Synthesis and Characterization of Starch-*g*-Polycaprolactone Copolymer

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Received September 14, 1998; Revised Manuscript Received August 30, 1999

ABSTRACT: The new biodegradable starch graft copolymer, starch-*g*-polycaprolactone (PCL), was synthesized by using the ring-opening graft polymerization of a ϵ-caprolactone (CL) monomer onto starch backbone. The grafting reactions were conducted with various starch/CL/water feed ratios to obtain starch-*g*-PCL copolymers with the various PCL graft structures. The detailed microstructure of the starch-*g*-PCL was characterized with one- and two-dimensional NMR spectroscopy, and the effect of feed composition on the resulting microstructure of the starch-*g*-PCL was investigated.

Introduction

Research and development on biodegradable polymers has been very active owing to concerns related to the environmental pollution by nondegradable plastics wastes. However, many of the candidates for biodegradable polymers have some limitations in their properties or costs. In general, high cost is one of the most serious limitations that restricts the application of biodegradable polymers.

Starch is a potentially useful material for biodegradable plastics because of its natural abundance and low cost. However, starch-based plastics have some drawbacks, including poor long-term stability caused by the water absorption, poor mechanical properties, and processability. To solve some of these problems, the various physical or chemical modifications of the starch molecule have been considered, including blending,[1−6] chemical derivation,[7−9] and graft copolymerization.[10,11]

Starch graft copolymer is representative of the modification of the starch molecule by chemical derivation. Starch graft copolymers such as starch-*g*-polymethylacrylate (PMA)[10] and starch-*g*-polystyrene (PS)[11] have been synthesized by generating free radicals on starch and reacting these free radicals with the respective vinyl monomers. However, these copolymers with vinyl polymer branches also have limited biodegradability because of the presence of their nondegradable branch units, although their properties are acceptable for applications.

This motivated us to newly synthesize a completely biodegradable polymer based on starch. The starch-*g*-PCL was synthesized by the grafting reaction between hydroxyl groups of the starch and ϵ-caprolactone monomers in the presence of water used as a swelling agent to gelatinize the starch granule. The detailed analysis on the microstructure of the resulting starch-*g*-PCL was also conducted by using one- and two-dimensional NMR spectroscopy. The starch-*g*-PCL was found to be a good compatibilizer of the completely biodegradable blend such as PCL/starch blend.[12]

Experimental Section

Materials. Cornstarch was received from Samyang Genex and ϵ-caprolactone was purchased from Aldrich Chemical. Tin(II) 2-ethylhexanoate used as a catalyst for the graft polymerization of CL monomer was also purchased from Aldrich Chemical. Water used as a plasticizer was prepared by distillation and deionization. Toluene, which was used for purification of the starch-*g*-PCL produced, was purchased from J. T. Baker. Dimethyl sulfoxide-d_6 (DMSO-d_6) and hexamethyldisiloxane (HMDS) used for NMR experiments were purchased from Aldrich and TCI Chemical, respectively. All of these materials were used as received without further purifications.

Synthesis of Starch-*g*-PCL. Starch-*g*-PCL was synthesized as described below:

Cornstarch (30 g; 0.185mol) was placed in a glass reactor that was previously flushed with high-purity (99.999%) N_2 gas for 2 h. The mixture of CL monomer and distilled water was then poured into the reactor and preswelling of the starch molecule was conducted with stirring of the starch/CL/water mixture at an elevated temperature (80 °C) for 16 h under nitrogen atmosphere. After the preswelling, Sn−Oct catalyst (0.2 wt % of total amount of the reactants) was added, and graft polymerization of CL onto starch proceeded at 100 °C for 20 h.

After the reaction product was allowed to cool to room temperature, it was poured with vigorous stirring into a beaker containing toluene to extract the unreacted CL monomer and the PCL homopolymer that can be produced by the initiation reaction of CL monomer with the hydroxyl groups of water molecules during the graft reaction. The extraction with toluene was performed at 60 °C for 2 days, and then, the final product, starch-*g*-PCL, was obtained by being filtered and dried under vacuum at 80 °C for 2 days.

All of the syntheses were conducted with different starch/CL/water ratios to find out the effect of feed composition on the yield and resulting structure of the starch-*g*-PCL product. To observe the influence of the preswelling on the graft polymerization, the reactions were also carried out without the preswelling procedure, and the results were compared with those from the reactions with preswollen starch.

NMR Measurements. The characterization of starch-*g*-PCL was conducted by using one- and two-dimensional nuclear magnetic resonance (NMR) spectroscopy: One-dimensional NMR measurements were performed on both ^{13}C and ^{1}H nuclei, and ^{13}C NMR spectra were obtained on a Bruker AMX 500 operating at 125 MHz for a carbon-13 isotope. The starch-*g*-PCL samples were dissolved in DMSO-d_6 at 60 °C, and the solution concentration was 15 w/v %. The spectra were obtained at 60 °C with a pulse angle of 25°, a delay time of 10 s, and an acquisition time of 2 s. All of the chemical shifts are reported in parts per million (ppm) using HMDS as a reference, which is usually used as an internal standard for NMR measurements at elevated temperatures.

Two-dimensional heteronuclear multiple quantum coherence (HMQC) spectroscopy was also used to obtain detailed

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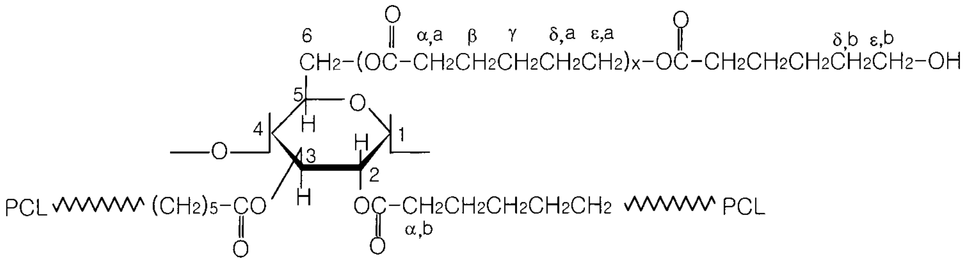

Figure 1. Structure of starch-*g*-PCL.

Table 1. Results of Starch-*g*-PCL Syntheses

trial	starch/CL/water (g/g/g)	starch-*g*-PCL (g)	yield (%)	coagulation of reactants
1[a]	30/30/30	36.3	60.5	yes
2[a]	30/30/40	38.0	63.3	yes
3[a]	30/30/55	45.8	76.3	no
4[a]	30/15/70	43.7	72.8	no
5[a]	30/30/70	54.9	91.5	no
6[a]	30/40/70	54.3	77.6	no
7[a]	30/45/70	41.8	69.7	yes
8[b]	30/30/70	33.8	56.3	no
9[b]	30/60/140	33.4	37.1	no

[a] With preswelling of starch. [b] Without preswelling of starch.

information on the direct C−H connectivity in the structure of starch-*g*-PCL molecule.

Results and Discussion

Yield of Starch-*g*-PCL. The reaction conditions and results of the starch-*g*-PCL syntheses are summarized in Table 1. Trials 1−3 and 5 were conducted with the various water contents at a fixed starch/CL feed ratio (30 g/30 g), and thus, the results could show the effect of water content on the grafting reaction. From these results, it is found that the yield of starch-*g*-PCL increases with the increase in water content in the feed. This seems to be due to the enhancement of starch gelatinization by the water. The starch gelatinization can generally induce the effective destruction and plasticization of granular structure of the starch and, consequently, promote the reactions between the starch and CL monomer.

On the other hand, trials 4−7 were carried out with various CL contents at a fixed starch/water feed ratio (30 g/70 g). The results from these trials show the existence of optimal CL content for the higher product yield. The reduction of yield at high CL content can be ascribed to the increase in hydrophobic character of the reaction medium, which reduces the plasticization of the hydrophilic starch molecule. In fact, we could observe that as the grafting reaction proceeded the coagulations of reactants occurred in some trials with relatively high CL/water ratio, such as the trials 1, 2, and 7. This phenomenon supports the importance of appropriate hydrophilicity of the reaction medium for the efficient grafting reaction.

Trials 8 and 9 were performed to find out the influence of preswelling of the starch on the grafting reaction. The results of these two trials show that the grafting reaction cannot proceed effectively without the preswelling of starch, irrespective of the starch/CL/water feed ratio. The much lower product yield of trial 8 especially, compared to that of trial 5 conducted with the same feed composition, indicates that the preswelling of starch enhances the grafting reaction very significantly.

Characterization of Starch-*g*-PCL. By the graft polymerization of CL monomer onto the starch backbone, it is expected that the molecular structure of repeat unit of starch should be changed. The structure of starch-*g*-PCL expected is illustrated in Figure 1. Because the structural repeat unit of starch has three hydroxyl groups, the three different grafts can be propagated in any given repeat unit. To obtain detailed information on the microstructure of starch-*g*-PCL, including the CL/starch mole ratio and the average length and number of the PCL grafts, one- and two-dimensional NMR experiments were performed.

Proton NMR spectroscopy is one of the most powerful tools for the quantitative analysis on the polymer microstructure. However, it has limitations in peak resolution in many cases due to the peak overlap caused by its narrow spectral range. Therefore, we assigned at first the peaks for all carbon species in the starch-*g*-PCL structure from its ^{13}C NMR spectrum, which has a spectral range wide enough to resolve easily each peak in the spectrum. Then, spectroscopy was used to find out the direct C−H connectivity between each carbon and the proton attached directly to it, and to correlate the ^{13}C NMR spectra with the ^{1}H NMR spectra. Figure 2 shows the typical HMQC spectrum of the starch-*g*-PCL sample. The longitudinal axis of the spectrum corresponds to the chemical shift of the one-dimensional ^{13}C NMR spectrum, and the transverse axis corresponds to that of the one-dimensional ^{1}H NMR spectrum.

The results of the peak assignment are summarized in Table 2. Numbers 1−6 denote the carbons in the starch unit, and the Greek symbols α−ϵ indicate the carbons in the CL unit as illustrated in Figure 1. In this assignment, we referred to the previous reports on the peak assignment for carbon species in the starch[13] and the PCL,[14] respectively. In fact, the peak for each carbon species in one-dimensional ^{13}C NMR spectrum (which is not shown) had some small sidebands originated from the magnetic environment slightly different from that of the main peak itself. Unfortunately, we could not characterize these sidebands accurately because their cross-peaks in the HMQC spectrum were highly overlapped with the main cross-peaks and thus could not be resolved. Only the chemical shifts of the main carbon peaks were thus summarized in Table 2.

It is found from this table that C_1 and C_6 carbons were connected with two kinds of protons, denoted by the subscripts a and b, respectively. Because this type of peak split is also observed in the case of pure starch, it is considered that this is not originated from the formation of PCL graft. Thus, $H_{1,a}$ and $H_{6,a}$ protons were assigned to the protons attached to the main C_1 and C_6 carbons, whereas $H_{1,b}$ and $H_{6,b}$ were assigned to the protons linked to the C_1 and C_6 carbons in the branch point of amylopectin unit.

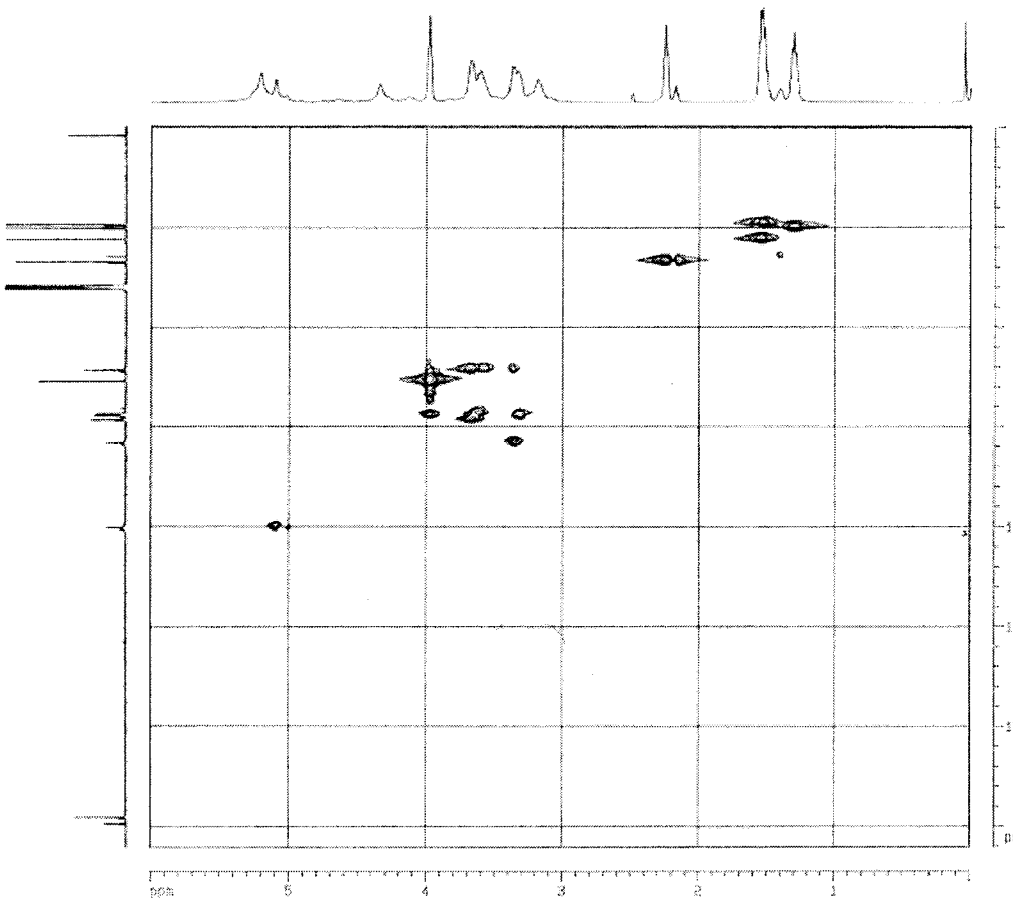

Figure 2. Typical HMQC spectrum of starch-*g*-PCL.

Table 2. Chemical Shifts for ^{13}C and ^{1}H Species in Starch-*g*-PCL

^{13}C	chemical shift (ppm)	^{1}H	chemical shift (ppm)
C_1	100.22	$H_{1,a}$	5.09
		$H_{1,b}$	5.02
C_2	73.37	H_2	3.67
C_3	72.19	H_3	3.32
C_4	79.10	H_4	3.36
C_5	71.77	H_5	3.60
C_6	60.78	$H_{6,a}$	3.67
		$H_{6,b}$	3.60
C_α	33.55	$H_{\alpha,a}$	2.24
		$H_{\alpha,b}$	2.17
C_β	25.02	H_β	1.30
C_γ	24.18	H_γ	1.53
C_δ	27.92	$H_{\delta,a}$	1.54
		$H_{\delta,b}$	1.40
C_ϵ	63.57	$H_{\epsilon,a}$	3.97
		$H_{\epsilon,b}$	3.37
C=O	172.77		

The C_α, C_δ, and C_ϵ carbons in the PCL grafts also have two corresponding protons, respectively; however, unlike the case of starch, these are induced by the differences in chemical environment between the corresponding protons. That is, the $H_{\alpha,a}$ can be assigned to the methylene proton in the type of $-CH_2(OC{=}O)\mathbf{CH_2}-$ linkage appearing at the internal α-position of the graft chain and the α-methylene unit at the initiating site of the graft from the C_6 carbon of the starch. On the other hand, the $H_{\alpha,b}$ corresponds to the methylene proton in the $-CH(OC{=}O)\mathbf{CH_2}-$ type linkage, which is present at the initiating site of the grafts from C_2 and C_3 carbons of the starch. A similar assignment is also possible for H_δ or H_ϵ protons. The $H_{\delta,a}$ and $H_{\epsilon,a}$ protons indicate the internal δ- and ε-methylene protons, respectively, in the $-\mathbf{CH_2CH_2}(OC{=}O)C-$ type linkage, whereas the $H_{\delta,b}$ and $H_{\epsilon,b}$ protons are the methylene protons attached to the hydroxyl end in the $-\mathbf{CH_2CH_2}OH$ unit of each PCL graft. These detailed assignments are also shown in Figure 1.

Microstructure Analysis of Starch-*g*-PCL. On the basis of the peak assignments shown in Table 2, the detailed microstructure of starch-*g*-PCL was analyzed by calculation with the peak intensity in ^{1}H NMR spectra.

The composition of the starch-*g*-PCL was determined with the signal intensities for the CL and the starch units. As shown in Table 2, the signals around 3.6−3.7 ppm contain the H_2, H_5, and H_6 protons of the starch unit, and it is clearly differentiated from the α−δ methylene protons of the CL unit that appear at around 1.3−2.3 ppm. Therefore, the relative mole ratio (CL/St) of starch and CL units within the starch-*g*-PCL sample can be calculated as follows:

$$\frac{\mathrm{CL}}{\mathrm{St}} = \frac{\text{intensity average of } \alpha-\delta \text{ methylene proton signals}}{\text{intensity average of } H_2,\ H_5, \text{ and } H_6 \text{ proton signals}}$$

The mole fraction of the CL component in the starch-*g*-PCL can also be obtained by simple calculation using this CL/St value. In addition, $N_{\mathrm{CL}} = \mathrm{CL/St} \times 100$, which is the total number of grafted CL units per 100 anhydroglucose units in starch, is introduced in the following characterization procedure for easier description on the graft structure. The compositional information of starch-

Table 3. Composition of Starch-*g*-PCL

trial	starch/CL/water (g/g/g)	CL/St	CL (mol %)	N_{CL}
1	30/30/30	0.30/1	23.1	30
2	30/30/40	0.38/1	27.5	38
3	30/30/55	0.75/1	42.9	75
4	30/15/70	0.65/1	39.4	65
5	30/30/70	1.18/1	54.1	118
6	30/40/70	0.81/1	44.8	81
7	30/45/70	0.56/1	35.9	56
8	30/30/70	0.18/1	15.3	18
9	30/60/140	0.16/1	13.8	16

Table 4. Structural Parameters of Starch-*g*-PCL

trial	$F_{\alpha,b}$	$F_{\delta,b}$	$NG_{2,3}$	NG_6	NG	DGP
1	0.38	0.51	11.3	3.9	15.2	2.0
2	0.44	0.54	16.8	3.7	20.5	1.9
3	0.24	0.30	18.1	4.6	22.7	3.3
4	0.30	0.38	19.6	5.0	24.6	2.6
5	0.17	0.21	19.5	5.6	25.1	4.7
6	0.24	0.31	19.8	5.0	24.8	3.3
7	0.35	0.45	19.6	5.3	24.9	2.2
8	0.67	0.78	12.0	2.0	14.0	1.3
9	0.82	0.91	13.1	1.5	14.6	1.1

g-PCL is summarized in Table 3.

To understand the more detailed graft structure of starch-*g*-PCL, we considered the structural differences between the C_2- and C_3-branches and the C_6-branch. The starting protons of the C_2- and C_3- branches are composed of $-CH(OC{=}O)CH_2-$ units that are assigned as α-methylene proton $H_{\alpha,b}$. However, the starting proton of the C_6 branch cannot be distinguished from the main CL units due to its identical structure of the type $-CH_2(OC{=}O)CH_2-$, which is denoted by $H_{\alpha,a}$.

Thus, the fraction of CL units at the starting site of C_2- and C_3-branches can be calculated by

$$F_{\alpha,b} = \frac{I_{\alpha,b}}{I_{\alpha,a} + I_{\alpha,b}}$$

where $I_{\alpha,a}$ and $I_{\alpha,b}$ represent the ^{1}H NMR signal intensities of $H_{\alpha,a}$ and $H_{\alpha,b}$, respectively. Because the N_{CL} is already known, the number of C_2- and C_3-branches per 100 anhydroglucose units, denoted by $NG_{2,3}$, can be obtained by the simple multiplication, $N_{CL} \times F_{\alpha,b}$.

A similar calculation is possible for δ-methylene groups in the end units of C_2-, C_3-, and C_6-branches. The fraction of δ-methylene groups in the CL end units of all grafts having the $-CH_2CH_2OH$ structure can be calculated by

$$F_{\delta,b} = \frac{I_{\delta,b}}{I_{\delta,a} + I_{\delta,b}}$$

where $I_{\delta,a}$ and $I_{\delta,b}$ represent the NMR signal intensities of the $H_{\delta,a}$ and $H_{\delta,b}$ protons. Then, we can obtain the total number of PCL grafts per 100 anhydroglucose units, NG, and number of C_6-branches per 100 anhydroglucose units, NG_6, as follows:

$$NG = N_{CL} \times F_{\delta,b}$$

$$NG_6 = NG - NG_{2,3}$$

Although $NG_{2,3}$ could be distinguished from NG_6, the degree of graft polymerization, DGP, could not be obtained separately for each PCL branch because all of the main CL units in C_2-, C_3- and C_6-branches showed similar chemical shifts in NMR spectra. Thus, the average DGP was calculated by the simple equation, DGP = N_{CL}/NG. All of the calculated results on the structural parameters of starch-*g*-PCL are summarized in Table 4.

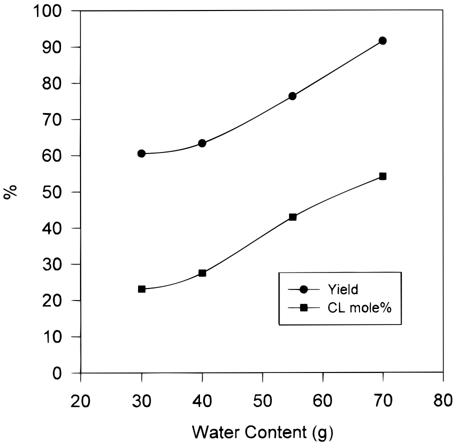

Figure 3. Yield and CL mol % of starch-*g*-PCL with water content at fixed starch/CL feed ratio.

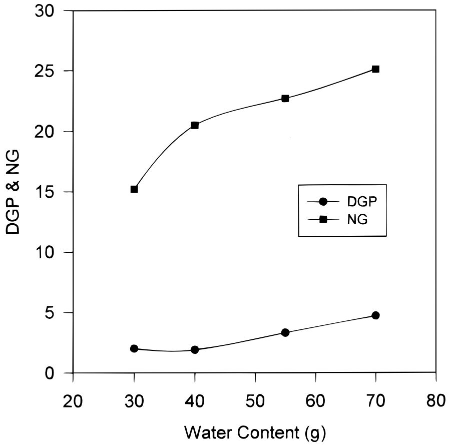

Figure 4. DGP and NG values of starch-*g*-PCL with water content at fixed starch/CL feed ratio.

Analysis on Reactivity of Graft Polymerization. Figure 3 shows the yield and compositional change of the starch-*g*-PCL with the water content in the feed at the fixed starch/CL ratio (30 g/30 g). This figure illustrates that as the water content increases the graft polymerization of CL monomer can be enhanced, and thus, both yield and CL mol % in the starch-*g*-PCL increase almost linearly with the water content. However, when the DGP and NG values of the starch-*g*-PCL are plotted as a function of the water content (Figure 4), the relationships between DGP and NG are different from each other. That is, the initial increase in water content in its low content range induces the exclusive increase in the NG value with no change of the DGP value. This represents that the water just acts as a polymer swelling agent that helps to increase the number of initiating sites for the grafting reaction.

However, the additional increase in the water content causes the increase in the DGP as well as in the NG. This means that the water enhances both initiation and propagation of the PCL graft in its higher content range. It is thus concluded that the sufficient water content should be required to lengthen the PCL graft in the starch-*g*-PCL.

To explain the abrupt change of NG value at low water content, a detailed structural analysis was con-

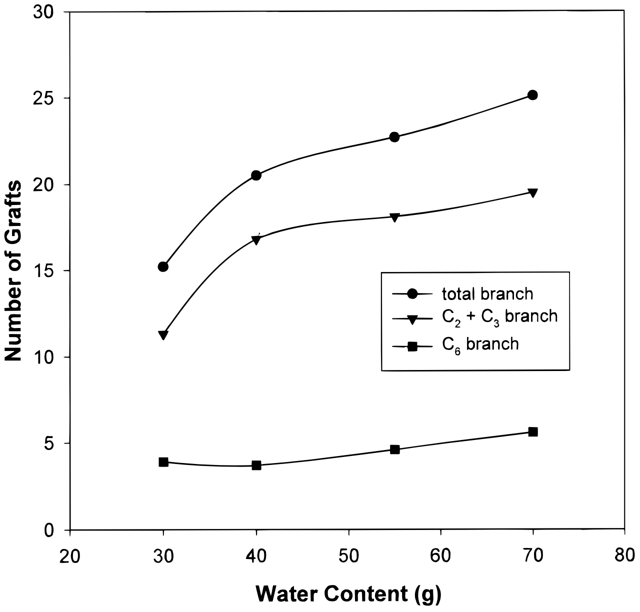

Figure 5. Changes of NG, $NG_{2,3}$, and NG_6 values with water content at fixed starch/CL feed ratio.

ducted. Figure 5 shows the effect of branch type on the increase in NG with water content. It is clearly seen that the initial abrupt increase in NG is mainly due to the increase in the number of C_2- and C_3-branches. This implies that the supply of water at its low content range enables the significant enhancement of reactivity of C_2-OH or C_3-OH group in starch. It is interesting to note that the C_6-OH group does not reveal the aspects similar to those of C_2-OH or C_3-OH group. It is thus supposed that the region near the C_2-OH and C_3-OH is more hydrophilic than the surroundings of C_6-OH in starch, and then, the hydrophilic water molecule would be more readily bound to the C_2-OH and C_3-OH groups and effectively loosen the region surrounding C_2-OH and C_3-OH groups. However, we think that further study should be performed to clarify this conjecture.

In comparing the actual reactivity of three hydroxyl groups in starch, it must be considered that the C_6-carbon at the branch point of amylopectin does not have a hydroxyl group but does have a C_6-O-C_1 ether linkage. In our system, the number of amylopectin branch per 100 anhydroglucose units in starch was 17, which was calculated by

$$\text{branch point fraction} = \frac{I_{1,b}}{I_{1,a} + I_{1,b}} \times 100$$

where $I_{1,a}$ and $I_{1,b}$ are the NMR intensities of the $H_{1,a}$ and $H_{1,b}$ protons, respectively. This means that the average number of C_2-OH or C_3-OH bonds is 100, whereas that of C_6-OH is 83 per 100 repeat units of starch before graft reaction. Therefore, the initiation reactivity of each hydroxyl group for the graft reaction could be calculated as follows:

$$\text{OH reactivity} = \frac{NG_{2,3}}{200} \times 100\ (\%) \quad \text{for } C_2-OH \text{ or } C_3-OH$$

$$\text{OH reactivity} = \frac{NG_6}{83} \times 100\ (\%) \quad \text{for } C_6-OH$$

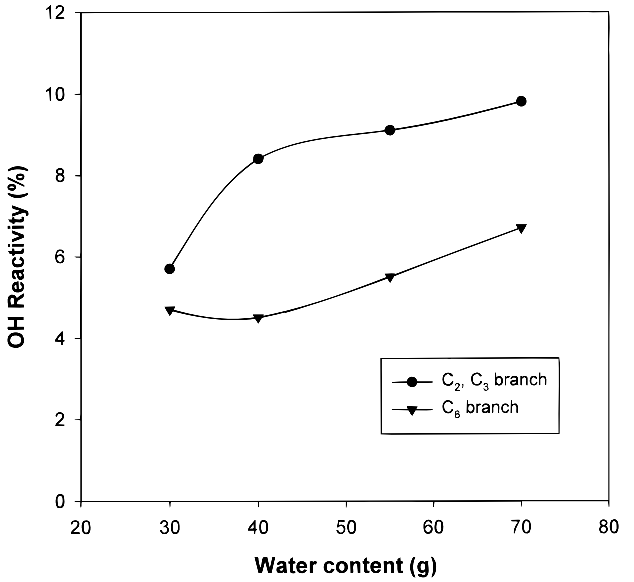

Figure 6. Hydroxyl group reactivity with water content at fixed starch/CL feed ratio.

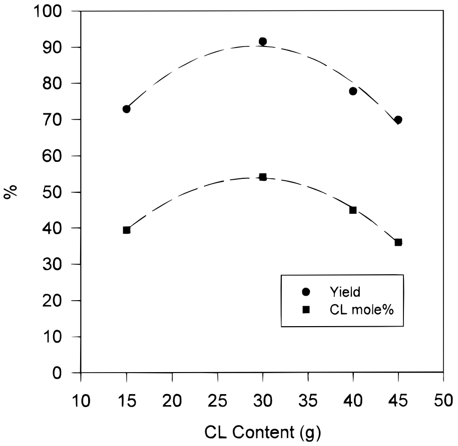

Figure 7. Yield and CL mol % of starch-*g*-PCL with CL content at fixed starch/water feed ratio.

The above calculation for C_2-OH or C_3-OH was conducted on the assumption that the C_2-OH and C_3-OH groups having the same structure would show equal reactivity for the graft reaction.

The results obtained are shown in Figure 6. The remarkable increase in reactivity of C_2-OH or C_3-OH is well correlated with the increase in $NG_{2,3}$ value. However, the higher reactivity of C_2-OH and C_3-OH compared to that of C_6-OH does not seem to be quite general. It might be ascribed to the insufficient swelling, which not enough to induce the enhancement of C_6-OH reactivity; however, this is not clearly understood in the present stage.

The influence of the CL content on the yield and the structure of the starch-*g*-PCL at a fixed starch/water ratio (30 g/70 g) is shown in Figures 7–10. As mentioned previously, the appearance of maxima in the yield and the CL mol % with the CL content in the feed would be due to the increase in hydrophobicity of the reaction medium in the high CL content range (Figure 7). The variations in the DGP and NG values with the CL content in Figure 8 enable the detailed analysis on this finding. It is very interesting to note that the NG value of starch-*g*-PCL is nearly unchanged with the CL content. It means that the NG is governed by the starch/

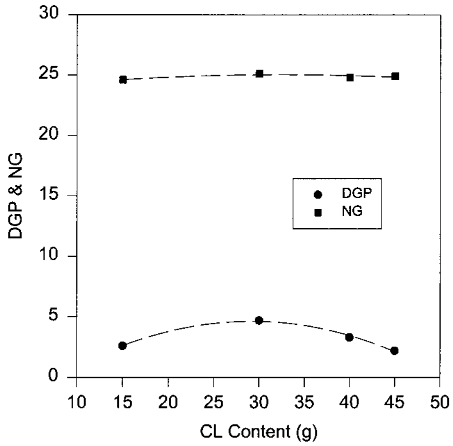

Figure 8. DGP and NG values of starch-*g*-PCL with CL content at fixed starch/water feed ratio.

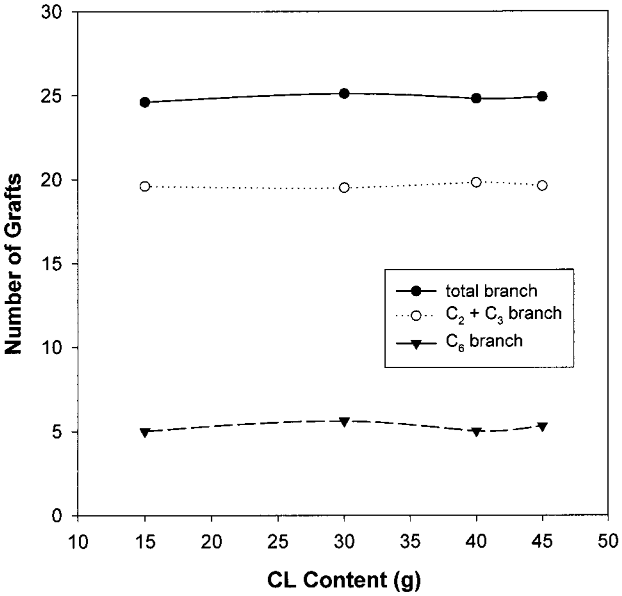

Figure 9. Changes of NG, $NG_{2,3}$, and NG_6 values with water content at fixed starch/water feed ratio.

water ratio in the feed irrespective of the CL content. Thus, it is easily understood that the reduction of yield at the high CL content results from the decrease not in NG but in DGP. In other words, the increase in CL content does not affect the initiation of grafting reaction but just reduces the propagation of the PCL graft. Because the reactivity of the initiation reaction is predominated with the starch/water ratio in the feed, the NG value remains almost constant despite the variation in the CL content. Figure 9 shows the similar tendency of all of the branches retaining nearly constant NG values with CL content irrespective of branch type.

The reason of the decrease in DGP value at the high CL content can be explained as follows:

As the propagation of the PCL graft proceeds, the swelling effect of water on the starch-*g*-PCL produced in the medium would be weakened because the solvating power of water to the starch-*g*-PCL molecule is reduced due to the gradual decrease in hydrophilicity of the starch-*g*-PCL caused by the formation and propagation of the PCL graft onto the starch. The higher water concentration is thus needed to solvate the starch-*g*-PCL. Therefore, if the water concentration of the reaction medium is not sufficiently high, the starch-*g*-PCL molecules produced cannot be stabilized and would be aggregated with each other in some cases. Consequently, the continuous propagation of the PCL graft should be hindered by this inappropriate reaction condition. This can be the reason for the decrease in DGP at the high CL content.

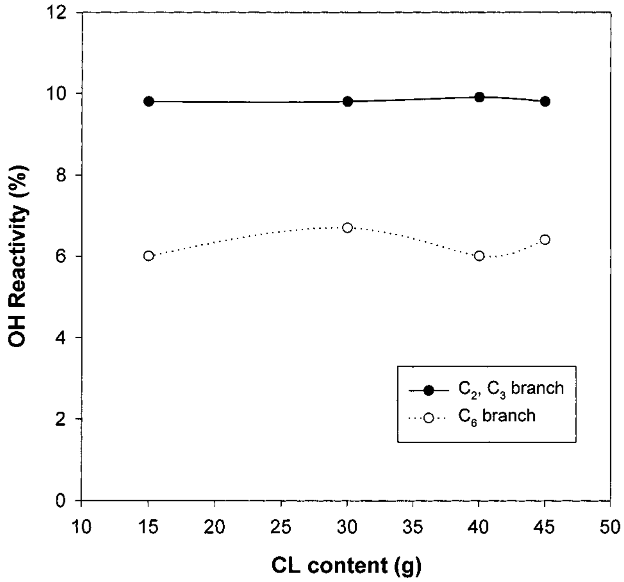

Figure 10. Hydroxyl group reactivity with water content at fixed starch/water feed ratio.

In terms of OH reactivity, the increase in CL content does not cause any significant increase in hydroxyl group reactivity, as illustrated in Figure 10. It means the initiation of graft reaction between the hydroxyl group of starch and the CL monomer is not affected by the CL content but is governed by the degree of swelling determined with the water content as already mentioned.

Conclusions

The graft polymerizations of CL monomer onto starch were successfully conducted with various starch/CL/water feed ratios to obtain starch-*g*-PCL copolymers with various graft structures. The initial increase in water content under the fixed starch/CL feed ratio induced the only increase in the number of PCL grafts, and the additional increase in water content lengthened even the PCL grafts. On the other hand, the change of CL content in the feed at the fixed starch/water ratio caused the maximum behavior in graft length and the constant number of PCL grafts. It seems that these phenomena are attributed to the change of hydrophilicity of the graft copolymers formed in the reaction medium affecting the reactivity of the grafting reactions.

Acknowledgment. This work was carried out with the support of the BioProcess Engineering Research Center in KAIST.

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MA981453F