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Thermal stability and degradation behavior of novel wholly aromatic azopolyamide-hydrazides

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Thermal stability and degradation behavior of a series of novel wholly aromatic azopolyamide-hydrazides have been investigated in nitrogen and in air atmospheres using differential scanning calorimetry, thermogravimetry, infrared spectroscopy and elemental analysis. The influences of controlled structural variations and molecular weight on the thermal stability and degradation behavior of this series of polymers have also been studied. The structural differences were achieved by varying the content of para- and metasubstituted phenylene rings incorporated within this series. The polymers were prepared by a low temperature solution polycondensation reaction of paminosalicylic acid hydrazide and an equimolar amount of 4,4'-azodibenzoyl chloride [4,4'-ADBC] or 3,3'-azodibenzoyl chloride [3,3'-ADBC] or mixtures of various molar ratios of 4,4'-ADBC and 3,3'-ADBC in anhydrous N,N'-dimethyl acetamide [DMAc] containing lithium chloride as a solvent at -10 °C. The results clearly reveal that these polymers are characterized by high thermal stability. Their weight loss occurred in three distinctive steps. The first was small and assigned to the evaporation of absorbed moisture. The second was appreciable and was attributed to the cyclodehydration reaction of the hydrazide groups into 1,3,4-oxadiazole rings by losing water, combined with elimination of azo groups by losing molecular nitrogen. This is not a true degradation but rather a thermo-chemical transformation reaction of the azopolyamide-hydrazides into the corresponding polyamide-1,3,4-oxadiazoles. The third was relatively severe and sharp, particularly in air, and corresponded to the decomposition of the resulting polyamide-1,3,4-oxadiazoles. In both degradation atmospheres, the improved resistance to high temperatures was always associated with increased content of para-phenylene moieties of the investigated polymer. Further, with exception of 160-200 °C temperature

range, where the lower molecular weight samples showed considerable weight losses which were most probably due to hydrogen bonded DMAc, all the wholly para-oriented phenylene type of polymer samples behaved similarly regardless of their respective molecular weight. This seems to indicate that the structural building units responsible for high thermal stability of the polymers are their characteristics groups, rather than the longer chain segments.