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Polymer 41 (2000) 473–480

polymer

Synthesis of copolymers of poly(amino acid)–urethane in *N*,*N*-dimethylformamide

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Received 13 November 1998; received in revised form 1 March 1999; accepted 9 March 1999

Abstract

The copolymers of poly(amino acid)–urethane (PAU) with multiblock–triblock structures have been synthesized in *N*,*N*-dimethylformamide (DMF). The use of triethylamine as an initiator of polymerizing NCA to both terminals of the PAU intermediate having urethane segments and a small amount of PMLG caused gelatinization, while the use of hydrazine gave a fluid solution with a whitish turbidity. Infrared (IR) spectra of the PAU in DMF demonstrated that the PMLG segments in the PAU obtained from TEA had an α-helix structure and PAU from hydrazine had a β-structure in addition to the α-helix structure. The X-ray diffraction pattern showed that the α-helix chains of the PMLG segments in the PAU obtained from hydrazine were oriented. Compared with the PMLG homopolymer, the elastic recovery and adhesion of the PAU significantly increased with a maintenance of a good sense of touch which is a unique quality of PMLG. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Copolymers of poly(amino acid)–urethane; *N*,*N*-dimethylformamide; Hydrazine

1. Introduction

Poly(γ-methyl-L-glutamate) (PMLG) [one kind of a poly(amino acid)] has been studied for use as fibers [1–15]. Also the use of PMLG as a synthetic leather has also been investigated [16–22]. In practice, the synthetic leather produced using PMLG having a similar primary chain structure to that of natural leather, looks and feels almost like natural leather, and high moisture permeability can be attained. However, a coating using only PMLG has a short lifetime because of its low elastic recovery and adhesion. It is thought that the low elastic recovery is caused by the phase transition of the PMLG from the α-helix structure to the β-structure induced by a slight elongation [23] and that the low adhesion can be attributed to the regular intramolecular hydrogen bonding along the α-helix structure. Recently, we reported that the poly(amino acid)–urethane copolymers (PAU) are prepared in 1,2-dichloroethane (EDC) and have significantly better physical properties such as elastic recovery and adhesion than the poly(γ-methyl-L-glutamate) (PMLG) homopolymer [24]. Furthermore, when the PAU is synthesized using triethylamine (TEA) as the initiator of the second stage reaction in the same manner as the PAU [24] using 1,2-dichloroethane solvent in *N*,*N*-dimethylformamide (DMF), (which is more extensively used as a solvent) then the PAU solution is transparently gelatinized. In contrast, the PAU synthesized using a hydrazine initiator produces a fluid solution with a white turbidity. Here we describe the characterization and physical properties of the PAU in DMF and the effects of initiators on the structure of the PAU.

2. Experimental

2.1. Materials

γ-Methyl-L-glutamate-*N*-carboxyanhydride (γ-MLG·NCA) with a ring-closure above 98% [25] and a Cl content below 0.03% was purchased from the Ajinomoto Co., Inc., Japan. Poly(tetramethylene ether)glycol [PTMG1000 (OH value = 114) [26]], which was made by the Mitsubishi Chemical Corp., Japan, was used. 4,4′-Diphenylmethane diisocyanate (MDI) (Mitsubishi Chemical Dow Co.) was purified as follows. The melted MDI was filtered using a pressure filtration funnel at 60°C, and then recrystallized from hexane in an ice-bath. Anhydrous hydrazine, (Nihon Suiyaku Co., Japan), triethylamine and *n*-butylamine, (Tokyokasei Co., Japan), were used. 1,2-Dichloroethane

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PII: S0032-3861(99)00191-3

(Sentoraru Glass Co., Japan) was purified by distillation just before use. The volume of water in the distilled 1,2-dichloroethane (EDC) was 0.02 wt.%. *N*,*N*-dimethylformamide (DMF, Nitto Chemical Co., Japan) was purified by distillation under reduced pressure after being dehydrated by molecular sieves. The water content was 0.02 wt.%. The water volume was measured by Karl Fischer's method using MCI moisture meter CA-03 (Mitsubishi Chemical Corp.).

2.2. Synthesis of urethane prepolymer (UPP)

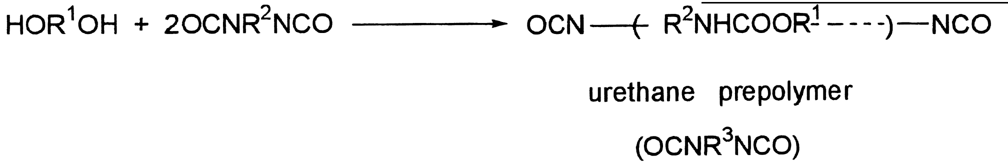
A urethane prepolymer (UPP) was prepared by the reaction of MDI and PTMG 1000 (2:1 mol/mol) according to the literature [reaction (1)] [24].

2.3. Synthesis of poly(amino acid)–urethane copolymer (PAU)

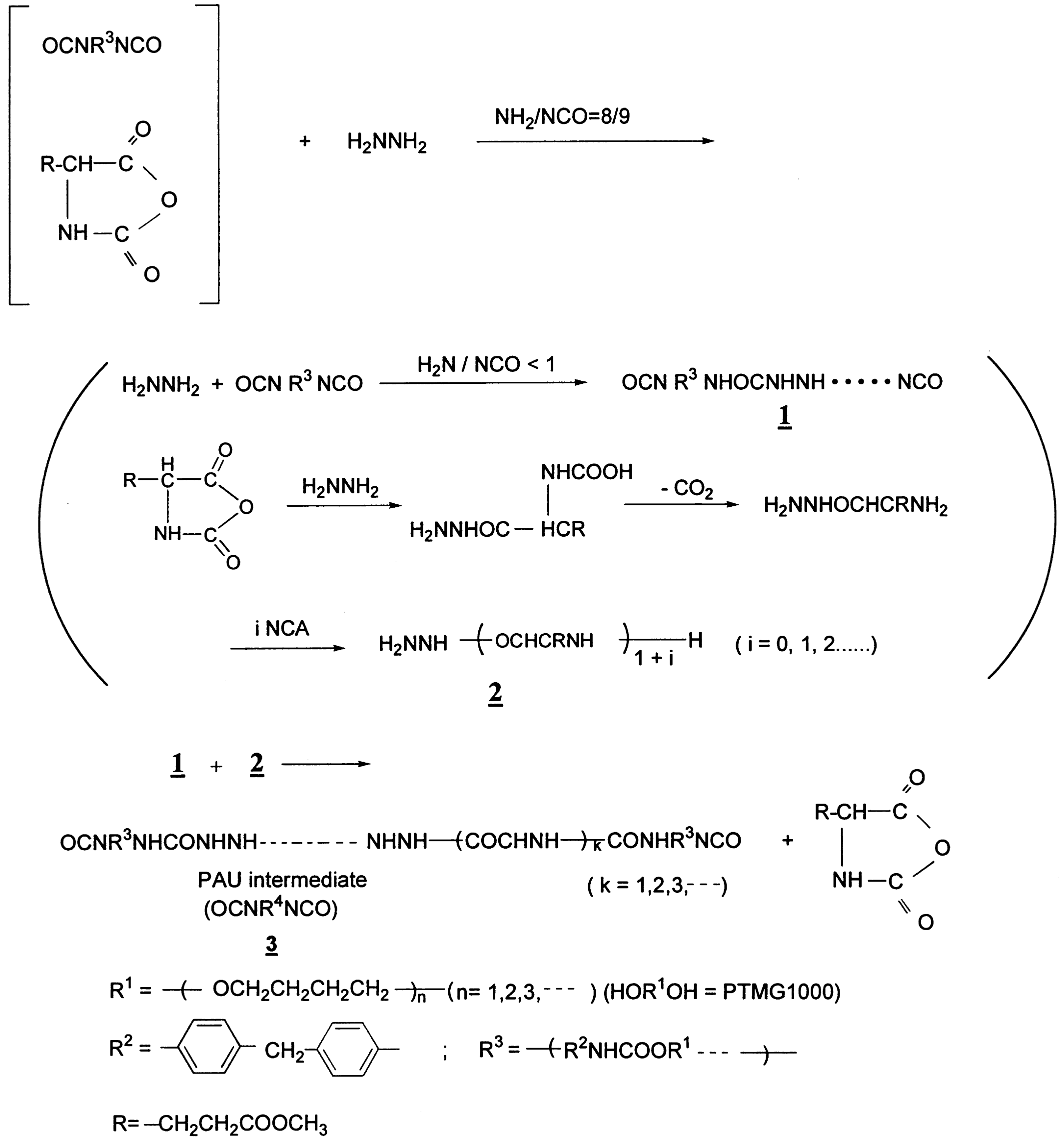
The poly(amino acid)–urethane copolymer (PAU) was synthesized by utilizing the chemical reactivities of the isocyanate groups and the mechanism of γ-MLG·NCA polymerization using primary amine initiator in DMF through two-stage processes expressed by reactions (2)[24] and (3).

2.3.1. First stage reaction

PAU intermediate with isocyanate groups at both terminals of chain was prepared by the previously described method [24][reaction (2)].



$$HOR^1OH + 2OCNR^2NCO \longrightarrow \underbrace{OCN{-}(R^2NHCOOR^1{-}{-}{-}{-}){-}NCO}_{\substack{\text{urethane prepolymer}\\(OCNR^3NCO)}} \qquad (1)$$



(2)

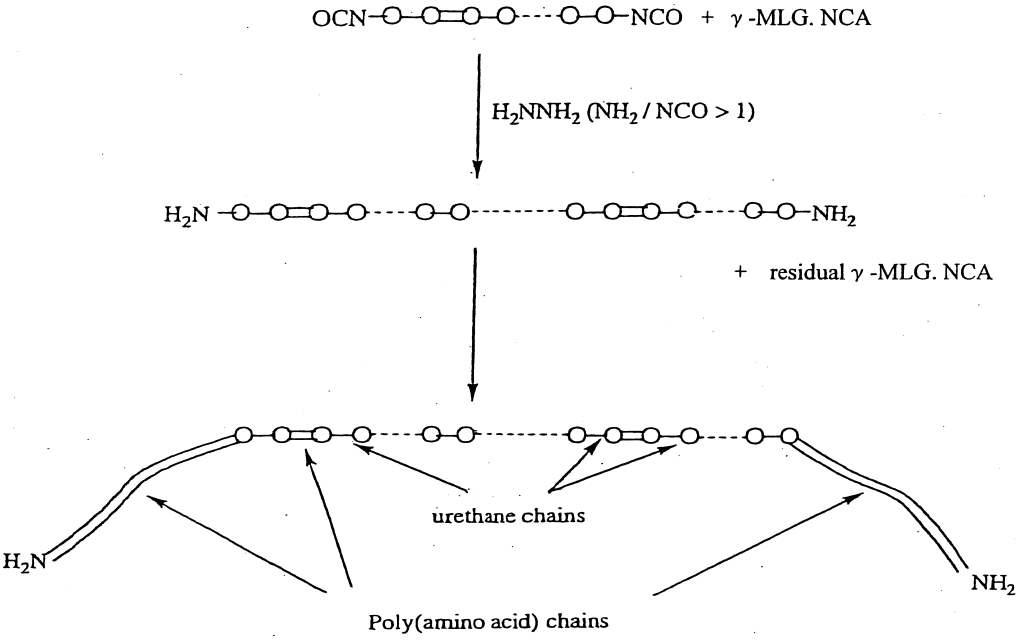


Fig. 1. Illustration of Eq. (3) process.

2.3.2. Second stage reaction

To the PAU intermediate solution, anhydrous hydrazine, [NCO of PAU intermediate: NH_2 of hydrazine = 9:10 (equivalent ratio)]was added as the initiator (triethylamine used as initiator in the literature [24] was replaced by anhydrous hydrazine). Hydrazine reacts with both γ-MLG·NCA and isocyanate groups of PAU intermediate. PAU intermediate is momentarily chain-extended by hydrazine and a small amount of total γ-MLG·NCA oligomers polymerized by hydrazine, resulting in a chain-extended PAU intermediate having NH_2 groups of both the terminals (NH_2–PAU intermediate) because the amino group equivalent of hydrazine is larger than the isocyanate groups of PAU intermediate. The residual γ-MLG·NCA (about 95% of the total γ-MLG·NCA) homogeneously polymerizes to both the terminals NH_2 groups of NH_2–PAU intermediates, resulting in PAU expressed by reaction (3).

Fig. 1 illustrates the polymerization mechanism expressed by reaction (3).

The fractionation of product PAU was carried out by the procedure, in which mixture of products was added, stirred and centrifuged in a solvent [DMF: methylethylketone = 1:1 (wt/wt)] for a urethane component (UPP and urethane chain-extending UPP using anhydrous hydrazine) and γ-MLG·NCA.

2.4. Measurements

2.4.1. Stress–strain test

Stress–strain test of PAU film was carried out using a Tensilon (Toyoseiki Seisakusho Co., Japan) with a tensile speed of 50 mm/min according to the literature [24].

Table 1
Analytical results of UPP, PAU intermediate and various PAUs (UPP:NCA = 40:60 (wt))

						Fractionated PAU			
	NCO	$Mn/10^3$	η_{sp}/c[a]	β-structure[b]	State	Yield	η_{sp}/c	β-structure	UPP (%)[c]
UPP	785	1.57	–	–	–	–	–	–	–
PAU Intermediate	9100	18.2	–	–	Sol	–	–	–	–
PAU (DMF)									
Hydrazine	–	–	0.91	Detected	Turbid sol	45	1.23	Detected	67
TEA	–	–	0.90	Not detected	Gelatinization	–	–	–	–
PAU (EDC)[d]									
TEA	–	–	1.19	Not detected	Sol	55	1.24	Not detected	90

[a] Reduced viscosity at 25°C of 0.5% solution in dichloroacetic acid.

[b] Determined from FTIR difference spectra.

[c] Copolymerization deg. of UPP calculated from ^{13}C-NMR spectrum.

[d] Prepared using TEA initiator in 1,2-dichloroethane (EDC) [23].

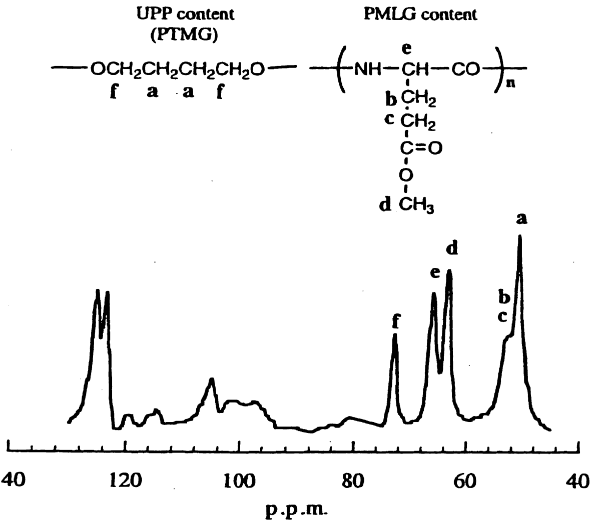


Fig. 2. ^{13}C-NMR spectrum of fractionated PAU.

2.4.2. Adhesion strength

The resin surface of the two sheets of cloth onto which the polyester–urethane resin was coated were adhered with a mixed solution of DMF containing 10 wt.% PAU and then treated by a previously described method [24].

Adhesion strength was determined by measuring the peel strength of the two sheets of cloth.

2.4.3. Moisture permeability

Moisture permeability was measured at 40°C in 90% relative humidity by the L-1099A-1 method. Samples for these measurements were prepared according to the literature [24].

2.4.4. Other measurements

The reduced viscosity, η_{sp}/c, of a dichloroacetic acid solution containing 0.5 wt.% PAU was measured at 25°C using an Ubbelhode type 1B Ostwald viscometer (Kusano Science Instrument Co., Japan). ^{13}C-NMR measurements were carried out using a FX-200 (200 MHz) (Nihon Electron Co., Japan). Infrared (IR) spectra were measured using a FT/IR-230 (Nihon Spectroscopy Co., Japan). X-ray diffraction measurements were carried out using Philips PW 1700 with CuKα ($= 1.5405$ Å) equipment.

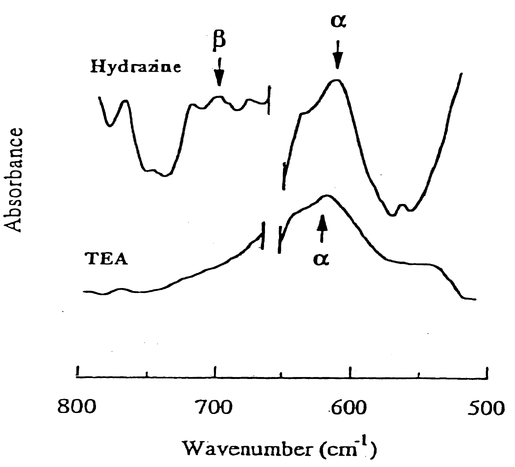


Fig. 3. FTIR difference spectra of PAUs prepared using hydrazine and triethylamine (TEA) in DMF.

2.5. Analyses

NCO equivalents of the UPP and PAU intermediate, and γ-MLG·NCA conversion in the PAU intermediate were determined by a previously described method [24].

3. Results and discussion

The analytical data of UPP, the PAU intermediate, PAUs obtained in DMF using TEA and hydrazine initiators, and PAU obtained in 1,2-dichloroethane using TEA are summarized in Table 1.

3.1. Synthesis of UPP

The infrared spectrum of the UPP showed a strong absorption band at 2250 cm^{-1} due to the two isocyanate groups. The NCO equivalent (785) of the UPP obtained was larger than the theoretical value of 750. This is attributed to the fact that the primary amine formed by the reaction between a small amount of water and the isocyanate group reacts with the isocyanate groups.

3.2. Synthesis of PAU

The PAU intermediate is obtained by the reaction expressed by reaction (2). The reaction proceeds through two-step processes: two prepolymers, which are obtained from the reactions between UPP and hydrazine as well as between and γ-MLG·NCA and hydrazine, are produced during the first stage, and then these prepolymers react with each other in second stage, leading to the production of the PAU intermediate. The PAU intermediate has the NCO equivalent of 9100 and the average molecular weight of 1.82×10^4. Although the theoretical number average molecular weight of the PAU is 1.52×10^4 because only five percent of the γ-MLG·NCA reacts, the observed number average molecular weight (1.82×10^4) is larger than the theoretical value.

This would be attributed to the fact that the theoretical NCO equivalent becomes small because the isocyanate group reacts with any trace of water in the reaction system.

The PAU is synthesized according to reaction (3). As the hydrazine initiator is added to the PAU intermediate solution under the condition of NH_2/NCO (equivalent ratio) = 10/9, the PAU intermediate momentarily reacts with the initiators and a small amount of γ-MLG·NCA oligomers forms, leading to the PAU intermediate having NH_2 groups in both the terminals (Fig. 1). The residual γ-MLG·NCA polymerize with NH_2 groups at both terminals

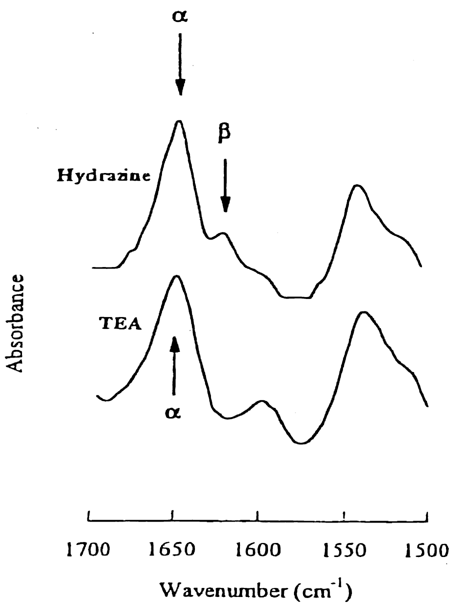


Fig. 4. FTIR spectrum of PAU membrane prepared using hydrazine and triethylamine (TEA) initiator in DMF.

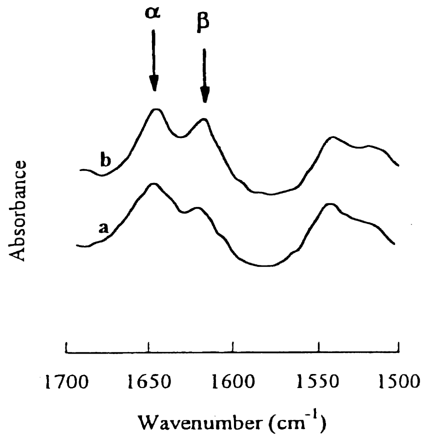


Fig. 5. FTIR spectra of PMLG homopolymer membranes using hydrazine initiator: (a) γ-MLG·NCA/Hydrazine = 142/1 (mol/mol); (b) γ-MLG·NCA/Hydrazine = 142/3 (mol/mol).

of the PAU intermediate according to the primary amine mechanism [28–34], leading to the production of PAU having NH_2 groups in the both terminals (Fig. 1). The resulting PAU is a white turbid solution having fluidity. The ^{13}C-NMR spectra of fractionated PAU show that the chemical shifts of carbons with an ether bond and methylene bond in the UPP appeared at 72.3 and 27.8 ppm, respectively (Fig. 2). In addition, the chemical shifts due to the PMLG segment are also observed. Furthermore, the IR spectra show an absorption band at 1110 cm^{-1} arising from the ether bond of poly(tetramethylene ether) glycol (PTMG1000) in the UPP segment. These results indicate that the PAU is the copolymer of poly(amino acid) and polyurethane. The fractionated PAU is obtained with a yield of 45%. The copolymerization degree is calculated from the ratio of the ^{13}C-NMR spectrum areas of the UPP part in the PAU before and after the fractionated treatment and is ca. 67%. It is thought that the reason why yield and the copolymerization degree is relatively small is because the urethane-rich copolymer is probably soluble in fractionating solvent. For the PAU obtained using the hydrazine initiator, the FTIR difference spectrum in DMF show absorption bands at 620 and 700 cm^{-1} due to the α-helix and β-structures [27], respectively (Fig. 3). The IR spectrum of the PAU membrane also shows absorption bands at around 1657 and 1625 cm^{-1} arising from α-helix and β-structures [27], respectively (Fig. 4). This is same as in the case of PMLG homopolymer using hydrazine initiator (Fig. 5). In contrast, the gelatinous PAU obtained using the TEA shows only an IR absorption band at 620 cm^{-1} due to the α-helix structure and does not show the absorption band at the 700 cm^{-1}. The gelatinous PAU is soluble in dichloroacetic acid. Therefore, this gelatinization is not caused by chemical cross-linking. The IR spectrum of the gelatinous PAU membrane shows only an absorption band at around 1657 cm^{-1} due to the α-helix structure and does not show the absorption band at around 1625 cm^{-1} (Fig. 4). This IR spectrum is the same as that of the PAU in the literature [24] in which PAU is synthesized using TEA initiator in 1,2-dichloroethane. Also the fluid PAU of the literature [24] gets gelatinized, when it is added in DMF and 1,2-dichloroethane is then vaporized in vacuum. Namely replacing the solvent 1,2-dichloroethane with DMF converts the fluid PAU into gelatinous PAU. These facts may indicate that the gelatinous PAU obtained using TEA initiator in DMF is the copolymer, which has the same structure as fluid PAU [24] prepared using TEA initiator in 1,2-dichloroethane. Furthermore, for the PAU solution obtained using the hydrazine initiator, the X-ray diffraction diagram showed a somewhat dilated peak at $2\theta = 8°$, indicating that the α-helix parts in the PMLG segments in the PAU solution have a certain orientation (Fig. 6). Presumably, such an orientation is induced by aggregation of the α-helix parts. Therefore, the PMLG chains in this PAU solution using the hydrazine initiator have both the α-helix parts with orientation and β-structure parts. In contrast, a PAU solution obtained using the TEA initiator does not show the dilated peak at $2\theta = 8°$ in the X-ray diffraction diagram. The PMLG chains in this PAU solution have the α-helix structure without orientation, but not the β-structure. Based on these facts, we postulate the structures of these PAUs in DMF as shown in Fig. 7. The PMLG α-helix segments in the TEA initiating PAU partially undergo partial association at random in DMF, forming a network structure due to the partial cross-linking. Consequently, the PAU solution is gelatinized. In contrast, the hydrazine initiating PAU has the β-sheet structure. The formation of such a β-sheet structure accelerates the crystallization of the α-helix parts in the PMLG segment because the α-helix part has a close-neighboring β-structure. Furthermore, the partial crystallization of the α-helix parts would be insoluble in DMF while other

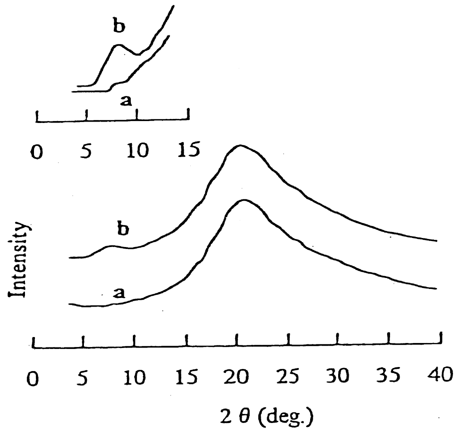
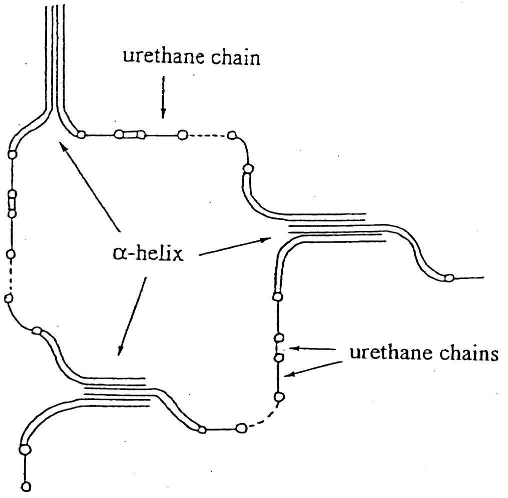


Fig. 6. X-ray diffraction diagrams of PAUs prepared using (a) TEA and (b) hydrazine initiators.

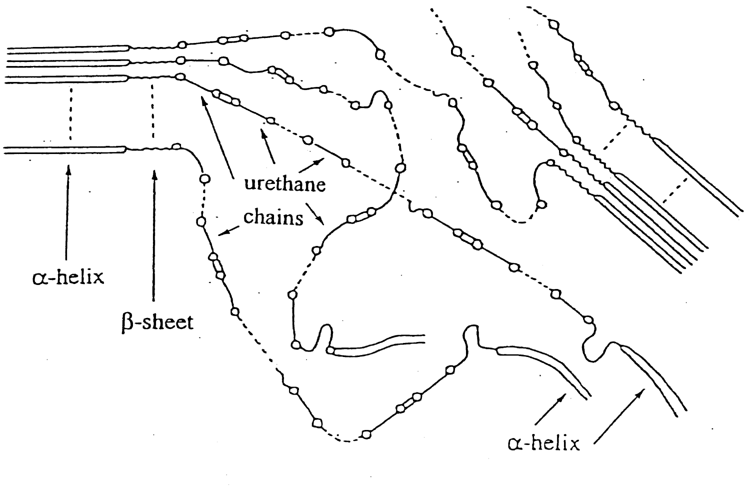
non-crystalline parts would be soluble. Therefore, the PAU in DMF is fluid solution with white turbidity.

3.3. Evaluation of physical properties of PAU resin

The physical properties of (solution and film of) PAU (DMFh) (PAU prepared using hydrazine initiator in DMF), PAU (EDCt) (PAU prepared using TEA initiator in 1,2-dichloroethane) and PMLG prepared using TEA initiator in 1,2-dichloroethane are summarized in Table 2. Here, the solution viscosity is measured using a rotational viscometer (E type). The viscosity of the PAU (DMFh) solution is larger than that of the PAU (EDCt), although the reduced viscosity of the PAU (EDCt) is larger than PAU (DMFh). This could be explained by the thixotropy property of PAU (DMFh). However, the tensile strength and



Transparent gelatinous PAU (TEA initiating)



Fluid solution with turbidity (Hydrazine initiating)

Fig. 7. Tentative Illustration of PAU structures in DMF.

Table 2
Physical properties of PAUs prepared in DMF and 1,2-dichloroethane and PMLG

	Solution property		Tensile properties of films				Adhesion
	Viscosity Cp[a]	Conc. wt.%	Elastic recovery %	M_{10}[b] kg/cm^2	Tb[c] kg/cm^2	Eb[d] %	kg/cm
PAU (DMFh)[e]	25 000	20	63	85	420	450	6.5
PAU (EDCt)[f]	3500	15	61	92	410	452	5.9
PMLG[g]	28 000	10	28	292	327	40	0.7

[a] Centipoise.
[b] Modulus of elasticity at 10% elongation.
[c] Tensile strength.
[d] Elongation at breaking.
[e] Prepared using hydrazine initiator in DMF.
[f] Prepared using triethylamine initiator in 1,2-dichloroethane.
[g] Prepared using triethylamine initiator in 1,2-dichloroethane (η_{sp}/c, 3.59).

elongation at breaking of the PAU (DMFh) film are almost similar to those of the PAU (EDCt) film, and the elastic recovery and adhesion are nearly equal. Furthermore, the PAU (DMFh) film has nearly the same sense of touch and moisture permeability as the PAU (EDCt) film (Table 3). These results indicate that the PAU prepared in DMF has almost the same physical properties of the PAU prepared in 1,2-dichloroethane, and has significantly better physical properties than PMLG.

4. Conclusions

We demonstrated the synthesis of a copolymer of poly-(amino acid) and urethane in DMF. The PAU (DMFt) (PAU prepared using the TEA initiator) is gelatinized in DMF, and when prepared using hydrazine initiator, it is a fluid solution with white turbidity. Such a phenomena can be explained by the difference in the stereo-structures between these PAUs; the PAU (DMFt) using the TEA initiator has an α-helix structure in the PMLG segment and the PAU (DMFh) using the hydrazine initiator has a β-structure in addition to the α-helix structure. The gelatinization is caused by the formation of a network structure induced by the physical cross-linked effect arising from the partial association of the α-helix chain in the PMLG segment. In contrast, in the PAU (DMFh) using the hydrazine initiator, the β-sheet structure is formed by aggregation of the β-structures segment with a concomitant orientation of the α-helix parts, which inhibits gelatinization and accelerates crystallization of the α-helix parts.

Table 3
The touch sense and moisture permeability of PAU (DMF)

	Touch sense	Moisture permeability (g/m^2 24 h) [Film thickness (μ m)]
PAU (DMF)	Dry	5700(7)
PAU (EDC)	Dry	5620(6)
PMLG	Dry	5290(6)

The physical properties of the PAU (DMFh) (PAU prepared using hydrazine initiator in DMF) are almost similar to those of a PAU (EDCt) (PAU prepared using TEA initiator in 1,2-dichloroethane). Also the PAU (DMFh) has nearly same sense of touch and moisture permeability as the PAU (EDCt); the elastic recovery and adhesion of the PAU (DMFh) are significantly larger than those of the PMLG with the maintenance of a good sense of touch which was a unique property of PMLG. When used as a top coat resin of synthetic leather, PAU gives a touch of dryness, none of tackiness and has good hand compared with urethane resin which is more conventionally used for a top coating material. These results indicate that the PAU can be synthesized by a choice of suitable initiators in DMF.

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