

# POLYESTERS FOR SUSTAINABLE ADHESIVE TECHNOLOGIES: FROM PSAS TO THERMOPLASTIC ELASTOMERS

Musan Zhang, Virginia Tech, Blacksburg, VA 24061-0212

Gozde I. Ozturk, Virginia Tech, Blacksburg, VA 24061-0212

Timothy E. Long, Virginia Tech, Blacksburg, VA 24061-0212

## Abstract

Melt polycondensation synthesis of polyesters presents a solvent-free and environmentally friendly approach of producing pressure sensitive adhesives (PSAs) due to their inherent biodegradability and low cost manufacturing process. Low glass transition temperature ( $-40\text{ }^{\circ}\text{C}$ ) all-aliphatic polyester PSAs were synthesized using melt polymerization. Careful selection of diester, diol, and monomer stoichiometry enabled tailoring of the glass transition temperature and adhesive properties as investigated using adhesive testing methods. Melt rheological experiments indicated a correlation between polyester molecular weight and adhesive performance. These studies enabled us to design a new family of segmented copolyesters for their potential in adhesive applications due to controlled sequence distribution and morphological consequences of microphase-separated block copolymers. Incorporating electrostatic interactions into copolymers also affords an avenue for the modification of thermally labile adhesive properties on the molecular level. We have recently developed a synthetic strategy that allows for melt transesterification of segmented block copolyesters using the sterically hindered and cyclic monomer, 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO). This monomer has also received significant industrial attention as a replacement for bisphenol-A based polycarbonates. High- $T_g$  polyester polyols containing CBDO and 0-5 mol% sulfonation were synthesized using conventional melt transesterification. Further reaction of the hard segment polyols with diesters and diols that comprise the resulting soft block demonstrates a one-pot synthetic method towards a new class of thermoplastic elastomers. Herein, we describe the influence of ionic interactions on sulfonated segmented copolyesters. Specifically, transesterification resistance studies and melt rheological experiments indicated a correlation between hard segment block content and sequence regularity to the adhesive and mechanical properties of the copolyesters. In addition, atomic force microscopy revealed the surface morphology of the copolyesters. These ion-containing segmented copolyesters permit modification of adhesive properties on both the molecular and morphological level.

## Introduction

Acrylic-based block copolymers are typical examples of pressure sensitive adhesives that have been traditionally synthesized using volatile organic solvents. Although this class of

adhesives serves an important role in commercial products, there remains a large demand for environmentally friendly solvent-free synthetic methods. In this report, we describe the synthesis of a novel class of low- $T_g$  pressure sensitive adhesive using melt polymerized polyesters. These polymers harness polyester degradability as well as their solvent-free polymerization techniques which can essentially lower production costs.

Polymer adhesive properties strongly depend upon the viscoelastic behavior of the polymers. Viscous behaviors heavily influence the polymer flow properties for processibility and product fabrication. However, elastic properties are needed to store and dissipate energy. Elastic properties of adhesives provide the mechanical integrity needed for strong adhesive bonding. Finally, the polymer glass transition temperature also plays a large role in design of novel polymers for PSA applications. Typical  $T_g$  values for room temperature pressure sensitive adhesives fall within the -20 to -60 °C range.

In this study, aliphatic low- $T_g$  based polyesters were synthesized using melt transesterification. The UV stability of aliphatic monomers provides an added advantage which allows these polyester based adhesives to be suitable for coatings and outdoor applications. Building upon the findings of our previous research, a new class of segmented block copolyesters has been formulated to improve the mechanical properties of these pressure sensitive adhesives.

Recent literature has revealed the importance of introducing secondary interactions into adhesives to improve upon the properties of PSAs.<sup>1</sup> Melt polymerization of polyesters have afforded polymers with various architectures such as cyclics, copolyesters, and hyperbranched polyesters. These architectures have been shown in the literature to affect morphology on the nanoscale and tune adhesive properties.<sup>2</sup> Due to transesterification of the ester linkages in the polyester backbone, it is often difficult to achieve segmented polyester. In order to reduce transesterification probability, we utilize the bulky and rigid cycloaliphatic diol 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO) to produce high- $T_g$  polyester polyols. CBDO has been researched extensively in the literature and has been shown to impart high glass transition temperatures as well as excellent impact resistance properties.<sup>3, 4</sup> We have found that these entirely polyester-based block copolymers formed well microphase-separated surface morphologies from atomic force microscopy. Secondary interactions provide physical and mechanical integrity, but unlike chemical crosslinks, these physical crosslinks are thermally labile which is important for processing methods.<sup>5-7</sup> Also, block copolymers allow us to introduce ionic domains into specific segments of the block copolymer to facilitate an understanding on the role of ionic interaction on pressure-sensitive adhesive properties.

## **Experimental**

### ***Materials***

Polyester monomers were provided by Eastman Chemical Company and used without further purifications. Titanium catalyst was purchased from Sigma Aldrich and diluted into a 0.01 g/mL 1-butanol solution.

### ***Synthesis of low- $T_g$ polyester pressure sensitive adhesives***

Polyesters were synthesized using conventional melt transesterification methods. A 1:1.5 molar ratio of diester to diol and titanium catalyst was charged into a 100-mL round-bottomed flask

equipped with a nitrogen inlet, mechanical stirrer, and condenser. Polyesters were made from a combination of diols (diethylene glycol, DEG, or triethylene glycol, TEG) and diesters (dimethyl cyclohexane dicarboxylate, DMCD, or dimethyl adipate, DMAP). The reaction was first purged and degassed 3 times before heating to 200-220 °C over a period of 5 h. The reaction temperature was subsequently increased to 275 °C and high vacuum (0.1 mmHg) was applied to the system. Samples were characterized without further purifications.

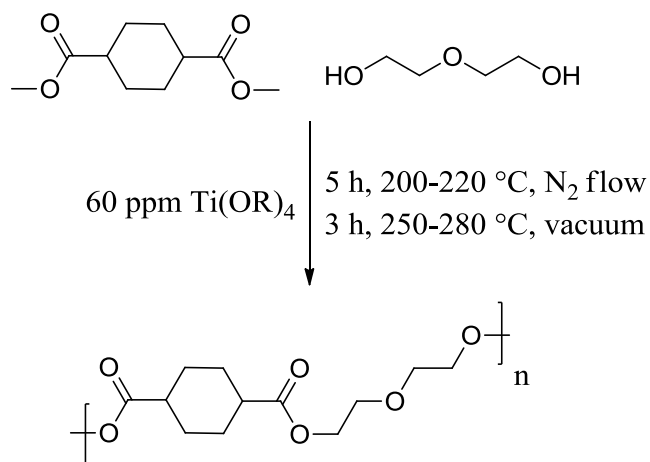
### Characterization

Low- $T_g$  polyesters were characterized with  $^1\text{H}$  NMR, differential scanning calorimetry, THF size exclusion chromatography and thermogravimetric analysis. Adhesive properties were characterized using 180° peel testing, loop tack and rolling ball tack, and holding power.<sup>8</sup> Polymer rheological behavior was investigated using melt rheology on a TA Instrument AR 100 stress controlled 8 mm parallel plate.

### Results

Low- $T_g$  polyesters were synthesized in a solvent-free method. The polyester aliphatic backbone contributes to advantages over traditional polystyrene-based PSAs. An aliphatic system enables coatings or adhesives for outdoor applications due to its increased UV stability over aromatic adhesive systems. In addition, ester linkages enable degradative properties which may be suitable for time-release adhesives or adhesives for biomedical applications. Thus, this approach allowed us to synthesize a new family of low- $T_g$  polyesters.

**Scheme 1** summarizes one class of polyesters, which incorporates a cycloaliphatic unit cyclohexane into the polymer backbone. Similarly, **Scheme 2** outlines the synthesis of polyesters comprised of the diester dimethyl adipate, which promotes a noncyclic comparison for DMCD-based polyesters. Diols used for these synthetic schemes were either DEG or TEG. Thus, these monomer choices allow us to investigate the thermal, rheological, and adhesive properties of cyclic versus noncyclic containing polyesters and the influence of an additional ether linkage on the polymer properties.

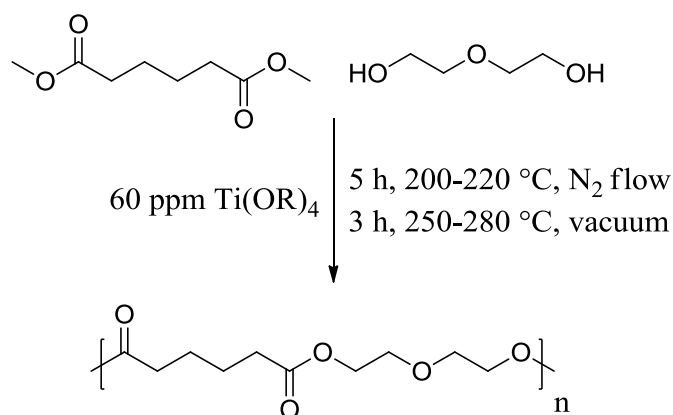


**Scheme 1.** Synthesis of DMCD-DEG polymer using melt transesterification techniques.

<sup>1</sup>H NMR spectroscopy confirmed the structure of these polymers. **Table 1** summarizes the polyester polymer composition as well as molecular weights and  $T_g$  values for these polymers. High molecular weights were obtained using melt transesterification methods. These polymers possessed adequately low glass transition temperatures ranging from -49 to -12 °C. The range in the glass transition temperature can be attributed to the monomer selection as well as the degree of ether linkages from the choice of diol used. In general, linear aliphatic polyesters provided lower glass transition temperatures compared to the cyclohexane-containing polyesters. This property is attributed to the loss of molecular stiffness and molecular bulk when the polyester contains a cyclohexane ring compared to the linear form. Moreover, the glass transition temperature is reduced by 10 °C for the DMCD-containing system when the diol is lengthened from DEG to TEG due to the increased flexibility arising from the ether linkage of TEG. These results demonstrate the role of monomer choice on the tailorable properties of these polyester PSAs.

**Table 1.** Composition, molecular weight and glass transition temperatures of low- $T_g$  polyester PSAs

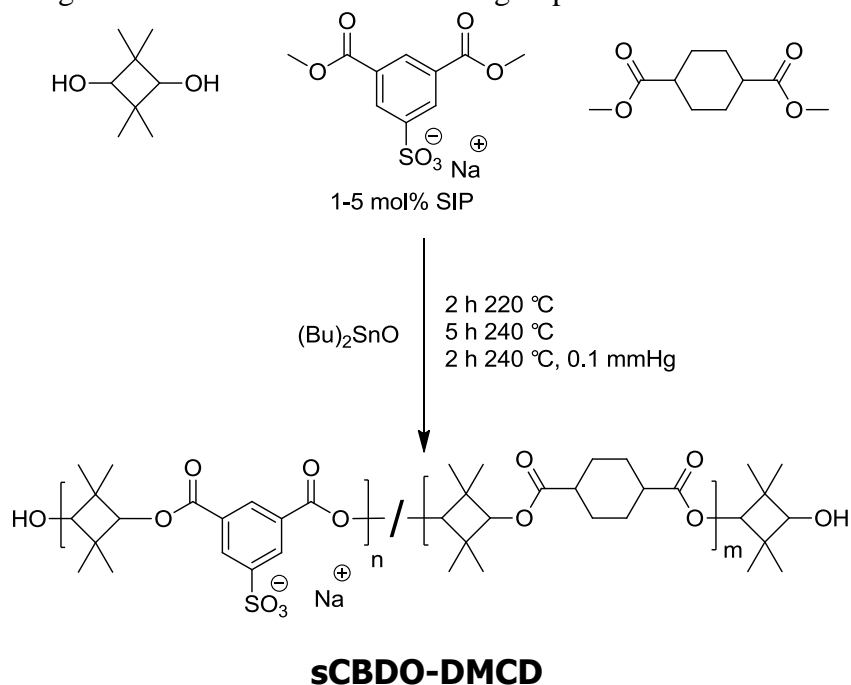
Composition	$M_w$ (g/mol)	$M_n$ (g/mol)	$M_w/M_n$	$T_g$ (°C)
DMAP-DEG	67,000	44,000	1.53	-47
DMAP-TEG	59,000	27,000	2.22	-49
DMCD-DEG	55,000	35,000	1.56	-12
DMCD-TEG	41,000	19,000	2.13	-25



**Scheme 2.** Synthesis of DMAP-DEG polymer using melt transesterification techniques.

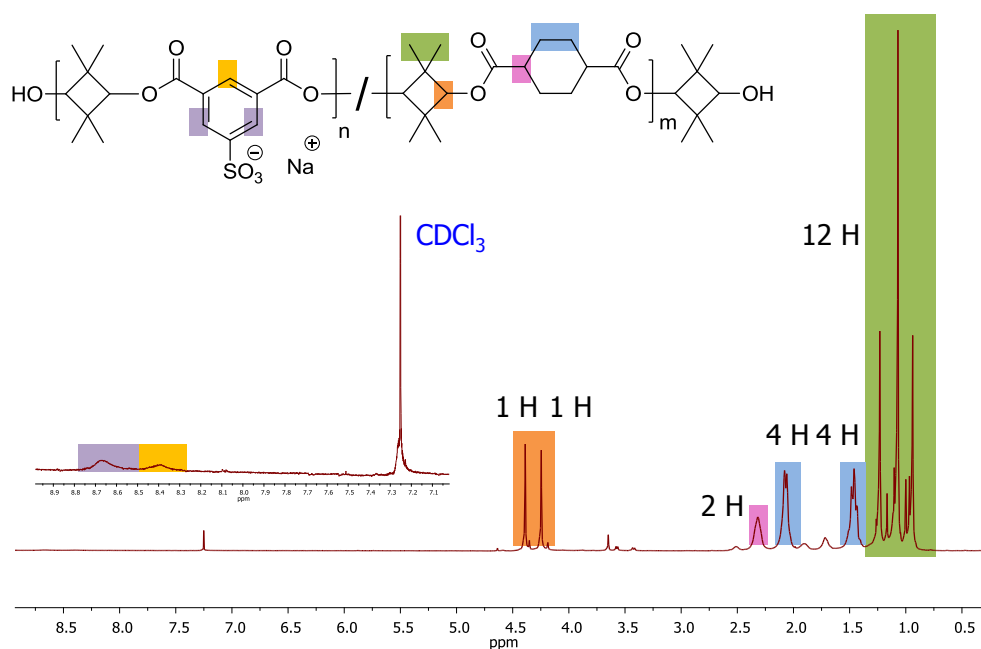
Block copolymers comprised of styrene and butadiene or isoprene blocks have been traditionally used in tailoring pressure sensitive adhesive properties. The drawbacks to these polymer systems are the use of volatile organic solvents in the synthesis of these polymers as well as the dependence on petroleum-derived monomers. Polyester block copolymers offer a solvent-free approach to synthesize degradable block copolymers for adhesive applications. To build upon the work summarized above, an entirely aliphatic-based block copolyester was

synthesized. These block copolymers comprised DEG-DMAp soft segment blocks due to the desirable adhesive and thermal properties we described.<sup>8</sup> Polyester polyols were synthesized using melt transesterification according to procedures summarized in **Scheme 3**.



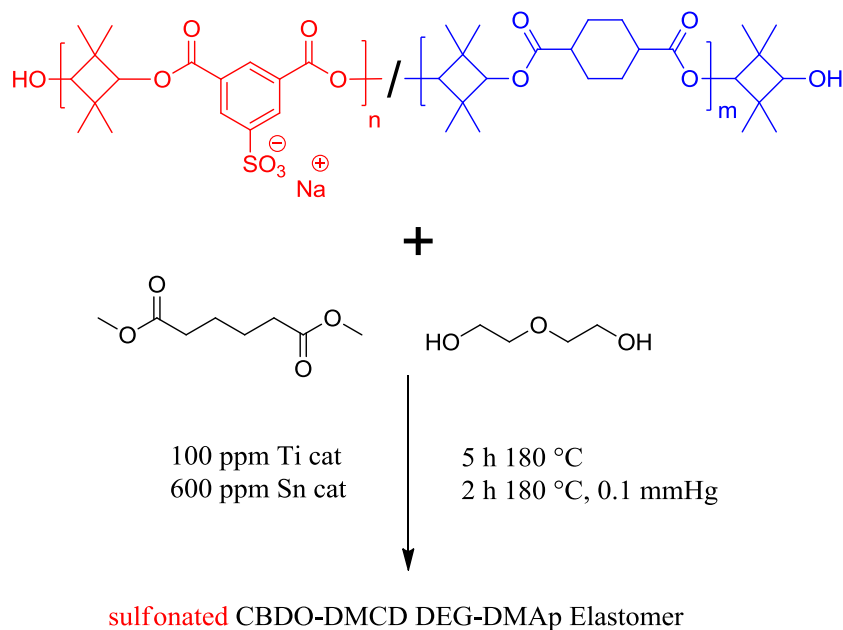
**Scheme 3.** Synthesis of sulfonated poly(CBDO-DMCD) using melt transesterification.

<sup>1</sup>H NMR spectroscopy confirmed the structure of the sulfonated and unsulfonated polyols systems (**Figure 1**).



Although chloroform SEC provided appropriate molecular weight results, sulfonated polyols showed aggregation in this solvent. Therefore, molecular weight of the sulfonated system was achieved through  $^1\text{H}$  NMR spectroscopy. Unsulfonated analogs using dimethyl isophthalate allowed comparison of the glass transition temperature attributed to ionic molar content.

Using previously determined transesterification study results, the polyester polyols were further utilized to synthesize segmented copolyesters with DMAP and DEG soft segments using melt transesterification as shown in **Scheme 4**.  $^1\text{H}$  NMR confirmed the structure of the segmented copolyesters and  $^{13}\text{C}$  NMR confirmed only two signals for the carbonyl ester corresponding to the carbonyl within the hard segment and within the soft segment.



**Scheme 4.** Melt transesterification of CBDO-DMCD-DEG-DMAp segmented copolyesters containing various sulfonation molar content.

Dynamic mechanical analysis revealed two thermal transitions corresponding to the soft and hard phases of the segmented copolyesters. The service temperature window ranged from -26 to 120 °C depending on whether the segmented copolyesters was sulfonated or not. The interesting decrease in the rubber plateau modulus prompted us to further investigate the segmented copolyesters surface morphology using atomic force microscopy.

## Conclusions

Segmented copolyesters offer an array of desirable attributes such as tunable mechanical properties and inherent biodegradability through the hydrolytic ester bond. We described a novel family of sulfonated segmented copolyesters based upon the melt transesterification of poly(CBDO-DMCD) polyols with low- $T_g$  monomers comprising the soft segment. These segmented copolyesters were characterized using  $^1\text{H}$  NMR spectroscopy, TGA, DSC, DMA, tensile tests, and AFM. The results suggested the absence of transesterification within the hard segment and microphase separation of the hard and soft blocks. The introduction of ionic groups

in the hard segment provides an avenue to tune mechanical and adhesive properties on the molecular level of these copolyesters as potential temperature-sensitive adhesives.

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