

Perylene as an electron-rich moiety in healable, complementary π – π stacked, supramolecular polymer systems

Article

Published Version

Creative Commons: Attribution 4.0 (CC-BY)

Open Access

Hart, L. R., Nguyen, N. A., Harries, J. L., Mackay, M. E., Colquhoun, H. M. and Hayes, W. ORCID: <https://orcid.org/0000-0003-0047-2991> (2015) Perylene as an electron-rich moiety in healable, complementary π – π stacked, supramolecular polymer systems. *Polymer*, 69. pp. 293-300. ISSN 0032-3861 doi: 10.1016/j.polymer.2015.03.028 Available at <https://centaur.reading.ac.uk/40290/>

It is advisable to refer to the publisher's version if you intend to cite from the work. See [Guidance on citing](#).

To link to this article DOI: <http://dx.doi.org/10.1016/j.polymer.2015.03.028>

Publisher: Elsevier

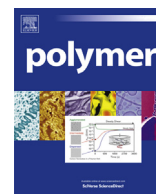
All outputs in CentAUR are protected by Intellectual Property Rights law, including copyright law. Copyright and IPR is retained by the creators or other copyright holders. Terms and conditions for use of this material are defined in the [End User Agreement](#).

www.reading.ac.uk/centaur

CentAUR

Central Archive at the University of Reading

Reading's research outputs online



Perylene as an electron-rich moiety in healable, complementary π – π stacked, supramolecular polymer systems



Lewis R. Hart ^a, Ngoc A. Nguyen ^b, Josephine L. Harries ^c, Michael E. Mackay ^{b, d}, Howard M. Colquhoun ^{a, *}, Wayne Hayes ^{a, *}

^a Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK

^b Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, USA

^c Domino UK Ltd, Trafalgar Way, Bar Hill, Cambridge CB23 8TU, UK

^d Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, USA

ARTICLE INFO

Article history:

Received 9 December 2014

Received in revised form

9 March 2015

Accepted 10 March 2015

Available online 25 March 2015

Keywords:

Healable polymers

π – π stacking

Polymer blends

ABSTRACT

A two-component, supramolecular polymer blend has been designed using a novel π -electron rich bis-*perylene*-terminated polyether. This polymer is able to self-assemble through electronically complementary π – π stacking interactions with a π -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.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

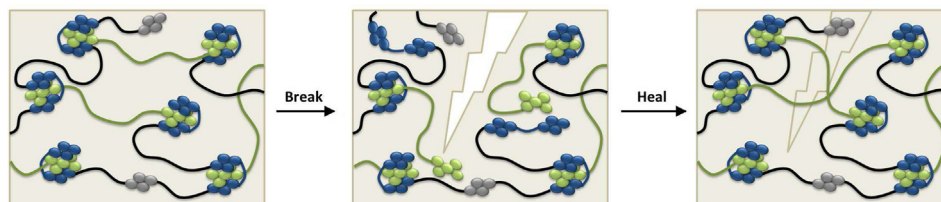
Directed, non-covalent interactions are an essential tool in the formation of supramolecular polymer assemblies [1]. Such materials typically comprise low- or medium-molecular weight species capable of strong, highly directional and stimuli responsive interactions. The ‘switchable’ nature of such supramolecular 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 π – π stacking interactions [25,36–40] have all been shown to exhibit healable characteristics. π – π 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 π -electron rich species such as *naphthalene* are also known to form stable complementary supramolecular complexes in solution and the solid state with π -electron deficient species [41–46]. However, there has been only limited investigation of the ability of other π -electron rich aromatics to form π -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 π – π 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*/chain-folding 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

* Corresponding authors. Tel.: +44 (0)118 378 6491; fax: +44 (0)118 378 6331.

E-mail addresses: h.m.colquhoun@reading.ac.uk (H.M. Colquhoun), w.c.hayes@reading.ac.uk (W. Hayes).



Scheme 1. Schematic of a complementary π – π stacking polymer-blend between a perylene terminated polymer (green) and chain-folding polydiimide (blue/black/grey), illustrating the process of breaking the polymer matrix by disengaging the weaker supramolecular interactions before applying an appropriate stimulus to facilitate healing. (The naphthalene-diiimide residues (grey) spaced by extended polymer residues do not form chain-folding sequences). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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 **1** which exhibits a pair of strong face-to-face π – π stacking interactions with the π -electron rich guest pyrene, **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, **3** (Scheme 2).

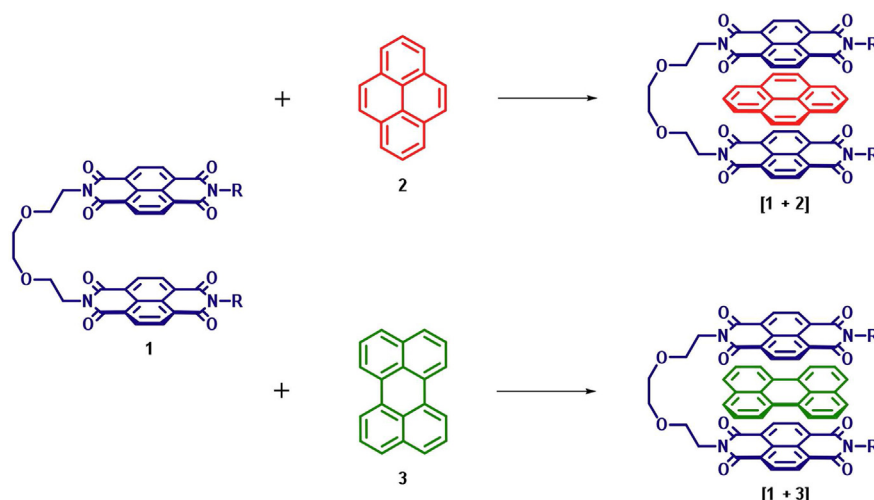
Computational modelling (SI Fig. S2) of the interaction between **3** and a simplified chain-folding bis-diimide motif predicted formation of a 1:1 π – π -stacked complex with an average distance of 3.5 Å between the carbon atoms of the complexing π -systems, close to the optimum van der Waals contact distance and consistent with values previously reported for π – π stacking interactions [41,49,50]. Experimentally, spectroscopic analysis of an equimolar blend of **1** (Scheme 2) and **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.

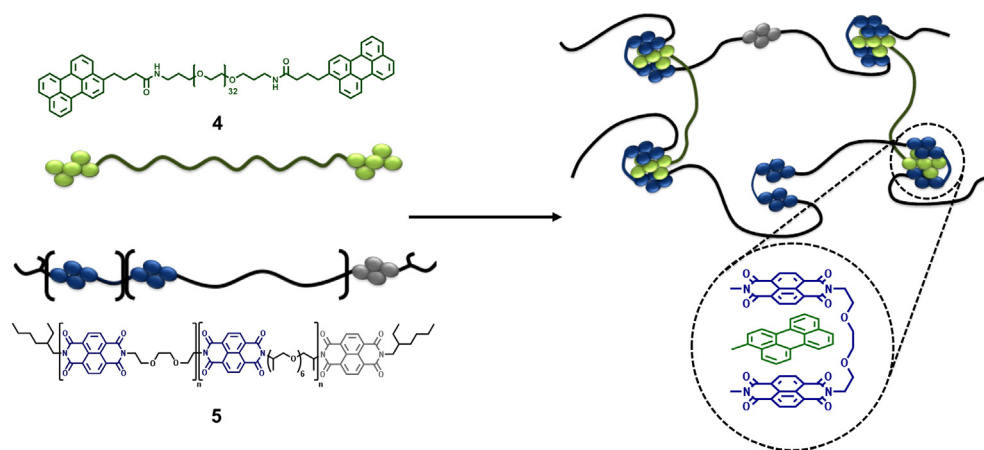
2.2. Polymer synthesis and characterisation

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, **4**, was identified as the next step in creating healable polymer blends with copolyimide **5** (Schemes 3 and 4).

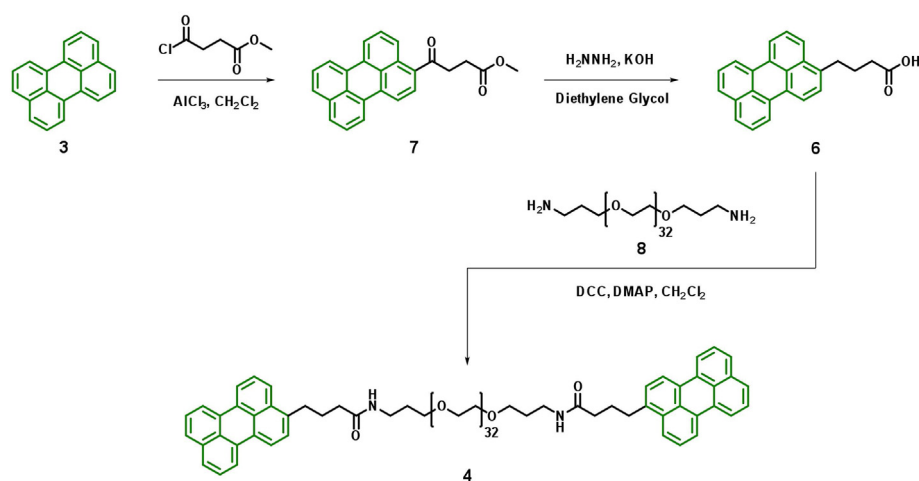
In order to generate perylene-terminated polymers for direct comparison with results on pyrene-based systems previously described by Hart et al. [39], 3-perylenebutrylic acid, **6**, was identified as a potentially valuable terminating unit (Scheme 4). Friedel–Crafts acylation of perylene, **3**, with the monomethyl ester-acyl



Scheme 2. Complexation of pyrene (**2**) and perylene (**3**) by complementary π – π -stacking with the chain-folding bis-diimide receptor **1** (R = 2-ethylhexyl).



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 triethylenedioxy 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) ($M_n = 1500$ Da) **8**.

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-Perylenebutyric 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**, ($M_n = 1500$ Da) was then end-capped with 3-perylenebutyric acid **6** via DCC-mediated coupling to afford a perylenyl-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, unfunctionalised 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 M_n at 2204.81 Da, $[\text{C}_{118}\text{H}_{176}\text{N}_2\text{O}_{35}\text{Na}]^+$, with an average of 32 repeating ethylene glycol units. This result is in good agreement with the value of M_n (2204.20 Da, $[\text{C}_{118}\text{H}_{176}\text{N}_2\text{O}_{35}\text{Na}]^+$) calculated for the divalent, perylene terminated polymer **4**. The mass difference between signals 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] ($M_n = 2240$ gmol^{-1} , $D_m = 1.87$) 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 obtained by mixing complementary polymer solutions (1×10^{-3} M with respect to binding motifs, CHCl_3/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

spectrum (SI Fig. S15) of the blended solutions [4 + 5], as was observed in the UV-visible spectra of the analogous model compounds (SI Fig. S3). Absorption at this wavelength is strongly indicative of a newly formed charge-transfer complex between the π -electron-rich perylene moiety and π -electron-deficient, chain-folding diimide [48].

Irradiation of a solution of the perylene terminated polymer **4** (CHCl_3/TFA , 9:1 v/v) with a standard laboratory UV-light source (310 nm) revealed a typical blue emission from the perylene end-groups (SI Fig. S16). On blending with the non-fluorescent polydiimide **5** in an equimolar ratio with respect to binding motifs, the perylene fluorescence was observed to diminish dramatically. To quantify this fluorescence-quenching further, fluorescence spectroscopy (SI Fig. S17) was used to probe the characteristics of the individual polymers (**4**, **5**) and the corresponding blend [4 + 5]. The emission spectrum of the perylene terminated divalent 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 [4 + 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 [4 + 5] (equimolar with respect to the binding motifs, 1×10^{-2} M, 10% TFA in CDCl_3 , (v/v)) were compared to spectra obtained for the individual components (SI Fig. S18). The singlet associated with the aromatic protons of the π -electron-poor naphthalenediimide residues **5** (8.80 ppm) experiences a significant upfield shift (>0.30 ppm) when blended, as a result of ring-current shielding by the intercalating perylene end-groups **4** within the chain-folding bis-diimide motif. In addition, the 'naphthyl' protons of the polydiimide polymer **5** split into distinct populations between bound sequences (8.50–7.60 ppm) and sequences which are non-binding (8.65 ppm). Resonances associated with the perylenyl end-group are also seen to shift upfield and become broader in appearance. The complex pattern observed for the bound naphthyl and perylenyl proton resonances in the polymer blend arises from the range of different binding sequences [56,57] within the random co-polymer backbone (i.e. dimer, trimer, etc.) whilst the broad nature of the proton resonances for both π -electron-rich and π -electron deficient species indicates that the system is approaching slow exchange on the NMR timescale.

Inherent viscosity (η_{inh}) 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** ($\eta_{\text{inh}} = 0.14 \text{ dL g}^{-1}$) and polydiimide **5** ($\eta_{\text{inh}} = 0.20 \text{ dL g}^{-1}$) in a 1:1 molar ratio with respect to binding units gave rise to a solution which demonstrated an increase in inherent viscosity ($\eta_{\text{inh}} = 0.27 \text{ dL g}^{-1}$; 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 [4 + 5], were drop-cast from 2,2,2-trichloroethanol onto a

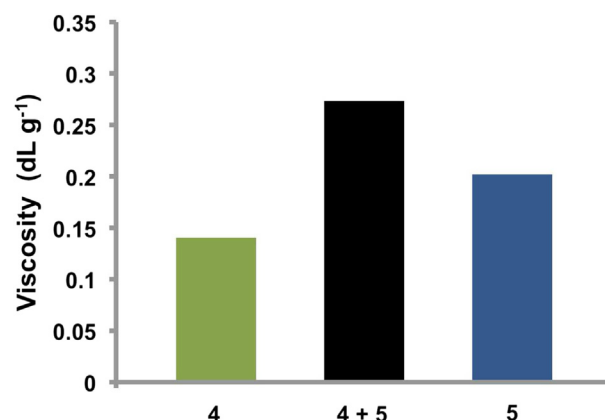


Fig. 1. Inherent viscosities of individual polymers (**4**, **5**) and the equimolar (with respect to binding motifs) polymer blend [4 + 5] at 10 mg mL^{-1} in chloroform/hexafluoroisopropanol (9:1, v/v). Viscosities are the mean of four repeat measurements in each case.

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-perylenyl-terminated poly(ethylene glycol) **4** was a viscous oil. Films cast from the divalent perylene end-capped polymer blended with the π -electron deficient polydiimide [4 + 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-peelable 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, a_T . 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, a_T 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 re-heal when compared to conventional thermoplastics.

Healing was initially demonstrated by heating a damaged film (ca. $50 \mu\text{m}$ wide cut) of the supramolecular polymer blend [4 + 5] at $10^\circ\text{C min}^{-1}$ 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 $10^\circ\text{C min}^{-1}$ under analogous conditions to the healable polymer blend [4 + 5].

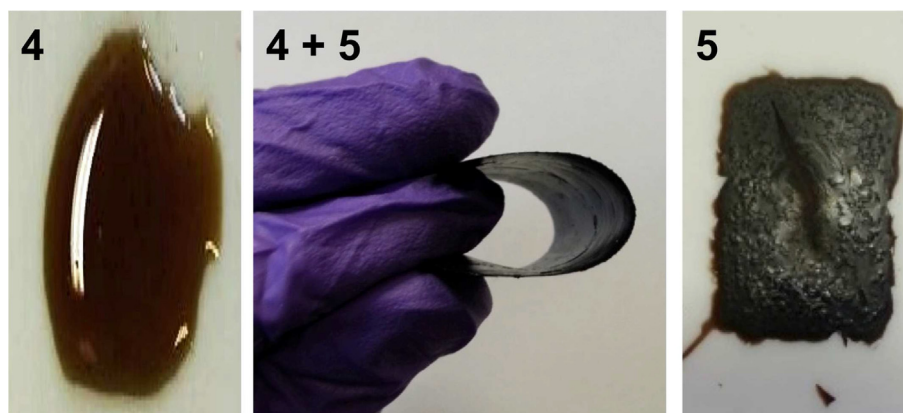


Fig. 2. Films of: (at left) the perylenyl terminated polyether **4**; (at right) the chain-folding polydiimide **5**; and (centre) the equimolar (with respect to binding motifs) blend **[4 + 5]**. All three films were cast from solution in 2,2,2-trichloroethanol and dried at room temperature for 24 h before drying at 40 °C for 24 h and finally at 80 °C for 24 h.

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 divalent 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 ($\lambda_{\text{max}} = 608$ nm). The new π – π -stacked complex demonstrated quenching of the characteristic perylene fluorescence and exhibited a much higher association constant ($K_a = 227$ M^{−1}) with the chain-folding bis-diimide **1** when compared to a pyrene analogue ($K_a = 50$ M^{−1}). Perylenebutyric acid **6** was readily synthesised and appended to a linear bis(3-aminopropyl) 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

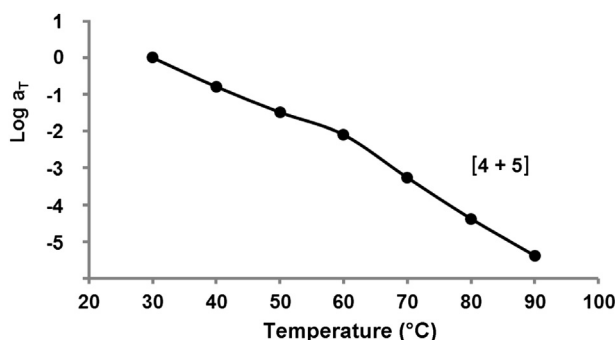


Fig. 3. Variation of rheometric shift factor, *a_T* (a function of melt-viscosity), with temperature for the supramolecular polymer system **[4 + 5]**.

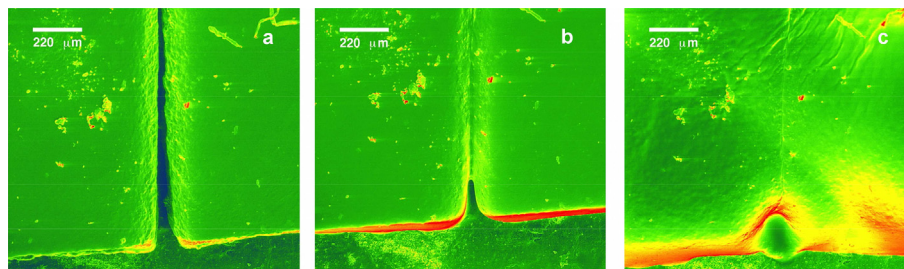


Fig. 4. False-colour ESEM images of the healable polymer blend [4 + 5] containing equimolar amounts (with respect to binding motifs) of perylene terminated polymer 4 and chain-folding polydiimide 5. Micrographs were taken at (a) 25 °C, (b) 75 °C and (c) 125 °C. The images demonstrate both formation of a homogenous blend and the healability of the polymer at elevated temperatures. Scale bar represents 220 μm .

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 ^{13}C NMR (100 MHz) spectra were obtained on a Bruker Nanobay 400 spectrometer using CDCl_3 or $\text{CDCl}_3/\text{trifluoroacetic acid}$ (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 cm^2 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 cm^2 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 analyte 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/hexafluoroisopropanol (9:1, v/v) on a Schott-Geräte 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 at a frequency of 100 rad s^{-1} were carried out before a frequency sweep from 0.1 rad s^{-1} to 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 a_T 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-perylen-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-dimethylamino-pyridine (0.10 g, 0.80 mmol) were mixed in dry dichloromethane

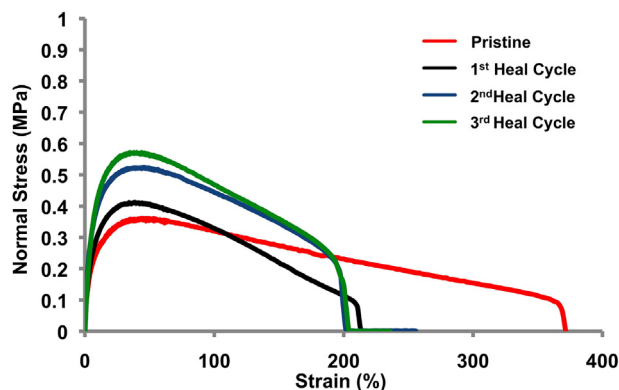


Fig. 5. Stress/strain curve demonstrating the elongation to break of the polymer blend [4 + 5] over three break/heal cycles.

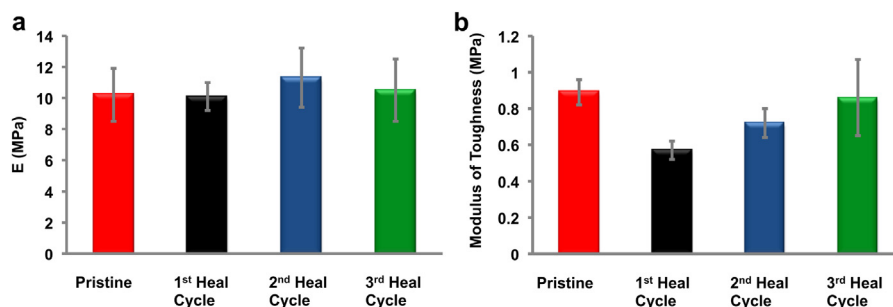


Fig. 6. (a) Tensile moduli and (b) Moduli of toughness of the blends containing the divalent perylenyl-polymer and chain-folding diimide [4 + 5], demonstrating the recovery of tensile modulus and modulus of toughness over 3 break/heal cycles.

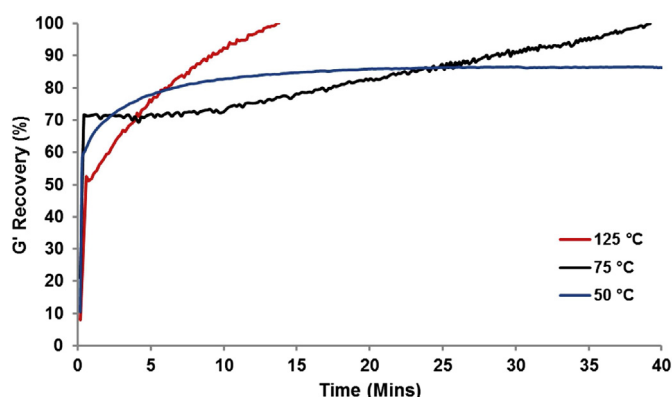


Fig. 7. Recovery of storage modulus as a function of healing time for samples of [4 + 5] at 50, 75, and 125 °C.

(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 $\nu_{\text{max}}/\text{cm}^{-1}$: 3525, 2868, 1644, 1547, 1465, 1387, 1343, 1279, 1241, 1101, 961, 841, 816, 765; ^1H NMR, (CDCl_3 , 400 MHz): δ (ppm) = 8.19–8.09 (8H, m, Ar–H), 8.7.91 (2H, d, J = 8.5 Hz, Ar–H), 7.65 (4H, t, J = 6.0 Hz, Ar–H), 7.53–7.44 (6H, m, Ar–H), 7.34 (2H, d, J = 7.5 Hz, Ar–H), 6.39 (2H, br, CH_2NHCO), 3.72–3.53 (192H, m, $[\text{O}(\text{CH}_2)_2]_n$), 3.38 (4H, q, J = 5.5 Hz, CH_2NHCO), 3.06 (4H, t, J = 7.5 Hz, $\text{CCH}_2\text{CH}_2\text{CH}_2\text{CO}$), 2.27 (4H, t, J = 7.5 Hz, $\text{CCH}_2\text{CH}_2\text{CH}_2\text{CO}$), 2.10 (4H, quin, J = 7.5 Hz, $\text{CCH}_2\text{CH}_2\text{CH}_2\text{CO}$), 1.77 (4H, quin, J = 6.0 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}$); ^{13}C NMR (CDCl_3 , 100 MHz): δ (ppm) = 172.7, 137.8, 134.6, 133.0, 131.7, 131.3, 129.6, 129.0, 128.5, 127.7, 127.4, 127.0, 126.6, 126.5, 123.9, 120.1, 120.0, 119.7, 70.5, 70.4, 70.0, 69.1, 37.9, 36.1, 32.7, 28.9, 26.3; GPC (THF) M_n = 1400 Da, M_w = 2258 Da, D_m = 1.61; MALDI-TOF MS (m/z) calc. for $\text{C}_{118}\text{H}_{176}\text{N}_2\text{O}_{35}\text{Na}$ = 2204.20 Da, found = 2204.81 Da \pm 44n Da; DSC: T_g = -44.8 °C.

Acknowledgements

We thank EPSRC and Domino Printing Sciences UK Ltd. for an Industrial CASE PhD studentship (No. 10002591) in support of LRH. Spectroscopic and thermal data were acquired using instrumentation in the Chemical Analysis Facility (CAF) of the University of Reading. The authors are grateful to the Electron Microscopy Laboratory (EMLab) of the University of Reading for providing access to

the ESEM microscope. Funding for work at the University of Delaware was provided by the Department of Materials Science and Engineering, NIST, and the Center for Neutron Science through award 70 NANOBI0 H256.

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

- [1] Sivakova S, Rowan SJ. *Chem Soc Rev* 2005;34:9–21.
- [2] Burattini S, Colquhoun HM, Greenland BW, Hayes W. In: Gale P, Steed J, editors. *Supramolecular chemistry: from molecules to nanomaterials*. John Wiley & Sons Ltd; 2012.
- [3] Hart LR, Harries JL, Greenland BW, Colquhoun HM, Hayes W. *Polym Chem* 2013;4:4860–70.
- [4] Murphy EB, Wudl F. *Prog Polym Sci* 2010;35:223–51.
- [5] Burattini S, Greenland BW, Chappell D, Colquhoun HM, Hayes W. *Chem Soc Rev* 2010;39:1973–85.
- [6] Bergman SD, Wudl F. *J Mater Chem* 2008;18:41–62.
- [7] Wool RP. *Soft Matter* 2008;4:400–18.
- [8] Hayes W, Greenland BW. *Healable polymer systems*. 1st ed. Cambridge: Royal Society of Chemistry Publishing; 2013.
- [9] Yang Y, Urban M. *Chem Soc Rev* 2013;42:7446–67.
- [10] Döhler D, Michael P, Binder WH. In: Binder WH, editor. *Self-healing polymers: from principles to applications*. Weinheim: Wiley-VCH Verlag GmbH & Co; 2013.
- [11] White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriman SR, et al. *Nature* 2001;409:794–7.
- [12] Cho SH, Andersson HM, White SR, Sottos NR, Braun PV. *Adv Mater* 2006;18:997–1000.
- [13] Keller MW, White SR, Sottos NR. *Adv Funct Mater* 2007;17:2399–404.
- [14] Toohy K, Sottos NR, Lewis J. *Nat Mater* 2007;6:581–5.
- [15] Caruso MM, Blaiszik BJ, White SR, Sottos NR, Moore JS. *Adv Funct Mater* 2008;18:1898–904.
- [16] Toohy KS, Hansen CJ, Lewis JA, White SR, Sottos NR. *Adv Funct Mater* 2009;19:1399–405.
- [17] Ghosh B, Urban M. *Science* 2009;323:1458–60.
- [18] Chen X, Dam MA, Ono K, Mal A, Shen H, Nutt SR, et al. *Science* 2002;295:1698–702.
- [19] Amamoto Y, Kamada J, Otsuka H, Takahara A, Matyjaszewski K. *Angew Chem Int Ed* 2011;50:1660–3.
- [20] Adzima BJ, Kloxin CJ, Bowman CN. *Adv Mater* 2010;22:2784–7.
- [21] Zheng P, McCarthy TJ. *J Am Chem Soc* 2012;134:2024–7.
- [22] Burnworth M, Tang L, Kumpfer JR, Duncan AJ, Beyer FL, Fiore GL, et al. *Nature* 2011;472:334–8.
- [23] Montarnal D, Cordier P, Soulié-Ziakovic C, Tournilhac F, Leibler L. *J Polym Sci A Polym Chem* 2008;46:7925–36.
- [24] Wang Q, Mynar JL, Yoshida M, Lee E, Lee M, Okuro K, et al. *Nature* 2010;463:339–43.
- [25] Burattini S, Greenland BW, Hermida Merino D, Weng W, Seppala J, Colquhoun HM, et al. *J Am Chem Soc* 2010;132:12051–8.
- [26] Montarnal D, Capelot M, Tournilhac F, Leibler L. *Science* 2011;334:965–8.
- [27] Capelot M, Montarnal D, Leibler L, Tournilhac F. *J Am Chem Soc* 2012;134:7664–7.
- [28] Barthel MJ, Rudolph T, Teichler A, Paulus RM, Vitz J, Hoepfner S, et al. *Adv Funct Mater* 2013;23:4921–32.
- [29] Köttritzsch J, Stumpf S, Hoepfner S, Vitz J, Hager MD, Schubert US. *Macromol Chem Phys* 2013;214:1636–49.

- [30] Cordier P, Tournilhac F, Soulié-Ziakovic C, Leibler L. *Nature* 2008;451:977–80.
- [31] Chen Y, Kushner AM, Williams GA, Guan Z. *Nat Chem* 2012;4:467–72.
- [32] Bosman AW, Sijbesma RP, Meijer EW. *Mater Today* 2004;7:34–9.
- [33] Folmer B, Sijbesma RP, Versteegen RM, van der Rijt JAJ, Meijer EW. *Adv Mater* 2000;12:874–8.
- [34] Herbst F, Seiffert S, Binder WH. *Polym Chem* 2012;3:3084–92.
- [35] Bode S, Zedler L, Schacher FH, Dietzek B, Schmitt M, Popp J, et al. *Adv Mater* 2013;25:1634–8.
- [36] Burattini S, Colquhoun HM, Fox JD, Friedmann D, Greenland BW, Harris PJF, et al. *Chem Commun* 2009:6717–9.
- [37] Burattini S, Colquhoun HM, Greenland BW, Hayes W. *Faraday Discuss* 2009;143:251–64.
- [38] Fox J, Wie JJ, Greenland BW, Burattini S, Hayes W, Colquhoun HM, et al. *J Am Chem Soc* 2012;134:5362–8.
- [39] Hart LR, Hunter JH, Nguyen NA, Harries JL, Greenland BW, Mackay ME, et al. *Polym Chem* 2014;5:3680–8.
- [40] Vaiyapuri R, Greenland BW, Colquhoun HM, Elliott JM, Hayes W. *Polym Chem* 2013;4:4902–9.
- [41] Iverson BL, Lokey RS. *Nature* 1995;375:303–5.
- [42] Nguyen JQ, Iverson BL. *J Am Chem Soc* 1999;121:2639–40.
- [43] Cubberley MS, Iverson BL. *J Am Chem Soc* 2001;123:7560–3.
- [44] Gabriel GJ, Iverson BL. *J Am Chem Soc* 2002;124:15174–5.
- [45] Reczek JJ, Iverson BL. *Macromolecules* 2006;39:5601–3.
- [46] Alvey PMP, Ono RJR, Bielawski CCW, Iverson BL. *Macromolecules* 2013;46:718–26.
- [47] Colquhoun HM, Zhu Z, Williams DJ, Drew MGB, Cardin CJ, Gan Y, et al. *Chem Eur J* 2010;16:907–18.
- [48] Greenland BW, Burattini S, Hayes W, Colquhoun HM. *Tetrahedron* 2008;64:8346–54.
- [49] Colquhoun HM, Zhu Z, Williams DJ. *Org Lett* 2003;5:4353–6.
- [50] Hansen JG, Feeder N, Hamilton DG, Gunter MJ, Becher J, Sanders JKM. *Org Lett* 2000;2:449–52.
- [51] Oskolkova OV, Saf R, Zenzmaier E, Hermetter A. *Chem Phys Lipids* 2003;125:103–14.
- [52] Zinke A, Troger H, Ziegler E. *Berichte Dtsch Chem Ges* 1940;73:1042–8.
- [53] Huang M. *J Am Chem Soc* 1946;68:2487–8.
- [54] Huang M. *J Am Chem Soc* 1949;71:3301–3.
- [55] Rico P. *Angew Chem Int Ed Engl* 1968;7:120–8.
- [56] Colquhoun HM, Zhu Z, Cardin CJ, Gan Y. *Chem Commun* 2004:2650–2.
- [57] Colquhoun HM, Zhu Z, Cardin CJ, Gan Y, Drew MGB. *J Am Chem Soc* 2007;129:16163–74.
- [58] Tian F, Jiao D, Biedermann F, Scherman OA. *Nat Commun* 2012;3:1207.