Supporting Information

사이클로덱스트린과 다이아민, 폴리아믹산 및 폴리이미드 구조를 활용한 포접복합체 제조 및 특성 분석

최재영[*,†] · **최민기**[*,**] · **최성훈**[*] · **송원성**[*] · **김윤호**[*,†] · **원종찬**[*,†]
[*] *한국화학연구원 고기능고분자연구센터,* [**] *한양대학교 화학공학과*

Preparation and Characterization of Inclusion Complexes Using Diamine, Poly(amic acid), and Polyimide Structures with Cyclodextrin

Jaeyeong Choi[*,†], Minki Choi[*,**], Seong Hun Choi[*], Wonseong Song, Yun Ho Kim[*,†], Jong Chan Won[*,†]

[*] *Advanced Functional Polymers Research Center, Korea Research Institute of Chemical Technology (KRICT), Daejeon, 34114, Republic of Korea*

[**] *Department of Chemical Engineering, Hanyang University, Seoul, 04763, Republic of Korea*

초록 통신기술의 개발로 인해 산업에 적용하기 위한 저유전성 필름이 요구되고 있다. 이러한 저유전성을 나타내는 대표적인 폴리이미드와 고리성분인 cyclodextrin (CD)을 활용한 포접복합체 형성과 특성을 연구하기 위하여, 모노머로 사용되는 다이아민과 중합 전구체인 폴리아믹산, 그리고 폴리이미드와 CD와의 혼합을 통하여, 포접복합체의 형성을 시도하였다. 각 성분과 CD를 혼합하고 dimethyl sulfoxide (DMSO)에 용해시켜 얻어진 용액의 FT-IR 스펙트럼 분석을 통해 CD의 많은 하이드록시기(-OH)의 존재로 인한 3100 ~ 3600 cm^{-1}의 넓은 밴드와 1150 cm^{-1} 부근의 CD 특유의 C-O-C 및 C-O의 신축 진동 밴드를 확인할 수 있었다. 또한, ^{1}H NMR 스펙트럼 분석을 이용하여, 모든 용액 상에서 CD의 chemical shift를 확인하여 포접복합체의 형성을 확인할 수 있었다.

ABSTRACT Due to the development of communication technology, a low dielectric film for application to the industry is required. In order to study the formation and properties of inclusion complexes using representative polyimide exhibiting such low dielectric properties and cyclodextrin (CD) as a ring component, through mixing diamine used as a monomer for polyimide, polyamic acid as a polymerization precursor, and polyimide was attempted. In order to research the formation and properties of inclusion complex using CD as ring components, an inclusion complex was formed by mixing diamine used as a monomer for polyimide, polyamic acid as a polymerization precursor, and polyimide. Through FT-IR spectrum analysis of the solution obtained by mixing each component and CD and dissolving it in dimethyl sulfoxide (DMSO), it was possible to confirm the wide band of 3100 to 3600 cm^{-1} due to the presence of many hydroxyl groups (-OH) in CD, and the stretchable vibration band of CD specific C-O-C and C-O around 1150 cm^{-1}. In addition, using ^{1}H NMR spectrum analysis, the inclusion complex formation could be confirmed by the chemical shift of CD in all solutions.

Keywords : *polyimide, cyclodextrin, inclusion complex, host-guest interaction, supramolecular chemistry*

[†]Corresponding Author: Jaeyeong Choi, Yun Ho Kim, Jong Chan Won
E-mail: mooki93@krict.re.kr, yunho@krict.re.kr, jcwon@krict.re.kr
Tel: (+) 82-10-9960-7086, 042-861-4151

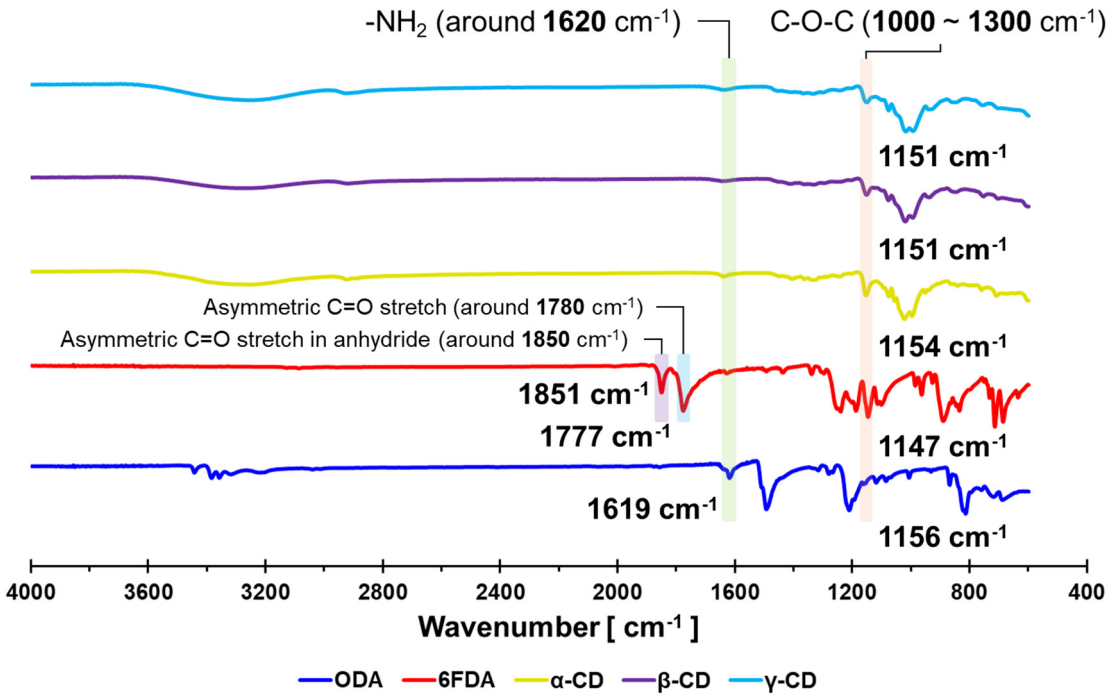

Figure S1. FT-IR spectra of elemental component in solid state.

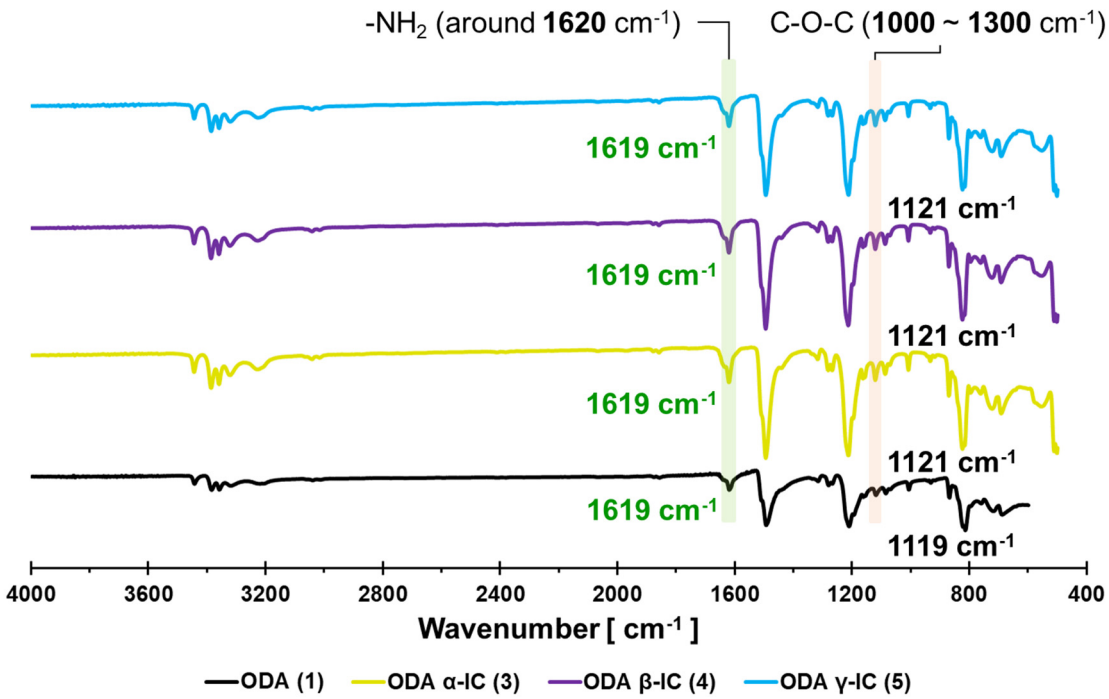

Figure S2. FT-IR spectra of ODA (**1**) and ODA CD-IC (**3** ~ **5**).

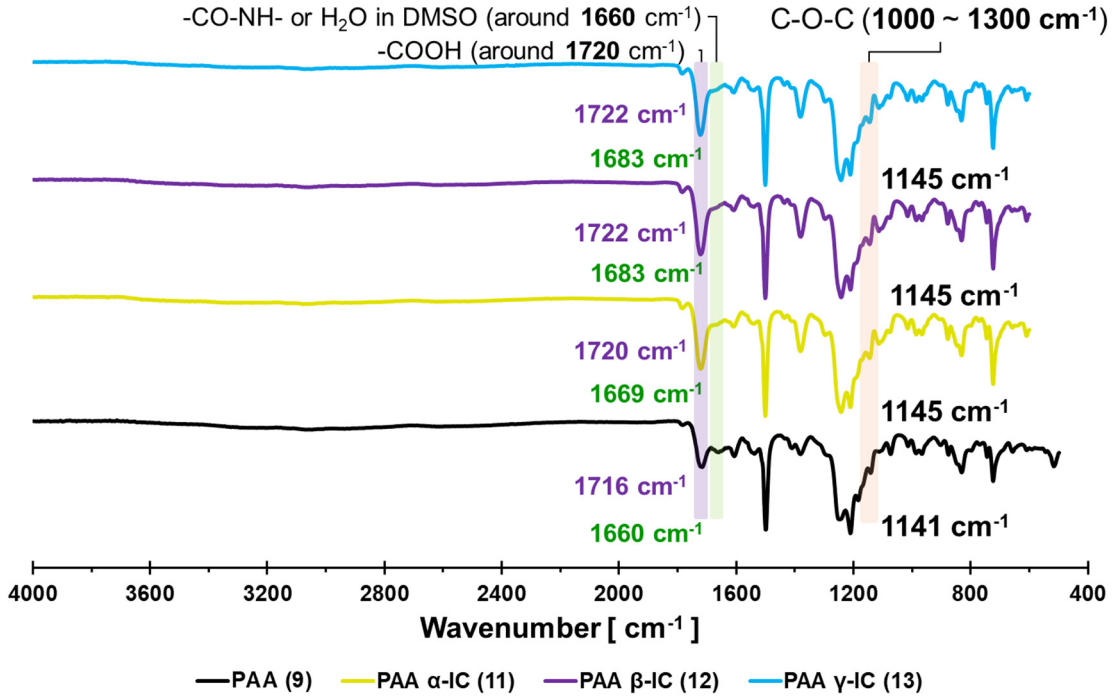

Figure S3. FT-IR spectra of PAA (**9**) and PAA CD-IC (**11** ~ **13**).

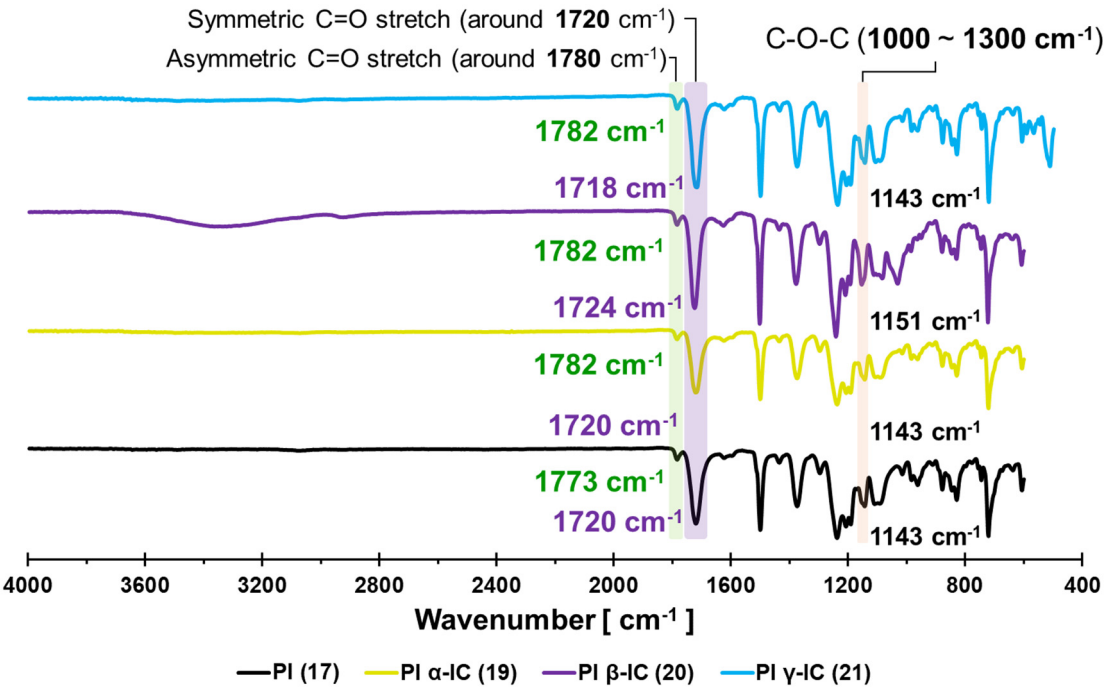

Figure S4. FT-IR spectra of PI (**17**) and PI CD-IC (**19** ~ **21**).

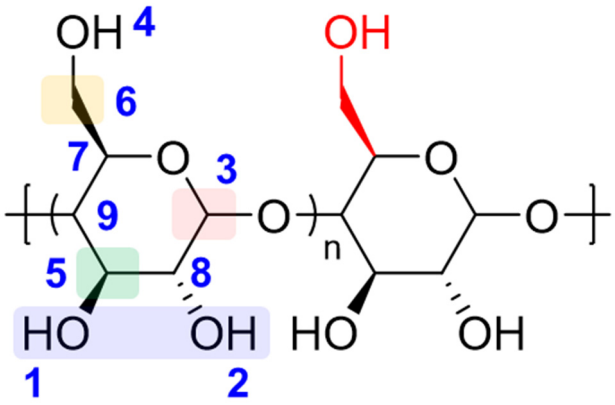

Figure S5. Chemical structure of CD and numbering representation according to H**.**

Table S1. Characteristic FT-IR bands of elemental component in solid state.

Sample	Main peaks (cm^{-1})	Assignment
ODA	1619, 1156	N–H bending (amide II), C–O–C stretching
6FDA	1851, 1777, 1147	Asym./sym. C=O stretch (anhydride)
α-CD	1154	C–O–C stretching (glycosidic bond)
β-CD	1151	C–O–C stretching (glycosidic bond)
γ-CD	1151	C–O–C stretching (glycosidic bond)

Table S2. Characteristic FT-IR bands of DMSO and CD Solution.

Sample	Main peaks (cm^{-1})	Assignment
DMSO	1619, 1156	C=O stretching (S=O)
α-CD (solution)	1662, 1149	C=O (S=O) and C–O–C stretching (glycosidic bond)
β-CD (solution)	1660, 1153	C=O (S=O) and C–O–C stretching (glycosidic bond)
γ-CD (solution)	1660, 1153	C=O (S=O) and C–O–C stretching (glycosidic bond)

Table S3. Characteristic FT-IR bands of the samples used in this study.

Sample	Main peaks (cm^{-1})	Assignment
ODA (**1**)	1619, 1119	N-H bending, C-O-C stretching
ODA Solution (**2**)	1642	N-H bending
ODA α-IC (**3**)	1619, 1121	N-H bending, C-O-C stretching
ODA β-IC (**4**)	1619, 1121	N-H bending, C-O-C stretching
ODA γ-IC (**5**)	1619, 1121	N-H bending, C-O-C stretching
ODA α-IC Solution (**6**)	1642, 1149	N-H bending, C-O-C stretching (glyosidic bond)
ODA β-IC Solution (**7**)	1646, 1153	N-H bending, C-O-C stretching (glyosidic bond)
ODA γ-IC Solution (**8**)	1642, 1153	N-H bending, C-O-C stretching (glyosidic bond)
PAA (**9**)	1716, 1660, 1141	Asym./sym. C=O (amide) stretching, C-O-C stretching
PAA Solution (**10**)	1714, 1669	Asym./sym. C=O (amide) stretching
PAA α-IC (**11**)	1720, 1669, 1145	Asym./sym. C=O (amide) stretching, C-O-C stretching (glyosidic bond)
PAA β-IC (**12**)	1722, 1683, 1145	Asym./sym. C=O (amide) stretching, C-O-C stretching (glyosidic bond)
PAA γ-IC (**13**)	1722, 1683, 1145	Asym./sym. C=O (amide) stretching, C-O-C stretching (glyosidic bond)
PAA α-IC Solution (**14**)	1718, 1667, 1149	Asym./sym. C=O (amide) stretching, C-O-C stretching (glyosidic bond)
PAA β-IC Solution (**15**)	1718, 1667, 1153	Asym./sym. C=O (amide) stretching, C-O-C stretching (glyosidic bond)
PAA γ-IC Solution (**16**)	1718, 1667, 1153	Asym./sym. C=O (amide) stretching, C-O-C stretching (glyosidic bond)
PI (**17**)	1773, 1720, 1143	Asym./sym. C=O (imide) stretching, C-O-C stretching
PI Solution (**18**)	1773, 1722	Asym./sym. C=O (imide) stretching
PI α-IC (**19**)	1782, 1720, 1143	Asym./sym. C=O (imide) stretching, C-O-C stretching (glyosidic bond)
PI β-IC (**20**)	1782, 1724, 1151	Asym./sym. C=O (imide) stretching, C-O-C stretching (glyosidic bond)
PI γ-IC (**21**)	1782, 1718, 1143	Asym./sym. C=O (imide) stretching, C-O-C stretching (glyosidic bond)
PI α-IC Solution (**22**)	1782, 1722, 1151	Asym./sym. C=O (imide) stretching, C-O-C stretching (glyosidic bond)
PI β-IC Solution (**23**)	1782, 1722, 1153	Asym./sym. C=O (imide) stretching, C-O-C stretching (glyosidic bond)
PI γ-IC Solution (**24**)	1782, 1722, 1153	Asym./sym. C=O (imide) stretching, C-O-C stretching (glyosidic bond)

Table S4. Summary of ^{1}H NMR chemical shift changes (Δδ) between free and CD-complexed samples.

Sample	Reference	$\Delta\delta_1$[a]	$\Delta\delta_2$[a]	$\Delta\delta_3$[a]	$\Delta\delta_4$[a]	$\Delta\delta_5$[a]	$\Delta\delta_6$[a]	$\Delta\delta_7$[a]	$\Delta\delta_8$[a]	$\Delta\delta_9$[a]
ODA α-IC (**3**)	α-CD	-								
ODA α-IC Solution (**6**)		0.20	0.23	0.03	-0.05	-0.10	0.01	-0.02	-0.04	0.01
PAA α-IC (**11**)		0.24		0.03	-0.06	broad region				
PAA α-IC Solution (**14**)		0.21	0.22	0.03	-0.06	-0.10	0	-0.01	-0.04	0
PI α-IC (**19**)		0.21	0.21	0.02	-0.06	broad region				
PI α-IC Solution (**22**)		0.20	0.23	0.03	-0.04	-0.10	0	-0.02	-0.04	0
ODA β-IC (**4**)	β-CD	-								
ODA β-IC Solution (**7**)		-0.21	-0.23	-0.03	0.03	0.11	-0.01	0.01	0.04	-0.03
PAA β-IC (**12**)		-0.18		-0.04	0.03	broad region				
PAA β-IC Solution (**15**)		-0.18	-0.25	-0.03	0.03	0.11	-0.01	0.01	0.04	-0.04
PI β-IC (**20**)		-0.18		-0.04	0.04	broad region				
PI β-IC Solution (**23**)		-0.20	-0.23	-0.03	0.03	0.11	-0.01	0.01	0.04	-0.02
ODA γ-IC (**5**)	γ-CD	-								
ODA γ-IC Solution (**8**)		0	0	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.03
PAA γ-IC (**13**)		0.02		-0.01	0	broad region				
PAA γ-IC Solution (**16**)		0.01	-0.02	-0.01	0	-0.01	-0.01	-0.01	0	-0.02
PI γ-IC (**21**)		0.02		-0.01	0	broad region				
PI γ-IC Solution (**24**)		0	-0.01	-0.01	-0.01	-0.02	-0.01	-0.01	0	-0.03

[a] $\Delta\delta_{H\ numbering\ of\ CD} = \delta_{H\ numbering\ of\ free\ CD} - \delta_{H\ numbering\ of\ complexed\ CD}$