

Modification of 6,6-Type Polyamide Containing Both γ -Lactone Ring and Hydrophilic Groups

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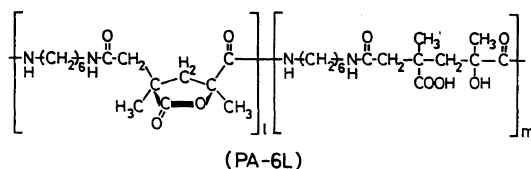
ABSTRACT: The interfacial polycondensation of (2*R**,4*S**)-4-chloroformyl-2-chloroformylmethyl-2,4-dimethyl-4-butanolide (BC) with 1,6-hexanediamine (HDA) gives a unique 6,6-type polyamide (PA-6L) with partial hydrolytic cleavage of the lactone moiety. PA-6L containing at random both γ -lactone ring and hydrophilic groups such as carboxyl and hydroxyl groups was modified by the following three methods: 1) ring-opening of the lactone groups in PA-6L by chemical treatment, 2) incorporation of nylon-66 (PA-66) sequence into PA-6L chain by interfacial copolycondensation, and 3) crosslinking of PA-6L with methylene bis(4-phenylisocyanate) (MDI). The ring-opening ratio of PA-6L increased by treating with either acids or alkalis, whereas $[\eta]$ decreased. In particular, the carboxylato-containing PA-6L prepared by the treatment with potassium hydroxide was highly soluble in water. In the interfacial copolycondensation of acid dichlorides, BC and adipoyl chloride (AC), with HDA, a methanol-soluble copolyamide PA-6L/66 was prepared at an $[AC]/([BC]+[AC])$ mole fraction of *ca.* 0.25. PA-6L crosslinked with MDI had a decomposition point of 303°C and showed a lower thermostability beyond 280°C than the original one.

KEY WORDS Modification / Hydrophilic 6,6-Type Polyamide / Lactone Ring-Opening / Water-Soluble Nylon / Copolycondensation / Crosslinking / Methylene Bis(4-phenylisocyanate) / Thermostability /

In a previous paper,¹ we reported the preparation of bifunctional lactone monomer, namely (2*R**,4*S**)-4-chloroformyl-2-chloroformylmethyl-2,4-dimethyl-4-butanolide (BC) by the chemical transformation of *t*-butyl methacrylate (TBMA) cyclic dimer, obtained from the telomerization of TBMA using bromotrichloromethane as a telogen. The interfacial polycondensation of BC with 1,6-hexanediamine (HDA) was accompanied by a partial hydrolytic cleavage of the γ -lactone ring, and gave unique 6,6-type polyamide (PA-6L) containing both γ -lactone ring and

hydrophilic groups such as carboxyl and hydroxyl groups. PA-6L was highly soluble in methanol, and a transparent and flexible film was prepared from the methanol solution by a casting technique.

In the preceding paper,² we reported the preparation of amphiphilic graft copolymers



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consisting of hydrophilic PA-6L as a backbone and hydrophobic oligostyrene as a branch by coupling between the PA-6L and chloroformyl-semitelechelic oligostyrene.

This paper deals with modification of PA-6L by the following three methods: 1) ring-opening of the lactone groups in PA-6L by chemical treatment, 2) incorporation of nylon-66 (PA-66) sequence into PA-6L chain by interfacial copolycondensation, and 3) crosslinking of PA-6L with methylene bis(4-phenylisocyanate) (MDI). The structure and characterization of modified PA-6L are discussed and compared with those of an untreated sample.

EXPERIMENTAL

Materials

The original PA-6L was prepared by the interfacial polycondensation of BC with HDA as described in the previous paper.¹ Adipoyl chloride (AC) was prepared by the chlorination of adipic acid with thionyl chloride. Commercial MDI was distilled *in vacuo* before use. Commercial *N,N*-dimethylacetamide (DMAc) was dried over calcium hydride and distilled before use. Other reagents and solvents were commercially obtained and used without further purification.

Characterization of Samples

IR spectra were measured with a JASCO IR REPORT-100 spectrophotometer. The ring-opening ratio, $m/(l+m)$, of PA-6L was determined from absorbance (A) on IR spectrum (film): $A_{1700}/(A_{1780} + A_{1700}) \times 100\%$: where, A_{1700} : absorbance at 1700 cm^{-1} , A_{1780} : absorbance at 1780 cm^{-1} . The water content of PA-6L was calculated as follows: $(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100\%$: where, W_{wet} : weight of swollen PA-6L at 95% relative humidity for 24 h, W_{dry} : weight of dry PA-6L. The intrinsic viscosity $[\eta]$ of PA-6L was measured with a Ubbelohde viscometer. The viscosity-average molecular weight (\bar{M}_v) of PA-6L was evaluated

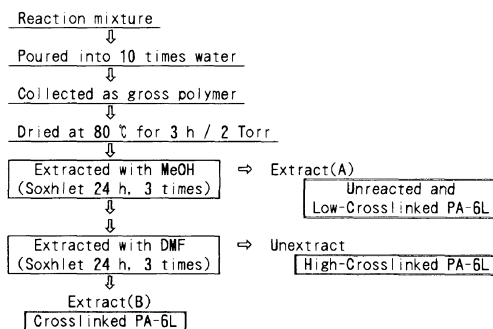
qualitatively by Elias's equation for PA-66.³ DSC curves of polymers were recorded on a SEIKO DSC-220C at a heating rate of $20^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. TG curves of polymers were measured with a SEIKO TG/DTA-220 under the same conditions as measurements of the DSC curves.

Chemical Treatment of PA-6L with Acids and Alkalis

To a solution of PA-6L (0.2 g, 2.13×10^{-2} mmol) in methanol (15 ml), a treatment agent (5 ml) was added at r.t. without stirring, and the mixed solution was immediately evaporated to dryness using a rotary vacuum evaporator. In the case of potassium hydroxide (KOH)-treatment, the residue was passed through a column packed with Sephadex G-10 (size, i.d. 22 mm \times L 120 mm; eluent, H_2O) to remove excess KOH.

Interfacial Copolycondensation⁴

A mixed solution of HDA (3 mmol) and sodium hydroxide (NaOH) (1.5 mmol) in water (20 ml) was poured onto a solution of acid dichlorides BC+AC (3 mmol) in the same volume of carbon tetrachloride. The reaction mixture was vigorously stirred using a homogenizer (1×10^4 rpm) for 5 min. The resulting copolyamide was collected, washed with water, and dried at 60°C under reduced pressure.



Scheme 1. Separation procedure of the crosslinked PA-6L.

Typical Crosslinking of PA-6L⁵

To a solution of PA-6L (0.4 g, 1.74×10^{-2} mmol) in DMAc (10 ml), a solution of MDI (0.13 g, 5.22×10^{-1} mmol) in DMAc (10 ml) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.05 ml) were added, and the reaction mixture was stirred at r.t. for 24 h under a nitrogen atmosphere. After the reaction, the reaction mixture was treated according to Scheme 1.

RESULTS AND DISCUSSION

Chemical Treatment of PA-6L

The original PA-6L was treated with acids and alkalis. The results are summarized in Table I. Chemical treatment of PA-6L was accompanied by increase in the ring-opening ratio and water content. Both values obtained suggest an adequate correlation. On the other hand, $[\eta]$ of PA-6L in methanol decreased by the chemical treatment, except for 0.6% KOH aq. The diminution rate is apt to rise with increase in ring-opening ratio. PA-6L modified by KOH also showed lower $[\eta]$ in formic acid compared with the original one. Besides the hydrolytic cleavage of γ -lactone ring, therefore, the hydrolytic scission of amide linkage in a main chain seems to be caused by chemical treatment.

Typical IR spectra of treated PA-6L samples are illustrated in Figure 1 compared with that of original PA-6L. Common carbonyl

absorptions owing to γ -lactone ring, carboxyl group, and amide linkage appeared at 1780, 1700, 1660, and 1530 cm^{-1} . In the case of KOH-treatment there appeared a new absorp-

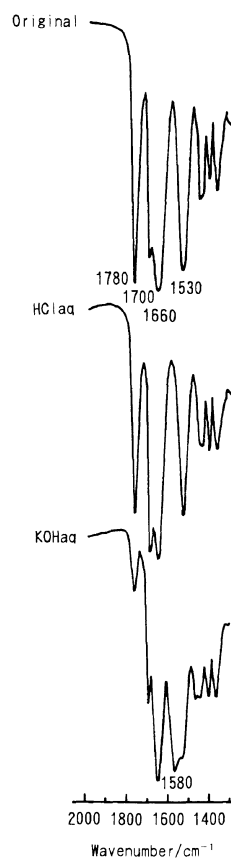


Figure 1. IR spectra of PA-6L modified by chemical treatment.

Table I. Chemical treatment of PA-6L

Treatment agent	Ring-opening ratio	Water content	$[\eta]^a$
		%	dl g^{-1}
Original	0.36	25	0.27 (0.42) ^b
90% HCOOH aq	0.42	37	0.24
37% HCl aq	0.59	43	0.22
28% NH_3 aq	0.61	41	0.20
0.6% KOH aq	0.75	85	0.38 (0.32) ^b

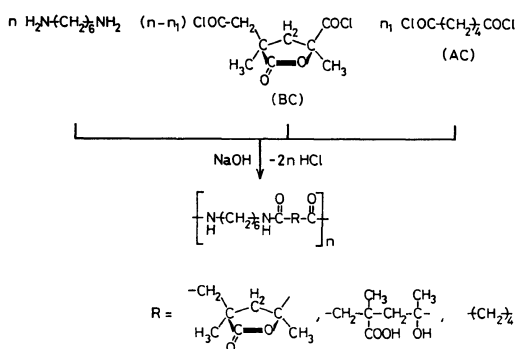
^a Measured in MeOH at 25°C.

^b 90% HCOOH aq was used in the place of MeOH.

tion band at 1580 cm^{-1} due to $-\text{COO}^-\text{K}^+$ formed by the hydrolytic cleavage of γ -lactone ring with KOH. The carboxylato-containing PA-6L was highly soluble in water (25 g dl^{-1} at 60°C). The unusual increase of $[\eta]$ in methanol of KOH-treated PA-6L must be caused by hydration owing to the formation of $-\text{COO}^-\text{K}^+$ group.

Preparation of Copolyamide-6L/66

Copolyamide-6L/66 was prepared by interfacial copolycondensation of acid dichlorides,



Scheme 2. Preparation of copolyamide-6L/66.

BC and AC, with HDA as shown in Scheme 2. As described in the previous paper,¹ the highest value of $[\eta]$ of PA-6L is achieved at $[\text{BC}]:[\text{HDA}]:[\text{NaOH}]=1:1:0.5$, whereas the best yield at a stoichiometric molar ratio, $[\text{BC}]:[\text{HDA}]:[\text{NaOH}]=1:1:2$. Therefore, the effect of mole fraction of $[\text{AC}]/([\text{BC}]+[\text{AC}])$ on yield, $[\eta]$ in formic acid, solubility in methanol, and water content of copolyamide-6L/66 was studied under the optimal conditions for preparation of high molecular weight PA-6L. As illustrated in Figure 2, the yield of copolyamide-6L/66 decreased linearly with increase in the mole fraction of AC, while $[\eta]$ increased linearly. This contrasting behavior indicates that the participation of AC under the unstoichiometric molar ratio, $[\text{acid dichlorides}]:[\text{HDA}]:[\text{NaOH}]=1:1:0.5$ makes a contribution to the preparation of high molecular weight copolyamide-6L/66 at the sacrifice of yield. As illustrated in Figure 3, both the solubility in methanol and water content of copolyamide-6L/66 decreased forming a curve with increase in the mole fraction of AC. The resulting co-

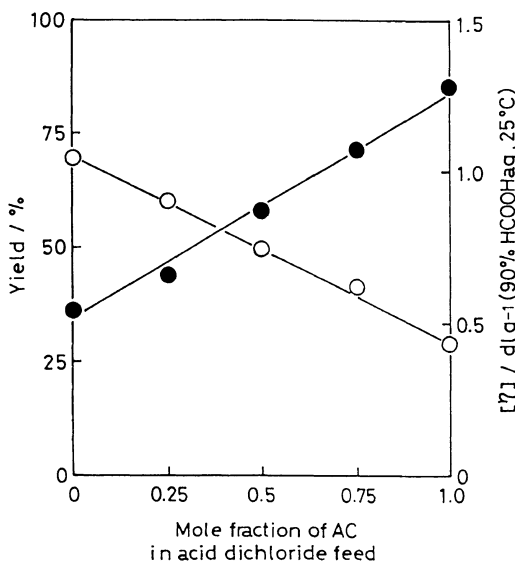


Figure 2. Effect of mole fraction of AC on yield (—○—) and intrinsic viscosity (—●—) of copolyamide-6L/66.

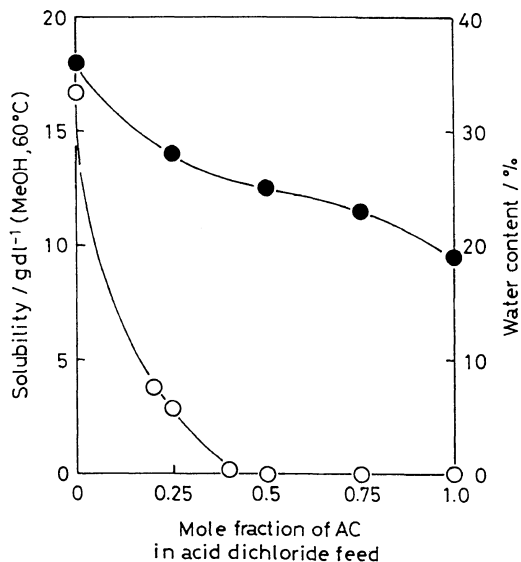


Figure 3. Effect of mole fraction of AC on solubility in MeOH (—○—) and water content (—●—) of copolyamide-6L/66.

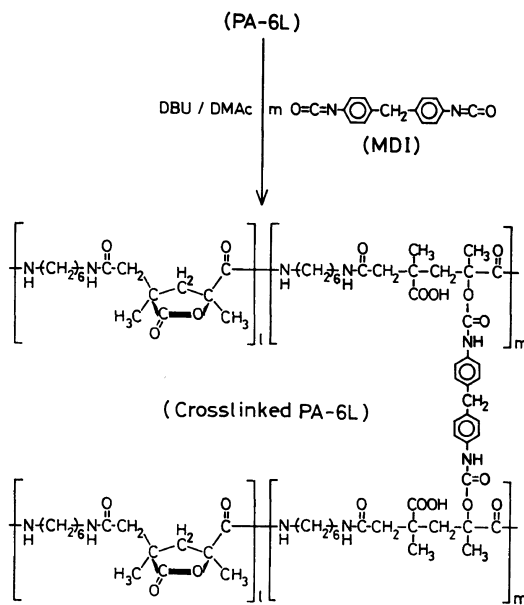
polyamide-6L/66 was no longer soluble in methanol when the mole fraction of AC was beyond 0.4. A methanol-soluble copolyamide-6L/66 was prepared at a mole fraction of AC of *ca.* 0.25.

Synthesis and Characterization of PA-6L Crosslinked with MDI

As shown in Scheme 3, crosslinked PA-6L was prepared by the addition of PA-6L with MDI in the presence of DBU as a catalyst. Table II shows the conditions for the synthesis of crosslinked PA-6L. After the reaction, the crosslinked PA-6L was separated according to the procedure shown in Scheme 1. The results of the fractionation of crosslinked PA-6L are shown in Table III. The compositions of extracts (A), (B) and unextract are supported by the comparisons of those IR and ^1H NMR spectra. The crosslinked PA-6L fractionated as extract (B) is a sample for the following spectroscopic and thermal analyses.

The IR spectrum of PA-6L (CPA-2) crosslinked with MDI is illustrated in Figure 4, and compared with those of original PA-6L and MDI. In addition to the carbonyl absorptions

owing to γ -lactone ring (1780), carboxyl group (1700), and amide linkage (1650 and 1540 cm^{-1}), there appeared new absorption peaks marked (\blacktriangle) in Figure 4 at 3320, 1700, 1600, and 1520 cm^{-1} . These absorption



Scheme 3. Preparation of crosslinked PA-6L.

Table II. Crosslinking conditions of PA-6L

Sample code	PA-6L			[MDI]	DBU	DMAc
	$\bar{M}_v \times 10^{-3}$	-OH ^a	g (mmol $\times 10^2$)	[PA-6L]	ml	ml
CPA-1	3.9	7	0.35 (9)	7	0.05	20
CPA-2	7.0	8	1.50 (21)	8	0.15	75
CPA-3	23.0	30	0.40 (2)	30	0.05	20

^a Average number of OH group: average degree of polymerization \times ring-opening ratio.

Table III. Fractionation of crosslinked PA-6L

Sample code	Yield ^a	wt%		
	g	Extract(A)	Extract(B)	Unextract
CPA-1	0.34	37	57	6
CPA-2	1.19	58	37	5
CPA-3	0.39	28	62	10

^a Weight of gross polymer.

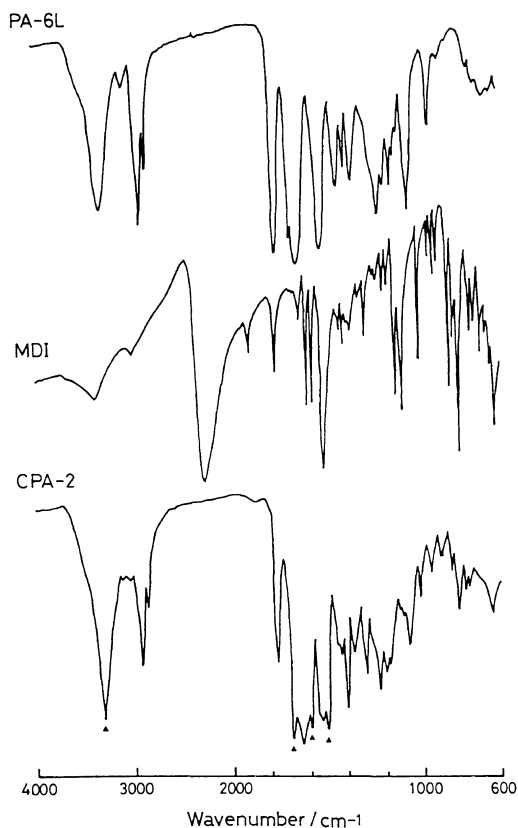


Figure 4. IR spectra of MDI and original crosslinked PA-6Ls.

peaks correspond to the urethane linkage and aromatic ring incorporated by the crosslinking of PA-6L with MDI. Furthermore, the crosslinking of PA-6L seems to be accompanied by a secondary cleavage of the γ -lactone ring because the carbonyl absorption owing to γ -lactone ring (1780) is weakening relative to those owing to amide linkage (1650 and 1540 cm^{-1}). Elemental analysis of CPA-2 indicated that one molecular unit of PA-6L backbone is crosslinked efficiently by more than eight molecular units of MDI (Found: C, 64.87%; H, 6.92%; N, 10.23%. Calcd as eight degrees of crosslinking: C, 61.32%; H, 7.35%; N, 9.53%). On the reactivity of MDI, it has been reported that the reactivity of the residual isocyanato group falls to one-third after the reaction of one of two isocyanato

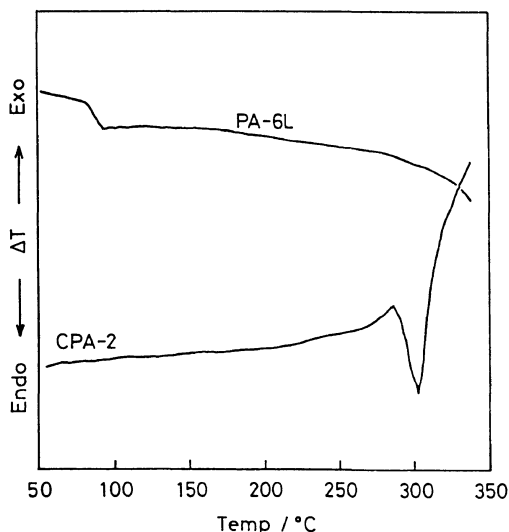


Figure 5. DSC curves of original and crosslinked PA-6Ls.

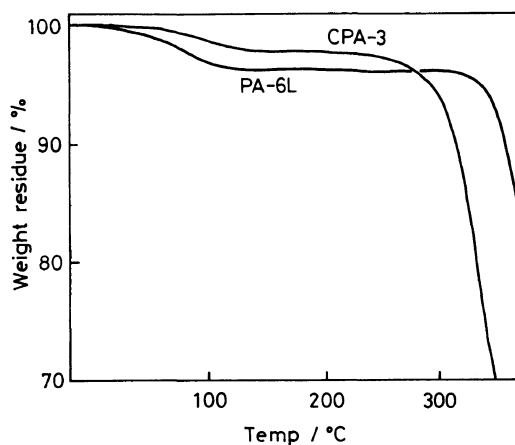


Figure 6. TG curves of original and crosslinked PA-6Ls.

groups.⁶ Therefore, taking into account the discrepancy from the calculated value, it does not necessarily follow that two isocyanato groups of MDI react perfectly with PA-6L. The PA-6L crosslinked with MDI results in a lowering of hydrophilicity (water content, 16%), and is characterized by the property of not dissolving in methanol, which is a good solvent for the original PA-6L.

Figure 5 shows the DSC curves of original

and crosslinked (CPA-2) PA-6L samples. A glass transition temperature (T_g) is clearly observed at 88°C for the original PA-6L. On the other hand, the CPA-2 sample has a sharp endothermic peak at 303°C instead of no T_g . This point corresponds to the decomposition of crosslinked PA-6L. Figure 6 shows the TG curves of the original and crosslinked (CPA-3) PA-6L samples. The weight loss of both samples at temperature near 100°C is presumed due to loss of absorbed water. As the original PA-6L is very hydrophilic, the weight loss of it is larger than that of the crosslinked one. However, the crosslinked PA-6L is accompanied by a precipitous loss of weight when the heating temperature rises to more than 280°C. Therefore, the thermostability of crosslinked PA-6L is unexpectedly inferior to that of the original one at temperature beyond 280°C.

CONCLUSION

The results on modification of PA-6L may be summarized as follows.

- 1) Adjustment of the ring-opening ratio of PA-6L is possible to a certain extent by treating with either acids or alkalis. However, PA-6L is subject to hydrolytic scission of the amide linkage through this treatment. The water-soluble polyamide can be prepared by treatment with KOH because of a stable $-\text{COO}^- \text{K}^+$ group.
- 2) Under optimal conditions for the preparation of high molecular weight PA-6L, the interfacial copolycondensation of acid dichlorides, BC and AC, with HDA gives a methanol-soluble copolyamide-6L/66 at a mole fraction of AC of *ca.* 0.25.
- 3) The weight loss of crosslinked PA-6L proceeds rapidly over 280°C, and is unexpectedly inferior to the original one in thermostability.

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