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Phenyl-methyl phosphazene derivatives for preparation and modification of hydrophobic properties of polymeric nonwoven textiles

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ABSTRACT

This paper focuses on the preparation of two types of hydrophobic nanolayers using electrospinning technology. The first synthetic approach consists in direct fiberizing of polymeric phenyl-methyl-polyphosphazene Ph-Me(p) with the aim to preparing nanolayers that have significant hydrophobicity and thermal stability. The preparation of Ph-Me(p) is a multi-step reaction which produces a relatively low amount of the product. The second area of our interest was the creation of nanofibers formed from a mixture of some commercially available organic polymers and a *cyclo*-phosphazene derivative. In this case, tri(phenyl)-trimethyl-*cyclo*-triphosphazene, Ph-Me(t), whose synthesis is less complicated than its polymeric form, was used as an additive. The influence of the Ph-Me(t) additive in the nanofibers on the affinity to water was compared with the affinity of nanolayers made from a pure commercial polymer, i.e. without any phosphazene additive. It was also shown that the hydrophobic properties of fibers formed from Ph-Me(p) dissolved especially in THF are better than those of the nanofibers composed of a commercial polymer with the addition of Ph-Me(t).

1. Introduction

There are many researchers who concentrate on the functionalization of nanofiber layers. However, this modifying process, influenced by the structure of the respective polymer, leads to newly created bonds that could modify significantly the properties of the final product [1]. It is usually expected that any additive to a polymer can preserve the polymer's original chemical structure wherein certain physical properties (such as hydrophobicity) of the modified polymer can be changed. [2].

It can be also expected that the original properties of a polymer and those of the additive merge into more suitable properties of the resulting material. A common *cyclo*-phosphazene derivative, containing non-polar organic side groups, could significantly increase the hydrophobic character of the whole *cyclo*-phosphazene molecule [10] as well as the hydrophobic character of the whole modified polymer. The mixture, containing a polymer and an additive, can be further shaped by various processing techniques, e.g. electrospinning, which is widely used for producing polymer nanofibers.

The following phosphazene compounds – trimeric tri(phenyl)-trimethyl-*cyclo*-triphosphazene, Ph-Me(t) (used as an additive), and polymeric phenyl-methyl-polyphosphazene, Ph-Me(p) – were synthesized according to the methods proposed by Patty Wisian-Neilson [3,4] (Schemes 1 and 2).

The electrospinning technology, which was used in the fiberizing process, is based on the creation of fibers in a high electrostatic field. The nanofibers are created from the surface of a polymer solution (or from its melt) placed on the top of the static powered rod. When the electrical field reaches its critical value, nanofibers are ejected from the positively-charged rod electrode towards the grounded negative electrode, called the collector. The solvent evaporates during this process and nanofibers are deposited on the supporting textile material, e.g. polypropylene foil (PP band), that the collector is covered with. [5–9] Fig.1 shows the scheme of the electrospinning device.

Nanotextiles, made commonly by electrospinning from commercial polymers, can be modified either by addition of the simple phosphazene Ph-Me(t), or they can be made directly from its polymeric form, i.e. Ph-Me(p). The polymeric nanolayers should exhibit, due to a higher number of organic –CH, –CF_3 groups and thin fibers, a relatively high hydrophobicity.

Abbreviations: Ph-Me(t), tri(phenyl)-trimethyl-*cyclo*-triphosphazene; Ph-Me(p), phenyl-methyl-polyphosphazene; PA6, polyamide 6; PS, polystyrene; ASA, acrylonitrile-styrene-acrylate; SAN, styrene- acrylonitrile; PESU, polyethersulphone; PP, polypropylene; THF, tetrahydrofurane; TFA, trifluoroacetic acid; DMS, dimethyl sulfide; AFA, mixture of acetic and formic acids; T_d^a, minimum thermal decomposition temperature; TGA, thermogravimetric analysis; SEE-system, Surface Energy Evalution system analysis; SEM, scanning electron microscope; EDX, X-ray photo-electron spectroscopy; ATR-FTIR, attenuated total reflectance Fourier transform infra-red; NMR, nuclear magnetic resonance.

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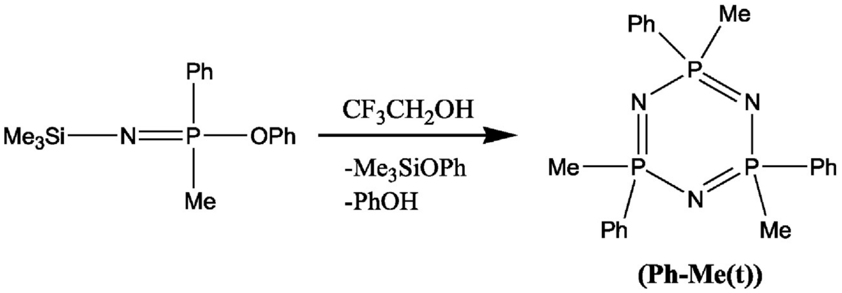
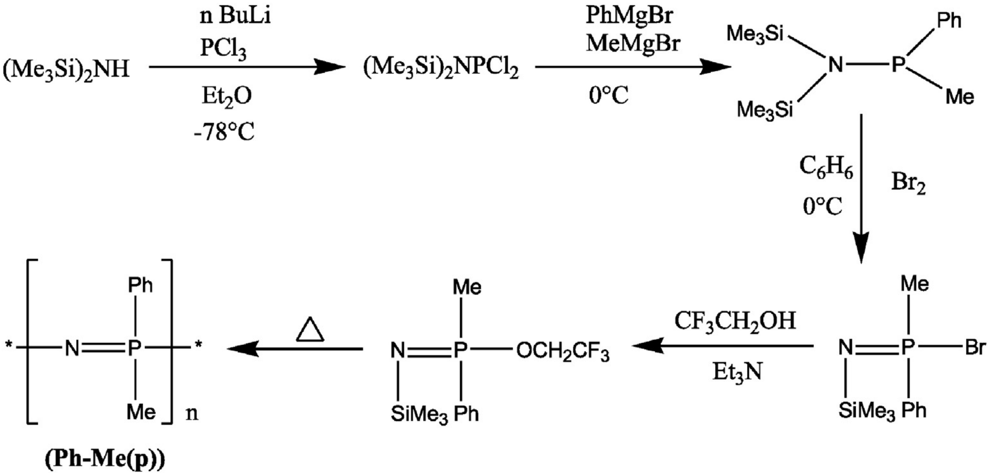


Scheme 1. Synthesis of Ph-Me(t).



Scheme 2. Synthesis of Ph-Me(p).

The resulting nanolayers can be manually removed from the supporting textile and used, e.g. as a protective material.

2. Experimental

2.1. The preparation of solution for electrospinning

Nanofibers were made from two different solutions, which differ in their composition.

- The commercial polymers – Polystyrene (PS), Polyamide 6 (PA6) or Polyethersulphone (PESU) – or copolymers – acrylonitrile-styrene-acrylate (ASA) or styrene-acrylonitrile (SAN) – were fiberized on their own (Fibers 1) and with Ph-Me(t) as an additive (Fibers 2).
- Ph-Me(p) was fiberized on its own (Fibers 3).

The properties of all the resulting types of nanofibers were compared with each other.

2.1.1. Solutions of commercial organic polymers with and without Ph-Me(t) as additive (Fibers 1, 2) and creation nanofibers from these solutions

The commercial polymers (PA6, PS, ASA, SAN, PESU) were produced by BASF, the solvents were delivered by Sigma Aldrich.

The above mentioned polymers were first dissolved in one of the following diluents — trifluoroacetic acid (TFA), a mixture of acetic and formic acids (AFA) or dimethylformamide (DMF). The prepared solutions of polymers were, for the following experiments, divided into two parts. The first part of the samples was fiberized on its own, i.e. nanofibers were created only from a single polymer or copolymer (Fibers 1). The second part of the samples was mixed with Ph-Me(t) (as an additive) (see Table 1). The content of Ph-Me(t) was either one or ten weight per cent related to the whole commercial polymer contained in the fiberized mixture. It follows from preliminary experiments that a 10 wt.% concentration of Ph-Me(t) is optimal for sufficient modification of fibers (Table 1). Therefore, more space in this article is devoted to fibers containing ten weight per cent of the Ph-Me(t) additive in the fiberized mixture.

The solutions were manually homogenized for 1 h using an electromagnetic stirrer before electrospinning.

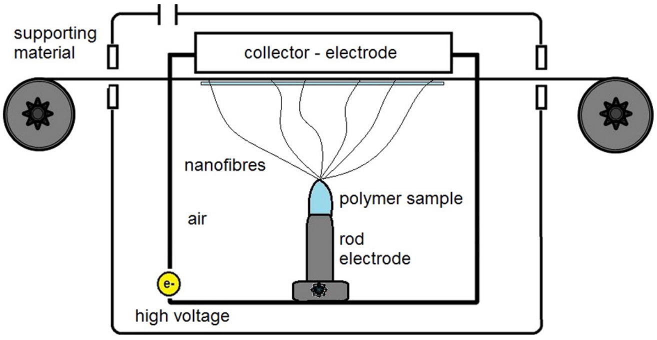


Fig. 1. Scheme of the electrospinning apparatus.