Synthesis of poly(aryleneethynylene)s bearing glucose units as substituents†

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A series of poly(aryleneethynylene)s functionalized with acetylated glucopyranosyl units were synthesized by the Pd-catalyzed reaction of trimethylsilylethynyl derivatives with aromatic halides in the presence of silver oxide.

Conjugated polymers represent a wide class of organic compounds with properties of electric conductors[1] or semiconductors[2] and, in the last two decades, they have attracted the interest of the scientific community for their promising applications in various electronic devices,[3] such as light-emitting diodes (LEDs),[3a] plastic lasers,[3b] and photovoltaic cells.[3c] Among the different typologies of conjugated polymers, which have come into focus in the last few years, poly-(aryleneethynylene)s (PAEs) are considered one of the most representative classes.[4] LEDs,[5] sensors,[6] molecular wires,[7] and polarizers for LC displays[8] have been fabricated using PAEs as active semiconducting materials, and, for this reason, a great multiplicity of molecular architectures have been produced.

An interesting structural modification lacking in the wide view of PAEs, and, in general, in the field of conducting polymers, is represented by conjugated materials having carbohydrate units as substituents. The few examples reported are related to polythiophenes[9] or polyazulenes[10] with D-glucopyranose pendant groups, obtained by oxidative or electrochemical polymerization of suitable monomers, or to sugar-coated polydiacetylene[11] obtained by UV polymerization reaction of amphiphilic butadiynes in liposomes or Langmuir–Schaefer films. This is rather surprising in view of the interest which is usually attributed to polymers, mainly of the poly(phenylenevinylene) family (PPVs), presenting various types of chiral nonracemic substituents.[12]

On the other hand, the introduction of monosaccharide functionalities as substituents in the chain of conjugated materials may induce solubility properties and features of potential interest in various fields of application of semiconducting organic polymers, such as LEDs emitting polarized light deriving from the presence of chiral nonracemic groups.[13]

Moreover, PAEs functionalized with monosaccharide units may act as multivalent glycosides ligands for proteins and peptides. Various dendritic or linear non-conjugated polymeric structures have been recently proposed for this purpose.[14] However, up to now, no example has been reported concerning conjugated polymers with this function. The consequence of the protein–polymer interaction may be the quenching of the intense fluorescence emission of these polymers,[6] which can be exploited in fabricating specific sensors for the interacting protein.

On the basis of these promising potentialities and in the framework of our efforts dealing with the synthesis and characterization of various classes of conjugated polymers,[15] we considered it of interest to investigate a synthetic strategy for carbohydrate substituted PAEs.

We have found that the PAEs **1a** and **1b** (Scheme 1), can be build up by cross-coupling between the trimethylsilyl derivative **2** and the diiodo arenes **3a** and **3b**, respectively (ESI†).

As shown in Scheme 1, the polymerization was performed adopting the Pd-catalyzed coupling reaction of trimethylsilyle-thynyl derivatives with aromatic halides in the presence of silver oxide[16] (Scheme 1). As shown by a comparative preliminary work, this methodology, with respect to the classic Cassar–Heck–Sonogashira cross-coupling process, is known to produce a lower amount of compounds deriving from oxidative homocoupling reaction of the ethynyl derivative, and has been successfully applied to the synthesis of different PAEs.[16]

In our case, the [1H] and [13C] NMR spectra of the copolymer **1b** demonstrates the complete absence of structural defects that could originate from the oxidative homocoupling reaction of the monomer **2**. In order to obtain other glucose substituted PAEs, the monomer **2** was also coupled with diiodotetrafluorobenzene **3c** and dibromothiophene **3d**, affording, in high yields, copolymers **1c** and **1d** (Scheme 1).

Molecular mass values are reported in Table 1 together with reactions yields, UV, and fluorescence data.

The lower molecular weight of copolymer **1a**, compared with that of **1b**, may be due to steric hindrance of monosaccharide substituents on the nearest benzenic rings that may prevent the growth of the polymeric chains. The higher molecular weight value measured in the case of polymer **4** (Scheme 2) supports this hypothesis.

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† Electronic supplementary information (ESI) available: experimental procedures and related references, and IR and NMR spectra of all the compounds. See http://www.rsc.org/suppdata/cc/b2/b207753a/
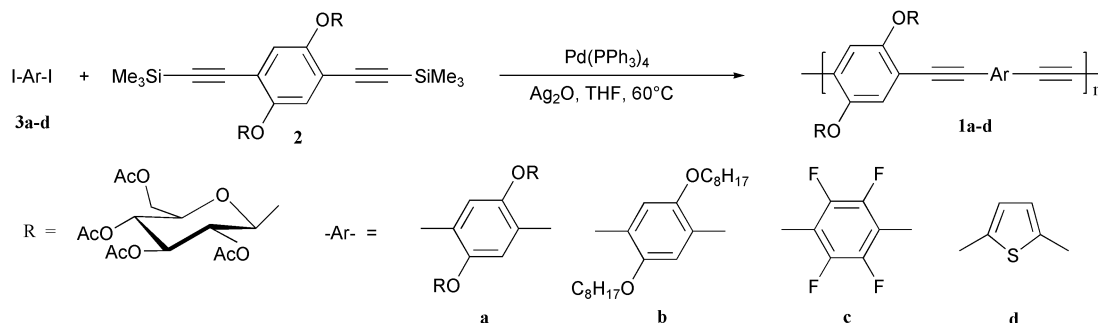
Scheme 1 Polymerization reaction.

Table 1 Molecular mass values and $\lambda_{\max}$ data for PAEs **1a-e**, **4**

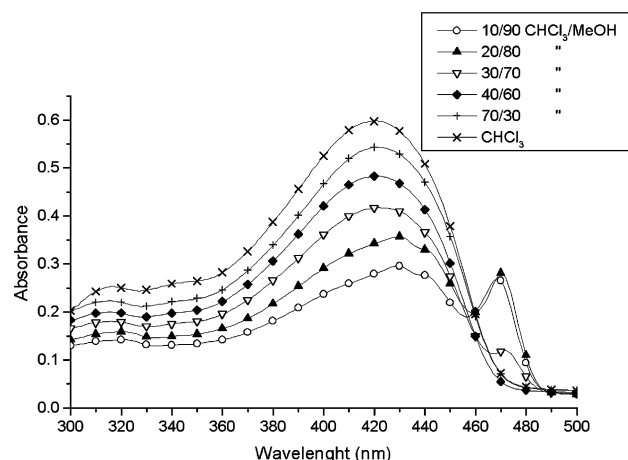| Polymer	Yields (%)	M_n^{ab} (Da)	M_w^{ac} (Da)	M_w/M_n	UV-Vis $\lambda_{\max}^{d}$(nm)	Fluorescence $\lambda_{\max}^{d}$ (nm)
1a	86	5000	6900	1.4	448	459
1b	86	19500	32500	1.7	421	464
1c	90	4200	14700	3.5	392	437
1d	90	2600	16000	6.4	427	472
1e	99	—	—	—	418[e]	459[e]
4	95	11650	27500	2.4	433	455

[a] Determined by gel permeation chromatography (GPC) with uniform polystyrene standards and THF as solvent. [b] Number average molecular mass. [c] Weight average molecular mass. [d] In chloroform solution. [e] In methanol solution.
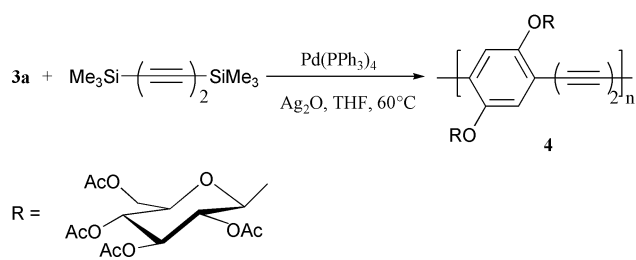
Scheme 2 Synthesis of polymer **4**.

Indeed, in the latter polymer the butadiyne units give a greater distance between the two nearest aromatic rings in the polymeric chain than the acetylenic groups. However, steric hindrance cannot be the only factor affecting the length of the polymer. A lower solubility of the growing chains may also lead to a lower degree of polymerization.

The hydrolysis of **1b**, easily conducted by an alkali $(MeO^-/MeOH)$ treatment, led to the corresponding deacetylated polymer **1e**, soluble in polar solvents (methanol, dimethyl sulfoxide) and moderately soluble in water.

Recently, aggregate and excimer formation in a mixture of solvent/non solvent (chloroform/methanol) has been proved for alkyl substituted PAEs by absorption and fluorescence spectroscopy.[17] Indeed, we have noticed a similar behaviour for the PAE **1b**. The absorption spectra of this polymer in a mixture of these two solvents starting from 60% up to 90% of methanol in chloroform showed the appearance of a sharper second red shifted band (469 nm), which could be ascribed to polymer aggregate formation as a consequence of the non solvent (methanol) presence (Fig. 1). On the contrary, for the deprotected polymer **1e** we did not found a similar tendency to aggregate in solution. Polymer **1e** is almost completely insoluble in chloroform, which acts in this case as non solvent. Absorption spectra in mixtures of methanol/chloroform from 90% to 60% of methanol are almost identical.‡ The strong interaction between the hydroxy groups on **1e** and methanol

may prevent the aggregate formation, even in the presence of relatively high concentration of non polar solvent.

In conclusion, we have succeeded in setting up a procedure for the preparation of a series of poly(aryleneethynylene)s substituted with glucose units, which may find useful applications in various fields of organic materials based devices. The advantages of our procedure are represented by (i) the versatility deriving from the possibility of placing the sugar moiety either on the disilyl derivative or on the aromatic diiodides (ii) the experimental simplicity, and (iii) the high yields in products which do not present structural defects due to homocoupling.

Notes and references

‡ In mixtures with chloroform concentration higher than 60% the polymer **1e** is insoluble.

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Fig. 1 Absorption spectra of polymer **1b** in various mixtures of chloroform/methanol.