

# Synthesis and Characterization of Poly(aryl ether sulfone)s with Metallophthalocyanine Pendant Unit

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**ABSTRACT:** A series of novel poly(aryl ether sulfone) copolymers containing dicyanophenyl group were prepared by the reaction of bis(4-chlorophenyl)sulfone with (3,4-dicyano)phenylhydroquinone and 4,4'-isopropylidenediphenol. On this basis, a series of poly(aryl ether sulfone)s containing metallophthalocyanine units were synthesized by the reaction of poly(aryl ether sulfone)s containing dicyanophenyl group with excessive amounts of 1,2-dicyanobenzene and the corresponding metal salt in quinoline. All these copolymers were found to have high glass transition temperature and thermal

stability. These copolymers were found to be soluble in common solvents, and capable of forming transparent films by solution casting. The copolymers containing metallophthalocyanine units showed strong optical absorption in the visible region, and exhibited blue photoluminescence in solution. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3457–3461, 2006

**Key words:** synthesis; metal-polymer complexes; poly(ether sulfones); copolymerization

## INTRODUCTION

Since the synthesis of phthalocyanines in the early 1930s,<sup>1</sup> a rich and varied chemistry and technology has developed around these interesting materials. There are literally thousands of publications and patents related to phthalocyanine and its analogs.<sup>2–5</sup> Owing to their application in optical data processing and catalytic activity, recently, there has been renewed interest in phthalocyanine compounds.<sup>6–15</sup> Phthalocyanine compounds have high thermal, hydrolytic, and oxidative stability. They show high absorption intensities at longer wavelengths. This latter property is even significant, since one of the goals of contemporary optical storage device design is to use solid semiconductor laser for writing purposes. These solid-state lasers emit at wavelengths greater than 800 nm, i.e., in the near infrared (IR) region. It was reported that the metallophthalocyanine end-capped poly(aryl ether sulfone)s were synthesized from the *o*-phthalonitrile end-capped polymers.<sup>16–19</sup> These polymers had high  $T_g$  and were soluble in common organic solvent. Some metals, for example Cu, Zn, Fe, Ni, Co, were used in the above preparation. It is always advantageous to synthesize amorphous polymers having high glass transition temperatures and excellent thermo-oxidative stability, as

they are soluble in common organic solvents, allow for easy solution processing and chemical modification.

In this article, we have prepared the new bisphenol containing dicyanophenyl pendant group. We report herein the synthesis of novel poly(aryl ether sulfone) copolymers containing dicyanophenyl and metallophthalocyanine moieties using the new bisphenol. These resulting copolymers are characterized using gel permeation chromatograph (GPC), infrared spectrometer (IR), thermogravimetric analysis (TGA), differential scanning calorimeter (DSC), UV-visible, and fluorescence spectroscopy.

## EXPERIMENTAL

### Materials

4,4'-Isopropylidenediphenol (BPA), phthalonitrile (Aldrich Chemicals), NMP, quinoline, toluene, chloroform, methanol, acetone, ethanol, and *n*-butanol were obtained from commercial sources and used as received. Bis(4-chlorophenyl) sulfone and 4-imidophthalonitrile were synthesized in our lab.

### Instrumentation

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker 510 instrument using dimethylsulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>) as the solvents. The IR spectra were recorded using the KBr pellet method with a Nicolet Impact 410FTIR spectrophotometer. The elemental analysis was carried out with a Thermoquest CHNS-

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Ovelemental analyzer. The GPC analysis was carried with a Waters 410 instrument with tetrahydrofuran as an eluent and polystyrene as the standard. The glass transition temperatures ( $T_g$ s) were determined using a modulated DSC (model Mettler DSC821<sup>e</sup>) instrument at a heating rate of 10°C/min under nitrogen flow of 100 mL/min. The reported  $T_g$  values were recorded from the second scan after first heating and quenching. The TGA was performed on a PerkinElmer Pyris 1 TGA under a protective nitrogen atmosphere (100 mL/min) at a heating rate of 10°C/min. The UV-visible absorption spectra were recorded on a UV2501-PC spectrophotometer and the fluorescence measurements were carried out with an LS 55 spectrophotometer.

## Synthesis

### Synthesis of (3,4-dicyano)phenyl hydroquinone (4)

To a 1000-mL beaker equipped with a mechanical stirrer, a dropping funnel, and a thermometer water (50 mL), ice (50 g), and 4-amidophthalonitrile (compound 1) (5.575 g, 0.025 mol) were added. Hydrochloric acid (21 mL) was added dropwise into the stirring mixture through the dropping funnel, and then a concentrated water solution of sodium nitrite (1.725 g, 0.025 mol) was added dropwise. The mixture was stirred for 1 h at 0–5°C, and changed into an opaque suspension. The resulting solution (containing complex 2) was filtered and added dropwise to a mixture of 1,4-benzoquinone (2.16 g, 0.02 mol), sodium bicarbonate (16.80 g, 0.2 mol), and water (100 mL). After that, the reaction mixture was stirred at 10–15°C for about 2 h and then at room temperature for 2 h. Then the precipitate was collected by filtration and washed thoroughly with water and kept at 60°C in a vacuum oven. Brown crystals (complex 3) were obtained after recrystallization from *n*-butanol.

In a 250-mL three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a condenser, compound 3 (11.70 g, 0.05 mol), zinc powder (9.75 g, 0.15 mol), and water (200 mL) were added. Hydrochloric acid (36%, 34 mL) was added dropwise into the mixture under stirring and reflux over a period of 1 h. After this addition, the reaction system was allowed to reflux for 0.5 h. The hot mixture was then filtered and the filtrate was poured into a large amount of water. Next, the solid was then collected and dried in a vacuum

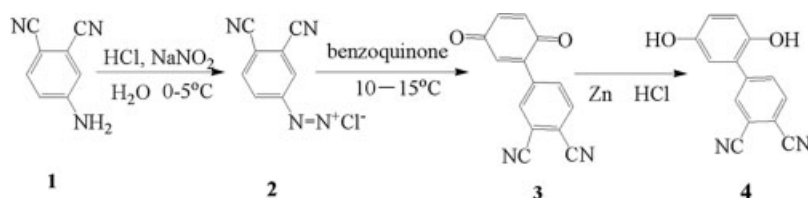
oven. A white solid (complex 4) was obtained after recrystallization from the mixture of water and ethanol (6/4, v/v). The Yield for this monomer is 66%, and its melting point (mp) is 262°C (DSC). Elem. Anal. Calcd. For C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub> (236.23 g/mol): C, 70.74%, H, 3.57%, N, 11.57%. Found: C, 71.18%, H, 3.41%, N, 11.86%. IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3308 (—OH), 2245 (—CN). <sup>1</sup>H NMR (DMSO,  $\delta$ , ppm): 9.37 (s, 1H, —OH), 9.00 (s, 1H, —OH), 8.27 (s, 1H), 8.14 (d, 1H,  $J = 8.5$ ), 8.08 (dd, 1H,  $J = 8.5$ ), 6.83 (d, 1H,  $J = 8.5$ ), 6.77 (s, 1H), 6.73 (dd, 1H,  $J = 8.5$ ). <sup>13</sup>C NMR (DMSO,  $\delta$ , ppm): 150.36, 147.07, 144.16, 133.98, 133.68, 123.99, 117.55, 117.21, 116.05, 114.35, 111.87.

### General procedure for synthesis of polymers (7)

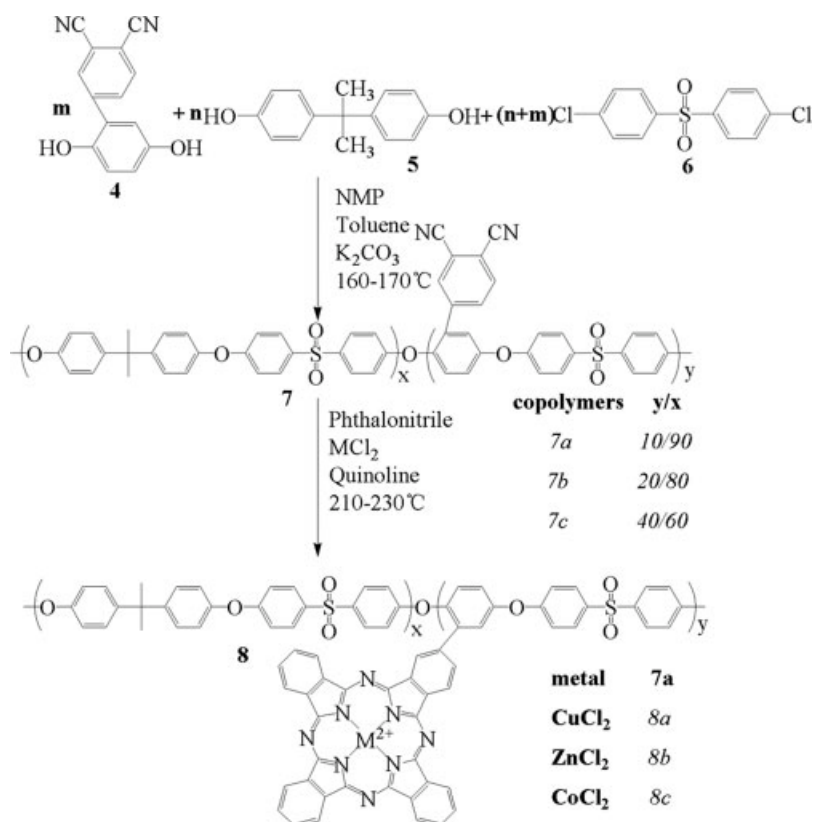
The procedure for synthesis of a series of copolymers 7 is as follows. For 7b, to a 100-mL three-necked round-bottom flask equipped with a magnetic stirrer, a Dean-Stark trap and condenser, and a nitrogen inlet, the monomer 4 (0.708 g, 3 mmol), 5 (BPA) (2.736 g, 12 mmol), 6 (4.172 g, 15 mmol), *N*-methylpyrrolidone (NMP) (25 mL), K<sub>2</sub>CO<sub>3</sub> (2.07 g, 15 mmol), and toluene (20 mL) were added. Under an atmosphere of nitrogen, the solution was heated to 130–140°C and maintained at that temperature for 2 h to remove all water by means of a Dean-Stark trap using toluene. The polycondensation was continued for 6–8 h at 170–180°C. Then the viscous solution was slowly poured into water and stirred vigorously. The thread-like polymer was pulverized into a powder after cooling. The powder was washed with hot methanol and water several times and dried at 100°C under vacuum for 24 h. The copolymers were prepared with varying mole fractions of 4 (*m*) and BPA(5) (*n*). The copolymers with different *m/n* ratio viz. 10/90, 20/80, and 40/60 were prepared and designated as 7a, 7b, and 7c, respectively.

### Procedure for synthesis of copolymers containing metallophthalocyanine (8)

For the synthesis of the copolymers containing metallophthalocyanine, the copolymer 7a was selected. To a 250-mL three-necked flask equipped with a condenser and nitrogen gas inlet, the copolymer 7a (1 g), phthalonitrile (1 g), the corresponding metal chloride (0.6 g), and 150 mL of quinoline were added. Under an atmosphere of nitrogen, the mixture was heated to 210–230°C



Scheme 1 Synthesis of monomer 4.



**Scheme 2** Synthesis of copolymer series 7 and 8.

for 6–8 h, and after this period; the reaction mixture became dark blue. The mixture was poured into a liquid mixture of 300 mL methanol and 20 mL of hydrochloric acid (11.8M), with vigorous stirring. The precipitated particles were washed with acetone, ethanol, and water. The precipitate was collected by filtration and extracted by chloroform, using a Soxhelt extractor. The chloroform solution was concentrated and precipitated into methanol. The dark blue fibrous material was

produced and dried at 110°C for 24 h. In the present work, copper, zinc, and cobalt chloride were used.

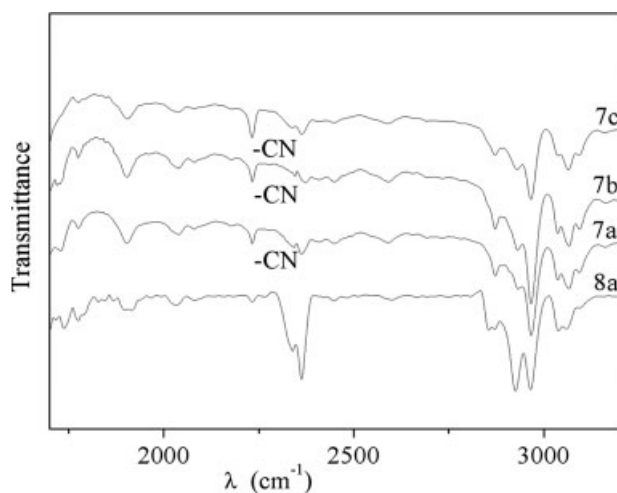
## RESULTS AND DISCUSSION

### Synthesis of bisphenol monomer

The synthetic route of the biphenol monomer **4** is shown in Scheme 1.

### Synthesis of copolymers containing metallophthalocyanine

The copolymers prepared as shown in the Scheme 2 were characterized by the FTIR, GPC, DSC, and TGA. The yield was found to be about 70%. The IR spectra for the copolymers **7a**, **7b**, **7c**, and **8a** are pre-



**Figure 1** IR spectra of copolymers **7a–7c** and **8a**.

**TABLE I**  
Properties of the Copolymer Series 7 and 8

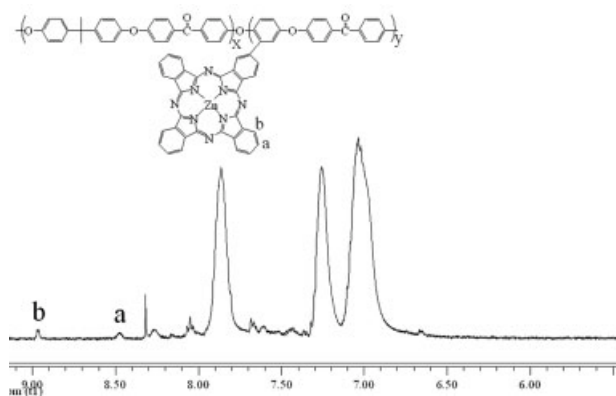
Polymer	$T_g$ (°C)	TGA-5% (°C)	$M_n$	$M_w$	Polydispersity	$\eta_{iv}$
<b>7a</b>	178.5	462	15,404	24,599	1.60	0.38
<b>7b</b>	179.9	429	11,636	15,799	1.36	0.30
<b>7c</b>	182.3	423	11,101	17,077	1.54	0.28
<b>8a</b>	188.0	450	19,416	36,793	1.90	0.38
<b>8b</b>	194.1	436	18,390	35,501	1.93	0.36
<b>8c</b>	180.0	461	18,034	35,171	1.95	0.36

**TABLE II**  
Elemental Analysis Result of Copolymer 8a–8c

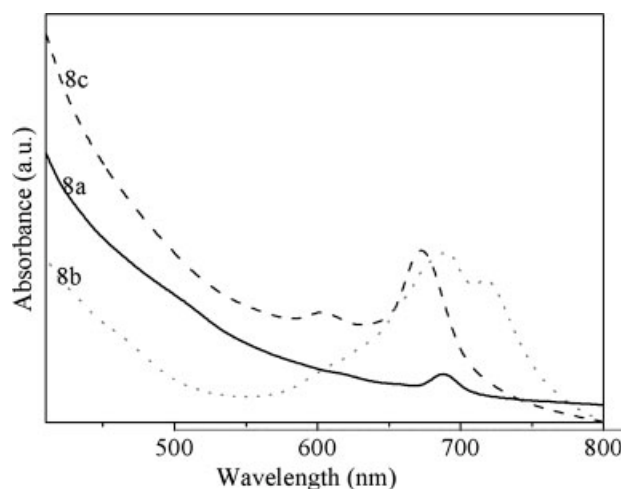
Polymer	H (mol %)	C (mol %)	N (mol %)	Pc (mol %)	Rate of conversion (%)
8a	4.933	71.40	1.039	8.36	83.6
8b	4.856	71.49	1.081	8.70	87.0
8c	4.849	71.45	1.086	8.71	87.1

sented in Figure 1. From the spectra, it is clearly evident that the intensity of the  $-\text{CN}$  band at  $2227\text{ cm}^{-1}$  is more for **7c** when compared to **7a** and **7b**. It is as expected that the mole fraction of  $-\text{CN}$  containing monomer is more in **7c** than in **7b** and in **7a**. However, from the spectrum for copolymer **8a**, it is clear that the peak at  $2227\text{ cm}^{-1}$  is missing indicating the completion reaction at this site.<sup>15–17</sup> The properties of copolymers **7a–7c** are listed in Table I. The glass transition temperature ( $T_g$ s) of the copolymers varied from  $178.5$  to  $182.3^\circ\text{C}$ . It is also evident from this table that  $T_g$ s of these copolymers is increasing with the content of compound **4**. The 5 wt % weight loss temperatures of these copolymers varied from  $423$  to  $462^\circ\text{C}$  indicating that these copolymers exhibited thermal stability.

The properties of the metal containing copolymer series **8** are presented in Table I. It can be seen that the polydispersity of the copolymers were 1.90, 1.93, and 1.95, respectively, which is larger than that of copolymer series **7**. As depicted in Scheme 2, the metal-complex ring can be formed by either intermolecular or intramolecular. The former would cause the crosslinking and insolubilization. The behavior can be avoided by using an excess 1,2-dicyanobenzene followed by extracting with chloroform as described in the experimental section. Presumably, the larger polydispersity of polymer series **8** comes from the GPC measurements because the incorporation of the very bulky metal contains rings pendants.<sup>16,17</sup> Also from the same table, we can see that  $T_g$  values varied from  $180$  to  $188^\circ\text{C}$ . These values are almost the same as those of the corresponding copolymer series **7**. The 5 wt % weight loss temperatures of **8a**, **8b**, and **8c** are  $450$ ,  $436$ ,



**Figure 2**  $^1\text{H}$  NMR spectra of polymer **8b**.



**Figure 3** UV-visible spectrum of copolymers **8a–8c** in chloroform solution (solution concentrations:  $5\text{ mg/mL}$ ).

and  $461^\circ\text{C}$ , which are close to that corresponding to the copolymer **7a**. These copolymers also exhibited good thermal stability. The contents of C, H, and N were obtained via elemental analysis. Then the contents of metallophthalocyanine in polymers were calculated (Table II). The rate of conversion was further calculated to be  $83.6$ – $87.1\%$ . Figure 2 shows the  $^1\text{H}$  NMR spectrum of copolymer **8b**, in which the signals of protons *a* and *b* appear at  $\delta$  8.47 and  $\delta$  8.99, respectively, as broad peaks. Because protons *a* and *b* are not very close to the core of the large metal-complex ring, the downfield shift effect of the metal-complex ring on the chemical shifts of protons *a* and *b* is not significant. However, the ring current affects the conjugated system, so the chemical shifts of protons *a* and *b* are high. The signal intensities of protons *a* and *b* are weak, because the content of the metal-complex units is about  $7.7\%$  as estimated from the NMR characterization. This value indicates that  $77\%$  of the dicyanobenzene groups were converted and incorporated into copolymer **8b**.

All the copolymers containing metallophthalocyanine were found to be nonbirefringent confirming their amorphous nature. These copolymers were found to be soluble in common solvents like *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), *N*-methylpyrrolidone (NMP), and chloroform, etc. It was also found that the copolymers were capable of forming transparent films by solution casting.

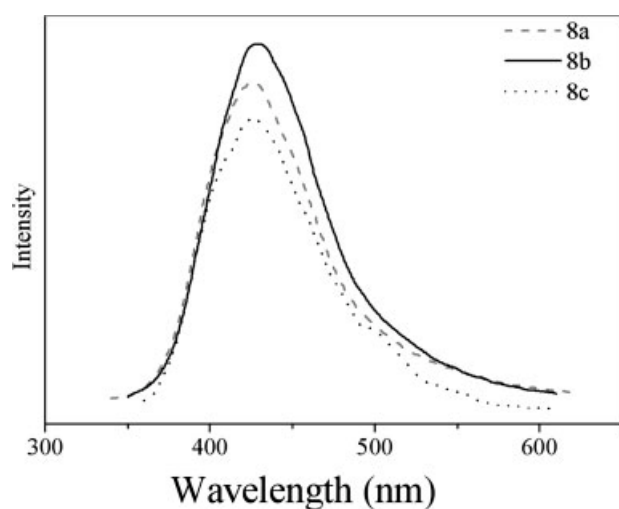
### Photoabsorption and photoluminescence

The absorption spectrums of copolymer **8a–8c** in dilute  $\text{CHCl}_3$  solution ( $5\text{ mg/mL}$ ) are shown in Figure 3. From the figure, it is clearly evident that strong absorption in the visible range existed for the copolymers **8b** and **8c**, whereas for **8a** is medium. These copolymers

containing metallophthalocyanine are found to be colored as expected. Figure 4 show the fluorescence emission spectra of the copolymers **8a–8c** in dilute CHCl<sub>3</sub> (5 mg/mL) at room temperature on excitation at 330 nm, the emission peaks were observed at 425–430 nm in the visible blue region. The absorption maxim values and fluorescence emission values of the copolymers **8a–8c** are presented in Table III.

### CONCLUSIONS

The novel bisphenol (3,4-dicyano)phenylhydroquinone was prepared in a three-step reaction. A series of novel poly(aryl ether sulfone) copolymers containing dicyanophenyl group were prepared by the reaction of bis(4-chlorophenyl)sulfone with (3,4-dicyano)phenylhydroquinone and 4,4'-isopropylidenediphenol. In addition, a series of poly(aryl ether sulfone)s containing metallophthalocyanine units were synthesized by the reaction of poly(aryl ether sulfone)s containing dicyanophenyl group with excess amounts of 1,2-dicyanobenzene and the corresponding metal salt in quinoline. All these copolymers were found to have high glass



**Figure 4** Fluorescent spectra of copolymers **8a–8c** in chloroform solution (solution concentrations: 5 mg/mL).

**TABLE III**  
Optical Properties of Copolymers **8a–8c**

Polymer	$\lambda_{vu}$ (nm)	$\lambda_{ex}$ (nm)	$\lambda_{em}$ (nm)	Color in the chloroform
<b>8a</b>	688	327	425	Light yellow
<b>8b</b>	603, 672	328	430	Dark green
<b>8c</b>	687, 716	330	429	Gray

transition temperature and thermal stability. These copolymers were found to be soluble in common solvents, and to be capable of forming transparent films by solution casting. The copolymers containing metallophthalocyanine units showed strong optical absorption in the visible region, and exhibited blue photoluminescence in solution. The polymers are being as fluorescent materials and electroluminescent materials.

### References

- Hay, S. R. *Macromolecules* 1992, 25, 1017.
- Snow, A. W.; Jarvis, N. L. *J Am Chem Soc* 1984, 106, 4706.
- Enokida, T.; Hirohashi, R. *J Imaging Sci Technol* 1990, 34, 234.
- Loutfy, R. O.; Hsiao, C. K. *J Imaging Sci Technol* 1985, 29, 116.
- Hay, S. R. *Macromolecules* 1992, 25, 1025.
- Ozoemena, K. I.; Tebello, N.; Philippe, W. *Electroanalysis* 2003, 14, 1762.
- Spadavecchia, J.; Rella, R. *Sens Actuators B* 2004, 100, 135.
- Cao, J.; Wang, W.; Wang, D. *J Thin Solid Films* 2003, 429, 152.
- Xu, H. H.; Bai, Y.; Cheng, Z. Y. *J Appl Polym Sci* 2001, 82, 70.
- Alexander, S.; Sophie, D. S.; Bernard, M. *J Am Chem Soc* 1996, 118, 7410.
- Zhang, Q. L.; Wang, D. J.; Xu, J. J.; Sun, J. Z.; Wang, W. *Mater Chem Phys* 2003, 82, 525.
- Masami, S.; Nagakazu, F. *Electrochim Acta* 2003, 48, 3953.
- Takashi, I.; Hirohito, M.; Hirofusa, S. *React Funct Polym* 2000, 43, 63.
- Sharma, V. B.; Jain, S. L. *Sain, B. Catal Lett* 2004, 94, 1.
- Meng, Y. Z.; Wan, W.; Xiao, M.; Hay, A. S. *Green Chem* 2004, 6, 249.
- Meng, Y. Z.; Abu-Yousef, I. A.; Hill, A. R.; Hay, A. S. *Macromolecules* 2000, 33, 9815.
- Wan, W.; Meng, Y. Z.; Zhu, Q.; Tjong, S. C.; Hay, A. S. *Polymer* 2003, 44, 575.
- Abu-Yousef, I. A.; Hill, A. R.; Hay, A. S. *Synth Commun* 1999, 29, 2915.
- Meng, Y. Z.; Hill, A. R.; Hay, A. S. *Polym Adv Technol* 2001, 12, 206.