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Soluble Polyimides Containing Alicyclic Structures

Kil-Yeong Choi*, Mi Hie Yi

Advanced Materials Division, Korea Research Institute of Chemical
Technology, P.O.Box 107, Yusong, Taejon, 305-600, Korea

SUMMARY : A series of novel aromatic diamines containing kinked cycloalkane structures between two phenyl rings were synthesized by HCl-catalyzed condensation reaction of excess aniline and corresponding cycloalkanone derivatives. The structures of the diamines were indentified by ^1H NMR, ^{13}C NMR, FT-IR spectroscopy and elemental analysis. The polyimides were synthesized from the obtained diamines with various aromatic dianhydrides by one-step polymerization in *m*-cresol. The polymerization was conducted for 6~8 h with refluxing, which was enough to obtain the polymers with high molecular weight. The inherent viscosities of the resulting polyimides were in the range of 0.37~1.66 dl/g. All polymers were readily soluble in common organic solvents such as chloroform, tetrachloroethane, dimethylacetamide, etc. and the glass transition temperatures were observed at 290 to 372°C. UV-visible spectra were obtained to measure the transparency of polymer films. Most of the polymers showed high transmission above 90 % in the wavelength of 450 ~ 600 nm.

Introduction

Polyimides have been noted for their excellent characteristics such as thermo-mechanical property, electrical properties, and chemical resistance[1)]. However, wholly aromatic polyimides with rigid structure were usually insoluble and intractable, which resulted in difficulties of processability. Furthermore, it was well known that intermolecular charge-transfer complexes(CTCs) formed between the electron-rich and electron-deficient moieties of polymer chains would be caused for dark color and high dielectric constant. Therefore, significant synthetic efforts have been focused on the synthesis of soluble, colorless and processable polyimides without the sacrifice of their excellent properties. One approach was to introduce the flexible linkages like amides and ether groups, or the incorporation of bulky pendant groups[2)]. Another approaches were the incorporation of alicyclic structures into the polymer backbone reported by Kurosaki et al.[3-10)] In this study, we would like to introduce the preparation of a class of soluble polyimides with high molecular weight from several kinds of aromatic diamines containing alicyclic moieties by one step polymerization in *m*-cresol. We have prepared a series of novel aromatic diamines containing various alicyclic structures

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between two phenyl rings and synthesized the new soluble polyimides from the prepared diamines and various aromatic dianhydrides. Also, the general properties of these polymers have been studied and compared with those of conventional aromatic ones [11-12].

Experimental

Materials. *m*-Cresol was freshly distilled under reduced pressure. *N*-methyl-2-pyrrolidone (NMP) was dried over calcium hydride for 12 h and distilled under reduced pressure. Pyromellitic dianhydride (PMDA, 99.2 %, Daicel Chemical Industry, Ltd.), 3,3'4,4'-benzophenonetetracarboxylic dianhydride (BTDA, 98.6 %, Daicel Chemical Industry, Ltd.), and 3,3'4,4'-biphenyltetracarboxylic dianhydride (BPDA, 99.6%, Mitsubishi Kasei) were used without further purification, because they were of highly purified grade for polyimide synthesis. 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA, Tokyo Chemical Industry Co., Ltd., >98%) and 3,3',4,4'-tetracarboxydiphenyl oxide dianhydride(ODPA, Tokyo Chemical Industry Co., Ltd., >98%) were used as received. Aniline (Aldrich Chemical Co., Inc., 99%, bp ;184 °C), cyclohexanone (Tokyo Chemical Industry Co., Ltd., >98%, bp;157°C), 4-methylcyclohexanone (Tokyo Chemical Industry Co., Ltd., >97%, bp;171°C), 3,3,5-trimethylcyclohexanone(Tokyo Chemical Industry Co., Ltd., >98%, bp;190°C) , 4-ethylcyclohexanone (Tokyo Chemical Industry Co., Ltd., >98%), 4-t-butylcyclohexanone (Tokyo Chemical Industry Co., Ltd., >98%, mp;50°C) and 4-n-pentylcyclohexanone(Tokyo Chemical Industry Co., Ltd., >90%) were used as received.

Measurements. Infrared spectra were obtained with a Bio-Rad Digilab Division FTS-165 FT-IR spectrophotometer and All NMR spectra were taken on a Bruker AMX 500 using $CDCl_3$ or dimethyl sulfoxide-d_6 (DMSO-d_6) as solvents. UV-Vis spectra were recorded on a Shimadzu UV 2100 UV-visible spectrotometer. Mass spectra and elemental analysis were measured with Jeol JMS-DX 303 mass spectrometer and FISONS Instruments EA-1108, respectively. The inherent viscosities of polymers were measured with a Ubbelohde viscometer at a concentration of 0.5 g/dL in *m*-cresol or NMP at 30 °C. The molecular weight of polymers were measured by Waters Model 150C ALC/GPC(Gel Permeation Chromatography) equipped with μ-Styragel columns in chloroform solution at 40 °C. The melting points of the prepared monomers were determined by DSC. Thermogravimetric analysis (TGA) was done with a Perkin Elmer TGA 7 at heating rate of 20 °C/min under nitrogen atmosphere. Differential scanning calorimeter (DSC) analysis was performed on a Du Pont model 910.

Monomer synthesis[11-13)]

1,1-Bis(4-aminophenyl)cyclohexane(BACH). BACH was prepared by the condensation reaction of cyclohexanone and excess aniline as follows.[14-15)] To a solution of cyclohexanone (40.0 g, 0.41 mol) in 145 mL of 35 % HCl aqueous solution in a 1 L autoclave equipped with a mechanical stirrer was added excess aniline (156.3 g, 1.68 mol) and the mixture was stirred at 120 °C for 20 h. After cooling , the solution was made basic with NaOH aqueous solution to pH 10 and the oily layer was separated and distilled to remove the unreacted excess aniline. The residual crude product was recrystallized from benzene to afford 86.4 g (79.4 % yield) of light yellow crystal: mp 112 °C; MS m/e 266 (M+); ^{1}H-NMR δ ($CDCl_3$) 1.40(6H, bs, H-3~8), 2.06(4H, bs, H-1,2,9,10), 3.20~3.70 (4H, bs, amine protons), 6.55~6.60 (4H, d, H-12,12',13,13'), 7.00~7.03 (4H, d, H-11,11',14,14') ppm; ^{13}C-NMR δ ($CDCl_3$) 22.6(C-2,4), 26.0(C-3), 36.6(C-1,5), 43.8(C-6), 113.7(C-9,11), 127.0(C-8,12), 136.4(C-7) 145.5(C-10) ppm; FT-IR (KBr pellet) 3343, 2932, 1627, 1513, 1469, 1362, 1279, 1189 cm^{-1} ; Elemental Anal. Calcd. for $C_{18}H_{22}N_2$: C, 81.09 ; H, 8.26 ; N,10.51 , Found: C, 80.91 ; H,8.50 ; N, 10.24 %

All other diamines were prepared in the similar procedure to that of BACH with the corresponding cyclohexanone derivatives instead of cyclohexanone.

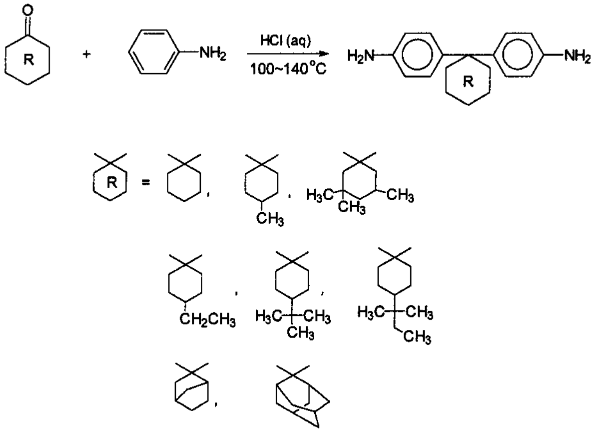
Polymer synthesis[11)]

Preparation of polyimides by chemical imidization. To a solution of BATM (5 mmol, 1.54 g) in 17.9 mL of NMP, BTDA (5 mmol, 1.61 g) was added with a solid content of 15 wt%. The solution was continuously stirred at room temperature for 24 h. To the reaction mixture were added 1.5 mL of acetic anhydride and 2.0 mL of pyridine and then the temperature was raised to 120 °C. After the reaction mixture was kept at 120 °C for 3 h, the resulting viscous solution was poured into excess methanol and filtered. The precipitated polymer was washed several times with water and methanol, and then the polymer was dried at 100 °C for 12 h in vacuo. The polymerization yield was almost quantitative.

Preparation of polyimides by one-step polymerization. To a solution of BATM (5 mmol, 1.54 g) in 19.0 mL of freshly distilled *m*-cresol, BTDA (5 mmol, 1.61 g) and isoquinoline(0.95 mL) as a catalyst were added at room temperature under nitrogen atmosphere. The reaction mixture was heated to 70~80 °C over 2 h and kept at that temperature for 2 h. And then the solution temperature was slowly raised to 200 °C over 2 h and refluxed for 6 h. The polymerization was performed under the gentle nitrogen stream to remove the water produced during imidization. The work-up process was same as the synthetic route (a).

Result and Discussions

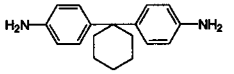
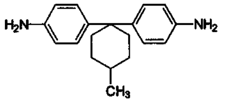
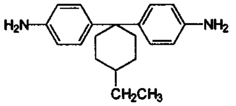
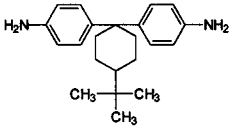
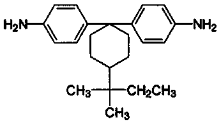
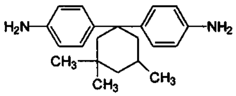
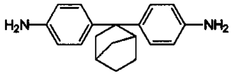
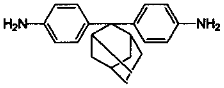
Monomer Synthesis. The synthetic route of the monomers is shown in Scheme 1. Seven kinds of new aromatic diamines containing cyclohexylidene moiety with different alkyl-substituents were synthesized by a HCl-catalyzed condensation reaction of the corresponding cyclohexanone derivatives with excess aniline in an autoclave at temperature of 100~140 °C for 20~24 h. The yields of the monomer preparation were in the range of 32.0~83.1 %. Aromatic diamines prepared from cyclohexanone or 4-alkylcyclohexanone were obtained with comparably high yields above 70 ~ 83 %. However, the yield of compounds such as BATM, BANB and BAAD were only 30 ~ 40 %. It can be explained by the steric hindrance of corresponding cyclohexanone derivatives. The addition reaction of 1st aniline proceeded from the less hindered direction of cyclohexanone derivatives, which resulted in hydroxonium intermediate[11] . However, steric hindrance of cyclohexane ring retarded the substitution reaction of 2nd aniline. This showed that the dehydration reaction occurred faster than the substitution reaction of 2nd aniline in the sterically hindered cyclohexanone derivatives like 3,3,5-trimethyl cyclohexanone. The structures of prepared monomers were characterized by FT-IR, ^{1}H- and ^{13}C-NMR spectroscopy. The results of monomer synthesis are summarized in Tab. I.

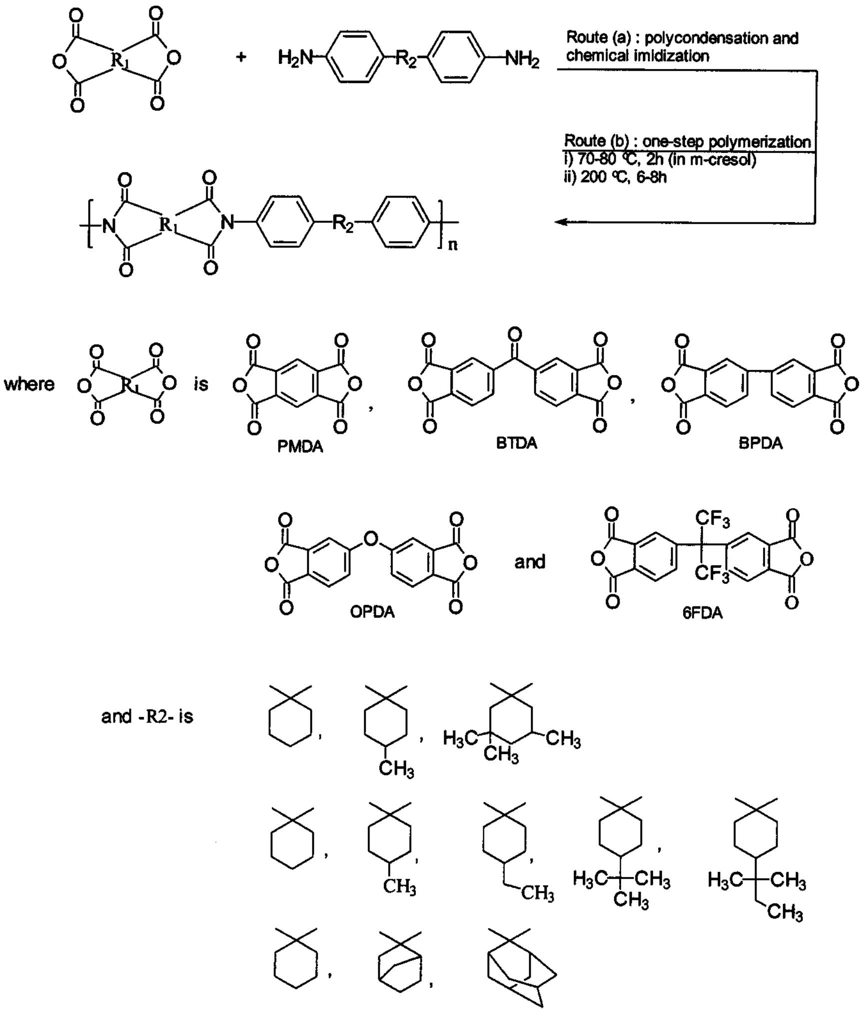


Scheme 1. Synthesis of monomers

Polymer Synthesis. For the synthesis of polyimides, two different synthetic routes were applied as shown in Scheme 2. At first, we had prepared the polyimides from BATM with aromatic dianhydrides by conventional polycondensation reaction followed by the chemical imidization using acetic anhydride and pyridine according to synthetic route (a). The inherent viscosities of the obtained polyimides were in the range of 0.55~0.68 dL/g, which might be due to the bended structure of BATM. However, one-step polymerization at high temperature as shown in synthetic route (b) could provide the enough energy even for the monomers with highly bent structure like BATM, which resulted in high viscosity as well as high molecular

Tab. I. Results of monomer synthesis

Monomer	Chemical Structures	m.p.(°C)	yield (%)
BACH		112.0	79.4
BAME		158.8	70.0
BAET		134.0	83.1
BABU		141.0	81.0
BAPE		98.0	81.0
BATM		46.0	40.0
BANB		203	35.2
BAAD		242	32.0



Scheme 2. Synthesis of polyimides

weight. The results of the polymerization are summarized in Tab. II. The inherent viscosities of polyimides obtained by one-step polymerization were in the range of 0.84~ 1.26 dL/g, which was remarkably increased as compared to those of polyimides prepared by chemically imidized two step polycondensation. Therefore, we have performed the one-step polyimidization in *m*-cresol at the temperature of 200 °C to obtain the polyimides with high molecular weights from the prepared diamines. Depending on the structure of dianhydrides, the solid contents were varied from 10 to 20 %. That is, the concentration had been kept low for the polymerization of PMDA with rigid structure to prevent the gel formation. The results of the polymerization are summarized in Tab. III. The inherent viscosities measured in *m*-cresol at 30 °C ranged from 0.37 to 1.66 dL/g. On the other hand, the relatively lower molecular weight of polyimides based on BACH resulted from their poor solubility to reaction medium. That is, polyimide(C-1) derived from BACH and PMDA was not soluble in *m*-cresol even at high temperature of 200 °C, which was precipitated out during polymerization without increasing molecular weight. The structures of the polyimides were characterized by FT-IR and ^{1}H- and ^{13}C-NMR spectroscopy. The FT-IR spectra of all polyimides exhibit the characteristic imide absorptions band in the regions of 1782, 1720 ($\nu_{C=O}$ asym. and sym. stretching, respectively), 1380-1350 (ν_{C-N}), and 750-720 (imide ring deformation) cm^{-1}.

Tab. II. Synthesis of new soluble polyimides by different synthetic routes

Polymer	Diamines[a]	Dianhydrides[b]	Polymerization Method	η_{inh} (dL/g)	GPC		
					Mn (g/mol)	Mw (g/mol)	PDI[f]
T-1	BATM	PMDA	one-step[c]	1.04	76,000[e]	129,000	1.70
T-2	BATM	BTDA	one-step[c]	1.21	87,000	133,000	1.53
T-3	BATM	BPDA	one-step[c]	1.25	74,000	132,000	1.78
T-4	BATM	ODPA	one-step[c]	1.26	92,000	159,000	1.97
T-5	BATM	6FDA	one-step[c]	0.84	91,000	142,000	1.46
T-(1)	BATM	PMDA	two-step[d]	0.68	60,000	109,000	1.82
T-(2)	BATM	BTDA	two-step[d]	0.66	38,800	89,000	2.31
T-(3)	BATM	BPDA	two-step[d]	0.56	40,000	94,000	2.32
T-(4)	BATM	ODPA	two-step[d]	0.55	44,000	74,000	1.68
T-(5)	BATM	6FDA	two-step[d]	0.55	60,000	102,000	1.70

[a] Abbreviations : BATM; 1,-Bis(4-aminophenyl)-3,3,5-trimethylcyclohexane

[b] Abbreviations : PMDA ; pyromellitic dianhydride, BTDA ; 3,3'4,4'-benzophenonetetracarboxylic dianhydride, BTDA; 3,3'4,4'-Biphenyltetracarboxylic dianhydride, ODPA; 3,3'4,4'-tetracarboxy-diphenyl oxide dianhydride, 6FDA;2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride

[c] 5.0 mmole of diamine and dianhydride were reacted in 19.0 mL of *m*-cresol at 70~80 °C for 2 h and at 200 °C for 6~8 h under nitrogen atmosphere in the presence of isoquinoline as a catalyst.

[d] Polymerization was performed with 5.0 mmol each of diamine and dianhydride in 10.5 mL of NMP at 20~25 °C for 24 h and followed by chemical imidization using Ac$_2$O/pyridine under nitrogen atmosphrene.

[e] Measured in chloroform solution at 40 °C with µ-Styragel column HT6E5E3,

[f] PDI; Poly Dispersity Index

Tab. III. Inherent viscosity (dL/g) of polyimides prepared by one-step polymerization[a]

Dianhydrides	PMDA[b]	BPDA	BTDA	6FDA	ODPA
Diamines	(1)	(2)	(3)	(4)	(5)
BACH(C)[c]	-	0.93	1.03	0.57	0.66
BAME (M)	1.18	1.31	1.58	0.89	1.02
BAET (E)	1.27	1.26	1.23	0.92	1.57
BABU(B)	0.93	1.01	0.95	0.91	1.51
BAPE(P)	1.24	1.66	1.14	1.00	0.74
BATM(T)	1.04	1.25	1.21	0.84	1.26
BANB(N)	0.88	1.02	0.92	0.59	0.90
BAAD(A)	0.37	0.44	0.52	0.34	0.49

[a] 5.0mmole of diamine and dianhydride were reacted in 19.0 mL of *m*-cresol at 70~80 °C for 2 h and at 200 °C for 6~8 h under nitrogen atmosphere in the presence of isoquinoline as a catalyst.

[b] Abbreviations : PMDA ; pyromellitic dianhydride, BTDA ; 3,3'4,4'-benzophenonetetracarboxylic dianhydride, BTDA; 3,3'4,4'-Biphenyltetracarboxylic dianhydride, ODPA; 3,3'4,4'-tetracarboxy-diphenyl oxide dianhydride, 6FDA;2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride

[c] Abbreviations : BAME;1-1-Bis(4-aminophenyl)4-methyl cyclohexane, BAET;1,1-Bis(4-aminophenyl)-4-ethylcyclohexane, BABU; 1,1-Bis(4-amino phen- yl)-4-n-butylcyclohexane, BAPE; 1,1-Bis(4-aminophenyl)-4-n-pentylcyclohexane, BATM; 1,-Bis(4-aminophenyl)-3,3,5-trimethylcyclohexane, BANB, 2,2-bis(4-aminophenyl)norbornane; BAAD, 2,2-bis(4-aminophenyl) adamantane.

Characterization of polyimides

Solubility. All of the polyimides containing subsitituted cyclohexylidene moiety prepared in this study were readily soluble in typical aprotic dipolar solvent such as NMP, dimethylacetamide(DMAc), dimethylsulfoxide (DMSO) as well as 1,1,2,2-tetrachloroethane (TCE). That is, the introduction of alicyclic structure decreased the inter-chain interaction of rigid aromatic polyimides, which resulted in the improvement of solubility. Tab. IV compared the solublility of the polyimides based on the aromatic diamines containing the methyl substituted cyclohexane ring with that of polyimide without methyl substituent. Most of the polyimides derived from BACH which has no methyl substituent were not soluble in common organic solvents. On the other hand, polyimides obtained from BATM having three methyl substituents showed the best solubility. The three methyl substitutions might decrease inter-chain interaction of rigid aromatic repeat units, resulting in the improved solubility.

Furthermore, the polyimides prepared from diamines containing the alkyl-substituted cyclohexylidene moieties or polyalicyclic structures showed good solubility to common organic solvent like chloroform. As shown in Tab. V, the solubility of polymers was improved significantly by the introduction of alkyl groups as well as the polycycloalkane structures, which might be due to the bulky structure of diamines used. And, most of polyimides could be cast into flexible, tough, and colorless films from TCE solutions.

Tab. IV. Effect of the number of the methyl substituents on the solubility

Poly-imides	Dianhydride	Diamine	Solvents						
			NMP a)	DMSO	TCE	Dioxane	THF	$CHCl_3$	Acetone
C-1	PMDA	BACH	– – b)	– –	+ +	– –	– –	– –	– –
M-1	PMDA	BAME	+ +	+ +	+ +	+ +	– –	– –	– –
T-1	PMDA	BATM	+ +	+ +	+ +	+ +	+ +	+ +	– –

a) Abbreviations : NMP, *N*-methyl-2-pyrrolidone, DMSO; dimethylsulfoxide, TCE; 1,1,2,2-tetrachloroethane, THF; tetrahydrofuran

b) Key : + + : soluble; + : soluble on heating ; + – : partially soluble ; – – : insoluble

Tab. V. Effect of the size of alkyl substituents on the solubility

Poly-imides	Dianhydride	Diamine	Solvents						
			NMP a)	DMSO	TCE	Dioxane	THF	$CHCl_3$	Acetone
C-1	PMDA	BACH	– – b)	– –	+ +	– –	– –	– –	– –
M-1	PMDA	BAME	+ +	+	+ +	+ +	– –	– –	– –
E-1	PMDA	BAET	+ +	+	+ +	+ +	+ +	+ +	– –
B-1	PMDA	BABU	+ +	+	+ +	+ +	+ +	+ +	– –
P-1	PMDA	BAPE	+ +	+	+ +	+ +	+ +	+ +	– –

a) Abbreviations : NMP, *N*-methyl-2-pyrrolidone, DMSO; dimethylsulfoxide, TCE; 1,1,2,2-tetrachloroethane, THF; tetrahydrofuran

b) Key : + + : soluble; + : soluble on heating ; + – : partially soluble ; – – : insoluble

Thermal Properites. The glass transition temperatures (Tgs) of the polyimides measured by Differential Scanning Calorimetry(DSC) were ranged from 290 to 372 °C, which was higher than that of polyimide, C-1 prepared from diamine (BACH) with non-substituted cyclohexylidene moiety. That is, the Tgs were increased by the introduction of alkyl-substituents onto cyclohexane ring. As shown in Tab. VI, it was also found that Tgs were increased with the number of methyl substituents because of the increasing restriction on the

Tab. VI. Effect of the number of methyl substituents of polyimides on the glass transition temperature(°C)[a]

Dianhydrides Diamines	PMDA	BPDA	BTDA	6FDA	ODPA
BACH	-[b]	-	305	293	290
BAME	349	355	346	306	300
BATM	-	~370(372)[c]	336(347)	323(332)	330(316)

[a] From the second heating traces of DSC measurements conducted with a heating rate of 10°C/min in nitrogen

[b] Not detectable

[c] Prepared by two-step chemical imidization

Tab. VII. Thermal properties of typical polyimides containing polyalicyclic structures

Polymers	Dianhydrides	Diamines	Tg(°C)[a]	IDT(°C)[d]	RW(%)[e]
N-1	PMDA	BANB	-	430	47.4
N-2	BPDA	BANB	-[b]	423	47.0
N-3	BTDA	BANB	347	384	47.3
N-4	6FDA	BANB	332	418	48.5
N-5	ODPA	BANB	- (327)[c]	432	46.3
A-1	PMDA	BAAD	-	472	43.2
A-2	BPDA	BAAD	- (323)[c]	463	46.8
A-3	BTDA	BAAD	363 (359)[c]	396	48.6
A-4	6FDA	BAAD	349	394	49.3
A-5	ODPA	BAAD	331	423	46.0
C-1	PMDA	BACH	-	423	44.4
C-2	BPDA	BACH	-	441	44.1
C-3	BTDA	BACH	305	405	48.4
C-4	6FDA	BACH	293	436	43.5
C-5	ODPA	BACH	290	456	42.6

[a] From the second heating traces of DSC measurements conducted with a heating a rate of 10 °C/min. under nitrogen atmosphere.

[b] Not detected.

[c] From MDSC(Modulated DSC) measurements conducted with a heating a rate of 2 °C/min. in nitrogen atmosphere.

[d] IDT : Initial decomposition temperature measured by TGA at a heating rate of 10 °C/min under nitrogen atmosphere.

[e] RW : residual weight at 800 °C

main chain rotational motion. Furthermore, as shown in Tab. VII, the Tgs of polyimides based on BAAD and BANB were higher than those of polyimides derived from BACH. That is, the incorporation of more rigid and bulky polycyclic structures restricted the free rotation of the polymer chain, which gave the higher Tgs. The thermal stabilities of polyimides were also investigated by thermogravimetric analysis(TGA) under nitrogen atmosphere.

The initial decomposition temperature of polyimides were more than 400 °C and the residual weight at 800 °C were above 30 %. Therefore, it can be concluded that the introduction of the cyclohexylidene moiety with alkyl-substituents along with the polyimide backbone improved the solubility with a retention of its high thermal stability.

Transmittance. UV-visible spectra of polymers based on BATM and various aromatic dianhydrides at a concentration of 5 x 10^{-3} mol/L in NMP solution were obtained . All the polymers showed high transmission above 90 % in the wavelength of 450~600 nm. That is, trimethylcyclohexylidene moiety increased the intermolecular chain distance and decreased the molecular interaction of the polymer chains, which resulted in good optical transparency. Especially, polyimides based on 6FDA exhibited better transparency than those of other polymer series. It can be seen that the electron conjugation of 6FDA moiety was also prohibited by the bulky trifluoromethyl structure. On the other hand, polyimides derived from PMDA showed strong absorption with a cut off between 330~ 450 nm, which was due to their electronic conjugation structure of PMDA.

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