ChemComm

Novel liquid-crystalline PPE-naphthalene copolymers displaying blue solid-state fluorescence

Neil G. Pschirer, Mary E. Vaughn, Y. B. Dong, Hans-Conrad zur Loye and Uwe H. F. Bunz*

Department of Chemistry and Biochemistry, The University of South Carolina, Columbia, South Carolina 29208, USA. E-mail: bunz@psc.sc.edu

Received (in Columbia, MO, USA) 14th September 1999, Accepted 5th October 1999

Synthesis of poly(*p*-phenyleneethynylene)s (PPEs) containing 1,5-diethynyl-3,7-di-*tert*-butylnaphthalene leads to novel phenylene-naphthylene-ethynylene copolymers which show strong blue luminescence in the solid state.

Conjugated polymers are organic semiconductors and find *inter alia* applications in electroluminescent devices[1,2] and 'plastic lasers'.[3] We have recently reported an efficient synthesis of high molecular weight poly(*p*-phenyleneethynylene)s (PPEs) by alkyne metathesis utilizing simple 'instant catalysts'.[4] PPEs are promising materials, because they show quantum yields of 1.0 and blue emission in dilute solution. However, in the solid state, the emission spectra of PPEs are much weaker and considerably red-shifted as a consequence of aggregation and concomitant excimer formation in the solid state.[5,6] Likewise poly(3,7-di-*tert*-butylnaphthyleneethynylene), which we recently synthesized, is effectively non-fluorescent as film or powder.[7]

Herein we repot the synthesis and characterization of the unsaturated copolymers **3** which are efficient blue emitters in the solid state (Fig. 1). The polymers **3** are obtained by adding defined amounts of 3,7-di-*tert*-butyl-1,5-dipropynylnaphthalene **2**[7] to 1,4-dipropynyl-2,5-dialkylbenzenes **1** (Scheme 1) in our alkyne metathesis protocol utilizing an instant catalyst formed of $Mo(CO)_6$ and 4-chlorophenol.[8]† The catalyst and a varying ratio of monomers **1** and **2** were stirred in 1,2-dichlorobenzene at 140 °C for 11–25 h under a flow of N_2. This protocol results in a series of high molecular weight copolymers **3**. Longer polymerization times give rise to higher degrees of polymerization, as examined in the PPE system in detail.[8]

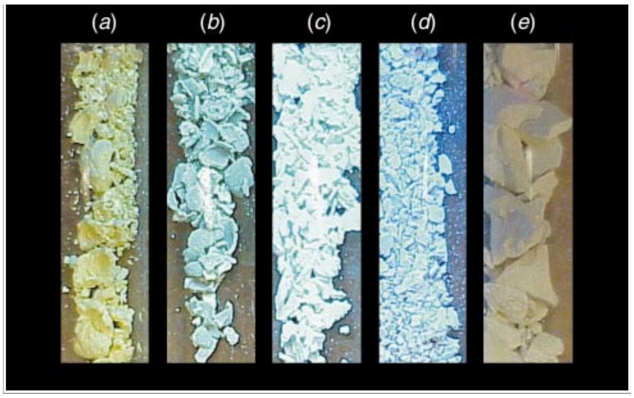
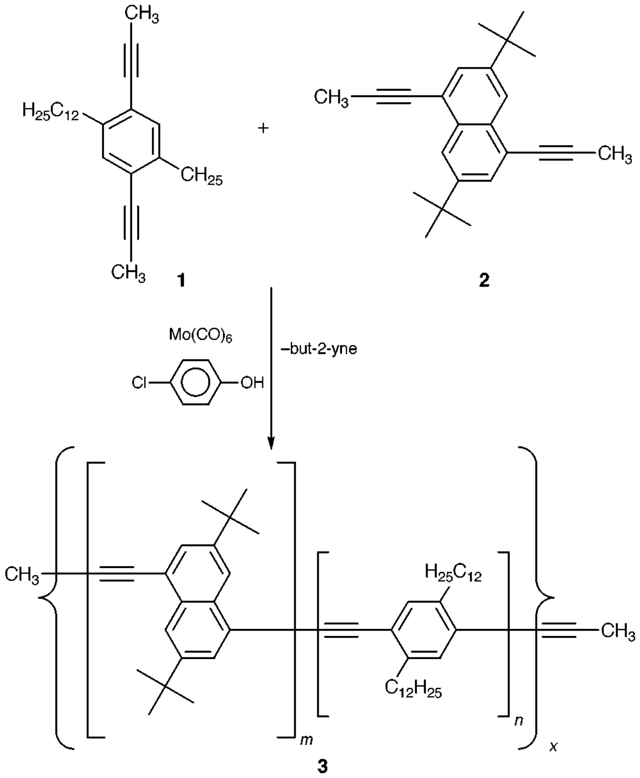


Fig. 1 Solid-state emission (hand held fluorescence lamp, λ_{max} = 366 nm) of PPE and PPE-napthalene copolymers **3**: (*a*) didodecyl-PPE; (*b*) polymer **3a**; (*c*) polymer **3c**; (*d*) polymer **3d**; (*e*) poly(3,7-di-*tert*-butylnaphtyleneethynylene).

The UV–VIS spectra of **3a–d** in dilute solution show a λ_{max} of 388–395 nm, very similar to that of dialkyl-PPEs (388 nm). To our surprise, thin film absorption spectra of **3a–d** are identical to those in solution, which is in stark contrast to the PPE case where a dramatic red-shift is observed. The unusual optical behavior prompted us to investigate fluorescence of **3a–d**. In solution an intense blue emission is observed (**3a**, 425 nm; **3d**, 419 nm), again similar to dialkyl-PPEs (425 nm). In the solid state, however, the situation is different, and in thin films



Scheme 1

Table 1 Characterization of **3a**–**d**

Entry	Ratio **1**:**2**	*t*/h	Yield (%)	GPC $D_p{}^a$	$P_n{}^a$	Absorbance/nm CHCl$_3$	Thin film	Emission/nm CHCl$_3$	Thin film
3a	5:1	25.5	86	96	2.9	395	395, 420	425, 446	446
3b	2:1	11	64	49	2.9	390	390, 420	422, 443	442
3c	1:1	17	79	56	4.7	391	391	421, 444	433
3d	1:2	12.5	77	42	2.3	388	388	419, 440	422

[a] Gel permeation chromatography results based on polystyrene standard.

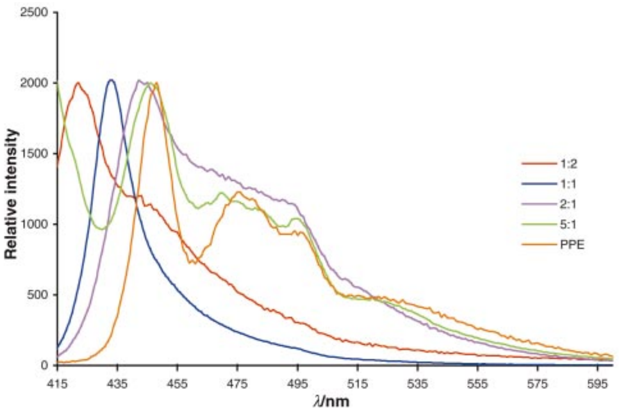


Fig. 2 Solid-state emission spectra of thin films of **3a**–**d** and PPE.

of **3a**–**d** we find emission maxima ranging from 446 (5 : 1, **3a**) to 422 nm (1 : 2, **3d**), (Fig. 2), thus allowing the manipulation of solid-state emission maximum from yellow–green to blue *via* the amount of added monomer **2**. The less PPE character the copolymer **3** has, the further its emission is blue-shifted towards that observed in dilute solution. We conclude that in the copolymers **3** aggregation and supramolecular ordering are efficiently suppressed by the presence of the bulky *tert*-butylnaphthyl groups.[9] This scenario must lead to a disordered solid state in **3**. To test this hypothesis we performed powder diffraction on polymers **3** (Fig. 3). The polymers **3a**–**c** display a broad diffraction peak of large intensity according to d = 4.2 Å. This diffraction peak can be attributed to the interchain distance of the polymers. A second, weak diffraction peak is observed at d = 8.8–11.7 Å, but is very weak in **3a**–**c**. In the naphthalene-rich polymer **3d** the small-angle diffraction at 11.7 Å is most prevalent. Molecular modeling indicates that this represents the distance between the two 3,7-*tert*-butyl groups on individual naphthalene units.[10]

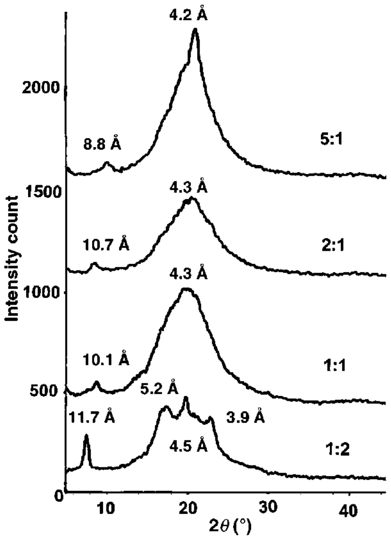


Fig. 3 Diffraction data of polymers **3a**–**d**.

For device purposes, liquid crystalline behavior offers the entry to polarized emission. DSC and polarizing microscopy performed upon **3a**–**c** shows that **3a**,**b** are thermotropic nematic (**3a**: isotropic → nematic 160 °C DSC; nematic → isotropic 170 °C → nematic 149 °C, evidenced by polarizing microscopy, cooling. **3b**: 194 °C polarizing microscopy, cooling isotropic → nematic), both displaying Schlieren textures. Copolymer **3c** displays a broad halo at 4.3 Å, and a weak small angle feature, suggesting either small domain sizes or a disordered structure. No identifiable textures develop upon thermal treatment. Only in the case of **3a** is the isotropic → nematic transition observed in the DSC and it is exothermic, with 0.27 kcal mol^{-1} per repeating unit, a small but not unexpected value.[11] Polymer **3d** is crystalline and does not show any phase transition up to 300 °C.

In conclusion we have presented the synthesis and characterization of a new series of liquid-crystalline PPE copolymers **3** which exhibit blue solid state fluorescence. The blue shift increases with the amount of naphthalene. Particularly attractive is the intensity of luminescence of **3** in the solid state. The increased solid-state fluorescence is attributed to the absence of aggregates and excimers, which normally reduce PPE's quantum efficiencies of emission in the solid state. Application of **3** in LEDs and sensory materials[12] is currently being explored.

We acknowledge Professor C. J. Murphy and L. Gearhart for help with the fluorescence spectra. This work was generously supported by the NSF (CHE 9814118, PI Bunz) and the Research Corporation.

Notes and references

† Sample coploymerization: **1** (0.35 g, 0.71 mmol), **2** (0.24 g, 0.71 mmol), Mo(CO)$_6$ (0.034 g, 0.07 mmol), 4-chlorophenol (0.091 g, 0.71 mmol) and 1,2-dichlorobenzene (20 mL) were held at 140 °C under a steady stream of N$_2$ for 17 h. Addition of chloroform acid and base washes and precipitation into methanol furnish **3c** in 80% yield. *Selected data* for **3c**: δ_H 8.58–8.54 (m), 8.07 (br s), 7.94 (br s), 7.60–7.42 (m), 3.02–2.89 (m), 2.13 (br s), 2.12 (br s), 1.79–1.68 (m), 1.51–1.22 (m), 0.88–0.87 (br s); δ_C 148.4, 141.9, 132.5, 131.3, 123.0, 122.8, 121.1, 93.5, 92.7, 35.1, 34.4, 32.0, 31.4, 31.3, 30.8, 29.8, 29.5, 29.4, 22.8, 14.2; ν_{max}(KBr)/cm^{-1} 3444, 2957, 2923, 2853, 2350, 1651, 1463, 1384, 1025, 886, 771.

1 D. Neher, *Adv. Mater.*, 1995, **7**, 691; A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem.*, 1998, **37**, 402; J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539.

2 S. A. Jenekhe and J. A. Osaheni, *Science*, 1994, **265**, 765; J. A. Osaheni and S. A. Jenekhe, *Macromolecules*, 1994, **27**, 739; X. Zhang, A. S. Shetty and S. A. Jenekhe, *Acta Polym.*, 1998, **49**, 52; E. Conwell, *Trends Polym. Sci.*, 1997, **5**, 218.

3 F. Hide, M. A. Diaz-Garcia, B. J. Schwartz and A. J. Heeger, *Acc. Chem. Res.*, 1997, **30**, 430.

4 L. Kloppenburg, D. Song and U. H. F. Bunz, *J. Am. Chem. Soc.*, 1998, **120**, 7973.

5 C. E. Halkyard, M. E. Rampey, L. Kloppenburg, S. L. Studer-Martinez and U. H. F. Bunz, *Macromolecules*, 1998, **31**, 8655; R. Fiesel, C. E. Halkyard, M. E. Rampey, L. Kloppenburg, S. L. Studer-Martinez, U. Scherf and U. H. F. Bunz, *Macromol. Rapid Commun.*, 1999, **20**, 107.

6 D. Ofer, T. M. Swager and M. S. Wrighton, *Chem. Mater.*, 1995, **7**, 418; Q. Zhou and T. M. Swager, *J. Am. Chem. Soc.*, 1995, **117**, 12 593; C. Weder and M. S. Wrighton, *Macromolecules*, 1996, **29**, 5157.

7 N. G. Pschirer, A. Marshall, C. Stanley, H. W. Beckham and U. H. F. Bunz, *Macromol. Rapid Commun.*, 2000, **21**, in the press.

8 L. Kloppenburg, D. Jones and U. H. F. Bunz, *Macromolecules*, 1999, **32**, 4194.

9 B. R. Hsieh, W. C. Wan, Y. Yu, Y. L. Gao, T. E. Goodwin, S. A. Gonzalez and W. A. Feld, *Macromolecules*, 1998, **31**, 631; W. J. Oldham, R. J. Lachicotte and G. C. Bazan, *J. Am. Chem. Soc.*, 1998, **120**, 2987; G. C. Bazan, Y. J. Miao, M. L. Renak and B. J. Sun, *J. Am. Chem. Soc.*, 1996, **118**, 2618; Z. H. Peng, J. H. Zhang and B. B. Xu, *Macromolecules*, 1999, **32**, 5152.

10 U. H. F. Bunz, V. Enkelmann, L. Kloppenburg, D. Jones, K. D. Shimizu, J. B. Claridge, H.-C. zur Loye and G. Lieser, *Chem. Mater.*, 1999, **11**, 1416; L. Kloppenburg, D. Jones, J. B. Claridge, H. C. zur Loye and U. H. F. Bunz, *Macromolecules*, 1999, **32**, 4460.

11 M. Altmann and U. H. F. Bunz, *Angew. Chem.*, 1995, **35**, 569.

12 J. S. Yang and T. M. Swager, *J. Am. Chem. Soc.*, 1998, **120**, 11 864.

Communication a907479a