Syringaldehyde Methacrylate as a Bio-Based Substitute for Styrenic-Derivatives in Acrylate Copolymers

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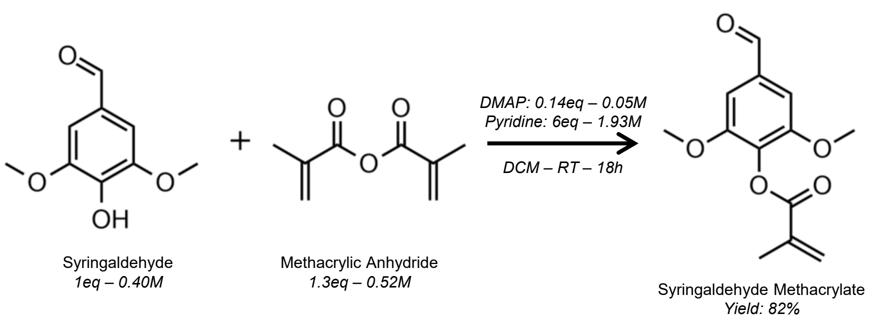
Introduction

The transition toward sustainable materials has intensified research on bio-based monomers for polymer synthesis [1]. To this end, syringaldehyde methacrylate (SyMA), a lignin-derived monomer, represents a promising alternative to styrene in acrylate copolymers, the latter having applications in coatings, adhesives, and paints [2]. However, its polymerization behaviour and the properties of the resulting copolymers require further investigation. In this study, SyMA was copolymerized with butyl acrylate (BuAc) using ARGET-ATRP, a controlled radical polymerization technique [3]. Reaction conditions were optimized by evaluating different amino-ligands, such as PMDETA, Me6TREN and BiPy, and initiators, e.g. EBiB, EBPA and TsCl. Kinetic studies were performed via ^{1}H-NMR and GPC to confirm the controlled nature of the process. The resulting copolymers were characterized by ^{1}H-NMR, GPC, DSC and TGA. Finally, mechanical properties of films with and without natural fillers, such as chitin and chitosan, were investigated through tensile tests.

1. Synthesis of Syringaldehyde Methacrylate



The synthetic procedure was modified by a reported procedure [4]. The use of methacrylic anhydride, instead of the classical methacrilic chloride, makes the synthetic process more susteinable.

3. Optimization of ARGET-ATRP copolymerization condition of SyMA and BuAc

Ligand Effect

Ligand	Initiator	Monomer/Reducing Agent Ratio	Yield (%)
PMDETA	EBiB	40:1	59
Me6TREN	EBiB	40:1	52
BiPy	EBiB	40:1	N.D.

Best Ligand: PMDETA

Initiator Effect

Ligand	Initiator	Monomer/Reducing Agent Ratio	Yield (%)
PMDETA	EBiB	40:1	59
PMDETA	EBPA	40:1	17
PMDETA	TsCl	40:1	N.D.

Best Initiator: EBiB

Monomer/Reducing Agent Ratio Effect

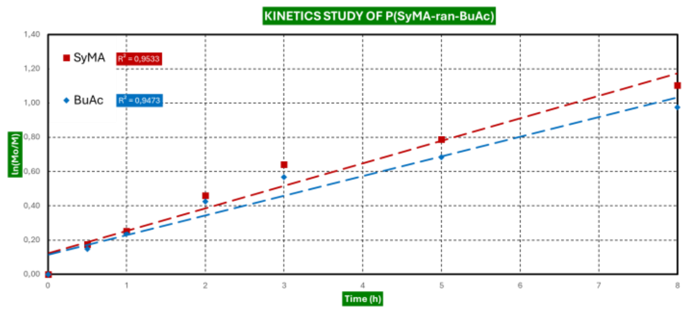
Ligand	Initiator	Monomer/Reducing Agent Ratio	Yield (%)
Me6TREN	EBiB	40:1	52
Me6TREN	EBiB	25:1	72
PMDETA	EBiB	40:1	59
PMDETA	EBiB	25:1	31

Best Monomer/Reducin Agent Ratio: 25:1 with Me6TREN as ligand

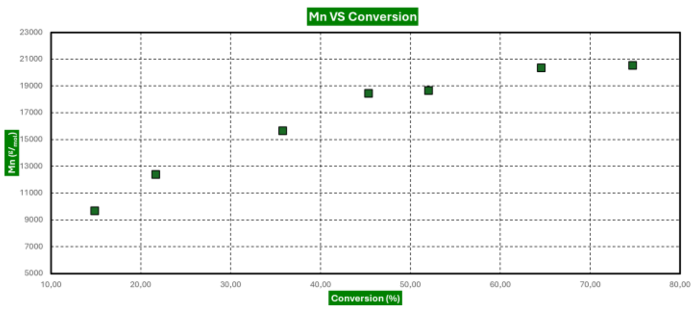
Best condition:
Total monomers/$CuBr_2$/Me6TREN/EBiB/$Sn(oct)_2$ at a molar ratio of 2000/1/1/10/80

Each polymerization was conducted under N_2 atmosphere, using toluene as solvent, at 90°C for 24h and with a total monomer concentration of 0,60M.

5. Kinetic Studies



Study made by ^{1}H-NMR analysis



Study made by GPC analysis

The Mw/Mn ratio was ≤ 1.3 for all the polymerizations. This finding, together with the linear trend of kinetic and of molecular masses vs conversion, confirmed the controlled polymerization. After 8 hours, the conversion of both monomers stopped.

6. Stress-Strain Measurements

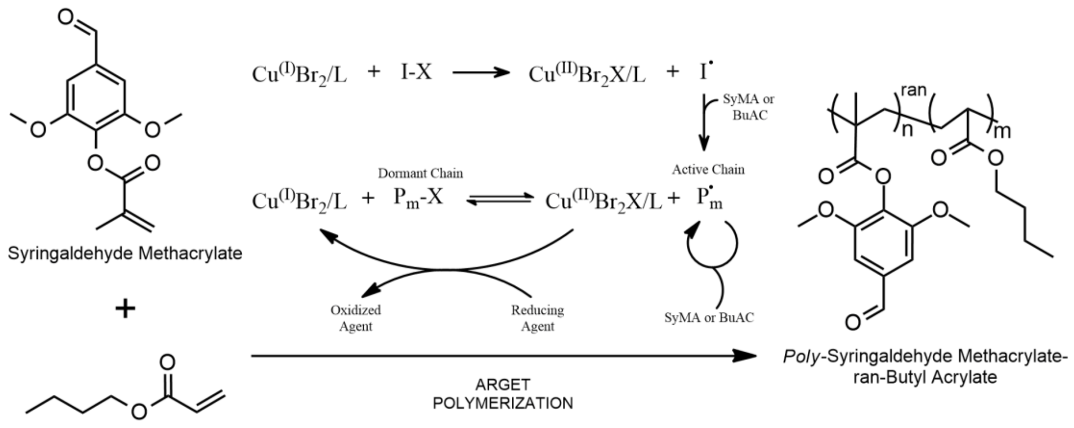
χ_{SyMA}	Filler	Stress σ (MPa)	Strain ε (%)
0.19	-	0.40	1000
0.19	Chitin	0.60	270
0.19	Chitosan	0.25	500

χ_{SyMA}	Filler	Stress σ (MPa)	Strain ε (%)
0.12	-	0.80	750
0.12	Chitin	1.60	150
0.12	Chitosan	1.20	170

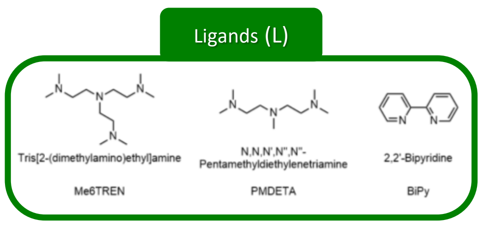
The presence of a filler decreases the max strain value. Film with higher content of SyMA (19%) show the highest elongation value (1000%) in absence of fillers

Tests made by Instron Machine

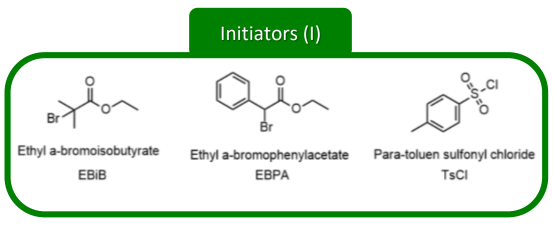
2. ARGET-ATRP copolymerization of SyMA and BuAc



Ligands (L)



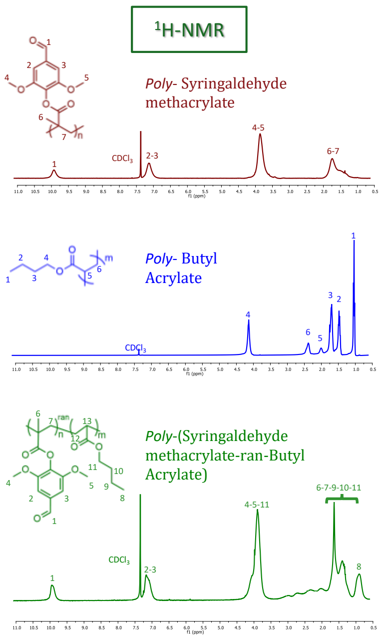
Initiators (I)



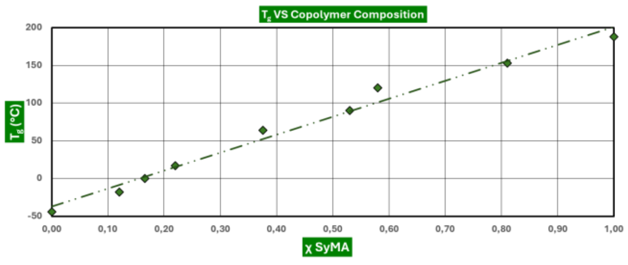
Reducing Agent: $Sn(oct)_2$

4. Characterization of copolymers

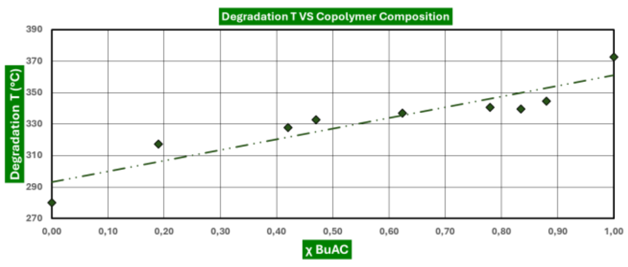
^{1}H-NMR



Thermal properties



T_g determinated by DSC analysis



Degradation temperature determined by TGA analysis

Conclusions

In this work, the copolymerization of SyMA and BuAc was investigated by the controlled and sustainable radical polymerization ARGET-ATRP. The polymerization was successfully optimized by using Me6TREN as ligand, and EBiB as initiator at 90°C. Copolymerizations were carried out by varying the monomer-to-reducing agent ratio, achieving a 71% of conversion, and kinetic studies performed via ^{1}H-NMR spectroscopy and GPC analysis confirmed the controlled nature of the process.

The copolymer composition significantly influenced the thermal properties, and the glass transition temperature (T_g) followed the Flory-Fox equation. Interestingly, the copolymer containing 55 wt% of SyMA exhibited a T_g of 64°C, notably higher than the one observed for a comparable styrene-based copolymer (34°C) [4]. Additionally, the thermal degradation temperature varied over a wide range, from 290°C to 370°C, increasing with increasing the BuAc content.

Mechanical tests on films with a content of SyMA less than 20% revealed high stretchability. The latter decreased in presence of fillers, especially chitin in comparison with chitosan. These findings suggest that SyMA-based copolymers can be tailored with and without fillers, for applications requiring adjustable thermal and mechanical properties.

Overall, this work highlights the potential of SyMA as a bio-based alternative to styrene in coatings, adhesives, and paints, contributing to the development of sustainable polymeric materials.

References

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