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Perylene as an electron-rich moiety in healable, complementary \( \pi-\pi \) stacked, supramolecular polymer systems

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A two-component, supramolecular polymer blend has been designed using a novel \( \pi \)-electron rich bis-perylene-terminated polyether. This polymer is able to self-assemble through electronically complementary \( \pi-\pi \) stacking interactions with a \( \pi \)-electron-deficient chain-folding polydiimide to afford thermally healable polymer blends. Model compounds were developed to assess the suitability of the deep green complexes formed between perylene residues and chain-folding bis-diimides for use in polymer blends. The polymer blends thus synthesised were elastomeric in nature and demonstrated healable properties as demonstrated by scanning electron microscopy. Healing was observed to occur rapidly at ca. 75 °C, and excellent healing efficiencies were found by tensometric and rheometric analyses. These tuneable, stimuli-responsive, supramolecular polymer blends are compared to related healable blends featuring pyrene-terminated oligomers.

1. Introduction

Directed, non-covalent interactions are an essential tool in the formation of supramolecular polymer assemblies [1]. Such materials typically comprise low- or medium-molecular weight species capable of strong, highly directional and stimuli responsive interactions. The 'switchable' nature of such supramolecular polymers has been investigated for a wide range of potential applications including adhesives, surface-coatings and, most recently, healable materials [2,3]. Polymers with the ability to repair themselves after damage [4–10] could extend the lifetime of materials in a variety of applications. Healable polymeric systems, both autonomic [11–16] and stimuli responsive [17–25], have been obtained through a variety of approaches, including the use of encapsulated liquid monomers and microvascular networks [11–16], irreversible covalent bond formation [17], reversible covalent bond formation [18,19,26–29], and reversible supramolecular interactions [3].

In the field of supramolecular polymers, materials based on hydrogen bonding [30–34], metal-ligand interactions [22,35], or \( \pi-\pi \) stacking interactions [25,36–40] have all been shown to exhibit healable characteristics. \( \pi-\pi \) Stacking interactions between pyrene and naphthalene diimides have been well-documented in the literature [25,36–40], and have recently been used to great effect in the formulation of healable materials. Alternative \( \pi \)-electron rich species such as naphthalene are also known to form stable complementary supramolecular complexes in solution and the solid state with \( \pi \)-electron deficient species [41–46]. However, there has been only limited investigation of the ability of other \( \pi \)-electron rich aromatics to form \( \pi \)-stacked complexes with naphthalene diimides. Perylene is known to form stable complexes with macrocyclic aromatic ether imide sulfones [47] and is an example of an alternative aromatic moiety which could be employed to form \( \pi-\pi \) stacking interactions with chain-folding aromatic diimides to yield healable materials (Scheme 1).

Here we report first on a model-compound study, aimed at determining the suitability of perylene/chaining-diimide complexes in supramolecular assembly. This revealed a five-fold increase in association constant \( K_a \) when compared to the analogous pyrene-based system. Guided by these findings, we developed
a perylene-terminated polyether that, when blended with a chain-folding polydiimide afforded a novel, healable supramolecular polymer system. The supramolecular polymer blend exhibited excellent retention of tensile modulus (10 MPa) over three break/heal cycles, as well as good recovery of the modulus of toughness.

2. Results and discussion

2.1. Model compound studies

To achieve a complementary, two component π–π stacking polymer blend, the design of the chain-folding diimide is crucial. Computational studies [48] have shown that two π-electron-deficient naphthalene diimide moieties, separated by a flexible linker and terminated with a branched alkyl group, give rise to a chain-folding motif which exhibits a pair of strong face-to-face π–π stacking interactions with the π-electron rich guest pyrene, Scheme 2 (Scheme 2 and SI Fig. S1). In the present work, a comparable study was carried out using the more extended fused-ring hydrocarbon perylene, Scheme 2 (Scheme 2).

Computational modelling (SI Fig. S2) of the interaction between Scheme 2 and a simplified chain-folding bis-diimide receptor 1 which exhibits a pair of strong face-to-face π–π stacking interactions with the π-electron rich guest pyrene, Scheme 2 (Scheme 2 and SI Fig. S1). In the present work, a comparable study was carried out using the more extended fused-ring hydrocarbon perylene, Scheme 2 (Scheme 2).

Computational modelling (SI Fig. S2) of the interaction between Scheme 2 and a simplified chain-folding bis-diimide receptor 1 which exhibits a pair of strong face-to-face π–π stacking interactions with the π-electron rich guest pyrene, Scheme 2 (Scheme 2 and SI Fig. S1). In the present work, a comparable study was carried out using the more extended fused-ring hydrocarbon perylene, Scheme 2 (Scheme 2).

Experimentally, spectroscopic analysis of an equimolar blend of Scheme 2 and Scheme 3 by UV-visible spectroscopy (SI Fig. S3), fluorescence (SI Fig. S4) and 1H NMR (SI Fig. S5) spectroscopy indeed showed that a dark green “charge-transfer” complex was formed, resulting in fluorescence quenching and a strong upfield shift in aromatic proton resonances as a consequence of mutual ring-current shielding. Determination of the binding constant for the 1:1 complex between the chain-folding bis-diimide and perylene (1 + 3) by 1H NMR spectroscopy revealed a ca. five-fold increase in association constant ($K_a = 227 \text{ M}^{-1}$) when compared to the analogous pyrene-based system (1 + 2, $K_a = 50 \text{ M}^{-1}$) (SI Figs. S6–S11 and SI Equation S1). This result was consistent with values previously reported [48] by Burattini et al. where the binding constant for the corresponding pyrenyl system (1 + 2) was calculated by UV-vis spectroscopy to be to be 80 M$^{-1}$ and also by Colquhoun and co-workers who demonstrated [47] that perylene bound more strongly than pyrene to a macrocyclic ether sulfone diimide by one order of magnitude.

2.2. Polymer synthesis and characterisation

Having completed a model compound study, which clearly demonstrated that perylene binds more strongly with the chain-folding bis-diimide motif than does pyrene, the synthesis of a perylene terminated polymer, Scheme 4, was identified as the next step in creating healable polymer blends with copolyimide Scheme 5 (Schemes 3 and 4).

In order to generate perylene-terminated polymers for direct comparison with results on pyrene-based systems previously described by Hart et al. [39], 3-perylenebutyric acid, Scheme 4, was identified as a potentially valuable terminating unit (Scheme 4). Friedel–Crafts acylation of perylene, Scheme 4, with the monomethyl ester-acyl
chloride of succinic acid at room temperature gave 3-(3-
perylenoyl)propanoic acid methyl ester 7 [51], in good yield
(75%). It is known that perylene is only acylated at the C3
position under these reaction conditions [52], yielding the mono-
substituted product after purification by flash chromatography.
3-Perylenecarboxylic acid 6 [51] was then obtained from 7 by the
Huang-Minlon modification [53,54] of the Wolff-Kishner reduction
[55]. The pre-polymer bis[3-(aminopropyl)]-terminated poly-
(ethylene glycol), 8, (Mn = 1500 Da) was then end-capped with 3-
perylenecarboxylic acid 6 via DCC-mediated coupling to afford a
perylentanyl-terminated, divalent poly(ethylene glycol) 4 (Scheme 4).
Analysis of the resulting polymer 4 by 1H NMR spectroscopy
revealed no mono-end-capped product, nor residual, unfunction-
alised pre-polymer. Mass spectrometric (MALDI-TOF) analysis was
also undertaken (SI Fig. S12) with a low intensity UV laser which
revealed a sodiated molecular ion corresponding to Mn at
2204.81 Da, ([C118H176N2O35Na]⁺), with an average of 32 repeating
ethylene glycol units. This result is good agreement with the value
of Mn (2204.20 Da, [C118H176N2O35Na]⁺) calculated for the divalent,
perylene terminated polymer 4. The mass difference between sig-
nals in the molecular ion series corresponds to 44 Da, the molecular
weight of one poly(ethylene glycol) repeat unit, with the overall
pattern corresponding to the molecular weight distribution present
in the pre-polymer.
A π-electron deficient polymer was also required in order to
produce an electronically-complementary system that might be
anticipated to show healing characteristics when blended with the
π-electron rich, perylene-terminated polymer 4. A chain-folding
diimide copolymer [36] (SI Fig. S13) with Jeffamine® D-400 mid-
blocks, 5, was therefore synthesised [36] (Mn = 2240 g mol⁻¹,
Dm = 1.87) to allow direct comparison with previous work in which
it was blended with a pyrenyl-terminated polyether [39].

2.3. Polymer complexation in solution

π−π-Stacked supramolecular polymer blends [4 + 5] were ob-
tained by mixing complementary polymer solutions (1 × 10⁻³ M
with respect to binding motifs, CHCl₃/TFA, 9:1 v/v) in equimolar
ratios with respect to equivalent weights of the binding motifs (SI
Fig. S14) as suggested by our model compound studies. A deep
green solution was formed instantaneously from solutions of the
pale yellow perylenyl polymer 4 and the orange/brown polydiimide
5. This dramatic change in colour results from the appearance of a
new, broad absorption band centred at 611 nm in the visible

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Scheme 3. Schematic of perylene terminated polymer 4 (green) and chain-folding polydiimide 5 (blue/black/grey) and their supramolecular blend. Insert shows the structure of the π−π stacked complex with π-electron rich perylene end-groups (green) and π-electron deficient naphthalene-diimide units (blue) linked by a triethyleneoxy unit to form a chain-folding, complexing sequence. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Scheme 4. Synthesis of perylene-terminated poly(ethylene glycol) 4 by DCC-mediated coupling of perylenebutyric acid 6 with bis(3-aminopropyl) terminated poly(ethylene glycol) (Mn = 1500 Da) 8.
and chain-folding polydiimide [eqmolecular blend between the bis-perylenyl terminated polymer]

...individual polymers (SI Fig. S17) was used to probe the characteristics of the polymer [eqmolecular blend between the bis-perylenyl terminated polymer]. The emission spectrum of the perylene terminated dimeric polymer 4 reveals characteristic bands for monomeric perylene at 484 and 512 nm, whilst the chain-folding polydiimide 5 was essentially non-fluorescent in agreement with visual observations. The supramolecular blend between the bis-perylenyl terminated polymer and chain-folding polydiimide [eqmolecular blend between the bis-perylenyl terminated polymer + 5] revealed almost complete quenching of the perylene monomer emissions, indicative of complementary π–π stacking as previously found in this work by computational modelling and model compound studies.

To further investigate the nature of the π–π stacking interaction between the bis-perylenyl terminated polymer 4 and the chain-folding polydiimide 5, 1H NMR spectroscopy was used in probing the solution behaviour of complementary π-electron-rich and π-electron-deficient polymers. Thus, 1H NMR spectra of the blended polymer [eqmolecular blend between the bis-perylenyl terminated polymer + 5] revealed a typical blue emission from the perylene end-groups (310 nm) and revealed a typical blue emission from the perylene end-groups (310 nm) revealed a typical blue emission from the perylene end-groups (310 nm) revealed a typical blue emission from the perylene end-groups (310 nm) revealed a typical blue emission from the perylene end-groups. The control blend was used to investigate the formation of π–π stacking interactions between the bound naphthyl and perylenyl proton resonances in the polydiimide and of the bound naphthyl and perylenyl proton resonances in the polydiimide [eqmolecular blend between the bis-perylenyl terminated polymer + 5] revealed a typical blue emission from the perylene end-groups (310 nm) revealed a typical blue emission from the perylene end-groups (310 nm) revealed a typical blue emission from the perylene end-groups (310 nm) revealed a typical blue emission from the perylene end-groups (310 nm) revealed a typical blue emission from the perylene end-groups (310 nm). The control blend was used to investigate the formation of π–π stacking interactions between the bound naphthyl and perylenyl proton resonances in the polydiimide and of the bound naphthyl and perylenyl proton resonances in the polydiimide.

Inherent viscosity (ηinh) measurements [10 mg mL⁻¹, chloroform/hexafluoroisopropanol (9:1, v/v), 25 °C] of the individual components and the blended solution gave further proof of supramolecular network formation between complementary polymers (Fig. 1). Blending the perylene terminated polymer 4 (ηinh = 0.14 dL g⁻¹) and polydiimide 5 (ηinh = 0.20 dL g⁻¹) in a 1:1 molar ratio with respect to binding units gave rise to a solution which demonstrated an increase in inherent viscosity (ηinh = 0.27 dL g⁻¹; c.f. calculated average of 0.17 dL g⁻¹) as a result of the formation of an extended supramolecular polymer network in solution.

2.4. Polymer films and healing studies

To investigate the formation of π–π stacked polymer complexes in the solid state, films of the individual components 4 and 5, and of the blend [eqmolecular blend between the bis-perylenyl terminated polymer + 5, were drop-cast from 2,2,2-trichloroethanol onto a PTFE plate and dried by progressively increasing the temperature to 80 °C (Fig. 2). The polydiimide 5 film was found to be extremely fragile, as described in the literature [25], whilst the new, bis-perylene-terminated poly(ethylene glycol) 4 was a viscous oil. Films cast from the dimeric perylene end-capped polymer blended with the π-electron deficient polydiimide [eqmolecular blend between the bis-perylenyl terminated polymer + 5] (1:1 with respect to binding motifs) gave rise to deep green peelable materials. The resulting robust, elastomeric films clearly demonstrated that complementary π–π stacking was not only retained in the solid state, but also led to formation of strong, self-supporting films from non-film-forming precursors. Previous studies [25,36,39] demonstrated not only the requirement for electronically complementary binding motifs in producing homogenous polymer blends, but also in generating healable polymeric materials. By way of a control experiment, the chain-folding polydiimide 5 was blended with the non-functionalised PEG pre-polymer 8 and films were cast under analogous conditions to test their film-forming properties. This “control blend” [5 + 8] produced a just-peeable but very fragile film (SI Fig. S19).

Rheometric analysis of the equimolar (with respect to binding units) blend between 4 and 5 revealed a sharp fall-off in melt viscosity with increasing temperature, as indicated by the change in rheometric shift factor, aT. This factor is approximately the ratio of the terminal viscosity at a given temperature to that at 30 °C, and is seen to fall precipitously with temperature, especially above 60 °C (Fig. 3). Overall, aT falls by more than five orders of magnitude between 30 and 90 °C, and the sharp increase in the gradient of this plot at about 60 °C suggests that, above this temperature, the new material should show a markedly enhanced ability to flow and heal when compared to conventional thermoplastics.

Healing was initially demonstrated by heating a damaged film (ca. 50 μm wide cut) of the supramolecular polymer blend [eqmolecular blend between the bis-perylenyl terminated polymer + 5] at 10 °C min⁻¹ in an environmental scanning electron microscope (ESEM) from ambient temperature (Fig. 4). Upon reaching ca. 75 °C healing of the damaged area was seen to initiate and the damaged area began to seal from the top of the cut down to its widest point.

After further heating to 100 °C and finally to 125 °C, the cut had demonstrated almost complete healing. To investigate whether the healing action was indeed the result of supramolecular interactions, ESEM analysis was carried out on a control blend between the poly(ethylene glycol) pre-polymer 8 without the π-electron rich perylene units and the chain-folding polydiimide 5 (SI Fig. S20). The control sample was cut and heated at 10 °C min⁻¹ under analogous conditions to the healable polymer blend [eqmolecular blend between the bis-perylenyl terminated polymer + 5].
The fracture was observed to narrow somewhat during the heating ramp, but crucially, no significant healing was demonstrated by the control material [5 + 8], and indeed the cut still remained very evident at 125 °C.

To quantify the healing efficiencies of the supramolecular polymer blends, a test-strip of film (0.2–0.3 mm in thickness and 4.0 mm in width) was elongated to failure by tensile tests over three test/break/heal/test cycles at 20 °C, at a Hencky strain rate of 0.1 s⁻¹ (Fig. 5) [25, 40].

The pristine film of the polymer blend [4 + 5] exhibited a tensile modulus (E) of 10 MPa (Fig. 6a), and the healing efficiency relative to the pristine material was maintained at 100% over three break/heal cycle. Samples were overlapped slightly to facilitate healing and then heated on a PTFE plate to 125 °C for 30 min, before cooling to room temperature. A decrease in tensile modulus was noted when compared to the tensile modulus of the analogous pyrenyl polymer blend (29 MPa) [39]. Although the association constant for perylene is greater than that of pyrene, it is possible that the ‘on-off’ rate [58] has a greater influence on the tensile properties of the material than the association constant in this instance. The modulus of toughness (Fig. 6b) of the pristine polymer blend is 0.89 MPa, compared to a value for the divergent pyrenyl analogue of 1.45 MPa. Although the magnitude of the modulus of toughness initially decreases by 36% (0.57 MPa) after the first break/heal cycle, a steady increase is observed, retaining up to 97% (0.86 MPa) of the original value after three break/heal cycles. This trend indicates that equilibrium is being reached within the polymer blend over a number of healing cycles. Whilst the strain to break decreases between the pristine and healed samples (370% to ca. 200%, Fig. 5), once broken a second and third time, the value remains constant. The reduction in breaking strain could be explained by loss (<5%) of water, as observed by TGA, which may be plasticising the polymer. Alternatively, as healing takes place at elevated temperatures, the polymeric chains may reorganise into a more ordered state, thus becoming less elastomeric and therefore possessing less freedom to elongate when strain is applied.

The rate of healing in the polymer blend [4 + 5] was also investigated (Fig. 7) by dynamic shear at three different temperatures (50, 75 and 125 °C, respectively). The initial modulus was obtained in the linear region from a strain sweep at a frequency of 100 rad s⁻¹ before the sample was broken by a use of a high strain amplitude of 100% and 100 rad s⁻¹ for 5 min at the corresponding temperatures. Time sweeps at the given temperature were then carried out to heal the sample. At 50 °C the sample recovered 87% of G’ after 40 min of healing, whereas full recovery of G’ was observed after 40 min at 75 °C. When the sample was heated to 125 °C, the material demonstrated 100% healing efficiency within 14 min, clearly demonstrating the tunable thermoreversibility of the supramolecular interaction.

3. Conclusions

A novel supramolecular binding motif between a known π-electron deficient chain-folding residue and the π-electron rich perylene unit has been designed, synthesised, implemented in polymer blends, and the properties of the derived materials explored. Computational modelling strongly suggested formation of π−π stacking interactions between the electronically complementary motifs, and model compounds were then synthesised and the binding interactions between a chain-folding bis-diimide 1 and perylene 3 investigated. This study confirmed the presence of new charge-transfer absorption in the visible spectrum, resulting in a dark green complex in solution (λmax = 608 nm). The new π−π-stacked complex demonstrated quenching of the characteristic perylene fluorescence and exhibited a much higher association constant (Kq = 227 M⁻¹) with the chain-folding bis-diimide 1 when compared to a pyrene analogue (Kq = 50 M⁻¹). Perylenebutyric acid 6 was readily synthesised and appended to a linear bis(3-amino propyl) terminated poly(ethylene glycol) to produce a polymer 4 which was formulated into an equimolar blend (with respect to binding motifs) of complementary π-electron deficient and π-electron rich polymers [4 + 5]. A film of [4 + 5] film was damaged by cutting and shown to heal on heating, as visualised by ESEM. Tensometry revealed the film to have a tensile modulus of 10 MPa.
which showed 100% recovery over three break/heal cycles. The modulus of toughness (0.89 MPa) was also recovered almost completely after three break/heal cycles. Temperature-dependent healing studies revealed the polymer to be fully healed after 40 min at 75 °C, or after 14 min at 125 °C, demonstrating the versatility of the new perylene-based supramolecular polymer system and the ability to tailor π−π stacking interactions to produce healable materials.

4. Experimental

4.1. Methods and materials

Reagents and solvents were purchased from Sigma Aldrich and were used without further purification, with the exception of dichloromethane which was dried by distillation from calcium hydride under argon. Proton NMR (400 MHz) and 13C NMR (100 MHz) spectra were obtained on a Bruker Nanobay 400 spectrometer using CDCl3 or CDCl3/trifluoroacetic acid (9:1 v/v) as solvent, with TMS as internal standard. Infrared (IR) spectroscopic analysis was carried out using a Perkin Elmer 100 FT-IR instrument with diamond-ATR sampling accessory and samples either as solids or oils. Environmental scanning electron microscopy was carried out using an FEI Quanta FEG 600 instrument equipped with a heating stage. Ultraviolet-visible spectra were measured on a Varian Cary 300 spectrophotometer with heating attachment, using 1 cm² quartz cuvettes, in the wavelength range 350–800 nm. Fluorescence spectroscopy was carried out in chloroform using a Varian Cary Eclipse fluorescence spectrophotometer and a 1 cm² quartz cuvette, exciting at 345 nm and recording emissions in the wavelength range 350–700 nm. Matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOF MS) were obtained using a Bruker Daltonics Ultraflex 1 spectrometer operating in reflection mode. The instrument was calibrated using a standard peptide mixture (Bruker Daltonics, calibration standard II), and 2,5-dihydroxybenzoic acid (DHB) was used as the matrix. A typical method of sample preparation follows: a solution of the anhydride in acetonitrile (3 μL, 5 mg mL⁻¹) was combined with 3 μL of a freshly prepared matrix solution (20 mg mL⁻¹ in 1:1 acetonitrile/water with 1% v/v TFA). Aliquots (1 μL) were then spotted onto a ground steel MALDI target plate and left to dry in air prior to analysis. Gel Permeation chromatography (GPC) data were collected using an Agilent Technologies 1260 Infinity Series chromatograph. Samples were dissolved in THF which was also used as the eluent, with poly(styrene) standards for calibration. Inherent viscosities were measured in chloroform/hexafluorisopropanol (9:1, v/v) on a Schott-Gerate CT-52 auto-viscometer using a size 03 Ubbelohde capillary in a thermostatted water bath at 25 °C. Differential scanning calorimetry (DSC) was carried out using a TA Instruments Q2000 calorimeter. Samples for DSC were heated to 110 °C to remove residual solvent, cooled to −90 °C, and then re-scanned from −90 to 250 °C. Dynamic mechanical analysis was carried out using a TA Instruments RSA III at 23 °C with a Hencky strain rate of 0.1 s⁻¹. Samples were 0.20–0.30 mm in thickness, cut to dimensions of approximately 4 × 40 mm. Uniform films with a thickness of 0.2–0.3 mm were tensile tested to break, and the edges of the broken samples were then overlapped, pressed gently on a pre-heated PTFE plate, and healed in an oven at 125 °C for 30 min. The rheological characteristics of the polymer were studied in a nitrogen atmosphere using a strain control rheometer, ARES-G2, from TA Instruments, using parallel stainless steel 8 mm diameter plates. The samples were pressed into discs with a diameter of 8 mm and a thickness of approximately 0.3–0.4 mm. Strain sweeps from a frequency of 100 rad s⁻¹ were conducted in the linear regions with a strain of 3–5% at different temperatures, including 30, 40, 50, 60, 70, 80, and 90 °C, respectively. The master curve at a reference temperature of 30 °C was constructed from these frequency sweeps, from which the shift factor at was extracted. Rheological healing studies were conducted at three different temperatures, 50, 75, and 125 °C. The initial modulus was obtained in the linear region from a strain sweep at a frequency of 100 rad s⁻¹. The samples were broken at a high strain of 100% and 100 rad s⁻¹ frequency for 5 min at the desired temperatures. A strain of 3% was used for samples at 50 and 75 °C, and 8% for healing at 125 °C, at a frequency of 100 rad s⁻¹ for time sweeps, to dynamically heal the samples after breaking.

4.2. Preparation of bis-perylene-terminated poly(ethylene glycol) (4)

Under an nitrogen atmosphere at 0 °C, bis(3-aminopropyl) poly(ethylene glycol) 8 (1.21 g, 0.81 mmol) and 4-dimethylaminopyridine (0.10 g, 0.80 mmol) were mixed in dry dichloromethane...
Fig. 6. (a) Tensile moduli and (b) Moduli of toughness of the blends containing the divalent perylenyl-polymer and chain-folding diimide [4 + 5], demonstrating the recovery of tensile modulus and modulus of toughness over 3 break/heal cycles.

(500 mL). Perylenebutyric acid 6 (0.60 g, 1.77 mmol) was added and stirred for 20 min at 0 °C, followed by dicyclohexylcarbodiimide (0.40 g, 1.93 mmol). The suspension was warmed to room temperature and subsequently stirred for 18 h before being cooled and filtered. The filtrate was concentrated in vacuo and precipitated in diethyl ether (300 mL) in a dry ice/acetone bath and filtered whilst cold. The crude polymer was further purified by column chromatography, eluting in chloroform/methanol (40:1) to yield 4 as an orange-brown oil (1.60 g, 88%); FT-IR spectroscopy, eluting in chloroform/methanol (40:1) to yield M

\[ \text{Na}\] (CDCl3, 400 MHz): 1547, 1465, 1387, 1343, 1279, 1241, 1101, 961, 841, 816, 765; 1H NMR, (4H, quin, J ¼ 50, 75, and 125 Hz), demonstrating the recovery of

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.03.028.

References
