

Thermal and Combustion Characteristics of Polyacrylonitrile Containing Covalently-bound Phosphonate Groups

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Main Message. A number of phosphorus-containing acrylic monomers were synthesised and copolymerised with acrylonitrile (AN), under radical initiation in an inert atmosphere, through an aqueous slurry route. It was found that the incorporation of phosphonate groups in polyacrylonitrile (PAN) chains resulted in improved flame-retardant characteristics. It was also observed that the actual chemical environment of phosphorus atom in the modifying groups has an influence on the thermal degradation and combustion attributes of the modified systems.

Key words. Polyacrylonitrile; Acrylic Phosphonates; Thermal Degradation; Combustion Characteristics; Flame Retardance

Introduction

Staple fibres based on PAN, being soft and resilient, are used as substitutes or diluents for wool, and fabrics made from them often demonstrate good crease resistance and retention. Owing to the relatively high melting point and significant carbon yields, PAN fibres are considered to be the most suitable precursors of high performance carbon fibres [1]. When exposed to prolonged heating PAN undergoes an extensive degradation involving the production of combustible volatile compounds such as acrylonitrile, ammonia, organic and inorganic nitriles as well as varying amounts of char; the latter strongly depending on the rate of heating [2]. Acrylic fibres are characterised by a Limiting Oxygen Index (LOI) value of around 18, and burn quite readily accompanied by melting and sputtering. Generally, the mechanism of PAN thermal degradation depends on the heating rate [3].

Experimental

All chemicals including initiators and solvents were purchased from Sigma Aldrich (UK) with the exception of acryloyl chloride, which was obtained from Alfa Aesar (UK). Acrylonitrile (AN) was freed from the inhibitor, 4-methoxyphenol, by passing it through a column of activated basic alumina and then consequently stored over molecular sieves (4 Å type) at 0-5°C. The solvents and other reagents were purified, if necessary, by standard literature procedures. The following comonomers were synthesised according to the method described in [4]: diethyl(acryloyloxymethyl)phosphonate (DEAMP); diisopropyl(acryloyloxymethyl)phosphonate (DiPAMP); diethyl(1-acryloyloxyethyl)phosphonate (DE1AEP); diethyl(acryloyloxyethyl)phosphonate (DEAEP); and diisopropyl(acryloyloxyethyl)phosphonate (DiPAEP).

Homo- and co-polymers of AN were prepared in an aqueous slurry phase, using a redox initiator system consisting of sodium metabisulfite and ammonium persulfate, at 40°C under argon, for about 24 hours. The polymers formed were collected by filtration, washed several times with de-ionized water, and were dried to constant weights in a vacuum oven before further examinations. ¹H and ³¹P NMR spectra were recorded on the solutions of the polymers dissolved in d₆-DMSO using a Bruker 500 MHz NMR spectrometer, under ambient probe conditions. Thermogravimetric analyses (TGA) were carried out on ca. 10 mg samples, on a Mettler Toledo TGA/SDTA 851^e instrument in the temperature range of 30-700°C, under both nitrogen and air atmospheres, at a heating rate of 10°C/min. Pyrolysis Combustion Flow Calorimetry (PCFC) measurements were carried out using a Fire Testing Technology Ltd (FTT) instrument, which works on a principle of oxygen consumption calorimetry. The instrument primarily generated plots of the Heat Release Rates (HRR) against time. It