10.1071/ CH06247_ AC

Accessory Publication: Aust. J. Chem., 2006, 59(10), 737–741.

# Reversible Addition-Fragmentation Chain Transfer (RAFT) Graft Polymerization of 2-Dimethylaminoethyl methacrylate onto Cellulose Fiber

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## Accessory Publication

### Experimental Section

**Materials.** All solvents, monomer, and other chemicals were purchased from Aldrich (Gillingham, Dorset, UK) at the highest purity available unless otherwise stated. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) (98%) was filtered before use through an activated basic alumina (Brockmann I) column. 2, 2′-Azobis-(isobutyronitrile) (AIBN) (Fluka, 98%) was purified by re-crystallization from ethanol and dried at room temperature in vacuum oven. The *S*-methoxycarbonylphenylmethyl dithiobenzoate (MCPDB) RAFT agent was synthesized following a procedure available in the literature.[1] A filter paper, Whatman no. 1, was used as cellulose substrate due to its high cellulose content (98 % α cellulose). The synthesis procedure for the cellulose-*s*- methoxycarbonylphenylmethyl dithiobenzoate RAFT agent (cellulose CTA) is described elsewhere.[2] All other chemicals and solvents were used as received.

**Elemental Analysis (EA)**.The cellulose samples before and after graft polymerization were analyzed for C, H, S and N contents at the Laboratory of Microanalysis, Chemistry Department, the University of Leeds, UK. The C, H and N contents were determined by combustion followed by chromatographic separation and thermal conductivity detection using a Carlo Erba EA 1108 Elemental Analyzer. The method for sulfur analysis is described elsewhere.[2] The accuracy of the analyses was +/- 0.3% absolute.

**Attenuated total reflectance Fourier transform infrared spectroscopy (ATR FT-IR).** ATR FT-IR spectra of the grafted and ungrafted cellulose samples were obtained on a Perkin-Elmer Spectrum One FT-IR Spectrometer using a single reflection horizontal ATR accessory. Each spectrum was collected in the range of 4,000-400 $cm^{-1}$ by cumulating 100 scans at a resolution of 4 $cm^{-1}$. The scan speed was set at 0.5 cm/s. Baseline was corrected for all spectra using the Perkin-Elmer Spectrum software.

**THF Size Exclusion chromatography (SEC).** The number-average molecular weight ($M_n$) and polydispersity index ($M_w/M_n$)) of free and cleaved poly(2-(dimethylamino)ethyl methacrylate) grafts were performed at Polymer Laboratories, UK, using SEC system equipped with a differential refractive index (DRI) detector (PL-GPC 50), and two PLgel 5.0 μm MIXED-C columns (300 x 7.5 mm) in series (Polymer Laboratories, UK). THF with 5% triethylamine (TEA) was used as the eluent at a flow rate of 1.0 mL $min^{-1}$ at ambient temperature. All samples were prepared accurately at nominally 2 mg/ml. The SEC system was calibrated with polymethylmethacrylate (PMMA) EasiVial narrow standards with molecular weights ranging from 690 to 1,944,000 g $mol^{-1}$.

**Nuclear magnetic resonance spectroscopy ($^1$H NMR**). $^1$H (400 MHz)) Nuclear Magnetic Resonance (NMR) spectra of free polymer formed in graft polymerization reactions were recorded on a Bruker 400 UltraShield Spectrometer at 25°C. Methylene chloride-d2 and *d*-chloroform were used as solvents. DMAEMA monomer conversion was assessed by measuring the disappearance of the vinyl protons (2H/mol monomer) of the monomer by respect to aromatic protons (5H/mol toluene) of toluene, which was used as polymerization solvent. Although, there is overlapping of chloroform protons with toluene protons, the contribution of the formers can be neglected. Indeed, the results were also verified using methylene chloride- $d_2$ in place of *d*-chloroform and we found a variation of conversion by only 1-2%.

**Grafting Ratio** The grafting ratio (G., wt-%) of each PDMAEMA-grafted filter paper was calculated using the following formula.

$$Grafting\ ratio\ (wt-\%) = \frac{Weight_{graft} - Weight_{cell-CTA}}{Weight_{cell-CTA}} \times 100 \quad (1)$$

Where "$Weight_{graft}$" is the dry weight of each cellulose CTA sample after grafting with PDMAEMA and Soxhlet extraction with tetrahydrofuran and "$Weight_{cell\text{-}CTA}$" is the initial weight of each cellulose CTA sample.

**General Procedure for the RAFT Graft Polymerization DMAEMA onto Cellulose with the Presence of Free Chain Transfer Agent.** All polymerizations were performed at 60°C in toluene with a thermal initiator (AIBN). The molar ratios of cellulose CTA to free CTA (MCPDB) ($[cell\text{-}CTA]_0/[free\ CTA]_0$) were varied from 1:0.5 to 1:2.5. A series of experiments was conducted keeping the initial monomer to cellulose-CTA ratio constant at 100:1 and initial monomer concentration at 2.0 M. Another batch was also carried out using different monomer to cellulose CTA ratio ($[M]_0/[cell\text{-}CTA]_0$ of 200:1, 100:1 and 50:1) keeping the amount of solvent constant. In all cases, the ratio cellulose CTA to initiator ($[cell\text{-}CTA]_0/[AIBN]_0$) was 1:0.1. The percentage monomer conversion in solution was measured by $^1$H NMR spectroscopy. The polymer solution was precipitated into a large amount of cold hexane. The

supernatant was removed and the polymer re-dissolved in dichloromethane and re-precipitated into cold hexane. Finally, the viscous polymer was dried overnight under reduced pressure. Molecular weight and polydispersity index of free PDMAEMA were determined by THF SEC. The grafting ratio of each PDMAEMA-grafted filter paper was calculated using formula (1).

**Cleaving of PDMAEMA Chains from Cellulose Backbone:** PDMAEMA chains were cleaved from the cellulose backbone under acidic condition. In a typical acid hydrolysis experiment, 0.1 g cellulose-*g*-PDMAEMA (23 wt-% grafting ratio, entry C4 in Table 1) sample was immersed into a round bottom flask containing 12 mL 6M HCl aqueous solution. The flask was stirred at 110 $^{o}$C for 48 h in a sand bath. The reaction mixture was filtered to separate the solid cellulose particles and the HCl aqueous solution was removed by evaporation, and the remaining polymer was dissolved in THF. Molecular weight ($M_n$) and molecular weight distribution ($M_w/M_n$) were determined by THF SEC.

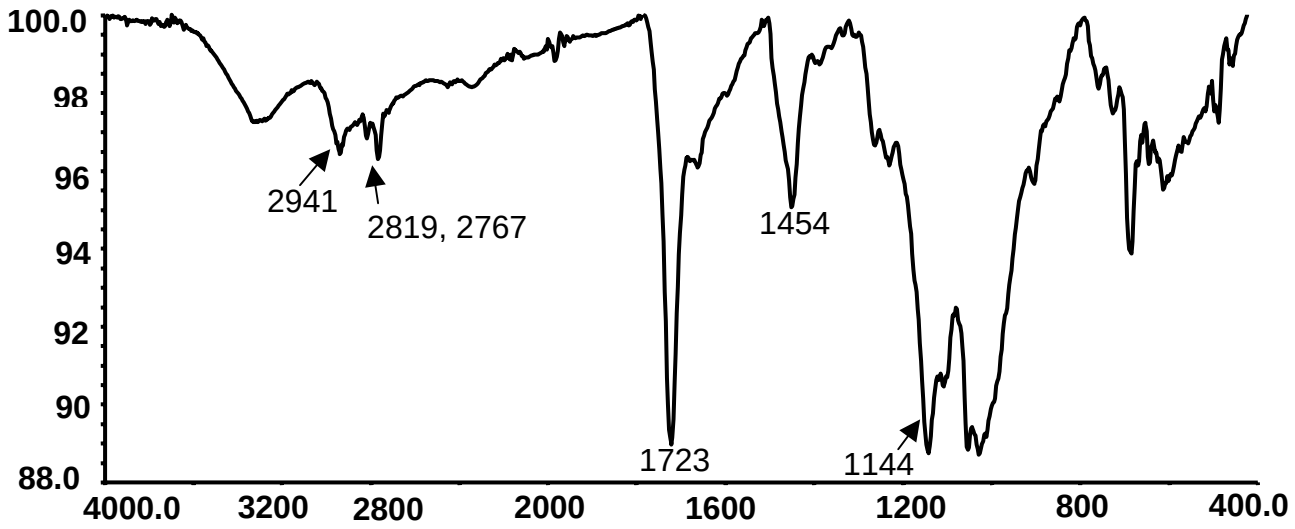


**Figure 1.** Typical ATR FT-IR spectra of cellulose-*g*-PDMAEMA (12 wt-% graft ratio, N-content (wt-%) =1.30)

## References

(1) Perrier, S.; Takolpuckdee, P.; Westwood, J.; Lewis, D. M. *Macromolecules* **2004**, *37*, 2709-2717.

(2) Roy, D.; Guthrie, J.T.; Perrier, S. *Macromolecules* **2005**, *38*, 10363.