the formation of a polysiloxane films. The reaction mechanism of the formation of thin film is shown at Fig. 2.

Results and discussion
It is well known that silanes do not deposit themselves in a uniform fashion, but rather deposit themselves as sea-island structures of varying thickness along the length of the fiber. For this reason, the morphology of the silane coating on E-glass fibers was investigated using scanning electron microscopy (SEM). The morphology of pp-VTEO film (Fig. 3a) and polysiloxane film prepared from the solution on glass fibers (Fig. 3b) is approximately of the same character. Atomic force microscopy (AFM) in contact mode was used to examine the surface roughness morphology of the silane coating on tested flat substrates. Pp-VTEO films (Fig. 4a) were more homogenous with regular porous structure in comparison to thin films deposited from aqueous solution of VTEO (Fig. 4b). Detailed chemical composition of pp-VTEO film deposited on glass slides was evaluated by X-ray photoelectron spectroscopy (XPS) and compared with XPS spectrum of polysiloxane film deposited from aqueous solution. Table 1 shows the atomic concentration of oxygen and carbon relative to the concentration of silicon atoms in the pp-VTEO films and thin film formed from silanol solution (sample A). Higher amount of carbon and oxygen in pp-VTEO film indicates different chemical structure. Surface adhesion and wettability was tested on deposited films by plasma polymerization and from solution on flat substrates by contact angle measurement against the following liquids: distilled water, glycerol, ethyleneglycol, and diiodomethane using DataPhysics Instruments contact-angle meter OCA 10. The obtained data were analyzed to estimate a dispersive and polar contribution to surface energy according to Owens-Wendt-Rabel-Kaelble method. The results of contact angle measurement are shown at the Table 2.

Table 1. XPS analysis of tested surfaces

<table>
<thead>
<tr>
<th>pp-VTEO film</th>
<th>Power [W]</th>
<th>C/Si [%]</th>
<th>O/Si [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continual plasma</td>
<td>50</td>
<td>4.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Continual plasma</td>
<td>2.5</td>
<td>4.2</td>
<td>2.1</td>
</tr>
<tr>
<td>Pulsed plasma</td>
<td>5</td>
<td>4.5</td>
<td>2.1</td>
</tr>
<tr>
<td>A</td>
<td>0.5% solution</td>
<td>2.4</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Table 2. Surface energy measuring of thin films

<table>
<thead>
<tr>
<th>Type of deposition on glass slides</th>
<th>Surface energy [mN.m⁻¹]</th>
<th>Polar part [mN.m⁻¹]</th>
<th>Dispersive part [mN.m⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet-chem. process</td>
<td>72.8</td>
<td>59.3</td>
<td>13.6</td>
</tr>
<tr>
<td>Plasma polymerization</td>
<td>30.7</td>
<td>4.7</td>
<td>26.0</td>
</tr>
<tr>
<td>Untreated E-glass</td>
<td>61.0</td>
<td>38.7</td>
<td>22.3</td>
</tr>
</tbody>
</table>

Conclusions
Thin films prepared from vinyltriethoxysilane monomer by plasma polymerization and wet-chemical process on planar and fibrous substrates have been compared and characterized in terms of surface morphology (AFM, SEM), chemical structure (XPS) and adhesion to the substrates (scratch test).

Pp-VTEO films are highly crosslinked polysiloxane materials with porous, but more homogenous and smoother surface morphology in comparison to siloxane films prepared by deposition from solution.

The influence of above mentioned coating techniques of glass fibers on quality of adhesion bonding in glass fiber/polyester system will be study using microbond test, short beam shear test and DMA.

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REFERENCES


L11 A NOVEL WELL-DEFINED LINEAR POLY(METHACRYLIC ACID) MACROMONOMERS FOR BIOMATERIAL APPLICATIONS: THE SYNTHESIS AND CHARACTERIZATION

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Introduction
Macromonomers (oligomers with $M_n$=10³–10⁴ that contain functional group suitable for further polymerizations) allow for control of a wide variety of properties of the species prior to polymerization into final product. The control of rheological properties, for example, is useful in coating and adhesive applications. Monomers, by definition, are of low molecular weight and because of their low viscosity do not possess favorable pro-
properties for these types of applications. In virtually every application of polymeric materials, strict control of properties is desired but are often not possible due to the polydisperse nature of polymers from conventional synthetic methods. In biomaterials and tissue-engineering applications strict control of properties is critical since all functional units within the body are structurally and functionally very specific and dynamically interact with its environment in a synergistic manner.2

Recently, the development of controlled/living free radical polymerization techniques known as Atom Transfer Radical Polymerization (ATRP), one of the most successful and versatile systems, has allowed for the synthesis of a variety of well-defined polymers with predetermined molecular weights (DP = $\delta$[M]/[P]) and low polydispersities ($M_w/M_n$ < 1.3). ATRP is applicable for hydrophobic monomers such as acrylates, methacrylates and styrenes as well as hydrophilic and functional monomers such as 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-(dimethylamino)ethyl methacrylate (DMAEMA) and 4-vinylpyridine. Functional end groups can be introduced by use of either a functional initiator or through the transformation of the halogen end group by a synthetic chemistry technique.3-10 As for macromonomers, Matyjaszewski et al. first reported the synthesis of poly(methylen)11,12 DMAEMA and methyl methacrylate (MMA).13 However, to the best of our knowledge, no synthesis of $\alpha$-allyl terminated macromonomers is reported. A disadvantage of ATRP is its sensitive to the presence of acids.14 Thus, monomers or initiators containing acid functionalities cannot be used for ATRP without protected acid groups. Although the deprotection of tert-butyl group from poly(tert-butyl acrylate) to afford poly(acrylic acid) has been successfully done using HCl/dioxane system, we found that this method does not work for removing of tert-butyl group from poly(tert-BMA).

This paper reports on the ATRP of tert-butyl methacrylate and the successful deprotection of tert-butyl group by trifluoroacetic acid (TFA) affording $\alpha$-allyl terminated poly(methacrylic acid) (poly(MAA)) macromonomers. These telechelic macromonomers with carboxyl functionality can be radiation cured (by UV or visible light) to form functionalized end-linked hydrogels with controlled chemical heterogeneity for biomedical/tissue engineering applications.

Experimental
Materials
Tert-butyl methacrylate (t-BMA, Aldrich 98%) and benzene (Fisher) were dried over CaH2 and then vacuum distilled. Tetrahydrofuran (THF, Acros HPLC grade) was vacuum distilled from purple Na/benzophenone. Copper bromide (CuBr, Aldrich 98%) was purified under argon blanket by stirring in glacial acetic acid, followed by filtering and washing with absolute ethanol and ethyl ether, and then dried under vacuum. Allyl 2-bromoisobutyrate (ABIJ), N,N,N',N,N',N'-hexamethyltriethylenetetramine (HMTETA), allyltributyltin (ATBT), aluminum oxide (alumina) and trifluoroacetic acid (TFA) were all purchased from Aldrich and used as received.

Characterization
Monomer conversion was determined using a Hewlett-Packard 5890 Gas Chromatograph (GC). Molecular weights and polydispersivities were estimated using Gel Permeation Chromatography (GPC) equipment with THF (1 mL/min) as the eluent against linear polystyrene standards. Molecular weight and polymer characterization results were confirmed using 1H NMR spectroscopy on a Bruker 400 MHz instrument. FT-IR measurements were performed using a KBr pellet on Perkin Elmer FTIR Spectrometer PARAGON 1000. MALDI-TOF mass spectra were recorded with Voyager-DE (AB Applied Biosystems, Framingham, MA) mass spectrometer equipped with nitrogen laser 337 nm (3 ns pulse width).

Synthesis
All reactions were run under argon unless noted.

$\alpha$-allyl terminated poly(t-BMA) via ATRP: CuBr (44.1 mg, 0.3 mmol), benzene (2.5 mL) and HMTETA (83.6 µL, 0.3 mmol), t-BMA (5 mL, 30 mmol) and dodecanes (0.2 mL, 0.2 mL, GC standard) were heated up to 60 °C. Then ABIB initiator (97.8 µL, 0.6 mmol) was added and an initial sample (time 0 min) was taken and reaction was stirred until it stopped by itself (in 90 min, very viscous dark green suspension). At that time GC analysis showed 65% of monomer conversion. Characterization by GPC: $M_w$ = 6198, $M_n$/Mw = 1.16. 1H NMR (CDCl3); tert-butyl -CH3 protons ($\delta$=1.4–1.5 ppm), methacrylate -CH2 protons ($\delta$=1.0–1.2 ppm), backbone -CH=CH2 protons ($\delta$=1.8–1.85 ppm) and allyl end group protons: CH2=$\delta$=2.5–5.4 ppm, -CH=$\delta$=5.8–6.0 ppm and -CH2-protons ($\delta$=4.5–4.7 ppm), MALDI-TOF: m/z = [a×142 (t-BMA) + 79/81 (Br)].

$\alpha$-allyl terminated poly(MAA): Benzene (2.5 mL) was injected into the polymer mixture after ATRP (one-pot reaction) followed by addition of allyltributyltin (571 µL, 1.8 mmol) and stirred for 13 hrs at 60 °C. The reaction solution was passed through a column of alumina (removing of copper catalyst) and precipitated into a 10-fold excess of a 50/50 v/v mixture of MeOH/DI. water and dried under vacuum overnight. 1H NMR (CDCl3); tert-butyl -CH3 protons ($\delta$=1.4–1.5 ppm), methacrylate -CH2 protons ($\delta$=1.0–1.2 ppm), backbone -CH=CH2 protons ($\delta$=1.8–1.85 ppm), and allyl end group protons: CH2=$\delta$=2.5–5.4 ppm, -CH=$\delta$=5.8–6.0 ppm, and -CH2-protons ($\delta$=4.5–4.7 ppm), MALDI-TOF: m/z = [a×142 (t-BMA)]

Scheme 1. The approach of synthesis of $\alpha$-allyl terminated poly(MAA) macromonomers.
Fig. 1. Plot of ln ([M]/[M]) vs time for ATRP of t-BMA in: THF at 60°C (□), benzene at 60°C (△) and acetone at 50°C (○) with [ABIB]/[CuBr]/[DMF]=1/1/
I= =0.6 mmol, [t-BMA]=30 mmol, t-BMA/THF=
=1/1 (v/v).

CH₂ protons (δ= 1.8–1.85 ppm), α-allyl end group protons:
CH₃ (δ= 2.5–5.4 ppm), =CH (δ= 5.9–6.0 ppm) and –CH₂ protons (δ= 4.5–4.7 ppm), α-allyl end group protons: CH₃ (δ= 5.0–5.1 ppm), =CH (δ= 5.6–5.8 ppm), MALDI-TOF: m/z=[m+142 (t-BMA)] + 41 (–CH₂=CH=CH₂)
α,ω-allyl Terminated poly(MAA): α,ω-allyl terminated poly(t-
-BMA) was dissolved in a minimum amount of concentrated TFA at room temperature. No solvent was used. In 10 min the TFA was removed by flushing the sample with argon. The polymer was purified by Soxhlet extraction in acetone, followed by drying under vacuum over night. ¹H NMR (d-DMSO) showed disappearance of t-butyl protons at δ= 1.4–1.5 ppm and rising of

Fig. 2. Plot of n vs conversion for ATRP of t-BMA in: THF at 60°C (□), benzene at 60°C (△) and acetone at 50°C (○) with [ABIB]/[CuBr]/[DMF]=1/1/
I= =0.6 mmol, [t-BMA]=30 mmol, t-BMA/solvent =1/1 (v/v). The solid line represents the theoretical value of n.

a new peak at δ= 12.3 corresponding to –COOH proton, FT-IR (KBr pellet): characteristic absorbance of carboxylic acid from 2800 to 3600cm⁻¹ was observed.

Results and Discussion

The approach utilized for synthesis of α,ω-allyl (CH₂=CH–
–CH₂) terminated poly(MAA) macromomers is shown in Scheme 1. α-allyl terminated poly(t-BMA) with terminal bromine was first prepared by ATRP method. Then the active bromine at the end of the polymer chain was transformed to a second allyl group by a free radical chain mechanism. Deprotection of the t-butyl group of the macromonomer by TFA produced the desired α,ω-allyl terminated poly(MAA) for end-linked hydrogels.

Fig. 3. Plot of Mₙ/M₀ vs conversion for ATRP of t-BMA in: THF at 60°C (□), benzene at 60°C (△) and acetone at 50°C (○) with [ABIB]/[CuBr]/[DMF]=1/1/
I= =0.6 mmol, [t-BMA]=30 mmol, t-BMA/solvent =1/1 (v/v).

Fig. 4. ¹H NMR spectroscopy of α-allyl terminated poly(t-
-BMA) in CDCl₃; [ABIB]/[CuBr]/[DMF]=1/1/
I= =0.6 mmol, [t-BMA]=30 mmol, t-BMA/solvent =1/1 (v/v). The reaction proceeded in THF at 60°C for 3h.

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Fig. 5. GPC of the first and second extending of the macromonomer chains. Original polymer (1): [ABIB]/[CuBr]/[HMTETA] = 1/0.5/0.5, [ABIB] = 0.6 mmol, [t-BMA] = 30 mmol, t-BMA/solvent = 1/0.5 (v/v). The reaction proceeded in benzene at 60 °C for 1.5 h, M_n = 6198, PDI = 1.16. One times extended polymer (2): [poly(t-BMA) no. 1]/[CuBr]/[HMTETA] = 1/1/1 = 0.098 mmol, [t-BMA] = 9.8 mmol. The reaction proceeded in bulk at 60 °C for 20 min, M_n = 11081 and PDI = 1.19. Two times extended polymer (3): [poly(t-BMA) no. 2]/[CuBr]/[HMTETA] = 1/1/1 = 0.098 mmol, [t-BMA] = 9.8 mmol. The reaction proceeded in bulk at 60 °C for 20 min, M_n = 13656 and PDI = 1.22.

ATRP Polymerization of t-BMA

The α-allyl terminated poly(t-BMA) was prepared by ATRP using commercially available allyl-2-bromoisobutyrate (ABIB) as an initiator. The latter has been already studied as an initiator for ATRP polymerization of DMAEMA but not for t-BMA.

The polarity of solvent can affect the homogeneity of the reaction solution (solubility of the catalyst) and thus also molecular weight and polydispersity of resulted polymer. Based on this idea the polymerization of t-BMA with [Cu(I)/HMTETA complex was studied in THF, benzene and acetone, the reaction proceeded at 60 °C, 60 °C and 50 °C, respectively. The conversion increased with time linearly and thus a kinetic plot of ln ([M]/[M]) vs time was first-order in all cases (Figure 1). The rates of reactions were very similar and conversions of monomer were approximately ~80% in 3 h. Figure 2 shows that the number average molecular weights (M_n) increased linearly with conversion and Figure 3 shows the narrowing of PDI (M_w/M_n) with conversion in all cases. The initiator efficiency was found to be in a range of 0.68–0.86, confirming that the resultant polymers had predictable molecular weights. The polymers produced were also characterized by 1H NMR spectroscopy (see Figure 4), which proved the incorporation of allyl group to the end of polymer. Further support for the validity of the NMR method was gained from the calculated Mn from 1H NMR, which was in a very good agreement with Mn found by GPC (M_n/N_Mn ~ 1.05).

Transformation of the Terminal Bromine

Bednarek et al. studied ATRP via MALDI-TOF mass spectrometry and found that in the later stages of polymerization side reactions lead to elimination of terminal bromine. Therefore, we tried to extend the polymer chain simply by using purified α-allyl terminated poly(t-BMA) (made in benzene) as the initiator for further ATRP of t-BMA to prove the existence of an active terminal bromine. The terminal bromine at the end of α-allyl terminated poly(t-BMA) macromonomer was found to be active when the following conditions were used: [t-BMA]/[benzene] = 1/0.5 (v/v), molar ratio of [t-BMA]/[ABIB]/[CuBr]/[HMTETA] = 50/1/0.5/0.5 at 60 °C. Suppression of the loss of bromine was proved by GPC where one sharp peak of extended polymer had M_n = 11081, higher than the starting macromonomer (M_n = 7130), and similar low polydispersity (1.18 vs.1.19). In addition, a second extension of this α-allyl terminated poly(t-BMA) macromonomer confirmed higher molecular weight (M_n = 13656) and low M_w/M_n = 1.22 (Figure 5).
After the optimization of reaction conditions, the active bromine at the end of the macromonomer was converted to a second allyl end group by a free radical chain mechanism using allyltri-n-butylstannane (ATBS). Coessens et al. has used ATBS for quenching the ATRP of MA at 90°C. Our transformation proceeded at 60°C and produced α,ω-allyl terminated poly(t-BMA) macromonomer whose structure was confirmed by 1H NMR spectroscopy (new peaks of α-allyl end group protons: \( \text{CH}_3 \) at \( \delta = 5.0 - 5.1 \) ppm and \(-\text{CH} \) at \( \delta = 5.6 - 5.8 \) ppm). Successful transformation was also proved by MALDI–TOF mass spectroscopy, in which the terminal bromine doublet peak with 79/81 molecular units was detected before transformation and it disappeared after the replacement of bromine by the second allyl group. New signal corresponds to 41 molecular units of \(-\text{CH} = \text{CH} = \text{CH} \) was detected.

**Deprotection of t-butyI Ester Group of Poly(t-BMA) Macromonomers**

The deprotection of t-butyI ester groups of poly(t-BA) polymers (hydrolysis) has been described by Coca et al. using an excess of HCl in refluxing dioxane for 4–6 h. This method, however, was not successful for poly(t-BMA) macromonomers. Methacrylate polymers are generally more hydrophobic than acrylate’s analogs and thus water, surrounding the polymer (hydrophobic interaction), suppresses the reaction of HCl with the ester groups. Thus, the poly(t-BMA) was dissolved in concentrated (99%) TFA and in 10 min the excess of TFA was removed by flushing the sample with argon. The polymer was purified via Soxhlet extraction in acetone and dried in vacuum oven. The 1H NMR spectroscopy in d-DMSO confirmed the complete deprotection of t-butyI groups from α,ω-allyl terminated poly(t-BMA) that afforded resulted α,ω-allyl terminated poly(MAA) macromonomers (Figure 6). The presence of the acidic group was also proven by FT-IR analysis (Figure 7) as a broad absorbance from 2800 to 3600 cm⁻¹.

**Conclusion**

Consideration of the mechanism of ATRP and optimization of the reaction conditions provided the basis for a synthesis of well-defined low molecular weight α-allyl terminated poly(t-BMA) macromonomers (\( M_w = 6198, M_n/M_w = 1.16 \)). Successful transformation of the terminal bromine to a second allyl group followed by subsequent deprotection of t-butyI groups using concentrated TFA produced well-defined α,ω-allyl terminated poly(MAA) macromonomers. By end-linking these telechelic poly(MAA) macromonomers via photo-curing, a new polymeric homogeneous network with controlled mechanical properties can be prepared. In addition, the carboxyl functional groups of poly(MAA) hydrogels serve as reactive sites for attaching peptides and often bio-active compounds required for biomedical/tissue engineering applications.

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**REFERENCES**