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Solvatochromic behavior of a novel soluble polydiacetylene with 2,4,6-tri(4-n-heptylphenyloxy)-3,5-difluorophenyl units directly attached to the conjugated backbone

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Abstract

The solvatochromic transition of a new polydiacetylene, with 2,4,6-tri(4-n-heptylphenyloxy)-3,5-difluorophenyl groups directly attached to the conjugated backbone, is described.

Keywords: Solvatochromic behavior; Polydiacetylene; Conjugated backbone; UV absorption spectra

1. Introduction

Polydiacetylenes (PDAs) are highly conjugated polymers produced by the solid-state topochemical 1,4-addition polymerization of macroscopical monomer crystals [1]. The rapid rise in interest in such materials is due mainly to the unusual thermo- and solvato-chromic transitions [2–5], nonlinear optical properties [6–8], photoconductivities [9], conductivities [10], etc. The general experimental and theoretical conclusion has suggested that PDAs which have aromatic rings directly attached to the conjugated main backbone for increasing the number of π-electrons in the repeat unit through π-conjugation between the main backbone and aromatic side groups might be good candidates for enhancing and modulating these functional properties [11–14]. To date, quite a number of soluble polydiacetylenes having flexible side-chains, such as the 9PA (poly-[10,12-docosadiyne-1,22-diol bis(phenylacetate) ester]) and PTS-12 (poly-[5,7-dodecadiyne-1,12-diol bis(*p*-toluenesulfonate)]), and flexible side-chains with the possibility of hydrogen bonding, such as n-BCMU (structures as shown in Fig. 1), have been prepared [12,15–17]. The solvatochromic and thermochromic transitions of poly{5,7-dodecadiyne-1,12-bis[(4-butoxycarbonyl)methylurethane]}, 4-BCMU, have been extensively investigated. In this communication, we would like to report the solvatochromic transitions of a new polydiacetylene which has 2,4,6-tri(4-n-heptylphenyloxy)-3,5-difluorophenyl units directly attached to the conjugated main backbone (structure as shown in Scheme 1).

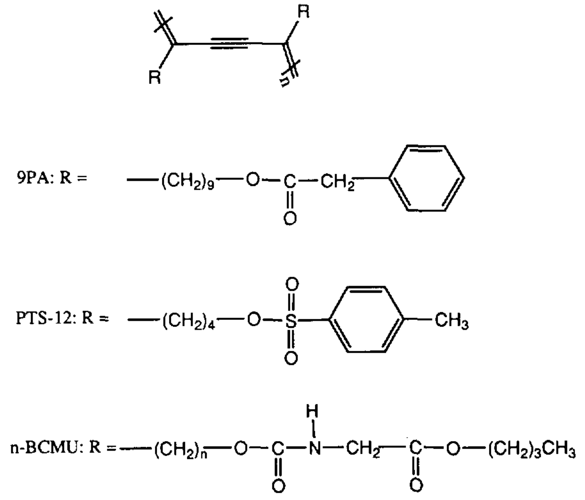

Fig. 1. Molecular structures of soluble polydiacetylenes with long flexible side-chains.

2. Experimental details

The diacetylene monomer, 1,4-bis[2,4,6-tri(4-n-heptylphenyloxy)-3,5-difluorophenyl]butadiyne, BTDB, was synthesized starting from pentafluoroiodobenzene as described in our previous papers [18,19]. Three 4-n-heptylphenyloxy

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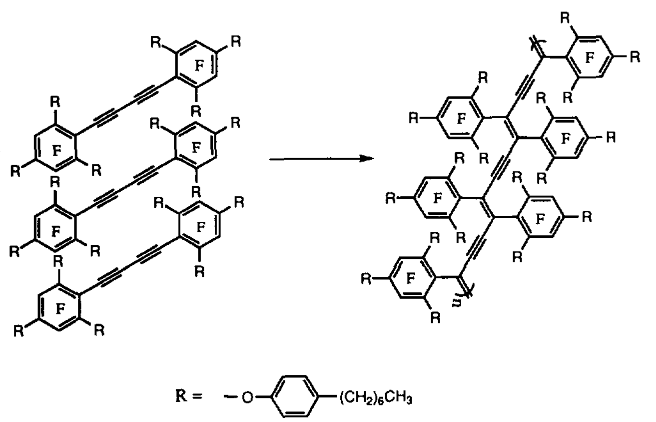

Scheme 1. Reagents and conditions: γ-ray irradiation.

groups could be introduced at an early stage to the 2,4,6-positions on each fluorobenzene ring of 1,4-bis(pentafluorophenyl)butadiyne using a nucleophilic substitution reaction on the polyfluoroaromatic rings. For other diacetylene systems without any fluoroaromatic rings, it is difficult to introduce multiflexible long chains to side aromatic rings. The solid-state polymerization was achieved by exposing polycrystalline monomer samples to γ-radiation from a ^{60}Co source. Polymerization of up to 38% of the monomer could be obtained with 150 Mrad of dosage, after which unreacted monomer was removed with ethanol.

The UV–vis spectra of the polymer solutions were recorded on a Shimadzu UV-3100 spectrophotometer at room temperature. Stock solutions were obtained by dissolving a known amount of polymer in chloroform. Such stock solutions were further diluted with chloroform and/or nonsolvent to obtain the desired concentration and solvent/nonsolvent ratios for the measurement of UV–vis spectra.

3. Results and discussion

The deep blue poly{1,4-bis[2,4,6-tri(4-n-heptylphenyloxy)-3,5-difluoro-phenyl]butadiyne}, PBTDB, was dissolved in chloroform (which is good solvent for PBTDB) to give a red solution with an absorption maximum at 562 nm. The strong absorption of PBTDB in the visible region of the spectrum in chloroform solution is due to the highly delocalized π-conjugated system which extends along the conjugated backbone. A lot of research work on molecular design and synthesis of PDAs has shown that only a few diacetylene monomers with an aromatic ring directly bound to the diacetylene moiety are polymerizable in the solid state, and their polymers are generally insoluble in common organic solvents [20–23]. It was found that PBTDB has a good solubility in common organic solvents, such as chloroform, due to the six flexible long chains attached to each repeating polymeric unit. This is the first report, to our knowledge, of a soluble polydiacetylene with two substituent aromatic groups directly attached to each conjugated repeating unit. The solutions of common soluble PDAs in good solvents are usually yellow with the absorption maximum at about 470 nm [24]. All these common soluble PDAs have flexible long chain spacers between the conjugated main backbone and side-groups. The differences in the absorption maximum in good solvents between common soluble PDAs and PBTDB might be due to the presence in the latter of the two fluorophenyl side-groups attached to each repeating unit of the conjugated main backbone. The electronic interactions between the backbone and side fluoroaromatic rings, and an increase in the effective delocalization length of the backbone due to the conjugated contribution of the aromatic side-groups, can shift the absorption maximum to a longer wavelength.

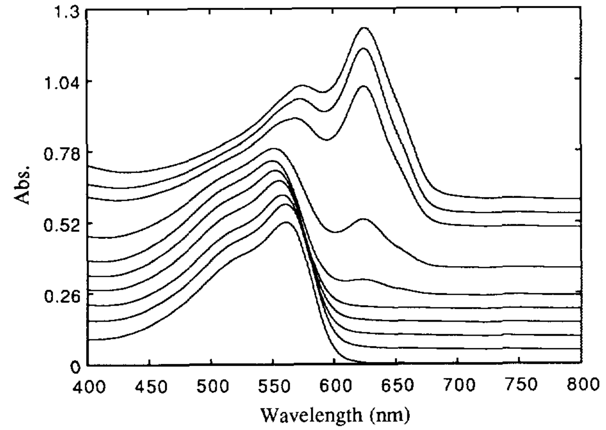

Fig. 2. Absorption spectra of PBTDB for various ratios of chloroform/methanol (v/v) at room temperature. From bottom to top: 10:0, 8:2, 6:4, 5:5, 4:6, 3:7, 2.5:7.5, 2.75:7.25, 2:8, and 1:9. The polymer concentration was 1.86×10^{-5} mol l^{-1}.

In a good solvent such as chloroform PBTDB solution is red. However, on addition of a nonsolvent such as methanol the polymer solutions undergo rapid dramatic color changes from red ($\lambda_{max} = 562$ nm) to blue (625 nm). The absorption spectra of solutions for PBTDB in various mixtures of chloroform and methanol are shown in Fig. 2. The color transition

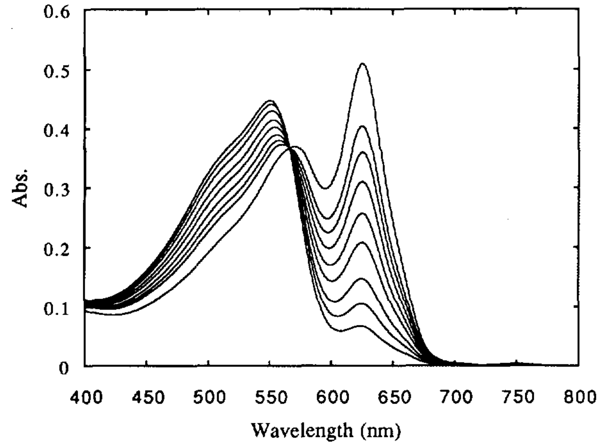

Fig. 3. Variation of the absorption spectrum of PBTDB with time in 3:7 chloroform/methanol (v/v) at room temperature. From bottom to top (625 nm): 0 min, 14 min, 35 min, 1.5 h, 2.5 h, 3.5 h, 5.5 h, 7.5 h and 24 h. The polymer concentration was 1.86×10^{-5} mol l^{-1}.

from red to blue occurs at a volume ratio of ca. 3:7 (v/v). It was found that if the volume ratios of chloroform/methanol were a little lower than 3:7 (v/v), the color transitions would become dramatically rapid. Fig. 3 shows the color changes of PBTDB with time in a 3:7 (v/v) chloroform/methanol mixture solution. The peak at 625 nm becomes sharper and more intense and the peak at 562 nm gradually shifts to 575 nm with elapse of time. The color changes from red to blue in PBTDB solutions may be due to an intermolecular polymer backbone conformational transition from nonplanar (red) to planar (blue). Such a color transition for soluble PDAs, first described by Patel et al. [25], is a fairly general feature of this class of polymers. There is good evidence to support the contention that the yellow to red color change in solution involves the backbone undergoing a nonplanar to planar conformational transition [25–28].

In conclusion, a novel soluble polydiacetylene, PBTDB, with aromatic substituents directly bound to the conjugated backbone has been obtained by solid-state γ-irradiation polymerization. A solvatochromic transition, which is a general feature of polydiacetylenes, has also been observed in this new type of polydiacetylene which has no hydrogen-bonded network. In comparison to common soluble PDAs, two aromatic substituents attached to one conjugated repeat unit of the polymer backbone shift the absorption maximum to longer wavelength due to the conjugation contribution of the side aromatic rings. Further work on the electric and optical properties of PBTDB is underway.

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