PAPER

NJC
www.rsc.org/njc

Observation of a non-conventional Horner–Wadsworth–Emmons olefination product and the effect of the lateral ethyl substitution on the solid state fluorescence†

Riju Davis,[a] Shibu Abraham,[a] Nigam P. Rath[b] and Suresh Das*[a]

[a] *Photosciences and Photonics Division, Regional Research Laboratory (CSIR), Trivandrum, 695019 India. E-mail: sdaas@rediffmail.com; Fax: +91-471-2490186; Tel: +91-471-2515318*
[b] *Department of Chemistry, University of Missouri-St. Louis, St. Louis, MO 63121 USA*

Received (in Montpellier, France) 9th June 2004, Accepted 30th June 2004
First published as an Advance Article on the web 18th October 2004

Donor-acceptor-substituted diphenylbutadienes, namely 1-(*p*-methoxyphenyl)-4-(*p*-cyanophenyl)buta-1*E*,3*E*-diene (MCB) and 1-(*p*-*N*,*N*-dimethylaminophenyl)-4-(*p*-cyanophenyl)buta-1*E*,3*E*-diene (ACB) exhibit fluorescence properties in their solid that are distinctly different from their fluorescence in solution. The red-shifted absorption and emission spectra observed in the solid state are attributed to the formation of *J* aggregates. Preparation of these derivatives *via* a Horner–Wadsworth–Emmons reaction, wherein the phosphonate obtained by treating *p*-cyanobenzyl bromide with triethyl phosphite was condensed with corresponding cinnamaldehydes, also yielded the non-conventional olefination products 1-(*p*-methoxyphenyl)-4-(*p*-cyanophenyl)-4-(ethyl)buta-1*E*,3*E*-diene (MCBE) and 1-(*p*-*N*,*N*-dimethylaminophenyl)-4-(*p*-cyanophenyl)-4-(ethyl)buta-1*E*,3*E*-diene (ACBE), which bear an ethyl group substituent on their butadiene chain. The formation of these products suggests a base-catalyzed 1,3-migration of an ethyl group from an oxygen center to the benzylic position in the initially formed phosphonate. The presence of the ethyl group in an otherwise planar molecule was observed to significantly hinder aggregation in the solid state, resulting in molecule-like fluorescence even in their bulk state.

Introduction

Non-covalent molecular interactions such as aggregation play a major role in controlling molecular organization in materials and an in depth knowledge of these interactions is fundamental for predicting their structure-property relationships.[1–4] The role of molecular packing in determining solid state fluorescence and other photophysical properties of organic molecules is an area that is still not well understood and it is of significant importance in the design of organic light emitting diodes (OLEDs).[5–7] Although a number of chromophores exhibiting blue emission in solution have been designed and synthesized, their solid state fluorescence is either quenched or red-shifted due to exciton coupling caused by molecular aggregation. In the field of OLEDs, the development of blue light emitting materials is of immense significance due to their applicability in the development of full color RGB displays.[8] Our studies on alkoxy-cyano-substituted diphenylbutadienes have shown that these molecules self-assemble in the bulk with the aid of π-stacking and intermolecular hydrogen bonding interactions, causing their fluorescence in the solid state to be drastically different from that of the individual molecules, as observed in solution phase studies.[9] Most conjugated molecules are known to self-assemble *via* extended π-stacks or form aggregates that usually result in bulk properties distinctly different from those of their constituent molecules. Minimization of molecular interactions and maintaining molecular level properties in the bulk has therefore been an important goal in material design. Introduction of molecular kinks within polymeric structures, for example, has been utilized in several studies to prevent molecular aggregation in materials.[10,11] The syntheses of most conjugated systems employ the Wittig, Arbuzov and Horner–Wadsworth–Emmons (HWE) reactions, which are fundamental reactions to generate double bonds with a high degree of geometric control.[12–18] The efficacy of these reactions is being exploited to obtain a variety of π-conjugated molecular materials for use in optoelectronic applications, including nonlinear optics[19] and light emitting diodes.[20–22] Here, we report the formation of a non-conventional olefination product following an HWE reaction and suggest a feasible reaction pathway. This observation can provide insights on generating a facile reaction to obtain laterally substituted olefins. The products obtained possess drastically different solid state fluorescence properties in comparison to the normal olefination product and this is attributed to restriction of molecular aggregation in the solid state, resulting in molecule-like fluorescence.

Experimental

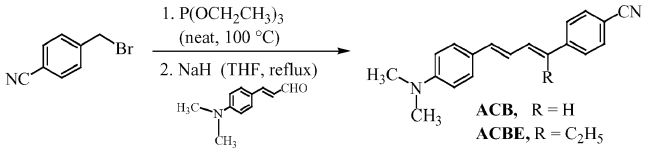
Solid state fluorescence spectra were recorded using the front face emission scan mode on a SPEX Fluorolog F112X spectrofluorimeter. Diffuse reflectance absorption spectra were recorded using a Shimadzu integrating sphere assembly attached to a Shimadzu UV-Vis-NIR 3101 PC spectrophotometer. $BaSO_4$ was used as the reflectance standard. Fluorescence quantum yields were determined by comparison with quinine sulfate in 0.1 M H_2SO_4 (Φ_F = 0.564), which was used as fluorescence standard.

Crystal data for ACBE

Single crystal XRD analyses were carried out on a Siemens SMART-1K CCD diffractometer with Mo source and graphite monochromator. $C_{21}H_{22}N_2$, M = 302.41, orthorhombic,

† Electronic supplementary information (ESI) available: colour figure showing solid state fluorescence of MCB and MCBE. See http://www.rsc.org/suppdata/nj/b4/b408748h/

DOI: 10.1039/b408748h



Scheme 1

a = 16.1420(3), b = 18.9857(4) and c = 11.1379(2) Å, α = β = γ = 90°, U = 3413.40(11) Å^3, T = 120(2) K, space group $Pna2_1$, Z = 8, μ = 0.069 mm^{-1}, 51849 reflections measured, 6697 unique (R_{int} = 0.079), final R indices [$I > 2\sigma(I)$]: R_1 = 0.0609, wR_2 = 0.1277; R indices (all data): R_1 = 0.1577, wR_2 = 0.1658.‡

Syntheses

Preparation of the phosphonate ester of *p*-cyanobenzylbromide (3). A mixture of *p*-cyanobenzyl bromide (100 mg, 0.5 mmol) and triethyl phosphite (1 mmol) was heated at 100 °C for 24 h.[23] After cooling, the unreacted triethyl phosphite was distilled out under reduced pressure, leaving behind the phosphonate ester of *p*-cyanobenzylbromide **3**, which was obtained as a viscous liquid. IR (KBr): ν_{max} 2990, 2913, 2227, 1615, 1512, 1445, 1393, 1249, 1166, 1043, 971, 863, 785 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.25 (t, 6H, CH_3), 3.20 (d, 2H, CH_2), 4.10 [q, 4H, $(CH_2)_2$], 7.43 (d, 2H, aromatic), 7.61 (d, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.1, 20.59, 32.93, 34.75, 62.25, 110.64, 118.45, 130.36, 132.01, and 137.45.

Preparation of 1-(*p*-*N*,*N*-dimethylaminophenyl)-4-(*p*-cyanophenyl)-4-(ethyl)buta-1*E*,3*E*-diene (ACBE). To the phosphonate ester **3**, NaH (61 mg, 2.5 mmol) was added, followed by dropwise addition of dry THF (10 mL) with efficient stirring. After about 10 min, a THF solution (10 mL) of *p*-*N*,*N*-dimethylaminocinnamaldehyde (89 mg, 0.5 mmol) was added dropwise and the resultant mixture was refluxed for 24 h under an argon atmosphere. The solvent was removed under reduced pressure and the residue was washed with water. The crude products were extracted using dichloromethane. Purification of the products by column chromatography over silica gel (100–200 mesh) using a mixture (1 : 19) of ethyl acetate and hexane as the eluent gave ACB (36%) and ACBE (4%).

ACBE: Mp 142–143 °C; IR (KBr): ν_{max} 3744, 3036, 2921, 2355, 2213, 1573, 1512, 1357, 1175, 960, 811 cm^{-1} UV (toluene): λ_{max} 396 nm (ε = 87 336 M^{-1}cm^{-1}); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.10 (t, 3H, CH_3), 2.69–2.77 (q, 2H, CH_2), 2.99 [s, 6H, $N(CH_3)_2$], 6.59–6.68 (m, 2H, olefinic), 6.68–6.71 (m, 2H, aromatic), 6.92–7.01 (dd, 1H, olefinic, J = 15.0 Hz), 7.36 (d, 2H, aromatic, J = 8.7 Hz), 7.52 (d, 2H, aromatic, J = 8.6 Hz), 7.59 (d, 2H, aromatic, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.01, 22.73, 40.36, 109.57, 112.33, 119.26, 120.70, 125.59, 126.22, 127.80, 130.50, 132.12, 135.83, 138.60, 146.87, 150.35. MS (EI): m/z 302 (M^+, $C_{21}H_{22}N_2$).

Preparation of 1-(*p*-methoxyphenyl)-4-(*p*-cyanophenyl)-4-(ethyl)buta-1*E*,3*E*-diene (MCBE). To the phosphonate ester **3**, NaH (61 mg, 2.5 mmol) was added and the mixture was heated at 100 °C for 24 h. NaH (61 mg, 2.5 mmol) was added, followed by dropwise addition of a THF solution (20 mL) of *p*-methoxycinnamaldehyde (83 mg, 0.5 mmol) and the resultant mixture was refluxed for 24 h under an argon atmosphere. The solvent was removed under reduced pressure and the residue was washed with water. The crude products were extracted with dichloromethane. Purification of the products by column chromatography over silica gel (100–200 mesh) using a mixture (1 : 99) of ethyl acetate and hexane as the eluent gave MCBE (30%) and MCB (30%).

MCBE: Mp 107–108 °C. IR ν_{max} (KBr): 2965, 2225, 1584, 1506, 1248, 1175, 1020, 963, 818 cm^{-1} UV (toluene): λ_{max} 360 nm (ε = 4842 M^{-1}cm^{-1}); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.04 (t, 3H, CH_3), 2.64–2.71 (q, 2H, CH_2), 3.77 (s, 3H, OCH_3), 6.52 (d, 1H, olefinic, J = 11 Hz), 6.63 (d, 1H, olefinic, J = 15 Hz), 6.83 (d, 2H, aromatic, J = 8 Hz), 6.92–7.01 (dd, 1H, olefinic, J = 15 Hz), 7.35 (d, 2H, aromatic, J = 8.7 Hz), 7.47 (d, 2H, aromatic, J = 8.5 Hz), 7.55 (d, 2H, aromatic, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.06, 22.85, 55.34, 110.96, 114.14, 119.18, 122.77, 126.41, 127.88, 129.92, 130.07, 132.18, 134.92, 140.27, 146.71. MS (EI): m/z 289 (M^+, $C_{20}H_{19}NO$).

Results and discussion

Syntheses, structure and formation mechanism

Alkoxy-cyano-substituted diphenylbutadienes have been reported to possess liquid crystalline phases and our initial interest was to investigate photoinduced isothermal phase transitions in these materials.[24] These derivatives were synthesized by base-catalyzed condensation of the phosphonate of *p*-cyanobenzyl bromide with *p*-alkoxycinnamaldehydes. These materials also exhibited strong solid state fluorescence.[9]

We were interested in 1-(*p*-*N*,*N*-dimethylaminophenyl)-4-(*p*-cyanophenyl)buta-1*E*,3*E*-diene (ACB), to study the effect of donor strength on the solid state fluorescence of these chromophores. Braatz *et al.* have studied the solution phase fluorescence and photoisomerization properties of ACB.[25] For the preparation of ACB, we used the HWE reaction, with triethyl phosphite as the phosphonating reagent (Scheme 1). Interestingly, apart from the expected product, ACB, the reaction also yielded 1-(*p*-*N*,*N*-dimethylaminophenyl)-4-(*p*-cyanophenyl)-4-(ethyl)buta-1*E*,3*E*-diene (ACBE). The structure of ACBE was unequivocally established on the basis of spectroscopic techniques and X-ray crystallographic analysis (Fig. 1).

Kucerovy *et al.* have observed a similar product formed during the synthesis of 5-[2-(2,5-dimethoxyphenyl)ethyl]-2-hydroxybenzoate.[26] To carry out an HWE reaction they used dimethyl phosphite as the phosphonating reagent and obtained trace amounts of an unexpected product bearing a methyl substitution on the unsaturated bond. The intermediate methyl phosphonate has been indicated to be the methylating agent.

The formation of ACBE may be rationalized in terms of the pathways shown in Scheme 2. The initial step, an Arbuzov reaction, involves the formation of the phosphonate **3**, which was isolated from the reaction mixture by column chromatography. The structure of **3** was confirmed using ^{1}H NMR, which clearly showed the presence of a two-proton doublet at δ 3.20 that corresponds to the benzylic protons. The phosphonate carbanion of **3**, formed in the presence of NaH, reacts with *p*-(*N*,*N*-dimethylamino)cinnamaldehyde, leading to the formation of ACB. The formation of ACBE will require an ethyl group at the benzylic carbon of the phosphonate carbanion. The only source of an ethyl group in the reaction mixture is triethyl phosphite. A probable route to the formation of ACBE involves the formation of the phosphonate **5** *via* an

‡ CCDC reference numbers 228416. See http://www.rsc.org/suppdata/nj/b4/b408748h/ for crystallographic data in .cif or other electronic format.

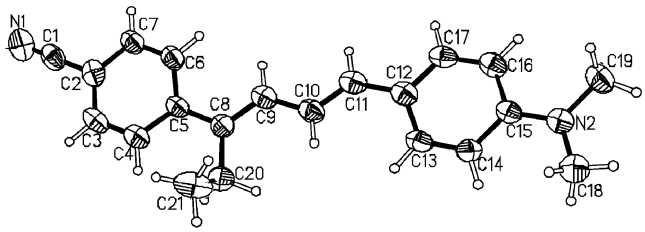
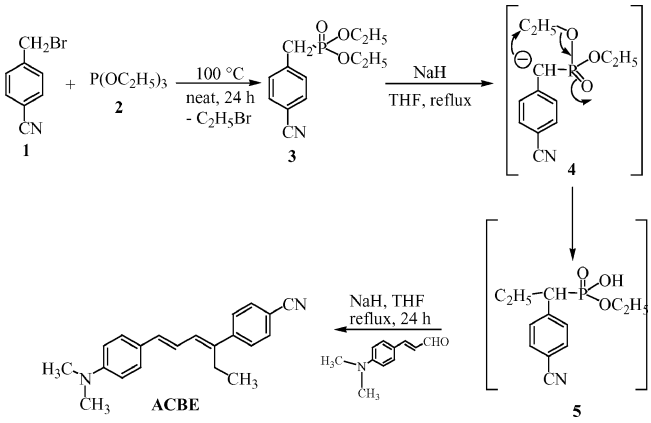


Fig. 1 ORTEP diagram of ACBE.



Scheme 2

intramolecular migration of an ethyl group as shown in Scheme 2.

We propose that the base-catalyzed transformation of **3** to **5** involves a four-membered transition state. The phosphonate carbanion of **5** can condense with *p*-(*N*,*N*-dimethylamino)cinnamaldehyde to form ACBE. However, formation of the ethyl-substituted product *via* an intermolecular mechanism cannot be ruled out.

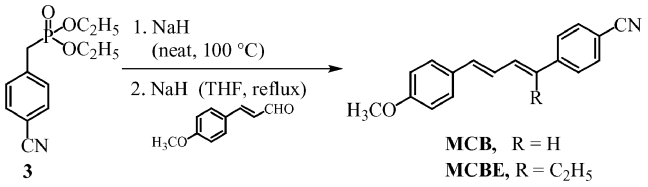
It is interesting to note that the analogous ethyl-substituted product was never observed during the synthesis of alkoxy-cyano-substituted diphenylbutadienes using similar reaction conditions.[24] This may be rationalized on the basis of the difference in the donor strengths of the amino and the alkoxy groups, which can have a pronounced effect on the electrophilicity of the carbonyl center in the corresponding cinnamaldehydes. The carbonyl center in *p*-(*N*,*N*-dimethylamino)cinnamaldehyde is rendered less electrophilic due to the strong positive mesomeric effect or the stronger electron-donating nature of the amino group compared to alkoxy groups in alkoxycinnamaldehydes. As a result, the reaction between the cinnamaldehydes and the phosphonate carbanion of **3** will be more facile in the case of the alkoxycinnamaldehydes. The less facile reaction of the aminocinnamaldehyde with the phosphonate carbanion of **3** can result in a competitive base-catalyzed formation of the phosphonate **5**, which can eventually lead to the formation of ACBE as proposed in Scheme 2.

To further investigate the mechanism of the formation of the ethyl-substituted product, phosphonate **3** was treated with NaH in the absence of aldehyde (Scheme 3). This reaction was carried out to generate the ethyl-migrated phosphonate **5**. Spectroscopic characterization of **5**, however, was not possible due to its unstable nature. Subsequent base-catalyzed condensation of phosphonate **5** with any aldehyde should result in the corresponding ethyl-substituted olefin. This was confirmed by treating the product mixture containing the phosphonate **5** with NaH in the presence of *p*-(methoxy)cinnamaldehyde, which resulted in the formation of 1-(*p*-methoxyphenyl)-4-(*p*-cyanophenyl)-4-(ethyl)buta-1*E*,3*E*-diene (MCBE). MCB was also formed by the reaction of *p*-(methoxy)cinnamaldehyde with phosphonate **3** also present in the reaction mixture.

Effect of the lateral substitution on molecular packing and its role in controlling solid state fluorescence

The fluorescence spectral data for the donor-acceptor-substituted butadienes in solution and in the solid state are summarized in Table 1. Both ACB and ACBE exhibit weak solution state fluorescence with emission maxima at 508 and 506 nm, respectively. The shapes of the fluorescence spectra of these derivatives in toluene were practically indistinguishable. The fluorescence spectra of MCB and MCBE in solution were also nearly identical (Table 1).

In the solid state, however, the fluorescence maxima of ACBE (576 nm) is blue-shifted compared to that of ACB (592 nm). Fig. 2 shows the solid state fluorescence spectra of ACB and ACBE measured under identical conditions. Apart from the blue shift a significant enhancement in fluorescence intensity was observed for ACBE compared to ACB. An interesting difference was also observed in the melting behavior



Scheme 3

Table 1 Solution and solid state fluorescence characteristics

Compound	Toluene λ_{max}/nm (Φ_F)	Solid state λ_{max}/nm	$\Delta\lambda_{max}$/nm
ACB	508 (0.02)	592	84
ACBE	506 (0.03)	576	70
MCB	435 (0.01)	495	60
MCBE	437 (0.03)	457, 479	20, 42

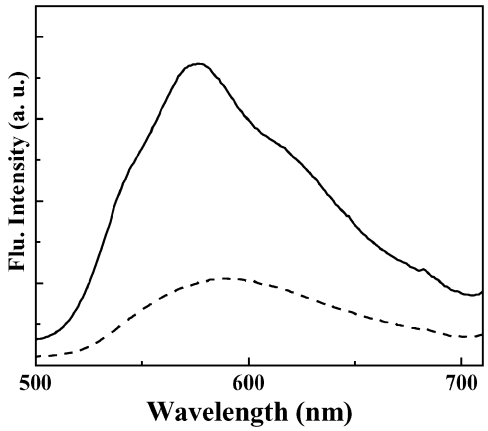


Fig. 2 Fluorescence spectra of ACB (———, powder) and ACBE (——, powder). Excitation wavelength: 375 nm.

of these derivatives. Whereas ACB undergoes decomposition at 250 °C, ACBE was observed to melt at 142 °C, and on cooling forms a thin yellow film.

The effect of the lateral ethyl group substitution on the solid state fluorescence of the methoxy-cyano-substituted diphenylbutadienes was much more pronounced. The solid state fluorescence spectrum of MCB possessed a maximum at 495 nm and its fluorescence was visually perceivable as green, whereas MCBE exhibited a substantially blue-shifted fluorescence spectrum with maxima at 457 and 479 nm; its fluorescence was visually perceivable as blue (Fig. 3 and ESI†). Both MCB and MCBE show Stokes' shift values of 73 and 74 nm, respectively in their solution state, with the corresponding values in their solid state being 92 nm and 79 nm, respectively.

The diffuse reflectance absorption spectrum of MCB possesses a broad absorption with a maximum centered at 404 nm (Fig. 4). In contrast the spectrum of MCBE is substantially narrower and blue-shifted compared to that of MCB. The absorption maximum of MCBE (378 nm) is significantly closer to its solution phase absorption maximum.

The similarity of the fluorescence spectra of the donor-acceptor-substituted butadienes measured in solution clearly indicates that the presence of the laterally substituted ethyl

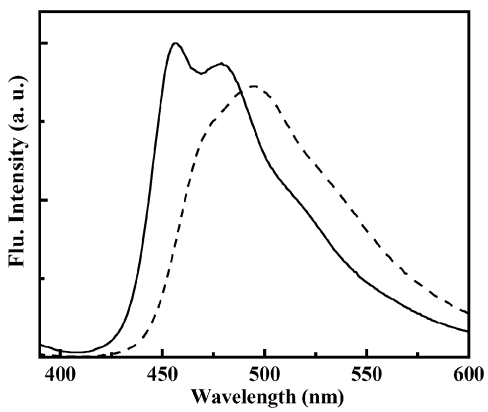


Fig. 3 Fluorescence spectra of MCB (———) and MCBE (——) in the solid state. Excitation wavelength: 360 nm.

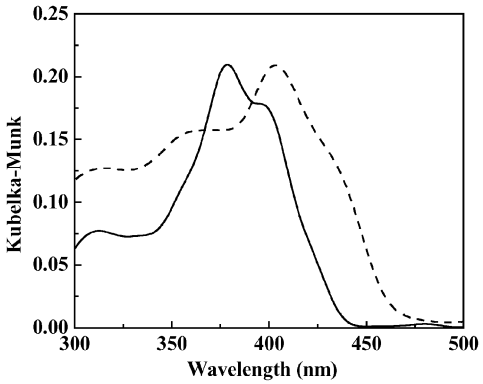


Fig. 4 Diffuse reflectance absorption spectra of MCBE (——) and MCB (——).

group does not affect their chromophore properties significantly. The effect of the lateral ethyl group substitution on the solid state fluorescence spectra of these derivatives can therefore be clearly attributed to changes in their molecular packing. Close packing of molecules in the solid state of ACB and MCB can result in ground state interactions leading to molecular aggregation, as indicated by the red shift and broadening of the absorption and emission spectra compared to that observed in solution. The red shift in the absorption and emission spectrum is indicative of the formation of *J*-type aggregates. The solid state fluorescence of alkoxy-cyano-substituted diphenylbutadienes has been shown to depend on its monomer : *J*-aggregate ratio.[9] When an ethyl group is introduced at the lateral position the molecules are no longer planar and are unable to interact as effectively with each other, resulting in destabilization of the aggregates.

Conclusions

In summary, we have reported the formation of a non-conventional olefination product bearing a lateral ethyl group substitution on the generated olefinic bond. The lateral ethyl group in these butadiene derivatives plays an active role in controlling their material properties, as evidenced from its effect on their solid state fluorescence properties. The presence of the ethyl group restricts molecular aggregation, thereby restoring molecule-like fluorescence even in the bulk. By suitable modification of the intermediate phosphonates in an HWE reaction, it may be possible to introduce other desired lateral substituents on unsaturated bonds and this aspect will be further explored.

Acknowledgements

We wish to thank Professor M. V. George for useful discussions. RD, SA and SD thank the Council of Scientific and Industrial Research (TF-CMM0010) and the Department of Science and Technology, Government of India for financial assistance. This is contribution No. RRLT-PPD-173 from RRL (CSIR), Trivandrum.

References

1 C. A. Hunter, K. R. Lawson, J. Perkin and C. J. Urch, *J. Chem. Soc., Perkin Trans. 2*, 2001, 651.
2 B. M. Krasovitskii and B. M. Bolotin, *Organic Luminescent Materials*, VCH, Weinheim, 1988.
3 M. J. Packer, M. P. Dauncey and C. A. Hunter, *J. Mol. Biol.*, 2000, **295**, 85.
4 F. D. Lewis and J.-S. Yang, *J. Phys. Chem. B*, 1997, **101**, 1775.
5 R. J. Davey, N. Blagden, G. D. Potts and R. Docherty, *J. Am. Chem. Soc.*, 1997, **119**, 1767.

6 B. M. Sheikh-Ali, M. Rapta, G. B. Jameson, C. Cui and R. G. Weiss, *J. Phys. Chem.*, 1994, **98**, 10 412.
7 A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 403.
8 L. M. Leung, W. Y. Lo, S. K. So, K. M. Lee and W. K. Choi, *J. Am. Chem. Soc.*, 2000, **122**, 5640.
9 R. Davis, N. P. Rath and S. Das, *Chem. Commun.*, 2004, 74.
10 T. Ahn, M. S. Jang, H. K. Shim, D. H. Hwang and T. Zyung, *Macromolecules*, 1999, **32**, 3279.
11 D. J. Liaw, B. Y. Liaw, P. N. Hsu and C. Y. Hwang, *Chem. Mater.*, 2001, **13**, 1811.
12 J. Boutagy and R. Thomas, *Chem. Rev.*, 1974, **74**, 87.
13 V. K. Aggarwal, J. R. Fulton, C. G. Sheldon and J. deVicente, *J. Am. Chem. Soc.*, 2003, **125**, 6034.
14 R. W. Hoffmann, *Angew. Chem., Int. Ed.*, 2001, **40**, 1411.
15 N. J. Lawrence, in *Preparation of Alkenes: A Practical Approach*, ed. J. M. J. Williams, Oxford University Press, London, 1996, pp. 19–58.
16 W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, 1961, **83**, 1733.
17 A. K. Bhattacharya and G. Thyagarajan, *Chem. Rev.*, 1981, **81**, 415.
18 S. Zheng, S. Barlow, T. C. Parker and S. R. Marder, *Tetrahedron Lett.*, 2003, **44**, 7989.
19 C. Cai, I. Liakatas, M. S. Wong, M. Bösch, C. Bosshard, P. Günter, S. Concilio, N. Tirelli and U. W. Suter, *Org. Lett.*, 1999, **1**, 1847.
20 M. S. Wong, Z. H. Li, Y. Tao and M. D'Iorio, *Chem. Mater.*, 2003, **15**, 1198.
21 A. M. Sarker, L. Ding, P. M. Lahti and F. E. Karasz, *Macromolecules*, 2002, **35**, 223.
22 L. H. Chan, R. H. Lee, C. F. Hsieh, H. C. Yeh and C. T. Chen, *J. Am. Chem. Soc.*, 2002, **124**, 6469.
23 A. P. H. J. Schenning, P. Jonkheijm, E. Peeters and E. W. Meijer, *J. Am. Chem. Soc.*, 2001, **123**, 409.
24 R. Davis, V. A. Mallia and S. Das, *Chem. Mater.*, 2003, **15**, 1057.
25 H. Braatz, S. Hecht, H. Seifert, S. Helm, J. Bendig and W. Rettig, *J. Photochem. Photobiol. A: Chem.*, 1999, **123**, 99.
26 A. Kucerovy, T. Li, K. Prasad, O. Repic and T. J. Blacklock, *Org. Process Res. Dev.*, 1997, **1**, 287.