



Catalyst-Free Thiol–Yne Click Polymerization: A Powerful and Facile Methodology for Preparation of Functional Poly(vinylene sulfide)s

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INTRODUCTION

The “thioclick” polymerization is a well expanded concept of click polymerization.¹ Among these polymerizations, the thiol–yne click polymerization is less developed and still in its infancy stage. In general, UV light, elevated temperature, amine or transition metal complexes are needed to catalyze the thiol–yne polymerization, which greatly complicates the experimental operation and limits its application.² Here, we developed a facile and powerful catalyst-free thiol–yne click polymerization for the preparation of functional poly(vinylene sulfide)s (PVSs).³

RESULTS AND DISCUSSION

Thiol–Yne Click Polymerization

Scheme 1. Syntheses of poly(vinylene sulfide)s by catalyst-free thiol–yne click polymerizations of diynes **1** and dithiols **2** or **3**.

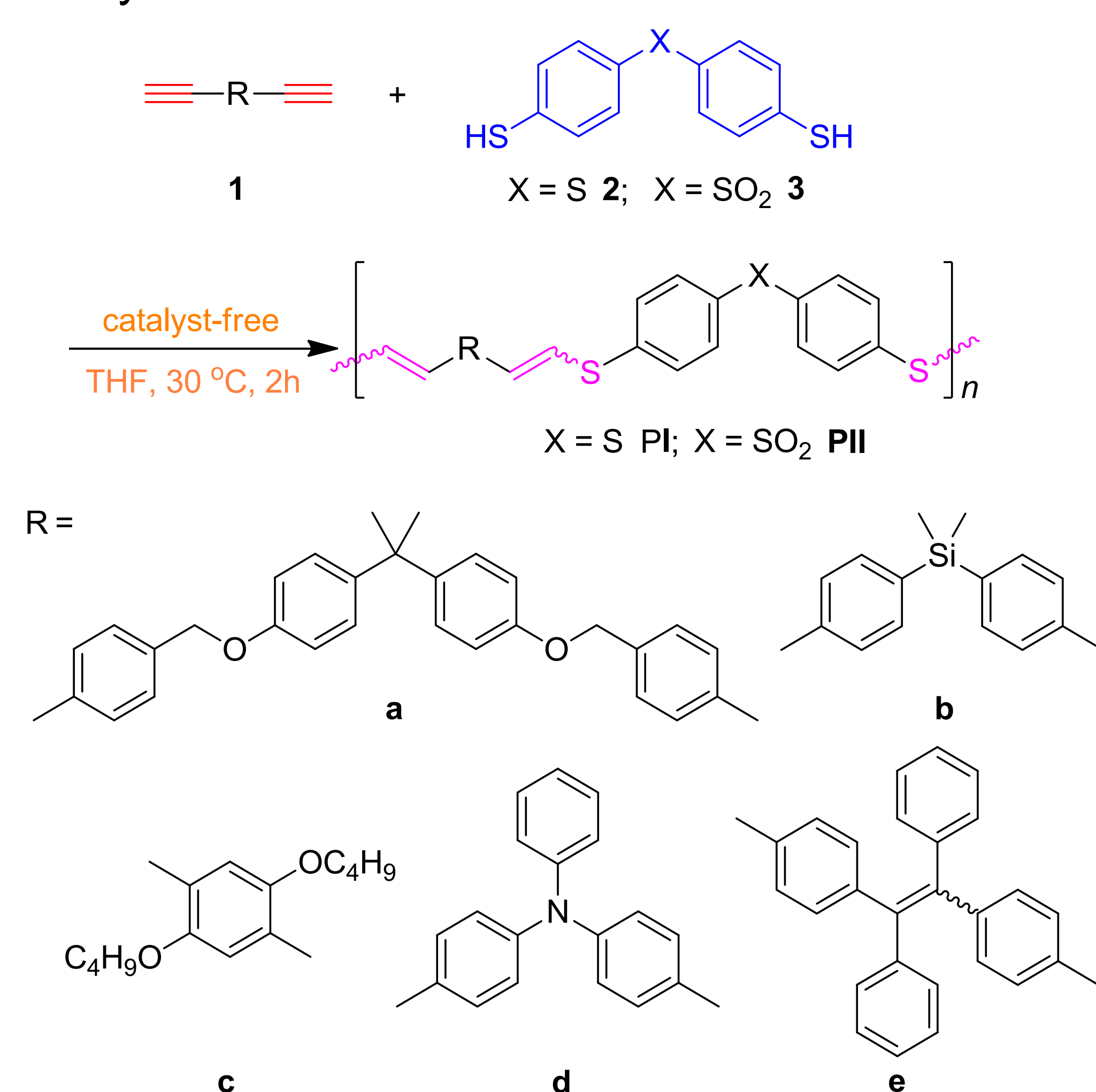


Table 1. The click polymerizations of diynes **1** with dithiols **2–4**.^a

No.	monomers	polymer	yield (%)	M_w^b	M_w/M_n^b
1	1a + 2	PIa	93	60100	1.85
2	1b + 2	PIb	92	17600	2.74
3	1c + 2	PIc	78	29900	3.11
4	1d + 2	PIId	90	53900	2.40
5	1e + 2	PIe	97	9100	2.48
6	1a + 3	PII	95	21300	1.49
7	1a + 4 ^c	PIII	75	6200	1.65

^a Carried out in THF at 30 °C under nitrogen for 2 h; $[M]_0 = 50$ mM. ^b Estimated by GPC in THF. ^c **4** = 1,5-pentanedithiol.

Structural Characterization

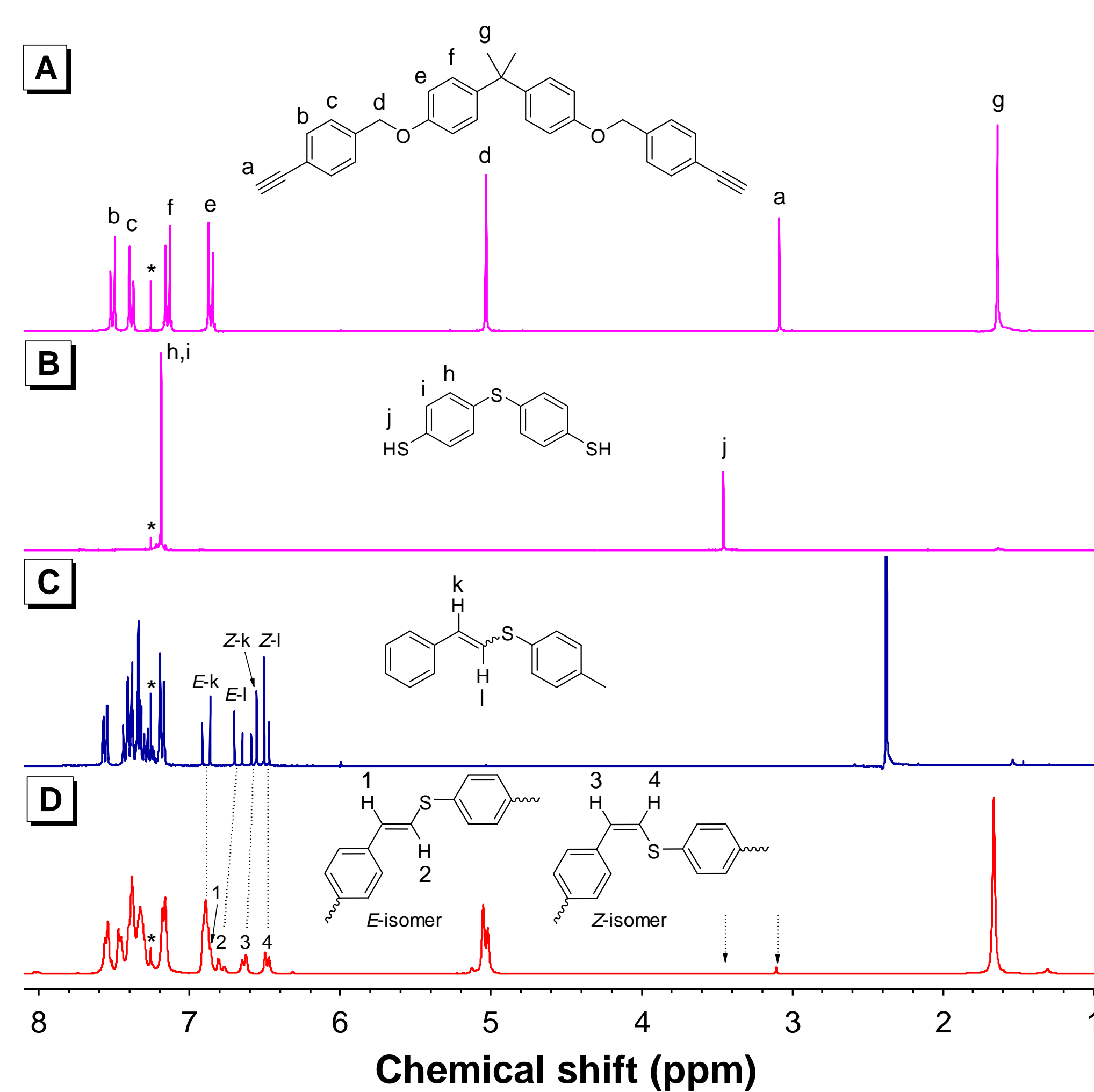


Figure 1. ¹H NMR spectra of monomers (A) **1a** and (B) **2**, (C) model compound, and (D) polymer **PIa** in CDCl₃.

Mechanism Study

Table 2. The polymerization of **1a** with **2** in the presence of γ -terpinene.^a

No.	[add] (mM) ^b	yield (%)	S ^c	M_w^d	M_w/M_n^d
1	0	97	√	60900	1.98
2	50	63	√	1400	1.50
3	100	53	√	1000	1.36

^a Carried out in THF at 30 °C under nitrogen for 2 h; $[M]_0 = 50$ mM. ^b add = γ -terpinene. ^c Solubility (S) tested in common organic solvents; √ = completely soluble. ^d Estimated by GPC in THF.

Light Refractivity

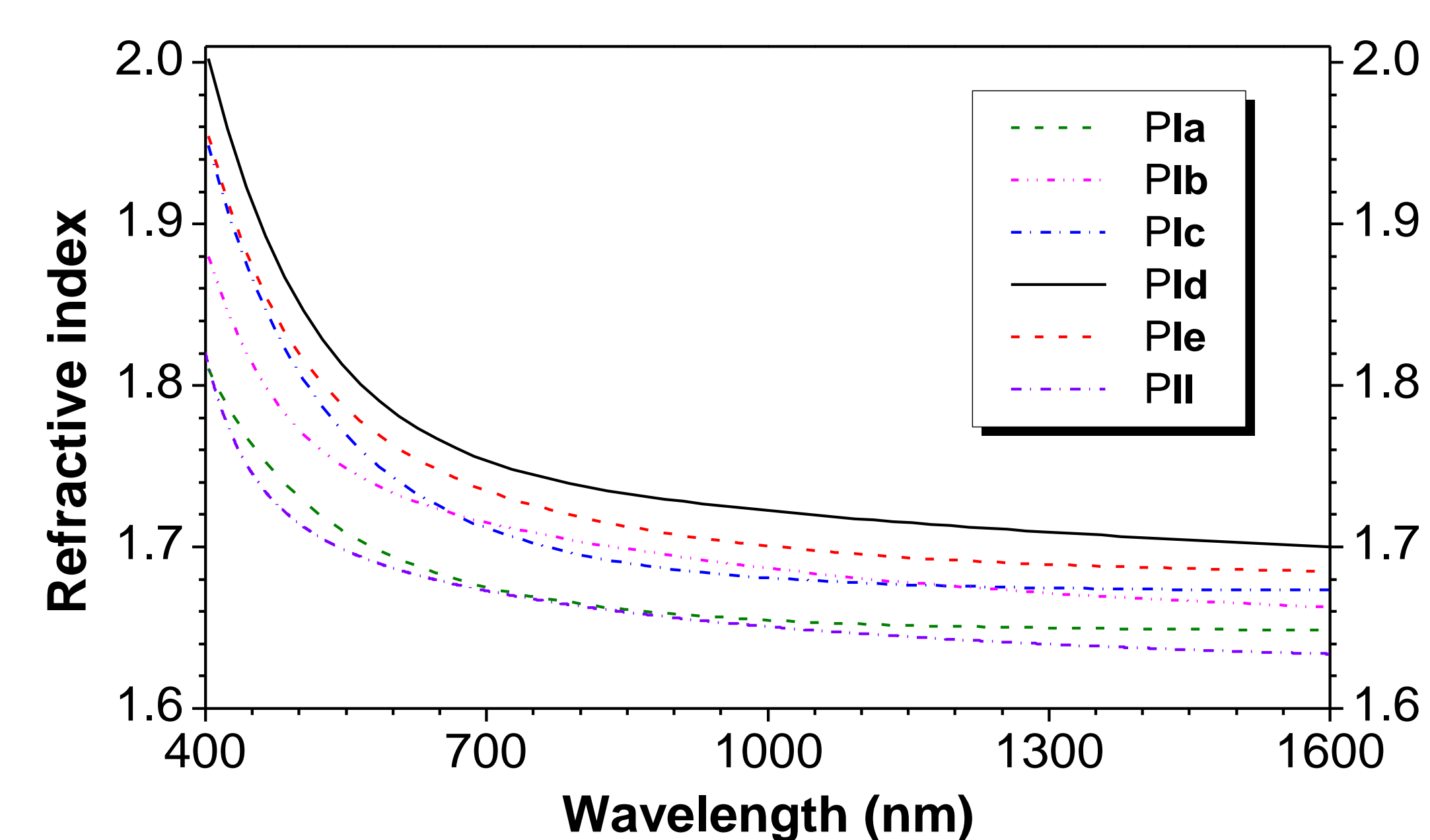


Figure 2. Light refraction spectra of thin solid films of polymers **PIa–PIe** and **PII**.

Aggregation-Induced Emission

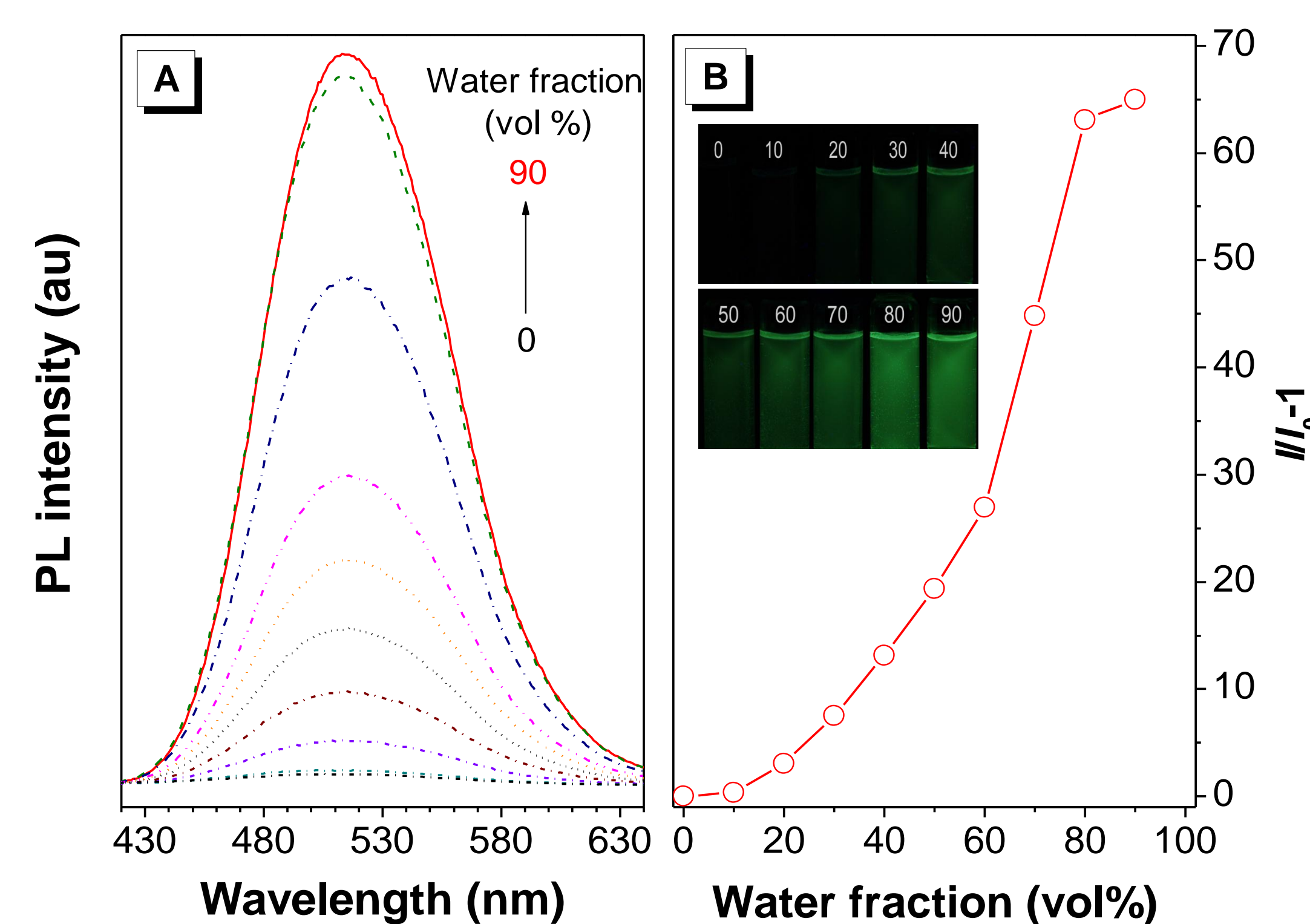


Figure 3. (A) PL spectra of **PIe** in THF and THF/water mixtures. Polymer concentration: 10 μ M. Excitation wavelength: 330 nm. (B) Plot of relative PL intensity versus water fraction in THF/water mixtures, where I = peak intensity and I_0 = peak intensity in pure THF. Inset: fluorescent images taken under a hand-held UV lamp.

CONCLUSIONS

Regioregular PVSs with high M_w were prepared by the catalyst-free click polymerization of aromatic diynes and dithiols under mild conditions. The PVSs possess good solubility and thermal stability, and excellent light refractivity in film state. The tetraphenylethene containing polymer **PIe** exhibits the unique aggregation-induced emission feature..

ACKNOWLEDGMENTS

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