Synthesis and Characterization of Copoly(amide-imide) Derivatives and Ultrafiltration Membrane Performances I
- Preparation of Copoly(amide-imide)s by One-step Method -

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Abstract : The diamide-diamine having carboxylic acid was prepared by direct condensation of 1,2,4-benzenetricarboxylic acid with bis[4-(3-aminophenoxy) phenyl]sulfone and bis(4-aminophenyl)-1,4-diisopropylbenzene in medium consisting of triphenylphosphite, LiCl, and N-methyl-2-pyrrolidone. Copoly (amide-imide) derivatives with high molecular weight could be synthesized by one-step polycondensation of prepared diamide-diamine having carboxylic acid and various dianhydride compounds. Depending on the chemical structure and composition of polymer backbones, the viscosities of polymers were found to range between 0.87~1.57 dL/g. All the polymers showed good thermal stability up to 320°C and the 10% weight loss temperature was observed in the range of 450~540°C in a thermogravimetric traces. The glass transition was recorded in the temperature range of 200~270°C. All the polymers showed an amorphous nature on a differential scanning calorimetric thermograms. These polymers generally had good mechanical properties and readily soluble in various polar solvents. Further, it was proved that their properties could be determined from the compositions

Keywords : *carboxylic acid, copoly(amide-imide), one-step polymerization*

Introduction

Polyimide derivatives have been important thermally stable and high-performance polymers, but their uses are limited because of their high melting temperatures and insolubility in common organic solvents [1-4]. To overcome these limitations for the versatile applications, copolyimides have been synthesized [5-10]. Among these copolymers, soluble copoly(amide-imide) derivatives with large molecular weights have been synthesized for sufficient applications. They were one of the important classes of materials having excel-

lent thermal and high-temperature mechanical properties and favorable balance of physical and chemical properties. In previous investigation[11], the poly(amide-imide) derivatives had been synthesized by the direct polycondensation of 1,2,4-benzenetricarboxylic acid and various diamines in the presence of metal salts and phosphorous compounds in NMP. The use of phosphorous compounds and metal salts has been investigated for the synthesis of high molecular weight polyamides directly from a dicarboxylic acid compound and a diamine one [12-14].

In this study, diamide-diamine having carboxylic acid was prepared through direct condensation of 1,2,4-benzenetricarboxylic acid with bis[4-(3-aminophenoxy) phenyl]sulfone and bis(4-aminophenyl)

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-1,4-diisopropylbenzene in the presence of LiCl and triphenylphosphite in NMP. Then copoly (amide-imide) derivatives were synthesized by one-step polymerization of prepared diamide-diamine having carboxylic acid and various dianhydride compounds. The main objective of this investigation was to relate characteristics of obtained copoly(amide-imide)s to their chemical structures and to compare with those of the corresponding copoly(amide-imide)s.

Experimental

Reagents

1,2,4-Benzenetricarboxylic acid (BTA, Aldrich Chemical Co.) was recrystallized from acetic acid before use. Bis[4-(3-aminophenoxy)phenyl]sulfone (BAPS, Wakayama Seika Kogyo Co.) and bis(4-aminophenyl)-1,4-diisopropylbenzene (BADB, Tokyo Kasei Co.) were purified by the recrystallization in ethanol. Pyromellitic dianhydride (PMDA), 3,3′, 4,4′-benzophenone tetracarboxylic dianhydride (BTDA), and 1,2,3,4-butanetetracarboxylic dianhydride (BTCA) were obtained from Aldrich Chemical Co. They were recrystallized from 4-methyl-2-pentanone followed by vacuum drying before use. N-Methyl-2-pyrrolidone (NMP) was dried by using CaH_2 and distilled before use. LiCl was recrystallized from methanol followed by vacuum drying and stored in a vacuum oven. Other laboratory-grade reagents were used without further purification.

Measurement

The viscosity was measured on 0.5 g/dL NMP solution at 25°C in an automated Ubbelohde viscometer. The analysis of gel permeation chromatography (GPC) was carried out by using a Waters Model 150 C equipped with microstyragel columns (porosity 10-10Å, solvent: DMF). The thermal properties were investigated by using a differential scanning calorimetry (DSC, Du Pont 2010) and a thermogravimetric analysis (TGA, Du Pont 2050). All samples were tested at a heating rate of
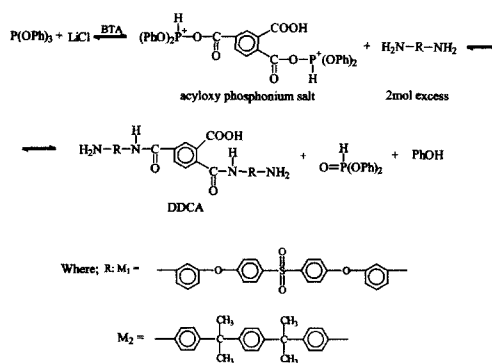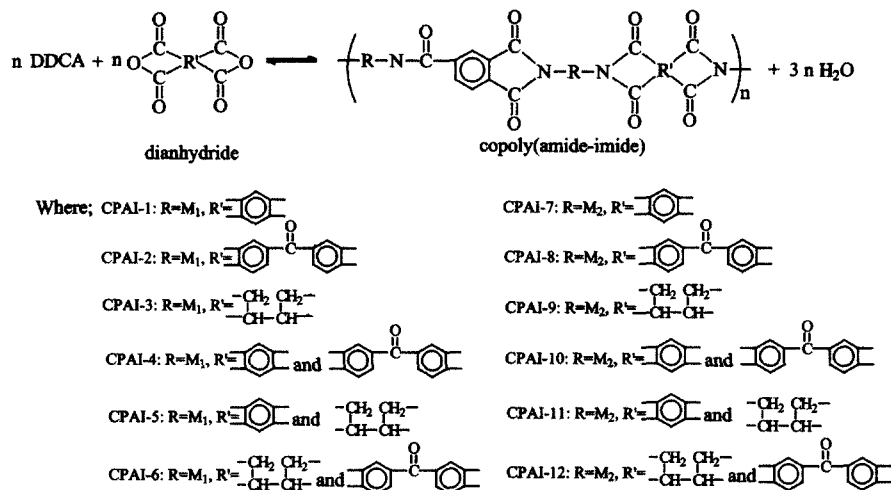

Scheme 1.

10°C/min. Second-run curve of TGA was considered after the first-run up to 300°C to eliminate rests of materials. The mechanical properties were measured at room temperature using a tensile strength testing machine (Testrometric M350, England). The test was used on the film specimens with 150 μm thickness, 10 mm width, and 5 mm length. IR spectrum was recorded in a film using a Perkin-Elmer PARAGON 500 FT-IR Spectrometer. Elemental analysis was carried out using a Perkin-Elmer 2400 elemental analyzer. To determine the solubility, the polymer film was immersed in the solvent and allowed with shaking at room temperature for 12 h.

Preparation of Diamide-diamine with Carboxylic Acid

Diamide-diamine having carboxylic acid (DDCA) was synthesized from BTA with BAPS and BADB as follows (scheme1); A four-neck round flask equipped with a seal Teflon stirrer, nitrogen gas inlet tube, reflux condenser, and thermometer, was charged with 2 wt% LiCl, equimol triphenylphosphite (TPP) referring to BTA, and NMP under flowing nitrogen. After the mixture had been stirred at a 100°C for 1 h, BTA was added into the mixture. When the solution was clear, 2 mol excess amount of a diamine that was dissolved in NMP was slowly added, and the reaction mixture was

Scheme 2.

kept at the temperature for 4 h with a stirred under flowing nitrogen. The solid content was 20%(w/w) in NMP. If the reaction was complete, the mixture was poured into hot water in which the DDCA was deposited and removed LiCl. The precipitate was separated by filtration, washed several times with hot water and cold ethanol to free of LiCl and residual TPP, and then vacuum dried at 90°C for 12 h. The pale yellow product was obtained. Elen. Anal., calc. for $C_{57}H_{42}N_4O_{12}S_2$ (M_1): C, 65.91%; H, 4.04%; N, 5.39%. Found: C, 64.86%; H, 4.22%; N, 5.52% and calc. for $C_{57}H_{58}N_4O_4$ (M_2): C, 78.82%, H, 6.67%, N, 6.45%. Found: C, 78.20%, H, 7.00%, N, 6.86%.

Preparation of Soluble Copoly(amide-imide)s by One-step Polymerization.

Copoly(amide-imide) derivatives (CPAI) that were soluble in organic solvents could be synthesized by one-step polymerization according to previous paper [15]. In this procedure, the prepolymer, poly(amic acid), having high molecular weight was synthesized at moderate temperature, and subsequently the dehydrocyclization was completed in solution without intermediating process. CPAI was synthesized from DDCA with various dianhydride compounds as

follows (scheme 2); DDCA was dissolved in NMP in a four-neck flask equipped with a seal Teflon stirrer, nitrogen gas inlet tube, reflux condenser with drying tube, and thermometer at 20°C and stirred till the solution was clear. Under flowing nitrogen, equivalent dianhydride compound was slowly added into the solution with vigorous agitation, and the mixture was kept at this conditions for 4 h to obtain prepolymer having high molecular weight. After the drying tube in the flask was exchanged with a distilling receiver having a reflux condenser, the mixture was rapidly heated to 180°C and kept at the temperature for 4 h under flowing nitrogen. The water liberated by dehydrocyclization was distilled off. At the end of the reaction, the viscous solution was cooled and poured into stirred methanol, giving rise to a precipitate, which was filtered off, washed thoroughly with methanol, collected by filtration, and dried under vacuum at 110°C for 6 h.

Results and Discussions

The formation of CPAIs was confirmed by means of FT-ir spectrum and elemental
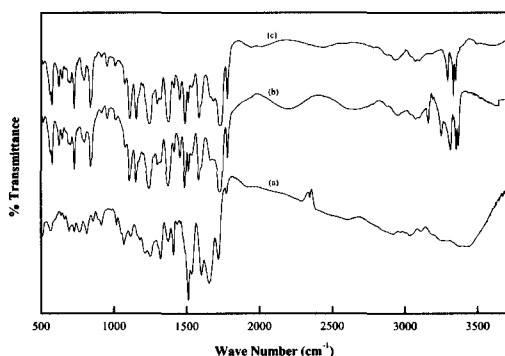
Fig. 1.

analysis. A typical FT-ir spectra of CPAI-1 are represented in Figure 1. The spectrum of CPAI-1 exhibited the characteristic absorption peaks of amide groups occurring around 1520, 1680, and 3350 cm^{-1}. The absorption of the

imide ring appeared at about 1780 cm^{-1} related to the stretching vibration of -C=O linkage of imide ring and at around 1380 and 725 cm^{-1} assigned to the -C-N stretching vibration of that ring. Elemental analysis values of the prepared polymers are listed in Table 1. In all case, the found values of carbon and nitrogen were slightly lower than those calculated for the formula structures. On the other hand, the hydrogen values were higher. The result probably related to the nature of amide and polar linkages of polymer main chains because of conforming electronic bonds between water and those groups of the polymers. The amount of absorbed moisture was in the range of 1. 5~3.6%, which was calculated from the weight loss of polymer samples dried under reduced pressure at 120°C for 12 h after exposure at room temperature, RH 65±3% for 24 h.

Table 1. Elemental Analysis of CPAIs

Polymer No.	Formular M_w		Elemental Analysis (%)			Moisture Uptake[a](%)
			C	H	N	
CPAI-1	$(C_{67}H_{38}N_4O_{15}S_2)_n$	Calc.	66.91	3.16	4.66	2.0
	$(1202.64)_n$	Found	64.20	3.65	4.14	
CPAI-2	$(C_{74}H_{42}N_4O_{16}S_2)_n$	Calc.	68.01	3.21	4.29	3.6
	$(1306.70)_n$	Found	65.16	3.57	3.65	
CPAI-3	$(C_{65}H_{42}N_4O_{15}S_2)_n$	Calc.	66.01	3.55	4.74	2.5
	$(1182.62)_n$	Found	63.79	4.27	4.21	
CPAI-4	$(C_{141}H_{80}N_8O_{31}S_4)_n$	Calc.	67.48	3.18	4.46	2.7
	$(2509.34)_n$	Found	64.36	3.85	3.87	
CPAI-5	$(C_{132}H_{80}N_8O_{30}S_4)_n$	Calc.	66.46	3.35	4.70	2.0
	$(2385.26)_n$	Found	65.02	4.03	4.00	
CPAI-6	$(C_{139}H_{84}N_8O_{31}S_4)_n$	Calc.	67.06	3.37	4.50	2.9
	$(2489.32)_n$	Found	65.10	3.88	4.16	
CPAI-7	$(C_{67}H_{54}N_4O_7)_n$	Calc.	78.38	5.26	5.46	1.5
	$(1026.60)_n$	Found	77.25	5.50	5.18	
CPAI-8	$(C_{74}H_{58}N_4O_8)_n$	Calc.	78.60	5.13	4.95	2.4
	$(1130.66)_n$	Found	76.97	5.90	4.97	
CPAI-9	$(C_{65}H_{58}N_4O_7)_n$	Calc.	77.56	5.76	5.56	1.8
	$(1006.58)_n$	Found	76.00	6.48	5.00	
CPAI-10	$(C_{141}H_{110}N_8O_{15})_n$	Calc.	78.57	5.10	5.20	2.0
	$(2155.26)_n$	Found	76.37	5.76	4.67	
CPAI-11	$(C_{132}H_{110}N_8O_{14})_n$	Calc.	78.05	5.42	5.51	1.9
	$(2031.18)_n$	Found	77.54	5.67	4.78	
CPAI-12	$(C_{139}H_{114}N_8O_{15})_n$	Calc.	78.18	5.34	5.25	2.0
	$(2135.24)_n$	Found	76.35	6.00	5.00	

[a] Moisture uptake(%) = $(W-W_0)/W_0$ x 100; W= weight of polymer sample after standing at room temperature, RH 65±3% for 24 h, and W_0 = weight of polymer sample after dried under reduced pressure at 120°C for 12 h.

Table 2. Viscosity and Yield of Copoly(amide-imide) Derivatives[a]

Polymer No.	DDCA	Dianhydride (mol ratio)	Viscosity[b] (dL/g)	Yield (%)	Remark[c]
CPAI-1		PMDA	1.45	> 98	H
CPAI-2		BTDA	1.21	> 98	H
CPAI-3		BTCA	0.87	> 98	H
CPAI-4	M₁	PMDA/BTDA(1 / 1)	1.30	> 98	H
CPAI-5		PMDA/BTCA(1 / 1)	1.24	> 98	H
CPAI-6		BTDA/BTCA(1 / 1)	1.03	> 98	H
CPAI-7		PMDA	1.57	> 98	H
CPAI-8		BTDA	1.52	> 98	H
CPAI-9		BTCA	1.09	> 98	H
CPAI-10	M₂	PMDA/BTDA(1 / 1)	1.54	> 98	H
CPAI-11		PMDA/BTCA(1 / 1)	1.27	> 98	H
CPAI-12		BTDA/BTCA(1 / 1)	1.10	> 98	H

[a] Reaction for solution dehydrocyclization was carried out 20 wt% of solid content in NMP at 180°C for 4 h under nitrogen.
[b] Measured at contents of 0.5 g/dL polymer in NMP at 25°C.
[c] Appearance of the mixture kept homogeneous solution(H) throughout the polymerization

The synthetic compositions of CPAIs are given in Table 2. All the polymers were obtained in quantitative yields with relatively high inherent viscosities of 0.87~1.57 dL/g. The values of viscosity might relate to the chemical structure and composition of reagents. The reaction of an amine and an anhydride was occurred by the nucleophilic substitution of amine groups at the carbonyl carbon atom of anhydride moiety [15-18]. Therefore, the extent of the reaction was strongly dependent on the electron affinity of carbonyl carbon atoms of the anhydride portion, and the nucleophilicity of nitrogen atom of the amine moiety. The stronger the electron-withdrawing anhydride moieties, the easier the nucleophilic substitution reaction at the carbonyl carbon atom of those. Those behaviors had a similar tendency to the previous papers [12,19].

The influences of chemical structure and composition on the mechanical properties of CPAIs were investigated and these results are summarized in Table 3. All the CPAI derivatives revealed comparatively good mechanical properties. The CPAIs had tensile strengths of 4.2~7.5 kg/mm², and elongations at a break

Table 3. Tensile Strength and Elongation of Copoly(amide-imide)s at Break Point[a]

Polymer No	Tensile strength (kg/mm²)	Elongation at break (%)
CPAI-1	7.2	11.5
CPAI-2	5.2	17.5
CPAI-3	5.4	15.0
CPAI-4	6.3	16.0
CPAI-5	6.0	12.0
CPAI-6	4.2	19.0
CPAI-7	7.5	11.0
CPAI-8	5.8	16.5
CPAI-9	6.0	15.0
CPAI-10	6.5	14.5
CPAI-11	7.0	11.0
CPAI-12	4.8	14.0
Ultem-1000[b]	5.6	6.7

[a] Measured at room temperature
[b] Obtained from general electric specialty plastics.

point of about 11.0~19.0%. These properties were also affected by chemical structure and composition of polymers. The tensile strength increased in proportion to increasing the fraction

Table 4. Thermal Behavior of Copoly(amide-imide) Derivatives[a]

Polymer No	T_i (°C)	T_{10} (°C)	T_{max} (°C)	T_g (°C)
CPAI-1	365	520	620	240
CPAI-2	350	470	580	220
CPAI-3	320	460	560	205
CPAI-4	350	490	600	225
CPAI-5	325	465	570	210
CPAI-6	320	450	560	200
CPAI-7	370	540	640	270
CPAI-8	355	480	590	240
CPAI-9	335	470	570	230
CPAI-10	360	525	610	245
CPAI-11	340	500	580	230
CPAI-12	330	460	565	220

[a] Measured at heating rate 10°C/min under nitrogen, second-run curve of TGA was considered after the first-run up to 300°C.

Fig. 2.

of segmental regularity in the polymer backbone because of increasing the force of molecular package [19-22]. On the other hand, elongation at a break point increased with introducing flexible linkages in the main chain because folding of the molecular chain was occurred.

Thermal properties of CPAI derivatives were evaluated by means of TGA and DSC under nitrogen conditions. Thermal properties of all CPAIs are summarized in Table 4. The relative thermal properties of polymers, the initial decomposition temperature T_i, which was taken as the onset temperature when the fastest weight loss process began, 10% weight loss T_{10}, and the maximum rate of weight loss T_{max}, for each step were obtained from TGA thermograms. Second-run results of TGA were considered after the first-run up to 300°C to eliminate rests of materials. The T_{max} was calculated from differential thermogravimetric trace. T_is of polymers in the range of 320~370°C, T_{10}s in the range of 450~540°C, and T_{max}s in the range of 560~640°C in nitrogen qualified these polymers as thermally stable.
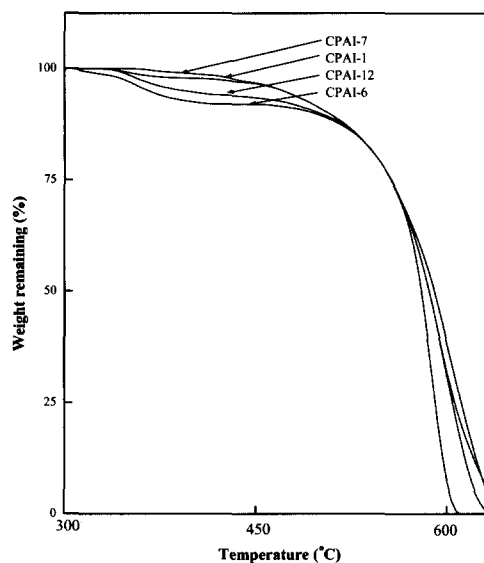
All of these polymers showed similar decomposition behaviors in Figure 2. In TGA traces, all the polymers possessed high thermal stability with no significant weight losses up to approximately 320°C in nitrogen. The relationship between the chemical structure and composition of main chains and thermal stability was observed from TGA traces. The polymers having the fraction of segmental regularity showed better stability than CPAIs with flexible linkages in the backbone. The results probably related to the structural regularity of polymers. The thermal stability decreased with introduction of flexible linkages because they might lead to loose packing strength of polymers [20-22].

The T_gs of CPAIs were in the range of 200~270°C. The melting temperature was not detected from DSC. All the polymers were probably amorphous. The relationship between the T_g and chemical structure was also investigated. As the fraction of flexible linkages in the main chains increased, T_g decreased. Even if the small moiety of a more flexible linkages was incorporated with the chain structure, the bending and rotating motions of the main

Table 5. Solubility of CPAIs[a]

Polymer No	Solvent[b]							
	NMP	DMAc	DMSO	H_2SO_4	m-cresol	Py	EtOH	MeOH
CPAI-1	+	+	+	+	+	−	−	−
CPAI-2	+	+	+	+	+	−	−	−
CPAI-3	+	+	+	+	+	−	−	−
CPAI-4	+	+	+	+	+	−	−	−
CPAI-5	+	+	+	+	+	±	−	−
CPAI-6	+	+	+	+	+	±	−	−
CPAI-7	+	+	+	+	+	−	−	−
CPAI-8	+	+	+	+	+	−	−	−
CPAI-9	+	+	+	+	+	−	−	−
CPAI-10	+	+	+	+	+	−	−	−
CPAI-11	+	+	+	+	+	−	−	−
CPAI-12	+	+	+	+	+	−	−	−

[a] Solubility: +, soluble; ±, swell; −, insoluble at room temperature.
[b] NMP, N-methyl-2-pyrrolidone; DMAc, N,N'-dimethylacetamide; DMSO, dimethylsulfoxide; Py, pyridine; EtOH, ethanol; MeOH, methanol.
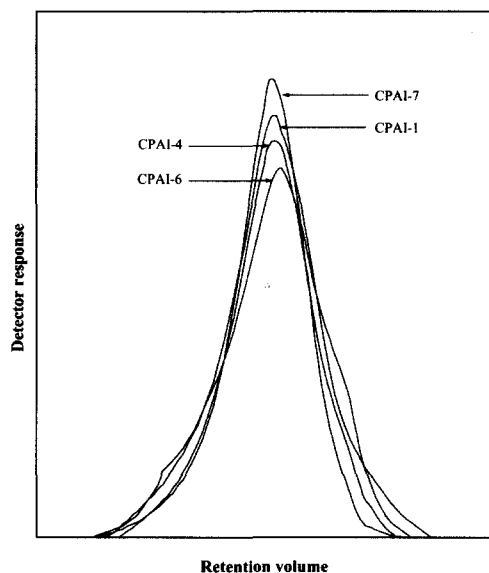
Fig. 3.

chains increased and reduction of T_g was induced. The result also related to the structural arrangements and composition of polymers and could be explained by the packing strength of main chains [19-22].

Figure 3 shows GPC of polymers. The molecular weight distribution of the CPAIs revealed a polydispersity index of 2.0~2.3.

The soluble characteristics of polymers in various solvents is summarized in Table 4. All the CPAIs were soluble in polar solvents such as NMP, DMSO, DMAc, and so on. The solubility of polymers could be improved with introducing the flexible and unsymmetric portions in the main chain. The presence of flexible linkages or more irregular segments order in polymer backbones might lead to loose packing strength, therefore the solvent molecules more easily penetrate into the polymer to soluble the polymer chains [21,22]. All the polymers had a good solubility in some solvents without much sacrifice in thermal and mechanical properties. Those soluble behaviors of the polymers might be advantageous for their applications.

Conclusion

The diamide-diamine having carboxylic acid was prepared by direct condensation of 1,2,4-benzenetricarboxylic acid with bis[4-(3-aminophenoxy) phenyl]sulfone and bis(4-aminophenyl)-1,4-

diisopropylbenzene in NMP using TPP and LiCl as condensing agents. Copoly(amide-imide) derivatives with high molecular weight could be synthesized by one-step polymerization of prepared diamide-diamine having carboxylic acid and various dianhydride compounds. Depending on the chemical structure and composition of polymers, the viscosities of polymers were found to range between 0.87~1.57 dL/g.

All the polymers showed good thermal and mechanical properties. An initial weight loss had not been shown up to 320°C and the 10% weight loss temperature was observed in the range of 450~540°C in a thermogravimetric traces. The glass transition was recorded in the temperature range of 200~270°C. All the polymers showed an amorphous nature on a differential scanning calorimetry thermograms. The CPAIs had tensile strengths of 4.2~7.5 kg/mm, and elongations at a break point of about 11.0~19.0%. These polymers dissolved well in various polar solvents. Further, it was proved that their properties could be determined from the chemical structure and composition of polymer main chains.

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