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DIRECT PYROLYSIS MASS SPECTROMETRY STUDIES ON THERMAL DEGRADATION CHARACTERISTICS OF POLY(PHENYLENE VINYLENE) WITH WELL-DEFINED PSt SIDE CHAINS

Y. Nur[1], *D. G. Colak*[2], *I. Cianga*[2,3], *Y. Yagci*[2] *and J. Hacaloglu*[1,*]

[1]Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey
[2]Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 34469, Turkey
[3]'Petru Poni' Institute of Macromolecular Chemistry, Iasi, Romania

Thermal degradation characteristics of a new macromonomer polystyrene with central 4,4'-dicarbaldehyde terphenyl moieties and poly(phenylene vinylene) with well-defined polystyrene (PPV/PSt) as lateral substituents were investigated via direct pyrolysis mass spectrometry. A slight increase in thermal stability of PSt was detected for (PPV/PSt) and attributed to higher thermal stability of PPV backbone. It was almost impossible to differentiate products due to the decomposition of PPV backbone from those produced by degradation of PSt.

Keywords: *poly(phenylene vinylene), polystyrene, pyrolysis mass spectrometry, thermal degradation*

Introduction

Conjugated polymers having π-electron delocalization along their backbones have interesting optical and electronic properties. Polyphenylene (PP) is a typical conjugated polymer with excellent mechanical properties and thermal and thermooxidative stability and has several practical applications. Thus, a great deal of research has gone into the study of PP and its derivatives [1–3]. Among the several conjugated polymers, poly(phenylene vinylene) (PPV) has attracted much attention for its electroluminescent property [4–7]. However, due to the insolubility of PPV, the light-emitting PPV films of these polymers can only be cast by a precursor route after high-temperature annealing. Thus, the applications of PPVs are still limited due to the rigid structures and inherent insolubilities. These problems are tried to be overcome by preparation of PPV derivatives (DP-PPV) with improved solubility, processability and stability.

In order to meet the requirements for high-tech applications, nanostructured photoactive conjugated oligo(phenylene vinylene) segments were attached as side chains to polystyrene (PSt) or poly(methyl methacrylate) (PMMA) backbones [8, 9]. Furthermore, block-copolymer series of PPV derivatives with fixed conjugation length were prepared. These alternating copolymers contained rigid – conjugated and flexible blocks [10, 11]. Significant improvement in solubility in common organic solvents was obtained for PPV derivatives with alkyl side chain and alkoxy groups on the polymer backbone [12]. Several PPVs with various substituents such as phenyl, linear or branched alkoxy side chain and fluorenyl groups have also been synthesized [13–15].

We have previously reported the synthesis and characterization of PPs and PPVs with well defined poly(ε-caprolactone) (PCL) or PSt as lateral substituents by combination of controlled polymerization methods with appropriate coupling and condensation reactions [16–18]. The resulting main chain conjugated graft copolymers were soluble as were the starting macromonomers and PPVs showed blue or green fluorescence in solution [18].

Thermal degradation characteristics of these architecturally complex polymeric materials are an important issue for developing a rational technology of polymer processing and applications. Notably, PPV has a higher degradation temperature (~500°C) than the other related polymers such as polyphenylene (450°C) or poly(*p*-xylene) (420°C) [19, 20]. This aspect is particularly important for their use in complex electronic circuits which requires exposure to high temperatures during manufacturing and processing. In our previous studies, we applied direct pyrolysis mass spectrometry technique to investigate thermal behavior of PPs with PCL and/or PSt as lateral substituents. It was observed that thermal degradation of poly(phenylene)-*graft*-poly(ε-caprolactone) copolymer (PP-*g*-PCL) occurred mainly in two steps; the decomposition of PCL chains was followed by the decomposition of the polyphenylene backbone [21, 22].

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[*] Author for correspondence: jale@metu.edu.tr

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Yet, a slight increase in the thermal stability of PCL chains was noted. When PP-*graft*-PCL/PSt copolymers were considered, thermally less stabile PCL side chains decomposed in the first step. In the second stage of pyrolysis, the decomposition of the polystyrene chains took place. A slight increase in the thermal stability of PCL chains for PP-*graft*-PCL/PSt copolymers was noted compared to copolymer PP-*graft*-PCL due to the interaction between PSt and PCL chains. This interaction was stronger when PSt chains were linked to 2-position of the repeating 1,4-phenylene ring.

In this work, the thermal degradation of PPV with well defined PSt chains as lateral substituents has been studied via direct pyrolysis mass spectrometry.

Experimental

Synthesis

The details of synthesis of PPV and initiators are given in our previous studies [18]. Shortly, atom transfer radical polymerization (ATRP) of styrene (St) in the presence of bifunctional initiator 1,4-dibromo-2-(bromomethyl)benzene provided well-defined low molecular mass polymers with dibromobenzene moieties. Suzuki coupling of these bromobenzene functions with 4-formylphenyl bromic acid yielded macromonomers having 4,4'-dicarbaldehyde terphenyl moieties. PPV with PSt chains as lateral substituents was synthesized by following a Witting polycondensation in combination with bis(triphenyl phosphonium) salts in the presence of potassium *tert*-butoxide. Experimental procedures are summarized in Scheme 1.

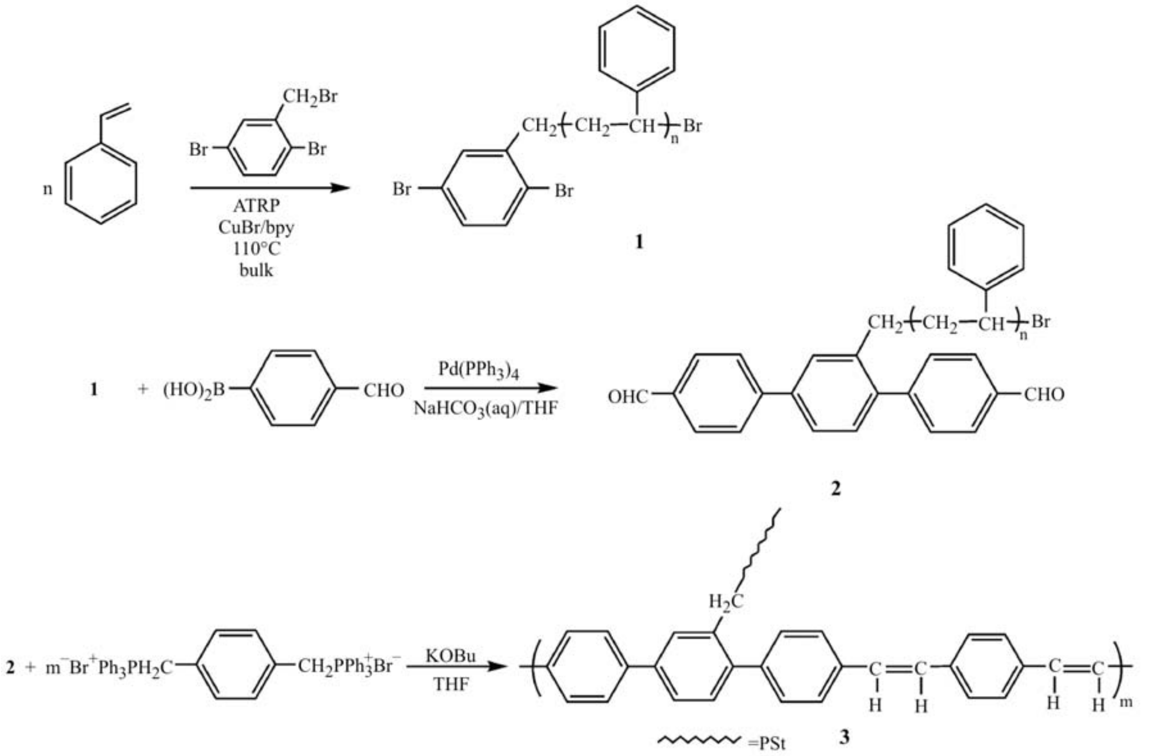
Instrumentation

Direct pyrolysis mass spectrometry analysis were carried out using (DPMS) system consisting a 5973 HP quadrupole mass spectrometer with a mass range of 10–800 Da which was coupled to a JHP SIS direct insertion probe (T_{max}=450°C). In each experiment, the temperature was increased up to 450°C at a heating rate of 10°C min^{-1}, and kept constant for an additional 10 min at 450°C. 0.010 mg samples were pyrolyzed in the flared glass sample vials. Pyrolysis experiments were repeated at least twice to ensure reproducibility.

TG experiments were performed using a Perkin Elmer Diamond TG/DTA Thermogravimetric Analyzer (TG) at a heating rate of 10°C min^{-1} under N_2 atmosphere (30–800°C).

Results and discussion

PPV with lateral substituent PSt, was prepared by a Wittig polycondensation of macromolecule **2** (low molecular mass PSt containing 4,4'-dicarbaldehyde



Scheme 1 Synthesis of poly(phenylene vinylene)s with well defined PSt as lateral substituent

terphenyl end groups) with bis(triphenyphoshonium) salts in the presence of potassium *tert*-butoxide. The macromonomer **2** was synthesized using Suzuki type coupling of macromonomer **1** (relatively low molecular mass PSt with 1,4-dibromophenylene end groups) with 4-formylphenyl bromic acid. Thus, all the samples under investigation involved the same PSt chains either as the main chain with different end groups or as a lateral substituent on PPV backbone [18]. In a recent study, the slight increase of molecular mass noticed for **2** with respect to **1** ($M_{n,GPC}$ and $M_{n,H\ NMR}$ were 2400 and 2270 for **1** and 2480 and 2420 for **2**, respectively) was attributed to introduction of new end groups on the central unit in accordance with expectations. $M_{n,\ GPC}$ value of 18600 determined for PSt substituted PPV was taken as the minimum estimate because of the highly branched structure [18]. In the same study, the thermogravimetric analysis of **1**, **2** and **3** under nitrogen indicated that the initial degradation temperature (IDT) increased significantly in the order **1**<**2**<**3** (180, 250 and 300°C for **1**, **2** and **3**, respectively). The temperature at which the mass loss was 10%, was almost identical for **1** and **2** (375 and 377°C, respectively) and for **3** it was 405°C. The direct pyrolysis of the samples under investigation yielded total ion current (variation of total ion yield as a function of temperature), (TIC), curves with a broad peak showing a maximum above 400°C (Fig. 1).

Pyrolysis mass spectra of all the samples were dominated by the peaks known to arise from the classical decomposition products of PSt. It is known that the thermal degradation of PSt takes place by a free-radical chain reaction, depolymerization, yielding mainly the styrene monomer [23–26]. Pyrolysis mass spectrometry analysis of **1** demonstrated that the products generated were essentially the same as those observed for the degradation of the other materials, namely **2** and **3**. All samples displayed similar behavior during dynamic ramping profiles and reached maximum decomposition yield around 420°C. The exceptions include HBr and Br whose intensities maximized around 240°C. In Fig. 2, the single ion pyrograms of C_6H_6 (m/z=78 Da), HBr and/or C_6H_8 (m/z=80 Da), C_7H_7 (m/z=91 Da), St monomer (m/z=104 Da), $C_6H_5C_3H_4$ (m/z=117 Da), St dimer (m/z=207 Da), trimer (m/z=312 Da) and tetramer (m/z=416 Da) are shown. The 79, 81, 80 and 82 Da peaks due to $H^{79}Br$ and $H^{81}Br$ emerged at about 190°C and reached maximum intensity near 240°C. Thus, it may be concluded that the thermal degradation started with the dissociation of labile C–Br bonds just above 190°C in accordance with TG data. Pyrolysis mass spectra contained no indication for a decreasing effect of HBr, evolved at initial stages of pyrolysis, on thermal stability of PSt chains. Actually, in the case of direct pyrolysis mass spectrometry, as the high vacuum system rapidly removes the degradation products from the heating zone, secondary and condensation reactions are avoided. Peaks due to decomposition of PSt chains, oligomers up to heptamer, were

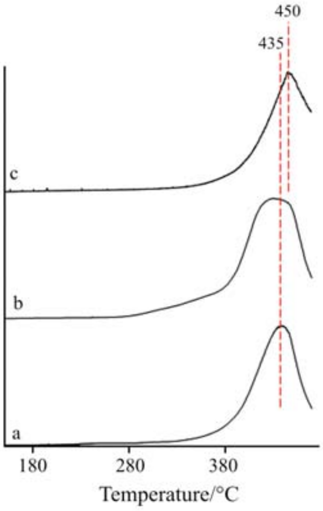


Fig. 1 TIC curves recorded during the pyrolysis of macromonomer a – **1**, b – **2**. c – PPV with alternating PSt side chains

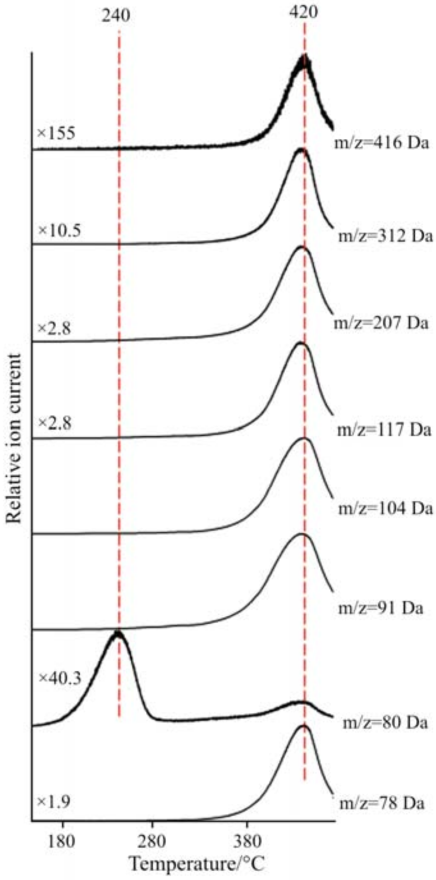


Fig. 2 Single ion pyrograms of some selected degradation products of PSt **1** with 1,4-dibromophenylene end groups

detected above 330°C. The relative intensities of the oligomers decreased drastically as the number of repeating units decreased. The monomer/dimer (M/D), monomer/trimer (M/T) monomer/tetramer (M/Te) ratios were 2.8, 10.5 and 155, respectively.

The TIC curve for the macromonomer **2** was quite broad. Inspection of single ion pyrograms for prominent and/or characteristic products indicated that thermal degradation again started by loss of end groups. In Fig. 3, the single ion evolution profiles of major and/or characteristic products detected during the pyrolysis of the macromonomer **2,** namely, CO (m/z=28 Da), C_6H_6 (m/z=78 Da), HBr (m/z=80 Da), C_7H_7 (m/z=91 Da), St monomer (m/z=104 Da), C_6H_5CHO, and/or C_8H_{10} (m/z=106 Da), $C_6H_5C_3H_4$ (m/z=117 Da), St dimer (m/z=207 Da), trimer (m/z=312 Da) and tetramer (m/z=416 Da), are shown. HBr evolution was almost totally disappeared in the pyrolysis mass spectra of **2** indicating that the Suzuki coupling process was highly effective. Evolution of CO started above 200°C and was maximized around 290°C. The single ion pyrogram of 106 Da product displayed two peaks, the weak and broad peak, emerging just above 290°C. These peaks were not present in the evolution profiles of other PSt based fragments and can directly be assigned to the loss of benzaldehyde. It should be noted that PSt based products followed identical evolution profiles as in the case of **1.** The PSt based fragment distribution was almost identical to what was observed for the macromonomer **1**. M/D, M/T and M/Te intensity ratios were measured as 2.8, 9.6 and 152, respectively. However, for **2,** the evolution of PSt based products were detected in a broader temperature range and their yields were maximized around 430°C, pointing out a slight increase in the thermal stability of PSt chains compared to **1**. Increase in thermal stability may directly be associated with higher bond energy of C–CO compared to that of C–Br. It is clear that the thermal degradation started by the elimination of CO. Yet, before the elimination of CO was completed, loss of benzaldehyde was also started. Thus, it may be considered that these two opposing decomposition pathways yielded PSt chains with two different end groups having slightly different thermal stabilities which in turn caused broadening in evolution profiles of PSt based products. The peaks at m/z=243 and 360 Da in the pyrolysis mass spectra recorded above 400°C, were readily be assigned to the presence of terphenyl units, $C_6H_5–C_7H_5–C_6H_5$ and $C_6H_5–C_6H_4CH_2(St)–C_6H_5$ fragments, respectively (Fig. 3).

The TIC curve for polymer **3** showed a single peak with a maximum at 450°C. The single ion evolution profiles of selected products, namely C_6H_6 (m/z=78 Da), HBr (m/z=80 Da), C_7H_7 (m/z=91 Da), St monomer (m/z=104 Da), C_6H_5CHO (m/z=106 Da), $C_6H_5C_3H_4$ (m/z=117 Da), St dimer (m/z=207 Da), trimer (m/z=312 Da), tetramer (m/z=416 Da) and $C_6H_5–C_7H_5–C_6H_5$ (m/z=243 Da) are given in Fig. 4. CO evolution was not detected during pyrolysis indicating that all the aldehyde functionalities were consumed and the Witting reaction was highly efficient. The decomposition of **3** was similar to that for **1** and **2**. However, the evolution profiles were sharper and shifted to higher temperatures compared to that ob-

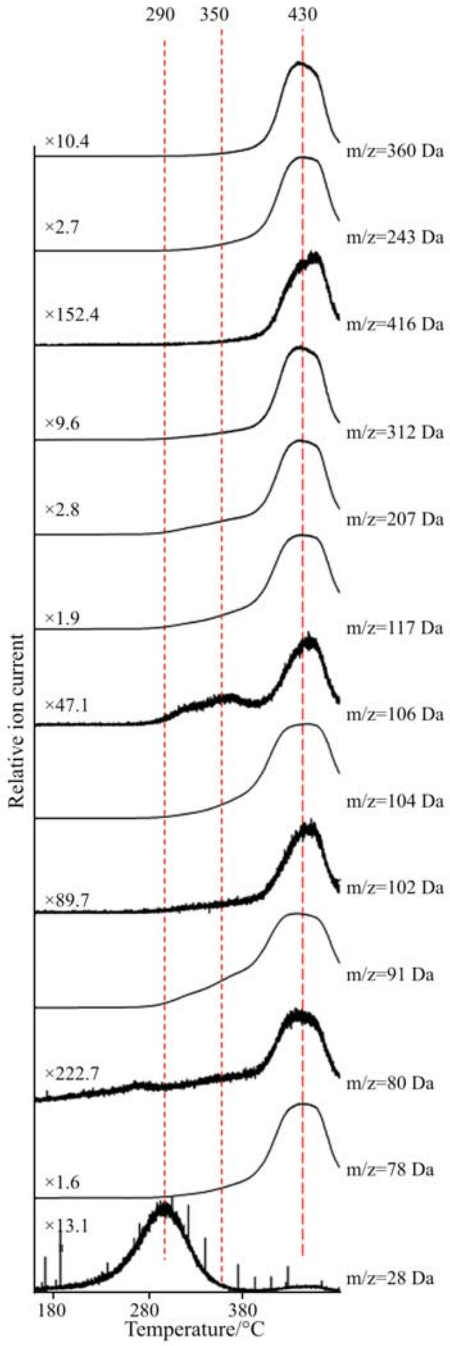


Fig. 3 Single ion pyrograms of some selected degradation products of PSt **2** with 4,4'-dicarbaldehyde terphenyl end groups

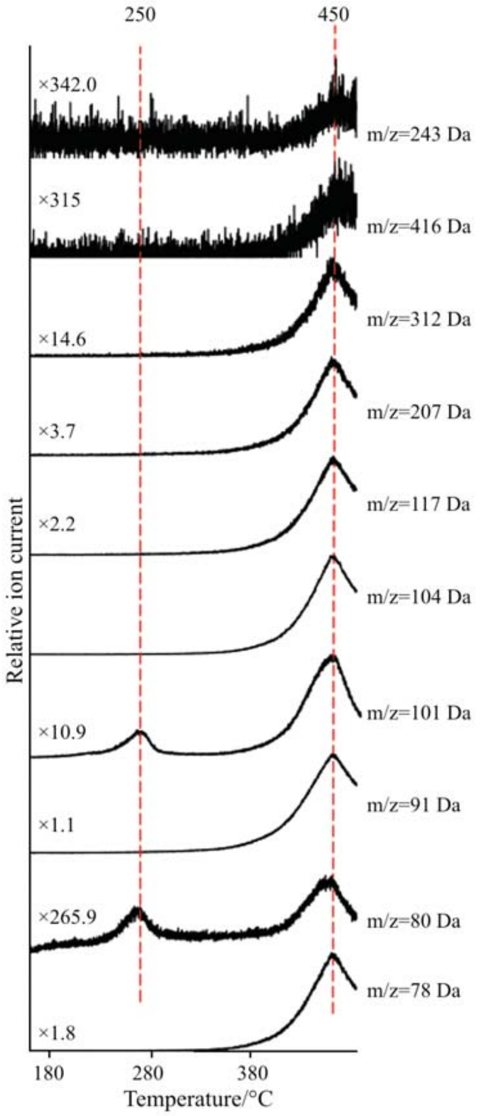


Fig. 4 Single ion pyrograms of some selected degradation products of PPV with alternating PSt side chains, **3**

served for **1** and **2**. Additionally, a noticeable decrease was observed in the relative intensities of the peaks corresponding to oligomers. For this sample**,** M/D, M/T and M/Te intensity ratios were 3.7, 14.6 and 315, respectively. Unfortunately, it is almost impossible to differentiate the products due to the decomposition of PPV backbone from those due to degradation of PSt. Actually, the backbone also contains terphenylene units. The phenylene vinylene units on both ends should restrict the evolution of the segments involving terphenyl units such as 243 and 360 Da fragments. Thus, the related peaks should either totally disappear or significantly diminish in the pyrolysis mass spectra of **3**. The pyrolysis data indicated very weak 243 Da peak in accordance with our expectations, confirming PPV formation. On the other hand, the noticeable increase in the relative yields of fragments involving hydrogen deficiency such as that of C_8H_5 (m/z=101 Da) fragment, was a direct evidence for the presence of vinylene phenylene units. The low temperature peak in the evolution profile of C_8H_5 fragment was assigned to unreacted *p*-xylenebis(triphenylphosphonium bromide). Detection of HBr evolution in the same region confirmed its presence.

The apparent, yet, slight increase in the thermal stability of PSt chains was attributed to higher thermal stability of PPV backbone. In a recent study, we discussed the thermal degradation characteristics of PCL substituted PPV. It was observed that the thermal stability of PCL side chains increased upon their substitution incorporation onto a thermally stable backbone. But, still the decomposition of the side chains and the PPV backbone occurred in two distinct regions. For PSt substituted PPV, degradation of both PSt chains and the PPV backbone occurred in the same temperature ranges. It is known that poly(phenylene vinylene) PPV has a higher degradation temperature (500°C) than that of polyphenylene (450°C). Thus, it can be concluded that the thermal stability of the PPV backbone is negatively impacted by the presence of thermally less stable side chains.

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