ELSEVIER

Thin Solid Films 363 (2000) 149–151

thin solid films

www.elsevier.com/locate/tsf

Synthesis and light-emitting properties of poly(carbazolylacetylenes)

Priscilla Pui-Sze Lee[a], Yanhou Geng[a], Hoi Sing Kwok[b], Ben Zhong Tang[a, b,*]

[a]*Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China*
[b]*Center for Display Research, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China*

Abstract

A group of new carbazole-containing polyacetylenes, poly[*n*–(9–carbazolyl)–1–alkynes] [$m = n - 2$; $m = 3$ (P2a), 9 (P2b)], poly[5–(3,6–dibromo–9–carbazolyl)–1–pentyne] (P3a), and poly[*n*–(9–carbazolyl)–1–chloro–1–alkynes] [$m = n - 2$; $m = 3$ (P4a), $m = 9$ (P4b)], have been synthesized using WCl_6–Ph_4Sn and $MoCl_5$–Ph_4Sn as catalysts. High molecular weight (up to 500 000) polymers have been obtained in high yields (up to 80%). The molecular structures of the polymers are characterized by spectroscopic methods. All the monomers except (P2a) are highly luminescent. The polymer with a long spacer length (P2b) emits intense deep-blue light when excited at 295 nm. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Light emission; Photoluminescence; Poly(carbazolylacetylenes)

1. Introduction

In the old days, electroluminescent materials were dominated by inorganic materials. Nowadays, there is increasing contribution of organic conjugated polymers to electroluminescent applications [1]. Carbazole is the best-known chromophore that is often used to construct polymers with photoconducting, photorefractive, and hole transporting properties [2–5]. In this study, we incorporated carbazole units into polyacetylene and investigated photoluminescence of the resultant carbazole-containing polyacetylenes.

2. Experimental section

2.1. Materials

Tetrahydrofuran (THF), toluene and acetone (all from Lab-Scan) were predried over 4 Å molecular sieves and distilled from sodium benzophenone ketyl immediately prior to use. Carbazole, thionyl chloride, sodium hydride, *t*-butyl lithium, tosyl chloride, tungsten(VI) chloride, tetraphenyltin (all from Aldrich), 5-chloro-1-pentyne, 11-undecyl-1-ol (both from Farchan), molybdenum(V) chloride (Acros), and pyridine (Nacalai Tesque) were used as received. Technical grade methanol and acetone was used for purification of the polymers by precipitation.

2.2. Instrumentation

^{1}H NMR spectra were measured on a Bruker ARX 300 NMR spectrometer using chloroform-*d* as solvent. Tetramethylsilane ($\delta = 0$) and chloroform ($\delta = 7.26$) were used as internal references for the NMR analysis. IR spectra were recorded on Perkin–Elmer 16 PC FTIR spectrometer. Molecular weights of the polymers were estimated by a Waters Associates gel permeation chromatography (GPC) using 12 monodisperse polystyrenes (molecular weight range 10^2–10^7) as calibration standards. Fluorescence spectra were measured on a SLM Aminco JD-490 spectrofluorometer.

2.3. Monomer synthesis

We synthesized three kinds of carbazole-containing acetylene monomers according to Scheme 1 and the corresponding polymers according to Scheme 2.

3. Results and discussion

Table 1 shows the polymerization results of the carbazole-containing monomers. Generally speaking, WCl_6–Ph_4Sn is a better catalyst system than $MoCl_5$–Ph_4Sn except in the cases of 2a and 4b whose spacer lengths are 9. With chlorine substituting the acetylene proton, molecular weight of the polymer dramatically increased when $n = 9$, and partially soluble polymer was produced when $MoCl_5$–Ph_4Sn was used as the catalyst.

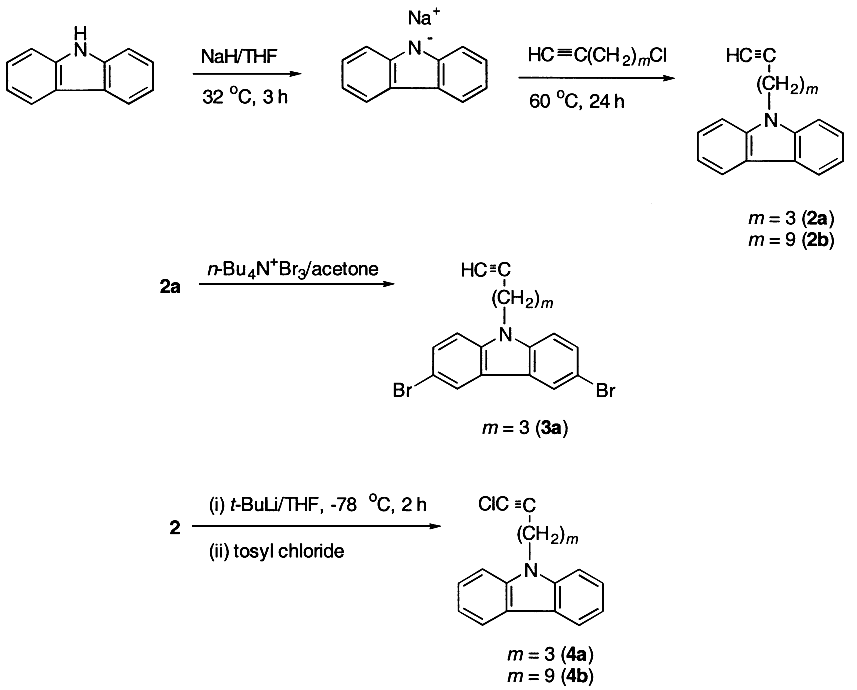
Fig. 1 shows the ^{1}H NMR spectra of carbazole-containing monomer 4b and its polymer P4b. All the peaks correspond

---

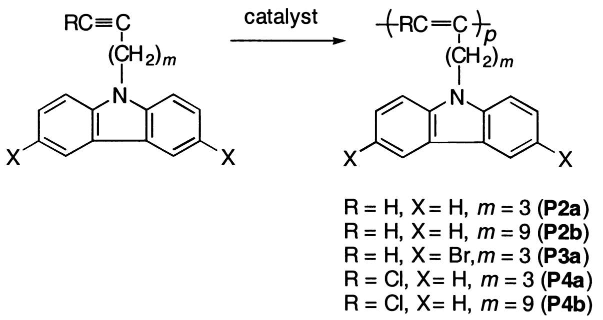
* Corresponding author. Tel.: + 852-2358-7375; fax: + 852-2358-1594.

E-mail address: tangbenz@ust.hk (B.Z. Tang)

0040-6090/00/$ - see front matter © 2000 Elsevier Science S.A. All rights reserved.
PII: S0040-6090(99)01029-9



Scheme 1. Synthesis of carbazole-containing acetylene monomers.



Scheme 2. Polymerization of carbazole-containing acetylene monomers.

Table 1
Polymerization of the carbazole-containing acetylene monomers[a]

Monomer	Catalyst	Yield (%)	M_w	M_w/M_n	Solubility[b]
2a	WCl_6-Ph_4Sn	64.8	66140	7.35	100
	$MoCl_5$–Ph_4Sn	35.6	20290	2.14	100
2b	WCl_6–Ph_4Sn	0			
	$MoCl_5$–Ph_4Sn	80.0	17170	2.49	100
3a	WCl_6–Ph_4Sn	62.0	59870	5.78	100
	$MoCl_5$–Ph_4Sn	7.0	22640	2.11	100
4a	WCl_6–Ph_4Sn	70.9	61220	4.91	100
	$MoCl_5$–Ph_4Sn	70.4	10850	1.83	100
4b	WCl_6–Ph_4Sn	0			
	$MoCl_5$–Ph_4Sn[c]	79.7	492800[d]	2.61	18

[a] Carried out at room temperature for 24 h in toluene under nitrogen, [catalyst] = 20 mM.

[b] In THF.

[c] $[M]_O = 0.25$ M, [catalyst] = 10 mM.

[d] THF-soluble fraction.

well with the expected structure. Fig. 2 shows the IR spectra of carbazole-containing monomer 2a and its polymer P2a. Stretching bands of the ≡CH and C≡C disappeared after polymerization.

Fig. 3 shows the photoluminescence spectra of the carbazole-containing monomers. When the spacer length is 3, the monomer does not show any fluorescence emission. When the spacer length increases to 9, the photoluminescence increases dramatically. Substitution by a chlorine atom greatly increases the photoluminescence even the spacer is as short as 3. When the spacer length increases from 3 in 4a to 9 in 4b, the photoluminescence, however, does not change much.

Fig. 4 shows the photoluminescence spectra of the polymers. Comparing P2a with P3a, P2a emits a very weak

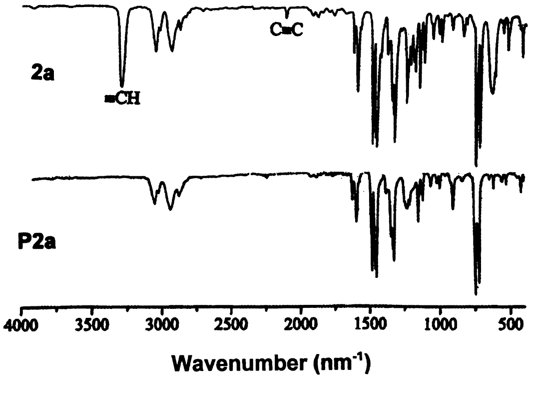


Fig. 2. IR spectra of carbazole-containing acetylene monomer 2a and polymer P2a.

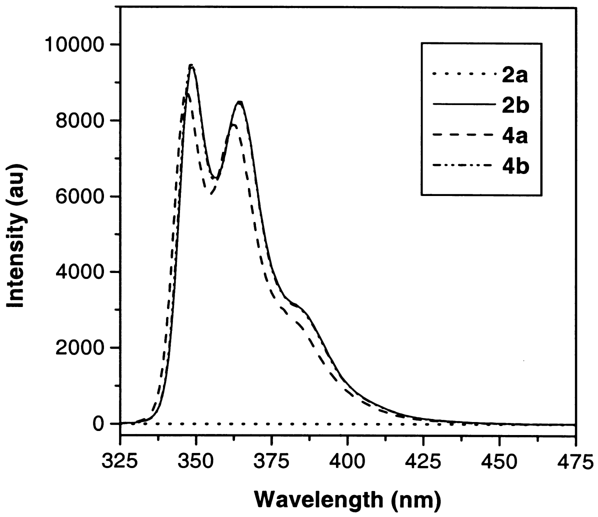


Fig. 3. Photoluminescence spectra of the carbazole-containing acetylene monomers (excited at 295 nm, concentration: 0.02 mg/ml).

fluorescence. When the spacer length increases to 9, surprisingly, the intensity of photoluminescence of P2b increases dramatically by eight folds. The introduction of a chlorine atom in the place of vinyl proton, however, did not increase the photoluminescence intensity.

4. Conclusion

Highly fluorescent polyacetylenes containing carbazole chromophore have been synthesized. Changing the spacer length greatly changes the photoluminescence intensity. The introduction of either a chlorine atom to the polyacetylene backbone in the place of the vinyl proton or two bromine atoms to the carbazole chromophore, does not greatly change the fluorescence emission. The fluorescence spectra of the monomers have also been examined, but no fluorescence emission is detected when the spacer length is short. When the spacer increases, photoluminescence efficiency enhances dramatically. The long spacer separating the polyacetylene backbone and the carbazole pendants may have effectively turned off the electronic communication between the main- and side-chains. The emission from the carbazole chromophore is, thus, not absorbed or quenched by the polyene backbone [6,7], accounting for the efficient luminescence from the polymers with the long spacer length.

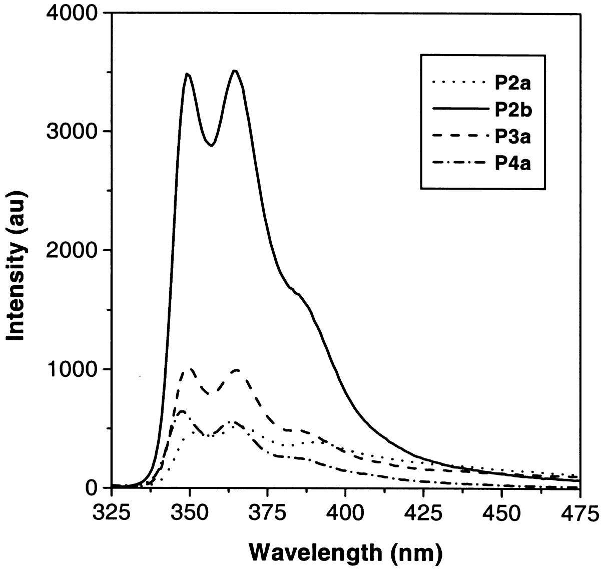


Fig. 4. Photoluminescence spectra of carbazole-containing polyacetylenes (excited at 295 nm, concentration: 0.02 mg/ml).

References

[1] A. Kraft, A.C. Grimsdale, A.B. Holmes, Angew. Chem. Int. Ed., 37 (1998) 402.

[2] Y.D. Zhang, T. Wada, H. Sasabe, J. Mater. Chem. 8 (4) (1998) 809.

[3] C. Maertens, C. Detrembleur, P. Dubois, R. Jérôme, Chem. Mater. 10 (1998) 1010.

[4] K.D. Belfield, C. Chinna, O. Najjar, Macromolecules 31 (1998) 2918.

[5] X.T. Tao, Y.D. Zhang, T. Wada, et al., Adv. Mater. 10 (1998) 226.

[6] Y.M. Huang, I.W.Y. Lam, K.K.L. Cheuk, W. Ge, B.Z. Tang, Macromolecules 32 (1999) 5976.

[7] Y. Huang, W. Ge, J.W.Y. Lam, B.Z. Tang, Appl. Phys. Lett. (1999) 74 in press.