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# High-Performance Pressure-Sensitive Adhesives from Renewable Triblock Copolymers

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Supporting Information

As part of broader efforts to develop sustainable alternatives to polymers derived from nonrenewable feedstocks,[1] biorenewable and biodegradable ABA triblock copolymers are being actively explored for thermoplastic elastomers and other applications.[2] A key technology for such copolymers is in pressure sensitive adhesives (PSAs), where, for example, the "stickies" problem in paper recycling could be mitigated by facilitating degradation of contaminating residues after paper pulping.[3] We recently developed renewable and hydrolytically degradable poly(lactide)-*b*-poly(menthide)-*b*-poly(lactide) (PLA-PM-PLA) triblock copolymers that were microphase separated, elastomeric, and effective as poly(L-lactide) crystallization nucleation agents.[2,4] High molar mass (∼100 kg/mol) PLA-PM-PLA samples containing small PLA (5−10 kg/mol) segments formulated with 40 wt % of a rosin ester tackifier miscible with the central PM component gave PSAs with respectable peel adhesion, probe tack and sheer strength values (3.2 N $cm^{-1}$, 1.1 N, and ∼2500 min at room temperature, respectively).[4e]

With a key goal being to improve performance at high temperatures for broader applicability, we developed variants with poly(α-methylene-γ-butyrolactone) (PMBL) end blocks that exhibit very high $T_g$ values (170−190 °C).[5] While these PMBL-PM-PMBL triblocks were found to exhibit excellent mechanical properties (e.g., high elongation at break values and low hysteresis), difficulties were encountered in efforts to explore PSA formulations due to their poor solubility in common organic solvents. We report herein the preparation of poly(γ-**methyl**-α-methylene-γ-butyrolactone)-*b*-poly(menthide)-*b*-poly(γ-**methyl**-α-methylene-γ-butyrolactone) (PMeMBL-PM-PMeMBL), the end blocks of which can be accessed from biomass via levulinic acid.[6] Characterization of the new triblock copolymer revealed the requisite elastomeric properties and enhanced solubility in organic solvents for the preparation of tackifier modified blends that exhibited impressive PSA properties significantly improved relative to previously reported sustainable polymer-containing formulations.

Samples of the triblock copolymer PMeMBL-PM-PMeMBL were synthesized using procedures similar to that used for the preparation of PMBL-PM-PMBL,[5] substituting γ-methyl-α-methylene-γ-butyrolactone (MeMBL; Figure 1) for α-methylene-γ-butyrolactone (see Supporting Information (SI) for details). $^1$H NMR spectroscopy and SEC data (Figure S1−S3) support the successful formation of two low dispersity triblocks containing 9.6 and 16.8 wt % PMeMBL (Table 1).

The triblocks were characterized by differential scanning calorimetry (DSC), atomic force microscopy (AFM), and small-angle X-ray scattering (SAXS) (Figures S4−S6). DSC traces of the PMeMBL-PM-PMeMBL samples revealed two glass transition temperatures around −26 and 210 °C, consistent with microphase-separated PM midblocks ($T_g$ ≈ −26 °C)[4a] and PMeMBL ($T_g$ ≈ 225 °C)[7] end blocks. Further support for microphase separation came from room temperature AFM images of thermally annealed (150 °C for 1 d) thin films that featured circular bright spots (smaller, hard PMeMBL domains) in a darker background (soft PM; Figure S6) consistent with spherical inclusions of PMeMBL in a matrix of PM. SAXS profiles of similarly annealed samples contained a principal reflection consistent with domain spacings of 21 and 22 nm for the 5-100-5 and 10-100-10 triblocks, respectively (Figure S5). Although well-defined higher-order reflections were not observed, broad features at higher $q$ values are consistent with form factor scattering from an array of spherical particles. Based on these data and considering the low hard segment (PMeMBL) contents, we posit that the copolymers adopt a microphase separated but disorganized spherical morphology.

Analysis of tensile stress−strain curves (Figure S7 and Table S1) for the triblock copolymers revealed tensile strengths (2−4 MPa) lower than those reported for PMBL-PM-PMBL (3−12 MPa) or commercial poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene) (SBS) TPEs (20−40 MPa),[5] but higher than PLA-PM-PLA (<1.7 MPa)[4a] and PMBL-PBA-PMBL (0.7 MPa).[8] Notably, the PMeMBL-PM-PMeMBL samples demonstrated strain values in excess of 1600% similar to what was reported for PMBL-PM-PMBL;[5] mechanical failure of these triblocks was not observed due to instrumental limitations.

Based on our earlier PLA-PM-PLA triblock studies,[4e] we formulated blends of the PMeMBL-PM-PMeMBL copolymers with the rosin ester (RE) tackifiers Sylvalite RE-85 and Sylvalite RE-10L (Arizona Chemicals). A representative PSA formulation was prepared by combining PMeMBL(10)-PM(100)-PMeMBL(10) (100 parts, 61 wt %) with Sylvalite RE-85 (40

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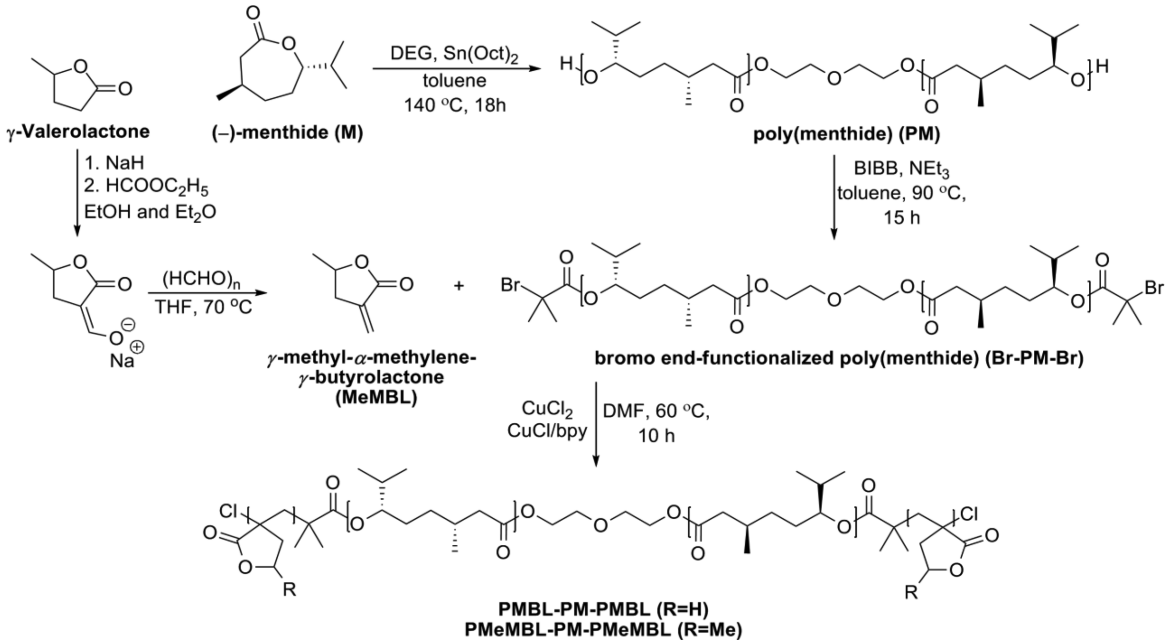


**Figure 1.** Renewable monomers and triblock copolymers.

**Table 1. Characterization Data for PMeMBL-PM-PMeMBL**[a]

| polymer | $[M]_0/[I]_0$[b] | $M_n$[c] (theo.) kg mol$^{-1}$ | $M_n$[d] (NMR) kg mol$^{-1}$ | $M_n$[e](SEC) kg mol$^{-1}$; $Đ$ | wt% PMeMBL |
|---|---|---|---|---|---|
| PMeMBL–PM-PMeMBL (5–100–5) | 350 | 111 | 111 | 113 (1.07) | 9.6[f] |
| PMeMBL–PM-PMeMBL (10–100–10) | 670 | 123 | 120 | 117 (1.07) | 17[f] |

[a]See Supporting Information for synthetic details. [b]M is γ-methyl-α-methylene-γ-butyrolactone (MeMBL) and I is dibromide-terminated poly(menthide) (Br-PM-Br) macroinitiator. [c]Calculated based on monomer conversion as determined by $^1$H NMR spectroscopy. [d]Calculated from relative integrations of PMeMBL and PM repeating units for PMeMBL-PM-PMeMBL by $^1$H NMR spectroscopy. [e]Determined by size exclusion chromatography (SEC) in $CHCl_3$ at 35 °C relative to poly(styrene) standards. [f]Mass percent of PMeMBL calculated from $^1$H NMR spectroscopy.

parts, 24 wt %) and Sylvalite RE-10L (25 parts, 15 wt %) in $CHCl_3$. The resulting solution was coated on a 2 mm polyester (Mylar brand PET) film using a Baker bar set at 8 mils (200 μm). The film was dried for 48 h and covered with release liner. The resultant coat weight was 22 g m$^{-2}$ (gsm). Preliminary adhesive tests using this single composition revealed high peel adhesion values {24.8 N/25 mm ($\sigma$ = 0.51)}. Loop tack, the property that controls the instant formation of a bonding interaction between the substrate and adhesive when they are brought into contact, was also high {11.2 N/25 mm$^2$ ($\sigma$ = 1.9)}.[9] Particularly notable was the superior shear adhesion failure temperature of this formulation. The shear adhesion temperature is the resistance to shear of a tape at constant load under rising temperatures and is defined as the temperature at which specimens bonded with adhesives delaminate under static load in shear.[10] The test was performed by hanging 500 g weights from the bottom of test strips having a contact area of 2.54 × 2.54 cm$^2$, while the oven temperature was raised at a rate of 25 °C h$^{-1}$. The heat-fail temperatures of these PSA formulations were in excess of 150 °C and in the realm of that typically observed for cross-linked systems. These values are superior to many common commercial formulations. For example, heat-fail temperatures for non-cross-linked styrenic block copolymer based PSA's, such as those used in commercial packaging, masking, and duct tapes, typically range from 90–125 °C.[11]

## ■ ASSOCIATED CONTENT

### Supporting Information

Detailed experimental procedures, $^1$H and $^{13}$C NMR data, SEC, DSC, AFM and SAXS profiles, and stress–strain curves for PMeMBL-PM-PMeMBL triblock copolymers. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.biomac.5b00754.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

(1) (a) Miller, S. A. *ACS Macro Lett.* **2013**, *2*, 550−554. (b) Wilbon, P. A.; Chu, F.; Tang, C. *Macromol. Rapid Commun.* **2013**, *34*, 8−37. (c) Olsén, P.; Borke, T.; Odelius, K.; Albertsson, A.-C. *Biomacromolecules* **2013**, *14*, 2883−2890. (d) Holmberg, A. L.; Reno, K. H.; Wool, R. P.; Epps, T. H., III *Soft Matter* **2014**, *10*, 7405−7424. (e) Olsén, P.; Undin, J.; Odelius, K.; Albertsson, A.-C. *Polym. Chem.* **2014**, *5*, 3847−3854. (f) Målberg, S.; Plikk, P.; Finne-Wistrand, A.; Albertsson, A.-C. *Chem. Mater.* **2010**, *22*, 3009−3014.

(2) Hillmyer, M. A.; Tolman, W. B. *Acc. Chem. Res.* **2014**, *47*, 2390−2396.

(3) Severtson, S. J.; Wang, X.; Kroll, M. S. *Ind. Eng. Chem. Res.* **2002**, *41*, 5668−5675.

(4) (a) Wanamaker, C. L.; O'Leary, L. E.; Lynd, N. A.; Hillmyer, M. A.; Tolman, W. B. *Biomacromolecules* **2007**, *8*, 3634−3640. (b) Wanamaker, C. L.; Bluemle, M. J.; Pitet, L. M.; O'Leary, L. E.; Tolman, W. B.; Hillmyer, M. A. *Biomacromolecules* **2009**, *10*, 2904−2911. (c) Wanamaker, C. L.; Tolman, W. B.; Hillmyer, M. A. *Biomacromolecules* **2009**, *10*, 443−448. (d) Wanamaker, C. L.; Tolman, W. B.; Hillmyer, M. A. *Macromol. Symp.* **2009**, *283*−*284*, 130−138. (e) Shin, J.; Martello, M. T.; Shrestha, M.; Wissinger, J. E.; Tolman, W. B.; Hillmyer, M. A. *Macromolecules* **2011**, *44*, 87−94.

(5) Shin, J.; Lee, Y.; Tolman, W. B.; Hillmyer, M. A. *Biomacromolecules* **2012**, *13*, 3833−3840.

(6) (a) Manzer, L. E. *ACS Symp. Ser.* **2006**, *921*, 40−51. (b) Manzer, L. E. *Appl. Catal. A: Gen.* **2004**, *272*, 249−256.

(7) Zhang, Y.; Gustafson, L. O.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2011**, *133*, 13674−13684.

(8) Juhari, A.; Mosnáček, J.; Yoon, J. A.; Nese, A.; Koynov, K.; Kowalewski, T.; Matyjaszewski, K. *Polymer* **2010**, *51*, 4806−4813.

(9) (a) Pocius, A. V. *Adhesion and Adhesives Technology: An Introduction*, 1st ed.; Hanser-Gardner: Cincinnati, OH, 1997; pp 251−259. (b) Benedek, I. *Pressure-Sensitive Adhesives and Applications*, 2nd ed.; Marcel Dekker: New York, 2004; pp 429−477.

(10) Benedek, I.; Feldstein, M. M. *Applications of Pressure-Sensitive Products*; CRC Press, Taylor and Francis Group: Boca Raton, FL, 2008; pp 8−56.

(11) (a) He, Q.; Hu, Y.; Pollock, A.; Mehaffy, J.; Harwell, M. G. European Patent Specification, EP2178974B1, 2008. (b) Muro, T.; Takeda, M. US Patent 5059487, 1991.



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