High temperature pyrolysis of poly(phenylene vinylene)s with poly(ε-caprolactone) or polystyrene side chains

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Abstract High temperature pyrolysis studies of poly (phenylene vinylene)s PPVs with lateral substituents poly(ε-caprolactone) (PPV–PCL) or poly(ε-caprolactone) and alternating Br (PPV–PCL–Br) or polystyrene (PPV–PSt) clearly showed that thermal stability of both the substituent and PPV were affected by the thermal stability of the other. In all the polymers under investigation, decomposition started by the degradation of the substituent. The thermal stability of the PPV backbone increased in the order PPV–PCL–Br < PPV–PCL < PPV–PSt. When the thermal stability of the substituent was significantly lower than that of the PPV backbone, as in the case of PPV–PCL and PPV–PCL–Br, then the radicals generated at early stages of pyrolysis coupled before the temperature reached to the values necessary for complete decomposition. This inturn yielded a thermally more stable crosslinked structure. The increase in thermal stability was greater upon coupling of the radicals generated on the PPV backbone.

Keywords Poly(phenylene vinylene) ·
Poly(ε-caprolactone) · Polystyrene · Thermal
degradation · Pyrolysis mass spectrometry

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Introduction

Poly(phenylene vinylene)s, (PPV), among the several conjugated polymers, have good mechanical properties and show high chemical and thermal stability. Yet, the applications of PPVs are limited due to the rigid structures and inherent insolubilities. These problems are overcome by the preparation of PPV derivatives with long alkyl chain or polymer substituents [1–9]. The resulting polymers exhibit improved solubility, processability and stability. Thermal degradation characteristics of these architecturally complex polymeric materials, is an important issue for developing a rational technology of polymer processing and applications. PPV has a higher degradation temperature (~ 500 °C) than other related polymers such as polyphenylene (450 °C), and poly(p-xylene) (420 °C) [10, 11]. Recently, we applied direct pyrolysis mass spectrometry technique to investigate thermal behavior of poly(phenylene)s and poly(phenylene vinylene)s with poly(ε-caprolactone) (PCL) and/or polystyrene (PSt) as lateral substituents at moderate temperatures up to 450 °C. It was shown that the conjugated backbones contribute to the improvement of the thermal stability of PCL and PSt chains [12–15].

For PPV with PCL as the lateral substituents, the decomposition of the side chains and PPV backbone were detected in two distinct regions [14]. The maximum yield for PCL based products, the protonated monomer, protonated oligomers and several fragments with various terminal groups such as COOH, $O=C(CH_2)_nCH=CH_2$ and $C(OH)=CH_2$, were detected around 415 °C. This value is almost about 100 °C higher than that recorded with the precursor poly(ε-caprolactone) macromonomer with a central 2,5-dibromo-1,4-benzene. The products forming from the decomposition of PPV backbone were observed at slightly higher temperatures and C_6H_5 and C_7H_7 evolutions

were maximized around 440 °C. For, PSt substituted PPV, only a slight increase in thermal stability of PSt substituents, about 20 °C, was detected and decomposition of both PSt and PPV backbone occurred almost in the same temperature range around 440 °C [15].

Regarding the unusual thermal behavior, it could not be definitely concluded whether the decrease in thermal stability is due to the presence of thermally less stable side chains or the limits of the pyrolysis system used. To resolve this issue, the present paper reports pyrolysis studies with a direct pyrolysis MS system coupled to a direct insertion probe capable of heating up to 650 °C in order to gain more insight on thermal degradation processes of PPVs with well defined PCL or PSt as lateral substituents.

Experimental

Synthesis

The details of synthesis of PPVs with PCL (PPV–PCL), or alternating PCL and bromide (PPV–PCL–Br) or PSt (PPV–PSt) as lateral substituents and initiators are given in our previous study [9]. Shortly, ring-opening polymerization (ROP) of ε-caprolactone (CL) or atom transfer radical polymerization (ATRP) of styrene (St) in the presence of bifunctional initiators 2,5-dibromo-1,4-(dihydroxymethyl)benzene and 1,4-dibromo-2-(bromomethyl)benzene, respectively, provided well-defined low molecular mass polymers with dibromobenzene moieties. Suzuki coupling of these bromobenzene functions with 4-formylphenyl bronic acid yielded macromonomers having 4,4'-dicarbaldehyde terphenyl moieties. PPVs with PCL or PSt as lateral substituents were synthesized by following a Wittig polycondensation in combination with bis(triphenyl phosphonium) salts in the presence of potassium terbutoxide. General synthetic procedures followed in this work are summarized in Scheme 1.

Instrumentation

Direct pyrolysis mass spectrometry (DPMS) system consisting a Waters Quattro Micro GC tandem mass spectrometer with an EI ion source and a mass range of 10–1500 Da was coupled a direct insertion probe (T_{max} = 650 °C). In each experiment, the temperature was kept constant at 50 °C for the first 5 min to remove any absorbed water and then increased to 650 °C at a heating rate of 10 °C min^{-1}, and kept constant for an additional 10 min at 650 °C. 0.010 mg samples were pyrolyzed in the quartz sample vials. Pyrolysis experiments were repeated at least twice to ensure reproducibility.

Results and discussions

The direct pyrolysis-MS system used in this study is totally different than the one that was used in our previous studies on thermal degradation of PPV with PCL or PSt as lateral substituents [14, 15]. Yet, the temperatures at which thermal degradation takes place and the peaks present in the pyrolysis mass spectra are almost identical up to 450 °C, the maximum attainable temperature for the previous system, indicating the reproducibility and the power

Scheme 1 Synthesis of PPVs with well defined PCL or PSt as lateral substituents
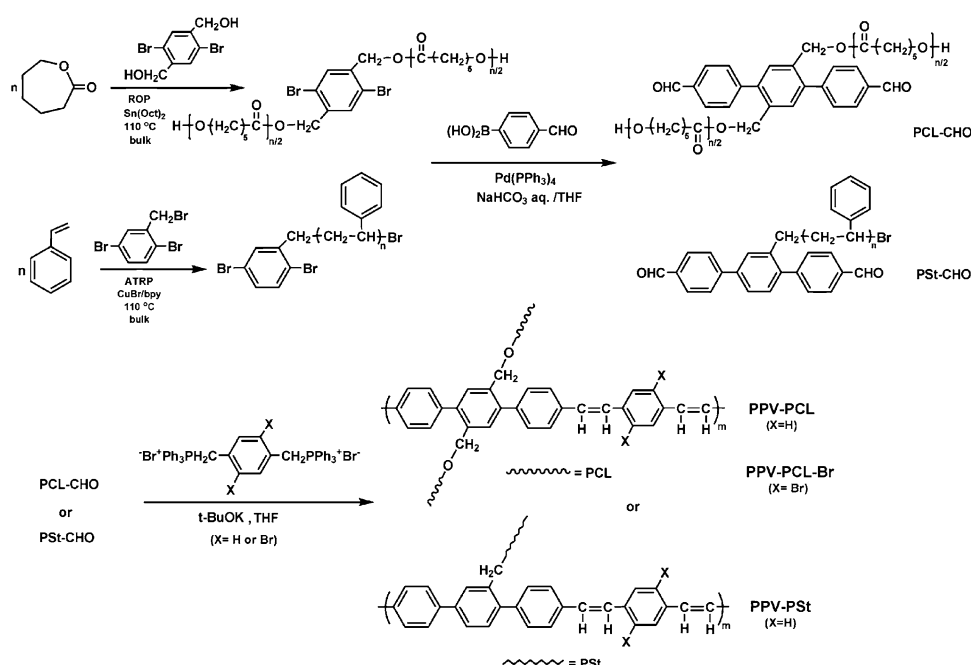
of the techniques used. Of course variations in peak intensities are detected not only because of the expected mass discrimination of two different analyzers with two different mass ranges but also because of the further heating up to 650 °C.

PPV with PCL as lateral substituents

Total ion current, (TIC), curve, (the variation in total ion yield as a function of temperature), for PPV with PCL as lateral substituents, PPV–PCL, showed a broad peak with a maximum at 415 °C and shoulders around 350 and 450 °C in accordance with our previous results. However, a weaker peak with maximum around 495 °C was also detected. The single ion pyrograms of the decomposition products of

PCL showed two peaks; a broad peak with a maximum at 410 °C and a weak one around 495 °C (Fig. 1). Though there were inconsistencies in the proposed degradation mechanism of PCL, the formation of ω-hydroxyl and ketene end groups have been confirmed by several groups [12, 14, 16–20]. Present results were in agreement with the reported findings as well as with our previous studies. The main decomposition products of PCL were the fragment with $m/z = 55$ Da attributed to $O=CCH=CH_2$ and the protonated monomer ($m/z = 115$ Da) [12, 14]. As the number of repeating unit increased, the peak with maximum at 410 °C was sharpened and the relative intensity of the shoulders on both sides decreased drastically as can be observed in the evolution profile of $O=C=CH(CH_2)_4O$ $(CL)_3CO(CH_2)_3CH=CH_2$ ($m/z = 552$ Da) fragment.
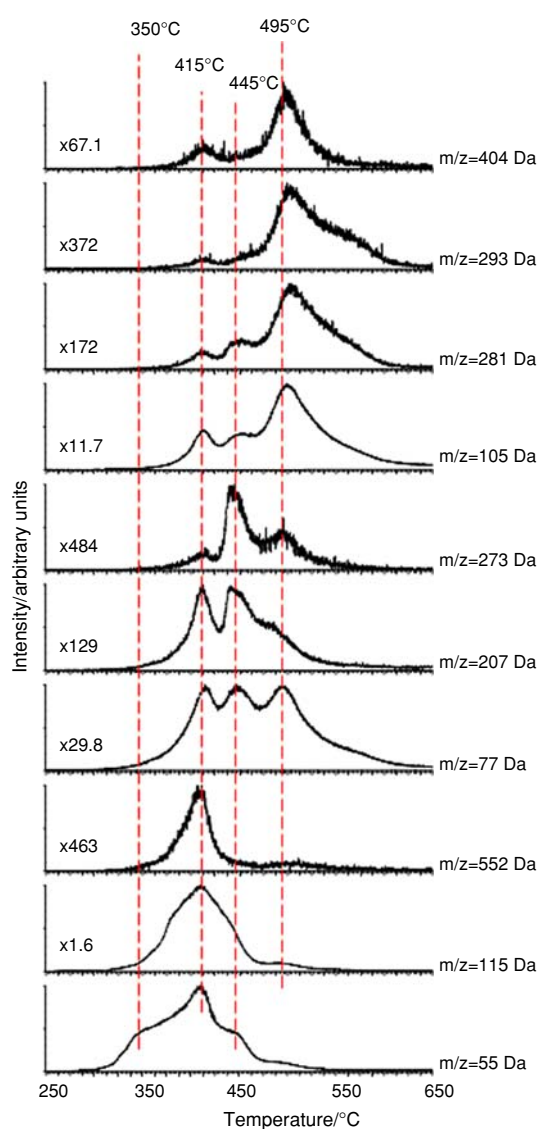

Fig. 1 Single ion pyrograms of some selected degradation products of PPV with PCL side chains, PPV–PCL
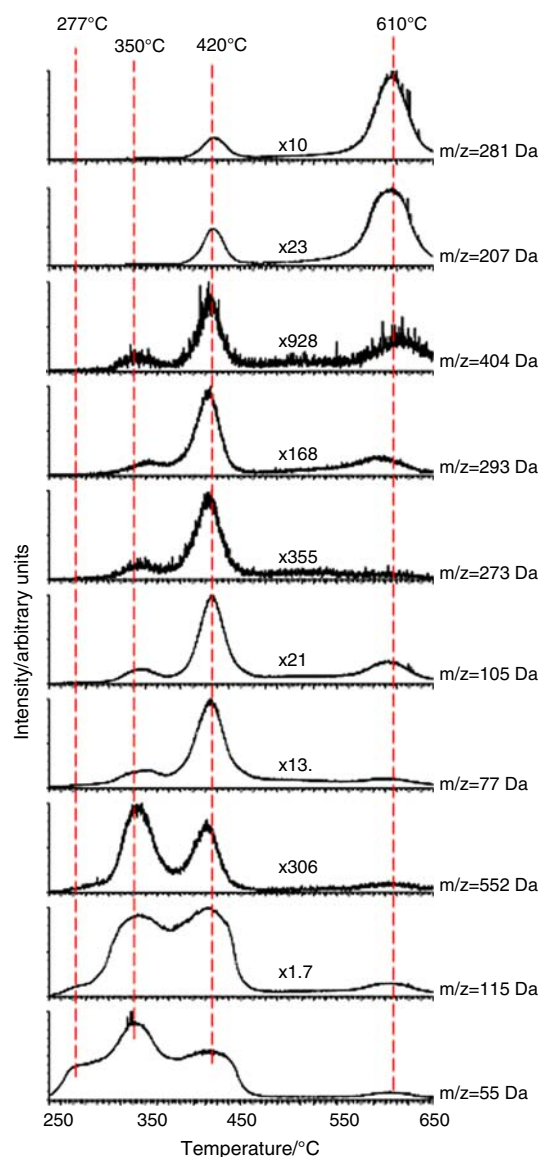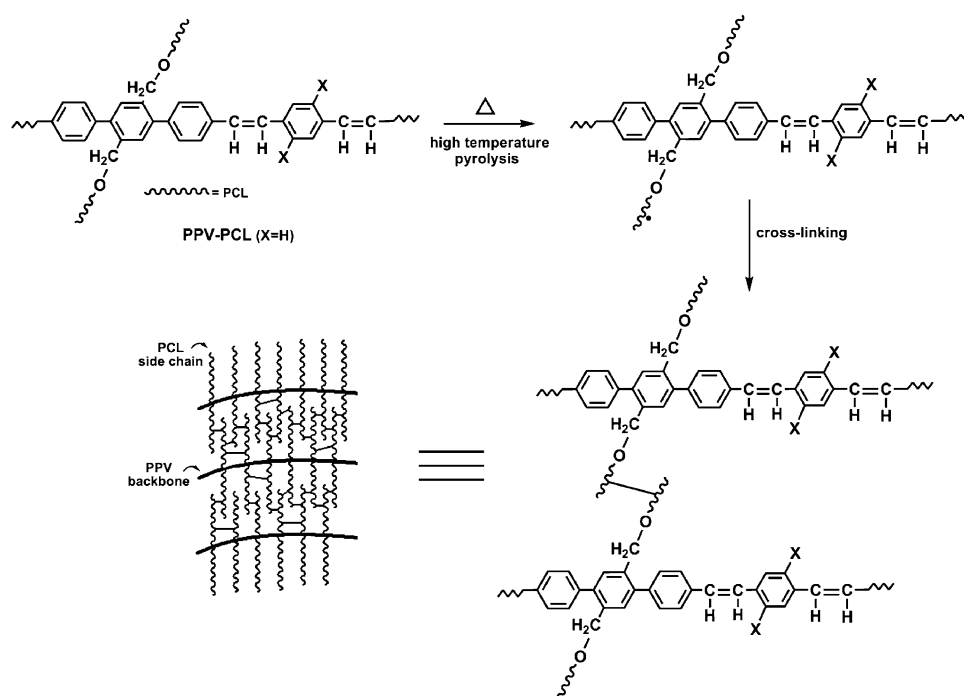
Fig. 2 Single ion pyrograms of some selected degradation products of PPV with alternating PCL side chains and Br, PPV–PCL–Br

Scheme 2 Formation of cross-linked networks by coupling of radicals formed on side chains during thermolysis of PPV–PCL

The evolution profiles of the products due to the degradation of PPV backbone showed three peaks with maxima at 415, 445 and 495 °C. The evolution of $C_6H_5C_2H_4$ ($m/z = 105$ Da) and C_6H_5 ($m/z = 77$ Da) was significant throughout the pyrolysis as expected since it can be generated by decomposition of units with different thermal stabilities. The evolution profiles of the fragments involving both PPV and PCL units such as hydroxymethylbenzene, $HC=CHC_6H_4C_6H_3CH_2OH$ ($m/z = 207$ Da) and $C_6H_5C_7H_6(CH_2OH)C_6H_5$ ($m/z = 273$ Da) showed an intense peak at around 445 °C. On the other hand, the intensities of the peaks associated with the fragments mainly due to decomposition of PPV backbone, involving phenylene vinylene units, namely $C_6H_5(C_6H_4CH=CH)_2$, ($m/z = 281$ Da), $CH_2C_6H_3(C_6H_4CH=CH)_2$, ($m/z = 293$ Da) and $C_{32}H_{20}$, ($m/z = 404$ Da) were maximized around 495 °C. Evolution of fragments such as $C_{32}H_{20}$ ($m/z = 404$ Da) that can directly be attributed to products involving H deficiency revealed presence of a crosslinked structure contrary to the results of Gedelian et al. [10]. In a recent study, they investigated the thermal degradation characteristics of heat treated PPV films by in situ mass spectroscopy and FTIR spectroscopy and found out that the decrease in film thickness was due to release of compounds such as toluene and xylene, but not to cross-linking or bond breaking [10]. In our case, however, PPV–PCL contains less stable aliphatic alkyl groups which may generate radicals directly or by hydrogen abstraction of the radicals formed during thermolysis. Regardless of their generation mode these radicals are capable of undergoing intermolecular coupling reactions to form insoluble cross-linked networks

(Scheme 2). Evolution of PCL based products also around 495 °C supports existence of such radical–radical coupling reactions.

It is clear that for PPV–PCL both PCL and PPV affected the thermal stability of the other significantly. The increase in the thermal stability of PCL chains, arising from the cross-linking described above, was more significant, being about 100 °C [14].

Notably, the thermal stability of PPV backbone also increased up to the literature values [10].

PPV with alternating PCL and bromine as lateral substituents

For comparison, pyrolysis studies with structurally similar PPV, but containing alternating bromine substituents, (PPV–PCL–Br) (See Scheme 1 for the structure) were also performed. The TIC curve of PPV–PCL–Br showed four peaks with maxima around 277, 350, 420 and 610 °C. Two intense peaks with maxima at 350 and 420 °C and weak peaks at 277 and 610 °C were detected in the evolution profiles of PCL based products (Fig. 2). Inspection of single ion evolution profiles of PCL based products attributed to $O=CCH=CH_2$ ($m/z = 55$ Da), protonated monomer ($m/z = 115$ Da) and $O=C=CH(CH_2)_4O(CL)_{3-}CO(CH_2)_3CH=CH_2$ ($m/z = 552$ Da) indicated that loss of low molar mass fragments was started just above 250 °C. Thus, it can be concluded that reactions of Br and/or HBr with PCL side chains caused loss of low mass fragments decreasing the thermal stability [14]. However, the

evolution profiles of the products that can directly be attributed to decomposition of PPV backbone also showed three peaks with maxima at 350, 420 and 610 °C, contrary to the single ion evolution profiles with a single peak with a maximum at 445 °C recorded previously [14]. In our previous study, the maximum attainable temperature was 450 °C, the temperature was increased to 450 °C at a rate of 10 °C min^{-1} and kept at this temperature for an additional 10 min. Present results indicated that the thermal degradation of PPV backbone was not completed at around 420 °C. Thus, the peak maximum in the evolution profiles of fragments involving C_6H_5 units might have been shifted to 445 °C as a result of continued decomposition. The base peak in the pyrolysis mass spectra recorded around 610 °C was at 207 Da and associated with $HC=CHC_6H_4C_6H_3$ CH_2OH. The yield of $C_6H_5(C_6H_4CH=CH)_2$ ($m/z = 281$ Da) was also noticeably high at elevated temperatures. These fragments were also detected during the pyrolysis of PPV with PCL as lateral substituents. Yet, they were quite weak. The high temperature shift of about 115 °C observed for the PPV based products revealed the formation of highly stable crossed-linked structure. In this case, the observed cross-linking occurs through the combination of the polymeric phenyl radicals formed from the loss of labile bromine atoms (Scheme 3). This is in contrast to the behavior of PPV–PCL where cross-linking occurs through lateral PCL substituents (see vide ante).

PPV with PSt as lateral substituents

It was reported that pyrolysis of the precursor macromonomers, namely PSt with 1,4 dibromo phenylene end groups and PSt with 4,4′-dicarbaldehyde terphenyl end groups, indicated depolymerization of PSt yielding mainly styrene. The single ion evolution profiles showed two overlapped peaks with maxima at around 410 and 445 °C
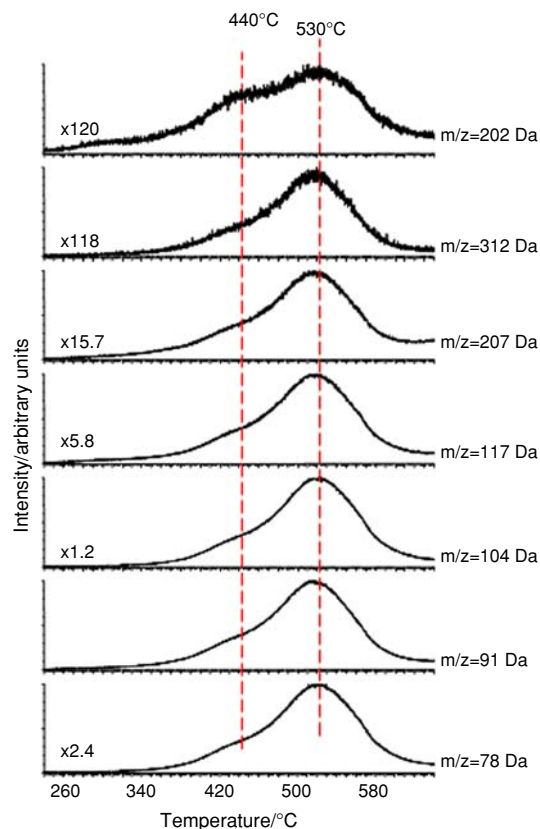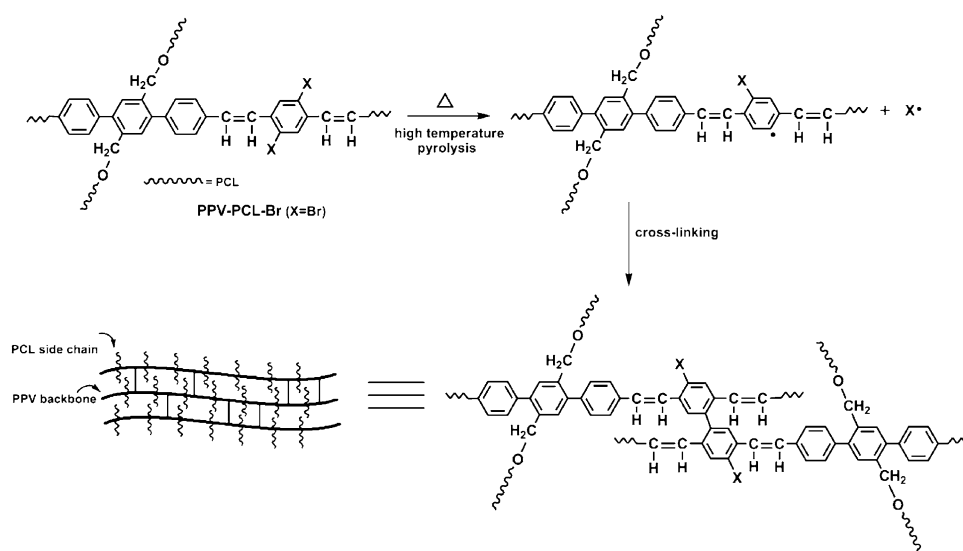

Fig. 3 Single ion pyrograms of some selected degradation products of PPV with PSt side chains, PPV–PSt

Scheme 3 Formation of cross-linked networks by coupling of radicals formed on PPV backbone during thermolysis of PPV–PCL–Br

[15]. The TIC curve of PPV derived form these macromonomers, PPV–PSt showed a broad peak with a maximum around 530 °C. Almost all the decomposition products showed identical evolution profiles; a broad peak with a maximum at 530 °C and a shoulder at 450 °C. Evolution profiles of intense and/or characteristic degradation products presented in Fig. 3, are in accordance with classical depolymerization decomposition mechanism of PSt [15, 21–23]. Unfortunately, it is almost impossible to differentiate the products either from the decomposition of PPV backbone or PSt side-chain.

Conclusions

High temperature pyrolysis studies of PPV with PCL, or PCL and alternating Br or PSt lateral substituents clearly showed that the thermal stability of PPV was affected by the thermal stability of the substituents. In all the polymers under investigation decomposition started by loss of and/or decomposition of the less stable lateral substituents. The thermal stability of the samples increased in the order PPV–PCL–Br < PPV–PCL < PPV–PSt as the stability of the substituent increased. On the other hand, when the thermal stability of the substituent was significantly lower than that of the PPV backbone, the radicals generated at early stages of pyrolysis coupled generating a more stable cross-linked structure. The increase in thermal stability is greater when the radicals generated were on the PPV backbone as in the case of PPV–PCL–Br involving alternating Br substituents. No crosslinking was detected for PPV–PSt for which thermal stability of PSt lateral substituents was comparable to the PPV backbone.

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