

Dedicated to the memory of
Professor Eugen Segal (1933-2013)

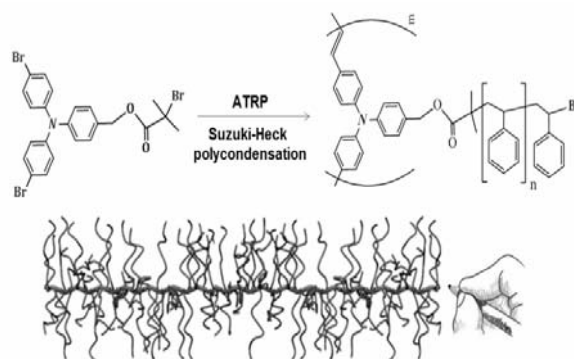
OLIGOSTYRENE GRAFTED POLY(4,4'-TRIPHENYLAMINE VINYLENE)S OBTAINED BY COMBINATION OF ATRP AND SUZUKI-HECK REACTIONS

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Grafted poly(4,4'-triphenylamine vinylene) with oligostyrene side chains has been synthesized by “grafting through” method, combining the atom transfer radical polymerization (ATRP) and Suzuki-Heck reaction. First, starting from a triphenylamine-based ATRP initiator, *i.e.*, 4-[bis(4-bromophenyl)amino]benzyl 2-bromo-2-methylpropanoate (BBMP), an oligostyrene macromonomer was synthesized by ATRP polymerization of styrene. Poly(4,4'-triphenylamine vinylene), with hairy-rod structure, where triphenylamine vinylene moiety is the main chain and oligostyrene are side chains, was obtained in the second step by Suzuki-Heck polycondensation of macromonomer with potassium vinyltrifluoroborate in the presence of palladium catalyst. The structure of the macromonomer and new graft copolymer was analyzed by FTIR, ¹H- and ¹³C-NMR spectroscopy and GPC measurements. Optical properties were studied by UV-Vis and fluorescence spectroscopy. The graft copolymer is soluble in common organic solvents and shows as well good processability as polystyrene while light emitting properties are specifically of polyarylene vinylenes.



INTRODUCTION

Poly(arylene vinylene)s are a very studied class of materials among conjugated polymers due to their interesting scientific aspects of synthesis and useful properties for many optoelectronic applications.¹ The seminal work of Cambridge group in England (1990)² has evidenced the presence of light emitting properties in poly(phenylene vinylene)s (PPV) and has renewed scientific interest for this class of polymers.³⁻⁵ Now, the potential application of PPVs in the next generation of full-color flat panel displays is

recognized and many researchers are interested to obtain new polymer structures with high emission efficiency.⁶⁻⁸ Unfortunately, most of poly(arylene vinylene)s are insoluble in many organic solvents, because they have a rigid structure which makes impossible to process them as thin films for applications. In order to improve solubility, processability and performances of these materials, a new approach based on attachment of flexible side chain substituents to the conjugated backbone has been reported.⁹

Graft copolymers are complex macromolecules in which several pendant chains are attached at

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various points to the polymer backbone. Current synthetic strategies to approach these targets normally involve multistep reactions and separation steps. The most explored methods to make graft copolymers are “grafting-onto”, in which side chains are separately performed and then attached to the backbone, “grafting-through”, in which the macromonomers are homo- or copolymerized with low molecular weight compounds and “grafting-from”, in which the monomer is grafted from the functional backbone.^{10,11}

The atom transfer radical polymerization (ATRP) method is the most versatile controlled free radical process employed to prepare a wide range of functionalized polymers and macromonomers with controlled molecular weights, narrow molecular weight distributions and chain end functionality due to its tolerance to a wide range of functional groups.¹²⁻¹⁴ The end groups of the polymers are determined by the structure of the initiator employed in the ATRP reaction. Various functional ATRP initiators have been used in the preparation of macromonomers with end-reactive groups that can imply them in polymer synthesis through chemical oxidative polymerization,¹⁵⁻¹⁸ or Suzuki, Stille and Yamamoto polycondensation¹⁹ for obtaining processable conjugated polymers.

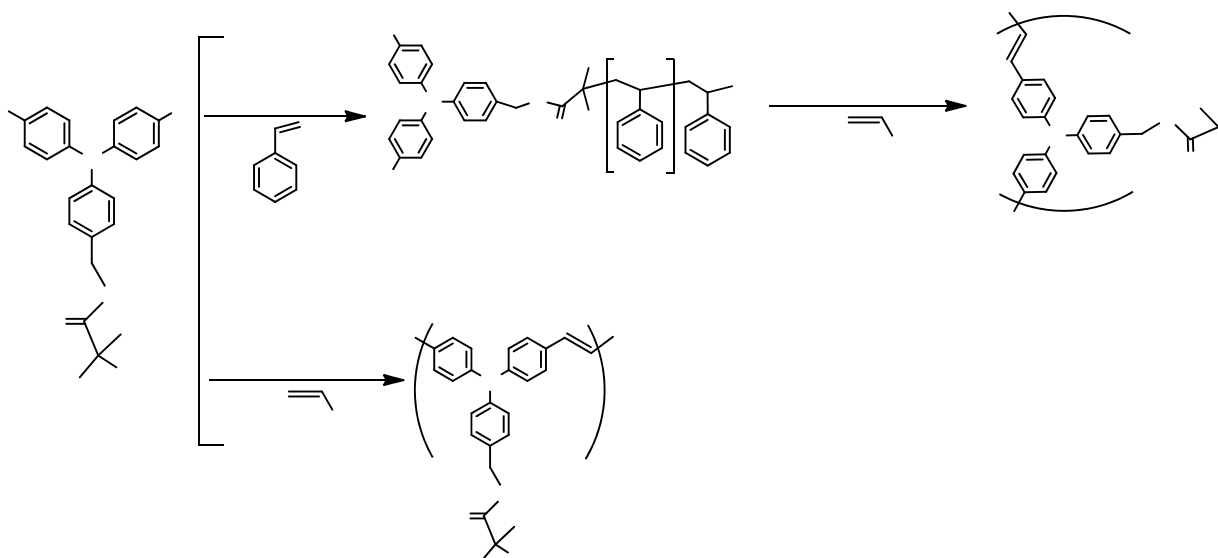
An interesting and recent development of the research on organic electroluminescent and photovoltaic materials based on poly(arylene vinylene)s is focused on triphenylamine due to its redox activity and hole-transporting properties.²⁰⁻²⁴ The introduction of triphenylamine group in

polyarylene vinylene structure may lead to new materials with interesting and useful properties. In this paper, it is reported for the first time, novel graft copolymers consisting of poly(triphenylamine vinylene)s main chain and oligostyrene side chains. They were successfully prepared starting from 4,4'-dibromo-triphenylamine based compounds, using in tandem the atom transfer radical polymerization and Suzuki-Heck polycondensation.

RESULTS AND DISCUSSION

Synthesis of graft copolymer by “grafting through” route

The synthetic strategy followed for the synthesis of intermediates (**M**, **PI**) and target poly(triphenylamine vinylene)s-*graft*-polystyrene (**G1**) is shown in Scheme 1. We have firstly applied the “grafting through” approach involving two steps: i) the synthesis of polystyrene-based macromonomer (**M**) with a well-defined molecular weight, narrow polydispersity and precise chain-end functionality (*i.e.*, 4,4'-dibromo-triphenylamine end) using ATRP of styrene with 4-[bis(4-bromophenyl)amino] benzyl 2-bromo-2-methylpropanoate (**BBMP**) as initiator, and ii) the Suzuki Heck coupling reaction of the macromonomer **M** having dibromo-triphenylamine end moiety with potassium vinyltrifluoroborate in the presence of palladium catalyst.



Scheme 1 – General procedure for synthesis of oligostyrene grafted poly(4,4'-triphenylamine vinylene)s: 1) “grafting through” route, and 2) “grafting from” route.

The ATRP initiator, 4-[bis(*p*-bromophenyl)amino]benzyl 2-bromo-2-methylpropanoate (**BBMP**, Scheme 1), was synthesized by a four-steps method starting from triphenylamine. 4-(Diphenylamino) benzaldehyde was obtained by monoformylation of triphenylamine using POCl₃/DMF reagent, as was described in the literature,²⁵ followed by bromination with bromine in CHCl₃ at 0°C²⁶ and reduction to 4-hydroxymethyl-N,N'-bis(4-bromophenyl)aniline with NaBH₄ in tetrahydrofuran/methanol mixture.²⁷ The further treatment of the alcohol with 2-bromo-2-methyl-propionyl bromide in toluene and presence of the triethylamine led to ATRP initiator in good yield. It was used as initiator for atom transfer radical polymerization of styrene to obtain macromonomers. The ATRP polymerization was carried out in dry toluene at 100°C, in the presence of initiator and CuBr/bipyridyl as catalyst, over 22h, using the feed molar ratio between components: [St]₀:[BBMP]₀:[CuBr]₀:[bipyridine]₀ = 20:1:1:2 to obtain an oligostyrene macromonomer (**M**) with Mn = 3000 g/mol and M_w/M_n = 1.15 (Scheme 1, route 1). The structure of the macromonomer was proved by ¹H-NMR and FT-IR. ¹H-NMR spectrum (CDCl₃, δ, ppm) shows characteristic peaks of polystyrene chain at 0.9-2.4 ppm (aliphatic protons) and 6.3-7.3 ppm (aromatic protons) (Fig. 1). Some signals of the aromatic protons from initiator are masked (partly overlapped) by the phenyl aromatic protons of polystyrene, but signal noted with "a" from 7.34-7.32 ppm is originating from the rest of the initiator. The peak from the last CH-Br protons appeared at about 4.54 ppm.

The FT-IR spectrum of macromonomer (Fig. 2) evidences the usual polystyrene strong absorptions: 3082 cm⁻¹, 3059 cm⁻¹, 3026 cm⁻¹ (aromatic CH stretching), 2923 cm⁻¹, 2851 cm⁻¹ (aliphatic CH stretching), 1601 cm⁻¹, 1492 cm⁻¹, 1452 cm⁻¹, (in-plane stretching vibrations of phenyl ring), 756 cm⁻¹ and 698 cm⁻¹ (CH out-of-plane deformation from monosubstituted phenyl rings). The peaks at 821 cm⁻¹ (CH out-of-plane deformation from disubstituted phenyl rings) and 1728 cm⁻¹ (is attributed to the group C=O) are from chain end.

The macromonomer containing 4,4'-dibromo-triphenylamine group as end chain was used as comonomer in the Suzuki-Heck coupling reaction with potassium vinyltrifluoroborate and Pd(acetate)₂/P(*o*-tolyl)₃ as catalyst. The experimental conditions used: an equimolar ratio between the reaction partners and reaction temperature (100 °C) and time (24h) were chosen so as to achieve grafted copolymer (**G1**) in high yield (83.3%) and soluble in chloroform. This step has a disadvantage, the equimolarity between coupling partners is very hard to be attained because the molecular weight of macromonomer **M** is not very precise known so graft copolymers have a short main conjugated chain. The graft copolymer **G1** has greenish-yellow color and an average molecular weight, Mn~9300 and a low polydispersity degree (1.9). The glass transition temperature determined by DSC is 89.8 °C for macromonomer **M** and slightly increased at 96.4 °C for graft copolymer **G1**, both being characteristic for polystyrene side chains. The slight increase of copolymer's Tg compared with macromonomer is due to the conjugated chain that decreases the mobility of polystyrene chains.

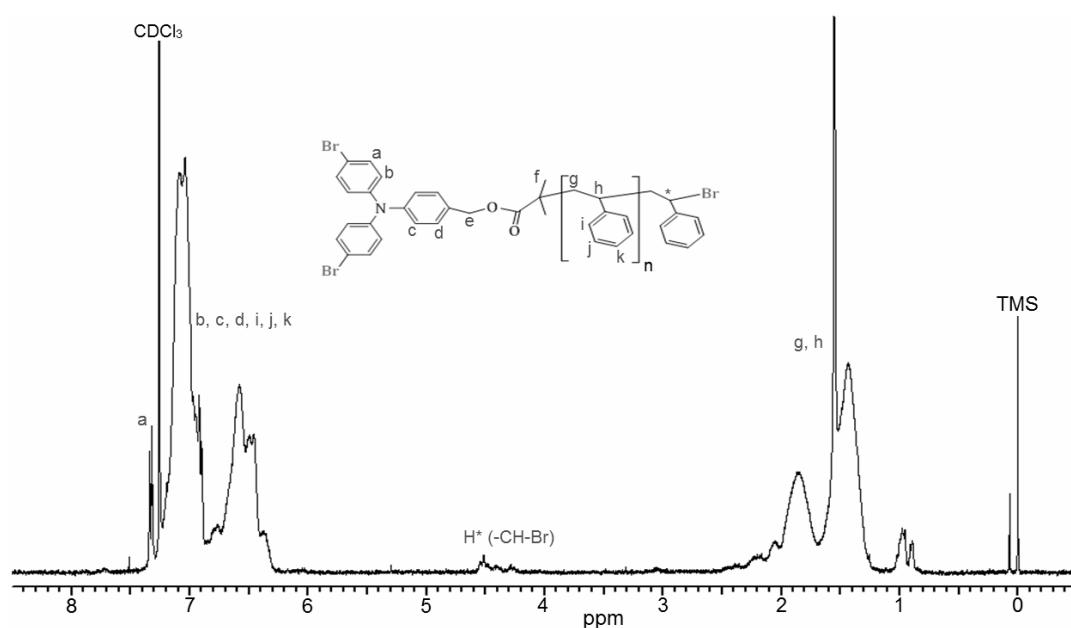


Fig. 1 – ¹H-NMR spectra (CDCl₃) of 4,4'-dibromo-triphenylamine functionalized macromonomer (**M**).

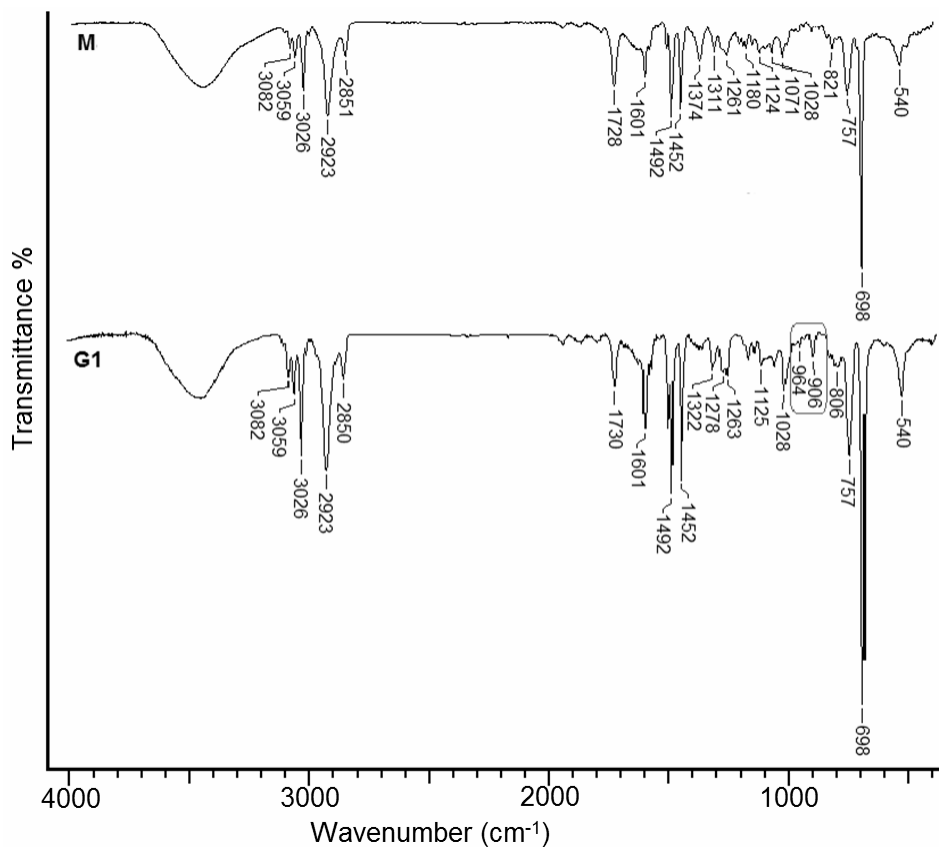


Fig. 2 – FT-IR spectra (KBr pellet) of macromonomer (M) and graft copolymer (G1).

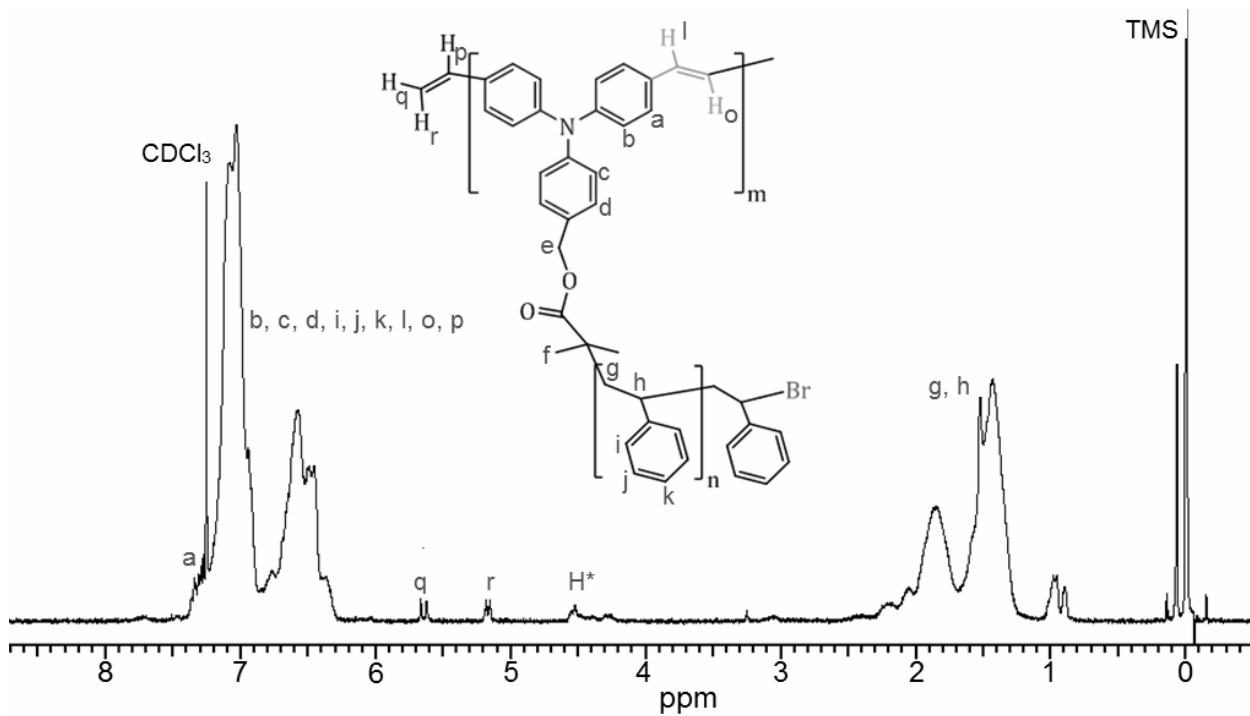


Fig. 3 – ¹H-NMR spectra (CDCl₃) of poly(4,4'-triphenylamine vinylene)-graft-poly(styrene) (G1).

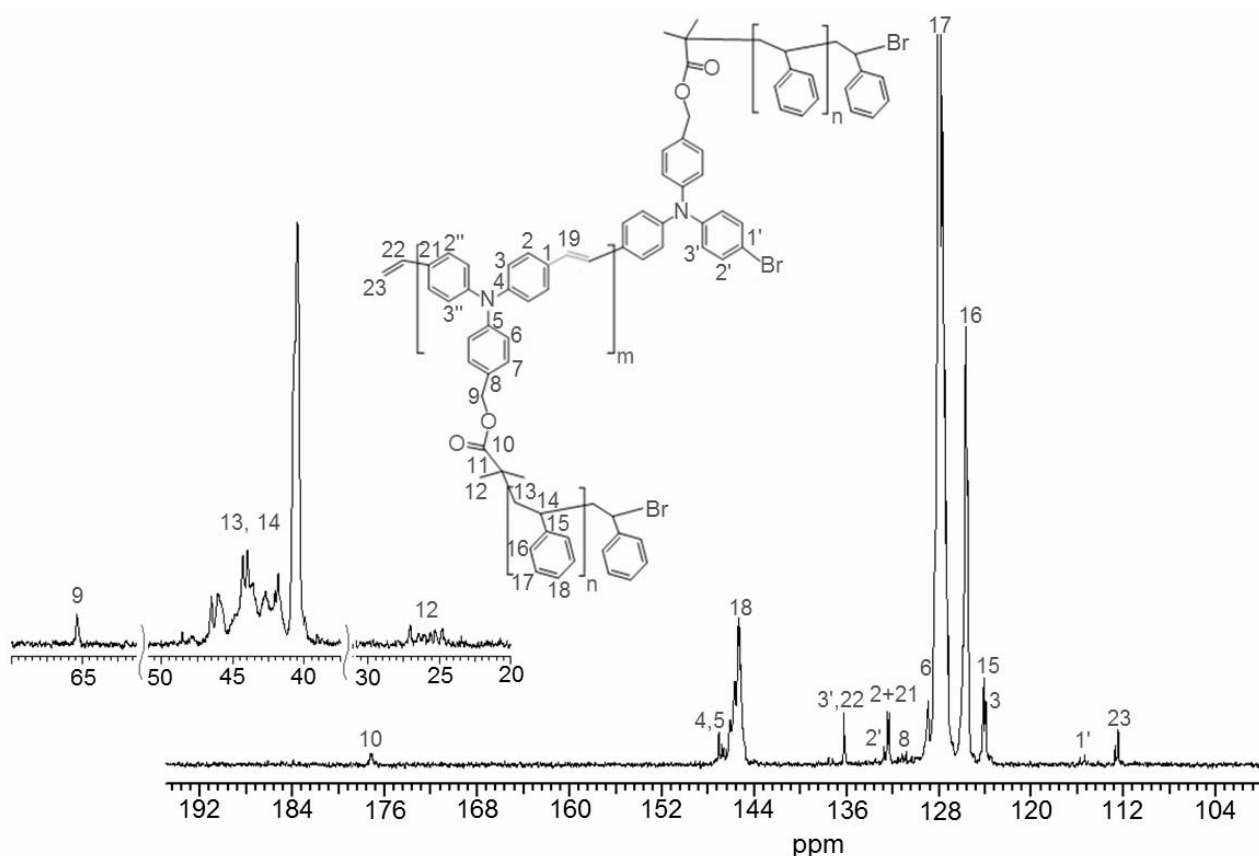


Fig. 4 – ^{13}C -NMR spectra (CDCl_3) of poly(4,4'-triphenylamine vinylene)-*graft*-poly(styrene) (G1).

FT-IR and NMR spectral measurements were used to check structure of the poly(triphenylamine-vinylene)-*s-graft*-poly(styrene). ^1H -NMR spectrum of **G1** is presented in Fig. 3. Comparing the spectrum of macromonomer with that of graft copolymer major changes can not be observed, but in the region of 5.0 to 6.8 ppm are observed signals in the form of doublet assigned to terminal vinyl protons at 5.17 ppm for H_r and 5.64 ppm for H_q . ^{13}C -NMR spectrum of the graft copolymer (Fig. 4) also shows the peaks specific to polystyrene, that could be identified at: 20-70 ppm (carbons 9, 13, 14 and 12), 124,02 ppm (15), 126,75 ppm (16), 127,69 ppm (17) and 145,69 ppm (18). In addition, it can also be identified peaks at 112.50 and 112.76 ppm for C23 assigned to the final vinyl carbons, 132.33-132.47 ppm (2 and 21), 136.14 and 136.23 (3' and 22). Additional evidences for the presence of new vinyl groups in structure of grafted copolymer are given by FT-IR spectrum (Fig. 2). A new absorbing band located at 964 cm^{-1} is assigned to out of plane vibration of the double bond in the *trans* isomer while the band at 906 cm^{-1} is attributed to rocking out of plane (wagging) the group = CH_2 .²⁸

Synthesis of graft copolymer by “grafting from” method

We have also tried the alternative route, the “grafting from” method, which suppose the obtaining of functional triphenylamine vinylene conjugated backbone firstly, followed by building of grafts by ATRP polymerization of styrene (Scheme 1). Thus, for synthesis of poly(4,4'-triphenylamine vinylene) chain (**PI**) the Suzuki-Heck cascade polymerization reaction starting from the ATRP initiator, 4-[bis(4-bromophenyl)amino] benzyl 2-bromo-2-methyl propanoate, with potassium vinyltrifluoroborate using $\text{Pd}(\text{OAc})_2$ as catalyst was tried. The polyconjugated chain should contain the initiator group in every structural unit and can be viewed as an ATRP polyinitiator (**PI**). Unfortunately, from the polycondensation reaction, the expected structure was not obtained. The heterogeneous material resulted from reaction was fractionated in chloroform-soluble (15.2 %) and chloroform-insoluble (65.3%) fractions. We previously synthesized poly(4,4'-triphenylamine vinylene)s by Suzuki-Heck polycondensation of 4,4'-*bis*ido

triphenylamine with potassium vinyltrifluoroborate in the same experimental conditions and the polymer was soluble.⁸ In this case, the insolubility of the polymer could be assigned to the side reactions leading to crosslinking of the material. The heterolytic dissociation of ester bond generating cations that could react through aromatic electrophilic substitution was reported for triphenylamine esters.^{29,30} Also, the side substituent (2-bromo 2-methyl propanoate group) contains reactive bromine atoms able to participate in side reactions. The FT-IR spectra of soluble and insoluble fractions of **PI** are given in Fig. 5 and evidence the vinylene structure of the main chain by presence of absorption band located in the range of 960-965 cm^{-1} which is attributed to the C-H out-of-plane bending vibration of *trans*-vinyl linkages. In addition, between the two polymer fractions (the soluble and the insoluble) are not major differences, both contain similar absorption peaks, thereby: 3027 and 3029 cm^{-1} (aromatic CH stretching), 2964 and 2924 cm^{-1} (aliphatic CH

stretching), 1600 and 1507 cm^{-1} (aromatic ring C=C vibration), 1316-1318 and 1271-1281 cm^{-1} (stretching vibration of tertiary amine from triphenylamine moiety) and 819-820 cm^{-1} (CH out-of-plane deformation from *p*-disubstituted phenyl rings). Also the absorptions at 1725 and 1728 cm^{-1} attributed to the valence vibration of C=O are observed but their intensity is diminished compared with BBMP. If in the BBMP spectrum the ratio of peak absorbances A_{1732}/A_{1271} is 1.09, in the polyinitiator (**PI**) spectra this ratio is ~ 0.795 that means part of ester functions are lost during the polycondensation and crosslinking process. Also, the $\nu_{\text{C-Br}}$ band from the initiator spectra (670 cm^{-1}) cannot be observed in the polymers spectra. As a conclusion, during the Suzuki-Heck polycondensation of BBMP at 100 °C side reactions took place with formation of crosslinked materials and loss of some functional groups. If the reaction was carried out at lower temperatures (65 °C) the Suzuki polycondensation was not effective.

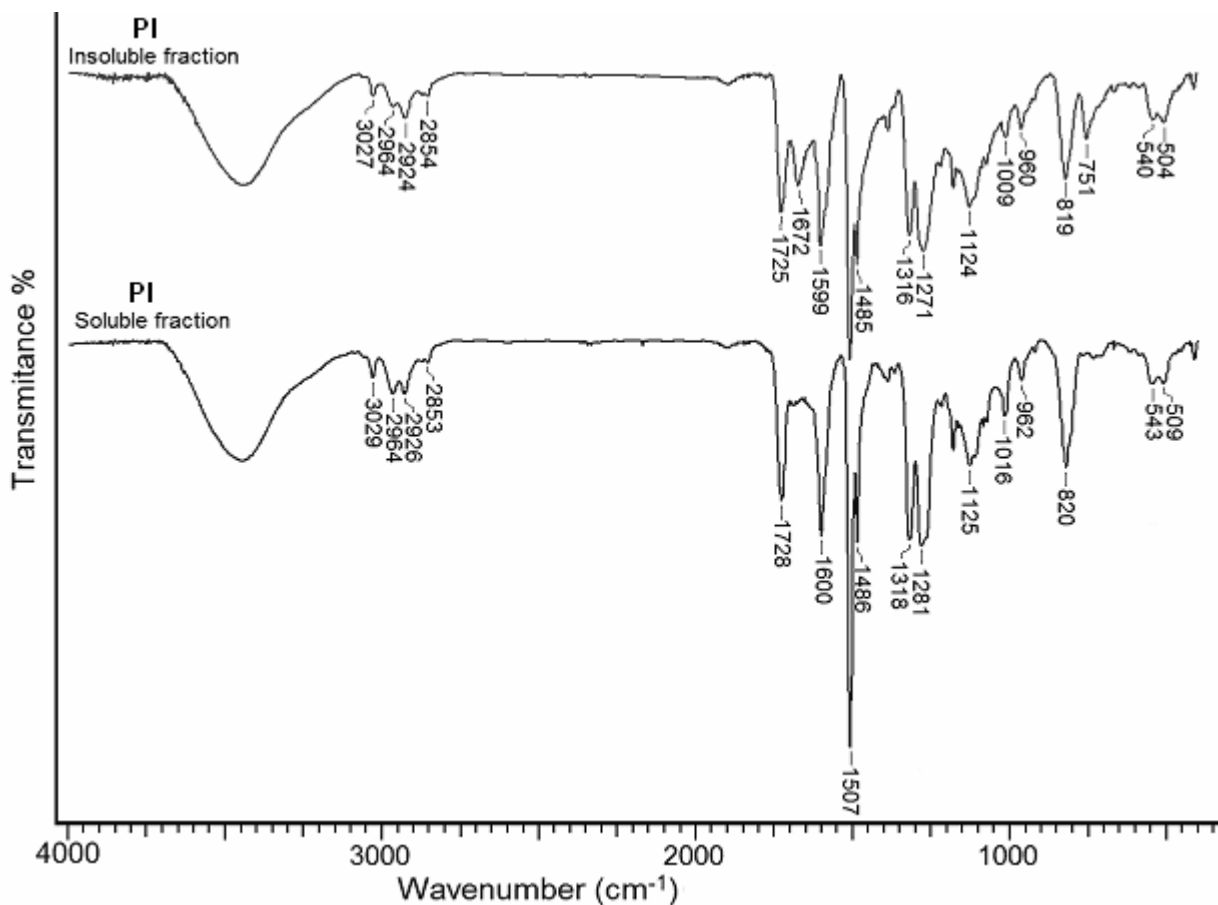


Fig. 5 – FT-IR spectra of polyinitiator (**PI**), soluble and insoluble fraction.

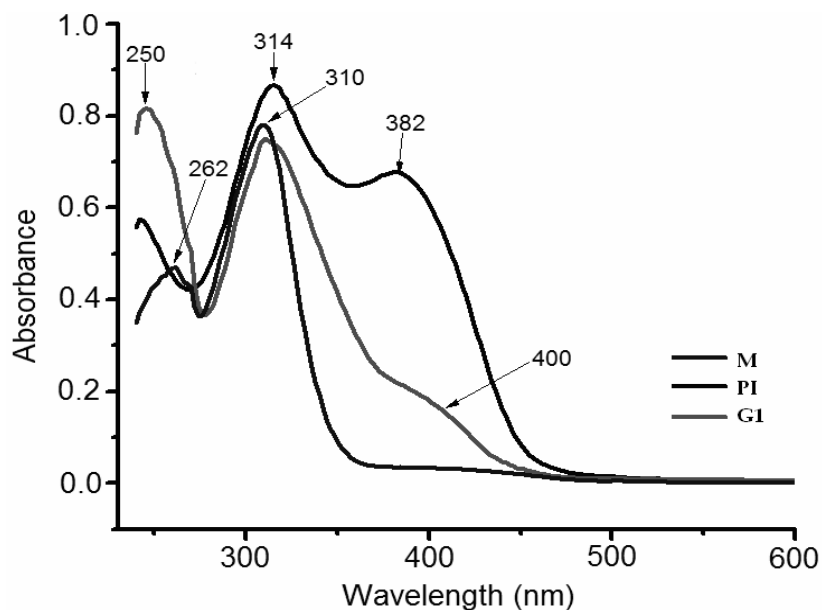


Fig. 6 – UV-Vis spectra (CHCl_3) of M, P1 and G1.

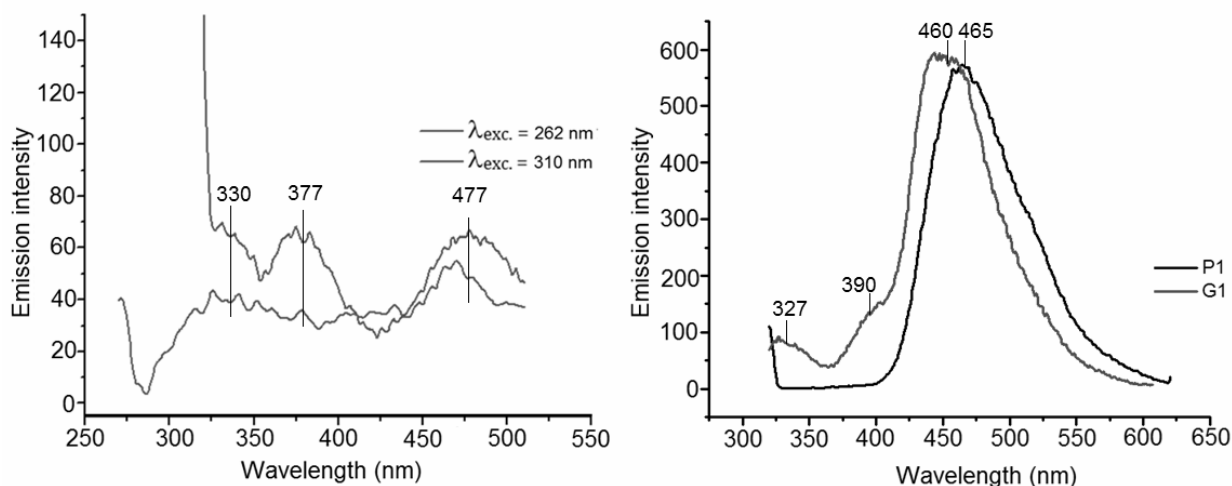


Fig. 7 – Emission spectra (CHCl_3) of: macromonomer (left) and graft copolymer (right).

The absorption and emission spectra of macromonomer and graft copolymer were investigated in dilute CHCl_3 solution (Fig. 6). The UV-Vis absorption spectrum of the triphenylamine shows absorption at a maximum wavelength of 302 nm, while for initiator (BBMP) the absorption maximum is slight red-shifted with 8 nm (310 nm), due to the contribution of electron-donating $-\text{CH}_2\text{-O}-$ group and bromine substituents. Styrene oligomers show absorptions between 250-290 nm assigned to $\pi\text{-}\pi^*$ transitions in phenyl rings. UV-Vis spectrum of macromonomer **M** shows absorption peaks characteristic both for oligostyrene and substituted triphenylamine, as is observed in Fig. 6. The two absorption maxima at 262 and 310 nm are mainly assigned to $\pi\text{-}\pi^*$ transitions in phenyl rings from polystyrene and

from TPA end groups, respectively. By Suzuki-Heck polymerisation, UV spectra of **P1** (soluble fraction) and graft copolymer **G1** show besides the two absorptions (250-262 nm, 310-314 nm), new and broader peaks at 382 nm (**P1**), and 400 nm (**G1**), respectively, assigned to $\pi\text{-}\pi^*$ transitions in poly(4,4'-triphenylamine vinylene) conjugated chain.

The fluorescence spectrum of the initiator (BBMP) shows a broad emission with two maxima at 388 nm and 477 nm assigned to emission from phenyl and triphenylamine groups ($\lambda_{\text{ex}} = 310$ nm). If the excitation was performed with $\lambda_{\text{ex}} = 375$ nm then the emission spectra present only the maximum at 477 nm. The emission spectrum of the macromonomer **M** (Fig. 7) when it is excited with a wavelength of 262 nm (phenyl rings from

oligostyrene) presents a broad emission with maxima located around 330 nm and 470 nm, values assigned emission from excited phenyl (from oligostyrene) and triphenylamine group, respectively. If the excitation was carried out with $\lambda_{\text{ex}} = 310$ nm then the emission spectra present only maxima associated with triphenylamine groups (377 nm and 477 nm). The emission spectrum of **G1** shows a complex form with three maxima at 327 nm, 390 nm (shoulder) and 460 nm ($\lambda_{\text{ex}} = 310$ nm) or a single maximum at 461 nm ($\lambda_{\text{ex}} = 400$ nm), while for **PI** (soluble fraction) due to the absence of oligostyrene grafts only one maximum at 465 nm ($\lambda_{\text{ex}} = 314$ nm or 382 nm) is observed. A slightly red shifting of the λ_{em} assigned to the increasing of conjugation length was observed from graft copolymer **G1** to **PI**.

EXPERIMENTAL

Materials

Styrene (Fluka, 99%) was washed with an aqueous solution of sodium hydroxide (5 %) and deionized water until neutral, dried over anhydrous sodium sulfate, and then distilled under vacuum. CuBr, 2-bromo-2-methyl-propionyl bromide, 2,2-bipyridine (bpy), palladium (II) acetate, potassium vinyl-trifluoroborate, tri(*o*-tolyl)phosphine (P(*o*-Tol)₃), triethylamine, and triphenylamine (98 %) were purchased from Aldrich, and used as received. Solvents (Aldrich) were dried by the usual methods or used as received. All manipulations were carried out under an inert atmosphere (nitrogen) using the Schlenk technique.

The ATRP initiator, 4-(bis(4-bromophenyl)amino)benzyl 2-bromo-2-methylpropanoate (BBMP), was synthesized by a four-steps method. Starting from triphenylamine, 4-(diphenylamino) benzaldehyde was synthesized by formylation reaction using POCl₃/DMF reagent, as was described in the literature,²⁵ followed by bromination with bromine in CHCl₃ at 0°C²⁶ and reduction to 4-hydroxymethyl-N,N'-bis(4-bromophenyl)aniline with NaBH₄ in tetrahydrofuran/methanol mixture.²⁷ The treatment of the alcohol with 2-bromo-2-methyl-propionyl bromide in toluene and presence of triethylamine led to ATRP initiator in good yield. Yield, 75%. ESI-MS = 582.9 (M+H)⁺. ¹H-NMR (CDCl₃, ppm): 7.4-6.8 (m, 12H_{Ar}), 5.08 (s, 2H, -CH₂O-) and 1.95 (s, 6H, -CH₃). ¹³C-NMR (CDCl₃, ppm): 171.52, 147.03, 146.28, 132.45, 129.30, 125.75, 124.75, 115.91, 77.01 (CDCl₃), 67.19, 55.73, 30.78.

Synthesis of poly(styrene) macromonomer (M)

The synthesis of macromonomer was carried out in a Schlenk tube in nitrogen for using molar ratios [St]₀: [BBMP]₀: [CuBr]₀: [bpy]₀ to 20:1:1:2. After degassing the solution three times by freeze-vacuum-thaw cycles, the mixture was immersed in an oil bath thermostated at 100°C and stirred. After 22 h, the tube was rapidly cooled in ice-water bath, diluted with THF and passed through a short column of silicagel to remove the metal salts. The white polymer was precipitated in methanol and purified by repeated precipitation. Yield = 86 %. The average-molecular weight is M_n = 3000 g/mol and PDI = 1.15.

Synthesis

of poly(triphenylamine-vinylene)s-graft-poly(styrene (G1)

Macromonomer (M_n ≈ 3000 g/mol, PDI = 1.154) (0.3 g, ~0.10 mmol), potassium vinyltrifluoroborate (0.015 g, 0.10 mmol), palladium acetate (0.0012 g, 0.005 mmol), tri(*o*-tolyl)phosphine (0.0076 g, 0.025 mmol) in triethylamine (0.04 mL; 0.030 g, 0.296 mmol), DMF (2.5 mL) and toluene (2.5 mL) were introduced in a 25 ml round bottomed flask and the reaction mixture was refluxed overnight. After cooling to room temperature, by immersion in ice bath, the reaction mixture was poured into methanol. The obtained solid was filtered, and dissolved in the minimum amount of chloroform for reprecipitation in methanol to give poly(4,4'-triphenylamine vinylene)-graft-poly(styrene). Color of compound is greenish-yellow. Yield = 83.3 %.

Synthesis of polyinitiator (PI)

A solution of 4-(bis(4-bromophenyl)amino)benzyl 2-bromo-2-methylpropanoate (0.431g, 0.74 mmol), potassium vinyltrifluoroborate (0.109 g, 0.8169 mmol), palladium acetate (8.32 mg, 0.0370 mmol), tri(*o*-tolyl)phosphine (5.64 mg, 0.018 mmol) in triethylamine (0.25 mL, 0.1875g, 1.85 mmol), DMF (3.0 mL) and toluene (3.0 mL) was refluxed overnight in a Schlenk tube. After cooling to room temperature by immersion in the ice bath, the reaction mixture was poured into methanol. The obtained solid was filtered, and dissolved in chloroform and reprecipitated in methanol to give functional poly(triphenylamine vinylene) (**PI**) as an dark yellow-brown powder. Yield = 15% soluble fraction. The molecular weight is M_n = 11400 g/mol and PDI = 1.90.

Characterization

¹H-NMR and ¹³C-NMR spectra were recorded at room temperature on a Bruker Avance DRX-400 spectrometer operating respectively at 400 MHz (for ¹H) and 100 MHz for (¹³C) as solutions in CDCl₃ with TMS as internal standard. Fourier transform infrared (FT-IR) spectra (KBr pellet) were recorded with a DIGILAB-FTS 2000 spectrometer. Gel permeation chromatography (GPC) was used to establish the molecular weight and molecular weight distribution (polydispersity) of the polymers. A PL-EMD 950 Evaporative Mass Detector chromatograph equipped with a set of six Ultrastaygel columns (10⁶, 10⁵, 10⁴, 10³, 500, and 100 Å) was used. Chloroform (1.0 mL min⁻¹) was used as eluent. UV-visible and fluorescence measurements were carried out in CHCl₃ solutions with a Specord 200 spectrophotometer and Perkin Elmer LS 55 apparatus, respectively. The differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC-12E apparatus, in nitrogen with a heating and cooling rate of 10°C/min.

CONCLUSIONS

In summary, macromonomers based on styrene with well-defined structure and characteristics, were successfully synthesized by atom transfer radical polymerization reactions, using 4-(bis[4-bromophenyl]amino)benzyl 2-bromo-2-methylpropanoate as initiator. Poly(4,4'-triphenylamine vinylene)s having PSt chains as lateral substituents

were synthesized by Suzuki-Heck cascade polymerization reaction from the macromonomer and potassium vinyltrifluoroborate using palladium catalysts. The synthesized new graft copolymer was analyzed by spectral methods and the thermal behavior was studied with DSC. The optical properties were studied with UV and fluorescence spectroscopy. Synthesis of conjugated polymers grafted with flexible side chains improved the solubility of the polymers and preserved their light emitting properties. Attempts to synthesize the same graft copolymer structure using an alternative approach, the “grafting from” route, failed due to the side reactions and loss of functional groups.

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