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One-pot synthesis of primary amino end-functionalized polymers by reaction of living anionic polybutadienes with nitriles

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Abstract

We present a convenient method to synthesize polymers with primary amino groups by end-capping of living anionic chain ends with nitriles followed by reduction in a one-pot process. As an example, the addition of pivalonitrile to the chain ends of oligobutadienyllithium in toluene, followed by the reduction with sodium borohydride quantitatively leads to ω-amino-oligo-1,4-butadiene, as demonstrated by ^{1}H and ^{13}C NMR, thin-layer chromatography and MALDI-ToF mass spectrometry.

Keywords: Butadiene; Anionic polymerization; Functionalization

1. Introduction

The synthesis of chain-end-functionalized polymers is of great importance due to the fact that they have various practical and potential applications such as waterproof membranes or coatings, adhesives, sealants, and others [1]. Living anionic polymerization is the preferred method for preparing such polymers because it leads to predictable molecular weights and narrow molecular weight distributions. Many possible end-functionalizations of living anionic polymers have been reported and well reviewed. Widely studied and successful examples are hydroxyl and carboxyl end-functionalized polymers that can be synthesized by the reaction of a living anionic polymers with ethylene oxide or carbon dioxide, respectively [2–8]. The resulting polymers have well defined structures (e.g. molecular weight and molecular weight distribution as well as a degree of end-functionalization). A deficiency of using hydroxyl terminated polybutadienes (HTPBs) and hydrogenated HTPBs is often caused by rather a weak nucleophilicity of the hydroxyl group at the chain end, which prevents its incorporation into formulations under commonly used process conditions. For example, the hydroxyl groups are usually not sufficiently reactive with bisphenol A (BPA) epoxy resins to be useful as crosslinkers or flexibilizers. In addition, when preparing resins for electric insulation, the reaction rate between the anhydride of maleic anhydride (MA)-modified polybutadiene and the hydroxyl group of HTPBs is too low at room temperature. Also, the curing reaction between the hydroxyl group of HTPBs and isocyanate groups in specific polyurethane applications is hindered or rendered incomplete, by the presence of other hydroxyl-containing additives which react at a comparable or faster rate [1]. Since, amines are stronger nucleophiles, the amino-terminated polybutadienes (ATPBs) would have been favored over corresponding HTPBs, except for the difficulty and expense of prior art methods of preparing ATPBs. In particular, α,ω-diamino-oligobutadienes could act as precursors of polyurethanes (via transformation to isocyanates), polyureas, polyamides, or crosslinked epoxides. Prior methods of preparation of amino-terminated polybutadienes comprised the use of functional anionic initiators or terminators. For example, Schulz and Halasa demonstrated the preparation of polyisoprenes and polybutadienes with amino end-groups by using the initiator *p*-lithio-*N*,*N*-bis(trimethylsilyl)aniline having a protected primary amino group [9]. The other and most widely utilized approach comprises the transformation of a living anionic chain end into aminofuctionality through the end-capping of living polymeric anions with 1,1-diphenylethylene derivatives [10] or the termination with protected ω-amino-functional-α-haloalkanes [11] or -chlorosilanes [12–14]. However, these methods require expensive reagents and a deprotection step after functionalization. An industrially feasible methodology

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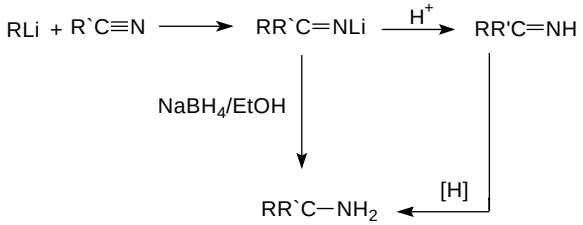


Scheme 1. Synthetic pathway to primary amino end-functionalization.

involves converting hydroxyl terminated polybutadienes into amino-terminated polybutadienes [1].

An efficient approach to ATPBs possessing one primary aminogroup, which excludes the disadvantages of previous methods, is introduced in this article. This approach is based on the addition reaction of organolithium compounds with nitriles [15,16], followed by reduction of the imide formed (Scheme 1). The use of difunctional initiators can lead to amino-telechelic polymers.

In our present study, we apply such addition reaction by reacting pivalonitrile (trimethylacetonitrile) with living oligobutadienyllithium. Pivalonitrile is a good choice for two main reasons: reactivity and characterization. The absence of protons on the carbon in α-position to the nitrile group allows us to exclude side reactions, and the *tert*-butyl group is well recognizable using different analytical techniques. To provide easy detection of functional groups in the final products, oligobutadienes with molecular weights of 500–1000 g/mol were chosen as model compounds.

After submission of the manuscript, one reviewer pointed us to a Japanese patent using a similar approach [17]. In the patent description, the authors give two examples: reaction of PMMA-Li and of SBS-Li with acetonitrile, followed by reduction with $LiAlH_4$ and a nickel catalyst, respectively. No characterization was reported except for end-group titration of the amine resulting in 88 and 91% functionalization, respectively. One reason for the incomplete functionalization might be proton abstraction from acetonitrile that cannot happen with pivalonitrile. In this publication, we report an extensive characterization of all intermediate and final products indicating 100% functionalization.

2. Experimental part

2.1. Materials

Toluene and cyclohexane (Sigma–Aldrich) were successively distilled over CaH_2 and potassium metal. 1,3-Butadiene (Riessner Gase, Germany) was purified by passing through activated alumina and 4 Å molecular sieves. Prior to use, it was condensed from di-*n*-butylmagnesium (Aldrich, 1.0 M solution in heptane) into a calibrated burette. Pivalonitrile (Acros, 98%) was stirred over freshly crushed CaH_2 and distilled under vacuum before use. The concentration of *sec*-butyllithium (Acros, 1.3 M in cyclohexane/hexane: 92:8) was determined by acid–base titration. TLC plates (200 μm, 50/p, with fluorescent indicator F-254) purchased from Carl Roth GmbH + Co (Germany) were employed.

2.2. Polymerization

Polymerizations were carried out under pure nitrogen atmosphere in a thermostated glass autoclave (Büchi, Switzerland). In a typical reaction, 250 mL of solvent were placed in the reactor which was heated to 40 °C. Upon insertion of 8.3 mL (10.7 mmol) of *sec*-BuLi via syringe, 16.3 mL (0.197 mol) of 1,3-butadiene were added under vigorous stirring. The course of the polymerization was followed by the drop of internal pressure. Before end-capping with pivalonitrile a 10 mL aliquot was withdrawn into degassed methanol to characterize the precursor polymer.

2.3. End-capping of oligobutadienyllithium

Pivalonitrile 1.4 mL (11.7 mmol, 1.1 M excess) was added to oligobutadienyllithium at 20 °C, the reaction mixture was allowed to stand for 10 min at room temperature. Subsequently, a solution of 0.484 g (12.7 mmol) $NaBH_4$ in 35 mL of absolute ethanol was added to the reaction mixture using an ampoule. Reduction was carried out at 50 °C and was completed within 1 h. Alternatively, the initially produced Li-imide was terminated with MeOH, isolated, and subsequently reduced by $NaBH_4$ in toluene/ethanol (6/1, v/v) solution.

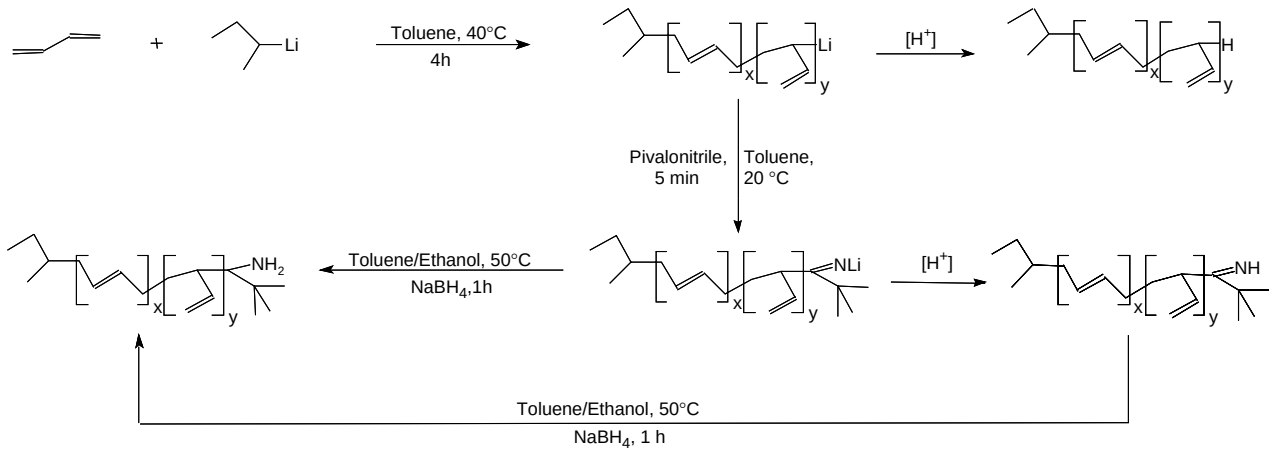
2.4. Analytical techniques

For ^1H and ^{13}C NMR spectroscopy a Bruker Avance (250 MHz) spectrometer was utilized. $CDCl_3$ and acetone-d_6 were used as solvents. MALDI-ToF mass spectrometry was performed on a Bruker Reflex III, equipped with a 337 nm N_2 laser, in the reflector mode and 20 kV acceleration voltage. 2-[(2*E*)-3-(4-*tert*-Butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) was used as matrix. Samples were prepared from THF solution by mixing sample, matrix (10 g L^{-1} each) and AgTFA in a ratio of 20:5:1. FT-IR spectroscopy was performed on a Bruker Equinox 55 using KBr pellets as substrates.

For size exclusion chromatography (SEC) PSS SDV gel columns (300 × 8 mm, 5 μm): 10^5, 10^4, 10^3, and 10^2 were used and 100 μL of a 0.4 wt% polymer solution was injected at room temperature. Measurements were performed at an elution rate of 1 mL min^{-1} using THF with 1 wt% of toluene as an eluent and RI detection. Poly(1,4-butadiene) standards were used to calibrate the columns and the internal standard was toluene.

3. Results and discussion

The polymerization of 1,3-butadiene in toluene was performed in a standard manner and resulted in narrowly distributed oligomers: M_n values ranged from 771 to 1197 g/mol and M_w/M_n varied from 1.09 to 1.15 (SEC). No end-functionalization was achieved in cyclohexane as a solvent, probably due to the stronger aggregation of the chains.



Scheme 2. Synthetic pathway towards amino-terminated oligobutadienes.

End-capping with pivalonitrile in toluene was followed directly by reduction using absolute ethanol as a protic solvent for $NaBH_4$ and terminator for Li-imide. This allows us to carry out one-pot, two-step amino end-functionalization. The polymerization and end-functionalization are depicted below in Scheme 2.

The aminated butadiene oligomers were easy to characterize with SEC. The SEC eluograms of unfunctionalized and amino-terminated polymers are presented in Fig. 1 and show monomodal distributions. The M_n of the end-capped oligomer increased by 73 (from 771 to 844) while the PDI remained as 1.11.

The completeness of end-functionalization in toluene was investigated by NMR, MALDI-ToF MS and thin-layer chromatography (TLC). The ^{1}H NMR spectrum of the unfunctionalized oligomer is shown in Fig. 2.

The spectrum of the unfunctionalized oligobutadiene initiated by *sec*-BuLi shows peaks typical for polybutadiene. The peaks in the 0.7–2.4 ppm region are assigned to the aliphatic part of the polybutadiene and *sec*-butyl initiator group (0.7–0.9 ppm). The peaks in the region 4.8–5.6 ppm are assignable to olefinic protons in the butadiene units. The 5.1–5.6 ppm region includes peaks for the protons from –C*H*=C*H*– units in the oligomeric butadiene chain possessing *cis*- and *trans*-1,4-microstructure as well as peaks for protons from vinyl groups (CH_2=C*H*–) in the 1,2-units. The vinylidene protons from the CH_2= groups in the 1,2-microstructure are assigned to resonance in the 4.8–5.0 ppm region [18]. The fraction of PB possessing 1,4-microstructure is 89% that is characteristic for polybutadiene polymerization in nonpolar solvents in absence of Lewis base additives.

A characteristic part in the spectrum of functionalized oligobutadiene is the *tert*-butyl group from pivalonitrile end-capping. The ^{1}H NMR spectrum (Fig. 3) shows new peaks in the region 1.08 ppm assignable to the protons of the imino group in oligobutadiene. The peak position is different from that of the *tert*-butyl group in pivalonitrile (1.39 ppm). The integral of the area corresponding to the aliphatic part of the polybutadiene in unfunctionalized and end-capped oligomer differed by nine units (nine protons of *tert*-butyl group), 38 protons being taken for the olefinic part (correlating with the molecular weight of 1277 g/mol by MALDI-ToF MS, Fig. 8).

After reduction of the ω-imino-oligobutadiene with $NaBH_4$, the proton spectrum showed a shift of the signals assigned to the *tert*-butyl group to higher field. The new peak is assigned to 0.89 ppm as shown in the Fig. 3. The ω-imino-oligobutadienes were stable enough to carry out NMR and other measurements before hydrolysis.

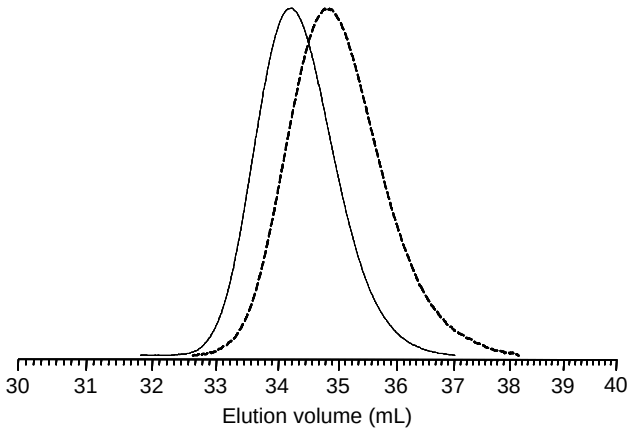


Fig. 1. SEC chromatograms of unfunctionalized (- - -) and amino-terminated oligobutadienes (—).

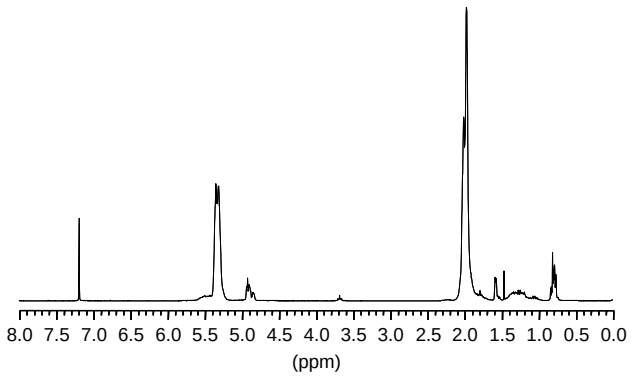


Fig. 2. ^{1}H NMR spectrum of the unfunctionalized oligobutadiene in $CDCl_3$.

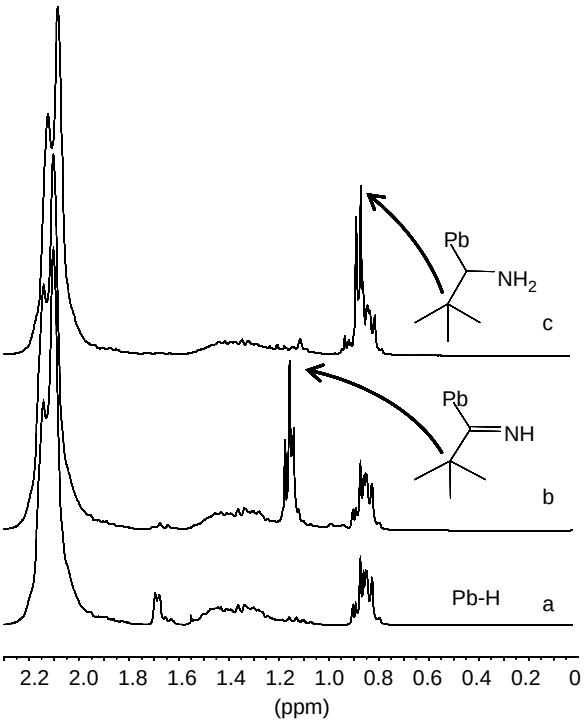


Fig. 3. Aliphatic parts of the ^{1}H NMR spectra in $CDCl_3$ of (a) unfunctionalized oligobutadiene, (b) ω-imino-oligobutadiene, (c) ω-amino-oligobutadiene.

To verify the end-functionalization, the polymers were also subjected to ^{13}C NMR measurements. The ^{13}C NMR spectrum of end-capped oligobutadiene shows the appearance of a signal at 189 ppm corresponding to the carbon of the terminal imino group (Fig. 4).

The signal assigned to the carbon in α-position to the amino group in the reduced ω-imino-oligobutadiene is observed at 77 ppm, overlapping with the solvent signal in $CDCl_3$, and at 70 ppm in acetone-d_6 (Fig. 5). The complete disappearance of the signal at 189 ppm demonstrates the successful reduction of

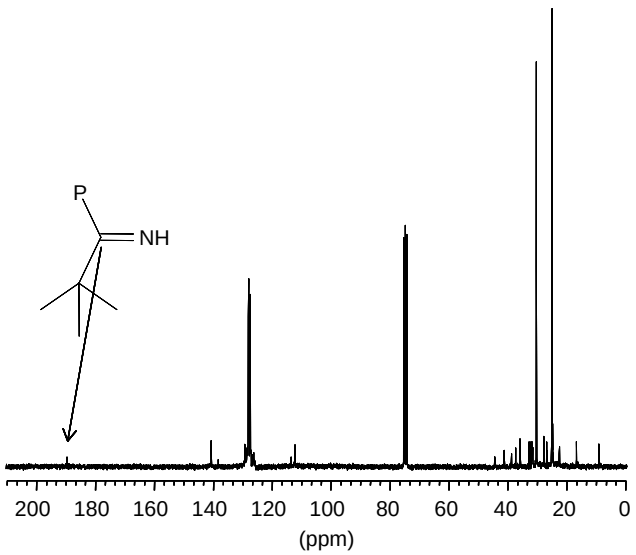


Fig. 4. ^{13}C NMR spectrum of ω-imino-oligobutadiene in $CDCl_3$ at room temperature.

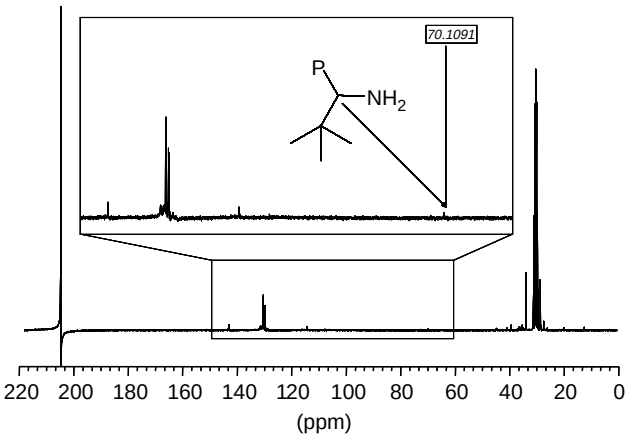


Fig. 5. ^{13}C NMR spectrum of ω-amino-oligobutadiene in acetone-d_6 at room temperature.

ω-imino-oligobutadiene to the corresponding amino-terminated polybutadiene.

Unfunctionalized oligobutadiene, imino-endcapped one as well as the reduction product were characterized using MALDI-ToF MS, which is a powerful method for a closer insight into the polymer structure [19]. This technique is able to provide information on the degree of end-functionalization. In the mass spectrum of the unfunctionalized oligobutadiene (Fig. 6), the difference between each monoisotopic peak was assigned to a molar mass of one monomeric unit of butadiene.

The minor distribution in the MALDI-ToF MS spectrum of unfunctionalized oligomer is assigned to products that appeared during ionization (with respect to TLC analysis). Fortunately, the oligobutadiene end-capped with pivalonitrile (ω-imino-oligobutadiene) was stable enough to perform MALDI-ToF MS measurements (Fig. 7). However, some badly assignable side series are detected.

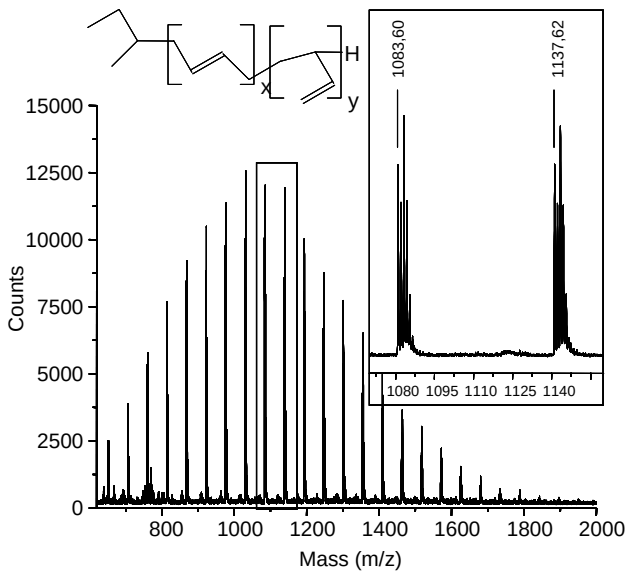


Fig. 6. MALDI-ToF mass spectrum of unfunctionalized oligobutadiene, possessing theoretical mass of $C_4H_9+(x+y)$ C_4H_6+H+cation ($x+y=17$, $C_{72}H_{112}Ag^{107}$, $M=1083.7$ g/mol). AgTFA was used as cationizing agent.

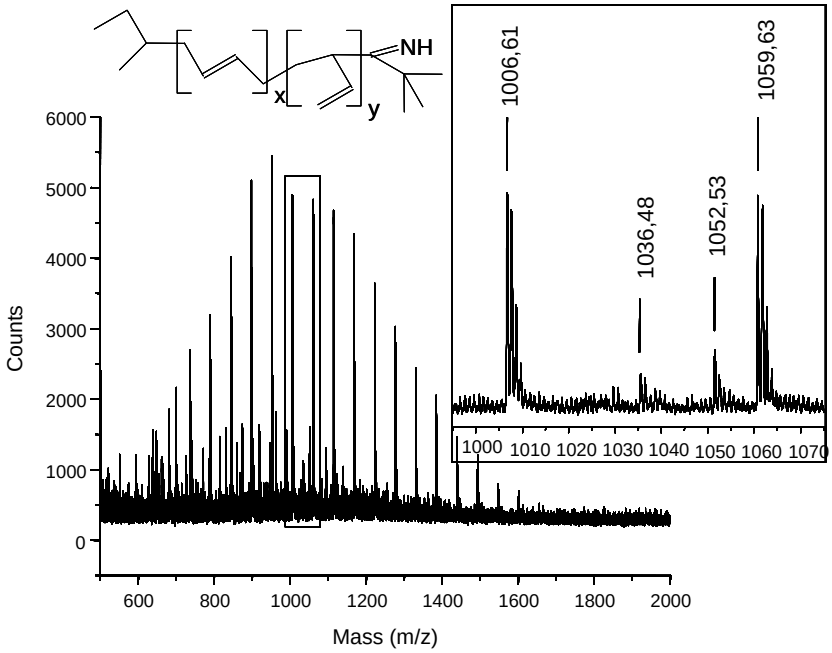


Fig. 7. MALDI-ToF mass spectrum of ω-imino-oligobutadiene with theoretical mass of $C_4H_9+(x+y)\,C_4H_6+C_5H_{10}N$ ($x+y=17$, $C_{77}H_{121}N$, $M=1059.85$ g/mol).

The molecular weight distribution of the primary amino end-functionalized oligobutadiene is depicted in Fig. 8. No side distributions were recognized.

As shown in Fig. 9, end-group analysis calculated for $C_{77}H_{123}NAg^{107}$ demonstrates full agreement with experimental data. The peak position of amino-functionalized oligomer increased by $m/z=86.06$ units which is consistent with the theoretical mass shift of 86.16 Da expected if a terminal hydrogen is replaced by the $C_5H_{10}NH_2$ end-group.

Comparison of the peaks for the monoisotopic distributions in MALDI-ToF spectra of the three polymers (Figs. 6–9) with those of simulated (the masses calculated for $C_{77}H_{123}NAg^{107}$, DP = 17) verifies completeness of the end-functionalization. In order to exclude any effects arising from different ionizabilities of functionalized and unfunctionalized oligobutadienes in MALDI-ToF analysis TLC was performed to verify the results.

TLC separation of polymers is based on the differences in their chemical structure, such as composition of block copolymers or end-group, rather than their molecular weight [20]. For development a mixture of toluene and methanol (99:1) was used. Two separate, very pronounced spots but no additional ones even after overloading of the plates were

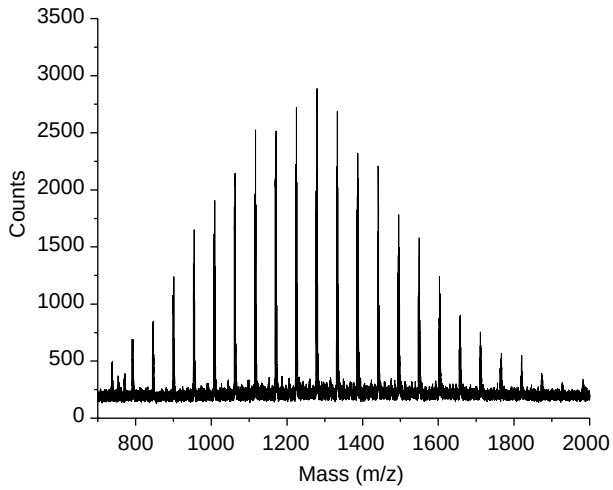


Fig. 8. MALDI-ToF mass spectrum of amino-functionalized oligobutadiene.

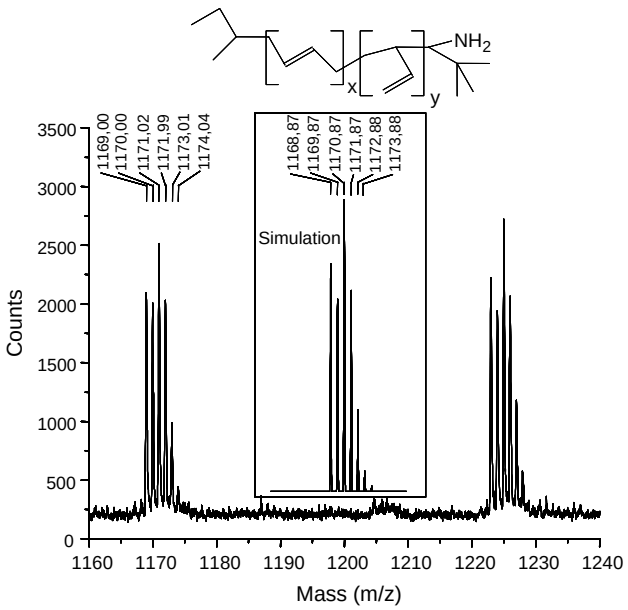


Fig. 9. Section of the MALDI-ToF mass spectrum of the amino-functionalized oligobutadiene with theoretical mass of $C_4H_9+(x+y)\,C_4H_6+C_5H_{12}N+$cation ($x+y=17$, $C_{77}H_{123}NAg^{107}$, $M=1168.75$ g/mol) and corresponding simulation.

observed. The R_f values of unfunctionalized and amino-terminated oligobutadienes are 0.9 and 0, respectively, and no other spots were observed. This clearly indicates the absence of unfunctionalized oligobutadiene which could be present and the minor distribution in MALDI-ToF MS is only a product formed in the mass spectrometer during ionization.

In the FT-IR spectrum of amino-functionalized oligobutadiene a characteristic absorbance band for the amino end-group was observed at 3630 cm^{-1}.

4. Conclusions

End-capping of living anionic chain ends with nitriles followed by reduction in a one-pot process is a convenient methodology of introducing terminal primary amino functionality at the ends of the polymer chains. This method excludes the disadvantages of the prior methods of preparing amino-terminated polybutadienes. The use of pivalonitrile rather than acetonitrile excludes the possibility of proton abstraction.

Acknowledgements

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