# Thermally Triggerable, Anchoring Block Copolymers for use in Aqueous Inkjet Printing

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## Introduction

Commercial inkjet printing onto hydrophobic materials, such as is used in the food and medical supply industries, rely heavily on harmful organic solvents for the deposition of hydrophobic inks that will adhere to the substrate whilst maintaining appropriate resolution of the printed information (**Figure 1**).

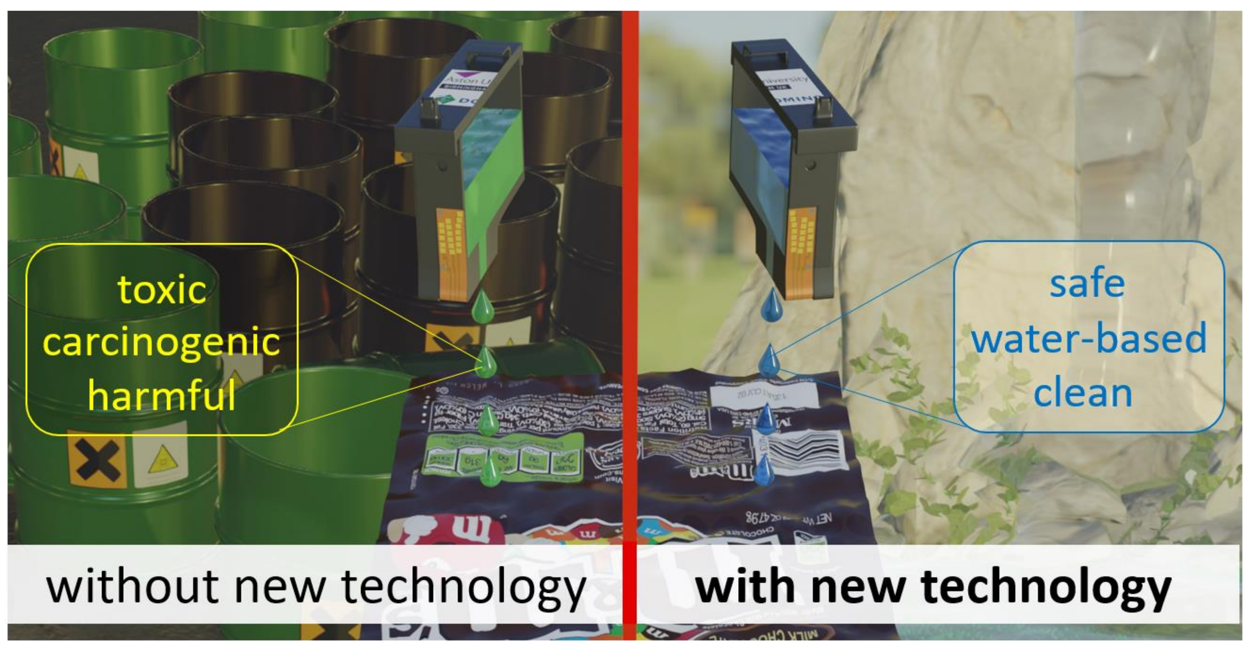


**Figure 1. Demonstration of the impact of the new polymer additive at <5% w/w loading to eradicate the need for harmful organic solvents in commercial inkjet printing. The block copolymer contains triggerable chemistry to allow water-based inkjet printing onto hydrophobic substrates (e.g. food packaging).**

## Methodology

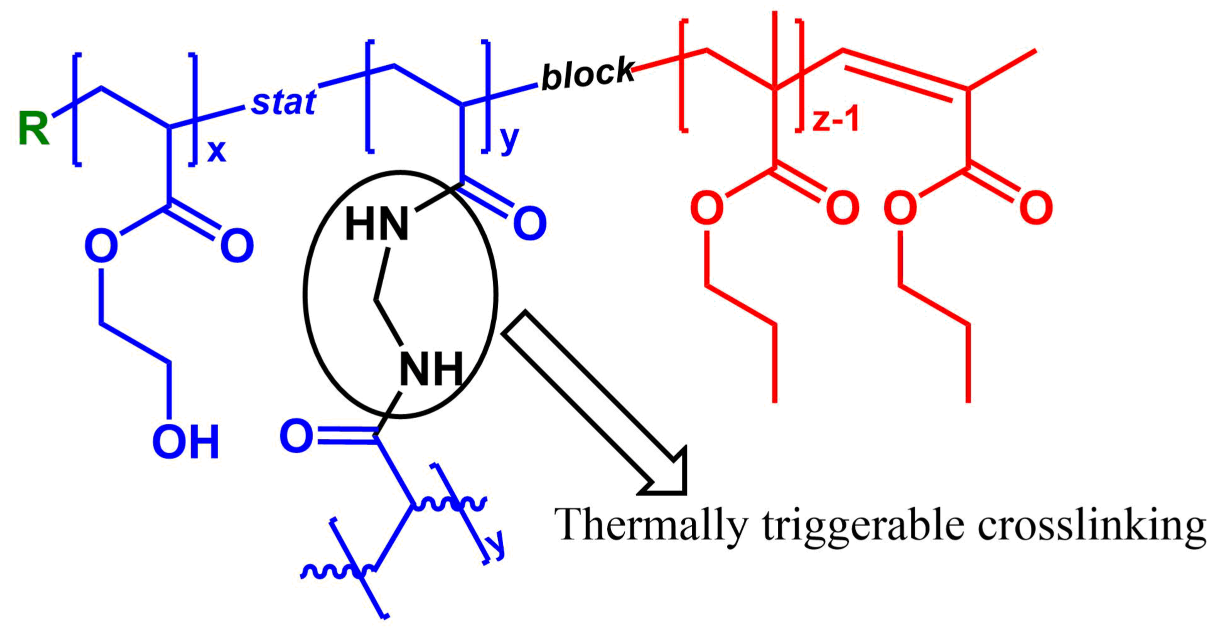


**Figure 2. Final crosslinked amphiphilic block copolymer structure highlighting the hydrophilic (blue) and hydrophobic (red) segments.**

A series of well-defined poly[(2-hydroxyethyl acrylate-*stat*-*N*-hydroxymethyl acrylamide)-*block*-propyl methacrylate], P[(HEA-*st*-HMAA)-*b*-PMA)], amphiphilic block copolymers (**Figure 2**) with varying P(HEA-*st*-HMAA) and PPMA contents were synthesized via RAFT polymerization and subjected to industrially designed tests to determine their suitability for use in aqueous ink formulations for printing onto hydrophobic substrates.

## Results

Five industrially designed adhesive tests were employed to fully examine the range of abrasive interactions that printed food packaging products undergo during their typical useable life-cycle (**Figure 3**). Each of these tests was assessed by a qualitative rating system (0 to 10, where 10 shows the highest adhesive performance) related to coverage (A = wetting) or percentage of sample remaining [B = finger rub, C = nail scratch, D = tape 610 and E = tape 810 (whereby tape 810 has stronger adhesive properties than tape 610)] post abrasion.

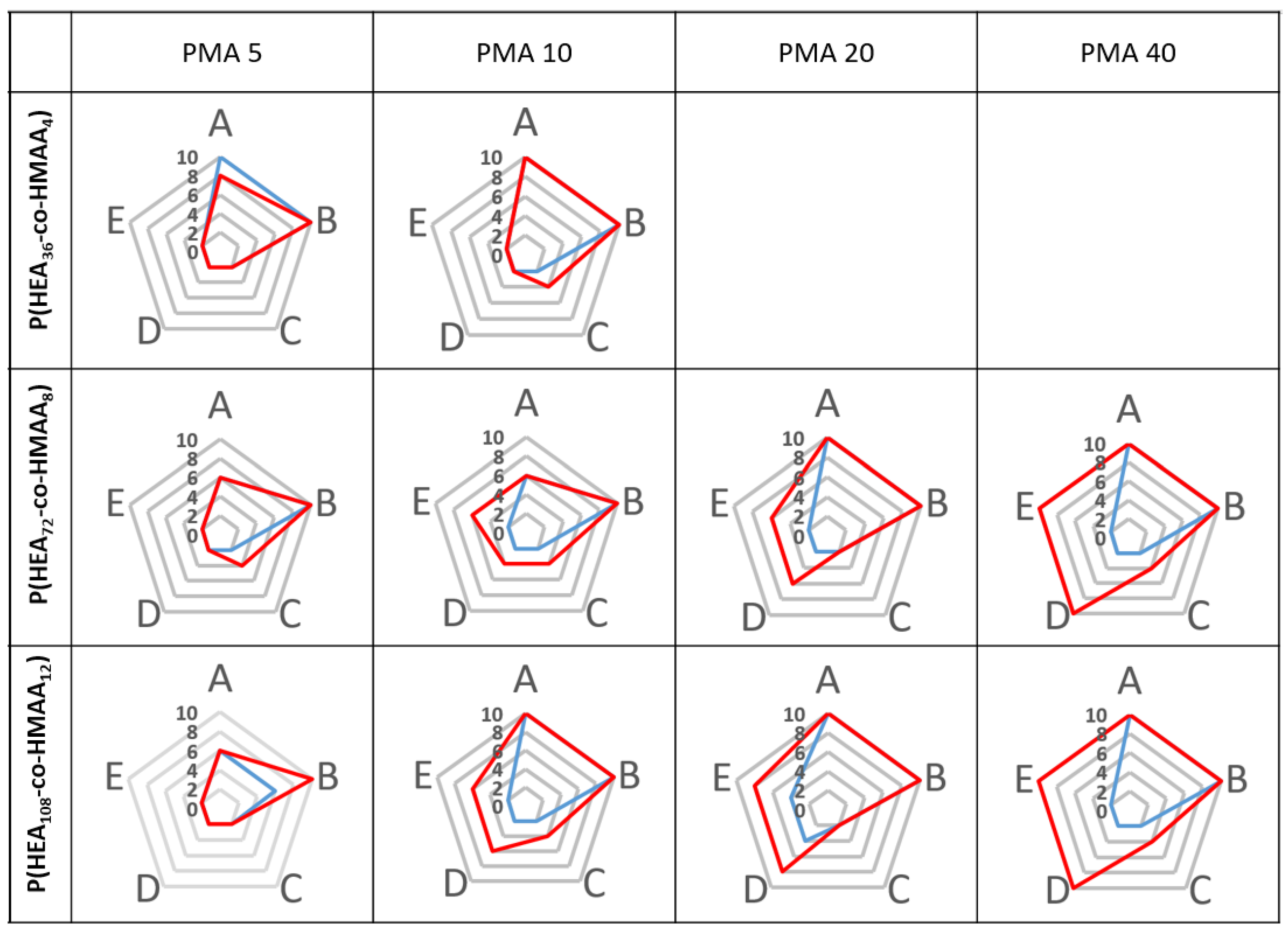


**Figure 3. Adhesive properties of four P[(HEA$_x$-*st*-HMAA$_y$)-*b*-PMA$_z$] block copolymer drawn down films on PET before (blue) and after (red) crosslinking *via* heating at 150 °C for 3 h.**

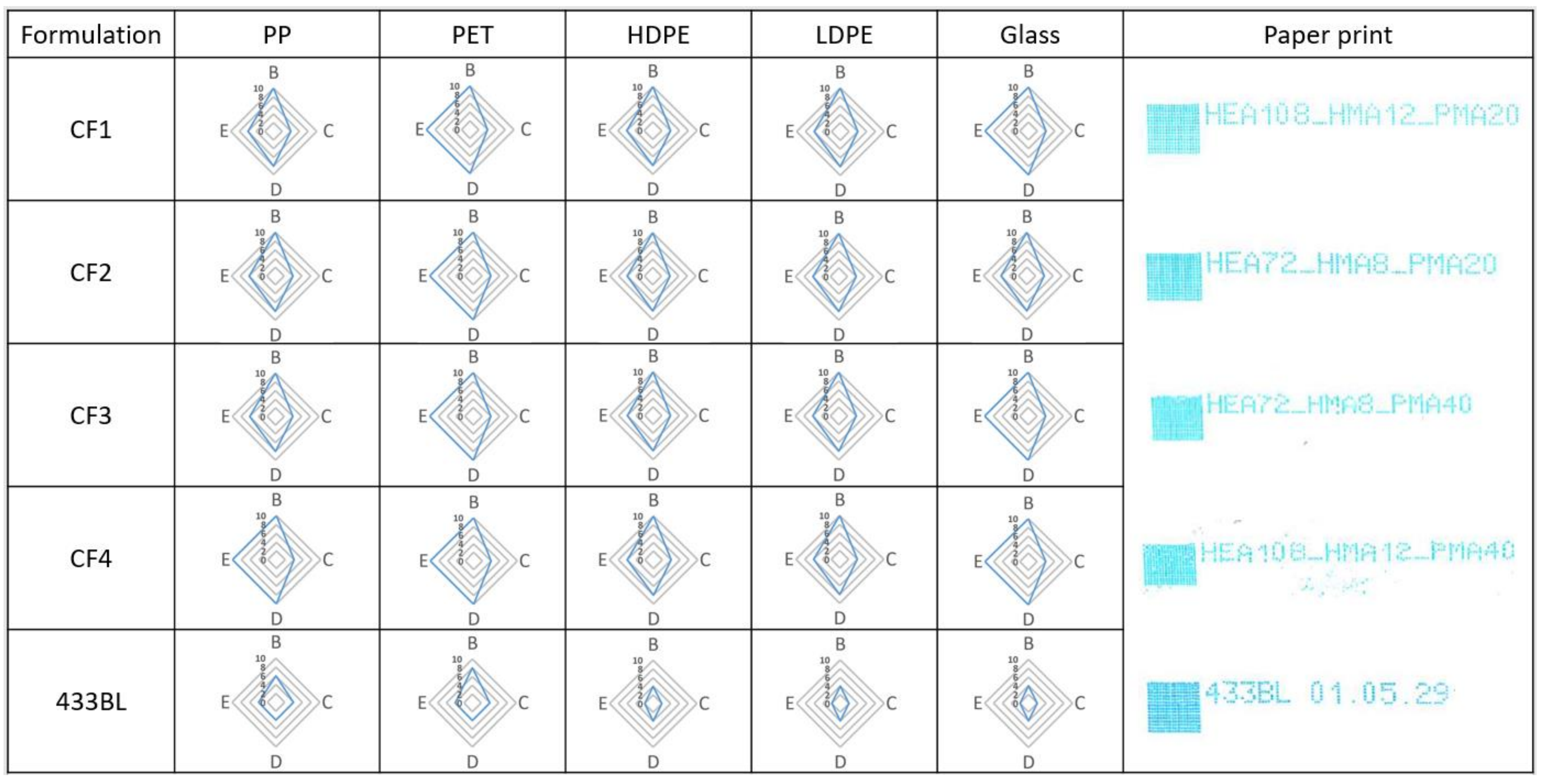


**Figure 4. Adhesion tests after printing block copolymer-containing ink formulations (CF1 – CF4) against a commercial formulation (433BL) onto PP, PET, HDPE, LDPE and glass after heating at 150 °C for 3 h.**

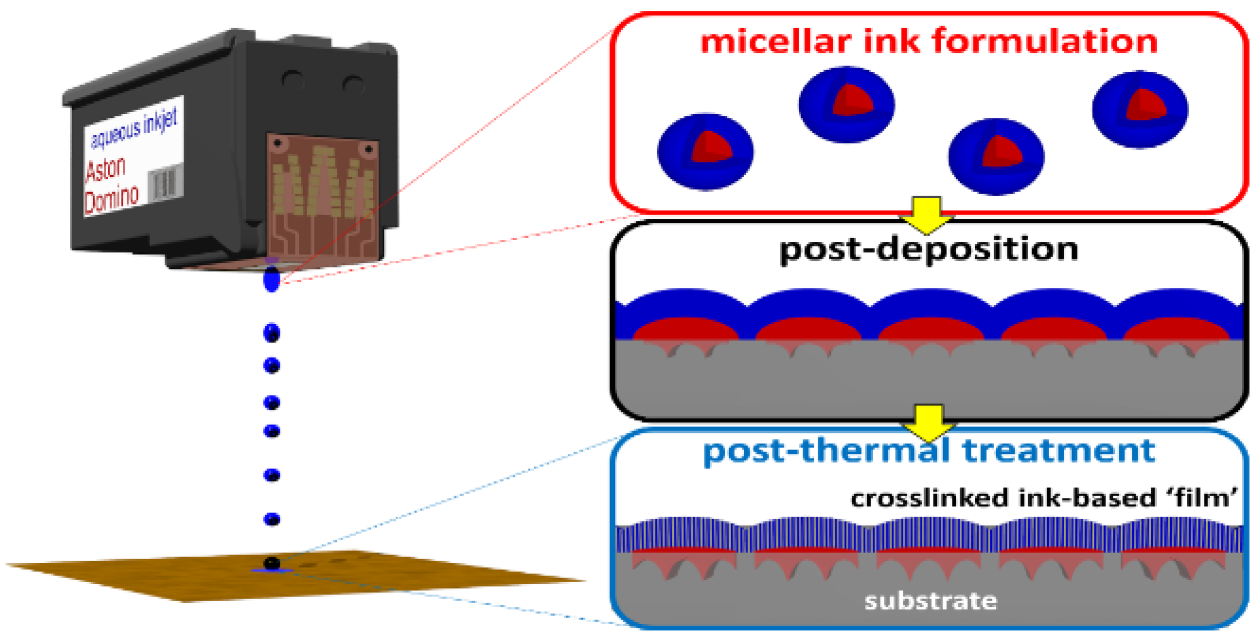


**Figure 5. Demonstration of the printing process and post-deposition thermal treatment for aqueous-based continuous inkjet printing.**

Ink formulations based on industrial standards at Domino Printing Sciences were prepared using the four block copolymers and the dye 'Brilliant Blue'. Formulations containing P[(HEA-*st*-HMAA)-*b*-PMA] block copolymers outperform commercial inks (**Figure 4**) when printed onto all hydrophobic substrates assessed in this study (**Figure 5**).

The following molecular design parameters for promising P[(HEA-*st*-HMAA)-*b*-PMA)] block copolymer ink additives were identified: (i) a high HMAA content (12.5 mol% HMAA within the hydrophilic block was shown to provide the maximum possible loading without promoting crosslinking events during polymerization), (ii) a long hydrophilic block (which reduces the required crosslinking time to below 60 minutes), and (iii) a high hydrophobic block volume fraction.

## Conclusion

Ink formulations that incorporated the P[(HEA-*st*-HMAA)-*b*-PMA] block copolymers were shown to be successfully printed from aqueous-based formulations to give comparable quality prints to commercial inks. Additionally, the polymers showed better adhesive properties in industrially designed tests on a variety of hydrophobic substrates, when compared to ink formulations that did not include the block copolymers. The crosslinked polymers (post-deposition) significantly outperformed the non-crosslinked polymers and demonstrate an exciting new technology for the future of commercial inkjet printing on hydrophobic substrates, which is a key step towards cleaner processes in the medical supply and food packaging industries.

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