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## pH responsive polymer brushes grafted from the surface of intravaginal rings for reversible switch on/off on-demand drug delivery

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A new pH sensitive reservoir type polyurethane intravaginal ring (PU IVR) was developed for on-demand drug delivery using a novel and versatile method. A combination of surface-initiated activator regenerated by electron transfer atom transfer radical polymerization (SI-ARGET-ATRP) and alkyne-azide click reaction was applied to graft pH responsiveness polymer brushes from the surface of PU IVR to achieve a rapid switchable release at specific pH environments. First, poly (propargyl acrylate) (PPA) brushes were grafted at the surface of PU IVR segments via SI-ARGET-ATRP to get the alkynyl handle terminated PU: PPA-PU. Secondly, pH sensitive monomers were bonded onto the surface of PPA-PU via alkyne-azide clic reaction. X-ray photoelectron spectroscopy (XPS) and Attenuated total reflectance Fourier transform infrared (ATR-FTIR) confirmed that polymer brushes were successfully grafted from the PU surface. The pH- responsive behaviour of untreated PU IVR segments and functionalized segments with pH-responsive polymer brushes were studied in PBS buffer solution at pH 4 and pH 7 over a minimum of 5 cycles using hydroxychloroquine (HCQ) as a model drug. The untreated PU IVR did not show any pH responsiveness upon pH changes. On the other hand, modified PU IVRs showed pH responsiveness upon changes in pH values. Release studies demonstrated that the “through pore mechanism” controls release of HCQ from pH sensitive reservoir-type IVR drug delivery systems. PU IVR grafted with anionic functional groups showed more release at acidic pH than basic pH. However, when cationic polymer brushes were grafted from the surface of PU IVR, more release was observed at basic pH than acidic pH.

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