polymer

Phase transitions of lignin-based polycaprolactones and their polyurethane derivatives

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Abstract

Alcoholysis and kraft lignin-based polycaprolactones (LigPCL) were synthesized by the polymerization of ε-caprolactone which was initiated by the hydroxyl (OH) group in lignin. LigPCL-based polyurethanes were also prepared from LigPCL. The caprolactone (CL)/OH ratio of the CAPCLs was changed from 1 to 25 mol mol^{-1}. Thermal properties of the LigPCL and LigPCL-based polyurethane (PU) sheets were studied by differential scanning calorimetry (DSC). Glass transition temperature (T_g), heat capacity difference at T_g (ΔC_p) cold crystallization temperature (T_{cc}) and melting temperature (T_m), were determined by DSC. The main chain motion of lignin is observed in the whole CL/OH ratio. When CL/OH ratio exceeds 5 mol mol^{-1} in the LigPCL samples and 10 mol mol^{-1} in the LigPCL-based PU samples, the crystalline region which is organized by the PCL chain association is observed. It was found that PCL chain association is controlled by both chain length and chemical cross linking. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Alcoholysis lignin; Kraft lignin; Caprolactone

1. Introduction

Lignin is usually considered as a polyphenolic material having an amorphous structure, which arises from an enzyme-initiated dehydrogenative polymerization of coniferyl, sinapyl and *p*-coumaryl alcohol [1]. Accordingly, the basic lignin structure is classified into two components; one is the aromatic part and the other is the alkyl (C3) chain. Available reaction sites in lignin are carbonyl, carboxyl and hydroxyl groups. However, both phenolic and alcoholic hydroxyl groups are the most useful reaction sites in the synthesis of lignin derivatives since the number of hydroxyl groups is the largest in the lignin structure [1].

In our previous studies, the hydroxyl group of plant components was used as an active reaction site for the preparation of various types of biodegradable polymers [2–11]. Lignin has attracted considerable attention in order to develop new plant component derivatives. It is known that lignin is a typical amorphous polymer whose glass transition (T_g) is observed at around 130–160 °C [12–15]. At the same time, lignin shows no viscous flow even at a temperature higher than T_g. It is usually considered

that lignin molecules are crosslinked with each other [1]. However, the crosslinking density is sufficient enough to prevent molecular movement at T_g [12–15]. Although the molecular motion of lignin is enhanced at a temperature higher than T_g, processability, such as flow ability, is insufficient in order to apply the usual processing methods used for synthetic polymers. In order to improve the processability of lignin, in this study, polycaprolactone (PCL) chain was attached to lignin. PCL is known as a representative biodegradable and biocompatible polymer [16,17]. At the same time, the higher order structure of PCL can be controlled by suitable thermal treatments [18,19]. It is considered that the higher order structure of lignin-based PCL can be expected to be controlled through appropriate processing. Moreover, both components, lignin and PCL, are biodegradable.

In this study, caprolactone chains with various lengths obtained by changing the number of caprolactone units are attached to lignin and their phase transition behavior is investigated by differential scanning calorimetry (DSC). In order to examine the effect of crosslinking on molecular motion, polyurethane (PU) derivatives were synthesized with various PCL chains. It is considered that molecular mobility is controllable by introducing inter-molecular chemical bondings, such as urethane linkage. We have

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also paid attention to the side chain association taking into account the thermal history and have compared the results with those of saccharide-based polycaprolactones which were newly synthesized in our laboratory [5].

2. Experimental

2.1. Sample preparation

Alcoholysis lignin (AL) (Alcel lignin®) was obtained from Repup Technologies Inc., and kraft lignin (KL) from Westvaco Co. Ltd. PCL with molecular weight 1.0×10^4 was purchased from Wako Pure Chemical Co. Ltd, Japan as reference material. PCL in pellet form was pressed at 120 °C under the pressure of 10 MPa using a Tester Industry Hot Presser SA-302.

Alcoholysis lignin-based PCL (ALPCL) and kraft lignin-based PCL (KLPCL) were synthesized by polymerization of ε-caprolactone (ε-CL) which was initiated by the hydroxyl (OH) group of the lignins. The amount of ε-CL was varied from 1 to 20 mol per OH group of each lignin (CL/OH ratio = 1, 2, 3, 4, 5, 10, 15, 20 and 25 mol mol^{-1}). The polymerization was carried out for 12 h at 150 °C with the presence of a small amount of dibutyltin dilaurate (DBTDL). ALPCL and KLPCL sheets were prepared by heat-pressing the synthesized polymers at 160–180 °C at ca. 10 MPa. The schematic chemical structures of the sample (LigPCL) are shown in Fig. 1.

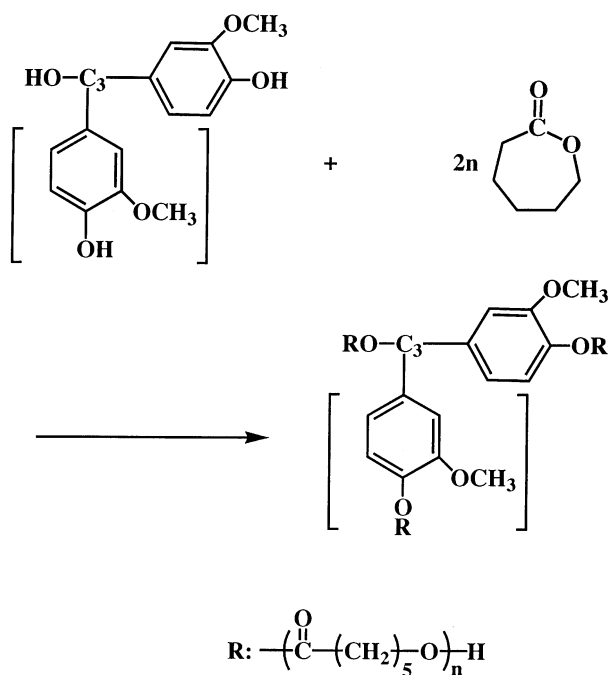PU samples of ALPCL and KLPCL were obtained by the following procedure. Lignin-based PCLs were dissolved in tetrahydrofuran (THF). Diphenylmethane diisocyanate (MDI) was reacted with the above solution for 30 min at room temperature with stirring. The obtained prepolymer was cast on a glass plate and the solvent was evacuated in a desiccator under dry conditions. The obtained ALPCL-based PU and KLPCL-based PU sheets were cured at 120 °C for 2 h. The schematic chemical structures of the sample (Lig PCLPU) are shown in Fig. 2.

PCL in pellet form was obtained from Daicell Chemical Industries Co. Commercial name of PCL was Placcel H5. Viscosity at 25 °C was 200–1000 MPa. PCL sheet with thickness of 2 mm was prepared using a hot press machine (Tester Indust. Test Press Type SA-303) under the pressure of 10^3 N cm^{-2} at 130 °C.

2.2. Differential scanning calorimetry

DSC was performed using a Seiko DSC 220 at a heating rate of 10 °C min^{-1} under a nitrogen flow (flow rate = 30 ml min^{-1}). Sample mass was 5–10 mg. Aluminum open pans were used. The AL and KL samples were heated to 200 °C and cooled at 40 °C min^{-1} to −120 °C. DSC scans were repeated two times. The results of the second run were used for determination of transition temperature and enthalpy. The melting temperature (T_m), enthalpy of melting (ΔH_m), cold crystallization temperature (T_{cc}), enthalpy of cold crystallization (ΔH_{cc}), pre-melt crystallization temperature (T_{pmc}), enthalpy of pre-melt crystallization (ΔH_{pmc}), glass transition temperature (T_g) and heat capacity gap at T_g (ΔC_p) were determined by the method reported previously [20]. Crystallinity (X_c) of samples was determined using the values ($\Delta H_m/\Delta H_{m100}$), where ΔH_{m100} is ΔH_m of 100% crystalline PCL, 139 J g^{-1} [21].

2.3. Thermogravimetry

Thermogravimetry (TG) was carried out in nitrogen (flow rate = 200 ml min^{-1}) using a Seiko TG 220 at a heating rate of 20 °C min^{-1} in the temperature range from 20 to 800 °C. Sample mass was ca. 5 mg. TG curves and derivatograms were recorded.

3. Results and discussion

By TG measurements, it was found that the samples used in this study decomposed at a temperature higher than 350 °C. Thermal decomposition of the lignin and PCL

Fig. 1. Schematic chemical reaction for the synthesis of lignin-based polycaprolactones (LigPCL).
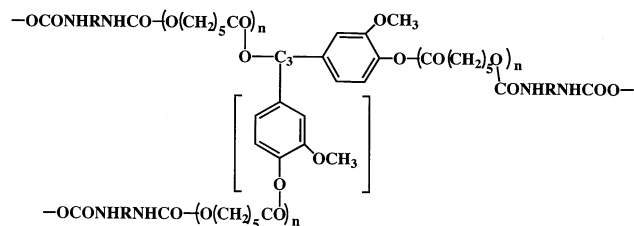

Fig. 2. Schematic chemical structures of polyurethane derived from lignin-based polycaprolactone (LigPCLPU).

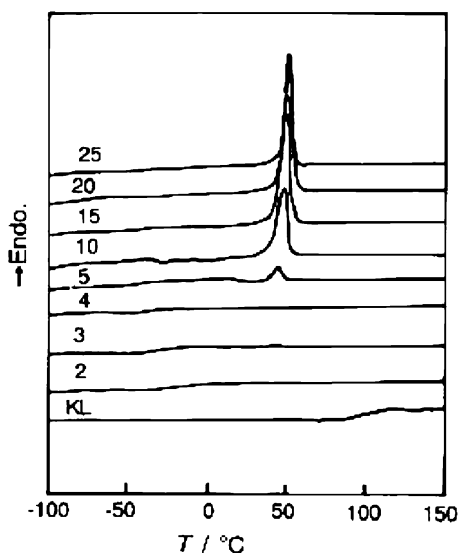Fig. 3. Stacked DSC curves of KLPCL with various CL/OH ratios heated at 10 °C min^{-1}. Numerals in the figure show CL/OH ratio, mol mol^{-1}.

measured by TG-Fourier transform infrared spectroscopy (TG-FTIR) was reported in our previous paper [22]. DSC measurements were carried out at a temperature where the samples are thermally stable.

Fig. 3 shows stacked DSC curves of KLPCL samples with various CL/OH ratios in a temperature from -100 to 150 °C. Fig. 4 shows stacked magnified DSC curves in a temperature range from -80 to 60 °C. As shown in the magnified curves (Fig. 4), a baseline deviation showing glass transition is clearly observed. T_g of KL is observed at around 100 °C and T_g of KLPCL decreases with increasing CL/OH ratio. T_g of lignin is detected even when CL/OH ratio exceeds 15 mol mol^{-1}. T_g of LigPCL decreases in the initial stage and increases slightly after reaching a leveling
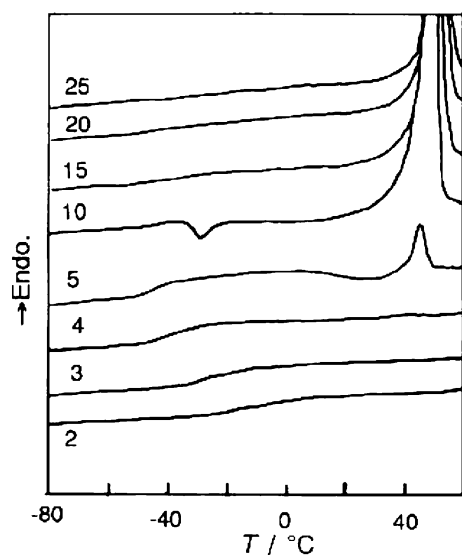
off point at around CL/OH = 10. An exothermic peak observed at around -40 °C for the samples with CL/OH ratio 10 is attributed to cold crystallization. The shallow exothermic peak observed at around 30 °C is attributed to pre-melt crystallization and it is observed for the sample with CL/OH ratio = 5 as shown in Fig. 4. An endothermic peak observed at around 50 °C for the samples with CL/OH ratio larger than 5 is attributed to the melting of coaggregated PCL side chains. Melting of pure PCL was observed in a temperature range from 59 to 64 °C [17]. Similar DSC curves were observed for ALPCL samples, although the pre-melt crystallization was more clearly observed for the samples with CL/OH ratio = 3 and 4 mol mol^{-1}.

Stacked DSC curves of KLPCL-based PU with various CL/OH ratios are shown in Fig. 5. A large difference between the results shown in Figs. 3 and 5 is that melting and cold crystallization are observed when the CL/OH ratio exceeds 15. Melting temperatures of KLPCL-based PU are almost 10 °C lower than those of KLPCL. ΔH_m (J g^{-1}) values of ALPCL-based PU are also lower than those of KLPCL. The results indicate that the higher order structure is strongly affected by the introduction of urethane linkage, i.e. the crystallinity of PCL chains increases not only by chain length but also by free molecular movement. A similar tendency was observed of the samples of ALPCL derived PU.

Fig. 6 shows a phase diagram of KLPCL and KLPCL-based PU and Fig. 7 shows a phase diagram of ALPCL and ALPCL-based PU. As already shown in the DSC curves (Figs. 3–5), melting, pre-melt crystallization, cold crystallization and glass transition are observed. Peak temperatures of melting, pre-melt crystallization and cold crystallization are shown in Figs. 6 and 7. Generally, no large difference is observed between melting and glass transition temperatures of KLPCL and those of ALPCL.
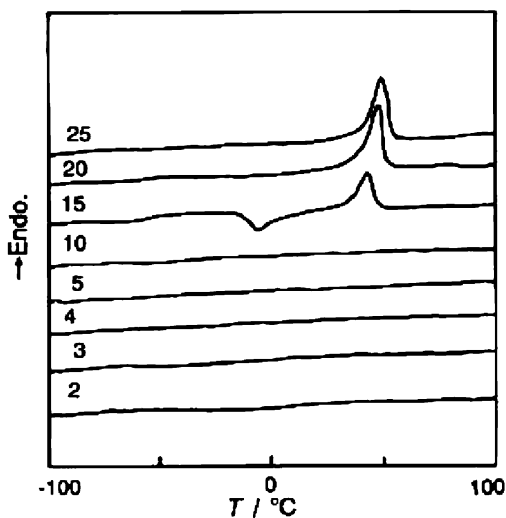

Fig. 4. Stacked magnified DSC curves of KLPCL with various CL/OH ratios heated at 10 °C min^{-1}. Numerals in the figure show CL/OH ratio.

Fig. 5. Stacked DSC curves of KLPCL-based PU with various CL/OH ratios heated at 10 °C min^{-1}. Numerals in the figure show CL/OH ratio.
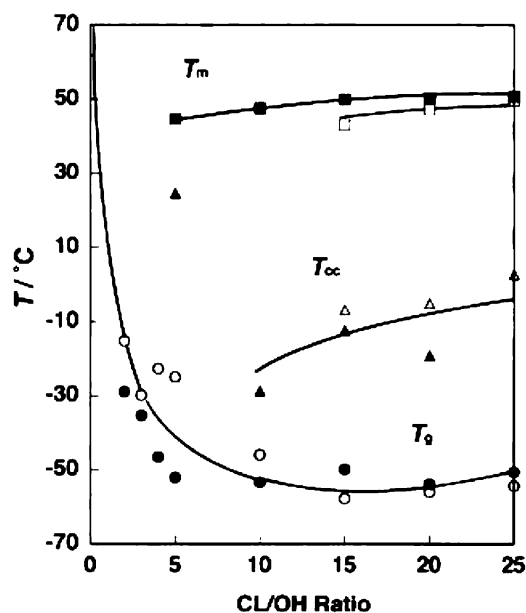
Fig. 6. Phase diagram of KLPCL and KLPCL-based PU. KLPCL (■) T_m, (▲) T_{cc}, (●) T_g. KLPCL-based PU: (□) T_m, (△) T_{cc}, (○) T_g.

Fig. 8. Relationship between crystallinity (X_c) and CL/OH ratio of ALPCL, ALPCL-based PU, KLPCL and KLPCL-based PU. I (●; ALPCL, ■; KLPCL). II (○; ALPCL-based PU, □; KLPCL-based PU).

However, a clear difference is found between lignin-based PU and LigPCL.

It is known that T_g of lignin is observed at around 130–160 °C depending on the lignin species, molecular weight and preparation methods [11–15]. T_g of KL used in this study was observed at 137 °C, and that of AL was 100 °C. As shown in Figs. 6 and 7, T_g decreases markedly by the introduction of PCL side chains. T_g decreased with
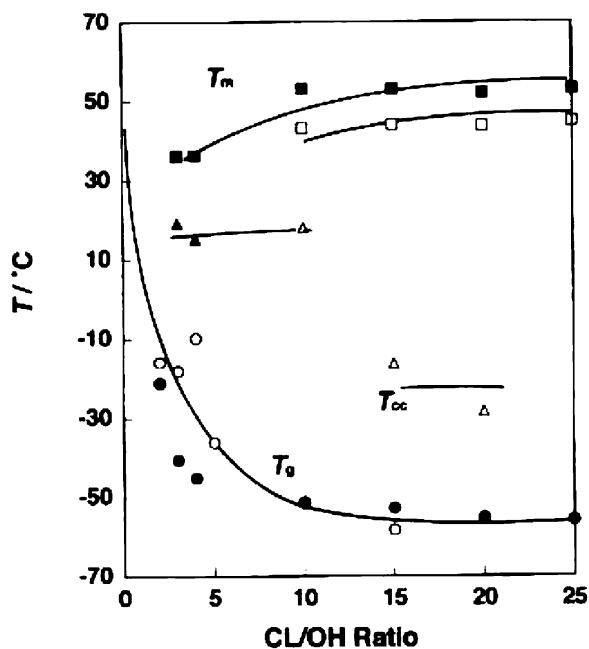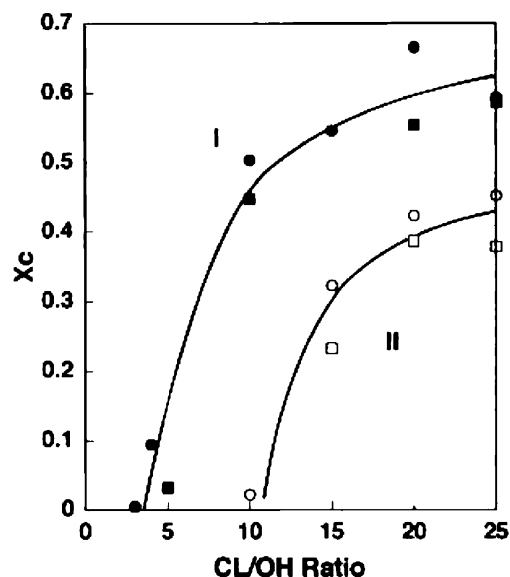

Fig. 7. Phase diagram of ALPCL and ALPCL-based PU. ALPCL (■) T_m, (▲) T_{cc} (●) T_g. ALPCL-based PU: (□) T_m, (△) T_{cc}, (○) T_g.

increasing CL/OH ratio and leveled off at around −55 °C at CL/OH ratio = 10 mol mol^{-1}. T_g of lignin-based PUs coincides with that of lignin PCL when CL/OH ratio exceeds 15 mol mol^{-1}. Pre-melt crystallization was particularly observed for the sample with CL/OH ratio = 5 mol mol^{-1}. T_m of KLPCL and ALPCL increases with increasing CL/OH ratio and levels off at around 50 °C. T_m of PU samples were observed at around 40 °C regardless of CL/OH ratio.

The enthalpy of melting of PCL with 100% crystallinity is reported to be 139 J g^{-1} [21]. Using the above value, the crystallinity (X_c) of each sample was calculated. Fig. 8 shows the relationships between X_c and CL/OH ratio mol mol^{-1}. When the length of PCL molecular chains exceeds 10 mol mol^{-1}, X_c reaches ca. 0.55. When the urethane linkage is introduced, it reaches 0.40 at a high CL/OH range. It is clear that side chain crystallization is restricted by inter-molecular urethane linkage.

Molecular mobility of lignin is affected by the crystallization of PCL side chains. Fig. 9 shows the relationships between T_g and X_c. For the samples of KLPCL and ALPCL, T_g decreases with increasing X_c. On the other hand, T_g of PUs derived from lignin-based PCL slightly decreases showing that inter-molecular crosslinking is the major factor affecting T_g. Lignins, whether AL or KL, hardly affect the T_g values.

The heat capacity difference at T_g is a criteria for the molecular enhancement of amorphous chains. Our previous study on heat capacity (C_p) measurements of lignin shows that C_p difference at T_g (ΔC_p) is almost similar to that of standard amorphous polymers, such as polystyrene [23]. Among synthetic amorphous polymers, it is known that ΔC_p is inversely proportional to T_g in a wide temperature
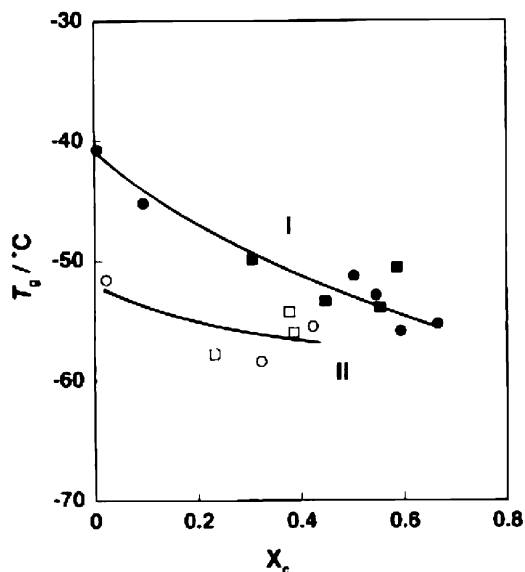
Fig. 9. Relationships between T_g and X_c of ALPCL, ALPCL-based PU, KLPCL and KLPCL-based PU. I (●; ALPCL, ■; KLPCL). II (○; ALPCL-based PU, □; KLPCL-based PU).

range from -100 to $300\,°C$ [23]. It is thought that the chemical structure having rigid components increases the T_g value. In the samples used in this experiment, ΔC_p values increases with increasing T_g as shown in Fig. 10, although ΔC_p values scatter in a certain range. These results suggest that molecular mobility of the lignin chain depends mainly on the length of side chain, i.e. crystallinity.

Fig. 11 shows the relationship between ΔC_p and CL/OH
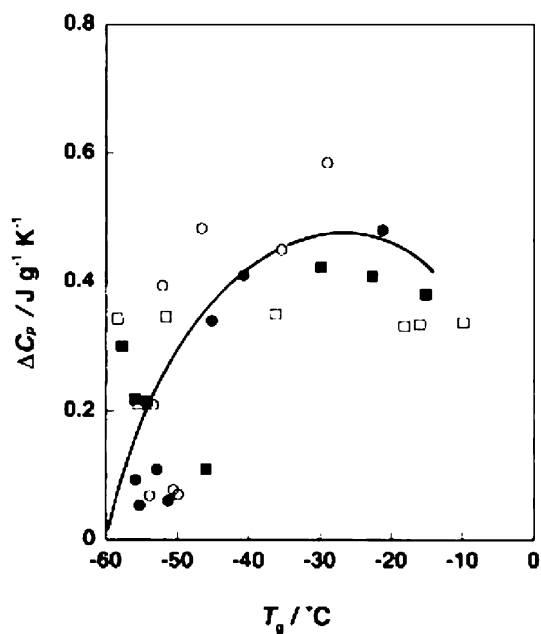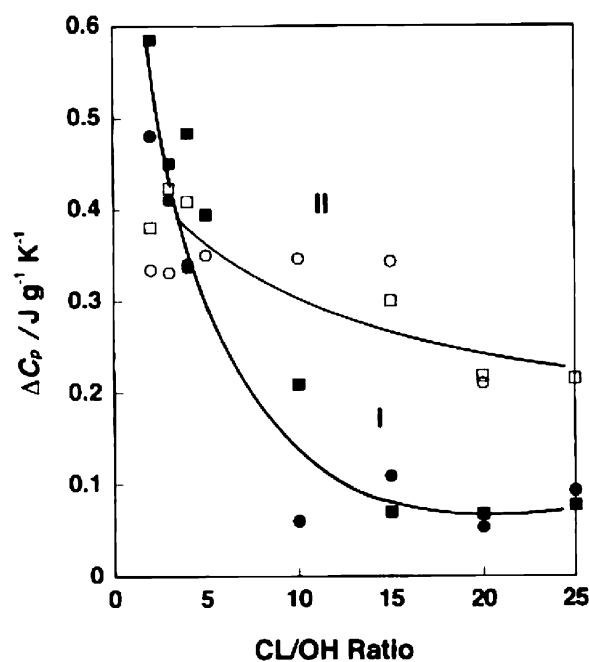

Fig. 11. Relationships between ΔC_p and CL/OH ratio of ALPCL, ALPCL-based PU, KLPCL and KLPCL-based PU. I (●; ALPCL, ■; KLPCL), II (○; ALPCL-based PU, □; KLPCL-based PU).

ratio. ΔC_p markedly decreases with increasing CL/OH ratio for the LigPCL samples. In contrast, ΔC_p of PUs derived from LigPCL decreases considerably with increasing CL/OH ratio. These results strongly suggest that ΔC_p depends on side chain coaggregation. Fig. 12 shows that ΔC_p linearly decreases with increasing X_c. Almost all data fit on a straight line, although several data are scattered as shown in Fig. 12.

Fig. 10. Relationships between T_g and ΔC_p of ALPCL, ALPCL-based PU, KLPCL and KLPCL-based PU. ●; ALPCL, ■; KLPCL, ○; ALPCL-based PU, □; KLPCL-based PU.
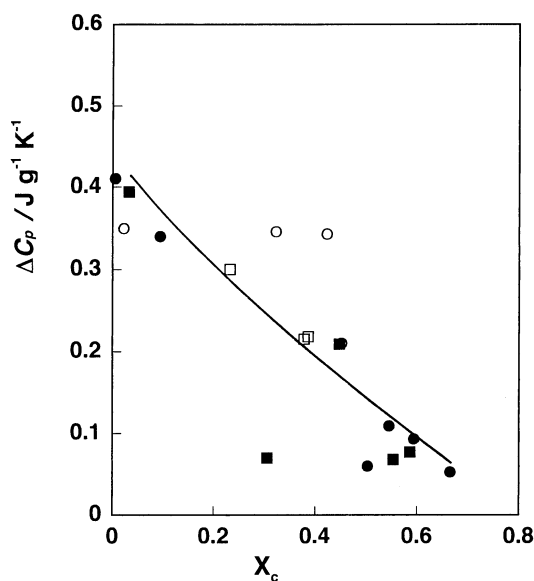

Fig. 12. Relationships between ΔC_p and X_c of ALPCL, ALPCL-based PU, KLPCL and KLPCL-based PU. ●; ALPCL, ■; KLPCL, ○; ALPCL-based PU, □; KLPCL-based PU.

The variation of T_g shown in Figs. 6 and 7 suggests that the main chain motion of lignin markedly decreases by the introduction of short side chain PCL molecules. T_g successively decreases with increasing PCL chain length. This indicates that inter-molecular hydrogen bonding of lignin decreases since OH groups converted into PCL chain. It is reasonable that T_g decreases from ca. 100 °C to a lower temperature due to the breakage of hydrogen bonding [24]. Large side chains expand the inter-molecular distance of lignin molecules, and the T_g of lignin decreases. At the same time, it is clear that the molecular motion of the main chain is restricted, when PCL long chain molecules form a well arranged crystalline structure which can be detected as X_c increases. This explains the fact that T_g value levels off when X_c reaches ca. 0.5 as shown in Fig. 9. It is noteworthy that the crystallinity of PCL side chains is high since the X_c of isolated PCL having the same thermal history was 0.45. It seems that molecular rearrangement of side chain molecules is not restricted by the presence of the lignin main chains in the case of LigPCL samples. In contrast, when the urethane linkage is introduced (PU derived from LigPCL) T_m and X_c decrease. Inter-molecular chemical linking disturbs the free side chain rearrangement. Cold crystallization observed at around −5 to 0 °C observed for the samples with CL/OH ratio at around 15 mol mol^{-1} is large enough and ΔH_{cc} is almost comparable to ΔH_m. The results suggest that the molecules are frozen in the amorphous state during the cooling process, and crystallization gradually takes place during the heating process. The fact that ΔC_p varies reciprocally with crystallinity indicates that the molecular mobility of lignins is restricted by the presence of the crystalline region established between lignin molecules.

From the above results, it can be said that the main chain motion of lignin chains is enhanced by both breakage of hydrogen bonding and expansion of inter-molecular distance when CL/OH ratio is low. When CL/OH ratio exceeds 15 mol mol^{-1}, PCL chains attached to lignin molecules are associated with each other and form a highly crystalline region. It can be said that molecular mobility is controllable by introducing inter-molecular chemical bonding, such as urethane linkage.

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