

Refractive Index Modulation by Photo-Fries Rearrangement of Main Chain-Type Aromatic Polyurethanes

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Aromatic polyurethanes were prepared from aromatic diisocyanates and dialcohol, and their photoreaction properties and concomitant refractive index change was investigated. Time-course UV–vis spectroscopy of the polyurethanes films under 254 nm irradiation showed clear spectral transition with an isosbestic point, indicating that selective photoreaction proceeded. FT-IR spectra of the irradiated aromatic polyurethanes films showed a consistent change to the targeted photo-Fries rearrangement. Ellipsometry revealed refractive index increase up to +0.0411 after the irradiation of the films for 60 min, presenting the good potential of aromatic polyurethanes as the functional moieties toward various optical materials that require photo-modulation of refractive index.

Keywords: Polyurethane, Refractive index change, Photo-Fries rearrangement, Film

1. Introduction

Polymeric materials capable of controlling their refractive indices (n) are of much interest, especially for the application to various optical materials such as optical switches and waveguides [1]. One of the efficient strategies to design those materials is utilization of functional molecular units that can undergo specific reactions accompanying a change in the ratio of molecular refraction $[R]$ versus molecular volume V that determines refractive index, according to the Lorentz–Lorenz equation (1) [2].

$$\frac{n^2 - 1}{n^2 + 2} = \frac{[R]}{V} \quad (1)$$

Particularly, isomerization and rearrangement reactions are useful classes of reactions for such purpose since they generally undergo variation of functionalities and/or saturation degree of bonds, leading to the change of molecular refraction. Horie and coworkers have reported refractive index decrease of a polyamide via photo-isomerization of norbornadiene to quadricyclane in the main chain with Δn of -0.006 [3], followed by

several improved norbornadiene derivatives that show Δn of up to -0.058 [4]. Afterward, Nishikubo and coworkers have reported photo-induced refractive index decrease of various ladder polysilsesquioxanes based on isomerization of norbornadiene (Δn : -0.073), *trans*–*cis* isomerization of azobenzene (Δn : -0.009), and dimerization of anthracene (Δn : -0.116) [5]. On the other hand, Kahn *et al.* have reported refractive index increase systems by photo-isomerization of thiocyanate to isothiocyanate in the polystyrene side chain to achieve Δn of $+0.03$ [6]. The same group has also reported refractive index increase of polyolefins via photo-Fries rearrangement of aromatic esters [7] and amides [8] in the side chains with Δn of $+0.07$ and $+0.1$, respectively, although some minor side reactions was also reported to accompany. Besides these photo-reaction systems, our group has previously reported refractive index increase by the thermal rearrangement reactions of *S*-(2-benzoxazolyl) thioester to 3-acylbenzoxazoline-2-thione (Δn : $+0.012$) [9] and triarylcyanurate to isocyanurate derivatives (Δn : $+0.051$) [10].

As another candidate of functional moieties for refractive index modulation, we focus on aromatic urethane structure that is known to undergo photo-Fries rearrangement [11]. In our previous study, we have demonstrated the domino-decomposition of a specifically designed aromatic polyurethane main chain in the block copolymer [11d], induced by the photo-Fries rearrangement of the polyurethane moiety. On the other hand, the Fries rearrangement of aromatic urethane produces aromatic amino group that possess high molecular refraction [12] and thus would lead to the increase of refractive index. However, to the best of our knowledge, the refractive index change through the photo-Fries rearrangement of urethane structure has not yet been reported despite the commonness and wide use of urethane motif. In this work, we prepared aromatic polyurethanes by polyaddition reaction using aromatic diisocyanates, and investigated their photoreaction behavior and photo-modulation of the refractive index.

2. Experimental

2.1. Materials

All solvents and reagents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Tokyo Chemical Industry (TCI), or Kanto Chemical, and used as received unless otherwise noted. DMSO was dried over CaSO_4 and distilled under reduced pressure before use.

2.2. Measurements

IR spectra were measured with JASCO Inc. FT/IR4600 spectrometer. ^1H -NMR measurements were carried out at 298 K with $\text{DMSO-}d_6$ solvent on a JEOL JNM-ECA-500 instrument at 500 MHz. UV-vis spectra were recorded on JASCO Inc. V-650 spectrometer. Number- and weight-average molecular weights (M_n and M_w) were determined by gel permeation chromatography (GPC) with Tosoh HLX8220 using RI detectors calibrated with polystyrene standards, using DMF solution of 10 mM LiBr and 10 mM phosphoric acid as the eluent at a flow rate of 1 mL/min. Differential scanning calorimetry (DSC) analysis were performed on a Seiko EXSTAR DSC 6200 at heating and cooling rate of 10 $^\circ\text{C}/\text{min}$ under N_2 flow. The refractive index and thickness of polymer films were determined by ellipsometry (DHA-OLX/S4, 633 nm, Mizojiri Optical Co. Ltd.).

2.3. Synthesis of P-1

Representative procedure is as follows: To a 50

mL flask were added methylenediphenyl 4,4'-diisocyanate (MDI, 1.79 g, 6.79 mmol) and 1,4-bis(hydroxymethyl)benzene (HMB, 0.966 g, 6.93 mmol), followed by DMSO (7.0 mL, 2.0 mol/L) and dibutyltin dilaurate (DBTDL, 0.0880 g, 0.139 mmol). The mixture was stirred under nitrogen atmosphere at room temperature for 24 h. After a few drops of methanol were added to quench the reaction, the product was reprecipitated in a mixed solvent of methanol and acetone (5/2, v/v). The precipitate was filtered, washed with methanol, and dried under reduced pressure at 75 $^\circ\text{C}$ to afford a white solid (1.96 g, 72%). ^1H -NMR (500 MHz, $\text{DMSO-}d_6$) δ (ppm): 9.64 (s, 2H), 7.41 (s, 4H), 7.34 (d, $J = 7.0$ Hz, 4H), 7.07 (d, $J = 7.0$ Hz, 4H), 5.11 (s, 4H), 3.77 (s, 2H). FT-IR (KBr, cm^{-1}): 3319 ($\nu_{\text{N-H}}$), 3030 ($\nu_{\text{C-H, Ar}}$), 2940 ($\nu_{\text{C-H, alkyl}}$), 1708 ($\nu_{\text{C=O}}$), 1596 ($\nu_{\text{C=C}}$), 1525 ($\nu_{\text{amide II}}$), 1052 ($\nu_{\text{C-O}}$).

2.4. Synthesis of P-2

P-2 was synthesized in the same manner as PU-1 using tolylene-2,4-diisocyanate (TDI), HMB, DMSO, and DBTDL and obtained as a white solid. ^1H -NMR (500 MHz, $\text{DMSO-}d_6$) δ (ppm): 9.66 (s, 1H), 8.92 (s, 1H), 7.52 (s, 1H), 7.41 (s, 4H), 7.14 (d, $J = 8.3$ Hz, 1H), 7.04 (d, $J = 8.3$ Hz, 1H), 5.11 (s, 4H), 2.09 (s, 3H). FT-IR (KBr, cm^{-1}): 3301 ($\nu_{\text{N-H}}$), 3022 ($\nu_{\text{C-H, Ar}}$), 2948 ($\nu_{\text{C-H, alkyl}}$), 1706 ($\nu_{\text{C=O}}$), 1597 ($\nu_{\text{C=C}}$), 1528 ($\nu_{\text{amide II}}$), 1051 ($\nu_{\text{C-O}}$).

2.5. Photo-irradiation experiment

All sample films were prepared by spin-casting of polyurethane solution on a fused silica plate for UV-vis, KBr plate for FT-IR, or Si wafer for refractive index measurement. Irradiation was performed using a xenon lamp (Asahi Spectra MAX-302) equipped with a band-pass filter at 254 nm with the intensity of 1.75 mW/cm².

3. Results and discussion

3.1. Synthesis and characterization of aromatic polyurethanes

Since photo-Fries rearrangement of *O*-aromatic urethanes afford *O*-aromatic esters that can further undergo another photo-Fries rearrangement, we chose HMB as the aromatic diol monomer to avoid the secondary rearrangement. We prepared two aromatic polyurethanes P-1 and P-2 by the polyaddition reaction using equimolar amount of HMB and MDI (for P-1) or TDI (for P-2) in the presence of DBTDL catalyst in DMSO solvent (Scheme 1, Table 1). IR spectra of P-1 and P-2

showed the N-H and C=O groups of urethane bond at around 3300 cm^{-1} and 1710 cm^{-1} , respectively, indicative of urethane bond formation. $^1\text{H-NMR}$ spectra of P-1 and P-2 were fully consistent to the corresponding structures (Fig. 1). GPC measurement confirmed the formation of polymeric structures of P-1 and P-2. DSC analysis of P-1a (M_n : 38,000, M_w/M_n : 1.71) showed no T_g in the region less than $250\text{ }^\circ\text{C}$, while P-2c (M_n : 18,700, M_w/M_n : 2.49) showed its T_g at $138\text{ }^\circ\text{C}$. Furthermore, P-1a dissolved only in aprotic polar solvents such as NMP, DMSO, and DMAc and did not dissolve in protic solvents and less polar solvents, whereas P-2c fully dissolved in THF and 1,4-dioxane in addition to P-1a-soluble solvents. These results suggest that the interchain interaction of P-1 is much stronger than P-2, plausibly because of the good linearity of P-1 with all para-substituted aromatic rings that would help hydrogen bonding and π - π stacking between the polymer main chains. On the other hand, P-2 possesses the less-symmetric TDI moiety with CH_3 group and meta-positioned two urethane bonds, which may hinder the close stacking of the polymer main chains.

3.2. Investigation of the photo-Fries rearrangement of the aromatic polyurethanes

The photo-reactivity of the obtained aromatic polyurethanes was evaluated by time-course UV-vis spectroscopy. To suppress the side reactions induced by the intermediate radical diffusion [13], we carried out the photoreaction experiments in the

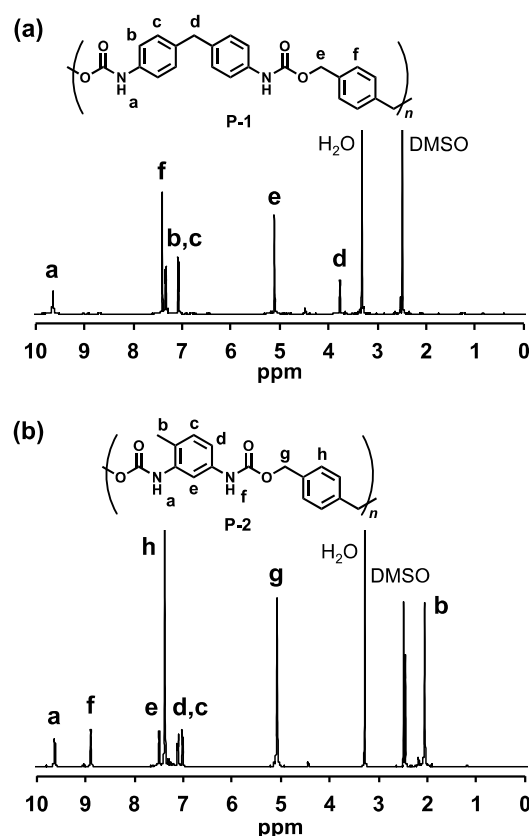
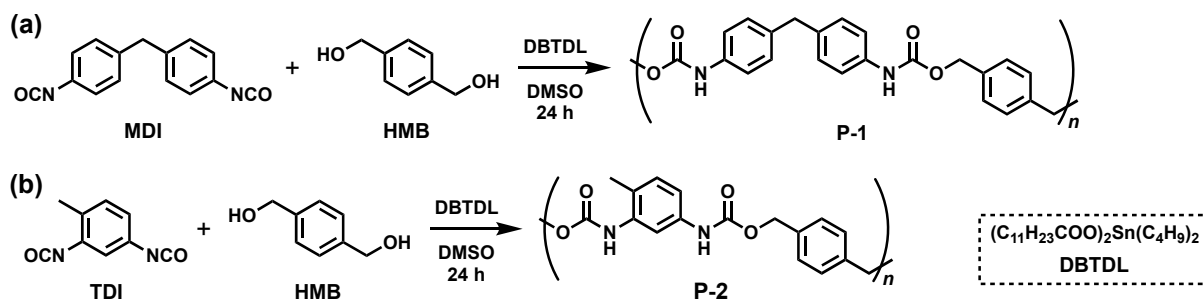


Fig. 1. Representative $^1\text{H-NMR}$ spectra of aromatic polyurethanes (a) P-1a and (b) P-2c.

film state. When irradiated at 254 nm , the UV-vis spectra of P-1a and P-2c films on fused silica plates showed decrease of the absorption at λ_{max} and increase of the absorbance at longer wavelength region (Fig. 2). Importantly, the existence of an isosbestic point in the each spectrum strongly



Scheme 1. Synthetic schemes of aromatic polyurethanes (a) P-1 and (b) P-2.

Table 1. Synthetic conditions and results of the aromatic polyurethanes

Polymer	Diisocyanate (eq.)	DBTDL (mol%)	DMSO (mol/L)	Temp. ($^\circ\text{C}$)	Yield (%)	M_n^a	M_w/M_n^a	$T_g^{b,c}$ ($^\circ\text{C}$)
P-1a	MDI (1.02)	2.15	1.96	rt	72	38,000	1.71	$>250^c$
P-1b	MDI (1.02)	2.18	1.88	60	94	12,800	1.54	—
P-1c	MDI (1.04)	2.33	1.95	80	72	57,900	2.14	—
P-2a	TDI (1.00)	2.14	1.98	rt	67	13,300	3.77	—
P-2b	TDI (1.05)	1.33	1.00	rt	81	15,800	3.35	—
P-2c	TDI (1.04)	1.02	0.973	60	56	18,700	2.49	138

^a) Estimated by GPC (RI) using polystyrene as the standard. ^b) Determined by DSC. ^c) Not observed in the range of -20 to $250\text{ }^\circ\text{C}$.

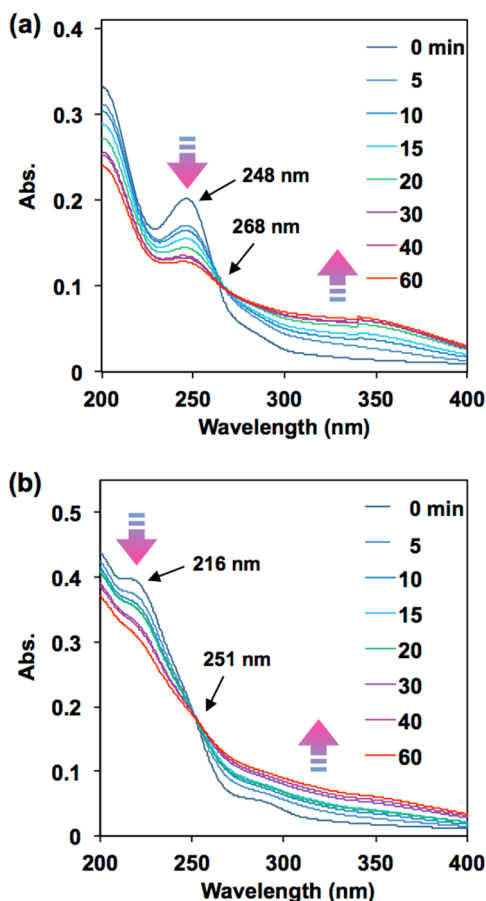


Fig. 2. UV-vis spectral change of (a) P-1a and (b) P-2c films during the photo-irradiation at 254 nm.

suggests that selective photoreaction proceeded without side reactions such as secondary photo-Fries rearrangement, as was aimed in advance. We next examined the structural characterization with FT-IR spectroscopy of the P-1a film prepared on a KBr plate. Although the FT-IR spectral change by the 254 nm irradiation for 60 min was somehow not as clear as the UV-vis, decrease of absorption at 1730 cm^{-1} (C=O), 1538 cm^{-1} (C(O)NH, Amide II), and 1220 cm^{-1} (C(O)NH, Amide III) that derive from urethane bond and increase at 3368 cm^{-1} of N-H (Fig. 3) were consistent with the expected structural changes induced by the photo-Fries rearrangement (Scheme 2), and thus suggests proceeding of the targeted photoreactions.

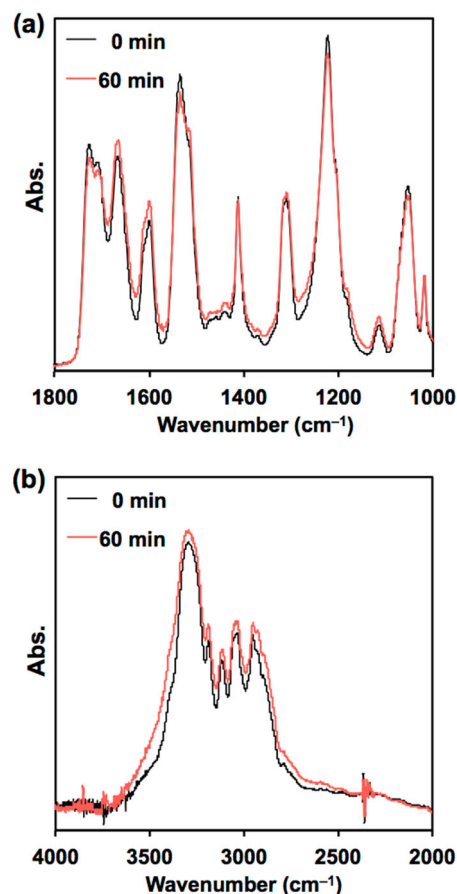
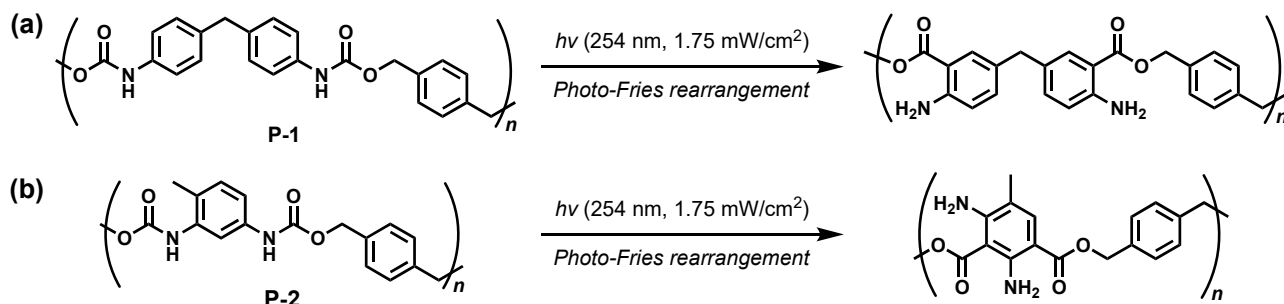


Fig. 3. Representative FT-IR spectra of aromatic polyurethane (P-1a) in the film state before and after photo-irradiation at 254 nm for 60 min.

3.3. Investigation of photo-induced refractive index change of the aromatic polyurethanes

The refractive index change of the aromatic polyurethanes was investigated using ellipsometry technique. The P-1a and P-2c films (thickness: *ca.* $0.1\text{ }\mu\text{m}$) prepared on Si wafers were irradiated at 254 nm, and their refractive indices and film thicknesses were measured. As a result, the both films showed increase of the refractive index as the irradiation (Fig. 4), and the Δn of P-1a and P-2c were up to +0.0411 and +0.0358, respectively, after 60 min (Table 2). These increases can be attributable to the formation of polar aromatic amino groups via photo-Fries rearrangement,



Scheme 2. Ideal reaction schemes of photo-Fries rearrangement of (a) P-1 and (b) P-2.

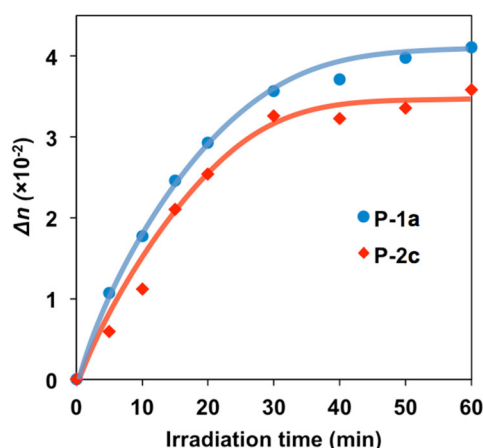


Fig. 4. Refractive index increase of P-1a and P-2c during photo-irradiation at 254 nm.

Table 2. Refractive indices of P-1a and P-2c^{a)}

Polymer	$n_{\text{before}}^b)$	$n_{\text{after}}^b)$	$\Delta n^c)$	$\Delta \text{Thick-ness (\%)}$
P-1a	1.6024	1.6435	+0.0411	−8.0
P-2c	1.5850	1.6208	+0.0358	−11.3

^{a)} Film thickness is ca. 0.1 μm . ^{b)} Refractive index at 633 nm before and after photo-irradiation at 254 nm ($1.75 \text{ mW}/\text{cm}^2$) for 60 min. ^{c)} $\Delta n = n_{\text{after}} - n_{\text{before}}$.

leading to the increase in the molecular refraction $[R]$. Herein, we also observed the decrease of the film thickness (P-1a: −8.0%, P-2c: −11.3%) after the irradiation for 60 min. This indicates the decrease of the film volume V , which would also contribute to the refractive index increase induced by the photo-Fries rearrangement of the aromatic polyurethanes [14].

4. Conclusion

In this work, we presented refractive index increase of aromatic polyurethanes induced by photo-Fries rearrangement. We prepared aromatic polyurethanes by the polyaddition reactions using aromatic diol HMB and aromatic diisocyanates MDI for P-1 and TDI for P-2 in the presence of DBTDL catalyst. UV-vis and FT-IR spectroscopy of the polyurethane films indicated that selective photo-Fries rearrangement proceeded under 254 nm irradiation. Ellipsometry of the polyurethane films before and after the photo-irradiation revealed that the refractive index increased up to 0.0411 through the photo-rearrangement reaction. Since urethane is one of the most commonly used structures in polymeric materials, the methodology of refractive index modulation developed herein would be promising as a versatile strategy in a broad range of polymeric materials.

References

1. H. Ma, A. K.-Y. Jen, and L. R. Dalton, *Adv. Mater.*, **14** (2002) 1339.
2. G. H. Meeten, "Optical Properties of Polymers", Elsevier Applied Science, London, 1989.
3. S. Morino, T. Watanabe, Y. Magaya, T. Yamashita, K. Horie, and T. Nishikubo, *J. Photopolym. Sci. Technol.*, **7** (1994) 121.
4. Y. Kato, H. Muta, S. Takahashi, K. Horie, and T. Nagai, *Polym. J.*, **33** (2001) 868.
5. H. Kudo, M. Yamamoto, and T. Nishikubo, *Macromolecules*, **39** (2006) 1759.
6. G. Langer, T. Kavc, W. Kern, G. Kranzelbinder, and E. Toussaere, *Macromol. Chem. Phys.*, **202** (2001) 3459.
7. (a) U. Daschiel, T. Höfler, G. Jakopic, V. Schmidt, and W. Kern, *Macromol. Chem. Phys.*, **208** (2007) 1190. (b) T. Höfler, T. Grießer, X. Gstrein, G. Trimmel, G. Jakopic, and W. Kern, *Polymer*, **48** (2007) 1930. (c) T. Griesser, T. Höfler, G. Jakopic, M. Belzik, W. Kern, and G. Trimmel, *J. Mater. Chem.*, **19** (2009) 4557. (d) T. Köpplmayr, M. Cardinale, G. Jakopic, G. Trimmel, W. Kern, and T. Griesser, *J. Mater. Chem.*, **21** (2011) 2965. (e) M. Edler, S. Mayrbrugger, A. Fian, G. Trimmel, S. Radl, W. Kern, and T. Griesser, *J. Mater. Chem. C*, **1** (2013) 3931.
8. T. Griesser, J.-C. Kuhlmann, M. Wieser, W. Kern, and G. Trimmel, *Macromolecules*, **42** (2009) 725.
9. M. Miyasaka, A. Higurashi, and A. Kameyama, *Chem. Lett.*, **40** (2011) 1363.
10. K. Tsuchiya, Y. Ishida, K. Higashihara, A. Kameyama, and M. Ueda, *Chem. Lett.*, **44** (2015) 1110.
11. (a) C. Wilhelm, A. Rivaton, and J. -L. Gradette, *Polymer*, **39** (1998) 1223. (b) L. Irusta and M. J. Fernandez-Berridi, *Polymer*, **40** (1999) 4821. (c) K. H. Chae, U. C. Yang, and M. K. Lee, *Polymer*, **55** (2014) 2362. (d) Y. Ishida, Y. Takeda, and A. Kameyama, *React. Funct. Polym.*, **107** (2016) 20.
12. J. A. Dean, "Lange's Handbook of Chemistry, 15th ed.", McGraw-Hill, 1998.
13. S. Koodanjeri, A. R. Pradhan, L. S. Kaanumalle, and V. Ramamurthy, *Tetrahedron Lett.*, **44** (2003) 3207.
14. A. Nagata, T. Sakaguchi, T. Ichihashi, M. Miya, and K. Ohta, *Macromol. Rapid Commun.*, **18** (1997) 191.