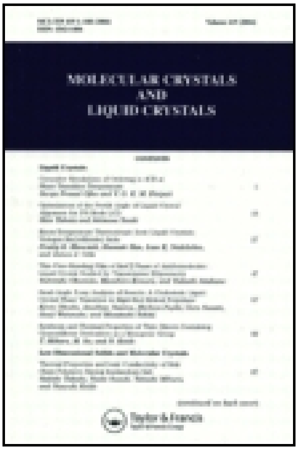


Molecular Crystals and Liquid Crystals

Synthesis and Electrochemical Properties of Pheneothiazine Dendrimers

Xiao-Hang Zhang [a], Kigook Song [a], Kwang-Hyun Ahn [a] & Sung Ik Yang [a]

[a] College of Environment and Applied Chemistry, Materials Research Center for Information Display, Kyung Hee University, Yongin, Republic of Korea

To cite this article: Xiao-Hang Zhang, Kigook Song, Kwang-Hyun Ahn & Sung Ik Yang (2007): Synthesis and Electrochemical Properties of Pheneothiazine Dendrimers, Molecular Crystals and Liquid Crystals, 464:1, 271/[853]-279/[861]

To link to this article: http://dx.doi.org/10.1080/15421400601031223

Mol. Cryst. Liq. Cryst., Vol. 464, pp. 271/[853]–279/[861], 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601031223

Synthesis and Electrochemical Properties of Pheneothiazine Dendrimers

Xiao-Hang Zhang
Kigook Song
Kwang-Hyun Ahn
Sung Ik Yang
College of Environment and Applied Chemistry, Materials Research Center for Information Display, Kyung Hee University, Yongin, Republic of Korea

Dendrimers have attracted much attention due to their potential applications in electronics and optoelectronics such as organic light emitting diodes and photovolatics cells. We have synthesized and characterized the electrochemical properties of conjugated dendrimers bearing phenothiazine derivatives as the peripheral group and phenylenevinylene as a core and corresponding monomer systems. We have found that the electrochemical properties and band gaps strongly depend on substituent and generation. These results can be explained in terms of π*-conjugation length changes as a function of generation.*

Keywords: cyclic voltammetry; dendrimer; electrochemical properties; phenothiazine

1. INTRODUCTION

Dendrimers have attracted extensive attention due to their potential applications in optical emitting devices [1], non-linear optical applications [2], solar energy harvesting antenna [3] and medicinal applications such as drug delivery systems [4]. Since Tomalia *et al.* and Newkome *et al.* reported the synthesis and characterization of the first family of dendrimers [5,6] and Hawker and Frechet introduced the convergent growth approach to dendrimer [7], there are vigorous

---

This research was supported by the "GRRC" Project of Gyeonggi Provincial Government, Republic of Korea (K.H.A., S.I.Y.)

Address correspondence to Kwang-Hyun Ahn or Sung Ik Yang, College of Environment and Applied Chemistry, Materials Research Center for Information Display, Kyung Hee University, Yongin, 449-701, Republic of Korea. E-mail: khahn@khu.ac.kr or siyang@khu.ac.kr

research activities on dendrimers. The advantage of dendrimers compared with monomer is that a number of chromophores can be held together, giving a high density chromophores. In addition, it is easy to introduce various kinds of functional group and to spatially control the active components, size and structures.

Electron rich phenothiazines have nonplanar ring structures since the center six membered ring showed bent form [8]. Phenothiazine has been used as electron donor components due to their low reversible oxidation potentials by virtue of the sulfur atom, which can facilitate the hole transport of the carrier [9]. Recently, phenothiazine-based conjugated polymers have been used as light-emitting materials [10].

In the present paper, we report the synthesis of dendrimers bearing phenothiazine derivatives as the peripheral group and phenylenevinylene as a core. We characterize the electrochemical properties of dendrimers and corresponding monomer systems.

2. EXPERIMENTAL

Materials

Chemicals were obtained from Aldrich and used as received if there is no special statement. All reactions were conducted under a nitrogen atmosphere. The synthetic starting materials were synthesized according to our previously reported methods [11]. Hexaethyl 1,3,5-benzenetriyltris(methylenephosphonate) was prepared according to literature [12].

3-Ethenyl-10-n-hexyl-10H-Phenothiazine(1)

(The general procedure also used for the preparation of **2** and **3**): A solution of 2.0 g (6.4 mmol) of 10-*n*-hexyl-10*H*-phenothiazine-3-carbaldehyde, 2.54 g (7.1 mmol) of methyltriphenylphosphonium bromide and 795 mg (7.1 mmol) of $KOBu^t$ in 50 ml of dry THF was stirred for 2 h at room temperature under N_2. Then the reaction was quenched by adding a small amount of saturated aqueous solution of NH_4Cl. The mixture was extracted with ethyl acetate and washed with water. The organic phase was dried over $MgSO_4$. Chromatography on silica gel (hexane) gave 1.65 g (84%) product **1** as a pale yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.87(m, 3 H), 1.26–1.31(m, 4 H), 1.43(m, 2 H), 1.78(m, 2 H), 3.81(t, $J = 7.2$ Hz, 2 H), 5.12(d, $J = 10.2$ Hz, 1 H), 5.59(d, $J = 16.8$ Hz, 1 H), 6.57(dd, $J = 10.8$ Hz, and $J = 17.4$ Hz, 1 H), 6.77(d, $J = 8.4$ Hz, 1 H), 6.83(d, $J = 8.1$ Hz, 1 H), 6.89(t, $J = 7.5$ Hz, 1 H), 7.10–7.18(m, 4 H). ^{13}C NMR (75 MHz , $CDCl_3$) δ 144.9, 144.7, 135.5, 132.0, 127.3, 127.2, 125.4, 124.8, 124.7, 124.3, 122.3, 115.2, 115.1, 112.0, 47.4, 31.4, 26.8, 26.6, 22.6, 14.0. HRMS (EI) m/z: calcd. $C_{20}H_{23}NS$ M^+ 309.1551, found 309.1550.

3-Ethenyl-10-n-hexyl-7-(2-phenyl-(E)-1-ethenyl)-10H-Phenothiazine (2)

Yellow oil, ^1H NMR ($CDCl_3$, 300 MHz): δ 0.88(m, 3 H), 1.30–1.53 (m, 6 H), 1.79(m, $J = 7.2$ Hz, 2 H), 3.81(t, $J = 7.2$ Hz, 2 H), 5.13 (d, $J = 10.8$ Hz, 1 H), 5.61(d, $J = 17.4$ Hz, 1 H), 6.58(dd, $J = 10.8$ Hz, $J = 17.4$ Hz, 1 H), 6.78(m, 2 H), 6.96(s, 2 H), 7.14–7.27(m, 5 H), 7.34 (t, $J = 6.9$ Hz, 2 H), 7.47(d, $J = 8.4$ Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.6, 26.5, 26.7, 31.4, 47.5, 112.1, 115.0, 115.1, 124.2, 124.4, 124.8, 124.9, 125.4, 125.8, 126.3, 127.0, 127.3, 128.6, 131.8, 132.1, 135.5, 137.4, 144.2, 144.3. HRMS (EI) m/z: calcd. $C_{28}H_{29}NSM^+$ 411.2021, found 411.2029.

3-Ethenyl-10-n-hexyl-7-(2-thien-2-yl-(E)-1-ethenyl)-10H-Phenothiazine (3)

Yellow oil, ^1H NMR ($CDCl_3$, 300 MHz): δ 0.86(t, $J = 6.9$ Hz, 3 H), 1.26–1.37(m, 6 H), 1.73(m, 2 H), 3.73(t, $J = 7.2$ Hz, 2 H), 5.11(d, $J = 10.5$ Hz, 1 H), 5.58(d, $J = 17.4$ Hz, 1 H), 6.55(dd, $J = 10.8$ Hz, $J = 17.4$ Hz, 1 H), 6.69–6.78(m, 3 H), 6.93–7.17(m, 8 H). ^{13}C NMR (75 MHz , $CDCl_3$) δ 14.0, 22.5, 26.5, 26.6, 31.4, 47.5, 112.1, 115.0,115.1, 120.1, 123.9, 124.0, 124.3, 124.6, 124.7, 125.4, 125.6, 127.0, 127.5, 131.3, 132.0, 135.4, 143.0, 144.0, 144.1. HRMS (EI) m/z: calcd. $C_{26}H_{27}NS_2M^+$ 417.1585, found 417.1601.

G1-PTZ3 (4)

The general procedure used for the Wittig-Horner reaction: 592 mg (1.90 mmol) of 10-*n*-hexyl-10*H*-phenothiazine-3-carbaldehyde and 335 mg (0.63 mmol) was dissolved 10 ml of dry THF. The resulting solution was added dropwise slowly to 564 mg (5.04 mmol) of $KOBu^t$ in 30 ml of dry THF at 0°C, then the reaction mixture was warmed to room temperature and stirred under N_2 for 12 h. The reaction was quenched by adding a small amount of saturated aqueous solution of NH_4Cl and extracted with ethyl acetate. The organic phase was dried over $MgSO_4$. Chromatography on silica gel (ethyl acetate/hexane 1:10) gave 525 mg (81%) of product **4** as a yellow solid. mp 94–96°C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88(t, $J = 6.9$ Hz, 9 H), 1.30–1.33(m, 12 H), 1.44 (m, 6 H), 1.81(m, 6 H), 3.84(t, $J = 7.2$ Hz, 6 H), 6.81–6.97(m, 12 H), 7.04(d, $J = 16.2$ Hz, 3 H), 7.12–7.17 (m, 6 H), 7.27–7.31(m, 6 H), 7.44(m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.00, 22.58, 26.62, 26.78, 31.43, 47.54, 115.32, 122.40, 123.29, 123.31, 124.20, 124.88, 124.95, 125.89, 126.68, 127.20, 127.39, 127.79, 131.71, 137.98, 144.55, 144.78;

HRMS (FAB) m/z calcd. $C_{66}H_{69}N_3S_3(M+H)^+$ 1000.4692, found 1000.4732.

The same procedure was used to prepare the dendrimers **5** and **6**:

G1-PTZ3-Ph (5):

Mp. 115–117°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88(t, $J = 6.6$ Hz, 9 H), 1.30–1.42(m, 18 H), 1.78(m, 6 H), 3.82(*br.* s, 6 H), 6.78–6.97(m, 18 H), 7.25–7.48(m, 30 H); ^{13}C NMR (75 MHz $CDCl_3$) δ 14.0, 22.6, 26.5, 29.6, 31.4, 47.4, 115.1, 124.0, 124.8, 125.9, 126.3, 127.3, 128.6, 131.8, 137.3, 143.9 (The ^{13}C-NMR gives poor resolution, so the number of C bar in the spectra is far less than the theoretical number); HRMS (FAB) m/z calcd. $C_{90}H_{87}N_3S_3$ $(M+H)^+$ 1306.8689, found 1306.6140.

G1-PTZ3-Th (6):

Mp. 127–129°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88(t, $J = 6.6$ Hz, 9 H), 1.25–1.40(m, 18 H), 1.76(m, 6 H), 3.74(*br.* s, 6 H), 6.74–7.26(m, 39 H), 7.38(s, 3 H); ^{13}C NMR (75 MHz , $CDCl_3$) δ 14.1, 22.6, 26.5, 29.6, 31.4, 47.5, 115.0, 120.0, 120.2, 123.3, 123.8, 124.1, 124.5, 124.7, 124.8, 125.1, 125.6, 125.9, 126.5, 126.6, 127.5, 128.1, 131.2, 131.6, 137.8, 143.0, 143.8; HRMS *(FAB)* m/z calcd. $C_{90}H_{87}N_3S_3$ $(M+H)^+$ 1324.9520, found 1324.4833.

Characterization

The ^{1}H and ^{13}C NMR spectra were collected on Jeol JNM-AL300 spectrometer at 300 MHz and 75 MHz, respectively. HRMS spectra were recorded on Jeol JMS-700 spectrometer. UV-vis absorption spectra were obtained on a Shimadzu UV-3100 spectrophotometer. Steady-state photoluminescence (PL) spectra were recorded on a Fluoro Max-2 spectrophotometer. The PL quantum yields of the compounds mentioned were determined relative to 9, 10-diphenylanthracene (DPA) as a standard in benzene ($\lambda_{exc} = 380$ nm, $\Phi_f = 0.91$).

Cyclic voltammetry (CV) experiments were performed on a BASi C3 Cell Stand under nitrogen in dry and degassed CH_2Cl_2 at room temperature and at scan rate of 100, 50 and 25 mV/s. The working electrode was 1.6 mm platinum disk, the counter electrode was platinum wire and a Ag/AgCl electrode was used as the reference electrode. The potentials values obtained in reference to Ag/Ag^+ were corrected to the internal standard of Fc/Fc^+ in $CH_2Cl_2(E_{ox}^{1/2} = 0.458\,V)$.

3. RESULTS AND DISCUSSION

Synthesis

In order to investigate the effect of the formation of dendritic architecture on the photophysical and electrochemical properties of materials, we synthesized the precursors (subunit molecules) of the dendrimers, **1–3**, which can be readily obtained from the Wittig reaction between corresponding heterocyclic aldehydes and methyltriphenylphosphonium bromide in good yield (Scheme 1). The typical Wittig-Horner reaction between heterocyclic aldehydes and the core building block, hexaethyl 1,3,5-benzenetriyltris(methylenephosphonate) was used for the synthesis of dendrimers, **4–6** [12].

The synthesized dendrimers **4–6** and their subunit molecules **1–3**, which are soluble in various organic solvents such as chloroform, dichloromethane, 1,2-dichloroethane and THF, were characterized by standard spectroscopic measurements. The ^{1}H NMR spectra ($CDCl_3$) of **G1-PTZ3** showed sharp and well resolved signals at room temperature. On the other hand, the signals of **G1-PTZ3-Ph** and **G1-PTZ3-Th** were broad at room temperature which might be due to the slow conformational change because of the extended chain length as shown by their ^{13}C NMR spectra. In addition, all the NMR spectra indicate that the dendrimers adopt highly symmetric conformations in solution.

Electrochemical Properties

Cyclic voltammetry (CV) experiments were conducted to probe the electrochemical properties of the dendrimers and subunit molecules (Figure 1 and Table 1). Compounds **1–3** show first reversible one-electron oxidation potential at 634–688 mV *vs*. Ag/AgCl, which were shifted cathodically with respect to the parent compound 10-n-hexyl-10H-Phenothiazine as a result of the extended π-conjugated skeleton. The observed peak separation for the reversible waves was $\sim$90 mV, which is larger than that of theoretical value (59 mV) of one-electron redox process. However, the internal standard, ferrocene gave a similar ΔEp (109 mV) under the same experimental conditions. Additionally, the studies of scan rate show the peak current (i_p) of the first reversible oxidation waves are proportional to the square root of the scan rate ($\nu^{1/2}$). But these are not the cases for second oxidation of **1–3**. Irreversible or quasi reversible oxidation waves were found at 1270–1468 mV for the sequential oxidation processes which can be attributed to the formation of unstable, highly reactive dication and/or or trication. It is worthy to note the introduction of electron-rich thiophene ring gives rise to more complex oxidation behavior (even exhibits an additional irreversible oxidation wave) and lower the oxidation potential as shown in Figure 1(f). On the other hand, the data suggested that as the conjugated length becomes longer, which leads to stabilize the radical cation(s) further, the oxidation potential becomes lower.

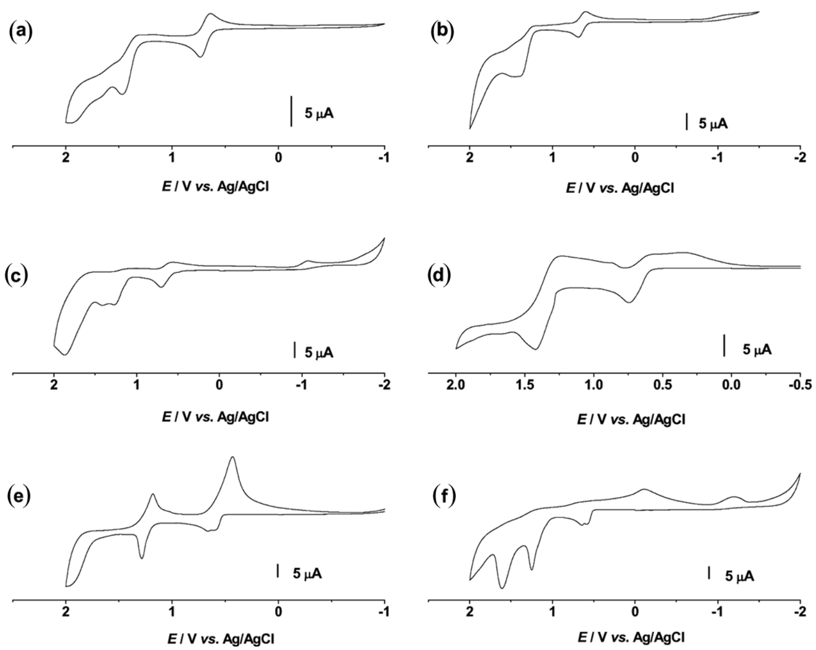


FIGURE 1 Cyclic voltammograms of compounds 1–6 (a–f) in CH_2Cl_2 containing 0.1 M Bu_4NPF_6, scan rate 0.05 V/s.

TABLE 1 Electrochemical Properties of **1**–**6**

	$E_{ox}(\Delta E$p) (mV)[a]	Absoption edge (nm)[d]	$E_g{}^{opt}$ (eV)	HOMO (eV)[e]	LUMO (eV)[e]
1	688(94)[b], 1468[c]	415	2.99	5.03	2.04
2	641(87)[b], 1457[c]	449	2.76	4.98	2.22
3	634(138)[b], 1270[c]	455	2.73	4.98	2.25
4	604(180)[b], 1317(197)[b]	449	2.76	4.95	2.19
5	545(212)[b], 1221(113)[b]	466	2.66	4.89	2.23
6	529(247)[b], 1250[c]	473	2.62	4.87	2.25
10-HP[f]	728	–	–	4.70	1.72

[a] E_{ox} and ΔEp data are in mV units with reference to Ag/AgCl.

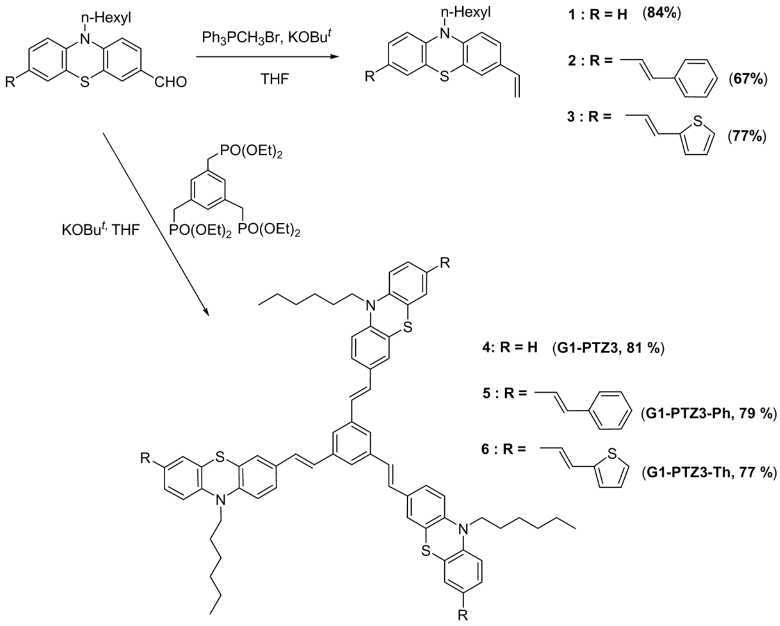
[b] Reversible oxidation half-wave potential.

[c] Irreversible oxidation peak potential.

[d] The E_g^{opt} optical band gap was derived from the intersection point of the normalized absorption and emission spectra ($E_g = 1240/\lambda_{onset}$).

[e] The energy of the HOMO was calculated with reference to ferrocene (4.8 eV *vs.* vacuum, $E_{HOMO} = E_{ox\ vs\ Fc/Fc^+} + 4.8$) and the energy of the LUMO was obtained by equation: $E_{LUMO} = E_{HOMO} - E_g^{opt}$.

[f] 10-HP stands for 10-hexylphenothiazine, respectively [13].



SCHEME 1 Synthetic route to dendrimer.

Upon extending the eletrophores from the subunits to dendrimers a significant difference in the oxidation behavior becomes apparent. **4** and **5** showed two overlapped oxidation peaks at the range of $0.4 \sim 0.8\,\mathrm{V}$ with current values of twice the height of the corresponding subunits **1–2**, which can be attributed to two consecutive reversible single-electron oxidation processes. Due to the complete or partial overlapping of the first and second oxidation waves, the anodic and cathodic peaks cannot be precisely determined. This result suggested the electronic interactions between the dendritic arms take place upon oxidation. The sequential oxidation of dendrimer **4** has an additional reversible oxidation wave at a half-wave potential ($E_{ox}^{1/2}$) of 1.317 V with a peak splitting $\Delta E\mathrm{p} = 197\,\mathrm{mM}$ and the peak current ($i_{pa} = 16.1\,\mu\mathrm{A}$) is nearly 4 times the value of the first reversible peak ($i_{pa} = 4.1\,\mu\mathrm{A}$) of **1**, which suggest two two-electron oxidation process were involved and gave hexacations eventually. The peak separation ($\Delta E\mathrm{p} = 113\,\mathrm{mM}$) of the reversible oxidation of **5** at $E_{ox}^{1/2} = 1.317\,\mathrm{V}$ and anodic peak current ($i_{pa} = 15.3\,\mu\mathrm{A}$) show this wave consists of four single-electron oxidation and correspond to the formation of hexacations. Although the formation of dendritic structure results in regular

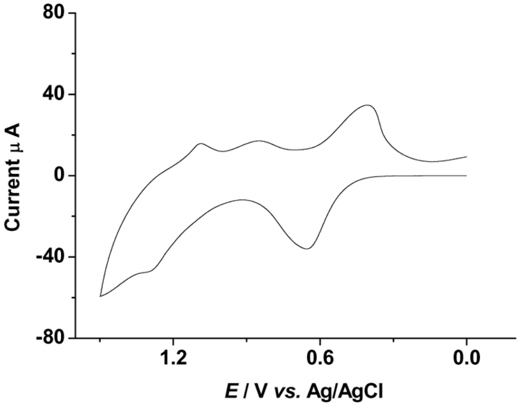


FIGURE 2 Cyclic voltammograms of compound 6 in CH_2Cl_2 containing 0.1 M Bu_4NPF_6, scan rate 0.10 V/s.

negative shift of the oxidation potential, the oxidation processes for **6** is more complex. Figure 1(f) shows the oxidation and reduction waves of **6** in the −2.0–2.0 V (*vs*. Ag/AgCl) scanning range. As demonstrated in the **5**, the anodic oxidation waves peaking at 0.58 and 0.64 can be contributed to the formation of radical cation and dication, respectively and the peak at 1.25 corresponds to the hexacation. The irreversibility of these three oxidation waves likely stems from the formation of unstable, polycation with a oxidation potential of 1.61 V. The formed highly reactive ploycation can readily react with reductive species to give rise a relative stable compound, to which the new reduction wave at −0.109 V most likely corresponds. Upon confining the scanning in the range of 0–1.4 V, dendrimer **6** show a reversible oxidation wave at a half-wave potential ($E_{ox}^{1/2}$) of 0.529 V. The peak splitting ($\Delta E\text{p} = 247\,\text{mM}$) indicate a two-electron oxidation process (Fig. 2). Additionally, there are another reversible oxidation wave ($E_{ox}^{1/2} = 1.193\,\text{V}$) and a cathodic reduction peak at 0.85 V.

The LUMO energy levels of compounds **1–6** determined by the HOMO and optical energy gap were tabulated in Table 1. All compounds have higher HOMO energy levels than the common hole-transporting materials. Therefore, one can expect the phenothiazine-containing compounds, especially the dendrimers to be excellent hole-transporting materials.

4. CONCLUSION

We have synthesized and characterized the electrochemical properties of dendrimers bearing phenothiazine derivatives as the peripheral group and phenylenevinylene as a core and their corresponding monomers. We have found that the electrochemical properties and band gaps strongly depend on substituent and generation which can be explained in terms of π-conjugation length changes.

REFERENCES

[1] Varnavski, O. P., Menkir, G., Burn, P., & Goodson, T. (2000). III. *Appl. Phys. Lett.*, *77*, 1120.

[2] Ma, H., Chen, B., Sassa, T., Dalton, L. R., & Jen, A. K. Y. (2001). *J. Am. Chem. Soc.*, *123*, 986.

[3] Adronov, A., Gilat, S., L., Frechet, J., M., J., Ohta, K., Neuwahl, F. V. R., & Fleming, G. R. (2000). *J. Am. Chem. Soc.*, *122*, 1175.

[4] Dass, C. R. (2002). *J. Pharm. Pharmacol.*, *54*, 3.

[5] Tomalia, D. A., Baker, H., Dewald, J., Hall, M., Kallos, G., Martin, S., Roeck, J., Ryder, J., & Smith, P. (1985). *Polym. J.*, *17*, 117.

[6] Newkome, G. R., Yao, Z., Baker, G. R., & Gupta, V. K. (1985). *J. Org. Chem.*, *50*, 2003.

[7] Hawker, C. J. & Frechet, J. M. J. (1990). *J. Am. Chem. Soc.*, *112*, 7638.

[8] Kramer, C. S., Zeitler, K., & Muller, T. J. J. (2000). *Org. Lett.*, *2*, 3723.

[9] Spreitzer, H. & Daub, J. (1996). *Chem. Eur. J.*, *2*, 1150.

[10] Kong, X., Kulkarni, A., P., & Jenekhe, S. A. (2003). *Macromolecules*, *36*, 8992.

[11] Zhang, X. H., Choi, S. H., Choi, D. H., & Ahn, K. H. (2005). *Tetrahedron Lett.*, *46*, 5273.

[12] Blanchard, P., Svenstrup, N., Rault-Berthelot, J., Riou, A., & Bercher, J. (1998). *Eur. J. Org. Chem.*, 1743.

[13] Kramer, C. S. & Muller, T. J. J. (2003). *Eur. J. Org. Chem.*, 3534.