

Controlled synthesis of radiolabelled amine methacrylate water-soluble polymers with end-groups of varying hydrophobicity and studies of adsorption behaviour

Mark Long, David W Thornthwaite, Suzanne H. Rogers, Francis R Livens
and Steve P Rannard

Supporting Information

Reagents and Suppliers

All reagents and solvents were purchased from the Sigma Aldrich Group unless otherwise stated. Prosafe liquid scintillation cocktail was purchased from Meridian Biotechnologies; PMMA GPC Standards were purchased from Polymer Laboratories; Partisil LK6DF Silica Gel 60A TLC Plates were purchased from BDH; ^{14}C Methyl Iodide (98.4%) was purchased from Amersham Biosciences; $^{14}\text{CH}_2$ Benzyl Alcohol (95%) was kindly supplied by Unilever. Buffer solutions were prepared using commercial Fixanal solutions

Substrates

Filter paper: Whatman Filter Paper 1 (Cellulose based hydrophilic filter paper)
Photographic Paper: Ilford Multigrade IV RC Delux Pearl Photo Paper (Medium Weight Polyethylene Hydrophobic Resin Coated Base)
"Virgin" Hair: Provided by Unilever and has been previously untreated. Water contact angle 103° (pH1)

Instrumentation Analysis and Sample Preparation

Nuclear Magnetic Resonance

All ^1H and ^{13}C NMR spectroscopy was conducted using a Bruker Advance DRX500 spectrometer. Sample preparation for ^1H NMR involved approximately 2mg of the sample dissolved in 1ml of CDCl_3 ; ^{13}C NMR involved approximately 50mg of the sample dissolved in 1ml of CDCl_3

Liquid Scintillation Counter

Analysis was conducted using a Packard Tri Carb 3100 TRC Liquid Scintillation Counter and results are presented as Disintegrations Per Minute (DPM)

Liquid Scintillation samples comprised a 20ml scintillation vial containing a known mass of radioactive compound dissolved in an appropriate solvent and 10ml of Prosafe Liquid Scintillation Cocktail containing:

- 60-75% Phenyl Xylyl Ethane
- 20-40% Alcohol Ethoxylate
- 2-8% Alcohol Ether Phosphate Ester
- 0.1-1.0% 2,5-Diphenyloxazole
- 0.1-1.0% 1,4-Bis(4-methyl-alpha-styryl)benzene

Gel Permeation Chromatography (GPC)

Analyses were conducted using THF as eluent. The GPC apparatus consisted of:

- Agilent 11100 Series RID
- 400C Eppendorf Oven
- Jasco PU 1580 Pump
- Jasco AS 590 Auto Samplers
- Polymer Laboratories PLgel 5 μm mixed-C and PLgel 5 μm mixed-D columns with a PL guard column

The eluent flow rate was 0.8 ml/min.

Calibration was conducted using poly(methyl methacrylate) standards with molecular weights ranging between 1000 and 1.5 million g/mol

Radio TLC (R-TLC)

R-TLC analysis was conducted using an AR 2000 BIOSCAN Radio TLC Imaging Scanner utilising a gas filled proportional counter filled with 90/10 Argon/Methane to detect the beta radioactive emissions from thin layer chromatography (TLC) plates.

The TLC samples (1.0% w/w) were prepared in an appropriate solvent and eluted using Whatman TLC plates (Partisil LK6DF silica Gel 60A with FL indicator) with a silica thickness of 250µm and 3cm pre adsorbent zone

The plates were eluted using an appropriate solvent to a standard 15cm solvent front. After drying the plates were analysed

UV-visible Spectrophotometry

Analysis was conducted using an Agilent 8453 UV-Visible Spectrophotometer comprising a photo diode array (PDA) for simultaneous measurement of the complete ultra violet light spectrum, with a wavelength range of 190-1100nm with a resolution of 2nm and < 0.03% stray light UV sample (0.025% w/v) was dissolved in 0.5ml ethanol.

Cyclone Phosphor Analysis of the Filter, Photo Papers and Hair Swatches

Storage Phosphor Imaging was conducted using a Packard Biosciences Cyclone Phosphor Imaging System

Quantitative assessment using OptiQuant software requires the exposure of a series of standards during the measurement of unknown samples. Initial exposure times were maintained at 7 days to generate the latent image. Radioactive standards were purchased from American Radiolabelled Chemicals.

Standard	Specific Activity (uCi/mg)	Radioactivity (DPM)
1	0.000068	75.5
2	0.000087	97
3	0.000130	144
4	0.000282	313
5	0.000530	588
6	0.000831	922
7	0.0011	1221
8	0.00213	2364
9	0.00358	3974
10	0.00447	4962
11	0.00898	9968
12	0.0184	20424
13	0.035	38850
14	0.0516	57276
14	0.117	129870
15	0.22	244200

Oxidation of Substrate Samples

Substrates were weighed accurately prior to oxidation (continuous flow of oxygen) using a Canberra Packard Model 307 Sample Oxidiser prior to Liquid Scintillation Counting

Synthetic Procedures

All synthetic procedures have been previously reported. Amounts of reagents, yields and radiochemical analysis are summarised below.

Methyl [¹⁴CH₃]2-bromoisobutyrate

Methyl [¹⁴CH₃] 2-bromoisobutyrate was synthesized using methyl [¹⁴CH₃] alcohol (0.0055moles, 5.5 mCi), triethylamine (1.1eq) dimethylaminopyridine (0.013eq) and 2-bromoisobutyryl bromide (1.1eq). Chemical yield = 813.4mg (81%), Radiochemical yield 97%, Total activity = 5.135 mCi, Specific activity = 6.313µCi/mg, Chemical purity > 95%, Radiochemical purity = 98%

Benzyl [¹⁴CH₂]2-bromoisobutyrate

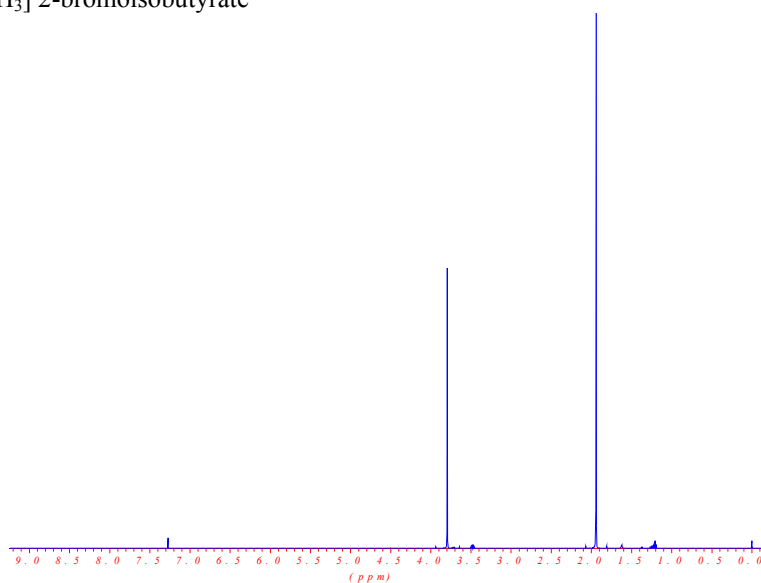
Benzyl [¹⁴CH₂]2-bromoisobutyrate was synthesized using benzyl [¹⁴CH₂] alcohol (0.0203moles, 13.56 mCi), triethylamine (1.1eq) dimethylaminopyridine (0.013eq) and 2-bromoisobutyl bromide (1.1eq). Chemical yield = 4.5g (87%), Radiochemical yield = 97%, Total activity = 13.13 mCi, Specific activity = 3.015 µCi/mg, Chemical purity > 95%, Radiochemical purity = 96%

9-Hydroxyfluorenyl [¹⁴CH₃] 2-bromoisobutyrate

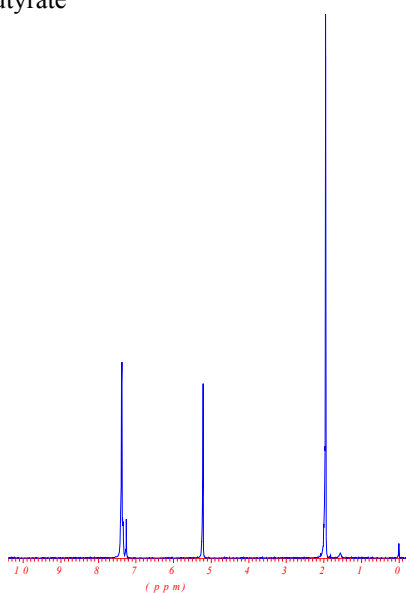
9-Hydroxyfluorenyl [¹⁴CH₃] 2-bromoisobutyrate was synthesized using 2-bromo [¹⁴CH₃] isobutyric acid (0.00077 moles, 2 mCi), 9-hydroxyfluorene (1.1eq) and 1, 1'-carbonyldimidazole (1.1eq). Chemical yield = 65.4mg (26%), Radiochemical yield = 22%, Total activity = 447 μCi, Specific Activity = 6.834 μCi/mg, Chemical purity > 95%, Radiochemical purity = 99%.

Figure S1: ^1H NMR Spectra for Initiators

A) Methyl [^{14}C] CH_3 2-bromoisobutyrate



B) Benzyl [^{14}C] CH_2 2-bromoisobutyrate



C) 9-Hydroxyfluorenyl [^{14}C] CH_3 2-bromoisobutyrate

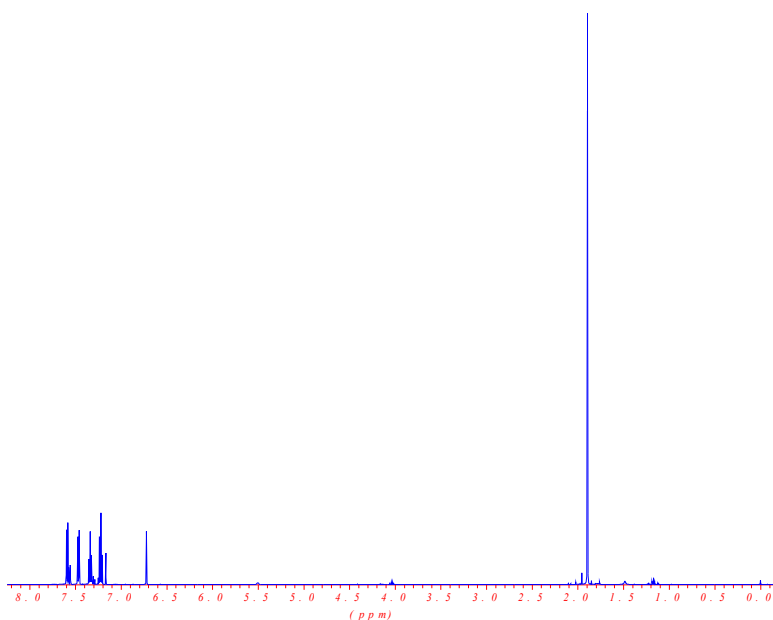
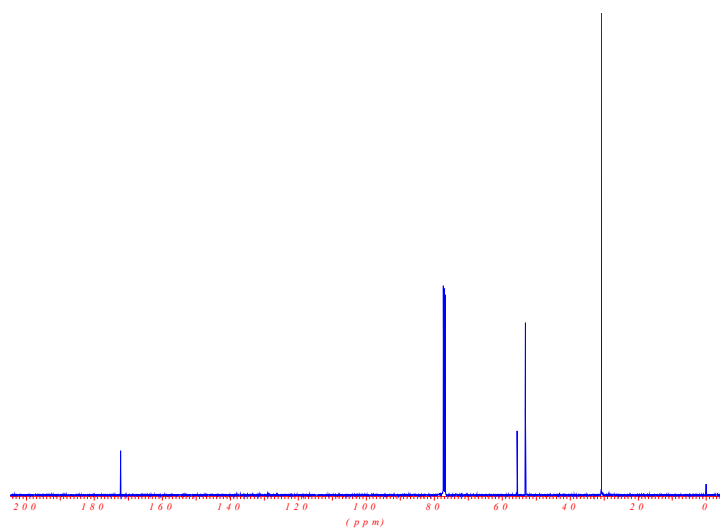
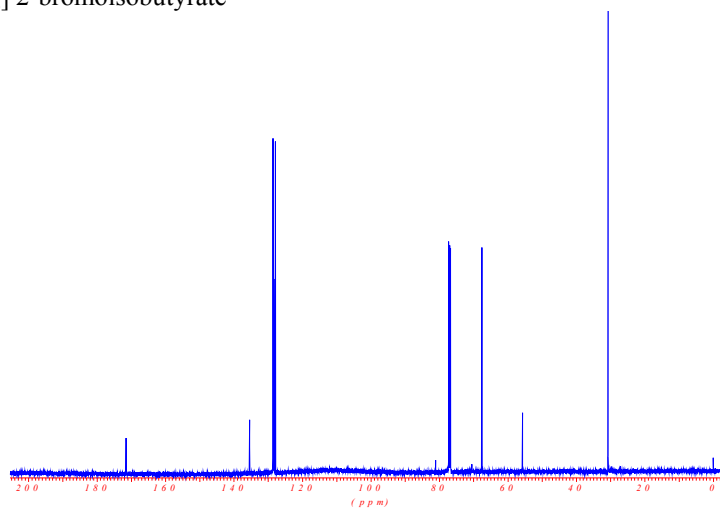


Figure S2: ^{13}C NMR Spectra of Initiators

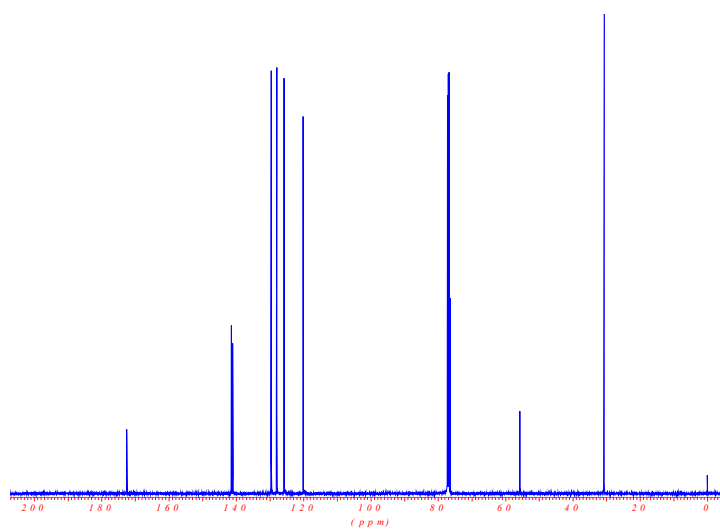
A) Methyl [$^{14}\text{CH}_3$] 2-bromoisobutyrate



B) Benzyl [$^{14}\text{CH}_2$] 2-bromoisobutyrate



C) 9-Hydroxyflourenyl [$^{14}\text{CH}_3$]2-bromoisobutyrate



Atom Transfer Radical Polymerisation (ATRP) of 2-(N,N-diethylamino) ethyl methacrylate (DEAEMA)

ATRP of DEAEMA using 2-propanol/water (90/10 v/v) followed previously reported procedures^{1,2}

A typical GPC chromatogram for a degree of polymerisation equal to 50 monomer units is shown in Figure S3.

Figure S3: GPC chromatogram of p(DEAEMA) with a target DP=50 monomer units using benzyl [¹⁴CH₂] 2-bromoisobutyrate (DRI detector)

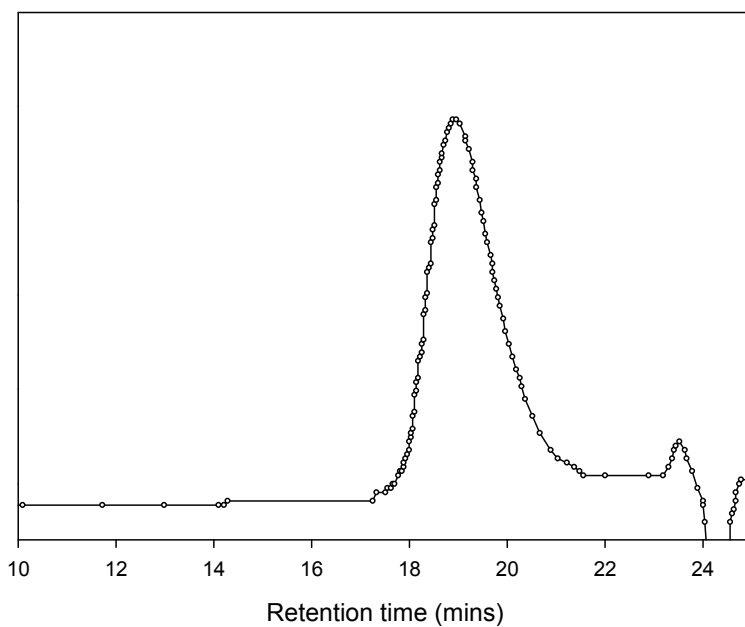


Figure S4: Adsorption of radiolabeled poly(2-(N,N-diethylamino) ethyl methacrylate onto different substrates – Comparison within each chain end group. A) methyl (red), B) benzyl (green) and C) 9-hydroxyfluorenyl (blue) groups. Data shown is determined by oxidation and liquid scintillation counting for hair (triangles), filter paper (circles) and photographic paper (squares).

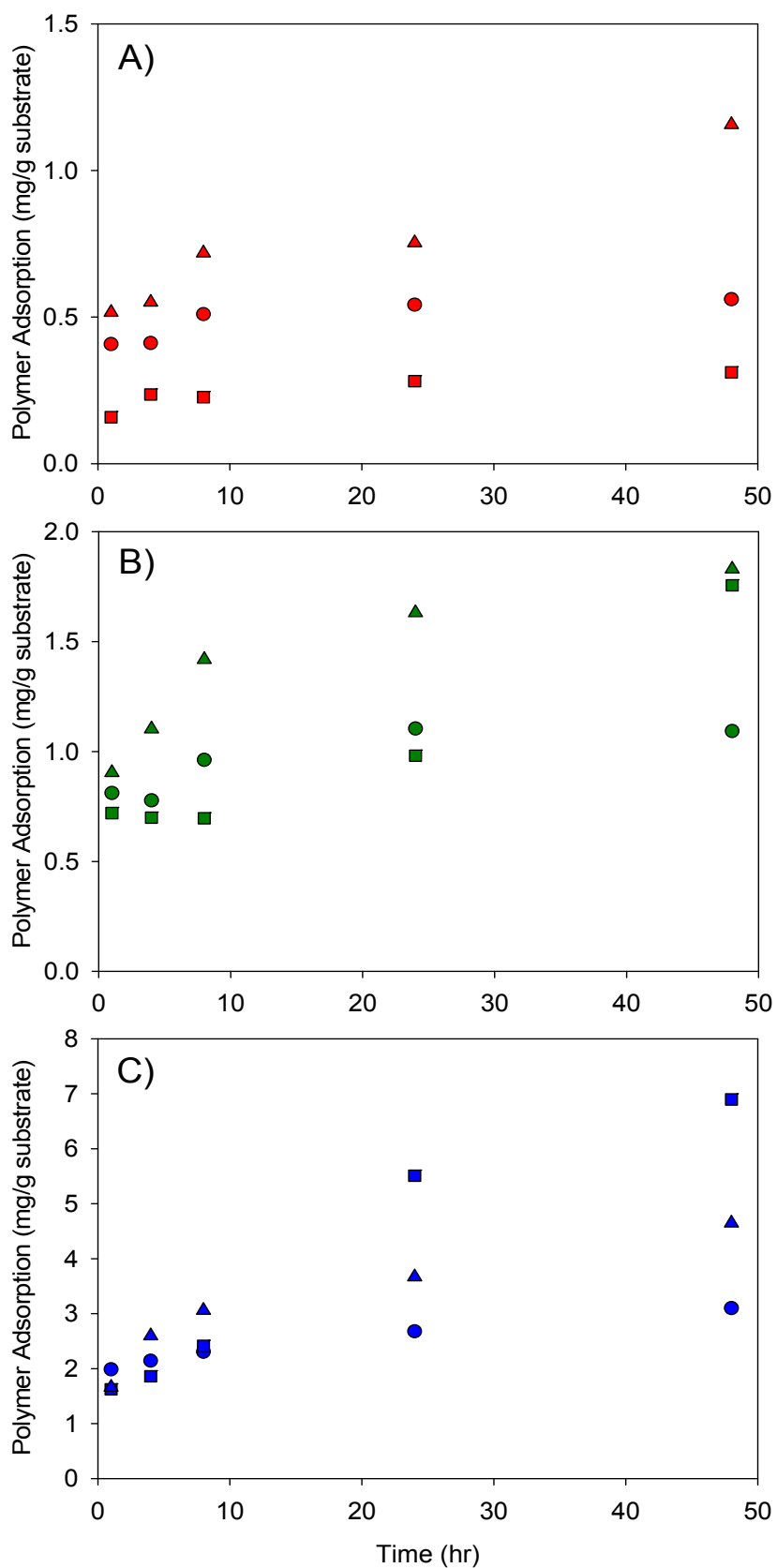
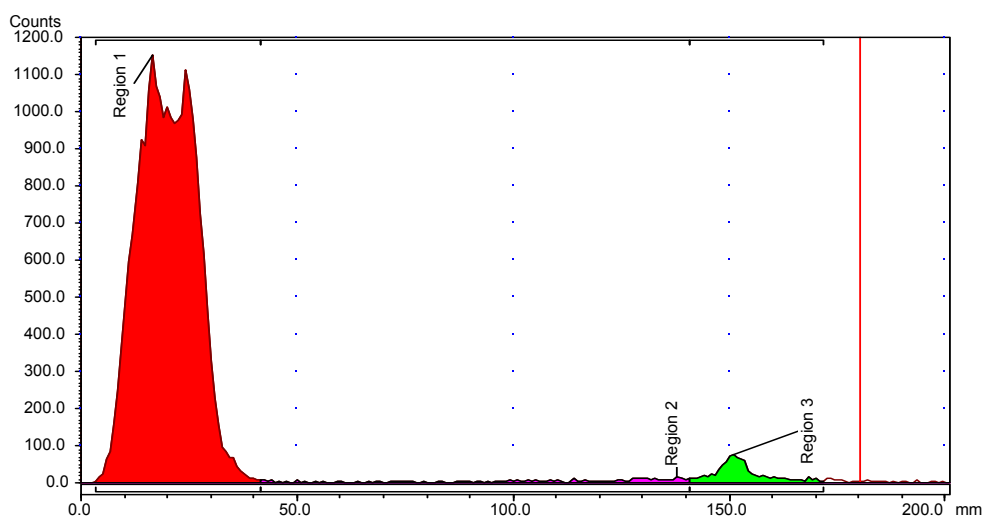
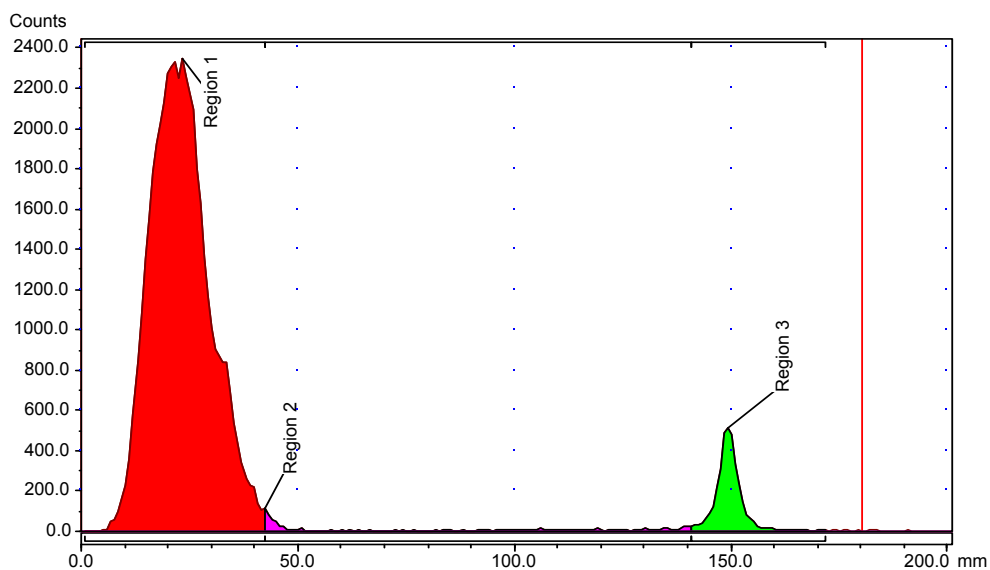


Figure S5: Radio- TLC of p(DEAEMA) polymers to determine unreacted initiator content
Each polymer was eluted with 90/10 (v/v) 40:60 Petroleum Ether/Acetic Acid

A) p(DEAEMA) polymer derived from methyl [^{14}C] 2-bromoisobutyrate



B) p(DEAEMA) polymer derived from benzyl [^{14}C] 2-bromoisobutyrate



C) p(DEAEMA) polymer derived from 9-hydroxyfluorenyl [^{14}C] 2-bromoisobutyrate

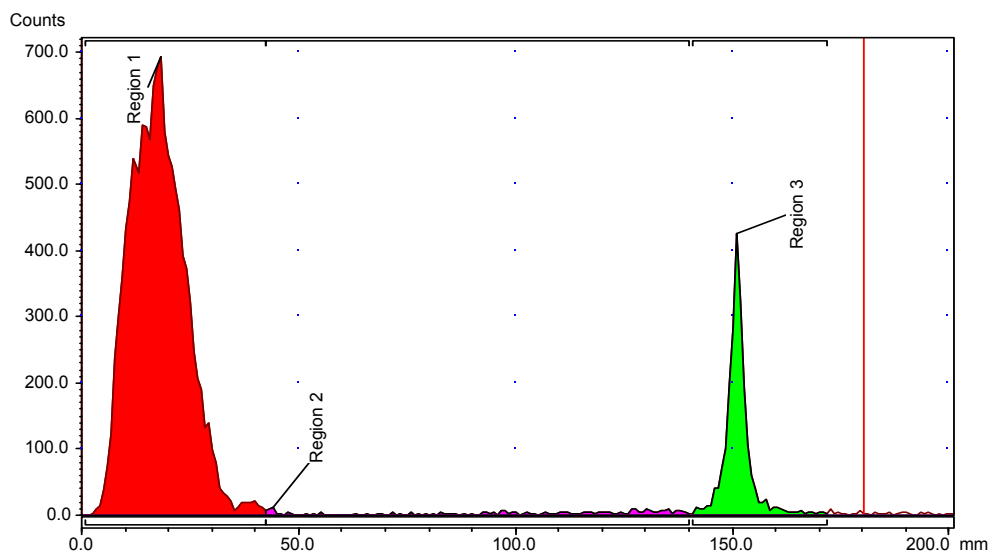
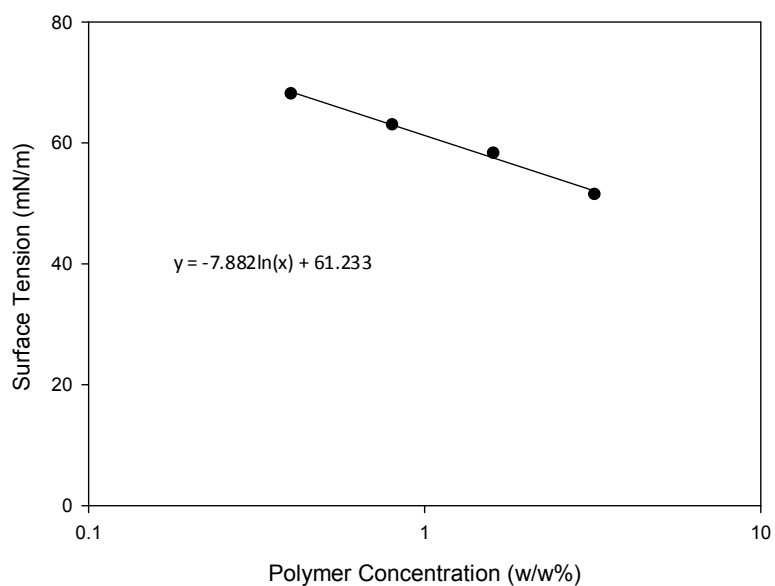
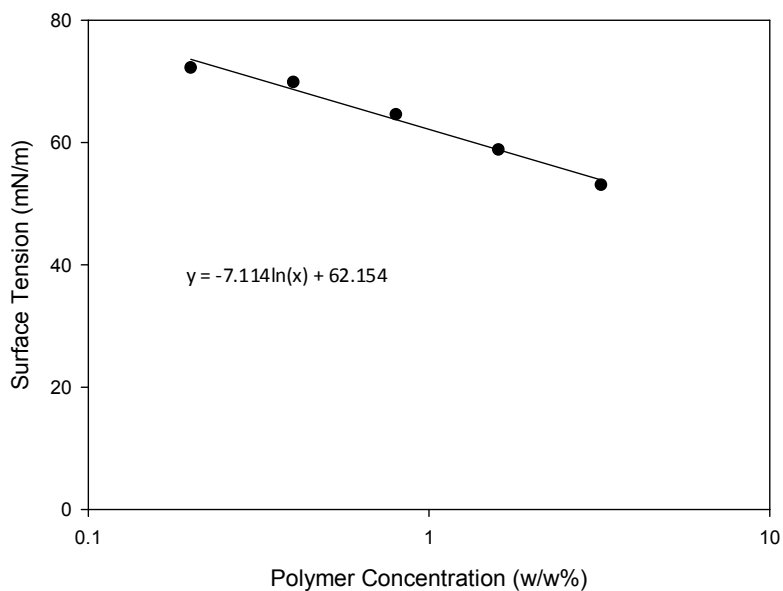


Figure S6: Regression of Linear Region of Surface Tension Measurements

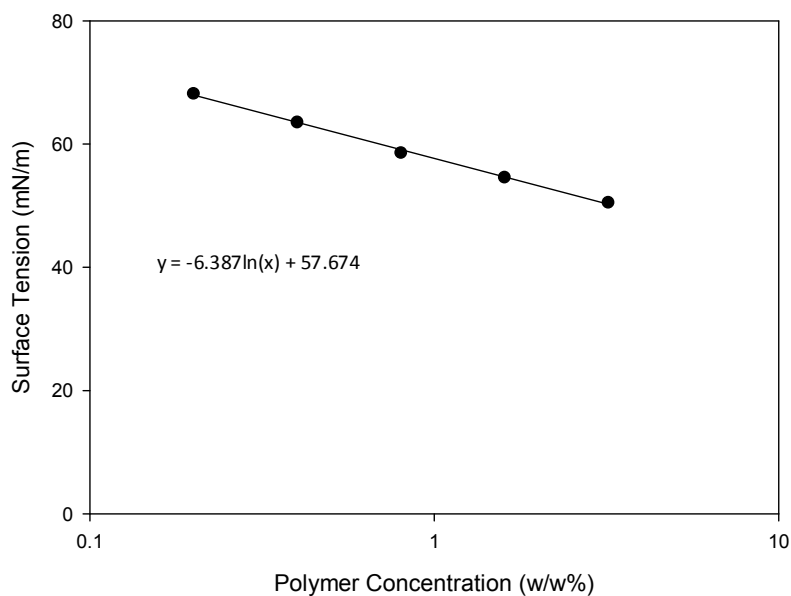
A) p(DEAEMA) derived from methyl [¹⁴CH₃] 2-bromoisobutyrate



B) p(DEAEMA) derived from benzyl [¹⁴CH₂] 2-bromoisobutyrate



C) p(DEAEMA) derived from fluorenyl [¹⁴CH₃] 2-bromoisobutyrate



References

- 1) S. McDonald and S. P. Rannard, *Macromolecules*, 2001, **34**, 8600. b) T. He, D. J. Adams, M. F. Butler, C. T. Yeoh, A. I. Cooper and S. P. Rannard, *Angew. Chem. Int. Ed.*, 2007, **46**, 9243. c) T. He, D. J. Adams, M. F. Butler, A. I. Cooper and S. P. Rannard, *J. Am. Chem. Soc.*, 2009, **131**, 1495.
- 2) a) M. Long, D. W. Thornthwaite, S. H. Rogers, G. Bonzi, F. R. Livens and S. P. Rannard, *Chem. Commun.*, 2009, **42**, 6406. b) M. Long, S. H. Rogers, D. W. Thornthwaite, F. R. Livens and S. P. Rannard *Polym. Chem.*, 2011, **2**, 581. c) S. Jana, S. P. Rannard and A. I. Cooper, *Chem. Commun.*, 2007, **28**, 2962.