

Research Article

Soluble Polyimides Bearing Long-Chain Alkyl Groups on Their Side Chain via Polymer Reaction

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Novel soluble polyimides having long-chain alkyl groups on their side chain were synthesized *via* polymer reaction with the polyimides having phenolic OH groups and 3,4,5-tris(dodecyloxy)benzoic acid (12GA) using *N,N'*-dicyclohexylcarbodiimide (DCC) as a dehydration reagent. The polyimides having phenolic OH groups were synthesized from the tetracarboxylic dianhydrides such as 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (cyclohexene-DA), 4,4'-hexafluoroisopropylidendi(phthalic anhydride) (6FDA), and 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA) and aromatic diamines such as 4,4'-diamino-3,3'-dihydroxybiphenyl (HAB). The polymer reactions were carried out in NMP and the progresses of polymer reactions were quantitatively monitored by ¹H NMR measurements (conversion; 12.2–98.7%). The obtained polyimides bearing long-chain alkyl groups have enough molecular weights, good film-forming ability, good solubility for various organic solvents, and enough thermal stability. The water contact angles of the polyimide films were investigated, and it is noted that the introduction of long-chain alkyl groups increases the hydrophobicity of polyimide surface. These polyimides are expected to be applicable as the functional materials for microelectronics such as the alignment layers of LCDs.

1. Introduction

Polyimides exhibit excellent thermal and mechanical properties and have extensive engineering and microelectronics applications [1, 2]. Aromatic polyimides such as polyimides based on pyromellitic dianhydride are prepared from aromatic diamines and aromatic tetracarboxylic dianhydrides *via* poly(amic acid)s. Since conventional aromatic polyimides are insoluble, these polymers are usually processed as the corresponding soluble poly(amic acid) precursors, and then either thermally or chemically imidized. However, owing to the instability of poly(amic acid)s and the liberation of water in the imidization process, problems can arise. Extensive research has been carried out to improve the solubility of polyimides and successful recent examples involve the incorporation of fluorine moieties [3], isomeric moieties [4], methylene units [5], triaryl imidazole pendant groups [6], spiro linkage groups [7], and sulfonated structure

[8]. Soluble polyimides bearing long-chain alkyl groups have also been reported [9–15], and their applications mainly involve their use as alignment layers for liquid crystal displays (LCDs).

Our research group has systematically investigated the synthesis and characterization of soluble polyimides based on aromatic diamines bearing long-chain alkyl groups such as alkyl diaminobenzophenone (ADBP-X, X = carbon numbers of alkyl chain) [16], alkoxydiaminobenzene (AODB-X) [17], diaminobenzoic acid alkylester (DBAE-X) [18], and alkyl diaminobenzamide (ADBA-X) [19], and the results from these research are described in the review papers [20]. Our recent paper has described soluble polyimides having dendritic moieties on their side chain, and it was found that these polyimides having dendritic side chains were applicable for the vertically aligned nematic liquid crystal displays (VAN-LCDs) [21]. These dendronized polyimides were synthesized using the novel diamine

monomer having a first-generation monodendron, 3,4,5-tris(*n*-dodecyloxy)benzoate, and the monomer having a second-generation monodendron, 3,4,5-tris[-3',4',5'-tri(*n*-dodecyloxy)benzyloxy]benzoate. The synthesis of dendronized polyimides using the similar diamine monomers containing multiple alkyl chains have been previously reported by another research groups [22–24].

In this paper, the introduction of multiple long-chain alkyl groups on the polyimide side chains *via* polymer reaction is described. Although above synthetic methods using the diamine monomers that have dendritic moieties are successful example, there are demerits such that monomer synthesis generally include the long synthetic route and difficult process, and that the molecular weights of polyimides are sometimes low because of the low reactivity of diamine monomers probably due to the steric hindrance based on huge dendritic moieties. Thus, the authors have investigated the alternative method for the introduction of such multiple long-chain alkyl groups to polymer backbones, namely, polymer reaction; in other words, postfunctionalization.

Polymer reaction is the synthetic technique sometimes used for the synthesis of photosensitive polyimides [25, 26], and 4,4'-diamino-3,3'-dihydroxy biphenyl (HAB) is one of the representative monomer for the introduction of the reactive phenolic OH groups to the polymer backbones. Thus, the synthesis of novel soluble polyimides having long-chain alkyl groups on their side chain was investigated *via* polymer reaction with the polyimides having phenolic OH groups and 3,4,5-tris(dodecyloxy)benzoic acid (12GA) using *N,N'*-dicyclohexylcarbodiimide (DCC) as a dehydration catalyst. The polyimides having phenolic OH groups were synthesized from the tetracarboxylic dianhydrides such as 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexane-1,2-dicarboxylic anhydride (cyclohexene-DA), 4,4'-hexafluoroisopropylidendi (phthalic anhydride) (6FDA), and 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA), and HAB and a codiamine monomer, 4,4'-diaminodiphenylether (DDE). The progress of polymer reactions were monitored by ¹H NMR, and the characterizations of obtained polyimides such as solubility, thermal stability, molecular weights (inherent viscosities and SEC measurements) were investigated, and the surface hydrophobicities characterized by long-chain alkyl groups were estimated from the results of water contact angle measurements.

2. Experimental

2.1. Materials. Cyclohexene-DA (EPICLON B-4400) was purchased from DIC Corporation and recrystallized from acetic anhydride (mp. 175.1°C). DSDA was purchased from New Japan Chemical Co., Ltd., and recrystallized from acetic anhydride (mp. 291.0°C). DDE from Seika Corporation, 6FDA from Central Glass Co., Ltd., HAB from Tokyo Chemical Industry Co., Ltd. (TCI), were used after drying in a vacuum oven. Ultrapure grade of *N*-methyl-2-pyrrolidone (NMP) was purchased from Kanto Chemical Co., Inc., and used as received. Other reagents were purchased from TCI or Wako Pure Chemical Industries (Wako) and used as received.

2.2. Measurements. ¹H NMR spectra were measured on a JEOL JNM-AL400 FT NMR in CDCl₃ or dimethyl sulfoxide-*d*₆ with tetramethylsilane (TMS) as an internal reference. The inherent viscosities of all polymers were measured using Cannon Fenske viscometers at a concentration of 0.5 g/dL in NMP at 30°C. Size exclusion chromatography (SEC) measurements were performed in NMP containing 10 mM LiBr at 40°C with a TOSOH HLC-8020 equipped with a TSK-GEL ALPHA-M. Number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity (M_w/M_n) were determined by TOSOH Multi Station GPC-8020 calibrated with a series of polystyrenes as a standard. The polyimide film samples for the measurement of thermomechanical analysis (TMA) were prepared by the following casting method. Five wt% polyimide solution in NMP were cast on aluminum cup and the solution were slowly evaporated by heating at approximately 100–120°C until the films were dried, then the films were dried in a vacuum oven at 100°C for 12 h. TMA was performed on a Shimadzu TMA-50 under nitrogen (30 mL/min) at a heating rate of 10°C/min with a 10 g load in the penetration mode using the film samples approximately 300 μm in thickness. Softening temperatures were taken as the onset temperature of the probe displacement on the second TMA scan after cooling from 220°C. Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50 in air or under nitrogen (50 mL/min) at a heating rate of 10°C/min using 5 mg of a dry powder sample, and initial decomposition temperatures (*T*_{d0}), 5% weight loss temperatures (*T*_{d5}), and 10% weight loss temperatures (*T*_{d10}) were calculated from the second heating scan after cooling from 250°C. Water contact angles were measured by contact angle meter (CA-D, Kyowa Interface Science Co., Ltd., Japan).

2.3. Synthesis of 3,4,5-Tris(*n*-dodecyloxy)benzoic Acid (12GA). 3,4,5-Tris(*n*-dodecyloxy)benzoic acid (12GA), known as the building blocks for Percec-type dendrons, was synthesized from 3,4,5-trihydroxybenzoic acid methyl ester (gallic acid methyl ester) followed by Williamson-etherification with *n*-dodecylbromide catalyzed by potassium carbonate, hydrolysis of ester groups by potassium hydroxide by the method in the previous papers [27, 28].

2.4. Preparation of Polyimides. Two step polymerization systems including poly(amic acid)s synthesis and chemical imidization were performed. The poly(amic acid)s were obtained by reacting the mixture of diamines with an equimolar amount of tetracarboxylic dianhydride at room temperature for 12 h under a nitrogen atmosphere. The polyimides were obtained by chemical imidization at 120°C in the presence of pyridine as a base catalyst and acetic anhydride as a dehydrating reagent. The experimental details are described in the previous papers [16–21].

2.5. Introduction of 12GA via Polymer Reaction. An equimolar amount of 12GA and DCC to the total amounts of phenolic OH groups were added to 5 wt% NMP solution of the polyimide containing HAB monomer units, and

TABLE 1: Polyimides and copolyimides containing phenolic OH groups based on HAB.

Tetracarboxylic dianhydride ^a	Diamine mol%		Poly(amic acid)s η_{inh}^b dLg ⁻¹	Solubility in NMP	Polyimides			
					η_{inh}^b dLg ⁻¹	Molecular weight ^c		
						Mn	Mw	Mw/Mn
Cyclohexene-DA	HAB	DDE	0.53	Soluble	0.14	15000	29700	2.0
	20	80						
	50	50						
6FDA	HAB	DDE	0.61	Soluble	0.16	14400	31900	2.2
	20	80						
	50	50						
DSDA	HAB	DDE	0.69	Soluble	0.29	17700	39100	2.2
	20	80						
	50	50						
6FDA	HAB	DDE	0.52	Soluble	0.58	53700	110000	2.0
	20	80						
	50	50						
DSDA	HAB	DDE	0.48	Soluble	0.48	35700	81500	2.3
	20	80						
	50	50						
DSDA	HAB	DDE	0.58	Soluble	0.65	30800	64200	2.1
	20	80						
	50	50						
DSDA	HAB	DDE	0.84	PS ^d	50400 ^e	132200 ^e	2.6 ^e	
	20	80						
	50	50						
DSDA	HAB	DDE	0.80	PS ^d	57100 ^e	149100 ^e	2.6 ^e	
	20	80						
	50	50						
DSDA	HAB	DDE	0.45	Soluble	0.61	73700	153400	2.1
	20	80						
	50	50						

^aEquimolar amount of tetracarboxylic dianhydride was used to the total amount of diamines. ^bMeasured at 0.5 g dL⁻¹ in NMP at 30°C. ^cDetermined by SEC in NMP containing 10 mM LiBr calibrated with a series of polystyrenes as a standard. ^dPartially soluble. ^eData of soluble parts in NMP.

the reaction mixture was stirred at room temperature for 12 h, and then poured into hot methanol. Precipitated polyimides were filtered, washed with excess hot methanol, and dried in a vacuum oven at 100°C for 1 day. It was confirmed that unreacted 12GA, DCC, and DCU (dicyclohexylurea) were dissolved in hot methanol.

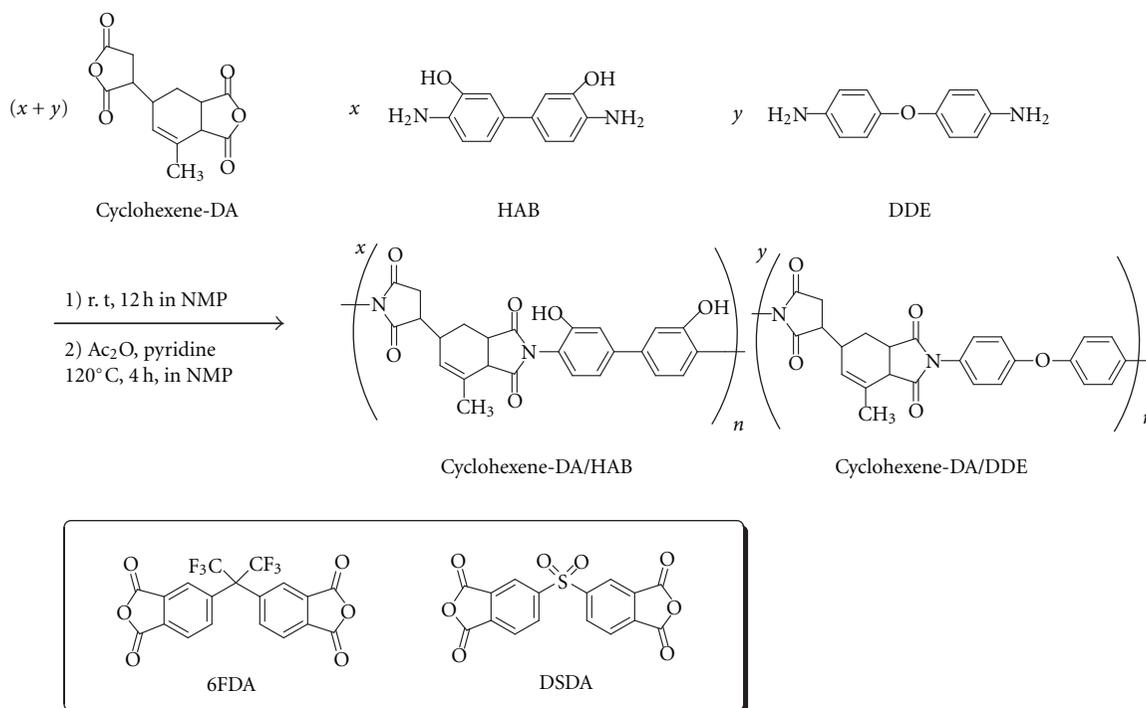
3. Results and Discussion

3.1. Synthesis of Polyimides and Copolyimides Containing Phenolic OH Groups Based on HAB. The synthetic route of the polyimides and copolyimides containing phenolic OH groups based on HAB is illustrated in Scheme 1. Two step polymerization systems including poly(amic acid)s synthesis and chemical imidization were performed. These are the optimized synthetic conditions previously developed for the synthesis of soluble polyimides in our laboratory [16–21]. If the polyimides were insoluble in the polymerization solvent, NMP, gelation or precipitation happened in the course of imidization process. Cyclohexene-DA, 6FDA, and DSDA known as the representative tetracarboxylic dianhydride monomers suitable for soluble polyimides were used. DDE, that is, a highly reactive and common aromatic diamine, was used as a diamine comonomer.

Experimental results of the synthesis of polyimides and copolyimides containing phenolic OH groups based on HAB are summarized in Table 1. Although all poly(amic acid)s were soluble in NMP that is a polymerization solvent, however, the solubility of obtained polyimides depended on the monomer composition. All of polyimides and copolyimides using cyclohexene-DA or 6FDA as a tetracarboxylic dianhydride were soluble, while the solubility of polyimides based

on DSDA depended on the HAB amounts. The homopolyimide based on DSDA/HAB was soluble in NMP, on the other hand, the copolyimides based on DSDA/HAB/DDE (100/20/80, 100/50/50) were only partially soluble. Although DSDA is known as a tetracarboxylic dianhydride suitable for soluble polyimides, it is considered that cyclohexene-DA containing flexible alicyclic structure and 6FDA containing both strong polar trifluoromethyl group and flexible isopropylidene structure are more effective for the enhancement of solubility than DSDA only containing polar sulfone group. In the case of DSDA/HAB polyimide, it is speculated that many hydroxyl groups based on HAB segments enhance the solubility of polyimide in NMP by H-bonding.

Inherent viscosities of HAB containing polyimides based on cyclohexene-DA were in the range of 0.14–0.29 dLg⁻¹, and the weight average molecular weights determined by SEC measurements were in the range of 29700 to 39100. These values indicated that the molecular weights of these polyimides are considered medium or rather lower values for polyimides; however, all polyimides show the good film formation ability. Inherent viscosities of HAB containing polyimides based on 6FDA, or DSDA were in the range of 0.48–0.65 dLg⁻¹, and the weight average molecular weights determined by SEC measurements were in the range of 64200 to 153400. These values indicated that the molecular weights of these polyimides are enough high, and it is considered that these higher molecular weights are based on the higher reactivity of aromatic tetracarboxylic dianhydride, 6FDA and DSDA in comparison with aliphatic tetracarboxylic dianhydride, cyclohexene-DA. Although the copolyimides based on DSDA/HAB/DDE (100/20/80, 100/50/50) partially precipitated in NMP during imidization process, however, after the filtration of these precipitated polyimide,



SCHEME 1: Synthesis of polyimides having phenolic OH groups.

the filtrate was poured in a large amount of methanol, and the soluble parts of polyimides were obtained. Therefore, the copolyimides based on DSDA/HAB/DDE (100/50/50, 100/20/80) are assigned as partially soluble in NMP, and the molecular weights of soluble parts were determined by SEC measurements (Table 1). As described above, a variety of soluble polyimides and copolyimides containing phenolic OH groups were synthesized and used for polymer reaction as base-polyimides.

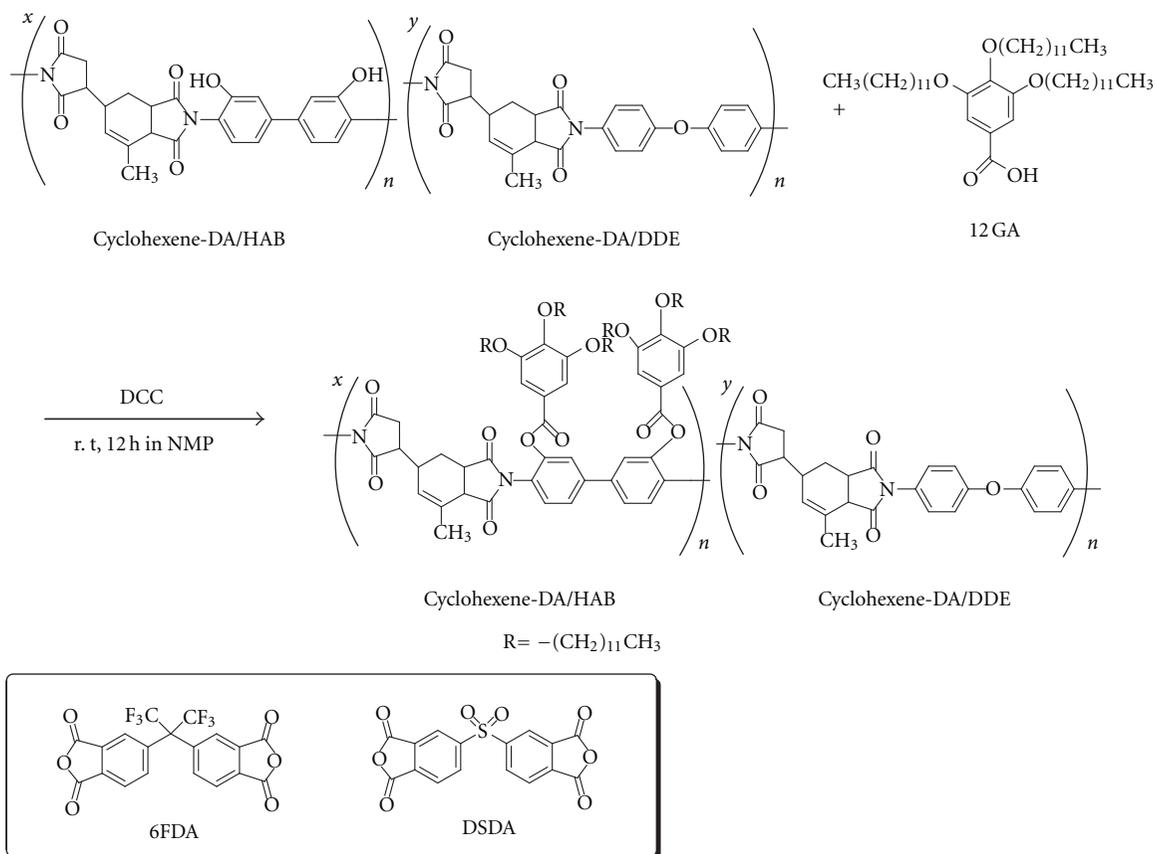
3.2. Introduction of 12GA via Polymer Reaction. The outline of the polymer reactions of HAB containing polyimides and 12GA is illustrated in Scheme 2 and the results are summarized in Table 2. The progresses of polymer reactions were quantitatively monitored by ¹H NMR measurements. For examples, Figure 1 shows the ¹H NMR of DSDA/HAB polyimides before and after polymer reaction with 12GA. ¹H NMR spectrum after polymer reaction, the CH₃ and (CH)₂ proton peaks based on long-chain alkyl groups appear in 0.69–0.87 ppm and 1.09–1.37 ppm, respectively. Thus, the addition reactions of 12GA to the polymer backbone were confirmed and the conversion of polymer reactions were calculated by comparing the integration ratios of aromatic protons and CH₃ and (CH)₂ protons (Table 2). It is considered that the conversions tend to decrease with the increase of phenolic OH contents (HAB contents) in the base-polyimides. It is speculated that the reactivity of bulky 12GA segments decrease with the increase of phenolic OH groups by steric hindrance. In the case of 6FDA/HAB polyimides and 6FDA/HAB/DDE copolyimides, the conversions of polymer reactions were relatively low in the

range of 12.2–66.4%. Since the solubility of these 6FDA based polyimides after polymer reactions was insufficient as described later, it appears that these relatively lower conversion values might reflect the decrease of solubility.

The effects of the enhancement of solubility based on the addition of 12GA segments that contains three long-chain alkyl groups were clearly observed in the case of DSDA/HAB/DDE copolyimides. Although the copolyimides based on DSDA/HAB/DDE (100/20/80, 100/50/50) are partially soluble in NMP before polymer reactions, these polyimides became to be soluble after the reactions with 12GA (conversions; 78.3–94.4%, Table 2). It is considered that these effects are certainly based on the entropy effect of long-chain alkyl groups.

However, with the increase of phenolic OH contents (HAB contents) in the base-polyimides, the solubility of the polyimides bearing 12GA segments tend to be decrease. Thus, Cyclohexene-DA/HAB (100/100), 6FDA/HAB (100/100), and DSDA/HAB (100/100) polyimides reacted with 12GA were partially soluble, even though their corresponding base-polymers were soluble. According to the our previous research, the excess attachments of long-chain alkyl groups sometimes reduce the polymer solubility probably due to the aggregation of long-chain alkyl segments [21].

The progress of the polymer reactions was confirmed also by SEC measurements. For example, Figure 2 shows the SEC traces of DSDA/HAB/DDE (100/50/50) base-polyimide, DSDA/HAB/DDE (100/50/50) polyimide reacted with 12GA, and the solution blend of DSDA/HAB/DDE (100/50/50) base-polyimide and 12GA. In the case of the solution blend, the elution peak of 12GA appears at around the region;



SCHEME 2: Polymer reactions of polyimides having phenolic OH groups and 12GA using DCC as a catalyst.

TABLE 2: Polyimides and copolyimides obtained from the polymer reaction of polyimides containing phenolic OH groups and 12GA.

Tetracarboxylic dianhydride ^a	Diamine mol%		12GA ^b mol%	Solubility in NMP	η_{inh}^c dLg ⁻¹	Molecular Weight ^d			Conversion ^e %
	HAB	DDE				Mn	Mw	Mw/Mn	
Cyclohexene-DA	HAB	DDE	40	Soluble	0.14	15400	30800	2.0	98.7
	20	80							
	50	50							
6FDA	HAB	DDE	100	Soluble	0.11	17200	34200	2.0	57.9
	20	80							
	50	50							
DSDA	HAB	DDE	200	PS ^f		24100 ^g	64800 ^g	2.7 ^g	49.1
	20	80							
	50	50							
6FDA	HAB	DDE	40	Soluble	0.61	51800	110000	2.0	66.4
	20	80							
	50	50							
DSDA	HAB	DDE	100	Soluble	0.45	31400	70700	2.2	23.0
	20	80							
	50	50							
6FDA	HAB	DDE	200	PS ^f		36800 ^g	74400 ^g	2.0 ^g	12.2
	20	80							
	50	50							
DSDA	HAB	DDE	40	Soluble	0.30	17100	37500	2.2	94.4
	20	80							
	50	50							
6FDA	HAB	DDE	100	Soluble	0.35	23700	61700	2.6	78.3
	20	80							
	50	50							
DSDA	HAB	DDE	200	PS ^f		77100 ^g	155400 ^g	2.0 ^g	64.7
	20	80							
	50	50							

^aEquimolar amount of tetracarboxylic dianhydride was used to the total amount of diamines. ^bEquimolar amount of 12GA was used to the total amount of phenolic OH groups, and the reaction was proceeded using an equimolar amount of DCC as a catalyst. ^cMeasured at 0.5 g dL⁻¹ in NMP at 30°C. ^dDetermined by SEC in NMP containing 10 mM LiBr calibrated with a series of polystyrenes as a standard. ^eCalculated from the intensity ratio of long-chain alkyl groups and aromatic protons. ^fPartially soluble. ^gData of soluble parts in NMP.

log Mw \cong 3.1; however, this peak clearly decreased after the polymer reaction. These phenomena were observed by all polymer reactions in our study, and the introduction of 12GA segment was confirmed. However, SEC peak analysis is less quantitative than ¹H NMR peak analysis, so that

the calculations of conversion were carried out using ¹H NMR peak analysis. The SEC traces after polymer reactions were moved to the low molecular weight region even though their actual molecular weight should increase by the attachment of 12GA segments. It can be imagined that

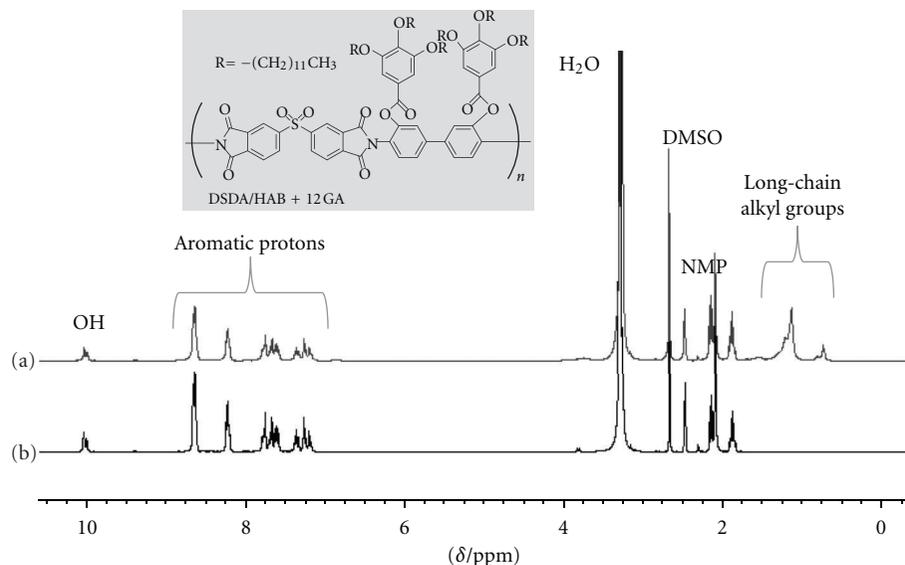


FIGURE 1: ^1H NMR spectra of polyimides based on DSDA/HAB and 12GA (a) after polymer reaction, (b) before polymer reaction.

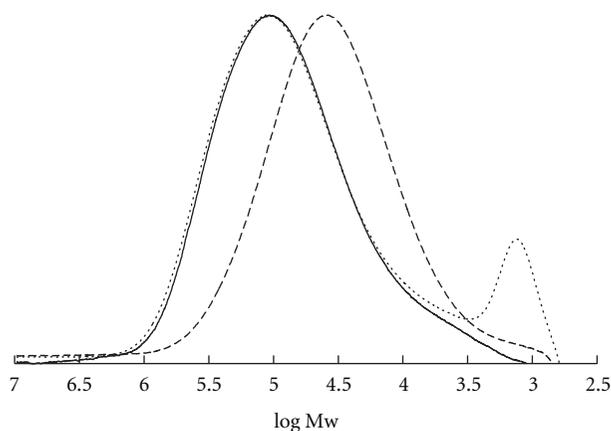


FIGURE 2: SEC traces of polyimides based on DSDA/HAB/DDE (100/50/50) and 12GA, (solid line); before polymer reaction, (dashed line); after polymer reaction, (dotted line); solution blends of DSDA/HAB/DDE (100/50/50) and 12GA.

the polymer structure became more spherical due to the attachment of multiple long chain alkyl groups, so apparent molecular weight observed by SEC measurements seem to decrease. Figure 3 shows the 3D molecular modeling (Chem3D) of DSDA/HAB/DDE (100/50/50) copolyimides and DSDA/HAB/DDE (100/50/50) copolyimides reacted with 12GA, and it can be imagined that the polymer chains of copolyimides reacted with 12GA seems to be more spherical than the base-polyimide. Although this molecular modeling is the simple simulation in the gas phase, it can be speculated that the similar shrinkage of the modified polymers in the eluent is occurred.

The thermal stabilities were evaluated by initial decomposition temperature (Td_0), 5% weight-loss temperatures (Td_5), and 10% weight-loss temperatures (Td_{10}) in TGA

measurements, and the glass transition temperatures (T_g) of these polyimides were determined by TMA measurements. All data are summarized in Table 3, and representative TGA traces are shown in Figures 4 and 5.

The thermal stabilities of both base-polyimides and 12GA reacted polyimides were evaluated in air and under nitrogen atmospheres using Td_0 , Td_5 , and Td_{10} for comparison. Td_0 of were in the range of 228~337°C in air and 273~419°C under nitrogen, Td_5 of these were in the range of 311~526°C in air and 346~550°C under nitrogen, and Td_{10} of these were in the range of 330~561°C in air and 380~574°C under nitrogen (Table 3). In most cases, Td values in air were lower than Td values under nitrogen following the general fact that oxidative degradation proceed rapidly in air. Also, Td_0 , Td_5 , and Td_{10} of these polyimides based on aromatic tetracarboxylic dianhydride, 6FDA, and DSDA were higher than those polyimides based on aliphatic tetracarboxylic dianhydride, cyclohexene-DA. As the incorporation of DDE resulted in a reduction of HAB component in the base-polyimides, Td of these polyimides tended to increase probably due to the fact that phenolic OH groups based on HAB tend to thermally decompose. It is generally described that Td values of the polyimides bearing long-chain alkyl groups after polymer reaction were lower than Td values of base-polyimides following the fact that thermal degradation of long-chain alkyl groups progress rapidly. In addition, Td values tend to be lower with the increase of long-chain alkyl group content. Consequently, above degradation temperatures are 100–200°C lower than the conventional fully aromatic polyimides; however, obtained polyimides bearing long-chain alkyl groups still can be ranked as heat resistant polymers.

T_g of all polyimides were not recognized by DSC measurements, probably due to the rigid imide linkages and ester linkages connecting the long-chain alkyl groups to the polymer backbones. Consequently, TMA measurements

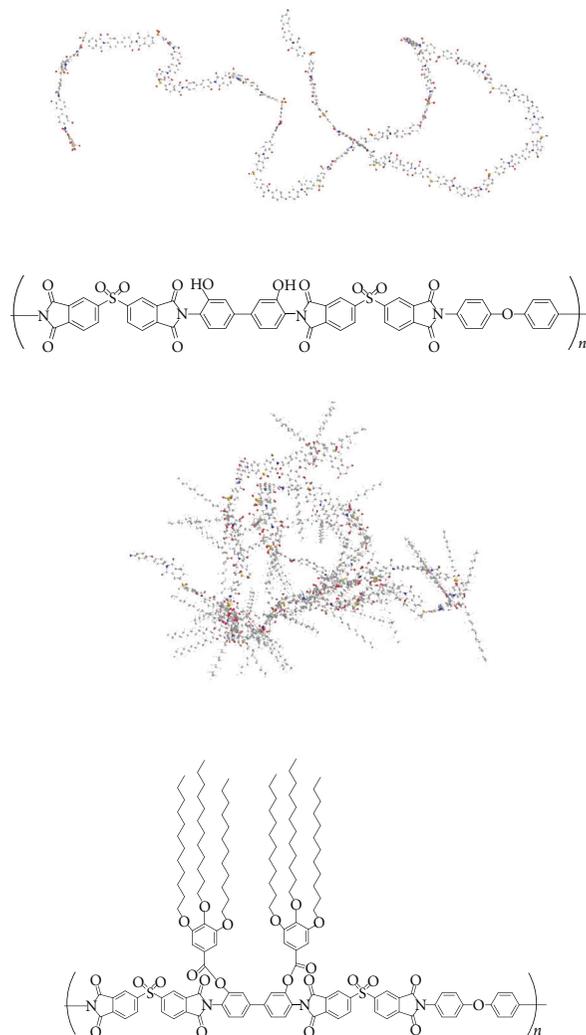


FIGURE 3: 3D Molecular modeling (Chem3D) of DSDA/HAB/DDE (100/50/50) copolyimides ($n = 10$) and DSDA/HAB/DDE (100/50/50) copolyimides ($n = 10$) reacted with 12GA.

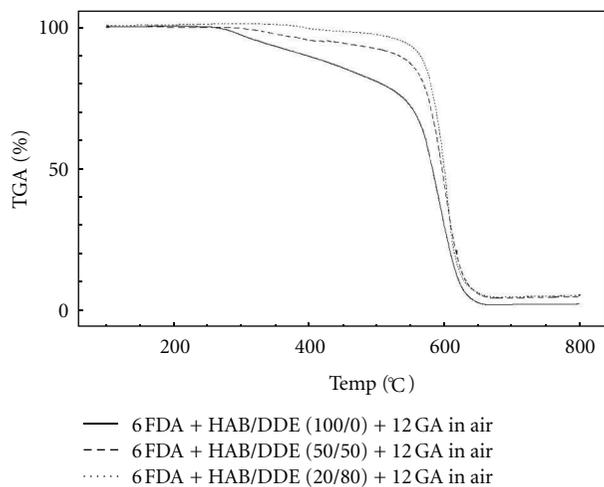


FIGURE 4: TGA traces of polyimides based on 6FDA/HAB/DDE and 12GA.

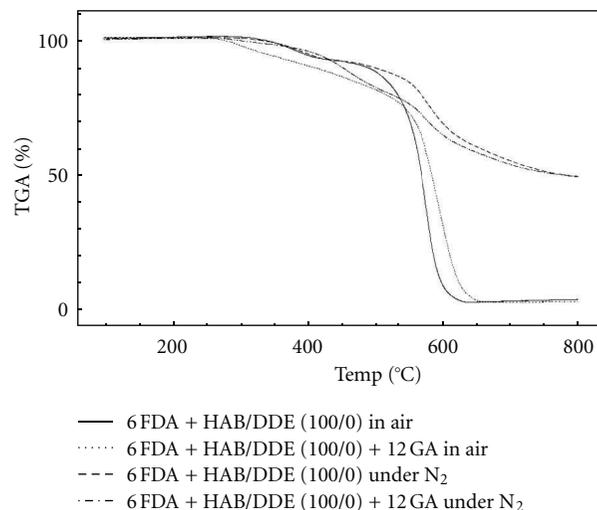


FIGURE 5: TGA traces of polyimides based on 6FDA/HAB/DDE and 12GA (continued).

TABLE 3: Thermal properties of polyimides and copolyimides containing phenolic OH groups and these polyimides reacted with 12GA.

Dianhydride ^a mol%	Diamine mol%		12GA ^b mol%	T_s^c °C	Thermal properties					
					Td_0^d		Td_5^e		Td_{10}^f	
					Air °C	N ₂ °C	Air °C	N ₂ °C	Air °C	N ₂ °C
Cyclohexene-DA	HAB	DDE								
	20	80	0	248	317	303	383	430	423	455
	50	50	0	233	303	284	357	391	385	430
	100	0	0	283	270	276	337	356	355	392
	20	80	40	249	255	371	311	441	387	459
	50	50	100	248	265	289	329	368	353	393
	100	0	200	226	228	289	304	367	330	387
6FDA	HAB	DDE								
	20	80	0	263	321	419	483	550	553	574
	50	50	0	244	311	403	406	522	522	562
	100	0	0	250	297	308	381	394	469	489
	20	80	40	276	337	383	526	549	561	574
	50	50	100	238	304	307	450	410	537	520
	100	0	200	250	253	268	325	404	397	446
DSDA	HAB	DDE								
	20	80	0	254	331	334	498	502	549	557
	50	50	0	242	304	315	392	410	484	489
	100	0	0	248	307	300	373	383	477	467
	20	80	40	251	314	321	421	460	474	524
	50	50	100	243	271	273	333	358	384	412
	100	0	200	252	268	291	314	346	338	380

^aEquimolar amount of tetracarboxylic dianhydride was used to the total amount of diamines. ^bEquimolar amount of 12GA was used to the total amount of phenolic OH groups, and the reaction was proceeded using a equimolar amount of DCC as a catalyst. ^cSoftening temperature, measured by TMA at a heating rate of 10°C/min in N₂ on second heating. ^dInitial decomposition temperature, measured by TGA at a heating rate of 10°C/min. ^e5% Weight loss temperature, measured by TGA at a heating rate of 10°C/min. ^f10% Weight loss temperature, measured by TGA at a heating rate of 10°C/min.

were performed to determine T_g of all polyimides. Many literatures described that the softening temperature (T_s) obtained from TMA measurements correspond the T_g of polymers [29, 30]. As can be seen from Table 3, T_s values obtained by TMA were in the ranged from 226–276°C, showing similar values observed in soluble polyimides bearing long-chain alkyl groups obtained from our laboratory. Above T_g (T_s) values of obtained polyimides are 100–150°C lower than the conventional fully aromatic polyimides, however, 100–150°C higher than the commodity thermoplastics.

The solubility of the obtained polyimides was determined in 12 common solvents at 5 wt% concentration (Table 4). These polyimides were soluble in various solvents in addition to NMP; however, the solubility depended on the structure of polyimides. The base-polyimides based on cyclohexene-DA or 6FDA show a good solubility in various solvents such as NMP, DMF, DMAc, DMSO, DMI, m-cresol, and several polyimides based on 6FDA are soluble in even THF and acetone. However, the solubility of the polyimides after polymer reactions tend to somewhat decrease in polar solvents such as NMP, DMF, DMAc, DMSO, and exceptionally increase in CH₂Cl₂ (Cyclohexene-DA/HAB/DDE

(100/20/80) + 12GA). It can be assumed that hydrophobicity of three long-chain alkyl groups may prevent the solubility in polar solvents, however, increase the solubility in dichloromethane. On the other hand, the polyimides based on DSDA tend to be soluble after reacted with 12GA. In these cases, the flexible long-chain alkyl groups seem to enhance the solubility of rigid DSDA based polyimides by entropy effects.

It is expected that the surface wettability of polyimide films are changed by the introduction of long-chain alkyl groups. The contact angles of obtained polyimide films to the water are summarized in Table 4. The water contact angles of base-polyimides based on cyclohexene-DA or DSAD are ranged from 71.4–77.6, and those based on 6FDA ranged from 82.0–86.4 showing relatively higher values probably due to the hydrophobic nature of trifluoromethyl groups in 6FDA. On the other hand, the water contact angles of the polyimides reacted with 12GA show higher values, 87.5–104.8 due to the hydrophobic nature of long-chain alkyl groups, and these contact angles are somewhat increase with the increase of the contents of long-chain alkyl groups.

TABLE 4: Solubility behavior and water contact angles of polyimides and copolyimides containing phenolic OH groups and these polyimides reacted with 12GA.

Dianhydride ^a mol%	Diamine mol%		12GA ^b mol%	Solubility ^c						Contact angle ^d deg (water)						
				NMP	DMF	DMAc	DMSO	DMI	<i>m</i> -Cresol	THF	CH ₂ Cl ₂	Acetone	Hexane	CHCl ₃	Ethyl acetate	
Cyclohexene-DA	HAB DDE															
	20	80	0	S	S	S	S	S	S	I	PS	I	I	PS	I	77.0
	50	50	0	S	S	S	S	S	S	I	PS	I	I	PS	I	71.4
	100	0	0	S	S	S	S	S	S	I	I	I	I	I	I	87.6
	20	80	40	S	S	S	S	S	S	I	S	I	I	PS	I	92.3
	50	50	100	PS	S	S	S(h)	S	S	I	PS	I	I	PS	I	100.3
	100	0	200	S(h)	S(h)	S(h)	S(h)	S(h)	S	I	PS	I	I	I	I	100.1
6FDA	HAB DDE															
	20	80	0	S	S	S	S	S	S	S	S	I	I	S	I	86.4
	50	50	0	S	S	S	S	S	S	S	S	PS	I	S	I	82.3
	100	0	0	S	S	S	S	S	S	S	PS	S	I	PS	I	82.0
	20	80	40	S	S	S	PS	S	S	S	S	I	I	S	I	87.5
	50	50	100	S	S(h)	S	PS	S	S	S	S	PS	I	S	I	101.2
	100	0	200	S	S(h)	S(h)	PS	S(h)	S	S	PS	S	I	PS	I	104.8
DSDA	HAB DDE															
	20	80	0	PS	PS	PS	PS	PS	PS	I	I	I	I	I	I	77.0
	50	50	0	PS	PS	PS	PS	PS	PS	I	I	I	I	I	I	76.2
	100	0	0	S	S	S	S	S	S	I	I	I	I	I	I	75.5
	20	80	40	S	PS	PS	S(h)	S	PS	I	I	I	I	I	I	95.9
	50	50	100	S	PS	PS	S(h)	S	PS	I	I	I	I	I	I	94.5
	100	0	200	S(h)	S(h)	S(h)	S(h)	S(h)	S(h)	I	I	I	I	I	I	101.3

^aEquimolar amount of tetracarboxylic dianhydride was used to the total amount of diamines. ^bEquimolar amount of 12GA was used to the total amount of phenolic OH groups, and the reaction was proceeded using a equimolar amount of DCC as a catalyst. ^cThe qualitative solubility was determined in the 3 mL of solvent at 5 wt% concentration. S: soluble after standing at room temperature for 12 h; S(h): soluble after heating at 70°C for 12 h; PS: partially soluble after standing at heating at 70°C for 12 h; I: insoluble even after heating at 70°C for 12 h. ^dWater contact angles (deg) using contact angle meter (CA-D, Kyowa Interface Science Co., Ltd., Japan).

4. Conclusions

The synthetic method for the novel soluble polyimides having multiple long-chain alkyl groups on their side chain is established using the polymer reaction with the polyimides having phenolic OH groups and 12GA using DCC as a dehydration catalyst. This method is an effective and a convenient method as an alternative method of the diamine synthesis containing multiple long-chain alkyl groups. The obtained polyimides bearing long-chain alkyl groups have enough molecular weights, a good film forming ability, good solubility for various organic solvents, and enough thermal stability. Remarkably, thin films of the obtained polyimides bearing long-chain alkyl groups show the high hydrophobicity, water contact angles; around 100°. As the surface of the polyimide is sometime denatured in the hydrophobicity in the field of the alignment layers of LCDs, the methods described in this study are expected to be applicable as the functional polyimide materials for microelectronics. We intend to conduct further studies on the synthesis and application of various functional polyimides such as the polyimides having long-chain alkyl substituted azobenzene

units either by the polymer reaction or the novel monomer synthesis, and these studies include the use of low molecular weight model compounds.

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