Azobenzene Functionalized Poly (disubstituted acetylenes): Polymer Synthesis, Fluorescent Property and Electronic Interaction between Side Chain and Main Chain

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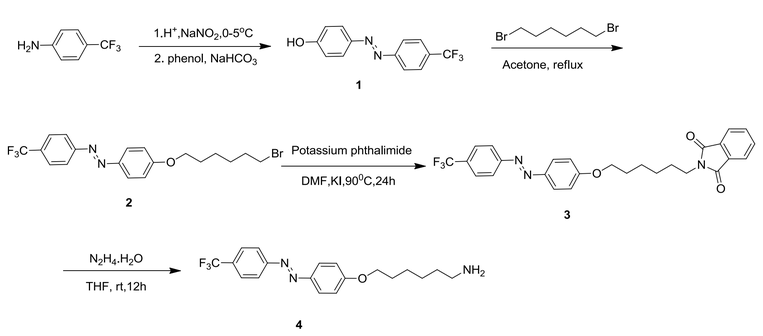
INTRODUCTION

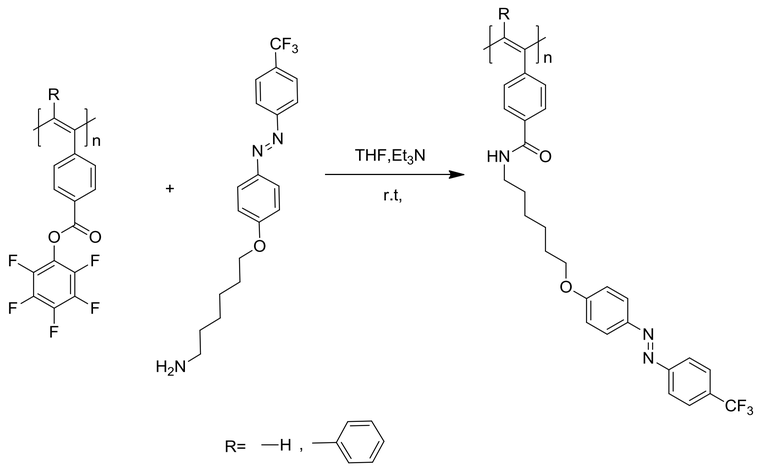
Functional poly(acetylenes) exhibit versatile properties such as electrical conductivity, optical nonlinearity, liquid crystal and fluorescence emission[1,2]. Generally, the properties are rendered by the mutal contribution from both the main and side chains. But in most cases, the interactions between the main and side chains are separately estimated. Herein, we synthesize poly(disubstituted acetylenes) with azobenzene-functionalities in the pendents to study the interactions by taking the advantages of the fluorescent property of the main chain and the fluorescent quenching property of the trans-azobenzene in the side chains. The photo-induced *trans-cis* isomerization of the azobenzene moieties discloses unprecedented details of the intramacromolecular electronic process.

RESULTS AND DISCUSSION

Synthetic Route



Scheme 1. Synthetic route to azobenzene derivative containing amine group



Scheme 2. Synthetic route to the mono-substituted (PMSA) and di-substituted poly(acetylene) (PDSA) with azobenzene-group in side chains

Photo-Isomerization Behavior

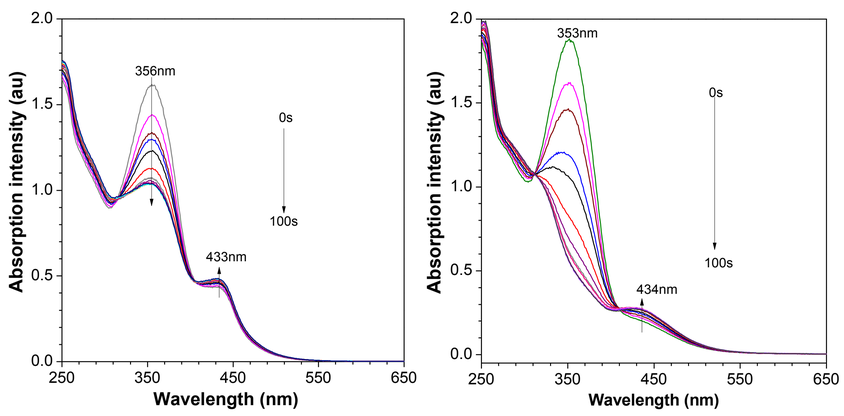


Fig.1. Variation of absorption features of PDSA-r-azo (Left) and PMSA-r-azo (Right) in THF solution with different irradiation times.Polymer concentration:10^{-4} M; Irradiation wavelength:365nm

Thermal Property

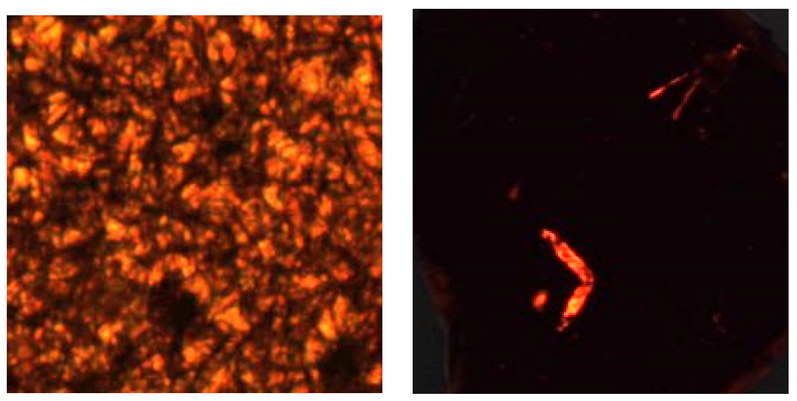


Fig. 2. Polarized optical microscopic images of azo-benzene-molecule **4** (Left) and PDSA-r-azo (Right).

Fluorescence Property

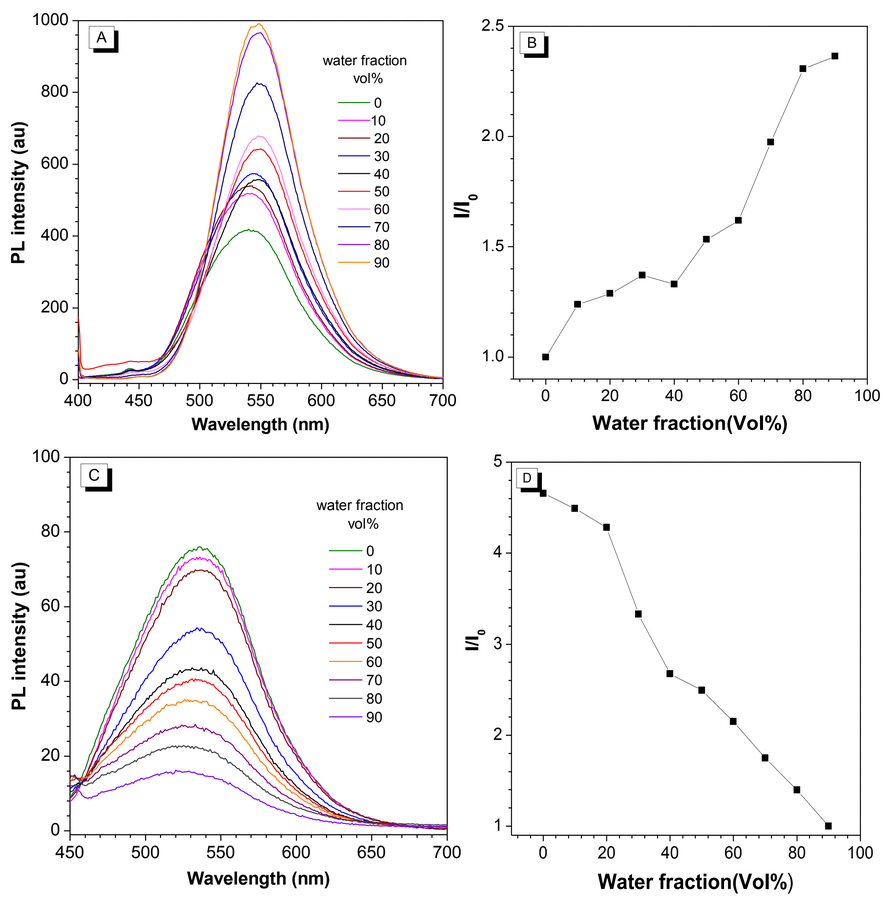


Fig. 3. (A) Photoluminescence (PL) spectra of PDSA in THF/water mixtures with different water fractions (f_w). (B) Plot of I/I_0 *vs* water fraction. (C) PL spectra of PDSA-r-azo in THF/water mixtures with different f_w. (D) Plot of I/I_0 *vs* water fraction, I_0 and I are the PL intensity of PDSA in pure THF solution and THF/water mixtures, respectively. λ_{ex} = 387 nm, polymer concentration = 10 μM.

SUMMARY

Two kinds of azobenzene functionalized poly(acetylene)s have been sythesized through activated ester strategy[3]. The chemical structure has been well characterized with comprehensive spectroscopic techniques. The monosubstituted poly(acetylene) (PMSA) shows more evident photoinduced isomerization than the disubstituted poly(acetylene) (PDSA) counterpart. PDSA shows an evident aggregation-induced emission enhancement , but the azobenzen-functionalized PDSA shows aggregation-caused quenching behavior in THF/water mixtures. Meanwhile, for azobenzen-functionalized PDSA, the liquid crystal property can hardly be observed due to the interactions between the rigid main chain and azobenzene mesogens in the side chains.

ACKNOWLEDGMENTS

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