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Potentially Biodegradable Polymers Based on α- or β-Pinene and Sugar Derivatives or Styrene, Obtained under Normal Conditions and on Microwave Irradiation

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The homopolymerisation of α- and β-pinene and their copolymerisation with styrene and hepta-*O*-benzyl-6′-*O*-methacryloyl-sucrose (BMS) have been examined in the presence of AIBN as free-radical initiator, either in toluene or without solvent at 80 °C at normal pressure and also in a synthetic microwave oven. A study of the effect of the reaction conditions, the monomer structure and the initial ratio of the comonomers on the properties of the final copolymers, each containing two natural products, has been carried out. A new procedure for synthesising poly(β-pinene), poly(α-pinene-co-styrene), and poly(β-pinene-co-styrene) in short reaction times and under mild conditions with microwave irradiation was found.

1. Introduction

The main constituents of pine resin distillate are α- and β-pinene, representing a significant source of economically important raw materials. Development of novel applications for these abundant and renewable biomass feedstocks would add to their value.[1]

Commercial polymers of these compounds have the common name "terpenic resins" and are normally obtained by Lewis acid-catalysed polymerisation. The most useful terpenes for production of these resins are β-pinene, dipentene, and α-pinene.[2] They have relatively low molecular weights and afford linear thermoplastic resins with light colours and weak mechanical properties, but show increased stability towards heat and UV irradiation. They find various applications as tackifying resins and additives in plastic compositions useful as adhesives,[3,4] electroconductive parts, thermoplastic mouldings etc.[5] Such compositions are used for drug-delivery and active compound release systems,[6,7] as well for other medicinal purposes.[8] The homopolymers of α- and β-pinene are also reported to have pesticidal properties (Wilt–Pruf Products, Inc.).

Many types of copolymers – including styrene with α- and β-pinene,[9–11] xylene with β-pinene,[12] maleic anhydride with β-pinene,[13] furfural with α-pinene for ion-exchange resins,[14] with methyl methacrylate[15] – have been reported. To the best of our knowledge, though, there are no reports on copolymers of pinene with sugar-derived monomers.

There are very few reports on the radical polymerisation of pinenes. The first dates from 1959, when Rozhkov reported the free radical copolymerisation of terpenes with methyl methacrylate[16] and acrylonitrile[17] in the presence of AIBN, whilst a British patent from 1964 deals with the same topic.[18] There followed other works by the same authors on the radical copolymerisation of limonene, but not of α-and β-pinene.[19,20] A free radical copolymerisation of α-pinene with acrylonitrile with benzoyl peroxide as catalyst[21] has been reported, as have a synthesis of graft copolymers of β-pinene with methyl methacrylate and butyl acrylate by a combination of living cationic and atom transfer radical polymerisation,[15] and copolymerisation with maleic anhydride using AIBN.[13] Kinetic studies of the free radical homo- and copolymerisation of α-and β-pinenes with styrene and methyl methacrylate with AIBN as an initiator have been carried out.[22,23]

Microwave irradiation has recently proved to be effective as an alternative to conventional heating for reactions with compounds that are sensitive and/or have low reactivity.[24] The energy is applied to the sample homogeneously, which in many cases allows the reactions to be performed in the absence of solvent, resulting in more efficient, more economic, and cleaner chemistry.[25] Monomodal microwave equipment has overcome the uncertainties associated with domestic microwave ovens. After fast acceptance in inorganic and organic syntheses, polymer chemists have also re-

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cently discovered this new kind of microwave reactor, and the growing interest in the use of microwave irradiation for polymerisations is reflected in an almost exponential increase in the number of publications in this field.[26] The main applications of microwave polymerisation are in the preparation of dental materials, polymer modification reactions, and curing processes.[27] So far, most polymerisations performed under microwave irradiation conditions have been of well investigated monomers such as styrene or methyl methacrylate,[28–30] most of them comparing thermal and microwave effects with or without initiator, or searching for controlled living or atom-transfer systems. To the best of our knowledge, there are no reports relating to microwave-assisted polymerisation of terpenes.

Growing attention[31,32] has recently been paid to the hypothesis that polymers with interesting biodegradability properties could be available from monomers such as vinyl sugars. In this work we have obtained homo- and copolymers of α- and β-pinene with styrene and sucrose monomers, comparing cationic and free radical polymerisation, as well as microwave irradiation and conventional heating. In order to incorporate the sucrose moieties into the polymer we opted to attempt a free radical approach, as this reaction is slower and more conducive to copolymerisation than cationic polymerisation. As a continuation of our work on the chemical transformation of sugars,[33–35] we studied the radical copolymerisation of a vinyl sugar starting material with α- and β-pinene. Copolymers with a wide range of compositions were synthesised and the influences of the experimental conditions on reactivity, incorporation ratios and average molecular mass, as well as some physical properties, were evaluated.

2. Results and Discussion

2.1. Synthesis of Acryl Sucrose Monomer and Its Application

Since sucrose has eight chemically active hydroxy groups, regioselective derivatisation is important for the selective synthesis of sucrose-containing linear polymers.[36,37] A route to selective derivatisation of the 6′-position of the sucrose, developed in our laboratory,[38,39] allowed us to obtain the fully protected sucrose with only the 6′-hydroxy unprotected, and from this intermediate we prepared unsaturated sucrose esters (Figure 1).[40] These monomers could be converted into pure linear polymers.

The homopolymerisation of α-and β-pinene, as well as their copolymerisation with styrene and the monomer BMS (hepta-*O*-benzyl-6′-*O*-methacryloyl-sucrose), were examined in the presence of $AlCl_3$ as a cationic and AIBN as a free-radical initiator, either in toluene or without solvent at 80 °C at normal pressure in a focused microwave oven or with conventional heating, followed by precipitation in cold methanol. A study of the effect of the reaction conditions, the monomer structure and the initial quantity of the comonomers on the sugar incorporation into the final copolymers has been carried out. As a result we obtained a number of copolymers with diverse protected sucrose content, with different chain lengths, reported in terms of the weight average molecular weight (M_w), polydispersity (M_w/M_n, M_n being the number average molecular weight), and with some physical properties such as optical rotations ($[\alpha]_D$) and glass transition temperatures (Tg).

2.2. Cationic and Radical Homopolymerisation of α- and β-Pinene

As a first approach to the synthesis of the desired materials, and for intercomparison of the materials, homopolymers of α- and β-pinene, as well as their copolymers with styrene, were prepared both by cationic polymerisation with $AlCl_3$ as catalyst and by radical polymerisation with AIBN under similar conditions. All the samples were characterised by ^{1}H NMR and IR. The structures of radical polymers would be expected to be analogous to the cationic ones[2,41,42] (Figure 2, Figure 3, Figure 4), as proposed by Roberts and Day, but to have lower molecular masses. The

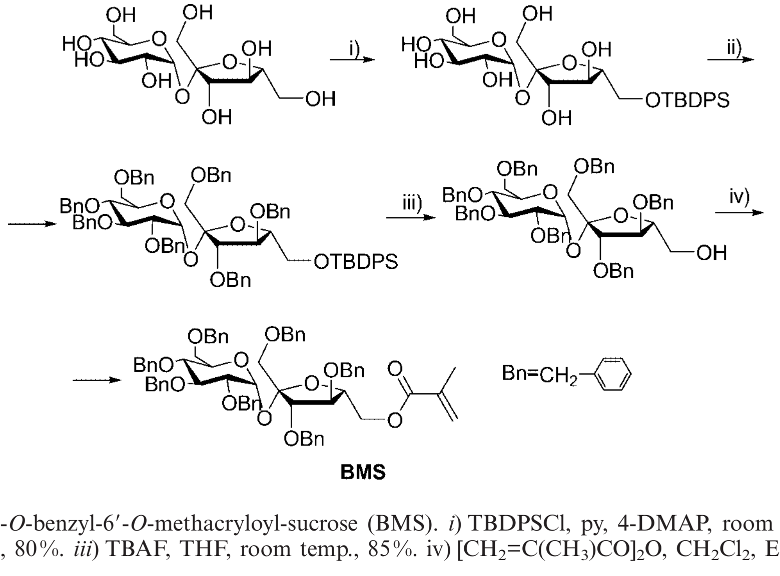

Figure 1. Synthesis of hepta-*O*-benzyl-6′-*O*-methacryloyl-sucrose (BMS). *i*) TBDPSCl, py, 4-DMAP, room temp., 85%. *ii*) BnBr/NaH, DMF, $Bu_4N^+I^-$, room temp., 80%. *iii*) TBAF, THF, room temp., 85%. iv) $[CH_2=C(CH_3)CO]_2O$, CH_2Cl_2, Et_3N, 4-DMAP, room temp., 73%.

two pinene isomers follow different polymerisation paths: β-pinene gives a polymer with a monocyclic monomer unit and, as shown in Figure 2, the chain grows by alternate isomerisation and addition steps, whilst the structure of poly(α-pinene) is not exactly known, as it represents a more complex case. Dimer formation occurs to a considerable extent and the main chain probably consists of two repeating units.[43]

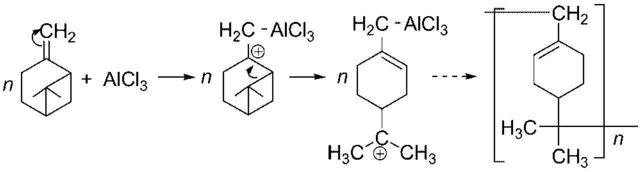

Figure 2. Cationic polymerisation of β-pinene.

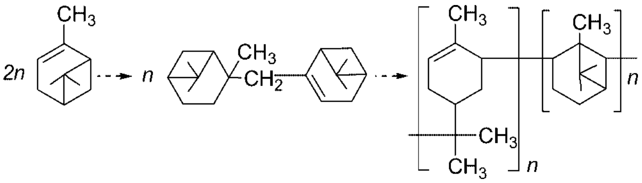

Figure 3. Cationic polymerisation of α-pinene (Ruckel, 1975).

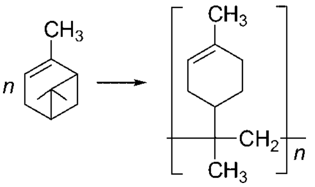

Figure 4. Cationic polymerisation of α-pinene (Roberts and Day, 1950).

Under microwave irradiation conditions, two different procedures for cationic and radical homopolymerisation of α- and β-pinene were tested. The first procedure involved working at constant power, with temperature monitoring, whilst the second entailed working at constant temperature, maintained by controlling the power. The experiments conducted under microwave irradiation conditions are marked in all the tables (see Supporting Information, Tables S1–S7) with the abbreviation “MW” in the column “Reaction conditions”. As can be seen from Table S1, cationic polymerisation (catalyst $AlCl_3$) afforded homopolymers with molecular weights similar to those reported in the literature (500–3000),[23] in relatively short times (10 min for β-pinene) both under classical conditions and under microwave irradiation conditions (Entries *1* and *4*), while with AIBN even 96 h were not enough. The general procedure for isolation of the obtained polymers from the reaction mixture is by precipitation through the addition of, in our case, cold MeOH, which is miscible with the monomers, the solvent, and the initiator, as well as with by-products (e.g., oligomers). The degree of conversion of the monomers to macromolecules is shown as the weight percent of the obtained solid phase polymers with regard to the initial monomer mixture.

The best result was achieved under microwave irradiation conditions at a constant power of 300 W (mild conditions, the reaction temperature was 54 °C) and with a short reaction time: by cationic polymerisation we obtained poly(β-pinene) in high yield and with a molecular mass identical to that of industrial polymers of this type formed under much harsher conditions.[44]

2.3. Radical Copolymerisation of α- and β-Pinene with Styrene

Radical copolymerisation of α-pinene and styrene was carried out under both “conventional” and microwave irradiation conditions with an initial 1:1 mol ratio of the monomers. The incorporation of pinene in poly(α-pinene-co-styrene) (Figure 5, Table S2, Supporting Information) was relatively low, due to the higher reactivity of styrene monomer under free radical conditions. The copolymers were obtained with higher conversion and higher incorporation of α-pinene under conventional conditions than under microwave irradiation conditions, probably due to the longer reaction time, whilst the copolymer obtained under MW conditions had higher molecular mass and a similar polydispersity, but contained mainly styrene units. The $[\alpha]_D$ and T_g values were in a range similar to those of similar copolymers reported in the literature.[23]

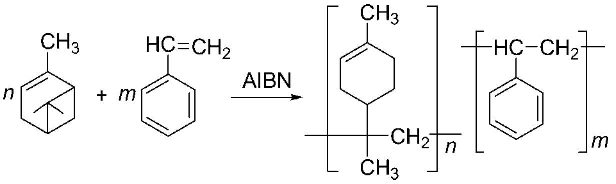

Figure 5. Radical copolymerisation of α-pinene with styrene.

The free radical copolymerisation of β-pinene with styrene was also studied under both conventional and microwave irradiation conditions, with an initial 1:1 mol ratio of the monomers. The polymers *1* and *2* (Figure 6, Table S3, Supporting Information) consisted only of polystyrene without any incorporation of β-pinene, as indicated by ^1H NMR, and were not characterised by SEC and DSC analyses. MW irradiation proved to be the only method by which to achieve incorporation of β-pinene in the copolymer (Entry *4*, Table S3) in short reaction times. After 4 h the obtained copolymer was a viscous oil and it was not possible to isolate it from the reaction mixture by precipitation, whilst after 5 h a powdery precipitate could be precipitated. The resulting copolymer represented a relatively low degree of conversion and incorporation of β-pinene, but had a high molecular mass, which was consistent with the literature data.[23]

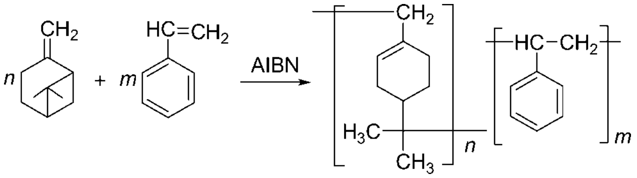

Figure 6. Radical copolymerisation of β-pinene with styrene.

2.4. Effect of the Reaction Time on Free Radical Copolymerisations of α- and β-Pinenes with Hepta-*O*-benzyl-6′-*O*-methacryloyl-Sucrose

With these results to hand we next examined free radical copolymerisations of α- and β-pinenes with hepta-*O*-benzyl-6′-*O*-methacryloyl-sucrose (Figure 7 and Figure 8). Unsaturated polyolefin-based materials can easily be vulcanised, resulting in elastomers. Through the incorporation of polar groups it is possible to eliminate one of the main technical limitations of polyethylene-based materials: their low binding ability.

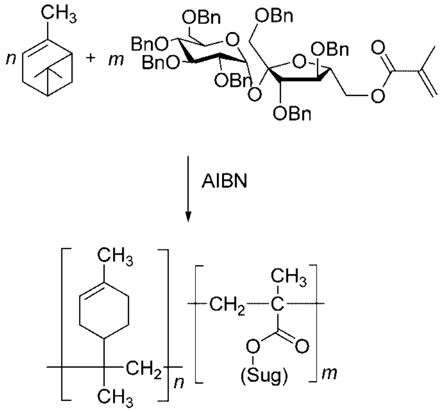

Figure 7. Radical copolymerisation of α-pinene with BMS.

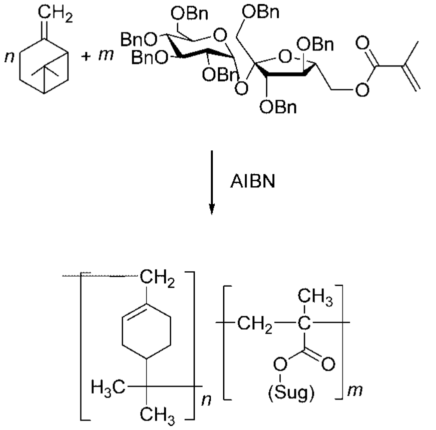

Figure 8. Radical copolymerisation of β-pinene with BMS.

A study of copolymerisation reactions as a function of the reaction time was carried out. The polymerisations were performed in closed vials without prior degassing and without stirring, with AIBN as initiator of the free radical polymerisation in two series: in toluene (Table S4, Supporting Information) and without solvent (Table S5, Supporting Information), heated at 80 °C in oil bath. The initial mol ratio in all experiments was [sug]/[pin] = 0.1.

From the experiments in the presence of solvent (Table S4), only oily oligomers consisting mainly of polypinene were isolated, as shown by their ^{1}H NMR spectra. As can be seen from the Table, the molecular mass and the rate of incorporation of sugar did not increase with longer reaction times, and the results obtained after 12 d reaction time in solution were the same as those after 5 d.

For most of the samples obtained by bulk polymerisation (Table S5), two polymerised fractions were isolated: (1) a higher molecular mass powder fraction (marked in the Tables as *powder*), and (2) a lower molecular mass resinous-like fraction (marked as *resin*). The resinous fraction was in all cases easily soluble in organic solvents such as $CHCl_3$ or CH_2Cl_2, whilst the powdery fraction was only partially soluble in these solvents, and in some cases (Entry *3*, Table S5) it was not possible to dissolve it in $CHCl_3$. It is likely to be a crosslinked part of the polymer, probably as a result of the presence of the double bonds in the pinene units. These samples did not show any thermal phenomenon during DSC analyses, which confirms a high degree of crosslinking. Since our studies required linear polymers, only the molecular masses of the resinous fractions were measured by SEC analyses. The chromatograms showed bimodal distributions with two overlapped distinct peaks, which means that there are two different polymer types present: either a mixture of polypinene and poly(pinene-co-sugar) copolymer, or the two homopolymers – polypinene and polysugar – blended together. At longer reaction times we obtained higher yields of the higher molecular mass fraction, but not greater incorporation of sugar. As expected, optical rotations were higher in the copolymers with greater incorporation of the optically active comonomer (Entries *2* and *3*, Table S6, Supporting Information). For comparison, the optical rotation of the monomer BMS is $[\alpha]_D^{20}$ = +46.88 (c = 1.23, $CHCl_3$)[35] and that of the polypinene $[\alpha]_D^{20}$ = –6.02 (c = 1.07, $CHCl_3$) (Table S1).

2.5. Effect of the Initial Monomer Ratio on the Free Radical Copolymerisation of α- and β-Pinenes with Hepta-*O*-benzyl-6′-*O*-methacryloyl-Sucrose

The rate of incorporation of the sugar monomer was studied by variation of the initial sugar/pinenes mol ratio in the presence of AIBN as free radical initiator and without solvent over the range [BMS]/[pin] = 0.05 to 2 (Tables S6 and S7, Supporting Information). The copolymer compositions were determined by ^{1}H NMR by comparison of the peak areas for the methylene and methyl protons in the pinene monomers with those for the 14 sucrose protons.

SEC analysis was not possible for all the product samples, due to their poor solubilities in chloroform. None of the polymers from samples *2–4*, or from powder fractions *5–9* (Table S6) and the powders *3–10* (Table S7), dissolved readily in chloroform, as the resin fractions did. In an attempt to dissolve the maximum amount of solid, the samples were stirred at room temperature for a total of seven days in 5 mL vials, after which the solutions were heated daily at 40 °C for 4 h for another seven days. Even after this treatment the polymers were still not completely dissolved. All the samples were filtered and subjected to size-exclusion chromatography. In the cases of Entries *2*, Table S6 and S4, Table S7, enough material had dissolved for the analysis.

None of the samples from Tables S6 and S7 showed any thermal phenomena during the DSC analyses. The DSC experiments with samples *2*, Table S6, and S4, Table S7, were carried out between –50 °C and 70 °C, at a heating rate of 10 °C min^{-1}, and no transitions were observed. The DSC thermograms of samples *3* and *5* (Table S7), were also measured in the range from 20 °C to 200 °C, at a heating rate of 10 °C min^{-1}, and again nothing was observed. The low solubility of the copolymer samples, the absence of any T_g temperature, and also the high molecular mass values of Entries *2*, Table S6, and S4, Table S7, suggested that they were crosslinked.

The molecular masses of the resin fractions were measured by Size Exclusion Chromatography (SEC) analysis and, as in previous series (Table S5), showed bimodal distributions of low molecular weight oligomer mixtures before the crosslinking occurred. The values of polydispersity obtained for the fractions were all very low, close to 1, indicating that they were highly homogeneous.

The results of experiments (Table S6 and S7) carried out under different conditions show that under microwave irradiation conditions and with lower reaction times the incorporation of the sucrose derivative in the copolymer was higher both for α- and β-pinene – [BMS]/[α-pin] = 0.84 and [BMS]/[β-pin] = 0.56 – when the initial ratio was 0.1.

Analysis of the experimental data showed that with conventional heating the greatest incorporation of sucrose derivative achieved was 0.19, for both α- and β-pinene (Entry *5*, Table S6 and Entry *8*, Table S7) and was achieved by starting from 2.0 and 0.5, respectively.

The relation between the molecular weights and the incorporation of the sugar monomer exhibited a maximum for copolymer *7*, Table S6, with the initial monomer ratio [BMS]/[pin] = 0.5, which also represented the highest monomer conversion (Figure 9).

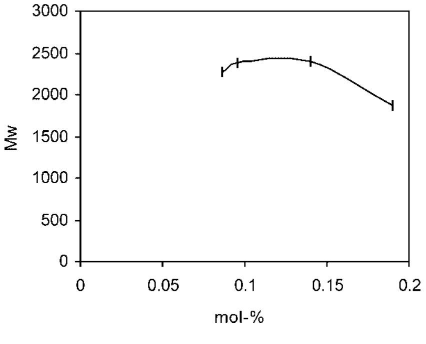

Figure 9. Molecular weights of the copolymers vs. mol percent of incorporation of BMS in poly(BMS-co-α-pinene).

In general, the copolymers with β-pinene showed decreased monomer conversion with higher incorporation of the sugar comonomer (determined by ^{1}H NMR) (Figure 10). This could be explained by the sugar monomer being less reactive in the polymerisation reaction, and also containing more functional groups, providing more possibilities for chain transfer reactions in the reaction mixture. The relationship between the molecular weights and incorporation of the sugar monomer for β-pinene copolymers also showed a maximum, for copolymer *9*, Table S7 with an initial monomer ratio [BMS]/[pin] = 0.1 (Figure 11).

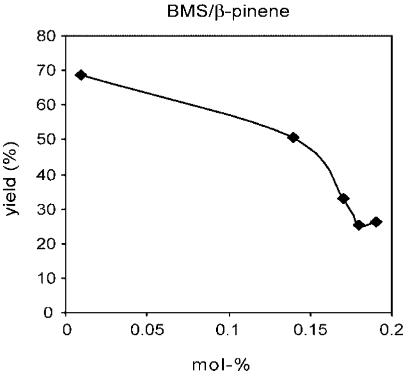

Figure 10. Degree of the monomer conversion vs. mol percent of incorporation of BMS in poly(BMS-co-β-pinene).

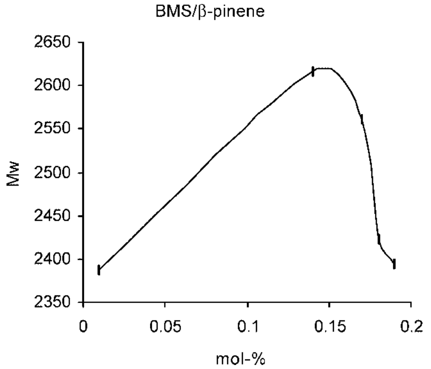

Figure 11. Molecular weights of the copolymers vs. mol percent of incorporation of BMS in poly(BMS-co-β-pinene).

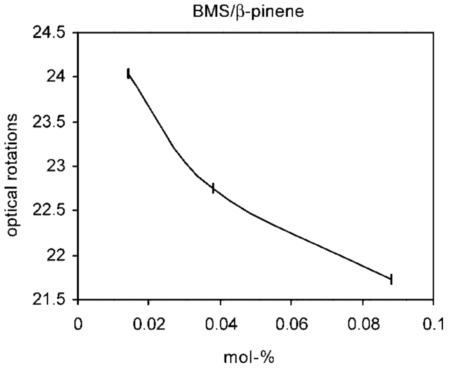

Figure 12. Optical rotations of the copolymers vs. mol percent of incorporation of BMS in poly(BMS-co-β-pinene).

Optical rotations were lower in the copolymers with greater incorporation (determined by ^{1}H NMR) of the sugar monomer for β-pinene copolymers (Figure 12, Table S7), but higher for the samples with greater initial proportions of sugar in α-pinene copolymers (Table S6).

3. Conclusion

In this work the use of α- and β-pinenes as comonomers for the synthesis of polyolefins containing side chain sucrose moieties by free radical-chain copolymerisation has been studied. A new procedure for synthesising poly(β-pinene), poly(α-pinene-co-styrene) and poly(β-pinene-co-styrene) in short reaction times under microwave irradiation conditions was found. Under these new conditions, it was possible to reduce the reaction time from several hours to 10 min for homopolymer formation. MW irradiation proved to be the only method by which to achieve incorporation of β-pinene in the copolymer with styrene, with reaction times in the 5 h range, rather than the 7 d previously reported.[23]

Regioisomerically pure vinyl sugar starting materials, obtained from sucrose by regioselective protection/deprotection sequences, were copolymerised with terpenic monomers. The characterisation of the polymer samples – the average molecular mass, as well as some physical properties of the resulting polymeric materials – permits an assessment of structural, thermal, mechanical and rheological information. Greater incorporation of the sucrose monomer was achieved under MW irradiation conditions for both α- and β-pinene. The resulting copolymers were formed exclusively from easy accessible natural products, and continue our program of research into the synthesis of polymeric materials from renewable starting materials.

4. Experimental Section

Reagents and solvents were purified before use.[45] The sucrose monomer 1′,2,3,3′,4,4′,6-hepta-*O*-benzyl-6′-*O*-methacryloyl-sucrose (BMS) was synthesised as reported.[35] Optical rotations were measured at 20 °C on an AA-1000 polarimeter (0.5-dm cell). NMR spectra were recorded at 400 MHz in $CDCl_3$ and are expressed as chemical shift values (δ) in ppm downfield from TMS. Average molecular weights were determined with a size exclusion chromatography (SEC) apparatus at 30 °C with chloroform as eluent and a series of three columns (10^3 Å, 10^4 Å and 10^5 Å). The calibration was performed with monodisperse polystyrene standards. Glass transition temperatures were measured in the second heating cycle with a rate of 10 °C min^{-1}.

General Procedure for Cationic Homopolymerisation of α- and β-Pinene:[41] A solution of the appropriate monomer in dry toluene (0.1 M) was cooled to 0 °C, $AlCl_3$ (5 wt.-%) was added under positive dry Ar pressure, and the mixture was stirred for an additional 2 h at 50 °C. The catalyst was removed by stirring with HCl (0.1 N, 10 mL/mmol monomer), and the organic phase was washed with NaOH (0.1 N) and H_2O and concentrated under vacuum. The residue was dissolved in toluene and precipitated in cold MeOH, the white solid was filtered and washed several times with cold MeOH, and the powder polymers were purified by repeated dissolution in toluene and reprecipitation in cold MeOH and dried under vacuum.

General Procedure for Radical Copolymerisation in Solution under Conventional Conditions: Copolymerisations of the sucrose derivative BMS with α- and β-pinene were carried out in dry toluene solutions (0.1 M) in the presence of AIBN as radical initiator (1% by weight with respect to the monomer mixture). The solutions were heated at 80 °C in oil bath for the estimated time (see Tables S4, S6, S7) and were then allowed to cool to room temp., and the product was precipitated by dropping it into a 10-fold amount of cold MeOH. The white solid was filtered and washed several times with cold MeOH. When possible (if the product was easily soluble), the powder polymers were purified by repeated dissolution in toluene and reprecipitation in cold MeOH and dried under vacuum. In the cases in which no solid polymer was obtained, the unreacted alkene monomers were distilled off under vacuum to provide a resin-like polymer.

General Procedure for Bulk Radical Copolymerisation under Conventional Conditions: Copolymerisations of the sucrose derivative BMS or styrene with α- and β-pinene were carried out by mixing the monomers with AIBN (1% by weight with respect to the monomer mixture). The mixtures were heated at 80 °C in oil bath for the estimated time (see Tables S2, S3, S5–S7) and were then allowed to cool to room temp., and the product was precipitated by dropping it into a 10-fold amount of cold MeOH. The white solid was filtered and washed several times with cold MeOH. When possible (if the product was easily soluble), the powder polymers were purified by repeated dissolution in toluene and reprecipitation in cold MeOH and dried under vacuum. The resin fractions were isolated by concentrating the filtrates and distilling off the unreacted alkene monomers under vacuum.

General Procedure for Polymerisation and Copolymerisation in a Focused Microwave Oven: (The experiments conducted under microwave irradiation conditions are marked in all the tables – see Supporting Information – with the abbreviation "MW" in the column "Reaction conditions").

The reactions were performed with a MicroSynth Labstation (MileStone, USA)[46] in closed vials. To the monomer mixture dissolved in dry toluene or without solvent was added AIBN (1% by weight with respect to the monomer mixture) under positive pressure of dry Ar. The vials were closed and a fibre optic sensor, connected to the system for automatic temperature control, was inserted in a reference vial. The desired temperature/potency/time protocol was programmed to work either at constant power, with temperature monitoring, or at constant temperature, maintained by controlling the power. After the estimated time (see Tables S1–S3, S6, S7), the vials were allowed to cool to room temp. and the product was precipitated by dropping it into a 10-fold amount of cold MeOH. The white solid was filtered and washed several times with cold MeOH, and the powder polymers were purified by repeated dissolution in toluene and reprecipitation in cold MeOH and dried under vacuum. In the cases in which no solid polymer was obtained, the unreacted alkene monomers were distilled off under vacuum to provide a resin-like polymer.

Supporting Information (see also the footnote on the first page of this article): Experimental conditions and analyses results for the obtained 43 polymer samples, summarised in seven tables with listing for each experiment of the initial mol ratio of the monomers, the presence/absence and type of solvent, type of catalyst, reaction temperature (indicating conventional heating or microwave irradiation), reaction time, obtained monomer ratio in the copolymer and percentage overall conversion, as well as the conversion for each monomer, weight average molecular mass, number average molecular mass, degree of polydispersity, optical rotation and glass transition temperature.

Acknowledgments

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