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Incorporation of Cyclotriphosphazenes as Pendant Groups to the Backbone of Natural Rubber

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INTRODUCTION

Cyclotriphosphazenes are flame retardant molecules that consist of skeletal phosphorus and nitrogen ($-P=N-$) atoms, forming a six-membered ring and with two substituents on each phosphorus¹. They are used as monomers or precursors for the development of high performance linear, cycloliner and cyclomatrix inorganic-organic polymers^{2,3}. The incorporation of cyclotriphosphazenes as pendant groups to the backbone of synthetic organic polymers affords a class of organic-inorganic polymers that exhibits useful thermal properties such as flame retardancy and self-extinguishability⁴⁻⁸.

In this paper, we describe two different methods for preparation of natural rubber derivatives with cyclotriphosphazenes as pendant groups.

EXPERIMENTAL

Materials

Hexachlorocyclotriphosphazene ($NPCl_2$)₃ (Fluka) was purified by recrystallisation from n-hexane and vacuum sublimation at 65°C and 0.03 Torr. Meta-aminophenol (Merck) was purified by sublimation at 90°C and 0.03 Torr. 1,4-dioxane (AJAX Chemicals) was freshly distilled prior to use from sodium benzophenone ketyl in an atmosphere of dry nitrogen gas. Trifluoroethanol (Fluka), Aluminium chloride hexahydrate, $AlCl_3 \cdot 6H_2O$ (Merck) and all other chemicals were used as commercially supplied. 50% Epoxidised Natural Rubber (ENR-50) was provided by Rubber Research Institute Malaysia (RRIM), Kuala Lumpur.

Instruments

Elemental (C, H, N) analysis were performed using CHN/O Analyzer, Perkin Elmer, Series II 2400. FT-IR spectra (KBr pellets and KBr windows) were recorded by using a Perkin Elmer- 2000. FT-NMR spectra were

acquired using Bruker DPX 400 spectrometer operating at 400 MHz for ¹H, 162 MHz for ³¹P and 101 MHz for ¹³C. Samples were dissolved or formed gel-like materials in $CDCl_3$ and chemical shifts were referenced to that of TMS (0.00 p.p.m.) for ¹H and ¹³C, and to that of 85% H_3PO_4 (0.00 p.p.m.) for ³¹P. Differential Scanning Calorimetry (DSC) analysis was carried out using Perkin-Elmer Pyris-1 DSC equipped with an internal cooler, 2P cooling accessory. Thermal weight loss measurements were made using Perkin-Elmer TGA-7 thermogravimetric analyzer (TGA). Scanning Electron Microscope (SEM) Leica Cambridge S-360 was used to study the surface morphology of the samples.

RESULTS AND DISCUSSION

In the first method, sodium 1,3,3,5,5-(trifluoroethoxy)-1-oxocyclotriphosphazenate [$N_3P_3(OCH_2CF_3)_5O^-Na^+$] was prepared and used as a nucleophile to react with ENR-50 in boiling 1,4-dioxane^{9,10}. The reaction is depicted in *Figure 1*. The nucleophile reacted exclusively and quantitatively with the epoxy moiety (oxirane) of ENR-50. Various amounts of the oxocyclotriphosphazenate, limited only by the number of oxirane available, could be bonded to the backbone of the organic polymer simply by varying the quantity of the nucleophile. Subsequent precipitation from slightly acidic aqueous media followed by drying under reduced pressure afforded the cyclotriphosphazene-incorporated natural rubber derivative (P1).

In the second method, treatment of ENR-50 with *meta*-aminophenol [$m-(HOC_6H_4)NH_2$] in the presence of catalytic amounts of $AlCl_3 \cdot 6H_2O$ in boiling 1,4-dioxane produced an intermediate with hydroxyl groups¹¹. This intermediate can be isolated, purified and then reacted with ($NPCl_2$)₃ to give P2. The overall two-step process is depicted in *Figure 2*. Alternatively, the subsequent reaction can be performed as a one-pot process: after Step 1, a solution of ($NPCl_2$)₃ in 1,4-dioxane is added to the reaction flask together with an excess amount of triethylamine (Et_3N) as

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