chemistry proceedings

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Synthesis of Bio-Based Methacrylic Polymer Using Camphor Terpene as a Renewable Resource †

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† The 27th International Electronic Conference on Synthetic Organic Chemistry, Spain, 15–30 November 2023; Available online: https://ecsoc-27.sciforum.net/

Abstract: Sustainable polymers derived from biomass have the potential to reduce environmental impact while offering significant performance and cost advantages over petrochemical-derived macromolecules. We present here a facile and efficient approach to the synthesis of a biomethacrylic monomer: isobornyl/bornyl methacrylate (IBOMA/BOMA) using the naturally available camphor terpene in the essential oil of the Algerian plant Artemisia arborescens (Absinthe) as a key intermediate. The essential oil of the aerial part of the Artemisia arborescens plant naturally distributed in northwest Algeria was isolated by hydrodistillation and analyzed using gas chromatography-mass spectrometry (GC/MS) techniques. Nine components were identified representing 90.7% of the total content. The main constituent of Artemisia arborescens essential oil is camphor (71.8%). Camphor was purified and modified to produce an 80% renewable carbon-based methacrylic monomer. This terpene-derived methacrylic monomer was free-radically polymerized to create a biosourced methacrylic polymer. Nuclear magnetic resonance (NMR) was used to characterize the structure of camphor terpene, isobornyl/bornyl methacrylate and poly (isobornyl/bornyl methacrylate) (PIBOMA)/(PBOMA).

Keywords: Artemisia arborescens; Camphor; Biobased polymers

Citation: Chabane, N.; Dergal, F.; Pata, H.; Chikhi, I. Synthesis of Bio-Based Methacrylic Polymer Using Camphor Terpene as a Renewable Resource. *Chem. Proc.* **2023**, *4*, x. https://doi.org/10.3390/xxxxx

Academic Editor: Firstname Lastname

Published: date

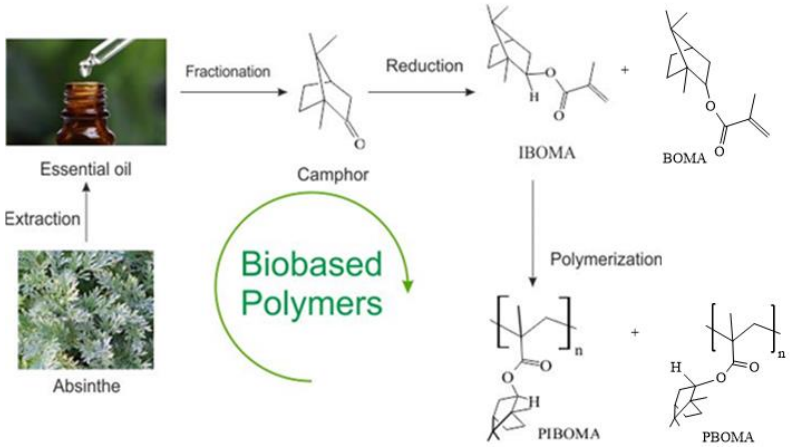
1. Introduction

In the contemporary landscape, a substantial portion of essential materials is currently derived from fossil fuels, yet a consensus among various research endeavors suggests a bleak prognosis: the depletion of all fossil resources within the next century. Consequently, an urgent call to action revolves around the transformation of chemical synthesis by adopting renewable resources, an ambitious quest vital for advancing sustainable development and, more specifically, the production of monomers [1-9].

The realm of renewable polymers has witnessed a transformative influence through the advent of natural molecular biomass. This biomass, akin to its petroleum-derived monomer counterparts, exhibits the versatility to serve as a direct source, whether in the form of terpenes or carbohydrates, or to undergo derivatization, ultimately evolving into a monomer suitable for uncontrolled or controlled polymerization processes [8]. Biomass-derived monomers can be broadly categorized into four principal classes, contingent upon the origin of their natural resources: Oxygen-rich monomers include carboxylic acids (lactic, succinic, itaconic, and levulinic acids) and furans. Hydrocarbon-rich monomers

encompass vegetable oils, terpenes, terpenoids, fatty acids, and bietic acids. Bio-olefins represent yet another group of hydrocarbon monomers, while carbon dioxide diverges as a non-hydrocarbon monomer. The development of novel bio-based methacrylic monomers and polymers from terpenes has garnered significant attention in recent years [10]. Terpenes, a family of naturally occurring, hydrocarbon-rich molecules prevalent in essential oils [11,12], exhibit a diverse array of structures. Terpenes featuring an isoprene moiety can be facilely polymerized through radical polymerization reactions [8,13]. Additionally, cyclic terpenes boasting alcohol or ketone functionalities can be strategically tailored for the pursuit of bio-sourced polymers [14,15].

This study is a focal point for the synthesis of a bio-based methacrylic monomer, with camphor terpene serving as a pivotal intermediate. The process involves the extraction of camphor from the Artemisia arborescens plant, followed by purification and modification to generate the bio-sourced methacrylic monomer. Subsequently, this monomer is subjected to free-radical polymerization, culminating in the creation of a bio-sourced thermoplastic methacrylic polymer, as exemplified in Scheme 1.



Scheme 1. Diagram summarizes the stages of our work.

2.2. . Experimental

2.1. Artemisia arborescens oil extraction

The aerial part of the A. arborescens plant was collected in Tlemcen, western Algeria. The station's relative GPS coordinates are 1°44′52″W longitude, 35°00′48″N latitude and 355 m above sea level. The essential oil of aerial part of Artemisia arborescens was obtained by hydro distillation for 3h employing Clevenger-type apparatus.

2.2. Reduction of camphor

Camphor was reduced to isoborneol/borneol in the presence of $NaBH_4$ in MeOH (figure 1). Camphor (0.01 mol) and methanol (3 mol) are introduced into a flask and stirred until a homogeneous solution is obtained. Next, 0.2g of sodium tetrahydruroborate ($NaBH_4$) was added. The mixture was heated to 60° C for 1h. The mixture was then removed and cooled. Finally, 20 ml of ice-cold water was added to the mixture and filtered.

2.3. Esterification of isoborneol

Into a 50 ml flask, 25 ml of dichloromethane were introduced. 1.5g of isoborneol/ borneol, then add 0.7ml of triethylamine. The mixture is stirred in an ice bath. Next, 0.9 ml methacryloyl chloride was added dropwise. After complete addition, the mixture was brought to room temperature and stirred for 24 hours. The product was washed with water (3x70 ml) and dried over anhydrous $MgSO_4$. Product purification was carried out on a silica gel chromatography column using a mixture of heptane and ether (90/10). For 1g of product, 30g of silica gel was used (figure 1).

2.4. Polymerization of Isobornyl methacrylate

We decided to work with the mixture (isobornyl/bornyl methacrylate) without separation. In a 25 ml flask, 0.01 mol of monomer (isobornyl/bornyl methacrylate) was introduced, then $9x10^{-4}$ g of AIBN was added. The mixture was bubbled with nitrogen for 15 min. Then stirred at 80°C for 6 h. The resulting polymer was purified by precipitation in methanol, filtered and dried in an oven at 60°C (figure 1).

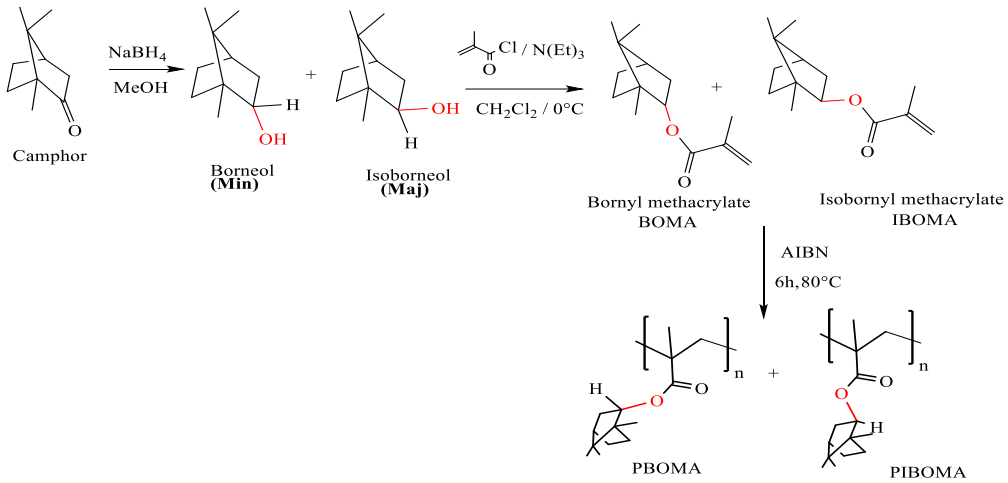


Figure 1. Reduction of camphor, Esterification of isoborneol/borneol and Polymerization of Isobornyl/bornyl methacrylate.

3.3. . Results and Discussion

GC/MS analysis of A. arborescens essential oil shows that the oil is dominated by camphor (71.8%) (Table 1).

Table 1. Chemical composition of essential oil of A. arborescens determined by GC/MS analysis.

N°	Compounds [a]	RI_a [b]	RI_a [c]	%
1	α-Thujene	913	914	3.6
2	Camphene	946	944	2.1
3	Artemisiatriene	922	924	2.5
4	α-Terpineol	1185	1183	1.0
5	β-Pinene	979	978	2.2
6	Terpinen-4-ol	1171	1169	1.7
7	Camphor	1143	1048	71.8
8	Sabinene	952	954	0.8
9	Chamazulene	1735	1734	4.8

a Order of elution are given on the apolar column (HP-5MS).
b Retention indices of literature (RIa) on the apolar column reported from the literature.
eRI: Retention Indices.
MS: Mass Spectrometry in electronic impact mode.

the structure of each synthesized compound was analyzed by NMR, and the polymer was analyzed by NMR and Raman. the band at 625 cm^{-1} attributed to C-C-C in planar bending (ring), 875 cm^{-1} for CH_2 rocking, 1470cm^{-1} for CH deformation, 1720 cm^{-1} and 2950 cm^{-1} for C=O and CH_2 stretching respectively[16] (figure 2).

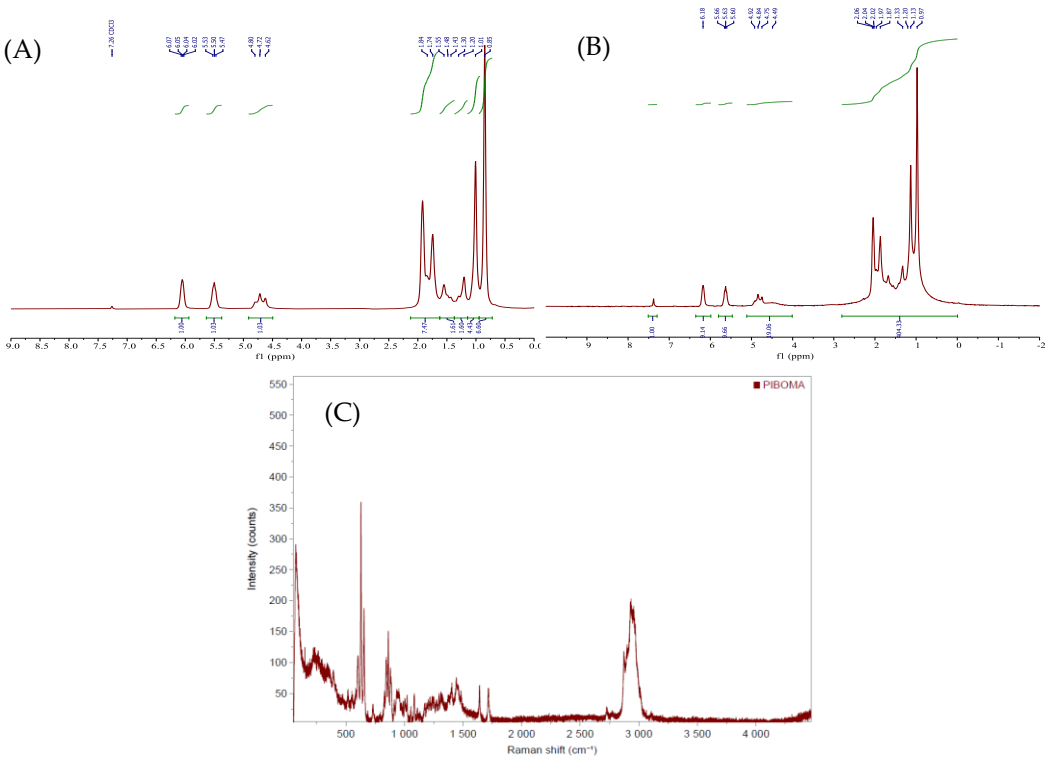


Figure 2. NMR spectra of Isobornyl/bornyl methacrylate IBOMA/BOMA (A) Poly (isobornyl/bornyl methacrylate) PIBOMA/PBOMA (B) and (C) Raman Spectra of Poly (isobornyl/bornyl methacrylate) PIBOMA/PBOMA. [16].

4. Conclusion

In conclusion, this work elucidates the synthesis of poly(isobornyl/bornyl methacrylate) by leveraging the camphor terpene, naturally occurring in the essential oil extracted from Artemisia arborescens, as a fundamental intermediate. The essential oil analysis conducted through Gas Chromatography/Mass Spectrometry (GC/MS) demonstrated a significantly high concentration of camphor terpene in the Artemisia arborescens plant extract. This finding underscores the potential of utilizing this natural resource as a crucial building block for synthesizing advanced materials.

The chemical modification of the camphor terpene offers a promising pathway for the development of a biopolymer characterized by an impressive 80 percent biobased carbon content. This innovative approach capitalizes on the renewable nature of terpenes, paving the way for the sustainable production of high-performance materials.

Throughout this study, each step involved in the separation of camphor and subsequent modifications leading to the formation of the biopolymer was meticulously executed, resulting in successful outcomes. This accomplishment signifies a significant advancement in the realm of biopolymer synthesis, showcasing the feasibility and efficacy of utilizing natural terpenes as precursors for eco-friendly material production.

The utilization of natural compounds, such as camphor terpene from Artemisia arborescens, not only presents an opportunity for reducing reliance on non-renewable resources but also contributes to the development of environmentally friendly materials. The successful completion of this synthesis process highlights the potential of bio-based polymers derived from natural sources, emphasizing the importance of sustainable methodologies in material science and engineering.

Author Contributions: Methodology, N.C.; validation, F.D.; writing—original draft preparation: N.C.; writing—review and editing, F.D.; supervision, I.C. and H.P. All authors have read and agreed to the published version of the manuscript.

Funding: The study is supported by the DGRSDT/MESRS in Algeria.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.
Data Availability Statement: Not applicable.

Acknowledgments: The authors very thankful to the DGRSDT/MESRS in Algeria for their financial support, as well as the Center for Scientific and Technical Research in Physico-Chemical Analysis (CRAPC), Tipaza, Algeria and University of Tlemcen, Algeria.

Conflicts of Interest: The authors declare no conflict of interest.

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