Chinese Journal of Polymer Science Vol. 24, No. 6, (2006), 619–625

Chinese Journal of
Polymer Science
©2006 World Scientific

POLYBINAPHTHYLS INCORPORATING (*R*)-2,2′-BINAPHTHO-20-CROWN-6 AND NAPHTHYL MOITIES[*]

Dan Zhu, Yi-xiang Cheng[**], Xiao-wei Zou, Ling-wu Chen, Jin-feng Song and Zhi-liu Wang
College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

Abstract Chiral polymer was synthesized by the polymerization of (*R*)-6,6′-bistributylstannyl-2,2′-binaphtho-20-crown-6 (M-1) with 1,4-dibromo-2,3-bisbutoxy-naphthyl (M-2) by $Pd(PPh_3)_4$ catalyzed Stille coupling reaction. Both monomer and polymer were analyzed by NMR, MS, FT-IR, UV, polarimetry, DSC-TGA, CD, fluorescent spectroscopy and GPC. The major difference between monomer and polymer is that a long wavelength Cotton Effect was observed for the polymer due to its more extended conjugation in the repeating unit and a highly rigid backbone in the polymer chain. Polymer has strong blue fluorescence due to the efficient energy migration from the extended π-electronic structure of the repeating unit of the polymer to the chiral binaphthyl core and is expected to have potential application in the materials of fluorescent sensors and chiral chromatographic packing for resolution of racemic amino acid.

Keywords: (*R*)-2,2′-Binaphtho-20-crown-6; Chiral polymer; Fluorescence; Stille reaction.

INTRODUCTION

(*R*) or (*S*)-1,1′-Binaphthol have been used as the starting materials for the preparation of conjugated polymers that have a main chain chiral configuration. These chiral binaphthyl-based polymers can lead to efficient and stable chiral induction and chiral discrimination, and they have exhibited potential applications in areas such as molecular recognition[1–3], asymmetric catalysis[4–6] and optoelectronic materials[7–9]. The polybinaphthyl hosts developed for molecular recognition purposes are mainly focused on crown ethers and cyclic amides. The molecular recognition capability of chiral crown ethers such as (*R*) or (*S*)-2,2′-binaphtho-20-crown-6 has been extensively studied by Cram[10–12]. BINOL-derived chiral crown ethers have been recognized as efficient selectors for the separation of chiral amines or α-amino acids in chiral HPLC, useful chiral ligands in asymmetric catalysis and highly selective chiral luminescent sensors. Shinbo employed 3,3′-dibenzo-2,2′-binaphtho-20-crown-6 as chromatographic packing for the separation of racemic amino acid. The results indicated that the chiral crown ether-coating packing was very powerful for the optical resolution of a variety of amino acids and optically active amines[13]. Japanese Daicel company has successfully used a chromatographic stable phase of Crownpak CR (+)™ and CR (−)™ for the resolution of amino acids and compounds with a primary amino group with an asymmetric center.

Pd-catalyzed Stille reaction was found to offer a simple access to the creation of new C—C bond-formation because Stille reaction can not only be done under mild conditions, but also introduce many functional groups to the reagents and substrates[14, 15]. This synthesis method has been investigated to synthesize the conjugated or other functional polymers with unique structure and properties[16–19]. Herein, the attachment of butoxy substitutents on M-2 as side chain of the polymers cannot only modify the electronic properties and conjugated structure of chiral polymers, but also dramatically improve their solubility in organic solvents. In this paper, we

---

[*] This work was supported by the National Natural Science Foundation of China (No. 20474028) and Jiangsu Provincial Natural Science Foundation (No. BK2004086).

[**] Corresponding author: Yi-xiang Cheng (成义祥), E-mail: yxcheng@nju.edu.cn

Received January 9, 2006; Revised February 9, 2006; Accepted February 24, 2006

report preliminary results of synthesis and structural characterization of polybinaphthyls incorporating (*R*)-2,2′-binaphtho-20-crown-6 and naphthyl moieties by Stille coupling reaction.

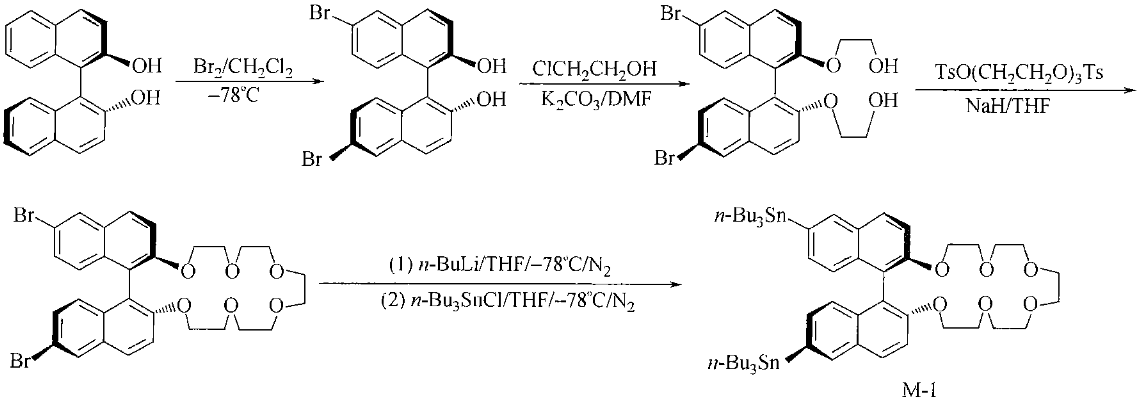
EXPERIMENTAL

^{1}H-, ^{13}C-NMR spectra (all in $CDCl_3$) were recorded on a 300-Bruker spectrometer with TMS as internal standard. FT-IR spectra were taken on a Nexus 870 FT-IR spectrometer. UV-Vis spectra were obtained from a Perkin-Elmer Lambda 25 spectrometer. DSC-TGA was preformed on a Perkin-Elmer Pyris-1 instrument under N_2 atomsphere. Fluorescent spectra were obtained from a 48000 DSCF spectrometer. MS was determined on Micromass GCT. Circular dichroism was determined with a JASCO J-810 spectropolarimeter. Molecular weight was determined by gel permeation chromatography (GPC) with Waters-244 HPLC pump and THF was used as solvent and relative to polystyrene standards. (*R*)-1,1′-Binaphthol was purchased from Changzhou High-Tech Biology Chemical Co., Ltd. and directly used without purification (>99.9% *e.e.*). All solvents and reagents were of commercially available A.R. grade. All reactions were performed under N_2 using Schlenk tube techniques.

Preparation of (R)-6,6′-bistributylstannyl-2,2′-binaphtho-20-crown-6 (M-1) (Scheme 1)

Synthesis of (R)-6,6′-dibromo-2,2′-bis(2-hydroxyethoxy)-1,1′-binaphthyl

A mixture of (*R*)-6,6′-dibromo-2,2′-binaphthol (3.89 g, 8.76 mmol), 2.34 mL 2-chloroethanol (35.04 mmol), 14.0 g K_2CO_3 (0.1 mol) and 50 mL DMF was stirred at 110°C for 17 h. The mixture was poured into 1 mol/L aqueous NaOH (200 mL) and precipitated the crude product. The solid was filtered and washed with water to pH = 7. The pale yellow solid (*R*)-6,6′-dibromo-2,2′-bis(2-hydroxyethoxy)-1,1′-binaphthyl was collected and dried under vacuum. The yield was 83% (3.88 g, 7.29 mmol) mp: 149–151°C; $[\alpha]_D = -43.8$ (*c* 0.3, THF); ^{1}H-NMR ($CDCl_3$, δ): 3.59–3.64 (m, 4H), 4.01–4.07 (m, 2H), 4.20–4.27 (m, 2H), 6.94 (d, $J = 9.0$ Hz, 2H), 7.30 (dd, $J = 9.1$, 1.8 Hz, 2H), 7.48 (d, $J = 9.1$ Hz, 2H), 7.91 (d, $J = 9.1$ Hz, 2H) and 8.06 (d, $J = 1.7$ Hz, 2H); IR: ν_{max} (KBr)/cm^{-1}: 3059.4, 2929.8, 2871.8, 1903.2, 1660.3, 1583.5, 1491.9, 1325.0, 1267.4, 1067.9, 933.1, 874.5 and 807.8.



Scheme 1 Synthesis route to M-1

Synthesis of (R)-6,6′-dibromo-2,2′-binaphtho-20-crown-6

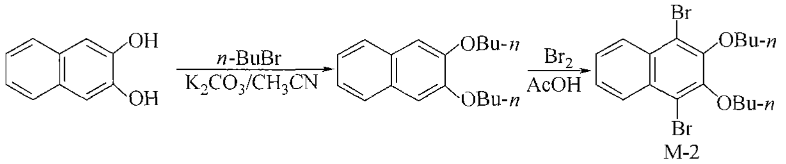
A solution of 1.72 g NaH and 3.88 g (*R*)-6,6′-dibromo-2,2′-bis(2-hydroxyethoxy)-1,1′-binaphthyl (7.29 mmol) in 25 mL THF was stirred and kept refluxing under N_2. A solution of 3.69 g $TsO(CH_2CH_2O)_3Ts$ (8.06 mmol)[20] in 40 mL THF was added dropwise for 1 h. The mixture was kept refluxing for 15 h. After being cooled to room temperature and filtered, the resulting solution was evaporated to remove solvent under reduced pressure, and the residue was extracted with CH_2Cl_2. The solution was washed with brine three times and dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure to give a viscous yellow product. The crude product was purified on silica column with the mixed solvents of petroleum ether and ethyl acetate (10:1, *V*/*V*) as eluent to afford a pale yellow product (2.35 g, 50%). $[\alpha]_D^{25} = +22.6$ (*c* 0.34, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, δ): 3.39 (t, $J = 4.0$ Hz, 4H,), 3.43–3.67 (m, 8H), 3.97–4.07 (m, 4H), 4.14–4.25 (m, 4H), 6.96 (d, $J = 9.0$ Hz, 2H), 7.25 (dd, J = 9.0, 2.5 Hz, 2H), 7.47 (d, J = 9.0 Hz, 2H), 7.82 (d, J = 9.2 Hz, 2H) and 7.99 (d, J = 1.9 Hz, 2H); ^{13}C-NMR (CDCl$_3$, δ): 69.75, 69.79, 70.49, 70.65, 70.87, 116.89, 117.51, 120.01, 127.11, 128.56, 129.65, 129.82, 130.41, 132.47 and 154.77; IR: $\nu_{\max}$ (KBr)/cm^{-1}: 3056.9, 2922.9, 2866.8, 1733.6, 1614.0, 1584.0, 1492.8, 1449.2, 1325.7, 1269.4, 1128.4, 1097.2, 1069.4, 936.0, 874.6 and 807.8; MS (m/z): 669 (M$^{+\cdot}$+Na, 100).

Synthesis of (R)-6,6'-bistributylstannyl-2,2'-binaphtho-20-crown-6

(R)-6,6′-dibromo-2,2′-binaphtho-20-crown-6 (1.44 g, 2.22 mmol) was dissolved in anhydrous THF (30 mL) under N$_2$, the solution was cooled to −78°C before 2.3 mL of n-butyllithium (2.2 mol/L in hexane, 4.89 mmol) was added to the above solution. The mixture was stirred at −78°C for 45 min, and then 1.64 mL of tributylstannyl chloride (6.07 mmol) was added dropwise. The reaction mixture was gradually warmed to room temperature and kept stirring for 12 h. The reaction was quenched with saturated aqueous NH$_4$Cl, and then the mixture was extracted with ether twice. The combined organic layer was washed with water and dried over anhydrous MgSO$_4$, and the solvent was evaporated under reduced pressure to give a viscous liquid. The crude product was purified on silica column with the mixed solvents of petroleum ether and ethyl acetate (20:1, V/V) as eluent to afford a colorless viscous liquid M-1 (1.76 g, 75%). $[\alpha]_D$ = −17.5 (c 0.2, THF); ^{1}H-NMR (CDCl$_3$, δ): 0.89 (t, J = 7.2 Hz, 18H), 1.09 (t, J = 7.9 Hz, 12H), 1.30–1.37 (m, 12H), 1.53–1.61 (m, 12H), 3.38–3.65 (m, 16H), 4.06–4.21 (m, 4H), 7.10 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 9.0 Hz, 2H), 7.90 (d, J = 9.0 Hz, 2H) and 7.94 (s, 2H); ^{13}C-NMR (CDCl$_3$, δ): 10.00, 14.08, 27.80, 29.54, 69.81, 70.17, 70.89, 71.03, 71.28, 116.12, 120.80, 124.89, 127.16, 129.30, 129.80, 133.92, 134.40, 136.80, 154.71; 128.56, 129.65, 129.82, 130.41, 132.47 and 154.77; IR:$\nu_{\max}$ (KBr)/cm^{-1}： 3050.5, 2955.1, 2924.8, 2870.3, 2853.1, 1611.5, 1575.8, 1463.4, 1323.8, 1278.7, 1251.0, 1137.4, 1099.6, 1075.8, 1060.7, 1045.0, 874.3, 820.6 and 690.3; MS (m/z): 1089 (M$^{+\cdot}$+H, 100).

Preparation of 1,4-dibromo-2,3-bisbutoxy-naphthyl (M-2) (Scheme 2)

M-2 was synthesized according to the literature[21], the overall yield of M-2 was 90%. ^{1}H-NMR (CDCl$_3$, δ): 1.04 (t, J = 7.3 Hz, 6H), 1.56–1.67 (m, 4H), 1.85–1.94 (m, 4H), 4.15 (t, J = 6.6 Hz, 4H), 7.56 (dd, J = 6.6, 3.2 Hz, 2H) and 8.25 (dd, J = 6.5, 3.3 Hz, 2H); IR:$\nu_{\max}$ (KBr)/cm^{-1}: 3057.4, 2958.2, 2933.7, 2872.4, 1577.2, 1541.4, 1454.3, 1360.1, 1336.1, 1325.0, 1116.9, 1020.5, 961.1 and 753.9.



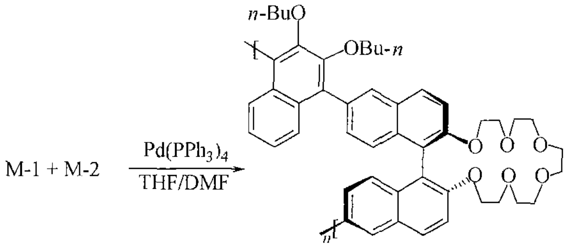
Scheme 2 Synthesis route to M-2

Preparation of Polymer

A mixture of M-1 (0.6655 g, 0.624 mmol) and M-2 (0.2684 g, 0.624 mmol) was dissolved in 15 mL mixed solvents of THF and DMF (1:1, V/V). After the solution was bubbled with N$_2$ for 10 min, Pd(PPh$_3$)$_4$ (47 mg, 0.0125 mmol) was added to the above solution. The solution was stirred and kept at 90°C for 72 h under N$_2$. After being cooled to room temperature, the mixture was passed through a short silica gel column into methanol (150 mL) to remove palladium black from the solution and precipitate out the crude product, which was washed several times with methanol. Further purification could be conducted by dissolving the polymer in THF to precipitate it again in methanol. Polymer was dried under vacuum to give 0.54 g in 91% yield. $[\alpha]_D$ = −156.5 (c 0.1, THF); M_w = 9500, M_n = 5700, PDI = 1.67; ^{1}H-NMR (CDCl$_3$, δ): 0.50–0.55 (m, 6H), 0.92–0.98 (m, 4H), 1.63–1.70 (m, 4H), 3.41–3.54 (m, 20H), 4.04–4.10 (m, 4H), 7.47–7.56 (m, 10H) and 7.87–7.93 (m, 4H); IR: $\nu_{\max}$ (KBr)/cm^{-1}: 3061.0, 2953.2, 2929.5, 2868.5, 1614.7, 1592.5, 1477.1, 1449.2, 1330.1, 1246.7, 1110.4, 823.4 and 760.3.

RESULTS AND DISCUSSION

(*R*)-6,6′-Dibromo-2,2′-binaphtho-20-crown-6 was synthesized from (*R*)-BINOL, which was different from the traditional synthesis routes by Cram[10]. Four synthesis routes to M-1 are shown in Scheme 1. Synthesis of M-1 should be handled under N_2 using Schlenk techniques with special care due to the toxicity of tributylstannyl chloride and side product hexa-*n*-butyldistannane. But the synthesis performance was easy. M-1 was purified by chromatography and relatively stable when compared with most organometallic reagents. In addition, M-1 can be safely stored and used for the chiral polymer synthesis because M-1 is not sensitive to either moisture or oxygen. Herein, a general Stille reaction condition was applied to the polymerization. The C—C cross coupling process was carried out by the polymerization of M-1 with M-2 (Scheme 2) in the presence of a catalytic amount (2 mol%) of $Pd(PPh_3)_4$ at 90°C under N_2 (Scheme 3)[16–19, 22, 23]. In order to synthesize higher molecular weight polymer and keep higher reaction temperature, the mixed solvents of THF-DMF (1:1, *V*/*V*) were chosen to improve the solubility of chiral polymer in the reaction medium. The polymerization could be produced in a good yield (about 90%). The result of polymer's GPC shows that it has moderate molecular weight. M-1 can be used as the monomer to prepare the desired chiral polymer. The chirality of binaphthyl compounds is derived from the restricted rotation of the two naphthalene rings. The rigid structure and C_2 symmetry of the chiral binaphthyl molecules can play an important role in chiral induction. The dihedral angle between two naphthalene rings of a binaphthyl molecule ranges from 60° to 120°, which leads to the kinked or twisted polymer main chain backbone[24, 25]. Polymer is an air stable solid with pale yellow color. Polymer shows good solubility in some common solvents such as THF, CH_2Cl_2, $CHCl_3$ and DMF. It can be attributed to the nonplanarity of the twisted polymer in the main chain backbone and the flexible alkyl substitutents on naphthyl units as side chain of the polymer. Polymer shows a glass transition temperature (T_g) at 130°C. Thermogravimetric analyses (TGA) of polymer was carried out under N_2 atmosphere at a heating rate of 10 K/min. Polymer has good thermal stability and only about 6% of weight loss from 260°C to 400°C due to the cleavage of the butyl group on the naphthyl unit. Under N_2 atmosphere, an apparent one-step degradation was observed at temperatures ranging from 410°C to 700°C (Fig. 1). Polymer will decompose completely at 660°C. A total of 50% weight loss was observed when heated to 700°C.



Scheme 3 Synthesis route to polymer

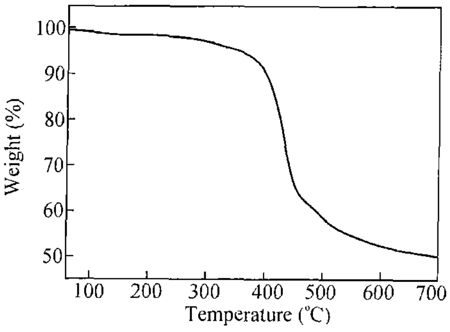


Fig. 1 TGA curve of polymer

Figure 2 illustrates the UV absorption and fluorescent spectra of monomer and polymer in THF solution or polymer as thin film. Polymer displays a stronger and broader UV-Vis absorption spectrum at the region from 250 to 400 nm. Pu *et al.* synthesized a series of conjugated polymers incorporating optically active polybinaphthyls in the main chain and compared their UV absorption wavelengths of the polymers with their corresponding repeating units, and found that there is almost no extended conjugation across the 1,1′-bond of the binaphthyl units in the backbone of such polymers[1, 26, 27]. In this paper, a large red-shift in the electronic absorptions of the conjugated polymer can be attributed to the effective π-π^* conjugated segment of the linker conjugated unit M-2 and naphthyl group in the main chain. The polymer has blue light under ultraviolet light (361 nm) or sunlight even at low concentration (1×10^{-4} mol/L). (*R*)-1,1′-Binaphtho-20-crown-6 and M-2 do not show fluorescence. But the maximum fluorescent wavelengths $\lambda^F{}_{max}$ of M-1 and polymer in THF solution show photoluminescent bands at 378 and 395 nm, respectively. But in thin film which was fabricated by spin coating on ITO glass with the rate of 3000 r/min, the fluorescent wavelength $\lambda^F{}_{max}$ of polymer shows red-shift of 28 nm relative to those measured in solution state. It can be attributed to a higher conjugated chain stacking in the solid than in the solution[28–30].

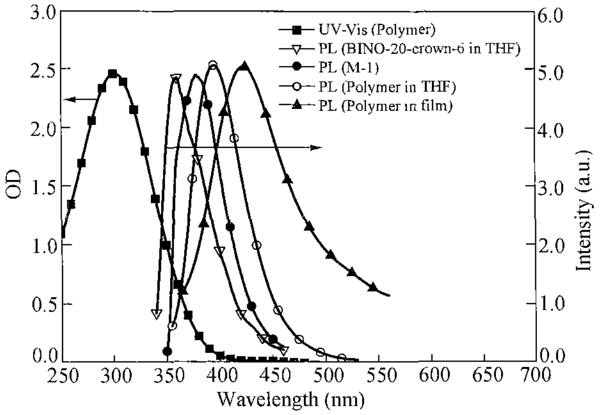


Fig. 2 UV spectrum of polymer and fluorescence spectra of M-1 and polymer
R-binaphtho-20-crown-6, λ_{ex} = 338 nm; M-1, λ_{ex} = 360 nm; polymer: solution, λ_{ex} = 350 nm; thin film, λ_{ex} = 360 nm

The special rotation value ($[\alpha]_D^{25}$) of monomer M-1 is −17.5, the corresponding chiral polymer is −134.5. The absolute values of the special rotation ($[\alpha]_D^{25}$) of polymer are much larger than those in monomer. Both M-1 and polymer exhibit intense CD signals with negative and positive Cotton Effects in their CD spectra (Fig. 3). The molecular ellipticity of (*R*)-1,1′-binaphtho-20-crown-6 is: $[\theta]_\lambda = +7.20 \times 10^5$ (225 nm), -1.61×10^6 (238 nm), $+5.22 \times 10^4$ (297 nm), and that of M-1 is: $[\theta]_\lambda = +8.70 \times 10^5$ (235 nm), -1.22×10^6 (248 nm), $+9.66 \times 10^4$ (284 nm). The molecular ellipticity of Polymer is: $[\theta]_\lambda = +5.34 \times 10^5$ (235 nm), -6.74×10^5 (261 nm), $+2.32 \times 10^5$ (338 nm). We can find great difference from CD spectra of (*R*)-1,1′-binaphtho-20-crown-6, M-1 and polymer (Fig. 3). The molar ellipticities of (*R*)-1,1′-binaphtho-20-crown-6 are nearly of the same magnitude as that of M-1 and stronger than the corresponding chiral polymer. CD signals of M-1 show red-shift of 10 nm relative to (*R*)-1,1′-binaphtho-20-crown-6. ^1B_b band of M-1 appears at 248 nm, but polymer appears red-shift to 261 nm. The long wavelength CD effect of polymer appears at 338 nm, which can be regarded as the more extended conjugated structure in the repeating unit and a highly rigid backbone in the polymer chain[31, 32].

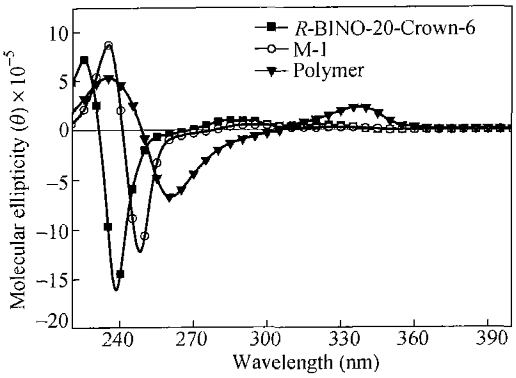


Fig. 3 CD spectra of (*R*)-1,1'-binaphtho-20-crown-6, M-1 and polymer (in THF)

CONCLUSIONS

Pd-catalyzed Stille reaction was found to offer a simple access to the desired chiral polymer. Polymer has thermal stability and shows good solubility in some common solvents due to the nonplanarity of the twisted polymers in the main chain backbone and flexible alkyl substitutents on naphthyl rings as side chain of the polymer. Polymer has strong blue fluorescence due to the efficient energy migration from the extended π-electronic structure of the polymer to the chiral binaphthyl core and is expected to have potential application in the materials for fluorescent sensors and chiral chromatographic packing for resolution of racemic amino acid. The major difference between monomer and polymer is that a long wavelength Cotton Effect is observed for the polymer due to its more extended conjugation in the repeating unit and a high rigidity of the polymer backbone.

REFERENCES

1 Pu, L., Chem. Rev., 1998, 98: 2405

2 Liu, T.J., Zhang, K.S., Chen, Y.J., Wang, D. and Li, C.J., Chin. J. Polym. Sci., 2001, 19: 521

3 Pu, L., Chem. Rev., 2004, 104: 1687

4 Fan, Q.H., Li, Y.M. and Chan, A.S.C., Chem. Rev., 2002, 102: 3385

5 Hu, Q.S., Huang, W.S., Vitharana, D., Zheng, X.F. and Pu, L., J. Am. Chem. Soc., 1997, 119: 12454

6 Moore, D. and Pu, L., Org. Lett., 2002, 4: 1855

7 Elshocht, S.V., Verbiest, T., Ma, L., Cheng, H., Musick, K.Y. and Pu, L., Chem. Phys. Lett., 1999, 309: 315

8 Zheng, L.X., Urian, R.C., Liu, Y.Q., Jen, A.K.Y. and Pu, L., Chem. Mater., 2000, 12: 13

9 Goto, H. and Akagi, K., Macromolecules, 2005, 38: 1091

10 Cram, D.J., Helgeson, R.C., Koga, K., Kyba, E.P., Madan, K., Sousa, L.R., Siegel, M.G., Moreau, P., Gokel, G.W., Timko, J.M. and Sogah, D.Y., J. Org. Chem., 1978, 43: 2758

11 Kyba, E.P., Helgeson, R.C., Madan, K., Gokel, G.W., Tarnowski, T.L., Moore, S.S. and Cram, D.J., J. Am. Chem. Soc., 1977, 99: 2564

12 Zhang, X.Z., Bradshaw, J.S. and Izatt, R.M., Chem. Rev., 1997, 97: 3313

13 Shinbo, T., Yamaguchi, T., Nishimura, K. and Sugiura, M., J. Chromatogr., 1987, 405: 145

14 Stille, J.K., Angew. Chem. Int. Ed. Engl., 1986, 25: 508

15 Farina, V., Kapadia, S., Krishnan, B., Wang, C. and Liebeskind, L.S., J. Org. Chem., 1994, 59: 5905

16 Koeckelberghs, G., Verbiest, T., Vangheluwe, M., Groof, L., Asselberghs, I., Picard, I., Clays, K., Persoons, A. and Samyn, C., Chem. Mater., 2005, 17: 118

17 Bao, Z.N., Chan, W.K. and Yu, L.P., J. Am. Chem. Soc., 1995, 117: 12426

18 Lere-Porte, J.P., Moreau, J.J.E., Serein-Spirau, F., Torreilles, C., Righi, A. and Sauvajol, J.L., J. Mater. Chem., 2000, 10: 927

19 Cheng, Y.X., Chen, L.W., Zou, X.W., Song, J.F. and Wang, Z.L., Polymer, 2006, 47: 435

20 Chen, Y.Y. and Gregory, L.B., J. Org. Chem., 1999, 64: 6870

21 Lau, K., Foster J. and Williams, V., Chem. Commun., 2003, 17: 2172

22 Koeckelberghs, G., Vangheluwe, M., Picard, I., Groof, L., Verbiest, T., Persoons, A. and Samyn, C., Macromolecules, 2004, 37: 8530

23 Farina, V., Krishnamurthy, V. and Scott, W.J., Org. React., 1997, 50: 1

24 Ma, L., Hu, Q.S., Vitharana, D., Wu, C., Kwan, C.M.S. and Pu, L., Macromolecules, 1997, 30: 204

25 Chow, H.F. and Ng, M.K., Tetrahedron: Asymmetry, 1996, 7: 2251

26 Musick, K.Y., Hu, Q.S. and Pu, L., Macromolecules, 1998, 31: 2933

27 Hu, Q.S., Vitharana, D., Liu, G., Jain, V. and Pu, L., Macromolecules, 1996, 29: 5075

28 Li, H., Powell, D.R., Firman, T.K. and West, R., Macromolecules, 1998, 31: 1093

29 Cheng, Y.X., Liu, T.D. and Chen, L.W., Chin. J. Polym. Sci. 2004, 22: 327

30 Cheng, Y.X., Chen, L.W., Zou, X.W. and Liu, T.D., Polym. J., 2005, 37: 355

31 Cheng, H., Ma, L. and Pu, L., Tetrahedron: Asymmetry, 1996, 7: 3083

32 Cheng, H. and Pu, L., Macromol. Chem. Phys., 1999, 200: 1274