

DEHYDROCHLORINATION OF POLY(VINYL CHLORIDE) AND CHLORINATED POLYETHYLENE BY PHOSPHONIUM IONIC LIQUIDSDAAN GLAS¹, JORIS HULSBOSCH¹, PHILIPPE DUBOIS², KOEN BINNEMANS³ AND DIRK E. DE VOS¹¹*Centre for Surface Chemistry and Catalysis, KU Leuven, Kasteelpark Arenberg 23, 3001 Leuven, Belgium – daan.glas@biw.kuleuven.be*²*Laboratory of Polymeric and Composite Materials, University of Mons, Place du Parc 23, 7000 Mons, Belgium*³*Division for Molecular Design and Synthesis, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium***Abstract**

Poly(vinyl chloride) (PVC) is the third most used synthetic polymer in the world. As this polymer contains about 55 % of chlorine, PVC waste is a major problem. During incineration of PVC HCl is formed which gives rise to corrosion of the equipment¹. In the recycling industry polymer mixtures free of PVC are preferred as HCl elimination in PVC starts at the low temperature conditions in which other polymers are remelted. HCl formation is a major risk for the recycling equipment. This problems can be overcome by full dehydrochlorination which is the elimination of HCl from the polymer chain. Thermally this is only achieved at high temperatures (400 °C)². In literature, 2 ionic liquids have shown to be catalysts for this reaction³.

In our research, a large range of ionic liquids (ILs) were investigated for their ability to dehydrochlorinate and/or dissolve the chlorinated polymers poly(vinyl chloride) (PVC) and chlorinated polyethylene (CPE). From this screening different phosphonium ionic liquids were selected as the best candidates for the dehydrochlorination reaction as they were able to successfully dissolve PVC and CPE at temperatures from 80°C onwards. Furthermore our results show that the dehydrochlorination activity of an IL depends mainly on its anion and is related to the high hydrogen bond accepting ability (beta-value) and basicity of the anion.

Subsequently quantitative measurements of the dehydrochlorination degree were performed. At 180 °C, the eventual dehydrochlorination degree of powder-form CPE after 60 min is highest (83 %) in tetrabutylphosphonium chloride ([P₄₄₄₄][Cl]), an IL with a high beta-value (0.95). The initial dehydrochlorination rate however is highest in ethyltributylphosphonium diethylphosphate ([P₄₄₄₂][(C₂H₅O)₂PO₂]), an IL with a basic anion. The investigation of the reaction kinetics showed that dehydrochlorination is favored by removal of the reaction product HCl but hindered by cross-linking of the formed double bonds. Powder-form PVC is dehydrochlorinated up to 98 % after 60 min in [P₄₄₄₄][Cl] at 180 °C. Calcium stearate stabilized PVC pieces (4 mm³) are dehydrochlorinated more slowly; conversions of 85 % and 96 % are reached after 1 and 8 h, respectively. Smaller polymer pieces are dehydrochlorinated faster. As the ionic liquid acts as catalyst and solvent many active centres are to be expected. This makes a higher loading possible. In our experiments a loading of 0.3 g stabilized PVC in 0.5 g IL was applied with only a minor loss of conversion. [P₄₄₄₄][Cl] proved to be stable during several consecutive dehydrochlorination reactions.

The structure of the dehydrochlorinated PVC was studied via ¹³C CP MAS NMR and FT-IR spectroscopy; the removal of chlorine and the formation of double bonds were confirmed. Carefully dehydrochlorinated CPE was processed further by ADMET depolymerization with ethylene and the Hoveyda-Grubbs 2nd-generation catalyst. A conversion of 34 % to α,ω -dienes and their isomerization products was achieved, with 1,5-hexadiene and 1,6-heptadiene being most abundant.¹

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