Organic Electronics 37 (2016) 169–177

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Solution-processable thiophene-based electrochromic polymers bearing trifluoromethyl rather than long side chains

Jian Liu, Sai Mi, Zhangping Xu, Jingchuan Wu, Jianming Zheng, Chunye Xu*

Hefei National Laboratory for Physical Sciences at the Microscale, CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, PR China

ARTICLE INFO

Article history:
Received 28 April 2016
Received in revised form
8 June 2016
Accepted 19 June 2016
Available online 30 June 2016

Keywords:
Solution-processable
Electrochromic
Trifluoromethyl
Long side chains
Thermal stability

ABSTRACT

A series of novel thiophene-based electrochromic (EC) polymers bearing trifluoromethyl group were designed and synthesized. Without long-chain alkyl or alkoxy group attached, the polymers still exhibit good solubility in conventional organic solvents, and much better thermal stability comparing with conventional non-fluorine EC soluble polymers. Optical, electrochemical, spectroelectrochemical and electrochromic switching properties of the polymers are characterized in detail as well as the solubility and thermal stability. Combining comprehensive properties of fluorine-containing molecules and electrochromic conjugated polymers, the polymers reported here are proven to provide a new strategy to design novel electrochromic conjugated polymers.

1. Introduction

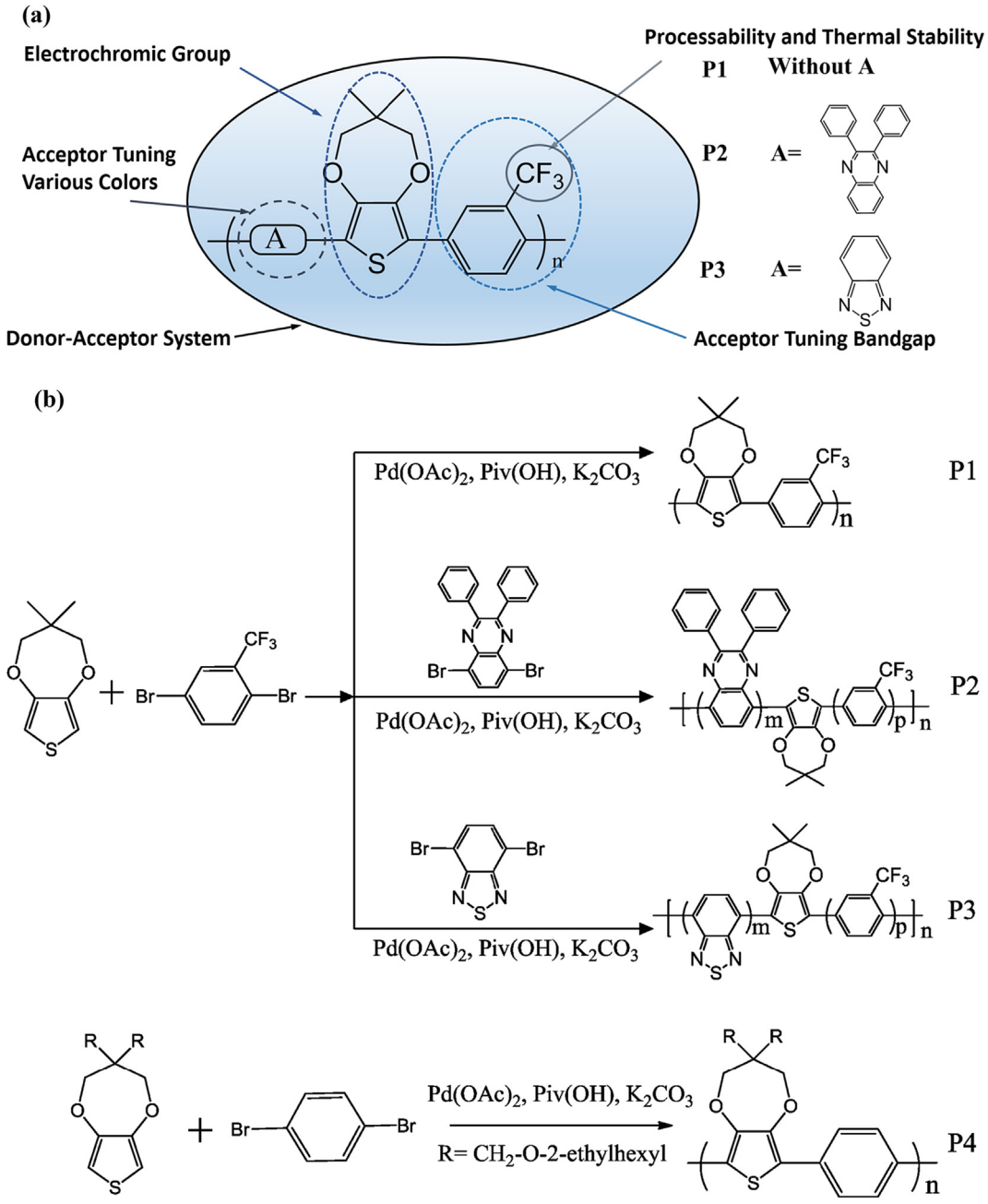
Electrochromic conjugated polymer achieves its reversible color change when being applied with electrochemical anodic or cathodic polarization. Owing to various colors [1,2], adjustable band gap [3], high coloration efficiencies [4], fast response time [5] and high optical contrast [6], they have received great attention in recent years. Wherein, solution-processable electrochromic conjugated polymers are particularly important since good solubility greatly facilitates the processibility of EC polymers in many application fields including smart window [7], organic light emitting devices [8], and large-area electrochromic displays [9].

Over past decades, great efforts has been made to optimize the solubility of conjugated polymers, the most common strategy is to introduce flexible long side chains such as ethythexyloxy [10–12], sulfonatoalkoxy [13] and siloxane-terminated alkoxy [14] on the conjugated backbone structure. The additional solubility may be ascribed to the synergistic effect of the van der Waals interactions between alkyl chains and solvent and the vibrational motions of the long side chains [15]. Recently, an alternative way was proposed by Chien-Lung Wang and his coworkers. Polymers with trifluoromethyl-substituted biphenyl were synthesized and used as organic field-effect transistors, and these polymer showed good solution-processability, as the formation of non-coplanar biphenyl structure resulted from the bulky trifluoromethyl could enhance the solubility [16]. However, to our knowledge, there is little information available about solution-processable conjugated polymers without long side chains in electrochromic field so far.

Since our group has been committing ourselves to the research and development of organic and inorganic electrochromic materials [17,18], we have developed various soluble EC conjugated polymers with long alkoxyl side chains [19,20]. In this paper, we have designed a series of novel polymers strategically based on the structure illustrated in Scheme 1a. We introduce the trifluoromethyl group into polymer backbone to replace traditional long side chains since it can modify the solubility and thermal stability of the conjugated polymers. Moreover, (trifluoromethyl) benzene group can be regarded as an acceptor due to the strong electron withdrawing ability of trifluoromethyl [21]. In contrast, 3,4-(2,2-dimethylpropylenedioxy)thiophene (ProDOT-Me_2) is an excellent electrochromic material with electron-donating effect [22]. As a result, the combined structure could form a donor-acceptor (D-A) system which can easily tune color state by

* Corresponding author.
E-mail address: chunye@ustc.edu.cn (C. Xu).

http://dx.doi.org/10.1016/j.orgel.2016.06.023
1566-1199/



Scheme 1. (a): Schematic design of soluble donor-acceptor polymers; (b): Synthetic route of the polymers.

regulating the molecular structure [23–25]. In order to investigate the concrete influence of the trifluoromethyl group on the polymers, we have synthesized three polymers of P1, P2 and P3 bearing different acceptors according to D-A theory. We expected that these polymers could possess both the characteristics of trifluoromethyl group and electrochromic properties of ProDOT-Me_2, Additionally, P4 carrying traditional long side alkoxy chains is also synthesized as a contrast experiment.

As might be expected, the solubility of these polymers of P1, P2 and P3 was excellent in conventional organic solvent such as chloroform, dichloromethane and tetrahydrofuran. The thermal stability, optical absorption, electrochemical and electrochromic properties of these polymers were characterized as presented below and the differences were also analyzed in detail.

2. Experimental section

2.1. Materials and instrumentation

All chemicals used in this paper were commercial products and used as received without further purification unless otherwise noted. Propylene carbonate (PC) was purchased from Sigma–Aldrich Chemical. HPLC tetrahydrofuran (THF) and N-methyl-2-pyrrolidone (NMP) were dried with 4A molecular sieves in argon atmosphere. 5,8-dibromo-2,3-diphenylquinoxaline and 3,3-bis(2-ethylhexyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxepine were prepared with previously reported methods [26,27].

NMR spectra were measured by Bruker Avance AV400. Molecular weights and molecular weight distributions were determined