

Thermal degradation of poly(2-vinylpyridine) copolymers

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ABSTRACT

The thermal degradation characteristics of block copolymers of poly(2-vinylpyridine) with polystyrene, PS-*b*-P2VP, polyisoprene, PI-*b*-P2VP and poly(methyl methacrylate), P2VP-*b*-PMMA, were investigated via pyrolysis mass spectrometry. DP-MS analyses indicated that the thermal degradation of each component of the copolymers, except P2VP-*b*-PMMA, occurred independently through the decomposition pathways proposed for the corresponding homopolymers. In case of P2VP-*b*-PMMA, significant decrease in the thermal stability of P2VP chains and evolution of products generated due to strong interaction between P2VP and PMMA chains were detected.

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1. Introduction

Nanostructures have received great attention recently due to their special optical, electronic, magnetic and chemical properties [1–3]. One approach in forming nanostructures is using nanoscale building blocks by self-assembled block copolymers [4–7]. Well-defined micelles with uniform diameters and shapes that are microcompartments with characteristic length scales between 10 and 100 nm can be formed from the diblock copolymers by using a selective solvent. Arrangement of these microcompartments on a superlattice leads the nanoparticles to integrate into the lattice which gives rise to the formation of nanostructured inorganic/polymer hybrid structures.

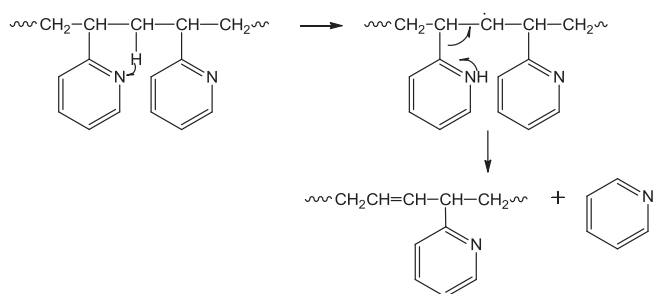
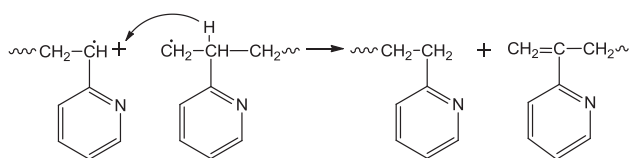
Diblock copolymers, having poly(vinylpyridine) (PVP) blocks as a polar group and polystyrene, or polyisoprene as the hydrophobic block have been used in coordination approaches commonly [8–13]. Few studies in which polymethacrylates were used as the hydrophobic block also appeared in the literature [14,15]. As the nitrogen atom on the pyridine has the capacity to coordinate with metals, poly(vinylpyridine)s (PVP) act as a matrix

for the metal nanoparticles. The micelle formation is achieved in an apolar solvent in the presence of hydrophobic blocks and hybrid materials are formed, when metals are incorporated into these kinds of polymer matrices [4,7].

Thermal degradation characteristics of such materials are one of the most important properties that determine the application areas. In a recent work, we discussed the change in thermal degradation characteristics of polystyrene-*b*-poly(2-vinylpyridine) copolymer upon coordination to cobalt metal [11]. A significant change in thermal stability and degradation mechanism of P2VP blocks were detected while PS blocks retained its original characteristics. Though several studies on preparation and application of these important materials have been carried out, the knowledge on effect of hydrophobic block on characteristics of the hybrid materials is limited [1,7]. In order to investigate the effect of metal coordination on thermal characteristics, the thermal degradation behavior of the copolymers has to be known. To our knowledge, only few studies that comprehensively address thermal degradation behavior of poly(vinylpyridine) block polymers appeared in the literature [11,16].

In this study, we report thermal degradation characteristics of three common diblock copolymers polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP), polyisoprene-*b*-poly(2-vinylpyridine) (PI-*b*-P2VP) and poly(2-vinylpyridine)-*b*-poly(methyl methacrylate) (P2VP-*b*-PMMA) investigated by direct pyrolysis mass spectrometry. Our future work will focus on the effect of coordination of metals on thermal characteristics of these block copolymers.

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a H-transfer to N atom in the pyridine ring**b** H-transfer to the chain ends

Scheme 1. H-transfer reactions generating unsaturated units and pyridine. (a) H-transfer to N atom in the pyridine ring. (b) H-transfer to the chain ends.

2. Experimental

2.1. Materials

PS-*b*-P2VP (PS: $M_n = 58,000$, P2VP: $M_n = 16,500$, PDI = 1.08), PI-*b*-P2VP (PI: $M_n = 19,200$, P2VP: $M_n = 12,200$, PDI = 1.03), and P2VP-*b*-PMMA (PMMA: $M_n = 56,000$, P2VP: $M_n = 57,000$, PDI = 1.09), were purchased from Polymer Source Inc. and used as received.

2.2. Instrumentation

Direct pyrolysis mass spectrometry, DP-MS, analyses were performed by Waters Micromass Quattro Micro MS/MS/MS Mass

Spectrometer with a mass range of 10–1500 coupled to a direct insertion probe. During the pyrolysis, the temperature was increased to 50 °C at a rate of 5 °C min⁻¹, then, was raised to 650 °C with a rate of 10 °C min⁻¹ and kept at 650 °C for five additional minutes. 0.01 mg samples were pyrolyzed in the flared quartz sample vials while recording 70 eV EI mass spectra at a mass scan rate of 1 scan s⁻¹. The analyses were repeated several times to ensure reproducibility. Each time, almost exactly the same trends were detected. It is known that direct pyrolysis mass spectra of polymers are usually very complex, as thermal degradation products further dissociate in the mass spectrometer during ionization and all fragments with the same mass to charge ratio make contributions to the intensities of the same peaks in the mass spectrum [17,18]. The pyrolysis mass spectra of copolymers are even more complicated, especially if similar units are present. Therefore, the trends in the single ion evolution profiles of diagnostic thermal degradation products of each block are used to determine the source of the product and/or the mechanism of thermal degradation.

In collision-induced dissociation (CID), experiments, daughter ions were produced by the collision of the selected particular ion with argon in the collision cell, the second quadrupole. The CID spectra were obtained by scanning of the third quadrupole mass analyzer.

3. Results and discussion

Unfortunately, copolymers involving P2VP blocks with almost the same M_n value were not available. However, in a recent study, DP-MS results indicated that thermal stability of P2VP is almost independent of the molar mass; maximum product yields were detected at 439 and 435 °C during the pyrolysis of P2VP with $M_n = 60,000$ and 11,000 respectively [11].

P2VP decomposes mainly by depolymerization yielding monomer and low molecular weight oligomers [11,20]. Yet, H-transfer reactions, which in turn increases thermal stability by coupling of the radicals generated yielding unsaturated linkages along the polymer backbone and/or cross-linking, and loss of pyridine also take place as shown in Scheme 1 [18].

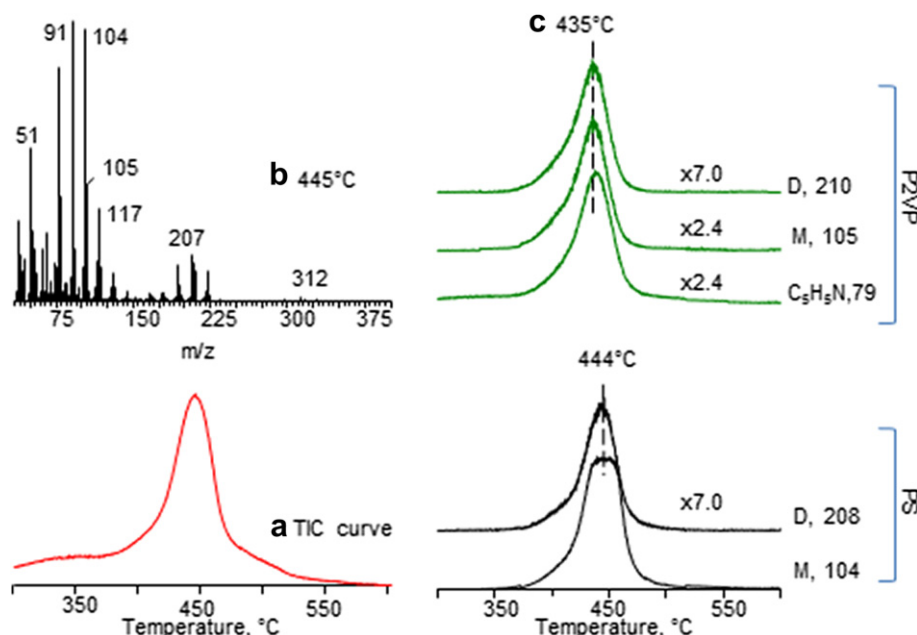


Fig. 1. (a) TIC curve, (b) pyrolysis mass spectrum at 445 °C and (c) single ion evolution profiles of some selected products detected during the pyrolysis of PS-*b*-P2VP.

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