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Nitroxide-functional polymers have garnered considerable interest in recent years and appear to hold promise for energy storage applications. However, their synthesis can be both expensive and time-consuming. Here, we propose a highly convenient method for the preparation of TEMPO-functional diblock copolymer nanoparticles directly in water. Epoxy-functional diblock copolymer worms are synthesized from a single monomer, glycidyl methacrylate (GlyMA), using a three-step, one-pot protocol in aqueous solution via polymerization-induced self-assembly (PISA). First, an initial aqueous emulsion of GlyMA was heated at 85 °C for 9 h to afford an aqueous solution of glycerol monomethacrylate (GMA). Then reversible addition-fragmentation chain transfer (RAFT) polymerization of GMA was conducted in aqueous solution using a dicarboxylic acid-based RAFT agent to produce a water-soluble PGMA homopolymer. Finally, chain extension of this pre-cursor block via RAFT aqueous emulsion polymerization of GlyMA at 50 °C produced amphiphilic diblock copolymer chains that self-assembled in situ to form a 15% w/w aqueous dispersion of diblock copolymer worms. These worms can be derivatized directly using 4-amino-TEMPO in aqueous solution, affording novel crosslinked anisotropic nanoparticles that contain a relatively high density of stable nitroxide radicals for potential charge storage applications.

Introduction

Non-conjugated redox-active organic radical polymers have recently gained considerable interest owing to their potential applications for energy storage and conversion.[1-4] In particular, the stable free radical species 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) has been widely investigated since the first TEMPO-based active electrode material reported by Nakahara *et al.* in 2002.[5] TEMPO-functional polymers can be prepared by (i) polymerization of a nitroxide precursor, (ii) direct polymerization of a nitroxide-functional monomer, or (iii) post-polymerization derivatization.[2, 6-7] Zhang *et al.* compared the conductivities of poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) prepared by various synthetic routes and showed that varying the preparation conditions did not affect the radical yield or conductivities.[8] Recently, Joo *et al.* reported an organic radical polymer exhibiting a remarkably high conductivity (20 S m^{-1}) when prepared as a thin film, which is comparable to values reported for semiconducting conjugated polymers.[6] This enhanced conductivity was postulated to be the result of a self-organized percolating structure. If this hypothesis is correct, then in principle highly anisotropic worm-like particles comprising stable free radicals may offer an important advantage for the design of an electrically conductive network at a relatively low volume fraction of active material.[9-10]

Polymerization-induced self-assembly (PISA) can be used to prepare diblock copolymer nanoparticles directly at much higher concentrations[11-12] than typical post-polymerization processing routes.[13-15] PISA involves the chain extension of a soluble homopolymer using a suitable second monomer. As this second block grows, it becomes insoluble in the reaction solution, thereby driving in situ self-assembly to form diblock copolymer nano-objects.[11-12, 16-17] In particular, reversible addition-fragmentation chain transfer (RAFT) dispersion polymerization has been utilized to prepare various examples of diblock copolymer worms in aqueous, alcoholic or non-polar media.[11-12, 18] In contrast, RAFT aqueous emulsion polymerization is very often limited to kinetically-trapped spheres. Exceptionally, Charleux and co-workers reported the synthesis of diblock copolymer worms via RAFT aqueous emulsion polymerization in 2010.[19] In this case, a water-soluble statistical copolymer precursor comprising poly(ethylene glycol) methyl ether acrylate (PEGA) and acrylic acid (AA) was chain-extended with styrene.[19-20] Well-defined worms were also obtained using a closely-related methacrylate-based stabilizer block.[21-23] More recently, D'Agosto and co-workers showed that statistical copolymerization of a relatively small amount of PEGA with N-acryloylmorpholine (NAM) also resulted in the formation of polystyrene-core worms under certain conditions.[24] There are also a few other reports of the synthesis of diblock copolymer worms by RAFT aqueous emulsion polymerization, but these routes typically require small quantities of either a surfactant or a plasticizer to access the worm morphology.[25-28] Unfortunately, efficient removal of such processing additives is

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essential prior to any potential applications, particularly in the context of biomaterials.

Recently, we reported that chain extension of a poly(methacrylic acid) stabilizer using 4-hydroxybutyl methacrylate (HBMA) via RAFT aqueous emulsion polymerization produced unusual 'monkey nut' nanoparticles.[29] This non-spherical morphology was attributed to the relatively high aqueous solubility of the HBMA monomer (20 g dm^{-3} at 70 °C). Subsequently, we investigated the RAFT aqueous emulsion polymerization of glycidyl methacrylate (GlyMA) at 50 °C, which has comparable aqueous solubility at this temperature. However, only kinetically-trapped spheres could be obtained when using a poly(glycerol monomethacrylate) (PGMA) steric stabilizer with a mean degree of polymerization (DP) of 45.[30] According to Blanazs *et al.*, a shorter PGMA stabilizer block should confer weaker steric stabilization, which should in turn lead to the formation of worms or vesicles rather than spheres.[31] This hypothesis is examined herein for the rational preparation of TEMPO-functional diblock copolymer worms, with high local concentrations of nitroxide groups within the worm cores.

Experimental

Materials

Glycerol monomethacrylate (GMA; >99%) was donated by GEO Specialty Chemicals (Hythe, UK) and was used without further purification. 4-((({2-(Carboxyethyl)thio)carbonothioyl)thio)-4-cyano-pentanoic acid (CECPA; 95%) was donated by Boron Molecular (Melbourne, Australia). Glycidyl methacrylate (GlyMA; 97%), 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-amino-TEMPO, 97%) and hydrochloric acid (HCl; 37%) were each purchased from Sigma-Aldrich UK and used as received. VA-044 (VA-044; ≥97%) was purchased from Wako Chemicals GmBH. Dimethyl sulfoxide-d_6 and CD_3OD were purchased from Goss Scientific Instruments Ltd. (Cheshire, UK). All other solvents were purchased from Fisher Scientific (Loughborough, UK) and used as received. Deionized water was used for all experiments. Biotech Cellulose Ester Dialysis Tubing was purchased from Spectrum Laboratories Inc. (USA) with a molecular weight cut off (MWCO) of 50 kDa.

Characterization

^{1}H NMR spectroscopy. ^{1}H NMR spectra were recorded at room temperature using a Bruker Avance III HD 400 MHz spectrometer using either CD_3OD or d_6-DMSO.

Solution state electron paramagnetic resonance (EPR) measurement was made at room temperature using a Bruker cw-ESR EMX spectrometer with an X-Band bridge. Solutions were prepared in DI water and diluted to 1 mM.

Dynamic light scattering (DLS). A Malvern Zetasizer NanoZS instrument was used to determine z-average diameters (D_z) and polydispersities (PDI) by DLS utilizing the cumulants method. All measurements were made on 0.1 % copolymer dispersions prepared using either deionized water and disposable plastic cuvettes, or DMF and glass cuvettes. All data were averaged over three consecutive runs.

Gel permeation chromatography (GPC). Copolymer molecular weights, M_n and M_w, and molecular weight distributions ($Đ$) were assessed using a GPC set-up comprising two Agilent PL gel 5 µm Mixed-C columns and a guard column connected in series to an Agilent 1260 Infinity GPC system equipped with both refractive index and UV–visible detectors (309 nm) operating at 60 °C. The GPC eluent was HPLC-grade DMF containing 10 mM LiBr at a flow rate of 1.0 mL min^{-1}. DMSO was used as a flow-rate marker. Calibration was achieved using a series of ten near-monodisperse poly(methyl methacrylate) standards (ranging in M_p from 625 to 618 000 g mol^{-1}). Chromatograms were analyzed using Agilent GPC/SEC software.

Transmission electron microscopy (TEM). Copper/palladium TEM grids (Agar Scientific, UK) were coated in-house to yield a thin film of amorphous carbon. The grids were subjected to a glow discharge for 30 s. The aqueous copolymer samples (10.0 µL, 0.1% solids) were subsequently placed onto freshly-treated grids for 20 s and then carefully blotted with filter paper to remove excess solution. To ensure sufficient electron contrast, uranyl formate (10.0 µL of a 0.75% w/w solution) was placed onto the sample-loaded grid for 20 s and then carefully blotted to remove excess stain. Each grid was then dried using a vacuum hose. Imaging was performed using a FEI Tecnai Spirit 2 microscope operating at 80 kV and equipped with an Orius SC1000B camera. The mean worm thickness was determined by analyzing more than 100 worms using ImageJ software.

Rheology. An AR-G2 rheometer equipped with a variable temperature Peltier plate and a 40 mL 2° aluminium cone was used for all experiments. Percentage strain sweeps were conducted at 25 °C using a fixed angular frequency of 1.0 rad s^{-1}. Angular frequency sweeps were conducted at 25 °C using a constant percentage strain of 1.0 %.

FT-IR spectroscopy. Spectra were recorded for freeze-dried copolymers at 20 °C (256 scans accumulated per spectrum) using a Thermo-Scientific Nicolet IS10 FT-IR spectrometer equipped with a Golden Gate Diamond ATR accessory.

Small angle X-ray scattering. SAXS patterns were collected at a synchrotron source (ESRF, station ID02, Grenoble, France) using monochromatic X-ray radiation (wavelength λ = 0.0995 nm, with q ranging from 0.0003 to 0.25 $Å^{-1}$, where $q = 4\pi \sin\theta/\lambda$ is the length of the scattering vector and θ is one-half of the scattering angle) and a Ravonix MX-170HS CCD detector. A flow-through capillary set-up was used as the sample holder, with a glass capillary (ø = 2 mm). Scattering data were reduced using standard routines available from the beamline and were further analyzed using Irena SAS macros for Igor Pro.[1] Water was used for the absolute intensity calibration. Measurements were conducted on a 1.0% w/w aqueous dispersion of $PGMA_{25}$-$PGlyMA_{45}$ diblock copolymer worms at a solution pH of 3.0.

Synthesis of glycerol monomethacrylate (GMA) from glycidyl methacrylate (GlyMA)

As previously described,[2] glycidyl methacrylate (5.00 g, 35.2 mmol) and deionized water (45.0 g, 2.50 mol, 10% w/w solution, pH ~6) were added to a round-bottomed flask, equipped with a magnetic flea and a condenser. The initial aqueous emulsion was stirred for 9 h at 85 °C in an oil bath and eventually became a homogeneous aqueous solution (pH ~5), with more than 98% conversion to glycerol monomethacrylate as judged by ^{1}H NMR. Conversion of GlyMA (142 g mol^{-1}) into GMA (160 g mol^{-1}) requires the addition of one mole of H_2O. This increase in monomer molecular weight means that the final aqueous solution contained 11.2% w/w GMA.

$PGMA_{25}$ macro-CTA synthesis

CECPA (0.264 g, 0.86 mmol) was added to 25.0 g of an 11.2% w/w aqueous solution of GMA (2.75 g, 17.2 mmol GMA) and heated to 50 °C in an oil bath for a few minutes to ensure complete dissolution. After cooling, VA-044 (69.4 mg, 0.21 mmol) was added and the solution pH was adjusted to pH 2.5-3.0 prior to degassing this reaction mixture via N_2 purge at 20 °C for 30 min. The degassed

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reaction mixture was then heated to 50 °C for 3 h, after which a small aliquot was removed for ^{1}H NMR spectroscopy studies in CD_3OD and GPC analysis in DMF. The resulting PGMA macro-CTA was either stored as a stock solution for scoping experiments, or chain-extended *in situ* for the one-pot syntheses. In one experiment, the PGMA macro-CTA was precipitated from water into diethyl ether three times prior to end-group analysis to determine its mean degree of polymerization using ^{1}H NMR spectroscopy.

Chain extension of $PGMA_{25}$ by RAFT aqueous emulsion polymerization of GlyMA

In a typical experiment targeting a mean PGlyMA DP of 45 at 15% w/w, 1.50 g of a 12.7% w/w stock solution of $PGMA_{25}$ macro-CTA (0.18 g $PGMA_{25}$, 0.042 mmol), GlyMA (0.268 g, 1.88 mmol) and VA-044 (3.40 mg, 0.011 mmol) were added along with acidified water (1.22 g) to maintain the solution pH between 2.5 and 3.0. This reaction mixture was degassed via N_2 purge in an ice bath for 30 min, then heated to 50 °C in an oil bath for 1 h. The final GlyMA conversion for the $PGMA_{25}$-$PGlyMA_{45}$ diblock copolymer was determined by ^{1}H NMR spectroscopy in d_6-DMSO and its molecular weight distribution was assessed by DMF GPC analysis.

One-pot synthesis of $PGMA_{25}$-$PGlyMA_{45}$ diblock copolymer worms starting from GlyMA

GlyMA (2.0 g, 14.1 mmol) and water (18.0 g, 1.0 mol, 10% w/w GlyMA aqueous emulsion) were added to a round-bottomed flask equipped with a magnetic flea and a condenser. The initial aqueous emulsion was stirred for 9 h at 85 °C in an oil bath and eventually became a homogeneous aqueous solution, with 98% conversion to GMA as judged by ^{1}H NMR spectroscopy. After the reaction mixture had cooled to 50 °C, CECPA (0.215 g, 0.70 mmol) was added directly to the reaction vessel and stirred at 50 °C for 2-3 min until complete dissolution had occurred. On cooling to 20 °C VA-044 (57 mg, 0.17 mmol) was added to the reaction mixture, which was degassed via N_2 purge for 30 min at the same temperature. The degassed reaction mixture was then heated to 50 °C in an oil bath for 3 h, after which a small aliquot of sample was removed for analysis by ^{1}H NMR spectroscopy in CD_3OD and DMF GPC. Previously degassed acidified water (15.4 mL, pH 3) and GlyMA (3.61 mL, 26.4 mmol) were added via syringe under N_2 to afford a 15% w/w aqueous emulsion, which was heated at 50 °C for a further 1 h. The final $PGMA_{25}$-$PGlyMA_{45}$ diblock copolymer worms formed a physical gel which was analyzed by rheological measurements. The diblock copolymer chains were analyzed by ^{1}H NMR spectroscopy in d_6-DMSO and DMF GPC.

Derivatization of $PGMA_{25}$-$PGlyMA_{45}$ diblock copolymer worms via epoxy-amine chemistry using 4-amino-TEMPO

The $PGMA_{25}$-$PGlyMA_{45}$ diblock copolymer worms were derivatized with 4-amino-TEMPO directly in water. Systematic variation of the copolymer concentration, reaction time, reaction temperature and 4-amino-TEMPO/epoxy molar ratio was undertaken in an attempt to optimize this epoxy-amine reaction (see Table S3).

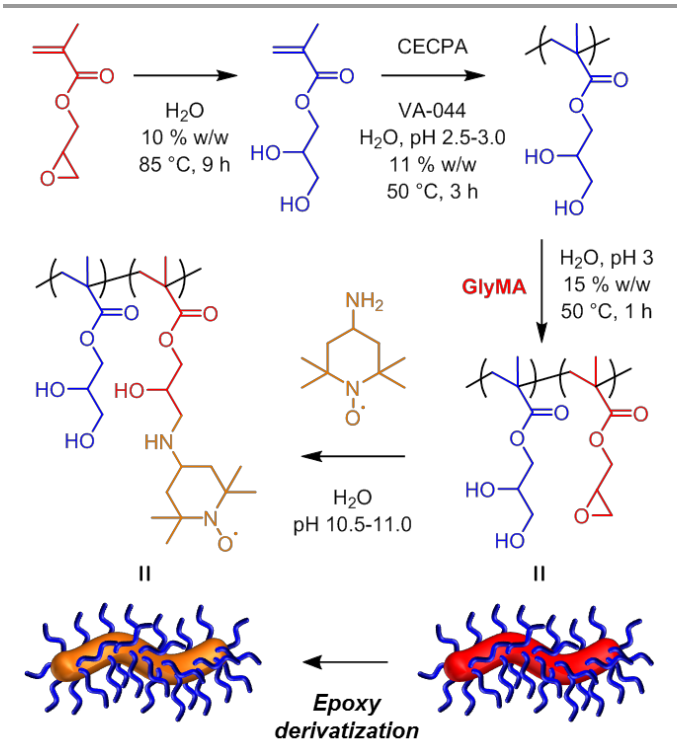
In a typical protocol, 5.0 % w/w $PGMA_{25}$-$PGlyMA_{45}$ diblock copolymer was reacted with 4-amino-TEMPO at 50 °C for 6 h using a 4-amino-TEMPO/epoxy molar ratio of 2.0. First, the original copolymer worm dispersion (10.0 g, 15 %w/w) was weighed into a glass jar and diluted with deionized water (20.0 g) with magnetic stirring to afford a 5.0 % w/w dispersion, which was then stirred for 48 h at 20 °C to ensure a high degree of dispersion with no visible aggregates. Subsequently, 4-amino-TEMPO (0.164 g, 0.96 mmol) was weighed into a sample vial, to which the appropriate mass of dispersed worms was also added (2.0 g of a 5.0 % w/w dispersion, 0.48 mmol epoxy groups). This reaction mixture was magnetically stirred while heating to 50 °C in an oil bath for 6 h. On cooling to room temperature, the resulting dispersion was purified by exhaustive dialysis against deionized water for three days. The purified $PGMA_{45}$-P(GlyMA-NH-TEMPO)$_{45}$ worms were characterized by DLS and EPR spectroscopy. The dried copolymer was isolated after freeze-drying from water overnight and characterized by elemental analysis and FTIR spectroscopy.

Results and discussion

Epoxy-functional diblock copolymer worms were prepared in aqueous solution using a single monomer (GlyMA) via a convenient three-step, one-pot protocol (Scheme 1). This convenient synthetic route allows for the direct derivatization of epoxy-containing diblock copolymer worms with 4-amino-TEMPO to give nitroxide-functionalized diblock copolymer worms. Owing to their highly anisotropic nature, such diblock copolymer worms are expected to form a percolating network at relatively low volume fractions[32] and hence may exhibit superior charge transport properties.[9-10]

Synthesis of diblock copolymer worms from GlyMA

An initial aqueous emulsion of GlyMA was converted into an aqueous solution of GMA by heating at 85 °C for 9 h.[33] ^{1}H NMR analysis indicated that the conversion of GlyMA to GMA was approximately 98%, see Fig. S1. The initial epoxy proton signals (CH_2 2.69 and 2.85 ppm, CH 3.26 ppm) shifted to 3.62, 3.75 and 3.92 ppm as the GlyMA was hydrolyzed to afford GMA. Then RAFT solution polymerization of GMA using a dicarboxylic acid-based RAFT agent (CECPA) and a low-temperature azo initiator (VA-044) at pH 2.5-3.0 afforded near-monodisperse PGMA chains with a mean DP of 25 (M_n = 7 900 g mol^{-1}, Đ = 1.14).



Scheme 1. Schematic representation of the one-pot synthesis of highly anisotropic PGMA-PGlyMA diblock copolymer worms from a single monomer (glycidyl methacrylate, GlyMA). These precursor epoxy-functionalized nanoparticles were then derivatized with 4-amino-TEMPO to introduce stable nitroxide species into the worm cores. [CECPA = 4-((({2-(carboxyethyl)thio)carbonothioyl)thio)-4-cyanopentanoic acid]

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Studies of the kinetics of GMA polymerization were conducted with a target mean DP of 20, see Fig. S2A. The polymerization reached 98% conversion within 3 h, a linear evolution of M_n with conversion was observed and dispersities ($Đ$) remained below 1.20. The resulting PGMA homopolymer precursor was isolated after purification (see Fig. S3). An integrated CH_2 signal (COOH-C$\underline{H_2}$-CH_2-S-C(=S)-S) assigned to CECPA at 2.73 ppm was compared to that of the five pendent [-C$\underline{H_2}$-C$\underline{H}$(OH)C$\underline{H_2}$OH] at 3.5-4.2 ppm to calculate an actual DP of 25 via end-group analysis using ^{1}H NMR spectroscopy. This suggested a CTA efficiency of ~80%, which was taken into account when targeting the PGMA DP in subsequent RAFT aqueous solution polymerizations. The latter syntheses proved to be highly reproducible (Table S1). The CTA efficiency indicated that up to 20% of the CTA did not react during the polymerization. Inspection of UV GPC chromatograms (Fig. S4) showed a small peak at 18.8 min corresponding to the CTA in addition to the peak expected for the $PGMA_{25}$ homopolymer. Following chain extension this peak at 18.8 min was still present. This suggested that the residual CTA does not react during the chian extension of $PGMA_{25}$ with GlyMA.

This $PGMA_{25}$ water-soluble precursor was subsequently chain-extended with GlyMA via RAFT aqueous emulsion polymerization at 50 °C, see Scheme 1. Initially, a stock solution of the $PGMA_{25}$ macro-CTA was used to investigate the target PGlyMA DP required to access a pure worm phase. GlyMA was added to the stock solution and the reaction mixture was degassed before heating to 50 °C for 1 h. PGlyMA DPs ranging between 25 and 60 were targeted (see Table S2). In each case more than 99% conversion was achieved and dispersities remained below 1.27. TEM analysis of these diblock copolymer nanoparticles revealed that targeting a composition of $PGMA_{25}$-$PGlyMA_{45}$ at 15% w/w solids resulted in well-defined worms (Fig. 1A inset and Fig. S5). It is perhaps worth emphasizing that our recent use of a somewhat longer $PGMA_{45}$ macro-CTA had only produced kinetically-trapped spheres.[30] Thus, in the present study we decided to evaluate a $PGMA_{25}$ macro-CTA in order to target worms because previous studies[31, 42] had demonstrated that relatively short steric stabilizer blocks are essential for accessing so-called 'higher order' morphologies.

Once an appropriate PISA formulation for the reproducible preparation of pure worms had been identified, a one-pot synthesis of $PGMA_{25}$-$PGlyMA_{45}$ diblock copolymer worms was developed. The hydrolysis of GlyMA to GMA and subsequent RAFT aqueous solution polymerization of GMA using CECPA and VA-044 was performed, as previously discussed. Degassed GlyMA monomer was then added to the reaction mixture after 3 h to conduct RAFT aqueous emulsion polymerization at 15% w/w solids which reached high conversion after a further 1 h reaction time (Fig. S2). The solution pH was maintained below the pK_a of CECPA during the polymerization to prevent ionization of its carboxylic acid end-groups during PISA. This precaution, combined with the relatively low mean DP used for the $PGMA_{25}$ stabilizer block, was essential to ensure the formation of PGMA-PGlyMA worms, as opposed to the kinetically-trapped spheres previously reported.[30] Conducting the same polymerization at pH 7.3 inhibited the formation of worms, yielding a free-flowing turbid dispersion of spherical nanoparticles (Fig. S6).

High GlyMA conversions and the concomitant formation of an aqueous physical gel were observed within 1 h at 50 °C when targeting a $PGMA_{25}$-$PGlyMA_{45}$ diblock composition, see Figs. S2, S6 and S7. Small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) analyses confirmed that a pure worm phase was obtained using this RAFT aqueous emulsion polymerization formulation (Fig. 1A). More specifically, the SAXS pattern recorded for a 1.0% w/w aqueous dispersion indicated a gradient of approximately -1 at low q, as expected for highly anisotropic worms.[34] The upturn at lower q (<0.03 Å^{-1}) suggests some degree of worm branching, for which TEM provides some evidence. The mean worm thickness, T_w, was calculated to be 11.6 ± 0.8 nm by fitting the SAXS pattern to a well-known worm-like micelle model.[35]

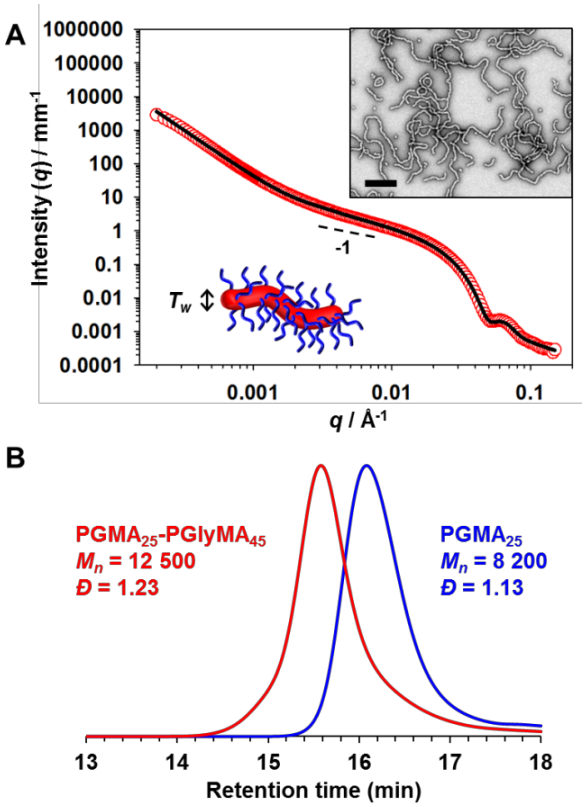


Figure 1. (A) SAXS pattern recorded for a 1.0% w/w aqueous dispersion of PGMA25-PGlyMA45 worms (inset: a representative TEM image, scale bar = 200 nm). The experimental data are denoted by red open circles while the solid black line indicates the data fit calculated using a worm-like micelle model.[34] (B) DMF GPC chromatograms for the PGMA25-PGlyMA45 diblock copolymer and the corresponding PGMA25 macro-CTA prior to chain extension.

Perusal of the PISA literature indicates that well-defined worms are seldom reported for RAFT aqueous emulsion polymerization formulations, which more typically produce kinetically-trapped spheres.[36-39] Moreover, the synthesis of well-defined diblock copolymer worms using just a *single* monomer (in this case GlyMA) is unprecedented. There are many literature examples of RAFT dispersion polymerization formulations producing pure worms, but their phase space is generally rather narrow.[31] Thus, it was not surprising that targeting alternative DPs for the current RAFT aqueous emulsion polymerization formulation yielded either spheres or mixed morphologies as judged by TEM, see Fig. S5. DMF GPC analysis revealed narrow molecular weight distributions (M_w/M_n < 1.30, see Table S2), with relatively high blocking efficiencies (Fig. 1B).

To derivatize the $PGMA_{25}$-$PGlyMA_{45}$ worms with 4-amino-TEMPO (see Scheme 1), the free-standing aqueous physical gel initially formed at 15% w/w was first diluted to 2.5-7.5% w/w to enable efficient stirring. Subsequently, 4-amino-TEMPO was added directly to the free-flowing aqueous dispersion followed by heating to 50, 60 or 70 °C for either 6 or 24 h at an unadjusted solution pH of 10.5-

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11.0. The 4-amino-TEMPO/epoxy molar ratio was varied from 1.0 to 4.0 and the extent of the epoxy-amine reaction was determined by nitrogen microanalysis after purification of the derivatized worms by exhaustive dialysis against deionized water followed by lyophilization (see Table S3). The theoretical maximum nitrogen content (6.92%) was calculated assuming that the 4-amino-TEMPO could react with all the epoxy groups. Longer reaction times led to higher degrees of derivatization for the 2.5% w/w dispersions, but no discernible improvement was observed at 5.0% w/w. Therefore, all subsequent epoxy-amine reactions at this higher concentration were conducted for 6 h. Greater degrees of derivatization were achieved when increasing the 4-amino-TEMPO/epoxy molar ratio from 1.0 to 4.0. Empirically, optimum epoxy-amine reaction conditions were found to be a 4-amino-TEMPO/epoxy molar ratio of 4.0 for a 5.0% w/w aqueous dispersion of copolymer worms after heating at 50 °C for 6 h, which afforded a mean degree of derivatization of 87%.

TEM studies of the resulting $PGMA_{25}$-P(GlyMA-NH-TEMPO)$_{45}$ worms indicated that the original copolymer morphology was preserved (Fig. 2A and 2B). However, a mixed phase of spheres and short worms was obtained when using a 4-amino-TEMPO/epoxy molar ratio of 1.0. Moreover, the surface of the worms appeared to be less smooth after epoxy-amine modification, although this could be a drying artefact. At higher copolymer worm concentrations (6.0-7.5% w/w), the initial free-flowing aqueous dispersions formed chemically crosslinked gels that could not be dissolved when exposed to a good solvent for both blocks such as DMF.

Once 4-amino-TEMPO reacts with an epoxy group within the worm cores, a secondary amine is generated that can react further with a neighboring epoxy group, which could lead to core-crosslinked worms. To examine whether this side reaction occurred in the present case, 4-amino-TEMPO derivatized worms were diluted to 0.1% w/w using DMF.

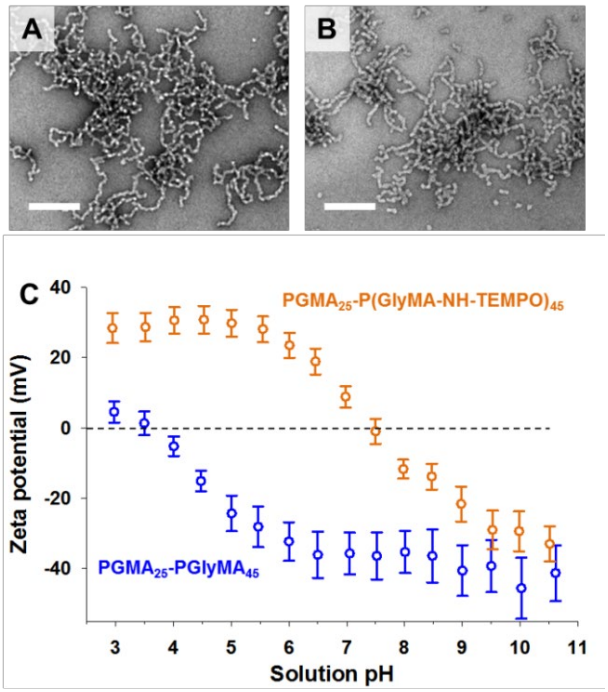


Figure 2. (A) TEM images recorded for $PGMA_{25}$-P(GlyMA-NH-TEMPO)$_{45}$ worms derivatized at 50 °C for 6 h using a 4-amino-TEMPO/epoxy molar ratio of (A) 1.5 and (B) 2.0. Scale bars = 200 nm. (C) Zeta potential vs. pH curves obtained for the precursor $PGMA_{25}$-$PGlyMA_{45}$ worms, and $PGMA_{25}$-P(GlyMA-NH-TEMPO)$_{45}$ worms (derivatized at 50 °C for 6 h using a 4-amino-TEMPO/epoxy molar ratio = 2.0).

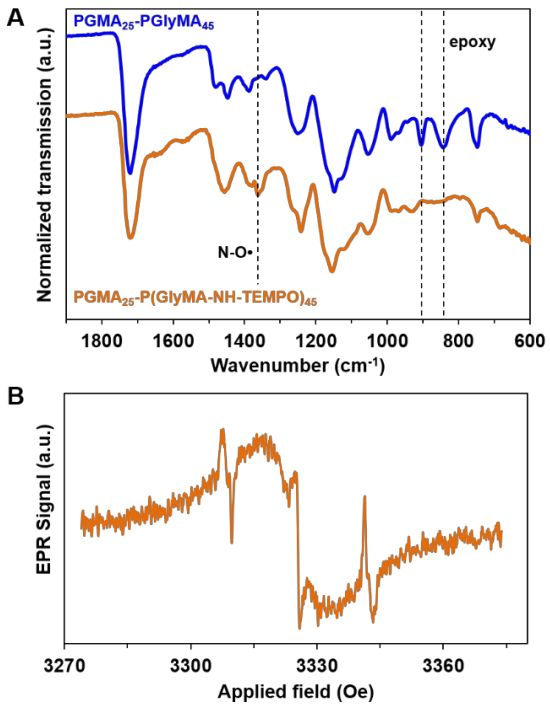


Figure 3. (A) ATR-FTIR spectra recorded for the linear precursor $PGMA_{25}$-$PGlyMA_{45}$ worms, and the crosslinked $PGMA_{25}$-P(GlyMA-NH-TEMPO)$_{45}$ worms obtained using a 4-amino-TEMPO/epoxy molar ratio of 2.0 at 50 °C for 6 h. (B) EPR spectrum recorded for the latter worms, showing both singlet and triplet signals for the stable nitroxide species.

DLS studies confirmed that the worms did not dissolve to produce individual copolymer chains under these conditions (see Fig. S8 and Table S4), which indicated that covalent crosslinking of the diblock copolymers had indeed occurred. In contrast, the linear $PGMA_{25}$-$PGlyMA_{45}$ precursor worms underwent molecular dissolution on dilution with DMF, as indicated by the relatively low derived count rate that is observed (Table S4). The electrophoretic behavior of the original $PGMA_{25}$-$PGlyMA_{45}$ worms and the corresponding 4-amino-TEMPO derivatized worms was investigated (see Fig. 2B).

Introducing secondary (and tertiary) amine groups into the worm cores leads to appreciable cationic character in acidic solution and an isoelectric point of around pH 7.5, as determined by zeta potential measurements. Similar observations were recently reported for the derivatization of $PGMA_{45}$-$PGlyMA_{100}$ spheres using diamines.[30] In contrast, the original linear $PGMA_{25}$-$PGlyMA_{45}$ worms exhibited an isoelectric point at pH 3.5 and anionic character from pH 4.0 to pH 10.5, owing to ionization of the carboxylic acid end-groups derived from the CECPA RAFT agent. Successful epoxy-amine reaction was supported by ATR-FTIR spectroscopy studies (Fig. 3A), which revealed a weak absorption band assigned to the nitroxide group at 1360 cm^{-1} and concomitant loss of characteristic asymmetric vibrational modes for the epoxy ring (904 and 843 cm^{-1}).

Incorporation of TEMPO groups within the worm cores was further confirmed by electron paramagnetic resonance (EPR) spectroscopy (Fig. 3B), which revealed the presence of both singlet and triplet signals. The latter feature is relatively weak and is assigned to isolated (non-interacting) TEMPO groups.[40-41] In contrast, the former signal is attributed to strongly interacting stable free radicals for which the characteristic hyperfine splitting pattern is quenched. This is consistent with the high local density of the nitroxide species within the crosslinked worm cores.[40-41] In contrast, the 4-amino-TEMPO precursor exhibits only triplet signals when characterized by

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EPR spectroscopy (see Figure S9). These TEMPO-functionalized worms will be investigated for their use in charge storage applications in the near future.

Conclusions

In summary, TEMPO-derivatized $PGMA_{25}$-$PGlyMA_{45}$ diblock copolymer worms were prepared directly in water via polymerization-induced self-assembly using a highly convenient one-pot, three-step protocol starting from a *single* monomer (GlyMA). Subsequent derivatization of the linear precursor worms was performed using 4-amino-TEMPO to yield TEMPO-functionalized crosslinked worms bearing a high local concentration of stable nitroxide groups within the worm cores. In principle, these new highly anisotropic nanoparticles could offer potential applications for charge storage and transport.

Conflicts of interest

There are no conflicts of interest to declare.

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