

Wood Preservation Based on *In situ* Polymerization of Bioactive Monomers

Part 1. Synthesis of Bioactive Monomers, Wood Treatments and Microscopic Analysis¹⁾

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Keywords

Wood preservation
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Fyrol 6 acrylate
Synthesis
Southern pine
Scanning electron microscopy
X-ray analysis

Summary

In situ polymerization of bioactive monomers was investigated as an alternative to conventional preservative treatments. The results are presented in a series of two papers. In Part 1 of the study, six acrylate monomers with covalently bonded, potentially bioactive moieties were synthesized: (1) pentachlorophenolyl acrylate (PCPA), (2) tributyltin acrylate (TBTA), (3) 8-hydroxyquinolyl acrylate (HQA), (4) 5,7-dibromo-8-hydroxyquinolyl acrylate (DBHQA), (5) diethyl-N,N-bis(acryloxyethyl) aminomethyl phosphonate (Fyrol 6 acrylate, F6A), and (6) tetrabromobisphenol A acrylate (TBBPAA). All of these acrylates, except F6A, were purified. Southern pine sapwood samples were treated with acrylate solutions (except TBBPAA) at different retention levels and various amounts of crosslinker (trimethylolpropane trimethacrylate, TMPTM), polymerized *in situ*, and then acetone leached. The relative amount and location of the polymer in earlywood and latewood of selected samples were determined by scanning electron microscopy and x-ray analysis. Distribution of the compounds varied with treatment. Biological and thermal properties of the treated wood are discussed in Part 2 of this series.

Introduction

A bioactive polymer is a polymer attached to a bioactive chemical that inhibits wood degradation (Rowell 1983). A bioactive polymer can be formed by condensation of the bioactive groups into the polymer or grafting them to the polymer, or by synthesizing the bioactive monomer and polymerizing it *in situ* in the cell voids.

Bioactive polymers have been grafted to cotton cellulose for the textile industry. The use of antibacterial and antifungal agents for preservation of textiles and paper started in the early 1940s; today, the main applications are for medical treatment, hygiene, and aesthetics. Vigo (1976 a,b) reviewed the representative classes of compounds, various chemical and physicochemical approaches for attaching these agents to fibers, mechanisms by which the product is effective against degradation, and test methods for evaluation. The compounds show antibacterial, antifungal, and broad-spectrum antimicrobial activity. Toxicity and cost vary with each compound.

One application of the synthesis of a bioactive monomer and *in situ* polymerization is for paint and coatings through polymer anchoring of mildewcides. In reviewing the literature on polymer anchoring of mildewcides in paint, Pittman (1976) found few examples in which a biocide had been directly anchored to the coating material, except in the case of antifouling marine coating (Steele and Drisko 1976). Antifouling coating is applied to underwater surfaces to

prevent the accumulation of organisms like barnacles and algae. Since then, Pittman and his research group have synthesized and evaluated the biological activity of many polymers with chemically bound biocides (Stahl and Pittman 1978; Pittman 1981; Pittman *et al.* 1978, 1982; Pittman and Lawyer 1982).

Bioactive polymers can be introduced into wood in three ways: (1) monomer or polymer grafting to reactive groups on the cell wall polymers, (2) nongrafted bulk polymer formation in the void structure of wood, or (3) chemical oxidation and derivatization of polymeric oligomers.

Grafting of organotin polymers to wood has been performed extensively (Mendoza 1977; Montemarano and Cohen 1976). Trialkyltin compounds are very toxic to marine fouling organisms (Andersen 1979) and wood-decay organisms (brown-rot, white-rot, and soft-rot fungi) (Subramanian *et al.* 1981 a,b). Sheldon (1975) showed that trialkyltin compounds eventually degrade to inorganic tin oxides by the action of ultraviolet (UV) light, microorganisms, etc.

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Treatment of wood with vinyl polymers is advantageous for not only preservation but also the improvement of mechanical properties and water repellency. Vinyl monomers can be polymerized by using catalysts (Meyer 1965) or radiation techniques (Siau *et al.* 1965). Raff *et al.* (1965) improved dimensional stability through polymerization of styrene and styrene-divinyl benzene in wood. Langwig *et al.* (1968) polymerized *t*-butylstyrene, epoxy monomers, and methyl methacrylate in wood by *in situ* impregnation. Hardness and static bending strength increased but mechanical properties showed little change. Gaylord (1973) developed a method for impregnating wood *in situ* with styrene and maleic anhydride monomers that formed a 1:1 charge transfer complex. At low temperatures, heating produced uncatalyzed polymerization.

Forest Products Laboratory researchers have been investigating bonding of fluorophenyl isocyanates to wood cell wall polymers and reaction of 8-hydroxyquinoline, pentachlorophenol, or β -naphthol with ethylene-maleic anhydride copolymer to cell wall polymers (Chen and Rowell 1986). The goal is to lower chemical load by using bonded biocides as controlled-release compounds.

Filling cell lumens with preformed bioactive polymers leads to problems with solubility and penetration. Because polymers have low solubility, high viscosity, and large molecular size, they are difficult to load into wood. Instead, it is possible to synthesize a monomer with a bioactive group, fill the wood with the monomer, and then polymerize or copolymerize *in situ* with a carrier monomer using a catalyst. This results in higher loading of the bioactive polymer into the wood.

Methyl methacrylate (MMA) polymerizes to a plastic material (poly(methyl methacrylate)) by chain or additional polymerization. A toxic group can be attached to the monomer through the ester linkage. The resulting bioactive methacrylate contains a toxic ester instead of the methyl ester. Rowell (1983) synthesized and treated wood with methacrylate derivatives of pentachlorophenol (PCPM), pentabromophenol (PBPM), and tributyltin oxide (TBTOM) at various concentrations. There was no increase in wood volume, indicating little or no cell wall penetration. Rowell found that all levels of MMA-PCPM and MMA-PBPM treatments were similar to MMA alone in weight loss during a soil block test with *Gloeophyllum trabeum*. Thus, biodegradation resistance is likely due to a moisture barrier and increase in density resulting from the polymer, not the release of the toxic chemical. The PCP and PBP esters were stable and did not release the active biocide. All levels of MMA-TBTOM were effective; no weight loss occurred when the treated wood was exposed to brown-rot fungi.

Treatment of wood with methacrylate polymers decreased the rate of moisture pick-up and improved mechanical properties, including modulus of elasticity and rupture, fiber stress at proportional limit, work to maximum load, maximum crushing strength, and hardness index, compared to those properties of untreated wood (Langwig *et al.* 1968; Rowell *et al.* 1982). However, treatment with methacrylate polymers causes high polymer weight gain and is expensive.

Materials and Methods

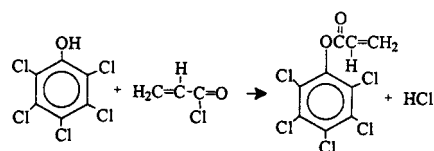
Pentachlorophenol (PCP) and tributyltin oxide (TBTO) were chosen for analysis because they are current wood preservatives; 8-hydroxyquinoline (HQ) is the only wood preservative approved for use in contact with food; and 5,7-dibromo-8-hydroxyquinoline (DBHQ), Fyrol 6 (F6) and tetrabromobisphenol A are fire retardants that may also provide biological resistance. The chemicals were obtained from commercial suppliers and used without further purification; Fyrol 6 was obtained from Akzo Chemical Inc. (Dobbs Ferry, NY) and the other chemicals from Aldrich Chemical Company (Milwaukee, MI).

Nuclear magnetic resonance (NMR) spectra were acquired on a Bruker WM-250 megahertz FT-NMR. Spectra were run in liquid state using 5-mm tubes and deuterated solvents (CDCl₃) with an internal standard of tetramethylsilane. The pulse angle was 30° with a relaxation delay of 2 s. All samples were run at room temperature (22 °C).

Electron impact and methane chemical ionization gas chromatography/mass spectrometry (GC/MS) spectrum were acquired with a Hewlett Packard 5890 Series 2 GC and a Finnigan Model 4500 MS. Superincos software was used. The volatilization temperature was 220°C and the ionizing energy 70 electron volts. The filament current was 0.2 mA.

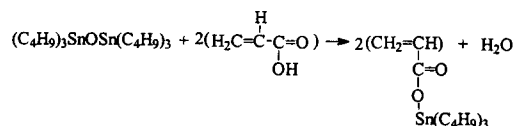
Synthesis of bioactive monomers

Pentachlorophenol acrylate (PCPA)



PCPA was prepared according to the literature (Rowell 1983) with some modification. Dry chloroform (500 ml), 66.63 g (0.25 mol) PCP, and 41.8 ml (0.30 mol) triethylamine (TEA) were placed into a 1000-ml three-neck round-bottom flask and stirred at room temperature until PCP dissolved. Acryloyl chloride (24.4 ml, 0.30 mol) was added dropwise to this mixture with mechanical stirring while cooled in an ice bath, so that the temperature did not exceed 35°C. After the acryloyl chloride was added, the solution was stirred for 2 h at room temperature. The chloroform solution was washed once with 1000 ml ice water and twice with 1000 ml water, separated from the water, and then dried over sodium sulfate. The solution was filtered and the chloroform removed under reduced pressure at 50 °C. The resulting solid was recrystallized from hot ethyl ether. Upon cooling, white crystals were obtained.

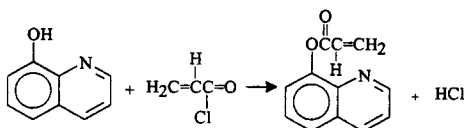
Tributyltin acrylate (TBTA)



TBTA was synthesized according to the literature (Rowell 1983; Mendoza 1977; Monterrosa *et al.* 1958) with some modification. Tri-*n*-butyltin oxide (TBTO), 202.6 g (173.2 ml, 0.34 mol), was dissolved in 500 ml carbon tetrachloride. Acrylic acid, 48.9 g (46.5 ml, 0.34 mol), and boiling chips were added to the solution. The mixture was refluxed for 3 h and then allowed to cool before adding sodium sulfate to remove the water byproduct. After filtering off the sodium sulfate, carbon tetrachloride was removed under reduced pressure, resulting in a crystalline solid. The solid was

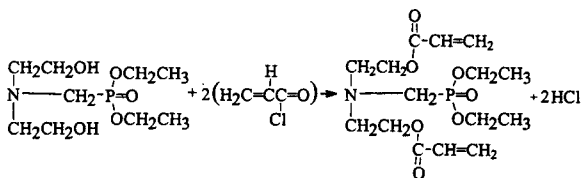
recrystallized by dissolving it in hot hexane, followed by cooling, filtration, and washing with cold hexane. The final product was a white needlelike crystalline material.

8-Hydroxyquinolyl acrylate (HQA)



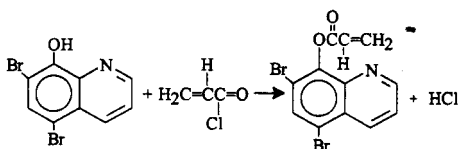
HQA was prepared according to the literature (Pittman *et al.* 1978) with some modification. Chloroform was used instead of benzene. Dry chloroform (100 ml), HQ (7.30 g, 0.05 mol), and TEA (8.5 ml, 0.06 mol) were placed in a 250 ml three-neck round-bottom flask fitted with a thermometer, addition funnel, and mechanical stirrer, and stirred until HQ dissolved. Acryloyl chloride (5.0 ml, 0.06 mol) was added dropwise to this mixture with mechanical stirring while cooled in an ice bath, so that the temperature did not exceed 35 °C. The solution was stirred for 3 h at room temperature (21 °C). The chloroform solution was washed once with 250 ml 5% NaHCO₃, then twice with 250 ml distilled water. The chloroform layer was dried over Na₂SO₄. The solution was filtered and the chloroform removed under reduced pressure at 50 °C, resulting in a light-brown syrup. The sample was cooled and yellow crystals were formed. White crystals of HQA were formed upon recrystallization from hot ethyl ether.

Diethyl-N₁N-bis(acryloxyethyl) aminomethyl phosphonate (Fyrol 6 acrylate, F6A)



Fyrol 6 (6.126 g, 0.024 mol), TEA (5 ml, 0.036 mol), and chloroform (60 ml) were placed in a three-necked round-bottom flask fitted with a thermometer and dropping funnel. Acryloyl chloride (5.84 ml, 0.072 mol) was added dropwise to this mixture with mechanical stirring while cooled in an ice bath, so that the temperature did not exceed 35 °C. The solution was then stirred for 3 h at room temperature (21 °C). The chloroform was removed under reduced pressure, leaving F6A as a light-brown viscous liquid.

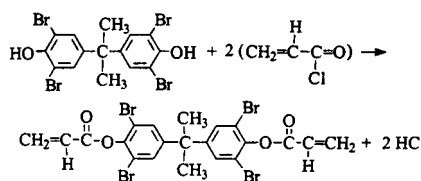
5,7-Dibromo-8-hydroxyquinolyl acrylate (DBHQA)



DBHQ (7.884 g, 0.026 mol) was dissolved in 750 ml chloroform with warming (30 °C) in a 1000-ml three-necked, round-bottom flask. Triethylamine (5.23 ml, 0.0375 mol) was added, followed by dropwise addition of acryloyl chloride (4.9 ml, 0.06 mol). The mixture was stirred for 5 h and then washed once with 1 l of 5% NaHCO₃ and twice with 1 l water. The solution was dried over Na₂SO₄ and then filtered. The chloroform layer was removed under reduced pressure and acetone was added to crystallize (1 h) the unreacted DBHQ, which was filtered off (3.63 g, 45.87% yield, mp 200 °C.) The acetone was removed under reduced pressure,

hexane was added, and the mixture was cooled to crystallize. The final product, DBHQA, was filtered from the solvent and dried.

Tetrabromobisphenol A acrylate (TBBPAA)



TBBPA (2.718 g, 0.005 mol) was dissolved in 65 ml toluene and 0.65 ml pyridine (0.008 mol). Acryloyl chloride (0.81 ml, 0.01 mol) was added dropwise to the solution. The temperature rose from 23 °C to 27 °C and a white precipitate instantly formed that was not identified by NMR. After 45 min, the temperature dropped to 23 °C. The solution was stirred for 3 h and then filtered to remove the precipitate formed in the reaction. Toluene was removed under reduced pressure, leaving a clear syrup that formed white crystals of TBBPAA on drying.

Wood treatments

Compound solutions were prepared in acetone or methanol just prior to treating at different retention levels (1%, 2%, 5%, 10%, 15%, and 20%). The crosslinking agent was trimethylolpropane trimethacrylate (TMPTM) (5%, 10%, 20%, 30%, 40%, and 50%). The catalyst was 0.4% 2,2'-azobis-(2,4-dimethylvaleronitrile) (Polysciences, Inc., Warrington, PA). All solvents used for synthesis and treatment were obtained from Aldrich Chemical Company.

Southern pine sapwood samples (2.54 by 2.54 cross section by 0.635 cm axial) were dried at 105 °C in a forced-draft oven for 24 h, cooled for 1 h at room temperature in a glass desiccator over phosphorus pentoxide, and weighed. (Subsequent weight measurements were performed in the same way.) Samples were then placed in a treating chamber (ASTM D 1413, ASTM 1976) and the system was evacuated for 30 min with a water aspirator (28 mmHg). The selected solution was placed in the treating chamber until it covered all the samples and was held there for 5 min. Samples were held in place with a glass weight to prevent floating. The vacuum was released and the chamber was brought to atmospheric pressure. Samples were allowed to soak in the solution for 30 min, and were then removed from the chamber, wiped of excess solution, weighed, and wrapped immediately in aluminum foil. They were then placed in a 52 °C oven, flushed with nitrogen, and left for 18 h to allow polymerization. The foil was then removed and the samples weighed. Samples were oven dried at 105 °C for 24 h and then weighed once more.

This experimental procedure varied for HQ and HQA. These samples were oven dried at 35 °C instead of 105 °C because of the low melting points of HQ (72 °C-74 °C) and HQA (51 °C-52 °C).

Leaching

Solubility in acetone (methanol for F6A) was determined for all bioactive compounds, monomers, and polymers. Polymer was prepared from each bioactive monomer and leached in hot acetone (methanol for F6A) for 2 h. The weight percentage of polymer remaining was calculated. Treated wood samples were leached to remove any unpolymerized monomer. Samples were placed in a Soxhlet extractor fitted with a 250-ml flat-bottom flask and extracted with acetone (methanol for F6A) for 2 h. Samples were then removed from the extractor, dried in a forced-draft oven at 105 °C for 24 h, and weighed.

Microscopic analysis

Scanning electron microscopy (SEM) was performed on selected samples with a Joel 840 instrument. Longitudinal sections were gold coated, and the earlywood and latewood were observed at 150 × and 250 × magnifications, respectively. Representative pictures were taken of both earlywood and latewood. X-ray microanalysis (EDXA) was performed on selected samples with a Tracor Northern 5500 energy dispersive spectrometer. Cross sections were carbon coated and observed at various magnifications. Representative pictures of both earlywood and latewood were taken.

Results and Discussion

Synthesis and identification of bioactive monomers

The synthesis of PCPA was scaled up to produce a larger amount of compound for treating wood samples. The melting point was the same as the literature value (81 °C), although the 91 % yield (72.54 g) was much higher than the literature value (58%) (Rowell 1983). Thin layer chromatography (TLC) on silica-gel-coated sheets in a solvent system of hexane/chloroform (1:1 v/v) showed an R_f of 0.76 for PCPA and R_{PCP} of 1.9. The R_f of PCP was 0.41. In the literature, the R_f of PCPA is 0.74, R_{PCP} is 3.1, and R_f of PCP is 0.25 (Rowell 1983). Short-wave UV light was used to locate the compounds on TLC plates.

The synthesis of THTA was also scaled up. Synthesis resulted in the same melting point of 74 °C, but a slightly higher yield (71.7 %, 175.9 g) compared with the literature value (60.7 %) (Shostakovskii *et al.* 1961; Rowell 1983).

In the synthesis of HQA, the solvent was changed from benzene (Pittman *et al.* 1978) to chloroform, resulting in a purer product. It was difficult to recrystallize the yellow crystals with warm ethyl ether, and the yield decreased from 81.3 %, 8.09 g (mp 48 °C-49 °C) to 74.4%, 7.4 g (mp 51 °C-52 °C). This was expected and the yield is still high given the resulting purity of the white crystalline product. The literature values are 36 °C for melting point and 79.3 % for yield (Pittman *et al.* 1978). TLC in a solvent system of hexane/chloroform (1:2 v/v) showed an R_f of 0.61 for HQA and R_{8-HQ} of 0.79. The R_f of 8-HQ was 0.48. The NMR spectra of HQA along with the chemical structure and peak assignments are shown in Figure 1. HQA showed a few impurities from 1-4 ppm, but otherwise was consistent with structure. The NMR literature values are (CCl₄) δ 4.9-5.7 (m, 3, CH₂ = CH), 5.9-6.4 (m, 3, Ar), and 6.5-7.3 (m, 3, Ar) (Pittman *et al.* 1978). Analysis for carbon, hydrogen,

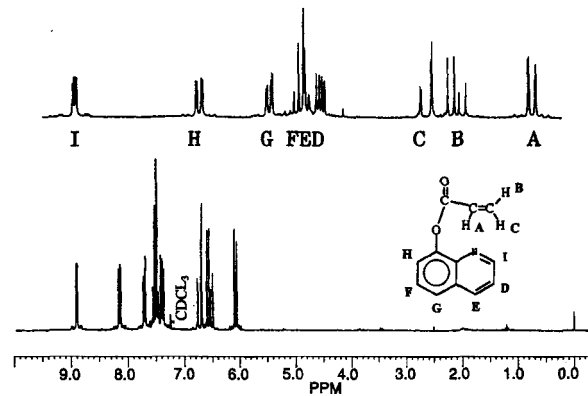


Fig. 1. ¹H NMR spectrum of 8-hydroxyquinolyl acrylate.

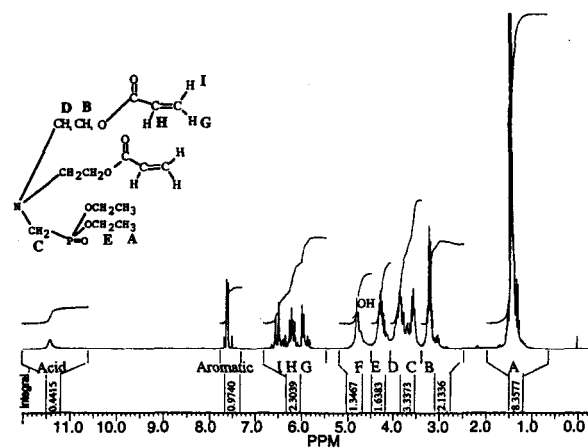


Fig. 2. ¹H NMR spectrum of Fyrol 6 acrylate.

and nitrogen (C-H-N analysis) yielded the following values for C₁₂H₉NO₂: calculated values were C, 72.35; H, 4.55; N, 7.03 and found values were C, 72.08; H, 4.66; N, 7.01.

Fyrol 6 (F6), a phosphonate ester, is specifically designed for use as a flame retardant in rigid urethane foams; the commercial product is only approximately 85 % pure. Two impurities may be ethanol (1%) and diethanolamine (0.1%). If Fyrol 6 acrylate (F6A) were to be used commercially, it would necessarily be impure since the bulk chemical (F6) has impurities. In the study reported here, F6A (14.8 g.) was prepared but not purified because

Table 1. Assignments for GC/MS spectra of F6A and TBBPA

Compound	Time	m/z	ID
F6A	5 min. 4 s	291.2	(M - CH ₂ = CHCOOH) + H ⁺
		278.2	(M - CH ₂ COOCH = CH ₂) ⁺
		226.2	(M - P(OEt) ₂ O) ⁺
TBBPA	13 min, 35 s	651.8	M ⁺
	2 acrylations	597.8	(M - C ₃ H ₂ O) ⁺
	8 min, 13 s	597.7	M ⁺
	1 acrylation	582.7	(M - CH ₃) ⁺
	5 min, 12 s	543.7	M ⁺
	no acrylations	528.8	(M - CH ₃) ⁺

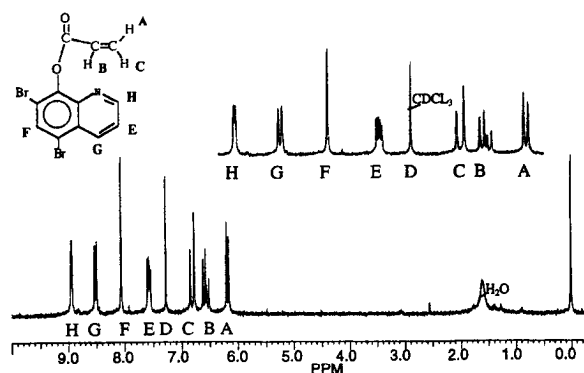


Fig. 3. ^1H NMR spectrum of 5,7-dibromo-8-hydroxyquinolyl acrylate.

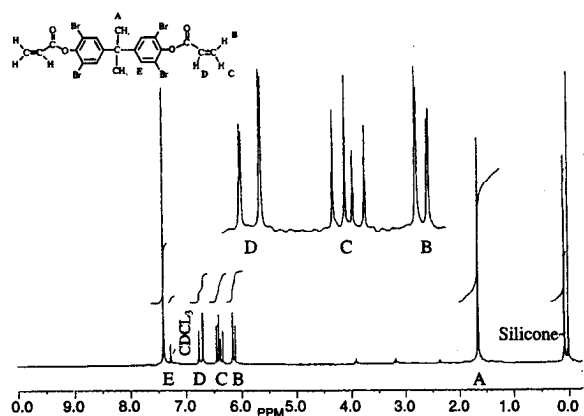


Fig. 4. ^1H NMR spectrum of tetrabromobisphenol A acrylate.

of the difficulty in removing the impurities due to the involvement of amino phosphonate moieties. The C-H-N analysis of $\text{C}_{15}\text{H}_{36}\text{NO}_7\text{P}$ yielded calculated value of C, 49.59; H, 7.16; N, 3.86 and found values of C, 38.85; H, 6.99; N, 4.48. The carbon content of synthesized F6A was 10.74% lower than the calculated value, hydrogen was 0.17% lower, and nitrogen was 0.62% higher. This indicates that the impurities in F6A contain nitrogen. The NMR spectrum shows consistency with structure but impurities as well (Fig. 2). The broad peak at 4.7 ppm is OH, and peaks occurred at 7.6 and 11.4 ppm. In the GC/MS spectrum of F6A, the acrylate appeared at 5 min, 4 s; another unidentified product appeared at 4 min, 5 s. Assignments are shown in Table 1.

In the synthesis of DBHQA, there was difficulty in crystallizing the acrylate. Acetone was added to precipitate out the starting material, DBHQ, because of its low solubility in acetone (10 mg/ml). The resulting yield was 45.1%, 4.19 g; mp was 115 °C compared to literature values of 106 °C–108 °C (Becke *et al.* 1974) and 114 °C–116 °C (Huber-Emden *et al.* 1971). The C-H-N analysis of $\text{C}_{12}\text{H}_7\text{Br}_2\text{NO}_2$ yielded calculated values of C, 40.34; H, 1.96; N, 3.92 and found values of C, 40.19; H, 2.10; N, 3.74. The NMR spectrum of DBHQA shows consistency with structure except for a water peak at 1.6 ppm (Fig. 3). The sample was not completely dry.

Table 2. Solubility of bioactive compounds, monomers, and polymers at room temperature (22 °C)

Chemical	Compound (mg/ml acetone)	Monomer (mg/ml acetone)	Polymer (wt % remaining)
MMA			97
PCP	60	250	99
TBTO	860	250	67
HQ	75	118	48
DBHQ	10	100	96
F6	Insoluble ^a	Insoluble ^b	89

^a Soluble in methanol 523.

^b Soluble in methanol 133.

TBBPA was synthesized with a few impurities (mp 98 °C–100 °C), but the yield was very low (15%). Therefore, TBBPA was not pursued as a treatment. The C-H-N analysis of $\text{C}_{21}\text{O}_4\text{H}_{16}\text{Br}$ yielded calculated values of C, 38.67; H, 2.46 and found values of C, 39.43; H, 2.83. The NMR spectrum of TBBPAA shows consistency with structure, with minor impurities between 2.3 and 4 ppm (Fig. 4). The peak at 0.1 ppm is silicone from the TLC plate, a technique used for purifying the compound. GC/MS showed acrylation of most of the compound at both hydroxyls (13 min, 35 s), less acrylation at one hydroxyl (8 min, 13 s), and the presence of a small amount of the starting material (5 min, 12 s). Assignments are shown in Table 1. The carbon and hydrogen values (0.76 and 0.37, respectively) of the synthesized TBBPAA were higher than the calculated values, indicating that the impurities contain both.

Leaching of treated wood samples

The solubility of the bioactive compounds and monomers is shown in Table 2. PCP, TBTO, HQ, and DBHQ dissolved in acetone; the most soluble chemical was HQA (48%). F6 and F6A were insoluble in acetone, but highly soluble in methanol (89%). After polymerization and leaching, the weight percentage of polymer remaining was high in MMA (97%), PCPA (99%), and DBHQA (96%), but low in TBTA (67%).

Microscopic analysis

Earlywood and latewood of the acetone-leached control sample are shown in Figures 5 and 6, respectively. For PCPA-treated samples, the polymer appeared globular (Fig. 7); treatment was not uniform throughout the wood, as confirmed by EDXA mapping of chlorine. The TBTA polymer appeared smooth and evenly distributed in both earlywood (Fig. 8) and latewood; the lumens were full, as confirmed by x-ray distribution mapping. For HQA-treated wood, polymer was present in latewood (Fig. 9) but not earlywood. In F6A samples, earlywood and latewood (Fig. 10) lumens were only lightly covered by polymer. In DBHQA samples, polymer was uniformly distributed in the lumens of both earlywood (Fig. 11) and latewood, as confirmed by x-ray distribution mapping and spectra.

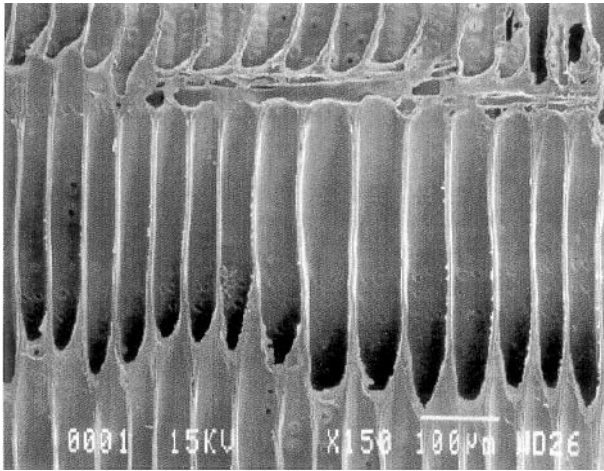


Fig. 5. SEM of leached earlywood control (150 ×).

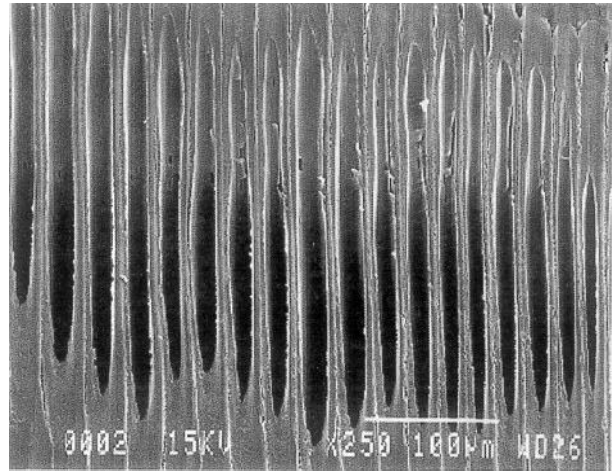


Fig. 6. SEM of leached latewood control (150 ×).

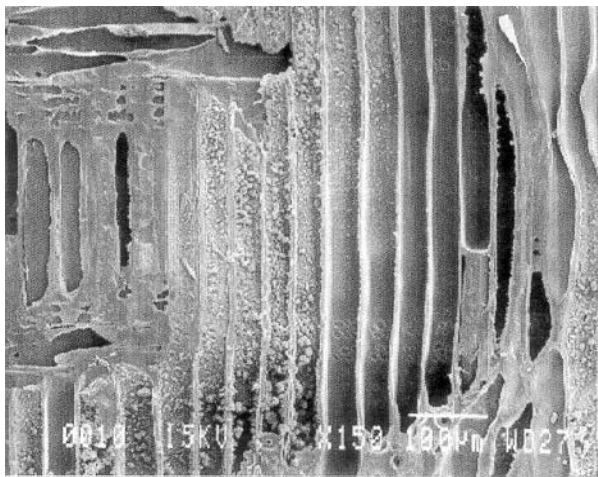


Fig. 7. SEM of leached PCAP-treated earlywood at 20% PCPA/5 % crosslinker loading (150 ×).

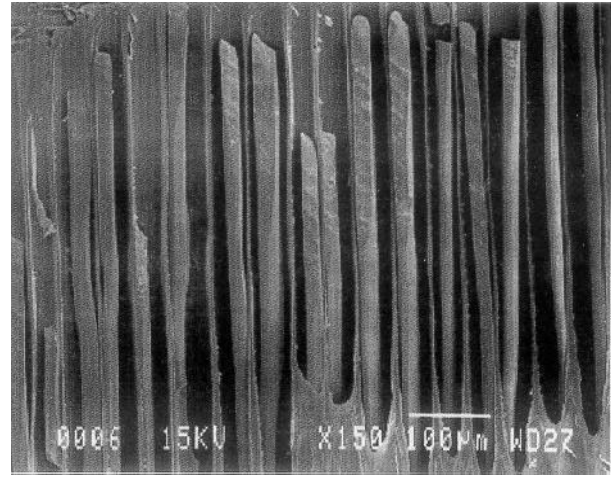


Fig. 8. SEM of leached TBTA-treated earlywood at 20% TBTA/5 % crosslinker loading (150 ×).

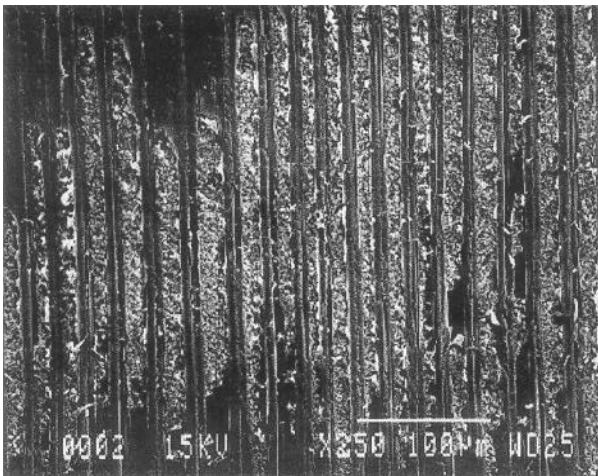


Fig. 9. SEM of leached HQA-treated latewood at 10% HQA/5 % crosslinker loading (250 ×).

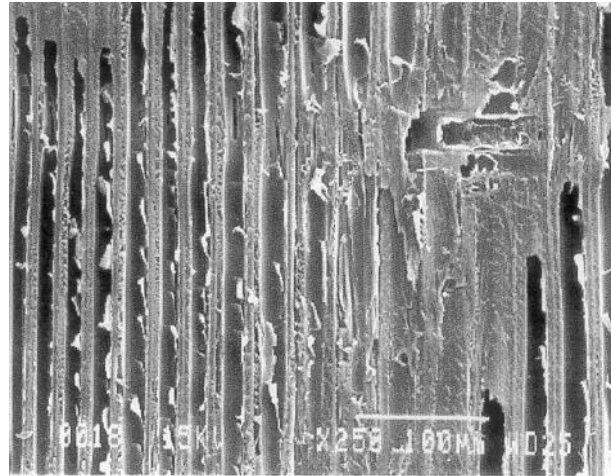


Fig. 10. SEM of leached F6A-treated latewood at 10% F6A/5 % crosslinker loading (250 ×).

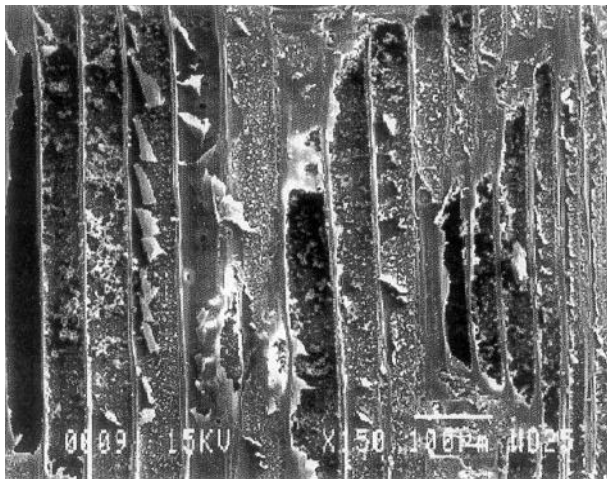


Fig. 11. SEM of leached DBHQA-treated earlywood at 5 % DBHQA/5 % crosslinker (150 ×).

Conclusion

Six potentially bioactive monomers were synthesized. All were polymerized in wood samples *in situ*, with the exception of TBBPAA because of its low yield. Microscopic analysis showed that the bioactive polymer is located in the lumens of the tracheids, but treatment uniformity varies with each polymer.

Acknowledgements

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