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Comparative Study of Homogeneous Solvents for the Esterification Crosslinking of Cellulose with 1,2,3,4-Butanetetracarboxylic Dianhydride and Water Absorbency of the Reaction Products

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ABSTRACT: Superabsorbent hydrogels were prepared via esterification crosslinking of cellulose with 1,2,3,4-butanetetracarboxylic dianhydride (BTCA) in three solvent systems: lithium chloride (LiCl)/*N*-methyl-2-pyrrolidinone (NMP), LiCl/*N*,*N*-dimethylacetamide (DMAc), and tetrabutylammonium fluoride/dimethyl sulfoxide (TBAF/DMSO). The absorbency of the hydrogels was strongly dependent on the BTCA feed to cellulose ratio as well as the nature of the solvent system used. The rate of cellulose esterification was enhanced in TBAF/DMSO relative to the other systems, and the highest water absorbency of the hydrogels (987 g g^{-1} polymer) was also achieved using this system. The hydrogels obtained in the TBAF/DMSO system had a similar degree of both crosslinking and grafting, indicating that both reactions were promoted to the same extent in this solvent, whereas crosslinking was preferentially enhanced over grafting in the LiCl/NMP and LiCl/DMAc systems. The difference in the composition of the hydrogels was attributed to the difference in the electronegativity of the fluoride and chloride anions in these solvents. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: cellulose; 1,2,3,4-butanetetracarboxylic dianhydride; superabsorbent hydrogel; cellulose-dissolving solvent; esterification crosslinking

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INTRODUCTION

Homogeneous functionalization of cellulose has been an area of active focus for cellulose research for a long time, even though homogeneous methods have not so far found industrial application in the production of cellulose derivatives. The homogeneous reaction of cellulose offers the advantages of creating options for incorporating functional groups, opening new avenues for design of the products, opening up the opportunity to control the degree of substitution (DS), etc. The homogeneous reaction of cellulose requires a solvent that is capable of dissolving cellulose and that provides a conducive reaction environment. However, the dissolution of cellulose is a formidable challenge because of the rigidity of the molecule that is composed of anhydroglucose units (AGUs) held together by 1,4-β-glucosidic linkages with structural close packing arising from numerous intermolecular and intramolecular hydrogen bonds.[1,2] To date, the number of solvent systems capable of disrupting the strong interactions because of the hydrogen bonds remains limited.

In recent years, ionic liquids, such as salts of *N*,*N*-disubstituted imidazolines, have been recognized as solvents for cellulose.[3] Good cellulose solvency has also been achieved using the combination of an aprotic, polar solvent and an inorganic salt and is particularly effective if the salt contains a hard cation. The structures of lithium chloride (LiCl)/*N*-methyl-2-pyrrolidinone (NMP)[4] and LiCl/*N*,*N*-dimethylacetamide (DMAc)[5] presented in Figure 1 illustrate that these systems possess the aforementioned characteristics and as such have good dissolution power for cellulose. One drawback of these systems, however, is that the dissolution process is time consuming and/or requires preswelling by sequential solvent change and heating.

Recently, good cellulose solvency was reported using a solution of tetrabutylammonium fluoride/dimethyl sulfoxide (TBAF/DMSO) presented in Figure 1.[6] This system can be used for rapid dissolution of celluloses having a very high degree of polymerization.[7] In addition, the system also proved useful as a reaction medium for chemical modifications of cellulose, such as acetylation,[6,8] succinylation,[9] carboxymethylation,[10] and

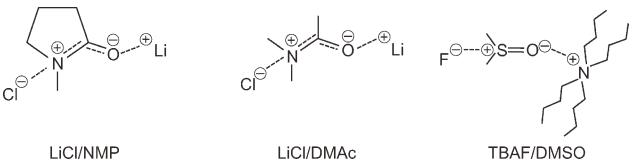

Figure 1. The hypothetical polar characteristics of the cellulose-dissolving solvent systems used in this study.

benzylation,[11] although the dissolution mechanism of the solvent system has not yet been fully elucidated.

We illustrated in a recent report,[12] as shown in Figure 2, that biodegradable superabsorbent hydrogels can be obtained from cellulose dissolved in a LiCl/NMP solvent system by esterification crosslinking of 1,2,3,4-butanetetracarboxylic dianhydride (BTCA) in the presence of 4-dimethylaminopyridine (DMAP) as an esterification catalyst. Fourier transform infrared (FTIR) and solid-state nuclear magnetic resonance (NMR) spectroscopic analyses of the hydrogels demonstrated that crosslinking and grafting of BTCA occurred simultaneously by the formation of diester and monoester linkages, respectively, in the stated reaction medium. Following neutralization with aqueous NaOH, the carboxyl group generated by the crosslinking and graft reactions is converted to sodium carboxylate, which enhances the affinity of the polymer to water, and consequently, the product is capable of absorbing water. The absorbency of the products was found to be strongly dependent on the average degree of polymerization (DP) of cellulose, and the use of cotton cellulose with a high DP of about 2400 produced a hydrogel with an absorbency of 720 times its dry weight. In addition, the hydrogels exhibited good biodegradability, with a maximum degradation of 95% within 7 days using cellulase. Thus, the product obtained by the esterification crosslinking of BTCA demonstrated exceptional potential as a substitute for conventionally used sodium polyacrylate (SPA) superabsorbent hydrogel, which suffers from the limitation of being nonbiodegradable.

The aim of this article is twofold. The first objective is to optimize the homogeneous reaction solvent system for the production of the superabsorbent hydrogels from cellulose and BTCA to maximize the efficiency of the biodegradable superabsorbent polymer synthesis. The second objective is to clarify the effect of the nature of various solvent systems on the esterification reaction. LiCl/NMP, LiCl/DMAc, and TBAF/DMSO (Figure 1) solvent systems, which are frequently used for the homogeneous derivatization of cellulose, were selected herein as the reaction media for the esterification reaction of cellulose and BTCA. A comparison of the water absorbency of the products obtained in each solvent system on the basis of their structure, as well as the effect of each solvent system on the interaction between the hydroxyl group of cellulose and acid anhydride of BTCA, which is considered to be one of the most important reactions in the study of interactions between cellulose and solvents, is presented.

EXPERIMENTAL

Materials

High-purity hardwood pulp with a DP of 800 determined on the basis of viscosity (Sulfate HJ, from Rayonier) was used as a cellulose source. The cellulose was dried to <1% moisture before use. NMP (Wako Chemicals, Japan) and DMAc (Kanto Chemicals, Japan) were distilled under reduced pressure and stored under nitrogen over Riedel-type 4-Å molecular sieves (Sigma-Aldrich). DMSO (Kanto Chemicals, Japan) was dried at 200°C under reduced pressure before use. LiCl and TBAF·3H_2O were purchased from Tokyo Kasei, Japan. BTCA and SPA were kindly supplied by Shin Nippon Rika, Japan, and Sundaiya Polymer, Japan, respectively. CMC (DP of 505 and DS of 0.72) was purchased from Junsei Chemicals, Japan. All other reagent used in this study were of analytical grade, which were purchased from Kanto Chemicals, Japan.

Dissolution of Cellulose in LiCl/NMP

Cellulose (1.0 g, 6.2 mmol based on AGU) pretreated by sequential preswelling with water and NMP was suspended in a mixture of NMP (95 g) and LiCl (5.0 g, 117 mmol) in a 300 mL of round-bottom flask. The mixture was stirred with Teflon impeller at 500 rpm of the rotation at 25°C for 2 days, yielding a clear solution.

Dissolution of Cellulose in LiCl/DMAc

Cellulose (1.0 g), pretreated using a literature[5] sequential preswelling method with water and DMAc, was suspended in DMAc (95 g) in a 300 mL of round-bottom flask equipped with a short path condenser. The suspension was stirred with the Teflon impeller at 500 rpm and heated to 150°C for 60 min, and 5.0 g of LiCl (117 mmol) was added. The mixture was subsequently heated to 170°C for 15 min, and the reaction mixture

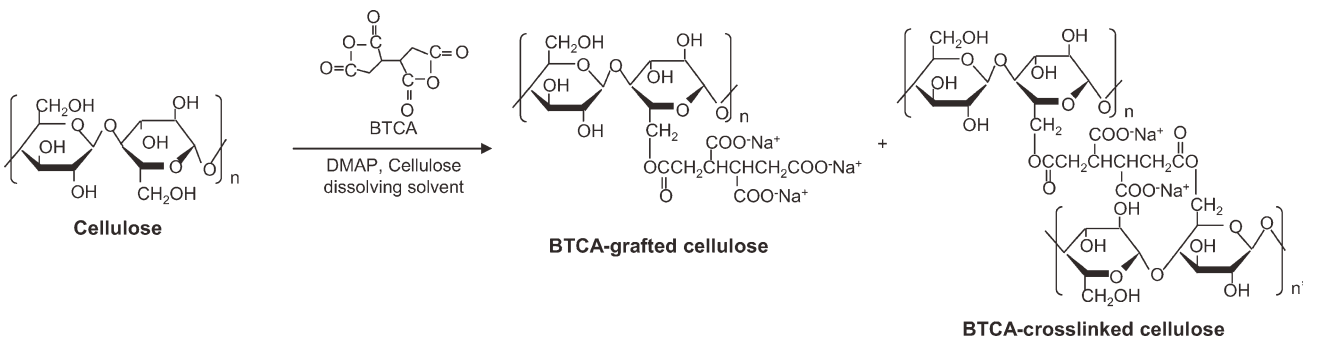

Figure 2. Synthesis of BTCA-crosslinked cellulose in cellulose-dissolving solvents using DMAP as a catalyst.

Table I. Reaction Conditions and Results of the Esterification Crosslinking of Cellulose with BTCA in LiCl/NMP, LiCl/DMAc, and TBAF/DMSO Solvent Systems

Solvent system	BTCA feed ratio to AGU	n_{COONa}/n_{ester}[a]	E[b] (mmol g^{-1})	C_{CR}[c] (%)	C_{GR}[d] (%)	n_{CR}[e]	n_{GR}[f]	n_{total}[g]	Absorbency[h] (g g^{-1})
LiCl/NMP[i]	0.5	1.16	0.715	85	15	0.06	0.01	0.07	25
	1	1.18	1.10	83	17	0.09	0.02	0.11	182
	2.5	1.25	2.05	78	22	0.20	0.06	0.26	308
	5	1.27	2.82	76	24	0.33	0.10	0.43	127
	7.5	1.32	2.89	72	28	0.34	0.13	0.47	100
LiCl/DMAc	0.5	1.22	1.22	80	20	0.11	0.03	0.13	220
	1	1.27	2.29	76	24	0.24	0.07	0.31	498
	2.5	1.24	3.01	79	21	0.37	0.10	0.47	264
	5	1.24	3.27	79	21	0.43	0.12	0.55	176
	7.5	1.28	3.39	75	25	0.46	0.15	0.61	168
TBAF/DMSO	0.5	1.68	2.46	49	51	0.23	0.24	0.47	726
	1	1.62	2.98	53	47	0.34	0.30	0.64	987
	2.5	1.64	3.18	52	48	0.39	0.36	0.75	596
	5	1.73	3.25	47	53	0.40	0.46	0.86	522
	7.5	1.75	3.29	45	55	0.41	0.50	0.91	475

[a]Molar ratio of sodium carboxylate group to ester linkage, which was determined by lineshape analysis of carbonyl carbon region the solid-state ^{13}C-NMR spectrum of each product., [b]Total ester linkages in 1 g of each product, obtained from the result of the titration method., [c]Molar percentages of crosslinked BTCA in total esterified BTCA in each product., [d]Molar percentages of grafted BTCA in total esterified BTCA in each product., [e]Average number of BTCA molecules involved in esterification crosslinking per AGU; $n_{CR} = n_{total}\ C_{CR}/100$., [f]Average number of BTCA molecules involved in esterification graft per AGU; $n_{GR} = n_{total}\ C_{GR}/100$., [g]Average number of BTCA molecules per AGU; $n_{total} = n_{CR} + n_{GR}$., [h]Water absorbency of each product after 72 h., [i]See Ref. 12.

was cooled to room temperature and stirred overnight for dissolution, yielding a clear, sandy-colored solution.

Dissolution of Cellulose in TBAF/DMSO

Cellulose (1.0 g) was suspended in a mixture of DMSO (92 g) and TBAF·3H_2O (8 g, 25 mmol) in a round-bottom flask. The mixture was stirred with Teflon impeller at 500 rpm at room temperature for about 2 h, yielding a clear solution.

Preparation of Superabsorbent Hydrogels

Superabsorbent hydrogels were prepared from cellulose according to the scheme presented in Figure 2. The procedure for the preparation of the hydrogel from cellulose pulp with the BTCA feed ratio of 2.5 in Table I was as follows. A total of 1.14 g of DMAP (9.3 mmol) was added to the cellulose solutions of the three solvent systems described above, each of which contained 1.0 g of cellulose (6.2 mmol). After complete dissolution of DMAP, 3.1 g of BTCA (15.5 mmol), which corresponds to 2.5 times the molar feed ratio to the AGU, was added to each cellulose solution. Esterification was allowed to proceed with stirring with a Teflon impeller (500 rpm) at room temperature for 24 h, after which the reaction mixture was poured into a mixture of methanol (800 g) and water (200 g) with stirring to precipitate the product, and then the product was neutralized to pH 7 with 10% (w/v) aqueous NaOH.[12] The precipitate was filtered by use of a glass filter and was then purified twice by reprecipitation with methanol and water. The purified product was dried under reduced pressure, finally cut with a mixer, and screened through a 16-mesh sieve to obtain a white granular product. Hydrogels from the cellulose sources listed in Table I were prepared according to a procedure similar to that described above by changing the molar feed ratio of BTCA or by changing cellulose source. The starting amount of cellulose was fixed to 1.0 g for the preparation of the all hydrogels.

Structural Analysis

FTIR spectra were recorded on a PerkinElmer Spectrum II spectrophotometer by diluting the samples in KBr powder. The powder mixture was compressed into a transparent disk and scanned from 4000 to 400 cm^{-1} using the average of 32 scans, with a resolution with 1 cm^{-1}. Dipolar decoupled solid-state ^{13}C-NMR spectra were recorded on a Bruker Biospin Avance II 500 spectrometer with 4-mm dual-tuned magic-angle spinning (MAS) probe at a MAS frequency of 10,000 Hz. ^{13}C-excitation pulse with the flip angle of 30°, date acquisition time, and repetition time were set to 1.5 μs, 20 ms, and 30 s, respectively. During the data acquisition period, two pulse phase modulation (TPPM) proton decoupling[13] was applied with a ^{1}H field strength of 72 kHz. The spectra were typically accumulated 2000–3000 times to achieve a reasonable signal-to-noise ratio. Chemical shifts were calibrated based on the carbonyl carbon resonance of glycine at 176.03 ppm, used as an external reference. The obtained NMR data were transferred to a Windows PC for line fitting. Lineshape analysis of the NMR spectra was performed using the Nuts software (Arcon NMR), and nonlinear least-squares methods were used for line fitting using the previously described Lorentzian function.[12,14–16]

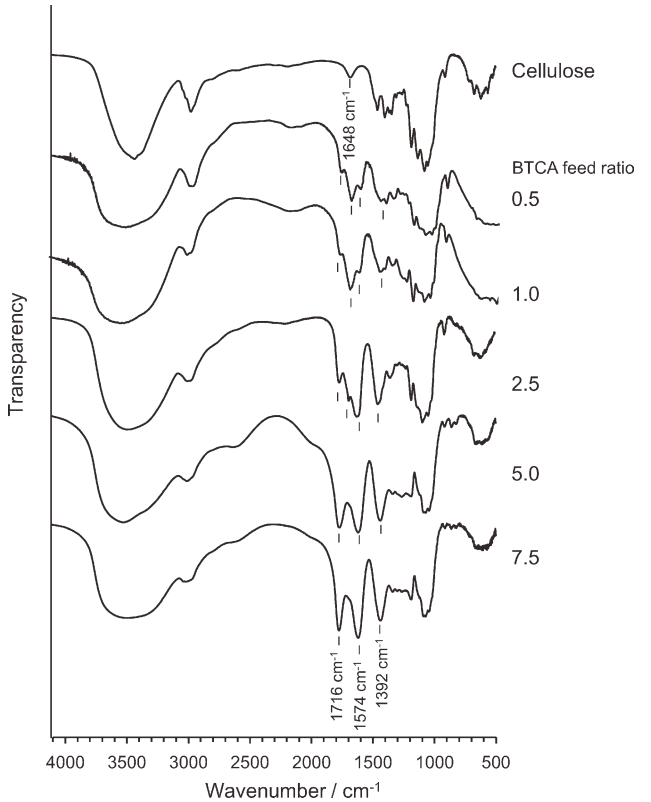

Figure 3. FTIR spectra of cellulose pulp and the hydrogels produced by crosslinking of BTCA with cellulose pulp in LiCl/DMAc solvent system.

Quantitative Determination of Ester Linkages in Hydrogel

Ester content in the product was determined by a titration method.[17] The procedure was as follows: 100–250 mg of product was weighed accurately and placed in a 200-mL flask and the mixture was stirred for 10 h at room temperature. A total of 30 mL of 0.1 mol L^{-1} NaOH was then added, and the mixture was heated at 50°C for 3 h for hydrolysis of ester linkages between BTCA and cellulose. The mixture was cooled to room temperature, and the NaOH consumed for ester hydrolysis was determined by the titration with aqueous 0.1 mol L^{-1} HCl using phenolphthalein as an indicator for the titration. Total ester linkages in 1 g of each product (E), which was in mmol g^{-1}, were determined by this procedure.

Water Absorbency

The water absorbency of the products was determined according to the previously described tea-bag method.[12,18] A nylon tea bag with dimensions of 100 mm × 200 mm was prepared from a nylon sheet with a pore size of 255 mesh using a heat sealer. Two hundred milligrams of the superabsorbent hydrogel sample was placed into the tea bag. The tea bag was then immersed in water at 25°C. After a prescribed time, the tea bag was removed from the water, and excess water was drained for 10 min. The weight of the tea bag including the swollen hydrogels (W_h) was measured, and the water absorbency was calculated using the following equation:

$$\text{Water absorbency} = (W_h - W_b - W_p)/W_p,$$

where W_b is the weight of the blank tea bag after water treatment and W_p is the weight of the dried superabsorbent hydrogel. Absorbency measurements were taken for five samples of each product, and the average of the five values was plotted against the absorbency time.

RESULTS AND DISCUSSION

Structure of Hydrogel

Figures 3 and 4 show the FTIR spectra of a series of products obtained by the esterification crosslinking of cellulose with BTCA dissolved in the LiCl/DMAc and TBAF/DMSO systems, respectively. Consistent with our previous report on the esterification crosslinking of cellulose with BTCA in the LiCl/NMP system,[12] the obtained products showed several new absorption peaks in addition to the original peaks of native cellulose. The new absorption band at 1716 cm^{-1} was assigned to the C=O stretching vibration of the ester group, and the absorption bands appearing at 1574 and 1392 cm^{-1} were assigned to the respective asymmetric and symmetric stretching vibrations of the carboxyl group.[19] The low intensity, broad band observed at 1648 cm^{-1} arises from the bending vibration of residual water molecules.[20] Thus, the IR analysis indicates the successful esterification of the hydroxyl group of cellulose with BTCA in the LiCl/DMAc and TBAF/DMSO systems as well as in the reported LiCl/NMP system, resulting in the formation of carboxylate anions as well as crosslinking between the cellulose chains.

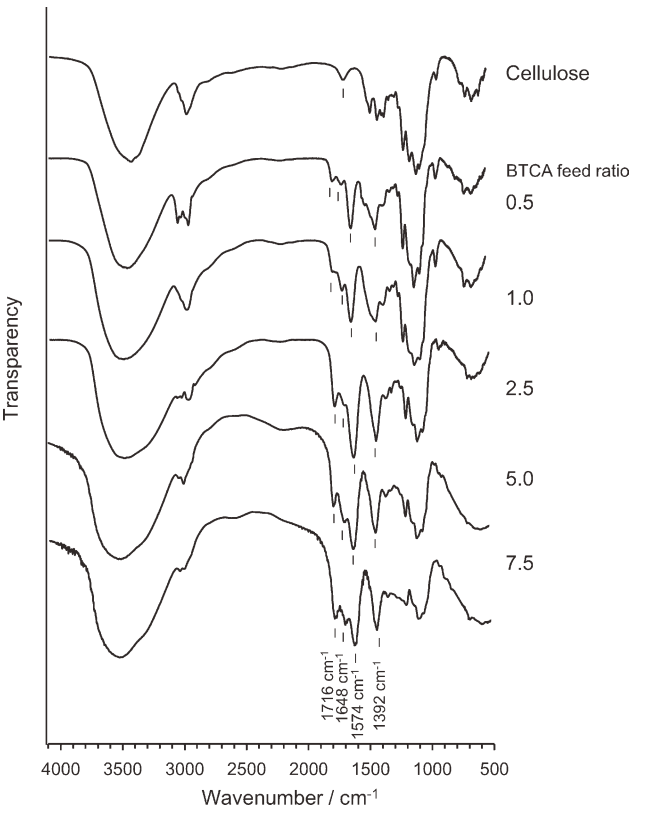

Figure 4. FTIR spectra of cellulose pulp and the hydrogels produced by crosslinking of BTCA with cellulose pulp in TBAF/DMSO solvent system.

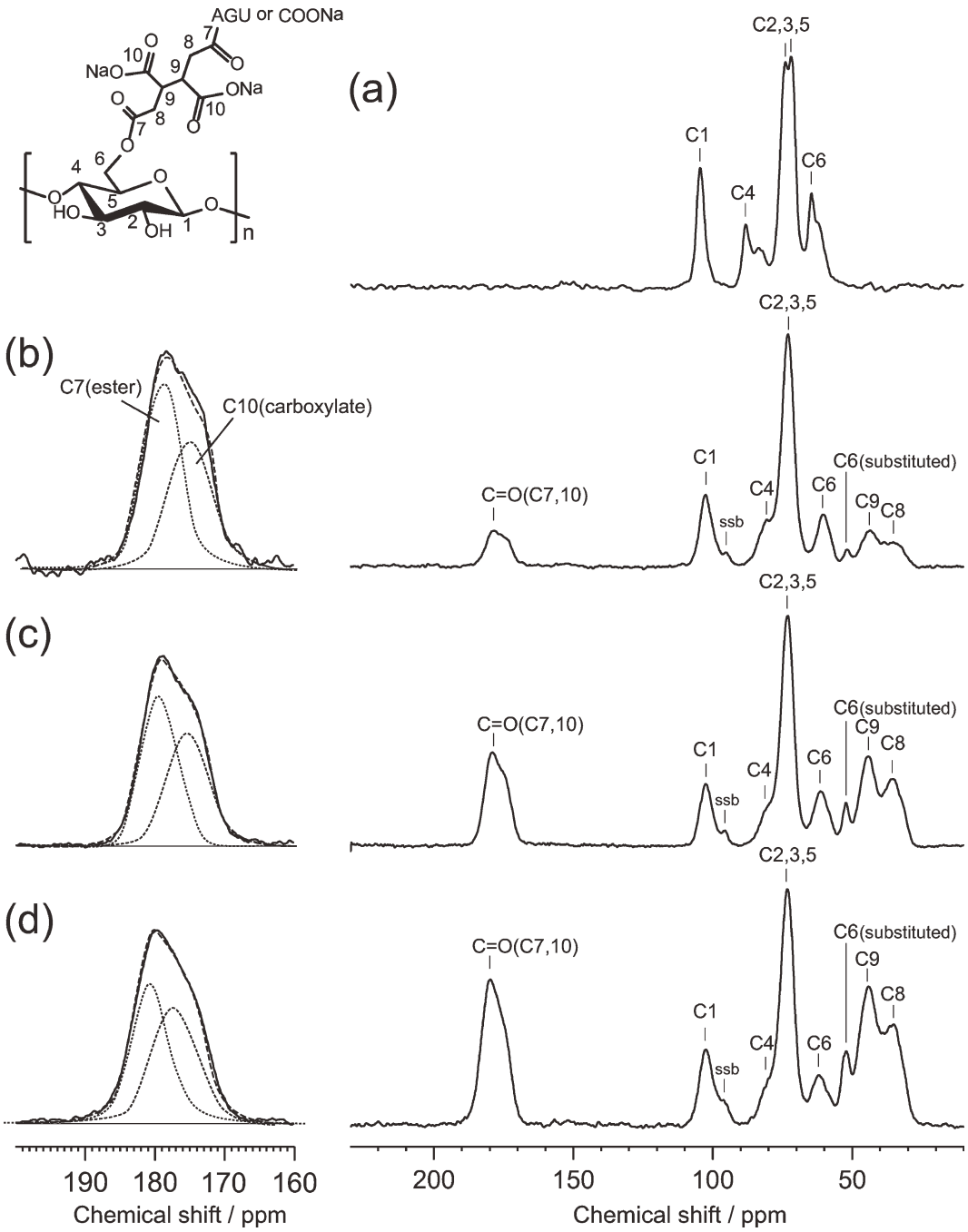

Figure 5. Solid-state ^{13}C-NMR spectra of pure cellulose pulp (a) and the products prepared in LiCl/NMP (b), LiCl/DMAc (c), and TBAF/DMSO (d) systems. The products were prepared from cellulose pulp with the BTCA feed ratio of 2.5. Expanded spectra of the carboxyl carbon region of the products and individual fit lines determined by the lineshape analysis are shown in this figure. The abbreviation "ssb" indicates spinning sideband of the carbonyl carbon resonances.

Figure 5 shows the solid-state ^{13}C-NMR spectra of the starting material of cellulose and the reaction products prepared from BTCA crosslinking with cellulose at the BTCA feed ratio of 2.5 in the three solvent systems. Compared with the spectrum of cellulose, four new resonance lines were observed in the spectra of the reaction product. The lines at 46 and 37 ppm proved the existence of CH_2 and CH groups of BTCA in the product, respectively, and the peak at 54 ppm was attributed to the BTCA-substituted C6 carbon of the AGU of cellulose.[12] The remaining resonance line in the region of 186–168 ppm was assigned to carbonyl carbons. The molar ratio of sodium carboxylate groups to the ester linkages formed in the product (n_{COONa}/n_{ester}) could be determined by the lineshape analysis of the solid-state ^{13}C-NMR spectra in the carbonyl carbon region

of 186–168 ppm, as previously reported.[12] Within this spectral region, the products exhibit carbonyl carbon resonances of the ester group at 181 ppm that are partially overlapped with and those of sodium carboxylate appearing at 176 ppm.[21] Following spectral deconvolution by means of lineshape analysis, the carbonyl carbon resonance was resolved into two Lorentzian lines with peaks at 181 and 176 ppm. The n_{COONa}/n_{ester} ratio was represented as an area ratio of the two lines at 181 and 176 ppm, and the values of which are summarized in Table I.

The synthesis scheme presented in Figure 2 illustrates that one diester and two sodium carboxylate groups are formed during the crosslinking reaction of BTCA with cellulose, whereas the graft reaction results in the formation of one ester and three sodium carboxylate groups. Ester formation between the carboxylate group newly formed in BTCA and hydroxyl group of cellulose was also considered, which results in triester and tetraester linkages. Number of the triester and tetraester was considered to be far less than that of monoester and diester because DMAP can promote the acylation of hydroxyl group with acid anhydride efficiently rather than that with carboxylate group.[22] Therefore, formation of the triester and tetraester was disregarded in this experiment. In 1 g of the product, it was supposed that there was X mmol of crosslinked BTCA and Y mmol of grafted BTCA. Therefore, the following simultaneous equations could be expressed as follows:

$$2X + Y = E \quad (1)$$

$$2X + 3Y = E \times n_{COONa}/n_{ester}, \quad (2)$$

where E (mmol g^{-1}) is the total ester linkages in 1 g of the product, which was determined by the titration method. The E value is given by the contribution of both crosslinked BTCA, $2X$, and grafted BTCA, Y, which could be obtained from the result of the titration method. The total sodium carboxylate groups in 1 g of the product was given by the contribution of the crosslinked BTCA, $2X$, and grafted BTCA, $3Y$, which could be determined by multiplying the E by the n_{COONa}/n_{ester}. By solving simultaneous eqs. (1) and (2) simultaneously, X and Y were given by

$$X = E \times (3 - n_{COONa}/n_{ester})/4$$

$$Y = E \times (n_{COONa}/n_{ester} - 1)/2.$$

Therefore, the molar percentages of crosslinked BTCA and grafted BTCA in the total BTCA molecules esterified with cellulose, represented by the symbols C_{CR} and C_{GR}, respectively, were given by

$$C_{CR}\ (\%) = X \times 100/(X + Y)$$

$$C_{GR}\ (\%) = Y \times 100/(X + Y).$$

As shown in Figure 1, the average molecular weight of the product is increased by 242 g mol^{-1} when one BTCA molecule crosslinks to hydroxyl group of cellulose per AGU. Similarly, grafting of one BTCA molecule per AGU increases the average molecular weight of the product by 282 g mol^{-1}. Therefore, the number of total BTCA molecules per AGU of cellulose (n_{total}) in the hydrogel sample could be determined using the following equation:

$$n_{total} = (X + Y)/[(1 - 242X/1000 - 282Y/1000)/162].$$

Moreover, the average numbers of crosslinked and grafted BTCA molecules per AGU, represented by the symbols n_{CR} and n_{GR}, respectively, were calculated from the following equations:

$$n_{CR} = n_{total} \times C_{CR}/100$$

$$n_{GR} = n_{total} \times C_{GR}/100$$

Table I summarizes the structural parameters of the hydrogels obtained in the homogeneous esterification of cellulose. The data presented in this table show an increase in the degree of ester formation between the acid anhydride of BTCA and the hydroxyl group of cellulose as the feed ratio of BTCA increased, in all of the solvent systems evaluated. Of the three systems studied, the rate of ester formation was most rapid in the TBAF/DMSO system versus the LiCl/NMP and LiCl/DMAc systems, whereas the E values of the products obtained in the LiCl/DMAc system were slightly higher than those in LiCl/NMP at the same BTCA feed ratio. In addition, the C_{CR} and C_{GR} values of the products obtained in TBAF/DMSO were markedly different from those obtained in the LiCl/NMP and LiCl/DMAc systems. The use of the TBAF/DMSO solvent system produced C_{CR} and C_{GR} values in the range of 45–53% and 47–55%, respectively, indicating that crosslinking and grafting of BTCA occurred with almost the same frequency. On the other hand, the C_{CR} value in the range of 72–85% that was obtained in the case of the LiCl/NMP and LiCl/DMAc systems shows that the crosslinking reaction of BTCA was dominant in these systems. The difference in the product composition achieved in the various solvent systems was also confirmed by a comparison of the FTIR spectra of products. Figure 4 shows the spectra of the products in the TBAF/DMSO system, from which it can be seen that the intensity of the absorptions at 1574 and 1392 cm^{-1} assigned to the sodium carboxylate carbonyl functionality was much higher than that at 1716 cm^{-1} assigned to ester group. In the case of the spectra of the products obtained in LiCl/DMAc (Figure 3), as well as LiCl/NMP, the peak intensity of the ester group appearing at 1716 cm^{-1} was comparable to those of carboxylate groups at 1574 and 1392 cm^{-1}.

Figure 6 represents the changes of the n_{total}, n_{CR}, and n_{GR} values of the products with respect to the BTCA feed ratio. Based on the observed curves, both crosslinking and grafting occurred simultaneously in all of the evaluated solvent systems, and the n_{total}, n_{CR}, and n_{GR} values of the hydrogels increased gradually with increasing BTCA feed ratio. However, the values obtained with the TBAF/DMSO system differed significantly from those obtained using the other two systems. The values of n_{total} in the hydrogels from the LiCl/TBAF system were considerably higher than those obtained in the LiCl/NMP and LiCl/DMAc systems for each BTCA feed ratio, which was mainly attributed to the high n_{GR} of the hydrogels from the TBAF/DMSO system. In particular, at the low BTCA feed ratios of 0.5 and 1, the n_{GR} values were extremely high for the hydrogels from the TBAF/

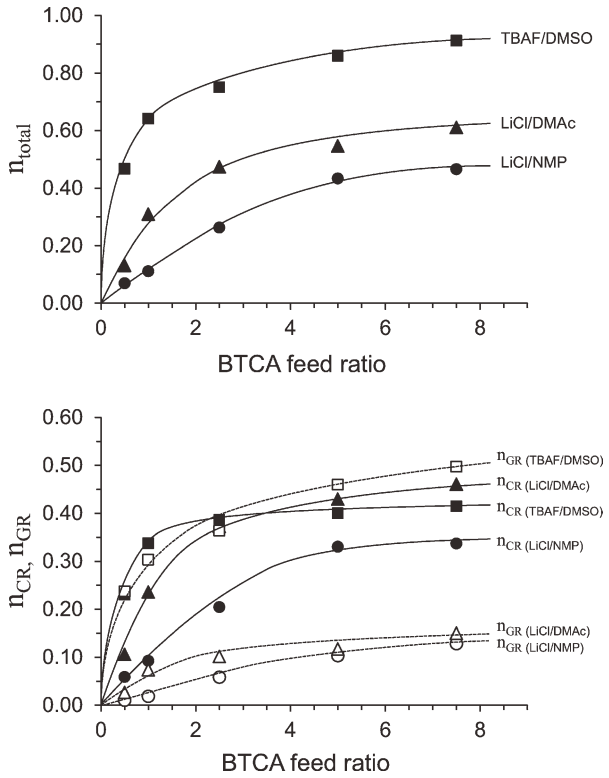

Figure 6. Average numbers of total (n_{total}; top), crosslinked (n_{CR}; bottom), and grafted (n_{GR}; bottom) BTCA molecules per AGU of hydrogels produced in TBAF/DMSO, LiCl/NMP, and LiCl/DMAc systems with various BTCA feed ratios.

DMSO system. With respect to the n_{CR} values, the products obtained in the TBAF/DMSO system were approximately equivalent to those of the LiCl/NMP and LiCl/DMAc systems, at the high BTCA feed ratios of 5 and 7.5, whereas at low BTCA feed ratios in the range of 0.5–2.5, the n_{CR} of the hydrogels from the

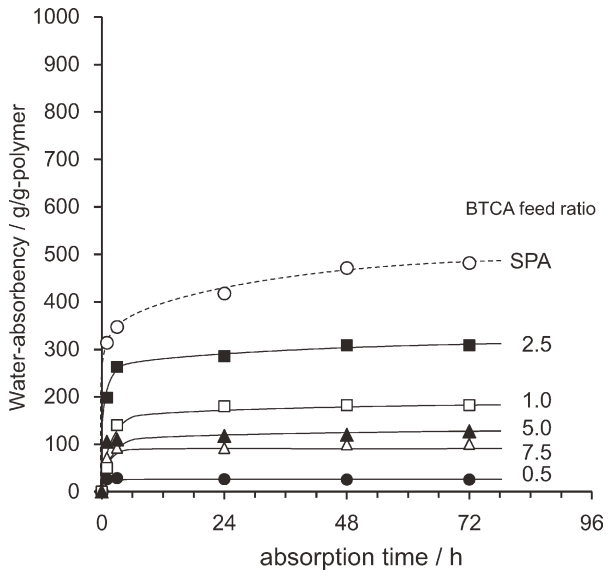

Figure 7. Absorbency of hydrogel products prepared in the LiCl/NMP solvent system. Dotted line shows the absorbency of SPA for comparison.

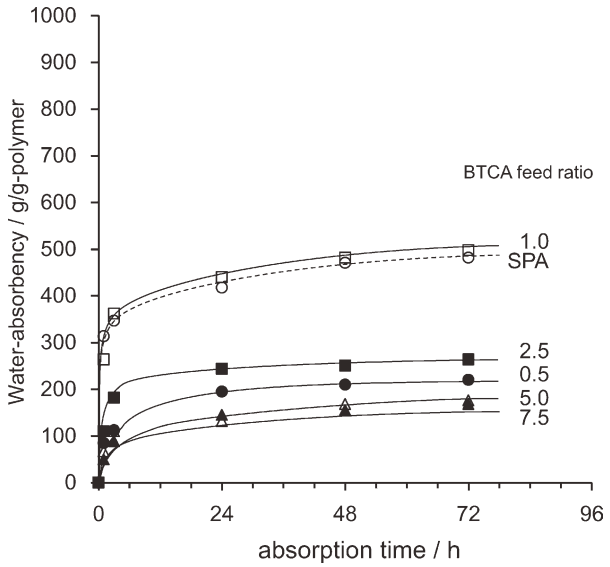

Figure 8. Absorbency of hydrogel products prepared in the LiCl/DMAc solvent system. Dotted line shows the absorbency of SPA for comparison.

TBAF/DMSO system was considerably higher than those of the other two systems. Therefore, the data indicate that the TBAF/DMSO system promoted both crosslinking and grafting of BTCA to cellulose even at low concentrations of BTCA, and the products obtained in the TBAF/DMSO system had a high percentage of grafted BTCA (45–53%) in comparison with the other two systems (72–85%). Although the structural parameters (n_{total}, n_{CR}, and n_{GR}) of the products obtained in the LiCl/NMP system were relatively close to the corresponding parameters in the LiCl/DMAc system, all of the parameters were slightly higher with the use of LiCl/DMAc than with LiCl/NMP.

Water Absorbency

The white granular powders obtained after the esterification crosslinking reaction of cellulose and BTCA absorbed water readily upon soaking, with concomitant alteration of their morphologies to form transparent hydrogels. The time dependence of water absorbency of the hydrogels produced in the LiCl/NMP, LiCl/DMAc, and TBAF/DMSO systems at varying BTCA feed to cellulose AGU ratios is shown in Figures 7–9, respectively. The dotted lines in these figures indicate the absorbency of SPA for comparison. The maximum absorbency of most samples was reached within 24 h, and little change in the absorbency was observed beyond 24 h. The absorbency of each sample after 72 h is shown in Table I.

Comparison of the absorbencies of the hydrogels prepared in the LiCl/NMP system at various BTCA feed ratios shows that the highest water absorbency of 308 g g^{-1} was obtained at a BTCA feed ratio of 2.5, which was much lower than that of SPA (482 g g^{-1}). The structural parameters of the product exhibiting the maximum absorbency were n_{total} of 0.26, and C_{CR} and C_{GR} values of 78% and 22%, respectively. In the case of the LiCl/DMAc system, the hydrogel with the highest water absorbency of 498 g g^{-1} was obtained at a BTCA feed ratio of 1.0, and the structural parameters of the hydrogel with the maximum absorbency were n_{total}, C_{CR}, and C_{GR} of 0.31, 76%, and 24%, respectively. The

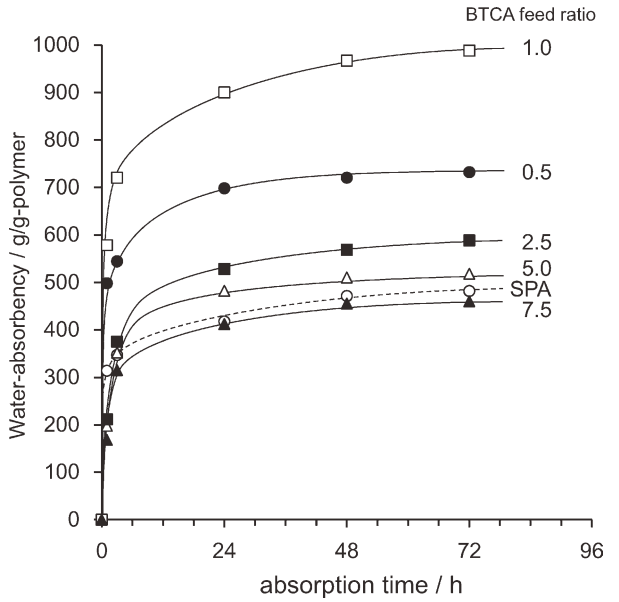

Figure 9. Absorbency of hydrogel products prepared in the TBAF/DMSO solvent system. Dotted line shows the absorbency of SPA for comparison.

hydrogels produced from the TBAF/DMSO system had a maximum water absorbency that was much higher than those produced in the other two systems. The hydrogel obtained at the BTCA feed ratio of 1.0, having structural parameters n_{total}, C_{CR}, and C_{GR} of 0.64, 53%, and 47%, respectively, gave the maximum absorbency of 987 g g^{-1}, which is twice the absorbency of conventionally used SPA. Based on the data presented in Table I, the n_{total} values for the products from each solvent system increased drastically as the feed ratio of BTCA increased, whereas the C_{CR} and C_{GR} values changed only marginally. C_{CR} and C_{GR} fell within the range of 72–85% and 15–28%, respectively, for the LiCl/NMP and LiCl/DMAc systems, whereas the C_{CR} and C_{GR} values of the products from the TBAF/DMSO system were 45–53% and 47–55%, respectively. This indicated that the molar ratio of grafted polymer to crosslinked polymer was nearly independent of the BTCA feed ratio. Therefore, for hydrogels having almost the same degree of crosslinking and grafting in the polymer composition, the n_{total} values had a strong influence on the optimum water absorbency, with an optimal n_{total} value of $\sim$ 0.3 for the products obtained in the LiCl/NMP and LiCl/DMAc systems and an optimum n_{total} value of ca. 0.64 for the crosslinked polymers from the TBAF/DMSO system. The difference in the optimum n_{total} of LiCl/NMP compared with the other two systems was attributed to the difference in the relative degrees of crosslinking and grafting because grafting of BTCA furnishes a number of carboxylate groups in the hydrogel compared with crosslinking. Because the n_{GR} values of the product obtained in the TBAF/DMSO system were much higher than those obtained in the other two systems (Table I), the TBAF/DMSO system is considered to offer merits for providing enhanced water absorbency of cellulose using BTCA as a crosslinker.

Effect of the Reaction Media on Esterification Crosslinking

The hypothetical polar characteristics of the cellulose solvent systems used in this study are shown in Figure 1. These systems comprise a combination of the salt of either LiCl or TBAF and a polar, aprotic solvent of NMP, DMAc, or DMSO. These solvents were considered to act as both soft and hard bases, whereas the salts (LiCl and TBAF) were considered to be polar, forming clusters with the solvent.[23,24] With the addition of cellulose to a given solvent system, the small electronegative anions such as Cl^- and F^- are expected to act as hydrogen bond acceptors, H-bonding with the hydroxyl groups of cellulose, thus dissolving the cellulose by breaking the native cellulosic intermolecular and intramolecular hydrogen bonds. In this study, the esterification of BTCA occurred more readily in the TBAF/DMSO system relative to the LiCl/NMP and LiCl/DMAc systems, suggesting that the F^- anions in the TBAF/DMSO system acted not only as strong hydrogen bond acceptors but also as esterification catalysts. Association with the F^- anion is expected to confer an effective negative charge on the hydroxyl proton of cellulose by an inductive effect in which electron density is drawn from oxygen to the hydrogen atom, thereby enhancing the nucleophilicity of the hydroxyl groups and facilitating attack of this group on the acid anhydrides of BTCA. This sequence of events is thought to account for the acceleration of the esterification reaction in the TBAF/DMSO system. The enhanced nucleophilicity of the cellulose hydroxyl groups is postulated on a comparative basis, considering that this effect was not observed in the LiCl/NMP and LiCl/DMAc systems that contain the Cl^- anion, which is less electronegative than the F^- anions. With respect to the catalytic effect of TBAF, Shimizu et al.[25] also reported that the polymerization of cyclic esters such as ε-caprolactone, L-lactide, and β-butyrolactone with hydroxyl-containing polymers was enhanced in TBAF/DMSO solution. Furthermore, Yoshimura et al.[18] prepared cellulose succinate by esterification using succinic anhydride and DMAP in LiCl/NMP and TBAF/DMSO systems and compared the swelling behavior of the cellulose succinates. Although they did not mention detailed structural information of the products such as grafting and crosslinking degrees as well as the catalytic effect of TBAF in the report, difference between the swelling behavior of the products prepared in LiCl/NMP and that in TBAF/DMSO was considered to be occurred by the catalytic effect of TBAF. The difference in the efficiency of the F^- and Cl^- ions to confer negative charge was also indicated by the difference in the dissolution power of the relevant solvent systems for cellulose. The LiCl/DMAc and LiCl/NMP systems require heating, longer time periods, and/or preswelling by sequential solvent change for dissolution of cellulose, whereas the TBAF/DMSO system facilitates rapid dissolution of cellulose without the need for complicated pretreatments.

In addition, the TBAF/DMSO system yielded products with approximately the same proportion of crosslinking and grafting, whereas the crosslinking reaction occurred preferentially in the LiCl/NMP and LiCl/DMAc systems. This distinction in the product composition was considered to be related to the fact that crosslinking with BTCA requires a two-step esterification reaction, whereas grafting is a single-step process. The initial step in the crosslinking process involves the attack of an acid anhydride group in BTCA by the hydroxyl group, after which another acid anhydride in the same BTCA molecule attaches to

another hydroxyl group. In the case of the TBAF/DMSO system, in light of the fact that the hydroxyl groups of cellulose were considered to be very nucleophilic, one acid anhydride group of BTCA is rapidly attacked by the hydroxyl group of cellulose, resulting in increased formation of the graft structure. As a consequence, the number of unreacted hydroxyl groups becomes relatively low, and the steric bulk of the cellulose chains is increased by grafting, which interferes with the esterification crosslinking of other unreacted acid anhydrides in the BTCA molecule grafted to cellulose. In the case of the LiCl/NMP and LiCl/DMAc systems, because the esterification reaction did not proceed as rapidly, it was considered that the acid anhydride group of BTCA grafted to cellulose could easily react with other hydroxyl groups.

CONCLUSIONS

This study demonstrated that superabsorbent hydrogels could be prepared from cellulose via simple esterification crosslinking with BTCA under mild conditions in homogeneous solvent systems comprising a combination of a salt of either LiCl or TBAF and a polar, aprotic solvent such as TBAF/DMSO, LiCl/DMAc, or LiCl/NMP. Simultaneous crosslinking and grafting of BTCA occurred in these solvent systems via the respective formation of diester and monoester linkages. The structure of the hydrogels depended strongly on both the BTCA feed to cellulose ratio and the nature of the homogeneous solvent system used as the reaction medium. Among the three solvent systems evaluated in this study, the TBAF/DMSO system was most effective for furnishing a product with high water absorbency. The maximum absorbency of the hydrogel produced in this system was 987 g g^{-1} at a BTCA feed ratio of 1, which is approximately two times as high as that of standard SPA.

In addition, this study revealed structural differences between the products obtained in the TBAF/DMSO system and those obtained in LiCl/NMP and LiCl/DMAc systems. The former solvent system contains hard and highly electronegative fluoride anions, which prompted rapid esterification of the hydroxyl group of cellulose, to yield products with approximately the same proportion of crosslinking and grafting. On the other hand, the latter systems containing the less electronegative chloride ion provided products with a highly crosslinked structure. In addition to these three solvent systems, a number of other solvents have been developed for dissolving cellulose. If the cellulose dissolution mechanism in each of these systems could be clarified, it might be possible to control the degree of grafting as well as crosslinking of BTCA.

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