

## 지속 가능한 블록 공중합체 기반 열가소성 탄성체

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## Sustainable Block Copolymer-based Thermoplastic Elastomers

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ABA 형태의 삼중블록공중합체는 고무상과 유리상의 상대적 성분에 좌우되는 열가소성 탄성체와 강화 플라스틱으로써 유용하다. 이러한 물질은 다른 고분자와 혼합하여 첨가제, 강화제, 상용화제로써 기능성을 줄 수 있다. 상업적으로 유용한 대부분의 블록 공중합체는 석유로부터 유래된다. 지구상의 유한한 화석자원 공급과 석유 사용 및 채굴에 관련된 경제, 환경적 비용을 고려하면 그 대안은 매력적이다. 이러한 흐름에 더하여 미래 지속 가능한 물질의 최종 용도를 위한 설계 및 그 실행이 요구되고 있다. 본 총설에서는 재생 가능한 ABA 형태의 삼중블록 공중합체 합성과 특성을 살펴보고, 특히 공중합체의 경성부분을 위한 높은 유리 전이온도 혹은 녹는점을 지닌 식물 유래 폴리올레핀과 다당류 유래 폴리락타이드와 공중합체의 연성부분을 위한 바이오 기반, 낮은 유리 전이온도, 무결정의 탄화수소계 고분자에 대해 논의하려고 한다. 이를 위해서 다양하게 제어된 고분자 중합법은 강력한 도구임이 증명되고 있다. 이러한 혼성 고분자의 정교한 합성에 관한 연구는 재생가능성, 생분해성, 고성능을 지닌 새로운 탄성체와 강화 플라스틱의 발전을 이끌고 있다.

Block copolymers including ABA triblock architectures are useful as thermoplastic elastomers and toughened plastics depending on the relative glassy and rubbery content. These materials can be blended with other polymers and utilized as additives, toughening agents, and compatibilizers. Most of commercially available block copolymers are derived from petroleum. Renewable alternatives are attractive considering the finite supply of fossil resources on earth and the overall economic and environmental expenses involved in the recovery and use of oil. Furthermore, tomorrow's sustainable materials are demanding the design and implementation with programmed end-of-life. The present review focuses on the preparation and evaluation of new classes of renewable ABA triblock copolymers and also emphasizes on the use of carbohydrate-derived poly(lactide) or plant-based poly(olefins) having a high glass transition temperature and/or high melting temperature for the hard phase in addition to the use of bio-based amorphous hydrocarbon polymers with a low glass transition temperature for the soft components. The combination of multiple controlled polymerizations has proven to be a powerful approach. Precision-controlled synthesis of these hybrid macromolecules has led to the development of new elastomers and tough plastics offering renewability, biodegradability, and high performance.

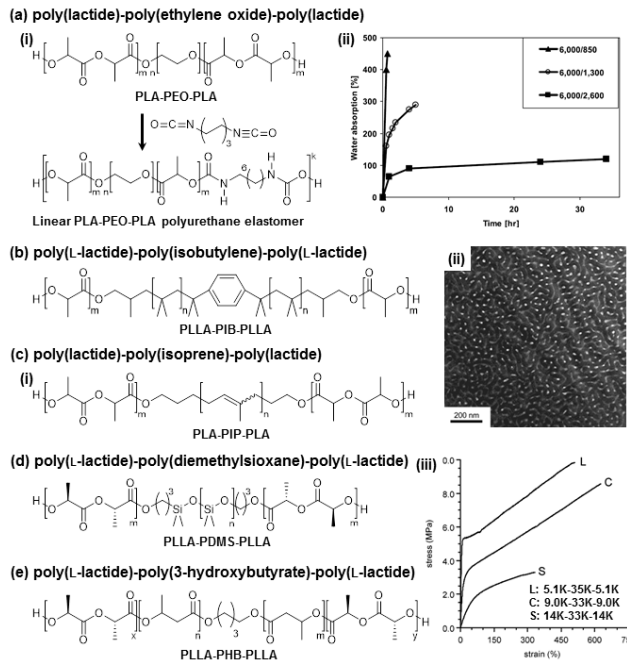
**Keywords:** ABA triblock copolymers; renewable; controlled polymerization; thermoplastic elastomers; toughening

### 1. Introduction

Thermoplastic elastomers (TPEs), offering both the processing advantages

of thermoplastics and the flexibility and extensibility of elastomeric materials, have found versatile applications in industry, including use in electronics, clothing, adhesives, and automotive components[1]. ABA triblock copolymers consisting of a soft segment between two hard segments are commercially available as TPEs. They have a microphase-separated morphology caused by an immiscible rubbery phase between two hard segments[2]. The application of triblock copolymers as TPEs requires careful control over their nanoscale structure. Given that the phase behavior of triblock copolymers has been well characterized[3-5], desired mechanical properties can be achieved by tuning the molecular composition and architecture.

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**Figure 1.** (a) Molecular structure of PLA-PEO (or PEG)-PLA and linear polyurethane elastomer with the triblock copolymer (i) and water absorption of three polyurethane elastomer comprising the same PEO segment (6000) and increasingly long PLA block as a function of time (ii). (b) Molecular structure of PLLA-PIB-PLLA. (c) Molecular structure of PLA-PIP-PLA (i), TEM image of triblock (9-33-9) (ii), and representative stress-strain curves for the triblocks (iii). (d) Molecular structure of PLLA-PDMS-PLLA. (e) Molecular structure of PLLA-PHB-PLLA.

When the glassy outer blocks self-assemble into cylindrical or spherical domains, the rubbery midblocks form bridges between the glassy domains. The resultant physical behavior of the polymer is that of an elastomeric material. When heated above the order-disorder transition temperature, the triblock copolymer becomes disordered and the elastomeric behavior disappears. Styrene-based linear ABA triblock copolymers, such as poly(styrene)-poly(butadiene)-poly(styrene) (SBS) and poly(styrene)-poly(isoprene)-poly(styrene) (SIS), are among the most important and widely used TPEs produced via living anionic polymerization. However, the styrenic triblock copolymers suffer from two drawbacks. First, the unsaturated carbon double bonds of the poly(butadiene) (PB) or poly(isoprene) (PI) block for the soft middle segment are easily oxidized and sensitive to UV degradation. Second, the upper service temperature is limited by  $T_g$  of the poly(styrene) block (ca. 100 °C)[6,7]. Additionally, these TPEs are derived from fossil fuels. The finite availability of fossil fuels and the environmental impact of petroleum manufacturing has led to increased interest in the development of alternative polymeric materials from sustainable sources[8]. Accordingly, there has been continuous efforts to replace poly(styrene) with thermoplastics having higher  $T_g$  and biodegradability to develop TPEs having improved characteristics beyond the triblock copolymers. Researcher have also sought to substitute PB or PI with more stable rubbery blocks via controlled polymerization techniques of various abundant renewable monomers obtained from plants to generate novel

bio-based polymers[9-13]. Controlled/living radical polymerization such as ringopening transesterification polymerization (ROTEP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) is now a powerful tool for preparing well defined block copolymers composed of immiscible segments that form self-assembling, ordered microphase-separated structures that depend on the monomer composition, the polymer molecular weights, and the segment sequence[14-16]. A variety of sustainable sources have been explored for polymers, including vegetable oils[17,18], plant sugars[19], terpenes[20], polysaccharides[21], rosins[22], and lignin[23]. Relatively few studies have focused on renewable resources for the derivation of TPEs. This article focused on lactide, renewable lactone derivatives, and bio-based acrylates from plants and vegetable oils as promising renewable monomers to produce high-performance TPEs with well-defined macromolecular architectures using precision polymerization. The aim of this review is to deliver a discussion on the definition of design strategies for renewable elastomers, and to describe recent advances in the synthesis, properties, and potential applications of these materials, especially in soft tissue engineering and drug delivery. Some of our insights on bio-based elastomers also are shared.

## 2. Lactide

Poly(lactide) (PLA) is a kind of biodegradable polyester and has been used for various biomedical purposes such as sutures, fracture fixation, oral implants, and drug delivery microspheres[24]. It can be synthesized by ring-opening transesterification polymerization (ROTEP) of the cyclic dimers of lactic acid. The polymerization of the racemic D,L-lactide usually results in atactic and amorphous polymers named poly(D,L-lactide) (PLA), whereas the polymerization of L-lactide or D-lactide results in isotactic and semicrystalline polymers called poly(L-lactide) (PLLA) or poly(D-lactide) (PDLA)[25,26]. PLA often fractures at very low strains (about 3%) after stretching, as such is not suitable for use in some fields where high elasticity and ductility are required. PLA related block copolymers, especially the ABA triblock copolymers, where A is a “hard”, high  $T_g$ , or semicrystalline PLA polymer and B is a “soft”, low  $T_g$ , or amorphous polymer, often present the properties of thermoplastic elastomers and usually possess high elasticity, appropriate biodegradability, and good biocompatibility for potential use in biomedical fields. These block copolymers are synthesized mostly by ROTEP of lactide initiated by hydroxyl-capped macromolecular monomers. Typical triblock copolymers with PLA are introduced in the following.

### 2.1. Poly(lactide)-poly(ethylene oxide or ethylene glycol)-poly(lactide) (PLA-PEO (or PEG)-PLA)

A series of PLA-PEO (or PEG)-PLA triblock copolymers, PLA-PEO (or PEG)-PLA, were synthesized by bulk ROTEP of D,L-lactide or L-lactide initiated by the hydroxyl terminal groups of PEO diol with a low toxicity stannous octoate, Sn(Oct)<sub>2</sub>, as a catalyst at elevated temperatures[27,28]. In order to develop highly flexible biodegradable polymers, chain extension of the triblock copolymers using hexamethylene diisocyanate (HDI) at 82 °C led to high molecular weight and superior mechanical properties of the multiblock poly(ether-ester-urethane)s (Fig-

ure 1a (i))[29]. In the design of the copolymers, amorphous PEO polymers spanning from 1 to 10 kg mol<sup>-1</sup> were selected to act as soft segments because of their high flexibility and allowance for fine tuning of hydrophilicity, while PLLA polymers ranging from approximately 0.2 to 3.6 kg mol<sup>-1</sup> were chosen to create the hard blocks because of their stiffness and allowance for fine tuning of hydrophobicity. PEO/PLLA multi-block copolymers displaying enhanced mechanical properties generated a phase segregated microstructure, where the PEO amorphous chains acted as a molecular spring and the crystalline PLLA blocks formed strong non-covalent crosslinking domains, as determined by differential scanning calorimetry (DSC) and X-ray analyses. These highly flexible thermoplastic elastomers attained ultimate tensile strength values as high as 30 MPa and elongation at break levels well above 1000%. Furthermore, the reinforcing effect of the crystalline and hydrophobic PLLA domains enabled some of these copolymers to retain noteworthy strength (8-9 MPa), even in their fully hydrated state. The equilibrium water uptake of the elastomers rose from 120 to 460% with increasing PEO content (Figure 1a (ii)).

### 2.2. Poly(L-lactide)-poly(isobutylene)-poly(L-lactide) (PLLA-PI-B-PLLA)

ROTEP of L-lactide at ambient temperature was accomplished with dipotassium-poly(isobutylene-alcoholate) telechelic polymer ( $M_n$  SEC = 7.4 kg mol<sup>-1</sup> and  $D = 1.17$ ) via dehydration with potassium metal, instead of tin(II) ethylhexanoate-catalyzed ROP at high temperature, to yield a PLLA-PIB-PLLA triblock copolymer ( $M_n$  SEC = 23.0 kg mol<sup>-1</sup> and  $D = 1.42$ ), a partially biodegradable thermoplastic elastomer (Figure 1b). The differential scanning calorimetry measurement of the copolymer showed two glass transitions ( $T_g = -69$  °C characteristic of PIB soft segment and  $T_g = 45$  °C characteristic of PLLA hard segment, showing strong evidence of microphase separation[30].

### 2.3. Poly(lactide)-poly(isoprene)-poly(lactide) (PLA-PI-PLA)

PI is an amorphous polymer with low  $T_g$ , and has been used to improve the properties (for example, toughening) and expand the applicability of traditionally brittle polymers such as poly(styrene). Poly(styrene)-poly(butadiene)-poly(styrene) (SBS) and poly(styrene)-poly(isoprene)-poly(styrene) (SIS) triblock copolymers are thermoplastic elastomers (TPEs) commonly used as blend compatibilizers, elastomers, asphalt modifiers, and pressure-sensitive adhesives[1]. The PI polymers have been used as soft segments to prepare PLA-PI-PLA block copolymers by the reaction of  $\alpha, \omega$ -dihydroxyl-terminated poly(isoprene) (HO-PI-OH) ( $M_n$  SEC = 4.5-72.0 kg mol<sup>-1</sup> and  $D = 1.08$ ) with lactide (PLA molar mass: 1.6-12 kg mol<sup>-1</sup>) at 90 °C using aluminum alkoxide (AlEt<sub>3</sub>) as a catalyst in toluene (Figure 1c (i))[31]. The copolymers could be fabricated in larger quantities and at higher reaction concentrations when aluminum triisopropoxide (Al(*i*OPr)<sub>3</sub>) was used instead of AlEt<sub>3</sub> [32]. The tensile strength of the copolymers increased with an increase of PLA content and the microphase alignment significantly influenced the resultant tensile properties. Three PLA-PI-PLA triblock copolymers were prepared with spherical, cylindrical, and lamellar morphologies, as confirmed by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) (Figure 1c (ii)). The morphology largely

determined the tensile properties including the Young's modulus and ultimate tensile strength. Tensile measurements demonstrated the elongation (650%) and elastomeric properties (1% residual strain after a 9% deformation) of the PLA-PI-PLA TPEs (Figure 1c (iii)) and noteworthy results were obtained for the cylindrical and spherical samples[33].

### 2.4. Poly(L-lactide)-poly(dimethylsiloxane)-poly(L-lactide) (PLLA-PDMS-PLLA)

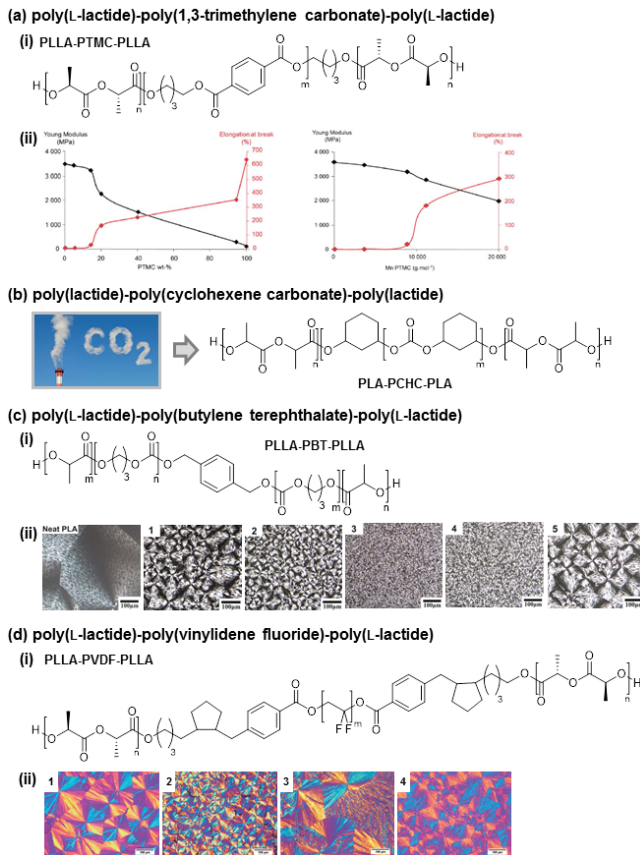
Various amounts of  $\alpha, \omega$ -dihydroxyl-terminated PDMS, having low  $T_g$ , high permeability for oxygen and water, and biocompatibility, were incorporated in PLLA main chains by ROTEP at very low contents of stannous octoate (Figure 1d)[34]. It was noteworthy that the peak of the proton is shifted from 3.7 to 4.0 ppm due to the methylene group of the  $\alpha, \omega$ -hydroxylpropyl-terminated PDMS linked to the PLLA ester group via ROP[35]. The molecular weight,  $T_g$ ,  $T_m$ , crystallinity, and heats of fusion of the synthesized polymers decreased as the composition of PDMS in the triblock copolymer increased. The molecular weight distribution broadened as the content of the PDMS increased, due to the occurrence of both initiation and propagation mechanisms. The incorporation of PDMS in the triblock copolymer improved its thermal stability compared to that of PLLA.

### 2.5. Poly(L-lactide)-poly(3-hydroxybutyrate)-poly(L-lactide) (PLLA-PHB-PLLA)

A telechelic PHB[36] was synthesized by ring-opening polymerization of [RS]- $\beta$ -butyrolactone ( $\beta$ -BL) in the presence of 1,4-butanediol (BD) with 1,3-dichlorotetrabutylstannoxane (DTD) as the catalyst. The produced polymer was found to have a syndiotactic-rich sequence with highly elastomeric properties (610% elongation at break). This polymer was found to be terminated by secondary hydroxyl groups, having an (oxytetramethylen)oxy group in the main chain. This telechelic [RS]-PHB was subjected to block copolymerization with L-lactide by the catalysis of tin (II) octoate to synthesize an ABA triblock copolyester having elastomeric [RS]-PHB as a soft segment and PLLA as a hard segment (Figure 1e). In this block copolymerization, the molecular weight and the unit composition of the produced copolymer were successfully controlled by changing the L-lactide/[RS]-PHB ratio in the feed. The DSC thermograms of the produced PLLA-[RS]-PHB-PLLA triblock copolymers suggested a microphase separation structure if segment crystallization was induced. The Young's modulus of the copolymer films increased from 30 to 160 MPa with increasing PLLA composition from 44 to 69% or increasing crystallinity from 9 to 23%. In contrast, the elongation at break decreased from 200 to 86%. Furthermore, the Young's modulus of the copolymer films was much higher than that of the syndiotactic [RS]-PHB and much lower than that of the PLLA, while their tensile strength was almost identical with that of [RS]-PHB. From these results PLLA-[RS]-PHB-PLLA can be used as a biodegradable thermoplastic elastomer[37].

### 2.6. Poly(L-lactide)-poly(1,3-trimethylene carbonate)-poly(L-lactide) (PLLA-PTMC-PLLA)

PTMC is a rubbery and amorphous polymer, degrading in vivo by



**Figure 2.** (a) Molecular structure of PLLA-PTMC-PLLA (i) and Young's modulus ( $E$ ) and elongation at break ( $\epsilon_b$ ) variation as a function of the PTMC weight fraction and the molar mass in the PTMC segment of the triblock copolymers (ii). (b) Molecular structure of PLA-PCHC-PLA. (c) Molecular structure of PLLA-PBT-PLLA (i) and polarized optical micrographs of neat PLA and the copolymers 1-5 (4.4:1, 16:1, 34:1, 77:1, and 97:1 for PLLA:PBT (wt:wt)) (ii). (d) Molecular structure of PLLA-PVDF-PLLA (i) and POM images 1-4 (PVDF isothermally crystallized at 125 °C, PVDF/PLLA blend isothermally crystallized at 145 °C, PLLA isothermally crystallized at 125 °C, PVDF/PLLA blend isothermally crystallized at 145 °C, and PLLA-PVDF-PLLA triblock copolymer isothermally crystallized at 145 °C) (ii).

surface erosion without release of acidic compounds[38]. Although several cell types have been successfully cultured on TMC-based copolymers, there is limited resistance to creep under long-term static or dynamic loading conditions in practical application. A series of PLLA-PTMC-PLLA block copolymers with PTMC as soft segments were prepared by using 1,3-trimethylene carbonate (TMC) and lactide (D-LA, L-LA, or D,L-LA) (Figure 2a (i)). First, the PTMC diols ( $M_n = 13.8-19.5 \text{ kg mol}^{-1}$ ) were synthesized by ROTEP of TMC initiated by 1,6-hexanediol with  $\text{Sn}(\text{Oct})_2$  as a catalyst at 130 °C for 72 h. The LA monomers were then added into the diols to polymerize and obtain the final copolymers ( $M_n = 18.9-26.6 \text{ kg mol}^{-1}$ ) including PLLA-PTMC-PLLA, PDLA-PTMC-PDLA, and PDLLA-PTMC-PDLLA. PDLLA-PTMC-PDLLA copolymer containing 35.2 mol % DLLA segments showed high tensile strength (1.8 MPa), elongation at break (880%) and a high creep

rate ( $1.4 \times 10^{-5} \text{ s}^{-1}$ ), but poor recovery after cyclic deformation (11.5%). Both PLLA-PTMC-PLLA copolymer containing 18 mol% lactide segments and PDLA-PTMC-PDLA copolymer containing 14 mol% lactide segments presented high flexibility and elasticity with low creep rates ( $2.7 \times 10^{-6}$  and  $2.5 \times 10^{-6} \text{ s}^{-1}$  respectively) and little permanent deformation in cyclic tensile testing (2.5 and 6.4% respectively) (Figure 2a (ii)). As a result, the block copolymers had good mechanical properties with low creep rates when crystalline PLA blocks of sufficient lengths were used to form the hard blocks ( $> 42 \text{ mol}\%$ ). For tissue engineering applications, the resistance to creep of the scaffolding materials under long-term cyclic deformation of 7–10% strain is very important[39,40]. PLLA-PTMC-PLLA shows significantly less permanent deformation (0.5%) than that of PTMC specimens (3.2%), while PS-PTMC-PS completely recovers, showing no permanent deformation even after 3,000 cycles. The copolymers are attractive for tissue engineering applications allowing dynamic cell culture. It was also reported that several metallic and organic catalytic systems successfully enabled controlled copolymerization of TMC and L-LA[41]. A stepwise approach from the "immortal" ROTEP of L-LA promoted by a PTMC-(OH)<sub>1,3</sub> pre-synthesized polymer or direct sequential copolymerization of the two monomers allowed the synthesis of both diblock (PTMC-PLLA) and triblock (PLLA-PTMC-PLLA), linear or star-shaped (GLY(PTMC-PLLA)<sub>3</sub>) copolymers.

## 2.7. Poly(lactide)-poly(cyclohexene carbonate)-poly(lactide) (PLA-PCHC-PLA)

The synthesis of a di-zinc catalyst ( $\text{Zn}(\text{O}_2\text{CCF}_3)_2$ ), with a macrocyclic ancillary ligand and trifluoroacetate co-ligand has been reported[42]. The complex is an efficient catalyst for the copolymerization of cyclohexene oxide (CHO) and carbon dioxide ( $\text{CO}_2$ ), under ambient pressures[43]. The PCHC produced is of low molecular weight ( $2.5-9.2 \text{ kg mol}^{-1}$ ) and a MALDI-ToF analysis shows exclusively hydroxyl end-groups. The di-hydroxyl terminated PCHC is used as a macroinitiator in the ring-opening polymerization of lactide, using an active yttrium co-initiator. Near complete conversions of the D,L-lactide or L-lactide ( $> 95\%$ ) were achieved, yielding ABA triblock copolymers ( $M_n = 17.3-51.0 \text{ kg mol}^{-1}$  and  $D = 1.28-1.38$ ) including PLA-PCHC-PLA and PLLA-PCHC-PLLA (Figure 2b), as determined through an analysis of the molecular weight using SEC and  $^1\text{H}$  NMR spectroscopy. The block nature of the copolymers was confirmed by DSC experiments, which revealed two glass transition temperatures. All the polymers showed a  $T_g$  of approximately 60 °C, corresponding to the lactide portion of the polymer[24]. In some cases, a second, low intensity  $T_g$  was observed at 80–95 °C, which corresponds to the  $T_g$  of low-weight PCHC.

## 2.8. Poly(L-lactide)-poly(butylene terephthalate)-poly(L-lactide) (PLLA-PBT-PLLA)

PBT is an important aromatic polyester with an acceptable crystallization rate and excellent moldability[44]. It was found that the crystallization rate of the PLLA phase in the blends of PLLA and PBT was accelerated with the addition of *para*-phenylene diisocyanate (PPDI)[45]. In order to reveal the potential effect of the copolymers on the crystallization of PLLA, a series of PLLA-PBT-PLLA triblock copoly-

mers were synthesized via ring-opening polymerization of L-lactide with hydroxyl-functionalized poly(butylene terephthalate) (HOPBT) as macroinitiator ( $M_n$  NMR = 1.6 kg mol<sup>-1</sup>) and stannous 2-ethylhexanoate (Sn(Oct)<sub>2</sub>) as the catalyst in 1,1,2,2-tetrachloroethane (TCE) (Figure 2c(i))[46]. The conversion of L-lactide was high (92–97%) and the PLA block in the copolymers ( $M_n$  SEC = 9.8–81.1 kg mol<sup>-1</sup> and  $\bar{D}$  = 1.42–1.55) showed high optical purity ( $[\alpha]_D = \text{ca. } -160^\circ$ ). DSC and WAXD results demonstrated that the two blocks of the copolymers formed the same crystal type as the respective homopolymer, i.e., PLA or PBT. The polarized light optical microscope (POM) (Figure 2c(ii)) and isothermal DSC results confirmed that these copolymers had a nucleation effect on the crystallization of PLA. Moreover, the nucleation effect depended on the composition of the copolymers. When the molecular weight of the PLLA-PBT-PLLA triblock copolymers was 1.6 kg mol<sup>-1</sup> PBT midblock and 10 kg mol<sup>-1</sup> PLLA endblock, the nucleation effect was optimal and even exceeded that of talc at the same content (5 wt %). This indicated that the spherulite diameter was effectively reduced to around 10  $\mu\text{m}$ , corresponding with the level of talc and, from neat the PLA to PLA blend containing 5 wt % the copolymer,  $t_0$  (the induction time) was shortened from 25.20 to 9.07 min and  $t_{1/2}$  (half crystallization time) was shortened from 109.91 to 19.18 min, respectively. The copolymer, even at a very low content (5 wt %), showed an unexpected favorable effect on the crystallization of PLA and on this basis is a potential polymeric nucleating agent for PLA.

### 2.9. Poly(L-lactide)-poly(vinylidene fluoride)-poly(L-lactide) (PLLA-PVDF-PLLA)

PVDF demonstrates outstanding thermal, chemical and mechanical stability[47], and is applied in the industrial fabrication of pipes, linings, and automotives. However, its most appealing features are the reported ferro-, pyro-, and piezoelectric properties of its  $\beta$ -crystalline phase[48,49]. Many techniques have been developed to increase this widely exploited  $\beta$ -polymorph in PVDF and PVDF-based materials. The incorporation of PVDF segments into block copolymers is highly attractive, since PVDF-containing block copolymers can function as potential precursors for ordered nanostructured materials with outstanding properties. Double-crystalline PLLA-PVDF-PLLA triblock copolymers (Figure 2d(i)) were successfully synthesized through ring opening polymerization of L-lactide and benzoyl peroxide initiated polymerization of vinylidene fluoride, followed by copper(I)-catalyzed azide-alkyne coupling of the functionalized PLLA and PVDF. Three triblock copolymers with different block ratios were prepared via this synthetic approach. The block copolymers were miscible in the melt, and an alternating crystalline lamellar nanostructure was formed upon crystallization from the homogeneous melt[50]. Two distinct crystallization temperatures were obtained due to the sequential crystallization of PVDF and PLLA. Crystallization behavior of the PLLA component depends strongly on the block composition. The crystallization temperature of the lower temperature crystallizing PLLA block increased considerably with respect to its parent homopolymer for rather symmetric block copolymers (49 and 58% of PLLA), indicating a strong nucleation effect. On the other hand, asymmetric block copolymers with low PLLA content (27%) demonstrated a large decrease of crystallization temperature, due to a fractionated crystallization process. A confined

crystallization mechanism for the PLLA blocks was suggested. This was indicated by the low degree of crystallization compared to the respective homopolymers, and confirmed by a microstructure analysis performed during isothermal crystallization. Contrary to PLLA, crystallization of the higher temperature crystallizing PVDF component within the block copolymer was not influenced by the block composition and similar crystallization behavior was observed with respect to PVDF homopolymers (Figure 2d(ii)).

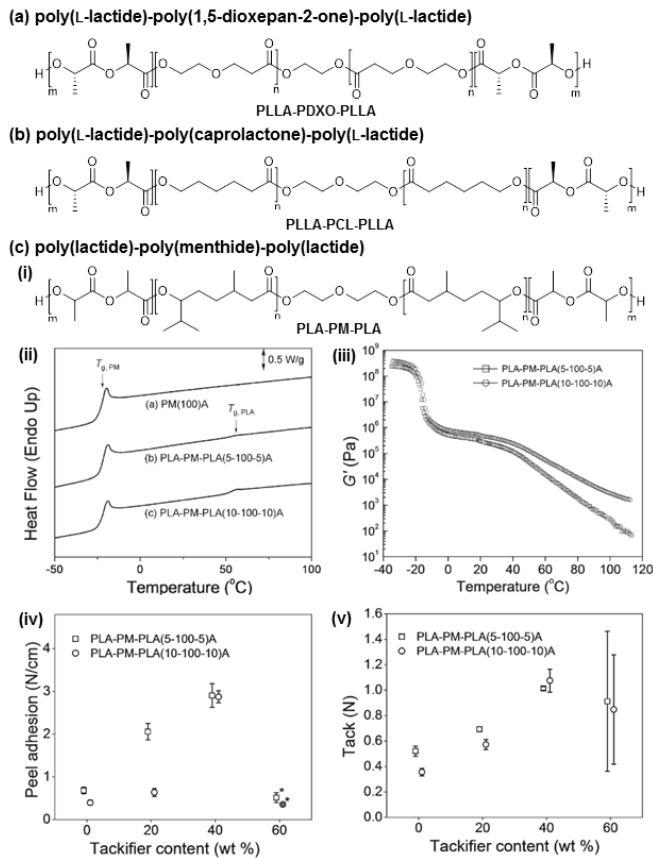
## 3. Lactone

One key to increasing the breadth of PLA applicability is through the controlled incorporation of other components, in particular in the form of block copolymers[51]. Particularly attractive targets are ABA triblock copolymers that incorporate PLA as the end blocks. With appropriate rubbery midblocks as “soft” amorphous, low  $T_g$  polymers, such TPEs can be used in a wide variety of consumer products such as footwear, asphalt additives, and hot melt and pressure sensitive adhesives[2]. The six or seven membered lactones derived from petroleum or bio-based materials are very interesting compounds that can be used as monomers in the syntheses of renewable or degradable polymers, providing aliphatic polyesters with  $T_g$  below  $-20^\circ\text{C}$ . Ring-opening polymerization transesterification polymerization (ROTEP) of lactones is the most commonly employed method. The ring size of monomer lactones is an important factor in their ability to ring-open; their propensity for ring-closing reactions, however, is equally important for achieving a high-molecular-weight polymer. The ideal ROTEP should exhibit a low depolymerization rate (a high equilibrium monomer concentration) and a high polymerization rate.

In searching for new lactones that enhance ductility for PLA, two critical aspects in addition to the flexibility of poly(lactone) are the reactivity of the individual lactone and copolymer segmental miscibility. If the reactivity of a lactone with PLA is low or if the addition is performed in sequence, blocky structures will be produced. If the resultant blocks also are immiscible, phase separation into harder and softer domains will occur. Harder PLA domains can subsequently act as physical cross-linking sites and result in a material with enhanced ductility[52]. Typical PLA related ABA triblock copolymers containing polyester from lactones as soft middle block are introduced in the following.

### 3.1. Poly(L-lactide)-poly(1,5-dioxepan-2-one)-poly(L-lactide) (PLLA-PDXO-PLLA)

A new family of ABA block copolymers (PLLA-PDOX-PLLA) containing PDOX (B) and PLLA (A) blocks has been synthesized (Figure 3a)[53]. The polymerization procedure was based on two-step sequential addition of monomers to a controlled polymerization system. In the first step, the middle block consisting of DXO ( $M_n$  SEC = 43.0–75.8 kg/mol and  $\bar{D}$  = 1.26–1.36) was polymerized through ROTEP to high monomer conversion (< 99%) using cyclic tin alkoxide 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclododecane as a cyclic difunctional initiator and the reaction was performed in chloroform at  $60^\circ\text{C}$ . In the second step, the L-lactide was added and subsequently poly-



**Figure 3.** (a) Molecular structure of PLLA-PDXO-PLLA. (b) Molecular structure of PLLA-PCL-PLLA. (c) Molecular structure of PLA-PM-PLA (i), DSC analysis for PM and PLA-PM-PLA triblock copolymers (ii), expanded storage moduli ( $G'$ ) for PLA-PM-PLA triblock copolymers (iii), effect of rosin ester tackifier on the peel adhesion of the PSA systems (iv), and effect of rosin ester tackifier content on the tack of the PSA system (v).

merized giving a triblock copolymer ( $M_{n \text{ SEC}} = 54.7\text{--}78.6 \text{ kg mol}^{-1}$  and  $D = 1.25\text{--}1.30$ ) and showing high conversion (72–99%). DSC and WAXD analyses indicated that the PLLA blocks formed crystalline domains in the solution-cast films by microphase separation. All triblock copolymers showed a  $T_m$  of approximately 153 °C and a  $T_g$  of roughly –33 °C, corresponding to the PLLA portion and PDXO of the polymer, respectively[54]. WAXD studies suggested that all the polymer compositions exhibited some degree of crystallinity. Even at the lowest L-lactide content of 7%, X-ray diffraction revealed the characteristic patterns of crystalline PLLA. The glass-transition temperature was only slightly affected by an increase in the amount of L-lactide although the melting temperature and the heat of fusion decreased as the L-lactide block length was reduced.

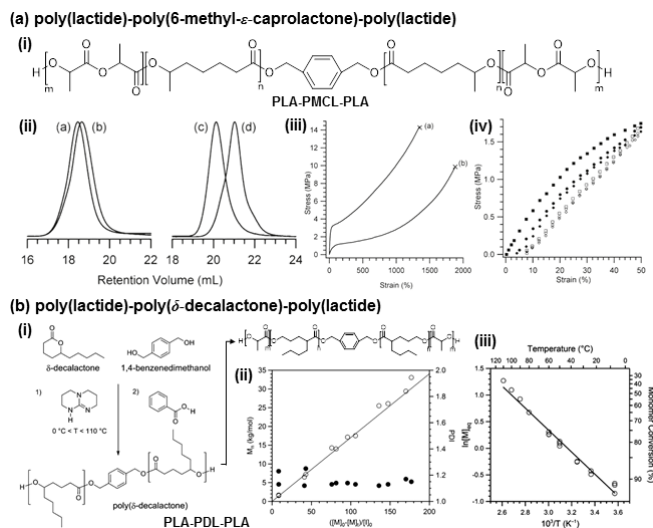
### 3.2. Poly(L-lactide)-poly(caprolactone)-poly(L-lactide) (PLLA-PCL-PLLA)

Biodegradable poly(ester-urethane) multiblock copolymers were prepared by using a chain-extended PLLA-PCL-PLLA block copolymer

and 1,6-hexamethylene diisocyanate (HDI) as an extender[55]. The PLLA-PCL-PLLA triblock copolymers (Figure 3b) were first synthesized by ROP of L-lactide initiated by PCL diols ( $M_n = 2 \text{ kg mol}^{-1}$  and  $D = 1.15\text{--}1.20$ ) with  $\text{Sn}(\text{Oct})_2$  as a catalyst at 145 °C for 1 h, and subsequently extended by using 1,6-HDI at 82 °C for 3 h under a nitrogen atmosphere to obtain chain-extended PLLA-PCL-PLLA block copolymers ( $M_{n \text{ SEC}} = 89\text{--}124 \text{ kg mol}^{-1}$  and  $D = 1.5\text{--}1.8$ ). As the molecular weight of the PLLA blocks increased from 0.6 to 6  $\text{kg mol}^{-1}$ , the chain-extended copolymers became increasingly stiffer, accompanying an increase in the modulus and a decrease in elongation at break. When the molecular weight of and the PCL and PLLA blocks was 2  $\text{kg mol}^{-1}$  and 2  $\text{kg mol}^{-1}$ , respectively, the initial molecular weight (190  $\text{kg mol}^{-1}$ ) of the chain-extended copolymers decreased to 83, 48, and 9.5  $\text{kg mol}^{-1}$  after 1, 3, and 6 months, respectively, of in vitro degradation. The produced multiblock copolymers displayed enhanced mechanical properties, with ultimate tensile strength values of around 32 MPa, Young's modulus as low as 30 MPa, and elongation at break values well above 600%. The longer the PLA block was, the slower in vitro degradation of the material proceeded, with all copolymers degrading faster than the respective homopolymers. A new biodegradable (AB) $_n$  type of multiblock copolymer derived from PCL and PLA ( $M_w = 5 \text{ kg mol}^{-1}$ ) was prepared via a chain extending reaction among PCL oligomers, PLA oligomers and HDI[56]. Fourier transform infrared spectra (FT-IR),  $^1\text{H}$  NMR, thermal gravity analysis (TGA) and derivative thermograms (DTG) were used to characterize the copolymers and the results showed that PCL and PLA were coupled by the reaction between –NCO groups and terminal –OH and –COOH groups of PCL and PLA, respectively. The material displayed enhanced mechanical properties: Young's modulus was as low as  $2.7 \pm 0.7 \text{ MPa}$ , tensile strength was as high as  $26 \pm 2.0 \text{ MPa}$ , and elongation at break value was above 790% at a PCL/PLA composition of 80/20 (w/w). Moreover, according to SEM micrographs, interfacial adhesion of the composites was improved. The thermal degradation temperature of the composites was higher than that of PLA but lower than that of PCL, which is advantageous for industry processes. A series of studies are currently being performed in the laboratory, including research on the effects of the composition of the copolymer on biodegradable properties and an experiment to assess compatibility between copolymers and cells.

### 3.3. Poly(lactide)-poly(menthlide)-poly(lactide) (PLA-PM-PLA)

ABA triblock copolymers were prepared using the renewable monomers menthlide and lactide by sequential ring-opening polymerizations. Initially, hydroxy telechelic polymenthlide was synthesized by diethylene glycol-initiated and tin (II) ethylhexanoate-catalyzed polymerization of menthlide. The resulting 100  $\text{kg mol}^{-1}$  ( $D = 1.07\text{--}1.09$ ) polymer was used as a macroinitiator for tin(II) ethylhexanoate-catalyzed ROTRP of D,L-lactide. Two PLA-PM-PLA triblock copolymers were prepared with 5 and 10  $\text{kg mol}^{-1}$  PLA end blocks (Figure 3c (i))[57]. Transesterification between the two blocks and PLA homopolymer formation were minimized, and triblock copolymers with narrow molecular weight distributions were produced ( $D = 1.07\text{--}1.09$ ). Microphase separation in these systems was corroborated by DSC (Figure 3c (ii)), dy-



**Figure 4.** (a) Molecular structure of PLA-PMCL-PLA (i), SEC traces PLA-PMCL-PLA (12-98-12), PMCL (98), PLA-PMCL-PLA (7-12-7), and PMCL (12) (ii), representative stress-strain of PLA-PMCL-PLA (25-98-25) and (12-98-12) triblocks (iii), and reciprocating tensile properties of PLA-PMCL-PLA (25-98-25) from 0 to 50% strain at  $\pm 5$  mm min<sup>-1</sup> for 20 cycles (iv). (b) Synthesis of PLA-PDL-PLA (i), polymerization thermodynamics for  $\delta$ -decalactone (ii), and molar mass control of poly( $\delta$ -decalactone) (iii).

dynamic mechanical analysis (Figure 3c (iii)), and SAXS measurements. The triblocks were combined with up to 60 wt % of a renewable tackifier, and the resulting mixtures were evaluated using probe tack, 180° peel adhesion, and shear strength tests. Maximum values of peel adhesion (3.2 N cm<sup>-1</sup>) (Figure 3c (iv)), tack (1.1 N) (Figure 3c (v)), and shear strength ( $\sim 2500$  min) were obtained at 40 wt % of the tackifier. In comparison, tests on commercial duct, paper, and electrical tapes under identical conditions gave peel adhesion of 1.9–4.2 N cm<sup>-1</sup>, tack of 0.4–0.6 N, and shear strength of  $\sim 1500$  min. However, while tackifiers can improve the cohesive strength in a pressure-sensitive adhesive (PSA) by the formation of a tackifier-rich soft phase[58,59], an excessive amount of tackifier (60 wt %) can lead to increases in the  $T_g$  of the PSA, actually reducing tack[60]. Taken together, the probe tack, peel adhesion, and shear strength test data demonstrate that mixtures of PLA-PM-PLA triblock copolymers and commercially available (and renewable) tackifiers are not only effective PSAs but also exhibit adhesive properties that are competitive with those of commercial samples

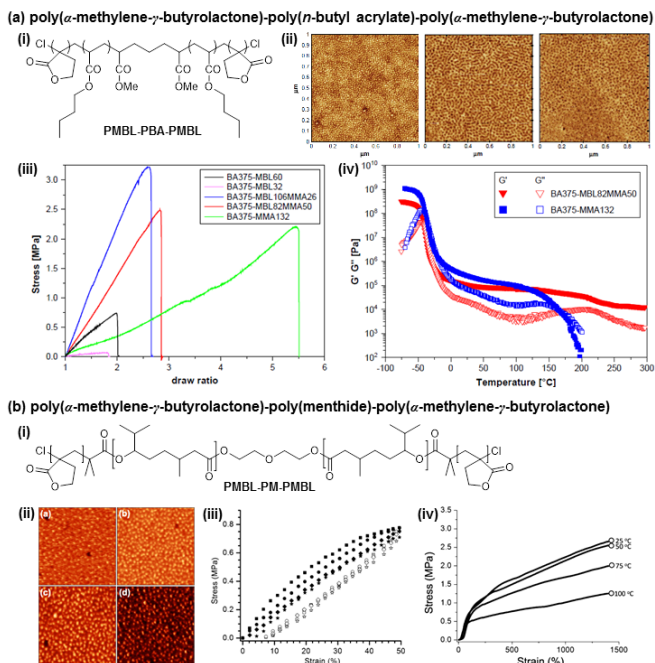
### 3.4. Poly(lactide)-poly(6-methyl- $\epsilon$ -caprolactone)-poly(lactide) (PLA-PMcCL-PLA)

Amorphous ABA type block aliphatic polyesters can be useful as degradable and biorenewable thermoplastic elastomers[61]. Additionally, a Baeyer–Villiger protocol that uses non-chlorinated solvents with higher atom economy was developed for the synthesis of 6-methyl- $\epsilon$ -caprolactone (MeCL) in high yield ( $> 99\%$ ). These materials can be prepared by sequential ROTEP reactions and can exhibit a range of physical properties and morphologies. In this work a set of amorphous

PLA-PMcCL-PLA aliphatic polyester ABA triblock copolymers (Figure 4a (i)) were prepared by consecutive controlled ROTEPs. ROTEP of neat 6-methyl- $\epsilon$ -caprolactone in the presence of 1,4-benzenedimethanol and tin (II) octoate afforded  $\alpha, \omega$ -hydroxyl-terminated PMcCL. High conversions of 6-methyl- $\epsilon$ -caprolactone ( $> 96\%$ ) afforded polymers with molar masses ranging from 12 to 98 kg mol<sup>-1</sup>, depending on the monomer-to-initiator ratios, and with narrow, unimodal molecular weight distributions (Figure 4a (ii)). An array of PLA-PMcCL-PLA triblock copolymers with controlled molecular weights and narrow molecular weight distributions were synthesized using telechelic PMcCL samples as macroinitiators for ring-opening polymerization of D,L-lactide. The composition of the triblocks was in good agreement with the feed composition. The bulk triblock properties were investigated using DSC, SAXS, DMA, and tensile experiments. In the range of molar masses studied, the PLA  $T_g$  is lower than its homopolymer equivalent. Several triblocks adopted well-ordered microphase-separated morphologies, and both hexagonally packed cylindrical and lamellar structures were observed. The Flory–Huggins interaction parameter was determined as  $\chi(T) = 61.2T^{-1} - 0.1[62-64]$ , based on the order-to-disorder transition temperatures of two symmetric triblocks using the calculated mean field theory result. The elastomeric mechanical behavior of two high molecular weight triblocks was characterized by tensile and elastic recovery experiments (Figure 4a (iv)), an exceptional elongation ( $> 1800\%$ ) and tensile strength ( $> 14$  MPa) were noted (Figure 4a (iii)). The combined properties of the PLA-PMcCL-PLA triblocks are promising for engineering degradable thermoplastic elastomers and related materials.

### 3.5. Poly(lactide)-poly( $\delta$ -decalactone)-poly(lactide) (PLA-PDL-PLA)

The bulk ROTEP of renewable  $\delta$ -decalactone (DL) using 1,5,7-triazabicyclo[4.4.0]dec-5-ene, a commercially available organo-catalyst[6-5,66], was carried out at temperatures between 7 and 110 °C (Figure 4b (i))[67]. The equilibrium monomer concentration for reactions within this temperature range was used to determine the polymerization thermodynamic parameters ( $\Delta H_p = -17.1 \pm 0.6$  kJ mol<sup>-1</sup>,  $\Delta S_p = -54 \pm 2$  J mol<sup>-1</sup> K<sup>-1</sup>)[68] for  $\delta$ -decalactone. The polymerization kinetics was established and high molar mass PDL with a glass transition temperature of  $-51$  °C was prepared. PDL samples with controlled molar mass and narrow molar mass distributions ( $M_n$  SEC = 84 kg/mol and  $D = 1.27$ ) (Figure 4b (ii)) were realized by controlling the monomer conversion (70–80%) and initiator concentration (Figure 4b (iii)). A high molar mass PLA-PDL-PLA triblock copolymer with a low polydispersity index ( $M_n$  SEC = 100 kg mol<sup>-1</sup> and  $D = 1.40$ ) was prepared by simple sequential addition of monomers. The product triblock exhibited two distinct glass transition temperatures at  $-51$  and  $54$  °C, corresponding to domains of PDL and PLA, consistent with microphase segregation. The low glass transition temperature of PDL makes it an attractive component for renewable triblock polymers with potential broad-based utility. Self-assembly and mechanical properties of the triblock copolymers that incorporate PDL will be actively being explored.



**Figure 5.** (a) Molecular structure of PMBL-PBA-PMBL (i), AFM phase images of PMBL-PBA-PMBL triblock copolymers (12.6 wt % PMBL to left, 19.3 wt% to middle, and 30.3 wt% to right) (ii), tensile mechanical properties of triblock copolymers with PMBL (iii), and comparison of the thermo-mechanical properties of triblock copolymers with PMBL (iv). (b) Molecular structure of PMBL-PM-PMBL (i), AFM images for PMBL-PM-PMBL (3-100-3) (upper and left), PMBL-PM-PMBL (5-100-5) (upper and right), PMBL-PM-PMBL (9-100-9) (lower and left), and PMBL-PM-PMBL (13-100-13) (lower and left) as spun (ii), tensile recovery properties of PMBL-PM-PMBL (5-100-5) from 0 to 50% strain at 5 mm min<sup>-1</sup> for 20 cycles (iii), and representative stress-strain curve of PMBL-PM-PMBL (5-100-5) at elevated temperatures (iv).

#### 4. Bio-based Acrylate

Polar vinyl molecules are interesting monomers for polymerization after which the poly(olefin) can be used as block segments in triblock copolymers. Among these, methyl methacrylate (MMA) has been the most extensively studied monomer. Some renewable cyclic analogs of MMA (i.e., vinyl butyrolactones) are emerging as very interesting monomers. Indeed,  $\alpha$ -methylene- $\gamma$ -butyrolactone, (MBL) also called Tulipalin A, is a natural product isolated from tulips[69]. A recent study reported its synthesis in high yield via enzyme-mediated conversion of tuliposide A, found in large quantities in tulip tissues (0.2-2% w/w of fresh weight)[70]. Its methyl derivative,  $\gamma$ -methyl- $\alpha$ -methylene- $\gamma$ -butyrolactone (MMBL), is obtained in two steps using a method developed by DuPont[71] starting from levulinic acid, derived from biomass and produced in 450 tons per year[72]. These butyrolactone-based vinyl monomers can be polymerized for hard segments in triblock copolymers due to their high  $T_g$ . On the other hand, vegetable oils and their fatty acids are a particularly attractive source due to their low toxicity, biodegradability, availability, relatively low price, and ease of functional-

ization[73]. The carbon-carbon double bonds on the triglyceride structure are amenable to a variety of functionalization chemistries that can lead to subsequent polymerization. The carboxylic acid end group of a fatty acid can be converted to a hydroxyl end group[74,75] and subsequently converted to an acrylate or methacrylate group[76]. These fatty acid-based vinyl monomers can be polymerized for soft segments in triblock copolymers due to their low  $T_g$ . The typical ABA triblock copolymers blocked with polyolefin based on bio-based acrylates are introduced in the following.

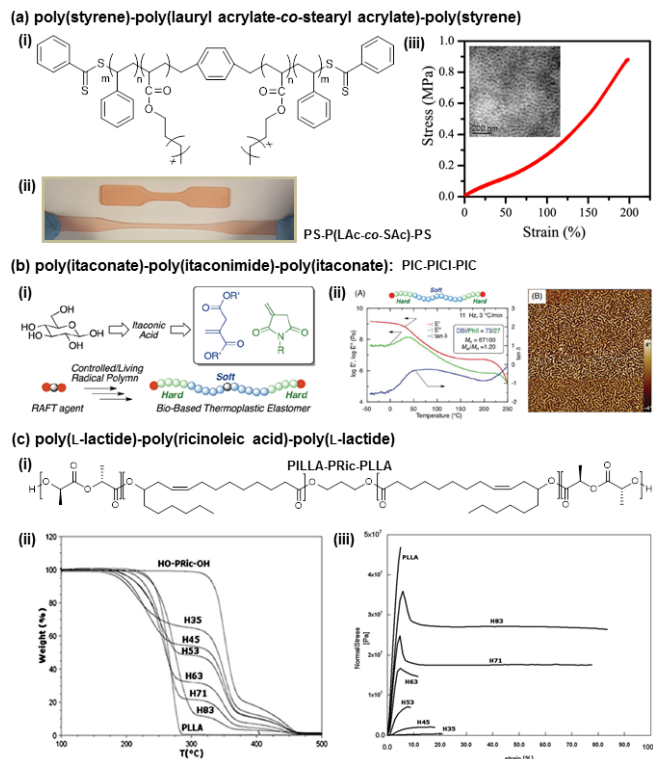
##### 4.1. Poly( $\alpha$ -methylene- $\gamma$ -butyrolactone)-poly(*n*-butyl acrylate)-poly( $\alpha$ -methylene- $\gamma$ -butyrolactone) (PMBL-PBA-PMBL)

As a bio-based acrylate, Tulipalin A (MBL), found in tulips, is the simplest member of butyrolactones, and is found and isolated from various plants[77]. Such natural products are renewable, environmentally friendly, biocompatible, and biodegradable. Furthermore, they may possess unique physical and biomedical properties. Because of its nearly planar five-membered ring and its exomethylene double bond, MBL is more reactive than MMA. PMBL is a rigid thermoplastic, with good durability, a relatively high refractive index (1.540), and a glass transition temperature ( $T_g$ ) of 195 °C[78]. A series of well-defined homopolymers as well as diblock and triblock copolymers containing middle soft PBA block and outer hard blocks of PMBL with low polydispersities and different molecular weights and compositions were synthesized by atom transfer radical polymerization (ATRP) using the aid of halogen exchange (Figure 5a (i))[79,80]. Phase separated morphologies of cylindrical (10.6–19.0 wt % of PMBL content) or spherical (6.1 wt % of PMBL content) hard block domains arranged in the soft PBA matrix were observed by AFM (Figure 5a (ii)) and SAXS. The thermo-mechanical properties of these new materials were thoroughly characterized using a variety of techniques. DMA studies confirmed the phase separated morphology of the copolymers, revealing a very broad elastic plateau in a storage shear modulus that extends over 250 °C between the glass transition temperatures of the two blocks (Figure 5a (iv)). The linear PMBL-PBA-PMBL triblock copolymers showed a relatively low elongation at break (*ca.* 150%) (Figure 5a (iii)) that was increased by replacing the PMBL hard blocks with less brittle PMBL-*random*-PMMA blocks. Due to the very high glass transition temperature and high thermal stability of PMBL, these materials could be suitable for high temperature applications. This illustrates the possibility of expanding the range of block copolymers accessible by ATRP[81,82].

##### 4.2. Poly( $\alpha$ -methylene- $\gamma$ -butyrolactone)-poly(menthene)-poly( $\alpha$ -methylene- $\gamma$ -butyrolactone) (PMBL-PM-PMBL)

As previously mentioned, MBL (tulipalin A) as a bio-based acrylate is a natural substance found in the common tulip *Tulipa gesneriana* L[83]. (-)-Menthol can be extracted from the plant *Mentha arvensis*, converted to (-)-menthone, and subsequently changed into (-)-menthene as a renewable seven-membered lactone by a simple Baeyer-Villiger oxidation[84]. Renewable ABA triblock copolymers were prepared by sequential polymerization of the plant-based monomers menthene and





**Figure 6.** (a) Molecular structure of PS-P(LAc-co-SAc)-PS (i), simple elastic test of PS-P(LAc-co-SAc)-PS (ii), and a representative stress-strain curve of the triblock copolymer (SAS1-61-24) and a TEM micrograph of the triblock (SAS1-100-23) (iii). (b) Synthesis of PIC-PICI-PIC (i) and dynamic tensile storage ( $E'$ ) and loss ( $E''$ ) moduli and  $\tan \delta$  as a function of temperature (left) and a AFM phase image for morphologies (right) (ii). (c) Molecular structure of PLLA-PRic-PLLA (i), TGA curves of HO-PRic-OH, PLLA and the triblock copolymers (ii), and stress-strain curves of PLLA and PLLA-PRic-PLLA block copolymers (iii).

MBL[85]. ROTEP of menthine using diethylene glycol as an initiator gave  $\alpha, \omega$ -dihydroxy poly(menthine) (HO-PM-OH) with high molar mass, low polydispersity ( $D = 1.07$ ), and a low glass transition temperature ( $T_g$ ) of  $-22^\circ\text{C}$ , and this was converted to  $\alpha, \omega$ -dibromo end-functionalized PM (Br-PM-Br) by esterification with excess 2-bromoisobutyryl bromide. The resulting  $100\text{ kg mol}^{-1}$  Br-PM-Br macro-initiator[86] was used for the ATRP of MBL. Four PMBL-PM-PMBL triblock copolymers (Figure 5b (i)) containing 6-20 wt% PMBL were prepared, as determined by NMR spectroscopy. Previous studies have shown that PLA is immiscible with PMBL[87] and PM[88], and PM and PMBL were expected to be incompatible given the polar nature of PMBL and the relatively nonpolar nature of PM (Figure 5b (ii)). Elongations in excess of 1300% without failure were observed between  $25\text{--}100^\circ\text{C}$  to evaluate the performance as the temperature was raised (Figure 5b (iv)). At 1,300% strain, the stress at  $50^\circ\text{C}$  was comparable to that at  $25^\circ\text{C}$  at all strains. However, at  $75$  and  $100^\circ\text{C}$ , the stress values at 1300% decreased to about 75 and 47% of the  $25^\circ\text{C}$  values, respectively. Nonetheless, even at  $100^\circ\text{C}$ , the mechanical behavior was respectable (stress at 1300% elongation  $\approx 1.0\text{ MPa}$ ). The tensile prop-

erties at both ambient and elevated temperature show that these materials are useful candidates for high-performance (Figure 5b (iii)) and renewable thermoplastic elastomer materials.

### 4.3. Poly(styrene)-poly(lauryl acrylate-co-stearyl acrylate)-poly(styrene) (PS-PLA-co-PSA-PS)

Vegetable oils are an attractive source for polymers due to their low cost, abundance, annual renewability, and ease of functionalization. Stearyl and lauryl acrylate, derived from vegetable oils such as soybean, coconut, and palm kernel oil, have been polymerized through reversible addition-fragmentation chain transfer polymerization (RAFT), and were well-controlled with a linear increase of molecular weight ( $39\text{--}82\text{ kg mol}^{-1}$ ) as a function of monomer conversion ( $> 85\%$ ) and relatively low values of the PDI (around 1.3) resulting in PS-P(LAc-co-SAc)-PS triblock copolymers (Figure 6a (i)) that act as TPEs (Figure 6a (ii))[89]. A copolymer of LAC and SAc has been chosen as the midblock of the triblock copolymers as these monomers offer a number of advantages, including low glass transition temperatures[90,91] and long alkyl side chains that are highly hydrophobic and provide greater resistance to degradation[92]. Varying the length of the side chain on the polyacrylate midblock (C18 and C12 in stearyl and lauryl acrylate repeat units, respectively) is a convenient tool for tuning the physical properties of the triblock copolymers. PS-P(LAc-co-SAc)-PS triblock copolymers exhibit properties that are appropriate for TPE applications. SAXS and transmission electron microscopy (TEM) experiments have elucidated the microphase-separated morphology of the triblock copolymers, consistent with a spherical morphology lacking long-range order. The physical properties of the polymers can be readily tuned by varying the acrylate midblock composition, including the melting temperature, viscosity, and triblock copolymer tensile properties. Tensile testing reveals elastomeric behavior with high elongation at break ( $\sim 200\%$ ) (Figure 6a (iii)). In all cases, the rheology data are consistent with an unentangled polymer. Therefore, it can be concluded that the PS-P(LAc-co-SAc)-PS triblock copolymers will contain P(LAc-co-SAc) midblocks that are not entangled. The unentangled matrices in the triblock copolymers result in lower tensile strengths as compared to styrenic block copolymer (SBC) TPEs. Although it may be a disadvantage for some TPE applications, many recent articles in the literature have focused on the use of polyacrylates for TPEs due to their hydrophobicity and soft matrix[93]. Surprisingly, the order-disorder transition temperature of the triblock copolymer is not dependent on the acrylate composition in the midblock. This indicates that the acrylate composition can be used as a tool to manipulate the physical properties of the triblock copolymers without affecting the order-disorder transition temperature or the processing temperature of the TPEs.

### 4.4. Poly(itaconate)-poly(itaconimide)-poly(itaconate) (PIC-PICI-PIC)

Controlled polymerizations of various abundant renewable vinyl monomers obtained from plants to generate novel bio-based polymers have been investigated[94]. A novel thermoplastic elastomer was developed via controlled/living radical polymerization of plant-derived itaconic acid derivatives, which are among the most abundant renewable

acrylic monomers obtained via the fermentation of starch[95]. Reversible addition-fragmentation chain-transfer (RAFT) polymerization of itaconic acid imide, such as *N*-phenylitaconimide and *N*-(*p*-tolyl)itaconimide, and itaconic acid esters, such as di-*n*-butyl itaconate and bis(2-ethylhexyl) itaconate, were examined using a series of RAFT agents to afford well-defined polymers (Figure 6b (i)). Among the various controlled/living radical polymerization systems, RAFT is one of the most facile and versatile systems in terms of its reaction procedure, applicable monomers, and controllability. The number-average molecular weights of these polymers increase with the monomer conversion while retaining relatively narrow molecular weight distributions. Based on successful controlled/living polymerization, sequential block copolymerization was subsequently investigated using mono and di-functional RAFT agents to produce block copolymers with soft PIC and hard PICI segments. In DSC analysis, all of the block copolymers exhibited typical features of micro-phase-separated morphologies. Two transition peaks, corresponding to the  $T_g$  values of the rubbery PIC segment below ambient temperature and the hard PICI blocks above 200 °C, were observed; however, the  $T_g$  values were slightly shifted in the low-molecular-weight block copolymer. The properties of the obtained triblock copolymer were evaluated as bio-based acrylic thermoplastic elastomers. The DMA analysis of the triblock copolymers revealed the dynamic tensile storage ( $E'$ ) and loss ( $E''$ ) moduli, as well as the  $\tan \delta$  ( $= E''/E'$ ), relative to the temperature for a typical sample of a PhII-DBI-PhII triblock copolymer (Figure 6b (ii)). The properties of the obtained triblock copolymer were evaluated as bio-based acrylic thermoplastic elastomers.

#### 4.5. Poly(L-lactide)-poly(ricinoleic acid)-poly(L-lactide) (PLLA-PRic-PLLA)

A set of ABA triblock PLLA-PRic-PLLA aliphatic copolyesters (Figure 6c (i)) were prepared by a two-step procedure: self polycondensation of methyl ricinoleate[96], produced from castor oil, in the presence of a small amount of 1,3-propanediol leading to a  $\alpha, \omega$ -dihydroxyl-telechelic poly(ricinoleic acid) (HO-PRic-OH) with a molar mass of 11 kg mol<sup>-1</sup>, followed by ring-opening polymerization of L-lactide from the hydroxyl functions, leading to triblock copolymers with a composition ranging from 35 to 83 wt % of PLLA[97]. The block structure was confirmed by several techniques. The copolymers displayed a multi-step thermal degradation with a temperature corresponding to 5 wt % loss in a range of 175–225 °C (Figure 6c (ii)). DSC analyses showed that the PRic block had a moderate effect on the PLLA melting behavior. The block structure of the copolymer enabled conservation of relatively high PLLA crystallinity and melting point after annealing. However, the PLLA crystallization kinetics was rather slow for high content of soft block in the copolymer indicating a significant effect of PRic on the nucleation step. The solid-state morphology of the so-formed copolymers was highly dependent on their chemical composition, as determined from SAXS and WAXD analyses. The high degree of separation of hard and soft phases was also confirmed by a dynamic mechanical analysis, as seen from the distinct  $\alpha$ -relaxations. Finally, the tensile properties of these block copolymers

ranged from thermoplastic to elastomeric depending on their composition (Figure 6c (iii)). This study verifies the feasibility of economical and environmentally friendly solutions for PLLA toughening by using castor oil derived polyesters. A forthcoming paper will address the effects of these block copolymers as compatibilizers in blends with PLA.

## 5. Conclusions and Perspectives

Renewable raw materials from various plants as well as carbohydrates have been used in polymer science for a long period of time. These renewable resources have proved to be useful for the synthesis of various monomers, such as lactide, lactone, and acrylate, which can be converted into block copolymers incorporating blocks of different types (i.e., polyolefins, polyesters, polyethers, polyurethane, and others). In this review we discussed their use for the synthesis of ABA block architectures. The chemical and physical properties as well as molecular characteristics of the obtained polymers were discussed and compared, showing that the application possibilities of these block copolymers are manifold. Moreover, gaps in knowledge were identified and possible further developments discussed. In our opinion, the study of well-defined block polymers derived from natural sources and obtained by controlled polymerization techniques, both to address sustainability objectives and to generate superior physical and chemical properties, will achieve goals involving both large commodity and specialty materials. Finally, consideration of sustainability reveals advantages for renewable raw materials considering gross energy requirements as well as life-cycle assessments. In summary, the recent developments highlighted in this contribution clearly show that there is still a large potential for developing interesting new monomers and block polymeric materials for thermoplastic elastomers and toughened plastics.

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