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Sustainable triblock copolymers as tunable and degradable pressure sensitive adhesives

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ABSTRACT

Pressure sensitive adhesives (PSAs) are widely used in a variety of applications (*e.g.,* sticky note and packing tape). As for most commercial polymer products, current PSA materials are primarily derived from fossil resources and not readily degradable, which has negative environmental consequences. Designing new PSA materials from sustainable resources possessing competitive adhesion properties and degradability is attractive for addressing sustainability concerns. In this work, we prepared a new aliphatic polyester with a long alkyl substituent, poly(pentadecyl caprolactone) (PPDCL), from cashewnut shell liquid derived lactones by ring opening transesterification polymerization in a controlled fashion. The PPDCL was used as the central block in a symmetric triblock copolymer with poly(lactide) end blocks. A series of ABA triblock copolymers were blended with a renewable tackifier to produce sustainable PSA materials. The resultant PSAs showed competitive adhesion properties with many common commercial adhesives. In addition, the ABA triblock copolymers hydrolytically degraded at 50 °C under acidic conditions suggesting they could be attractive sustainable and degradable PSA materials.

Keywords: Polyesters, Pressure sensitive adhesives, Degradable polymers, Sustainable polymers, Cashewnut shell liquids

INTRODUCTION

Pressure sensitive adhesives (PSAs) are widely used in many applications such as sticky notes, labels, tape, and stamps due to their facile adhesion to substrates with minimal applied force.[1] The global PSA market is growing at about 10% annually with a projected total market of 13 billion USD in 2023.[1,2] Most commercial PSAs contain two important components: polymer and tackifier.[3] Among many possibilities, the ABA triblock copolymer architecture has been recognized as particularly useful; it is typically comprised of glassy/minority A-end blocks and rubbery/majority B-central block.[1,4] The microphase-separated glassy A-blocks can act as physical crosslinks, thereby providing strength and resistance to creep while a high level of adhesion mostly originates from the rubbery B-block matrix.[1,4] For example, poly(styrene)-poly(isoprene)-poly(styrene) (SIS)[1,5-6] and poly(styrene)-poly(butadiene)-poly(styrene) (SBS)[7,8] are presently being used in commercial PSAs. In general, these commercial triblock copolymers are blended with a tackifier to increase the adhesion by diluting entanglements in the central block thus lowering the modulus; lower modulus materials can better establish contact with the substrate of interest over larger areas.[1,5,9,10] For example, SBS exhibits high storage modulus given the low entanglement molar mass (M_e) of poly(butadiene) (PB) (≈ 1.7 kg mol^{-1}), resulting in poor adhesion.[2,8,10-12] Therefore, a tackifier is blended into the PB block to dilute entanglements, providing improved adhesion.[1,8,10]

Most commercial PSA materials are derived from fossil resources and often have poor degradability, which raises a number of sustainability concerns. With recent attentions on polymer sustainability, PSA materials from renewable feedstocks are of interest as potential alternatives to fossil resource derived counterparts (*e.g.*, SIS and SBS).[2,9,13-17] To rationally design sustainable ABA triblock copolymers, a number of sustainable A-blocks with high glass transition temperature (T_g) have been considered as substitutes to the traditional styrenic hard block ($T_{g,PS}$ ≈ 100 °C); examples include poly(lactide)

(PLA),[4,15,16] poly(isosorbide acrylate),[17] poly(glucose acrylate),[18] poly(propylsyringyl acrylate),[2] poly(γ-methyl-α-methylene-γ-butyrolactone)[19], and poly(lactone acrylate).[46] In contrast, the development of alternative rubbery B-blocks has been focused on polymers with low T_g, such as poly(menthide) (PM),[16,19] poly(β-methyl-δ-valerolactone) (PβMδVL),[4] and poly(ε-decalactone) (PDL).[15] Some of these sustainable PSA systems exhibited competitive adhesion properties to commercial products (*e.g.,* duct tape). Among the possible sustainable ABA combinations, completely degradable triblock copolymers (*e.g.* PLA-*b*-PM-*b*-PLA)[16,20] are particularly attractive because they can potentially degrade before or during the paper recycling process, solving the "adhesive residue" problem in pulping facilities.[13,14,19]

To date, most of the reported sustainable and degradable rubbery B-blocks have lower M_e (*e.g.,* $M_{e,\mathrm{P}\beta\mathrm{M}\delta\mathrm{VL}} \approx 4$ kg mol^{-1}, $M_{e,\mathrm{PDL}} \approx 5$ kg mol^{-1}, $M_{e,\mathrm{PM}} \approx 13$ kg mol^{-1})[15,16,21] than the typical non-hydrolytically degradable rubbery B-blocks, such as poly(isoprene) ($M_e \approx 7$ kg mol^{-1})[12,22] or poly(n-butyl acrylate) ($M_e \approx 28$ kg mol^{-1})[12], which can limit adhesion performance. Shin and co-workers engineered PDL-based PSAs by blending with a tackifier and plasticizer together to both dilute entanglements and control viscosity.[15] The incorporation of bulky side groups in the B-central block polymer is another strategy to reduce entanglements by increasing M_e.[23] For example, the M_e of poly(*n*-alkyl-*δ*-valerolactones) significantly increases with increasing the length of alkyl substituents without impacting the T_g.[21] With this knowledge, we identified poly(pentadecyl caprolactone) (PPDCL) containing the long alkyl (C15) substituent as an attractive rubbery B-block. PPDCL is relatively inexpensive, rubbery, expected to have a high M_e, and potentially degradable, making it an attractive alternative rubbery B-block for PSAs. Moreover, its lactone precursor can be synthesized from cashewnut shell liquids (CNSLs), which are by-products of the cashew industry (**Figure 1**).[24-26] The cashew industry produces >2.2 million tons of cashews per year, and CNSLs are being produced from the cashewnut shells through a straightforward extraction process, supplying over 450,000 metric tons of CNSLs per year at low cost.[26] In the present study, PPDCL was synthesized from a CNSLs-derived lactone in a controlled manner through ring opening transesterification polymerization (ROTEP) for the first time. The synthesized PPDCL was used as the rubbery B-central block in ABA triblock copolymers containing glassy PLA as A end blocks. The resultant PSAs exhibited adhesion properties competitive with commercial versions with the added benefit of hydrolytic degradability. We conclude that the PPDCL based polymers have potential as future sustainable and degradable PSA materials.

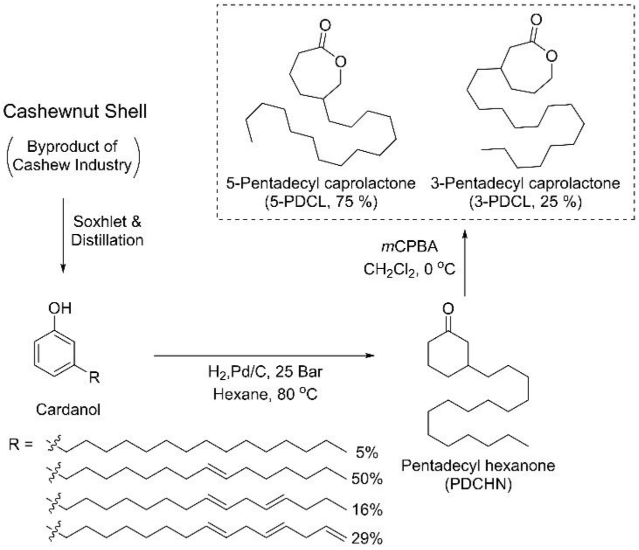

Figure 1. Plausible synthetic route of PDCL from cashewnut shells. PDCL was synthesized from cardanol in this study.

RESULTS AND DISCUSSION

Monomer synthesis. Cardanol, an ingredient in CNSLs, was used as the starting material to synthesize pentadecyl caprolactone (PDCL). Note that the synthesis of PDCL from CNSLs is reported by Lemaire and co-workers: all of the monomer synthetic procedures (ketones and lactones) were from a previous report.[24] Briefly, cardanol was reduced by Pd-catalyzed hydrogenation, yielding a mixture of 3-pentadecyl cyclohexanol and 3-pentadecyl cyclohexanone (PDCHN) (**Figure 1**). Note that high pressure (>35 bar) and a reaction time of 6 h is critical to achieve high yields of PDCHN (≈ 70%). The PDCHN was converted to the caprolactone form (PDCL) by Baeyer–Villiger oxidation with *meta*-chloroperoxybenzoic acid (*m*CBPA), yielding a regioisomeric mixture containing 75% 5-PDCL and 25% 3-PDCL. This 5- and 3-PDCL mixture is referred to simply as PDCL in this study. ^{1}H NMR and FT-IR characterization data are shown in the Supporting Information, and are consistent with previously reported results (Figures S1–S4).[24]

Bulk Polymerization. Bulk polymerization of PDCL was carried out at 110 °C using $Sn(Oct)_2$ as a catalyst and 1,4-benzenedimethanol (BDM) as an initiator (**Figure 2** and Figure S5 for ^{1}H NMR). The bulk polymerization was monitored over time by analyzing aliquots using ^{1}H NMR spectroscopy and size exclusion chromatography equipped with multiangle light scattering (MALS-SEC) at 25 °C using tetrahydrofuran (THF) eluent. The conversion of PDCL reached 87% after 6 h, plateauing at about 92% after 9 h (**Figure**

3a). The kinetic plot indicates the polymerization is first-order in monomer (**Figure 3**a; inset), and the pseudo first-order rate constant was 1.4 × 10^{-4} s^{-1} at $[Sn(Oct)_2]_0$ = 0.015 M. By assuming first order dependence on catalyst concentration as for ROTEP of other cyclic esters,[27,28] the second-order rate constant was determined to be 9.1 × 10^{-3} M^{-1} s^{-1}. This is smaller than those of other substituted poly(caprolactones) such as PM (1.4 × 10^{-2} M^{-1} s^{-1} at $[Zn\ alkoxide]_0$ = 0.009 M, 30 °C in toluene)[29] and PγMCL (5.1 × 10^{-2} M^{-1} s^{-1} at $[Sn(Oct)_2]_0$ = 0.016 M, 130 °C in bulk).[28] This is likely because the long alkyl substituent causes significant steric congestion around the ester linkages.[21] A linear relationship between the conversion and molar mass was observed, suggesting a controlled polymerization process (**Figure 3**b). The increase in dispersity that occurs at 92% conversion is presumably due to inter- or intra-molecular transesterification.[30,31] The molar mass of PPDCL increased linearly with increasing $[PDCL]_0/[BDM]_0$ at fixed conversion, resulting in molar mass up to 115 kg mol^{-1} ($M_{n,NMR}$), which is additional evidence for a controlled polymerization (**Figure 3**c). Note that 5-PDCL was more reactive than 3-PDCL during the polymerization (Figure S6) likely due to the thermodynamic preference.[21] This is consistent with the previous report; 5-methyl caprolactone (5-MCL) is more reactive than 3-MCL.[44]

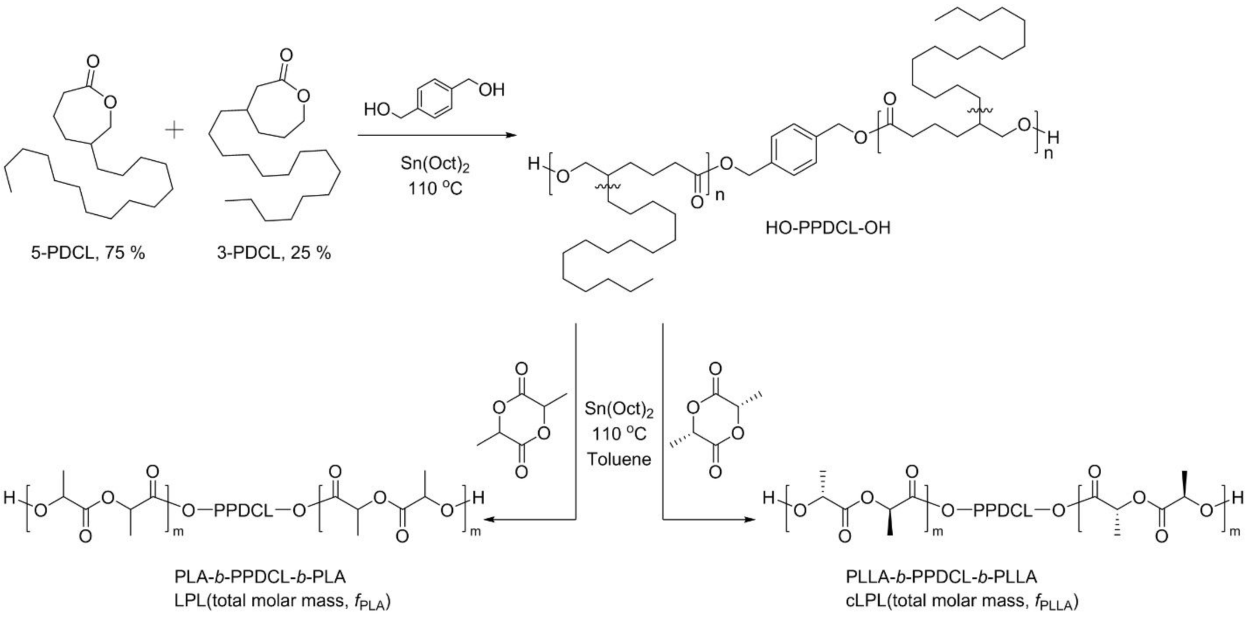

Figure 2. Synthesis of PPDCL, LPL, and cLPL.

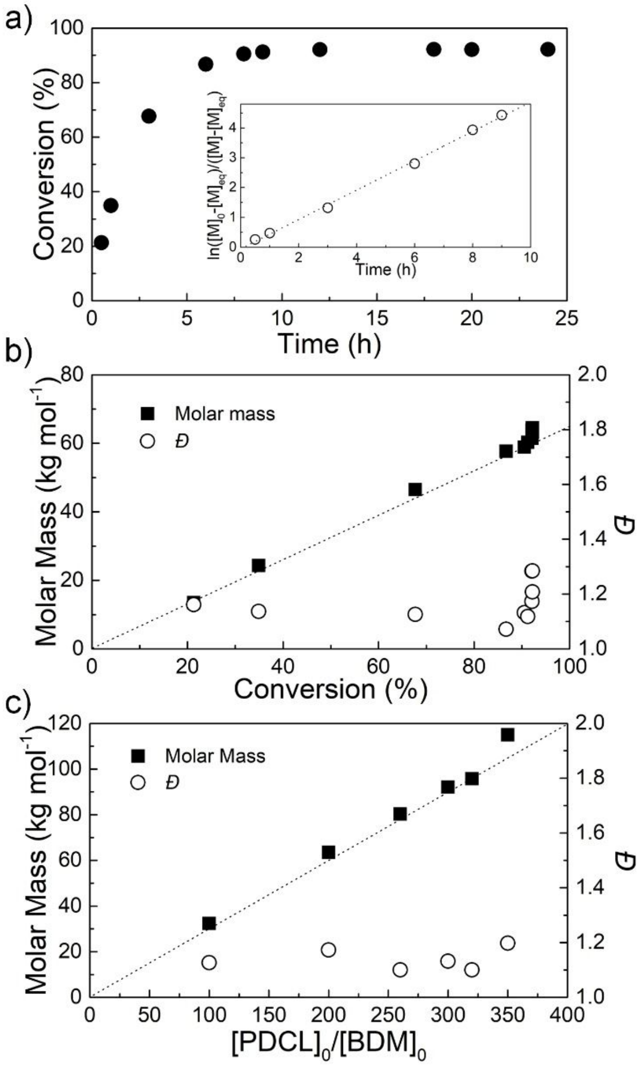

Figure 3. Bulk polymerization of PDCL at 110 °C, $[PDCL]_0$ = 2.91 M, $[Sn(Oct)_2]_0$ = 0.015 M. (a) Conversion of PDCL as a function of reaction time ($[BDM]_0$ = 0.015 M). The inset shows linear fit of kinetic data up to 9 h ($[M]_{eq}$ = 0.23 M). (b) Linear relationship between conversion and molar mass ($[BDM]_0$ = 0.015 M). (c) Molar mass control of PPDCL. Each polymerization was performed to the equilibrium conversion and the dashed lines indicate

the theoretical molar mass at the equilibrium conversion. Conversion of PDCL and molar mass were determined by ^{1}H NMR spectroscopy. Dispersity ($Đ$) was determined by MALS-SEC (THF, 25 °C).

The thermodynamics of the ROTEP of PDCL were investigated by measuring the equilibrium monomer concentration at different polymerization temperatures. By defining standard monomer concentration ($[M]_{ss}$) as 1.0 M,[21,32] the thermodynamic parameters were calculated using equation 1.

$$\ln{[M]_{eq}} = \frac{\Delta H_P^{\circ}}{RT} - \frac{\Delta S_P^{\circ}}{R} \qquad \text{(eq. 1)}$$

From a linear plot of $\ln[M]_{eq}$ versus T^{-1}, the enthalpy and entropy of PDCL polymerization were determined to be ΔH_P° = –16.9 ± 2.1 kJ mol^{-1} and ΔS_P° = –31.2 ± 5.3 J mol^{-1} K^{-1}, respectively (see Figure S7). The determined enthalpy (the parameter of ring strain) is consistent with those of the polymerization of other caprolactones such as *ε*-caprolactone (–17.0 kJ mol^{-1})[33] and menthide (–16.8 kJ mol^{-1}).[29] The entropy of the PDCL polymerization was more unfavorable than those of *ε*-caprolactone (–4.0 kJ mol^{-1})[33] and menthide (–27.4 kJ mol^{-1}),[29] which could be due to the more restricted rotational freedom in the polymer; this might originate from the long alkyl substituent as compared to caprolactone, as previously discussed.[21]

Synthesis of ABA triblock copolymers. The PLA-*b*-PPDCL-*b*-PLA triblock copolymers (LPLs) were synthesized by the ROTEP of lactide using high molar mass (≈ 100 kg mol^{-1}) hydroxy telechelic PPDCL as a macro-initiator (**Figure 2**). Typical styrenic triblock copolymers for PSA applications have small PS volume fractions.[1] Therefore, small volume fractions of PLA end blocks (f_{PLA} = 0.06 and 0.13) were targeted (**Table 1**, Figures S8–S9 for ^{1}H NMR spectra, S10 for SEC traces). Upon completion of the reaction, the signal for the terminal methylene protons of PPDCL at δ ~3.6 ppm was no longer present in the ^{1}H NMR spectrum, and a signal for the new terminal methine protons of the PLA end blocks appeared at δ ~4.35 ppm, consistent with efficient initiation by the PPDCL chain ends (**Figure 4**). Given that the SEC trace of LPL(114k, 0.06) showed a lower molar mass shoulder (Figure S10), it may contain PPDCL homopolymer fraction likely because a low PLA fraction was targeted. The LPL with a high PLA composition (f_{PLA} = 0.50), LPL(82k, 0.50), was also synthesized for clearer observation of the $T_{g,PLA}$, which will be discussed below. ^{13}C NMR spectra revealed no evidence of transesterification between PPDCL and PLA blocks, indicating that the block copolymers have the desired ABA architecture (Figure S11). In addition, PLLA-*b*-PPDCL-*b*-PLLA, cLPL(107k, 0.14), containing similar PLLA fractions was synthesized by the ROTEP of *L*-lactide using hydroxy telechelic PPDCL macro-initiator. This enables an investigation of the effect of crystallinity in the hard segments on the adhesion properties (Figure S12 for ^{1}H NMR data).

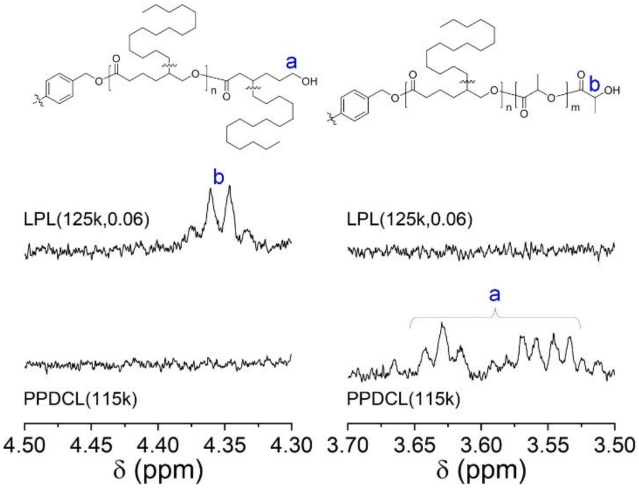

Figure 4. Expanded ^{1}H NMR spectra (500 MHz, $CDCl_3$) of PPDCL(115k) and LPL(125k, 0.06).

Table 1. Molecular characterization data for the synthesized polymers.

Polymer	$M_{n,PPDCL}$[a]	$M_{n,PLA}$[a]	$M_{n,total}$[a]	$M_{n,MALS-SEC}$[b]	$M_{w,MALS-SEC}$[b]	$Đ$[b]	f_{PLA}[c]
PPDCL(92k)	92	0	92	71	89	1.3	0
LPL(125k, 0.06)	115	10	125	102	124	1.2	0.06
LPL(114k, 0.13)	96	18	114	107	129	1.2	0.13
LPL(82k, 0.50)	35	47	82	67	86	1.3	0.50
cLPL(107k, 0.14)	88	19	107	96	114	1.2	0.14

[a]Determined by ^{1}H NMR spectroscopy (kg mol^{-1}). [b]Determined by MALS-SEC (THF, 25 °C) (molar mass unit, kg mol^{-1}). [c]Calculated using ρ_{PPDCL} = 0.943 g cm^{-3} at 0 °C and ρ_{PLA} = 1.25 g cm^{-3} at 25 °C.

Polymer Properties. Thermal, morphological, and rheological properties of the polymers were evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), small-angle X-ray scattering (SAXS), and dynamic mechanical analysis (DMA), respectively. PPDCL(92k) showed comparable thermal stability ($T_{d,5\%}$ ≈ 282 °C) to those of other aliphatic polyesters (Figure S13).[28] The triblock copolymers showed mass loss starting at ≈ 200 °C likely due to the decomposition of the low molar mass PLA component. PPDCL(92k) showed a clear melting endotherm at 27 °C which can be attributed to the long alkyl (C15) side chains in PPDCL (**Figure 5**a, See Figure S14 for the same DSC data over a wider temperature range). This $T_{\mathrm{m,PPDCL}}$ is comparable to the T_{m} of poly(n-alkyl acrylates) (n = 14–18).[34] No clear transition could be assigned to $T_{\mathrm{g,PPDCL}}$, due in part to its large melting endotherm. Instead, $T_{\mathrm{g,PPDCL}}$ was determined by DMA, which displayed a broad tan δ peak at –70 °C (Figure S15). This is comparable to $T_{\mathrm{g,P}\gamma\mathrm{MCL}}$ (–60 °C).[21, 28] Block copolymers containing small PLA fractions showed $T_{\mathrm{m,PPDCL}}$ ≈ 27 °C, whereas $T_{\mathrm{g,PLA}}$ was not clearly observable, likely because of the small PLA content.[17] Nonetheless, the $T_{\mathrm{g,PLA}}$ of LPL(125k, 0.06), LPL(114k, 0.13), and cLPL(107k, 0.14) were observed at 45 °C, 55 °C, and 59 °C, respectively, by DMA (Figure S16). Additionally, LPL(82k, 0.50) exhibited a distinct $T_{\mathrm{g,PLA}}$ ≈ 48 °C and $T_{\mathrm{m,PPDCL}}$ ≈ 27 °C by DSC. The $T_{\mathrm{m,PPDCL}}$ of block copolymers are close to that of PPDCL homopolymer regardless of the volume fraction of PLA, suggesting that the two blocky components are microphase separated. The presence of microphase-separation was corroborated by small angle X-ray scattering profiles of the block copolymers (**Figure 5**b). All of the block copolymers showed prominent principle scattering peaks with higher-order reflections.

Although the morphologies of block copolymers containing low PLA content ($f_{\mathrm{PLA}} < 0.15$) are difficult to assign definitively due to the broadness and weak intensity of the higher-order reflections, we speculate that they are spherical morphologies given the peak position ratio as indicated in Figure S17. Similar scattering patterns of triblock copolymers have been assumed to be a disorganized spherical morphology with the absence of long-range order.[17,19] The LPL(82k, 0.50) sample exhibits lamellae, which is consistent with the expectation for a symmetric block copolymer ($f_{\mathrm{PLA}} \approx 0.5$).

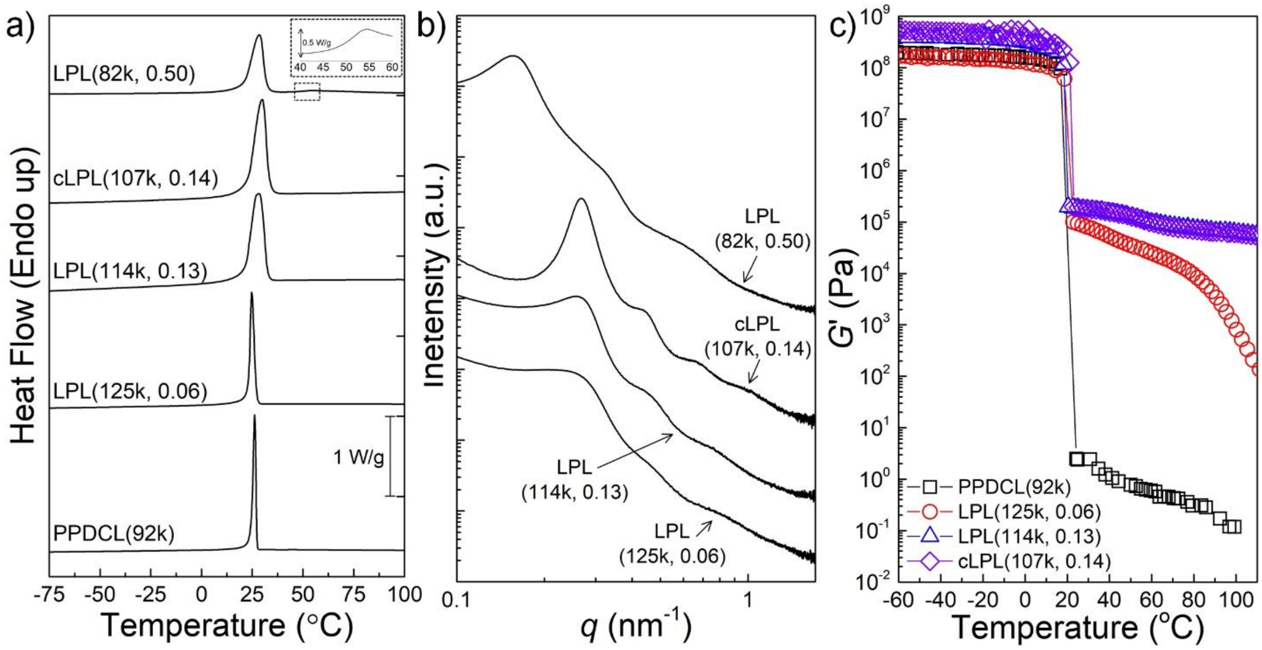

Figure 5. (a) DSC data (2nd heating, 10 °C min^{-1}), (b) SAXS data (at 40 °C, vertically shifted for clarity), and (c) storage moduli (cooling, 10 °C min^{-1}, 1 rad s^{-1}) of the synthesized polymers.

The dynamic elastic modulus is one of the most important parameters governing the wetting of a substrate by PSA.[4,35] According to the Dahlquist criterion, the storage modulus (G') of PSAs at their application temperature should be less than 3×10^5 Pa to achieve wetting under low pressure .[35] All of the block copolymers showed a significant decrease in G' in the vicinity of $T_{\mathrm{m,PPDCL}} \approx 21$ °C, then exhibited plateau moduli (**Figure 5**c). The plateau moduli of LPL(125k, 0.06), LPL(114k, 0.13), and cLPL(107k, 0.14) (9.4×10^4, 1.9×10^5, and 1.9×10^5 Pa at 25 °C, respectively) were all below the Dahlquist criterion. LPL(125k, 0.06) showed a lower modulus than those of LPL(114k, 0.13) and cLPL(107k, 0.14) in the entire temperature range of interest due to the lower PLA content. The M_{e} of PPDCL was estimated by employing the Guth–Smallwood equation.[4,16,28,36] Based on the plateau moduli of LPL(125k, 0.06) and LPL(114k, 0.13) at 25 °C, $M_{\mathrm{e,PPDCL}}$

≈ 20–28 kg mol^{-1} was approximated (Detailed calculations in the Supporting Information). The $M_{e,PPDCL}$ is comparable to the M_e of poly(*n*-butyl acrylate) (≈ 28 kg mol^{-1})[12] but larger than the other central blocks used for degradable ABA triblock copolymers for PSAs, *e.g.,* PM (≈ 13 kg mol^{-1})[16] and PDL (≈ 5 kg mol^{-1}).[15] Therefore, LPL-based PSAs are expected have high levels of adhesion to substrates.

Adhesion Properties. A series of PSA formulations were prepared by solution mixing LPLs with a renewable rosin ester tackifier (Sylvalite 2E 80HP). By adding the tackifier, additional tuning of adhesion and cost reduction are possible.[3] Increasing the tackifier content leads to a decrease in $T_{m,PPDCL}$ as well as a decrease in crystallinity of the PPDCL (**Figures 6** and S18), suggesting PPDCL and tackifier are miscible. In contrast, $T_{g,PLA}$ measured by DMA was essentially unaffected (55 °C) at 20 wt% tackifier loading (Figure S19), indicating that PLA is not miscible with the tackifier. Therefore, the tackifier is miscible with only the less polar PPDCL central block, consistent with other PLA-containing ABA triblock copolymers.[4,15,16]

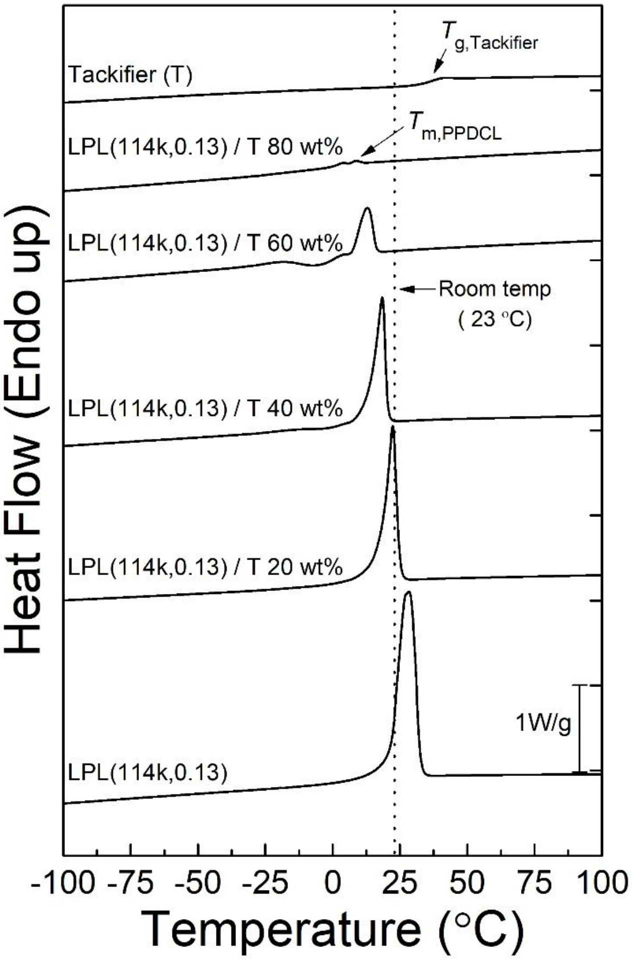

Figure 6. DSC data (2nd heating, 10 °C min^{-1}) of LPL(114k, 0.13) with different tackifier compositions. Vertical dashed line indicates room temperature (23 °C).

The adhesion properties of the resultant PSAs such as peel, loop tack, and shear strengths were evaluated (**Figure 7**, Figures S20–S25, and Table S1 for specific values). In contrast to our expectation that the neat block copolymers with relatively high $M_{e,PPDCL}$

should exhibit high peel and loop tack strengths, they exhibited a low level of adhesion (peel force ≈ 0.19 N cm^{-1}, loop tack force ≈ 0.15 N cm^{-1}) (**Figure 7**a and **7**b), which is comparable to that used for repositionable sticky notes. The peel and loop tack strengths were not improved even after the incorporation of 20 wt% tackifier. This is likely because the semi-crystalline PPDCL block cannot readily flow and adhere to the surface since $T_{\mathrm{m,PPDCL}}$ (≈ 27 °C) is above the room (operating) temperature (≈ 23 °C) (**Figure 6**). For neat block copolymers or PSA formulations containing 20 wt% tackifier, the peel strength (measured at room temperature) increased up to 0.7 N cm^{-1} when the substrate surface was heated to 38 °C for 15 s to improve the flow during adhesion. This suggests that these adhesives would also be useful as heat-activated adhesives, and even could be activated by body temperature. Increasing tackifier content beyond 20 wt% led to a significant improvement in peel and loop tack strengths due to decreases in $T_{\mathrm{m,PPDCL}}$ below room temperature, enabling adequate flow upon light pressure. For example, a peel force of 4.71 ± 0.46 N cm^{-1} and a loop tack force of 5.51 ± 1.00 N cm^{-1} were obtained for LPL(114k, 0.13) with 40 wt% tackifier content, which are comparable to commercial tapes. Increasing the tackifier content further to 60 wt% achieves excellent peel and loop tack strengths, which are superior to commercial adhesives. Given that the T_m of the PSA is still higher than 0 °C, PPDCL can partially crystallize at somewhat lower temperatures. When an adhered adhesive surface was cooled down by an ice cube for 20 s, the peel force decreased and exhibited adhesive failure (i.e., no adhesive residue on a substrate after failure by visual inspection (Figure S26). This suggests that the adhesive can strongly adhere to a substrate and can be detached easily and cleanly on demand, which could be useful for indoor applications.

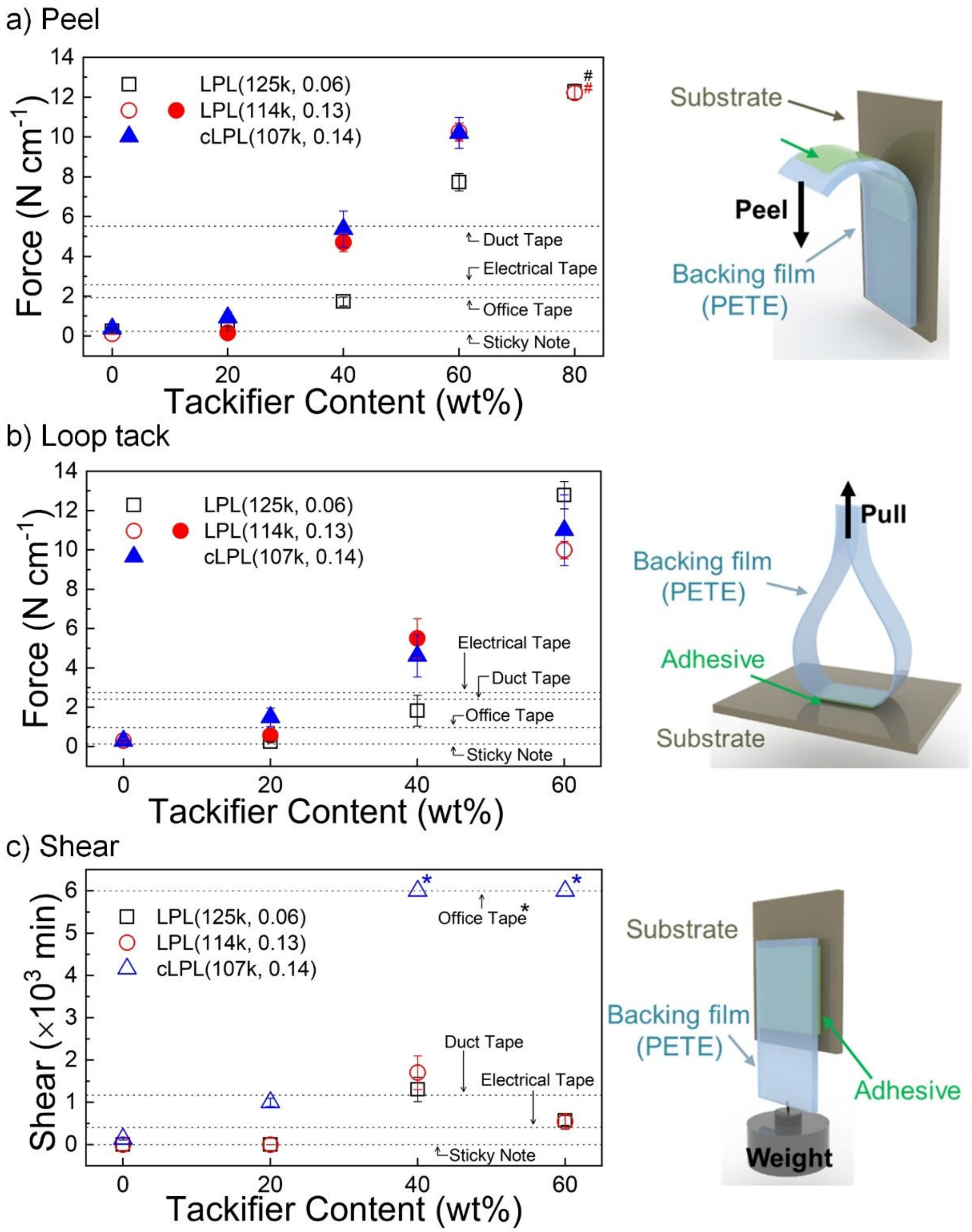

Figure 7. Adhesion properties of LPLs, cLPL, and commercial adhesives; (a) peel adhesion, (b) loop tack adhesion, and (c) shear resistance. Open and filled symbols indicate cohesive and adhesive failure, respectively. Horizontal lines indicate the

adhesion properties of commercial adhesives. All of the peel and loop tack adhesion tests were performed at the rate of 305 mm min^{-1}, otherwise noted. $^{\#}$measured at a peel rate of 31 mm min^{-1}. *No failure for 6000 min, and then the experiment was manually terminated. See Table S1 for specific values.

Mostly, LPL(114k, 0.13) and cLPL(107k, 0.14) with higher PLA content exhibited similar or stronger peel/loop tack strengths than LPL(125k, 0.06) at most tackifier compositions.[15,17] Adhesive failure was observed for cLPLs over the entire range of tackifier compositions, suggesting that they would be useful for removable PSA applications. This is likely because the crystallinity of the PLLA end blocks reduced failure of the physical crosslinks by, for example, chain-end pullout, leading to a stronger adhesive that is less likely to fail cohesively.[37] The increased strength of the semi-crystalline block polymers is also consistent with the high values of shear strength (**Figure 7**c and discussed below). Surprisingly, transparent PSAs with 80 wt% tackifier were prepared without phase separation between the LPLs and the tackifier. However, stick slip failures were observed for those samples when the peel test was performed at a peel rate of 305 mm min^{-1} (Figures S20e and S21e) possibly due to the partial coverage of the substrate by free tackifier.[6] However, reliable peel strength data were obtained at a slow peel rate of 31 mm min^{-1} (Figures S20f and S21f). Note that common tackifier compositions for PSAs are lower than 60 wt% for two reasons: either an increase in T_g to near/above use temperature or phase separation between the polymer and the tackifier are observed.[4,6,16] For example, a significant drop in peel strength was observed when PLA-PM-PLA was blended with 60 wt% tackifier.[16] The LPL system reported here can apparently tolerate more tackifier than other ABA triblock copolymer systems (*e.g.* PLA-*b*-PM-*b*-PLA and PLA-*b*-P*β*M*δ*VL-*b*-PLA),[4,16] possibly due to the more nonpolar nature of PPDCL.

To examine the resistance of PSA to flow under a constant load, shear tests were carried out by suspending a 500 g weight on the adhesive film (contact area: 1.27 cm × 1.27 cm) adhered to the substrate. Particularly, LPLs with 40 or 60 wt% tackifier failed after ~1700 and ~500 min, respectively (**Figure 7**c and Table S1). This is due to the weak resistance to flow of LPLs, which results from the low modulus of PPDCL and weak physical crosslinking of non-crystalline PLA hard segments that can fail by, for example, chain pullout. While, cLPL(107k, 0.14) with 40 or 60 wt% tackifier showed no shear failure up to 6000 min, likely because the strong physical crosslinking of crystalline domains in the PLLA hard segments provide strong resistance to creep.[15] To summarize the adhesion of LPL-based PSAs, the adhesion can be tuned over a wide range from the low level of adhesion (*e.g.*, sticky notes) to strong adhesion (*e.g.*, stronger than duct tape) by controlling the PLA length, crystallinity of PLA, and/or tackifier composition.

Hydrolytic Degradation. The hydrolytic degradation of PPDCL and LPLs at 50 °C in 0.1 M HCl/THF or 0.1M NaOH/THF mixtures (1/1 vol.) was monitored by MALS-SEC. When polymers were exposed to acidic conditions, all polymers exhibited more than 90 % loss of molar mass ($M_{\mathrm{n,MALS\text{-}SEC}}$) after 28 days compared (**Figure 8**), suggesting that PPDCL degrades by acid-catalyzed hydrolysis as for poly(caprolactone) under similar conditions.[38,39] This result demonstrates that the LPL-based PSAs could be useful for solving the “adhesive residue” problem in pulping facilities. The small differences in degradation rates are likely due to the small differences in hydrophilicity, original molar mass, and PLA content.[40,41] A decrease in molar mass was accompanied by the broadening of SEC traces (Figure S27), which is evidence of homogeneous and random chain scission.[42,43] ^{1}H NMR spectra of the degradation products also confirm the structural change of PPDCL and PLA upon hydrolytic degradation (**Figure 9**).[45] The methine proton in PLA (δ ~5.2 ppm, see red triangle region) disappeared almost completely while a new carboxylic acid proton appeared at δ ~10.5 ppm. Methylene protons, assigned as g (δ~4.0 ppm) and f (δ~2.2 ppm), were also shifted and broadened, indicative of PPDCL chain scission. The degradation of PPDCL was slower when exposed to basic conditions (Figure S28).

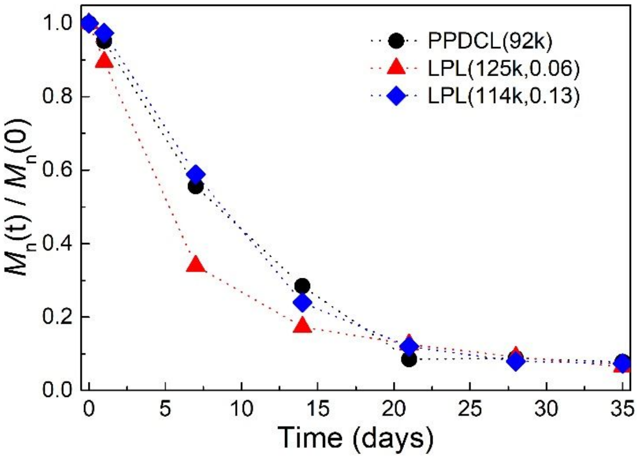

Figure 8. Relative remaining molar mass ($M_{\mathrm{n,MALS\text{-}SEC}}$) of PPDCL and LPLs under hydrolytic degradation conditions at 50 °C in 0.1 M HCl(*aq*)/THF mixture solution (1/1 vol.).

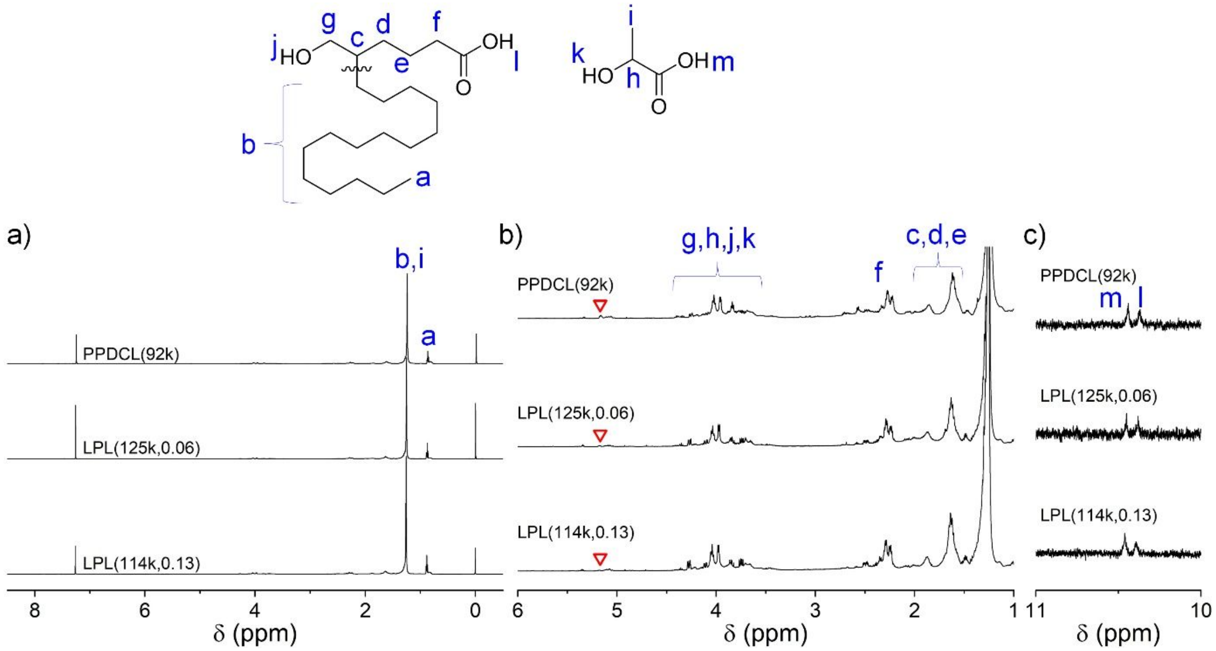

Figure 9. (a) ^{1}H NMR spectra (500 MHz, $CDCl_3$) of PPDCL and LPLs after 4 weeks of hydrolytic degradation conditions at 50 °C in 0.1 M HCl(*aq*)/THF mixture solution (1/1 vol.). (b) and (c) expanded ^{1}H NMR spectra corresponding to methylene/methine and carboxylic acid protons, respectively.

CONCLUSIONS

A new aliphatic polyester (PPDCL) with a long alkyl substituent was synthesized in a controlled manner from a cardanol based lactone. The PPDCL was used as the B-central block in an ABA triblock copolymer with PLA as A-end blocks. This triblock copolymer (LPL) was evaluated as a PSA, by either using it as a neat material or blending with a renewable tackifier. The resultant PSAs exhibited a wide range of adhesion properties, which are comparable or superior to commercial PSAs. The unique and beneficial characteristics of LPL-based PSAs are attributed to the long alkyl substituent in the PPDCL block. In addition, the LPLs degraded in 0.1 M HCl(*aq*)/THF mixture solution at 50 °C within a reasonable time frame. The properties of these polymeric materials can be further tuned by controlling molar mass, architecture, and composition for other future applications. PPDCL is a promising degradable alternative to other non-degradable rubbery polymers such as poly(*n*-alkyl acrylates).

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge.

Additional experimental details, polymerization thermodynamics, supplementary characterization data (^{1}H and ^{13}C NMR, FT-IR spectroscopy, SEC, DSC, Rheology, SAXS), adhesion test, hydrolytic degradation data.

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Notes

The authors declare no competing financial interest.

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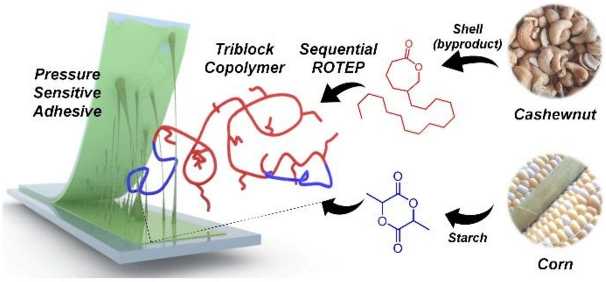

Tunable and degradable pressure sensitive adhesive materials have been prepared from renewable resources.