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New synthetic method for the polymerization of alkylthiophenes

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Abstract

The polymerization of 2-iodo-3-alkylthiophenes using a Heck-type reaction with Pd(OAc)$_2$ / NBu$_4$Br as catalytic system is reported leading to expected functionalized oligomers with good yields.

Keywords: Heck reactions, Oligomerization, Thiophene derivatives

Introduction

Due to their numerous potential applications, organic conducting polymers have been intensively studied in the last twenty years. Particularly, poly(thiophenes) lead to materials showing an important environmental and thermal stability, with good conductivity. Poly(alkylthiophenes) are moreover soluble in common organic solvents which facilitates their processability and widens the field of their application [1,2]. It is now well established that the physical properties of conducting polymers are closely linked to the structure of their monomeric precursor and to the polymerization conditions. The synthesis of substituted thiophene rings is well documented [3-5], allowing the obtention of various heterocycles. McCullough has very recently reviewed exhaustively the syntheses of the corresponding poly(thiophenes) [6]. Their polymerization can be classified in two categories, *i.e.* the oxidative electrochemical or chemical polymerization and the organometallic couplings leading to neutral polymers. These methods give rise to polymers with various structures, especially considering the chain length or the regioregularity of the linking, for substituted monomers. The electrochemical anodic polymerization has been extensively studied [7]. This method presents the advantage that the doped conducting polymer is directly grafted onto the electrode surface, which is of particular interest for electrochemical applications or *in situ* characterization by electrochemical analyses. However, considering the homocoupling of alkylated thiophenes, the best head-to-tail regioregularity observed is 70% [8]. Sugimoto et al. have reported a chemical polymerization of thiophene derivatives that implies the monomer oxidation by iron trichloride [9]. Poly(alkylthiophenes) obtained by this method are often high-molecular-weight polymers which have a low amount of irregular couplings. One of the most used chemical preparation of poly(thiophene) is the metal-catalyzed polycondensation polymerization of 2,5-dihalogenothiophene essentially via Kumada-Corriu

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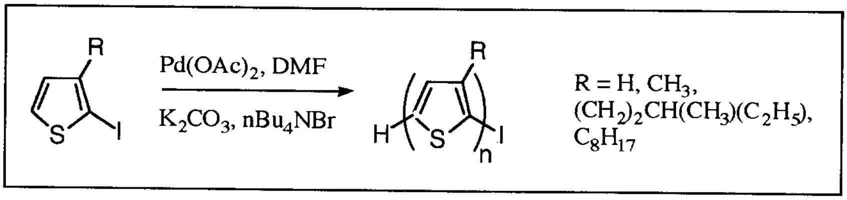
cross-coupling [10]. McCullough et al. reported the first synthesis leading almost exclusively to head-to-tail couplings [11]. They succeeded the homopolymerization of 2-bromo-5-(bromomagnesio)-3-alkylthiophenes with catalytic amount of Ni(II). Alternatively, Rieke et al. prepared 2-bromo-3-alkyl-5-(iodozincio)-thiophenes to be also regioregularly polymerized in the presence of a nickel catalyst [12]. Very recently, the use of 2-iodo-3-alkyl-5-tri-*n*-butylstannyl-thiophene derivatives [13] or 2-iodo-3-alkyl-5-thienyl-boronic esters [14] has been described for the obtention of regioregular head-to-tail poly(3-alkylthiophenes) by the Stille or the Suzuki coupling reactions, respectively. These last methods offer the possibility to prepare pure head-to-tail poly(alkylthiophenes) with high molecular weights and conductivities. The only inconvenient is the difficult access to the monomeric precursors, with high purity.

Recently, the direct thiophene monoarylation using a Heck-type reaction with $Pd(OAc)_2$ / NBu_4Br as catalytic system has been reported by our group leading to expected coupling products with good yields [15]. We report here a new method for the polymerization of 2-iodo-3-alkylthiophenes using this catalytic system.



Synthesis

We have tested this new methodology on four thiophene derivatives : 2-iodothiophene, 2-iodo-3-methylthiophene, 2-iodo-3-octylthiophene and (S)-2-iodo-3-(3-methyl-pentyl)-thiophene. The synthesis of 3-octylthiophene [16] and (S)-3-(3-methyl-pentyl)thiophene [17] was reported elsewhere. The corresponding iodinated derivatives have been regiospecifically synthesized according to a procedure described by Miller et al., involving the use of mercuric oxide and iodine in benzene [18]. A selectivity superior to 95%, in 2-monoiodination with regards to diiodination, is obtained in all cases. Pure compounds, according to GC and NMR analyses, were obtained after fractional distillation.

The general procedure used for the Heck-homocoupling implies the reaction of the iodinated thiophene derivative with catalytic amounts of $Pd(OAc)_2$, equimolar quantity of tetrabutylammonium bromide and excess potassium carbonate as base in DMF at 80°C. In all cases, the precipitated polymeric products have been purified by several washings before characterization and obtained in good yields (see table 1).

Characterization of the polymers

One of the main advantage of poly(alkylthiophenes) bearing alkyl groups, at least as large as a butyl substituent, is their solubility in common organic solvents which facilitates largely their characterization. The polymers obtained by our method have been described by Gel Permeation Chromatography, elemental and mass analyses, NMR and UV-Vis spectroscopy.

Gel permeation chromatography was conducted in THF where all the obtained polymers were soluble. Very usually, number-average- ($\overline{M}_n$) and weight-average molecular weights ($\overline{M}_w$) are determined relative to polystyrene standards. We have run our calculations from such a calibration curve which was moreover precised thanks to injection of authentic short thiophene oligomers (dimers to tetramers). Results obtained by this method are reported in table 1. Both monomers, bearing a C6 or C8 substituent, lead to the formation of polymers with similar degree of polymerization and polydispersities around 2.

Table 1
Characterization of the polymers by UV-Vis spectroscopy (in $CHCl_3$), Gel Permeation Chromatography (DP : degree of polymerization, PDI : polydispersity) and Elemental Analysis.

R	UV (nm)	GPC					Elemental Analysis				Yield (%)
		$\overline{M}$n	$\overline{M}$w	DP	PDI		C	H	S	I	
$-(CH_2)_2-{}^*CHMeEt$	421	2905	5856	16	2.01	exp.	68.7	8.0	17.6	5.1	89
						calc.	68.9	8.1	18.4	4.6	
C_8H_{17}	421	3071	6422	15	2.09	exp.	70.4	8.9	15.0	3.9	93
						calc.	71.0	9.0	15.8	4.2	

Elemental analyses have been performed which confirmed the results obtained by GPC : a good suitability has indeed to be noticed between the experimental and calculated results (respectively DP = 16 and DP = 15) for both poly((S)-3-(3-methyl-pentyl)thiophene) and poly(3-octylthiophene). FAB-Mass analyses have ensured that these polymers are functionalized by a iodine atom at the chain end. Similar sets of analyses have been run for the polymers obtained from thiophene or 3-methylthiophene, indicating the formation of a mixture of iodinated and mainly deiodinated materials. Obviously, the polymerization pathway is here competing with two possible transformations : the reduction of the C-I bonding to an inactive C-H linkage and/or the homocoupling of two monomeric (or oligomeric) units by an Ullman-like reaction leading also to a loss of activated C-I bondings [19]. We assume that these reactions are indeed more likely for thiophene derivatives bearing short alkyl chains, where the steric hindrance towards a possible transformation of the C-I bonding is smaller. We have tested anyway, without success, the homocoupling of 2-iodo-3-octylthiophene under Ullman-coupling conditions [20].

NMR studies on poly((S)-3-(3-methyl-pentyl)thiophene) and poly(3-octylthiophene) have been run in chloroform. Many articles have reported results concerning NMR spectroscopy of such polymeric structures. The resonance of the isolated aromatic proton in the 4-position of thiophene has been undoubtedly assigned for the four possible triad sequences that arise from the different alignment of the monomer [21]. Hence, a peak at $\delta = 6.98$ has been ascribed to the Head-to-Tail configuration (HT) of triad sequences and should be the only representative in the aromatic region for a regioregular polymer. The poly(octylthiophene) synthesized by our methodology possesses some additional signals at the aromatic region beside the main peak at δ=6.98. We propose that these peaks correspond to hydrogens on thiophene rings at the chain ends. Indeed, with a degree of polymerization of 15, the aromatic proton on the fifth position of the starting thiophenic ring is recognizable, centered at δ=7.15. Integration of this signal with regard to the whole aromatic peaks confirms furthermore the length of the polymeric chains, already obtained from GPC, mass and elemental analyses. Comparable results and interpretation have been reported by Iraqi et al.

[13] for the description of similar octylthiophene oligomers (DP = 13). Work is anyway in progress to confirm these assumptions particularly by performing 2-D NMR analyses.

Absorption spectra on these polymers in chloroform have been measured (see table 1) and show maximum absorptions at λ_{max} = 421 nm. As comparison, 449 nm is the value reported for higher molecular mass polymers due to the extent of electronic delocalisation [6].

Conclusion

We have developed a new method for obtaining soluble oligo(alkylthiophenes) starting from easily available functionalized monomers. This reaction is based on a Pd(OAc)$_2$ Heck-like coupling of iodo-alkylthiophenes, in the presence of potassium carbonate as base and tetraalkylammonium salts. The macromolecules thus obtained are regioregular functionalized oligomers bearing an iodide at the chain end susceptible to be involved in subsequent reactions. Work is in progress to study the influence of the solvent nature and of the mixture concentration on the structure of the obtained polymers.

general procedures

2-iodo-3-alkylthiophenes have been prepared according to ref [18]. 2-iodo-3-methylthiophene : yield 79%, sample identical to reported analyses ref[22]. (S)-2-iodo-3-(3-methyl-pentyl)thiophene : (102-108°C, 0.1mm Hg), yield 81%, ^{1}H NMR : δ 7.39 (d, 1H, J=5.4Hz), 6.77 (d, 1H, J=5.4Hz), 2.61-2.51 (m, 2H), 1.65-1.14 (m, 5H), 0.95 (d, 3H), 0.90 (t, 3H). ^{13}C NMR : δ 147.40 (C$_3$), 130.41 (C$_5$), 127.94 (C$_4$), 73.88 (C$_2$), 36.89 and 29.89 (2 x CH$_2$), 34.15 (CH), 27.88 (CH$_2$-allylic), 19.20 (CH$_3$), 11.41 (CH$_3$). 2-iodo-3-octylthiophene : yield 67%, sample identical to reported analyses ref[14].

Polymerization of 2-iodo-3-alkylthiophenes : to a solution of 2-iodo-3-alkylthiophenes (5 mmol in 6 mL DMF) was added under nitrogen potassium carbonate (12.5 mmol) and tetrabutylammonium bromide (5 mmol). The mixture was heated to 80°C with stirring and palladium acetate (0.25 mmol) was added. The mixture was stirred at 80°C for 48h. The precipitate was then filtered out, washed with water and methanol, finally dissolved in chloroform. This solution was washed again with water. The organic layer was dried over MgSO$_4$. Solvent was removed by rotatory evaporation to give a deep red residue. In the case of poly(thiophene) and poly(3-methylthiophene), the obtained deep red solids were only washed several times with water/methanol before analyses. The characterization of the obtained polymers is precisely described in the general part of this article.

References

[1]. Jen K-J, Miller GG, Elsenbaumer RL. J.Chem.Soc. Chem.Commun. 1986; 1346-1347.
[2]. Sato M, Tanaka S, Kaeriyama K. J.Chem.Soc. Chem.Commun. 1986; 873-874.
[3]. Gronowitz S. The Chemistry of Heterocyclic Compounds : Thiophene and Its Derivatives, ed. Gronowitz S. vol. 44, Wiley&Sons, Inc., New York, 1985, part 1, pp. 1-213.
[4]. Schulz E, Fahmi K, Lemaire M. Acros Organics Acta 1995; 1: 10-17.
[5]. Ye X-S, Yu P, Wong HNC. Liebigs Ann./Recueil 1997; 459-466.
[6]. McCullough RD. Adv.Mater. 1998; 10: 93-116.
[7]. Roncali J. Chem.Rev. 1992; 92: 711-738. Chem.Rev. 1997; 97: 173-205.
[8]. Leclerc M, Martinez Diaz F, Wegner G. Makromol.Chem. 1989; 190: 3105-3116.
[9]. Sugimoto R, Takeda S, Gu HB, Yoshino K. Chem.Express 1986; 1: 635-638.
[10]. Yamamoto T, Sanechika K, Yamamoto A. J.Polym.Sci., Polym.Lett.Ed. 1980; 18: 9-12.
[11]. McCullough RD, Lowe RD, Jayaraman M, Anderson DL. J.Org.Chem. 1993; 58: 904-912.
[12]. Chen TA, Wu X, Rieke RD. J.Am.Chem.Soc. 1995; 117: 233-244.
[13]. Iraqi A, Barker GW. J.Mater.Chem. 1998; 8: 25-29.
[14]. Guillerez S, Bidan G. Synth.Met. 1998; 93: 123-126.
[15]. Gozzi C, Lavenot L, Ilg K, Penalva V, Lemaire M. Tetrahedron Lett. 1997; 38: 8867-8870.
[16]. Schulz E, Kinderli P, Perrard A, Lemaire M. Applied Catal. A:General 1996; 293-304. Synthesis at the industrial scale.
[17]. Papillon J, Schulz E, Gélinas S, Lessard J, Lemaire M. Synth.Met. 1998; 96: 155-160.
[18]. Miller LL, Yu Y. J.Org.Chem. 1995; 60: 6813-6819.
[19]. Fanta PE. Synthesis 1974; 1: 9-21.
[20]. Hassan J, Lavenot L, Gozzi C, Lemaire M. to be published in Tetrahedron Lett.
[21]. Sato M-A, Morii H. Macromolecules 1991; 24: 1196- 1200.
[22]. Wu R, Schumm JS, Pearson DL, Tour JM. J.Org.Chem. 1996; 61: 6906-6921.