A controlled radical polymerization route to polyepoxidated grafted hemicellulose materials

Ulrica Edlund[1)], Ann-Christine Albertsson[1),*)]

DOI: dx.doi.org/10.14314/polimery.2014.060

For a long-lasting friendship, a never-ending devotion to polymer science, and priceless tutoring contributions to graduate student courses at Royal Institute of Technology, we thank Professor Stanislaw Penczek and dedicate this original research work to him with our heartfelt congratulations on his 80th birthday

Abstract: Polyfunctional copolymers were prepared from the major softwood hemicellulose polysaccharide, *i.e. O*-acetylated galactoglucomannan (AcGGM) through a grafting-from controlled radical polymerization. AcGGM was functionalized with brominated pendant groups that served as initiating species in the subsequent Cu(0) mediated radical polymerization of glycidyl methacrylate (GMA). A linear relationship of $\ln[GMA]_0/[GMA]$ (the index 0 refers to the initial value) versus reaction time up to conversions of 80 % suggests a first order rate of propagation and a "living" polymerization.

Keywords: *O*-acetylated galactoglucomannan, hemicellulose, renewable resources, single-electron-transfer living radical polymerization.

Otrzymywanie epoksydowanych szczepionych materiałów hemicelulozy metodą kontrolowanej polimeryzacji rodnikowej

Streszczenie: Kopolimery wielofunkcyjne wytworzono z głównego polisacharydu będącego składnikiem hemicelulozy pochodzącej z drewna miękkiego, tj. *O*-acetylowanego galaktoglukomannanu (AcGGM) poprzez szczepienie w procesie kontrolowanej polimeryzacji rodnikowej. AcGGM funkcjonalizowano przyłączając bromowane grupy boczne, które służyły jako inicjatory w kolejnym procesie, katalizowanej za pomocą Cu(0), reakcji polimeryzacji rodnikowej metakrylanu glicydylu (GMA). Liniowa zależność $\ln[GMA]_0/[GMA]$ (indeks 0 odnosi się do wartości początkowej) od czasu reakcji obserwowana do osiągnięcia 80 % konwersji, pozwala przypuszczać, że reakcja propagacji jest pierwszego rzędu i ma charakter polimeryzacji żyjącej.

Słowa kluczowe: *O*-acetylowany galaktoglukomannan, hemiceluloza, surowce odnawialne, rodnikowa polimeryzacja żyjąca z przeniesieniem pojedyńczego elektronu.

INTRODUCTION

The design of renewable and sustainable functional materials is an area of immediate concern to the society and generates ever increasing interest. Renewable material resources from the vast and diverse group of polysaccharides offer plentiful opportunities to design polymeric materials with functionalities and performances that render them attractive alternatives to conventional fossil-based materials, especially those polysaccharides where material utilization is not competing with the constantly and globally growing food demand. The group of hemicelluloses is very attractive as such, being more or less branched heteropolysaccharides of pentose and hexose sugars with large structural variations depending on origin, and major constituents of wood and higher plants [1]. Hemicelluloses are generally much more soluble than cellulose and are typically released to the aqueous phase when plants and woody biomass are industrially processed, *e.g.* for pulp, board, or food production. The isolation and recovery of hemicelluloses from the residual process liquors allow for subsequent utilization of this renewable resource in higher value applications, including barrier films [2—6], hydrogels [7, 8] or hemicellulose derived fuel and chemicals [9, 10].

As all polysaccharides, hemicellulose properties may potentially be varied over a broad range by covalent structural modification, especially considering the abundance of hydroxylated pendant groups on the sugar ring backbone. By chemical modification, the typical limitations of hemicelluloses such as moisture sensitivity and lack of plasticity, could be circumvented and the spectrum of possible applications significantly broadened.

[1)] Royal Institute of Technology (KTH), Fibre and Polymer Technology, Teknikringen 56, SE-100 44 Stockholm, Sweden.

[*)] Author for correspondence; e-mail: aila@kth.se

The challenge is to find robust, facile and environmentally benign synthetic pathways for said modifications, without detrimental effects to the polysaccharide backbone which is readily hydrolyzed under basic and acidic conditions. Preferably, such a pathway should provide control over molecular weight and architectures, proceed homogeneously, and be tolerant to water. Recently we showed that a new method for the living and controlled radical polymerization — single-electron-transfer living radical polymerization (SET-LRP), may be developed and applied for hemicellulose modification [11—14]. In SET-LRP a transition metal, typically elemental Cu, is the catalyst in very low amounts offering facile and complete removal of the catalyst from the reaction mixture with no further need for tedious purification of catalyst traces. *Via* a single electron transfer from the transition metal catalyst, propagating polymer chain ends are generated and they undergo a reversible termination with a halogen species released from the initiator molecule, thus transferring the growing chain end to a dormant state where no true termination can occur, hence preserving the chain end "living". Since first presented in 2006, the interest in SET-LRP has skyrocketed, thanks to its versatility to a broad range of solvents and monomers, its robustness to water and traces of air, and "living" character [15—23]. By applying SET-LRP to hemicelluloses, it is possible to combine vinyl polymerization with polysaccharide chemistry and to derive hybrid copolymer materials with innovative combinations of properties.

Our aim was to utilize the glucomacroinitiator methodology in the preparation of a polyepoxidated functionalized hemicellulose material by exploring the potential of the major spruce hemicellulose acetylated galactoglucomannan (AcGGM) to initiate a controlled grafting-from polymerization of glycidyl methacrylate.

EXPERIMENTAL PART

Materials

N,*N*'-carbonyldiimidazole (CDI, 97 %, Aldrich), α-bromo isobutyric acid (αBrIBA, 98 %, Aldrich), imidazole (≥99.5 %, Sigma), copper wire (American wire gauge AWG 20), tris[2-(dimethylamino)ethyl]amine (Me_6-TREN, Aldrich), 2-propanol (99 %, Labscan), and dimethyl sulfoxide (DMSO, ≥ 99.5 %, Fluka) were used as received. Glycidyl methacrylate (GMA, 97 %, Aldrich) was passed through a column of neutral aluminum oxide before use and then stored cold. *O*-acetyl-galactoglucomannan (AcGGM) was recovered from the aqueous phase used in the thermomechanical pulping of spruce (*picea abies*). The liquid phase was purified by ultrafiltration (membrane cut off 1000 Da) and then lyophilized on a LyoLab 3000 instrument. AcGGM had a number-average molecular weight ($\overline{M}_n$) of 5150, a dispersity ($Đ$) of ~1.3, and a degree of acetylation of 0.30 as determined according to a published protocol [24].

AcGGM macroinitiator (AcGGM-Br) preparation

AcGGM was esterified to yield pendant brominated groups according to a procedure published previously [11—13]. Briefly, 9.7 g of CDI and 10 g of α-bromo isobutyric acid (αBrIBA) was dissolved in 80 mL of DMSO and allowed to react at room temperature for 60 min, forming a imidazoyl-activated intermediate. Next, the reaction mixture was heated to 50 °C. Imidazole (4 g) and AcGGM (2.6 g) dissolved in 100 mL of DMSO was added under stirring. The reaction was allowed to proceed for another 60 min. The reaction mixture was drop-wise added to cold 2-propanol and the precipitate was collected and subjected to Soxhlet extraction in 2-propanol over 2 days. Finally, the product AcGGM-Br was dissolved in water, lyophilized and characterized with ^{1}H NMR. $\overline{M}_n$ of AcGGM-Br, measured by SEC, was 3540.

Graft polymerization of GMA

AcGGM-Br (16.4 mg) was dissolved in 3 mL of DMSO. GMA in an amount needed to obtain a $[GMA]_0/[AcGGM\text{-}Br]_0$ ratio (here and below the index 0 refers to the initial value, before reaction) of either 50/1 or 200/1 was added to the solution together with 0.7 μL of Me_6-TREN. The mixture was transferred to a Schlenk tube and subjected to a freeze-pump-thaw degassing cycle four times, flushing with N_2. A control reaction, not subjected to freeze-pump-thawing was also performed. Polymerizations were started by adding the catalyst, 6.25 cm copper wire, to the reaction mixture. Each polymerization reaction was allowed to proceed at 25 °C for a predetermined time, then a small aliquot of the reaction mixture was sampled for ^{1}H NMR analysis while the remainder of the reaction mixture was precipitated in cold water or ethyl acetate. The off-white precipitate was washed in water and finally vacuum dried.

Characterization of substances

^{1}H NMR spectra were recorded with a Bruker DMX-500 nuclear magnetic resonance spectrometer operating at 500 MHz. For AcGGM and AcGGM-Br, D_2O was used as the solvent while GMA and polymerization products were dissolved in DMSO-d_6 (Larodan Fine Chemicals AB) in sample tubes with an outer diameter of 5 mm. MestReNova software was used for data acquisition.

— Structural analysis was also done by FT-IR ATR using a Perkin Elmer Spectrum 2000 Fourier Transform Infrared Spectrometer with an Attenuated Total Reflectance crystal accessory. All spectra were recorded as the mean of 16 individual scans at a resolution of 2 cm^{-1} in the interval between 4000 and 600 cm^{-1}. Corrections were made for atmospheric water and CO_2.

— Molecular weights of AcGGM and AcGGM-Br were determined with a Shimadzu Size Exclusion Chromatography (SEC) system using *N*,*N*-dimethylacetamide

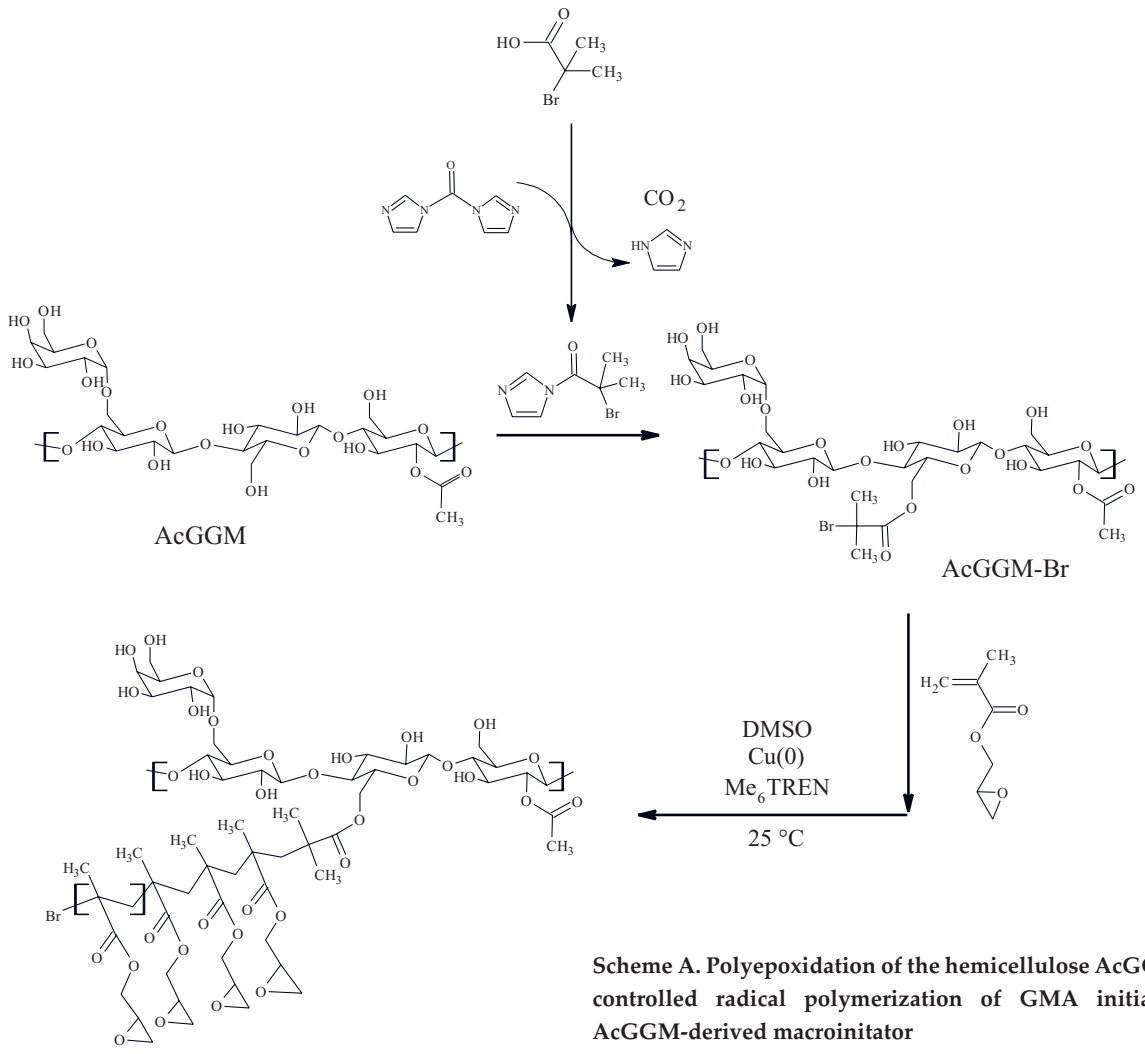
(DMAc) containing LiCl (0.5 wt. %) as the eluent running at a flow rate of 0.5 mL/min at 80 °C. All samples were filtered (0.45 μm, Millipore) prior to analysis and then a sample volume of 200 μL was manually injected into the system consisting of four PLgel 20 μm Mixed-A columns. Pullulan standards with narrow molecular weight distributions were used for calibration and LC Solution software from Shimatzu was used for data acquisition and calculations.

RESULTS AND DISCUSSION

Polyepoxidated hemicellulose materials were prepared by converting the polysaccharide into a macroinitiator bearing spatial bromo moieties that initiates the controlled radical polymerization of GMA, resulting in a graft copolymer. The strategy is schematically presented in Scheme A.

The conversion of AcGGM to a brominated macroinitiator was confirmed using ^{1}H NMR and FT-IR ATR (Fig. 1). The native AcGGM display a triplet at 2.1 ppm originating from the acetyl pendant groups. As the degree of acetylation has previously been determined to be 0.3, this peak was used for the calculation of the degree of substitution with -C(CH$_3$)$_2$-Br pendant functions (DS_{Br}) following the esterification reaction with αBrIBA. The introduced isobutyric methyl groups give rise to signals between 2 and 1.4 ppm depending on their position on the sugar ring repeating units. Relating the isobutyric methyl group integrals to the integral at 2.1 relating to an acetylation degree of 0.3 gives a macroinitiator DS_{Br} of 0.15 which corresponds to about 6 brominated moieties on each hemicellulose chain. The DS_{Br} can be increased by prolonging the esterification reaction time [14], however, a low value of DS_{Br} was targeted to avoid intramolecular termination caused by propagating sites being situated too close to one another on the macroinitiator in its active state.

AcGGM-Br was used as a macroinitiator in the controlled radical polymerization of GMA according to the SET-LRP process. A copper wire is used as the catalyst allowing for facile and complete removal of the catalyst after polymerization. The structural progression of the polymerization was followed by ^{1}H NMR as shown in Fig. 2. The peaks at 6.03 ppm and 5.69 ppm stemming from the vinyl group of the GMA monomer are gradually disappearing while alkyl main chain proton signals at 1—0.77 ppm of the growing polymers are increasing in



Scheme A. Polyepoxidation of the hemicellulose AcGGM *via* the controlled radical polymerization of GMA initiated by a AcGGM-derived macroinitator

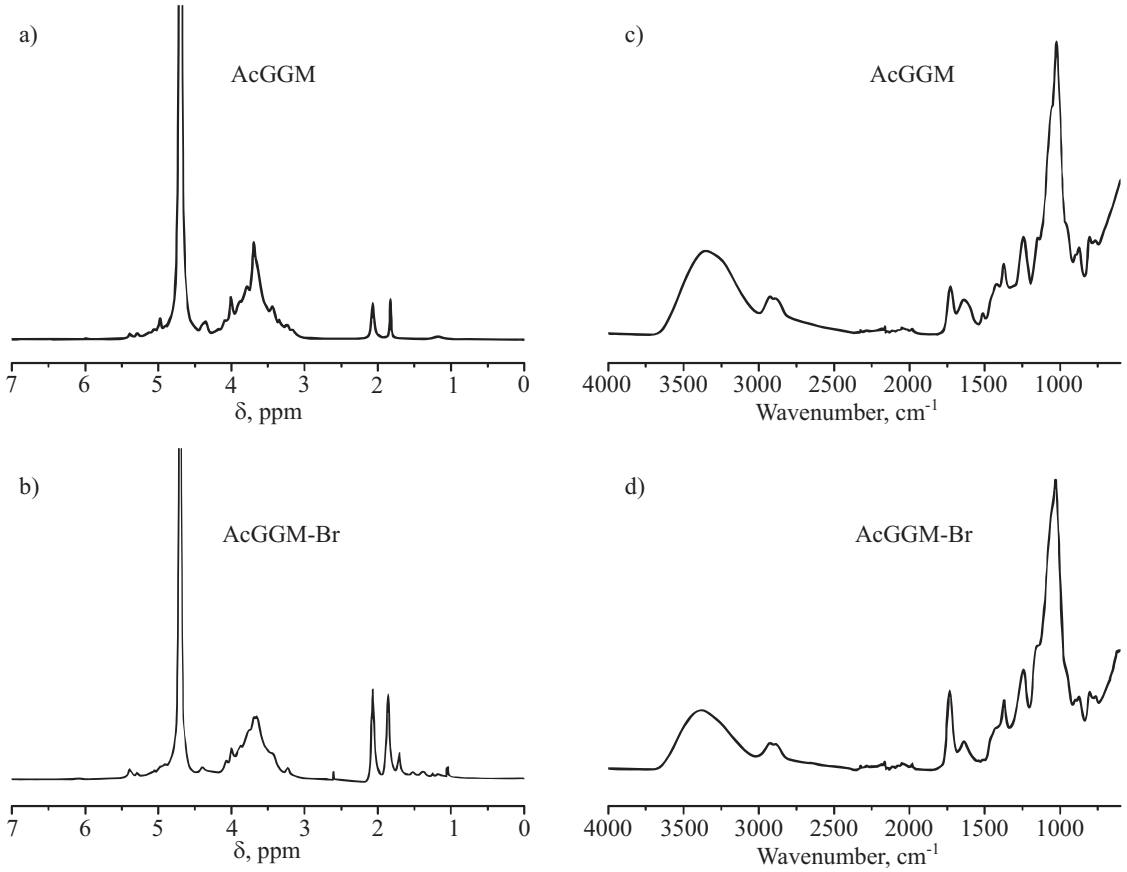


Fig. 1. ^{1}H NMR in D_2O (a and b) and FT-IR ATR (c and d) spectra of AcGGM before and after bromo substitution converting AcGGM to a macroinitiator for controlled radical polymerization

intensity. Following progressing polymerization, the signals from the oxirane protons and the -CH_2- protons adjacent to the oxirane ring are shifting to slightly lower shifts. This is clearly seen for the oxirane proton signals at 4.44 ppm and 3.87 ppm which shift to less resolved peaks at 4.27 ppm and 3.71 ppm, respectively, as the polymerization proceeds. The anomeric protons of the AcGGM macroinitiator constitute a small part of the reaction mixture at the $[GMA]_0/[AcGGM\text{-}Br]_0$ ratio of 200/1 and are partly overlaid by the GMA signals. Hence, they are difficult to distinguish in the NMR spectra in Fig. 2.

FT-IR ATR results more clearly shows the coexistence of AcGGM and the GMA grafts in the resulting copolymer (Fig. 3). A broad hydroxyl band peaking at ~3360 cm^{-1} stems from the polysaccharide chains. The ester C=O in each GMA unit gives rise to a strong band at 1715 cm^{-1} which is overlaying the AcGGM pendant acetyl C=O peaks at 1740 cm^{-1}. The peak at 1650 cm^{-1} in the GMA spectrum originates from primary alkene C=C stretching vibrations and is not present in the copolymer product where the vinyl groups have reacted to form graft chain alkyl groups which give rise to C-H stretching vibrations bands at 3100—2800 cm^{-1}.

The kinetics of the GMA polymerization was more closely followed with ^{1}H-NMR as shown in Fig. 4. The time dependence of $\ln[GMA]_0/[GMA]$ and conversion is close to linear suggesting pseudo-first order rate of propagation and a "living" polymerization up to conversions of 80 %. A high conversion is reached within 5 h. The apparent rate constant of propagation (k_p^{app}) from the kinetic plot is 0.0035 min^{-1}. The identical k_p^{app} values for both an $[GMA]_0/[AcGGM\text{-}Br]_0$ ratio of [200]/[1] or [50]/[1] further sustains a controlled polymerization. Noteworthy, when performing an identical polymerization experiment with $[GMA]_0/[AcGGM\text{-}Br]_0/[Me_6\text{-}TREN]_0 = 200/1/0.2$ in DMSO but without subjecting the reaction mixture to freeze-pump-thaw deoxygeneation prior to reaction, the polymerization still proceeds to ~ 80 % conversion at a rate not significantly more sluggish than in the degassed reactions. Tolerance to air is an important feature facilitating up-scaling and industrial implementation.

To keep the viscosity from increasing too much during the course of polymerization, both the initiator and monomer concentrations were purposely kept low. Still, a macroscopic and homogeneous sol-gel transition was observed as conversions approached 80 % as shown in Fig. 5. At this point, conversions did not increase much further due to inhibited diffusion in the gel-like product. The products were still soluble in DMSO and could be recovered by dilution in DMSO followed by precipitation. Water solubility, typical for the native AcGGM, is lost around 40 % conversion of GMA grafting. The solubility of AcGGM-*graft*-GMA at 80 % conversion in a range of com-

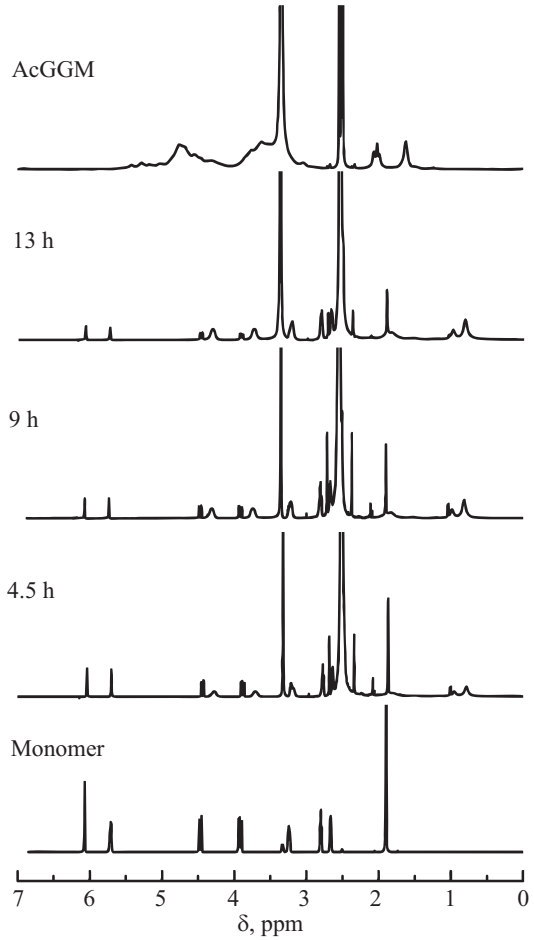


Fig. 2. ^{1}H NMR in DMSO-d_6 (AcGGM in D_2O) of the progressing polymerization of GMA initiated by AcGGM-Br at different reaction times. $[GMA]_0/[AcGGM\text{-}Br]_0/[Me_6\text{-}TREN]_0$ = 200/1/0.2

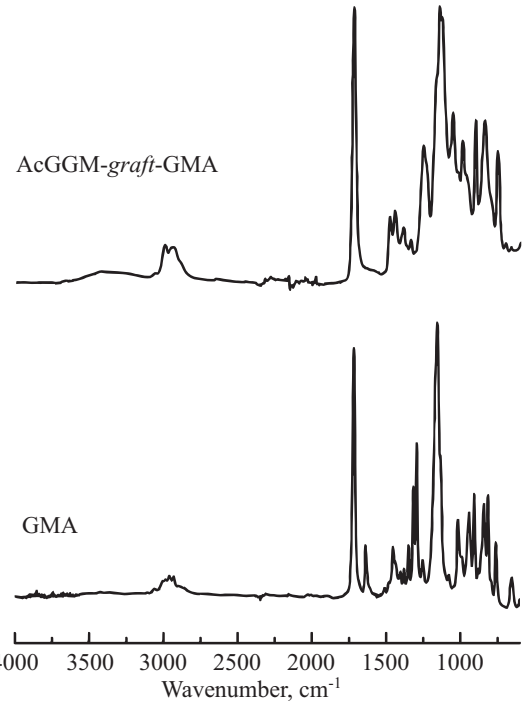


Fig 3. FT-IR ATR spectra of the monomer GMA and the polymerization product of GMA initiated by the macroinitiator AcGGM-Br

mon solvents is shown in Table 1. The low solubility in solvents being eluents of available SEC systems impaired the measurements to the point where molecular weights of the graft copolymers could not be determined. The alternative molecular weight determination will instead be a topic of further study. The derived graft co-polymer material is moldable into plastic-like films and do, unlike AcGGM, display a distinct glass transition temperature at 80—85 °C ($[GMA]_0/[AcGGM\text{-}Br]_0$ = 200/1, 80—68 % conversion). Also, the imported oxirane functionalities offer many opportunities of subsequent coupling of other molecules to the grafted AcGGM so that a wide range of combinatory materials can be prepared.

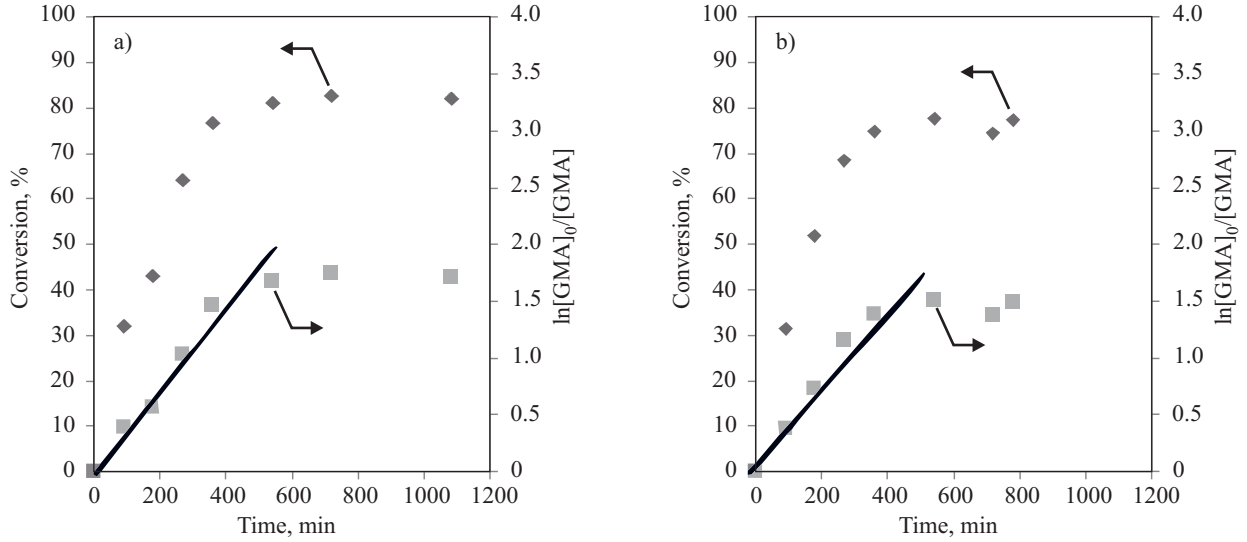


Fig. 4. Kinetic plots for polymerization at 25 °C of GMA initiated by the AcGGM-Br macroinitiator (each data point represents an individual experiment): a) $[GMA]_0/[AcGGM\text{-}Br]_0/[Me_6\text{-}TREN]_0$ = 200/1/0.2, b) $[GMA]_0/[AcGGM\text{-}Br]_0/[Me_6\text{-}TREN]_0$ = 50/1/0.2

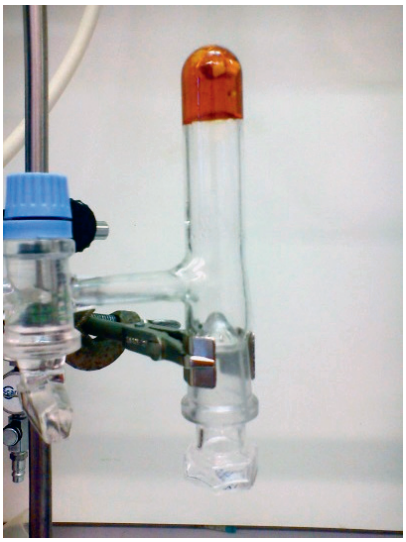


Fig. 5. Reaction product from AcGGM-Br initiated GMA graft polymerization at 80 % conversion. $[GMA]_0/[AcGGM\text{-}Br]_0/[Me_6\text{-}TREN]_0 = 200/1/0.2$

T a b l e 1. Comparative solubility data of AcGGM and AcGGM-*-graft*-GMA (I — insoluble, SS — slightly soluble, S — soluble)

Solvent	AcGGM	AcGGM-*graft*-GMA (at 80 % conversion)
H_2O	S	I
Methanol	I	I
Ethanol	I	I
Acetone	I	I
Diethyl ether	I	I
DMSO	S	S
DMAc	S	SS
$CHCl_3$	I	SS
THF	I	SS

CONCLUSIONS

The major hemicellulose spruce, AcGGM, was converted to a functional macroinitiator that mediated the controlled polymerization of glycidyl methacrylate (GMA). Pseudo-first order kinetics and a "living" polymerization and conversions of 80 % were achieved in less than 5 h producing a branched AcGGM-*graft*-GMA copolymer. Successful polymerization in a "living" manner was also achieved without the rigorous deoxygeneation conventionally required in controlled radical polymerization.

REFERENCES

1. Albertsson A.-C., Edlund U., Varma I. K.*: "New materials for sustainable films and coatings"* in *"Biopolymers"* (Ed., Plackett D.), Chapter 7, John Wiley & Sons Ltd. 2011, pp. 133—150.
2. Xiao C., Lu Y., Gao S., Zhang L.: *J. Appl. Polym. Sci.* **2001**, *79*, 1596.
3. Hartman J., Albertsson A.-C., Sjöberg J.: *Biomacromolecules* **2006**, *7*, 1983.
4. Hansen N. M. L., Plackett D.*: Biomacromolecules* **2008**, *9*, 1493.
5. Edlund U., Ryberg Y. Z., Albertsson A.-C.: *Biomacromolecules* **2010**, *11*, 2532.
6. Saadatmand S., Edlund U., Albertsson A.-C., Danielsson S., Dahlman O.: *Environ. Sci. Technol*. **2012**, *46*, 8389.
7. Lindblad M. S., Ranucci E., Albertsson A.-C.: *Macromol. Rapid Commun*. **2001**, *22*, 962.
8. Li X., Pan X.: *J. Biobased Mater. Bioenergy* **2010**, *4*, 289.
9. Ji X., Huang H., Nie Z.-K., Qu L., Xu Q., Tsao G. T.: *Adv. Biochem. Eng./Biotechnol.* **2012**, *128*, 199.
10. Girio F. M., Fonseca C., Carvalheiro F., Duarte L. C., Marques S., Bogel-Lukasik R.: *Biores. Technol*. **2010**, *101*, 4775.
11. Voepel J., Edlund U., Albertsson A. C., Percec V.: *Biomacromolecules* **2011**, *12*, 253.
12. Voepel J., Edlund U., Albertsson A. C.: *J. Polym. Sci., A Polym. Chem.* **2011**, *49*, 2366.
13. Edlund U., Albertsson A.-C.: *J. Polym. Sci., A Polym. Chem.* **2011**, *49*, 4139.
14. Edlund U., Albertsson A.-C.: *J. Polym. Sci., A Polym. Chem.* **2012**, *50*, 755.
15. Percec V., Guliashvili T., Ladislaw J. S., Wistrand A., Stjerndahl A., Sienkowska M. J., Monteiro M. J., Sahoo S.*: J. Am. Chem. Soc.* **2006**, *128*, 14 156.
16. Lligadas G., Percec V.: *J. Polym. Sci., A Polym. Chem*. **2008**, *46*, 4917.
17. Percec V., Rosen B. M.: *Chem. Rev*. **2009**, *109*, 5069.
18. Percec V., Jiang X. A., Rosen B. M.: *J. Polym. Sci., A Polym. Chem*. **2010**, *48*, 2716.
19. Fleischmann S., Rosen B. M., Percec V**.:** *J. Polym. Sci., A Polym. Chem*. **2010**, *48*, 1190.
20. Ding A., Lu G., Guo H., Zheng X., Huang X.: *J. Polym. Sci., A Polym. Chem*. **2013**, *51*, 1091.
21. Levere M. E., Nguyen N. H., Leng X., Percec V.: *Polym. Chem*. **2013**, *4*, 1635.
22. Zhang Q., Wilson P., Li Z., McHale R., Godfrey J., Anastasaki A., Waldron C., Haddleton D. M.: *J. Am. Chem. Soc.* **2013**, *135*, 7355.
23. Leng X., Nguyen N. H., van Beusekom B., Wilson D. A., Percec V.*: Polym. Chem*. **2013**, *4*, 2995.
24. Jacobs A., Dahlman O.: *Biomacromolecules* **2011**, *2*, 894.