



# Poly(ethylene glycol) as a 'green solvent' for the RAFT polymerization of methyl methacrylate

Andrew G. West<sup>a</sup>, Christopher Barner-Kowollik<sup>b</sup>, Sébastien Perrier<sup>a,\*</sup>

<sup>a</sup>Key Centre for Polymers & Colloids, The University of Sydney, Sydney, NSW 2006, Australia

<sup>b</sup>Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe, Germany

## ARTICLE INFO

### Article history:

Received 20 January 2010

Received in revised form

10 June 2010

Accepted 10 June 2010

Available online 18 June 2010

### Keywords:

Living radical polymerization (RAFT)

Polyethylene glycol

Green solvents

## ABSTRACT

We demonstrate the use of a range of poly(ethylene glycol)s (PEGs) to control the polymerization of methyl methacrylate (MMA) using reversible addition-fragmentation chain transfer (RAFT) polymerization. The use of PEG as the solvent ( $M_n = 4600 \text{ g mol}^{-1}$ ) resulted in an increase in the rate of the reaction over that of other solvents by a factor of 5 at 60 °C, allowing MMA to be polymerized to high conversions with a DP of 100 much more rapidly than in standard solvents, while maintaining control over the molecular weight with polydispersities as low as 1.05. Interestingly, whilst the same rate increase is seen when polymerizing to a DP of 500, PEG appears to limit the achievable molecular weight to differing degrees depending on its chain length. Advantages of using PEG include its very low toxicity and other environmentally friendly aspects of its nature that allow it to be classed as a 'green' solvent.

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## 1. Introduction

Radical polymerization is one of the most frequently employed methods in both academia and industry as a key method for the production of commodity polymers. Considerable effort has been directed towards optimising these processes to generate well-defined polymers for numerous applications. In the past two decades, research into the synthesis of polymers has moved away from large bulk processes producing commodity polymers into techniques that allow greater control over the molecular weight and size distribution of polymeric chains. The advent of controlled/living radical polymerization has revolutionised the manufacture of polymers on a laboratory scale, and is attracting increased interest from industry. Living radical polymerization (LRP) has received considerable exposure recently due to the ease in which it can be undertaken. Many systems are currently under investigation, including Nitroxide Mediated Polymerization (NMP) [1,2], Iodine Transfer Polymerization (ITP) [3,4], Atom Transfer Radical Polymerization (ATRP) [5,6] and Reversible Addition-Fragmentation chain Transfer or Macromolecular Design by Interchange of Xanthates (RAFT/MADIX, hereafter RAFT) [7–10]. Since its inception in 1998 [11], RAFT polymerization has become one of the most

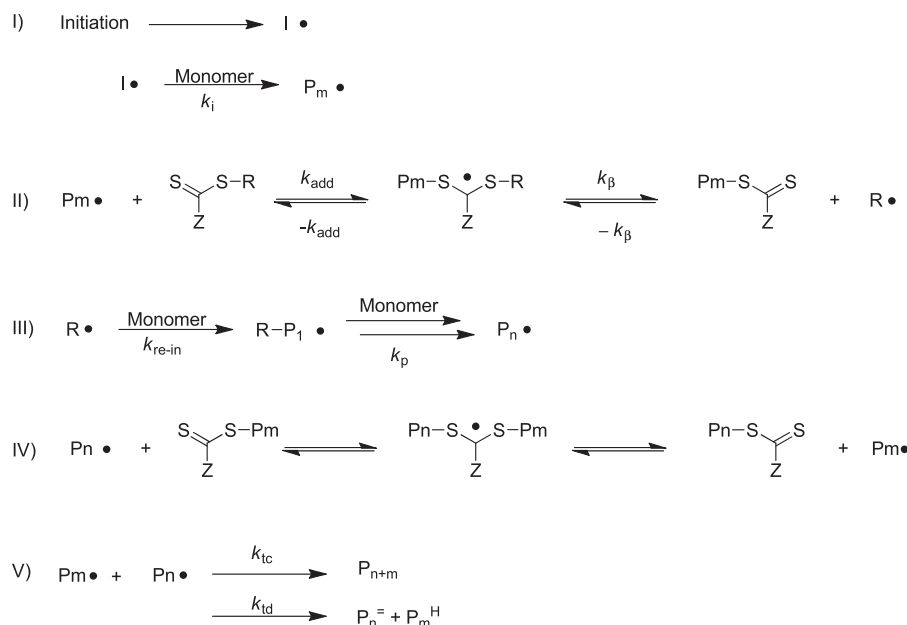
powerful and versatile LRP techniques. Unlike many other controlled radical techniques, RAFT does not require any special conditions and may be carried out in the same manner as conventional free radical polymerization, with the addition of a small amount of chain transfer agent. It is able to polymerize a wide range of commodity monomers such as acrylates, methacrylates, acrylamides, methacrylamides and styrenics [9], and is one of the few techniques able to control the polymerization of vinyl acetate [12,13] (Scheme 1).

Recently, significant research has gone into improving chemical processes in order to combat increasing levels of pollution, both on a laboratory and industrial scale. In 1998, the United States Environmental Protection Agency released a list of twelve 'Principles of Green Chemistry', originally published by Anastas and Warner [14]. Of these, many are achievable through more care and awareness during the designing and planning of reactions. When carrying out laboratory scale experiments, especially organic and polymerization reactions, it is difficult to avoid the use of volatile organic solvents. This is more prevalent in radical polymerization reactions, as the products are inherently difficult to process at high conversions in bulk, and a solvent is commonly employed to mitigate the Trommsdorff effect [15] and possible auto-acceleration. Unfortunately, these solvents typically have a high volatile organic compounds (VOCs) content [16].

The trend towards 'green chemistry' has increased recently due to rising concern towards the environment. Significant research has

\* Corresponding author.

E-mail address: [sebastien.perrier@sydney.edu.au](mailto:sebastien.perrier@sydney.edu.au) (S. Perrier).



**Scheme 1.** Generally accepted mechanism for RAFT/MADIX polymerization.

been geared towards the use of 'green solvents' for polymerization reactions, such as supercritical carbon dioxide [17–19], water [20], and ambient temperature ionic liquids [21–24]. While all exhibit various 'green solvent' characteristics, they do not fulfil all requirements for the reactions themselves to be bracketed for use in 'green chemistry' reactions, as defined by Anastas and Warner [14]. Research into polymerization in 'green' solvents is a relatively new aspect of RAFT [21,25,26]. As yet, RAFT polymerizations have been reported in ambient temperature ionic liquids under relatively mild conditions [21–24] and supercritical carbon dioxide under high pressure [17–19]. Polymerizations undertaken in these solvents have shown good control, living characteristics and narrow molecular weight distributions.

One solvent that has not yet received much interest is poly(ethylene glycol) (PEG). PEG has previously been investigated as a green reaction medium for organic reactions [25], but its use as a solvent for polymerization reactions is scarce [26–29]. From a 'green chemistry' point of view, the use of PEG as a solvent has many advantages in living/controlled radical polymerization. These include its low volatile organic content, low cost and low toxicity, as well as the availability of a large range of molecular weights (related to its viscosity). PEG is water soluble, and various moderate and high molecular weight PEGs are also solid at ambient temperature and as such are easy to transport. Various molecular weights are approved for use by the Food and Drug Administration of the United States for medical use, and find applications in a variety of commercial products, such as in skin creams, toothpaste and some soft drinks, as well as therapeutic applications, such as drug delivery [30]. All these characteristics make PEG a green solvent of choice [26].

Perrier and colleagues were the first to investigate the use of PEG as a green solvent for ATRP reactions [26]. It was found that not only could polymerization be undertaken in low molecular weight PEG with good control over molecular weight and molar-mass dispersity (polydispersity, PDI), but also that the PEG chain would interact with the copper catalyst, and improve its removal from the final polymer product. Here, we extend our investigation of the use of PEG as a solvent to another living/controlled radical polymerization technique, the RAFT process.

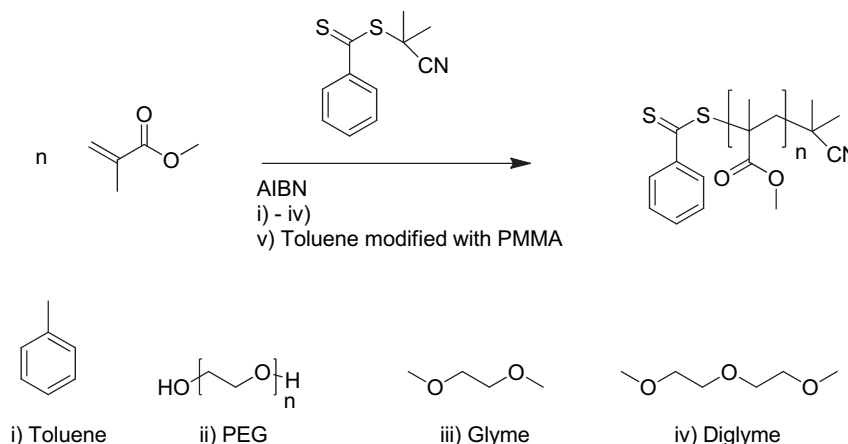
## 2. Experimental

### 2.1. Materials

Methyl methacrylate (99%) was purchased from Sigma–Aldrich and was passed over basic alumina prior to use to remove the inhibitor. 2,2'-Azobis(isobutyronitrile), AIBN, was purchased from Sigma–Aldrich and was twice recrystallised from methanol and dried under vacuum at ambient temperature. 2-Cyanopropan-2-yl benzodithioate, CPBD, was synthesised according to the literature [9]. High molecular weight poly(methyl methacrylate) was synthesised according to the literature [31]. Toluene was purchased from Univar and used as received. Poly(ethylene glycol) (PEG) was obtained from Sigma–Aldrich ( $M_n = 400, 4600 \text{ g mol}^{-1}$ ) and Fluka ( $M_n = 10,000 \text{ g mol}^{-1}$ ) and used without further purification. Molecular weight distributions were obtained using gel permeation chromatography (GPC) at 40 °C with a system equipped with a guard column and two PLGel Mixed-B columns with a molecular weight range of 200– $2 \times 10^6 \text{ g mol}^{-1}$  (Polymer Laboratories) with a Shimadzu RID-10A differential refractive-index detector. Tetrahydrofuran (THF) was used as the eluent with a flow rate of  $1 \text{ mL min}^{-1}$ , with toluene used as a flow rate marker. The system was calibrated with poly(methyl methacrylate) standards ranging from 690 to  $1,944,000 \text{ g mol}^{-1}$ .  $^1\text{H}$  NMR spectra were recorded on a Bruker Avance 300 MHz instrument for solutions in  $\text{CDCl}_3$  containing 0.03% tetramethylsilane (TMS). Dynamic viscosities were determined using a Brookfield viscometer (DV II). 20 mL of the solution were placed in a thermostated bath at 70 °C until equilibrated. For viscosities above 200 cP, a 62 spindle was used, and for solutions lower, a 61 spindle was used. Solutions were degassed using an ultrasonic bath before measurement (Scheme 2).

### 2.2. Polymerization procedures

Polymerizations were carried out in a 50 mL 2-neck round bottom flask under nitrogen. Solutions were treated variably depending on their composition according to one of the following techniques. When PEG was employed as a solvent, technique 1 was used due to the nature of the solvent. Technique 2 was used for



**Scheme 2.** Reaction scheme depicting the polymerization of methyl methacrylate mediated by CPDB in various solvents.

work involving high molecular weight PMMA. For glyme, diglyme and toluene, technique 3 was used (Table 1).

**Technique 1.** The solvent was heated to 70 °C under vacuum in the reaction vessel for a period of time to remove any oxygen present. Two sealed vials, one containing a solution of chain transfer agent, initiator and a small amount of monomer, the other containing the remaining monomer, were degassed by nitrogen purge (30 min in ice). The degassed monomer was transferred to the solvent and stirred for 2 min and then the solution of monomer, initiator and chain transfer agent was added by cannula. The solution was reacted at 70 °C under nitrogen with samples taken at various time intervals. Conversion was obtained by both NMR and gravimetry. Molecular weights were determined via GPC.

**Technique 2.** High molecular weight PMMA was degassed under vacuum before addition of degassed toluene and dissolved using sonication and heating. A solution of monomer, chain transfer agent and initiator was degassed by nitrogen purge and added to the solvent system via cannula before reaction at 70 °C with samples taken at various intervals. Conversion was obtained by both NMR and gravimetry. Molecular weights were determined via GPC.

**Technique 3.** A solution of solvent, monomer, initiator and chain transfer agent was added to the reaction vessel and degassed by nitrogen purge whilst immersed in ice. The solution was reacted at 70 °C under nitrogen with samples taken at various intervals. Conversion was obtained by both NMR and gravimetry. Molecular weights were determined by GPC.

### 3. Results and discussion

RAFT polymerization of MMA was undertaken in the presence of PEG of approximate molecular weight 4600 g mol<sup>-1</sup> as a solvent. Polymerizations targeting DP 100 (at quantitative monomer to polymer conversions) reached full conversion in close to 7 h, exhibiting a 5-fold increase in rate when compared to similar polymerizations in toluene (approx. 40% conversion in 7 h) (see Fig. 1). The polymerization was very well controlled, as illustrated by the linear evolution of the molecular weight with conversion, which adheres closely to the predicted target molecular weights,

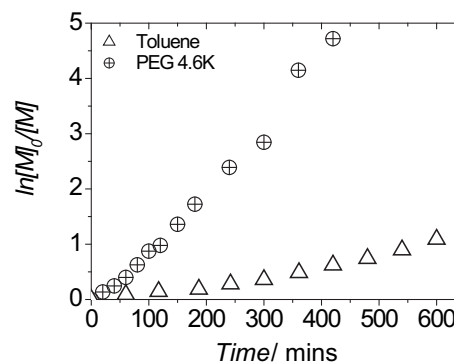
**Table 1**  
Overview of the amounts of reactants employed in the current study.

	Monomer	CTA	Initiator
Ratio	500/(100) <sup>a</sup>	1	0.1
[conc.]/moles	0.05	1 × 10 <sup>-4</sup> /(5 × 10 <sup>-4</sup> )	1 × 10 <sup>-5</sup> /(5 × 10 <sup>-5</sup> )
Mass/g	5.00	0.022/(0.11)	0.0032/(0.016)

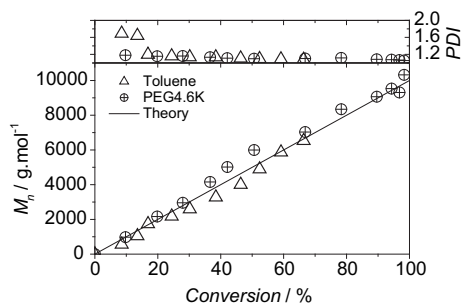
<sup>a</sup> Bracketed amount shows amount used for reaction at a DP of 100.

and polydispersities remain low during polymerization (PDI < 1.2, Fig. 2). PEG therefore offers a viable alternative as a green solvent, leading to PMMA with well-controlled molecular weight and a rate of reaction that is significantly faster than that of a corresponding RAFT polymerization in toluene.

Polymerizations targeting a DP of 500 exhibit a similar increase in rate when compared to polymerizations undertaken in toluene (Fig. 3). The induction period observed when targeting a higher DP is common to RAFT polymerizations mediated by dithiobenzoate chain transfer agents, which exhibit low propagating radical concentrations [32–35]. Interestingly, the molecular weights obtained at moderate conversions are lower than those expected from theory, although the polydispersities remain low (close to 1.1) throughout the polymerization (Fig. 4). We propose that the lower than expected molecular weights obtained at a DP of 500 may result from PMMA chains not being fully solvated at longer chain lengths. Current data indicates that these polymers stop growing at a certain molecular weight, as evidenced by the low PDI of the system and the plateau reached by the molecular weight at increasing conversions; this critical length depends on the molecular weight of the PEG used. Such an effect has been documented in the literature for poor solvents for PMMA, such as methanol, and highly viscous solvents, such as ionic liquids [21–24]. In addition, a number of studies have demonstrated that a local phase separation is observed for blends of poly(ethylene oxide) (PEO) and PMMA. Whilst this is most evident in PEO-rich blends, it is also observed in other blend compositions, as well as under shear conditions. It was also found that this phase separation effect is



**Fig. 1.** First order kinetic plot for the polymerization of MMA in PEG 4600 g mol<sup>-1</sup> (⊗) and toluene (Δ). Reaction conditions: [MMA]<sub>0</sub>:[CPDB]<sub>0</sub>:[AIBN]<sub>0</sub> = 100:1:0.1 at 70 °C. [Monomer]:[Solvent] = 1:1 w/w.

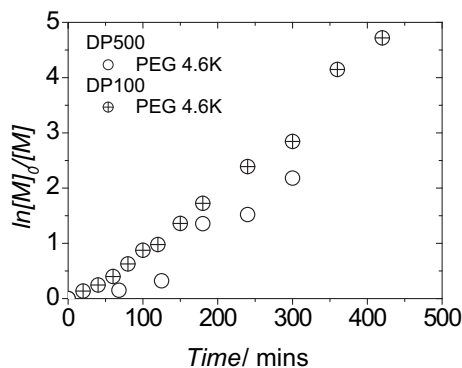


**Fig. 2.** Molecular weight and PDI vs. conversion for the polymerization of MMA in PEG 4600 g mol<sup>-1</sup> (⊗) and toluene (Δ). Reaction conditions: [MMA]<sub>0</sub>:[CPDB]<sub>0</sub>: [AIBN]<sub>0</sub> = 100:1:0.1 at 70 °C. [Monomer]:[Solvent] = 1:1 w/w.

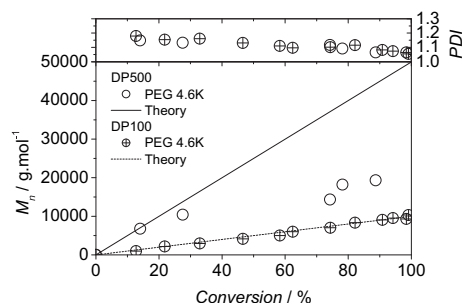
increased when the chain length of the PEO is increased [36], which agrees with results recorded here. It is noteworthy that no obvious phase separation was observed since the blend is created *in situ*, therefore MMA polymerization stops before macroscopic phase separation can be observed. One of the reviewers of this paper suggested that the occurrence of irreversible chain transfer side reactions, and/or initiation from an unknown source, could justify the fact that polymerization proceeds to full conversion whilst exhibiting a lower than expected molecular weight. It is also worth noting that this effect may also be present in polymerizations targeting a lower DP, but it may be undetectable by GPC. However, the chain-transfer-to-solvent constant ( $C_S$ ) of MMA to ethylene glycol ( $0.28 \times 10^4$  at 60 °C) [37] and the chain-transfer-to-polymer ( $C_P$ ) of MMA to poly(ethylene glycol) ( $0.6 \times 10^4$  at 50 °C) [38] are comparable to the  $C_S$  of MMA to toluene ( $0.567 \times 10^4$  at 70 °C) [39], thus suggesting that chain transfer side reactions are unlikely. We are currently investigating this effect further.

When aiming at a DP of 500, it is of particular interest that the molecular weight of the PEG solvent affects both the rate of polymerization and the PMMA molecular weights obtained. Increasing the size of the PEG chain to approximately 10,000 g mol<sup>-1</sup> resulted in a similar rate of polymerization to that of the polymerizations undertaken in PEG 4600 g mol<sup>-1</sup>, yet leads to a reduction in the molecular weight of the generated PMMA. By decreasing the molecular weight of the PEG chain to 400 g mol<sup>-1</sup>, a rate of polymerization intermediate to that noted for reactions in toluene and higher molecular weight PEG was observed, and the molecular weight increased linearly throughout the reactions, although values were lower than predicted (see Figs. 5 and 6).

An increase in molecular weight of PEG has a direct effect on the polarity of the medium. In free radical polymerization, the polarity



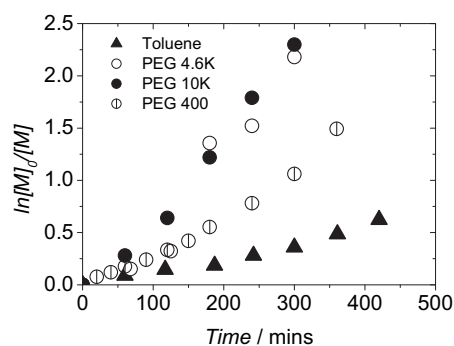
**Fig. 3.** First order kinetic plot for the polymerization of MMA in PEG 4600 g mol<sup>-1</sup>. Reaction conditions: [MMA]<sub>0</sub>:[CPDB]<sub>0</sub>: [AIBN]<sub>0</sub> = 100:1:0.1 (⊗) and 500:1:0.1 (○) at 70 °C. [Monomer]:[Solvent] = 1:1 w/w.



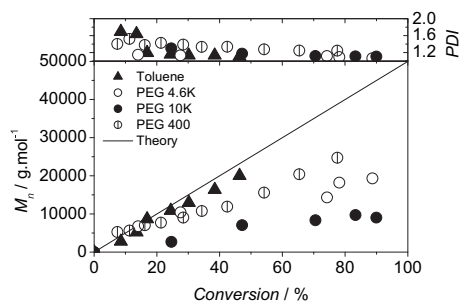
**Fig. 4.** Molecular weight and PDI vs. conversion for the polymerization of MMA in PEG 4600 g mol<sup>-1</sup>. Reaction conditions: [MMA]<sub>0</sub>:[CPDB]<sub>0</sub>: [AIBN]<sub>0</sub> = 100:1:0.1 (⊗) and 500:1:0.1 (○) at 70 °C. [Monomer]:[Solvent] = 1:1 w/w.

of the solvent appears to have no effect on the rate of polymerization [40,41]. Such a notion is consistent with the non-polar nature of the propagating species. In transition metal mediated living radical polymerization systems such as atom transfer radical polymerization (ATRP), however, high polarity solvents (such as DMSO) appear to have a detrimental effect on the rate of polymerization [42], whereas in single electron transfer living radical polymerization (SET-LRP) the use of a polar solvent is shown to increase the overall rate of polymerization, although this is thought to be due to a solvent–catalyst interaction [43]. The effect of polar solvents in RAFT has not been thoroughly investigated for the polymerization of MMA, although the use of acetonitrile and dimethylformamide (DMF) has been demonstrated to result in low polydispersities, yet at the expense of monomer to polymer conversions, over those undertaken in benzene [44]. Use of a more polar solvent for the polymerization of methyl acrylate (MA) yielded similar results to those undertaken in toluene [45].

We investigated the influence of solvent polarity by using glyme and diglyme as solvents, as they are analogues to PEG in structure, yet feature a viscosity comparable to that of toluene. A similar number of  $-(CH_2-CH_2-O)-$  repeat units with respect to each MMA molecule, when compared to the amount of repeat units used in polymerizations in PEG, were introduced (as shown in Table 2). Both kinetic data and molecular weight evolution demonstrated that the solvent polarity did not affect the RAFT polymerization. The polymerizations carried out in glyme and diglyme exhibit similar rates of polymerization to that of toluene, with little acceleration evident (see Fig. 7). In addition, the molecular weight evolutions in both solvents followed closely theory, unlike the reactions carried out in PEG (see Fig. 8). It is noteworthy that at high conversion, the molecular weight of PMMA is lower than expected



**Fig. 5.** First order kinetic plots for the polymerization of MMA in PEG's of molecular weights 400 (⊕), 4600 (○) and 10,000 g mol<sup>-1</sup> (●) and toluene (▲). Reaction conditions: [MMA]<sub>0</sub>:[CPDB]<sub>0</sub>: [AIBN]<sub>0</sub> = 500:1:0.1 at 70 °C. [Monomer]:[Solvent] = 1:1 w/w.



**Fig. 6.** Molecular weight and PDI vs. conversion for the polymerization of MMA in PEG's of molecular weight 400 ( $\diamond$ ), 4600 ( $\circ$ ) and 10,000  $\text{g mol}^{-1}$  ( $\bullet$ ) and toluene ( $\blacktriangle$ ). Reaction conditions:  $[\text{MMA}]_0:[\text{CPDB}]_0:[\text{AIBN}]_0 = 500:1:0.1$  at  $70^\circ\text{C}$ .  $[\text{Monomer}]:[\text{Solvent}] = 1:1$  w/w.

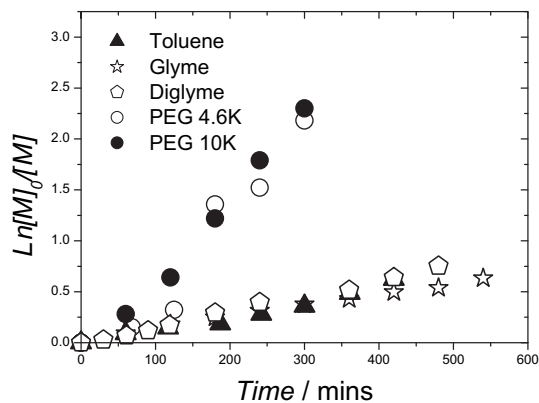
for the polymerization undertaken in glyme. It is likely that high molecular weight PMMA chains are less soluble in glyme than in diglyme, thus leading to a microphase separation similar to that observed for polymerizations undertaken in poor solvents such as methanol.

Since the polarity of the solvent does not seem to affect the polymerization, the effect of the viscosity of the medium of polymerizations was investigated. Studies using other polymerization systems, such as catalytic chain transfer polymerization, have determined that the bulk viscosity of the solvent has a detrimental effect on the rate of polymerization [31,46–48]. It was determined that the rate of polymerization decreases as the viscosity of the medium increases, which is in contradiction with our observations. Reasons for the increase in rate of polymerization in PEG are thought to stem from the so-called 'microviscosity' of the solvent, as opposed to the bulk viscosity. The rate of propagation of methyl methacrylate in a free-radical system was investigated by Russell and colleagues, who suggest that the polymerization does not depend on the bulk viscosity of the solvent, but on the 'solvent viscosity' (i.e. the 'microviscosity') [49]. The so-called 'bulk/macroviscosity' of the solvent is defined as the viscosity measured using macroscopic techniques (in this case, a viscometer). The solvent/microviscosity is defined as the viscosity of the solvent in greatest percentage within the solution medium. This is not strictly speaking the same value as that of the bulk viscosity.

In order to establish the effect of bulk viscosity vs. microviscosity on the rate of polymerization, toluene was modified with PMMA of molecular weight  $2 \times 10^6 \text{ g mol}^{-1}$  generated via free radical polymerization. The viscosities of the high molecular weight PMMA modified toluene solutions were comparable to the PEGs used, as shown in Table 3. Polymerizations undertaken in PMMA modified toluene indicated little increase in rate of polymerization over that of unmodified toluene. When compared to toluene – a solvent of low viscosity – reactions in all types of PEG are shown to be much faster. For the two systems most comparable in viscosity, PEG 4.6 K and toluene modified with 3% PMMA, PEG displays a significantly increased rate of polymerization, despite a higher viscosity than that of the solution of toluene + PMMA (see Fig. 9). In comparison, reactions in PEG of 10,000  $\text{g mol}^{-1}$  also

**Table 2**  
Approximate numbers of  $-(\text{CH}_2-\text{CH}_2-\text{O})-$  repeat units per monomer unit

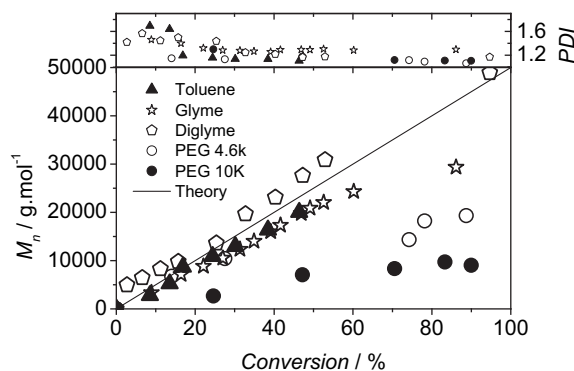
Solvent	Approx. number of ethylene oxide units
PEG 400	2
PEG (approx. 10,000 $\text{g mol}^{-1}$ )	2
PEG (approx. 4600 $\text{g mol}^{-1}$ )	2
Glyme	1
Diglyme	1.5



**Fig. 7.** First order kinetic plots for the polymerization of MMA in PEG's of molecular weight 4600 ( $\circ$ ) and 10,000  $\text{g mol}^{-1}$  ( $\bullet$ ), glyme ( $\star$ ), diglyme ( $\diamond$ ) and toluene ( $\blacktriangle$ ). Reaction conditions:  $[\text{MMA}]:[\text{CPDB}]:[\text{AIBN}] = 500:1:0.1$  at  $70^\circ\text{C}$ .  $[\text{Monomer}]:[\text{Solvent}] = 1:1$  w/w.

exhibit increased polymerization rates over the toluene and 3% PMMA system with a viscosity six times higher. In addition, reactions in PEG of 10,000  $\text{g mol}^{-1}$  displayed a significantly higher rate of polymerization than those carried out in toluene modified with 5% high molecular weight PMMA, which has a lower viscosity. It should be noted that while the system utilising toluene modified with 3% high molecular weight PMMA shows a slight increase in the rate of reaction over that of toluene, the molecular weight also evolves linearly with theory (see Fig. 10). Analysis of the polymerization employing a mixture of toluene and high molecular weight PMMA (5% w/w) shows linear growth of the polymeric chains, as well as low polydispersities (less than 1.2) throughout the polymerization process (see Fig. 10). Molecular weights are significantly lower for the 5% PMMA system than for toluene (5000  $\text{g mol}^{-1}$  at 30% conversion compared to 11,500  $\text{g mol}^{-1}$  in toluene).

Whilst the reason for the increase in rate of polymerization may only be speculated upon, it is thought that the addition of a high molecular weight PMMA to toluene alters the bulk viscosity (or macroviscosity) without changing the microviscosity (or solvent viscosity) of the solvent, giving similar polymerization rates compared to those reactions undertaken in toluene. In contrast, employing PEG as a solvent changes both the micro- and bulk viscosity of the system, leading to an increase in the overall rate of polymerization and a decrease in the (average) termination rate coefficient,  $\langle k_t \rangle$ . It has been shown that diffusion-controlled rate coefficients, such as  $k_t$ , in bulk free radical polymerization



**Fig. 8.** Molecular weight and PDI vs. conversion plot for the polymerization of MMA in PEG's of molecular weight 4600 ( $\circ$ ) and 10,000  $\text{g mol}^{-1}$  ( $\bullet$ ), glyme ( $\star$ ), diglyme ( $\diamond$ ) and toluene ( $\blacktriangle$ ). Reaction conditions:  $[\text{MMA}]_0:[\text{CPDB}]_0:[\text{AIBN}]_0 = 500:1:0.1$  at  $70^\circ\text{C}$ .  $[\text{Monomer}]:[\text{Solvent}] = 1:1$  w/w.

**Table 3**

Solvents and solvent systems employed in the polymerization of MMA and their associated dynamic viscosities

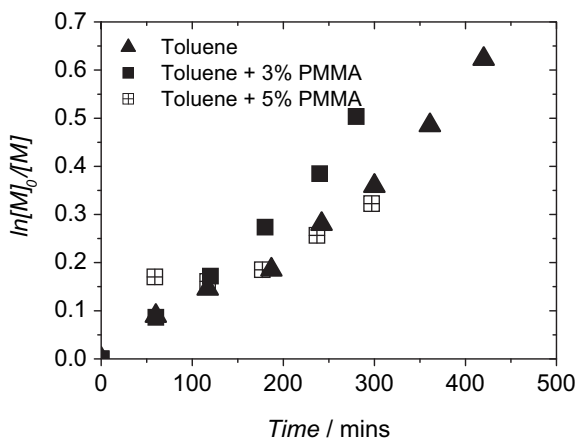
Solvent <sup>a</sup>	Additive	Viscosity (cP) <sup>b</sup>
Toluene	–	0.25
PEG 400	–	10.8
PEG 4.6 K	–	55.2
PEG 10 K	–	205
Toluene	3% PMMA <sup>c</sup>	33.5
Toluene	5% PMMA <sup>c</sup>	115

<sup>a</sup> Solvent: Monomer ratio = 1:1 w/w.

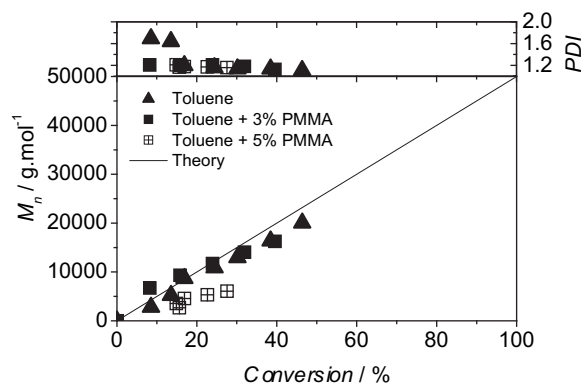
<sup>b</sup> Viscosities measured at 50 rpm and 70 °C.

<sup>c</sup> Percentage refers to amount of PMMA in total solution volume by mass.

with an increased bulk viscosity are constant until over 20% conversion [50,51], indicating that these rate coefficients do not necessarily scale with macroviscosity [31]. This effect would be increased for polymerizations in solution. By increasing the microviscosity of the solvent, the rate of diffusion for longer polymer chains is decreased, while that of the smaller molecules such as monomers and chain transfer agents is relatively unaffected. This results in a decrease in bimolecular termination (by both combination and disproportionation) between the relatively immobile high molecular weight polymers generated during the polymerization, and as such an increase in the overall rate of polymerization. The data suggests that rather than determining the rate of polymerization, it is useful to study small molecule diffusion coefficients, as these coefficients decrease slowly over the course of polymerization, with the rate of these reactions depending on the Smoluchowski equation, for which there is no viscosity term. However, the Stokes–Einstein equation (in which  $D \sim 1/\text{viscosity}$ ) is substituted into the Smoluchowski equation to show that  $k \sim 1/\text{viscosity}$ . Investigations by Schulz and co-workers concluded that by varying the solvent viscosity by orders of magnitude – whilst keeping other reaction conditions (including solvent power) constant – it was found that  $k_t$  scales inversely with viscosity, which one would expect for a diffusion-controlled reaction, assuming the Stokes–Einstein relationship holds true (when substituted into the Smoluchowski equation) [52]. However, this is not the case when using PEG. Work by Heuts et al. on catalytic chain transfer polymerization (CCT) concerning the bulk viscosity of solutions found a strong correlation between the rate coefficient of chain transfer,  $k_{tr}$ , and monomer viscosity [31]. By increasing the bulk viscosity by several orders of magnitude,



**Fig. 9.** First order kinetic plot for the polymerization of MMA in toluene ( $\blacktriangle$ ), toluene modified with 3% PMMA ( $\blacksquare$ ) and toluene modified with 5% PMMA ( $\square$ ) by mass. Reaction conditions:  $[MMA]_0:[CPDB]_0:[AIBN]_0 = 500:1:0.1$  at 70 °C.  $[Monomer]:[Solvent] = 1:1$  w/w.



**Fig. 10.** Molecular weight and PDI vs. conversion for the polymerization of MMA in toluene ( $\blacktriangle$ ), toluene modified with 3% PMMA ( $\blacksquare$ ) and toluene modified with 5% PMMA ( $\square$ ) by mass. Reaction conditions:  $[MMA]_0:[CPDB]_0:[AIBN]_0 = 500:1:0.1$  at 70 °C.  $[Monomer]:[Solvent] = 1:1$  w/w.

these authors found that  $k_{tr}$  did not decrease, indicating that the propagation rate coefficient,  $k_p$ , is not dependent on viscosity, as indicated by the similar rates of polymerization for reactions undertaken in differing bulk viscosities.

In conclusion, the current work demonstrates that by increasing the microviscosity of the solvent, it is possible to carry out polymerizations in a system in which the rate of diffusion of longer polymer chains is decreased, leading to a decrease in  $k_t$ , whilst  $k_p$  remains constant, leading to an increased overall rate of polymerization.

#### 4. Conclusions

The current work has demonstrated that poly(ethylene glycol) is a viable ‘green’ solvent for the RAFT polymerization of methyl methacrylate at degrees of polymerization of up to 100, leading to a 5-fold increase in rate of polymerization when PEG of  $4600 \text{ g mol}^{-1}$  is employed as a solvent, whilst maintaining predictable control over the molecular weight. Although the degree of polymerization is limited to 100, these molecular weights are typical of most applications of polymers obtained via living radical polymerization. The main advantages of using PEG as a solvent include a large increase in the rate of polymerization, ease of availability and simple purification.

At higher targeted degrees of polymerization, the polymerizations still exhibit a large increase in the rate of polymerization, although molecular weights are lower than expected. These lower molecular weights may be explained by the low solubility of PMMA chains in PEG once a certain molecular weight is reached. This limiting molecular weight may be targeted by altering the chain length of the employed PEG. Of significant interest is the large increase in the rate of polymerization. Polymerizations undertaken in order to mimic both the bulk viscosity and polarity of the PEG indicated no increase in the rate of polymerization. The current results suggest that the rate of termination is determined not by bulk viscosity, but by the so-called ‘microviscosity’, in which the micro domain of a solvent determines how a molecule diffuses through a solvent.

#### Acknowledgements

The authors acknowledge the School of Chemistry, University of Sydney for funding. C.B.-K. acknowledges continued funding from the Karlsruhe Institute of Technology (KIT) in the context of the Excellence Initiative for leading German universities. The authors

additionally acknowledge Associate Prof. Greg Russell and Dr. Hans Heuts for their helpful and insightful comments.

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