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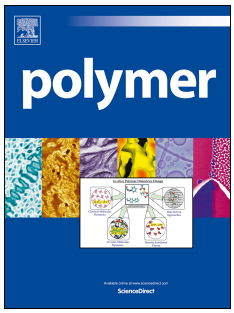


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# A Hyperbranched Mechanically Interlocked Rotaxane-Type Polymer

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## ABSTRACT

The interaction of the diacid chloride (**2**) of N,N'-bis(5"-carboxypentyl)-4,4'bipyridnium bis(hexafluorophosphate) (**1**) with *m*-phenylene-5'-hydroxymethyl-1',3'-phenylene-32-crown-10 (**3**) at -70 $^{o}$C led to the *in situ* formation of a pseudorotaxane **4** as an $AB_2$ monomer, which was allowed to polymerize by raising the temperature and adding a catalytic amount of pyridine. The resulting hyperbranched polymer was held together via mechanical bonds formed by threading of the crown ether units by the bipyridinium (paraquat) moieties. The polymer was initially precipitated into aqueous $NH_4PF_6$ to remove any unreacted, water soluble diacid **1** to form **5b** and then precipitated from DMSO into aqueous $NH_4PF_6$ to remove any pyridinium monoester **8** complexed with crown ether units in the polymer, leading to **6**. The hyprerbranched polyester was characterized by $^{1}$H NMR and NOESY spectroscopies, FAB and MALDI-TOF mass spectrometry and viscometry. NMR spectroscopy confirmed complete esterification of the crown ether alcohol; **5b** contained 60% monoesterified paraquat units (**8**) and 40% diester moieties (**9**), while **6** contained only 24% monoester moieties, which existed primarily as "focal point" units (**10**), but also as uncomplexed linker units (**11**). A variety of mechanically linked structures