



Pressure-sensitive adhesives from polyester pentablock copolymers

Cite this: *Polym. Chem.*, 2026, **17**, 21

Received 23rd October 2025,
Accepted 21st November 2025

DOI: 10.1039/d5py01006c

rsc.li/polymers

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Pressure sensitive adhesives (PSAs) are widely used materials in a number of applications, such as sticky notes and tapes, but for most commercial products they are derived from petrochemicals. Here, a series of pentablock polymers, with an ABABA structure featuring poly(cyclohexene oxide-*alt*-phthalic anhydride) 'A' blocks and poly(ϵ -decalactone) (PDL) 'B' blocks, are prepared as pressure-sensitive adhesives from bio-sourced monomers. The pentablock polymers are prepared by controlled polymerisation techniques, using a single catalyst, in a one-pot process. Polymer properties are tuned through varying the hard block (A) content between 16–39 wt%. Below 25 wt% hard block, the pentablock polymers show low-tack adhesive performance (0.2–0.6 N cm⁻¹) and are removed by adhesive failure. Their adhesive performance compares favourably to low-tack commercial adhesives.

Introduction

Pressure-sensitive adhesives (PSAs) are an important class of materials used as tapes, glues and labels in packaging, automotive components, and electronics.¹ They are characterised by their ability to self-adhere quickly under light pressure, resist shear forces during use, and be removed without leaving adhesive residue.^{2–5} To achieve this, PSAs should have a balance between the viscous flow required for substrate wetting and elasticity for mechanical integrity and removability.⁶ Most PSAs consist of polyacrylates, natural rubbers or styrenic copolymers which are combined with tackifier and other additives.^{4,7–9} Amongst these formulations, tackified styrenic block copolymers stand out for their tuneable viscoelastic and mechanical properties. These materials are typically ABA triblocks which comprise 10–30 wt% of the hard/glassy 'A' block with a glass transition temperature (T_g) > room temperature and the remainder a soft/rubbery 'B' block (T_g < room temperature). Block phase separation is desirable, with

the rubbery matrix enabling substrate wetting and surface contact, while the hard domains act as physical crosslinks to provide cohesive strength and resist shear forces.^{4,10}

With the exception of natural rubber based-PSAs, most formulations are petrochemically derived (*e.g.* polyacrylates or styrenics). Development of alternative sustainable materials to the petrochemically sourced polymers is essential to reduce the 1.8 Gt of carbon dioxide (CO₂)-equivalents emitted annually from petrochemical polymer manufacturing.^{11–15} Oxygenated block polymers offer attractive alternatives as they can be derived from renewable feedstocks and their high oxygen content should improve substrate adhesion.^{16–18} Polyester-based PSAs are well precedented, with their potential established by Long and co-workers.^{19–21} Triblock polyester PSAs made by cyclic ester ring opening polymerisation (ROP) were initially demonstrated by Hillmyer and co-workers utilising monomers from biomass feedstocks; since then, many successful examples have been developed from renewable monomers such as lactide (from corn starch), menthene (from mint), and ϵ -decalactone (from castor oil).^{22–30} In most cases, the block polymers require further formulation with additives and tackifiers to deliver the desired adhesive behavior. Although certain additives, such as rosin esters, can be renewably sourced, multi-component adhesives are inherently more complex, posing challenges for future recycling and waste management.

Single-component PSAs based on oxygenated block copolymers have been reported by our team and others.^{31–35} These materials were accessed by switchable polymerisation catalysis which allows for coupling of ring opening copolymerisation (ROCOP) of epoxide with CO₂ or anhydride and cyclic ester ring opening polymerisation (ROP), using a single catalyst, in a one-pot process.^{36,37} This highly controlled catalysis results in the production of block polyesters with predictable high molar masses, and monomodal distributions, with high end-group fidelity, and obviates the requirement for intermediary polymer purification steps.^{38–41} Our prior reports utilise a heterodinuclear [Zn(II)Mg(II)] catalyst to produce ABA triblock

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Fig. 2 (a) Frequency sweep of PB-2 (25 °C). (b) PSA performance windows of pentablock polyesters constructed from the bonding ($\omega = 0.1 \text{ rad s}^{-1}$) and debonding frequencies ($\omega = 100 \text{ rad s}^{-1}$).

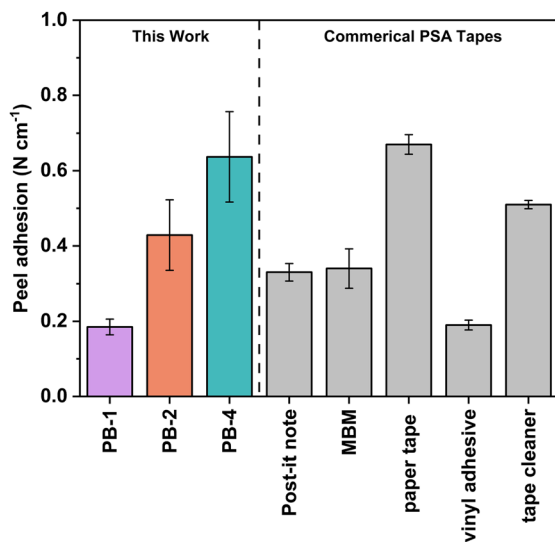


Fig. 3 180° Peel adhesion properties on stainless steel substrates of PB-1, PB-2, and PB-3 with comparisons to commercial low tack PSAs.

cm⁻¹), PB-2 (0.43 N cm⁻¹), and PB-3 (0.64 N cm⁻¹) showed an increase with greater P(CHO-*alt*-PA) hard block content (16 to 26 wt%) across the series (Fig. 3). PB-1 and PB-2 demonstrated desirable adhesive failure with clean removal and no residue (Fig. S20). PB-3 failed cohesively, leaving polymer residue on the substrate, which would be a disadvantage for a removable application. Adhesive failure results from bridging of the hard domains by the rubbery soft block in the block copolymers, which form fibrils during PSA debonding and increase cohesive strength of the PSA.^{28,63} The lower hard block content of PB-1 and PB-2 promotes effective fibril formation and elongation during the PSA debonding, leading to adhesive failure. Whereas, this mechanism is more hindered in PB-3, which has higher hard block content, and resulted in cohesive failure. The low adhesion force of these materials is compar-

able to reported values for commercial low tack PSAs used for removable/repositionable tapes or surface protection films, such as MBM (0.34 N cm⁻¹), Post-it note (0.33 N cm⁻¹), low tack paper tape (0.67 N cm⁻¹), low tack vinyl adhesive (0.19 N cm⁻¹), and 3M tape cleaner (0.51 N cm⁻¹).²⁶ The pentablock polyesters provide low strength peel adhesion without the need for additional of additives such as tackifiers for PSA applications.

The stress-strain behaviour of PB-3 and PB-4 were studied by uniaxial tensile testing, at an extension rate of 10 mm min⁻¹ (Table S2 and Fig. S21). Dumbbell shaped specimens were cut from the polymer films, according to ISO 527-2, specimen type 5B using a cutting press. PB-3 and PB-4 both exhibit elastomeric behaviour. PB-3 shows low ultimate tensile strength (0.76 MPa) and a strain at break of 261%. At increased hard block content, PB-4 showed an improvement in tensile strength (2.61 MPa) and strain at break (405%). PSAs with higher hard block content often have a G' that is too large, hindering substrate wetting and tackiness and thus limiting adhesive performance of PB-4.

A series of pentablock polymers with high molar mass and increasing hard block content were selectively prepared using a single catalyst, in a one-pot procedure. Polymerisations were highly controlled and selective, enabling the formation of multiblock polymers at varying block compositions. The polyesters were effective low-tack pressure sensitive adhesives, without the addition of tackifier resin or additives. They showed comparable adhesive performance to existing commercial materials, with favourable adhesive failure at lower hard block content (< 20 wt%) making them most suitable for temporary applications. These results showcase the utilisation of switchable catalysis to selectively prepare pentablock polymers which act as effective low-tack PSAs. It is expected that further manipulation of polymer composition, molar mass, and block ratios would allow further tuning of material properties.



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