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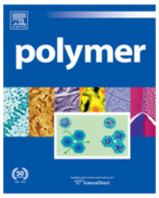

# Synthesis and characterization of a novel graft copolymer with poly-(*n*-octylallene-*co*-styrene) backbone and poly(ε-caprolactone) side chain

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## A B S T R A C T

A novel graft copolymer consisting of poly(*n*-octylallene-*co*-styrene) (PALST) as backbone and poly (ε-caprolactone) (PCL) as side chains was synthesized with the combination of coordination copolymerization of *n*-octylallene and styrene and the ring-opening polymerization (ROP) of ε-caprolactone. Poly(*n*-octylallene-*co*-styrene) (PALST) backbone was prepared from the copolymerization of *n*-octylallene and styrene with high yield by using the coordination catalyst system composed of bis[N,N-(3,5-di-tert-butylsalicylidene)anilinato]titanium(IV) dichloride ($Ti(Salen)_2Cl_2$) and tri-isobutyl aluminum($Al(i\text{-}Bu)_3$). The molar ratio of each segment in the copolymer, and the molecular weight of the copolymer as well as the microstructure of the copolymer could be adjusted by varying the feeding ratio of both styrene and *n*-octylallene. The hydroxyl functionalized copolymer PALST–OH was prepared by the reaction of mercaptoethanol with the pendant double bond of PALST in the presence of radical initiator azobisisbutyronitrile (AIBN). The target graft copolymer [poly(*n*-octylallene-*co*-styrene)-g-poly-caprolactone] (PALST-g-PCL) was synthesized through a grafting-from strategy via the ring-opening polymerization using PALST–OH as macroinitiator and $Sn(Oct)_2$ as catalyst. Structures of resulting copolymer were characterized by means of gel permeation chromatography (GPC) with multi-angle laser light scattering (MALLS), $^{13}C$ NMR, $^{1}H$ NMR, DSC, polarized optical microscope (POM) and contact angle measurements.

## 1. Introduction

Allene derivatives are attractive monomers because they have cumulated double bonds, which can be regarded as the isomers of propargyl derivatives. Allene derivatives are good candidates to produce reactive polymers bearing exomethylene substituents attached to the polymer backbone or those having internal double bonds in the main chain by the polymerization of either part (1,2- or 2,3-polymerization) of the cumulated double bonds [1]. Moreover, allene derivatives can also be used as attractive synthetic precursors for synthesizing functional materials due to the versatility of the addition reactions of the double bonds.

Allene derivatives can be polymerized with different polymerization mechanisms including radical, cationic, coordination and zwitterionic polymerization [1]. Endo and co-workers developed the living coordination polymerization of allene derivatives by π-allylnickel catalysts [2–7]. More recently, the living coordination polymerization of an allene monomer having homochiral binaphthyl and phenylcarbamoyloxy moieties was performed by $[(\pi\text{-ally})NiOCOCF_3]_2/PPh_3$ catalyst, yielding a polymer with a single-handed helical conformation in aprotic solvents [8]. The living coordination polymerization of allene derivatives in protic solvents can accelerate the polymerization and increase 1,2-polymerization selectivity [9]. Due to the stability of the living π-allylnickel ends of the polymers, the block copolymerizations of different allene derivatives [10,11], and allene derivatives with isonitrile [12] or isocyanides [13] proceed in a two-stage coordination polymerization process. However, the polymerizations of common vinyl monomers such as styrene and acrylate cannot be initiated by π-allylnickel catalysts, and consequently the copolymerization of allene derivatives with common vinyl monomers was not reported till now. Huang et al [14–16] synthesized graft copolymers with a polyallene-based backbone and poly(acrylate) side chains by the combination of π-allylnickel catalyzed living coordination polymerization of 6-methyl-1,2-heptadien-4-ol and atom transfer radical polymerization (ATRP) of methyl methacrylate or *tert*-butyl acrylate. Huang et al. also synthesized a new double bond based amphiphilic graft copolymer containing hydrophilic PEG side chains via coupling reaction between the

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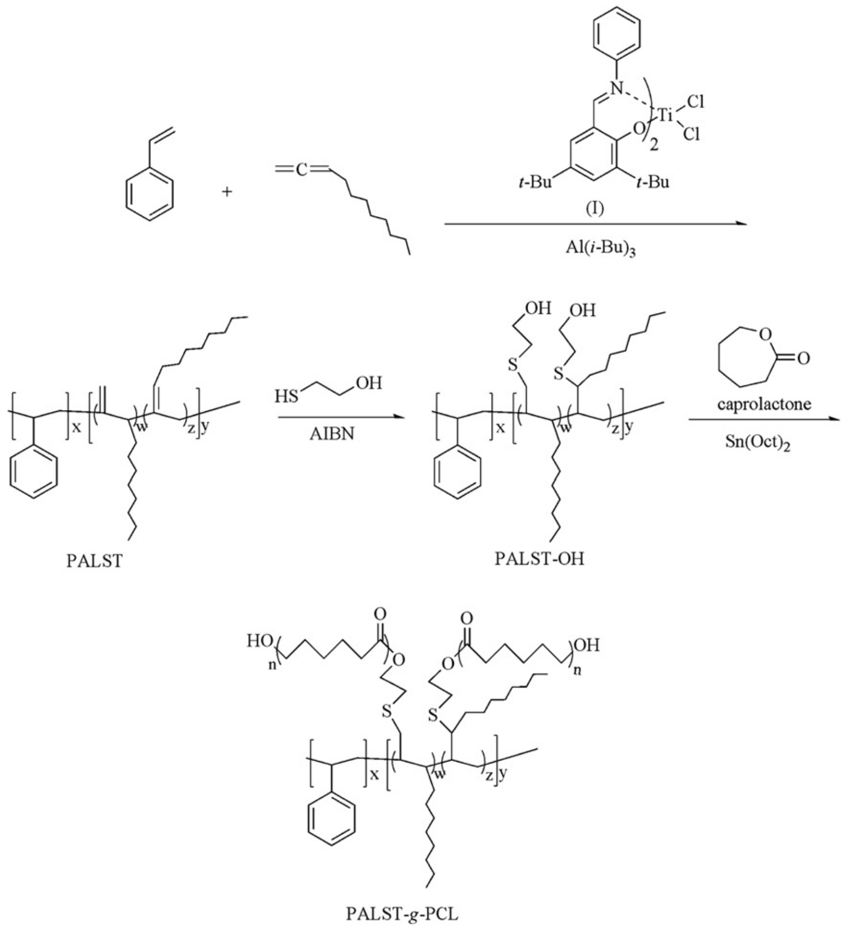

**Scheme 1.** Synthesis of novel graft copolymer PALST-*g*-PCL.

pendant hydroxyls of 6-methyl-1,2-heptadien-4-ol homopolymer and acyl chloride end group of functionalized MPEG using 4-dimethylamino as catalyzer [17]. Copolymers are of importance as materials whose functions are difficult to attain by any homopolymer systems [18]. The polymerization of vinyl-end monomers are quite useful methods for the designed synthesis of graft copolymers [19,20]. Allene moieties might be attractive polymerizable groups in terms of the improvement of the polymerizability and reactivity of the resulting double bond containing polymers. However, only the hydrosilylation and the oxidation reaction of polymers having polyallene units were reported [12,21].

**Table 1**
Copolymerization of *n*-Octylallene(A) and Styrene(St).[a]

| Run | [A]/[Ti] | [St]/[Ti] | $M_w$[b] ($10^4$) | $M_w/M_n$[b] | Yield (%) | Composition of copolymer | |
|---|---|---|---|---|---|---|---|
| | | | | | | A:St[c] | unit ratio(%)[d] |
| 1 | 100 | 100 | 1.69 | 1.58 | 100 | 47:53 | 37:63 |
| 2 | 100 | 200 | 2.61 | 1.61 | 100 | 34:66 | 31:69 |
| 3 | 100 | 500 | 3.14 | 1.63 | 86 | 24:76 | 21:79 |
| 4 | 100 | 1000 | 5.24 | 1.64 | 85 | 22:78 | 14:86 |
| 5 | 100 | 1500 | 8.13 | 1.68 | 87 | 14:86 | 12:88 |
| 6 | – | 400 | – | – | <1 | – | – |
| 7 | 50 | 350 | 4.61 | 1.72 | 100 | 15:85 | 12:88 |
| 8 | 100 | 300 | 3.81 | 1.76 | 100 | 28:72 | 17:83 |
| 9 | 150 | 250 | 2.87 | 1.49 | 100 | 35:65 | 22:78 |
| 10 | 200 | 200 | 1.80 | 1.58 | 100 | 50:50 | 36:64 |
| 11 | 250 | 150 | 1.27 | 1.49 | 100 | 66:34 | 42:58 |
| 12 | 300 | 100 | 1.21 | 1.66 | 100 | 74:26 | 54:46 |

[a] Polymerization conditions: [Al]/[Ti] = 50, aged at 80 °C for 3h, polymerized at 80 °C for 16h in bulk.

[b] Determined by GPC against the standard PSt samples.

[c] The molar ratio of two segments determined by $^1$H NMR.

[d] The molar ratio of 1,2-polymerized units(w) and 2,3-polymerized units(z) of the poly(*n*-octylallene) moieties in the main chain, determined by $^1$H NMR.

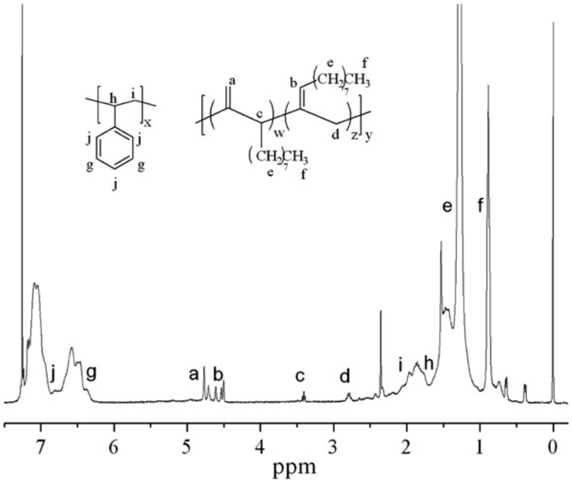

**Fig. 1.** $^1$H NMR spectrum of PALST (Run 1 in Table 1).