

# Synthesis of Poly(glycerol methacrylate) and Its Application to Dimensional Stabilization of Wood

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**ABSTRACT:** The dimensional stabilization of wood is investigated using poly(glycerol methacrylate) (PGMA) prepared from polyglycerol and glycidyl methacrylate instead of the well-known poly(ethylene glycol). PGMA allows waterborne treatment of wood, which after polymerization leads to the formation of a wood polymer composite with improved dimensional stability. Microscopic observations and a picture analysis permit the location of PGMA in the

wood cell walls and explains the dimensional stabilization by its bulking effect. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 743–749, 2003

**Key words:** polyglycerol; glycidyl methacrylate; poly(glycerol methacrylate); dimensional stabilization of wood; polymerization

## INTRODUCTION

Polyglycerol (PG) is an industrial by-product that is prepared from glycerine, a versatile chemical produced throughout the world from animal fats and vegetable oils. PGs are used in the food, cosmetic, and pharmaceutical industries as surfactants, emulsifiers, lubricants, gelling agents, humectant adhesives, urethane intermediates, and textile fiber finishes.<sup>1–6</sup> Highly soluble in water, PGs are polyethers, which present several similarities to the poly(ethylene glycols) (PEGs) that are widely used in the field of the dimensional stabilization of wood<sup>7–12</sup> (Scheme 1). Impregnation with PEG aqueous solutions allows the bulking of wood cell walls, preventing shrinkage, but leads only to the deposition of chemicals in the wood that are nonbonded and consequently easily leachable. Poly(glycerol methacrylate) (PGMA) represents an attractive way to avoid leaching of impregnated chemicals. Indeed, PGMA, which is soluble in water, allows the waterborne treatment of wood that after *in situ* polymerization leads to the formation of a tridimensional network that is insoluble in water and able to bulk the wood cell walls. This keeps the latter in a

partially swollen state, improving its dimensional stability.

The aim of the present article is to describe the synthesis of PGMA, its polymerization with or without impregnation in wood, its effect on the dimensional stabilization of wood, its localization in wood, and its leachability from treated wood.

## EXPERIMENTAL

### Materials

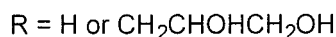
Glycidyl methacrylate (GMA) and methyl ethyl ketone peroxide (MEKP) were purchased from Fluka–Sigma–Aldrich Chimie SARL (St Quentin Fallavier, France). PG was obtained from Novance (Compiègne, France) as a mixture of compounds with an average molecular weight of 242 ( $n \sim 3$ ).

### Instruments

The <sup>1</sup>H-NMR spectra were recorded in water on a Bruker AM 400 spectrometer. Solid-state cross-polarization with magic angle spinning (CP/MAS) <sup>13</sup>C-NMR spectra were recorded on a Bruker MSL 300 spectrometer at a frequency of 75.47 MHz. Chemical shifts were calculated relative to TMS. An acquisition time of 0.026 s was used with about 1200 transients. All the spectra were run with a relaxation delay of 5 s, a CP time of 1 ms, and a spectral width of 20,000 Hz. The spinning rates were 3.5 KHz. The chemical shifts are expressed in parts per million. The IR spectra were recorded as thin films between NaCl plates or KBr

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PG

PEG

**Scheme 1** The chemical structure of polyglycerol (PG) and poly(ethylene glycol) (PEG).

disks on a Perkin Elmer FTIR Spectrum 2000 spectrometer.

### Synthesis of PGMA

The PG (30 g) was mixed in a mechanical stirrer in a 100-mL flask with dimethylamino pyridine (300 mg). The mixture was then heated at 70°C to decrease its viscosity and GMA (35.2 g) was added dropwise over 2 min. The reaction was kept at the same temperature for 15 min and then cooled to room temperature, and the product was used without further purification. <sup>1</sup>H-NMR (D<sub>2</sub>O) (δ): 1.88 (s, allylic CH<sub>3</sub>), 3.35–4.20 (m, CH and CH<sub>2</sub>), 5.63 (s, vinylic CH), 6.06 (s, vinylic CH). IR (NaCl disk): 3400 (νOH), 1718 (νCO), 1635 cm<sup>-1</sup> (νC=C).

### Chemical modification of blocks

Weighed (*m*<sub>0</sub>) oven-dried beech (*Fagus sylvatica*) and pine (*Pinus sylvestris*) blocks (15 × 20 × 50 mm) were used throughout this study. Solutions of PGMA (10, 20, 30, and 50 mass %) were prepared in distilled water, and MEKP (2 mass %) was added just before use. The blocks were placed in a beaker inside a desiccator and a vacuum of 5 mbar was drawn for 15 min using a pump. They were then covered with the solution of PGMA and the pressure returned to atmospheric. After 2 h of soaking, the blocks were drained for 5 min and cured at 80°C for 3 days.

The weight percentage gain (WPG) was calculated from the initial and treated oven-dried weight according to

$$\text{WPG} = (m_1 - m_0)/m_0 \times 100$$

where *m*<sub>0</sub> is the initial oven-dried weight of the sample and *m*<sub>1</sub> is the treated oven-dried weight.

### Chemical leachability

The leachability of the impregnated chemicals was determined by placing four samples in 800 mL of distilled water under agitation for different times (1, 2, 4, 8, 16, and 48 h) with a change of water between each time. The leached blocks were then dried at 80°C for 2

days (*m*<sub>2</sub>) and the quantity of leached chemical (LC) expressed as a percentage of the initially impregnated chemicals.

$$\text{LC} (\%) = (m_1 - m_2)/m_1 - m_0 \times 100$$

### Antiswelling-efficiency (ASE) measurements

The ASE was determined by measuring the increase in the volume of treated and untreated pine blocks. The blocks were placed in a climatic chamber (WTB Binder type KBF 115) at 25°C and 95% relative humidity for approximately 2 months. After stabilization of their weight, the blocks were measured. The volumetric swelling coefficients were calculated according to the following formula:

$$S (\%) = [(V_2 - V_{0 \text{ or } 1})/V_{0 \text{ or } 1}] \times 100$$

where *V*<sub>2</sub> is the volume of water saturated wood and *V*<sub>0 or 1</sub> is the volume of dry untreated or treated wood.

The percentage of swelling was calculated from the wet and oven-dried volumes of treated and untreated blocks according to

$$\text{ASE} (\%) = [(S_c - S_m)/S_c] \times 100$$

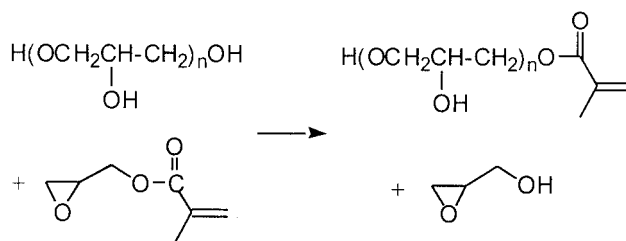
where *S*<sub>c</sub> is the volumetric swelling coefficient of unmodified samples and *S*<sub>m</sub> is the volumetric swelling coefficient of modified samples.

### Microscopic analysis

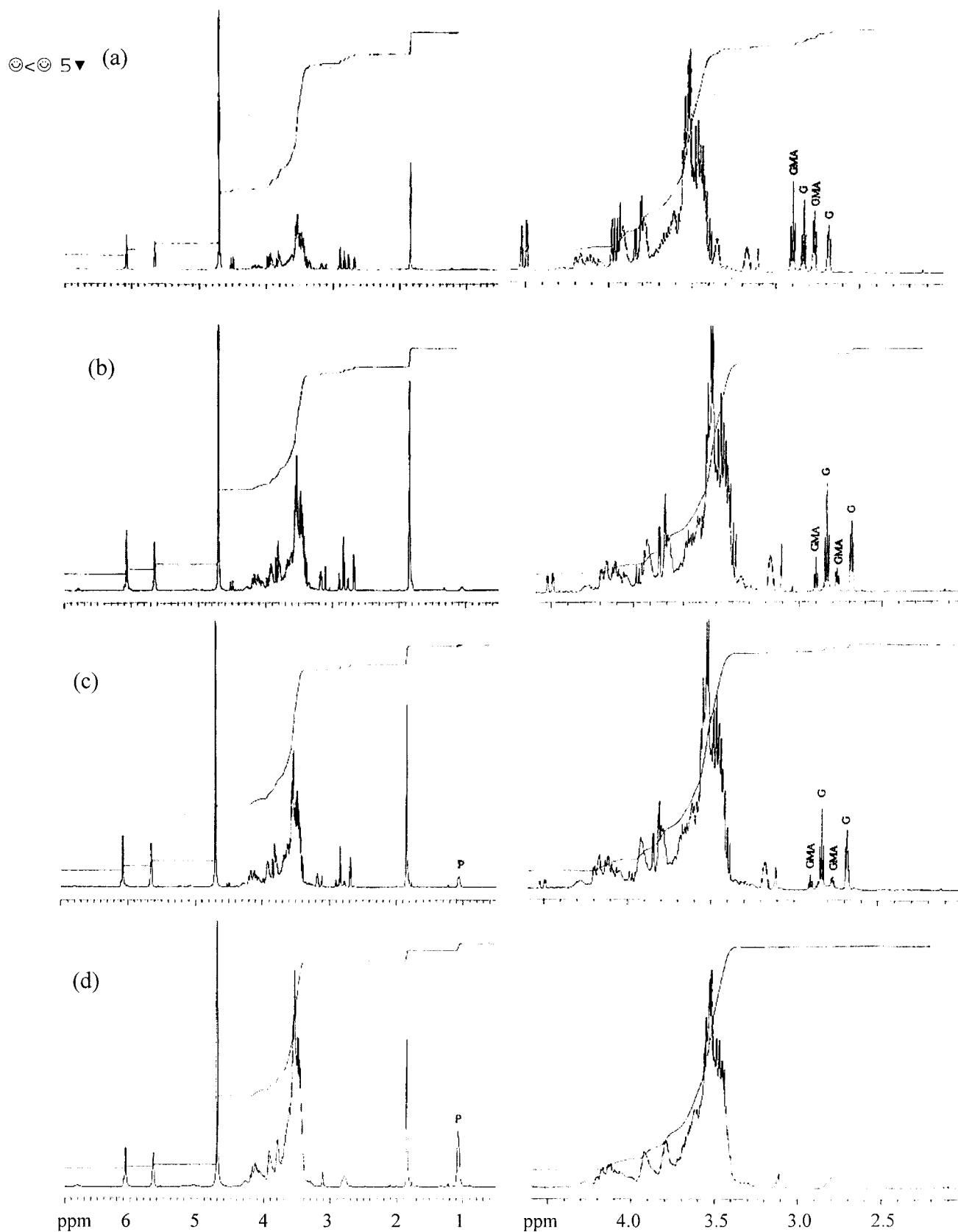
The microscopic analysis was performed with reflected light on a Axioplan Zeiss microscope equipped with a numerical camera (Coolsnap, RS Photometrics) connected to a computer for picture acquisition. Samples were prepared by dry polishing of the radial/tangential face to obtain very clean surfaces.

### Picture analysis

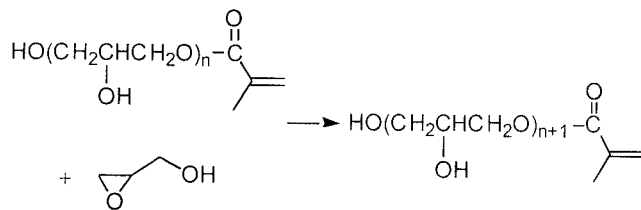
The swelling effect of the treatment was investigated using picture analysis software (Visilog version 3.1, Noesis). This treatment consisted of an automatic thresholding that separates the lumens (pixel value



**Scheme 2** The reaction of polyglycerol with GMA.



**Figure 1** The  $^1\text{H-NMR}$  spectrum of the crude products obtained from the reaction of PG3 (1 eq) and GMA (2 eq) at  $70^\circ\text{C}$  and solubilized in  $\text{D}_2\text{O}$  after (a) 5 min, (b) 15 min, (c) 1 h, and (d) 4 h.



**Scheme 3** The nucleophilic attack of the epoxy group.

= 1, white) and the walls (pixel value = 0, black) of the cells. The software can then calculate the percentage of lumen and wall in the picture.

## RESULTS AND DISCUSSION

### Synthesis of PGMA

The synthesis of PGMA was first investigated from methacrylic acid using standard esterification conditions. Several attempts made in toluene with 4-methoxyphenol or hydroquinone as a radical scavenger systematically leads to poly(methacrylic acid) before any esterification reaction. (No water was observed in the Dean stark trap.) Bulbing of air into the reaction mixture also has no effect on the inhibition of the polymerization. The explanation for these failures is probably the poor solubility of PG in toluene. Other attempts using methacryloyl chloride in dichlo-

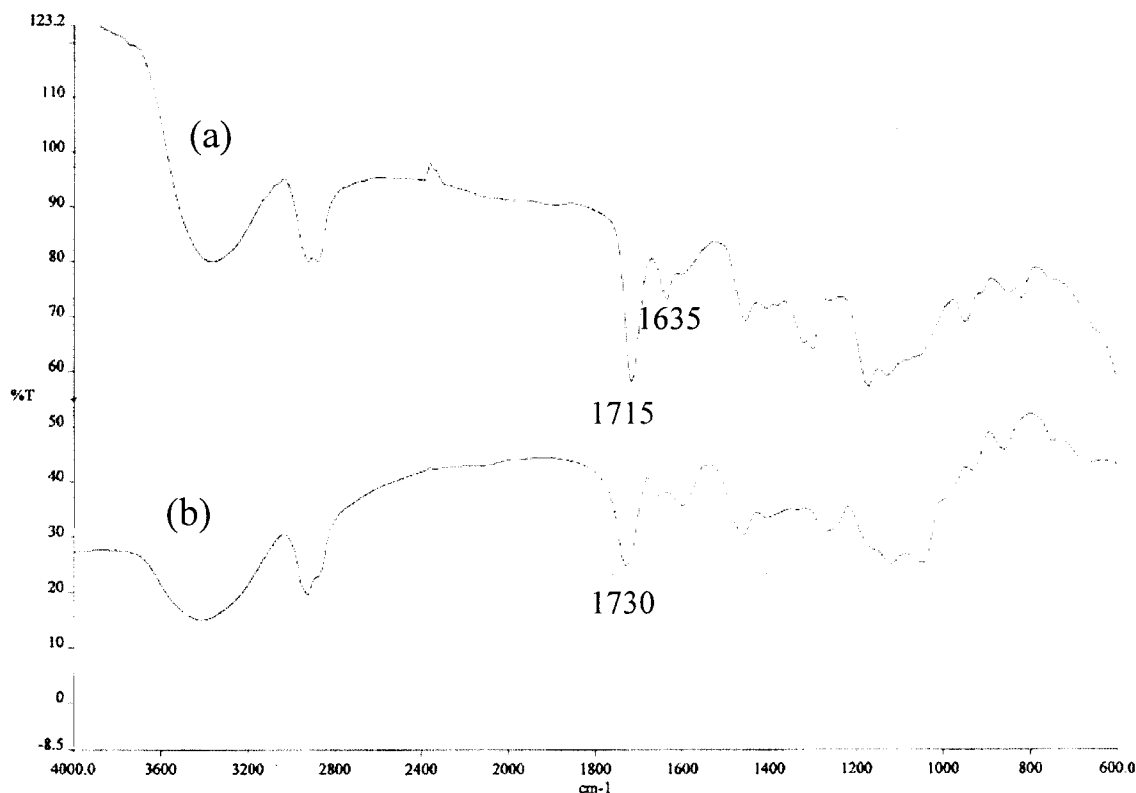
romethane were also unsuccessful. Therefore, we investigated the reaction of PG with GMA by analogy with the results concerning the synthesis of GMA derivatized dextran.<sup>13,14</sup> Similar to the results reported by van Dijk Wolthuis et al.,<sup>13,14</sup> the reaction of PG with GMA occurs via transesterification of the methacryloyl group, yielding PGMA and glycidol (Scheme 2).

A <sup>1</sup>H-NMR analysis of the crude reaction products solubilized in D<sub>2</sub>O shows that glycidol is formed initially during the reaction with a concomitant decrease in the amount of GMA (Fig. 1). Further analysis indicates the disappearance of the glycidol signals due to its reaction with the free hydroxyl of PG via nucleophilic opening of the epoxy group (Scheme 3).

PGMA polymerizes rapidly using either UV activation<sup>15</sup> or thermal activation in the presence of a radical initiator as demonstrated by the displacement of the characteristic IR carbonyl band from 1715 to 1730 cm<sup>-1</sup> and the disappearance of the ethylenic band at 1635 cm<sup>-1</sup> (Fig. 2). The <sup>13</sup>C-MAS/CP NMR analysis also indicates polymerization of PGMA (the nonconjugated carbonyl signal at 178 ppm and no ethylenic signals, Fig. 3).

### Dimensional stabilization of wood

PGMA was investigated for wood treatment using standard vacuum/pressure impregnation. The PGMA



**Figure 2** The FTIR spectrum of poly(glycerol methacrylate) before (spectrum a) and after (spectrum b) thermal treatment in the presence of MEKP.

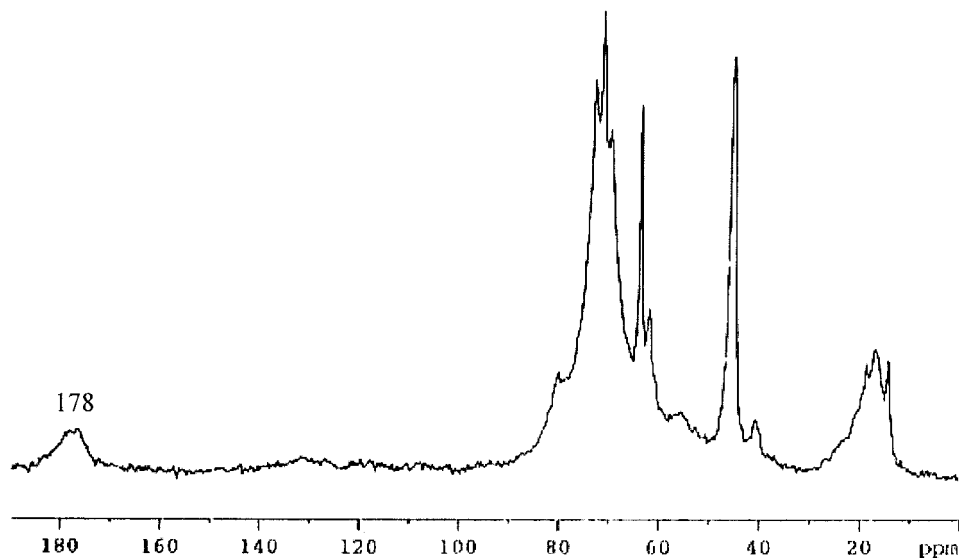


Figure 3 The  $^{13}\text{C}$ -CP/MAS NMR spectrum of poly(glycerol polymethacrylate).

diluted in water (10, 20, 30, and 50 mass %) in the presence of MEKP (2 mass %) was impregnated in pine or beech blocks. After curing at  $80^\circ\text{C}$  for 3 days, the blocks were subjected to ASE measurements. The results are given in Table I (Fig. 4). However, in spite of this tendency, the relationship between the ASE and chemical uptake is not linear. This lack of linearity could be explained by the strong heterogeneity of wood (the structure and chemical composition), which explains the high differences calculated for the same range of values. The weight gain and ASE are directly connected to the amount of chemical used for impregnation. The dimensional stability of treated wood is considerably increased compared to untreated wood. The level of polymerization of PGMA was investigated after leaching of unreacted products (Fig. 5). Indeed, the polymerization of PGMA was carried out without solvent in the presence of MEKP, which leads to the formation of a water insoluble polymer. Thus, the chemicals still present after leaching correspond principally to polymerization products insoluble in

water. Polymerization increases with the concentration of PGMA used, indicating that the dilution of PGMA into the wood is important for such types of treatments and particularly for their durability in outdoor applications.

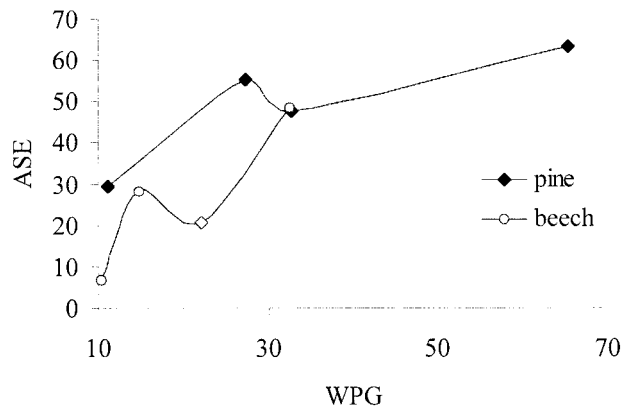
#### Microscopic analysis

The localization of PGMA in the wood was investigated using optical microscopy. Penetration of chemicals into the wood structure principally depends on the volumetric swelling coefficient of the solvent used for impregnation.<sup>16</sup> A polar solvent like water swells the wood structure and permits penetration of PGMA into the wood cell wall. After polymerization, PGMA remains in the cell walls when the wood is dried. This bulking action prevents the wood from shrinking, increasing its dimensional stability. Microscopic analysis associated with picture analysis allows the estimation of the area corresponding to either the cell walls ( $A_{\text{cw}}$ ) or lumen ( $A_l$ ) of wood. The  $A_l/A_{\text{cw}}$  ratio permits

TABLE I  
Impregnation of Blocks with Aqueous Solution of PGMA in Presence of MEKP (2%) Followed by Heating at  $80^\circ\text{C}$  for 3 Days

Species	PGMA (%)	$m_0$ (g)	$m_1$ (g)	WPG (%)	ASE (%)
Pine	10	$7.92 \pm 0.2$	$8.81 \pm 0.2$	$11.22 \pm 1.3$	$29.47 \pm 10.6$
Pine	20	$8.39 \pm 0.9$	$10.66 \pm 0.9$	$27.39 \pm 3.4$	$55.48 \pm 10.2$
Pine	30	$10.02 \pm 0.3$	$13.29 \pm 0.3$	$32.69 \pm 5.3$	$47.79 \pm 3.6$
Pine	50	$8.88 \pm 0.9$	$14.58 \pm 0.7$	$65.38 \pm 16.1$	$63.41 \pm 17.0$
Beech	10	$12.27 \pm 0.4$	$13.55 \pm 0.4$	$10.47 \pm 0.6$	$6.61 \pm 3.6$
Beech	20	$14.10 \pm 0.4$	$16.18 \pm 0.3$	$14.75 \pm 1.5$	$28.27 \pm 14.5$
Beech	30	$14.47 \pm 0.6$	$17.67 \pm 0.4$	$22.14 \pm 2.3$	$20.90 \pm 6.0$
Beech	50	$13.87 \pm 0.4$	$18.35 \pm 0.8$	$32.54 \pm 9.7$	$48.36 \pm 10.1$

The values are the average of five replicates.

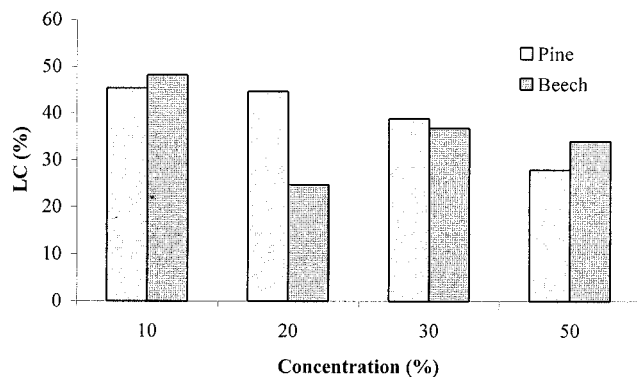


**Figure 4** The relationship between the ASE and chemical uptake.

the quantification of the swelling effect of the treatment, which is in direct connection with the dimensional stabilization (Table II). In the case of pine earlywood the  $A_l/A_{cw}$  ratio, which is higher for the untreated sample than for the treated one, indicates an important bulking effect of the treatment (compare 4.55 to 2.37). These results show that PGMA is able to swell the cell walls of wood, explaining its higher dimensional stability after treatment. Such an approach was more difficult to apply to beech because of its important morphological heterogeneity. Figures 6 and 7 show micrographs of polished transversal cutting of treated or untreated pine or beech blocks. It is evident from these micrographs that the thickness of the cell walls is considerably increased. This is particularly evident in beech, where the lumen of the fibers is practically obstructed.

### CONCLUSION

PGMA was synthesized in good yields starting from PG and GMA. Soluble in water, PGMA allows waterborne treatment of wood, limiting the use of volatile organic compounds. After *in situ* polymerization, the treated wood shows increased dimensional stability



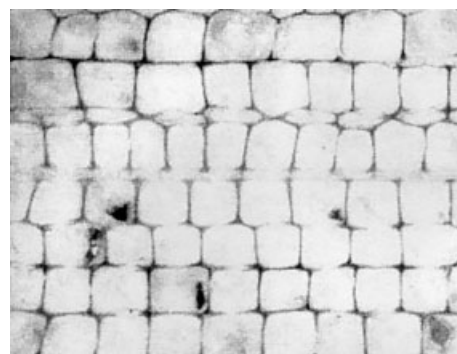
**Figure 5** The leachability of chemicals from treated wood.

**TABLE II**  
Picture Analysis of Treated PGMA (50% in Water) and Untreated Pine Earlywood

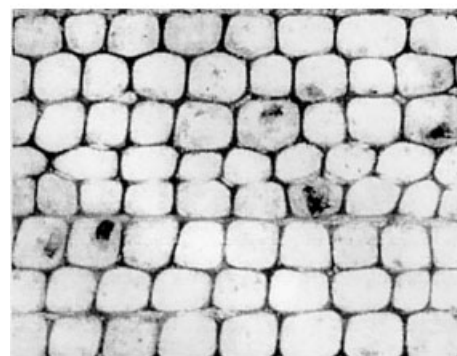
Sample	Area (%)		$A_l/A_{cw}$
	Cell wall	Lumen	
Untreated pine	16.14	83.86	
Untreated pine	17.98	82.02	
Untreated pine	16.67	83.33	
Untreated pine	20.82	79.18	
Untreated pine	18.38	81.62	
Untreated pine <sup>a</sup>	18.00 ± 1.8	82.00 ± 1.8	4.55 ± 1.8
Treated pine	27.59	72.41	
Treated pine	31.45	68.55	
Treated pine	27.48	72.52	
Treated pine	30.88	69.12	
Treated pine	30.86	69.14	
Treated pine <sup>a</sup>	29.66 ± 1.9	70.34 ± 1.9	2.37 ± 1.8

<sup>a</sup> The average value.

compared to the untreated wood. The dimensional stabilization and the level of polymerization are in direct relation with the amount of PGMA used for the impregnation solution. Microscopic observation coupled with picture analysis indicates that poly[glycerol-

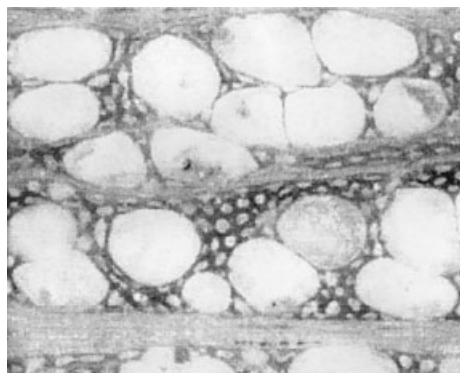


(a)

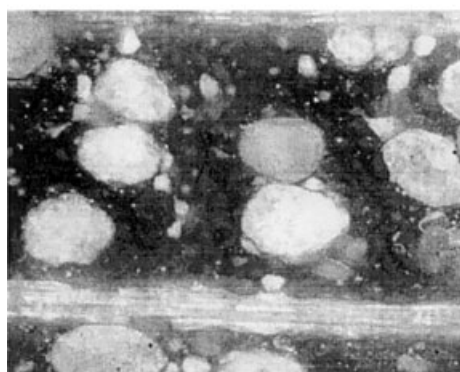


(b)

**Figure 6** Cross-sectional views of pine earlywood (a) before and (b) after treatment with poly(glycerol methacrylate).



(a)



(b)

**Figure 7** Cross-sectional views of beech earlywood (a) before and (b) after treatment with poly(glycerol methacrylate).

poly(methacrylate)] is able to bulk the cell walls, explaining the observed dimensional stabilization.

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