

# One-Pot Reversible Complexation Mediated Polymerization (RCMP) from Benzylic Alcohols for Facile Access to Polymer-Grafted Lignin

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**Abstract:** One-pot synthesis of methacrylic and acrylic polymers from benzylic alcohols (R-OH) used as initiating moieties was developed. R-OH was converted to alkyl iodide (R-I), and the generated R-I was used as an initiator without purification or isolation in the subsequent reversible complexation mediated polymerization (RCMP), leading to one-pot RCMP from R-OH. As a useful application, this technique was exploited for one-pot polymer-grafting from lignin that is the second most abundant renewable carbon-source on earth and bears benzylic alcohols. The direct initiation from lignin eliminates tedious initiator attachment and purification, offering a facile access to polymer-grafted lignin. The obtained polymer-grafted lignin was utilized to form an efficient UV-absorbing film with high transparency in visible region. One-pot RCMP may serve as a practical method to obtain value-added functional lignin-polymer composites.

## Introduction

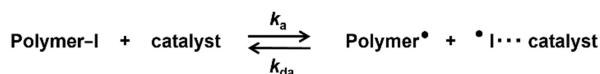
Lignin accounts for approximately 30% of wood weight and is the second most abundant renewable polymer on earth after cellulose and its derivatives.<sup>1</sup> Paper pulping industry annually produces 100 billion tons of lignin globally. However, only a small fraction (less than 2%) of the lignin is currently utilized commercially and mostly used in its original form (as unmodified lignin) for, e.g., agricultural, pelleting, and antimicrobial agents.<sup>1-3</sup>

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.<sup>4,5</sup> However, physical blending of lignin with synthetic polymers gives only heterogeneous composites with limited properties because lignin is immiscible with most synthetic polymers.<sup>6</sup>

In order to improve the miscibility, chemical grafting of synthetic polymers from lignin is a useful approach.<sup>1,3,6-16</sup> 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)<sup>1,3,6,9-14</sup> and reversible addition-fragmentation chain-transfer (RAFT) polymerization<sup>3,14-18</sup> are often used. For example, ATRP was used to graft poly(methyl methacrylate) (PMMA).<sup>1,10</sup> The obtained PMMA-grafted lignin (PMMA-g-Lignin) was blended with pure PMMA to generate PMMA/lignin composites with tuned mechanical properties<sup>1</sup> and was blended with poly( $\epsilon$ -caprolactone) (PCL) to generate a nanofibrous composite.<sup>10</sup> 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<sup>16</sup> and graft poly(poly(ethylene glycol) methacrylate) for sunscreen applications.<sup>17,18</sup> The abundant hydroxyl groups present in lignin were used to immobilize initiators of ATRP and RAFT polymerization.<sup>11,14</sup>

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.

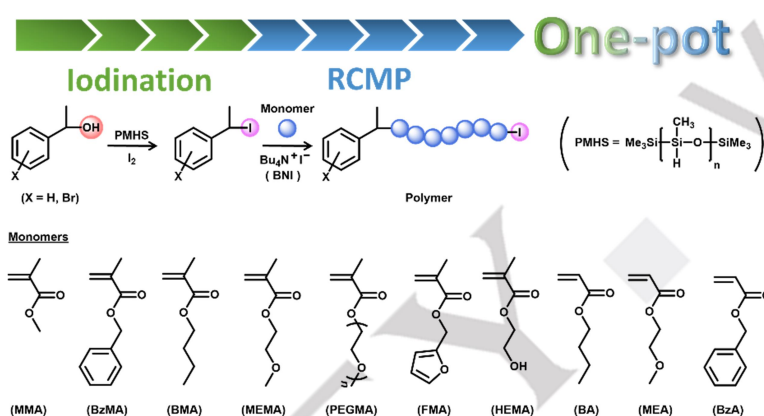


Scheme 1. Reversible activation mechanism of RCMP.

Our research group has developed an organocatalyzed LRP, termed reversible complexation mediated polymerization (RCMP), which uses alkyl iodide (R-I) initiators and organic catalysts such as tetra-*n*-

butylammonium iodide ( $\text{Bu}_4\text{N}^+\text{I}^-$ ) (BNI).<sup>19-23</sup> Mechanistically (**Scheme 1**), a polymer-iodide (Polymer-I) dormant species coordinates a catalyst ( $\text{I}^-$ ) to yield a halogen-bonding complex (Polymer-I $\cdots\text{I}^-$ ), which subsequently reversibly generates a propagating radical (Polymer\*) and  $\text{I}_2^{*-}$ . Advantages of RCMP are no use of special capping agents or metals, amenability to various functional monomers, and accessibility to a range of polymer structures. A potential problem of RCMP is the instability of isolated R-I initiators upon long-term storage. To overcome this problem, an in-situ generation of R-I initiators from their stable precursors during the polymerization was developed via a combination of stable molecular iodine ( $\text{I}_2$ ) and azo compound<sup>20,24</sup> and a combination of stable alkyl bromides and sodium iodide (NaI).<sup>25</sup>

In the present work, we explored another 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 (**Figure 1**), a benzylic alcohol (R-OH) reacts with iodinating agents ( $\text{I}_2$  and polymethylhydrosiloxane (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.

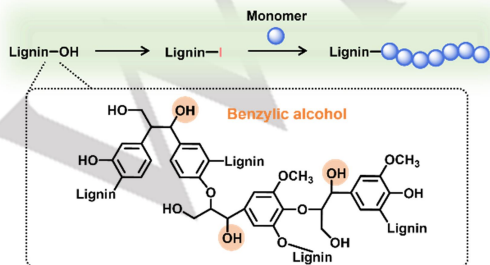


**Figure 1.** Schematic illustration of one-pot RCMP and structures of PMHS and studied monomers.

#### (a) Two-pot LRP (literature)



#### (b) One-pot RCMP (this work)



**Figure 2.** Schematic illustration of one-pot grafting of polymer from lignin

In the present work, as a particularly useful application, we explored one-pot RCMP from lignin. Lignin contains secondary benzylic alcohols, primary aliphatic alcohols, and phenolic alcohols (**Figure 2**). Via direct initiation from the benzylic alcohols, we attained one-pot grafting of polymers from lignin (**Figure 2**) without tedious initiator attachment

and purification, giving a practical breakthrough (a reduction in the costly additional processes) in the polymer-grafting 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.

## Results and Discussion

### Optimization of Iodination Condition

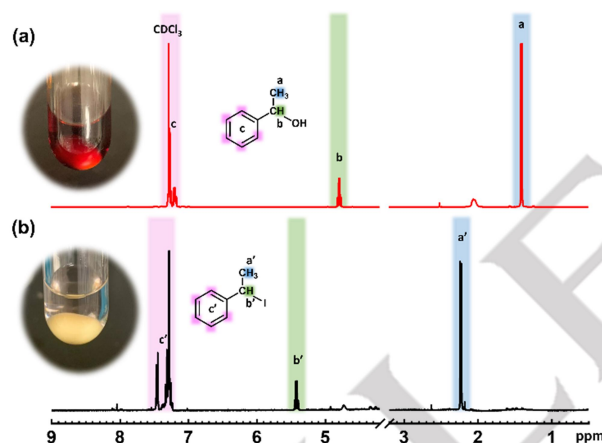
Das et al. reported a fast and full conversion of benzylic alcohols to benzylic iodides using  $\text{I}_2$  and PMHS as iodinating agents in the field of organic chemistry of small molecules.<sup>26</sup> Mechanistically, the Si-H in each repeat unit of PMHS reacts with  $\text{I}_2$  to in situ generate 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  $\text{I}_2$  (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.<sup>26</sup> In our one-pot RCMP (described below), we will use higher iodination concentrations of R-OH. Hence, we first screened the iodination conditions at higher concentrations of R-OH (**Table 1**).

**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 (°C)	t (min)	Conv. (%) <sup>a</sup>
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

<sup>a</sup>The conversion of R-OH to R-I was determined using  $^1H$  NMR.



**Figure 3.** 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**).

We studied two secondary benzylic alcohols (**Figure 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, we elevated the temperature 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 (**Figure 3**) and was also easily monitored by the disappearance of the red colour of  $I_2$  (full consumption of  $I_2$ ) (**Figure 3**). 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.

### One-pot polymerization of methyl methacrylate (MMA)

We studied one-pot RCMP of several monomers (**Figure 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.

**Figure 4** 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 (red circles in **Figure 4**), 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 (blue triangles in **Figure 4**), 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) (**Figures S1 and S2** in Supporting Information) 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

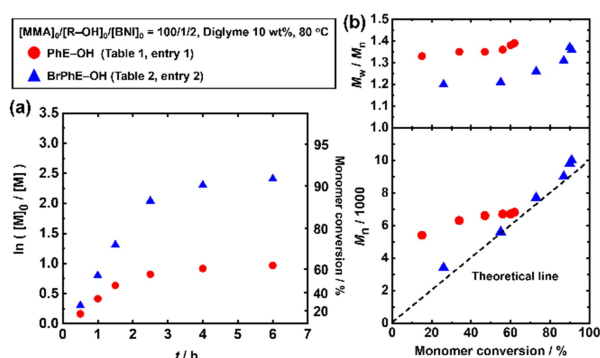
aryl protons in the initiating alcohol moieties and the methoxy protons in the MMA monomer units, we estimated that approximately 100% of the polymer contained the initiating alcohol moieties for both PhE-OH and BrPhE-OH systems, respectively (Table S1 in Supporting Information). The results demonstrate 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.

**Table 2.** One-pot RCMP of several monomers.

Entry	R-OH	Monomer	[Monomer] <sub>0</sub> /[R-OH] <sub>0</sub> /[BNI] <sub>0</sub> <sup>a</sup>	T (°C)	t (h)	Monomer Conv. (%) <sup>b</sup>	M <sub>n</sub> <sup>c</sup> (M <sub>n,theo</sub> ) <sup>d</sup>	Đ <sup>c</sup>
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

<sup>a</sup>A solution of R-OH (1 equiv.), I<sub>2</sub> (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. <sup>b</sup>Monomer conversion determined with <sup>1</sup>H NMR. <sup>c</sup>M<sub>n</sub> and Đ values determined with PMMA-calibrated DMF-GPC (entry 6) or THF-GPC (other entries). <sup>d</sup>Theoretical M<sub>n</sub> value calculated according to ([monomer]<sub>0</sub>/[R-OH]<sub>0</sub>) × (monomer conversion) × (molecular weight of monomer) + (molecular weight of R-I generated from R-OH).



**Figure 4.** 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.

### 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

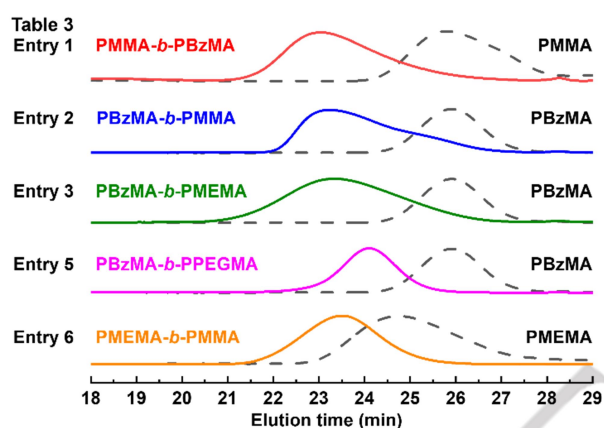
methacrylate (BMA), 2-hydroxyethyl methacrylate (HEMA), 2-methoxyethyl methacrylate (MEMA), furfuryl methacrylate (FMA), and poly(ethylene glycol) methyl ether methacrylate (PEGMA) (average molecular weight = 300) (Figure 1). Relatively low-dispersity polymers ( $\bar{D} = 1.18$ –1.48) were obtained up to 51–95% monomer conversions (Table 2, entries 4–9) with high initiation efficiencies (74–100%) from BrPhE-OH (Figures S3–S8 and Table S1 in Supporting Information) for all cases.

We also studied a different family of monomers, i.e., acrylates. 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 ( $\bar{D} = 1.38$ –1.45) at 40–87% monomer conversions (Table 2, entries 10–12) with high initiation efficiencies (73–91%) from BrPhE-OH (Figures S9–S11 and Table S1 in Supporting Information). 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.

**Table 3.** Synthesis of block copolymers using macroinitiators synthesized via one-pot RCMP.

Entry	Macroinitiator	Monomer	[Monomer] <sub>0</sub> /[Macroinitiator] <sub>0</sub> /[BNI] <sub>0</sub>	T (°C)	t (h)	Monomer Conv. (%) <sup>a</sup>	M <sub>n</sub> <sup>b</sup> (M <sub>n,theo</sub> <sup>c</sup> )	Đ <sup>b</sup>
1	PMMA-I <sup>d</sup>	BzMA	100/1/2	80	8	60	14100 (14400)	1.46
2	PBzMA-I <sup>e</sup>	MMA	100/1/2	80	8	75	10100 (11800)	1.56
3	PBzMA-I <sup>e</sup>	MEMA	100/1/2	80	8	61	12300 (13100)	1.59
4	PBzMA-I <sup>e</sup>	HEMA	100/1/2	80	24	40	8000 (9500)	1.27
5	PBzMA-I <sup>e</sup>	PEGMA	50/1/1	80	24	42	13300 (10600)	1.21
6	PMEMA-I <sup>f</sup>	MMA	100/1/2	80	8	73	9800 (12400)	1.37

<sup>a</sup>Monomer conversion determined with <sup>1</sup>H NMR. <sup>b</sup>M<sub>n</sub> and Đ values determined with PMMA-calibrated DMF-GPC (entry 4) or THF-GPC (other entries). <sup>c</sup>Theoretical M<sub>n</sub> value calculated according to ([monomer]<sub>0</sub>/[macroinitiator]<sub>0</sub>) × (monomer conversion) × (molecular weight of monomer) + (molecular weight of macroinitiator). <sup>d</sup>M<sub>n</sub> = 3800 and Đ = 1.26. <sup>e</sup>M<sub>n</sub> = 4300 and Đ = 1.14. <sup>f</sup>M<sub>n</sub> = 5100 and Đ = 1.34.



**Figure 5.** 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 3**, entries 1–3, 5, and 6. The GPC chromatograms with DMF eluent for **Table 3**, entry 4 is given in Supporting Information.

### Synthesis of block copolymers

Exploiting the living character of the obtained polymers, we studied block polymerizations (**Table 3** and **Fig. 5**). 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 (Supporting Information)), 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 3**, entries 1–3 and 6), hydrophobic-amphiphilic (**Table 3**, entry 5), and hydrophobic-hydrophilic (**Table 3**, entry 4) segments with  $M_n = 8000$ –14100 and  $\bar{D} = 1.21$ –1.59. The GPC chromatograms (**Figure 5**) 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.

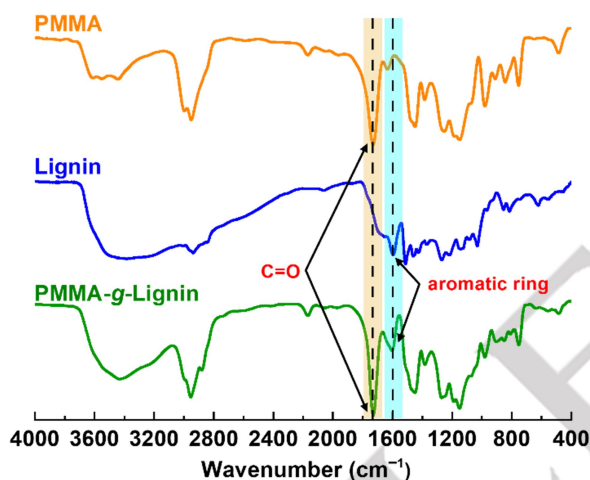
### One-pot grafting of polymers from lignin

We studied one-pot grafting from lignin by initiating from its benzylic alcohols (**Table 4**, entry 1). We first heated a mixture of lignin ( $M_n = 600$ ) (1 equiv. of lignin molecules and approximately 0.45 equiv.<sup>27,28</sup> of benzylic alcohols), I<sub>2</sub> (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. 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 4**, entries 2–4). We obtained PMMA-grafted lignin with varied PMMA/lignin compositions from 95/5 to 67/33 (w/w) (**Table 4**, 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 S2** in Supporting Information). 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 4.** One-pot RCMP from lignin.

Entry	Monomer	Lignin (wt% of Monomer)	[Monomer] <sub>0</sub> /[Lignin] <sub>0</sub> /[BNI] <sub>0</sub> <sup>a</sup>	T (°C)	t (h)	Monomer Conv. (%) <sup>b</sup>	M <sub>n</sub> <sup>c</sup>	Đ <sup>c</sup>	Polymer/Lignin Composition (w/w) <sup>d</sup>	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	BzA	1.2	300/1/1.5	110	24	71	49000	2.17	98/2	PBzA-g-Lignin (98/2)

<sup>a</sup>A mixture of lignin (1 equiv. of lignin molecules and approximately 0.45 equiv. of benzylic alcohols), I<sub>2</sub> (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. <sup>b</sup>Monomer conversion determined with <sup>1</sup>H NMR. <sup>c</sup>M<sub>n</sub> and Đ values determined with PMMA-calibrated DMF-GPC (entry 6) or THF-GPC (other entries). <sup>d</sup>Polymer/Lignin Composition = [(initial weight of monomer) × (monomer conversion)] / (initial weight of lignin).

**Figure 6.** FT-IR spectra of pure PMMA, pure lignin, and PMMA-g-Lignin (95/5) (Table 4, entry 1 for 72 h).

**Figure 6** shows infra-red (IR) spectra of pure PMMA, pure lignin, and PMMA-g-Lignin (95/5) (Table 4, 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<sup>-1</sup>) and carbonyl group originated from PMMA (at ca. 1730 cm<sup>-1</sup>), confirming the successful grafting of PMMA from lignin.

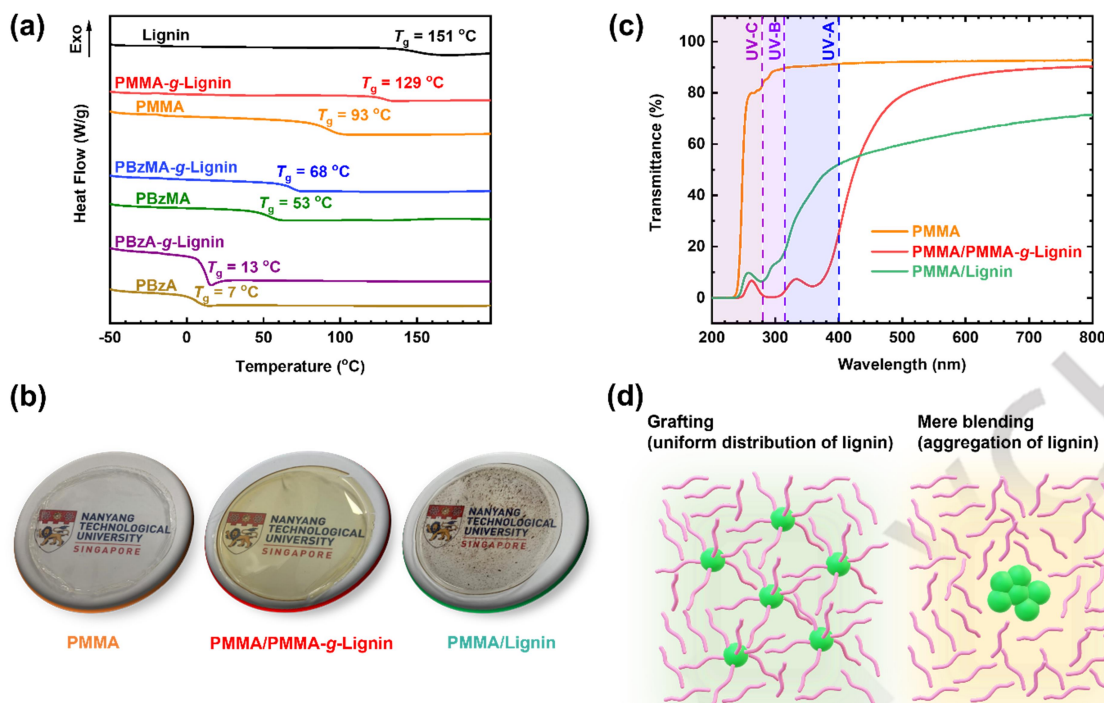
We also successfully grafted another methacrylate BzMA and an acrylate BzA from lignin to yield polymer-grafted lignin (aggregates) with M<sub>n</sub> = 49000–420000 and Đ = 1.52–2.17 (Table 4, entries 5 and 6). The monomer

conversion of BzMA (58% for 48 h) (Table 4, entry 5) was higher than those of MMA (14–22% for 48 h) (Table 4, entries 1–4) because of the large propagation rate constant (k<sub>p</sub>) for BzMA.

#### Thermal properties of polymer-grafted lignin

We studied thermal properties of the obtained polymer-grafted lignin using differential scanning calorimetry (DSC) (Figure 7a) and thermogravimetric analysis (TGA) (Figure S20 in Supporting Information). The polymer-grafted lignin had a significantly higher glass transition temperature (T<sub>g</sub>) than the neat polymer because of the high T<sub>g</sub> value of lignin (151 °C) (Figure 7a). The T<sub>g</sub> 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<sub>g</sub> value instead of two distinct T<sub>g</sub> values for polymer and lignin for all cases, suggesting that the polymer-grafted lignin is not phase-separated 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<sub>d5%</sub>) 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 (Figure S20 in Supporting Information), suggesting stable grafting of polymer from lignin.



**Figure 7.** (a) DSC curves of PMMA-g-Lignin (95/5), PBzMA-g-Lignin (98/2), and PBzA-g-Lignin (98/2) (Table 4, 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).

### UV absorption of PMMA/PMMA-g-Lignin composite film

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.<sup>29,30</sup> However, mere physical blending of lignin with synthetic polymers causes phase-separation and gives opacity or limited UV-shielding properties due to their immiscibility.<sup>31</sup>

The immiscibility problem can be solved by using polymer-grafted lignin. We prepared an approximately 100  $\mu\text{m}$  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 (Figure 7b). A neat PMMA film exhibited more than 80% transmittance in a 260–400 nm UV region (Figure 7c (orange line)). 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% (Figure 7c (red line)). 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 (Figure 7c (green line)) because of the incompatibility between PMMA and lignin. By the mere physical blending (Figure 7d), lignin formed large aggregates in the PMMA matrix because of

the immiscibility, making the film less transparent. In sharp contrast (Figure 7d), 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:

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

where CF is a correction factor (10 as a constant), EE ( $\lambda$ ) is an erythemal spectral effectiveness with wavelength  $\lambda$ ,  $I(\lambda)$  is a solar intensity with wavelength  $\lambda$ , Abs ( $\lambda$ ) is a spectrophotometric absorbance value at wavelength  $\lambda$  (Table S3 in Supporting Information).<sup>32</sup> 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).<sup>16,33</sup> The PMMA/PMMA-g-Lignin film

was slightly yellow in color (**Figure 7b**) 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.

## Conclusions

We developed 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. 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/I<sub>2</sub> 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.

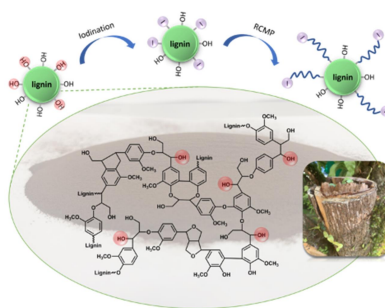
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**Keywords:** Lignin • grafting • living radical polymerization • one-pot • UV absorption

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## Entry for the Table of Contents



We report the first one-pot synthesis of methacrylic and acrylic polymers from benzylic alcohols (R-OH) via reversible complexation mediated polymerization (RCMP) (organocatalyzed living radical polymerization). This method enabled direct initiation from benzylic alcohols of lignin to yield polymer-grafted lignin in one pot as a practically useful application.