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The multi-component Debus-Radziszewski reaction in macromolecular chemistry

S. Saxer,^a C. Marestin^{a†}, R. Mercier^a and J. Dupuy^b

The well-known Debus-Radziszewski reaction is over one century old. However, this reaction has only been considered very recently as a new tool to design original imidazole and imidazolium-containing polymers by direct formation of the imidazole ring during the polymerization process. This article reports recent advances concerning the use of this newly emerging reaction in macromolecular chemistry.

Introduction

Multicomponent reactions (MCRs) avoiding long multi-step synthetic pathways have been extensively studied by organic chemists, as witnessed by many dedicated reviews¹⁻³ or books⁴. Although most of the MCRs are known for a long time (Strecker (1850), Mannich (1912), Biginelli (1893), Passerini (1921)...), these reactions regain interest for the design and synthesis of various organic compounds of biological and therapeutic interest⁵ as well as for material science applications. In the polymer chemistry domain, MCRs have been rather overlooked up to now^{6,7}. Excepted few articles published in the nineteen seventies, most works related to multi-component polycondensation are very recent (less than a decade) and provide evidences that highly functionalized polymers can be easily synthesized. Most of these studies concern the synthesis of linear and aliphatic polymers by Mannich reaction⁸, isocyanide-based multicomponent reactions (Passerini and Ugi)^{9,10}, metal catalyzed reactions (CuMCR¹¹, «A³» coupling¹²). Recent reviews¹³ report last advances on these topics. On the other hand, the synthesis of macromolecular structures-containing heterocyclic units obtained by MCR are scarcely described. Few examples concern the incorporation of thiazolidinones by the mercaptoacetic acid locking imine (MALI)¹⁴ reaction, of dihydropyridines by Hantzsch reaction^{15,16}, of dihydropyrimidinones by Biginelli reaction¹⁷⁻²⁰, or by the formation of pyrrole groups^{21,22}. In the frame of on going research in this field, the Debus-Radziszewski MCR appears particularly promising. Indeed, both heterocyclic imidazole rings or aromatic substituted imidazoles can be obtained from this reaction based on an α -dicarbonyl compound, an aldehyde and ammonia. When the reaction involves glyoxal, an imidazole ring is formed (Fig. 1A)²³. This reaction occurs in mild conditions (room temperature), in acidic media. When the α -dicarbonyl compound is a 1,2-diketone, a 2,4,5-trisubstituted imidazole core²⁴ (well known as lophine) (Fig. 1-B) is obtained. In this case, higher reaction temperatures are required. High reaction yields and highly pure products can be obtained in various experimental conditions (in AcOH, EtOH, under thermal or microwave heating, and in the presence of different acidic catalysts). Such compounds are considered as key components for the development of new therapeutic agents (for their anti-inflammatory²⁵ or antibacterial properties²⁶). Their optical properties²⁷⁻²⁹ have also attracted significant interest from material scientists for the elaboration of blue light emitting materials³⁰, the design of luminophore for optoelectronic applications, chromophore for non-linear optics, molecular photonics and sensing... Different modifications of the pristine reaction have been described over time³¹. When two primary amines are reacted with glyoxal, imidazolium compounds can be easily formed (Fig. 1-C). When 1,2-diketones are reacted with both an amine and ammonia, complex 1,2,4,5-tetrasubstituted imidazoles are obtained (Fig. 1-D).

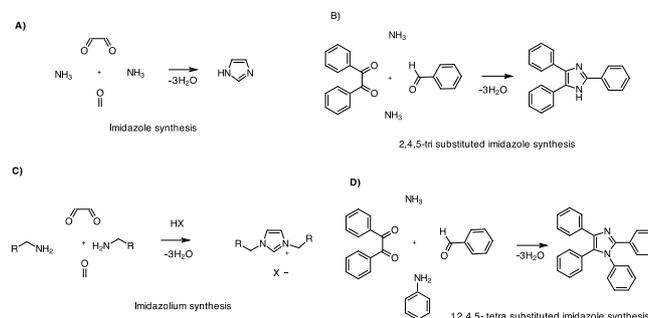


Fig. 1 Debus-Radziszewski reactions

Due to their intrinsic properties, the incorporation of imidazoliums and substituted arylimidazoles rings in macromolecular backbones has attracted a particular interest. Different strategies can be envisioned in order to incorporate such groups in polymers: 1) by chemical modification of a pre-existing precursor, 2) by preliminary

synthesis of an imidazolium / substituted arylimidazole monomer and its subsequent polymerization, 3) by direct formation of the heterocyclic ring during the polymerization process. The purpose of this article is to review the recent use of Debus-Radziszewski reaction for the elaboration of innovative heterocyclic macromolecular structures. As mentioned above, depending on the nature of the reactants and on the experimental conditions, Debus-Radziszewski reaction can lead to either imidazoliums or substituted arylimidazoles. Whereas the first part of this article will be devoted to the synthesis of poly(imidazolium)s, the second part will deal with the synthesis of poly(tri and tetra-substituted arylimidazole)s.

The Radziszewski reaction for the synthesis of poly(imidazolium)s

Imidazolium-containing polymers have attracted considerable interest in recent years for the development of poly(ionic liquid)s (PILs)³². Such polymers can be easily synthesized by post-modification of precursors. The most widely used approach concerns the chemical modification of halogeno-alkane-containing polymers, by N-alkylation of alkyl imidazoles compounds. This approach has been widely described, on various polymer substrates (Polyarylether ketones³³, copolymers of polystyrene and vinylbenzylchloride³⁴...). Among the different existing methods allowing the synthesis of imidazole, few of them are of industrial importance (essentially the Debus-Radziszewski reaction)³⁵. However, in this article, we do not intend to review the works done on the chemical grafting of pre-formed imidazole derivatives. In the following examples, special emphasis is placed on post-modification reactions leading to the direct formation of imidazolium heterocycles.

Antonietti et al.³⁶ reported a water-based coupling reaction either to efficiently couple amino-terminated poly(ethylene oxide) oligomers or to enable the intra and intermolecular coupling of poly(L-lysine) by formation of imidazolium linkages (Fig. 2).

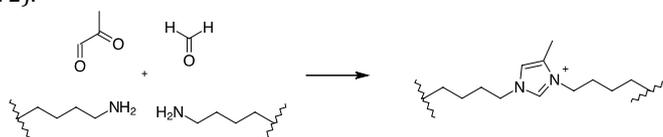


Fig. 2 Formation of imidazolium rings as crosslinking reaction

Sirvio et al.³⁷ described the effective crosslinking of chitosan using glyoxal (or methyl glyoxal) and propionaldehyde (or benzaldehyde) to link chitosan free pendant amine groups by formation of imidazolium bridges, as represented in Figure 3. The reaction is performed in 10% acetic acid aqueous solution, at room temperature. The resulting crosslinked material was obtained as a water-insoluble aerogel that presents excellent adsorption capacity of anionic dyes.

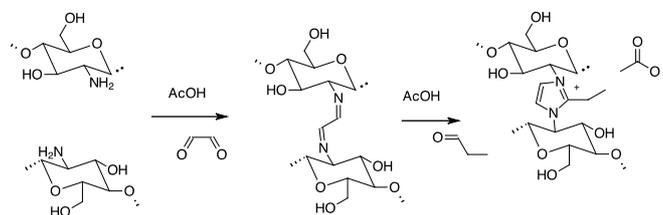


Fig. 3 Chitosan crosslinking by formation of imidazolium linkages

Zhao and coworkers³⁸ reported the reticulation of polyamidoamine PANAM dendrimers to generate novel imidazolium-crosslinked ionogels by the same reaction, in the presence of methylglyoxal. The physico-chemical characterization of these ionogels shows conductivities up to 6.8 mS⁻¹ at 25 °C and high elastic modulus (10³-10⁶ Pa at room temperature).

Nanoparticles functionalized with polyimidazolium groups were the subject of many works. Thus functionalized magnetic nanoparticles were prepared and evaluated for the extraction of preservatives in vegetables³⁹, as adsorbent for organophosphorus pesticides from tea drinks¹⁴, or for the analysis of some drugs in pharmaceutical formulations, in plasma and urine⁴⁰. While many research work concerning the manufacturing of these functionalized nanoparticles are based on multi-step reactions, Castro-Grijalba et al.⁴¹ used with success the one-step Debus-Radziszewski reaction involving magnetic nanoparticles coated with amine groups. The resulting materials were evaluated as sorbent for different non-steroidal anti-inflammatory drugs such as salicylic acid, ketoprofen and naproxen present in saliva samples.

Hajipour et al.⁴² reported the synthesis of N-heterocyclic carbene-cobalt complex supported on carbon nanotubes. In this synthesis, the Debus-Radziszewski reaction is a key step for the immobilization of imidazolium functions on the

aminated carbon nanotube surface (Fig. 4). A high catalytic activity and efficiency was evidenced for these carbenes, in the Mizoroki-Heck reaction.

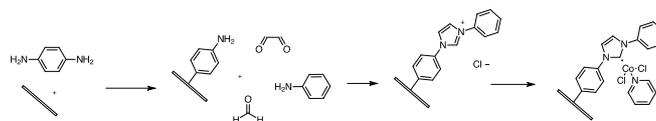


Fig. 4 Immobilization of N-heterocyclic carbene-cobalt complex on carbon nanotubes

Synthesis of a monomer containing the imidazolium group and its subsequent polymerization

Compared to the post-functionalization route, the direct polymerization of a precursor containing an imidazolium group helps improving the control of the final macromolecular structures. Most polyimidazoliums synthesized according to this strategy are obtained by radical polymerization of imidazolium-containing vinyl, styrenic, acrylic or methacrylic monomers⁴³. However, some recent examples also describe the synthesis of polyesters^{44,45} or polyimides⁴⁶, by polycondensation of specific precursors. To date, such monomers are usually synthesized by classical multi-step syntheses and involve pre-formed imidazole heterocycles as reactants. However, Esposito et al. have described the synthesis of various symmetric bifunctional imidazolium compounds by direct Debus-Radziszewski multi-component reaction⁴⁷ from various aliphatic amines, with excellent yields. Wan et al.⁴⁸'s work broadens the scope of this reaction with aromatic substrates (Fig. 5).

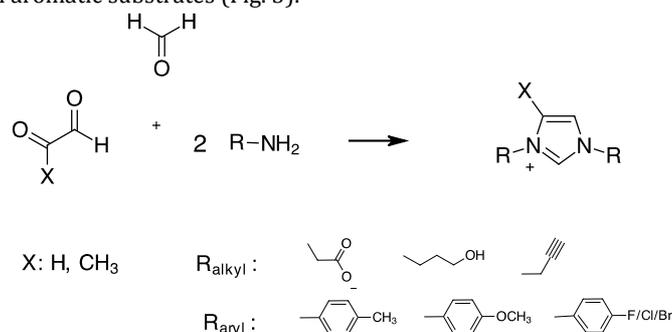


Fig. 5 One-pot synthesis of difunctional imidazolium-containing compounds

Industrial interest in the synthesis of dialkylimidazolium by Debus-Radziszewski reaction has been as well shown for long time by Du Pont de Nemours⁴⁹. This highly efficient synthetic pathway opens wide perspectives for the synthesis of new functional precursors and macromolecular structures.

Synthesis of polyimidazolium structures. Formation of the imidazolium heterocycles during the polymer chain growth

The preliminary synthesis of functional precursors, their isolation, purification and subsequent polymerization is a rather long process. However, the unique properties associated with the materials obtained give rise to a wide range of possibilities for the material chemist⁵⁰. This is probably the reason why the development of new polymerization processes allowing the direct formation of imidazolium ring during the polymer chain growth is particularly promising.

Recently, a research group from BASF has shown a great interest in this field, as witnessed by two recent patents^{51,52}. Moreover, Lindner⁵³ reported latest advances on the direct synthesis of polyimidazolium by a one pot /one step Debus-Radziszewski reaction, from glyoxal, formaldehyde and various diamines, as represented in Figure 6.

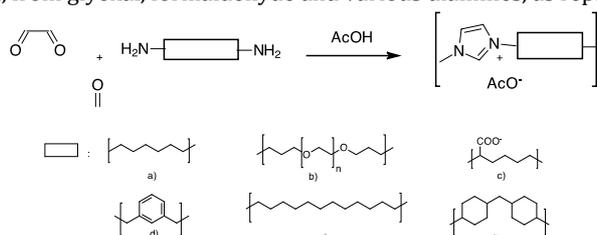


Fig. 6 Poly(imidazolium)s synthesis by direct formation of heterocyclic ring during the polymer chain growth

The Radziszewski polycondensation reaction (RPR) was found very efficient. High monomer conversions were evidenced by ^1H NMR, after one hour reaction at 100 °C. The reaction can be also performed at room temperature (21 °C) as well for longer reaction times. The polymers synthesized in the presence of a slight carbonyl compound excess were found to have the highest molecular weight values. Depending on the diamine structure, the glass transition temperature of the polymers can be easily tuned, on a wide range of temperatures flexible long alkyl sequences (a), b), d), e),) result in very low T_g 's values (from -46 °C to -9 °C) whereas zwitterionic structure of lysine (c) or more rigid scaffold of bis-cyclohexyl (f) tends to increase T_g around 45 °C. The mild reaction conditions, the versatility and industrial availability of the monomers have brought a huge interest in this aqueous polymerization process. According to a similar synthetic pathway, Grygiel and coworkers⁵⁴ have considered the incorporation of an aromatic diamine (p-phenylene diamine). The reaction is performed in an aqueous medium, at room temperature. The resulting rigid polymer contains alternating imidazolium and aryl rings (Fig. 7). Acetate anion exchange with dicyanamide anion affords a nitrogen-doped polyimidazolium. The chemical structure was confirmed by ^1H NMR and the molecular weight were evaluated by size exclusion chromatography (20% MeOH / 80% acetate buffer). The physico-chemical characterizations of this structure attest for a high glass transition temperature (153 °C) and high thermal stability materials.

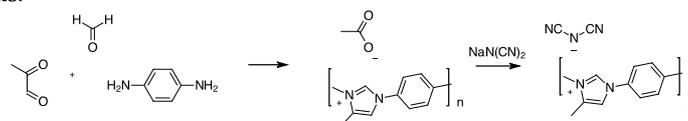


Fig. 7 Aromatic diamines as reactants for the direct synthesis of poly(imidazolium)s

The synthesis of meso /microporous polymers was also addressed by RPR⁵⁵. In this case, the synthesis is performed with the tetrakis(4-aminophenyl) methane, which is considered as one of the most commonly used tetrahedral scaffold for the synthesis of microporous polymers. Because of the four available reactive amine groups, the multi-component reaction results in the direct formation of a polymer network (Fig. 10). Intrinsic porosity of the material is related to the specific steric hindrance of the tetramine. The reaction takes place at room temperature. However, slight heating (80 °C for 24 hours) was required to achieve completion of the reaction. Excellent performances towards carbon dioxide adsorption of the resulting materials were evidenced. Similar work was reported by a sequential imine formation / subsequent reaction with p-formaldehyde on a tetrahedral core containing four 2,6-diisopropyl aniline groups⁵⁶.

The Radziszewski reaction for the synthesis of 2,4,5-,trisubstituted imidazoles or 1,2,4,5-,tetrasubstituted imidazoles-containing polymers.

By synthesis of a substituted arylimidazole-containing functional precursor and its subsequent polymerization

The synthesis of an imidazole-containing precursor, and its subsequent polycondensation by conventional methods (amidation, aromatic nucleophilic substitution...) has been investigated in the past. The preparation of polyamides by Akutsu et al.⁵⁷ in 1987 can be considered as pioneering work using this synthesis methodology.

A trisubstituted arylimidazole-containing dicarboxylic acid compound was obtained by a two-step reaction from diethyl-4,4'-benzildicarboxylate, benzaldehyde and ammonium acetate, in acetic acid, followed by an hydrolysis under alkaline conditions (Fig. 8).

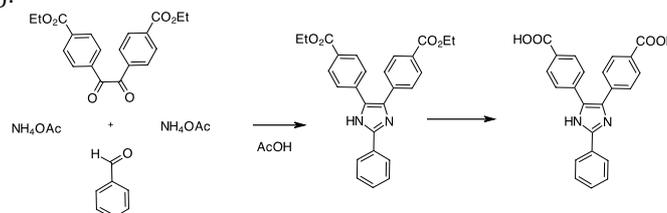


Fig 8. Synthesis of triarylimidazole-containing dicarboxylic acid

This monomer was condensed with different aromatic diamines. The resulting polyamides are very rigid ($T_g > 292$ °C) and show high thermal stabilities ($T_{d5\%} > 444$ °C). This was attributed to the incorporation of the stiff imidazole rings in the polymer chain. Interestingly, these improved properties were not obtained at the expense of the solubility in

common organic solvents. These improvements were accounted for by the asymmetric structure of the polymer backbone, the polar nature of the imidazole ring (and its affinity with polar solvents) as well as the effect of the bulky phenyl substituent. In the frame of some work dedicated to the development of high performance polymers for aerospace application, Connell et al.^{58,59} used a similar strategy to synthesize poly(arylene ether imidazole)s from the direct polycondensation of trisubstituted-containing imidazole bisphenols (Fig. 9), via an aromatic nucleophilic substitution reaction. High molecular weight polymers were synthesized and characterized. These macromolecular structures could be solution-cast into thin tough films. The polymers present good mechanical properties as well as adhesives and composites properties.

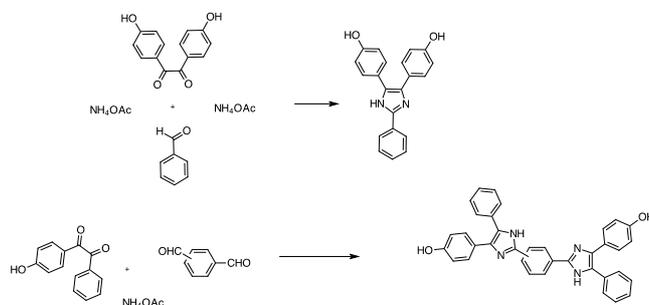


Fig 9. Synthesis of triarylimidazole-containing bisphenols

The incorporation of bulky, polar trisubstituted arylimidazole groups in polyimide backbones was also considered. For this purpose, the two-step or multi-step synthesis of new diamine-containing tri-substituted arylimidazole groups were developed as illustrated in Figure 10.

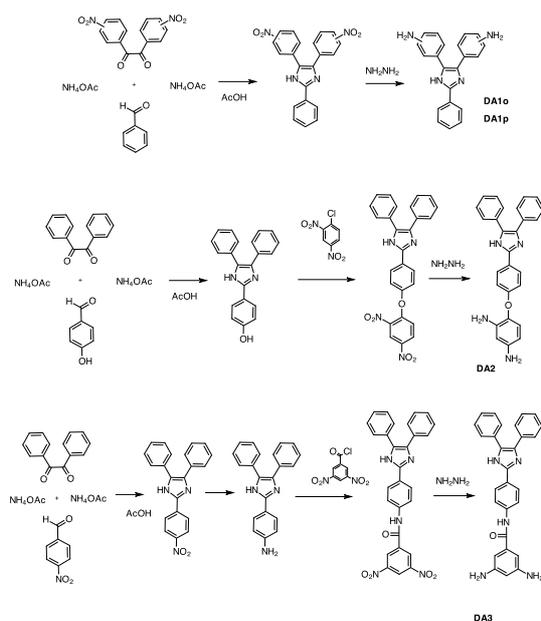


Fig 10. Synthesis of triarylimidazole-containing diamines

4,5-di(4-aminophenyl)-2-phenylimidazole (DA1p)⁶⁰ and 4,5-di(3-aminophenyl)-2-phenylimidazole (DA1o)⁶¹ were synthesized by condensation of 4,4'-dinitrobenzil or 3,3'-dinitrobenzil, with benzaldehyde and ammonium acetate, and subsequent reduction of nitro groups. By direct polycondensation of these diamine monomers with different dianhydrides, various polyimides were synthesized. The resulting polymers have very high T_g (>279 °C) and high thermal stability ($T_{d10\%}$ >567 °C). Such rigid structures are still rather fairly soluble in common polar aprotic solvents (DMSO, DMAC, NMP). A similar approach was explored by Ghaemy et al.⁶², with the synthesis of diamine DA2. In this case, a specific attention was paid to incorporate a diphenylether spacer in the precursor, in order to remove the imidazole ring from the macromolecular chain in the final polymer. As expected, highly soluble polymers were obtained in this case. This result was attributed to the better solvation of the polymer chains related to the solvent penetration due to the free volume generated by the bulky pendant groups. Depending on the dianhydride comonomer, the polymer T_g are ranging from 232 °C to 325 °C. Despite the presence of bulky and rather flexible side-chains, the glass transition temperature of the polymers is not much affected, but thermal stability seems slightly reduced ($T_{d10\%}$ >368 °C). Analogous results were very recently reported by Rafiee et al.⁶³ for polyimides based on

DA3 ($T_g > 261$ °C and $T_{d10\%} > 406$ °C). Hariharan et al.⁶⁴ described the synthesis of a new tetrasubstituted arylimidazole diamine (DA4) by a four component reactions involving benzil, nitrobenzaldehyde, nitroaniline and ammonium acetate (Fig. 11).

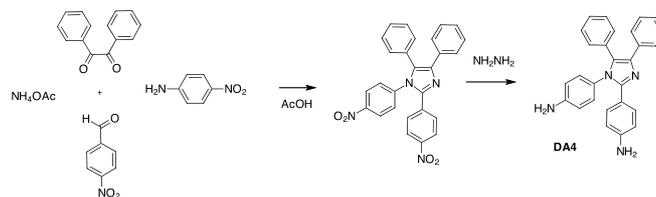


Fig 11. Synthesis of a tetrasubstituted arylimidazole-containing diamine

The incorporation of such diamines in polyimides results in very high glass temperatures polymers (398 -453 °C). Furthermore, the presence of tetrasubstituted units imparts very good solubility of these macromolecular structures (DMAC, DMSO, DMF, NMP, THF and even partial solubility in CHCl_3). Besides their outstanding thermal stability, some of these polymers present interesting electrochemical properties (low band gap value of 2.37 V) as well as optical properties (photoluminescence quantum yield of 65%). Muellen et al.⁶⁵ designed a dihalogenated bisimidazole precursor (Fig. 12). This reactant was involved in the synthesis of a poly(p-phenylene) by a Nickel(0)-mediated Yamamoto-type polycondensation. However, only low molecular weight oligomers were successfully obtained. Nevertheless, it was proven that the incorporation of the conjugated bisimidazole chromophore induces a strong modification of the optical properties of the polymer compared with poly(paraphenylene). Blue-green emitting properties were evidenced for this polymer.

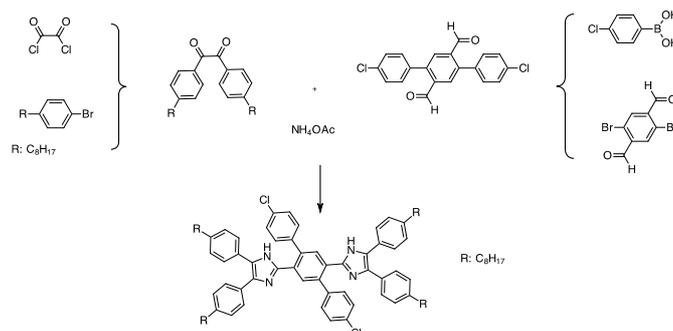


Fig 12. Synthesis of a dihalogenated bisimidazole precursor.

By formation of the tri-or tetrasubstituted imidazole ring during the polymer chain growth

Although the synthesis of tri or tetra-substituted arylimidazoles-containing polymers by direct polycondensation via Radziszewski reaction appears very challenging, very little results have been so far reported in literature.

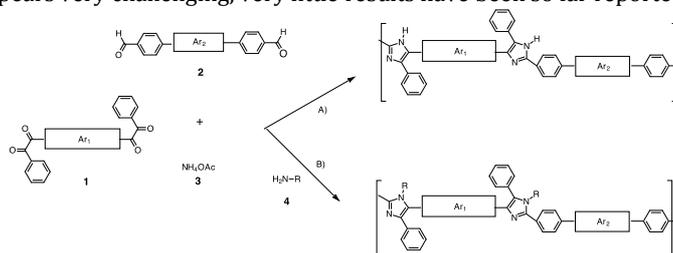


Fig. 13 Poly(arylimidazole)s synthesis

To the best of our knowledge, the first work relative to the synthesis of poly(triarylimidazole)s was described in 1967⁶. However, only low molecular weight oligomers were isolated. More recently, high molecular weight polymers were successfully synthesized from a microwave-assisted polymerization (Fig. 13A)⁶⁶. Based on a similar process, the same research group has investigated the synthesis of tetrasubstituted

poly(arylimidazole)s (Fig. 13B)⁶⁷. Different polymers with high molecular weight were obtained and display very good thermal stabilities (357 °C $< T_{d5\%} < 513$ °C). Holdcroft and co-workers⁶⁸ reported the elaboration of high performance cationic polyelectrolytes based on poly(arylene-imidazolium)s (Fig. 14). These structures were

synthesized as described above and a subsequent alkylation of the imidazole groups was achieved by reaction of methyl iodide. The resulting polymers were cast into tough anionic conductive membranes. Preliminary results evidences excellent anionic conductivities ($280 \pm 80 \text{ mS}\cdot\text{cm}^{-1}$) and performances ($818 \text{ mW}\cdot\text{cm}^{-2}$ at $1.8 \text{ A}\cdot\text{cm}^{-1}$) for these membranes in anionic exchange membrane fuel cell tests (AEMFC)s.

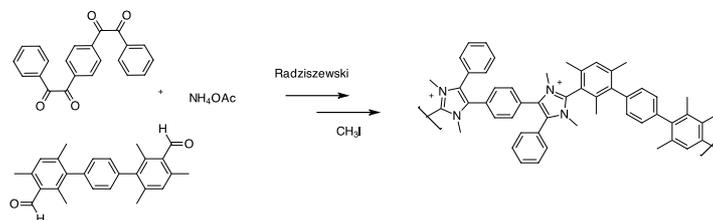


Fig. 14 Synthesis of poly(arylene-imidazolium)s

Conclusions

Recent developments in the design of innovative and high performance polymers have recently led to a renewed interest in old organic reactions. In this connection, The multicomponent Debus-Radziszewski reaction enables the formation of a wide range of imidazole derivatives. This reaction can be considered as an efficient way to design functional oligomers and polymers, either by a post-modification reaction, to synthesize complex and innovative monomers, or by direct formation of imidazole derivatives during the polymer chain growth. As evidenced by the reported results, the incorporation of imidazole derivatives in macromolecular structures provides unique physico-chemical features for the resulting polymers and opens wide perspectives and possibilities. Most recent advances in this field points out the huge potential of the Debus-Radziszewski reaction as a newly emerging polymerization technique.

Conflict of interest

There are no conflicts to declare.

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