

Synthesis and Optoelectronic Properties of Novel Polyamides with *N,N'*-Di-2-naphthyl-*N,N'*-diphenyl-1,4-phenylenediamine Units

NSC 100-2221-E-027-025

Su-Jung Yeh (葉素蓉), Hui-Min Wang (王惠民), Sheng-Huei Hsiao (蕭勝輝)*

Department of Chemical Engineering and Biotechnology, National Taipei University of Technology

(國立臺北科技大學化學工程與生物科技系)

E-mail: shhsiao@ntut.edu.tw

Abstract

A new series of electroactive polyamides were synthesized from *N,N'*-bis(4-aminophenyl)-*N,N'*-di-2-naphthyl-1,4-phenylenediamine (**2**) with four dicarboxylic acids via the phosphorylation polyamidation technique. These polyamides were amorphous with good solubility in many organic solvents and could be solution-cast into flexible and strong films. They exhibited moderately high thermal stability with glass transition temperatures in the range of 247-289 °C. The polyamide **4a** derived from a cycloaliphatic dicarboxylic acid revealed stronger fluorescence emission than those derived from aromatic ones, and it also showed a remarked solvent effect on the fluorescence profile. All the electroactive polymer films showed reversible electrochemical oxidation accompanied by strong color changes from colorless neutral state to green and blue oxidized states.

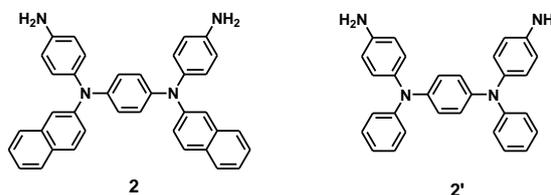
1. Introduction

Electrochromism refers to the reversible electromagnetic absorbance/transmittance and color change resulting from the oxidation or the reduction of the material in response to an externally applied potential by electrochemical means.¹ At present, the most promising uses of electrochromic materials are in smart windows for cars and buildings and in antiglare rear-view mirrors. Potential applications in information storage, electrochromic displays, and adaptive camouflages can also be envisioned. Among the different types of electrochromic materials, conjugated polymers such as polyanilines, polypyrroles, polyselenophenes, polythiophenes, and in particular, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives attract increasing interest because of mechanical flexibility, ease in band-gap/color-tuning via structural control, and the potential for low-cost processing for large-area devices.²

Triarylamine derivatives are well known for photo- and electroactive properties that find optoelectronic applications as photoconductors, hole-transporters, and light-emitters.³ Polymers bearing triarylamine units are receiving considerable interest as ideal hole-transporting materials in various optoelectronic device applications such as organic light-emitting diodes (OLEDs) due to the strong electron-donating and hole-transporting/injecting properties of triarylamine units. Triarylamines can be easily oxidized to form stable radical cations, and the oxidation process is always associated with a noticeable change of coloration. Thus, many triarylamine-based electrochromic polymers have been reported in literature.⁴ In recent years, we have developed a number of high-performance polymers such as aromatic polyamides and polyimides carrying the triarylamine unit as an electrochromic functional moiety.⁵ Our strategy was to synthesize the triarylamine-containing monomers such as diamines and dicarboxylic acids that were then reacted with the corresponding comonomers

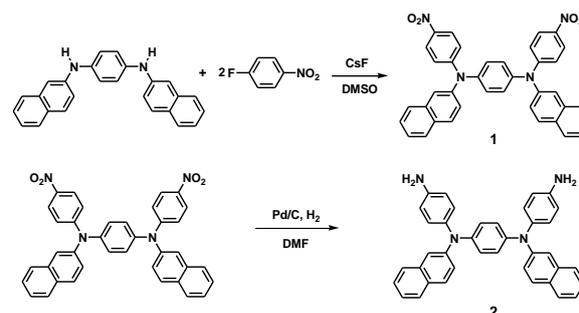
through conventional polycondensation techniques. The obtained polymers possessed a well-defined structure, characteristically high molecular weights, and high thermal stability. Because of the incorporation of packing-disruptive, three-dimensional triarylamine units along the polymer backbone, most of these polymers exhibited good solubility in polar organic solvents. They may form uniform, transparent amorphous thin films by solution casting and spin-coating methods. This is advantageous for their ready fabrication of large-area, thin-film devices.

In this work, we extended our effort to the synthesis and characterization of novel triarylamine-based polyamides, using *N,N'*-bis(4-aminophenyl)-*N,N'*-di-2-naphthyl-1,4-phenylenediamine (**2**) as the diamine monomer. The electrochemical, electrochromic, and luminescent properties of these polymers are also described herein and are compared with those of structurally related ones from *N,N'*-bis(4-aminophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine (**2'**).⁶ The polymers synthesized here are expected to exhibit enhanced thermal stability and solubility because of the bulkier 2-naphthyl group.



2. Monomer synthesis

According to a literature procedure,⁷ the target diamine monomer **2** was prepared by hydrogen Pd/C-catalyzed reduction of the intermediate dinitro compound **1** resulting from CsF-mediated *N,N'*-diarylation of *N,N'*-di-2-naphthyl-1,4-phenylenediamine with 4-fluoronitrobenzene (Scheme 1). The structures of all the synthesized compounds were confirmed by IR and NMR analyses. Figure 1 illustrates the ¹H NMR and ¹³C NMR spectra of **2**. These spectra are in good agreement with its proposed molecular structure.



Scheme 1. Synthetic route to target diamine monomer **2**.

3. Polymer synthesis

According to the phosphorylation polyamidation technique described by Yamazaki and coworkers,⁸ a series of polyamides **4a-4d** with *N,N'*-di-2-naphthyl-*N,N'*-diphenyl-1,4-phenylenediamine units were synthesized from the diamine monomer **2** with four commercially available dicarboxylic acids (**3a-3d**) (Scheme 2). The polymerization was carried out via solution polycondensation using triphenyl phosphite and pyridine as condensing agents. All polymerization reactions proceeded homogeneously and gave high molecular weights. The obtained polyamides had inherent viscosities in the range of 0.52–0.57 dL/g and could be solution-cast into flexible and tough films.

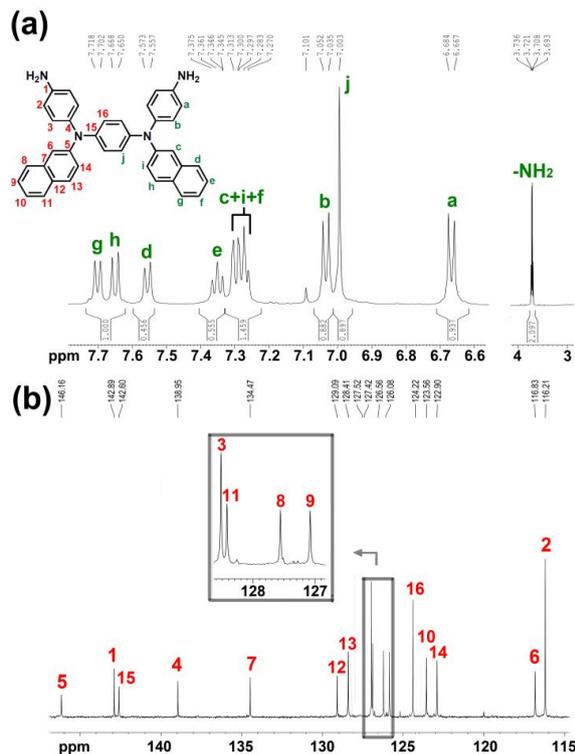
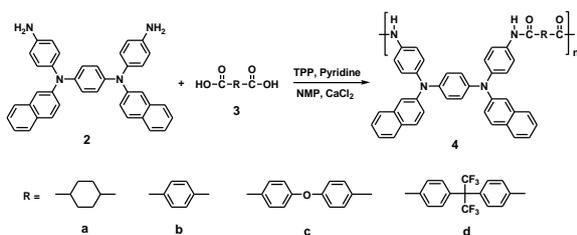


Figure 1. (a) ¹H NMR and (b) ¹³C NMR spectra of diamine monomer **2** in CDCl₃.



Scheme 2. Synthesis of polyamides **4a-4d**.

4. Organo-solubility and thermal properties

All the polyamides were highly soluble in polar solvents such as NMP, DMAc, DMF, and DMSO, and the high solubility could be attributed in part to the introduction of bulky naphthyldiphenylamine moiety into the repeat unit. Thus, the excellent solubility makes these polymers potential candidates for practical applications by spin-coating or inkjet-printing processes to afford high performance thin films for optoelectronic devices.

The thermal properties of the polyamides were investigated by TGA and DSC techniques. The thermal behavior data are included in Table 1. The glass-transition temperatures (T_g) of wholly aromatic ones of the prepared

polyamides were observed in the range of 267–289 °C by DSC. As compared to the **4'** series analogs, the present series polyamides exhibit a slightly higher T_g as a result of the presence of rigid naphthalene segments. The 10 % weight-loss temperatures (T_d) of the wholly aromatic polyamides in nitrogen and air were recorded in the range of 531–562 °C and 521–541 °C, respectively. The amount of carbonized residue (char yield) of these polymers was more than 69 % at 800 °C in nitrogen. Apparently, the high char residues of these aromatic polyamides can be explained by their high aromatic contents in their polymer chains. The lower T_g and T_d values of polyamide **4a** are reasonable when considering the less rigid and less thermally stable aliphatic segment.

Table 1. Thermal Properties of Polyamides

Polymer code	T_g (°C) ^a	T_d at 10% weight loss (°C) ^b		Char yield (wt %) ^c
		N ₂	Air	
4a	247 (241) ^d	440	449	55
4b	289 (278)	562	539	79
4c	267 (257)	554	541	77
4d	276 (273)	531	521	69

^a Midpoint temperature of the baseline shift on the second DSC heating trace (rate = 20 °C/min) of the sample after quenching from 400 to 50 °C (rate = 200 °C/min) in nitrogen. ^b Decomposition temperature at 10 % weight loss was recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 20 cm³/min. ^c Residual weight percentage at 800 °C in nitrogen. ^d Values in parentheses are data of analogous polyamides **4'** having the corresponding diacid residue as in the **4** series.

5. Absorption and fluorescence

All the polyamides were examined by UV-Vis absorption and PL spectroscopy both in solution and in solid state, and the results are presented in Table 2. These polyamides in dilute NMP solution exhibited strong UV-vis absorption bands around 332–343 nm, assignable to the π - π^* transitions resulting from the conjugation between the aromatic rings and nitrogen atoms. In the solid state, the polyamides showed UV-vis absorption characteristics similar to those observed in solutions, with low-energy absorption $\lambda_{\max}^{\text{abs}}$ centered at 330–343 nm and absorption onsets at 418–447 nm corresponding to optical band gaps of 2.86–3.02 eV. Their PL spectra in dilute NMP solution showed maximum bands around 450–507 nm in the blue-green region with fluorescence quantum yields (Φ_F) ranging from 0.05 % to 3.61 %. The semi-aromatic polyamide **4a** exhibited higher fluorescence quantum yields compared with the aromatic polyamides **4b-4d**. This could be attributed to the less charge transfer complexing between the aliphatic segment in the diacid component and the triarylamine unit in the diamine component.

In contrast to absorption spectra, a strong medium effect is observed in the fluorescence spectra of these polyamides. For instance, polyamide **4a** displays a blue-shifted emission profile in solid film ($\lambda_{\max} = 462$ nm) when compared to that observed for NMP solution ($\lambda_{\max} = 507$ nm), as shown in Figure 2. This latter observation suggests that the polarity in the solid film is less than that in NMP solution. This may be accounted for by the planarity violation of the naphthyldiphenylamine segment in the solid state due to the more restricted bond rotation. As can be seen from Figure 2, the dilute solution of polyamide **4a** in less polar THF exhibited an emission profile ($\lambda_{\max} = 476$ nm) similar to that in the solid film. Therefore, the emission maximum or color of these naphthyldiphenylamine-based polyamides is dependent upon the solvent polarity, i.e., they display a solvatochromic behavior.

Table 2. Optical and Electrochemical Properties of Polyamides

Polymer code	Absorption and Photoluminescence							Cyclic voltammetry				
	In solution ^a			As film				Oxidation potential (V) ^f			Energy levels (eV)	
	$\lambda_{\max}^{\text{abs}}$ (nm)	$\lambda_{\max}^{\text{PL}}$ (nm) ^b	Φ_{F} (%) ^c	$\lambda_{\max}^{\text{abs}}$ (nm)	$\lambda_{\text{onset}}^{\text{abs}}$ (nm)	$\lambda_{\max}^{\text{PL}}$ (nm) ^b	$E_{\text{g}}^{\text{opt}}$ (eV) ^e	E_{onset}	$E_{1/2}^{\text{Ox1}}$	$E_{1/2}^{\text{Ox2}}$	HOMO ^g	LUMO ^h
4a	332	507	3.61	331	425	462	2.92	0.46	0.61	0.93	4.97	2.05
4b	341	484	0.13	330	433	- ^d	2.86	0.47	0.62	0.97	4.98	2.12
4c	342	505	0.21	343	410	-	3.02	0.46	0.62	0.96	4.98	1.96
4d	343	450	0.05	336	418	-	2.97	0.49	0.65	0.97	5.01	2.04
4'a	322	410	2.58	325	397	413	3.12	0.45	0.59	0.94	4.95	1.83

^a Measured in dilute solutions in NMP at a concentration of about 1×10^{-5} mol/L. ^b Excited at the absorption maximum for both solution and the solid film state. ^c The fluorescent quantum yield was calculated in an integrating sphere with quinine sulfate as the standard ($\Phi_{\text{PL}} = 54.6\%$). ^d Difficult to be defined due to low PL intensity. ^e Optical band gap obtained from $E_{\text{g}} = 1240/\lambda_{\text{onset}}$. ^f vs Ag/AgCl. ^g The HOMO energy levels were calculated from $E_{1/2}$ and were referenced to ferrocene (4.8 eV). ^h LUMO = HOMO - E_{g}

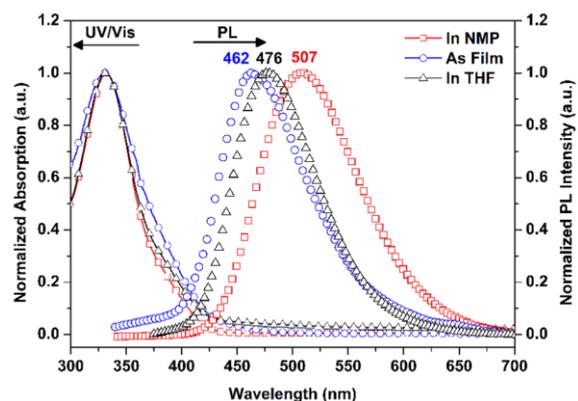


Figure 2. The normalized UV-Vis absorption and PL spectra of polyamide **4a** in dilute NMP and THF solutions (1×10^{-5} M), as well as in the solid film.

6. Fluorescence solvatochromism

In order to further investigate the solvatochromic properties, we investigated the absorption and fluorescence of polyamide **4a** in solvents with different polarity. **Figure 3** showed the normalized PL spectra of polyamide **4a** in dilute solution in various solvents, together with fluorescence images of its solutions. The absorption and PL emission data are collected in **Table 3**.

The solution absorption spectra of **4a** are similar, with little shift in the peak maximum (absorption $\lambda_{\max} = \sim 332$ nm). This clearly indicates that the solvent polarity exerts little effect on its ground-state electronic transition. In contrast, the PL emission spectra of **4a** show strong solvent-polarity dependence, revealing a dominant broad emission band that undergoes remarkable bathochromic shifts with an increase of the solvent polarity. The emission color changes from blue in toluene (PL $\lambda_{\max} = 424$ nm) to green in DMSO ($\lambda_{\max} = 522$ nm). The solvatochromism could be attributed to the fast intramolecular charge-transfer process resulting in a large change of dipole moment in the excited state.⁹ Such solvatochromic behavior is associated with the stabilization of the polar emissive excited states by the polar solvents.

Table 3. Solvatochromic Properties of Polyamide

Solvent ^a	ϵ^b	$\lambda_{\max}^{\text{abs}}$ (nm)	$\lambda_{\max}^{\text{PL}}$ (nm)
Toluene	2.4	332	424
CHCl₃	4.8	323	434
THF	7.5	331	476
CH₂Cl₂	9.1	323	492
NMP	32.2	332	508
DMSO	47.0	333	522

^a Measured at a polymer concentration of ca. 10^{-5} M. ^b Dielectric constant of the solvent.

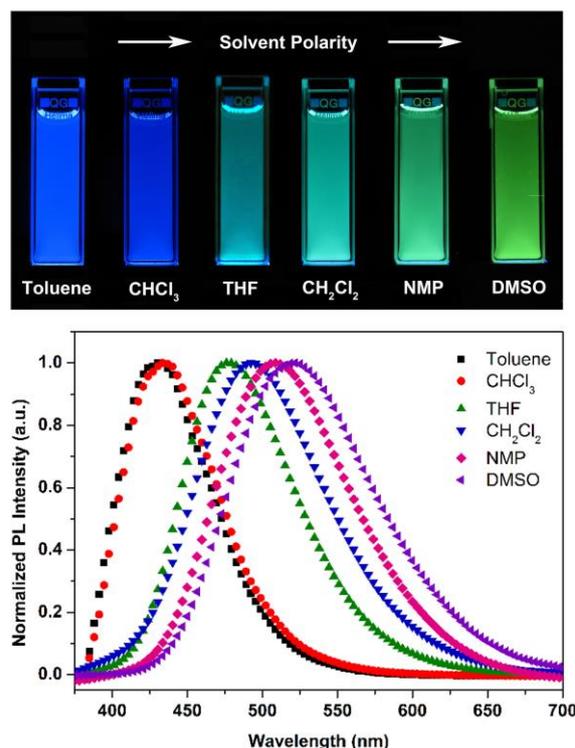


Figure 3. Normalized PL spectra the dilute solutions of polyamide **4a** (ca. 1×10^{-5} M) in solvents of various polarity. Photographs were taken under illumination of a 365 nm UV light.

7. Electrochemical properties

The electrochemical behavior of the polyamides was investigated by cyclic voltammetry (CV) conducted for the cast film on an ITO-coated glass substrate as working electrode in dry acetonitrile (CH_3CN) containing 0.1 M of Bu_4NClO_4 as an electrolyte under nitrogen atmosphere. The derived oxidation potentials are summarized in **Table 2**. The representative cyclic voltammograms for polyamides **4a** and **4'a** are illustrated in **Figure 4** for comparison. There are two reversible oxidation redox couples with half-wave potentials ($E_{1/2}$) of 0.61 V and 0.93 V for polyamide **4a** and 0.59 V and 0.94 V for polyamide **4'a**, respectively. The pronounced potential difference ($\Delta E_{1/2} = 0.32$ V) indicates that efficient resonance delocalization of the radical cation occurs in the diamine residue. Because of the good stability of the films and excellent adhesion between the polymer and ITO substrate, these polyamides exhibited good reversibility of electrochromic characteristics by continuous ten cyclic scans between 0.0 and 1.2 V, changing color from the original pale yellowish to green, and then to blue upon electrochemical oxidations of the

N,N'-di-2-naphthyl-*N,N'*-diphenyl-1,4-phenylenediamine segment in the polymer chain. The redox potentials of the polyamides as well as their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels (below vacuum) are also listed in Table 2. The external ferrocene/ferrocenium (Fc/Fc⁺) redox standard has $E_{1/2}$ of 0.44 V vs Ag/AgCl in acetonitrile. Under the assumption that the HOMO level for the ferrocene standard was 4.80 eV with respect to the zero vacuum level, the HOMO levels for polyamides 4 series were evaluated to be 4.97-5.01 eV calculated from $E_{1/2}$. The lower ionization potential could suggest an easier hole injection into films from ITO electrodes in electronic device applications.

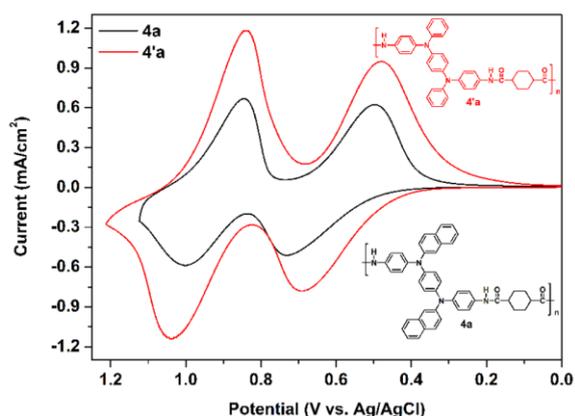


Figure 4. Cyclic voltammograms of the cast films of polyamides **4a** and **4'a** on the ITO-coated glass substrate in 0.1 M Bu₄NClO₄/CH₃CN at a scan rate of 50 mV/s.

8. Spectroelectrochemical properties

Spectroelectrochemical measurements were performed on films of polymers drop-coated onto ITO-coated glass slides immersed in electrolyte solution. The electrode preparations and solution conditions were identical to those used in the CV experiments. Figure 5 presents the UV-vis-NIR absorption spectra of polyamide **4a** film at various applied potentials. In the neutral form, polyamide **4a** exhibited strong absorptions at 333 nm, characteristic for π - π^* transitions, but it was almost transparent in the visible and NIR regions. Upon electro-oxidation of the **4a** film (increasing applied voltage from 0 to 0.73 V), the absorption of π - π^* transition at 333 nm gradually decreased while a new absorption peak at 421 nm and a broadband having its maximum around 1083 nm in the NIR region grew up. We attribute this spectral change to the formation of a stable monocation radical from the naphthylidiphenylamine moiety. The absorption band in the NIR region is assigned to an intervalence charge-transfer (IV-CT) between states in which the positive charge is centered at different amino centers.¹⁰ Upon further oxidation at applied voltages to 1.0 V, the intensity of the IV-CT band gradually decreased, with a formation of a new strong absorption band centered at about 869 nm. The observed electronic absorption changes in the film of **4d** at various potentials are fully reversible and are associated with strong color changes; indeed, they even can be seen readily by the naked eye. From the photos shown in Figure 5 inset, it can be seen that the film changed from a transmissive neutral state (nearly colorless) to a highly absorbing semi-oxidized state (green) and a fully oxidized state (blue).

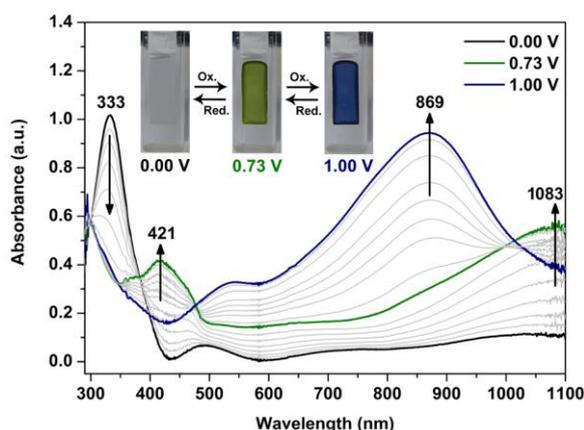


Figure 5. Spectral changes of the cast film of polyamide **4a** on an ITO-coated glass in 0.1 M Bu₄NClO₄/CH₃CN at various applied potentials (vs Ag/AgCl). The inset shows the color changes of the polymer films at indicated electrode potentials.

9. Conclusions

New polyamides containing *N,N'*-di-2-naphthyl-*N,N'*-diphenyl-1,4-phenylenediamine chromophores were readily prepared from diamine monomer **2** with various dicarboxylic acids via the phosphorylation polyamidation reaction. Because of the introduction of the bulky triarylamine unit into the polymer backbone, all the polymers had good solubility in many polar aprotic solvents and exhibited excellent film-forming ability. In addition to high T_g , high thermal stability, notable fluorescence and solvatochromism, the polymers also revealed interesting electrochromic characteristics with multi-electrochromic behavior (highly transmissive-to-green and then to-blue switching) Thus, these polyamides have great potential for use in optoelectronic applications as new charge-transporting, light-emitting, and electrochromic materials.

References

- 1 Monk, P. M. S.; Mortimer, R. J.; Rosseinsky D. R. *Electrochromism and Electrochromic Devices*, Cambridge University Press, Cambridge, UK, 2007.
- 2 Beaujuge, P. M.; Reynolds, J. R. *Chem. Rev.* **2010**, *110*, 268.
- 3 Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953.
- 4 Liou, G.-S.; Hsiao, S.-H.; Ishida, M.; Kakimoto, M. A.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3815.
- 5 (a) Cheng, S.-H.; Hsiao, S.-H.; Su, T.-H.; Liou, G.-S. *Macromolecules* **2005**, *38*, 307. (b) Kung, Y.-C.; Hsiao, S.-H. *J. Mater. Chem.* **2011**, *21*, 1746. (c) Wang, H.-M.; Hsiao S.-H. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 337. (d) Yen, H.-J.; Liou G.-S. *Polym. Chem.* **2012**, *3*, 255.
- 6 Liou, G.-S.; Hsiao, S.-H.; Ishida, M.; Kakimoto, M. A.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2810.
- 7 Wang, Y.-F.; Chen, T.-M. Okada, K.; Uekawa M.; Nakaya T.; Kitamura M.; Inoue H. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2032.
- 8 Yamazaki, N.; Matsumoto M; Higashi, F. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1375.
- 9 Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.
- 10 Lambert, C.; Noll, G. *Angew. Chem. Int. Ed.* **1998**, *37*, 2107.