Copper (0)-Mediated Radical Polymerisation in a Self-Generating Biphasic System

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ABSTRACT. Herein, we demonstrate the synthesis of well-defined poly(n-alkyl acrylate)s via copper (0)-mediated radical polymerisation in a self-generating biphasic system. During the polymerisation of n-butyl acrylate in DMSO the polymer phase separates to yield a polymer-rich layer without trace of copper salts (XPS analysis). The poly(n-butyl acrylate) has been characterized by a range of techniques, including GPC, NMR and MALDI-TOF, to confirm both the controlled character of the polymerisation and the end group fidelity. Moreover, we have successfully chain extended poly(n-butyl acrylate) in this biphasic system several times with n-butyl acrylate to high conversion without intermediate purification steps. A range of other alkyl acrylates have been investigated and the control over the polymerisation is lost as the hydrophobicity of the polymer increases as the alkyl chain length increases indicating that it is important for the monomer to be soluble in the polar solvent.

KEYWORDS: Copper(0)-mediated polymerisation, dispersed system, controlled/living radical polymerisation.

Introduction

A range of transition metal-mediated radical polymerisation (ATRP) techniques,[1] including initiators for continuous activator regeneration (ICAR),[2-6] activators regenerated by electron transfer (ARGET),[7-9] and activators generated by electron transfer (AGET),[10] have been developed which can control the polymerisation of a large range of monomers and allow routine access to complex polymer architectures such as multi-block copolymers, star polymers and variations thereof. Recently, it has been demonstrated that copper(0)-mediated radical polymerisation in polar solvents (also referred to as SET-LRP) results in extremely high end-group fidelity, an indication of excellent livingness, to very high monomer conversion in the case of acrylates.[11-18] A main drawback of conventional transition metal-mediated polymerisation techniques in general (including Cu(0)/SET-LRP) is the presence of metal/copper complexes in the final polymer. Traces of metal salts could result in polymer degradation due to potential catalytic oxidation,[19,20] contribute to the presence of residual colour and may even contribute to biological toxicity.[21] A variety of different routes have been explored to decrease the amount of metallic residues.[5,22,23] A range of methods has been reported which keeps the catalyst insoluble in the polymerisation phase including the use of fluorous biphase systems,[24-27] supported catalysts[28-31] and ionic liquids.[32-35] A solid supported catalyst can be easily removed,[36,37] but diffusion of reactants to the catalytic site can present a problem.[38,39] One of us has also explored the use of [N-alkyl-(2-pyridyl)methanimine]copper(I) complexes which had tuneable solubility in certain organic solvents used in this type of polymerisation.[40] Other homogeneous approaches have included the reduction of the amount of copper employed during the polymerisation (ARGET and ICAR),[4,5,41] the use of a redox system (e.g. ascorbic acid or radical), which have made it possible to decrease the amount of copper to ppm levels.[5]

In this present work, we report a convenient polymerisation methodology using a self-generating, surfactant-free biphasic system, which allows separation and removal of the copper catalyst from the polymer product without complex purification procedures. In this initial work, the method has been successfully applied to the polymerisation of n-butyl acrylate (BA) in DMSO using Cu(0)-

mediated radical polymerisation at ambient temperature. The polymer starts to phase separate from the reaction mixture after reaching a molecular weight of ~2,500 g/mol, corresponding to approximately 50% conversions under the conditions studied, to give a biphasic system; comprising an upper polymer-rich phase and a lower DMSO-rich phase. Surprisingly, this phase separation does not significantly affect the polymerisation process in terms of control/livingness as evidenced by both narrow polydispersity (PDI) and high end group fidelity.

Experimental Part:

Materials:

Ethyl 2-bromoisobutyrate (EbiB, Aldrich, 98 %), copper (II) bromide (Cu$_2$Br, Sigma-Aldrich, 99 %), tetrahydrofuran (THF, Sigma, 99 %) and dimethyl sulphoxide (DMSO, UNIVAR, AR) were all used as received. Copper wire (diameter = 1.25 mm) was activated by washing in sulfuric acid for 10 min. Tris(2-(dimethylamino)ethyl)amine (Me$_6$TREN) was synthesised according to literature procedure[42] and stored under nitrogen prior to use. Monomers, such as *n*-butyl acrylate (nBA, Aldrich, 99%), lauryl acrylate, *iso*-butyl acrylate, *tert*-butyl acrylate and 2-ethylhexyl acrylate were de-inhibited by percolating over a column of basic alumina (Ajax, AR).

Methods:

Synthesis of difunctional initiator: ethylene bis(2-bromoisobutyrate) (2F-BiB)

Ethylene glycol (1.80 mL, 32.4 mmol) and an excess of triethylamine (9.90 mL, 71.3 mmol) were added to a 500 mL round bottom flask with a stirrer bar, and was flushed with nitrogen for 15 minutes on an ice bath. Anhydrous THF (150 mL) was added to the flask via an airtight syringe, and allowed to cool to 0 °C. Under a nitrogen atmosphere, 2-bromoisobutyryl bromide (8.40 mL, 68.1 mmol) was added slowly via a dropping funnel. Care must be taken in order to minimise the exotherm generated by the reaction. The solution was then left to stir overnight at ambient temperature. The reaction mixture was filtered in order to remove the triethylammonium bromide salt formed, and the solution concentrated by rotary evaporation. The resulting yellow/brown solution was then stirred with 0.10 M aqueous sodium carbonate to hydrolyze any remaining 2-bromoisobutyryl bromide. The crude product was then extracted with dichloromethane (3x50ml) using a separating funnel and the combined dichloromethane extracts dried with anhydrous magnesium sulfate, the filtered. The solvent was removed via rotary evaporation, yielding yellow crystals upon cooling. The product was purified using flash column

chromatography using 3:1 ethyl acetate:hexane to give white crystals (8.2 g, 70.3 %) ^{1}H NMR (CDCl$_3$): δ (ppm) 4.44 (t, 4H), 1.94 (s, 12H).

A typical Cu(0)-meditated polymerization using ethyl 2-bromoisobutyrate (mono-functional initiator):

n-Butyl acrylate (nBA, 2.4 mL, 16.9 mmol, 39 eq), DMSO (2.4 mL), EbiB (0.064 mL, 0.431 mmol, 1.00 eq), Me$_6$TREN (0.018mL, 0.069 mmol, 0.16 eq), CuBr$_2$ (4.8 mg, 0.022 mmol, 0.05 eq) and a magnetic stir bar were charged to a polymerization flask fitted with a rubber septum and the mixture was degassed with nitrogen for 10 min. A slight positive pressure of nitrogen was then applied and the pre-activated copper wire (0.7 cm) was carefully added under a nitrogen blanket. The polymerization flask was then resealed and polymerised at ambient temperature for 24 h. Sample of the reaction mixture were carefully removed periodically for ^{1}H NMR, GPC and mass spectroscopy analysis. The samples for ^{1}H NMR were simply diluted with CDCl$_3$, while samples for GPC and mass spectroscopy analysis were first diluted with THF, then passed over an aluminium oxide column to remove metal salts.

For the chain extension, a further 2.4 mL of a degassed monomer in DMSO (50 vol-%), was then carefully added via gas tight syringe and again the solution was allowed to polymerize at ambient temperature for another 24 h with stirring.

A typical Cu(0)-meditated polymerization using ethylene bis(2-bromoisobutyrate) (*difunctional initiator*):

n-butyl acrylate (BA, 5 mL, 35 mmol, 20 eq), DMSO (5 mL), ethylene bis(2-bromoisobutyrate) (2F-BiB) (0.3g, 0.88 mmol, 1.00 eq C-Br), CuBr$_2$ (9.8 mg, 0.044 mmol, 0.05 eq) and pre-activated copper wire (5 cm) wrapped around magnetic stir bar were added to a Schlenk tube. A rubber septum was then fitted and the reaction mixture degassed via nitrogen bubbling for 10 minutes. Degassed Me$_6$TREN (0.048 mL, 0.16 mmol, 0.18 eq) was then added via an airtight syringe and the reaction left to polymerize overnight at ambient temperature (25°C).

Samples of the reaction mixture and polymer were removed for ^{1}H NMR, GPC and MALDI-TOF MS analysis. The samples for ^{1}H NMR was simply diluted with CDCl$_3$, while the samples for GPC were diluted with CHCl$_3$, then passed over an alumina column to remove metal salts.

Results and Discussion

Cu(0)-mediated radical polymerisation of BA has been carried out using ethyl bromoisobutyrate, $CuBr_2$ and Me_6TREN in DMSO at ambient temperature. The polymerisation proceeds rapidly with full monomer conversion (>95%) achieved in less than 3 h, as determined by ^{1}H NMR. The monomer conversion is calculated using the signals at 5.5-6.5 ppm and 4.0 ppm attributed to acrylic and CH_2O groups, respectively. The polymerisation fulfils all the criteria of a controlled/living radical polymerisation. Interestingly, $\ln[M]_t/[M]_0$ increases linearly with time up until one hour (56% conversion) consistent with a constant concentration of propagating radicals at the polymerisation loci. After one hour, the polymerisation rate increases significantly. Finally, over 90% monomer conversion is observed in less than 120 min (**Figure 1A**). When PBA reaches a molecular weight in the range 2,000-3,000 g/mol (~50% conversion), the system becomes biphasic due to the low solubility of PBA in DMSO (the phase separation is difficult to detect unless the magnetic stirring is stopped), resulting in an upper polymer-rich phase and a lower DMSO-rich phase which contains monomer and catalyst. From this point onwards in the reaction, further chain extension (i.e. polymerisation) is confined to the polymer-rich phase. After phase separation has occurred, the system comprises one phase consisting mainly of PBA with low amounts of DMSO (< 5 wt-%) and BA monomer (< 5 wt-%) at 80% monomer conversion as determined by ^{1}H NMR, and another second phase comprising DMSO, BA, copper (copper wire) and copper complex(es) (ligand/Cu(II)) as seen by a green colouration. The formation of the second phase in the polymerisation mixture is accompanied by a distinct *increase* in the polymerisation rate ($\ln[M]_t/[M]_0$ vs. time shows a step change in the gradient whilst remaining linear). Remarkably, the polymerisation proceeds with excellent control under these biphasic conditions as indicated by the low PDI values (approx. 1.20-1.30). The PDI values decrease from 1.23 to 1.13 in the first phase of the polymerisation (until 1 hour, corresponding to the homogenous system), and after this critical point, the PDI values increase slightly to approximately 1.32. This good correlation between the experimental molecular weight and the theoretical values (**Figure 1B**) also confirms the controlled/living character of the polymerisation. The theoretical values were calculated using the

equation: $M_{n, \text{theo.}} = \alpha \times ([M]_0/[\text{Init}]_0) \times M_W^{BA} + M_W^{Init}$. Throughout the polymerisation, GPC chromatograms indicate a mono-modal distribution shifting to higher molecular weights with increasing conversion (**Figure 1C**), with no apparent influence of the phase separation
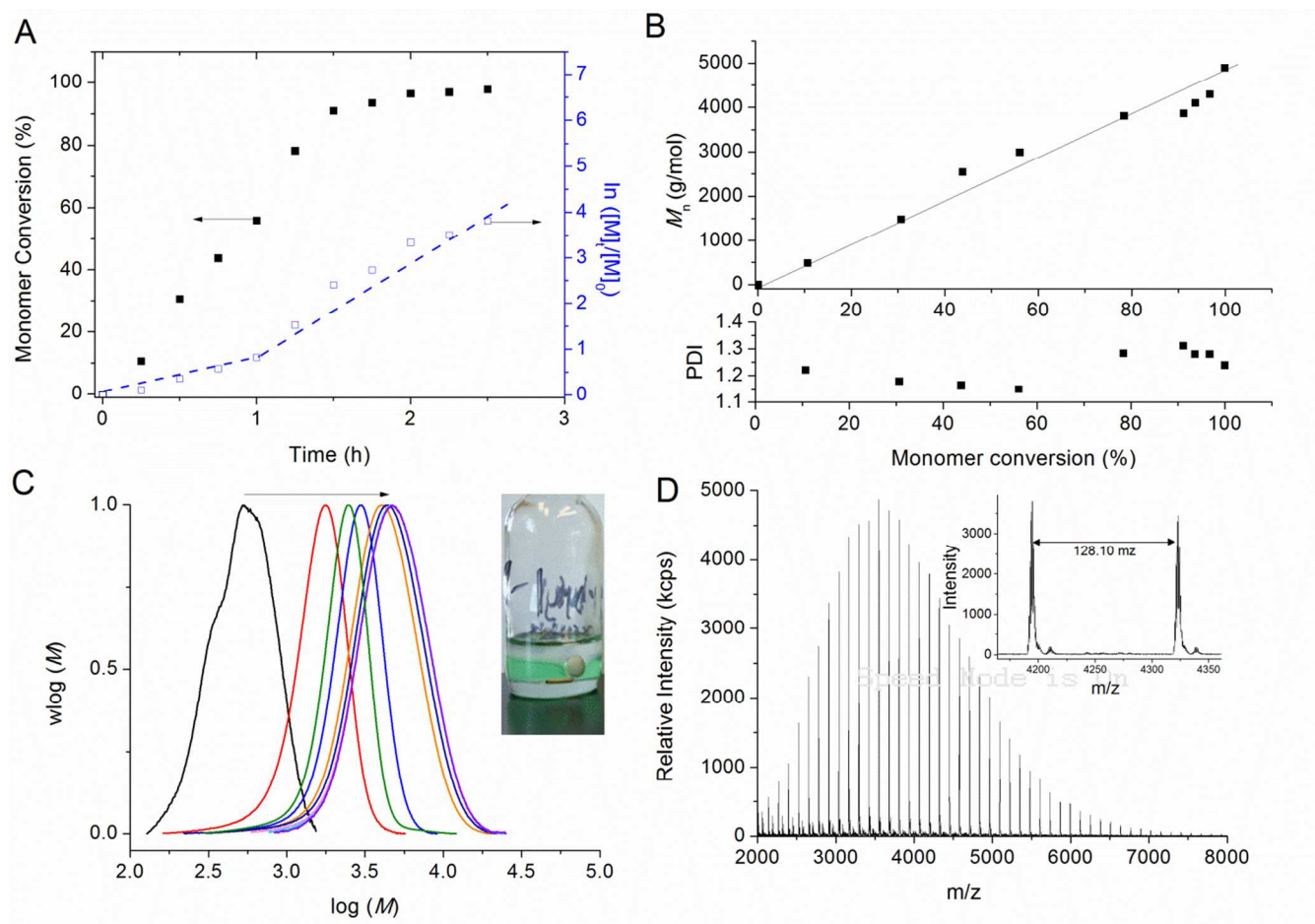

Figure 1. Cu(0)-mediated radical polymerisation of *n*-butyl acrylate in DMSO at ambient temperature. (A) Monomer conversion and ln([M]₀/[M]) vs. time (h); (B) theoretical (full line) and experimental (square) molecular weights and PDI values vs. monomer conversion; (C) w(log*M*) versus log*M* at different monomer conversions (inset: picture of the mixture after polymerisation); (D) MALDI-TOF spectrum of poly(*n*-butyl acrylate) obtained at >99% monomer conversion (inset: magnified MALDI-TOF spectrum).

Following polymerisation, the polymer is present as a clearly distinguishable colourless top layer (inset in **Figure 1C**), while the bottom DMSO layer contains the vast majority of the copper/ligand complexes as indicated by the green colour from Cu(II) complexes (as well as the Cu wire). After separation of the top layer at >99% monomer conversion, the polymer was analyzed by a range of techniques, including NMR, MALDI-TOF and GPC. ^{1}H NMR analysis of the top layer (polymer phase without any purification) reveals the absence of monomer and the presence of pure polymer with a small peak of DMSO. Interestingly, the presence of a low intensity peak of DMSO observed by ^{1}H NMR suggests that the polymer is swelling. Another important observation is that the polymer phase remains colourless after prolonged exposure to air. This observation suggests the absence of copper(I) species in this phase as trace amounts of copper(I) should quickly oxidize to Cu(II) species with a typical green/blue colour characteristic of d^9 complexes. To confirm this assumption, the polymer phase was analyzed by XPS (**Figure S1 in the Electronic Supplementary Information**) and by ICP-MS. XPS fails to detect the presence of copper in this phase, confirming that the catalyst (copper/ligand) is indeed confined to the bottom layer, or is present in the upper layer in a quantity of less than 0.05 atomic-% (XPS detection limit) (**Table S1 in the Electronic Supplementary Information**). ICP-MS confirms that the amount of copper is 0.016 wt-% in the polymer. This value is relatively low as conventional ATRP usually produces polymers with approximately 1 wt-% of copper.

It has been reported previously that Cu(0)-mediated radical polymerisation allows the preservation of very high end group fidelity to high conversion in polar solvents.[14,43-46] MALDI-TOF analyses before and after phase separation during the polymerisation confirm "perfect" end group fidelity under these polymerisation conditions. Two major distributions separated by 128 Daltons are observed, attributed to PBA-Br/ Na$^+$ and PBA-Br/K$^+$ species, respectively (**Table S2 in the Electronic Supplementary Information**). It is very surprising and quite remarkable that the polymerisation proceeds with excellent control/livingness considering that the Cu wire and the Cu/ligand complexes are (primarily) located in the lower DMSO-rich phase as opposed to in the polymer-rich phase (where polymerisation must occur).

The PBA synthesized was systematically chain extended using our previously developed iterative polymerisation methodology.[43,46] At full monomer conversion (>99%), a fresh degassed solution of BA in DMSO was added to the polymerisation mixture. It is important to note that the reaction system remains fully biphasic. The conversion and evolution of molecular weight were monitored by NMR and GPC, respectively (**Figure 2A**). Interestingly, we observe that the polymerisation rate is lower in this second chain extension, as the polymerisation requires 5 hours to reach 90% monomer conversion. This effect can be attributed to the dilution of the reaction mixture due to the addition of monomer and DMSO. In the biphasic systems, PBA is successfully chain extended with near perfect control over the molecular weight and PDI (**Figure 2B**). Again, this result is quite remarkable as one would expect limited accessibility of the monomer to the locus of polymerisation (the polymer-rich phase where the propagating radicals must reside) in this biphasic system. GPC chromatograms confirm the absence of low molecular weight populations and coupling products (**Figure 2A**). MALDI-TOF spectroscopy after one chain extension confirms a single population (**Figure S2 in the Electronic Supplementary Information**) corresponding to bromide terminated polymer confirming high end group fidelity.
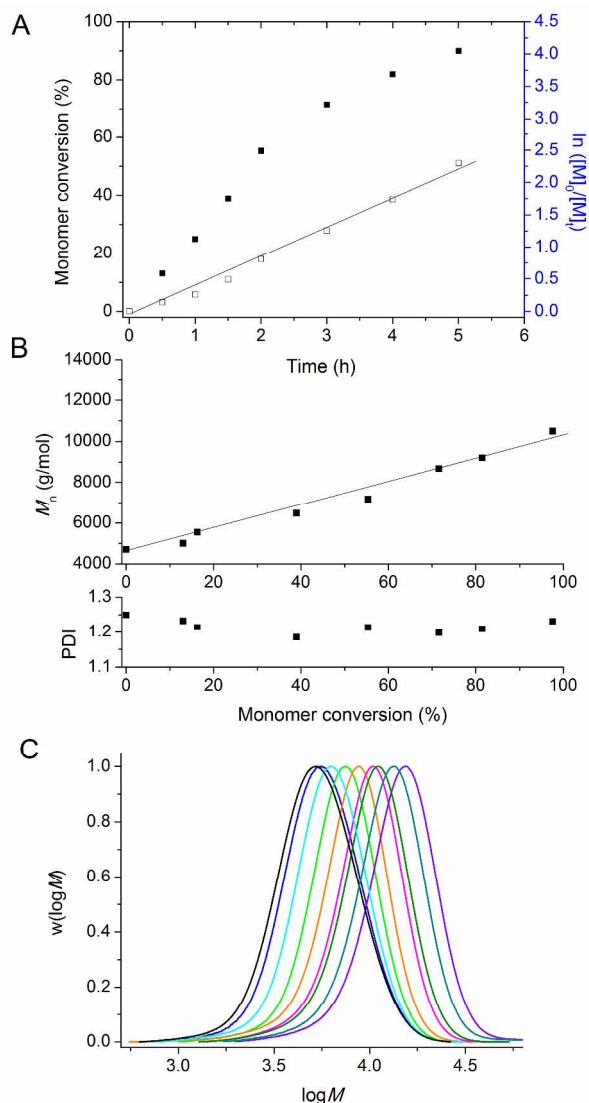
Figure 2. Chain extension of poly(*n*-butyl acrylate) (using poly(*n*-butyl acrylate) from >99% in Figure 1 as macroinitiator) (PBA) in DMSO using Cu(0)-mediated polymerisation using PBA as macroinitiator. (A) Monomer conversion and $\ln([M]_0/[M]_t)$ vs. time (h); (B) theoretical (full line) and experimental (square) molecular weight and PDI values vs. monomer conversion; (C) w($\log M$) vs. $\log M$ at different monomer conversions.

Polymers could be chain extended in an iterative fashion at least 4 times (each time reaching near full conversion) in DMSO without significant loss of control/livingness. The molecular weights determined by GPC analysis are in near perfect agreement with the theoretical values for each chain extension (**Figure 3A**). The mass fraction of living polymers chains were determined by deconvolution of the

GPC detector response vs. time traces, revealing in excess of 95 wt-% living polymer after four chain extensions. This result (as well as the fact that the first stage proceeds with control/livingness) is extremely surprising as the catalyst (copper wire and copper complex/ligand) is not located in the same phase as the polymer. It would appear that an interfacial mechanism is likely to be involved in the activation/deactivation process, although mechanistic details remain to be elucidated. The evolution of the PDI (**Figure 3A**) and molecular weight suggest that the activation and deactivation reactions are not adversely affected by the biphasic system during the successive chain extensions.
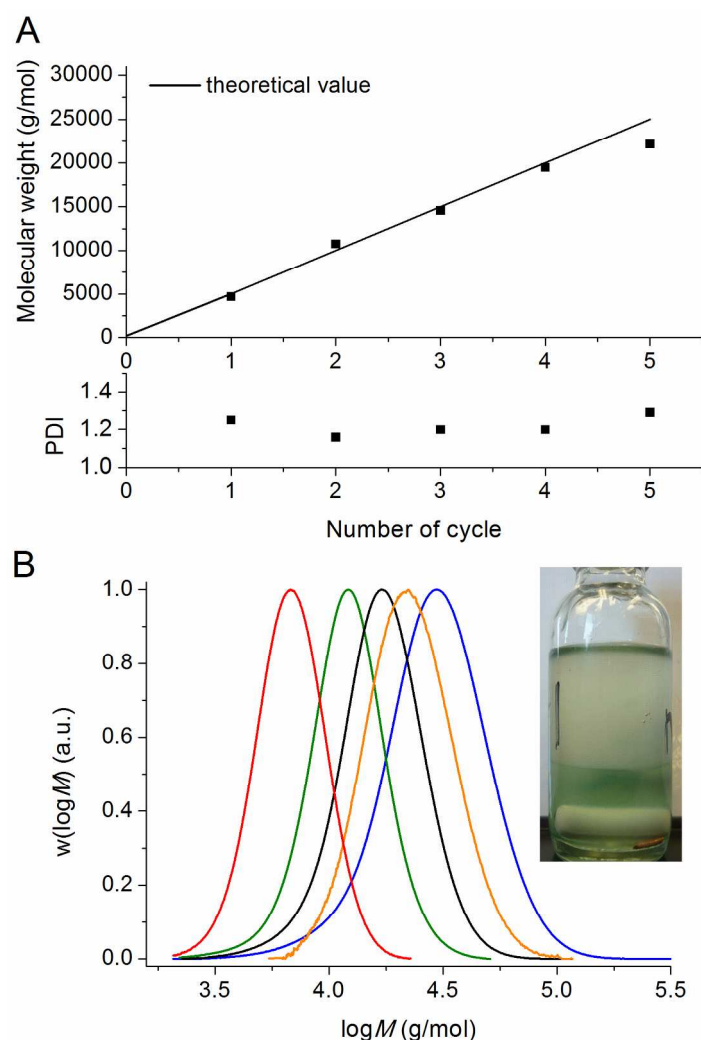

Figure 3. Number-average molecular weights, PDI values and molecular weight distributions for five successive chain extensions of poly(*n*-butyl acrylate) >99.% conversion in Figure 1 with *n*-butyl acrylate by use of Cu(0)-mediated radical polymerisation in DMSO at ambient temperature.

In addition, we have also applied this methodology using a difunctional initiator, ethylene bis(2-bromoisobutyrate) (2F-BiB). During these experiments the effects of steric requirements of the monomer and alkyl chain length of the monomer were also investigated.

In an analogous way to the polymerisation of *n*-butyl acrylate above, polymerisation from 2F-BiB also resulted in the same phase separation. Complete monomer conversion, as determined by ^{1}H NMR, is achieved in 3 hours to yield a polymer with a PDI = 1.08 (**Figure 4**), again showing that the phase separation does not negatively impact the control of the polymerisation.
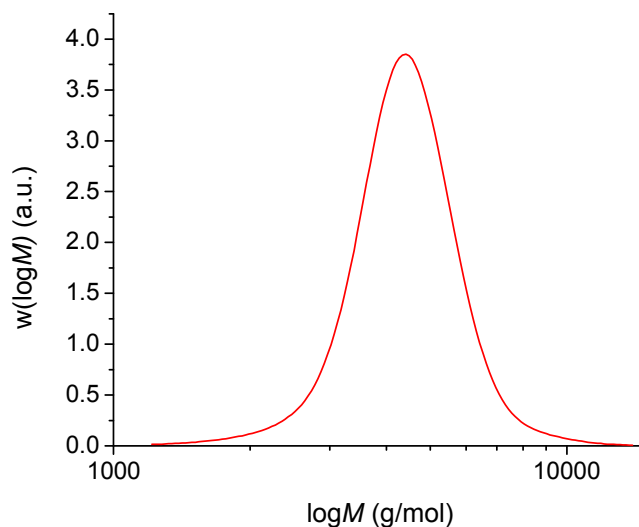

Figure 4 Cu (0)-mediated radical polymerisation of *n*-butyl acrylate using a bifunctional initiator in DMSO at ambient temperature.

MALDI-TOF MS analysis of this polymer shows two major distributions, unlike the monomodal distribution seen using GPC. The main distribution corresponds to the desired bifunctional polymer, the end group fidelity of which is confirmed by both the m/z values which are in close agreement with theoretical values and the isotopic pattern which indicate the presence of two bromide terminal groups (**Figure 5**). The second, lower molecular weight distribution is that of polymer which has been

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terminated at one end via loss of a bromide but continued to grow; this again is elucidated by the agreement with theoretical mass values and splitting patterns. We have attributed this effect to chain transfer to ligand in the early stages of the reaction, where the ligand can react with the initiator at a comparable rate to the monomer. Further studies have shown that this second distribution can be increased or suppressed depending on the level of ligand in the system (i.e. increased ligand content gives increased termination), however, this work will be presented in a future publication as it is outside the focus of this current work.
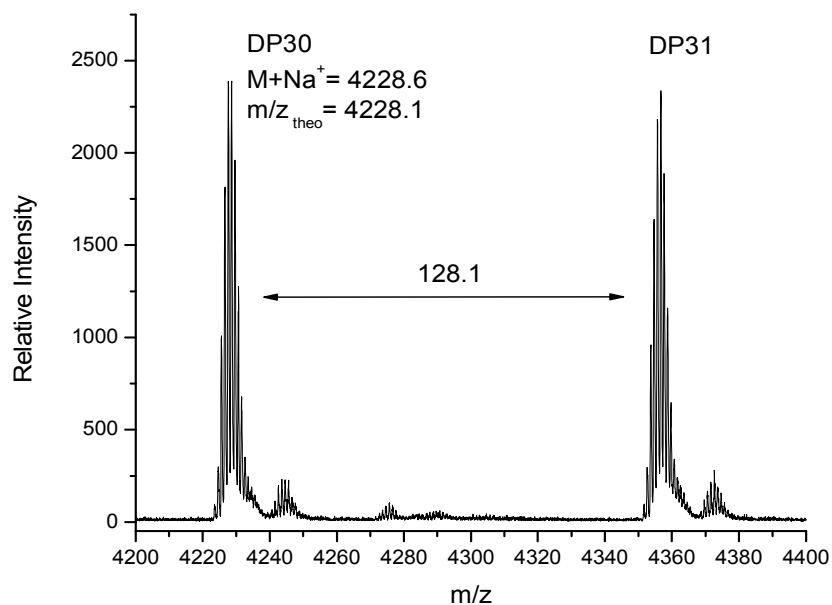
A
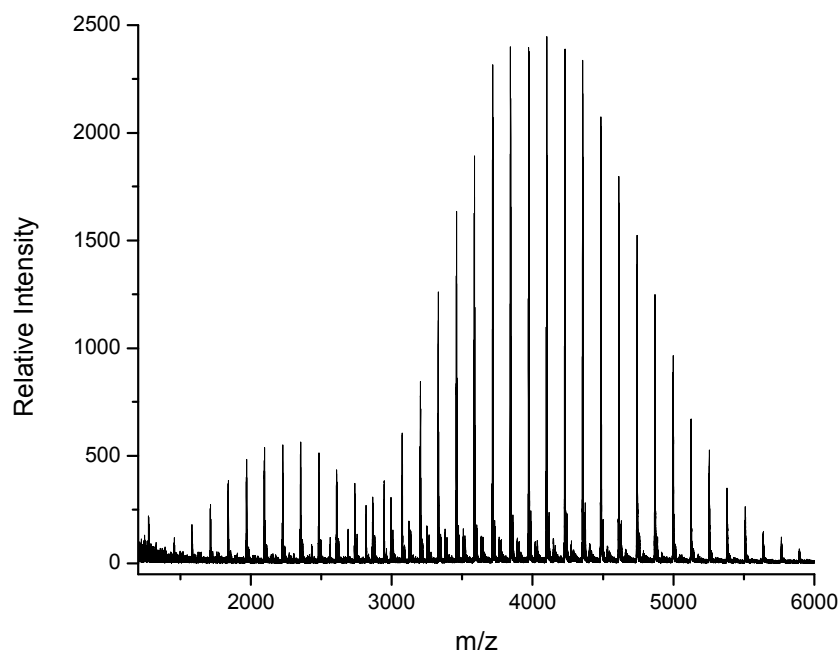
B

Figure 5 (a) MALDI-TOF MS spectra obtained at 99% monomer conversion (b) expansion from 4200-4400 m/z.

The polymerisation was repeated but with isomers of *n*-butyl acrylate (*iso*- and *tert*-) (**Table 1**). Phase separation is also observed and the polymerisations proceed with good control, however, a small

increase in the PDI can be observed. We have attributed this effect simply due to the increase in steric

bulk from *n-* to *iso-* to *tert-*.

We were interested in achieving higher molecular weight poly(acrylates), and thus poly(*n*-butyl

acrylate) of higher molecular weight (12 000 g/mol) was targeted and subsequently chain extended via

addition of extra monomer in DMSO upon reaching complete monomer conversion. We were able to

obtain a polymer with an M_n = 15 000 g/mol and PDI = 1.24, demonstrating that the good control is not

just limited to polymers with a low target molecular weight. The subsequent chain extension to 21,500

g/mol was successful, although an increase in the PDI was observed (**Figure 6**). The large PDI is

attributed to the presence of dead poly(*n*-butyl acrylate) obtained during the initial polymerization.
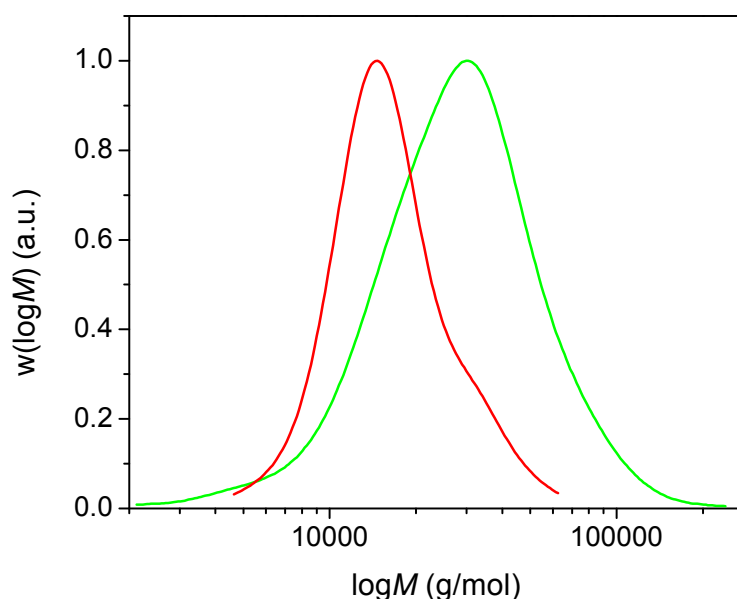

Figure 6 Molecular weight distributions for poly(*n*-butyl acrylate) M_n = 15 000 g/mol and with

subsequent chain extension using a diphasic process.

Finally, we examined the effect of some more hydrophobic acrylates (lauryl and 2-ethyl hexyl acrylate)

(**Table 1**). As these monomers are insoluble in DMSO at ambient temperature, the reaction mixture was

in two phases at the start of the polymerisation. Polymerisation was achieved as indicated by a high

monomer conversion (>90%), however, the large molecular weights and high PDI achieved indicate that control of the reaction has been lost. Thus, it is important for the monomers to be soluble in the polar solvent whilst the polymer becomes insoluble.

Monomer	Target M_n g/mol	$M_{n\ (GPC)}$	PDI
n-butyl acrylate	3 000	4 200	1.10
iso-butyl acrylate	3 000	4 300	1.16
tert-butyl acrylate	3 000	2 900	1.42
*n*BA High M_n	12 000	15 000	1.24
*n*BA High M_n chain extension	25 000	21 500	1.55
lauryl acrylate	3 000	22 300	2.23
2-ethylhexyl acrylate	3 000	4 500	5.75

Table 1 Summary table showing monomers, target molecular weights, number-average molecular weights and PDI obtained using CHCl$_3$ GPC.

Conclusion:

In summary, we have developed a self-generating biphasic polymerisation system that is compatible with Cu (0)-mediated radical polymerisation at ambient temperature. This approach provides a facile method to remove residual copper from the polymer without complex purification procedures, as the polymer phase does not contain detectable levels of copper species by XPS analysis. The method has been exploited to conduct the first ever Cu (0)-mediated radical polymerisation of *n*-butyl acrylate with a very good control of the molecular weight. We explored this biphasic approach for the synthesis of a

range of poly(acrylates) with longer aliphatic chains. However, for these more hydrophobic acrylates, we observed that the polymerization is not well controlled.

Electronic Supplementary Information Available. Experimental details, **Figures S1 to S2** and **Tables S1-S2** are available free of charge via internet.

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Electronic Supplementary Information

Copper (0)-Mediated Radical Polymerisation in a Self-Generating Biphasic System

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Characterization

NMR Spectroscopy

^{1}H NMR spectra were recorded using a Bruker ACF300 (300 MHz) spectrometer employing $CDCl_3$ as solvent. Monomer conversions were determined via ^{1}H NMR spectroscopy, comparing the signal areas from the vinyl protons ($\delta \sim$ 6.50-6.00 ppm) 3H/mol to the signal area of OCH_2 signal (at 4.0 ppm) attributed to $-CH_2O$ (*n*-BuA).

Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) was conducted using THF as the mobile phase. GPC analyses were performed at 40 ^{o}C (flow rate = 1 mL/min) using a Shimadzu modular system comprising an LC-20AT pump, SIL-10AD auto-injector, CTO-16AC column oven and RID-10A RI detector. Molecular weight separation was achieved via a column set comprising a PL 5.0-mm bead-size guard column (50 × 7.8 mm) followed by four Phenomenex PHENOLGEL GPC columns (300 × 7.8mm; 5µm; 10^{-2}, 10^{-3}, 10^{-4} and 10^{-6}A). A calibration curve was generated with commercial linear polystyrene standards ranging from 500 to 10^6 g/mol. SEC was conducted on Varian 390-LC system in $CHCl_3$ at ambient temperature, equipped with refractive index and viscometry detectors, 2 × PLgel 5 µm mixed-D columns (300 × 7.5 mm), 1 × PLgel 5 µm guard column (50 × 7.5 mm) and autosampler.

X-ray Photoelectron spectrometer (XPS)

A Kratos Axis ULTRA XPS incorporating a 165 mm hemispherical electron energy was used. The incident radiation was monochromatic A1 X-rays (1486.6 eV) at 225 W (15 kV, 15 ma). Survey (wide) scans were taken at an analyzer pass energy of 160 eV and multiplex (narrow) higher resolution scans at 20 eV. Survey scans were carried out over 1200 eV binding energy with 1.0 eV steps and a dwell time of 100 ms. Poly(n-butyl acrylate) sample was placed on silica plate and analysed by XPS.

MALDI-TOF Mass Spectrometry

MALDI-TOF MS experiments were carried out on a Bruker UltraFLEX II TOF/TOF-MS instrument equipped with a 337 nm nitrogen laser, ion acceleration voltage of 25 kv and pulse extraction delay time of 90 ns. The instrument was operated in reflectron mode unless otherwise stated and with each spectra being the summation of typically 1000 laser shots in order to maximise the signal to noise ratio.

Sample preparation: Each polymer (0.5 mg/mL) was prepared in THF with sodium iodide (1 mg/mL) and saturated 2,5 dihydroxybenzoic acid (DCTB) matrix in a 1:0.1:1 ratio (sample : salt:matrix). 0.5μ of the mixture was then spotted onto the target plate and analysed.

Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS has been carried out PerkinElmer quadrapole Nexion ICPMS. The instrument has been previously calibrated using copper solution in water. Sample preparation: un-purified poly(n-butyl acrylate) (10 mg) obtained by copper (0) mediated radical polymerization in DMSO has been dissolved in THF (0.200 mL), and then, the solution was drop wise added to water (9.8 mL, 0.1 M of HCl). The solution was mixed for 14 hours before analysis by ICP-MS to determine copper concentration. Each sample was analysed four times, and the average of the four values was calculated.
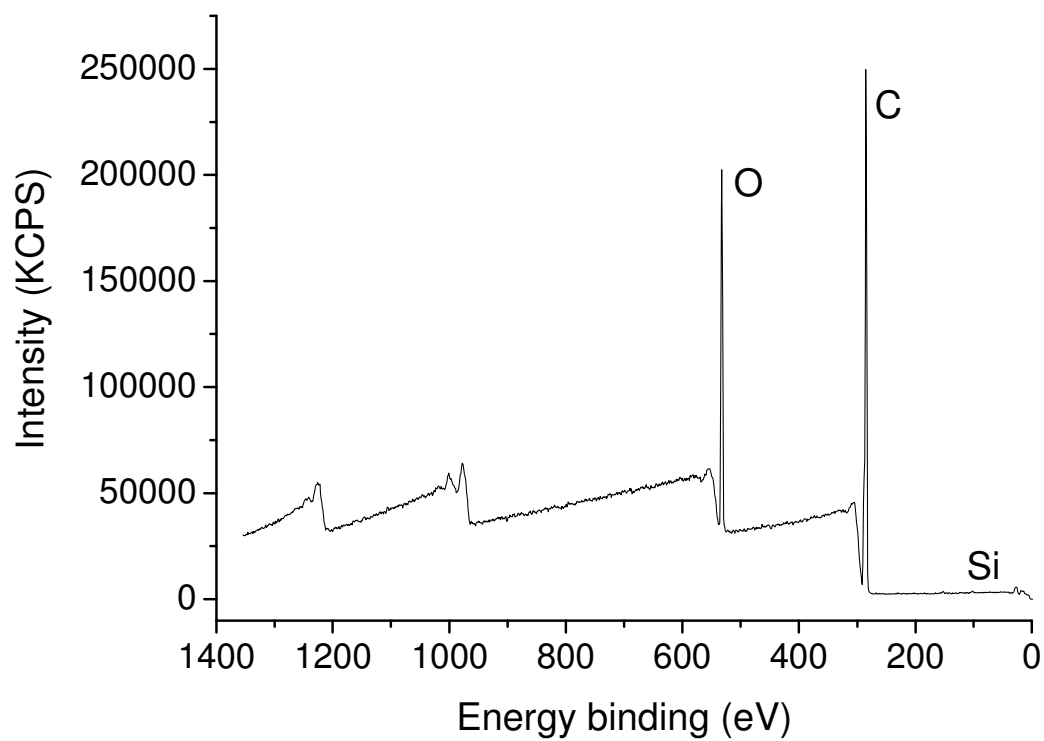
Figure S1. Wide XPS spectrum of crude poly(*n*-butyl acrylate) obtained by copper (0) mediated radical polymerization in biphasic system.
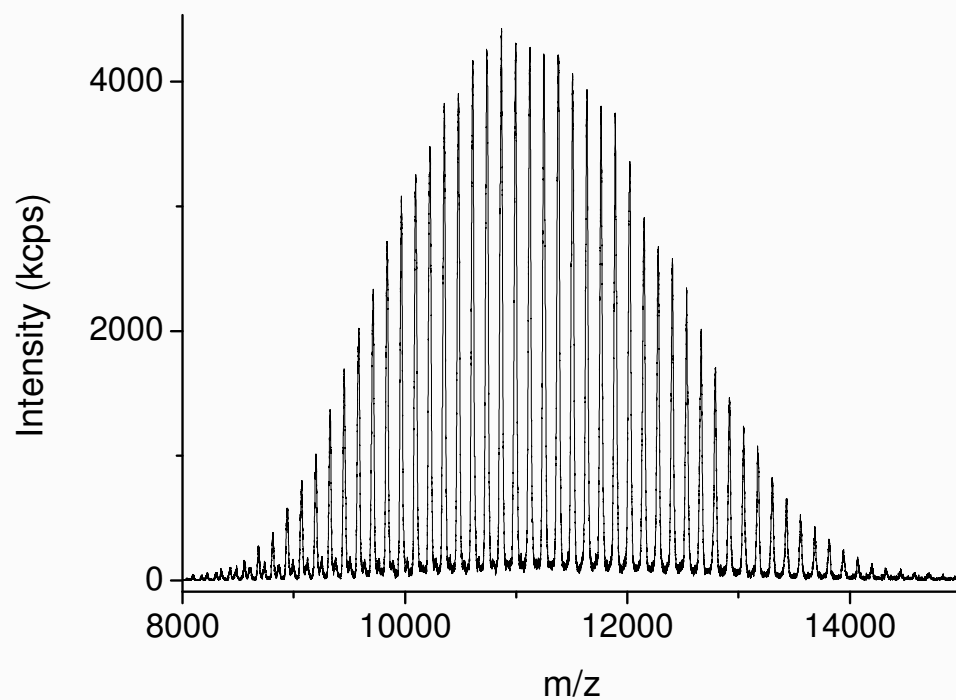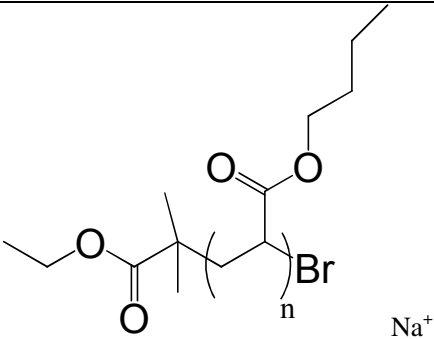
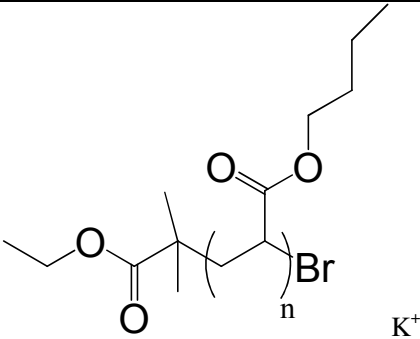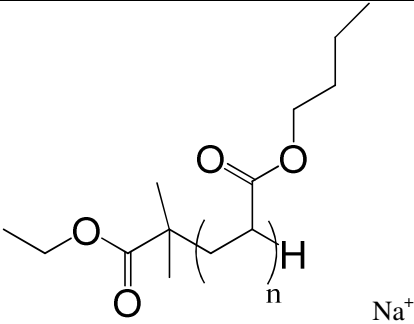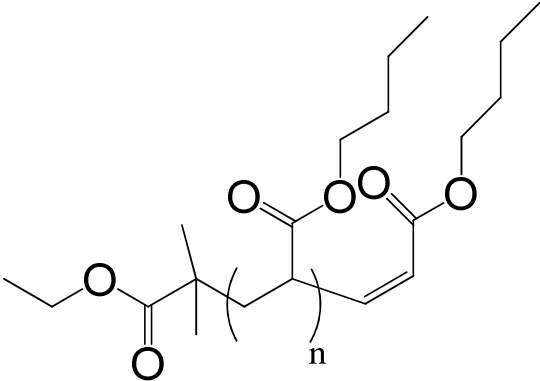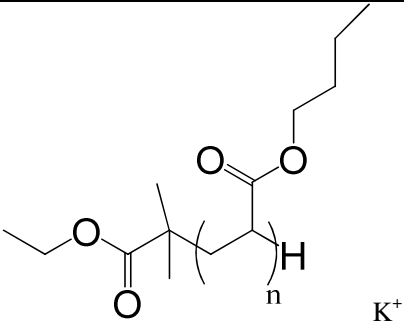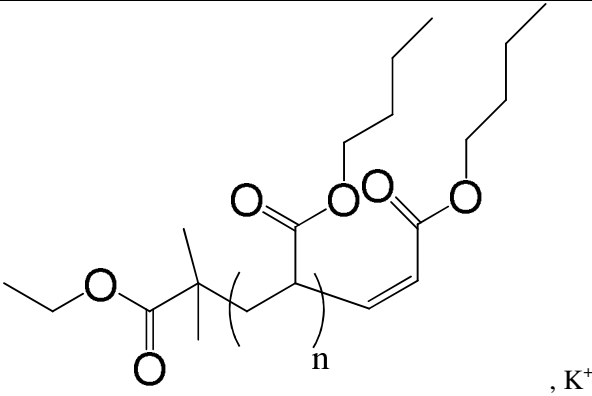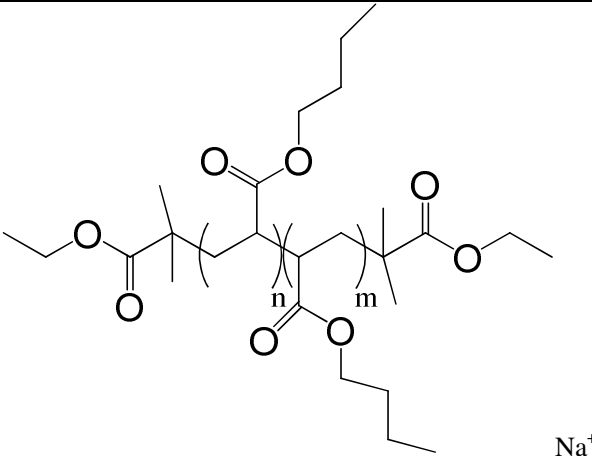**Figure S2.** MALDI-TOF spectrum of poly(*n*-butyl acrylate) after chain extension using copper (0) mediated polymerization in the presence of *n*-butyl acrylate in DMSO.
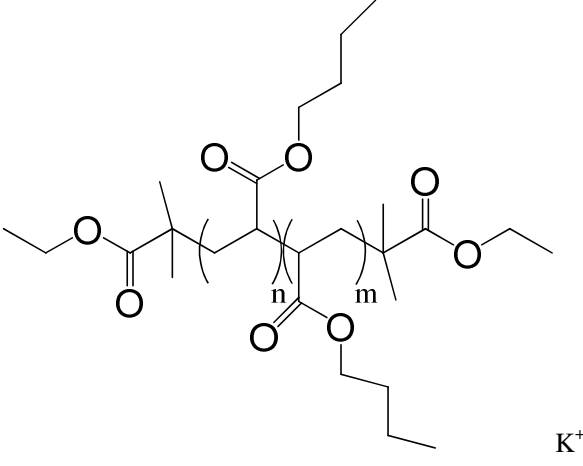
Table S1. Amount of different elements determined by XPS for non-purified poly(*n*-butyl acrylate) obtained by copper (0) mediated radical polymerization in biphasic system.

Type	Energy Binding (eV)	AT-%
C 1s		68.68
O 1s	282-2.89	20.05
Si-O 2p	105.6	0.27
Cu 3s	124-125	Non-detectable
Cu 2p1/2	932-933	Non-detectable
Cu 2p3/2	934-935	Non-detectable

Table S2. Possible populations obtained during the copper(0) mediated radical polymerization.

Species	Theoretical m/z	Experimental m/z
	3422.48 (n= 24)	3422.3
	3438.54 (n= 24)	3438.7
	3342.32 (n= 24)	Not observed
	3340.32 (n= 23)	Not observed

ESI7

Na⁺		
K⁺	3358.48 (n= 24)	Not observed
, K⁺	3356.48 (n =23)	Not observed
Na⁺	3327.20 (n+m= 23)	Not observed

	3343.38 (n+m= 23)	Not observed

ESI9