

TECHNICAL REVIEW

Synthesis and properties of polyester imides based on 2,2-bis(4-hydroxyphenyl)propanedibenzoate-3,3',4,4'-tetracarboxylic acid dianhydride

Hiroyuki Furutani¹, Hiroyuki Tsuji² and Keisuke Sogabe³

Evidence for the Higgs boson, for which the Nobel Prize in physics was awarded in 2013, was discovered by the European Organization for Nuclear Research (CERN) in 2012, using the Large Hadron Collider (LHC). PIXEO BP-S exhibited superior resistance to both radiation and cryogenics and this polymer played a crucial role in the operation of the LHC, thus contributing to the Higgs boson discovery. Herein, we report the synthesis and characterization of various polyester imides for a cryogenic and radiation-resistant polyimide adhesive tape. These polyester imides (**3**) were synthesized from 2,2-bis(4-hydroxyphenyl)propanedibenzoate-3,3',4,4'-tetracarboxylic acid anhydride (ESDA) and various diamines (**1a–1f**). All polymers showed high solubility in various solvents, especially **3a**, which was synthesized from ESDA and 4,4'-bis(3-aminophenoxy)diphenyl sulfone and dissolved even in ether solvents such as dioxane and dioxolane. Dynamic mechanical analysis and X-ray diffraction studies indicated that the excluded volume of the polyester imides had a length of 150 Å, and that this volume affected the thermoplastic properties and solubilities of the polymers. The degree of imidization of **3a** dissolved in dimethyl sulfoxide was examined by ¹H-Nuclear magnetic resonance (NMR) imaging utilizing a ¹⁵N-enriched amine model compound in conjunction with ¹H-¹⁵N heteronuclear single quantum coherence 2-dimensional NMR and was found to be 99.5%.

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INTRODUCTION

In 2013, the Nobel Prize in Physics was awarded to Dr François Englert and Dr Peter W Higgs for their work on the Higgs boson.¹ Evidence for the existence of this particle had been obtained the previous year by the European Organization for Nuclear Research (CERN), using the Large Hadron Collider (LHC).²

In the late 1990s, CERN announced that the Large Electron-Positron Collider, located 100 m below ground at a site approximately 27 km from Geneva, would be replaced by the LHC as part of their efforts to discover proof of the existence of the Higgs boson shown in Figure 1. At the time, CERN had a requirement for a polyimide film and a polyimide adhesive tape with good resistance to radiation and cryogenics. In response to this requirement, 24.5 MT of a polyimide adhesive tape and 66.5 MT of a polyimide film itself were provided to CERN between 2000 and 2005.

The use of a polyimide tape that can be adhered at low temperatures and pressures on the superconducting wires was important so as to avoid quench cracking phenomenon.^{3,4} Towards this purpose, we successfully designed a series of solvent soluble thermoplastic polyester imides that could be coated on a base polyimide film. Upon wrapping of this coated film on to the cables, it exhibited good adherence when subjected to low pressure–temperature conditions. The polyimide tape was lapped on

to the superconducting strands by a 50% overlap of each winding for thorough coverage and insulation. The robust property of this material allowed it to withstand radiation (alpha particles) and exposure to cryogenic temperatures (liquid helium flow) from the collider, thus meeting all requirements set by CERN.

As a result of the contribution of the polyimide adhesive tape to the discovery of the Higgs Boson, this product has been presented with the Award of the Society of Polymer Science, Japan (2014). Herein, we report the synthesis of polyester imides for a polyimide adhesive tape, as well as the characterization of these materials.

POLYESTER IMIDES

Importance and novelty of polyester imides

Loncrini⁵ first reported the synthesis of polyester imides from 2,2-bis(4-hydroxyphenyl)propanedibenzoate-3,3',4,4'-tetracarboxylic acid anhydride (ESDA) via trimellitate acetate, bisphenol-A and various diamines in the late 1960s. Although Kurita⁶ has reviewed the subsequent progress of research into polyester imides, there have been only a few literature reports concerning the use of ESDA to date.

In the present study, the HOMO and LUMO energy levels of ESDA were calculated and compared with those of other dianhydrides. As can be seen from Table 1, it was found that the LUMO energy level of ESDA was lower than those of Da and Db (see Table 1 for the full

¹Kaneka US Material Research, Kaneka Americas Holding Inc, College Station, TX, USA; ²Electric and Electronics Material Division, Kaneka Corporation, Tokyo, Japan and ³Kaneka Techno Research Corporation, Osaka, Japan

Correspondence: Dr H Furutani, Kaneka US Material Research, Kaneka Americas Holding Inc, 800 Raymond Stotzer Pkwy, Suite #2105, College Station, 77845 TX, USA. E-mail: hiroyuki.furutani@kaneka.com

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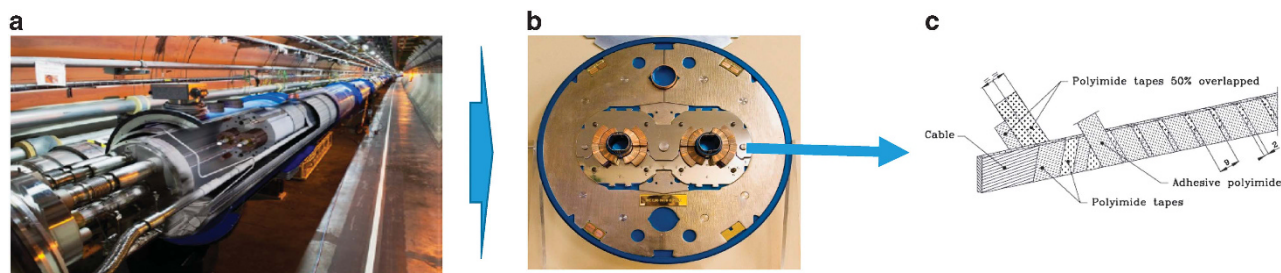


Figure 1 (a) The Large Hadron Collider at CERN (Home Page of High Energy Accelerator Research Organization (KEK), http://semrl.t.u-tokyo.ac.jp/supercom/85/85_1.html). (b) The cross section of LHC Dipole, and (c) polyimide tape lapping.

Table 1 MOPAC3 Calculation results for HOMO and LUMO orbital levels of dianhydrides

Entry	Dianhydride	HOMO (eV)	LUMO (eV)
1	PMDA	-11.668	-2.669
2	BPDA	-10.600	-2.058
3	BTDA	-11.228	-2.052
4	ODPA	-10.487	-1.942
5	ESDA	-9.624	-1.841
6	TMHQ	-10.116	-1.837
7	Da	-10.097	-1.681
8	Db	-10.196	-1.478

Abbreviations: BPDA, 3,3',4,4'-biphenyltetracarboxylic acid dianhydride; BTDA, 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride; Da, 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride; Db, 1,4-bis(3,4-dicarboxyphenoxy)butane dianhydride; ESDA, BisPhenol-A bis(trimellitate)dianhydride; ODPA, oxydiphthalic acid dianhydride; PMDA, pyromellitic acid dianhydride; TMHQ, hydroquinone bis(trimellitate)dianhydride.

names of all compounds), nearly equal to that of TMHQ, and higher than those of ODPA, BTDA, BPDA, and PMDA. It has been proposed that LUMO energy levels⁷ have a significant effect on the reactivities of dianhydrides during electrophilic attack (an S_N2 -type reaction) by diamines. Therefore, it follows that a lower LUMO energy level should result in higher reactivity. In keeping with this theory, ESDA was found to have moderate reactivity among the series of dianhydrides listed in Table 1. ESDA was thus considered as one of several potential dianhydrides for polyimide syntheses.

Syntheses of polyester imides

A series of polyester imides (**3**) were synthesized from the reaction of ESDA with various diamines (**1a–1l**) by a newly developed rapid thermal imidization method using polyamic acid intermediates (**2**). The chemical structures of the resulting polyester imides are presented in Figure 2. Each of these polymers showed high solubility in various solvents, especially **3a**, which was synthesized from 4,4'-bis(3-aminophenoxy) diphenyl sulfone and ESDA, and was soluble even in the ether solvents dioxane and dioxolane.

The imidization ratios of the polyester imides were determined by a newly developed method based on a ^1H - ^{15}N heteronuclear single quantum coherence (HSQC) 2-dimensional (2D) nuclear magnetic resonance (NMR) imaging technique utilizing a ^{15}N -enriched amine model compound.

Characteristics of polyester imides

Table 2 summarizes the solubilities of the polyester imides in various common solvents. It was found that **3a**, **3c**, **3d**, **3e** and **3f**, all of which had ether linkages, ester linkages or were meta-substituted, showed solubility in THF and some other ether solvents. Compounds **3a** and

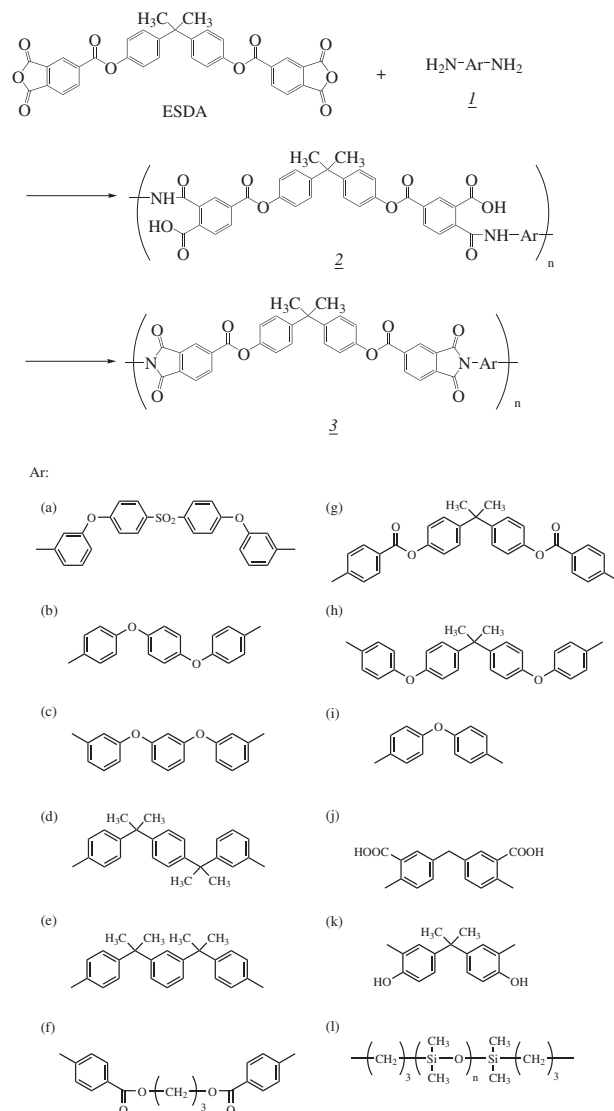


Figure 2 Chemical structures of polyester imides (**3**) derived from ESDA and various diamines (**1**).

3c were particularly soluble in dioxane and dioxolane, while **3l** was also soluble in CHCl_3 .

Casting of **3a** from a dioxolane solution generated a transparent, light yellow film with the properties summarized in Table 3.

Dynamic mechanical analysis (DMA) of the resulting polymers was also performed, and a typical DMA plot is presented in Figure 3. This

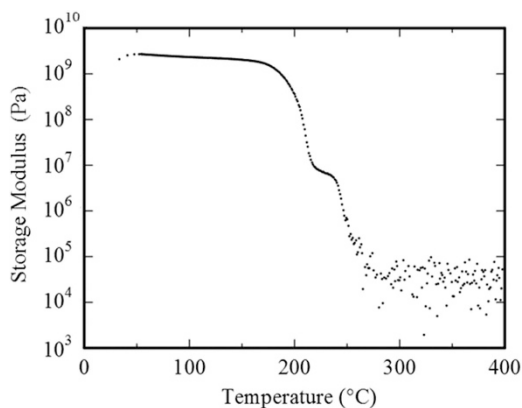
Table 2 Solubilities of polyester imides (**3**)

Polyester imide (3)	Solubility ^a								
	DMF	DMAc	NMP	DMSO	m-Cresol	CHCl ₃	THF	Dioxane	Dioxolane
3a	+	+	+	+	+	-	+	+	+
3b	+	+	+	+	+	-	+	±	±
3c	+	+	+	+	+	-	+	+	+
3d	+	±	±	±	+	-	±	±	±
3e	±	±	±	±	±	-	±	-	-
3f	±	±	±	±	±	-	±	±	±
3g	±	±	±	±	±	-	±	±	±
3h	±	±	±	±	±	-	-	-	-
3i	±	±	±	±	±	-	-	-	-
3j	NM	NM	NM	+	NM	-	-	±	±
3k	NM	NM	NM	+	NM	-	NM	±	±
3l	+	+	+	+	NM	+	NM	NM	NM

Abbreviation: NM, not measured.

^a+, soluble; ±, partially soluble or swollen; -, insoluble.Table 3 Film properties of polyester imide **3a**

Properties	Units	Method	Conditions	Values
Thickness	μm	—	20 °C	25
Elongation at break	%	ASTM D882	20 °C	62
Flexural strength	MPa	ASTM D882	20 °C	121
Flexural modulus	GPa	ASTM D882	20 °C	2.28
Water absorption	%	ASTM O-570	D-24/20	0.4
ε	—	ICP-TM-650	1 MHz, 20 °C	2.9
Density	g cm ⁻³	—	—	1.32
α	p.p.m.	TMA	20–100 °C	49
Insulation resistance	Ω cm	ASTM D257	500 V, 20 °C	> 5 × 10 ¹⁵
Thermal conductivity	cal cm ⁻¹ °C	—	—	6 × 10 ⁻⁴
Flammability	—	UL94	—	VTM-0

Figure 3 DMA curve of polyester imide **3a**.

plot shows that above its glass transition temperature (T_g) of 185 °C, the storage elastic modulus of the material (E') drops rapidly to a value of approximately 10^5 . In the temperature range above its T_g , **3a** thus exhibited excellent flow properties.

X-ray diffraction (XRD) crystalline structure analysis of ESDA was performed after obtaining a pure crystal from DMF solution. An ORTEP drawing of the ESDA repeat unit is shown in Figure 4.

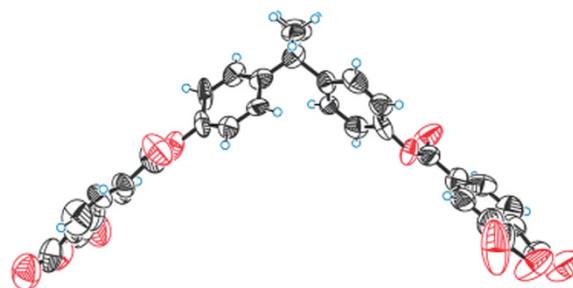


Figure 4 ORTEP drawing of an ESDA repeat unit.

The high solubility of this polyester imide can be attributed to the bent structure of its repeat units. The 3D structure of **3i**, composed of ESDA and **1i**, was calculated with Gaussian 03 HF/STO-3G using the ORTEP data for ESDA, and is shown in Figure 5.

The DMA and XRD data indicated that the excluded volume of the polyester imide was 150 Å in length, and that this volume was associated with the unique thermoplastic properties and solubility of the polymer.^{8,9} As a result, it can be said that the properties of polyester imide **3i** result from its amorphous nature.^{10,11}

The determination of imidization ratios by infrared spectroscopy measurements has been reported, although not in a quantitative manner.¹² Imidization ratios of polyimides in organic solvents have also been assessed using ¹H-NMR spectroscopy, but there are associated difficulties in confirming the N–H peak positions.¹³ Therefore, it was necessary to develop a new method to assess the degree of imidization of these polyester imides. For this purpose, **3a** was dissolved in DMSO and studied using a ¹⁵N-enriched amine model compound and ¹H–¹⁵N HSQC 2D NMR.^{14,15} In addition, a ¹⁹F-NMR method capable of elucidating the trifluoroamide-NH structures of the derivatized polymer was employed.

The chemical structure of the model compound A, composed of ESDA and aniline-¹⁵N, is shown in Figure 6, and the ¹H-NMR spectra of A in its original and its imidized forms are presented in Figures 7a and b, respectively. These spectra confirmed that the N–H peak is found at 10.5 p.p.m. and the COO–H peak at 13.5 p.p.m. The ¹H–¹⁵N HSQC spectrum of compound A is given in Figure 7c. From this, the N–H peak of compound A was found to appear at 10.4–10.6 p.p.m.

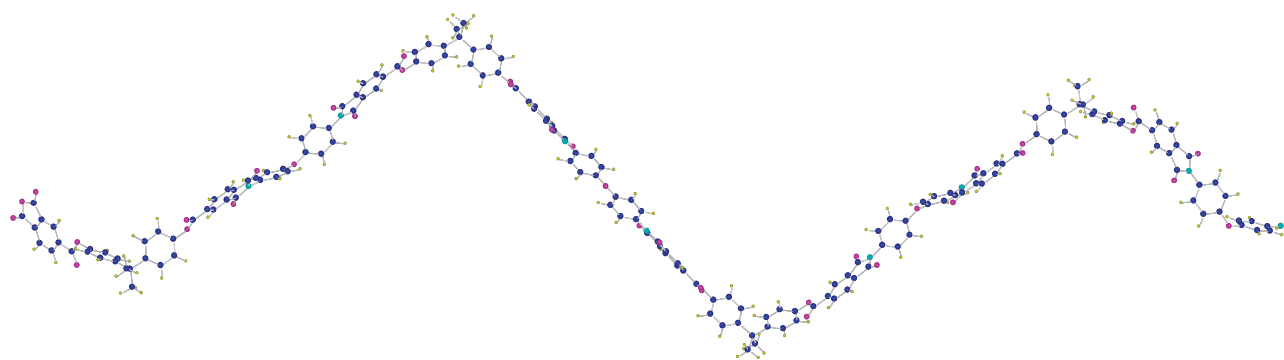


Figure 5 3D structure of the polyester imide from ESDA data.

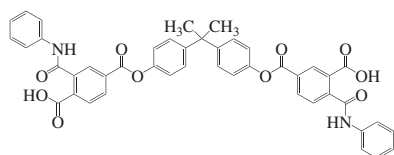


Figure 6 Chemical structure of model compound A composed of aniline- ^{15}N and ESDA.

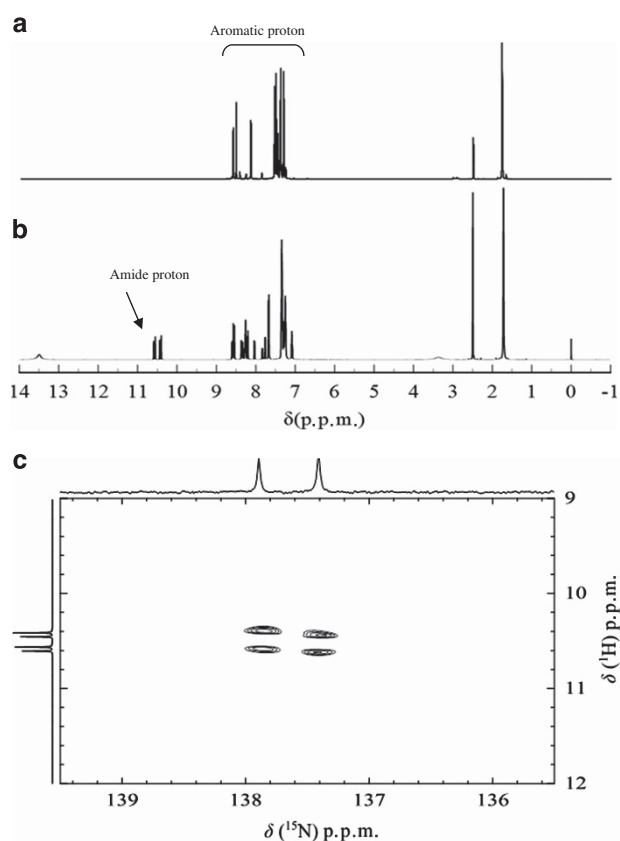


Figure 7 ^1H -NMR spectra of (a) the imidized form of model compound A, (b) the model compound A, and (c) the ^1H - ^{15}N HSQC spectrum of A in $\text{DMSO}-d_6$.

The ^1H -NMR spectrum of **3a** is shown in Figure 8.

In Figure 8, an N-H peak is observed at 10.5 p.p.m. and the protons of the aromatic group appear from 7 to 9 p.p.m.

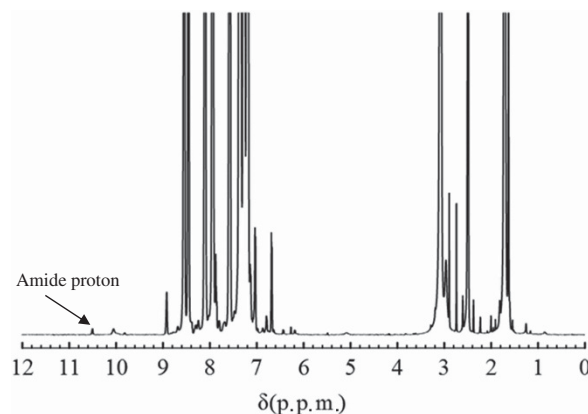


Figure 8 ^1H -NMR spectrum of **3a** in $\text{DMSO}-d_6$.

From these data, the imidization ratio of **3a** was calculated using Equation (1).

$$\text{Imidization ratio}(\%) = 100 \times \left\{ 1 - \left[\left(\frac{A_{\text{am}}}{2} \right) / \left(\frac{A_{\text{ar}}}{30} \right) \right] \right\} \quad (1)$$

Here A_{am} and A_{ar} represent the integration values of the N-H and aromatic protons. Based on Figure 8 and Equation (1), the imidization ratio of **3a** was determined to be 99.5%.

CONCLUSION

Evidence for the existence of the Higgs boson, for which the Nobel Prize in Physics was awarded in 2013, was discovered by CERN in 2012, using the LHC. During this work, a polyester imide having both high radiation resistance and superior cryogenic properties, was adopted as the superconducting magnet insulation adhesive tape within the LHC. In this study, we synthesized various polyester imides, including **3a**, and examined the properties of these polymers. Recently, in 2013, it was further confirmed during a maintenance and repair process of LHC that the PIXEO BP-S polyimide adhesive tape still retained its radiation and cryogenic temperature resistance as same as when it was received.¹⁶

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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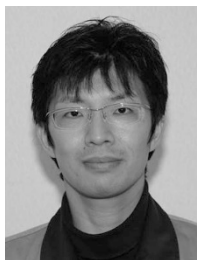
- 1 Sogabe, K., Miyauchi, M., Kikuchi, T., Tsuji, H., Ida, J. & Furutani, H. Characteristics of polyesterimides consisting of 2,2-Bis(4-hydroxyphenyl)propane-dibenzoate-3,3',4,4'-tetracarboxylic acid anhydride (ESDA) and various diamines. *Kobunshi Ronbunshu* **70**, 647–654 (2013).
- 2 Nihon Syoken Shinbun (Evening Edn, 15 October 2013).
- 3 Fessia, P., Kummer, H., Kuribayashi, H., Tommasini, D. & Van de Velde, F. Curing of LHC main dipole coils insulated with all polyimide PIXEO_ adhesive tape. *IEEE Trans. Appl. Sup.* **16**, 1782–1785 (2006).
- 4 LHC Project Document No. LHC-VCX-AP-0001 (2002).
- 5 Loncrini, D. F. Aromatic polyesterimides. *J. Polym. Sci.* **4**, 1531–1541 (1966).
- 6 Kurita, K. *Polymer Applications* **37**, 74–78 (1988).
- 7 Furutani, H., Ida, J., Tanaka, K. & Nagano, H. Novel soluble ethynyl-terminated ester-imide prepolymers: their syntheses and characteristics. *High Perf. Polym.* **12**, 461–469 (2000).
- 8 Stewart, J. J. P. MOPAC version 6.0 (QCPE #455).
- 9 Hirano, T. MOPAC version 6.01 (JCPE P049).
- 10 Miyauchi, M. Development of novel asymmetric and addition-type imide resin with high solubility and excellent processability. *Kobunshi Ronbunshu* **69**, 580–587 (2012).
- 11 Furutani, H. in *Proceedings 21st Japan polyimides and aromatic polymers conference, recent progress of polyimides*, 29–32 (Tokyo, 2013).
- 12 Karamanchevaa, V., Stefov, B., Šoptrajanov, D. G., Spasovad, E. & Assad, J. FTIR spectroscopy and FTIR microscopy of vacuum-evaporated polyimide thin films. *Vib. Spectrosc.* **19**, 369–374 (1999).
- 13 Matsuura, T., Hasuda, Y., Nishi, S. & Yamada, N. Polyimide derived from 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl. 1. Synthesis and characterization of polyimides prepared with 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride or pyromellitic dianhydride. *Macromolecules* **24**, 5001–5005 (1991).
- 14 Bodenhausen, G. & Ruben, D. Natural abundance nitrogen-15 NMR by enhanced heteronuclear spectroscopy. *J. Chem. Phys. Lett.* **69**, 185–189 (1980).
- 15 Grzesiek, S. & Bax, A. The importance of not saturating water in protein NMR. Application to sensitivity enhancement and NOE measurements. *J. Am. Chem. Soc.* **115**, 12593 (1993).
- 16 Rossi, L. in *Cryogenics and Superconductivity Society of Japan's Presentation* (University of Kyoto, 2013).



Dr Hiroyuki Furutani was born in Okayama, Japan, in 1961. He received his BS, MS, and PhD degrees in engineering from Okayama University in 1985, 1987 and 2001, respectively. He joined Kaneka Corporation in 1987. His main responsibility was new polyimide materials research for over 20 years. He was a Visiting Scientist at the University of Akron Ohio, USA from 1990 to 1991. He is an author of *ca.* 30 original papers and oral presentations, and *ca.* 200 patent applications. He received three Technical Awards, 45th Technical Award for Chemistry, Kinki Chemical Society, Japan, in 1992; 46th Annual JCIA Technology Award, Grand Prize, Japan Chemical Industry Association (JCIA), Japan, in 2014; and 47th ICHIMURA Industrial Award, The New Technology Development Foundation, Japan in 2015. He was also a recipient of the Award of the Society of Polymer Science, Japan, in 2015.



Mr Hiroyuki Tsuji was born in Fukuoka, Japan, in 1968. He received his BS and MS degrees in agriculture from Okayama University in 1990 and 1992, respectively. He joined Kaneka Corporation in 1992. He is now the technical manager of the Electric & Electronics Department. He received 46th Annual JCIA Technology Award, Grand Prize, Japan Chemical Industry Association (JCIA), Japan, in 2014; and 47th ICHIMURA Industrial Award, The New Technology Development Foundation, Japan, in 2015. He was also a recipient of the Award of the Society of Polymer Science, Japan, in 2015.



Dr Keisuke Sogabe was born in Aichi, Japan, in 1972. He received his BS and MS degrees in engineering from Nagoya Institute of Technology in 1995 and 1997, respectively. He joined Kaneka Corporation in 1997. He received his PhD degree in engineering from Tokushima University in 2014. His main responsibilities have been composition analysis and NMR analysis of organic material for over 18 years. He is now the group leader of the analysis department of Kaneka Techno Research Corporation. He was also a recipient of the Award of the Society of Polymer Science, Japan, in 2015.