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A new chemical polymerization process for substituted anilines Application to the synthesis of poly(*N*-alkylanilines) and poly(*o*-alkylanilines) and comparison of their respective properties

A. Falcou[a], A. Duchêne[a], P. Hourquebie[b], D. Marsacq[b], A. Balland-Longeau[b,*]

[a] *Faculté des Sciences, Laboratoire PIMIR, Parc de Grandmont, 37200 Tours, France*
[b] *Commissariat à l'Energie Atomique, Le Ripault, 37260 Monts, France*

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Abstract

A new chemical polymerization process has been developed for the synthesis of polyaniline derivatives. Various poly(*N*-alkylanilines) and poly(*o*-alkylanilines) bearing different alkyl chain lengths (3–18 carbons) can be prepared by oxidation with ammonium persulfate in a mixture comprising methanesulfonic acid, water, hexane and a cosolvent (THF). Using this general process and further purification procedures, we found that numerous polymers can be produced in their dedoped forms with very high purity and reproducibility. The physical, spectral and thermal properties of poly(*N*-alkylanilines) and poly(*o*-alkylanilines) were studied and compared. As expected, the solubility of these substituted polyanilines in their dedoped form increased with alkyl chain length, and doped polymers containing long alkyl chains were also totally soluble in the usual organic solvents.

Keywords: *N*-Alkylanilines; *o*-Alkylanilines; Polymerization; Properties of poly(*N*-alkylanilines) and poly(*o*-alkylanilines)

1. Introduction

Conjugated polymers were first extensively studied for their electrical conductivity and valuable optical and electroluminescence properties [1]. Polyaniline (PANI) occupies a very significant place among these materials because of its high conductivity in the doped state.

Recent developments have shown that PANI and its derivatives can also be used in the field of polymer-based light-emitting diodes as an interface layer between the metal electrode and the emitting polymer layer to ease charge injection [2]. Moreover the unusual dielectric properties of conjugated polymers make them valuable for the design of microwave absorbing materials [3] and materials with improved dielectric breakdown strength [4]. For such applications, conjugated polymers or their blends with thermoplastics do not need to be highly conducting.

To be used in such applications and on a large scale, materials must be soluble in common solvents or melt-processable. Polyaniline itself does not satisfy these requirements and many studies have therefore focused on improving the solubility and fusibility of polyaniline.

In most cases PANI is doped with specific acids [5,6] such as dodecylbenzene sulfonic acid or camphor sulfonic acid and, the resulting salts are partially soluble in solvents such as NMP or *m*-cresol. Polyaniline films can be thus spin-coated in the conducting form onto substrates.

Another approach to improve solubility in more usual solvents is the polymerization of monomers obtained from the modification of aniline. Different substituents (hydrophilic or organophilic) have been attached to the nitrogen of aniline and at the *ortho* or *meta* position of the aromatic ring of aniline. The most frequently studied have been poly(*ortho*-

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* Corresponding author. Tel.: +33 247 34 48 35; fax: +33 247 34 51 68.
E-mail address: alexia.longeau@cea.fr (A. Balland-Longeau).

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alkyl [7–15], -alkoxy [16] and -sulfonated [17] anilines) and poly(*N*-alkylanilines) [18–24]. Flexible alkyl chains and alkylsulfonic acid chains have also been incorporated directly into the polyaniline [17a,21–23].

These studies have shown that polyaniline derivatives in the doped state are less conducting than PANI but solubility is substantially improved in solvents such as chloroform, THF or DMF. Furthermore, copolymers of aniline and substituted aniline have proved to be more conducting than substituted homopolymers and more soluble than PANI. Nevertheless, this class of component has not been further developed or well characterized, principally because it is difficult to polymerize or copolymerize substituted anilines and to purify the resulting polymers.

Moreover most studies concerning substituted aniline polymerization have been carried out with commercially available substituted anilines containing short alkyl chains (containing 1–4 carbons) using chemical or electrochemical methods. In contrast, there have been few investigations into polymerization and characterization of polyanilines bearing longer substituents [12–15,18]. Indeed, these monomers do not polymerize under the conditions usually employed for the polymerization of aniline, e.g. ammonium persulfate in 1 M aqueous HCl. Under these conditions, it has been reported that the hydrochloride salts of such substituted monomers precipitate due to their hydrophobic properties which hamper polymerization [12]. More generally, we have found that the polymerization reaction occurs only if monomers are truly solubilized in the medium. We therefore investigated ways of preparing poly (*N*- and *ortho*-substituted anilines) which are difficult to obtain by classical oxidative methods.

Other techniques with specific acids or oxidants have been published. For example, Chevalier et al. showed that *N*-alkylanilines were chemically polymerized in aqueous $HClO_4$ solution [18]. The authors noted the need to heat the polymerization medium in the case of monomers containing long alkyl chains in order to keep a homogeneous mixture. Polymers were obtained in their ClO_4^--doped form but it is difficult to remove these ions during post-processing. Geniès et al. reported chemical oxidation of alkylanilines in an anhydrous medium constituted of NH_4F, 2.35 HF [13–15]. However, this process was found to be more convenient for electrochemical polymerization. Alternative methods have been described consisting of performing the polymerization reaction in organic solvents in which monomers and oxidant are soluble [25,26]. We attempted to polymerize our monomers according to the conditions described by Inoue et al. [26]. (CH_3CN, copper perchlorate) but we obtained only oligomers or polymers of very low molecular weight, especially with monomers bearing long alkyl chains.

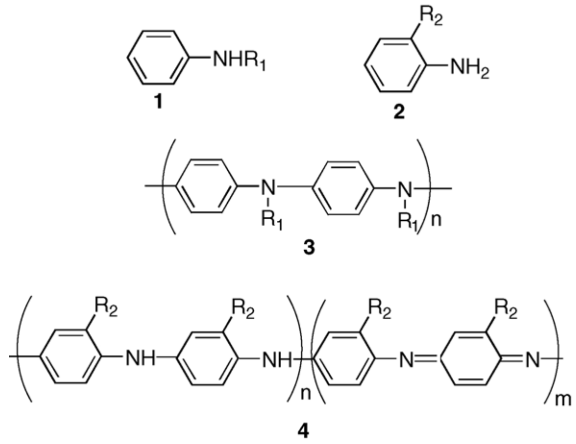
We finally decided to develop a new chemical method which allows more general access to pure polyaniline derivatives. We present here the synthesis of poly(*ortho*-alkylanilines) and poly(*N*-alkylanilines) bearing various alkyl chains in a mixture of hexane, water and THF. The properties of these materials, including solubility and thermal behavior, were compared and correlated with the substituent nature of the polymers. The effects of side chain length on the physical properties were investigated by spectroscopic and steric exclusion chromatography measurements.

2. Results and discussion

Our investigations first focused on the development of a new polymerization process which could be adapted to chemically different monomers, i.e. *N*-alkylanilines (**1**) and *o*-alkylanilines (**2**), bearing short to very long alkyl chains (Plate 1). The second aim was to optimize the purification phase since access to pure N-substituted and ring-substituted polyanilines (**3**) and (**4**) was required in their dedoped state in order to compare the physicochemical, thermal and electrical properties of these two types of polymer.

2.1. Synthesis, solubility and molecular weight

Several investigators have developed an emulsion polymerization process to polymerize aniline in the presence of specific dopants [27]. We decided to adapt this concept to our wide range of substituted monomers **1** and **2**. In fact, the latter possess both hydrophobic and hydrophilic parts. We therefore hypothesized that a mixture containing a polar solvent (water) and an apolar solvent (hexane) would allow polymerization of these monomers. We decided to use methanesulfonic acid and not DBSA because we wanted easy access to the undoped and pure forms of polymers for their full characterization. Taking into account the greater or lesser hydrophobic character of these monomers, we had to adapt our basic process by adding a small quantity of cosolvent, such as THF. The addition of such a cosolvent does not affect the polymerization process but allows better solubilization of specific monomers **1e** and **2b**–**2d** in the reaction mixture.



R_1 = *n*-butyl, *n*-hexyl, *n*-decyl, *n*-octadecyl

R_2 = H, *n*-propyl, *n*-hexyl, *n*-nonyl, *n*-undecyl

Plate 1. Chemical structures of *N*-alkylanilines (**1**) and *o*-alkylanilines (**2**) and their corresponding polymers (**3** and **4**).