



Thermal decomposition of polystyrene-*b*-poly(2-vinylpyridine) coordinated to co nanoparticles

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ABSTRACT

Direct pyrolysis mass spectrometry analyses of polystyrene-block-poly(2-vinylpyridine), PS-*b*-P2VP, indicated that the thermal degradation of each component occurred independently through the decomposition pathways proposed for the corresponding homopolymers; depolymerization for PS and depolymerization and loss of protonated oligomers for P2VP by a more complex degradation mechanism. On the other hand, upon coordination to cobalt nanoparticles, thermal decomposition of the P2VP blocks was initiated by loss of pyridine units, leaving an unsaturated and/or crosslinked polymer backbone that degraded at relatively high temperatures.

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1. Introduction

During the last decades, the incorporation of nanomaterials with block polymers has been the subject of many studies because of the potential applications in optics, catalysis, biosensors, microelectronics and magnetic data storage [1–9]. As a consequence of the strong affinity of amines to various ions and polar groups, polymers containing a pyridine moiety can make strong bonds with various metal ions or nanoparticles and have attracted increasing attention. PS-*b*-P2VP copolymer has been extensively studied and has also been used in nanoparticle assembly into block copolymers.

Enhancement of thermal stability of the polymer is expected as a result of metal and/or metal ion coordination [10–15]. Khairou investigated the thermal stability of poly(4-vinylpyridine) and its complex with transition metal chlorides and found that the degradation products mainly consist of 4-vinylpyridine monomer and traces of pyridine [11]. Lyons and co-workers studied the thermal degradation characteristics of poly(2-vinylpyridine) (P2VP) and its complexes with copper chloride via TGA and GC–MS and proposed changes in the thermal degradation mechanism of P2VP [12], but they were unable to propose related thermal

degradation mechanisms. In the case of pyrolysis GC–MS analysis, since thermal decomposition occurs in a closed container/system, secondary reactions cannot be avoided and only low molecular weight volatile species can be detected. Thus, in most cases, with the use of pyrolysis GC–MS data, the investigation of the thermal decomposition mechanism is almost impossible [16].

In the present study we applied direct pyrolysis mass spectrometry to investigate the thermal degradation behaviour of polystyrene-block-poly(2-vinylpyridine), PS-*b*-P2VP, and PS-*b*-P2VP coordinated to cobalt nanoparticles in order to elucidate the effect of metal coordination on thermal characteristics by direct pyrolysis mass spectrometry to investigate the changes in thermal behaviour.

2. Experimental

2.1. Materials and synthesis

The block copolymers PS-*b*-P2VP, were synthesized by sequential polymerization of the corresponding monomers by anionic polymerization using high vacuum techniques [17]. After the complete polymerization of styrene in tetrahydrofuran at –78 °C with *n*-BuLi as initiator, 2-vinylpyridine was distilled into the reactor and the polymerization was allowed to proceed for 1 h before being terminated with degassed methanol. The block copolymers were recovered by precipitation in methanol. The molecular

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characteristics of the block copolymers, as shown in Table 1, were determined by size exclusion chromatography (SEC), low angle laser light scattering (LALLS) and ^1H NMR spectroscopy. Two additional block copolymers were purchased from Polymer Source Inc. (PS: $M_n = 58,000$, P2VP: $M_n = 16,500$, PDI = 1.08 and PS: $M_n = 25,000$, P2VP: $M_n = 15,000$, PDI = 1.04).

Co_2CO_8 used in the synthesis of Co functional copolymer was purchased from Aldrich Chemical Company and used without further purification. Cobalt functional PS-*b*-P2VP polymers were prepared according to the literature methods [18]. In brief, 150 mg PS-*b*-P2VP were completely dissolved in 15 mL toluene (bp: 108–109 °C). To this solution, 300 mg (0.877 mmol) $\text{Co}_2(\text{CO})_8$ were added. The mixture was refluxed under deoxygenated nitrogen atmosphere for 8 h at the boiling point of toluene, 110 °C. Finally, the solvent was evaporated under vacuum. The resulting product was analyzed by means of TEM, FTIR and direct pyrolysis mass spectrometry.

2.2. Instrumentation

Thermogravimetric analyses (TGA and DTA) were conducted on Perkin Elmer Pyris 1 TGA equipment, heating at 10 °C/min under nitrogen atmosphere from ambient temperature to 700 °C.

The FTIR spectra of the samples milled with KBr were recorded on a Nicolet 510 FTIR Spectrometer.

TEM imaging of the nanoparticles was carried out with a Philips CM20 instrument at 200 kV (iNANO – The University of Aarhus, Denmark). The nanoparticles were dispersed on the carbon-coated copper grid from their diluted suspension of toluene.

Direct pyrolysis mass spectrometry, DP-MS, analyses were performed on a Waters Micromass Quattro Micro GC Mass Spectrometer with a mass range of 10–1500 Da and EI ion source, coupled to a direct insertion probe. During the pyrolysis, the temperature was increased to 50 °C at a rate of 5 °C/min, and was then raised to 650 °C with a rate of 10 °C/min and kept at 650 °C for 5 additional minutes while recording the 70 eV EI mass spectra at a mass scan rate of 1 scan/s. The analyses were repeated several times to ensure reproducibility. Each time, almost exactly the same trends were detected.

3. Results and discussion

The direct pyrolysis mass spectra of the polymers, especially those of copolymers, are usually very complex since thermal degradation products further dissociate in the mass spectrometer during ionization. Furthermore, all the fragments with the same mass to charge ratio contribute to the intensity of the same peak in the mass spectrum. Thus, for the analysis of metal functionalized PS-*b*-P2VP block copolymers, DP-MS analyses of both the PS-*b*-P2VP block copolymers and refluxed copolymers were also carried out under the same conditions in the absence of the Co-carbonyl complex, for comparison, in order to investigate the effect of the metal on the thermal behaviour of copolymer.

Table 1
Molecular characteristics of diblock copolymers PS-*b*-P2VP.

Sample	$M_w^a \times 10^{-3}$	$\text{PDI} = M_w/M_n^b$	wt% PS ^c	wt% P2VP ^c
1	50	1.06	90.0	10.0
2	50	1.09	80.0	20.0
3	10	1.16	44.0	56.0
4	18	1.08	50.0	50.0
5	33	1.19	42.0	58.0

^a Determined by LALLS in THF at 25 °C.

^b Determined by SEC in THF at 40 °C.

^c Determined by ^1H NMR in CDCl_3 at 25 °C.

3.1. Polystyrene-*block*-poly(2-vinylpyridine), PS-*b*-P2VP

It is known that PS degrades in a single step by a depolymerization reaction to yield, mainly, the monomer, styrene and some low molecular weight oligomers [19]. In a recent study, we proposed a complex degradation mechanism for P2VP, in contrast to that of PS, to produce protonated oligomers in addition to the depolymerization reactions and associated the evolution of protonated oligomers with the position of nitrogen atom in the pyridine ring and the σ effect [20]. DP-MS studies revealed that during the pyrolysis of the copolymer, each component decomposed independently via the decomposition pathways identified for the corresponding pure homopolymers. The total ion current, TIC, curves (variation of total ion yield as a function of temperature) of the diblock copolymers, having variable compositions showed only a slight shift to high temperatures with increasing molecular mass of the copolymer, indicating that the change in the composition or molecular weight in the ranges studied did not have a significant effect on the thermal stability of the copolymer. Furthermore, pyrolysis mass spectra of all the samples were dominated by identical peaks corresponding to monomer and low mass oligomers of both components and to protonated oligomers of P2VP, as well as to fragments generated by dissociative EI ionization, indicating that not only the thermal stability but also the thermal degradation mechanism were independent of the composition and molecular mass of the sample in the range studied. The only noticeable difference was the variations in the relative intensities of the peaks; as the PS content increased the relative intensities of the diagnostic peaks of PS also increased, as expected.

The TIC curve and the pyrolysis mass spectra at 375 °C and 428 °C, at the peak maximum and the shoulder present in the TIC curve, recorded during the pyrolysis of PS-*b*-P2VP ($M_n(\text{PS}) = 58,000$; $M_n(\text{P2VP}) = 16,500$ and $\text{HI} = 1.08$) are shown in Fig. 1. The characteristic peaks of PS were relatively more intense than those of P2VP in the pyrolysis mass spectra of the block copolymer, as expected, considering the composition of the diblock copolymer. Peaks due to styrene (St) and 2-vinylpyridine (VP) monomers and low mass oligomers were among the most intense (Table 2).

To obtain a better understanding of the degradation behaviour of the diblock copolymer, the evolution profiles of characteristic products associated with each block were studied in detail. Some examples are given in Fig. 2. The trends in the evolution profiles indicated a lower thermal stability for P2VP block compared to PS block. The yield of the thermal degradation products of P2VP blocks was maximized at around 428 °C, at slightly lower temperatures than the corresponding value for the PS block that maximized at around 437 °C. Evolution of protonated trimer and tetramer of V2P, produced by a complex mechanism due to the proton transfer from the main chain to the N at σ position, was detected at slightly higher temperatures compared to the evolution of oligomers generated through a depolymerization mechanism as in the case of P2VP homopolymer [20]. The yields of the protonated oligomers were higher than the corresponding oligomers and were maximized at around 441 °C.

3.2. Polystyrene-*block*-poly(2-vinylpyridine) coordinated to Co nanoparticles, co-PS-*b*-P2VP

Theoretically, nanoparticle formation starts by the coordination of the electron-rich segment of the copolymer (2-vinylpyridine here) to the metal atom with the exclusion of the ligands. As a result of bonding of the pyridine nitrogen to the metal atom, the pyridine stretching and bending modes should be affected [21]. A comparison of FTIR spectra for the polymers PS-*b*-P2VP and Co-PS-*b*-P2VP

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