

ONE-POT GRAFTING OF POLYMERS FROM ALCOHOLS AND BIOMASSES

Field of Invention

The present disclosure generally relates to grafting of polymers, and more particularly relates to one-pot grafting of polymers from alcohols and biomasses.

Background

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Lignin accounts for approximately 30% of wood weight and is the second most abundant renewable polymer on earth after cellulose and its derivatives. Paper pulping industry annually produces 100 billion tons of lignin globally. However, only a small fraction (less than 2%) of the lignin is currently utilized commercially and mostly used in its original form (as unmodified lignin) for, e.g., agricultural, pelleting, and antimicrobial agents.

To offer value-added products, growing attention has been paid to prepare lignin-polymer composites by blending lignin with commercially available synthetic polymers. Lignin affords thermal stability, mechanical strengths, biodegradability, antioxidant properties, and UV-barrier properties to synthetic polymer films, plastics, coatings, and textiles, offering value-added biomass-containing polymer materials. However, physical blending of lignin with synthetic polymers gives only heterogeneous composites with limited properties because lignin is immiscible with most synthetic polymers.

In order to improve the miscibility, chemical grafting of synthetic polymers from lignin is a useful approach. Compared with the original lignin, polymer-grafted lignin can enhance miscibility with synthetic polymers to generate homogeneous composites and can reduce aggregation (macroscopic phase separation) of lignin in the composites to afford high durability in long-term use. As grafting techniques, living radical polymerizations (LRPs) (also known as reversible deactivation radical polymerizations) such as atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain-transfer (RAFT) polymerization are often used. For example, ATRP was used to graft poly(methyl methacrylate) (PMMA). The obtained PMMA-grafted lignin (PMMAg-Lignin) was blended with

pure PMMA to generate PMMA/lignin composites with tuned mechanical properties and was blended with poly(ϵ -caprolactone) (PCL) to generate a nanofibrous composite. RAFT polymerization was used to, e.g., graft poly(*n*-butyl acrylate-co-1-vinylimidazole) for possible skin-adhesive, UV-protective, and self-healable applications and graft poly-(poly(ethylene glycol) methacrylate) for sunscreen applications. The abundant hydroxyl groups present in lignin were used to immobilize initiators of ATRP and RAFT polymerization.

However, the mentioned ATRP and RAFT polymerization approaches require a two-pot procedure including (pot 1) attachment of the initiator (alkyl bromide or sulfur compound) to hydroxyl groups of lignin and subsequent purification and (pot 2) polymerization. The tedious initiator attachment and purification in pot 1 limit industrial applications. Also, ATRP uses heavy metals, and RAFT polymerization uses odorous sulfur species. The high cost of the agents and the removal of toxic and odorous agents from the resultant products limit practical use.

Therefore, there exists a need for new processes for grafting of polymers from alcohols and biomasses.

Summary of Invention

Aspects and embodiments of the invention will now be discussed by reference to the following numbered clauses.

1. A process to form a polymeric material, the process comprising the steps of:
 - (a) providing a substrate having one or more alcohols and converting at least one of the one or more alcohols to an iodide group to provide a modified substrate;
 - (b) mixing the modified substrate with a first monomer and a first catalyst to provide a first mixture, and subjecting the first mixture to reaction conditions that provide a first polymeric or oligomeric material formed from the first monomer, wherein:
 - the modified substrate acts as an initiator for polymerisation and provides a terminal group in at least one part of the first polymeric or oligomeric material; and
 - the reaction conditions comprise an elevated temperature.
2. The process according to Clause 1, wherein step (b) involves adding in a second monomer after a period of time to provide a block copolymer.

3. The process according to Clause 1 or Clause 2, wherein the first catalyst is tetrabutylammonium iodide (TBAI).

4. The process according to any one of the preceding clauses, wherein the modified substrate is obtained by reacting the substrate having one or more alcohols with iodine and polymethylhydrosiloxane.

5. The process according to any one of the preceding clauses, wherein the first monomer is selected from one or more of the group consisting of acrylonitrile, styrene, methoxystyrene, butoxystyrene, chloromethyl styrene, chlorostyrene, methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, t-butyl acrylate, hexyl acrylate, 2-ethyl hexyl acrylate, n-octyl acrylate, nonyl acrylate, decanyl acrylate, benzyl acrylate, tetrahydrofurfuryl acrylate, glycidyl acrylate, cyclohexyl acrylate, 2-methoxyethyl acrylate and butoxyethyl acrylate, tris(trialkylsiloxy) derivative-acrylates, and fluoroalkyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, hexyl methacrylate, 2-ethyl hexyl methacrylate, n-octyl methacrylate, nonyl methacrylate, decanyl methacrylate, benzyl methacrylate, tetrahydrofurfuryl methacrylate, glycidyl methacrylate, cyclohexyl methacrylate, 2-methoxyethyl methacrylate, butoxyethyl methacrylate, tris(trialkylsiloxy) derivative-methacrylates, fluoroalkyl methacrylates, hydroxy styrene, styrene sulfonic acid, sodium styrene sulfonic acid, styrene boronic acid, acrylamide, N-isopropyl acrylamide, N,N-dimethyl acrylamide, N-methylol acrylamide, N-hydroxyethyl acrylamide, methacrylamide, N-isopropyl methacrylamide, N,N-dimethyl methacrylamide, N-methylol methacrylamide, N-hydroxyethyl methacrylamide, acrylic acid, hydroxyalkyl acrylate (e.g. 2-hydroxy ethyl acrylate), 2-hydroxypropyl acrylate, glyceryl monoacrylate, diethylene glycol acrylate, polyethylene glycol acrylate, methoxy tetraethylene glycol acrylate, methoxypolyethylene glycol acrylate, 2-(dimethylamino) ethyl acrylate, 3-chloro-2-hydroxypropyl acrylate, 2-hydroxy-3-phenoxypropyl acrylate, 2-acryloyloxyethyl phosphorylcholine, 2-(N,N-diethyl-N-methyl amino) ethyl acrylate +/trifluorosulfonyliminium salt, 2-(N-ethyl-N-methyl-N-hydrogenation amino) ethyl acrylate +/trifluorosulfonyliminium ($N(CF_3SO_2)^{2-}$) salt, 1-ethyl-3-methyl imidazolium acrylate +/fluorohydrogenation ($(FH)_nF^-$) salt, methacrylic acid, 2-hydroxy ethyl methacrylate, 2-hydroxypropyl methacrylate, glyceryl monomethacrylate, diethylene glycol methacrylate and polyethylene glycol methacrylate, methoxy tetraethylene glycol methacrylate, methoxypolyethylene glycol methacrylate, 2-(dimethylamino) ethyl methacrylate, 3-chloro-2-hydroxypropyl methacrylate, 2-hydroxy-3-phenoxypropyl methacrylate, 2-acryloyloxyethyl phosphorylcholine, 2-(N,N-diethyl-N-methyl amino) ethyl methacrylate +/trifluorosulfonyliminium salt, 2-(N-ethyl-N-methyl-N-

hydrogenation amino) ethyl methacrylate +/trifluorosulfonyliminium ($N(CF_3SO_2)_2^-$) salt, and 1-ethyl-3-methyl imidazorium methacrylate+/ fluorohydrogenation ($(FH)_nF^-$) salt, diethylene glycol dimethacrylate, diethylene glycol diacrylate, vinyl acetate, N-vinyl pyrrolidone, N-vinyl carbazol, butadiene, ethylene, propylene, butene, pentene, hexene, heptane, octene, vinyl ethers, vinyl ketones, vinyl chloride, acetylene, and phenyl acetylene, optionally wherein the first monomer is selected from one or more of the group consisting of methyl methacrylate, benzyl methacrylate, 2-hydroxyethyl methacrylate, 2-methoxyethyl methacrylate, furfuryl methacrylate and poly(ethylene glycol) methyl ether methacrylate.

6. The process according to any one of the preceding clauses, wherein one or both of the following apply:

- (aa) the first monomer comprises a mixture of two or more monomers; and
- (ab) the alcohols in the substrate having one or more alcohols are primary or secondary alcohols.

7. The process according to any one of the preceding clauses, wherein the substrate having one or more alcohols is selected from one or more of the group consisting of 1-phenylethanol, 1-(4-bromophenyl) ethanol, (S)-1-phenylethanol, (+)-1-phenylethanol, 1-(4-methylphenyl)ethanol, 4-methylbenzyl alcohol, 1-phenyl-1-propanol, benzyl alcohol, 2-methylbenzyl alcohol, 3-methylbenzyl alcohol, 1-phenylmethanediol, 1-hydroxy-1-phenylethyl, α -isodecyl-benzenemethanol, α -silylbenzenemethanol, 4-hydroxybenzyl alcohol, 4-ethylbenzyl alcohol, 3-hydroxybenzyl alcohol, 4-mercaptobenzenemethanol, 1,4-benzenedimethanol, 3-ethylbenzenemethanol, α -mercaptobenzenemethanol, α -methyl-p-sec-pentyl-benzyl alcohol, p-sec-decyl- α -methyl-benzyl alcohol, α -methyl-4-sec-nonyl-benzyl alcohol, α -methyl-4-sec-octyl-benzyl alcohol, 4-sec-heptyl- α -methyl-benzyl alcohol, p-sec-hexyl- α -methyl-benzyl alcohol, 2-aminobenzyl alcohol, 3-aminobenzyl alcohol, 4-aminobenzyl alcohol, α -ethynylbenzenemethanol, 2-mercaptobenzenemethanol, 3-mercaptobenzenemethanol, 4-propylbenzenemethanol, (2-ethylphenyl)methanol, [4-(hydroxymethyl)phenyl]lithium, 4-silylbenzenemethanol, ($\pm$)-phenylethanolamine, 1-phenyl-2-propen-1-ol, 2-methyl-1-phenyl-1-propanol, 1-phenyl-1-butanol, 4-ethynylbenzenemethanol, 3,5-dimethylbenzyl alcohol, 1-phenyl-1,2-propanediol, α -phosphinobenzenemethanol, 1-phenylethanol, α -(mercaptomethyl)benzenemethanol, α -iodobenzenemethanol, 4-(mercaptomethyl)benzenemethanol, 4-(hydroxymethyl)benzeneethanol, 2-selenobenzenemethanol, 4-methoxybenzyl alcohol, mandelonitrile, 4-iodobenzyl alcohol, 4-vinylbenzyl alcohol, 2-phenyl-2-butanol, 4-(hydroxymethyl)benzonitrile, α -methylbenzenemethan-d-ol, 3-(aminomethyl)benzenemethanol, α -bromobenzenemethanol,

benzonitrile, α -(borylmethyl)benzenemethanol, 4-isononylbenzenemethanol, α -(methyl-d3)benzenemethanol, α -methylbenzene-2,3,4,5,6-d5-methanol, 4-chlorobenzyl alcohol, 4-bromobenzyl alcohol, 4-fluoro- α -methylbenzyl alcohol, 1-(p-tolyl)ethanol, 4-fluorobenzyl alcohol, 4-(methylthio)benzenemethanol, α -ethyl- α -methylbenzenemethanol, (1S,2R)-(+)-norephedrine, α -hydroxybenzeneacetaldehyde, 5-methyl-1,3-benzenedimethanol, 4-methoxy- α -methylbenzyl alcohol, 2-phenyl-2-propanol, α -methyl-2-naphthalenemethanol, 4-bromo- α -methylbenzyl alcohol, 1-(2,4-dimethoxyphenyl)ethanol, 1-(4-chlorophenyl)ethanol, (1RS)-1-(6-methoxynaphthalen-2-yl)ethanol, (1S,2S)-(+)-pseudoephedrine, 1-(2,4,6-trimethoxyphenyl)ethanol, lignin, methanol, ethanol, 1-butanol, isopropyl alcohol, tert-butanol, 1,3-butanediol, 2-butanol, propanediol, 4,4,4-trifluoro-1-butanol, 2-amino-1-butanol, 4-phenyl-2-butanol, 3-methyl-2-butanol, 4-chloro-1-butanol, 4-bromo-1-butanol, 2-methyl-2-butanol, 3-methoxy-1-butanol, 4-phenyl-1-butanol, 1-amino-2-butanol, 3-(methylamino)-1-butanol, 3-(dimethylamino)-1-butanol, 4-(methylthio)-1-butanol, 1-bromo-2-butanol, 2-(methyldiphenylsilyl)ethanol, 2-(isopropylamino)ethanol, 2-(methylthio)ethanol, 2-(methylphenylamino)ethanol, 2-(isobutylsulfanyl)ethanol, 2-(phenylsulfonyl)ethanol, 2-(trifluoromethoxy)ethanol, lactic acid, ethyl lactate, 2-(trimethylsilyl)ethanol, 1-(4-methylcyclohexyl)ethanol, 2-(2-quinoliny)ethanol, 2-[2-(diethylamino)ethoxy]ethanol, furfuryl alcohol, ($\pm$)-1-(2-furyl)ethanol, tetrahydrofurfuryl alcohol, tetrahydropyran-2-methanol, 1,2,6-hexanetriol, isosorbide, isoidide, isomannide, glycerol, sorbitol, farnesol, cetyl alcohol, stearyl alcohol, octanol, decanol, cetearyl alcohol, behenyl alcohol, arabinol, maltitol, xylaric acid, mannosylerythritol, arabitol, ribitol, isoborneol, myristyl alcohol, lauryl alcohol, oleyl alcohol, 1,1-bis(triphenylsilyl)ethanol, glucose, maltose, xylitol, erythritol, mannitol, ethylene glycol, propylene glycol, trimethylolpropane, pentaerythritol, cellulose, lignocellulose, 2-hydroxyethyl cellulose, ethyl cellulose, hydroxypropyl cellulose, (hydroxypropyl)methyl cellulose, cellulose triacetate, methyl cellulose, cellulose acetate, cyanoethylated cellulose, cellulose acetate butyrate, cellulose acetate propionate, sodium carboxymethyl cellulose, and hydroxyethyl-cellulose, optionally wherein the substrate is lignin or cellulose.

8. The process according to any one of the preceding clauses, wherein the substrate having one or more primary or secondary alcohols is a benzylic alcohol, optionally wherein the benzylic alcohol is selected from one or more of the group consisting of 1-phenylethanol, 1-(4-bromophenyl) ethanol, (S)-1-phenylethanol, (+)-1-phenylethanol, 1-(4-methylphenyl)ethanol, 4-methylbenzyl alcohol, 1-phenyl-1-propanol, benzyl alcohol, 2-methylbenzyl alcohol, 3-methylbenzyl alcohol, 1-phenylmethanediol, 1-hydroxy-1-phenylethyl, α -isodecyl-benzenemethanol, α -silylbenzenemethanol, 4-hydroxybenzyl alcohol, 4-ethylbenzyl alcohol, 3-hydroxybenzyl alcohol, 4-mercaptobenzenemethanol, 1,4-

benzenedimethanol, 3-ethylbenzenemethanol, α -mercaptobenzenemethanol, α -methyl-p-sec-pentyl-benzyl alcohol, p-sec-decyl- α -methyl-benzyl alcohol, α -methyl-4-sec-nonyl-benzyl alcohol, α -methyl-4-sec-octyl-benzyl alcohol, 4-sec-heptyl- α -methyl-benzyl alcohol, p-sec-hexyl- α -methyl-benzyl alcohol, 2-aminobenzyl alcohol, 3-aminobenzyl alcohol, 4-aminobenzyl alcohol, α -ethynylbenzenemethanol, 2-mercaptobenzenemethanol, 3-mercaptobenzenemethanol, 4-propylbenzenemethanol, (2-ethylphenyl)methanol, [4-(hydroxymethyl)phenyl]lithium, 4-silylbenzenemethanol, ($\pm$)-phenylethanolamine, 1-phenyl-2-propen-1-ol, 2-methyl-1-phenyl-1-propanol, 1-phenyl-1-butanol, 4-ethynylbenzenemethanol, 3,5-dimethylbenzyl alcohol, 1-phenyl-1,2-propanediol, α -phosphinobenzenemethanol, 1-phenylethenol, α -(mercaptomethyl)benzenemethanol, α -iodobenzenemethanol, 4-(mercaptomethyl)benzenemethanol, 4-(hydroxymethyl)benzeneethanol, 2-selenobenzenemethanol, 4-methoxybenzyl alcohol, mandelonitrile, 4-iodobenzyl alcohol, 4-vinylbenzyl alcohol, 2-phenyl-2-butanol, 4-(hydroxymethyl)benzonitrile, α -methylbenzenemethanol-d-ol, 3-(aminomethyl)benzenemethanol, α -bromobenzenemethanol, benzonitrile, α -(borylmethyl)benzenemethanol, 4-isononylbenzenemethanol, α -(methyl-d3)benzenemethanol, α -methylbenzene-2,3,4,5,6-d5-methanol, 4-chlorobenzyl alcohol, 4-bromobenzyl alcohol, 4-fluoro- α -methylbenzyl alcohol, 1-(p-tolyl)ethanol, 4-fluorobenzyl alcohol, 4-(methylthio)benzenemethanol, α -ethyl- α -methylbenzenemethanol, (1S,2R)-(+)-norephedrine, α -hydroxybenzeneacetaldehyde, 5-methyl-1,3-benzenedimethanol, 4-methoxy- α -methylbenzyl alcohol, 2-phenyl-2-propanol, α -methyl-2-naphthalenemethanol, 4-bromo- α -methylbenzyl alcohol, 1-(2,4-dimethoxyphenyl)ethanol, 1-(4-chlorophenyl)ethanol, (1RS)-1-(6-methoxynaphthalen-2-yl)ethanol, (1S,2S)-(+)-pseudoephedrine, 1-(2,4,6-trimethoxyphenyl)ethanol, and lignin, further optionally wherein the benzylic alcohol is lignin.

9. The process according to any one of the preceding clauses, wherein the molar concentration ratio of the modified substrate to the first monomer in step (b) of Clause 1 is from 1:5 to 1:2,000, such as from 1:6 to 1:1,600, such as from 1:9 to 1:300, such as from 1:10 to 1:100.

10. The process according to any one of the preceding clauses, wherein the molar concentration ratio of the modified substrate to the first catalyst in step (b) of Clause 1 is from 1:0.1 to 1:10, such as from 1:0.3 to 1:1.

11. The process according to any one of the preceding clauses, wherein the first mixture further comprises a radical initiator, optionally wherein the radical initiator is azobisisobutyronitrile.

12. The process according to any one of the preceding clauses, comprising the further step of:

- (c) terminating the polymerisation reaction of step (b) in Clause 1 to provide the first polymeric or oligomeric material as a macroinitiator; and
- (d) mixing the macroinitiator with a third monomer to provide a second mixture, and subjecting the second mixture to reaction conditions that provide a second polymeric material formed from the third monomer and the macroinitiator.

13. The process according to Clause 12, wherein terminating the polymerisation reaction in step (c) involves cooling the first mixture to a temperature of from 0 to 50 °C, such as around 25 °C.

14. The process according to Clause 12 or Clause 13, wherein the third monomer is selected from one of more of the group consisting of acrylonitrile, styrene, methoxystyrene, butoxystyrene, chloromethyl styrene, chlorostyrene, methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, t-butyl acrylate, hexyl acrylate, 2-ethyl hexyl acrylate, n-octyl acrylate, nonyl acrylate, decanyl acrylate, benzyl acrylate, tetrahydrofurfuryl acrylate, glycidyl acrylate, cyclohexyl acrylate, 2-methoxyethyl acrylate and butoxyethyl acrylate, tris(trialkylsiloxy) derivative-acrylates, and fluoroalkyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, hexyl methacrylate, 2-ethyl hexyl methacrylate, n-octyl methacrylate, nonyl methacrylate, decanyl methacrylate, benzyl methacrylate, tetrahydrofurfuryl methacrylate, glycidyl methacrylate, cyclohexyl methacrylate, 2-methoxyethyl methacrylate, butoxyethyl methacrylate, tris(trialkylsiloxy) derivative-methacrylates, fluoroalkyl methacrylates, hydroxy styrene, styrene sulfonic acid, sodium styrene sulfonic acid, styrene boronic acid, acrylamide, N-isopropyl acrylamide, N,N-dimethyl acrylamide, N-methylol acrylamide, N-hydroxyethyl acrylamide, methacrylamide, N-isopropyl methacrylamide, N,N-dimethyl methacrylamide, N-methylol methacrylamide, N-hydroxyethyl methacrylamide, acrylic acid, hydroxyalkyl acrylate (e.g. 2-hydroxy ethyl acrylate), 2-hydroxypropyl acrylate, glyceryl monoacrylate, diethylene glycol acrylate, polyethylene glycol acrylate, methoxy tetraethylene glycol acrylate, methoxypolyethylene glycol acrylate, 2-(dimethylamino) ethyl acrylate, 3-chloro-2-hydroxypropyl acrylate, 2-hydroxy-3-phenoxypropyl acrylate, 2-acryloyloxyethyl phosphorylcholine, 2-(N,N-diethyl-N-methyl amino) ethyl acrylate +/trifluorosulfonyliminium salt, 2-(N-ethyl-N-methyl-N-hydrogenation amino) ethyl acrylate +/trifluorosulfonyliminium $(N(CF_3SO_2)^{2-})$ salt, 1-ethyl-3-methyl imidazolium acrylate +/fluorohydrogenation $((FH)_nF^-)$ salt,

methacrylic acid, 2-hydroxy ethyl methacrylate, 2-hydroxypropyl methacrylate, glyceryl monomethacrylate, diethylene glycol methacrylate and polyethylene glycol methacrylate, methoxy tetraethylene glycol methacrylate, methoxypolyethylene glycol methacrylate, 2-(dimethylamino) ethyl methacrylate, 3-chloro-2-hydroxypropyl methacrylate, 2-hydroxy-3-phenoxypropyl methacrylate, 2-acryloyloxyethyl phosphorylcholine, 2-(N,N-diethyl-N-methyl amino) ethyl methacrylate +/-trifluorosulfonyliminium salt, 2-(N-ethyl-N-methyl-N-hydrogenation amino) ethyl methacrylate +/-trifluorosulfonyliminium ($(\text{N}(\text{CF}_3\text{SO}_2)_2)^+$) salt, and 1-ethyl-3-methyl imidazorium methacrylate+/- fluorohydrogenation ($(\text{FH})_n\text{F}^-$) salt, diethylene glycol dimethacrylate, diethylene glycol diacrylate, vinyl acetate, N-vinyl pyrrolidone, N-vinyl carbazol, butadiene, ethylene, propylene, butene, pentene, hexene, heptane, octene, vinyl ethers, vinyl ketones, vinyl chloride, acetylene, and phenyl acetylene, optionally wherein the third monomer is selected from one or more of the group consisting of methyl methacrylate, benzyl methacrylate, 2-hydroxyethyl methacrylate, 2-methoxyethyl methacrylate, furfuryl methacrylate and poly(ethylene glycol) methyl ether methacrylate, further optionally wherein the third monomer is different from the first monomer.

15. The process according to any one of Clauses 12 to 14, wherein the molar concentration ratio of the macroinitiator to the third monomer in step (d) of Clause 12 is from 1:5 to 1:2,000, such as from 1:6 to 1:1,600, such as from 1:9 to 1: 300, such as from 1:10 to 1:100.

16. The process according to any one of Clauses 12 to 15, wherein the molar concentration ratio of the macroinitiator to a total amount of catalyst in step (d) of Clause 12 is from 1:0.1 to 1:10, such as from 1:0.3 to 1:1, wherein the total amount of catalyst refers to the first catalyst alone or, where present, a combination of the first catalyst and a second catalyst.

17. The process according to Clause 16, wherein where present, the second catalyst is tetrabutylammonium iodide (TBAI).

18. A process to form an iodide material, the process comprising the steps of:

- (ai) providing a substrate having one or more aliphatic alcohols; and
- (aii) converting at least one of the one or more alcohols to an iodide group to provide a modified substrate.

19. The process according to Clause 18, wherein the modified substrate is obtained by reacting the substrate having one or more alcohols with iodine and polymethylhydrosiloxane.

20. The process according to Clause 18 or Clause 19, wherein the substrate having one or more aliphatic alcohols is selected from one or more of the group consisting of methanol, ethanol, 1-butanol, isopropyl alcohol, tert-butanol, 1,3-butanediol, 2-butanol, propanediol, 4,4,4-trifluoro-1-butanol, 2-amino-1-butanol, 4-phenyl-2-butanol, 3-methyl-2-butanol, 4-chloro-1-butanol, 4-bromo-1-butanol, 2-methyl-2-butanol, 3-methoxy-1-butanol, 4-phenyl-1-butanol, 1-amino-2-butanol, 3-(methylamino)-1-butanol, 3-(dimethylamino)-1-butanol, 4-(methylthio)-1-butanol, 1-bromo-2-butanol, 2-(methyldiphenylsilyl)ethanol, 2-(isopropylamino)ethanol, 2-(methylthio)ethanol, 2-(methylphenylamino)ethanol, 2-(isobutylsulfanyl)ethanol, 2-(phenylsulfonyl)ethanol, 2-(trifluoromethoxy)ethanol, lactic acid, ethyl lactate, 2-(trimethylsilyl)ethanol, 1-(4-methylcyclohexyl)ethanol, 2-(2-quinoliny)ethanol, 2-[2-(diethylamino)ethoxy]ethanol, furfuryl alcohol, ($\pm$)-1-(2-furyl)ethanol, tetrahydrofurfuryl alcohol, tetrahydropyran-2-methanol, 1,2,6-hexanetriol, isosorbide, isoidide, isomannide, glycerol, sorbitol, farnesol, cetyl alcohol, stearyl alcohol, octanol, decanol, cetearyl alcohol, behenyl alcohol, arabinol, maltitol, xylaric acid, mannosylerythritol, arabitol, ribitol, isoborneol, myristyl alcohol, lauryl alcohol, oleyl alcohol, 1,1-bis(triphenylsilyl)ethanol, glucose, maltose, xylitol, erythritol, mannitol, ethylene glycol, propylene glycol, trimethylolpropane, pentaerythritol, cellulose, lignocellulose, 2-hydroxyethyl cellulose, ethyl cellulose, hydroxypropyl cellulose, (hydroxypropyl)methyl cellulose, cellulose triacetate, methyl cellulose, cellulose acetate, cyanoethylated cellulose, cellulose acetate butyrate, cellulose acetate propionate, sodium carboxymethyl cellulose, and hydroxyethyl-cellulose, optionally wherein the substrate is cellulose.

Drawings

Fig. 1 depicts illustration of one-pot reversible complexation mediated polymerization (RCMP) and structures of polymethylhydrosiloxane (PMHS) and studied monomers.

Fig. 2 depicts photos of the reaction mixture and ^1H NMR spectra (a) before and (b) after iodination of PhE-OH (1 M, 1 equiv.) using I_2 (1 equiv.) and PMHS (5 equiv. of the Si-H unit) in diglyme at 70 °C for 100 min (Table 1, entry 6).

Fig. 3 depicts ^1H NMR spectrum of PMMA (initiated from PhE-OH) (Table 2, entry 1) (400 MHz, 298 K, CDCl_3).

Fig. 4 depicts NMR spectrum of PMMA (initiated from BrPhE–OH) (Table 2, entry 2) (400 MHz, 298 K, CDCl₃).

Fig. 5 depicts ¹H NMR spectrum of PBzMA (initiated from BrPhE–OH) (Table 2, entry 4) (400 MHz, 298 K, CDCl₃).

Fig. 6 depicts ¹H NMR spectrum of PBMA (initiated from BrPhE–OH) (Table 2, entry 5) (400 MHz, 298 K, CDCl₃).

Fig. 7 depicts ¹H NMR spectrum of PHEMA (initiated from BrPhE–OH) (Table 2, entry 6) (400 MHz, 298 K, DMSO-d₆).

Fig. 8 depicts ¹H NMR spectrum of PMEMA (initiated from BrPhE–OH) (Table 2, entry 7) (400 MHz, 298 K, CDCl₃).

Fig. 9 depicts ¹H NMR spectrum of PFMA (initiated from BrPhE–OH) (Table 2, entry 8) (400 MHz, 298 K, CDCl₃).

Fig. 10 depicts ¹H NMR spectrum of PPEGMA (initiated from BrPhE–OH) (Table 2, entry 9) (400 MHz, 298 K, CDCl₃).

Fig. 11 depicts ¹H NMR spectrum of PBA (initiated from BrPhE–OH) (Table 2, entry 10) (400 MHz, 298 K, CDCl₃).

Fig. 12 depicts ¹H NMR spectrum of PMEAA (initiated from BrPhE–OH) (Table 2, entry 11) (400 MHz, 298 K, CDCl₃).

Fig. 13 depicts ¹H NMR spectrum of PBzA (initiated from BrPhE–OH) (Table 2, entry 12) (400 MHz, 298 K, CDCl₃).

Fig. 14 depicts plots of (a) $\ln([M]_0/[M])$ vs time (t) and (b) M_n and M_w/M_n vs monomer conversion for the MMA/R–OH/BNI (100/1/2) systems at 80 °C (Table 2, entries 1 and 2), where $[M]$ is the concentration of monomer (MMA). The symbols are indicated in the figure.

Fig. 15 depicts GPC chromatograms (with THF eluent) of purified block copolymers (solid lines) obtained from macroinitiators (dashed lines) that were synthesized via one-pot RCMP. The reaction conditions are given in Table 4, entries 1–3, 5, and 6. The GPC chromatograms with DMF eluent for Table 4, entry 4 is provided in Figs. 19 and 20.

Fig. 16 depicts ^1H NMR spectrum of PMMA-*r*-PBzMA (400 MHz, 298 K, CDCl_3).

Fig. 17 depicts ^1H NMR spectrum of PMMA-*r*-PHEMA (400 MHz, 298 K, CDCl_3).

Fig. 18 depicts ^1H NMR spectrum of PBA-*r*-PMEA (400 MHz, 298 K, CDCl_3).

Fig. 19 depicts DMF-GPC chromatogram of PBzMA-*b*-PHEMA (Table 4, entry 4).

Fig. 20 depicts THF-GPC chromatogram of PBzMA-*I* macroinitiator (Table 4, entry 4).

Fig. 21 depicts one-pot RCMP of MMA from aliphatic primary alcohol and phenolic alcohol (Table 7).

Fig. 22 depicts FT-IR spectra of pure PMMA, pure lignin, and PMMA-*g*-Lignin (95/5) (Table 6, entry 1 for 72 h).

Fig. 23 depicts (a) differential scanning calorimetry (DSC) curves of PMMA-*g*-Lignin (95/5), PBzMA-*g*-Lignin (98/2), and PBzA-*g*-Lignin (98/2) (Table 6, entries 1, 5, and 6) and neat PMMA, PBzMA, and PBzA (Table 2, entries 2, 4, and 12). (b) Digital photographs and (c) UV/Vis transmittance curves for PMMA, PMMA/PMMA-*g*-Lignin (95/5) composite, and PMMA/Lignin blend films. The PMMA/PMMA-*g*-Lignin (95/5) composite film contained 94 wt % of PMMA and 6 wt % of PMMA-*g*-Lignin (95/5), which corresponds to 99.7 wt % of PMMA and 0.3 wt % of lignin as a whole. The PMMA/Lignin blend film contained 99.7 wt % of PMMA and 0.3 wt % of lignin. (d) Illustration of distribution of lignin in PMMA/PMMA-*g*-Lignin (95/5) composite film (grafting) and PMMA/Lignin blend film (mere blending).

Fig. 24 depicts thermal gravimetric analysis (TGA) curves of polymer-grafted lignin and the corresponding neat polymers: PMMA-*g*-Lignin (95/5) (Table 6, entry 1), PBzMA-*g*-Lignin (98/2) (Table 6, entry 5), PBzA-*g*-Lignin (98/2) (Table 6, entry 6), neat PMMA (Table 2, entry 2), neat PBzMA (Table 2, entry 4), neat PBzA (Table 2, entry 12), and neat lignin.

Fig. 25 depicts illustration of one-pot grafting of polymer from lignin.

Fig. 26 depicts ^1H NMR spectrum of PMMA-b-PBzMA (initiated from BrPhE-OH) (Table 4, entry 1) (400 MHz, 298 K, CDCl_3).

Fig. 27 depicts ^1H NMR spectrum of PBzMA-b-PMMA (initiated from BrPhE-OH) (Table 4, entry 2) (400 MHz, 298 K, CDCl_3).

Fig. 28 depicts of PBzMA-b-PMEMA (initiated from BrPhE-OH) (Table 4, entry 3) (400 MHz, 298 K, CDCl_3).

Fig. 29 depicts of PBzMA-b-PHEMA (initiated from BrPhE-OH) (Table 4, entry 4) (400 MHz, 298 K, $\text{DMSO}-d_6$).

Fig. 30 depicts ^1H NMR spectrum of PBzMA-b-PPEGMA (initiated from BrPhE-OH) (Table 4, entry 5) (400 MHz, 298 K, CDCl_3).

Fig. 31 depicts ^1H NMR spectrum of PMEMA-b-PMMA (initiated from BrPhE-OH) (Table 4, entry 6) (400 MHz, 298 K, CDCl_3).

Description

It has been surprisingly found that polymers may be derived from one-pot reversible complexation mediated polymerization (RCMP) of alcohols. As will be appreciated, the one-pot RCMP disclosed herein may be amenable to several hydrophobic, functional, and amphiphilic methacrylates and acrylates, demonstrating a wide monomer scope of this technique. RCMP is free from heavy metals and odour and utilizes only inexpensive compounds so it provides cost-saving. Further, the one-pot RCMP disclosed herein may serve as a practically useful technique to obtain value-added biomass-polymer composites.

Thus, in a first aspect of the invention, there is provided a process to form a polymeric material, the process comprising the steps of:

- (a) providing a substrate having one or more alcohols and converting at least one of the one or more alcohols to an iodide group to provide a modified substrate;

(b) mixing the modified substrate with a first monomer and a first catalyst to provide a first mixture, and subjecting the first mixture to reaction conditions that provide a first polymeric or oligomeric material formed from the first monomer, wherein:

the modified substrate acts as an initiator for polymerisation and provides a terminal group in at least one part of the first polymeric or oligomeric material; and
the reaction conditions comprise an elevated temperature.

In embodiments herein, the word “comprising” may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word “comprising” may also relate to the situation where only the components/features listed are intended to be present (e.g. the word “comprising” may be replaced by the phrases “consists of” or “consists essentially of”). It is explicitly contemplated that both the broader and narrower interpretations can be applied to all aspects and embodiments of the present invention. In other words, the word “comprising” and synonyms thereof may be replaced by the phrase “consisting of” or the phrase “consists essentially of” or synonyms thereof and *vice versa*.

The phrase, “consists essentially of” and its pseudonyms may be interpreted herein to refer to a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than 97% pure, such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

The phrase, “consists essentially of” and its pseudonyms may be interpreted herein to refer to a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than 97% pure, such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

As used herein, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a composition” includes mixtures of two or more such compositions, reference to “an oxygen carrier” includes mixtures of two or more such oxygen carriers, reference to “the catalyst” includes mixtures of two or more such catalysts, and the like.

The term substrate relates to an organic material (in the chemical sense) that has one or more alcohols as part of its structure. Each of the one or more alcohols may be a primary alcohol,

a secondary alcohol or a tertiary alcohol. While all three types of alcohols may work, without wishing to be bound by theory, it is believed that primary and secondary alcohols may be generally more suitable. As such, in certain embodiments of the invention, the one or more alcohols may comprise primary and secondary alcohols, and it may be these alcohols that react to provide an iodide group. It will be noted that a substrate may have primary, secondary and tertiary alcohols or any combination thereof.

The process described above may be one in which (b) may involve adding in a second monomer after a period of time to provide a block copolymer.

Any suitable catalyst may be used as the first catalyst, provided that it can catalyse a polymerisation reaction between an iodide material as formed in step (a) and a first monomer. In embodiments of the invention that may be mentioned herein, the first catalyst may be tetrabutylammonium iodide (TBAI).

Any suitable method may be used to form the modified substrate, provided that an iodide is produced by displacement of an alcohol group. However, in embodiments of the invention, the modified substrate may be obtained by reacting the substrate having one or more alcohols with iodine and polymethylhydrosiloxane. It is noted that the use of this method, which is detailed in more detail in the experimental section hereinbelow, may be particularly suited for a one-pot reaction.

The first monomer may be any suitable that can react with the modified substrate. The term "monomer" when used herein refers to the ability of a material to undergo polymerisation. This may mean a simple organic chemical (e.g. styrene) or it may be a more complex material, such as polyethylene glycol monomethacrylate, which contains a methacrylate group which can be subjected to polymerisation, while having a polyethylene glycol side chain. Suitable first monomers include, but are not limited to, acrylonitrile, styrene, methoxystyrene, butoxystyrene, chloromethyl styrene, chlorostyrene, methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, t-butyl acrylate, hexyl acrylate, 2-ethyl hexyl acrylate, n-octyl acrylate, nonyl acrylate, decanyl acrylate, benzyl acrylate, tetrahydrofurfuryl acrylate, glycidyl acrylate, cyclohexyl acrylate, 2-methoxyethyl acrylate and butoxyethyl acrylate, tris(trialkylsiloxy) derivative-acrylates, and fluoroalkyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, hexyl methacrylate, 2-ethyl hexyl methacrylate, n-octyl methacrylate, nonyl methacrylate, decanyl methacrylate, benzyl methacrylate, tetrahydrofurfuryl methacrylate, glycidyl methacrylate,

cyclohexyl methacrylate, 2-methoxyethyl methacrylate, butoxyethyl methacrylate, tris(trialkylsiloxy) derivative-methacrylates, fluoroalkyl methacrylates, hydroxy styrene, styrene sulfonic acid, sodium styrene sulfonic acid, styrene boronic acid, acrylamide, N-isopropyl acrylamide, N,N-dimethyl acrylamide, N-methylol acrylamide, N-hydroxyethyl acrylamide, methacrylamide, N-isopropyl methacrylamide, N,N-dimethyl methacrylamide, N-methylol methacrylamide, N-hydroxyethyl methacrylamide, acrylic acid, hydroxyalkyl acrylate (e.g. 2-hydroxy ethyl acrylate), 2-hydroxypropyl acrylate, glyceryl monoacrylate, diethylene glycol acrylate, polyethylene glycol acrylate, methoxy tetraethylene glycol acrylate, methoxypolyethylene glycol acrylate, 2-(dimethylamino) ethyl acrylate, 3-chloro-2-hydroxypropyl acrylate, 2-hydroxy-3-phenoxypropyl acrylate, 2-acryloyloxyethyl phosphorylcholine, 2-(N,N-diethyl-N-methyl amino) ethyl acrylate +/-trifluorosulfonyliminium salt, 2-(N-ethyl-N-methyl-N-hydrogenation amino) ethyl acrylate +/-trifluorosulfonyliminium ($N(CF_3SO_2)_2^-$) salt, 1-ethyl-3-methyl imidazolium acrylate +/-fluorohydrogenation ($(FH)_nF^-$) salt, methacrylic acid, 2-hydroxy ethyl methacrylate, 2-hydroxypropyl methacrylate, glyceryl monomethacrylate, diethylene glycol methacrylate and polyethylene glycol methacrylate, methoxy tetraethylene glycol methacrylate, methoxypolyethylene glycol methacrylate, 2-(dimethylamino) ethyl methacrylate, 3-chloro-2-hydroxypropyl methacrylate, 2-hydroxy-3-phenoxypropyl methacrylate, 2-acryloyloxyethyl phosphorylcholine, 2-(N,N-diethyl-N-methyl amino) ethyl methacrylate +/-trifluorosulfonyliminium salt, 2-(N-ethyl-N-methyl-N-hydrogenation amino) ethyl methacrylate +/-trifluorosulfonyliminium ($N(CF_3SO_2)_2^-$) salt, and 1-ethyl-3-methyl imidazolium methacrylate+/- fluorohydrogenation ($(FH)_nF^-$) salt, diethylene glycol dimethacrylate, diethylene glycol diacrylate, vinyl acetate, N-vinyl pyrrolidone, N-vinyl carbazol, butadiene, ethylene, propylene, butene, pentene, hexene, heptane, octene, vinyl ethers, vinyl ketones, vinyl chloride, acetylene, and phenyl acetylene, optionally wherein the first monomer is selected from one or more of the group consisting of methyl methacrylate, benzyl methacrylate, 2-hydroxyethyl methacrylate, 2-methoxyethyl methacrylate, furfuryl methacrylate, poly(ethylene glycol) methyl ether methacrylate, and combinations thereof.

As noted above, the first monomer may itself be a mixture of two or more monomers (e.g. selected from the above list) and therefore the process described herein may be used to make a random copolymer. As will be appreciated, a random copolymer will be provided if the two or more monomers have similar reaction kinetics. However, if the reaction kinetics of the monomers are different, then it may be possible to generate block copolymers using the process even if one simply supplies all monomers at the same time.

As noted above, any suitable substrate having one or more alcohols may be used herein. For example, the substrate having one or more alcohols may be selected from, but not limited to, 1-phenylethanol, 1-(4-bromophenyl) ethanol, (S)-1-phenylethanol, (+)-1-phenylethanol, 1-(4-methylphenyl)ethanol, 4-methylbenzyl alcohol, 1-phenyl-1-propanol, benzyl alcohol, 2-methylbenzyl alcohol, 3-methylbenzyl alcohol, 1-phenylmethanediol, 1-hydroxy-1-phenylethyl, α -isodecyl-benzenemethanol, α -silylbenzenemethanol, 4-hydroxybenzyl alcohol, 4-ethylbenzyl alcohol, 3-hydroxybenzyl alcohol, 4-mercaptobenzenemethanol, 1,4-benzenedimethanol, 3-ethylbenzenemethanol, α -mercaptobenzenemethanol, α -methyl-p-sec-pentyl-benzyl alcohol, p-sec-decyl- α -methyl-benzyl alcohol, α -methyl-4-sec-nonyl-benzyl alcohol, α -methyl-4-sec-octyl-benzyl alcohol, 4-sec-heptyl- α -methyl-benzyl alcohol, p-sec-hexyl- α -methyl-benzyl alcohol, 2-aminobenzyl alcohol, 3-aminobenzyl alcohol, 4-aminobenzyl alcohol, α -ethynylbenzenemethanol, 2-mercaptobenzenemethanol, 3-mercaptobenzenemethanol, 4-propylbenzenemethanol, (2-ethylphenyl)methanol, [4-(hydroxymethyl)phenyl]lithium, 4-silylbenzenemethanol, ($\pm$)-phenylethanolamine, 1-phenyl-2-propen-1-ol, 2-methyl-1-phenyl-1-propanol, 1-phenyl-1-butanol, 4-ethynylbenzenemethanol, 3,5-dimethylbenzyl alcohol, 1-phenyl-1,2-propanediol, α -phosphinobenzenemethanol, 1-phenylethanol, α -(mercaptomethyl)benzenemethanol, α -iodobenzenemethanol, 4-(mercaptomethyl)benzenemethanol, 4-(hydroxymethyl)benzeneethanol, 2-selenobenzenemethanol, 4-methoxybenzyl alcohol, mandelonitrile, 4-iodobenzyl alcohol, 4-vinylbenzyl alcohol, 2-phenyl-2-butanol, 4-(hydroxymethyl)benzonitrile, α -methylbenzenemethanol-d-ol, 3-(aminomethyl)benzenemethanol, α -bromobenzenemethanol, benzonitrile, α -(borylmethyl)benzenemethanol, 4-isononylbenzenemethanol, α -(methyl-d3)benzenemethanol, α -methylbenzene-2,3,4,5,6-d5-methanol, 4-chlorobenzyl alcohol, 4-bromobenzyl alcohol, 4-fluoro- α -methylbenzyl alcohol, 1-(p-tolyl)ethanol, 4-fluorobenzyl alcohol, 4-(methylthio)benzenemethanol, α -ethyl- α -methylbenzenemethanol, (1S,2R)-(+)-norephedrine, α -hydroxybenzeneacetaldehyde, 5-methyl-1,3-benzenedimethanol, 4-methoxy- α -methylbenzyl alcohol, 2-phenyl-2-propanol, α -methyl-2-naphthalenemethanol, 4-bromo- α -methylbenzyl alcohol, 1-(2,4-dimethoxyphenyl)ethanol, 1-(4-chlorophenyl)ethanol, (1RS)-1-(6-methoxynaphthalen-2-yl)ethanol, (1S,2S)-(+)-pseudoephedrine, 1-(2,4,6-trimethoxyphenyl)ethanol, lignin, methanol, ethanol, 1-butanol, isopropyl alcohol, tert-butanol, 1,3-butanediol, 2-butanol, propanediol, 4,4,4-trifluoro-1-butanol, 2-amino-1-butanol, 4-phenyl-2-butanol, 3-methyl-2-butanol, 4-chloro-1-butanol, 4-bromo-1-butanol, 2-methyl-2-butanol, 3-methoxy-1-butanol, 4-phenyl-1-butanol, 1-amino-2-butanol, 3-(methylamino)-1-butanol, 3-(dimethylamino)-1-butanol, 4-(methylthio)-1-butanol, 1-bromo-2-butanol, 2-(methyldiphenylsilyl)ethanol, 2-(isopropylamino)ethanol, 2-(methylthio)ethanol, 2-(methylphenylamino)ethanol, 2-(isobutylsulfanyl)ethanol, 2-(phenylsulfonyl)ethanol, 2-

(trifluoromethoxy)ethanol, lactic acid, ethyl lactate, 2-(trimethylsilyl)ethanol, 1-(4-methylcyclohexyl)ethanol, 2-(2-quinoliny)ethanol, 2-[2-(diethylamino)ethoxy]ethanol, furfuryl alcohol, ($\pm$)-1-(2-furyl)ethanol, tetrahydrofurfuryl alcohol, tetrahydropyran-2-methanol, 1,2,6-hexanetriol, isosorbide, isoidide, isomannide, glycerol, sorbitol, farnesol, cetyl alcohol, stearyl alcohol, octanol, decanol, cetearyl alcohol, behenyl alcohol, arabinol, maltitol, xylaric acid, mannosylerythritol, arabitol, ribitol, isoborneol, myristyl alcohol, lauryl alcohol, oleyl alcohol, 1,1-bis(triphenylsilyl)ethanol, glucose, maltose, xylitol, erythritol, mannitol, ethylene glycol, propylene glycol, trimethylolpropane, pentaerythritol, cellulose, lignocellulose, 2-hydroxyethyl cellulose, ethyl cellulose, hydroxypropyl cellulose, (hydroxypropyl)methyl cellulose, cellulose triacetate, methyl cellulose, cellulose acetate, cyanoethylated cellulose, cellulose acetate butyrate, cellulose acetate propionate, sodium carboxymethyl cellulose, hydroxyethyl-cellulose, and combinations thereof. In particular embodiments that may be mentioned herein, the substrate may be lignin or cellulose.

It is noted that the substrate having one or more alcohols may be one where the alcohol is benzylic (e.g. as in lignin) or aliphatic (e.g. as in cellulose). While not wishing to be bound by theory, it is believed that the benzylic alcohols may undergo a greater conversion to iodides and hence provide a greater amount of initiation sites for the polymerisation to occur. Nevertheless, aliphatic alcohols are able to undergo the conversion to iodides and hence undergo initiation for polymerisation. As will be appreciated, if the efficiency of initiation is close to 100% (as for iodides derived from benzylic alcohols), then there may be multiple initiation sites on a modified substrate derived from lignin (which contains multiple benzylic alcohols). Even if the initiation rate for aliphatic alcohols is as low as 1%, then for a modified substrate such as cellulose, which may have more than 100 aliphatic alcohols per cellulose molecule, there is sufficient initiation sites for polymerisation to occur. In both cases, the products obtained may be commercially useful.

The reaction conditions for conversion of benzylic and aliphatic alcohols to iodides are similar, as is their polymerisation conditions. For example, the only difference may be that the polymerization temperature may be typically 70 °C for modified substrates derived from benzylic alcohols and typically 80 °C or slightly higher for modified substrates derived from aliphatic alcohols.

As noted above, the substrate having one or more primary or secondary alcohols may be a benzylic alcohol in certain embodiments. In such embodiments, the benzylic alcohol may be, but is not limited to, 1-phenylethanol, 1-(4-bromophenyl) ethanol, (S)-1-phenylethanol, (+)-1-

phenylethanol, 1-(4-methylphenyl)ethanol, 4-methylbenzyl alcohol, 1-phenyl-1-propanol, benzyl alcohol, 2-methylbenzyl alcohol, 3-methylbenzyl alcohol, 1-phenylmethanediol, 1-hydroxy-1-phenylethyl, α -isodecyl-benzenemethanol, α -silylbenzenemethanol, 4-hydroxybenzyl alcohol, 4-ethylbenzyl alcohol, 3-hydroxybenzyl alcohol, 4-mercaptobenzenemethanol, 1,4-benzenedimethanol, 3-ethylbenzenemethanol, α -mercaptobenzenemethanol, α -methyl-p-sec-pentyl-benzyl alcohol, p-sec-decyl- α -methylbenzyl alcohol, α -methyl-4-sec-nonyl-benzyl alcohol, α -methyl-4-sec-octyl-benzyl alcohol, 4-sec-heptyl- α -methyl-benzyl alcohol, p-sec-hexyl- α -methyl-benzyl alcohol, 2-aminobenzyl alcohol, 3-aminobenzyl alcohol, 4-aminobenzyl alcohol, α -ethynylbenzenemethanol, 2-mercaptobenzenemethanol, 3-mercaptobenzenemethanol, 4-propylbenzenemethanol, (2-ethylphenyl)methanol, [4-(hydroxymethyl)phenyl]lithium, 4-silylbenzenemethanol, ($\pm$)-phenylethanolamine, 1-phenyl-2-propen-1-ol, 2-methyl-1-phenyl-1-propanol, 1-phenyl-1-butanol, 4-ethynylbenzenemethanol, 3,5-dimethylbenzyl alcohol, 1-phenyl-1,2-propanediol, α -phosphinobenzenemethanol, 1-phenylethenol, α -(mercaptomethyl)benzenemethanol, α -iodobenzenemethanol, 4-(mercaptomethyl)benzenemethanol, 4-(hydroxymethyl)benzeneethanol, 2-selenobenzenemethanol, 4-methoxybenzyl alcohol, mandelonitrile, 4-iodobenzyl alcohol, 4-vinylbenzyl alcohol, 2-phenyl-2-butanol, 4-(hydroxymethyl)benzonitrile, α -methylbenzenemethanol-d-ol, 3-(aminomethyl)benzenemethanol, α -bromobenzenemethanol, benzonitrile, α -(borylmethyl)benzenemethanol, 4-isononylbenzenemethanol, α -(methyl-d3)benzenemethanol, α -methylbenzene-2,3,4,5,6-d5-methanol, 4-chlorobenzyl alcohol, 4-bromobenzyl alcohol, 4-fluoro- α -methylbenzyl alcohol, 1-(p-tolyl)ethanol, 4-fluorobenzyl alcohol, 4-(methylthio)benzenemethanol, α -ethyl- α -methylbenzenemethanol, (1S,2R)-(+)-norephedrine, α -hydroxybenzeneacetaldehyde, 5-methyl-1,3-benzenedimethanol, 4-methoxy- α -methylbenzyl alcohol, 2-phenyl-2-propanol, α -methyl-2-naphthalenemethanol, 4-bromo- α -methylbenzyl alcohol, 1-(2,4-dimethoxyphenyl)ethanol, 1-(4-chlorophenyl)ethanol, (1RS)-1-(6-methoxynaphthalen-2-yl)ethanol, (1S,2S)-(+)-pseudoephedrine, 1-(2,4,6-trimethoxyphenyl)ethanol, lignin, and combinations thereof. In particular embodiments that may be mentioned herein, the benzylic alcohol may be lignin.

The term "and combination thereof" when used herein may refer to the use of 2, 3, 4, 5, 6, 7, 8, 9, 10 or more (e.g. 2, 3, or 4, such as 2 or 3) components of the type mentioned.

The molar concentration ratio of the modified substrate to the first monomer in step (b) may be any suitable molar ratio. For example, the molar concentration ratio of the modified

substrate to the first monomer in step (b) may be from 1:5 to 1:2,000, such as from 1:6 to 1:1,600, such as from 1:9 to 1:300, such as from 1:10 to 1:100.

For the avoidance of doubt, it is explicitly contemplated that where a number of numerical ranges related to the same feature are cited herein, that the end points for each range are intended to be combined in any order to provide further contemplated (and implicitly disclosed) ranges. Thus, as an example, the molar concentration ratio of the modified substrate to the first monomer in step (b) may be:

from 1:5 to 1:6, from 1:5 to 1:9, from 1:5 to 1:10, from 1:5 to 1:100, from 1:5 to 1:300, from 1:5 to 1:1,600 from 1:5 to 1:2,000;

from 1:6 to 1:9, from 1:6 to 1:10, from 1:6 to 1:100, from 1:6 to 1:300, from 1:6 to 1:1,600 from 1:6 to 1:2,000;

from 1:9 to 1:10, from 1:9 to 1:100, from 1:9 to 1:300, from 1:9 to 1:1,600 from 1:9 to 1:2,000;

from 1:10 to 1:100, from 1:10 to 1:300, from 1:10 to 1:1,600 from 1:10 to 1:2,000;

from 1:100 to 1:300, from 1:100 to 1:1,600 from 1:100 to 1:2,000;

from 1:300 to 1:1,600 from 1:300 to 1:2,000; and

from 1:1,600 to 1:2,000.

The molar concentration ratio of the modified substrate to the first catalyst in step (b) may be any suitable molar ratio. For example, the molar concentration ratio of the modified substrate to the first catalyst in step (b) may be from 1:0.1 to 1:10, such as from 1:0.3 to 1:1.

In certain embodiments of the invention, the first mixture may further comprise a radical initiator. Any suitable radical initiator that is compatible with the reagents used in the process may be used herein. For example, the radical initiator may be azobisisobutyronitrile.

The process described herein may be conveniently used to generate block copolymers. This may be conveniently achieved by the further steps of:

(c) terminating the polymerisation reaction of step (b) in Claim 1 to provide the first polymeric or oligomeric material as a macroinitiator; and

(d) mixing the macroinitiator with a third monomer to provide a second mixture, and subjecting the second mixture to reaction conditions that provide a second polymeric material formed from the third monomer and the macroinitiator.

The term "terminating" herein simply means stopping the polymerisation reaction by any suitable means. This may be, for example simply by reducing the reaction temperature to a

point where polymerisation stops. Thus, in embodiments of the invention that may be mentioned herein, the polymerisation reaction in step (c) may involve cooling the first mixture to a temperature of from 0 to 50 °C, such as around 25 °C.

Any suitable material may be used as the third monomer. For example, the third monomer may be selected from, but not limited to, acrylonitrile, styrene, methoxystyrene, butoxystyrene, chloromethyl styrene, chlorostyrene, methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, t-butyl acrylate, hexyl acrylate, 2-ethyl hexyl acrylate, n-octyl acrylate, nonyl acrylate, decanyl acrylate, benzyl acrylate, tetrahydrofurfuryl acrylate, glycidyl acrylate, cyclohexyl acrylate, 2-methoxyethyl acrylate and butoxyethyl acrylate, tris(trialkylsiloxy) derivative-acrylates, and fluoroalkyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, hexyl methacrylate, 2-ethyl hexyl methacrylate, n-octyl methacrylate, nonyl methacrylate, decanyl methacrylate, benzyl methacrylate, tetrahydrofurfuryl methacrylate, glycidyl methacrylate, cyclohexyl methacrylate, 2-methoxyethyl methacrylate, butoxyethyl methacrylate, tris(trialkylsiloxy) derivative-methacrylates, fluoroalkyl methacrylates, hydroxy styrene, styrene sulfonic acid, sodium styrene sulfonic acid, styrene boronic acid, acrylamide, N-isopropyl acrylamide, N,N-dimethyl acrylamide, N-methylol acrylamide, N-hydroxyethyl acrylamide, methacrylamide, N-isopropyl methacrylamide, N,N-dimethyl methacrylamide, N-methylol methacrylamide, N-hydroxyethyl methacrylamide, acrylic acid, hydroxyalkyl acrylate (e.g. 2-hydroxy ethyl acrylate), 2-hydroxypropyl acrylate, glyceryl monoacrylate, diethylene glycol acrylate, polyethylene glycol acrylate, methoxy tetraethylene glycol acrylate, methoxypolyethylene glycol acrylate, 2-(dimethylamino) ethyl acrylate, 3-chloro-2-hydroxypropyl acrylate, 2-hydroxy-3-phenoxypropyl acrylate, 2-acryloyloxyethyl phosphorylcholine, 2-(N,N-diethyl-N-methyl amino) ethyl acrylate +/trifluorosulfonyliminium salt, 2-(N-ethyl-N-methyl-N-hydrogenation amino) ethyl acrylate +/trifluorosulfonyliminium ($(\text{CF}_3\text{SO}_2)^{-}$) salt, 1-ethyl-3-methyl imidazolium acrylate +/fluorohydrogenation $((\text{FH})_n\text{F}^-)$ salt, methacrylic acid, 2-hydroxy ethyl methacrylate, 2-hydroxypropyl methacrylate, glyceryl monomethacrylate, diethylene glycol methacrylate and polyethylene glycol methacrylate, methoxy tetraethylene glycol methacrylate, methoxypolyethylene glycol methacrylate, 2-(dimethylamino) ethyl methacrylate, 3-chloro-2-hydroxypropyl methacrylate, 2-hydroxy-3-phenoxypropyl methacrylate, 2-acryloyloxyethyl phosphorylcholine, 2-(N,N-diethyl-N-methyl amino) ethyl methacrylate +/trifluorosulfonyliminium salt, 2-(N-ethyl-N-methyl-N-hydrogenation amino) ethyl methacrylate +/trifluorosulfonyliminium ($(\text{CF}_3\text{SO}_2)^{-}$) salt, and 1-ethyl-3-methyl imidazolium methacrylate+/ fluorohydrogenation $((\text{FH})_n\text{F}^-)$ salt, diethylene glycol dimethacrylate, diethylene glycol diacrylate, vinyl acetate, N-vinyl pyrrolidone, N-vinyl carbazol, butadiene, ethylene,

propylene, butene, pentene, hexene, heptane, octene, vinyl ethers, vinyl ketones, vinyl chloride, acetylene, phenyl acetylene, and combinations thereof.

In particular embodiments of the invention, the third monomer may be selected from one or more of the group consisting of methyl methacrylate, benzyl methacrylate, 2-hydroxyethyl methacrylate, 2-methoxyethyl methacrylate, furfuryl methacrylate and poly(ethylene glycol) methyl ether methacrylate. As will be appreciated, the third monomer may be selected to be different from the first monomer.

The molar concentration ratio of the macroinitiator to the third monomer in step (d) may be any suitable molar ratio. For example, the molar concentration ratio of the macroinitiator to the third monomer in step (d) may be from 1:5 to 1:2,000, such as from 1:6 to 1:1,600, such as from 1:9 to 1:300, such as from 1:10 to 1:100.

The molar concentration ratio of the macroinitiator to a total amount of catalyst in step (d) may be any suitable molar ratio. For example, the molar concentration ratio of the macroinitiator to a total amount of catalyst in step (d) may be from 1:0.1 to 1:10, such as from 1:0.3 to 1:1. The total amount of catalyst may refer to the first catalyst alone or, where present, a combination of the first catalyst and a second catalyst. That is, where a second catalyst is added to the reaction mixture along with the third monomer. For example, the second catalyst may be tetrabutylammonium iodide (TBAI).

In a second aspect of the invention, there is provided a process to form an iodide material, the process comprising the steps of:

- (ai) providing a substrate having one or more aliphatic alcohols; and
- (a ii) converting at least one of the one or more alcohols to an iodide group to provide a modified substrate.

Any suitable method may be used to form the modified substrate, provided that an iodide is produced by displacement of an alcohol group. However, in embodiments of the invention, the modified substrate may be obtained by reacting the substrate having one or more alcohols with iodine and polymethylhydrosiloxane. It is noted that the use of this method, which is detailed in more detail in the experimental section hereinbelow, may be particularly suited for a one-pot reaction.

Any suitable substrate having one or more aliphatic alcohols may be used herein, for example, the substrate having one or more aliphatic alcohols may be selected from one or more of the group consisting of methanol, ethanol, 1-butanol, isopropyl alcohol, tert-butanol, 1,3-butanediol, 2-butanol, propanediol, 4,4,4-trifluoro-1-butanol, 2-amino-1-butanol, 4-phenyl-2-butanol, 3-methyl-2-butanol, 4-chloro-1-butanol, 4-bromo-1-butanol, 2-methyl-2-butanol, 3-methoxy-1-butanol, 4-phenyl-1-butanol, 1-amino-2-butanol, 3-(methylamino)-1-butanol, 3-(dimethylamino)-1-butanol, 4-(methylthio)-1-butanol, 1-bromo-2-butanol, 2-(methyldiphenylsilyl)ethanol, 2-(isopropylamino)ethanol, 2-(methylthio)ethanol, 2-(methylphenylamino)ethanol, 2-(isobutylsulfanyl)ethanol, 2-(phenylsulfonyl)ethanol, 2-(trifluoromethoxy)ethanol, lactic acid, ethyl lactate, 2-(trimethylsilyl)ethanol, 1-(4-methylcyclohexyl)ethanol, 2-(2-quinoliny)ethanol, 2-[2-(diethylamino)ethoxy]ethanol, furfuryl alcohol, ($\pm$)-1-(2-furyl)ethanol, tetrahydrofurfuryl alcohol, tetrahydropyran-2-methanol, 1,2,6-hexanetriol, isosorbide, isoidide, isomannide, glycerol, sorbitol, farnesol, cetyl alcohol, stearyl alcohol, octanol, decanol, cetearyl alcohol, behenyl alcohol, arabinol, maltitol, xylaric acid, mannosylerythritol, arabitol, ribitol, isoborneol, myristyl alcohol, lauryl alcohol, oleyl alcohol, 1,1-bis(triphenylsilyl)ethanol, glucose, maltose, xylitol, erythritol, mannitol, ethylene glycol, propylene glycol, trimethylolpropane, pentaerythritol, cellulose, lignocellulose, 2-hydroxyethyl cellulose, ethyl cellulose, hydroxypropyl cellulose, (hydroxypropyl)methyl cellulose, cellulose triacetate, methyl cellulose, cellulose acetate, cyanoethylated cellulose, cellulose acetate butyrate, cellulose acetate propionate, sodium carboxymethyl cellulose, and hydroxyethyl-cellulose, optionally wherein the substrate is cellulose.

Therefore, there is disclosed herein:

- 1) a one-pot synthetic technique for grafting polymers from benzylic alcohols is disclosed herein. The technique is termed one-pot reversible complexation mediated polymerization (one-pot RCMP);
- 2) a one-pot synthetic technique for grafting polymers from lignin that bears hydroxyl groups is disclosed herein; and
- 3) a one-pot RCMP can be extended for grafting polymers from other hydroxyl-bearing biomass molecules and substrates such as cellulose.

As will be appreciated, the present invention may provide one or more of the following advantages.

- 1) One-pot RCMP enables direct grafting of polymers from benzylic alcohols without additional mid-step purification (step 1). This technique allows grafting of polymers

from a variety of commercially available inexpensive or functional benzylic alcohol, reducing the cost of RCMP and providing functional polymers.

- 2) One-pot RCMP enables direct grafting of polymers from lignin, solving the problem (tedious initiator attachment and purification) of the current two-pot techniques, simplifying the manufacturing processes and reducing the costs. The present invention gives an industrial breakthrough in lignin applications.
- 3) One-pot RCMP is free from heavy metals and odor and uses only inexpensive agents, overcoming another important problem (removal of toxic and odorous agents and high cost of agents) of the current two-pot techniques. The present can serve as a cost-effective industrial technology to obtain value-added lignin-polymer composites.
- 4) One-pot RCMP has a wide monomer scope and accessibility to a range of copolymer and branched polymer structures and can serve as a platform technology for designing a range of polymer-grafted lignin composites.
- 5) One-pot RCMP can be extended for grafting polymers from other biomass molecules and substrates and can generate a library of polymer-grafted biomass composites.
- 6) Lignin absorbs UV light and can serve as bio-based sunscreens and anti-aging agents of organic plastics and films. However, mere physical blending of lignin with synthetic polymers causes phase-separation and gives opacity or limited UV-shielding properties due to immiscibility of lignin and synthetic polymers. Chemical grafting of synthetic polymers from lignin can solve the immiscibility problem. We blended the obtained polymer-grafted lignin with a pure polymer and formed a UV-absorbing film, which achieved a direct UV protection percentage of 95.4%. This excellent UV-barrier property is comparable to those of petroleum- and inorganic-based commercial sunscreen products but is achieved by biomass-based composites in this invention.

It will also be appreciated that the present invention can serve as a cost-effective manufacturing process for value-added polymer-grafted lignin and polymer-grafted biomass composites. Promising applications are biomass-containing plastics, films, packaging, coatings, textiles, and adhesives with thermally stability, mechanical toughness, biodegradability, antioxidation, and UV-absorption, for example, which would be attractive for chemical companies seeking sustainable products.

Further aspects and embodiments of the invention will now be described by the following non-limiting examples.

Examples

Materials

Polymethylhydrosiloxane (PMHS) (average molecular weight = 2500) (98%, BLDpharm, China), iodine (I_2) (>98%, Tokyo Chemical Industry (TCI), Japan), 1-phenylethanol (PhE-OH) (98%, Sigma-Aldrich, USA), 1-(4-bromophenyl) ethanol (BrPhE-OH) (>99%, TCI), 4-methoxyphenol ($\geq 99\%$, Sigma-Aldrich), 2-phenylethanol ($\geq 99\%$, Sigma-Aldrich), tetrabutylammonium iodide ($Bu_4N^+I^-$ (BNI)) (>98%, TCI), methyl methacrylate (MMA) (>99.8%, TCI), benzyl methacrylate (BzMA) (>98%, TCI), butyl methacrylate (BMA) (>99%, TCI), 2-hydroxyethyl methacrylate (HEMA) (>95%, TCI), 2-methoxyethyl methacrylate (MEMA) ($\geq 98\%$, TCI), furfuryl methacrylate (FMA) (97%, Sigma-Aldrich), poly(ethylene glycol) methyl ether methacrylate (PEGMA) (average molecular weight = 300) (98%, Sigma-Aldrich), butyl acrylate (BA) (>99%, TCI), 2-methoxyethyl acrylate (MEA) (>98%, TCI), benzyl acrylate (BzA) (>98%, TCI), styrene (St) (>99%, TCI), 2-ethylhexyl methacrylate (EHMA) (>99%, TCI), dodecyl methacrylate (LMA) (>97%, TCI), stearyl methacrylate (SMA) (>97%, TCI), chloroform ($\geq 99.8\%$, Fisher Chemical, USA), toluene (99.8%, Sigma-Aldrich), butyl acetate (>99%, TCI), diethylene glycol dimethyl ether (diglyme, >99%, TCI), acetone ($\geq 99.5\%$, Fisher Chemical), ethanol ($\geq 99.8\%$, Fisher Chemical), hexane (ACS reagent grade, VWR International, USA), diethyl ether (ACS reagent grade, VWR Chemicals), tetrahydrofuran (THF) ($\geq 99.8\%$, Fisher Chemical), *N,N*-dimethylformamide (DMF) (>99.5%, Kanto Chemical, Japan), and potassium bromide (KBr) ($\geq 99\%$, trace metals basis, Sigma-Aldrich) were used as received. PMMA (number-average molecular weight (M_n) = 5000) (powder, Sigma-Aldrich) was used for blending. Lignin (average molecular weight = 600) (alkali, 5% moisture, Sigma-Aldrich), cellulose (average molecular weight = 70000) (powder, Sigma-Aldrich), and (hydroxypropyl)methyl cellulose (average molecular weight = 90000) (HPM cellulose, powder, Sigma-Aldrich) were dried under vacuum overnight before use.

Analytical techniques

Proton nuclear magnetic resonance (1H NMR) spectroscopy

The spectra were recorded at ambient temperature on a Bruker (Germany) BBFO400 spectrometer (400 MHz). Chloroform- d ($CDCl_3$, Cambridge Isotope Laboratories, USA) or DMSO- d_6 (Cambridge Isotope Laboratories) was used as the NMR solvent. The residual non-deuterated solvents and tetramethylsilane (TMS) were used as the internal standards for 1H NMR analysis (calibration of chemical shift).

Gel permeation chromatography (GPC)

The GPC analysis was performed on a Shimadzu (Kyoto, Japan) LC-2030C Plus liquid chromatograph. The sample detection was conducted using a refractive index detector (RID-20A). The eluent was THF or DMF. The DMF eluent contained LiBr (10 mM). The flow rate was 0.7 mL/min (THF) (40 °C) or 0.34 mL/min (DMF) (40 °C). The columns for the THF eluent were a Shodex (Tokyo, Japan) LF-804 mixed gel column (300 × 8.0 mm; bead size = 6 µm; pore size = 3000 Å) and a Shodex KF-804L mixed gel column (300 × 8.0 mm; bead size = 7 µm; pore size = 1500 Å). The columns for the DMF eluent were two Shodex LF-804 columns (300 × 8.0 mm; bead size = 6 µm; pore size = 1500 Å) and one Shodex KD-802 column (300 × 8.0 mm; bead size = 6 µm; pore size = 150 Å). For both THF and DMF eluents, the column system was calibrated with standard poly(methyl methacrylate)s (PMMA)s.

Fourier-transform infrared spectroscopy (FT-IR)

The FT-IR analysis was carried out on a Bruker ALPHA FT-IR (Bruker, US) spectrometer. KBr was used as a matrix for FT-IR.

Differential scanning calorimetry (DSC)

The DSC curves were recorded with QSeries DSC Q50 model device (TA instrument, New Castle, US). The DSC analysis was conducted using aluminium sample pans under nitrogen flow at a flow rate of 50 mL/min. The samples were cooled down to −60 °C and heated up to 200 °C with a heating rate of 10 °C/min.

Thermal gravimetric analysis (TGA)

The TGA curves were recorded with TGA Q500 model device (TA instrument). The TGA analysis was carried out in platinum pans under flowing nitrogen at a flow rate of 60 mL/min with a heating rate of 20 °C/min at a temperature range of 25–800 °C.

Ultraviolet-visible (UV-Vis) spectroscopy

The UV-Vis absorption measurements were performed on a Shimadzu UV-3600 (Kyoto, Japan) at room temperature with a quartz cell with an optical path length of 1 cm.

Example 1. Optimization of iodination conditions

Iodination reaction

A typical iodination reaction was conducted as follows (Table 1, entry 1). To a solution of PhE-OH (0.06 g, 0.5 mmol) and PMHS (0.15 g, 2.5 mmol of Si-H unit) in chloroform (2 mL), iodine (0.126 g, 0.5 mmol) was added under an argon atmosphere (using standard Schlenk

technique). The mixture was stirred at room temperature for 120 min. The initial dark red color of the mixture turned colorless. The mixture was then analyzed with ^1H NMR.

Table 1. Optimization of iodination condition using R-OH (1 equiv.), I_2 (1 equiv.), and PMHS (5 equiv. of the Si-H unit).

Entry	R-OH	Solvent	[R-OH] (M)	T ($^{\circ}\text{C}$)	t (min)	Conv. (%) ^a
1	PhE-OH	Chloroform	0.25	r.t.	120	> 99
2	PhE-OH	Toluene	0.25	r.t.	180	> 99
3	PhE-OH	Toluene	0.25	70	15	> 99
4	PhE-OH	Butyl acetate	0.25	70	15	> 99
5	PhE-OH	Diglyme	0.25	70	15	> 99
6	PhE-OH	Diglyme	1	70	100	> 99
7	BrPhE-OH	Diglyme	0.25	70	15	> 99
8	BrPhE-OH	Diglyme	1	70	90	> 99

^aThe conversion of R-OH to R-I was determined using ^1H NMR.

Results and discussion

Das *et al.* reported a fast and full conversion of benzylic alcohols to benzylic iodides using I_2 and PMHS as iodinating agents in the field of organic chemistry of small molecules (B. Das *et al.*, *Tetrahedron Lett.* **2007**, *48*, 3201-3204). Mechanistically, the Si-H in each repeat unit of PMHS reacts with I_2 to in situ generate hydrogen iodide (HI), which then reacts with R-OH to form R-I. PMHS is a byproduct generated in silicone industry and inexpensive, allowing the iodination process to be cost-effective. In the literature, the iodination was studied in a dilute condition ($[\text{R-OH}]_0 = 0.1 \text{ M}$ (1 equiv.)) in chloroform (solvent) at room temperature using I_2 (1 equiv.) and PMHS (1.5 equiv. of the Si-H unit), generating R-I with a high isolated yield (up to 96%) for a short reaction time (< 30 min). 0.5 equiv. of I_2 was used to R-I, and the other 0.5 equiv. of I_2 was bonded with Si in PMHS (B. Das *et al.*, *Tetrahedron Lett.* **2007**, *48*, 3201-3204). In our one-pot RCMP (described in the Examples below), higher concentrations of R-OH were used. Hence, we first screened the iodination conditions at higher concentrations of R-OH (Table 1).

We studied two secondary benzylic alcohols (Fig. 1), i.e., 1-phenylethanol (PhE-OH) and 1-(4-bromophenyl) ethanol (BrPhE-OH). We used R-OH (1 equiv.), I_2 (1 equiv.), and PMHS (5 equiv. of Si-H) at the fixed molar ratio. At a higher concentration of R-OH (0.25 M), the iodination of PhE-OH required longer times (120–180 min) to reach full conversions (>99%)

in chloroform and toluene (solvents) at room temperature (Table 1, entries 1 and 2). This was partly because of the limited solubility (saturation) of I_2 in those solvents at the higher concentration of I_2 (0.25 M) at room temperature. Thus, the temperature was elevated to 70 °C, which significantly reduced the reaction time to 15 min to reach full conversions (>99%) in toluene, butyl acetate, and diglyme (solvents) for both PhE-OH and BrPhE-OH probably because of an increased solubility of I_2 and increased relevant reaction rate constants (Table 1, entries 3–5 and 7). We studied an even higher concentration of R-OH (1 M), which required prolonged reaction times but attained full conversions (> 99%) in reasonably short times of 90–100 min at 70 °C for both PhE-OH and BrPhE-OH (Table 1, entries 6 and 8). The full conversion was confirmed using 1H NMR (Fig. 2) and was also easily monitored by the disappearance of the red colour of I_2 (full consumption of I_2) (Fig. 2). Similar reaction times were required for PhE-OH and BrPhE-OH, suggesting that the electron-withdrawing bromide in BrPhE-OH does not significantly affect the iodination. However, the bromide somewhat affected the initiation (activation) of the resultant R-I in the polymerization (RCMP) as described below. We used diglyme as a solvent in the following one-pot RCMP because of its low toxicity and high boiling point.

Example 2. One-pot polymerization of monomers

One-pot RCMP

A typical one-pot RCMP was conducted as follows (Table 2, entry 2). To a solution of BrPhE-OH (0.05 g, 0.25 mmol) and PMHS (0.075 g, 1.25 mmol of Si-H unit) in diglyme (0.28 g), iodine (0.063 g, 0.25 mmol) was added under an argon atmosphere. The mixture was stirred at 70 °C for 120 min. The initial dark red color of the mixture turned colorless. To this mixture, MMA (2.5 g, 25 mmol) and BNI (0.184 g, 0.5 mmol) were added under an argon flow. The mixture was then heated to 80 °C. An aliquot (0.1 mL) of the mixture was taken out by a syringe at prescribed times, cooled to room temperature, and analyzed with GPC and 1H NMR. After 6 h, the mixture was diluted with THF, and the generated polymer was purified by reprecipitation in a mixture of hexane/ethanol (8/2 (v/v)) three times. The purified polymer was dried in vacuo and analyzed with 1H NMR.

In the purification of polymers, the dilution solvent was DMF for poly(2-hydroxyethyl methacrylate) (PHEMA) and THF for the other polymers. The precipitation solvent (non-solvent) was a mixture of water/ethanol (5/5 (v/v)) for poly(butyl acrylate) (PBA), a mixture of diethyl ether/ethanol (9/1 (v/v)) for poly(furfuryl methacrylate) (PFMA), and a mixture of hexane/ethanol (8/2 (v/v)) for the other polymers.

Table 2. One-pot RCMP of several monomers.

Entry	R-OH	Monomer	[Monomer] ₀ / [R-OH] ₀ / [BNI] ₀ ^a	T (°C)	t (h)	Monomer Conv. (%) ^b	M _n ^c (M _{n,theo}) ^d	D ^c
1	PhE-OH	MMA	100/1/2	80	6	62	6800 (6400)	1.39
2	BrPhE-OH	MMA	100/1/2	80	6	91	10000 (9300)	1.36
3	BrPhE-OH	MMA	100/1/0	80	24	0	NA	NA
4	BrPhE-OH	BzMA	100/1/2	80	8	95	18000 (16900)	1.33
5	BrPhE-OH	BMA	100/1/2	80	8	80	10300 (11600)	1.18
6	BrPhE-OH	HEMA	100/1/2	80	24	56	9700 (7500)	1.30
7	BrPhE-OH	MEMA	100/1/2	80	18	75	11400 (11000)	1.47
8	BrPhE-OH	FMA	100/1/2	80	8	78	11900 (13200)	1.48
9	BrPhE-OH	PEGMA	50/1/1	80	24	51	6800 (7900)	1.39
10	BrPhE-OH	BA	100/1/2	110	48	50	6000 (6600)	1.38
11	BrPhE-OH	MEA	100/1/2	110	48	40	5000 (5400)	1.45
12	BrPhE-OH	BzA	100/1/2	110	24	87	9800 (14300)	1.42
13	BrPhE-OH	Styrene	100/1/2	110	48	0	NA	NA

^aA solution of R-OH (1 equiv.), I₂ (1 equiv.), and PMHS (5 equiv. of Si-H) was heated in diglyme at 70 °C for 90 min (entries 4, 5, and 7–12) or 120 min (entries 1–3, 6 and 13) to convert R-OH to R-I (iodination). The concentration of R-OH in the iodination process was 0.84 M (entries 1–3), 0.53 M (entry 4), 0.57 M (entry 5), 0.74 M (entry 6), 0.60 M (entry 7), 0.58 M (entry 8), 0.63 M (entries 9 and 10), 0.59 M (entry 11), 0.57 M (entry 12), or 0.81 M (entry 13). In the same pot (unpurified solution), monomer and BNI were added, and the polymerization was conducted. The diglyme/monomer ratio was 10/90 (w/w) during the

polymerization step. ^bMonomer conversion determined with ¹H NMR. ^c M_n and $\bar{D}$ values determined with PMMA-calibrated DMF-GPC (entry 6) or THF-GPC (other entries). ^dTheoretical M_n value calculated according to $([\text{monomer}]_0/[\text{R-OH}]_0) \times (\text{monomer conversion}) \times (\text{molecular weight of monomer}) + (\text{molecular weight of R-I generated from R-OH})$.

Determination of a fraction of initiating benzylic alcohol moiety contained in PMMA (Table 2, entries 1 and 2)

A fraction of the initiating benzylic alcohol moiety contained in the PMMA obtained via one-pot RCMP (F_i) was calculated according to equation (1):

$$F_i = \frac{DP_n}{DP_n(\text{NMR})} \quad (1)$$

DP_n is the number-average degree of polymerization determined with PMMA-calibrated GPC. $DP_n(\text{NMR})$ is the DP_n determined from the ¹H NMR peak areas of the aromatic protons (originated from the initiating benzylic alcohol) and the methoxy protons (originated from the MMA monomer units), assuming all PMMA chains were initiated from benzylic alcohols. Fig. 3 shows the ¹H NMR spectrum of the polymer obtained in the PhE-OH system (Table 2, entry 1), where peaks f and g (7.08–7.20 ppm) (aromatic protons) and peak e (3.46–3.71 ppm) (methoxy protons) were used for the determination of $DP_n(\text{NMR})$. Fig. 4 shows the ¹H NMR spectrum of the polymer obtained in the BrPhE-OH system (Table 2, entry 2), where peak f (6.97–7.06 ppm) (aromatic protons) and peak e (3.46–3.71 ppm) (methoxy protons) were used for the determination of $DP_n(\text{NMR})$.

Determination of a fraction of initiating benzylic alcohol moiety contained in other polymers (Table 2, entries 4–12)

The F_i values were similarly calculated for the other polymers (Table 2, entries 4–12) according to equation (1). The M_n values determined with GPC are not absolute values but PMMA-calibrated values for the other polymers. Hence, for the other polymers, the theoretical DP_n value calculated according to $([\text{monomer}]_0/[\text{R-OH}]_0) \times (\text{monomer conversion})$ was used for DP_n in equation (1). Table 3 summarizes the F_i values.

Table 3. Initiation efficiencies (F_i) of the polymers obtained in Table 2 (entries 1, 2, and 4–12) (Figs. 3–13).

Table	2	1	2	4	5	6	7	8	9	10	11	12
Entry												
Initiation	100	100	100	78	86	75	99	74	75	91	73	

efficiency (F_i) (%)											
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Results and discussion

One-pot polymerization of methyl methacrylate (MMA)

One-pot RCMP of several monomers was studied (Fig. 1 and Table 2). We first heated a solution of R-OH (PhE-OH or BrPhE-OH) (0.84 M, 1 equiv.), I_2 (1 equiv.), and PMHS (5 equiv. of Si-H) in diglyme at 70 °C for 90–120 min to convert R-OH to R-I (PhE-I or BrPhE-I) (iodination). In the same pot (unpurified solution (10 wt%)), we added monomer (90 wt%) (100 equiv.) and BNI ($Bu_4N^+I^-$) as an RCMP catalyst (2 equiv.) and heated the reaction mixture at 80 °C for methacrylates or 110 °C for acrylates to conduct RCMP in one pot. Assuming a full conversion of R-OH to R-I, the theoretical degree of polymerization (DP) was 100 ($[monomer]_0/[R-OH]_0 = 100$) at a full (100%) monomer conversion.

Fig. 14 shows one-pot RCMP of methyl methacrylate (MMA) from PhE-OH and BrPhE-OH (Table 2, entries 1 and 2). The monomer conversion reached 62% and 91% for 6 h of polymerization for PhE-OH and BrPhE-OH, respectively. For the PhE-OH system (circles in Fig. 14), the number-average molecular weight (M_n) deviated from the theoretical value ($M_{n,theo}$) at an early stage of polymerization and became closer to the theoretical value as the polymerization proceeded, suggesting a relatively slow initiation from the generated PhE-I. For the BrPhE-OH system (triangles in Fig. 14), the M_n value agreed with the theoretical value from an early stage of polymerization, suggesting a fast initiation from the generated BrPhE-I. The dispersity ($\mathcal{D} = M_w/M_n$) was 1.3–1.4 and 1.2–1.4 for the PhE-OH and BrPhE-OH systems, respectively, where M_w is the weight-average molecular weight. The 1H NMR spectra of the polymers generated at 6 h of polymerization and subsequently purified ($M_n = 7300$ and $\mathcal{D} = 1.31$ for PhE-OH and $M_n = 10200$ and $\mathcal{D} = 1.35$ for BrPhE-OH after purification) (Figs. 3 and 4) clearly showed the aryl proton peaks at 7.08–7.33 ppm for the PhE-OH system and at 6.97–7.43 ppm for the BrPhE-OH system, confirming the presence of the initiating alcohol moieties in the polymers. From the DP (M_n) values determined with GPC and the 1H NMR peak areas of the aryl protons in the initiating alcohol moieties and the methoxy protons in the MMA monomer units, we estimated that approximately 100% of the polymer contained the initiating alcohol moieties for both PhE-OH and BrPhE-OH systems, respectively (Table 3). The results demonstrate successful one-pot RCMP from R-OH with high efficiencies for yielding polymers with relatively low dispersities. The BrPhE-OH system without the addition of BNI (RCMP catalyst) (Table 2, entry 3) resulted in no polymerization, meaning that the propagating radical was generated from R-I via the catalysis with BNI.

One-pot polymerization of functional (meth)acrylates

The results for MMA suggest a higher initiating efficiency using BrPhE-OH than PhE-OH. Thus, we used BrPhE-OH in the following studies. To expand the monomer scope, we studied several hydrophobic, functional, and amphiphilic methacrylates, i.e., benzyl methacrylate (BzMA), butyl methacrylate (BMA), 2-hydroxyethyl methacrylate (HEMA), 2-methoxyethyl methacrylate (MEMA), furfuryl methacrylate (FMA), and poly(ethylene glycol) methyl ether methacrylate (PEGMA) (average molecular weight = 300) (Fig. 1). Relatively low-dispersity polymers ($\bar{D} = 1.18\text{--}1.48$) were obtained up to 51–95% monomer conversions (Table 2, entries 4–9) with high initiation efficiencies (74–100%) from BrPhE-OH (Figs. 5–10 and Table 3) for all cases.

A different family of monomers (i.e., acrylates) was also studied. A higher temperature was used for acrylates (110 °C) than methacrylates (80 °C) in the polymerization because of the stronger secondary alkyl carbon-iodine bond in acrylate polymers compared with the tertiary alkyl carbon-iodine bond in methacrylate polymers. The one-pot RCMP of butyl acrylate (BA), 2-methoxyethyl acrylate (MEA), and benzyl acrylate (BzA) yielded polyacrylates with relatively low-dispersities ($\bar{D} = 1.38\text{--}1.45$) at 40–87% monomer conversions (Table 2, entries 10–12) with high initiation efficiencies (73–91%) from BrPhE-OH (Figs. 11–13 and Table 3). Thus, the results illustrate a wide monomer scope for one-pot RCMP. We also studied styrene, but no polymerization took place (Table 2, entry 13) because of the relatively low catalytic activity of BNI for RCMP of styrene.

Example 3. Synthesis of block copolymers*One-pot synthesis of macroinitiators and their copolymerization*

The one-pot synthesis of PMMA-I macroinitiator (Table 4, entry 1) was conducted as follows. To a solution of BrPhE-OH (0.05 g, 0.25 mmol) and PMHS (0.075 g, 1.25 mmol of Si-H unit) in diglyme (0.28 g), iodine (0.063 g, 0.25 mmol) was added under an argon atmosphere. The mixture was stirred at 70 °C for 120 min. To this mixture, MMA (2.5 g, 25 mmol) and BNI (0.184 g, 0.5 mmol) were added under an argon flow. The mixture was then heated at 70 °C for another 1 h (monomer conversion = 27%). The mixture was diluted with chloroform, and the generated PMMA-I was purified by reprecipitation in a mixture of hexane/ethanol (8/2 (v/v)) three times. The purified PMMA-I ($M_n = 3800$ and $\bar{D} = 1.26$) was dried in vacuo for 3 h and used as a macroinitiator for subsequent block polymerization.

The one-pot synthesis of PBzMA-I macroinitiator (Table 4, entries 2–5) was conducted as follows. To a solution of BrPhE-OH (0.05 g, 0.25 mmol) and PMHS (0.075 g, 1.25 mmol of Si-H unit) in diglyme (0.49 g), iodine (0.063 g, 0.25 mmol) was added under an argon atmosphere. The mixture was stirred at 70 °C for 90 min. To this mixture, BzMA (4.4 g, 25 mmol) and BNI (0.184 g, 0.5 mmol) were added under an argon flow. The mixture was then heated at 70 °C for another 1 h (monomer conversion = 25%). The mixture was diluted with chloroform, and the generated PBzMA-I was purified by reprecipitation in a mixture of hexane/ethanol (8/2 (v/v)) three times. The purified PBzMA-I ($M_n = 4300$ and $\bar{D} = 1.14$) was dried in vacuo for 3 h and used as a macroinitiator for subsequent block polymerizations.

The one-pot synthesis of PMEMA-I macroinitiator (Table 4, entry 6) was conducted as follows. To a solution of BrPhE-OH (0.05 g, 0.25 mmol) and PMHS (0.075 g, 1.25 mmol of Si-H unit) in diglyme (0.4 g), iodine (0.063 g, 0.25 mmol) was added under an argon atmosphere. The mixture was stirred at 70 °C for 90 min. To this mixture, MEMA (3.6 g, 25 mmol) and BNI (0.184 g, 0.5 mmol) were added under an argon flow. The mixture was then heated at 70 °C for another 2 h (monomer conversion = 36%). The mixture was diluted with chloroform, and the generated PMEMA-I was purified by reprecipitation in a mixture of hexane/ethanol (8/2 (v/v)) three times. The purified PMEMA-I ($M_n = 5100$ and $\bar{D} = 1.34$) was dried in vacuo for 3 h and used as a macroinitiator for subsequent block polymerization.

A typical block copolymerization was conducted as follows (Table 4, entry 1). A mixture of PMMA-I ($M_n = 3800$ and $\bar{D} = 1.26$) (0.2 g, 0.053 mmol), BzMA (0.93 g, 5.3 mmol), and BNI (0.039 g, 0.106 mmol) was heated in a Schlenk flask at 80 °C under argon atmosphere with magnetic stirring for 8 h. The mixture was cooled to room temperature. An aliquot (0.1 mL) of the mixture was analyzed with GPC and ^1H NMR. The rest of the mixture was diluted with THF, and the generated polymer was purified by reprecipitation in a mixture of hexane/ethanol (8/2 (v/v)) three times. The purified polymer was dried in vacuo and analyzed with GPC and ^1H NMR.

Table 4. Synthesis of block copolymers using macroinitiators synthesized via one-pot RCMP.

Entry	Macroinitiator	Monomer	$[\text{Monomer}]_0 / [\text{Macroinitiator}]_0 / [\text{BNI}]_0$	T (°C)	t (h)	Monomer Conv. (%) ^a	M_n^b ($M_{n,\text{theo}}^c$)	$\bar{D}^b$
1	PMMA-I ^d	BzMA	100/1/2	80	8	60	14100 (14400)	1.46
2	PBzMA-I ^e	MMA	100/1/2	80	8	75	10100 (11800)	1.56

3	PBzMA-I ^e	MEMA	100/1/2	80	8	61	12300 (13100)	1.59
4	PBzMA-I ^e	HEMA	100/1/2	80	24	40	8000 (9500)	1.27
5	PBzMA-I ^e	PEGMA	50/1/1	80	24	42	13300 (10600)	1.21
6	PMEMA-I ^f	MMA	100/1/2	80	8	73	9800 (12400)	1.37

^aMonomer conversion determined with ¹H NMR. ^b M_n and $\bar{D}$ values determined with PMMA-calibrated DMF-GPC (entry 4) or THF-GPC (other entries). ^cTheoretical M_n value calculated according to $([\text{monomer}]_0/[\text{macroinitiator}]_0) \times (\text{monomer conversion}) \times (\text{molecular weight of monomer}) + (\text{molecular weight of macroinitiator})$. ^d $M_n = 3800$ and $\bar{D} = 1.26$. ^e $M_n = 4300$ and $\bar{D} = 1.14$. ^f $M_n = 5100$ and $\bar{D} = 1.34$.

Results and discussion

Exploiting the living character of the obtained polymers, we studied block polymerizations (Table 4 and Fig. 15). Using purified PMMA-I ($M_n = 3800$ and $\bar{D} = 1.26$), PBzMA-I ($M_n = 4300$ and $\bar{D} = 1.14$), and PMEMA-I ($M_n = 5100$ and $\bar{D} = 1.34$) as macroinitiators (synthesized via one-pot RCMP (described in Example 2)), we conducted block polymerizations of BzMA, MMA, MEMA, HEMA and PEGMA, where PMMA, PBzMA, and PMEMA are poly(methyl methacrylate), poly(benzyl methacrylate), and poly(2-methoxyethyl methacrylate), respectively. For the macroinitiators, relatively low molecular-weight polymers were synthesized at relatively low monomer conversions (25–36%) to ensure high iodide-chain-end fidelity. We obtained block copolymers with hydrophobic-hydrophobic (Table 4, entries 1–3 and 6), hydrophobic-amphiphilic (Table 4, entry 5), and hydrophobic-hydrophilic (Table 4, entry 4) segments with $M_n = 8000$ –14100 and $\bar{D} = 1.21$ –1.59. The GPC chromatograms (Fig. 15) smoothly shifted, suggesting that large portions of the macroinitiators were extended to block copolymers (high block efficiencies). The results demonstrate accessibility to a range of block copolymers using macroinitiators synthesized via one-pot RCMP.

Random copolymerizations using BrPhE-OH as the initiator were also conducted on monomer couples of MMA/BzMA, MMA/HEMA and BA/MEA. Relatively low-dispersity random copolymers ($\bar{D} = 1.16$ –1.46) were obtained with 35–82% monomer conversions (Table 5, entries 1–3) at high initiation efficiencies (58–75%) from BrPhE (Figs. 16–18) for all cases. These results illustrate the one-pot RCMP from alcohols contributes to the construction of various polymer architectures.

Table 5. Synthesis of random copolymers via one-pot RCMP.

Entry	Alcohol	M1	M2	$\frac{[M1]_0/[M2]_0}{[R-OH]_0/[BNI]_0^a}$	T (°C)	t (h)	M_n^b $\langle M_{n,theo}^c \rangle$	$\bar{D}^b$	Conv. (%) ^d
1	BrPhE- OH	MMA	BzM A	4000/4000/80/160	80	5	14200 <11300>	1.46	M1
									82%
									M2 80%
2	BrPhE- OH	MMA	HEM A	4000/4000/80/160	80	24	5200 <4500>	1.37	M1
									42%
									M2 35%
3	BrPhE- OH	BA	MEA	4000/4000/80/160	110	48	7400 <5700>	1.16	M1
									45%
									M2 41%

^aThe solvent was diglyme. The solvent/monomer ratio was 10/90 (w/w) during the polymerization step; ^b M_n and $\bar{D}$ values determined using THF-GPC for all other entries, which were calibrated with PMMA standard; ^cTheoretical M_n ($M_{n,theo}^c$) calculated according to $([M1]_0/[R-OH]_0) \times \text{conversion} \times (\text{molecular weight of monomer 1}) + ([M2]_0/[R-OH]_0) \times \text{conversion} \times (\text{molecular weight of monomer 2}) + (\text{molecular weight of alkyl iodide generated from R-OH})$; ^dMonomer conversion determined using ¹H NMR.

Example 4. One-pot grafting of polymers from lignin

One-pot grafting of polymers from lignin

A typical one-pot grafting of polymer from lignin was conducted as follows (Table 6, entry 1). To a dispersion of lignin (0.05 g, 0.08 mmol) and PMHS (0.075 g, 1.25 mmol of Si-H unit) in diglyme (0.83 g), iodine (0.032 g, 0.125 mmol) was added under an argon atmosphere. The mixture was stirred at 70 °C for 120 min. To this mixture, MMA (2.5 g, 25 mmol) and BNI (0.092 g, 0.25 mmol) were added under an argon flow. The mixture was then heated at 80 °C. After prescribed times, an aliquot (0.1 mL) of the mixture was taken out by a syringe, cooled to room temperature, and analyzed with GPC and ¹H NMR. After 6 h of polymerization at 80 °C, the mixture was diluted with THF and purified by reprecipitation in a mixture of hexane/ethanol (8/2 (v/v)) three times. The purified PMMA-g-Lignin was dried in vacuo for further analysis and film fabrication.

Table 6. One-pot RCMP from lignin.

Entry	Monomer	Lignin (wt % of Monomer)	[Monomer] ₀ ^a / [Lignin] ₀ ^a / [BN] ₀ ^a	T (°C)	t (h)	Monomer Conv. (%) ^b	M _n ^c	D ^c	Polymer/Lignin Composition (w/w) ^d	Sample Code
1	MMA	2	300/1/1.5	80	24	10	130000	1.45	83/17	PMMA-g-Lignin (83/17)
					48	22	270000	1.70	92/8	PMMA-g-Lignin (92/8)
					72	36	400000	1.75	95/5	PMMA-g-Lignin (95/5)
2	MMA	4	150/1/1.5	80	48	18	150000	2.26	82/18	PMMA-g-Lignin (82/18)
3	MMA	6	100/1/1	80	48	14	94000	2.11	70/30	PMMA-g-Lignin (70/30)
4	MMA	8	75/1/0.75	80	48	16	78000	1.92	67/33	PMMA-g-Lignin (67/33)
5	BzMA	1.1	300/1/1.5	80	48	58	420000	1.52	98/2	PBzMA-g-Lignin (98/2)
6	Bz	1.2	300/1/1.5	110	24	71	49000	2.17	98/2	PBzA-g-Lignin (98/2)

^aA mixture of lignin (1 equiv. of lignin molecules and approximately 0.45 equiv. of benzylic alcohols), I₂ (1.5 equiv.), and PMHS (15 equiv. of Si-H) was heated in diglyme at 70 °C for 2 h to convert R-OH to R-I (iodination). In the same pot (unpurified solution), monomer and BNI were added, and the polymerization was conducted. The diglyme/monomer ratio was 25/75 (w/w) during the polymerization step. ^bMonomer conversion determined with ¹H NMR. ^cM_n and D values determined with PMMA-calibrated DMF-GPC (entry 6) or THF-GPC (other entries). ^dPolymer/Lignin Composition = [(initial weight of monomer) × (monomer conversion)] / (initial weight of lignin).

Results and discussion

We studied one-pot grafting from lignin by initiating from its benzylic alcohols (Table 6, entry 1). We first heated a mixture of lignin ($M_n = 600$) (1 equiv. of lignin molecules and approximately 0.45 equiv. (D. V. Evtuguin *et al.*, *J. Agric. Food Chem.* **2001**, *49*, 4252–4261; and P. M. Froass, A. J. Ragauskas & J.-e. Jiang, *J. Wood Chem. Technol.* **1996**, *16*, 347–365) of benzylic alcohols), I_2 (1.5 equiv.), and PMHS (15 equiv. of Si-H) in diglyme at 70 °C for 2 h for iodination. Lignin was not fully dissolved in diglyme (solvent) but was dispersed, as the mixture appeared turbid. To this mixture (25 wt%), we added MMA (75 wt%) (300 equiv.) and BNI (1.5 equiv.) and heated the reaction mixture at 80 °C, where the amount of lignin was 2 wt% of MMA. Although the polymerization was relatively slow, the monomer conversion gradually increased to reach 10, 22, and 36% for 24, 48, and 72 h of polymerization, respectively. In contrast to the original lignin, the PMMA-grafted lignin exhibited improved solubility, as the polymerization mixture appeared transparent by eyes although lignin molecules would still form nanometer-sized aggregates at molecular levels. The M_n value of the resultant PMMA-grafted lignin (aggregates) increased from 130000 to 400000 from 24 h to 72 h with $\bar{D}$ values of 1.45–1.75, suggesting the growth of the grafted polymer chains. We also varied the lignin content from 2 wt% to 4, 6, and 8 wt% of MMA, yielding PMMA-grafted lignin (aggregates) with M_n values of 78000–150000 and $\bar{D}$ values of 1.92–2.26 (Table 6, entries 2–4). We obtained PMMA-grafted lignin with varied PMMA/lignin compositions from 95/5 to 67/33 (w/w) (Table 6, entries 1–4). The relatively large $\bar{D}$ values of 1.45–2.26 would be ascribed to nanometer-sized random aggregation of lignin at molecular levels. To obtain indirect but possible information of the grafting position of PMMA on lignin, we conducted model experiments. Namely, we studied one-pot polymerization from 2-phenylethanol and 4-methoxyphenol as models of aliphatic alcohol and phenolic alcohol of lignin, respectively (Table 7). No polymerization took place from the two alcohols, suggesting that benzylic alcohol of lignin (rather than aliphatic alcohol or phenolic alcohol of lignin) would be the grafting position.

Table 7. One-pot RCMP of MMA from aliphatic primary alcohol and phenolic alcohol.

Entry	R-OH	Monomer	[Monomer] ₀ /[R-OH] ₀ /[BNI] ₀ ^a	T (°C)	t (h)	Monomer Conv. (%) ^b	M_n	$\bar{D}$
1	2-Phenylethanol	MMA	100/1/2	80	24	0	NA	NA
2	4-Methoxyphenol	MMA	100/1/2	80	24	0	NA	NA

^aA solution of R-OH (1 equiv.), I_2 (1 equiv.), and PMHS (5 equiv. of Si-H) was heated in diglyme at 70 °C for 120 min (both entries). The concentration of R-OH in the iodination process was 0.84 M (both entries). In the same pot (unpurified solution), monomer and BNI

were added, and the polymerization was conducted. The diglyme/monomer ratio was 10/90 (w/w) during the polymerization step. ^bMonomer conversion determined with ¹H NMR.

Fig. 22 shows infra-red (IR) spectra of pure PMMA, pure lignin, and PMMA-*g*-Lignin (95/5) (Table 6, entry 1 for 72 h) purified via reprecipitation in a hexane/ethanol mixed solvent (8/2 (v/v)). The PMMA-*g*-Lignin clearly showed peaks for both aromatic ring originated from lignin (at ca. 1600 cm⁻¹) and carbonyl group originated from PMMA (at ca. 1730 cm⁻¹), confirming the successful grafting of PMMA from lignin.

We also successfully grafted another methacrylate BzMA and an acrylate BzA from lignin to yield polymergrafted lignin (aggregates) with $M_n = 49000\text{--}420000$ and $\bar{D} = 1.52\text{--}2.17$ (Table 6, entries 5 and 6). The monomer conversion of BzMA (58% for 48 h) (Table 6, entry 5) was higher than those of MMA (14–22% for 48 h) (Table 6, entries 1–4) because of the large propagation rate constant (k_p) for BzMA.

We studied thermal properties of the obtained polymergrafted lignin using DSC (Fig. 23a) and thermogravimetric analysis (TGA) (Fig. 24). The polymer-grafted lignin had a significantly higher glass transition temperature (T_g) than the neat polymer because of the high T_g value of lignin (151 °C) (Fig. 23a). The T_g value was 129 °C for PMMA-*g*-lignin (95/5), which is higher than 93 °C for neat PMMA, 68 °C for PBzMA-*g*-lignin (98/2), which is higher than 53 °C for neat PBzMA, and 13 °C for PBzA-*g*-lignin (98/2), which is higher than 7 °C for neat PBzA. The polymer-grafted lignin had a single T_g value instead of two distinct T_g values for polymer and lignin for all cases, suggesting that the polymer-grafted lignin is not phaseseparated but is present homogeneously. Thus, compared with neat polymer, polymer-*g*-lignin clearly improved the thermal stability of polymers.

The decomposition temperature (5% weight loss temperature) ($T_{d5\%}$) of the polymer-grafted lignin was enhanced by 22–27 °C comparing with that of the neat polymer and remained >300 °C for all cases (Fig. 24), suggesting stable grafting of polymer from lignin.

Fig. 24 shows TGA curves of polymer-grafted lignins, pure polymers, and pure lignin. The 5% decomposition temperatures (5% weight loss temperatures) ($T_{d5\%}$) of the polymer-grafted lignins (307–352 °C) were higher than those of the neat polymers (285–325 °C) by 22–27 °C, although that of pure lignin was 259 °C, which is lower than those of the neat polymers (285–325 °C). The exact reason for the observed higher $T_{d5\%}$ values of the polymer-grafted lignins than those of the pure polymers is unclear at the moment. A possible explanation would

be as follows. Pure lignin decomposed at a broad range of temperature. A majority of pure lignin was still stable even above 350 °C. The 50% decomposition temperature (50% weight loss temperature) ($T_{d50\%}$) of pure lignin is as high as 478 °C. As a whole, a majority of lignin components have high thermal stability, which would afford additional thermal stability to polymers in polymer-grafted lignins and thereby increase the $T_{d5\%}$ values of the polymer-grafted lignins compared to those of the neat polymers. This explanation is not conclusive but is viewed as a possible hypothesis.

Thus, in the present disclosure, as a particularly useful application, we explored one-pot RCMP from lignin. Lignin contains secondary benzylic alcohols, primary aliphatic alcohols, and phenolic alcohols (Fig. 25). Via direct initiation from the benzylic alcohols, we attained one-pot grafting of polymers from lignin (Fig. 25) without tedious initiator attachment and purification, giving a practical breakthrough (a reduction in the costly additional processes) in the polymergrafting from lignin. Furthermore, RCMP is free from metals and odour and uses only inexpensive agents, which also solves other important issues, i.e., removal of metallic and odorous agents and high cost of agents. Thus, one-pot RCMP may serve as a practically useful approach to obtain value-added lignin-polymer composites.

Example 5. UV absorption of PMMA/PMMA-g-Lignin composite film

Film fabrication for UV absorption measurements

PMMA-g-Lignin (95/5) (0.015 g, 6 wt%) and PMMA ($M_n = 5000$, 0.225 g, 94 wt%) were fully dissolved in THF (1.5 g) to form a homogeneous solution. The solution was then casted in a 5 cm diameter glass Petri dish and put in an oven at 70 °C. The complete evaporation of THF from the casting solution resulted in the formation of PMMA/PMMA-g-Lignin composite film (99.7 wt% of PMMA and 0.3 wt% of lignin as a whole). The thickness of the prepared film was about 100 μm . A neat PMMA film and a PMMA/Lignin-blended film containing 99.7 wt% of PMMA and 0.3 wt% of lignin were also similarly prepared as references.

Results and discussion

Lignin absorbs UV light encompassing all of UV-A (315–400 nm), UV-B (280–315 nm) and UV-C (200–280 nm) and serves as natural broad-spectrum sunscreens and anti-aging agents of organic plastics and films owing to the abundance of aromatic rings present in lignin (X. Liu *et al.*, *Int. J. Biol. Macromol.* **2015**, *81*, 521–529; and Y. Li *et al.*, *ACS Sustainable Chem. Eng.* **2022**, *10*, 11856–11866). However, mere physical blending of lignin with synthetic polymers

causes phase-separation and gives opacity or limited UV-shielding properties due to their immiscibility (F. Isnard *et al.*, *Biomacromolecules* **2022**, 23, 3174–3185).

The immiscibility problem can be solved by using polymer-grafted lignin. We prepared an approximately 100 μm thick film by mixing pure PMMA (94 wt%) with PMMA-*g*-Lignin (95/5) (6 wt%), which contained 99.7 wt% of PMMA and 0.3 wt% of lignin as a whole (Fig. 23b). A neat PMMA film exhibited more than 80% transmittance in a 260–400 nm UV region (Fig. 23c). The obtained PMMA/PMMA-*g*-Lignin film reduced transmittance of UV-A to 2.7–25.3%, UV-B to 0.2–2.7%, and UV-C to 0–6.7% (Fig. 23c). A physical blending film of pure PMMA and unmodified lignin exhibited absorption in the UV region to some extent, but its transmittance (transparency) in the visible region significantly decreased (Fig. 23c) because of the incompatibility between PMMA and lignin. By the mere physical blending (Fig. 23d), lignin formed large aggregates in the PMMA matrix because of the immiscibility, making the film less transparent. In sharp contrast (Fig. 23d), PMMA-*g*-Lignin was uniformly embedded in the PMMA matrix because of the high miscibility, affording more optical transparency in the visible region. UV-B is particularly harmful to skin, and the protection from UV-B is crucial to commercially available UV-absorption products. The UV-B protection is quantitatively evaluated by Sun Protection Factor (SPF) defined as:

$$\text{SPF} = \text{CF} \times \sum_{290}^{320} \text{EE}(\lambda) \times \text{I}(\lambda) \times \text{Abs}(\lambda)$$

where CF is a correction factor (10 as a constant), EE (λ) is an erythral spectral effectiveness with wavelength λ , I (λ) is a solar intensity with wavelength λ , Abs (λ) is a spectrophotometric absorbance value at wavelength λ (Table 8) (E. A. Dutra *et al.*, *Rev. Bras. Cienc. Farm.* **2004**, 40, 381–385). The SPF value for the PMMA/PMMA-*g*-Lignin composite film was 21.9, which is much higher than that of the neat PMMA (0.5) film or the PMMA/Lignin blend film (8.4). The direct UV protection percentage, which is calculated as $100 - (100/\text{SPF})$, was 95.4% for the PMMA/PMMA-*g*-Lignin film. The result indicates an excellent UV-B barrier property that is comparable to commercial sunscreen products (93–99% for SPF15–100 products) (W. Wang *et al.*, *Chem. Eng. J.* **2021**, 404, 126358; and F. J. Moloney, S. Collins & G. M. Murphy, *Am. J. Clin. Dermatol.* **2002**, 3, 185–191). The PMMA/PMMA-*g*-Lignin film was slightly yellow in color (Fig. 23b) but still maintained high transparency in a visible region (above 80% transmittance at >500 nm). The results demonstrate a successful application of PMMA-*g*-Lignin for a UV-absorbing film.

Table 8. SPF calculation.

Wavelength	290 nm	295 nm	300 nm	305 nm	310 nm	315 nm	320 nm
EE × I	0.0150	0.0817	0.2874	0.3278	0.1864	0.0839	0.0180
Abs (PMMA)	0.064	0.055	0.052	0.051	0.049	0.047	0.046
Abs (PMMA/Lignin)	1.006	0.911	0.873	0.846	0.804	0.740	0.659
Abs (PMMA/PMMA-g-Lignin)	2.644	2.662	2.488	2.189	1.863	1.564	1.349

Example 6. One-pot grafting polymerization from large weight percent of lignin

One-pot grafting polymerization also conducted from larger weight of lignin to produce higher content of lignin in lignin-g-PMMA. Similar to the previous study of polymerization from small weight percent of lignin, the experiments start with initiating from the benzylic alcohols. We first heated a mixture of lignin ($M_n = 600$) (0.32 equiv.), I_2 (0.5 equiv.), and PMHS (5 equiv. of silane units) in diglyme at 70 °C for 2 h for iodination. Lignin was not fully dissolved in diglyme (solvent) but was dispersed, as the mixture appeared turbid. Several reaction mixtures with different mol ratio of MMA, BNI and Azobisisobutyronitrile (AIBN) are conducting as shown in Table 9. All the reaction mixture was heated at 80 °C. The polymerization was relatively faster after addition of azo initiator AIBN and increment dosage of BNI catalyst. The monomer conversion gradually increased in a short period of polymerization time. In this study, few sets of experiments were conducted to produce Lignin-g-PMMA with different higher lignin contents (20 wt.% to 50 wt.% of MMA), which is higher from previous section, giving polymer-grafted lignin (aggregates) with M_n values of 2100 to 110000 with $\bar{D}$ values of 1.28 to 1.60 (Table 9, entries 1-8).

Table 9. One-pot grafting polymerization from large weight percent of lignin (Source: Sigma).

Entry	Sample Code	Diglyme (%) ^a	Lignin (wt.%)	[M] ₀ /[Lignin] ₀ /[BN] ₀ /[AIBN]	T (°C)	t (h)	M _n ^b	Đ ^b	Conv. (%) ^c
1	Lignin-g-PMMA(20%-5)	40	20	3000/100/100/0	80	5	23000	1.35	8
2	Lignin-g-PMMA(20%-5)	40	20	3000/100/20/30	80	5	13000	1.42	15
3	Lignin-g-PMMA(20%-5)	40	20	3000/100/100/30	80	5	110000	1.58	80
4	Lignin-g-PMMA(30%-5)	50	30	1200/100/100/30	80	5	65000	1.60	71
5	Lignin-g-PMMA(40%-5)	60	40	900/100/100/50	80	5	48000	1.57	77
6	Lignin-g-PMMA (50%-5)	60	50	600/100/20/10	80	5	26000	1.28	10
7	Lignin-g-PMMA(50%-5)	60	50	600/100/20/30	80	5	32000	1.31	14
8	Lignin-g-PMMA(50%-5)	60	50	600/100/100/50	80	5	2100	1.28	60

^aDiglyme percentage determined is the weight percentage of diglyme over total weight of monomer, lignin and diglyme; ^bM_n and Đ values determined by THF-GPC calibrated with PMMA standard; ^cMonomer conversion determined using ¹H NMR.

Table 10. One-pot grafting polymerization from large weight percent of lignin using different solvent (Source: Sigma).

Entry	Sample Code	Solvent	Solvent (%) ^a	Lignin (wt.%)	[M] ₀ /[Lignin] ₀ /[BN] ₀ /[AIBN]	T (°C)	t (h)	M _n ^b	Đ ^b	Conv. (%) ^c
1	Lignin-g-PMMA(20%-5)	Butyl Acetate	80	40	900/100/100/50	80	5	24000	1.58	53
2	Lignin-g-PMMA(20%-5)	Toluene + DMSO (1:1)	50	40	900/100/100/50	80	5	2500	1.56	13
3	Lignin-g-PMMA(20%-5)	Toluene	40	40	900/100/100/50	80	5	2100	1.48	10
4	Lignin-g-PMMA (20%-5)	1-4 Dioxane	40	40	900/100/100/50	80	5	14000	1.43	42

^aDiglyme percentage determined is the weight percentage of diglyme over total weight of monomer, lignin and diglyme; ^bM_n and Đ values determined by THF-GPC calibrated with PMMA standard; ^cMonomer conversion determined using ¹H NMR.

The one-pot grafting polymerization was also conducted in different solvent as shown in Table 10. Butyl acetate, toluene, and 1,4-dioxane, and combination of toluene with DMSO (1:1) are used. Higher percentage of butyl acetate is added during the one-pot grafting polymerization as it is a relatively non-polar solvent which may not be compatible to dissolve the polar and hydrogen bonding functional present in lignin. As a result, the lignin may have absorbed or absorbed the butyl acetate, leading to a gel-like mixture rather than homogenous solution (A. Dastpak *et al.*, *Ind. Crops Prod.* **2020**, 148, 112310). Toluene is a non-polar aromatic solvent. In this case, lignin has limited solubility in toluene, leading to heterogeneous reaction condition and low conversion of MMA monomer. 1,4-Dioxane is less polar than butyl acetate. This difference in polarity can affect the solvation of the growing polymer chains and the monomer (MMA), potentially influencing the conversion of MMA during polymerization.

Another two alternative lignin are used to produce Lignin-g-PMMA. Table 11 shows the results of one-pot grafting polymerization from another source of lignin. The conversion of MMA is higher after the increment dosage of AIBN.

Table 12 shows the results of one-pot grafting polymerization using lignin from Ingevity. The experiment conditions of polymerization using Ingevity is the same as the no source stated lignin. However, the conversion of MMA after polymerization with Ingevity lignin is lower than no source stated lignin. This is due to the degree of iodination can vary depending on the reactivity of the lignin structure, which is influence by their functional groups and accessibility of reactive sites. In other words, different lignin sources will exhibit different degrees of iodination, leading to different concentrations of initiating sites for the polymerization reaction, affecting the conversion of MMA (A. K. Sangha *et al.*, *J. Phys. Chem. B*, **2014**, 118, 164-170).

Table 11. One-pot grafting polymerization from large weight percent of lignin (no source stated).

Entry	Sample Code	Diglyme (%) ^a	Lignin (wt.%)	[M] ₀ /[Lignin] ₀ /[BNI] ₀ /[AIBN]	T (°C)	τ (h)	M _n ^b	Đ ^b	Conv. (%) ^c
1	Lignin-g-PMMA(3%-4)	20	3	160000/100/75/10	80	4	NA	NA	24
2	Lignin-g-PMMA(10%-4)	50	10	6000/100/75/10	80	4	NA	NA	40
3	Lignin-g-PMMA(20%-4)	60	20	3000/100/75/10	80	4	NA	NA	38
4	Lignin-g-PMMA(20%-4)	40	20	3000/100/75/10	80	4	NA	NA	60
5	Lignin-g-PMMA(20%-4)	50	20	3000/100/162/10	80	4	NA	NA	50
6	Lignin-g-PMMA(20%-4)	60	20	3000/100/75/40	80	4	NA	NA	94

^aDiglyme percentage determined is the weight percentage of diglyme over total weight of monomer, lignin and diglyme; ^bM_n and Đ values determined by THF-GPC calibrated with PMMA standard; ^cMonomer conversion determined using ¹H NMR.

Table 12. One-pot grafting polymerization from large weight percent of lignin (Source: Ingevity).

Entry	Sample Code	Diglyme (%) ^a	Lignin (wt.%)	[M] ₀ /[Lignin] ₀ /[BN] ₀ /[AIBN]	T (°C)	t (h)	M _n ^b	D ^b	Conv. (%) ^c
1	Lignin-g-PMMA(3%-4)	20	3	16000/100/75/10	80	4	NA	NA	13
2	Lignin-g-PMMA(10%-4)	50	10	6000/100/75/10	80	4	NA	NA	21
3	Lignin-g-PMMA(20%-4)	60	20	3000/100/75/10	80	4	NA	NA	14
4	Lignin-g-PMMA(20%-4)	40	20	3000/100/75/10	80	4	NA	NA	30
5	Lignin-g-PMMA(20%-4)	50	20	3000/100/162/10	80	4	NA	NA	33
6	Lignin-g-PMMA(20%-4)	60	20	3000/100/75/40	80	4	NA	NA	88

^aDiglyme percentage determined is the weight percentage of diglyme over total weight of monomer, lignin and diglyme; ^bM_n and D values determined by THF-GPC calibrated with PMMA standard; ^cMonomer conversion determined using ¹H NMR.

Example 7. One-pot grafting polymerization from cellulose

Inspired by the results of lignin-grafted polymers, we also studied one-pot grafting from cellulose (Table 13, entry 1). We first heated a mixture of cellulose ($M_n = 70000$) (0.0028 equiv., 1.23 equiv. by unit), I_2 (0.5 equiv.), and PMHS (5 equiv. of silane units) in diglyme at 70 °C for 2 h for iodination. Cellulose was not dissolved in diglyme (solvent) but was dispersed, as the mixture appeared turbid. To this mixture (25 wt. %), we added MMA (75 wt. %) (100 equiv.) and BNI (0.5 equiv.) and heated the reaction mixture at 80 °C, where the amount of cellulose was 8 wt. % of MMA. Although the polymerization was relatively slow, the monomer conversion gradually increased and reached 26% for 48 h of polymerization. In contrast to the original cellulose, the polymer-grafted cellulose exhibited improved solubility in organic solvents such as THF, as the polymerization mixture appeared transparent by eyes although cellulose molecules would still form nanometer-sized aggregates at molecular levels. The M_n value of the resultant polymer-grafted cellulose (aggregates) determined by PMMA-calibrated GPC was 1140000 with a $\bar{D}$ value of 2.02. We also studied one-pot grafting from (hydroxypropyl)methyl cellulose (HPM cellulose) with the same content of 8 wt. %, giving polymer-grafted HPM cellulose (aggregates) with M_n values of 290000 with a $\bar{D}$ value of 1.75 (Table 13, entry 2).

We also studied one-pot grafting from cellulose with varying MMA content (Table 14, entries 1-3). We first heated a mixture of cellulose (1 equiv. by unit), I_2 (1 equiv.), and PMHS (5 equiv. of silane units) in diglyme at 70 °C for 2 h for iodination. Cellulose was not dissolved in diglyme (solvent) but was dispersed, as the mixture appeared turbid. To this mixture, we added varying MMA (10 - 100 equiv.) and BNI (2 equiv.) and heated the reaction mixture at 80 °C. In contrast to the original cellulose, the polymer-grafted cellulose exhibited improved solubility in organic solvents such as THF. Additionally, by varying the MMA contents between 10 – 100 equiv, we were able to synthesize MMA-grafted cellulose with M_n values of 85000–940000 with $\bar{D}$ values of 2.24–5.79.

We also successfully grafted another methacrylate, BzMA and an acrylate, BzA from cellulose to yield polymer-grafted cellulose with $M_n = 52000$ –64000 and $\bar{D} = 1.96$ –2.69 (Table 14, entries 4 and 5).

Table 13. One-pot grafting polymerization from cellulose.

Entry	Sample Code	(HPM) cellulose (wt. %)	Solvent ^a	[M] ₀ /[HPM cellulose] ₀ /[BNI] ₀ ^a	T (°C)	τ (h)	M _n ^b	Đ ^b	Conv. (%) ^c
1	Cellulose-g-PMMA(8%-48)	8	Diglyme	8000/0.23/40	80	48	1140000	2.02	26
2	HPM cellulose-g-PMMA(8%-48)	8	Diglyme	8000/0.18/40	80	48	290000	1.75	16

^aThe solvent was 25/75 (w/w) to the monomer, sourced from the iodination step. [HPM cellulose]₀ means the molar concentration of β-glucose unit.; ^bM_n and Đ values determined by THF-GPC calibrated with PMMA standard; ^cMonomer conversion determined using ¹H NMR.

Table 14. One-pot grafting polymerization from cellulose.

Entry	Sample Code	Cellulose (wt. %)	Solvent ^a	[M] ₀ /[cellulose] ₀ /[BNI] ₀ ^a	T (°C)	τ (h)	M _n ^b	Đ ^b
1	Cellulose-g-PMMA	1.2	Diglyme	8000/1/160	80	24	940 000	5.79
2	Cellulose-g-PMMA	2.4	Diglyme	4000/1/160	80	24	500 000	3.70
3	Cellulose-g-PMMA	10.5	Diglyme	800/1/160	80	24	85 000	2.24
4	Cellulose-g-PBzMA	0.7	Diglyme	8000/1/160	80	24	52 000	1.96
5	Cellulose-g-PBMA	1.1	Diglyme	8000/1/160	80	24	140 000	1.28
6	Cellulose-g-PLMA	0.6	Diglyme	8000/1/160	80	24	13 000	1.65
7	Cellulose-g-PDMAEMA	1.0	Diglyme	8000/1/160	80	24	67 000	3.14
8	Cellulose-g-PHEMA	1.2	Diglyme	8000/1/160	80	24	43 000	1.83
9	Cellulose-g-PBzA	0.7	Diglyme	8000/1/160	100	24	64 000	2.69

^aThe solvent was 25/75 (w/w) to the monomer (Cellulose and Comonomer). [cellulose]₀ means the molar concentration of β-glucose unit.; ^bM_n and Đ values determined by DMF-GPC for entries 7 and 8 and THF-GPC for the other entries calibrated with PMMA standard.

Example 8. Optimization of the ratio of iodine and PMHS in one-pot grafting polymerization

We conducted different sets of mixtures of different lignin ($M_n = 600$), I_2 and PMHS in diglyme at 70 °C for 2 h for iodination as shown in Table 15. After the iodination, polymerization was conducted for each set. All the reaction mixture was heated at 80 °C. In the present disclosure, the experiments were conducted to produce Lignin-g-PMMA with higher lignin contents (50 wt.% of MMA), (Table 15, entries 1-4) and (Table 16, entries 1-4). The findings from both no source lignin and Ingevity lignin revealed that when the iodine and PMHS are in excess, it has the potential to lead to solubility issues, which might contribute to lower MMA conversion.

Table 15. Optimization of iodination reaction for polymerization. (Source: No source).

Iodination	Entry	Solvent	Lignin (M)	Iodine (M)	PMHS (M)	T (°C)	t (h)	Polymerization	[MMA] ₀ /[Lignin] ₀ /[BNI] ₀ /[AIBN] (M)	T (°C)	t (h)	Conv. (%) ^a
	1	Diglyme	1	1.5	15	70	2					
	2	Diglyme	1	0.15	1.5	70	2					
	3	Diglyme	1	0.15	1.5	70	2					
	4	Diglyme	1	0.015	0.15	70	2					

a. The reaction conversion was determined by ¹H-NMR.

Table 16. Optimization of iodination reaction for polymerization. (Source: Ingevity).

Iodination	Entry	Solvent	Lignin (M)	Iodine (M)	PMHS (M)	T (°C)	t (h)	Polymerization	[MMA] ₀ /[Lignin] ₀ /[BNI] ₀ /[AIBN] (M)	T (°C)	t (h)	Conv. (%) ^a
	1	Diglyme	1	1.5	15	70	2					
	2	Diglyme	1	0.15	1.5	70	2					
	3	Diglyme	1	0.15	1.5	70	2					
	4	Diglyme	1	0.015	0.15	70	2					

5 a. The reaction conversion was determined by ¹H-NMR.

Example 9. One-pot grafting polymerization of different monomer from large weight percent of lignin (in diglyme)

5 One-pot grafting polymerization was conducted from larger weight of lignin to produce higher content of lignin in lignin-g-PMMA. The experiments started with initiating from the benzylic alcohols. A mixture of lignin (0.015 M), I_2 (0.15 M), and PMHS (0.15 M) was first heated at 70 °C for 2 h for iodination in diglyme. Different monomers were polymerized as shown in Table 17 and Table 18.

Table 17. Optimization of iodination reaction for polymerization. (Source: No source).

Entry	Sample Code	Monomer	Diglyme (%) ^a	Lignin (wt.%) ^b	[M] ₀ /[Lignin] ₀ /[BN] ₀ /[AIBN]	T (°C)	t (h)	Conv. (%) ^c
1	Lignin-g-BMA(50%-4)	BMA	50	50	420/100/80/40	80	4	98
2	Lignin-g-BzMA(50%-4)	BzMA	50	50	340/100/80/40	80	4	89
3	Lignin-g-SMA(50%-4)	SMA	50	50	180/100/80/40	80	4	78

a. Diglyme percentage determined is the weight percentage of diglyme over total weight of monomer, lignin and diglyme; b. Lignin percentage determined is the weight percentage of lignin over total weight of monomer and lignin; c. Monomer conversion determined using ¹H NMR.

5

Table 18. Optimization of iodination reaction for polymerization. (Source: Ingevity).

Entry	Sample Code	Monomer	Diglyme (%) ^a	Lignin (wt.%) ^b	[M] ₀ /[Lignin] ₀ /[BN] ₀ /[AIBN]	T (°C)	t (h)	Conv. (%) ^c
1	Lignin-g-BMA(50%-4)	BMA	50	50	420/100/80/40	80	4	98
2	Lignin-g-BzMA(50%-4)	BzMA	50	50	340/100/80/40	80	4	98
3	Lignin-g-SMA(50%-4)	SMA	50	50	180/100/80/40	80	4	97

a. Diglyme percentage determined is the weight percentage of diglyme over total weight of monomer, lignin and diglyme; b. Lignin percentage determined is the weight percentage of lignin over total weight of monomer and lignin; c. Monomer conversion determined using ¹H NMR.

Example 10. One-pot grafting polymerization of different monomer from large weight percent of lignin (in butyl acetate)

5 One-pot grafting polymerization was conducted from larger weight of lignin to produce higher content of lignin in lignin-g-PMMA. The experiments started with initiating from the benzylic alcohols. A mixture of lignin (0.015 M), I_2 (0.15 M), and PMHS (0.15 M) was first heated at 70 °C for 2 h for iodination in butyl acetate. Different monomers were polymerized as shown in Table 19 and Table 20.

Table 19. Optimization of iodination reaction for polymerization. (Source: No source).

Entry	Sample Code	Monomer	Butyl Acetate (%) ^a	Lignin (wt. %) ^b	[M] ₀ /[Lignin] ₀ /[BN] ₀ /[AIBN]	T (°C)	t (h)	Conv. (%) ^c
1	Lignin-g-EHMA(50%-4)	EHMA	50	50	310/100/80/40	80	4	51
2	Lignin-g-BA(50%-4)	BA	50	50	470/100/80/40	110	4	98
3	Lignin-g-Styrene(50%-4)	Styrene	50	50	580/100/80/40	110	4	74
4	Lignin-g-BMA(50%-4)	BMA	50	50	430/100/80/40	80	4	33
5	Lignin-g-LMA(50%-4)	LMA	50	50	240/100/80/40	80	4	44
6	Lignin-g-BzMA(50%-4)	BzMA	50	50	340/100/80/40	80	4	98
7	Lignin-g-SMA(50%-4)	SMA	50	50	180/100/80/40	80	4	22

a. Butyl Acetate percentage determined is the weight percentage of butyl acetate over total weight of monomer, lignin and butyl acetate; b. Lignin percentage determined is the weight percentage of lignin over total weight of monomer and lignin; c. Monomer conversion determined using ¹H NMR.

Table 20. Optimization of iodination reaction for polymerization. (Source: Ingevity).

Entry	Sample Code	Monomer	Butyl Acetate (%) ^a	Lignin (wt. %) ^b	[M] ₀ /[Lignin] ₀ /[BN] ₀ /[AIBN]	T (°C)	t (h)	Conv. (%) ^c
1	Lignin-g-EHMA(50%-4)	EHMA	50	50	310/100/80/40	80	4	51
2	Lignin-g-BA(50%-4)	BA	50	50	470/100/80/40	110	4	99
3	Lignin-g-Styrene (50%-4)	Styrene	50	50	580/100/80/40	110	4	68
4	Lignin-g-BMA(50%-4)	BMA	50	50	430/100/80/40	80	4	59
5	Lignin-g-LMA(50%-4)	LMA	50	50	240/100/80/40	80	4	21
6	Lignin-g-BzMA(50%-4)	BzMA	50	50	340/100/80/40	80	4	95

7	Lignin-g-SMA(50%-4)	SMA	50	50	180/100/80/40	80	4	30
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a. Butyl Acetate percentage determined is the weight percentage of butyl acetate over total weight of monomer, lignin and butyl acetate; b.Lignin percentage determined is the weight percentage of lignin over total weight of monomer and lignin; c. Monomer conversion determined using ¹H NMR.

Example 11. One-pot grafting polymerization of different monomer from large weight percent of lignin (in 2-butanone)

5 One-pot grafting polymerization was conducted from larger weight of lignin to produce higher content of lignin in lignin-g-PMMA. The experiments started with initiating from the benzylic alcohols. A mixture of lignin (0.015 M), I_2 (0.15 M), and PMHS (0.15 M) was first heated at 70 °C for 2 h for iodination in 2-Butanone. Different monomers were polymerized as shown in Table 21 and Table 22.

Table 21. Optimization of iodination reaction for polymerization. (Source: No source).

Entry	Sample Code	Monomer	2-Butanone (%) ^a	Lignin (wt.%) ^b	[M] ₀ /[Lignin] ₀ /[BNi] ₀ /[AIBN]	T (°C)	t (h)	Conv. (%) ^c
1	Lignin-g-MMA(50%-4)	MMA	50	50	600/100/80/40	70	4	95
2	Lignin-g-EHMA(50%-4)	EHMA	50	50	310/100/80/80	70	4	99
3	Lignin-g-BzMA(50%-4)	BzMA	50	50	340/100/80/40	70	4	99
4	Lignin-g-BMA(50%-4)	BMA	50	50	430/100/80/40	70	4	96
5	Lignin-g-LMA(50%-4)	LMA	50	50	240/100/80/40	70	4	97

a. 2-Butanone percentage determined is the weight percentage of 2-butanone over total weight of monomer, lignin and 2-butanone; b.Lignin percentage determined is the weight percentage of lignin over total weight of monomer and lignin; c. Monomer conversion determined using ¹H NMR.

Table 22. Optimization of iodination reaction for polymerization. (Source: Ingevity).

Entry	Sample Code	Monomer	2-Butanone (%) ^a	Lignin (wt.%) ^b	[M] ₀ /[Lignin] ₀ /[BNi] ₀ /[AIBN]	T (°C)	t (h)	Conv. (%) ^c
1	Lignin-g-MMA(50%-4)	MMA	50	50	600/100/80/40	70	4	95
2	Lignin-g-EHMA(50%-4)	EHMA	50	50	310/100/80/80	70	4	99
3	Lignin-g-BzMA (50%-4)	BzMA	50	50	340/100/80/40	70	4	98
4	Lignin-g-BMA (50%-4)	BMA	50	50	430/100/80/40	70	4	94
5	Lignin-g-LMA(50%-4)	LMA	50	50	240/100/80/40	70	4	94

a. 2-Butanone percentage determined is the weight percentage of 2-butanone over total weight of monomer, lignin and 2-butanone; b.Lignin percentage determined is the weight percentage of lignin over total weight of monomer and lignin; c. Monomer conversion determined using ¹H NMR.

Conclusion

In the present disclosure, we explored a unique method to in situ generate R-I initiators, i.e., from benzylic alcohols, and developed one-pot RCMP using benzylic alcohols as stable precursors. Mechanistically (Fig. 1), a benzylic alcohol (R-OH) reacts with iodinating agents (I₂ and PMHS) to in situ generate an R-I initiator, and the generated R-I is used without purification for polymerization, leading to one-pot RCMP from R-OH. The one-pot RCMP enables direct polymerization from benzylic alcohols in contrast to the two-pot ATRP and RAFT polymerization from alcohols. A variety of commercially available inexpensive or functional benzylic alcohols can be used as precursors (pre-initiators), significantly widening the initiator scope of RCMP.

Thus, one-pot RCMP from secondary benzylic alcohols based on fast and quantitative iodination of secondary benzylic alcohols and the subsequent RCMP via the direct initiation from the generated benzylic iodides without their purification or isolation was developed. One-pot RCMP was amenable to several hydrophobic, functional, and amphiphilic methacrylates and acrylates, demonstrating a wide monomer scope of this technique. The obtained polymers have high iodide-chain-end fidelities and were successfully used as macroinitiators to yield several block copolymers. As a particularly useful application, one-pot RCMP was used to graft polymers from biomass lignin which bears secondary benzylic alcohols. MMA, BzMA, and BzA were polymerized from surfaces of nanometer-sized lignin aggregates via one-pot RCMP. The obtained PMMA-grafted lignin was mixed with pure PMMA to form a UV absorbing film, achieving 95.4% UV protection with a 0.3 wt% lignin content. The direct initiation from lignin eliminates tedious initiator attachment and purification, offering a facile access to polymer-grafted lignin. The iodination step utilizes a low-cost PMHS/I₂ reducing process. RCMP is free from heavy metals and odour and utilizes only inexpensive compounds. One-pot RCMP may serve as a practically useful technique to obtain value-added lignin-polymer composites.

Claims

1. A process to form a polymeric material, the process comprising the steps of:
 - (a) providing a substrate having one or more alcohols and converting at least one of the one or more alcohols to an iodide group to provide a modified substrate;
 - (b) mixing the modified substrate with a first monomer and a first catalyst to provide a first mixture, and subjecting the first mixture to reaction conditions that provide a first polymeric or oligomeric material formed from the first monomer, wherein:
 - the modified substrate acts as an initiator for polymerisation and provides a terminal group in at least one part of the first polymeric or oligomeric material; and
 - the reaction conditions comprise an elevated temperature.
2. The process according to Claim 1, wherein step (b) involves adding in a second monomer after a period of time to provide a block copolymer.
3. The process according to Claim 1 or Claim 2, wherein the first catalyst is tetrabutylammonium iodide (TBAI).
4. The process according to any one of the preceding claims, wherein the modified substrate is obtained by reacting the substrate having one or more alcohols with iodine and polymethylhydrosiloxane.
5. The process according to any one of the preceding claims, wherein the first monomer is selected from one or more of the group consisting of acrylonitrile, styrene, methoxystyrene, butoxystyrene, chloromethyl styrene, chlorostyrene, methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, t-butyl acrylate, hexyl acrylate, 2-ethyl hexyl acrylate, n-octyl acrylate, nonyl acrylate, decanyl acrylate, benzyl acrylate, tetrahydrofurfuryl acrylate, glycidyl acrylate, cyclohexyl acrylate, 2-methoxyethyl acrylate and butoxyethyl acrylate, tris(trialkylsiloxy) derivative-acrylates, and fluoroalkyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, hexyl methacrylate, 2-ethyl hexyl methacrylate, n-octyl methacrylate, nonyl methacrylate, decanyl methacrylate, benzyl methacrylate, tetrahydrofurfuryl methacrylate, glycidyl methacrylate, cyclohexyl methacrylate, 2-methoxyethyl methacrylate, butoxyethyl methacrylate, tris(trialkylsiloxy) derivative-methacrylates, fluoroalkyl methacrylates, hydroxy styrene, styrene sulfonic acid, sodium styrene sulfonic acid, styrene boronic acid, acrylamide, N-isopropyl acrylamide, N,N-dimethyl acrylamide, N-methylol acrylamide, N-hydroxyethyl acrylamide, methacrylamide, N-isopropyl methacrylamide, N,N-dimethyl methacrylamide, N-

methylol methacrylamide, N-hydroxyethyl methacrylamide, acrylic acid, hydroxyalkyl acrylate (e.g. 2-hydroxy ethyl acrylate), 2-hydroxypropyl acrylate, glyceryl monoacrylate, diethylene glycol acrylate, polyethylene glycol acrylate, methoxy tetraethylene glycol acrylate, methoxypolyethylene glycol acrylate, 2-(dimethylamino) ethyl acrylate, 3-chloro-2-hydroxypropyl acrylate, 2-hydroxy-3-phenoxypropyl acrylate, 2-acryloyloxyethyl phosphorylcholine, 2-(N,N-diethyl-N-methyl amino) ethyl acrylate +/trifluorosulfonyliminium salt, 2-(N-ethyl-N-methyl-N-hydrogenation amino) ethyl acrylate +/trifluorosulfonyliminium ($(\text{N}(\text{CF}_3\text{SO}_2)_2)^+$) salt, 1-ethyl-3-methyl imidazolium acrylate +/fluorohydrogenation ($(\text{FH})_n\text{F}^-$) salt, methacrylic acid, 2-hydroxy ethyl methacrylate, 2-hydroxypropyl methacrylate, glyceryl monomethacrylate, diethylene glycol methacrylate and polyethylene glycol methacrylate, methoxy tetraethylene glycol methacrylate, methoxypolyethylene glycol methacrylate, 2-(dimethylamino) ethyl methacrylate, 3-chloro-2-hydroxypropyl methacrylate, 2-hydroxy-3-phenoxypropyl methacrylate, 2-acryloyloxyethyl phosphorylcholine, 2-(N,N-diethyl-N-methyl amino) ethyl methacrylate +/trifluorosulfonyliminium salt, 2-(N-ethyl-N-methyl-N-hydrogenation amino) ethyl methacrylate +/trifluorosulfonyliminium ($(\text{N}(\text{CF}_3\text{SO}_2)_2)^+$) salt, and 1-ethyl-3-methyl imidazolium methacrylate+/ fluorohydrogenation ($(\text{FH})_n\text{F}^-$) salt, diethylene glycol dimethacrylate, diethylene glycol diacrylate, vinyl acetate, N-vinyl pyrrolidone, N-vinyl carbazol, butadiene, ethylene, propylene, butene, pentene, hexene, heptane, octene, vinyl ethers, vinyl ketones, vinyl chloride, acetylene, and phenyl acetylene, optionally wherein the first monomer is selected from one or more of the group consisting of methyl methacrylate, benzyl methacrylate, 2-hydroxyethyl methacrylate, 2-methoxyethyl methacrylate, furfuryl methacrylate and poly(ethylene glycol) methyl ether methacrylate.

6. The process according to any one of the preceding claims, wherein one or both of the following apply:

- (aa) the first monomer comprises a mixture of two or more monomers; and
- (ab) the alcohols in the substrate having one or more alcohols are primary or secondary alcohols.

7. The process according to any one of the preceding claims, wherein the substrate having one or more alcohols is selected from one or more of the group consisting of 1-phenylethanol, 1-(4-bromophenyl) ethanol, (S)-1-phenylethanol, (+)-1-phenylethanol, 1-(4-methylphenyl)ethanol, 4-methylbenzyl alcohol, 1-phenyl-1-propanol, benzyl alcohol, 2-methylbenzyl alcohol, 3-methylbenzyl alcohol, 1-phenylmethanediol, 1-hydroxy-1-phenylethyl, α -isodecyl-benzenemethanol, α -silylbenzenemethanol, 4-hydroxybenzyl alcohol, 4-ethylbenzyl alcohol, 3-hydroxybenzyl alcohol, 4-mercaptobenzenemethanol, 1,4-benzenedimethanol, 3-ethylbenzenemethanol, α -mercaptobenzenemethanol, α -methyl-p-

sec-pentyl-benzyl alcohol, p-sec-decyl- α -methyl-benzyl alcohol, α -methyl-4-sec-nonyl-benzyl alcohol, α -methyl-4-sec-octyl-benzyl alcohol, 4-sec-heptyl- α -methyl-benzyl alcohol, p-sec-hexyl- α -methyl-benzyl alcohol, 2-aminobenzyl alcohol, 3-aminobenzyl alcohol, 4-aminobenzyl alcohol, α -ethynylbenzenemethanol, 2-mercaptobenzenemethanol, 3-mercaptobenzenemethanol, 4-propylbenzenemethanol, (2-ethylphenyl)methanol, [4-(hydroxymethyl)phenyl]lithium, 4-silylbenzenemethanol, ($\pm$)-phenylethanolamine, 1-phenyl-2-propen-1-ol, 2-methyl-1-phenyl-1-propanol, 1-phenyl-1-butanol, 4-ethynylbenzenemethanol, 3,5-dimethylbenzyl alcohol, 1-phenyl-1,2-propanediol, α -phosphinobenzenemethanol, 1-phenylethanol, α -(mercaptomethyl)benzenemethanol, α -iodobenzenemethanol, 4-(mercaptomethyl)benzenemethanol, 4-(hydroxymethyl)benzeneethanol, 2-selenobenzenemethanol, 4-methoxybenzyl alcohol, mandelonitrile, 4-iodobenzyl alcohol, 4-vinylbenzyl alcohol, 2-phenyl-2-butanol, 4-(hydroxymethyl)benzonitrile, α -methylbenzenemethanol-d-ol, 3-(aminomethyl)benzenemethanol, α -bromobenzenemethanol, benzonitrile, α -(borylmethyl)benzenemethanol, 4-isononylbenzenemethanol, α -(methyl-d3)benzenemethanol, α -methylbenzene-2,3,4,5,6-d5-methanol, 4-chlorobenzyl alcohol, 4-bromobenzyl alcohol, 4-fluoro- α -methylbenzyl alcohol, 1-(p-tolyl)ethanol, 4-fluorobenzyl alcohol, 4-(methylthio)benzenemethanol, α -ethyl- α -methylbenzenemethanol, (1S,2R)-(+)-norephedrine, α -hydroxybenzeneacetaldehyde, 5-methyl-1,3-benzenedimethanol, 4-methoxy- α -methylbenzyl alcohol, 2-phenyl-2-propanol, α -methyl-2-naphthalenemethanol, 4-bromo- α -methylbenzyl alcohol, 1-(2,4-dimethoxyphenyl)ethanol, 1-(4-chlorophenyl)ethanol, (1RS)-1-(6-methoxynaphthalen-2-yl)ethanol, (1S,2S)-(+)-pseudoephedrine, 1-(2,4,6-trimethoxyphenyl)ethanol, lignin, methanol, ethanol, 1-butanol, isopropyl alcohol, tert-butanol, 1,3-butanediol, 2-butanol, propanediol, 4,4,4-trifluoro-1-butanol, 2-amino-1-butanol, 4-phenyl-2-butanol, 3-methyl-2-butanol, 4-chloro-1-butanol, 4-bromo-1-butanol, 2-methyl-2-butanol, 3-methoxy-1-butanol, 4-phenyl-1-butanol, 1-amino-2-butanol, 3-(methylamino)-1-butanol, 3-(dimethylamino)-1-butanol, 4-(methylthio)-1-butanol, 1-bromo-2-butanol, 2-(methyldiphenylsilyl)ethanol, 2-(isopropylamino)ethanol, 2-(methylthio)ethanol, 2-(methylphenylamino)ethanol, 2-(isobutylsulfanyl)ethanol, 2-(phenylsulfonyl)ethanol, 2-(trifluoromethoxy)ethanol, lactic acid, ethyl lactate, 2-(trimethylsilyl)ethanol, 1-(4-methylcyclohexyl)ethanol, 2-(2-quinoliny)ethanol, 2-[2-(diethylamino)ethoxy]ethanol, furfuryl alcohol, ($\pm$)-1-(2-furyl)ethanol, tetrahydrofurfuryl alcohol, tetrahydropyran-2-methanol, 1,2,6-hexanetriol, isosorbide, isoidide, isomannide, glycerol, sorbitol, farnesol, cetyl alcohol, stearyl alcohol, octanol, decanol, cetearyl alcohol, behenyl alcohol, arabinol, maltitol, xylaric acid, mannosylerythritol, arabitol, ribitol, isoborneol, myristyl alcohol, lauryl alcohol, oleyl alcohol, 1,1-bis(triphenylsilyl)ethanol, glucose, maltose, xylitol, erythritol, mannitol, ethylene glycol, propylene glycol, trimethylolpropane, pentaerythritol, cellulose, lignocellulose, 2-hydroxyethyl cellulose, ethyl cellulose, hydroxypropyl cellulose, (hydroxypropyl)methyl cellulose, cellulose

triacetate, methyl cellulose, cellulose acetate, cyanoethylated cellulose, cellulose acetate butyrate, cellulose acetate propionate, sodium carboxymethyl cellulose, and hydroxyethyl-cellulose, optionally wherein the substrate is lignin or cellulose.

8. The process according to any one of the preceding claims, wherein the substrate having one or more primary or secondary alcohols is a benzylic alcohol, optionally wherein the benzylic alcohol is selected from one or more of the group consisting of 1-phenylethanol, 1-(4-bromophenyl) ethanol, (S)-1-phenylethanol, (+)-1-phenylethanol, 1-(4-methylphenyl)ethanol, 4-methylbenzyl alcohol, 1-phenyl-1-propanol, benzyl alcohol, 2-methylbenzyl alcohol, 3-methylbenzyl alcohol, 1-phenylmethanediol, 1-hydroxy-1-phenylethyl, α -isodecyl-benzenemethanol, α -silylbenzenemethanol, 4-hydroxybenzyl alcohol, 4-ethylbenzyl alcohol, 3-hydroxybenzyl alcohol, 4-mercaptobenzenemethanol, 1,4-benzenedimethanol, 3-ethylbenzenemethanol, α -mercaptobenzenemethanol, α -methyl-p-sec-pentyl-benzyl alcohol, p-sec-decyl- α -methyl-benzyl alcohol, α -methyl-4-sec-nonyl-benzyl alcohol, α -methyl-4-sec-octyl-benzyl alcohol, 4-sec-heptyl- α -methyl-benzyl alcohol, p-sec-hexyl- α -methyl-benzyl alcohol, 2-aminobenzyl alcohol, 3-aminobenzyl alcohol, 4-aminobenzyl alcohol, α -ethynylbenzenemethanol, 2-mercaptobenzenemethanol, 3-mercaptobenzenemethanol, 4-propylbenzenemethanol, (2-ethylphenyl)methanol, [4-(hydroxymethyl)phenyl]lithium, 4-silylbenzenemethanol, ($\pm$)-phenylethanolamine, 1-phenyl-2-propen-1-ol, 2-methyl-1-phenyl-1-propanol, 1-phenyl-1-butanol, 4-ethynylbenzenemethanol, 3,5-dimethylbenzyl alcohol, 1-phenyl-1,2-propanediol, α -phosphinobenzenemethanol, 1-phenylethanol, α -(mercaptomethyl)benzenemethanol, α -iodobenzenemethanol, 4-(mercaptomethyl)benzenemethanol, 4-(hydroxymethyl)benzeneethanol, 2-selenobenzenemethanol, 4-methoxybenzyl alcohol, mandelonitrile, 4-iodobenzyl alcohol, 4-vinylbenzyl alcohol, 2-phenyl-2-butanol, 4-(hydroxymethyl)benzonitrile, α -methylbenzenemethanol-d-ol, 3-(aminomethyl)benzenemethanol, α -bromobenzenemethanol, benzonitrile, α -(borylmethyl)benzenemethanol, 4-isononylbenzenemethanol, α -(methyl-d3)benzenemethanol, α -methylbenzene-2,3,4,5,6-d5-methanol, 4-chlorobenzyl alcohol, 4-bromobenzyl alcohol, 4-fluoro- α -methylbenzyl alcohol, 1-(p-tolyl)ethanol, 4-fluorobenzyl alcohol, 4-(methylthio)benzenemethanol, α -ethyl- α -methylbenzenemethanol, (1S,2R)-(+)-norephedrine, α -hydroxybenzeneacetaldehyde, 5-methyl-1,3-benzenedimethanol, 4-methoxy- α -methylbenzyl alcohol, 2-phenyl-2-propanol, α -methyl-2-naphthalenemethanol, 4-bromo- α -methylbenzyl alcohol, 1-(2,4-dimethoxyphenyl)ethanol, 1-(4-chlorophenyl)ethanol, (1RS)-1-(6-methoxynaphthalen-2-yl)ethanol, (1S,2S)-(+)-pseudoephedrine, 1-(2,4,6-trimethoxyphenyl)ethanol, and lignin, further optionally wherein the benzylic alcohol is lignin.

9. The process according to any one of the preceding claims, wherein the molar concentration ratio of the modified substrate to the first monomer in step (b) of Claim 1 is from 1:5 to 1:2,000, such as from 1:6 to 1:1,600, such as from 1:9 to 1: 300, such as from 1:10 to 1:100.

10. The process according to any one of the preceding claims, wherein the molar concentration ratio of the modified substrate to the first catalyst in step (b) of Claim 1 is from 1:0.1 to 1:10, such as from 1:0.3 to 1:1.

11. The process according to any one of the preceding claims, wherein the first mixture further comprises a radical initiator, optionally wherein the radical initiator is azobisisobutyronitrile.

12. The process according to any one of the preceding claims, comprising the further step of:

(c) terminating the polymerisation reaction of step (b) in Claim 1 to provide the first polymeric or oligomeric material as a macroinitiator; and

(d) mixing the macroinitiator with a third monomer to provide a second mixture, and subjecting the second mixture to reaction conditions that provide a second polymeric material formed from the third monomer and the macroinitiator.

13. The process according to Claim 12, wherein terminating the polymerisation reaction in step (c) involves cooling the first mixture to a temperature of from 0 to 50 °C, such as around 25 °C.

14. The process according to Claim 12 or Claim 13, wherein the third monomer is selected from one or more of the group consisting of acrylonitrile, styrene, methoxystyrene, butoxystyrene, chloromethyl styrene, chlorostyrene, methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, t-butyl acrylate, hexyl acrylate, 2-ethyl hexyl acrylate, n-octyl acrylate, nonyl acrylate, decanyl acrylate, benzyl acrylate, tetrahydrofurfuryl acrylate, glycidyl acrylate, cyclohexyl acrylate, 2-methoxyethyl acrylate and butoxyethyl acrylate, tris(trialkylsiloxy) derivative-acrylates, and fluoroalkyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, hexyl methacrylate, 2-ethyl hexyl methacrylate, n-octyl methacrylate, nonyl methacrylate, decanyl methacrylate, benzyl methacrylate, tetrahydrofurfuryl methacrylate, glycidyl methacrylate, cyclohexyl methacrylate, 2-methoxyethyl methacrylate, butoxyethyl methacrylate, tris(trialkylsiloxy) derivative-methacrylates, fluoroalkyl methacrylates, hydroxy styrene,

styrene sulfonic acid, sodium styrene sulfonic acid, styrene boronic acid, acrylamide, N-isopropyl acrylamide, N,N-dimethyl acrylamide, N-methylol acrylamide, N-hydroxyethyl acrylamide, methacrylamide, N-isopropyl methacrylamide, N,N-dimethyl methacrylamide, N-methylol methacrylamide, N-hydroxyethyl methacrylamide, acrylic acid, hydroxyalkyl acrylate (e.g. 2-hydroxy ethyl acrylate), 2-hydroxypropyl acrylate, glyceryl monoacrylate, diethylene glycol acrylate, polyethylene glycol acrylate, methoxy tetraethylene glycol acrylate, methoxypolyethylene glycol acrylate, 2-(dimethylamino) ethyl acrylate, 3-chloro-2-hydroxypropyl acrylate, 2-hydroxy-3-phenoxypropyl acrylate, 2-acryloyloxyethyl phosphorylcholine, 2-(N,N-diethyl-N-methyl amino) ethyl acrylate +/trifluorosulfonyliminium salt, 2-(N-ethyl-N-methyl-N-hydrogenation amino) ethyl acrylate +/trifluorosulfonyliminium ($N(CF_3SO_2)_2^-$) salt, 1-ethyl-3-methyl imidazolium acrylate +/fluorohydrogenation ($(FH)_nF^-$) salt, methacrylic acid, 2-hydroxy ethyl methacrylate, 2-hydroxypropyl methacrylate, glyceryl monomethacrylate, diethylene glycol methacrylate and polyethylene glycol methacrylate, methoxy tetraethylene glycol methacrylate, methoxypolyethylene glycol methacrylate, 2-(dimethylamino) ethyl methacrylate, 3-chloro-2-hydroxypropyl methacrylate, 2-hydroxy-3-phenoxypropyl methacrylate, 2-acryloyloxyethyl phosphorylcholine, 2-(N,N-diethyl-N-methyl amino) ethyl methacrylate +/trifluorosulfonyliminium salt, 2-(N-ethyl-N-methyl-N-hydrogenation amino) ethyl methacrylate +/trifluorosulfonyliminium ($N(CF_3SO_2)_2^-$) salt, and 1-ethyl-3-methyl imidazolium methacrylate+/ fluorohydrogenation ($(FH)_nF^-$) salt, diethylene glycol dimethacrylate, diethylene glycol diacrylate, vinyl acetate, N-vinyl pyrrolidone, N-vinyl carbazol, butadiene, ethylene, propylene, butene, pentene, hexene, heptane, octene, vinyl ethers, vinyl ketones, vinyl chloride, acetylene, and phenyl acetylene, optionally wherein the third monomer is selected from one or more of the group consisting of methyl methacrylate, benzyl methacrylate, 2-hydroxyethyl methacrylate, 2-methoxyethyl methacrylate, furfuryl methacrylate and poly(ethylene glycol) methyl ether methacrylate, further optionally wherein the third monomer is different from the first monomer.

15. The process according to any one of Claims 12 to 14, wherein the molar concentration ratio of the macroinitiator to the third monomer in step (d) of Claim 12 is from 1:5 to 1:2,000, such as from 1:6 to 1:1,600, such as from 1:9 to 1: 300, such as from 1:10 to 1:100.

16. The process according to any one of Claims 12 to 15, wherein the molar concentration ratio of the macroinitiator to a total amount of catalyst in step (d) of Claim 12 is from 1:0.1 to 1:10, such as from 1:0.3 to 1:1, wherein the total amount of catalyst refers to the first catalyst alone or, where present, a combination of the first catalyst and a second catalyst.

17. The process according to Claim 16, wherein where present, the second catalyst is tetrabutylammonium iodide (TBAI).

18. A process to form an iodide material, the process comprising the steps of:

- (ai) providing a substrate having one or more aliphatic alcohols; and
- (a ii) converting at least one of the one or more alcohols to an iodide group to provide a modified substrate.

19. The process according to Claim 18, wherein the modified substrate is obtained by reacting the substrate having one or more alcohols with iodine and polymethylhydrosiloxane.

20. The process according to Claim 18 or Claim 19, wherein the substrate having one or more aliphatic alcohols is selected from one or more of the group consisting of methanol, ethanol, 1-butanol, isopropyl alcohol, tert-butanol, 1,3-butanediol, 2-butanol, propanediol, 4,4,4-trifluoro-1-butanol, 2-amino-1-butanol, 4-phenyl-2-butanol, 3-methyl-2-butanol, 4-chloro-1-butanol, 4-bromo-1-butanol, 2-methyl-2-butanol, 3-methoxy-1-butanol, 4-phenyl-1-butanol, 1-amino-2-butanol, 3-(methylamino)-1-butanol, 3-(dimethylamino)-1-butanol, 4-(methylthio)-1-butanol, 1-bromo-2-butanol, 2-(methyldiphenylsilyl)ethanol, 2-(isopropylamino)ethanol, 2-(methylthio)ethanol, 2-(methylphenylamino)ethanol, 2-(isobutylsulfanyl)ethanol, 2-(phenylsulfonyl)ethanol, 2-(trifluoromethoxy)ethanol, lactic acid, ethyl lactate, 2-(trimethylsilyl)ethanol, 1-(4-methylcyclohexyl)ethanol, 2-(2-quinoliny)ethanol, 2-[2-(diethylamino)ethoxy]ethanol, furfuryl alcohol, ($\pm$)-1-(2-furyl)ethanol, tetrahydrofurfuryl alcohol, tetrahydropyran-2-methanol, 1,2,6-hexanetriol, isosorbide, isoidide, isomannide, glycerol, sorbitol, farnesol, cetyl alcohol, stearyl alcohol, octanol, decanol, cetearyl alcohol, behenyl alcohol, arabinol, maltitol, xylaric acid, mannosylerythritol, arabitol, ribitol, isoborneol, myristyl alcohol, lauryl alcohol, oleyl alcohol, 1,1-bis(triphenylsilyl)ethanol, glucose, maltose, xylitol, erythritol, mannitol, ethylene glycol, propylene glycol, trimethylolpropane, pentaerythritol, cellulose, lignocellulose, 2-hydroxyethyl cellulose, ethyl cellulose, hydroxypropyl cellulose, (hydroxypropyl)methyl cellulose, cellulose triacetate, methyl cellulose, cellulose acetate, cyanoethylated cellulose, cellulose acetate butyrate, cellulose acetate propionate, sodium carboxymethyl cellulose, and hydroxyethyl-cellulose, optionally wherein the substrate is cellulose.