary Hydroxyl Group by 4-Methoxytrityl Chloride

Regioselective substitution was studied with protection and deprotection chemistry. The more reactive hydroxyl group at the C-6 position was protected with a 4-methoxytrityl group with a 4-methoxytrityl chloride reagent. The synthetic route for the chemical reaction is shown in Scheme 1, as per a previous procedure.⁶ Cellulose (10.0 g, 61.7 mmol) was suspended in 200 mL of anhydrous DMAc and stirred at 120°C for 2 h. The slurry was then cooled to 100°C, and LiCl (15.0 g, 353.9 mmol) was added and stirred for 15 min. The mixture was cooled to room temperature and stirred overnight. Anhydrous pyridine (22.5 mL, 278.2 mmol) and 4-methoxytrityl chloride (57.5 g, 186.2 mmol) were added to the homogeneous solution. The solution was heated to 70°C and stirred for 4 h under nitrogen. The reaction mixture was allowed to cool to room temperature, and the polymer was isolated by precipitation in methanol. Further purification was achieved by the redissolution of the crude polymer in 200 mL of DMF and reprecipitation in methanol to produce a white powder. The resulting product was dried in a hood overnight; this was followed by vacuum drying at 60°C for 4 h. The obtained yield was 57.9 wt %.

Substitution of 2-Isocyanatoethylmethacrylate

An amount of 1 g of 6-*O*-(4-methoxytrityl) cellulose was dissolved in 300 mL of dimethyl sulfoxide (DMSO); this was followed by the addition of five drops of DBTDL and BHT (inhibitor, 0.78 mg). A solution of 2-isocyanatoethylmethacrylate (78 mg) was dissolved in 100 mL of DMSO and added dropwise to the mixture with vigorous stirring. The mixture was then continuously stirred overnight at 40°C to ensure a complete reaction. The product, 6-*O*-(4-methoxytrityl)-2,3-di-*O*-



Scheme 2. Nonregioselective substitution reaction of cellulose.

isocyatoethylmethacrylate cellulose, was precipitated in cold methanol. The product was dried in an oven at 60°C *in vacuum oven* for 4 h. The obtained yield was 50 wt %.

Deprotection of the Primary Hydroxyl Group

Removal of the bulky trityl group from methacrylate substituted cellulose [6-*O*-(4-methoxytrityl)-2,3-di-*O*-substituted cellulose] was performed according to a previous procedure.^{5,6} Six hundred milligrams of 6-*O*-(4-methoxytrityl)-2,3-di-*O*-isocyatoethylmethacrylate cellulose was dissolved in 52 mL of THF, and 2.51 mL of concentrated HCl was added dropwise. Stirring was continued for 5 h at room temperature to ensure complete deprotection. The isolated cellulose was dried *in vacuum oven* and named regioselective methacrylate-grafted cellulose (RC). The resulting dried product was obtained with a yield of 50 wt %.

Synthesis of Nonregioselectively Substituted Celluloses

Substitutions of 2-isocyanatoethylmethacrylate at different molar ratios of AGU to monomer (1 : 2 and 1 : 3) are shown in Scheme 2 (the substituent could actually present randomly at all C-2, C-3, and C-6 positions with a probably higher degree of substitution at C-6 because it was relatively more reactive). Cellulose dissolved in a DMAc/LiCl system was treated with 2-isocyanatoethylmethacrylate in the presence of BHT (inhibitor) and DBTDL (catalyst) and stirred at 40°C overnight to ensure a complete reaction. The modified cellulose was isolated by precipitation in methanol, and this was followed by drying *in vacuum oven*. The polymer was named nonregioselective double-bonded cellulose (NRC-1 : 2 or NRC-1 : 3). The obtained yield was 71 wt %.

Characterization

¹H-NMR spectra of the samples were obtained at 300 MHz (Gemini 2000, Varian, CA) with hexadeuterated DMSO as the

solvent. Cross-polarization/magic angle spinning (CP-MAS) ¹³C-NMR spectra of samples were collected with a VNMRS 400 spectrometer (Varian), operating at a frequency of 400 MHz. Fourier transform infrared (FTIR) spectroscopy was carried out with a Nicolet 6700 FTIR spectrometer (Thermo Scientific, Madison, WI) with the KBr disc technique. Spectra were recorded in the region 400–4000 cm⁻¹, and each spectrum was recorded with a total of 32 scans. Thermogravimetric analysis (TGA) was examined on a PYRIS6 (PerkinElmer, MA, Waltham, Massachusetts, USA) with 11–25-mg samples predried for 4 h *in vacuum oven* at 60°C. Thermograms were run in a nitrogen atmosphere at a constant heating rate of 10°C/min from room temperature to 700°C. X-ray diffraction (XRD) was carried with a D8-Advance (Bruker AXS GmbH, Karlsruhe, Germany) with Ni-filtered Cu K α radiation ($\lambda = 1.5460\text{\AA}$) at 40 kV and 40 mA. Scattered radiation was detected in the range of 2θ from 2 to 50° at a scanning rate of 2°/min. The crystallinity index (CI) of cellulose was calculated from a height of the 200 peak (I_{200} ; $2\theta = 21^\circ$) and the intensity minimum between the 200 and 110 peaks (I_{am} ; $2\theta = 12^\circ$) with the Segal method [eq. (1)].^{10,11} I_{200} represents both crystalline and amorphous material, where I_{am} represents the amorphous material:

$$\text{CI}(\%) = \left(1 - \frac{I_{\text{am}}}{I_{200}} \right) \quad (1)$$

RESULTS AND DISCUSSION

Regioselective and Nonregioselective Substitution of 2-Isocyanatoethylmethacrylate

The tritylation reaction of cellulose was conducted in a homogeneous solution system of DMAc/LiCl (Scheme 1). The cellulose dissolved in DMAc/LiCl was treated with 4-methoxytrityl chloride in the presence of pyridine. The tritylation was confirmed by ¹H-NMR spectra (Figure 1), where the chemical shift

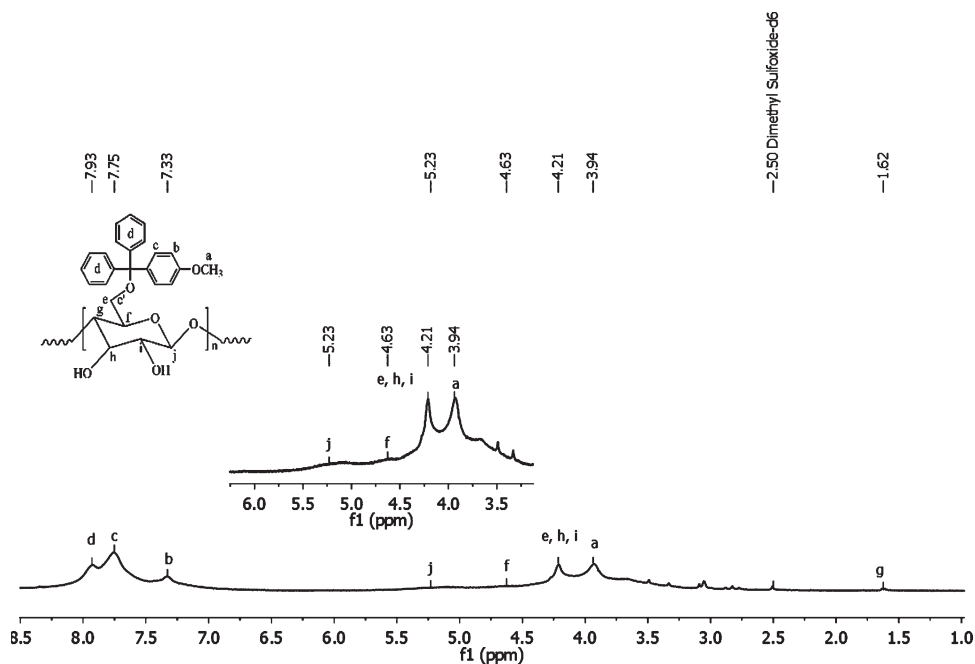


Figure 1. $^1\text{H-NMR}$ spectra of the protected cellulose.

in the range 7–8.0 ppm could be attributed to the aromatic protons of the trityl group, and those at 3–5.5 ppm were due to cellulose backbones. The presence of aromatic peaks confirmed the successful protection of the primary alcohol group. The residual hydroxyl groups were combined with a 2-isocyanatoethyl-methacrylate monomer through urethane linkage in the presence of DBTDL.¹²

Compared to virgin cellulose, the cellulose with incorporated bulky trityl groups led to the suppression of the hydrogen-bond-

ing interactions between cellulose chains. The primary hydroxyl group is a moiety highly responsible for hydrogen bonding. Therefore, its solubility, in common organic solvents, was significantly altered, and a homogeneous reaction solution was obtained with DMSO; this was important for the availability of residual hydroxyl groups from the backbone chain of the cellulose macromolecules (Figure 2). The residual hydroxyl groups in the protected cellulose acted as active sites for further functionalization reactions.⁶ The removal of the 4-methoxytrityl group was

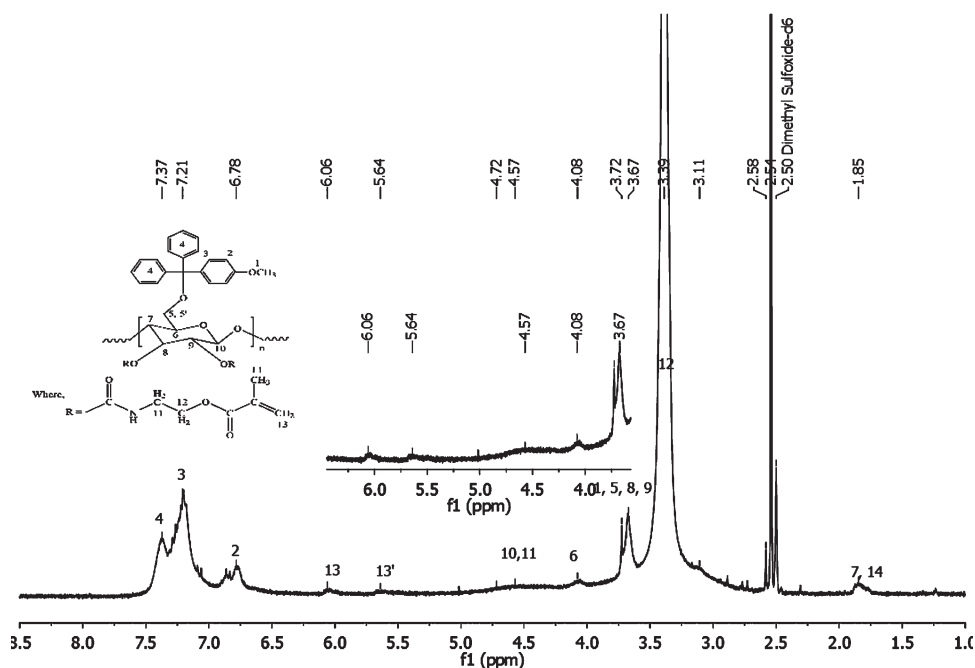


Figure 2. $^1\text{H-NMR}$ spectra of the substituted cellulose.

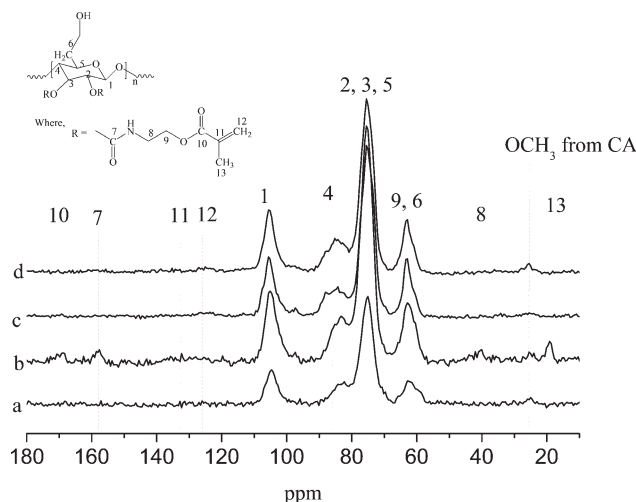


Figure 3. CP-MAS ^{13}C -NMR spectra of (a) cellulose, (b) RC, (c) NRC-1 : 3, and (d) NRC-1 : 2.

accomplished with concentrated HCl in THF. Deprotection was confirmed by CP-MAS ^{13}C -NMR, through the monitoring of aromatic peaks of the trityl group, as shown in Figure 3.

The nonregioselective substituted cellulose was synthesized with 1 : 2 and 1 : 3 molar ratios of AGU to methacrylate units. The homogeneous chemical reaction proceeded without the protection of the C-6 OH group. The routes for the chemical reactions are shown in reaction Scheme 2 and follow the same synthesis route as the regioselective scheme without the protecting and deprotecting steps.

Both cellulose derivatives were nearly insoluble in most common organic solvents. However, for RC, the protected samples were soluble in DMSO, although they became insoluble again after the removal of the trityl group. Before deprotection, the substitution was confirmed by ^1H -NMR, as shown in Figure 2. The aromatic protons from the trityl group were confirmed at 6.6–7.5 ppm and methacrylate unsaturation at 5.6 and 6.15 ppm. The presence of aromatic protons and methacrylate unsaturation confirmed that the 2-isocyanatoethyl methacrylate was covalently attached to the cellulose backbone chain.

The CP-MAS ^{13}C -NMR spectra were used to confirm the structures after chemical modification, as shown in Figure 3. The NMR spectra of cellulose showed relevant peaks between 120 and 50 ppm at 63 (C-6), 76 (C-2, 3, and 5), 85 (C-4), and 105 (C-1) ppm. For RC, the peaks were at 158 (C-7), 41 (C-8), 63 (C-9), 169 (C-10), 132 (C-11), 126 (C-12), and 18.5 (C-13) ppm. However, in both NRCs, some peaks of C-7, C-8, C-11, and C-12 were not clearly visible and may have been due to a lower substitution rate of 2-isocyanatoethyl methacrylate for cellulose. All of the samples showed small peaks at 25.5 ppm; this indicated OCH_3 from cellulose acetate.

All of the substituted celluloses were obtained as white powders and were used for further characterization. In the study of Mayumi et al.,¹³ the degree of substitution for regioselective substitution of cyclic esters was 0.5–0.7 in a DMAc/LiCl solvent system. Samaranyake et al.¹⁴ obtained cellulose derivatives with

a lower degree of substitution of less than 0.1 and 2.5 in DMAc/LiCl solvent. In this case, the degree of substitution was similarly low, and it was difficult to clearly assess by NMR.

Chemical Structure Analysis with FTIR Spectroscopy

FTIR spectroscopy is an appropriate technique for confirming the chemical structure of substituted cellulose after chemical modification.^{15,16} Figure 4 shows the FTIR results of cellulose (starting material), RC, NRC-1 : 3, and NRC-1 : 2. The FTIR spectrum of cellulose showed relevant bands at 3400 cm^{-1} (O—H stretching vibrations), 2900 cm^{-1} (C—H stretching), 1630 cm^{-1} (O—H bending), 1156 cm^{-1} (C—O—C stretching), and about 1020 cm^{-1} (stretching vibrations of the hydroxyl group). All the substituted cellulose spectra showed a slight decrease in the peak intensity at 3400 cm^{-1} , which was related to the decrease in the total number of OH groups in the cellulose main chains. The urethane bands were also visible at 3300 and $1515\text{--}1560\text{ cm}^{-1}$ (C—N stretching and N—H bending, respectively) and confirmed the substitution reaction. Finally, it was possible to verify the presence of C=C double bonds by the detection of the corresponding peak at 2880 cm^{-1} . These results confirmed the 2-isocyanatoethylmethacrylate monomer was covalently bonded to cellulose macromolecules. Similar peaks have been reported in the literature where 2-isocyanatoethyl methacrylate was attached to dextran.¹⁵

Thermal Stability Analysis

The examination of the thermal stability of substituted celluloses is important for highlighting the influence of selective substitution. Figure 5 shows the TGA curves of RC, NRC-1 : 3, and NRC-1 : 2; these illustrate the differences in thermal behavior caused by the substitution of a 2-isocyanatoethylmethacrylate moiety. In all cases, a small weight loss was observed in the range $25\text{--}100^\circ\text{C}$ due to the gradual evaporation of bounded moisture in the materials or of low-molecular-weight compounds.^{12,17} The thermal decomposition of substituted cellulose displayed a maximum degradation around 350°C . Both substitution processes increased the thermal stability of cellulose. The initial decomposition temperature (IDT) of cellulose was about 190°C , and those of the substituted celluloses were significantly

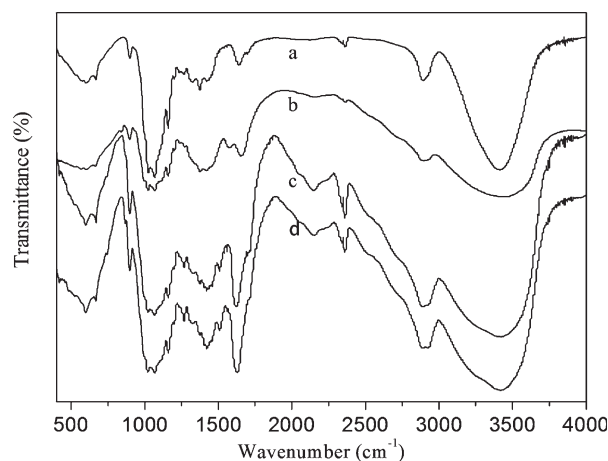


Figure 4. FTIR spectra of (a) cellulose, (b) RC, (c) NRC-1 : 3, and (d) NRC-1 : 2.

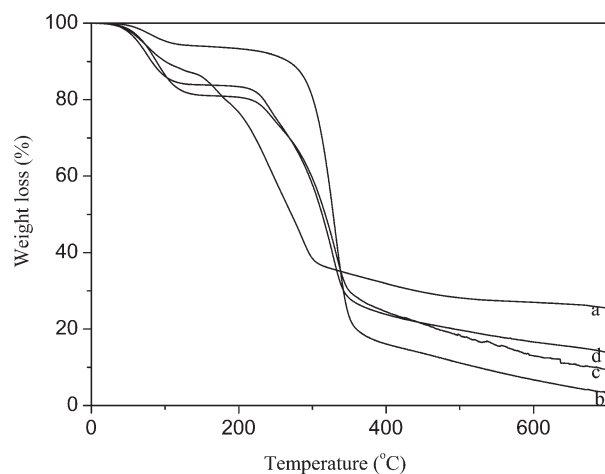


Figure 5. TGA curves of (a) cellulose, (b) RC, (c) NRC-1 : 3, and (d) NRC-1 : 2.

higher. Notably, the IDT of RC was the highest at 310°C; this was a dramatic improvement from that of cellulose.

Among the substituted celluloses, RC had a lower char yield than NRC and cellulose. At 700°C, the char yield was 4% for RC. The higher char yields of cellulose and NRC remained up to the final decomposition temperature of 700°C (26 and 11–15%, respectively). This likely indicated the presence of laevoglucose, a product obtained at higher temperatures by depolymerization and possibly due to the crystalline phase of cellulose.^{18,19} The decrease in char yield in the cases of substituted celluloses was probably related to the reduced crystalline phase of the original cellulose polymorph.

XRD Analysis

The crystallinity of the substituted celluloses was examined by XRD, and the results are shown in Figure 6. The cellulose showed typical diffraction peaks at 12 and 20°, and its CI, as calculated from the Segal method, was 22%. Both the NRC-1 : 3 and NRC-1 : 2 displayed strong crystalline peaks at 21° (the CI values calculated from the Segal method were 52 and 50%, respectively). RC displayed a broad halo between 5 and 25° and a crystalline peak near 13°. The broad halo, which usually spans 10–25°, is characteristic of amorphous material. The broad halo seemed to exist in all of the samples but was smallest in the case of NRC, where a relatively high crystallinity was observed.

The diffraction patterns of RC and NRC were apparently different from that of cellulose. Therefore, the simple result of the Segal method, that the crystallinity decreased in the order of NRC, cellulose, and RC, was misleading. Both RC and NRC appeared to have a different polymorph or crystal orientation because their XRD patterns were quite different in terms of both peak position and shape.

In a study by Yan et al.,¹⁷ cellulose-*g*-Poly(L-lactide) (PLLA) copolymers had an amorphous diffraction pattern, which may have been caused by the expansion of intermolecular distance and the enhancement of chain mobility due to the introduction of a relatively long PLLA side chain.¹⁷ Similarly, the bulky 2-isocyanatoethylmethacrylate side chain enhanced the cellulose

chain mobility by expanding the intermolecular distance and decreasing the cellulose–intrinsic polymorphic phase. At the same time, the enhanced crystallization of a different crystal polymorph (different crystal structure) due to the substitution of the OH group at the C-6 position could have been expected. Because the free OH group at the C-6 position is involved in intermolecular hydrogen bonding, its substitution can destroy the original crystal structures. However, if a different crystal structure available for the substituted cellulose chains is adapted, the expanded intermolecular distance and enhanced mobility could induce more effective crystallization to improve crystallinity and depress the amorphous phase content. Indeed, the 12° peak almost completely decreased, whereas the 21° peak increased in the cases of NRC; this suggested that a different crystal polymorph developed with a depressed amorphous phase. Therefore, it was the case that the crystallinity could not be assessed simply by the Segal method.

DISCUSSION

The regioselective substitution of 2-isocyanatoethylmethacrylate was successfully performed to produce novel polymers useful for conjugation and reactive compatibility with most vinyl monomers. The regioselectively substituted cellulose showed an interesting combination of improved thermal stability and a depressed cellulose–intrinsic polymorphic phase. This cellulose was compared with its nonregioselective counterparts prepared under the same reaction conditions without the protecting and deprotecting steps.

The results of XRD and TGA (different diffraction patterns and better thermal stability) consistently suggested the formation of a new polymorph different from the original cellulose crystal structure. The possible new polymorph endowed novel properties to cellulose in addition to the novel chemical structure of the branches.

The solubility of substituted celluloses, which was studied in common organic solvents at room temperature and at 50°C, was not better than that of cellulose. The substituted celluloses were insoluble in DMAc, DMF, DMSO, THF, ethanol, and

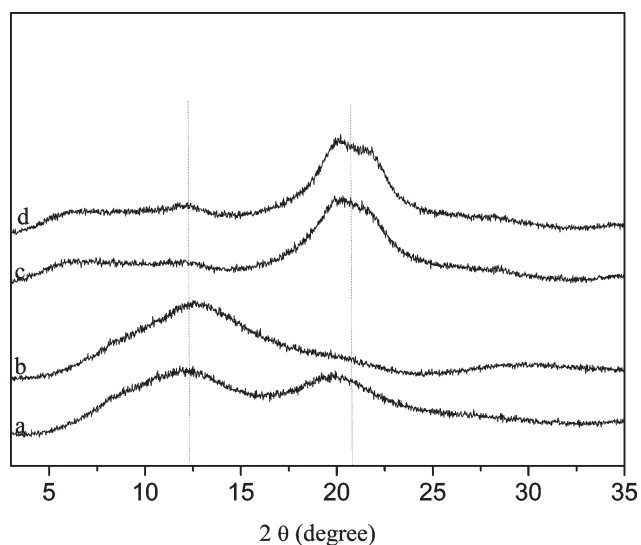


Figure 6. XRD results of (a) cellulose, (b) RC, (c) NRC-1 : 3, and (d) NRC-1 : 2.

chloroform. The insolubility might have been related to the lower substitution rates and the possible chemical crosslinking of substituted methacrylate groups; this remains to be determined by future research efforts.

CONCLUSIONS

Regioselective and nonregioselective substitutions of 2-isocyanatoethylmethacrylate monomer to cellulose by a homogeneous synthesis method were developed, and their influence on the properties of cellulose was investigated. NMR and FTIR confirmed that the 2-isocyanatoethylmethacrylate monomer was covalently attached to cellulose in both cases. Nonregioselectively substituted cellulose showed a lower IDT and a higher char yield than regioselectively substituted cellulose, whereas both of the substituted celluloses had significantly higher IDTs and lower char yields than pure cellulose. The good thermal stability of the substituted celluloses might have arisen from their crystallinity. On the basis of the thermal and XRD analyses, the methacrylate-grafted celluloses may have had different crystal structures, which provided unique properties. The high crystallinity of the nonregioselectively substituted cellulose was noticeable in the XRD analysis.

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