A Novel Synthetic Route to Functional Poly(diphenylsubstituted acetylenes) *via* Phenol-Yne Click Reactior

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Abstract: We report a new synthetic strategy to derive functional poly(disubstituted acetylenes) (PDSAs) through "phenol-yne click reaction". The phenol-containing PDSA was prepared by the polymerization of the triisopropylsilan (TIPS)-protected 4-((4-fluorophenyl)ethynyl)phenol monomer and the subsequent a de-protection step. Then, different functional groups (e. g., ester and amide) were grafted onto the PDSA side chains via the highly efficient "phenol-yne click reaction". The post-polymerization modification was carried out in mild conditions for a short time (4 h). The structures of the products were well characterized by GPC, NMR, and FTIR techniques and satisfactory data were collected.. This is the first example of the preparation of phenol-containing PDSA and the use of it as a precursor to prepare functional PDSAs.

Introduction

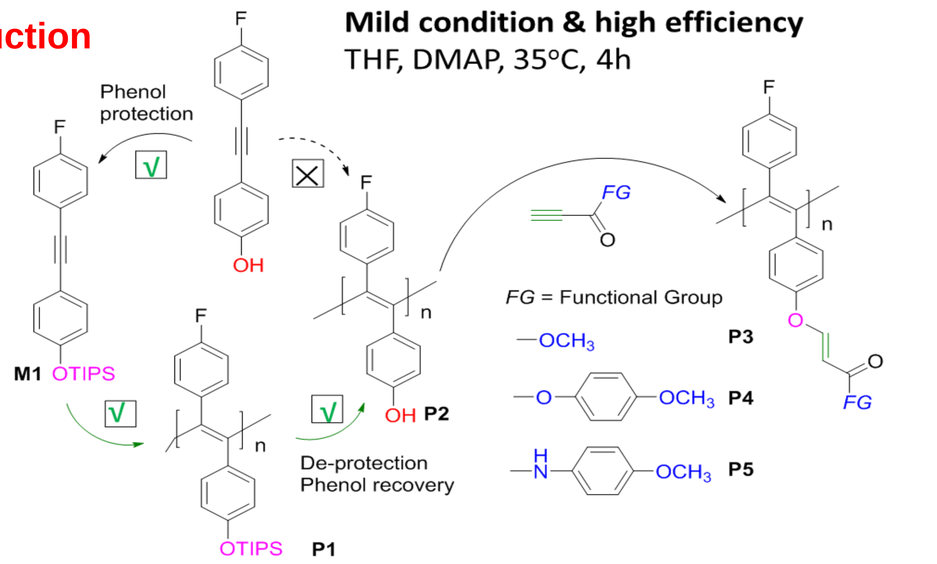

Fig. 1. Synthetic route of the functionalized PDSAs and the post polymerization modification via "phenol-yne click reaction"

Polymerization & Characterization

Table 1. Polymerization of M**1** catalyzed by MCl_x –Ph_4Sn[a]

No	Temperature(℃)	Catalyst	*Mn*[b]	*Mw*[b]	*Mw*[b]/ *Mn*[b]	Yield (%)
1	80	WCl_6-Ph_4Sn	18600	48500	2.60	54.2
2	90	WCl_6-Ph_4Sn	14800	47900	2.82	39.6
3[c]	80	WCl_6-Ph_4Sn	15200	46600	3.06	27.1
4[c]	90	WCl_6-Ph_4Sn	14300	25500	1.78	18.4
5	90	$MoCl_5$-n-Bu_4Sn	trace			
6[d]	80	$TaCl_5$-n-Bu_4Sn	0.98×10^6	1.73×10^6	1.75	35.2

[a] MClx = WCl_6, $MoCl_5$, $TaCl_5$. Carried out in toluene under N_2 for 24 h. Aging time : 10 min. [WCl_6] : [Ph_4Sn] = 1 : 1 [M**1**] = 0.5 M. [b] Determined by GPC in THF.

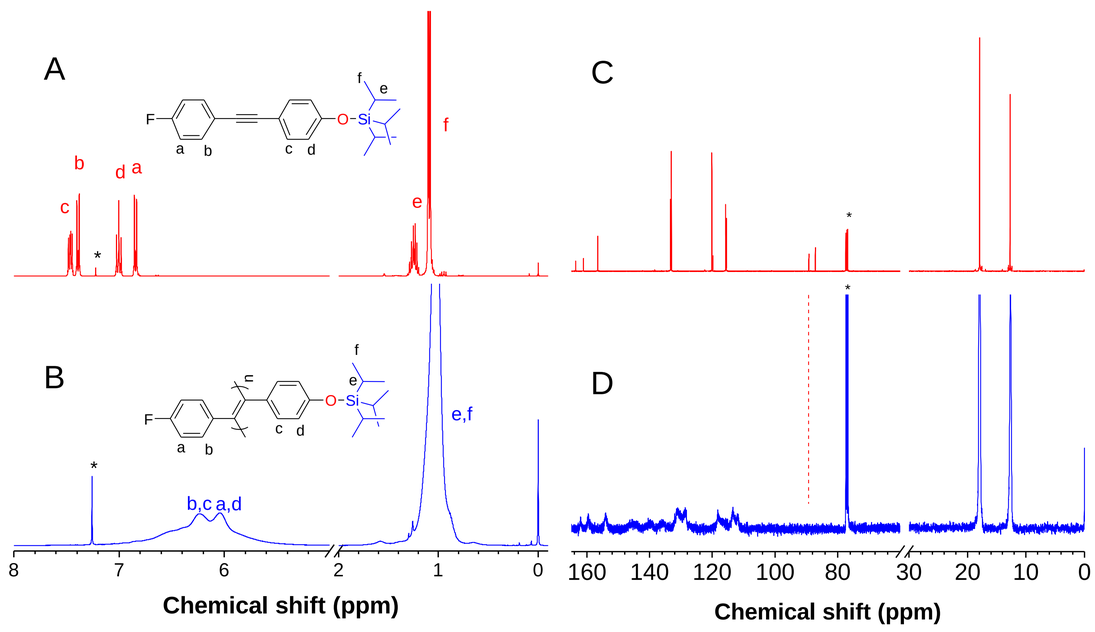

Fig.2 . (Left) ^{1}H NMR spectra of (A) M**1** and (B) P**1**; (Right) ^{13}C NMR spectra of (C) M**1** and (D) P**1** in chloroform-*d*.

Post Polymerization modification & Characterization

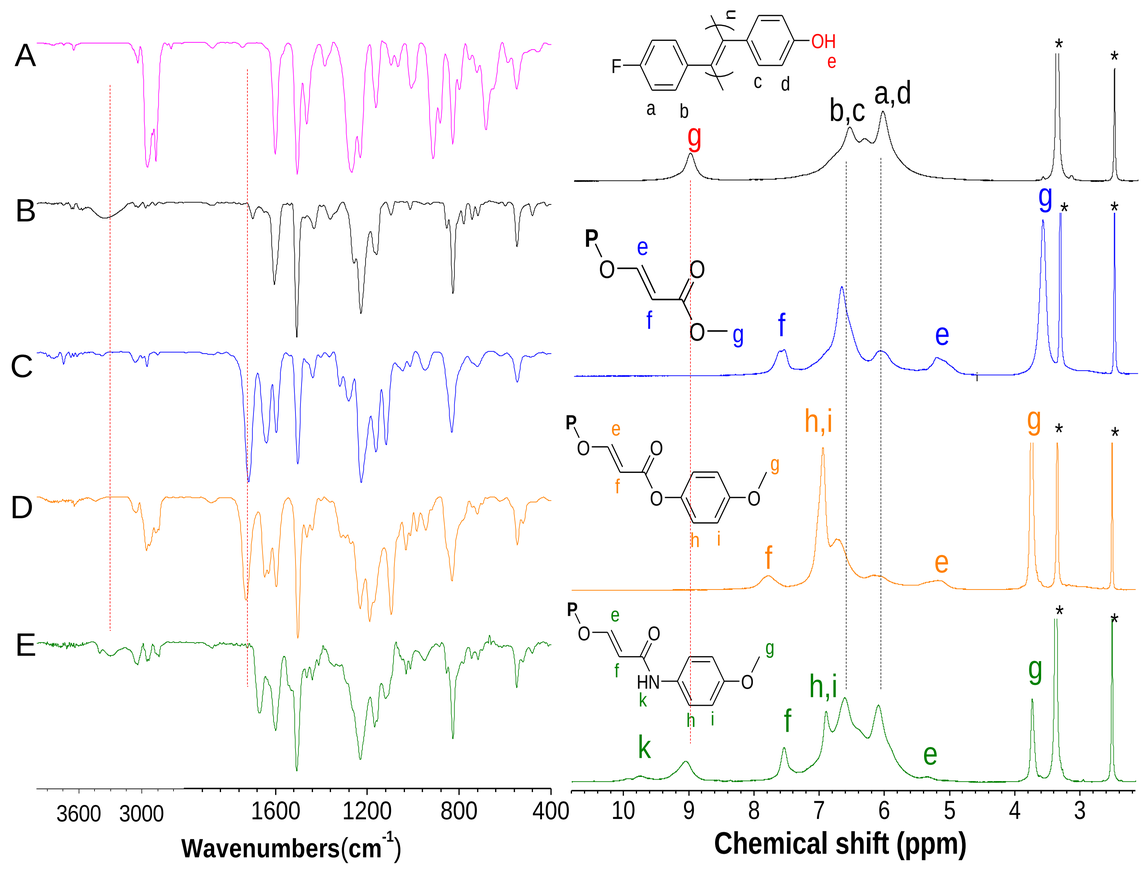

Fig. 3. Measurement results of the polymeric products before and after the "phenol-yne reaction". FTIR spectra of P**1** -P**5** (A-E) and ^{1}H NMR spectra of P**1**-P**5.**

Fluorescent & thermal properties

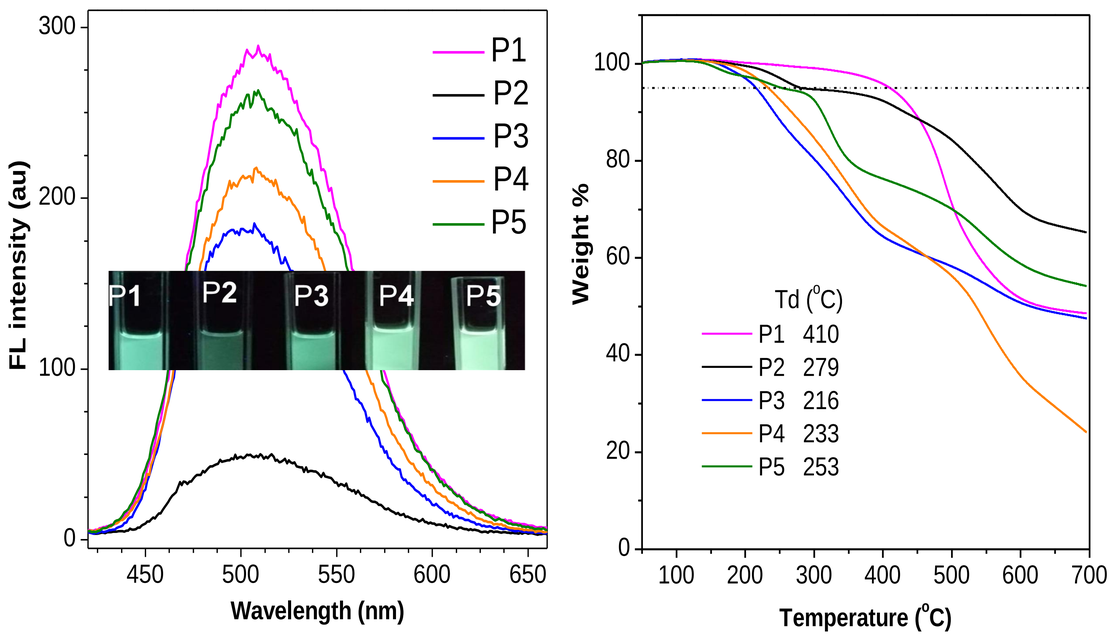

Fig. 4. Fluorescence (FL) spectra of P**1**~P**5** in THF solution (10 μm). Inset: FL images excited under 365 nm, from left to right: P**1**~P**5**.

Fig. 5. TGA thermograms of polymers P**1**-P**5**. T_d represents the temperature of 5% weight loss. Heating in the N_2 at the rate of 10 °C/ min.

Conclusions

PDSA with phenol functionality (P2) has been facilely synthesized with moderate yield via precursor PDSA (P1) by polymerization of the protected monomer M1. Phenol-yne click reaction has been firstly applied to modify P2 with high efficiency in mild condition to afford functional PDSAs (P3-P5). All these polymers emit green fluorescence and show good thermal stability.

Acknowledgement

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References

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[2] Gao, Y.; Wang, X.; Sun, J. Z., Tang, B. Z. *Chem. Rec*., 2015, 15, 524.