



**Confined polymerisation of bis-thyminyll monomers within
nanoreactors: Towards molecular weight control**

Journal:	<i>Polymer Chemistry</i>
Manuscript ID	PY-ART-04-2020-000523.R1
Article Type:	Paper
Date Submitted by the Author:	01-Jun-2020
Complete List of Authors:	Alqarni, Yanallah; Monash University, Centre for Green Chemistry; Imam Abdulrahman Bin Faisal University, Department of Basic Sciences Ishizuka, Fumi; The University of New South Wales, School of Chemical Engineering Bell, Toby; Monash University, School of Chemistry Tabor, Rico; Monash University, School of Chemistry Zetterlund, Per; The University of New South Wales, School of Chemical Engineering Saito, Kei; Monash University, Centre for Green Chemistry



Journal Name

ARTICLE

Confined polymerisation of bis-thymynyl monomers within nanoreactors: Towards molecular weight control

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Yanallah Alqarni^{a,b}, Fumi Ishizuka^c, Toby D.M. Bell^a, Rico F. Tabor^a, Per B. Zetterlund^c and Kei Saito^{*a}

This paper reports the molecular weight control of polymers from bis-thymynyl monomers via confined photo-polymerisation inside different sized nanoreactors. Bis-thymynyl monomers were hosted inside nanoreactors (oil-in-water microemulsion, water-in-oil microemulsion, and miniemulsion) and topochemically polymerised using UV-light. UV-VIS and NMR spectroscopy and gel permeation chromatography (GPC) were used to confirm polymer formation and the molecular weight of formed polymers. The molecular weight of the formed polymer could be increased by increasing the diameter of the nanoreactors, which demonstrates that it is possible to control polymer molecular weight by modifying the nanoscopic reaction vessel size. This confined polymerisation provides polymers with a narrow molecular weight distribution when compared with conventional topochemical polymerisation.

Introduction

Polymer molecular weight is a vital characteristic, as many properties of polymers are controlled by molecular weight, including physical, thermal and mechanical properties.¹⁻⁶ Researchers have for many decades sought different techniques to control the molecular weight and molecular weight distribution (MWD) of polymers to achieve desired properties.⁷⁻⁹ Reversible deactivation radical polymerisation (RDRP) has in the past twenty years revolutionized the ability to control the molecular weight and MWD of addition polymers formed via radical polymerisation.^{10, 11} The concept of controlling the molecular weight and MWD by confining the polymerisation to a nanodimensional confined space has also been explored, e.g. the use of mesoporous silica and metal-organic frameworks (MOFs) as nanoreactors. Multiple studies have reported advantageous features of polymerisation within such confined spaces, e.g. minimisation of side reactions and enhancement of reaction rates.¹²⁻¹⁸ Several studies have explored the effects of RDRP inside mesoporous silica on polymer molecular weight control.¹⁹⁻²² For example, Blas *et al.* used nitroxide-mediated polymerisation (NMP), which is a type of RDRP, to polymerise styrene on the inner and outer surfaces of mesoporous silica.²³ Their results showed that the polymer molecular weight was affected by the structure and size of the mesoporous silica porous. It is well-known that the progression of a radical polymerisation, including RDRP, can be strongly influenced by

use of the nanoreactor concept, perhaps most significantly by reducing the rate of bimolecular termination reactions.²⁴⁻²⁷

MOFs, also known as porous coordination polymers (PCPs), have been used as nanoreactors in some polymerisations. Although common applications of MOFs include gas storage, separation and purification,^{28, 29} several researchers have revealed that MOFs can also be used to control the molecular weights of some polymers, as well as other properties. For example, radical polymerisation of styrene in different MOF structures showed that MOFs are capable of controlling the molecular weight of polystyrene.³⁰ Additionally, Uemura's group reported several studies about the advantages of using MOFs in polymerisation.³¹⁻³⁵ Comotti and co-workers prepared polyacrylonitrile with high molecular weight using porous organic cages as nanoreactors for polymerisation.³⁶ Porous dipeptide crystals have also been used as nanoreactors.³⁷ Polymerisations of acrylic and diene monomers within one-dimensional nanochannels in dipeptide crystals were conducted utilizing gamma-ray irradiation. This method resulted in high molecular weight polymers. Recently, Tarnacka *et al.* reported on the advantages of using nanoporous aluminium oxide membranes as nanoreactors in ring-opening polymerisation (ROP) of ϵ -caprolactone.³⁸ The obtained molecular weight had moderate dispersity (less than 1.41) and was extremely high compared with the molecular weight that resulted from ROP under conventional macroscale conditions.

Polymerisation in microemulsions, where nanodimensional micelles/particles provide a nanoreactor environment, has also revealed the ability to produce polymers with high molecular weight.³⁹⁻⁴⁹ As mentioned above, there are numerous examples of successful synthesis of polymers with high molecular weight in confined space. However, there are very

^a School of Chemistry, Monash University, Clayton, Victoria 3800, Australia.

^b Department of Basic Sciences, Imam Abdulrahman Bin Faisal University, Dammam 34212, Saudi Arabia.

^c Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, The University of New South Wales, Sydney, New South Wales 2052, Australia.

few examples of controlling the molecular weight of polymers in confined spaces using light without initiators or additives. In addition, most polymerisations conducted within confined spaces fall in the category of addition polymerisation.

In the present study, we aim to control the polymer molecular weight via a facile method based on confining the monomer inside nanoreactors, and subsequently conducting topochemical polymerisation using UV irradiation (Figure 1). Topochemical polymerisation is a monomer crystal to polymer crystal transformation utilising a stimulus, and is a green way of polymer synthesis in a solvent-free environment without the need for an initiator or other chemicals.^{50, 51} The present study focuses on polymerisation of bis-thymine monomer, which undergoes topochemical polymerisation via $[2\pi + 2\pi]$ -cycloaddition of thymine units.⁵² Our previous study⁵² revealed that bis-thymine monomer fulfils the criteria of Schmidt's topochemical postulates,⁵³ where the reactive C=C bond separation distance is 4.2 Å and monomers stack into tight offset layers and align parallel to one another in the crystal.⁵⁴ A single crystal contains several layers of monomer which in turn form several polymer chains. As this is a crystalline solid state polymerisation, the polymer molecular weight should be controlled by the size of the crystal such that a larger crystal leads to higher molecular weight as the length of the monomer layers are fixed by the size of the crystal. The molecular weight of the formed polymer depends mainly on the length of the monomer layer, not the monomer conversion. In this study, we have used microemulsion and miniemulsion systems to create equal size crystals of monomers which leads to equal molecular weight polymer chains in larger quantities.

The hypothesis here is that if the amount of monomer within similar size nanoreactors can be controlled and if a single crystal from all the monomers in each nanoreactor is converted into polymer chains of equal length, the molecular weight and the MWD of the formed polymer can be controlled. Hypothetically, each nanoreactor can form one crystal which consists of stacked layers of monomer units. Each layer within the crystal can form a polymer chain after irradiation and the length of the layer is fixed by the size of the crystal, which in turn means the single crystal can produce several polymer chains in equal length as depicted schematically in Figure 1.

Bis-thymine monomer units should be in appropriate alignment and exist as fixed layers to proceed and form the oligomers and polymers via topochemical polymerisation inside the nanoreactor. In this case, the nanoreactor diameter is expected to be a more valid indicator of the number of monomer units per nanoreactor as the monomer molecules will not occupy the entire available volume inside the nanoreactor.

In this study, we use globular microemulsions and miniemulsion as nanoreactors to perform topochemical polymerisation. Topochemical polymerisation inside nanoreactors is implemented after evaporating the solvent, i.e. precipitating the monomers, thus allowing the monomers to form the fixed crystalline monomer layer within the

nanoreactor. This fixed crystalline monomer layer is transformed into a polymer chain after UV irradiation. Microemulsions consist of two immiscible liquid phases (one of which is usually water) and a surfactant that reduces the interfacial tension between the liquid phases to an ultra-low value. One of the liquid phases (the dispersed phase) is dispersed in the other (the continuous phase) as droplets, stabilized by interfacial adsorption of surfactants with or without co-surfactant.^{55, 56} Microemulsions were chosen due to several appealing features, including their thermodynamic stability, optical transparency, small droplet size and thus large overall internal interfacial area.⁵⁷ Moreover, microemulsion preparation does not require multiple steps or high energy. The effect of nanoreactor size was also explored by use of Shirasu porous glass (SPG) membrane emulsification to generate somewhat larger nanosized droplets.⁵⁸

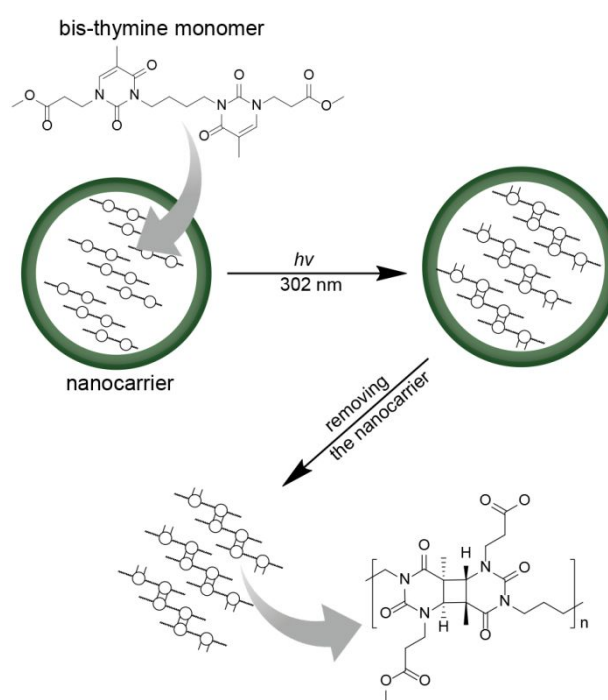


Fig. 1 Schematic representation of polymerisation inside nanoreactors.

Experimental section

Materials

Thymine, methyl acrylate, 1,4-diiodobutane, Triton X-100 (TX-100), poly(ethylene glycol) p-(1,1,3,3-tetramethylbutyl)-phenyl ether where the average ethoxylation number = 9.5), hexadecane, hexadecyltrimethylammonium bromide (CTAB), pentanol and sodium dodecyl sulphate (SDS) were purchased from Sigma–Aldrich Castle Hill, NSW, Australia. Triethylamine (Et₃N), potassium carbonate (K₂CO₃), anhydrous magnesium sulfate (MgSO₄), anhydrous dimethylformamide (DMF), ethanol, hexane, chloroform and deuterium oxide D₂O were obtained from Merck. Reagents of the highest purity were purchased and used without further purification.

Synthesis of bis-thyminyl monomer

The bis-thyminyl monomer was prepared according to the procedure described in our previous report⁵² and obtained as white solid in 67% yield. Mp: 190.1–192.2 °C. ¹H-NMR (400 MHz, CDCl₃): δ 1.68–1.71 (m, 4H), 1.91 (d, *J* = 1.2 Hz, 6H), 2.78 (t, *J* = 6.1 Hz, 4H), 3.71 (s, 6H), 3.97 (t, *J* = 6.1 Hz, 8H), 7.15 (d, *J* = 1.2 Hz, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 12.9, 25.3, 32.9, 41.1, 45.8, 52.0, 109.5, 139.4, 151.6, 162.9, 170.0. Selected IR bands: 2965 m, 2869 m, 1728 s, 1700 s, 1630 s, 1451 m, 1388 m, 1357 m, 1217 s, 1198 s. MS (ESI)⁺ calcd for C₂₂H₃₀N₄O₈: *m/z* 478.5; found: *m/z* 479.5 (M+H)⁺, 501.5 (M+Na)⁺.

Preparation of oil-in-water microemulsion

The base formulation of oil-in-water (o/w) microemulsion used herein consisted of 25 mL of distilled water, 4.2 mL of Triton X-100 (a non-ionic surfactant) and 0.1 mL of chloroform (oil phase), which contained the maximum concentration of the monomer (0.1 M) in terms of monomer solubility. The microemulsion was formed by shaking the compositions vigorously in glass vials for 1 min, which were subsequently sonicated for 5 min. After sonication, the mixture changed from a cloudy to transparent mixture, indicating formation of the microemulsion.

Preparation of water-in-oil microemulsion

Water-in-oil (w/o) microemulsions were prepared using different ratios of CTAB (a cationic surfactant), distilled water, DMF containing 0.01 M monomer, pentanol (a co-surfactant) and hexane (Tables S1–S4 in Supporting Information). Water-in-oil microemulsions were combined in sealed glass vials and shaken vigorously for 1 min and then sonicated for 5 min. The microemulsions were left to equilibrate at room temperature until they formed transparent solutions.

Preparation of miniemulsion

A miniemulsion was prepared by SPG membrane emulsification using a hydrophilic membrane of pore size of 100 nm in connection with an SPG module (external pressure type micro kit) purchased from SPG Technology (Japan). SDS surfactant was dissolved in water to prepare the continuous

phase, while CHCl₃, which contained the monomer, was mixed with hexadecane to act as the dispersed phase. The dispersed phase was used in the emulsification process with a connection to SPG membrane emulsification, as represented by the schematics shown in Figure S1 in Supporting Information. After filling the dispersion phase tank with dispersed phase liquid (0.2 g of hexadecane with 4 g CHCl₃ containing 0.1 M monomer), the dispersed phase was permeated into the continuous phase (0.12 g of SDS in 40 g of H₂O) at 250 kPa. The continuous phase was agitated continuously at 160 rpm.

Droplet size measurements

Dynamic light scattering (DLS) and small-angle neutron scattering (SANS) were used to measure droplet diameters. Microemulsions were filtered through a membrane filter (0.22 μm pore size) before measurements were made. The miniemulsion was not subjected to such filtration. Average sizes and size distributions of droplets were measured via DLS at ambient temperature using a Malvern Zetasizer nano at the Melbourne Centre for Nanofabrication. SANS measurements were conducted using the QUOKKA beamline at the Australian Centre for Neutron Scattering, ANSTO, Lucas Heights, Australia, at a sample temperature of 25°C.

Polymerisation process

Polymerisations were conducted within microemulsion/miniemulsion droplets of a range of different sizes. For (o/w) microemulsions and miniemulsions, the monomer was dissolved in CHCl₃, while it was dissolved in DMF in the (w/o) microemulsions. In all cases, bis-thyminyl monomers were hosted inside the droplets, which were irradiated with an Ultraviolet Products CL1000M UV lamp (302 nm). After irradiation, an excess of either ethanol or acetone was added to the system, followed by centrifugation (4500 rpm for 30 min) at room temperature. White solids were obtained, washed several times using water, then dried in a vacuum oven at 40 °C overnight. ¹H-NMR (400 MHz, CDCl₃): δ_H 1.38 (s, 6H), 1.63 (br. s, 4H), 2.59–2.66 (m, 2H), 2.76–2.85 (m, 2H), 3.23–3.33 (m, 2H), 3.69 (s, 6H), 3.88 (br. t, 4H), 3.96 (s, 2H), 3.98–4.05 (m, 4H), ¹³C-NM (100 MHz, CDCl₃): δ_C 18.84, 25.63, 31.90, 40.74, 43.82, 45.81, 51.85, 61.98, 151.37, 171.91. Selected IR bands: 2948 m, 2865 w, 1728 s, 1696 s, 1670 s, 1511 w, 1467 s, 1435 s, 1390 s, 1370 s, 1282 m, 1202 s, 1157 m, 1106 m, 985 m, 841 m, 762 m.

Molecular weight determination

The number average molecular weight (*M_n*) and dispersity of the MWD (*D*) of the polymer was determined using gel permeation chromatography (GPC) equipped with a refractive index detector and ultraviolet (UV) detector (λ = 280 nm) using Tosoh alpha 4000 and 2000 columns. Calibration curves were obtained using polystyrene standards ranging between *M_n* 500 - 2.11 × 10⁶ g·mol⁻¹. DMF containing 10 mM LiBr was used as the eluent with a flow rate of 1.0 mL per min⁻¹.

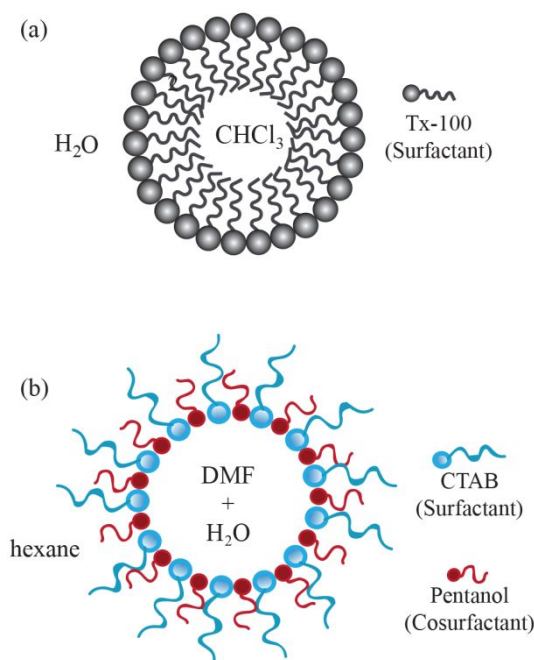


Fig. 2 (a) Oil-in-water microemulsion, where the oil phase (CHCl_3) contains 0.1 M monomer. (b) Water-in-oil microemulsion, where the dispersed aqueous phase is a mixture of water and DMF containing 0.01 M monomer.

Atomic force microscopy

The morphology of the polymer was characterized using atomic force microscopy (AFM) using alternating contact (AC) mode on a JPK Nanowizard 3 AFM, employing Bruker NCHV cantilevers (nominal spring constant 40 N/m, resonant frequency 340 kHz). The untreated polymer emulsions were dried onto freshly cleaved mica discs using spin coating (2,000 rpm) before imaging.

Results and discussion

Polymerisations were conducted within nanoreactors of different size with the ultimate aim being to exercise control over the molecular weight of the polymer formed through control of the amount of monomer contained within each nanoreactor. Bis-thyminyll monomer was selected due to its ability to undergo topochemical polymerisation via UV-light. Previously, our group has reported the molecular weight of the formed polymer from bis-thyminyll monomer in the solid state (not using the concept of nanoreactors) as 19,000 ($D = 4.0$).⁵² Polymerisation was conducted inside various nanoreactors using UV-light at 302 nm (12 h, 60 J.cm⁻¹).

Polymerisation in (o/w) microemulsions

The first type of nanoreactor explored comprised an oil-in-water (o/w) microemulsion (Figure 2a) using chloroform and the nonionic surfactant Triton X. Chloroform was used as the oil phase due to the high monomer solubility (monomer concentration = 0.1 M).

DLS analysis of the (o/w) microemulsion indicated that the diameter of the droplets was 5 nm prior to polymerisation. This result is in good agreement with that obtained from SANS, where a droplet diameter of 5.8 nm was previously reported.⁵⁹ The irradiation of the system was conducted after evaporating chloroform by a desiccator under vacuum. We showed that this microemulsion can only contain two bis-thyminyll monomer molecules at a monomer concentration of 0.1 M (the maximum concentration), and thus cyclic dimers would predominantly form via topochemical reaction.⁵⁹ GPC data after polymerisation revealed that the number-average molecular weight M_n of the product was 1,300 g mol⁻¹ which matches with the molecular weight of two monomer units (Table 1, entry 1). As a consequence, the microemulsion droplet size needed to be increased in order to investigate the effect of droplet size on molecular weight. The droplet size can be increased by increasing the amount of oil.^{60, 61} However, in the present case, microemulsions did not form at higher oil content. Several co-surfactants such as *n*-butanol and *n*-pentanol were explored in order to further stabilise the system, however, microemulsions did not form.

It was obvious that alternative larger nanoreactors were required to examine the effect of nanoreactor size on polymer molecular weight; these were found in the form of water in oil (w/o) microemulsions (Figure 2b), also referred to as reverse microemulsions.

Polymerisation in (w/o) microemulsions

Because of the poor solubility of the bis-thyminyll monomer in water, the monomer was dissolved in a water-miscible solvent, DMF. As monomer solubility in DMF is not as high as in chloroform, a concentration of 0.01 M was used. A reverse (w/o) microemulsion was formed using CTAB (surfactant), water, DMF, pentanol (co-surfactant) and hexane.

According to DLS measurements, the droplet diameter of this (w/o) microemulsion was 10 nm, which was nearly twice the diameter of the (o/w) microemulsion (5 nm). In the same manner used for the (o/w) microemulsion, the confined monomer inside the microemulsion was exposed to UV-light at 302 nm (12 h, 60 J.cm⁻¹). Following UV irradiation, ultraviolet-visible spectroscopy (UV-Vis) was used to examine the polymerisation. This polymerisation occurs via $[2\pi+2\pi]$ -cycloaddition, where an electron from the double bond in thymine is excited by UV-light to transfer from the ground state of the highest occupied molecular orbital (HOMO). The $[2\pi + 2\pi]$ -cycloaddition occurs when the excited-state HOMO of one thymine interacts with the lowest unoccupied molecular orbital (LUMO) of the second thymine to produce cyclobutane. Before irradiation, the olefinic double bonds in the monomer showed high absorption at 268 nm, whereas the absorption of the photo product decreased sharply at the same wavelength, as shown in Figure 3. This result indicates that the bis-thyminyll monomer underwent a $[2\pi+2\pi]$ -cycloaddition reaction to form the corresponding cyclobutene.

Table 1 Polymer molecular weight obtained from polymerisation in different types of nanoreactors

Entry	Type of nanoreactors	DLS		GPC		Number of units Theoretical ^a / experimental ^b
		Size of nanoreactors (nm)	PDI	M_n	\bar{D}	
1	(o/w) microemulsion	5	0.10	1,300	-	2/ 2
2	(w/o) microemulsion	10	0.12	2,700	1.05	4-6/ 6
3	(w/o) microemulsion	12	0.24	3,000	1.04	5-7/ 6
4	(w/o) microemulsion	18	0.31	6,000	1.98	7-11/ 12
5	(w/o) microemulsion	22	0.42	8,000	2.37	7-13/ 16
6	mini-emulsion	140	0.02	32,800	2.95	65-68/ 68

^a monomer unit before polymerisation based on the nanoreactors diameter divided by the length of monomer (2.12 nm).

^b monomer units after polymerisation based on the molecular weight of the resulting polymer (by GPC) divided by the molecular weight of monomer.

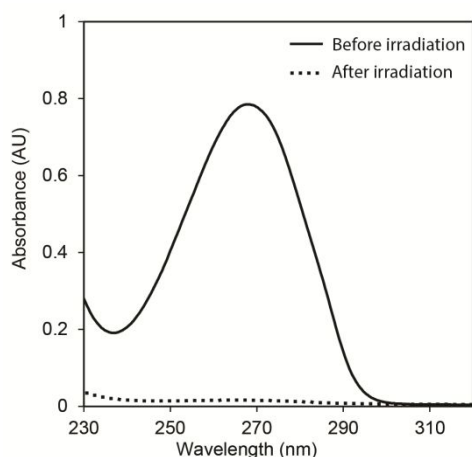


Fig. 3 UV-Vis absorption spectra of the monomers before irradiation and the polymers after irradiation

¹H NMR spectroscopy provided additional supportive evidence for the success of the polymerisation. The ¹H NMR spectrum of the monomer showed two peaks at δ 1.92 and δ 7.15 ppm which correspond to the -CH₃ and olefinic protons respectively; these peaks were absent in the photo-product spectrum. In contrast, the photo-product spectrum revealed two new peaks at δ 1.38 and δ 3.98 ppm which correspond to cyclobutane protons, indicating the success of the polymerisation.

The resulting polymer was subsequently analysed using GPC, which notably showed that the molecular weight of the polymer extracted from the (w/o) microemulsion nearly doubled compared to that obtained from the (o/w) microemulsion (Table 1, entry 1 and 2). Due to these outcomes, which imply a correlation between polymer molecular weight and microemulsion droplet diameter, different droplet diameters of microemulsions were prepared in order to further study this correlation.

One of the difficulties we encountered was in preparing microemulsions with specific diameters because of the multiple parameters that control droplet diameter within microemulsions, such as the type and concentration of surfactant, co-surfactant and oil phase, and the molar ratio of microemulsion components.⁶²

Hence, a range of (w/o) compositions were prepared utilizing different ratios of microemulsion components (Tables S1-S4 in Supporting Information). Nevertheless, the number of microemulsions produced successfully was limited, as shown in Table 2.

These microemulsions did, however, reveal a clear trend in the values of M_n that depended on the droplet diameter and the length of each monomer unit, which is 2.12 nm based on single-crystal X-ray diffraction.⁵²

The number of monomer units can be calculated by considering the overall monomer concentration in the dispersed phase and the volume of the nanoreactor, as shown in Table S5 in Supporting Information. However, the volume of nanoreactor is not a suitable tool to predict the number of monomer units, because the monomer units will not exist in all the available spaces inside the nanoreactor. As mentioned early in the introduction, bis-thymynyl monomer molecules are not free to move as individual molecules within the nanoreactor to proceed topochemical polymerisation. In fact, the success of the topochemical polymerisation relies on the appropriate alignment of the monomers inside nanoreactors and bis-thymynyl monomer molecules should be stacked into tight offset layers from one end of the space to the other within the nanoreactor.

Table 2 DLS and SANS measurements for water-in-oil microemulsions^a

CTAB (g)	Pentanol (mL)	H ₂ O (mL)	Droplet diameter (nm)	
			DLS	SANS
0.2	2	0.5	10	10.8
0.3	3	0.9	12	11.6
0.4	2	0.8	18	12.0
0.5	3	0.4	22	13.5

^a The amounts of hexane and DMF were constant (27.3 mL and 0.3 mL, respectively).

As they are in this fixed layer structure within the nanoreactor, theoretically, the diameter of nanoreactor could play an important role in determining the expected molecular weight. The number of monomer units in the nanoreactor can be

expected based on the diameter of nanoreactor and the length of the monomer unit. Hence, the number of expected monomer units in the nanoreactor, approximately, is the diameter of the nanoreactor divided by the length of monomer (2.12 nm).

For example, the nanoreactor with 5 nm diameter can include two monomer units. This can be calculated by dividing the diameter of the nanoreactor 5 nm by the length of monomer 2.12 nm = 2.35 \approx 2 units (this is the expected unit numbers that in Table 1, entry 1). The nanoreactor with 10 nm diameter will be able to host four to six monomer units and again this can be calculated by dividing the diameter of nanoreactor 10 nm by the length of monomer 2.12 nm = 4.75 \approx 5 \pm 1 units due to the PDI of nanoreactor, and so on.

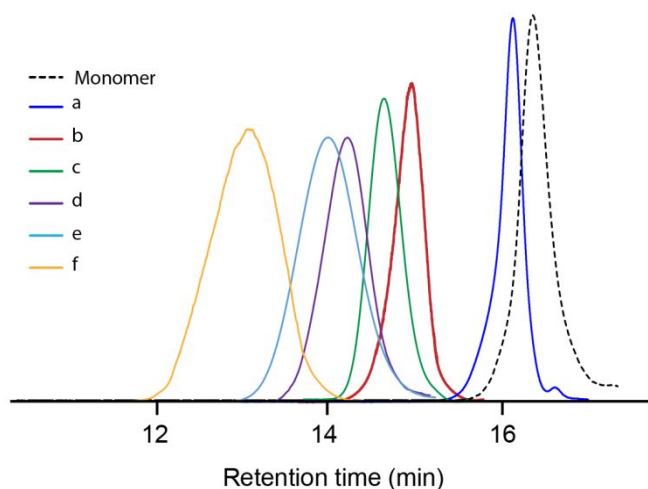


Fig. 4 Correlation GPC elution curves of polymerisation inside nanoreactors of diameter a) 5 nm, b) 10 nm, c) 12 nm, d) 18 nm, e) 22 nm, and f) 140 nm.

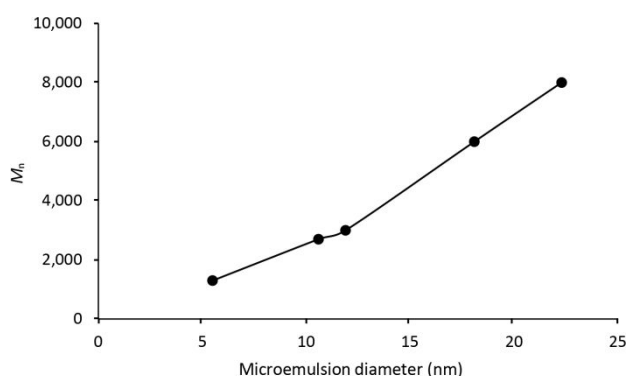


Fig. 5 Correlation between polymer molecular weight and microemulsion diameter.

Polymerization inside the droplet of diameter 10 nm gave an oligomer with $M_n = 2,700$ which is similar to the expected molecular weight of an oligomer with 6 units ($M_n = 2,874$) as shown in Table 1 (entry 2). The number of expected units in the

microemulsions increased by increasing the diameter to 8-10 for microemulsions with a diameter 18 nm ($M_n = 6,000$). A slight change in microemulsion droplet diameter was accompanied by small changes in molecular weight (Table 1, entry 2 and 3), while a noticeable increase was observed in molecular weight when droplet diameters increased from 12 nm to 18 nm. GPC data of all samples are shown in Figure 4.

These results indicate that the size of microemulsion droplets could present a means of controlling the molecular weight of the formed polymer. As illustrated in Figure 5, there is an almost linear correlation between polymer molecular weight and microemulsion droplet diameter. The molecular weight in entry 4 and 5 was slightly higher than expected, which might be attributed to the high polydispersity of the droplets (0.31 and 0.42, respectively). The DLS data on droplet diameters refer to the situation before the evaporation of chloroform. The actual diameters of the droplets might be slightly different.

The shape and dimensions of polymer that resulted from polymerisation inside (w/o) microemulsions (22 nm) was investigated using AFM. After purifying the polymer from the nanoreactors, the shape of the polymer particles was approximately spherical (Figure 6), with little evidence of any shape anisotropy. Their size (obtained from height traces of the polymer particles) was around height: 2–3 nm and width: 40–50 nm.

Photo-polymerisation in the largest diameter (22 nm) of reverse microemulsions produced a polymer with molecular weight 8,000 Da. All attempts to create (w/o) microemulsions larger than 22 nm were unsuccessful. As a consequence of this, membrane emulsification was used as an alternative approach to generate droplets with larger size.⁶³

Polymerisation in miniemulsions

An SPG membrane was chosen to produce large uniform emulsion droplets. Indeed, SPG membrane emulsification technology is simple, does not require high energy, can provide narrow pore-sized distributions, and has the ability to generate near monodisperse droplets. As can be seen in Figure S1, a positive nitrogen gas pressure pushes the dispersed phase, which contains the monomer, into the continuous phase through the SPG membrane pores (pores size is 100 nm) to prepare miniemulsions. After completion of the emulsification process (24 h), droplets were analysed using DLS.

The miniemulsion droplet diameters (140 nm) were large compared to previous microemulsions and relatively uniform (PDI = 0.026). The confined monomers in the droplets produced were irradiated in the same fashion as for previous systems. Following 12 h of irradiation, GPC data revealed a high molecular weight, M_n 32,800. This high molecular weight was expected due to the large space available for polymerisation, as compared to the smaller polymerisation spaces in the (o/w) and (w/o) microemulsions.

The increased molecular weight was accompanied by an increase in the dispersity of the MWD (Table 1). The lack of

success in keeping the MWD narrow is likely due to the difficulty of controlling the amount of monomers inside the miniemulsion droplets. More precisely, in the case of few monomers units inside small nanoreactors (for example 12 nm) all monomer units can polymerise to form equal length chains. In contrast, if the nanoreactors contain a large number of monomers, there is a possibility to form several chains with different lengths, as different groups of monomers that are not equal in number can be polymerised. An increase in the MWD after increasing the nanocarrier diameter would thereby result.

Although the nanoreactors did not effectively contribute to controlling the MWD, it was clear that the different sizes of nanoreactors did play a role in determining the molecular weight of polymer.

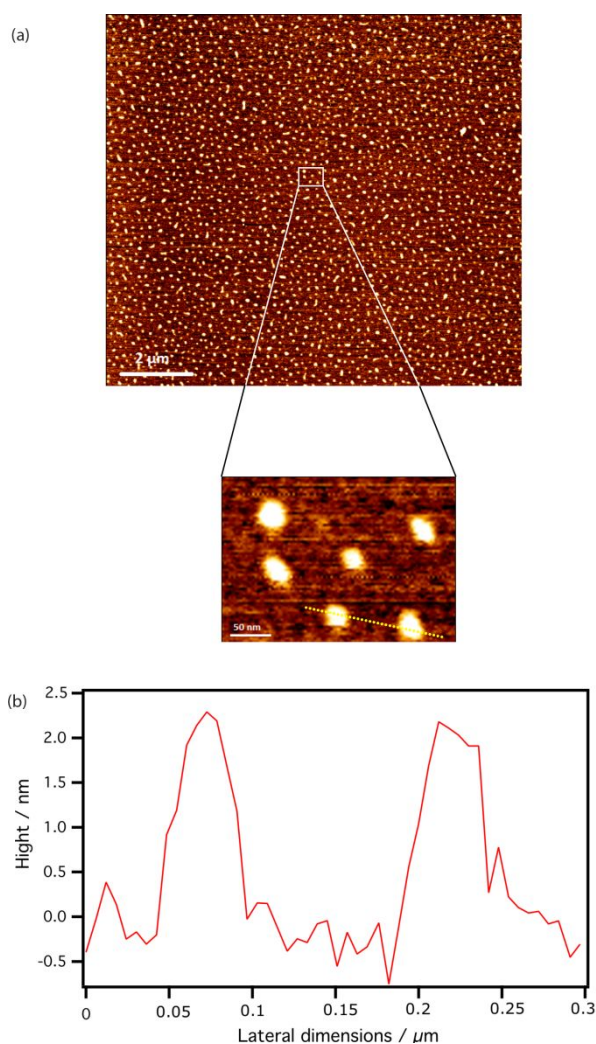


Fig. 6 AFM image of the polymer after irradiation inside nanoreactors (diameter = 22 nm, Table 1, entry 5). The height profile in (b) corresponds to the yellow dotted line in (a).

Polymerisation without nanoreactors

For the purpose of further studying the role of the nanoreactors, polymerisation was conducted in the absence of nanoreactors to examine the resulting M_n . In a separate experiment, polymerisation was carried out in the same conditions as polymerisation in (w/o) microemulsions, but without the microemulsion phase present, in order to investigate the role of droplet size in determining the molecular weight of polymer.

Figure 7a shows the GPC elution curves of the monomer and the obtained polymer from (w/o) microemulsion (with a droplet diameter of 10 nm). As a result of using microemulsions, there was one narrow peak on the GPC curves that represented the polymer. GPC measurements determined that the molecular weight of the polymer was 2,700. These results can be explained by observing the space available for polymerisation. As previously mentioned, the diameter of this microemulsion was 10 nm, which is approximately appropriate to host only 4-6 monomer units, where each unit is 2.12 nm in length.⁵²

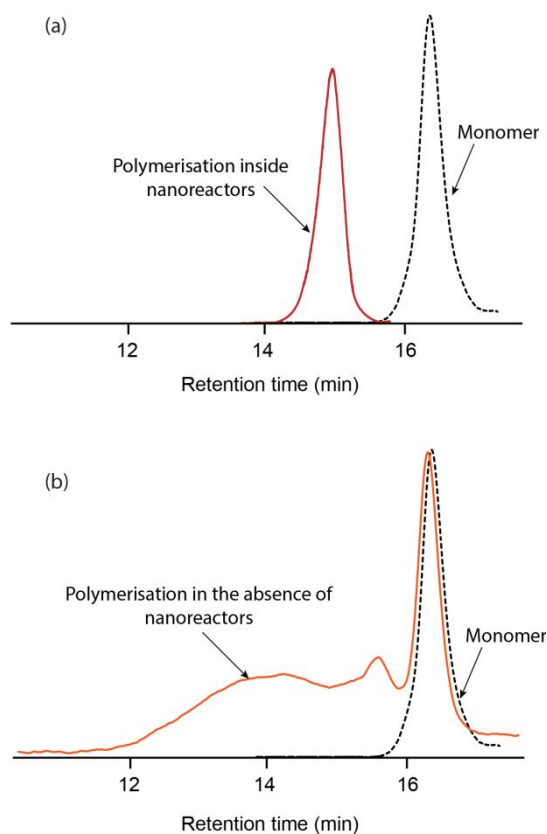


Fig. 7 GPC elution curves obtained by (a) polymerisation inside nanoreactors (diameter = 10 nm) and (b) polymerisation in the absence of nanoreactors.

In contrast, when polymerisation was conducted without a microemulsion (Figure 7b), the GPC data revealed three peaks. The broad peak represents a polymer with a molecular weight M_n of 9,000 Da ($\mathcal{D} = 2.94$), and the other two peaks reflect oligomers and some residual monomers. This increase in the molecular weight, as well as the mixture of polymer, oligomer and monomer, was due to the absence of nanoreactors, which yielded a large amount of available space for polymerisation, compared to polymerisation space available in the (w/o) microemulsion; hence polymerisation had not been controlled. In other words, in the presence of nanoreactors, monomers are confined in a specific space and this forces them to polymerise together on application of UV-light to give only a polymer. The number of monomer units can be increased by increasing droplet diameter, thus producing a polymer with higher molecular weight. In brief, the presence of nanoreactors plays an important role in controlling the molecular weight of formed polymers.

Conclusions

In summary, topochemical polymerisation reactions of bis thyminyll monomers were successfully conducted inside different nanoreactors using 302 nm UV-light irradiation. Soft template nanoreactors were used in different sizes to control the molecular weight of the polymer. Under the conditions of topochemical polymerisation, the polymer molecular weight increased as the diameters of the nanoreactors increased. In the absence of nanoreactors, polymerisation created a polymer with a high molecular weight, accompanied by some oligomers and residual monomers. This outcome reinforces the key role that nanoreactors play in determining the molecular weight of polymers from topochemical polymerisations.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

This work was supported by PRESO, JST, JPMHPR1515. We acknowledge the support of the Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation, in providing the neutron research facilities used in this work.

Notes and references

- [1] S. Cheng, A. P. Holt, H. Wang, F. Fan, V. Bocharova, H. Martin, T. Etampawala, B. T. White, T. Saito and N. G. Kang, *Phys. Rev. Lett.*, 2016, **116**, 038302.
- [2] C. Bruner and R. Dauskardt, *Macromolecules*, 2014, **47**, 1117-1121.
- [3] S. Y. Kim and C. F. Zukoski, *Macromolecules*, 2013, **46**, 6634-6643.
- [4] R. Machado and A. Bolzan, *Chem. Eng. J.*, 1998, **70**, 1-8.

- [5] L. Fetters, D. Lohse, D. Richter, T. Witten and A. Zirkel, *Macromolecules*, 1994, **27**, 4639-4647.
- [6] R. W. Nunes, J. R. Martin and J. F. Johnson, *Polym. Eng. Sci.*, 1982, **22**, 205-228.
- [7] N. Corrigan, R. Manahan, Z. T. Lew, J. Yeow, J. Xu and C. Boyer, *Macromolecules*, 2018, **51**, 4553-4563.
- [8] D. T. Gentekos, L. N. Dupuis and B. P. Fors, *J. Am. Chem. Soc.*, 2016, **138**, 1848-1851.
- [9] T. Ando, M. Kato, M. Kamigaito and M. Sawamoto, *Macromolecules*, 1996, **29**, 1070-1072.
- [10] P. B. Zetterlund, S. C. Thickett, S. Perrier, E. Bourgeat-Lami and M. Lansalot, *Chem. Rev.*, 2015, **115**, 9745-9800.
- [11] W. A. Braunecker and K. Matyjaszewski, *Prog. Polym. Sci.*, 2007, **32**, 93-146.
- [12] G. Distefano, H. Suzuki, M. Tsujimoto, S. Isoda, S. Bracco, A. Comotti, P. Sozzani, T. Uemura and S. Kitagawa, *Nat. Chem.*, 2013, **5**, 335-341.
- [13] T. Uemura, G. Washino, S. Kitagawa, H. Takahashi, A. Yoshida, K. Takeyasu, M. Takayanagi and M. Nagaoka, *J. Phys. Chem. C*, 2015, **119**, 21504-21514.
- [14] T. Kitao, S. Bracco, A. Comotti, P. Sozzani, M. Naito, S. Seki, T. Uemura and S. Kitagawa, *J. Am. Chem. Soc.*, 2015, **137**, 5231-5238.
- [15] P. Sozzani, S. Bracco, A. Comotti, R. Simonutti, P. Valsesia, Y. Sakamoto and O. Terasaki, *Nat. Mater.*, 2006, **5**, 545-551.
- [16] K. Tajima and T. Aida, *Chem. Commun.*, 2000, **0**, 2399-2412.
- [17] K. Renggli, N. Sauter, M. Rother, M. G. Nussbaumer, R. Urbani, T. Pfohl and N. Bruns, *Polym. Chem.*, 2017, **8**, 2133-2136.
- [18] B. Helms, S. J. Guillaudeu, Y. Xie, M. McMurdo, C. J. Hawker and J. M. J. Fréchet, *Angew. Chem. Int. Ed.*, 2005, **44**, 6384-6387.
- [19] M. Chen, L. Qin, Y. Wei, Y. Liu and F. Zhang, *J. Porous Mater.*, 2019, **26**, 7-17.
- [20] H. Yang, H. Pu and F. Gong, *J. Polym. Sci., Part A: Polym. Chem.*, 2016, **54**, 1508-1516.
- [21] J. Ma and H. Zhang, *J Polym Res*, 2014, **21**, 590.
- [22] M. Save, G. Granvorka, J. Bernard, B. Charleux, C. Boissière, D. Grosso and C. Sanchez, *Macromol. Rapid Commun.*, 2006, **27**, 393-398.
- [23] H. Blas, M. Save, C. Boissière, C. Sanchez and B. Charleux, *Macromolecules*, 2011, **44**, 2577-2588.
- [24] S. C. Thickett and R. G. Gilbert, *Polymer*, 2007, **48**, 6965-6991.
- [25] P. B. Zetterlund and M. Okubo, *Macromolecules*, 2006, **39**, 8959-8967.
- [26] P. B. Zetterlund, *Polym. Chem.*, 2011, **2**, 534-549.
- [27] P. B. Zetterlund and D. R. D'hooge, *Macromolecules*, 2019, **52**, 7963-7976.
- [28] S. Kitagawa, R. Kitaura and S. i. Noro, *Angew. Chem. Int. Ed.*, 2004, **43**, 2334-2375.
- [29] A. Schoedel, M. Li, D. Li, M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2016, **116**, 12466-12535.
- [30] T. Uemura, Y. Ono, K. Kitagawa and S. Kitagawa, *Macromolecules*, 2008, **41**, 87-94.
- [31] T. Uemura, *Chem. Eur. J.*, 2014, **20**, 1482-1489.
- [32] T. Uemura, N. Yanai and S. Kitagawa, *Chem. Soc. Rev.*, 2009, **38**, 1228-1236.
- [33] T. Uemura, S. Horike, K. Kitagawa, M. Mizuno, K. Endo, S. Bracco, A. Comotti, P. Sozzani, M. Nagaoka and S. Kitagawa, *J. Am. Chem. Soc.*, 2008, **130**, 6781-6788.
- [34] T. Uemura, D. Hiramatsu, Y. Kubota, M. Takata and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2007, **46**, 4987-4990.
- [35] T. Uemura, K. Kitagawa, S. Horike, T. Kawamura, S. Kitagawa, M. Mizuno and K. Endo, *Chem. Commun.*, 2005, **0**, 5968-5970.

- [36] A. Comotti, S. Bracco, M. Mauri, S. Mottadelli, T. Ben, S. Qiu and P. Sozzani, *Angew. Chem. Int. Ed.*, 2012, **51**, 10136-10140.
- [37] G. Distefano, A. Comotti, S. Bracco, M. Beretta and P. Sozzani, *Angew. Chem. Int. Ed.*, 2012, **51**, 9258-9262.
- [38] M. Tarnacka, A. Dzienia, P. Maksym, A. Talik, A. Zięba, R. Bielas, K. Kaminski and M. Paluch, *Macromolecules*, 2018, **51**, 4588-4597.
- [39] S. Tomoeda, Y. Kitayama, J. Wakamatsu, H. Minami, P. B. Zetterlund and M. Okubo, *Macromolecules*, 2011, **44**, 5599-5604.
- [40] N. M. B. Smeets, R. W. K. Lam, R. P. Moraes and T. F. L. McKenna, *Polym. Chem.*, 2012, **3**, 514-524.
- [41] S. Liu, K. D. Hermanson and E. W. Kaler, *Macromolecules*, 2006, **39**, 4345-4350.
- [42] K. D. Hermanson and E. W. Kaler, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 5253-5261.
- [43] M. Nomura and K. Suzuki, *Macromol. Chem. Phys.*, 1997, **198**, 3025-3039.
- [44] D. C. Steytler, A. Gurgel, R. Ohly, M. Jung and R. K. Heenan, *Langmuir*, 2004, **20**, 3509-3512.
- [45] J. Wakamatsu, M. Kawasaki, P. B. Zetterlund and M. Okubo, *Macromol. Rapid Commun.*, 2007, **28**, 2346-2353.
- [46] Y. Kagawa, M. Kawasaki, P. B. Zetterlund, H. Minami and M. Okubo, *Macromol. Rapid Commun.*, 2007, **28**, 2354-2360.
- [47] P. B. Zetterlund, J. Wakamatsu and M. Okubo, *Macromolecules*, 2009, **42**, 6944-6952.
- [48] K. D. Hermanson, S. Liu and E. W. Kaler, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 6055-6070.
- [49] Y. Kitayama, S. Tomoeda and M. Okubo, *Macromolecules*, 2012, **45**, 7884-7889.
- [50] K. Biradha and R. Santra, *Chem. Soc. Rev.*, 2013, **42**, 950-967.
- [51] K. Tanaka and F. Toda, *Chem. Rev.*, 2000, **100**, 1025-1074.
- [52] P. Johnston, C. Braybrook and K. Saito, *Chem.Sci.*, 2012, **3**, 2301-2306.
- [53] G. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647-678.
- [54] A. Udagawa, P. Johnston, A. Sakon, R. Toyoshima, H. Uekusa, H. Koshima, K. Saito and T. Asahi, *RSC Advances*, 2016, **6**, 107317-107322.
- [55] M. Fanun, *Microemulsions: properties and applications*, Taylor & Francis Inc, United States, 2008.
- [56] C. Stubenrauch, *Microemulsions: background, new concepts, applications, perspectives*, John Wiley and Sons Ltd, United Kingdom, 2009.
- [57] F. Grasset, R. Marchand, A. M. Marie, D. Fauchadour and F. Fajardie, *J. Colloid Interface Sci.*, 2006, **299**, 726-732.
- [58] N. Nauman, N. Zaquen, T. Junkers, C. Boyer and P. B. Zetterlund, *Macromolecules*, 2019, **52**, 4492-4499.
- [59] Y. Alqarni, T. D. M. Bell, R. F. Tabor and K. Saito, *J. Org. Chem.*, 2019, **84**, 8596-8601.
- [60] D. Han, H. Yang, C. Shen, X. Zhou and F. Wang, *Powder Technol.*, 2004, **147**, 113-116.
- [61] S. Qiu, J. Dong and G. Chen, *J. Colloid Interface Sci.*, 1999, **216**, 230-234.
- [62] J. N. Solanki and Z. V. P. Murthy, *Ind. Eng. Chem. Res.*, 2011, **50**, 12311-12323.
- [63] S. M. Joscelyne and G. Tragardh, *J. Memb. Sci.*, 2000, **169**, 107-117.

Table of Contents Graphic

Controlling polymer molecular weight by topochemical polymerisation inside nanoreactors

