# Articles

# Synthesis and Characterization of Bifunctional Polymers Carrying Tris(bipyridyl)ruthenium(II) and Triphenylamine Units

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ABSTRACT: The synthesis, characterization, and properties of a highly soluble bifunctional polymer are described in which a tris(bipyridyl)Ru(II) unit acts as dye and triphenylamine units act as charge transport moieties. First a macroligand, a bipyridine carrying two poly(4-bromostyrene) chains, was synthesized by atom transfer radical polymerization (ATRP) of 4-bromostyrene in bulk using CuCl/ PMDETA as the catalytic system and bis(chloromethyl) bipyridine as the initiator. The target polymer was then obtained via a polymer amination reaction in which the bromophenyl group was converted into a triphenylamine followed by metallation of the bipyridine unit of the macroligand with Ru(II) bis(bipyridine). The reaction conditions of ATRP and polymer amination reaction were optimized, and the degree of conversion for both steps was determined by gas chromatography (GC) analysis of rest monomer content and elemental analysis of unreacted bromine, respectively. The control in molecular weight was achieved maintaining a narrow distribution in the desired low molecular weight range of bulk polymerization of 4-bromostyrene. The polymer amination reaction using the  $Pd(OAc)_2$  and P(t-Bu)<sub>3</sub> system was found to be very efficient, and the reaction was complete within 2 h. The metallation reaction could be followed by UV/vis spectroscopy. MALDI-TOF MS of the three polymers was carried out to obtain absolute molecular weights and their distribution. A comparison of these molecular weights gave additional information about the degree of polymer amination and metallation reaction. The thermal properties of the different polymers suggest that the thermal stability as well as the glass transition temperature increases from the starting macroligand which carries poly(4-bromostyrene) chains to the intermediate polymer having poly(vinyItriphenyIamine) chains and finally to the bifunctional Ru(II) polymer complex.

### Introduction

Polymer technology involving optical and electronical functional materials demand the design and synthesis of new polymers with well-defined structure, control in molecular weight, and low polydispersity. As most of the electrooptical applications demand versatile functions like light absorption or emission and charge injection/ transport properties, the conventional way of realizing this is to design multicomponent single-layer devices or multilayer devices. In most cases, these devices are very thin; therefore, the various interfaces play a considerable role in the overall performance of the device, and in certain cases, as for example in solar cells, they even decide the degree of charge separation and hence the efficiency of the cell. It has been shown that the concept of copolymerization of different functional monomers is a simple way of incorporating two different material functions into a polymer chain.<sup>1-4</sup> But in random copolymerization there is no control of polydispersity or molecular weight, and the interface between the two functional moieties is also not present in the bulk due to lack of phase separation of the functional domains. On the other hand, living polymerizations and controlled radical polymerizations deliver block copolymers with

separation between two functional domains. Thus, it is advisable to define the interface between the two functionalities exactly by attaching the two different functional moieties by a covalent bond and if possible to manipulate the interface formation between these two moieties using intrinsic polymeric properties like phase separation and aggregation in block copolymers.<sup>5,6</sup> Some synthetic attempts in this regard have been successfully tried out by Hadziioannou et al. by developing bifunctional diblock copolymers carrying *p*-phenylenevinylene and fullerene units.<sup>7</sup> For successful exploitation of the desired morphology which creates the internal interface and which in turn guarantees charge separation at these internal interfaces, as for example in a solar cell, a good control of the building up of phase domains of the block copolymer is required. In the specific case of a dye-sensitized TiO<sub>2</sub> solar cell in which ruthenium(II)-(bipyridyl) dye is chemisorbed onto TiO<sub>2</sub> surface and a triphenylamine derivative functions as the hole conductor, the interface between the chemisorbed monomolecular dye layer and hole conductor is very crucial for charge separation and transport.<sup>8</sup> The state-of-theart preparation of this interface is just by spin-coating of a solution of the hole conductor onto the dye-coated TiO<sub>2</sub> surface. This results in insufficient contact between dye and hole conductor which leads to low performance

a narrow polydispersity which favor nanoscale phase

 $\ast$  Corresponding author: e-mail Mukundan. Thelakkat@ uni-bayreuth.de. of the cell. One way to overcome this problem is to use additional bifunctional/bipolar compatibilizers which bridge the interface between dye and hole conductor. A chemical approach to solve this problem is to bind the dye with hole transport polymers and use such bifunctional systems alone or in combination with the conventional dyes and hole conductors.

Keeping this in mind, we wanted to realize a bifunctional polymer carrying a strongly absorbing polar dye unit attached to well-defined polymer chains carrying charge transport moieties based on triarylamines. The controlled polymerization of the monomer, vinyltriphenylamine (VTPA), using anionic polymerization<sup>9,10</sup> as well as by TEMPO (2,2,6,6-tetramethylpiperidine oxide)-mediated radical polymerization<sup>11</sup> is reported in the literature. Here we report the successful synthesis of "poly(vinyltriphenylamine)" using a different route as the above-reported methods in the literature. Fraser et al. have reported the atom transfer radical polymerization (ATRP) of styrene starting from bis(chloromethyl)bipyridine or from the corresponding ruthenium complex as initiator to obtain poly(styrene) attached to a ruthenium core.<sup>12</sup> It is also possible to carry out ATRP of other substituted styrenes like 4-bromostyrene using conventional initiators like 1-phenylethyl bromide as reported by Matyjaszewski et al.13

We made use of a combination of the above two concepts to polymerize 4-bromostyrene in bulk using bis-(chloromethyl)bipyridine as initiator for the first time in order to obtain two poly(4-bromostyrene) chains with well-defined molecular weights and low polydispersity attached to a bipyridyl unit. Then we adopted a polymer analogous amination reaction on this macroligand to convert the bromophenyl group into a triphenylamine moiety. In a final step, the bipyridine moiety was complexed with bis(bipyridyl)Ru(II) precursors to obtain a highly polar dye functionality covalently bound to two hole transport polymer chains of vinyltriphenylamine. Although the direct polymerization of the vinyltriphenylamine monomer using bis(chloromethyl)bipyridine as initiator was feasible, this route was not favored due to lack of reproducibility in the control of polymerization under the conditions that we used.

This paper describes the details of synthesis, characterization, and different physical properties of a series of metal-free macroligands, poly(4-bromostyrene)s or poly(vinyltriphenylamine)s, and the final Ru(II) polymer complexes having variable chain lengths. The main aim here was to find out a synthetic route for bifunctional systems which can be synthesized over a wide range of molecular weights. It is usually difficult to obtain high control of molecular weight distribution in the oligomeric regime in bulk polymerization. For preparing a series of polymers with two different material functions varying in their weight fractions, the method adopted here is seemly efficient. Moreover, this method is also of general nature and is applicable for the incorporation of other organo-metal complex dyes and other charge transport units like carbazoles and phenothiazines as well.

#### **Results and Discussion**

A multistep synthetic route was selected to obtain functional polymers with defined chain length and narrow molecular weight distribution for tuning the electrooptical properties of the resulting material. The function of the dye is fulfilled by a tris(bipyridyl)Ru(II)

#### Scheme 1. Scheme of Polymerization of 4-Bromostyrene via ATRP in Bulk Using 4,4'-Bis(chloromethyl)-2,2'-bipyridine as Initiator and CuCl/PMDETA as Catalytic System at 60 °C<sup>a</sup>



<sup>*a*</sup> Molar ratio of reagents is [monomer]:[initiator]:[CuCl]: [PMDETA] = 150:1:1:2.

unit, and the charge transport function is taken care of by a triphenylamine moiety. All the analytical data for the polymers from NMR, FT-IR, MALDI-TOF MS, and UV/vis spectroscopy are given in the Experimental Section.

The first step of the synthesis as shown in Scheme 1 involves the controlled free radical bulk polymerization of 4-bromostyrene using CuCl/PMDETA (1,1,4,7,7-pentamethyldiethylenetriamine) as the catalytic system. PMDETA acts as complexing ligand for the CuCl/CuCl<sub>2</sub> system which controls the equilibrium between active radical and dormant bromide species in the reaction mixture. In ATRP usually bipyridine derivatives are used as ligands and phenylethyl bromide or ethyl 2-bromopropionate as initiators.<sup>13</sup> But Fraser and coworkers have shown that an initiator. bis(chloromethyl)bipyridine (1) in combination with a conventional catalytic system like CuCl/PMDETA can be used for the controlled radical polymerization of styrene.<sup>12</sup> Therefore, 4,4'-bis(chloromethyl)-2,2'-bipyridine was used here as initiator in combination with PMDETA/CuCl in order to polymerize 4-bromostyrene in bulk. A series of polymerization reactions were performed with the molar ratio [monomer]:[initiator]:[CuCl]:[PMDETA] = 150:1: 1:2 in order to optimize the reaction. The initiator **1** was synthesized from the corresponding 4,4'-(trimethylsilvlmethyl) derivative by a modified procedure of the CsF method described in the literature, and it is given in the Experimental Section.<sup>14</sup>

To obtain well-defined low molecular weight polymers, the reaction was quenched by cooling and exposing the reaction mixture to air at desired time intervals. Since the polymerization was terminated at low degrees of conversion, there is always rest monomer left in the reaction mixture which makes a proper precipitation of 2 either in methanol or in *n*-hexane difficult. For this reason, it is important to remove the remaining monomer in high vacuum to obtain reasonable precipitation of the polymer 2. The rest of the Cu salts in polymer 2was removed by repeated washing of the polymer with aqueous NH<sub>4</sub>Cl solution (see Experimental Section).

The molecular weight and polydispersity obtained from GPC (THF and 0.25 wt % *tert*-butyl bromide as eluent, polystyrene standards) for two different batches of polymerization are shown in Table 1. As expected, the polydispersity becomes lower with higher degree of polymerization, and depending on the conditions used,



**Figure 1.** (A) GPC elution curves for a series of polymers **2** with increasing molecular weights. (B) Dependence of numberaverage molecular weights  $M_n$  and weight-average molecular weights  $M_w$  on time for ATRP of 4-bromostyrene in bulk at 60 °C (GPC data obtained with THF containing 0.25 wt % *tert*butylammonium bromide as eluent and calibration with polystyrene standards).

Table 1. GPC Data (Obtained with THF Containing 0.25 wt % *tert*-Butyl Ammonium Bromide as Eluent and Calibration with Polystyrene Standards) of Two Sets of Macroligand 2 Obtained at Various Time Intervals via ATRP in Bulk Using 4,4'-Bis(chloromethyl)bipyridine as Initiator, CuCl, and PMDETA as Catalytic System

| batch | time [min] | $M_{ m w}$ [g/mol] | M <sub>n</sub> [g/mol] | PDI  |
|-------|------------|--------------------|------------------------|------|
| 1     | 180        | 4348               | 3060                   | 1.42 |
|       | 240        | 5811               | 4267                   | 1.36 |
|       | 300        | 7535               | 5756                   | 1.31 |
|       | 360        | 9779               | 7559                   | 1.29 |
| 2     | 60         | 2764               | 1803                   | 1.53 |
|       | 120        | 3309               | 2610                   | 1.27 |
|       | 180        | 5130               | 3540                   | 1.45 |
|       | 240        | 6987               | 4959                   | 1.41 |
|       | 300        | 9159               | 6558                   | 1.40 |
|       | 360        | 11000              | 8237                   | 1.34 |

molecular weights can be tuned in the oligomeric range. At higher conversion, high molecular weight polymer **2** with  $M_n$  in the range of 30 000 g/mol was obtained. It was rather easy to obtain high molecular weight polymers than low molecular weight polymers with narrow molecular weight distribution using ATRP of 4-bromostyrene in bulk. This observation is similar to that reported for bulk polymerization of styrene under similar conditions.<sup>12</sup> But our special interest was to obtain polymer chains with less number of repeating units in order to obtain high dye content as well as good filling properties for the polymer **1**, the individual GPC curves and the dependence of the corresponding molecular weights on time of reaction are shown in Figure 1.



**Figure 2.** Dependence of number-average molecular weight  $M_n$  and polydispersity  $M_w/M_n$  on degree of monomer conversion in bulk-ATRP of 4-bromostyrene; conversion determined by GC measurements with anisole as external standard.

It can be clearly seen that the monodisperse eluograms show constant increase in molecular weight. Both number-average molecular weight  $M_n$  and weight-average molecular weight  $M_w$  show a linear dependence on reaction time, which is a measure of conversion.

The conversion at different time intervals was determined by gas chromatography (GC) analysis of the amount of unreacted monomer. For this purpose, samples were taken from the reaction mixture at designated time intervals and they were diluted with THF, and a defined amount of anisole was added as external GC standard. The data obtained from GC analysis plotted vs the corresponding molecular weights and polydispersities obtained from GPC are shown in Figure 2. The attained polydispersity of 1.3 for a conversion of about 40% in the low molecular weight range of about 10 000 g/mol is appreciably good for ATRP in bulk. Since we are interested in synthesizing materials with low molecular weights in order to use these materials as bifunctional compatibilizers, this method offers an elegant way of achieving this goal. Further lowering of polydispersity is possible by optimizing the conditions of polymerization which affect the concentration of active species and rate of polymerization, as for example, to carry out the polymerization in suitable solvents.

Thus, it was possible to obtain a macroligand of bipyridine carrying two poly(4-bromostyrene) chains as arms which can be later complexed with Ru(II) bis-(bipyridine)s for the incorporation of the dye function. Moreover, the bromo substituents of the resulting poly-(4-bromostyrene) provide an ideal opportunity to attach a charge transport moiety like triphenylamines by polymer analogous amination with diphenylamine. For the latter we require a fast and efficient method of amination of aryl halide.

The polymer amination reaction with diphenylamine was carried out as shown in Scheme 2. Similar polymer amination reactions of poly(4-bromostyrene) using amines like carbazoles or phenazines were found to proceed smoothly with a high degree of substitution.<sup>15</sup> For the conversion of macroligand **2** to macroligand **3**, a general method of Pd-catalyzed amination reaction of aryl halides was used, which was developed and studied by Hartwig et al. and Buchwald et al.<sup>16,17</sup> It is known from literature that side reactions involving incorporation of phosphor and hydrodehalogenation are possible if aryl halides containing electron-poor substituents are used. To avoid any undesired product and to obtain complete conversion in appreciably short periods, different com-



**Figure 3.** <sup>1</sup>H NMR spectra of polymer **2** and polymer **3** (in CHCl<sub>3</sub>, 250 MHz) which shows the disappearance of the two doublets from polymer **2** and the appearance of multiplets corresponding to polymer **3** aryl hydrogen signals after a reaction for about 1 h.

Scheme 2. Schematic Representation of Pd-Catalyzed Polymer Analogous Amination of Polymer 2 with Diphenylamine Using Pd(OAc)<sub>2</sub> and P(t-Bu)<sub>3</sub> as Catalytic System



binations of Pd catalysts and ligands were tested to find out the most efficient system, and it turned out that a combination of  $Pd(OAc)_2$  and  $P(t-Bu)_3$  in the presence of NaOt-Bu gave the best results. With the described catalytic system it was possible to achieve high conversion of the aryl bromide to triphenylamine unit in less than 2 h. The working-up procedure for further purification is also simple. After cooling the reaction mixture to room temperature and filtration over alumina to remove the residual Pd, half of the solvent was evaporated, and polymer **3** was precipitated in methanol. Further reprecipitation by adding the THF solution of the polymer into MeOH yielded 90% of the desired product **3**.

The polymer amination reaction was followed via NMR spectroscopy (see Figure 3). After about 1 h of reaction, the aryl hydrogen signals of polymer **2** completely disappear (which usually appear as doublets at 6.29 and 7.17 ppm) and the multiplet signals corresponding to triphenylamine protons appear, and therefore the reaction seems to be complete within the errors



**Figure 4.** Plot of bromine content (weight percentage) determined from elemental analysis for polymers **3** at different time intervals of conversion along with the corresponding triphenylamine content as calculated from the number of repeating units taking into consideration the number-average molecular weight of 30 481 g/mol for the starting polymer **2** as obtained from GPC. The lines are exponential fits of the data points.

of NMR detection. To verify the above results obtained from NMR spectroscopy, elemental analysis was carried out to determine the content of bromine in the resulting polymer **3**. The conversion of polymer **2** to polymer  $\mathbf{3}$ could be calculated from weight percentage of remaining bromine as determined by elemental analysis for a series of samples taken at different time intervals. For polymer **2** with a number-average molecular weight  $M_{\rm n}$ (GPC) of 3107 g/mol, the number of repeating units was calculated as 16. This gives a theoretical weight of bromine as 41.2%. The elemental analysis gave exactly the same value of 41.2% for bromine content, and after 2 h of polymer analogous reaction, the rest bromine content in polymer 3 was 7.56%, which corresponds to a conversion of 82%. We also estimated the degree of conversion for the polymer analogous reaction for a polymer 2 with higher molecular weight. For example, a batch of polymer **2** with  $M_n = 30$  481 g/mol (repeating units = 135, theoretical Br content = 43.2%) gave 43.9%Br in elemental analysis, which is in agreement with the theoretical value bearing in mind that the molecular weight obtained from GPC is not absolute. After a reaction time of 65 min the Br content falls to 7.20%, corresponding to a conversion of 84% and after 2 h of reaction time; the rest of the Br content is only 0.5%, which corresponds to 99% conversion. Figure 4 depicts the rest of the bromine content in polymer 3 for case two (high molecular weight polymer) plotted against time of conversion, and it follows an exponential behavior as expected for a polycondensation reaction. Using the number-average molecular weight obtained from GPC for this series of polymer 3 and the bromine content from elemental analysis, the triphenylamine content can also be calculated by taking into consideration the number of repeating units of  $\bar{4}$ -bromostyrene and vinyltriphenylamine present at different degrees of conversion. These values are also plotted in Figure 4 for a comparison. From the TPA content, the conversion value at 65 min comes to 88 wt %. Thus, it is very obvious that the polymer analogous reaction is complete within 1-2 h.

The UV/vis spectroscopy of polymer **3** in CHCl<sub>3</sub> solution shows additional strong absorption at about 305 nm due to the introduction of the triphenylamine unit; the absorption maximum  $\lambda_{max}$  of the simple triphenylamine molecule is 305 nm whereas the starting polymer **2** has a maximum absorption at 276 nm. The FTIR spectrum of polymer **3** shows no  $\nu$ (C–Br) band at 1073





cm<sup>-1</sup> which was originally present in polymer **2** and instead exhibits additional bands for C–N streching at 1312 and 1275 cm<sup>-1</sup> which are evidently absent in polymer **2**. Thus, elemental analysis, FTIR, NMR, and UV/vis absorption data indicate that the Pd-catalyzed polymer reaction provided the desired product **3** in which triphenylamine is the pendant group.

The final step of metallation of polymer 3 with Ru-(bpy)2Cl22H2O was carried out according to Scheme 3 using the activated silver salt method.<sup>18</sup> For this reaction,  $Ru(bpy)_2Cl_22H_2O$  together with the silver salt,  $CF_3$ -SO<sub>3</sub>Ag, was stirred at room temperature in acetone for 3 h, and the precipitated AgCl was removed by filtration. The deep red precursor complex Ru(bpy)<sub>2</sub>(CF<sub>3</sub>- $SO_3)_2$ (acetone)<sub>2</sub> is much more active than  $Ru(bpy)_2Cl_2$ -2H<sub>2</sub>O, and so it was reacted with polymer **3** by refluxing a solution of **3** and precursor complex in DMF overnight. After precipitation of the polymer into methanol, the product was filtered out and washed with methanol several times to remove any unreacted Ru(bpy)<sub>2</sub>(CF<sub>3</sub>- $SO_3_2$ (acetone)<sub>2</sub> or other low molecular Ru complexes formed during the reaction. The metallation reaction can be well-followed by observing the shift of MLCT (metal-to-ligand charge transfer) absorption maximum in UV/vis spectroscopy of the bis(bpy) system, Ru(bpy)2-(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>(acetone)<sub>2</sub>, at 550 nm to the tris(bpy) system, tris(bipyridyl)Ru(II) unit, at 456 nm. The UV/vis absorption spectrum of polymer 4 after 24 h of reaction is given in Figure 5, and it shows a clear absorption band at 456 nm and no absorption at 550 nm. With NMR spectroscopy it was possible to detect the bipyridine hydrogen signals in the low molecular weight polymers **3** and **4**. The bipyridine ligands show broad signals in the region from 7.4 to 8.3 ppm, which could not be resolved in detail (see Experimental Section). For high molecular weight polymers 3 and 4, the bipyridyl proton signals became weaker due to the decreasing weight percentage of bipyridyl unit in the polymer chain.

A comparison of the molecular weights of the metalfree macroligands **2** and **3** with the polymer complex **4** using a common GPC was not possible due to the difference in intrinsic viscosities and hydrodynamic volumes of these polymers and also due to lack of calibration standards for these new types of polymers. The macroligand **3** and polymer complex **4** carrying triphenylamine units seem to interact strongly with the stationary phase, leading to delayed elution and tailing



**Figure 5.** UV/vis spectrum of polymer **4** ( $M_n = 3940$  g/mol from MALDI-TOF MS) with a degree of metallation of 83% and correspondingly 2.1% Ru content recorded in CHCl<sub>3</sub> solution. The inset shows the magnified absorption maximum  $\lambda_{max}$  of hexacoordinated Ru(II) core at 456 nm present only in polymer **4** and which is absent in polymer **3**.

effect as compared with polymer 2. This results in low values of molecular weights for polymer 3 compared to its precursor polymer 2 using the polystyrene calibration which is not the reality. To overcome this, elution was also carried out in the presence of added salts in THF or dimethylacetamide as solvent, but without any success. The calibration of molecular weights for the polymer 3 using light scattering has large margins of error due to the low molecular weight nature of these polymers. An alternative is to use MALDI-TOF MS analysis, and it was carried out for all the three polymers 2, 3, and 4 resulting from one reaction batch. Under the used conditions of our measurement, we observed that the flow of polymer 2 to the detector was comparably better than those of polymers 3 and 4. For the MALDI-TOF MS analysis we selected the starting polymer 2 with an  $M_n$  value of 3107 g/mol as obtained from GPC. In MALDI-TOF an M<sub>n</sub> value of 2720 g/mol was determined for polymer 2, which is in agreement with the GPC value. The M<sub>n</sub> values for the corresponding polymers 3 and 4 are 3350 and 3940 g/mol, respectively, giving proof of polymer amination and metallation in terms of absolute molecular weights. The peak molecular weights for all the three polymers from MALDI-TOF are 2570, 3340, and 3930 g/mol, respectively. The MALDI-TOF curves are given in Figure 6.



**Figure 6.** Comparison of MALDI-TOF mass spectra of polymers 2-4 from one batch of reaction (recorded with dithranol as matrix and silvertriflate as additive).

It can be obviously seen that all the three polymers are monodisperse, and the difference in peak molecular weights between polymer **2** and polymer **3** corresponds to 92% conversion for polymer amination. The weight difference between polymer **3** and polymer **4** is 590 mass units, which exactly corresponds to 83% conversion for the metallation reaction. Thus, the successful conversion of the macroligand carrying poly(*p*-bromostyrene) chains to poly(vinyltriphenylamine) chains and its final metallation could be verified, and the degree of conversion for each step could be determined from the absolute molecular weights obtained from MALDI-TOF MS analysis.

Using the method described here, the weight fraction of ruthenium dye in final polymer can be varied over a wide range by varying the length of poly(4-bromostyrene) chains (from 5 wt % dye content for a molecular weight of 12 300 g/mol up to 25 wt % dye content for a molecular weight of 2670 g/mol). These polymers are highly soluble in the metal-free form as well as in the complexed form in usual solvents like CHCl<sub>3</sub>, toluene, etc., and they form uniform and smooth films by spincoating.

# **Thermal Properties**

Thermal characterization of all the polymers 2, 3, and 4 obtained from the same batch as the one used for MALDI-TOF analysis was performed by TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry). The starting polymer 2 has  $M_n$  value of 3107 g/mol as obtained from GPC and 2720 g/mol as determined from the absolute method, MALDI-TOF MS analysis. A comparison of second heating curves for the polymers 2, 3, and 4 as obtained from DSC measurement is shown in Figure 7. The absence of any melt peak or recrystallization peaks points toward amorphous nature of these polymers. Polymers with structure 2 show 4% weight loss at about 230 °C, which can be attributed to the removal of chlorine end groups. In all cases, glass transitions were evident in the DSC curves at about 110 °C similar to any standard poly(styrene) in the low molecular weight regime. Polymers 3 having triphenylamine pendant groups exhibit 4.7% weight loss at 238 °C and a glass transition temperature at about 130 °C, an increase of about 20 °C corresponding to the substitution of bromine with diphenylamine. After metallation, an increase in thermal stability is observed for polymer 4 compared to polymers 2 and 3. The onset of weight loss in TGA for polymer 4 is at about 287 °C, which is almost 50–60 °C higher than that for polymers



**Figure 7.** Comparison of second heating curves for the polymers 2-4 as obtained from DSC measurement (heating rate 10 K/min). Polymers **3** and **4** were obtained from polymer **2** with an  $M_n$  value of 3107 g/mol (GPC) and 2720 g/mol (MALDI-TOF MS).

**2** and **3**. This gives hints about a good thermal stability of the final polymer containing a hexacoordinated tris-(bipyridyl)Ru(II) complex. Moreover, the glass transition temperature is also improved to 145 °C compared to 110 and 130 °C for polymers **2** and **3**, respectively.

# Conclusion

ATRP in bulk was adapted to synthesize poly(4bromostyrene) with controlled molecular weight and low polydispersity starting from bis(chloromethyl)bipyridine as initiator for the first time. A series of polymers with well-defined molecular weights and narrow distribution could be obtained. The polymer amination reaction using  $Pd(OAc)_2$  and  $P(tBu)_3$  offered a fast and efficient method to introduce the charge transport moiety, with triphenylamine as pendant groups. The final complexation of the bipyridyl unit present in the polymer led to a highly soluble bifunctional polymer in which charge transport polymer chains are attached to a tris(bipyridyl)Ru(II) core. MALDI-TOF MS analysis gave the absolute molecular weights for all the three types of polymers, and the degree of conversion of polymer amination and metallation determined from these absolute molecular weights agree well with those obtained from elemental analysis. We expect that the Rucontaining polymer shows aggregation behavior due to its bipolar nature, and this can lead to interesting morphologies in bulk as a result of dye aggregation and phase separation. At present, the film formation properties of these polymers from different solvent combinations and under different thermal treatments are under investigation.

#### **Experimental Section**

**Materials.** 4-Bromostyrene from Aldrich was vacuumdistilled and stored in a refrigerator under an argon atmosphere. Cu(I) chloride (Merck) was purified as described by Keller.<sup>19</sup> Sodium *tert*-butylate and CsF were dried by heating under vacuum and stored under argon. Toluene was distilled from Na prior to use; DMF was refluxed over CaH<sub>2</sub> and distilled under vacuum. 4,4'-Bis(trimethylsilyl)-2,2'-bipyridine was synthesized as described by Fraser et al.<sup>14</sup> PMDETA, Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (Lancaster), palladium acetate, tri-*tert*butylphosphine, and diphenylamine (Aldrich) were purchased and used as received.

**Instrumentation.** <sup>1</sup>H NMR spectra were acquired on a Bruker AC 250 spectrometer (250 MHz); the molecular weights of polymers were determined by gel permeation chromatography (GPC) in THF + 0.25 wt % *tert*-butylammonium bromide with UV and RI detectors (Waters). UV/vis spectra were recorded using a Hitachi U-3000 spectrometer, IR spectroscopy

was carried out with a BioRad Digilab FTS-40 (FTIR), and GC analysis was done in a GC 8000 series from Fisons Instruments using anisole for calibration. The thermal degradation of the polymers was studied using a Netzsch TGA STR 409 with a standard heating rate of 10 K/min under N<sub>2</sub> atmosphere, and the differential scanning calorimetry was carried out with a Perkin-Elmer DSC 7. The MALDI-TOF MS analysis was performed using a Bruker Reflex III equipped with a 337 nm N<sub>2</sub> laser, an acceleration voltage of 20 kV with dithranol as matrix, and silver triflate as additive.

Synthesis. 4,4'-Bis(chloromethyl)-2,2'-bipyridine (1). To a solution of 4,4'-bis(trimethylsilylmethyl)-2,2'-bipyridine (43 mmol, 14.13 g) and Cl<sub>3</sub>CCCl<sub>3</sub> (86 mmol, 20.26 g) in 150 mL of dry DMF under an inert atmosphere anhydrous CsF (86 mmol, 13.06 g) was added. The reaction mixture was stirred at room temperature until the starting TMS compound was fully used up. The reaction mixture was poured into a mixture of EtOAc and H<sub>2</sub>O (200 mL each), the organic layer was separated, the aqueous layer was extracted three times with 100 mL of EtOAc each, and the combined organic fractions were dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and evaporation of the solvent gave a yellowish product which can be purified by washing with cold toluene cooled using liquid N<sub>2</sub> to yield a white solid: 5.00 g (46%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ : 4.58 (s, 2 H), 7.35 (d, 1 H), 8.39 (s, 1 H), 8.66 (d, 1H). IR (KBr, v, cm<sup>-1</sup>): 3001, 1594, 1558, 1457, 1376, 1279, 1216, 855. m/z 252  $(M^{+}).$ 

4,4'-Bis[poly(4-bromostyryl)methyl]-2,2'-bipyridine (2). A solution of 4-bromostyrene (115 mmol, 21 g) and 4,4'-bis-(chloromethyl)-2,2'-bipyridine (1) (0.77 mmol, 129.1 mg) was placed in an argon-flushed three-neck flask. The mixture was degassed in three cycles by the freeze-pump-thaw method<sup>13</sup> followed by the addition of CuCl (0.77 mmol, 75.8 mg). The mixture turns first deep brown and then becomes light brown when the ligand PMDETA (1.53 mmol, 265.1 mg) was added. Equipped with a septum and a condenser, the flask was immersed in an oil bath maintained at 60 °C, and the initial time was recorded. Samples (2 mL) were taken out of the reaction mixture at certain time intervals through the septum with an argon-flushed syringe. They were cooled and exposed to air to terminate the polymerization and were used for GC analysis after dilution with THF. After precipitation in nhexane the slightly bluish polymers were filtered, dried, and washed first with methanol and then with an aqueous solution of NH<sub>4</sub>Cl to remove the residual copper catalyst. The polymers were reprecipitated from THF into methanol to give a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz) δ: 1.25 (m, 2 H), 1.56 (m, 1 H), 6.29 (d, 2 H), 7.16 (d, 2 H). IR (KBr, v, cm<sup>-1</sup>): 2924, 1592, 1486, 1407, 1073, 1009, 822. UV/vis (CHCl<sub>3</sub>):  $\lambda_{max} = 276$  nm. Rest Cu content after one washing with  $\rm NH_4Cl$  solution: 0.048 wt %. Elemental analysis: C = 52.28% (calcd 54.1%); H =3.82% (3.9%); N = 1.22% (0.9%); Br = 41.2% (41.2%); Cl = 1.78% (2.3%); the calculated values are obtained by taking the  $M_{\rm n}$  value of 3107 g/mol as determined from GPC.  $M_{\rm n}$  (from MALDI-TOF) = 2720 g/mol.

4,4'-Bis[poly(vinyltriphenyamino)methyl]-2,2'-bipyridine (3). A mixture of polymer (2) (5.46 mmol of monomer unit, 1 g) and diphenylamine (16.38 mmol, 2.77 g) was dissolved in 30 mL of dry toluene. Sodium tert-butylate (8.19 mmol, 0.79 g), palladium acetate (0.14 mmol, 30.60 mg), and  $P(t-Bu)_3$  (8.19 mmol, 165 mg) were added to the solution at room temperature. The dark brown reaction mixture was stirred at 110 °C for 1 h under an argon atmosphere. The reaction was quenched by cooling and flushing with air. After the removal of half of the toluene in a vacuum the triphenylamine polymer was precipitated in methanol, filtered, and dried. For further purification the product can be reprecipitated from THF into methanol to yield a pale yellow solid: 1.34 g (90%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz) δ: 1.57 (m, 2 H), 1.97 (m, 1 H), 6.48–6.99 (m, 9 H). IR (KBr, v, cm<sup>-1</sup>): 3058, 3024, 2920, 2850, 1588, 1492, 1312, 1275, 826, 751, 694. UV/vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}} = 303 \text{ nm.} M_n \text{ (from MALDI-TOF)} = 3350 \text{ g/mol.}$ 

Complexation of Polymer 3 with Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O. CF<sub>3</sub>SO<sub>3</sub>Åg (0.375 mmol, 96.3 mg) and Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (0.187 mmol, 97.5 mg) were dissolved in 30 mL of dry acetone and stirred under argon for 3 h. After filtration of AgCl over a filter paper, acetone was removed under vacuum at room temperature. The dark red residue was dissolved in 30 mL of dry DMF, and polymer 3 (2.6 mmol of monomer unit, 0.7 g) was added. The reaction mixture was refluxed for 24 h. At the end of reaction about 75% of the DMF was removed, and the rest was dissolved in a small amount of CHCl<sub>3</sub>. The product (4) was precipitated out by adding the CHCl<sub>3</sub> solution into MeOH, filtered, and washed repeatedly with MeOH until the washings are colorless. After drying in a vacuum an orange powder was obtained in ca. 83% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz) δ: 1.57 (m, 2 H), 2.00 (m, 1 H), 6.59-6.89 (m, 9 H), 7.41 (m, 0.06 H), 7.54 (m, 0.06 H), 7.74 (m, 0.08 H), 7.91 (m, 0.12 H), 8.33 (m, 0.08 H). IR (KBr, v, cm<sup>-1</sup>): 2940, 2899, 1567, 1492, 1437, 1318, 1235, 1063, 801. UV/vis (CHCl<sub>3</sub>):  $\lambda_{max} = 456$  nm;  $M_n$  (from MALDI-TOF) = 3940 g/mol.

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