

## Study on the Effects of Trifluoromethyl Substitution into Poly(L-Lactide) for Improving Thermal Stability

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**Abstract.** An aprotic solvent, dimethyl sulfoxide (DMSO), was employed for detecting the location of substitution (regioselectivity) as a trifluoromethyl-substituted poly(L-lactide) (PLLA). The trifluoromethylation results revealed different melting temperatures and viscoelastic properties. The maximum substitution yields (by using H-NMR with shifted peaks were following the substituted CF<sub>3</sub>) were 16% of trifluoromethyl group into PLLA, which was obtained at 80 °C with 35 wt% sodium trifluoromethanesulfinate (Langlois reagent, CF<sub>3</sub>SO<sub>2</sub>Na), 3.0 wt% tert-butyl hydroperoxide (TBHP) in dimethyl sulfoxide (DMSO). These were demonstrated by <sup>19</sup>F-NMR, DSC, and DMA with various trifluoromethylation conditions. The trifluoromethyl-substituted structures of PLLA were presented -CHCF<sub>3</sub>, HC-OCF<sub>3</sub>, and CF<sub>3</sub>C=O that substituted PLLA shown the maximum melting temperature at 231°C. These results are expected to use as materials where were needed for high thermal stability.

**Keywords:** Substitution, trifluoromethylation, thermal stability, polylactide, biodegradable.

### 1 Introduction

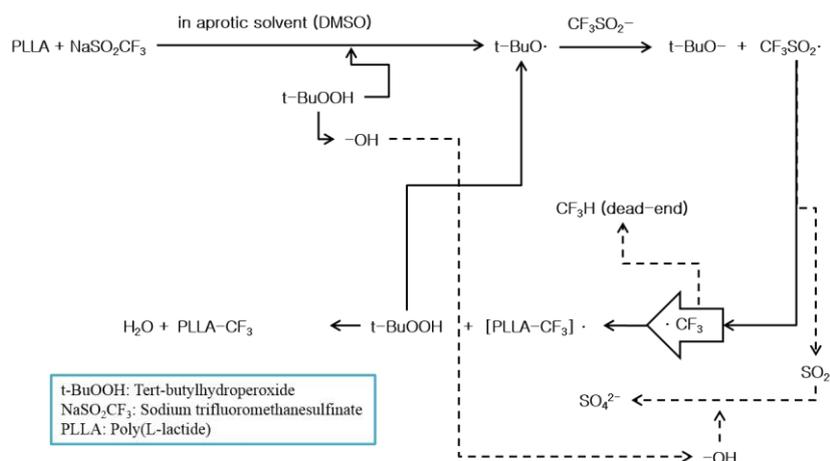
Various methods have been used to modify the properties of materials, among which trifluoromethylation has been used to bring about remarkable changes. In the past two decades, the study of new organofluoro-substituted compounds has increased, because of their improved properties compared with nonfluorinated analogues [1-3]. The introduction of fluorine into organic molecules often brings about significant changes in their physical, chemical, and biological properties [4-5].

Trifluoromethylation in the field of substituted polymers can effectively provide improved mechanical properties, such as metabolic stability, lower friction, higher lipophilicity, and thermal resistance [6-8]. Its energetic electron-withdrawing ability and small size cause powerful electro-negativity and lead to significant effects in both regio-selectivity and reactivity [9], [10].

Leroux et al. [11] reported on the synthesis and properties trifluoromethyl ethers using nucleophilic substitution, fluorodesulfurization, and CF<sub>3</sub>-transfer agents. The results of studies on the properties and structure have increased interest in the utility

of trifluoromethylation. Heo and Park [8] studied the curing behavior and thermal and mechanical properties of fluorine-group-substituted acrylates under different steric hindrance and polarizability. Matsuura et al. [12] described the properties of polyimides with trifluoromethyl side chains in the diamine unit, which had a higher coefficient of thermal expansion and polymer decomposition temperature than those with methyl side chains. However, polyimides with trifluoromethyl side chains have lower intrinsic viscosities. These results showed that the trifluoromethyl group leads to significant changes upon trifluoromethyl substitution into organic materials. Therefore, we have focused on the investigation of trifluoromethyl-substituted poly(L-lactide) to improve the thermal resistance.

Ji et al. functionalized the inherently reactive positions of a substrate, and reported the innate C-H trifluoromethylation of heterocycles with Langlois reagent [13]. There were two reasonable results: a 'putative mechanism' of trifluoromethylateion with Langlois reagent and tert-butyl hydroperoxide, and differences in selectivity with different solvent systems. In another report, Kino et al., Chen and Bozzelli, and Kumar and Malhotra described the position selectivity in various systems, in which the reaction was achieved smoothly with both a nucleophilic radical species and electrophilic trifluoromethyl radicals. The fusion of previous studies with these data allowed for a putative mechanism of trifluoromethyl-substituted poly(L-lactide) to be proposed, as shown in Fig. 1.



**Fig. 1.** Putative mechanism of trifluoromethylation into the poly(L-lactide)

Poly(lactide) or poly(lactic acid) (PLA) have gradually replaced the currently existing oil-based polymers. It is the front runner in the emerging bioplastics market, with the best availability and the most attractive cost structure. PLA is a thermoplastic material with rigidity and clarity, which are good for making transparent films. However, there are a few drawbacks, in that it is highly brittle and has low thermal stability. PLA should be modified to be suitable for use in applications, especially where the thermal stability for materials of electronic devices are important, such as in high melting temperature resin. Therefore, in this study, new types of PLA resins

have been developed to satisfy such requirements via trifluoromethyl-substituted PLA. Focus was centered on the structural analysis in different substitution conditions. The characteristics of thermal and structural differences compared to the original PLA resins are shown. As far as we know, this is the first attempt for the trifluoromethylation of PLA. Structural analysis by nuclear magnetic resonance (NMR) is presented, and the thermal properties determined by differential scanning calorimetry (DSC) in different solvent systems are discussed.

## 2 Conclusions

Trifluoromethyl-substituted PLLA was prepared by a catalyst-free system with Langlois reagent in DMSO and DCM. A maximum trifluoromethyl group substitution yield of 16% was obtained with 35 wt% Langlois reagent and 3 wt% TBHP in DMSO, and 5.5% maximum substitution yield was accomplished with 35 wt% Langlois reagent and 0.75 wt% TBHP in DCM. The  $^{19}\text{F}$ -NMR spectrum provided information about the structures and mechanisms of trifluoromethyl-substituted PLLA. Among these structures, the  $\text{CHCF}_3$  (replacement of methyl group) type was a common structure in both solvents (DMSO and DCM) of which none of the thermal and mechanical properties were affected. However,  $\text{HC-O-CF}_3$  and  $\text{CH-CF}_3$  (from carbonyl) were characterized to lead to an increase of the melting temperature to over  $230\text{ }^\circ\text{C}$ , and to decrease the brittleness by having an increased loss tangent. These experimental results and it became the first in the trifluoromethylation of PLA. Therefore, further studies are needed, the results of which would be fundamental research in this field. Table 1 shows the results of thermal characteristics of trifluoromethylation.

**Table 1.** Thermal characteristics of  $\text{CF}_3$ -substituted PLLA at 3.0 wt% TBHP in DMSO.

Sample No.	$\text{CF}_3\text{SO}_2\text{Na}^*$ wt%	$T_c$ $^\circ\text{C}$	$T_{m1}, T_{m2}, T_{m3}$ ( $^\circ\text{C}$ )	Case No.
T1	15	98	151, 160, 230	C1, C2, C3
T2	35	93	133, 147, 231	C1, C2, C3
T3	50	74	140, 163, 230	C1, C2, C3
T4	65	93	137, 162, 230	C1, C2, C3

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