Plasticization of Cellulose Diacetate by Graft Copolymerization of ε-Caprolactone and Lactic Acid

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ABSTRACT: Graft copolymerization of ε-caprolactone (CL) and lactic acid (LA) onto cellulose diacetate (CDA) at the residual hydroxyl positions was conducted to obtain thermoplastic CDA. The effects of the reaction temperature and time and the CL/LA molar ratio in the feed on the progress of the graft copolymerization were investigated. The molecular weight of CDA was increased by this graft copolymerization. The oxycaproyl and lactyl molar substitutions (MS_{CL} and MS_{LA}, respectively) in grafted CDA (*g*-CDA) were determined through ^{1}H-NMR spectral analysis. These MS values were controllable by changing the reaction conditions adequately. The flow temperature and melt viscosity of *g*-CDA decreased with an increase in the total substitution of MS_{CL} and MS_{LA}, and transparent polymer sheets could be obtained from the resulting *g*-CDA by hot pressing at around 200°C without adding any plasticizer. The mechanical properties of the molded *g*-CDA samples varied widely, depending on the different combinations of the MS_{CL} and MS_{LA} values; the *g*-CDA sheets became elastic when the MS_{CL} was larger than the MS_{LA}, and their tensile strengths were enhanced as the MS_{LA} was increased. It was thus found that CDA was successfully plasticized by this graft copolymerization. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2621–2628, 2002

Key words: graft copolymerization; cellulose diacetate; ε-caprolactone; lactic acid; thermoplasticity; mechanical property

INTRODUCTION

Recently, thermoplastic cellulose esters have become highly significant as potentially biodegradable polymer materials for the composting of plastic waste. Cellulose diacetate (CDA) is one of the cellulose organic esters that is widespread in industrial production. It is known that CDAs with a degree of substitution (DS) of <2.5 exhibit biodegradability.[1–3] However, this cellulosic material shows a high glass-transition temperature, which results in limited processibility when compared with conventional synthetic plastics. In practice, low molecular weight plasticizers are usually utilized to plasticize cellulose acetate, because of their low cost and facility of compounding. A serious problem of this convenient method of plasticization may be plasticizer migration, which manifests itself more or less in the course of time; it is responsible for the lowering of the mechanical properties of molded CDA products.

To solve this migration problem, some attempts have been made[4–12] to improve the processibility of cellulose acetate. For example, Yoshioka et al. reported ring-opening graft copolymerization of ε-caprolactone (CL) and lactide (LA) onto cellulose acetate (LACD).[5] In this method the graft reaction proceeded rapidly to

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completion within 10–30 min. However, the reaction process had to be carried out under a strictly dried condition, and it was difficult to control the chemical composition in the grafted side chain, because of the much higher reactivity of LACD than CL.

Instead of the use of LACD, direct condensation polymerization of LA is known as an alternative route to prepare poly(lactic acid) (PLA). In this case, a PLA product with a relatively high molecular weight can be obtained without any isolation of the intermediate LACD.[13] In the present work this direct condensation method was applied for the graft copolymerization of CL and LA onto CDA, so that the extent of plasticization of the cellulose ester may be expected to be controlled more easily.

EXPERIMENTAL

Materials

The CDA was supplied by Daicel Chemical Industries Co. Ltd. The DS of the CDA was 2.4 (combined acetic acid ≈55%) and its degree of polymerization was about 160. The CL was also provided by Daicel Chemical Industries, and it was used after vacuum distillation. The LA (88.5% aqueous solution) was purchased from Nakalai Tesque Co. Ltd. and used without further purification. Diphenyl ether, SnO, and other organic solvents were purchased from Nacalai Tesque Co. Ltd., these were all guaranteed reagent grade and used as received.

Graft Copolymerization of CDA with CL and LA

Weighed amounts of CDA (10 g), CL (10–60 g), LA (10–60 g), diphenyl ether (reaction solvent, 100 mL), and SnO (catalyst, 0.238 g) were charged into a flask with a Soxhlet extractor filled with 3-Å molecular sieves; the vaporized solvent was resupplied to the reactor, under reduced pressure through the molecular sieves. In this reaction apparatus the flask was placed in an oil bath thermoregulated at a desired temperature ranging from 130 to 170°C, and azeotropic dehydration was carried out under a pressure of 10–15 mmHg. After the grafting reaction was continued over a prescribed time period, 200 mL of acetone was poured into the reaction mixture. The resulting homogeneous solution was added dropwise into a vigorously stirred large excess of methanol containing aqueous 1*N* HCl at 1% concentration. The suspension thus obtained was allowed to stand overnight with slow stirring. Then the precipitate was filtrated off using a 0.5 μm Teflon membrane filter; dissolved in acetone, and reprecipitated in a large excess of methanol, which was followed by standing with slow stirring and collection by filtration. Via further repetition of this purification procedure, the collected grafted product (*g*-CDA) was dried at 60°C *in vacuo*.

GPC Analysis

The molecular weight distribution of purified *g*-CDA was determined on a Tosoh HLC-8020 gel permeation chromatograph equipped with a refractive index detector and using two TSK-GEL GMHHR columns connected to each other. The measurement was conducted by using tetrahydrofuran (THF) as the mobile phase at a flow rate of 1.0 mL/min. The concentration of the test samples was 0.5% in THF and the quantity of injection was 100 μL. The system was calibrated with monodisperse polystyrene standards.

NMR Spectroscopic Measurements

The 300-MHz ^{1}H-NMR and 75-MHz ^{13}C-NMR spectra of purified *g*-CDA samples were measured by using a Bruker ARX 300 NMR apparatus at 300 K. The solvent that was used was $CDCl_3$, the solute concentration was 30 mg/mL, and the internal standard was tetramethylsilane. The pulse width was 3.0 μs for 32 (^{1}H) and about 10,000 (^{13}C) scans.

Thermal Flow Properties

The apparent flow temperatures of the *g*-CDA samples were measured by a constant heating test with a Shimadzu CFT-500A flow tester. The starting temperature was 50°C at a heating rate of 5°C/min. The die orifice size was 1-mm diameter and 10-mm length. Measurements of the apparent melt viscosity were conducted with the same equipment at a constant 230°C.

Melt Molding and Tensile Tests

The *g*-CDAs were hot pressed at 180–220°C with a Toyo-Seiki hot-pressing apparatus to obtain polymer sheets for the tensile tests. For the molding a pressure was gradually applied to the respective molten sample to reach 5.0 MPa in 3–5 min; subsequently, it was quickly increased to 15.0 MPa, followed by maintaining this applica-

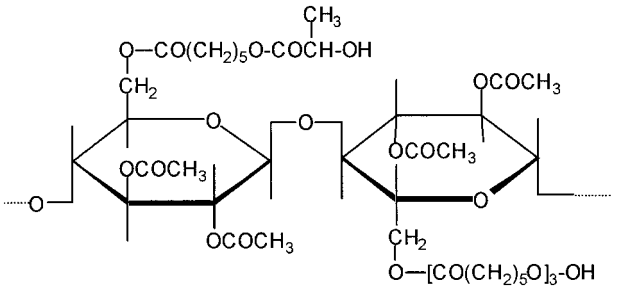

Figure 1 A possible molecular structure of *g*-CDA copolymerized with CL and LA.

tion for 30 s at the selected temperature. Immediately after the pressure was released, the samples were transferred to another compressing apparatus and cold pressed at 15.0 MPa and 25°C for 2 min. After being rereleased from the compressed state, the molded polymer sheets were finally conditioned at 20°C and 60% relative humidity (RH) for 48 h.

Rectangular specimens (80 × 5 × 0.4 mm) were cut from the molded sheets. Tensile tests were performed for these specimens by using a Shimadzu Autograph AGS-5kNG at 20°C and 60% RH. The strain rate and span length were 0.5 mm/min and 40 mm, respectively. Ten specimens of each *g*-CDA sample were used for the measurement, and the averaged data were adopted.

RESULTS AND DISCUSSION

Graft copolymerization of CL and LA onto CDA was conducted to obtain thermoplastic CDA. This reaction proceeds in the presence of the water that the LA contains, whereupon cyclic CL can be easily converted into 6-hydroxy caproic acid. However, an excess amount of water should be removed in order to shift the reaction equilibrium toward copolymerization; therefore, this reaction was performed under reduced pressure. The present method of graft copolymerization is an expanded application of catalytic, direct condensation polymerization of LA.[13] A possible structure of the *g*-CDA is illustrated in Figure 1. It is depicted with an oxycaproyl molar substitution (MS_{CL}) of 2, a lactyl molar substitution (MS_{LA}) of 0.5, and an acetyl DS of 2.

Figure 2 exemplifies a comparison of the molecular weight distribution curves of CDA that were obtained before and after an actual graft reaction. The CDA maintained a high molecular weight, or its molecular weight tended to increase as a consequence of this graft copolymerization. Thus, the hydrolysis allowable in the coexistence of water and organic acid was substantially less effective in the lowering of the molecular weight of CDA. Furthermore, it was also found that the reprecipitation procedure applied for purification in this study successfully removed some by-products of oligomers and/or residual monomers of CL and LA, because no corresponding GPC peak was observed in the low molecular weight region of the distribution curves.

The average number of introduced oxycaproyls (MS_{CL}) and lactyls (MS_{LA}) per anhydroglucose residue of CDA was determined by ^{1}H-NMR. Figure 3 shows a ^{1}H-NMR spectrum obtained for a *g*-CDA sample. In the spectrum we designate the resonance peak area derived from the methyl protons of acetyl groups as A, an averaged area of the resonance signals from the methylene protons of oxycaproyls as B, and the area from the methyl protons of lactyls as C. The MS_{CL} and MS_{LA} can be calculated by the following equations:

$$MS_{CL} = DS \times 3B/2A$$

$$MS_{LA} = DS \times C/A$$

where DS denotes the acetyl DS of the original CDA used. In the present study the MS_{CL} and MS_{LA} were first evaluated for *g*-CDAs prepared in the same reaction time (4 h) with equimolar amounts of the two monomers as a function of the reaction temperature for the graft copolymeriza-

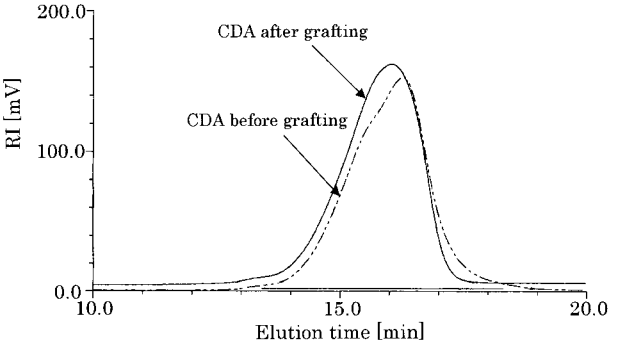

Figure 2 Molecular weight distribution curves of CDA measured before and after a graft reaction carried out under the following conditions: a (CL + LA)/CDA weight ratio of 6, a CL/LA molar ratio of 1, a catalyst content of 0.34 wt %, a reaction time of 3 h, and a temperature of 150°C. RI, refractive index.

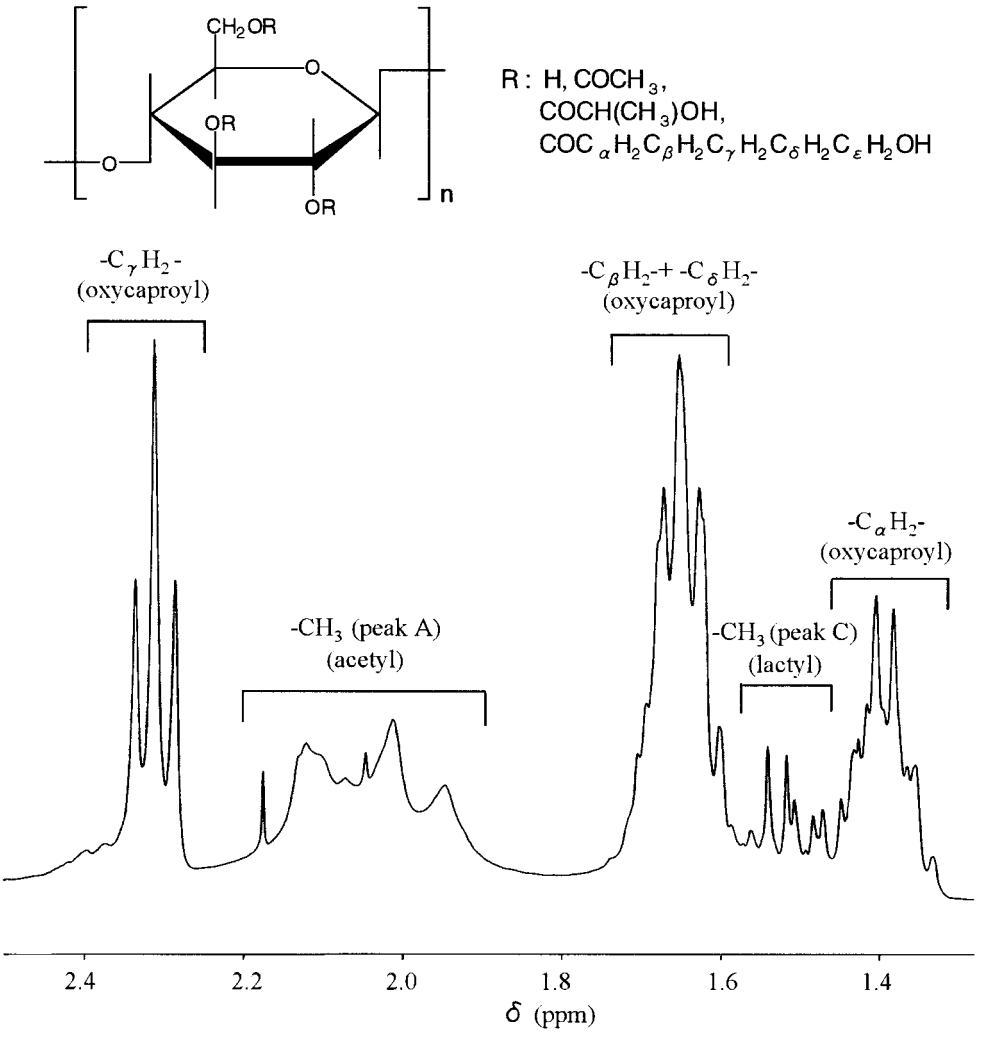

Figure 3 The ^{1}H-NMR spectrum of a *g*-CDA copolymerized with CL and LA.

tion. The results are summarized in Figure 4. It can be seen here that the MS_{CL} and MS_{LA} increase rapidly from 0.3 to 0.7 and 0.01 to 0.2, respectively, with the increase in the reaction temperature from 130 to 150°C. Above 150°C both substitution values level off, indicating that the graft reaction proceeds with the temperature elevation having no appreciable effect on the degree of copolymerization in this temperature range.

Figure 5 shows the dependence of the MS_{CL} and MS_{LA} on the reaction time, which was examined at 150°C and again with equimolar CL and LA monomers in the feed. The MS_{CL} and MS_{LA} values both increased sharply with a reaction time of up to 4 h; then they leveled off. Thus, 4 h is a sufficient reaction time to obtain the maximum values of the molar substitutions of oxycaproyls and lactyls.

Concerning the data given in Figures 4 and 5, it is also interesting to note that the absolute value of the MS_{CL} is always larger than the corresponding value of the MS_{LA}, irrespective of the reaction temperature and time, reflecting that CL has a higher reactivity than that of LA in the present reaction system. Contrary to this, in the ring-opening graft copolymerization of (LACD),[5] the molar substitution of CL was usually about one-half that of LACD. Such an observation of the apparently opposite situation of the MS_{CL} for the two kinds of *g*-CDAs may be ascribed to a large difference in the reactivity between the CL partners (LA and LACD) with mutually different molecular structures. Consequently, it can be said

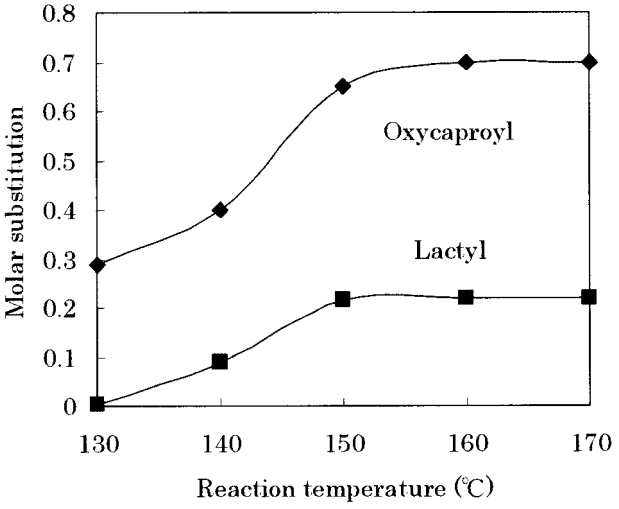

Figure 4 The effect of the reaction temperature on the molar substitutions (MS_{CL} and MS_{LA}) under the following grafting conditions: a (CL + LA)/CDA weight ratio of 6, a CL/LA molar ratio of 1, a reaction time of 4 h, and a catalyst content of 0.34 wt %.

that the graft copolycondensation employed in this work is a very useful method for the synthesis of copolymers with a CL content higher than the LA content, which was hardly realized by ring-opening copolymerization.

In the present reaction system it followed that the values of the total substitution of oxycaproyl and lactyl groups were generally lower than the

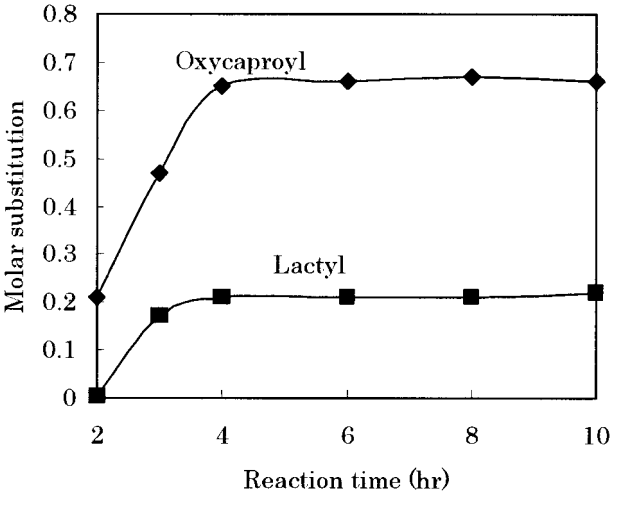

Figure 5 The effect of the reaction time on the molar substitutions (MS_{CL} and MS_{LA}) under the following grafting conditions: a (CL + LA)/CDA weight ratio of 6, a CL/LA molar ratio of 1, a reaction temperature of 150°C, and a catalyst content of 0.34 wt %.

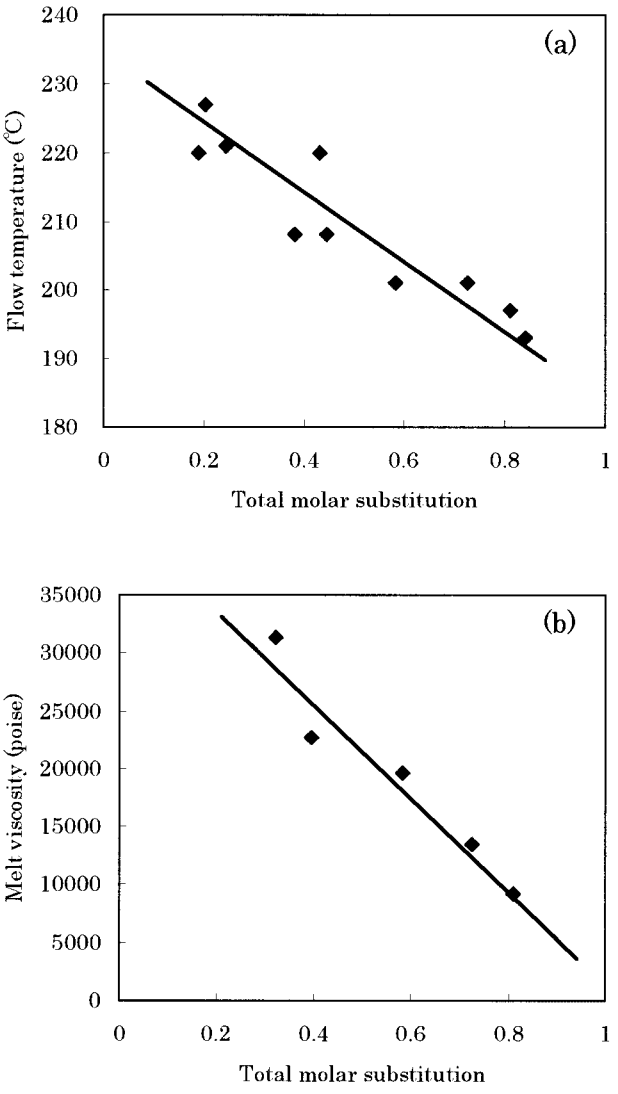

Figure 6 Plots of the (a) flow temperature and (b) melt viscosity (at 230°C) of *g*-CDA versus the total molar substitution (MS_{CL} + MS_{LA}).

corresponding ones obtained by the ring-opening copolymerization method.[5] In spite of the lower substitution (<1.0), however, the synthesized *g*-CDAs showed sufficient flow properties at 180–230°C. Figure 6 compiles the data of their flow temperature and melt viscosity plotted as a function of the total MS of CL and LA. Both plots follow a linear relation with a relatively large, negative slope in the substitution range of about 0.2–0.9. The flow temperature, which was about 255°C in the ungrafted state, is lowered to 190°C when the total substitution [MS(CL + LA)] increases to approximately 0.9. On the other hand, the melt viscosity of CDA, which was originally too high to be measurable at 230°C, falls to less

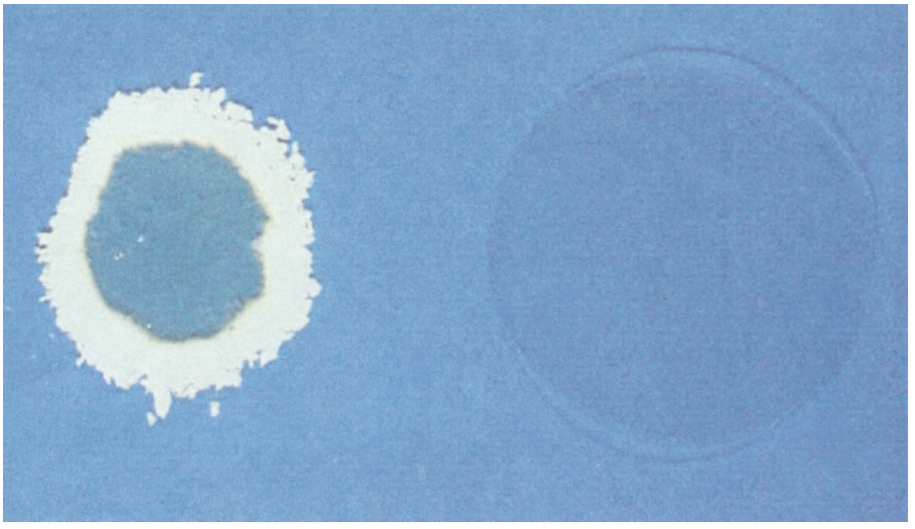

Figure 7 Photographs of CDA sheets hot pressed at 200°C, showing an effect of plasticization due to the graft copolymerization. The original CDA after pressing (left) and the *g*-CDA hot pressed into a clear sheet (right). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

than 10^4 P with an increase in the MS(CL + LA) to 0.8. These observations indicate that the present grafting is quite effective in providing thermoplasticity to CDA. Because of the thermoplasiticity, it was actually possible to mold the *g*-CDAs into film sheets at 180–220°C without adding any other plasticizers. The sheets were transparent and homogeneous visually, as demonstrated in Figure 7.

The good moldability of *g*-CDA may be primarily attributed to the preferential grafting of flexible oxycaproyls with as many as five methylene units onto the carbohydrate backbone. In addition to this primary factor, it would be plausible to presume that there may be another structural feature characteristic of the graft copolymers synthesized here, which contributes to the marked enhancement of the fluidity with a slight increase in the grafting amount. Acting on the expectation of finding the structural details of *g*-CDAs, we next examined the sequence distribution of their side chains by ^{13}C-NMR measurements.

Figure 8 shows the NMR spectrum obtained for a *g*-CDA with MS_{CL} = 0.63 and MS_{LA} = 0.15, which is depicted on an enlarged scale to make the resonance region of the methyl and methylene carbons clearer. In this figure the notations C and L designate oxycaproyl and lactyl, respectively, and the assignment of the sequences was performed according to the literature.[14–17] The sample has a total MS of (0.78) less than unity; nevertheless, in the ^{13}C-NMR spectrum, the respective resonance signals of oxycaproyl and lactyl carbons are split into plural peaks, which decidedly come from the formation of various sequences in the graft chains. From this result it can be reasonably assumed that the residual hydroxyl groups of the original CDA were not esterified in an even proportion by monomer reagents; therefore, the resulting graft chains were located irregularly but with an adequate enough length to yield the monomer sequence distribution. The local introduction of such bulky side chains onto the cellulose backbone would produce extreme weakening of the self-associating nature of CDA molecules based on some possible attractive interaction such as hydrogen bonding, resulting in the improvement of the inherent poor fluidity.

The changing manner of the MS degrees of *g*-CDA with a variation of the CL/LA ratio in the feed was investigated. The result is shown in Figure 9; the data were obtained under an equivalent reaction condition of 150°C for 3 h. The MS_{CL} increases sharply as the CL feed amount increases, whereas the increase of the MS_{LA} with an increasing LA amount is gradual. This clearly demonstrates again the difference in reactivity between the two monomers. However, it should be emphasized that the MS_{LA} becomes higher than the MS_{CL} in a CL/LA range of 1/5–2/4 in the feed molar ratio, although the total MS assumes a considerably low value. Thus, in the present

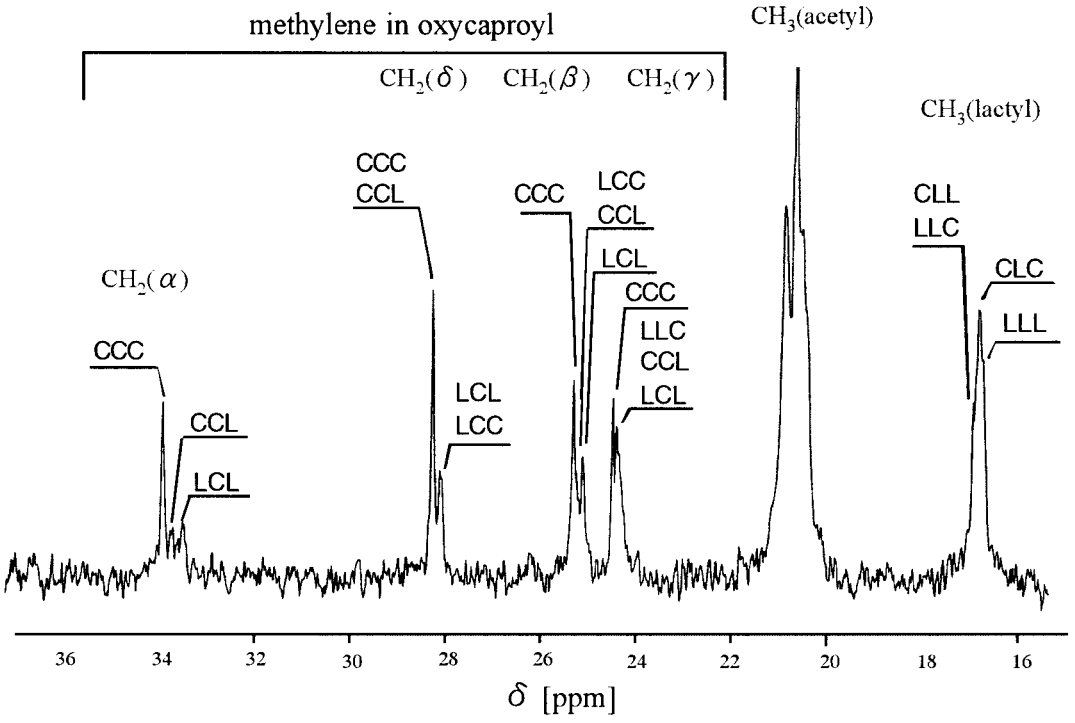

Figure 8 The ^{13}C-NMR spectrum of a *g*-CDA with MS_{CL} = 0.63 and MS_{LA} = 0.15 and displayed on an enlarged scale for the resonance region of methyl and methylene carbons.

grafting method it was possible to prepare *g*-CDAs with a variety of proportions of MS_{CL} and MS_{LA} by adjusting the CL/LA feed ratio. As a matter of course, film sheets obtained from the *g*-CDAs by hot pressing are expected to exhibit wide-ranging mechanical properties, which are sensitively variable according to the different combinations of MS_{CL} and MS_{LA} values.

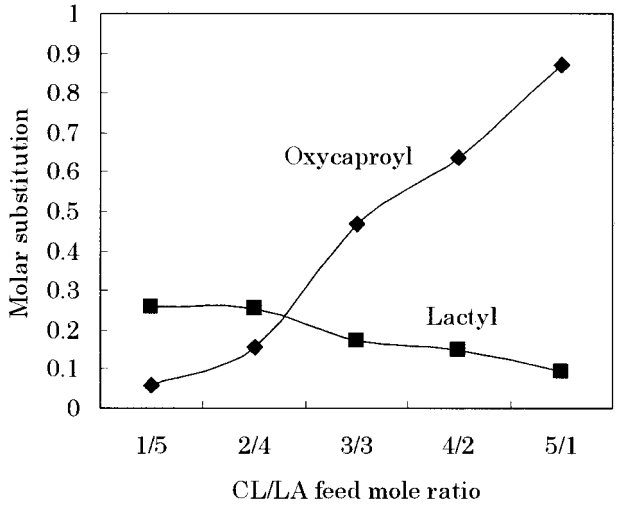

Figure 9 The relation between the molar substitutions of CL and LA in *g*-CDA and the feed composition of the two monomers. The graft products examined were all synthesized at 150°C for 3 h.

In Figure 10 the data of the tensile strength, elongation at rupture, and Young's modulus for the molded *g*-CDA samples are plotted as a function of the MS_{CL} and MS_{LA}. There are a number of observations worth noting in the results of the tensile testing: The *g*-CDA sheets were ductile and more or less endowed with elasticity when the MS_{CL} was higher than the MS_{LA}; however, there a fairly steep rise of the tensile strength and modulus occurred with an increase in the MS_{LA} value. More than an 80-MPa tensile strength and about 70% elongation at break were attained for LA-rich and CL-rich compositions respectively in the present measurements. This variability of the mechanical properties of the *g*-CDA sheets may be interpreted as being due to the following effects: the grafting of a large amount of CL groups with a very flexible methylene sequence should serve to make the *g*-CDA sample soft and elastic while some extent of copolymerization of comparatively semiflexible LA segments, leading to a higher density of ester linkages in the graft side

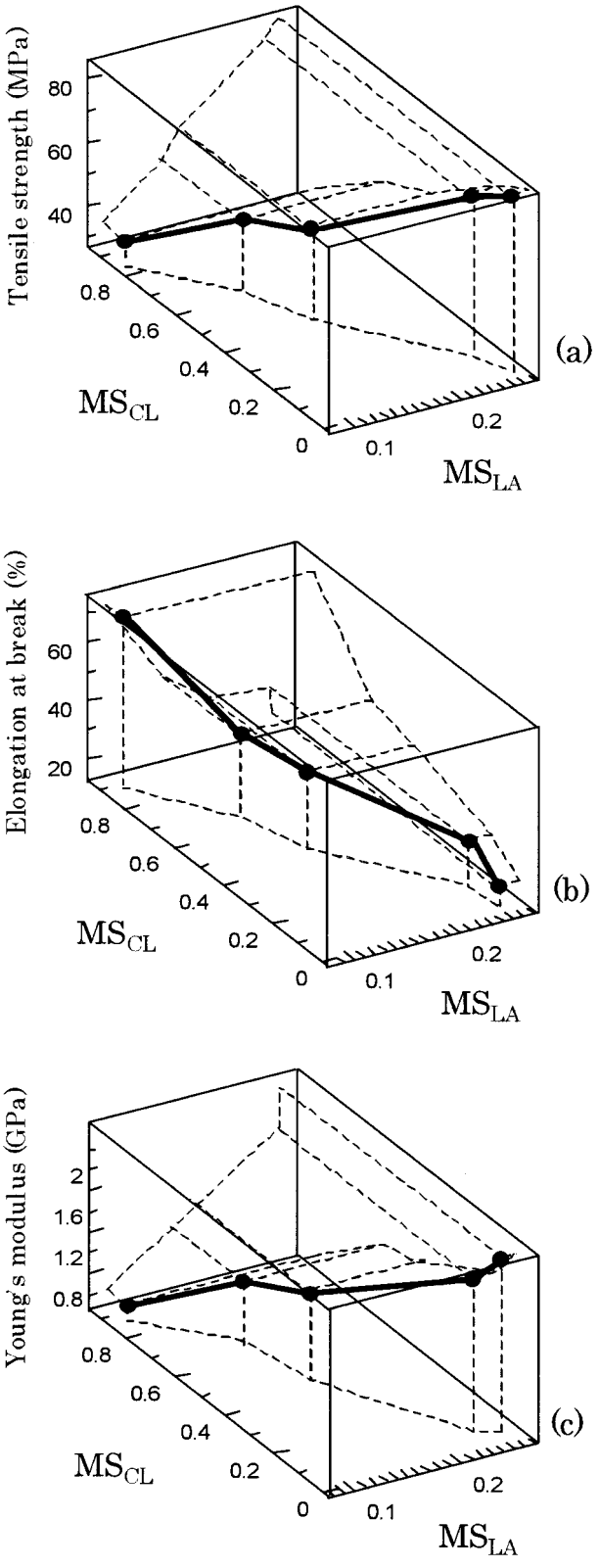

Figure 10 The mechanical properties of *g*-CDA: (a) tensile strength, (b) elongation at break, and (c) Young's modulus; each is plotted as a function of the MS_{CL} and MS_{LA}.

chain, would allow the *g*-CDA material to be rather tough.

CONCLUSION

In conclusion, thermoplastic *g*-CDAs were synthesized successfully by the grafting method based on a direct condensation copolymerization of CL and LA; the original poor moldability of CDA was remarkably improved, and the mechanical properties of film sheets obtained from the *g*-CDAs varied widely with different combinations of the MSs (MS_{CL} and MS_{LA}). The control of the relative proportion of the two substitution degrees was possible by selecting the appropriate reaction conditions including the temperature, time, and feed composition of the two monomers.

Further characterization of the thermal and optical properties of *g*-CDAs will be described in a subsequent article. In parallel with the general studies of physical properties, a detailed examination of the biodegradability of *g*-CDAs is now in progress in our laboratory.

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