Polymer 50 (2009) 4464–4470

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

The kinetics of dithiocarbamate-mediated polyurethane-*block*-poly(methyl methacrylate) polymers

Alpesh Patel, Kibret Mequanint*

Department of Chemical and Biochemical Engineering, The University of Western Ontario, London, ON, Canada N6A 5B9

ARTICLE INFO

Article history:
Received 28 April 2009
Received in revised form
8 July 2009
Accepted 22 July 2009
Available online 6 August 2009

Keywords:
Polyurethane macroiniferter
Dithiocarbamate
Polymerization kinetics

ABSTRACT

One important advantage offered by polymeric iniferters is the possibility that polycondensation polymers could be further reacted with vinyl monomers to produce novel block copolymers with interesting properties. The objective of this work was the kinetic investigation of polyurethane-*block*-poly(methyl methacrylate) (PU-*b*-PMMA) using dithiocarbamate (DC)-based polyurethane macroiniferter (PUMI) at different concentrations. It is shown that the copolymerization reactions followed the first order dependency. A linear increase of molecular weight with monomer conversion demonstrated that the copolymerization followed the mechanism of controlled radical polymerization. The rate of polymerization (R_p) at specific reaction time increased as the PUMI concentration increased from 0.34×10^{-3} mol/L to 2.74×10^{-3} mol/L, pass through a maxima, and decreased as PUMI concentration was increased beyond 2.74×10^{-3} mol/L. The thermogravimetric analysis showed that both PUMI and PU-*b*-PMMA degraded in three distinctive stages but the PU-*b*-PMMA is thermally more stable than the PUMI especially at lower temperatures. Thus, a combination of polycondensation and free radical photopolymerization methods, as demonstrated in this study, could be used to synthesize polyurethane-based block copolymers with tailored chain lengths of different blocks suitable for biomedical applications.

1. Introduction

Many important commercial polymers are manufactured using free radical polymerization technique. Even though free radical polymerization is applicably simple and versatile, the difficulties to control the molecular weight, polydispersity index and polymer end groups limit the final properties of the polymers obtained. The limitations are largely due to irreversible bimolecular and/or disproportionation terminations in conventional free radical polymerization making it hard to achieve well-defined architectures with required chemoselectivity such as segmented block copolymers with controlled block lengths. Such irreversible terminations can be avoided by either of the following: (i) by stopping the physical contacts of the growing chain ends using specific guards or; (ii) by providing a reversible termination and/or chain transfer agent with specific free radicals that do not involve in the initiation reaction [1]. Based on either of these two approaches, different controlled radical polymerization techniques such as atom transfer radical polymerization (ATRP) [2,3], reversible addition-fragmentation chain transfer polymerization (RAFT) [4], nitroxy-mediated polymerization (NMP) [5] and iniferter [6] have been developed. Iniferter (**Ini**tiator-chain trans**fer**-**ter**minator) is a controlled radical polymerization method that utilizes the concept of reversible termination [7].

Iniferter molecules photochemically or thermally dissociate into transient radicals (A•), with high reactivity towards unsaturated monomers, and persistent radicals (B•), with high reactivity towards free radicals. The transient radicals initiate the polymerization and incorporate monomers to the polymer chain, based on their kinetic constants. The growing polymer chains reversibly terminate with the persistent radicals that can reinitiate to incorporate further monomers into the polymer chains. The controlled repetition of re-initiation, monomer insertion and reversible termination gives high molecular weight polymer with lower polydispersity index than conventional free radical polymerization. In addition, both the molecular weight of the polymer and monomer conversion increases linearly with reaction time. Since the polymerization is carried out through monomer insertion into the iniferter bonds, such polymers always have iniferter fragments at the chain ends [8]. In order to provide controlled radical polymerization, the reversible termination constant of the growing chain with the persistent radicals has to be higher than the irreversible termination constants at any conversion. In addition, the rate of reversible termination reaction has to be greater than the rate of

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* Corresponding author. Tel.: +1 519 661 2111x88573; fax: +1 519 661 3498.
E-mail address: kmequani@eng.uwo.ca (K. Mequanint).

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doi:10.1016/j.polymer.2009.07.045

the propagation reaction. Thus, in the case of iniferter, the chemical nature of the persistent radicals is the key factor towards driving controlled radical polymerizations in the desired direction [9].

The three main characteristics of iniferter radical polymerization method are: (i) the end groups of the polymers are iniferter fragments; (ii) both the molecular weight of the polymer and monomer conversion increase with reaction time and; (iii) the polymer prepared through iniferter technique should, if needed, act as polymeric iniferter to produce block copolymers. Since the seminal work conducted by Ostu [7], considerable progress was made on the mechanism of iniferter polymerization. Dithiocarbamate (DC)-based photoiniferters are among the earliest to be investigated for the controlled polymerization of vinyl monomers [6]. Since then, DC derivatives such as benzyl-*N*,*N′*-diethyldithiocarbamate (BEDC) [10], (2-*N*,*N′*-diethyldithiocarbamyl) isobutylic acid (DTCA) [11,12], (4-cyano-4-diethyldithiocarbamyl) pentanoic acid (CDPA) [11,12], *p*-xylylenebis(*N*,*N′*-diethyldithiocarbamate) (XDT) [13], diethyl dithiocarbamato-(1,2)-propane diol (DCPD) [14], benzyl-*N*,*N′*-dimethyl dithiocarbamate (BMDC) [15], *N*,*N′*-(tetramethyl) thiuram disulfide (TMTD) [15], O,O′-diisopropylxanthic disulfide (DPXD) [15], diethyl-2,3-dicyano-2,3-di(*p*-*N*,*N′*-diethyldithiocarbamymethyl) phenylsuccinate (DDDCS) [16], *N*,*N′*-(tetraethyl) thiuram disulfide (TETD) [10], and 1,2,4,5-tetrakis(*N*,*N′*-diethyldithiocarbamylmethyl) benzene (DDCMB) [17] had been studied as photoiniferters in the syntheses of diblock [14,15], triblock [16], star-block [10] and graft [18–21] copolymers. Many of these studies, however, focused on small dithiocarbamyl (DTC)-centered persistent radicals at the end of the growing polymeric chains. In order to prepare multiblock copolymers, DC derivatives can also be incorporated in the polymer backbone to provide long polymeric DTC-centered persistent radicals [22]. Since DC-based iniferters that are part of the polymer backbone can be affected by diffusion, the long polymeric persistent radicals may behave differently and potentially influence the overall rate of polymerization compared with the small persistent radicals.

One important advantage offered by polymeric iniferters is the possibility that polycondensation polymers could be reacted with vinyl monomers to produce novel block copolymers with interesting properties. In this regard, our laboratory has been investigating polyurethane-based macroiniferters to synthesize novel hydrogels for biomedical applications [22–24]. These hydrogels had a wide variety of physical, mechanical, thermal and biological properties expanding the possibilities towards emerging areas of applications. While a minimal kinetic work was conducted on polyurethane macroiniferters derived from 1,1,2,2-tetraphenyl-1,2-ethanediol [25], kinetic data for polyurethane macroiniferters derived from DC is notably absent in the literature. Detailed kinetic analysis of such macroiniferter provides advanced information to tune the final properties of the block copolymers. Previously, we have synthesized a DC-based polyurethane macroiniferter (PUMI) and utilized it to prepare physically cross-linked polyurethane hydrogels for biomedical applications [22]. Our approach is one of only a few reports describing the incorporation of DC groups into polycondensation polymers in order to synthesize block copolymers [26–28]. In this manuscript, the kinetics of DC-based polyurethane macroiniferter is examined using methyl methacrylate as a model monomer.

2. Experimental

2.1. Materials

All chemicals were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Methyl ethyl ketone (MEK) and dimethylformamide (DMF) were distilled at reduced pressure prior to use. Polytetramethylene oxide with a molecular weight of 1000 g/mol (PTMO 1000) was dried at 90 °C and at reduced pressure of 200 mmHg for 2 h. 4, 4′ Diphenylmethane diisocyanate (MDI) was purified by filtering it from the melt. Methyl methacrylate (MMA) was used after passing through an inhibitor remover column (Sigma-Aldrich, WI). All other chemicals and reagents were of the highest purity available and used without further purification.

2.2. Synthesis of N,N′-diethyl-N,N′-bis(2-hydroxyethyl)-thiuram disulfide (DHTD) and segmented polyurethane macroiniferter (PUMI)

DHTD was prepared from 2-ethylaminoethanol and carbon disulfide using the method we described previously [22]. The PUMI was synthesized from MDI, PTMO 1000 and DHTD as reported in our previous publication [22]. The final products were characterized using ^{1}H NMR and FTIR spectroscopy.

^{1}H NMR ($CDCl_3$) (1) DHTD: $\delta = 1.10$–1.30 ($-CH_2C\underline{\mathbf{H}}_3$), 3.50 ($-O\underline{\mathbf{H}}$), 3.60–4.00 ($-C\underline{\mathbf{H}}_2CH_3, -S_2CNC\underline{\mathbf{H}}_2-$) and 4.35 ($-C\underline{\mathbf{H}}_2OH$) ppm; (2) PUMI: $\delta = 1.25$ ($-C\underline{\mathbf{H}}_3CH_2N-$), 1.42 ($-CH_3C\underline{\mathbf{H}}_2N-$), 1.61 ($-C\underline{\mathbf{H}}_2CH_2-$), 1.71 ($-C\underline{\mathbf{H}}_2N$), 3.40 ($-OC\underline{\mathbf{H}}_2-$), 3.86 ($-C_6H_4C\underline{\mathbf{H}}_2C_6H_4-$), 4.15 ($-COOC\underline{\mathbf{H}}_2-$) and 7.00–7.25 (aromatic) ppm.

FTIR: (1) DHTD: 3400 (b, OH), 2975–2935 (b, aliphatic), 1180 (st, C=S), 1040 (st, C–S) and 750 (st, S–S); (2) PUMI: 3295 (st, NH), 2940–2850 (b, aliphatic), 1725 (st, C=O), 1604 (st, aromatic ring, MDI), 1530 (b, NH), 1480–1445 (aliphatic deformation), 1410 (b, $-CH_2$ in MDI), 1220 (st, C–N, urethane), 1090 (st, C–O–C) and 817 (aromatic, out of plane).

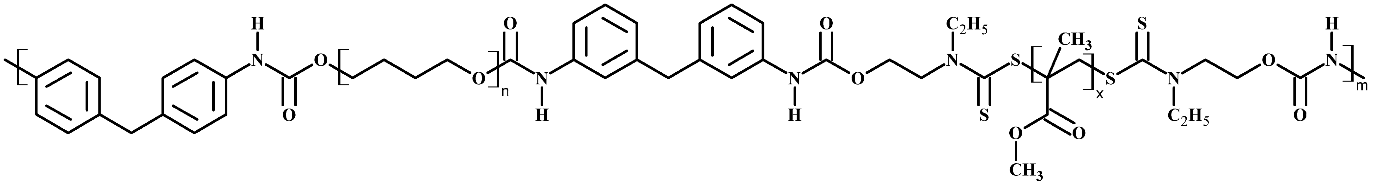
2.3. Synthesis of polyurethane-block-poly(methyl methacrylate) (PU-b-PMMA)

A solution of known amounts of PUMI (as shown in Table 1) and 12.00 g of MMA in 80 mL DMF was purged with nitrogen for 10 min. The solution was then sealed and irradiated with UV light (100 W, model B100AP; UVP Inc., CA) at the distance of 6 cm (≈ 20 mW/cm^2). Samples were taken at stipulated times, poured into pre-weighed Petri dishes and the solvent was evaporated at 60 °C and at reduced pressure of 200 mmHg for 2 h. The conversions were calculated using a gravimetric method. In order to calculate the rate of polymerization (R_p) for kinetic studies, the molecular weight of the repeating unit in PUMI (1828 g/mol) was used for molar concentration calculations. For molecular weight analyses, samples were taken in intervals of 6 h and the PU-*b*-PMMA (Scheme 1) was precipitated using tenfold excess cold methanol. The product was dried at 30 °C in a vacuum oven overnight. Unreacted MMA residues and possible homo-PMMA were extracted using acetonitrile. Since precipitation of the block copolymers after 8 h reaction was very difficult for PUMI concentrations below 10 g/L, kinetic data above 8 h reaction was not obtained for these concentrations.

Table 1
Block copolymerization of MMA using PUMI under UV radiation in DMF.

Run	PUMI (g)	MMA (g)	DMF (mL)	PUMI (g/L)	Iniferter concentration[a] (mol/L) × 10^3	MMA (mol/L)
1	0.05	12.00	80.00	0.625	0.342	1.50
2	0.10	12.00	80.00	1.25	0.684	1.50
3	0.20	12.00	80.00	2.50	1.368	1.50
4	0.40	12.00	80.00	5.00	2.735	1.50
5	0.80	12.00	80.00	10.00	5.470	1.50
6	1.20	12.00	80.00	15.00	8.206	1.50
7	2.40	12.00	80.00	30.00	16.411	1.50
8	3.20	12.00	80.00	40.00	21.882	1.50

[a] The PUMI used in the reaction in units of g/L has been converted to mol/L by dividing it with the molecular weight of the repeating unit (1828 g/mol).



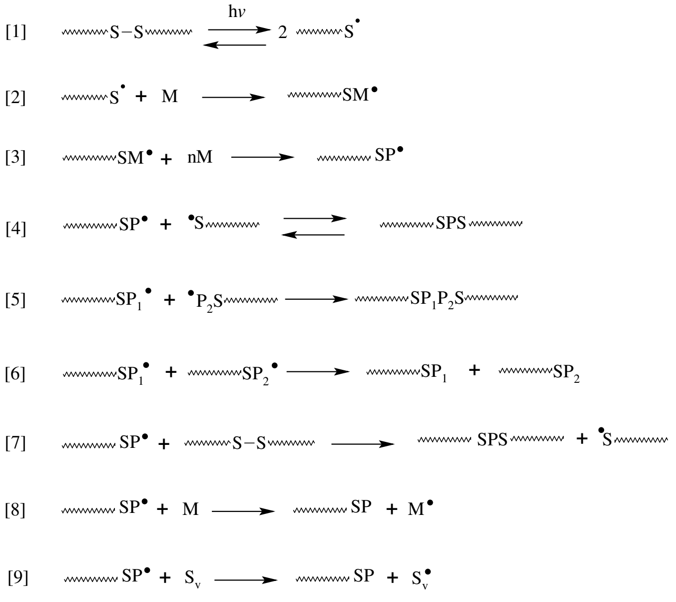
Scheme 1. The chemical structure of PU-*b*-PMMA.

^{1}H NMR ($CDCl_3$) PU-*b*-PMMA: $\delta = 0.78$ ($-C\underline{H}_3CR_3$, syndiotactic), 0.95 ($-C\underline{H}_3CR_3$, atactic), 1.18 ($-C\underline{H}_3CR_3$, isotactic), 1.37 ($-CH_3C\underline{H}_2N-$), 1.55 ($-C\underline{H}_2CH_2-$), 1.74 ($-CH_2C\underline{H}_2N$), 1.81 ($-C\underline{H}_2-CR_2-C\underline{H}_2$), 3.34 ($-OC\underline{H}_2-$), 3.53 ($-C\underline{H}_3OCO$), 3.81 ($-C_6H_4C\underline{H}_2C_6H_4-$), 4.09 ($-COOC\underline{H}_2-$) and 7.00–7.25 (aromatic) ppm.

FTIR of PU-*b*-PMMA: 3297 (st, NH), 2940–2860 (b, aliphatic), 1725 (st, C=O), 1598 (st, aromatic ring, MDI), 1535 (b, NH), 1485–1440 (aliphatic deformation), 1410 (b, CH_2 in MDI), 1275 (st, C–O, PMMA), 1220 (st, C–N, urethane), 1100 (st, C–O–C) and 817 (aromatic, out of plane).

2.4. Characterization methods

Fourier Transform Infrared (FTIR) spectra were recorded on solid samples by using Bruker Vector 22 spectrophotometer. For every specimen, 32 Scans at 4 cm^{-1} resolution were collected. Nuclear Magnetic Resonance (^{1}H NMR) spectra were recorded on a Varian® INOVA 400 (400 MHz) in $CDCl_3$. ACD/2D NMR software was used to analyze the peaks. The molecular weights of the PU-*b*-PMMA were determined using a Waters 2695 separations module equipped with a Waters 2414 differential refractometer and two PLgel 5 μm mixed-D (300 × 7.5 mm) columns from Polymer Laboratories. The samples, dissolved in DMF with 0.1 M LiBr and 1% (v/v) triethylamine, were injected at 85 °C to the PLgel column using a flow rate of 1 mL/min. Calibration was done using polystyrene standards. Empower 2 software was used to integrate the eluted curves. TGA was carried out using a TA Instruments Q-series TGA Q 500 analyzer. The specimens were dried at 50 °C in a vacuum oven overnight, weighed in the range of 5–10 mg and heated from 25 °C to 700 °C at a heating rate of 10 °C/min under nitrogen. TA Instruments Universal Analysis 2000 software was used to analyze the data.



Scheme 2. The polymerization mechanism of DC-based macroiniferter. Reactions 1–4 are the idealized controlled iniferter polymerization; reactions 5 and 6 are possible irreversible terminations whereas reactions 7–9 are possible chain transfer reactions.

3. Results and discussion

The chemistry of dithiocarbamate-based photoiniferters was first proposed by Ostu and coworkers [7]. As presented in Scheme 2, the S–S bond in the DC units of the polyurethane can cleave easily in the presence of UV light between 320 and 380 nm wavelengths [17]. Thus, the photolysis of S–S bonds produce two stable DTC-centered radicals that have higher than 20 μS lifetime [15] (reaction 1). These radicals barely react with MMA monomer (M) to initiate the polymerization, since they are more receptive to terminate the

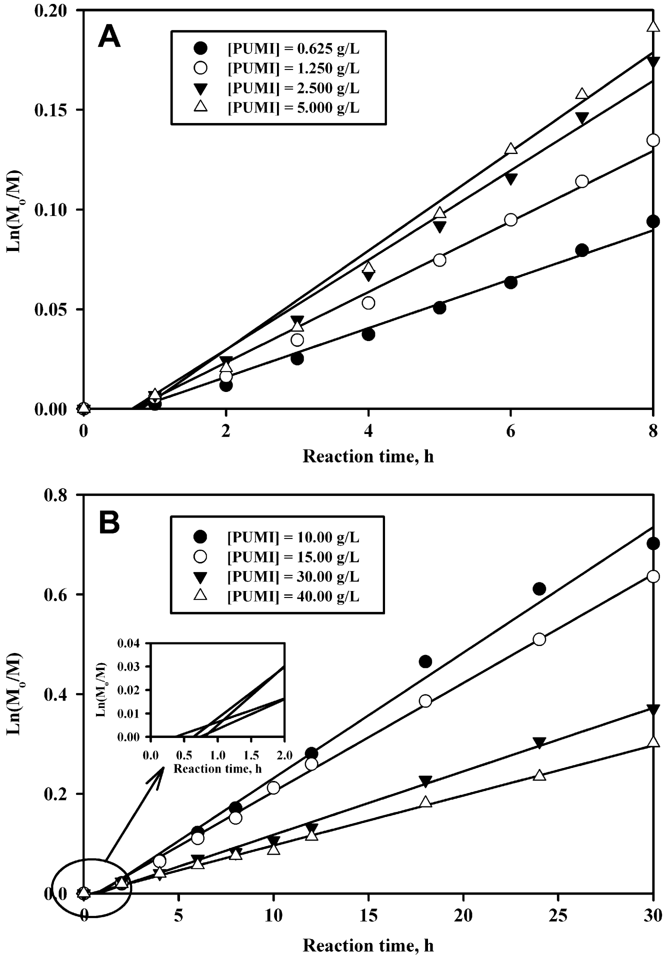


Fig. 1. Ln(M_o/M) versus time plots for the MMA copolymerization with different concentrations of PUMI in DMF under the induction of UV light. Since precipitation of the block copolymers after 8 h reaction was very difficult for PUMI concentrations below 10 g/L, kinetic data above 8 h reaction was not obtained for these concentrations.

polymerization. The only driving force towards the initiation reaction is a high monomer to DTC-centered radical ratio. Once the DTC-centered radicals initiate and propagate the polymerization (reactions 2 and 3), the resulting carbon (C)-centered radicals recombine either through reversible primary radical termination (reaction 4) or through irreversible bimolecular termination (reaction 5). The C–S bond length ($\approx$ 1.8 Å) formed due to these terminations [29], is also long enough to be cleaved upon further induction of UV light (reaction 4). The re-initiation provides again C-centered radicals having short lifetime and hence participates into the propagation reaction (reaction 3). The DTC-centered radicals generated through this re-initiation, on the other hand are more stable and proceed through subsequent primary radical termination reaction (reaction 4). During the polymerization, C-DTC reversible termination is more preferable than C–C bimolecular irreversible termination, since the rate constant of C–C termination is at least one order of magnitude lower than that of C-DTC termination reaction [13]. Thus, in the absence of irreversible terminations and other side reactions, the DC-based macroiniferter proceeds through controlled radical polymerization mechanism. In Scheme 2, reaction 6 shows the irreversible termination by disproportionation, whereas reactions 8 and 9 show the irreversible termination through transfer to monomer and solvent respectively. The extent of these irreversible termination reactions compete with the controlled mechanism and potentially increases the polydispersity. In this study, we first prepared high molecular weight polyurethane macroiniferter containing DC segments. PU-*b*-PMMA copolymers were then prepared by solution polymerization of MMA with PUMI. The DC segments within the PUMI backbone followed the photoiniferter chemistry, added PMMA segments in the polyurethane backbone and thus allowing multiblock PU-*b*-PMMA copolymers to be facilely prepared (Scheme 1).

In order to minimize the possibility of irreversible terminations and other chain breaking side reactions, we used low intensity ($\approx$20 mW/cm^2) UV light. Accordingly, we prepared PU-*b*-PMMA copolymers at different PUMI concentrations and studied the influence of macroiniferter concentrations on the rate of copolymerization. The first order dependency of the copolymerization reactions at different PUMI concentrations are shown in Fig. 1. Here, M_0 represents the initial monomer concentration and M represents the monomer concentration at a specific reaction time of interest. The semi-logarithmic plots represent that the polymerization reactions followed the first order reaction kinetics. Instantaneous chain growth was not observed at almost all PUMI concentrations. Thus a lag phase for the first hour of the reaction is evident in Fig. 1. The possible reasons are explained as follows. As mentioned earlier, initial macroiniferter decompositions provide only DTC-centered radicals and these radicals hardly initiate the polymerization reaction. Once the C–S bonds are formed; the re-initiation, monomer addition and reversible combination proceeded through the first order reaction kinetics. This mechanism is not unique to our polymeric iniferters as small molecule iniferters are also known to initiate at a slower rate. However, the lag phase was not observed when small molecules were used as iniferters [10,11,13]. Therefore we believe that the size of the iniferter molecule played a role and

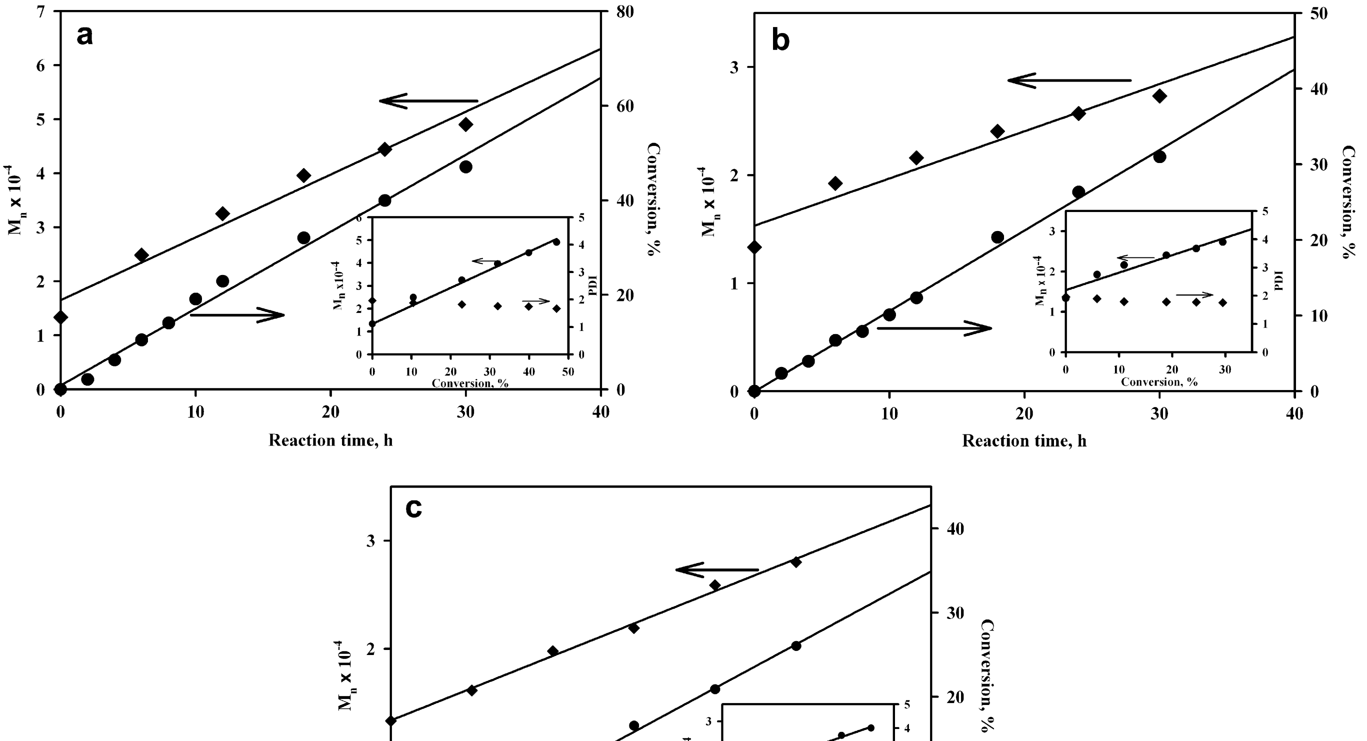


Fig. 2. Molecular weight and monomer conversion plots versus time for the copolymerization of MMA with different PUMI concentrations in DMF. (a) [PUMI] = 15 g/L, (b) [PUMI] = 30 g/L and (c) [PUMI] = 40 g/L. The insert shows the molecular weight and PDI as a function of monomer conversion.

exacerbated the observed lag phase. Our polyurethane macroiniferter has a molecular weight of 13,000 g/mol and is very large to diffuse through the reaction solution and initiate the polymerization instantaneously.

During the course of the polymerization, a linear increase in both molecular weight and conversion with reaction time had been observed for different PUMI concentrations (Fig. 2). This allows controlling the length of PMMA segments within the polyurethane backbone by adjusting the radiation time. At every PUMI concentrations, a linear increase in molecular weight, with respect to the conversion, is consistent with the monomer conversion that proceeds via a controlled radical polymerization mechanism. The polydispersity indices (PDI) remained unaffected or decreased slightly and supported the hypothesis that the monomer addition into polyurethane backbone progress in a controlled manner. Interestingly Fig. 2a–c also highlights that as the PUMI concentration increased from 15 g/L to 40 g/L, both molecular weight and conversion decreased for fixed reaction times. This observation is in sharp contrast to conventional radical polymerization whereby an increase of initiator concentration increases conversion. Fig. 3 shows the GPC traces of PU-*b*-PMMA for different polymerization times and at different PUMI concentrations. For all PUMI concentrations used, the peaks obtained were unimodel and moved distinctively towards lower elution volumes as the reaction time increases, indicating a molecular weight increase. Turner and Blevins [30] reported that when dithiocarbamate end-capped poly(methy1 methacrylate) was chain extended with MMA, the molecular weight first increased and then decreased at higher conversion. Using dithiocarbamate end-capped polystyrene and poly(methyl methacrylate) macroiniferters for sequential block copolymerization, the same authors also showed that the addition of MMA as a second monomer resulted higher homopolymerization than styrene [30] although studies carried out by Otsu and coworkers demonstrated the reverse effect [31,32]. Because we used the dithiocarbamate-containing diol for the synthesis of the polyurethane, there are 7–8 iniferter units per mole of polyurethane as part of the polymer backbone. These iniferter units are part of the polymer backbone and, the radicals generated at any time will have a polyurethane backbone. In dithiocarbamate end-capped inferter systems, the main reason for homopolymer formation is the recombination of the persistent radicals followed by re-initiation [33]. In our case, such recombination results polyurethane segments with iniferter units. Upon re-initiation, MMA can only be added into yet polyurethane bearing PMMA radical making the likelihood of MMA homopolymer formation rare. Therefore the use of polycondensation polymers as macroiniferter is advantageous over the end-capped macroiniferter [27,28]. However, the propagating PMMA radical is known to undergo predominantly termination by disproportionation that may lead to the formation of PU-*b*-PMMA diblocks instead of the multiblock final product. Given that we started with a high molecular weight macroiniferter, such diblock polymer chains should either reduce the molecular weights of the final product or result in a bimodal distribution corresponding to the diblock and multiblock polymers. GPC traces showed neither of these effects (Fig. 3) indicating the possibility that PMMA propagating radicals towards disproportionation termination is less pronounced in the presence of polymeric DTC-centered radicals. Further, the photolysis of dithiocarbamate iniferters is shown to release some CS_2 leading to the loss of the living nature of the

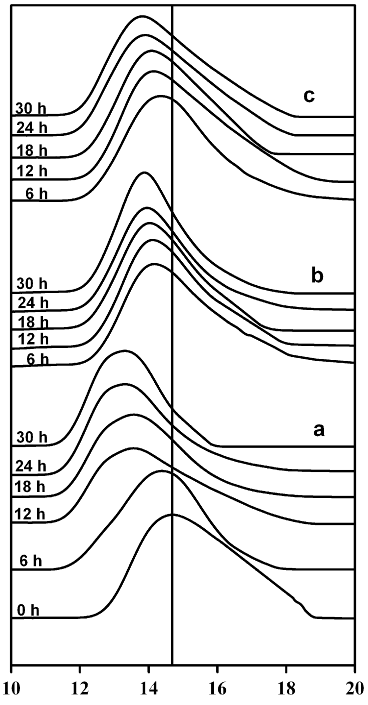


Fig. 3. GPC elution curves for the PU-*b*-PMMA with different concentrations of PUMI in DMF. (a) [PUMI] = 15 g/L, (b) [PUMI] = 30 g/L and (c) [PUMI] = 40 g/L.

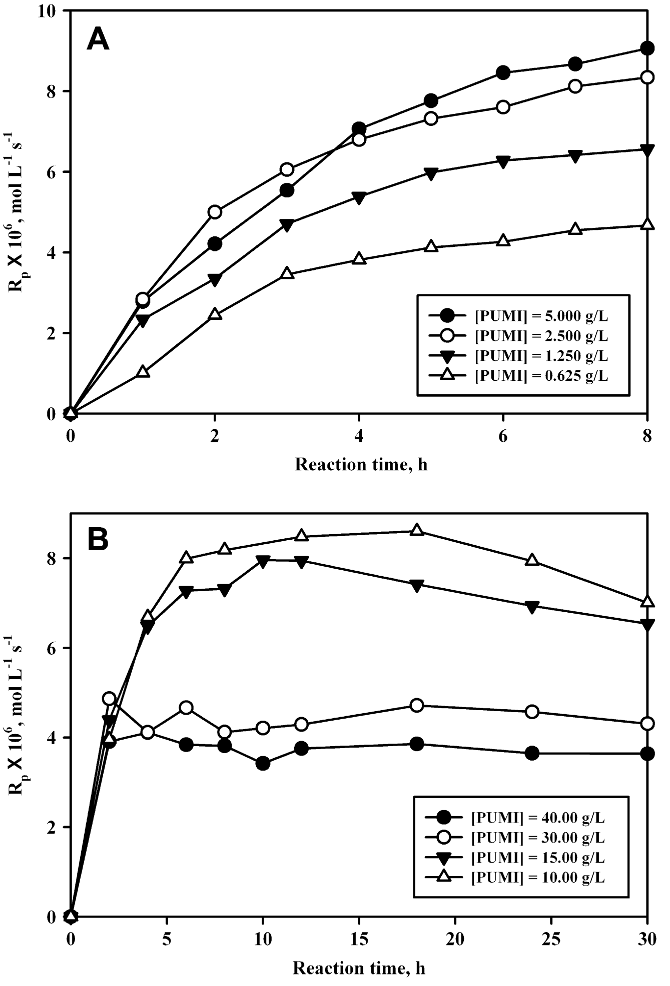


Fig. 4. Rate of polymerization versus time curves for MMA copolymerization with different PUMI concentrations in DMF. Since precipitation of the block copolymers after 8 h reaction was very difficult for PUMI concentrations below 10 g/L, kinetic data above 8 h reaction was not obtained for these concentrations.

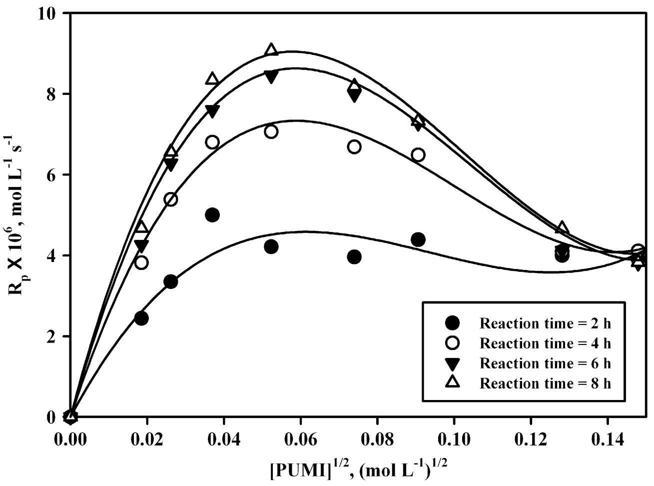


Fig. 5. Plots of rate of polymerizations as a function of PUMI concentrations for various reaction times.

polymerization [30,34]. That was the case when dithiocarbamate-terminated poly(methy1 methacrylate) was chain extended with methyl methacrylate [30] and when *n*-butyl acrylate was polymerized by *n*-butyl-2-(*N*,*N*′-diethyldithiocarbamyl)propionate [34]. Contrary to these, when dithiocarbamate-terminated poly(*n*-butyl acrylate) was chain extended with *n*-butyl acrylate, it followed a (pseudo-linear) molecular weight increase with conversion despite CS_2 evolution (see table 6 in [34]). This suggests that the extent of CS_2 evolution is highly system-dependent rather than simply the monomer choice. Despite all these possibilities, our study showed a linear molecular weight increase with conversion (Fig. 2a–c) and support the notion that the system followed a predominantly controlled manner. On a final note we should point out that the kinetics of macroiniferters are likely to be more complicated than the ideal living polymerization.

The change in the rate of copolymerization with reaction time is shown in Fig. 4. Initially lower rate of polymerization is observed due to the slow rate of initiation (refer Fig. 1). After 4 h of reaction time, the rate of polymerization appeared to plateau. For PUMI concentrations of 10 g/L and 15 g/L, the plateau is followed by a decrease in the rate of polymerization. There are three possible reasons for this: (i) For these two PUMI concentrations, high monomer conversions were observed specifically above 18 h which in turn affects the monomer concentration. Usually, for an effective iniferter, the reversible termination is always faster than the propagation and the only factor that promotes the propagation reaction is the high ratio of monomer to DTC-centered radicals. At high monomer conversion this ratio may decrease to the level where the effect of reversible termination becomes the controlling factor compared with the rates of propagation and; the rate of polymerization starts to fall. (ii) With increased conversion, the viscosity of the reaction mixture increases which may also be a considerable factor in decreasing the rate of polymerization [28]. (iii) The presence of irreversible terminations may also reduce the free radical concentrations with reaction time and hence R_p decreases. Such irreversible terminations should have contributed to increase the PDI which was not observed in our study (Fig. 2). Thus, the possibility of irreversible terminations is rare. Overall, the rates of polymerization in our study are much lower than those of conventional free radical polymerization which is consistent with controlled polymerization methods [35]. As a final point, due to the significant depletion of monomer concentration above 50% conversion, the first order kinetic seems to deviate from linearity.

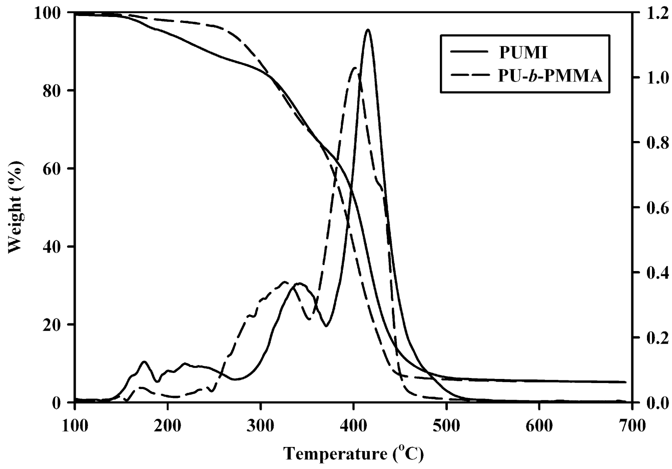


Fig. 6. TGA primary and derivative mass losses for PUMI and PU-*b*-PMMA.

The effect of PUMI concentrations on the rates of polymerization is shown in Fig. 5. The rates of polymerization initially increased with an increase of PUMI concentrations, passes through a maxima and then falls off as a function of PUMI concentrations. In this work the optimal PUMI concentration to achieve the highest R_p is 5 g/L (2.74×10^{-3} mol/L). The iniferter to monomer ratio play an important role in iniferter chemistry. At lower PUMI to monomer ratio, the rate of polymerization increases with iniferter concentration similar to the conventional radical polymerization. As the PUMI to monomer ratio increases, the concentration of transient radicals also increases which, in turn, increases the rate of reversible termination and reduces the overall rate of polymerization. Thus the rate of polymerization increases until certain critical iniferter concentration and then decreases with increasing iniferter concentration [36]. Moreover, at the optimal PUMI concentration of 5 g/L (2.74×10^{-3} mol/L), maximum conversion as well as maximum molecular weight can be obtained at a fixed reaction time. On the other hand, in conventional radical polymerization the rate of polymerization always increases linearly with square root of initiator concentration [35].

The TGA thermographs of the PUMI and PU-*b*-PMMA copolymers are presented in Fig. 6. Conventional polyurethanes are known to degrade in two stages that are related to the soft and hard segments degradations [37]. Fig. 6 shows that the PUMI and PU-*b*-PMMA degraded in three distinctive stages. The first degradation stage is related to the decomposition and release of CS_2, whereas the second and third stage degradations are related to the hard and soft segment decompositions respectively. PU-*b*-PMMA showed higher thermal stability than the PUMI especially in the early stages of the degradation.

4. Conclusions

Several PU-*b*-PMMA copolymers were prepared using a macroiniferter technique which followed the controlled radical polymerization with first order kinetics. The linear increase in molecular weight and conversion with reaction time supported that the DC-derived PUMI is an effective photo-macroiniferter. Thus, the ratio of the block lengths of PU/PMMA can be easily controlled by selecting the molecular weight of PTMO in PUMI synthesis and by monomer conversion in the PU-*b*-PMMA synthesis. The dome shape curves of the rates of polymerization versus square roots of PUMI concentrations showed a typical controlled polymerization system. The three stage thermal degradations of both PUMI and PU-*b*-PMMA were related to the CS_2

release, hard segment and soft segment degradations respectively. The studied DC-derived PUMI offers a facile way for the preparation of polyurethane-based elastomeric block copolymers with tuned segmental lengths of different blocks for biomedical applications.

Acknowledgements

This work was supported by Natural Sciences and Engineering Research Council (NSERC) of Canada.

References

[1] Sebenik A. Prog Polym Sci 1998;23(5):875–917.
[2] Tong L, Shen Z, Zhang S, Li YJ, Lu GL, Huang XY. Polymer 2008;49(21):4534–40.
[3] Tsarevsky NV, Matyjaszewski K. J Polym Sci Part A Polym Chem 2006;44(17):5098–112.
[4] Moad G, Rizzardo E, Thang SH. Polymer 2008;49(5):1079–131.
[5] Sciannamea V, Jerome R, Detrembleur C. Chem Rev 2008;108(3):1104–26.
[6] Otsu TJ. J Polym Sci Part A Polym Chem 2000;38(12):2121–36.
[7] Otsu T, Yoshida M. Makromol Chem Rapid Commun 1982;3(2):127–32.
[8] Liu P. E-Polymer 2007;62:1–31.
[9] Otsu T, Matsumoto A. Adv Polymer Sci 1998;136:75–137.
[10] Otsu T, Matsunaga T, Doi T, Matsumoto A. Eur Polym J 1995;31(1):67–78.
[11] Ishizu K, Katsuhara H, Kawauchi S, Furo M. J Appl Polym Sci 2005;95(2):413–8.
[12] Ishizu K, Katsuhara H, Itoya K. J Polym Sci Part A Polym Chem 2006;44(10):3321–7.
[13] Kannurpatti AR, Lu SX, Bunker GM, Bowman CN. Macromolecules 1996;29(23):7310–5.
[14] Bhuyan PK, Kakati DK. J Appl Polym Sci 2005;98(5):2320–8.
[15] Lalevee J, El-Roz M, Allonas X, Fouassier JP. J Polym Sci Part A Polym Chem 2007;45(12):2436–42.
[16] Qin SH, Qiu KY. Polymer 2001;42(7):3033–42.
[17] Nemoto Y, Nakayama Y. J Polym Sci Part A Polym Chem 2008;46(13):4505–12.
[18] Ward JH, Bashir R, Peppas NA. J Biomed Mater Res 2001;56(3):351–60.
[19] Luo N, Hutchison JB, Anseth KS, Bowman CN. J Polym Sci Part A Polym Chem 2002;40(11):1885–91.
[20] Al-Kaabi K, van Reenen AJ. J Appl Polym Sci 2008;108(4):2528–34.
[21] Reddy SK, Sebra RP, Anseth KS, Bowman CN. J Polym Sci Part A Polym Chem 2005;43(10):2134–44.
[22] Patel A, Mequanint K. J Polym Sci Part A Polym Chem 2008;46(18):6272–84.
[23] Mequanint K, Patel A, Bezuidenhout D. Biomacromolecules 2006;7(3):883–91.
[24] Patel A, Mequanint K. Macromol Biosci 2007;7(5):727–37.
[25] Tharanikkarasu K, Radhakrishnan G. Eur Polym J 1997;33(10–12):1779–86.
[26] Cakmak I. Eur Polym J 1998;34(10):1561–3.
[27] Nair CPR, Clouet G, Brossas J. J Macromol Sci Chem 1988;A25(9):1089–126.
[28] Nair CPR, Clouet G. Macromolecules 1990;23(5):1361–9.
[29] Ishizu K, Katsuhara H, Itoya K. J Polym Sci Part A Polym Chem 2005;43(1):230–3.
[30] Turner SR, Blevins RW. Macromolecules 1990;23(6):1856–9.
[31] Otsu T, Kuriyama A. Polym Bull 1984;11(2):135–42.
[32] Otsu T, Kuriyama A. Polym J 1985;17(1):97–104.
[33] Manga JD, Polton A, Tardi M, Sigwalt P. Polym Int 1998;45(1):14–21.
[34] Manga JD, Tardi M, Polton A, Sigwalt P. Polym Int 1998;45(3):243–54.
[35] Odian J. Principles of polymerization. 4th ed. New York: John Wiley & Sons; 2004 [chapter 3].
[36] Kongkaew A, Wootthikanokkhan J. Polym Bull 1999;43(4–5):327–32.
[37] Bajsic EG, Rek V, Agic A. J Elast Plast 2003;35(4):311–23.