DIRECT FUNCTIONALIZATION OF KEVLAR® WITH COPOLYMERS CONTAINING SULFONYL NITRENES

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14. ABSTRACT

Generating innovative methods to functionalize fibers and interfaces are important strategies for developing coatings that impart new or improved properties to a given material. In this work, we present a method for functionalizing highly inert poly(p-phenylene terephthalamide) (Kevlar®) fibers via thermal generation of an electrophilic nitrene, while preserving the mechanical properties of the aramid. Because of the high affinity of the sulfonyl nitrene singlet state for aromatic rings, the use of a sulfonyl azide-based copolymer allows the covalent grafting of a wide variety of common commercial polymers to Kevlar. Also, by using reactive ester copolymers, an avenue for the attachment of more exotic or delicate functionalities like small molecules, dyes, and biomolecules through postpolymerization modification is described.

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FIBERS	POLYMERS	ARAMID FIBERS	TENSILE PROPERTIES
AZIDES	SYNTHESIS	EPOXY COMPOSITES	CHEMICAL PROPERTIES
KEVLAR	MONOMERS	SURFACE MODIFICATION	
TEXTILES	DEGRADATION	AMBIENT TEMPERATURE	
SURFACES	MODIFICATION		

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PAPER

Direct functionalization of Kevlar® with copolymers containing sulfonyl nitrenes†

Jeremy Yatvin,[a] Shalli A. Sherman,[b] Shaun F. Filocamo[b] and Jason Locklin*[a]

Generating innovative methods to functionalize fibers and interfaces are important strategies for developing coatings that impart new or improved properties to a given material. In this work, we present a method for functionalizing highly inert poly(*p*-phenylene terephthalamide) (Kevlar®) fibers *via* thermal generation of an electrophilic nitrene, while preserving the mechanical properties of the aramid. Because of the high affinity of the sulfonyl nitrene singlet state for aromatic rings, the use of a sulfonyl azide-based copolymer allows the covalent grafting of a wide variety of common commercial polymers to Kevlar. Also, by using reactive ester copolymers, an avenue for the attachment of more exotic or delicate functionalities like small molecules, dyes, and biomolecules through postpolymerization modification is described.

Introduction

Since the development of poly(*p*-phenylene terephthalamide) fibers by Stephanie Kwolek at DuPont in 1965,[1] Kevlar® and other polyaramids have found utility in hundreds of different applications due to their remarkable chemical and mechanical properties. Pristine Kevlar fibers display high tensile strength,[2] thermal stability,[3] and resistance to mechanical degradation.[4] These superior properties are primarily derived from the highly conjugated and extensively hydrogen bonded nature of the aramid backbone. This same high degree of conjugation, along with the deactivated nature of the aryl backbone and lack of reactive functional groups, also makes Kevlar and other aramids difficult to process and derivatize using reactive coating methods, which are effective strategies used to impart new properties onto textiles such as anti-wrinkle technology,[5] hydrophobic,[6] or antimicrobial coatings.[7]

Current methods that have been used to functionalize Kevlar include epoxy resins,[8] electrochemical deposition,[9] impregnation,[10] isocyanates,[11] radiation, plasma, or chemical radical generation,[12] conventional solution-based electrophilic aromatic substitution,[13] silanation,[14] or hydrolysis with strong acids to generate reactive end groups.[15] Each of these approaches has critical issues that limit their widespread

utility. Most employ harsh chemistry that leads to degradation of the fibers or a functionalizing moiety, while others involve exotic strategies and unstable compounds. Among these approaches are techniques that do not generate covalent bonds between the coating and the aramid fibers, and therefore produce coatings that are subject to dewetting, delamination, and leaching. It is also important to note that several of these techniques depend on exposure to chloride ions, which are known to damage Kevlar.[16]

In order to circumvent these issues, we have developed a simple strategy that utilizes a *p*-styrene sulfonyl azide (SSAz) monomer[17] to generate covalent graft points between a copolymer coating and Kevlar fabric. SSAzs can form covalent bonds *via* an excited nitrene,[18] which is generated through the decomposition and subsequent elimination of nitrogen gas from the azide. The elimination occurs in the presence of UV light or heat.[19] This reactive nitrene can perform several chemistries: C–H or O–H insertions, addition across double bonds to form aziridines, trigger homolytic cleavage of C–H bonds followed by recombination, or electrophilic addition to aromatic rings.[20] There are two mechanisms of nitrene C–H insertion: either a direct insertion from the singlet state into a double bond, or hydrogen atom extraction by a triplet state nitrene and subsequent radical–radical recombination between the radical center and the sulfonyl nitrogen radical, both of which lead to covalent bond formation.

SSAzs differ from other C–H grafting chemistries like diradicaloid benzophenone,[7a,21] or carbenes derived from diaryl-diazonium salts,[22] α-diazoesters,[23] or diazirines[24] in several important ways. First, polymers incorporating SSAz as a comonomer afford the unique combination of long-term stability under ambient conditions, easy synthetic accessibility,

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a choice of either photochemical or thermal activation, and the high affinity of the sulfonyl nitrene singlet state for aromatic rings. Perfluorophenylazide based grafting chemistry, which has been used extensively by the Yan group,[25] has a similar reactivity as SSAzs; however the high fluorine content of perfluorophenylazides leads to incompatible wetting on different polymer interfaces, which prevents thin coatings with consistent thickness and uniformity. SSAzs on the other hand are generally more compatible with respect to wetting and do not suffer from this issue. The SSAz copolymers described in this work were all synthesized from low-cost, commercially available starting materials and are stable indefinitely under ambient conditions.

The SSAz monomer starts to undergo thermal decomposition and nitrene generation at approximately 120 °C, with maximum nitrene generation kinetics occurring at 180 °C.[17] The most important aspect of these materials for this work is that while sulfonyl azides facilely insert into *alkyl* C–H bonds, this functionality is even more reactive towards *aryl* groups,[19b] which is critical in covalent grafting to substrates like Kevlar with high aryl content. One recent example that demonstrates the reactivity of nitrenes with a polyaramid substrate is work by McVerry *et al.* in which a perfluorophenyl azide-terminated polyethyleneglycol was grafted onto a polyaramid reverse-osmosis filter using photochemical activation.[26]

The copolymerization of SSAz with other monomers allows for the grafting of a large variety of heat or UV stable polymeric functionalities to the surface of Kevlar *via* the mechanism in Scheme 1. Since Kevlar and other polyaramids are known to have high thermal stability but are susceptible to UV-catalyzed degradation,[27] we have used thermal grafting in this work. Thermal grafting also provides access to the entire geometry of the fibers, rather than just the immediate surface where UV light is limited by substrate transparency and penetration depth. To demonstrate the versatility of thermal grafting onto aramid substrates, we have synthesized several different SSAz containing copolymers. Common monomers such as acrylonitrile and 4-vinylbenzyl chloride were copolymerized with SSAz to display the effectiveness of covalent grafting despite highly variable polymer wettability and solubility conditions. Poly-4-vinyl-*N*-benzyl-*N*-methylbutan-1-amine and polymethacrylic acid copolymers were also synthesized as suitable cationic and anionic base polymers for layer-by-layer (LBL) deposition on the surface of Kevlar. This was followed with precipitation of TiO_2 in order to directly observe the coating *via* EDS (energy-dispersive X-ray spectroscopy), WDS (wavelength-dispersive X-ray spectroscopy) and SEM (scanning electron microscopy). We also copolymerized SSAz with the pentafluorophenol acrylate (PFPA) monomer, an activated ester with superior utility for post-polymerization modification of surfaces.[28] The use of PFPA allows the attachment of more delicate or complex functionality that would not survive the initial polymerization or grafting procedures, or would be difficult to synthesize as a copolymer. Most of the previous work for functionalizing Kevlar surfaces focused on small molecule derivatization; however by using SSAz we can take advantage of the fact that
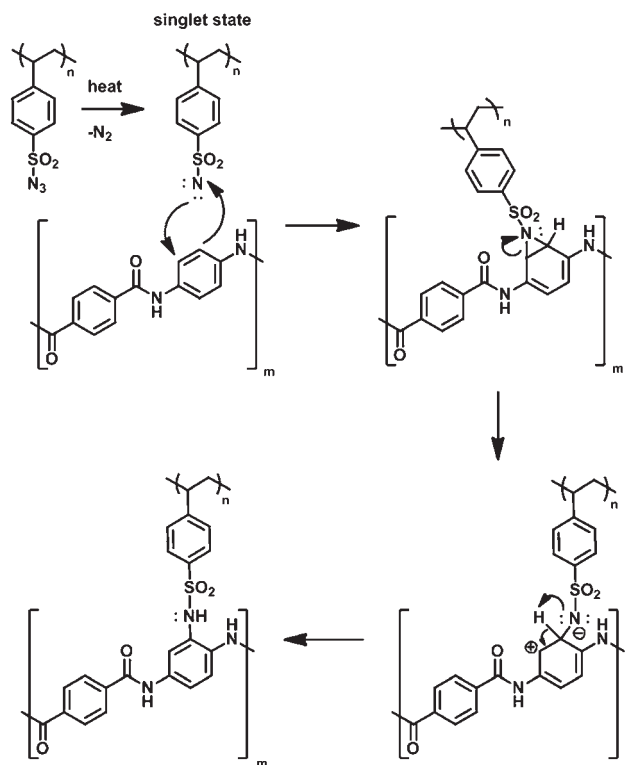
Scheme 1 Arrow pushing mechanism of the grafting of a styrene sulfonyl azide containing copolymer onto a Kevlar substrate.

polymeric materials are easier to process and have superior coating properties.

Materials and procedure

Materials

All compounds were purchased from Alpha-Aesar, TCI, or Sigma-Aldrich and unless otherwise noted were used as received. Methyl methacrylate and 4-vinylbenzyl chloride were purified by flashing through basic alumina plugs. Acrylonitrile was purified by flashing though a neutral alumina plug. Methacrylic acid was purified by vacuum distillation. Pentafluorophenol acrylate was synthesized according to a previously published procedure.[29] 850 Denier Kevlar KM2 was obtained from Barrday, and was cleaned by sonicating in acetone for 30 minutes, sonicating in hexane for 30 minutes, stirring in 2% w/w sodium borate solution for 1 h at 85 °C, and then stirring in water at 75 °C for 1 h, followed by drying in a vacuum oven at room temperature.

Equipment

^{1}H NMR and ^{13}C NMR of small molecules were taken on a Varian Mercury 300 MHz NMR. Polymer spectra were taken on a Varian Inova 500 MHz NMR. FTIR studies were done using a Thermo-Nicolet model 6700 spectrometer equipped with a variable angle grazing angle attenuated total reflection

(GATR-ATR) accessory (Harrick Scientific) at 64 scans with 4 cm^{-1} resolution. Electron dispersive spectroscopy and wavelength dispersive spectroscopy were taken on a JEOL JXA-8600 Electron Microprobe at 20 kV. Scanning electron microscopy was taken on a FEI Inspec F FEG SEM at 20 kV. Fluorescence microscopy pictures were taken using an 8 megapixel digital camera on a Zeiss AX10 Observer inverted microscope with an X-cite Series 120 fluorescent light source and Chroma Technology filter model 11 000 FITC UV filter (350 nm excitation, >430 nm emission). Tensile testing was done on an Instron 5500R Series Model 4302 with reported values being the average of 15 pulled yarns from the warp direction of the Kevlar sample. The tensile testing procedure from ASTM D279/D7269M was used, with a 1 kN load cell, and 10 inch yarns with 2.8 twists per inch in the Z direction. A Mettler Toledo TGA/SDTA851 was used to perform thermogravimetric analysis on samples at a heating rate of 10 °C min^{-1}. Nitrogen at 50 mL min^{-1} was used as the carrier gas.

Styrene sulfonyl chloride

Synthesized using the procedure developed by Schuh et al.[17] The crude product was passed through a silica plug in 1:1 ethyl acetate–hexane (78% yield) and stored in the freezer at −20 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 7.99 (td, J = 8.4 Hz, 2.4 Hz, 2H, H–C=C–SO$_2$) 7.60 (td, J = 6.9 Hz, 1.5 Hz, 2H, H–C=C–CH$_2$) 6.78 (dd J = 17.7 Hz, 10.8 Hz, H–C=CH$_2$) 5.97 (d, J = 17.7 Hz, H_{cis}CH–C=CH$_2$) 5.54 (d, J = 10.8 Hz, H_{trans}CH–C=CH$_2$). ^{13}C NMR (75 MHz, CDCl3) δ = 144.4 (C$_{ar}$–SO$_2$N$_3$), 142.9 (C$_{ar}$–CH), 134.7 (CH=CH$_2$), 127.4 (2 × C$_{ar}$), 1 27.1 (2 × C$_{ar}$), 119.3 (–CH$_2$=CH).

Styrene sulfonyl azide (1)

Synthesized according to Schuh et al. (74% yield).[17] When handling the SSAz monomer, it is important to note that it is stable under cold (−20 °C) storage, but will form an insoluble solid if stored neat at room temperature overnight after 24 hours in the presence of light. It should also not be subjected to temperatures above ~30 °C in a concentrated form, as this can also result in an insoluble mass. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 7.91 (d, 8.4 Hz, H–C=C–SO$_2$) 7.61 (d, 8.4 Hz, H–C=C–CH$_2$) 6.78 (dd, 17.1 Hz, 11.1 Hz, H–C=CH$_2$) 5.95 (d, 17.7 Hz, H_{cis}CH–C=CH$_2$) 5.52 (d, 10.8 Hz, H_{trans}CH–C=CH$_2$). ^{13}C NMR (75 MHz, CDCl$_3$) δ = 143.7 (C$_{ar}$–SO2N3), 136.7 (C–CH$_{ar}$), 134.6 (CH=CH$_2$), 127.6 (2 × C$_{ar}$), 126.9 (2 × C$_{ar}$), 118.6 (CH$_2$=CH). IR (neat cm^{-1}): 3094, 3069 2128, 1593, 1400, 1372, 1190, 1169, 1088, 989, 927, 844, 759, 748, 650, 597.

Polymethyl methacrylate-co-styrene sulfonyl azide (pMMA-co-SSAz) (2)

1.0 g (9.98 mmol) methyl methacrylate, 104 mg (0.5 mmol) styrene sulfonyl azide, and 18 mg (0.11 mmol) of AIBN were added to an oven dried Shlenk flask with 10 mL dry toluene. The solution was degassed for 30 minutes with argon, before placing on a Shlenk line under nitrogen for reaction, and the headspace purged. The reaction was conducted at 65 °C for 24 hours, then precipitated into cold methanol and suction fil-

tered to obtain 270 mg of off-white solid (23% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 7.87 (bd, 2H) 7.20 (bd, 2H) 3.60 (bs, 27H) 3.01 (bm, 2H) 0.5–2.1 (bm, 46H).

Poly-4-vinylbenzyl chloride-co-styrene sulfonyl azide (p4VBC-co-SSAz) (3)

2 g (13.1 mmol) of 4-vinylbenzyl chloride, 144 mg (0.69 mmol) styrene sulfonyl azide, and 47 mg (0.28 mmol) of AIBN were added to an oven dried Shlenk flask with 10 mL dry toluene. The solution was degassed for 30 minutes with argon, before placing on a Shlenk line under nitrogen for reaction, and the headspace purged. The reaction was conducted at 65 °C for 54 hours, then precipitated into cold methanol and suction filtered to obtain 1.95 g of off-white solid (91% yield).). ^{1}H NMR (500 MHz, DMSO-d$_6$) δ = 7.5–7.6 (bm, 4H) 6.9–7.5 (bm, 20H) 6.3–6.9 (bm, 20H) 4.6–4.9 (bs, 20H) 1.0–2.3 (bm, 30H).

Poly-4-vinyl-N-benzyl-N-methylbutan-1-amine-co-styrene sulfonyl azide (p4VBA-co-SSAz) (4)

0.94 g of P4VBC-co-SSAz was dissolved in 18 mL dry THF, and 1.17 g (13.4 mmol) of 4-methyl-butan-1-amine which had been dried over molecular sieves for 24 hours was added and the reaction conducted on a Shlenk line under nitrogen at room temperature. After 72 hours the developed amine salt was vacuum filtered off, the solvent removed by evaporation, and the crude product redissolved in boiling acetone. The polymer was precipitated by quickly adding this solution to water and suction filtering the solid to obtain 1.25 g of off-white solid. (95% yield) Note: this polymer should be stored as a stock solution in chloroform. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 6.4–8.0 (bd, 5H) 3.2–3.7 (bs, 2H) 0.7–2.9 (bm, 16 H).

Polyacrylonitrile-co-styrene sulfonyl azide (pAN-co-SSAz) (5)

1 g (18.8 mmol) of acrylonitrile, 210 mg (1 mmol) styrene sulfonyl azide, and 68 mg (0.4 mmol) of AIBN was added to an oven dried Shlenk flask with 10 mL dry toluene. The solution was degassed for 30 minutes with argon, before placing on a Shlenk line under nitrogen for reaction, and the headspace purged. The reaction was conducted at 65 °C for 24 hours. Toluene was evaporated off, and the solid was redissolved in DMF and precipitated into ethyl acetate twice. The solid polymer was suction filtered to obtain 0.40 g of yellow solid (33% yield). ^{1}H NMR (500 MHz, DMSO-d$_6$) δ = 7.4–8.2 (bm 4H) 3.0–3.3 (bm, 11H) 1.6–2.3 (bm 28H).

Polymethacrylic acid-co-styrene sulfonyl azide (pMAA-co-SSAz) (6)

1 g (11.6 mmol) of methacrylic acid, 130 mg styrene sulfonyl azide, and 42 mg (0.25 mmol) of AIBN was added an oven dried Shlenk flask with 10 mL dry acetonitrile. The solution was degassed for 30 minutes with argon, before placing on a Shlenk line under nitrogen for reaction, and the headspace purged. The reaction was conducted at 65 °C for 24 hours, then 10 mL of methanol was then added to the reaction to fully solubilize the crude polymer. The solution was then precipitated into ethyl acetate and suction filtered to obtain 0.67 g of off-white solid (59% yield). ^{1}H NMR (500 MHz, DMSO-d$_6$)

δ = 12.1–12.5 (bs, 20H) 7.9–8.0 (bm, 2H) 7.6–7.7 (bm, 2H) 1.3–2.1 (bm, 40H) 0.5–1.3, 60H).

Polypentafluorophenolacrylate-*co*-styrene sulfonyl azide (pPFPA-*co*-SSAz) (7)

1.0 g (4.2 mmol) of pentafluorophenol acrylate, 46 mg (0.22 mmol) styrene sulfonyl azide, and 15 mg (0.09 mmol) AIBN were added to an oven dried Shlenk flask with 10 mL benzene. The solution was degassed for 1 hour, before placing on nitrogen line for reaction, and the headspace purged. The reaction was conducted at 65 °C for 24 hours, then the solvent was removed by rotary evaporation. The clear viscous liquid remaining was redissolved in THF, precipitated into cold methanol, and suction filtered to obtain 0.42 g of white solid (26% yield).). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 7.87 (bd, 2H) 7.41 (bd, 2H) 1.5–3.1 (bm, 65H).

Kevlar coating

A clean 2.54 cm × 2.54 cm swatch of Kevlar was dipcoated in a 10 mg mL^{-1} solution of polymer in a favorable solvent, then dried in a vacuum oven at room temperature. The swatch was then placed on a hotplate held at 180 °C in a nitrogen atmosphere under a piece of stainless steel that had been previously heated to the same temperature. After 1 hour, the swatch was removed, heavily sonicated in the original coating solvent and dried in a vacuum oven at room temperature.

Layer-by-layer (LbL) deposition and titania precipitation

A coated swatch of Kevlar was soaked for 2 minutes in 0.1 mM HCl solution (pH = 4). Dipcoating was done by alternating between 0.1% w/w polystyrene sulfonate and 0.1% w/w branched polyethyleneimine solutions, with a deionized water washing step between each dip. This process was repeated to form 5 layers. After LbL, the swatch was dried in a vacuum oven at room temperature. TiO$_2$ was precipitated by placing the coated swatch in 25 mL of a 25 mM (0.076 g/25 mL) Tris buffer solution, then adding 0.5 mL of 50% w/w aqueous dihydroxybis(ammoniumlactato)titanium(IV) and placing on a shaker at 250 rpm for 6 hours.[30] The swatch was removed, rinsed with deionized water, and dried in a vacuum oven at room temperature.

Attachment of 1-pyrenemethylamine

A Kevlar swatch was dipped in 50 mg mL^{-1} PPFPA-*co*-SSAz THF solution, dried at room temperature in a vacuum oven, then cured for 1 h at 180 °C. After curing, the swatch was sonicated in THF to remove any physisorbed polymer. The swatch was then placed in an oven dried Shlenk flask under inert atmosphere. Solutions of 40 mM 1-pyrenemethylamine hydrochloride and 80 mM triethylamine were prepared in DMF and added to the flask, and the mixture was stirred for 1 hour at room temperature under nitrogen. The swatch was Soxlet extracted with acetone overnight in the dark to wash away excess 1-pyrenemethylamine and dried in a vacuum oven at room temperature.

Results and discussion

Scheme 2 shows the variety of monomers that were copolymerized with SSAz (1) in this work, including: methyl methacrylate (2), 4-vinylbenzyl chloride (3), poly-4-vinyl-*N*-benzyl-*N*-methyl-butan-1-amine (4), acrylonitrile (5), methacrylic acid (6), and pentafluorophenol acrylate (7), a monomer easily synthesized in one step from methacryloyl chloride and pentafluorophenol.[28] All of these polymerizations were successful, provided the reaction was conducted under suitably dilute conditions. It is of importance to note that all SSAz free radical polymerizations should be performed at concentrations of no more than ~10–20% v/v monomer, as more concentrated reactions gel after several hours at polymerization temperature. Regardless of feed monomer, this gel was insoluble in common solvents, likely indicating a crosslinked polymer network. Nitrene formation at 65 °C is negligible, however Breslow *et al.* found that in the presence of a hydroperoxide radical initiator, benzene sulfonyl azide showed evidence of decomposition to a benzene sulfonyl radical.[19b] It follows that in this system, AIBN can initiate the radical decomposition of SSAz, creating free radicals along the polymer backbone, leading to premature crosslinking. By avoiding more concentrated or neat polymerizations, this side reaction can be circumvented.

All the polymers synthesized in this work contained the SSAz crosslinker at 5 mol%, which was chosen to provide a balance between sufficient crosslinking points for grafting while still preserving the properties of a homopolymer prepared from the primary monomer. The resulting polymers were stable for months under ambient conditions with one exception. To produce an amine functionalized polymer, poly-4-vinylbenzyl chloride-*co*-styrene sulfonyl azide (p4VBC-*co*-
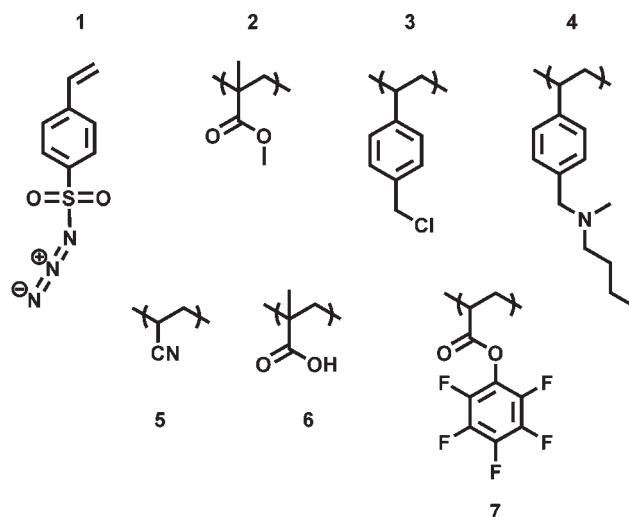
Scheme 2 Styrene sulfonyl azide monomer (**1**) and copolymer structures used in this work: polymethyl methacrylate (**2**), polyvinylbenzyl chloride (**3**), poly-4-vinyl-*N*-benzyl-*N*-methylbutan-1-amine (**4**), poly-acrylonitrile (**5**), polymethacrylic acid (**6**), and polypentafluorophenol acrylate (**7**).

SSAz) was post-polymerization modified with *N*-butylmethyl-amine to yield poly-4-vinyl-*N*-benzyl-*N*-methylbutan-1-amine-*co*-styrene sulfonyl azide (**p4VBA-*co*-SSAz**). After purification, if left in the dry state, pVBA-*co*-SSAz becomes completely insoluble after several hours. This is surprising because the precursor, p4VBC-*co*-SSAz, is stable under ambient conditions. Because water is used to precipitate the polymer and remove leftover *N*-methylbutylamine, we hypothesize that a small proportion of the benzyl chloride groups may remain after post-polymerization modification, which can result in the amine catalyzed formation of dibenzyl ether crosslinks. Sufficient crosslinking renders the polymer insoluble. However, p4VBA-*co*-SSAz is stable for months if immediately dissolved and kept in an anhydrous chloroform solution.

The polymers produced in this study were cured onto Kevlar swatches at 180 °C for 1 hour, and produced coatings such as those seen in the SEM images in Fig. 1A and B. These images of polymer coated Kevlar demonstrate the nature of the attachment chemistry. The clearest features are the crosslinked polymer bridges that extend between Kevlar strands (Fig. 1A), and the highly smooth coating on the yarn surface (Fig. 1B). The coating is homogeneous across all the strands in a given sample, which indicates uniform distribution and wetting. There were few, if any, defects or voids observed *via* SEM.

By using SSAzs to attach a base polymer like pVBA-*co*-SSAz or polymethacrylic acid-*co*-styrene sulfonyl azide (pMAA-*co*-SSAz), a surface was prepared that was conducive to LbL deposition of anionic polystyrenesulfonate and cationic poly-ethyleneimine. After 5 dipping cycles, a coating of titania nanoparticles were precipitated on the Kevlar substrate using previously described methods.[30] The titania nanoparticles were observable by SEM, EDS, and WDS. Fig. 1C shows an increased surface roughness along with a morphological change due to the precipitated TiO_2, and under high magnification (Fig. 1D), TiO_2 nanoparticles are evident. The presence of titanium on the surface is also apparent in the elemental maps (Fig. 1F–H) generated from EDS and WDS from the Ti Kα peak at 4.511 keV.

To determine whether the mechanical properties were damaged during the curing process or by the presence of the polymer coating, Kevlar yarns were subjected to tensile testing on an Instron, the results of which are shown in Table 1. p4VBA-*co*-SSAz coated and cured (PCC) Kevlar was compared to Kevlar that had been thermally cured without any coating (TC), and to virgin Kevlar. The results indicated that there was minimal difference in the mechanical properties between all three samples. With respect to the virgin Kevlar and the TC
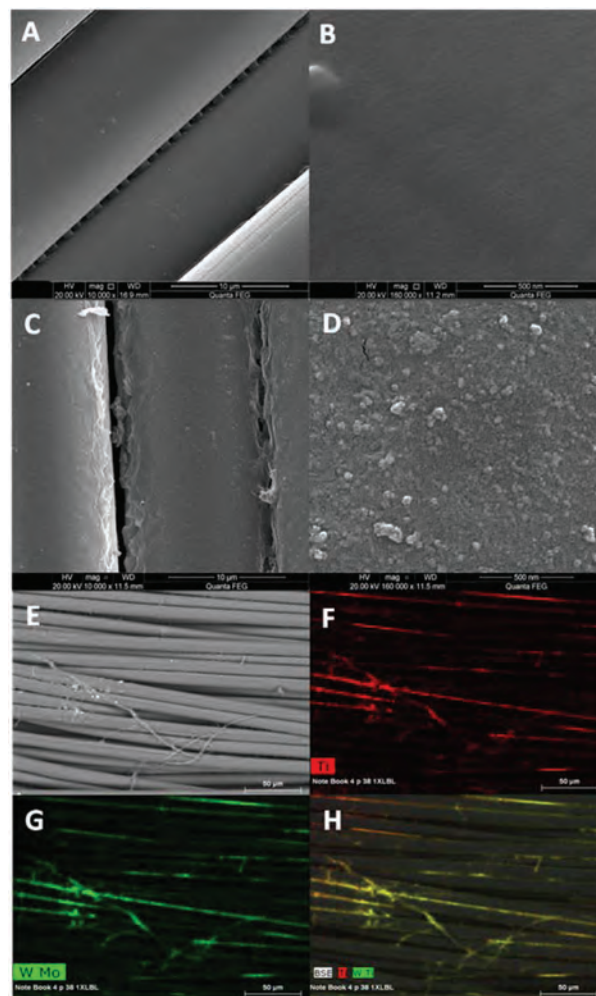

Fig. 1 (A–D) Scanning electron microscope images of (A) SSAz copolymer coated Kevlar with SSAz copolymer cross-bridges; (B) high magnification image of the coated Kevlar fibers which shows the smooth morphology; (C) LBL coated Kevlar with precipitated TiO_2; (D) high magnification image of TiO_2 nanoparticles precipitated on coated Kevlar. (E–H) SSAZ copolymer coated Kevlar elemental mapped at 4.511 keV (Ti Kα line) using (E) backscattered electrons (F) EDS, (G) WDS, and (H) overlaid EDS and WDS data.

Kevlar, there was a slight decrease in tensile stress at max load and energy at break, and a slight increase in Young's modulus. There is essentially no statistical difference in these properties between the PCC Kevlar and the TC Kevlar. The net difference between the virgin Kevlar and the PC Kevlar across the properties measured is 6–14%, which borders the standard devi-

Table 1 Tensile data for untreated Kevlar, thermally cured Kevlar, and Kevlar cured in the presence of p4VBA-*co*-SSAz

	Tensile stress at max load (MPa)	Young's modulus (gf per den)	Energy at break (J)
Virgin Kevlar	20.158 ± 0.818	726.985 ± 7.531	0.923 ± 0.070
Thermal Control (TC)	19.281 ± 0.757	743.618 ± 6.991	0.837 ± 0.055
pVBA-*co*-SSAz (PCC)	18.930 ± 0.783	744.818 ± 10.376	0.808 ± 0.062

ation (4–7%) of the measurements. The close values of the TC and PCC Kevlar tensile results also indicated that the small change in mechanical properties is unrelated to the polymer coating. The thermal curing is done under nitrogen atmosphere to avoid oxidative damage, and it is likely that some molecular rearrangement of water between the amorphous and crystalline regions in the Kevlar is the source of slight mechanical losses.[31] There was, however, a greater tensile strength loss when curing with pMAA-co-SSAz (ESI†). Curing with this polymer derivative caused a 14% loss in tensile stress at max load and modulus, and a 25% loss of energy at break. We hypothesize that acid-catalyzed hydrolysis at the curing temperature is causing some chain-scission in Kevlar, resulting in more significant deterioration of the mechanical properties with this acid containing coating.

Thermogravimetric analysis of a PMMA-co-SSAz coated Kevlar sample showed little change in the thermal properties of the material as compared to the control sample (ESI†). The coated sample had a ~5% weight loss between 250–550 °C, before the decomposition temperature of Kevlar that occurs around 550 °C, which likely corresponds to the degradation of the PMMA-co-SSAz coating.

The pMMA-co-SSAz copolymer was also used to provide direct spectroscopic evidence of the incorporation of a PSAz containing polymer onto Kevlar. Polymethylmethacrylate (PMMA) has two distinct IR peaks at 1728 cm^{-1} and 1149 cm^{-1} (attributed to the ester C=O and C–O stretches) that can be differentiated from bulk Kevlar. Both pMMA-co-SSAz and commercial pMMA were applied to and cured at 180 °C on Kevlar swatches, and the FTIR spectra recorded. Kevlar has a primarily C=O amide I (1645 cm^{-1}), an amide II primarily N–H mode, a C=C$_{aromatic}$ band (1515 cm^{-1}), an amide III with complex contributions (1319 cm^{-1}), a C–O$_{aromatic}$ stretch (1262 cm^{-1}), and a C–H$_{aromatic}$ in-plane vibration peak (1018 cm^{-1}). Fig. 2 shows that after curing and prior to rinsing, both pMMA and pMMA-co-SSAz coated Kevlar contain the pMMA ester carbonyl peak at 1728 cm^{-1} and the C–O peak at 1149 cm^{-1}. However after sonication in dichloromethane, only the Kevlar cured with the pMMA-co-SSAz retains the ester C=O and C–O peaks, indicating that the polymer is still covalently attached.

Finally, in order to demonstrate the flexibility and modularity of this thermal grafting approach, the activated ester monomer PFPA was copolymerized with SSAz. PFPA is notable for its fast and selective reactions with amines (surface confined pseudo-first order rate constant of 0.246 s^{-1} with primary alkyl amines), and reduced susceptibility to hydrolysis.[28] pPFPA-co-SSAz allows the functionalization of Kevlar with moieties not amenable to high temperature curing or inclusion directly as a monomer by acting as an excellent substrate for post-polymerization modification. To demonstrate that the PFPA functionality remains reactive after grafting to Kevlar, 1-pyrenemethylamine was reacted with the coated surface to produce a copolymer containing pendant pyrene moieties. Fig. 3 shows fluorescence microscopy images of the pPFPA-co-SSAz functionalized Kevlar after post-polymeriz-
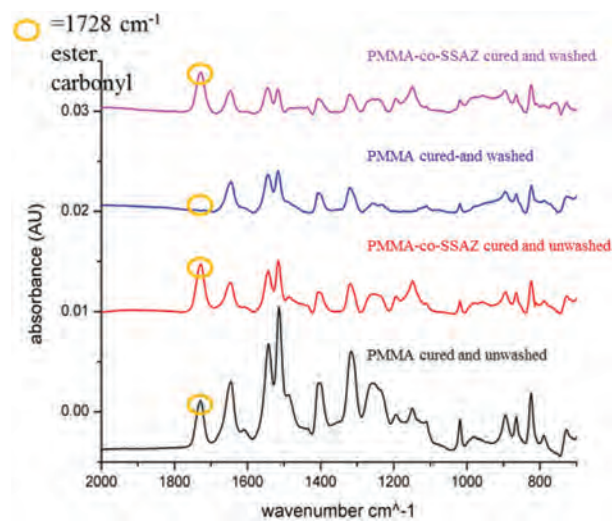

Fig. 2 FTIR spectra demonstrating the robust attachment of PMMA-co-SSAz copolymer to Kevlar. After coating with PMMA or PMMA-co-SSAz the Kevlar swatches display the methacrylic 1728 cm^{-1} ester peak. After rinsing, it is evident that the coating is retained only on the swatch that underwent thermal grafting PMMA-co-SSAz.

ation modification with 1-pyrenemethylamine. The polymer containing pendant pyrene moieties shows a strong blue fluorescence (Fig. 3D), whereas the controls (plain Kevlar, plain Kevlar exposed to 1-pyrenemethyl amine, and Kevlar cured with pPFPA-co-SSAz) only exhibit the inherent green fluorescence of Kevlar (Fig. 3A–C).
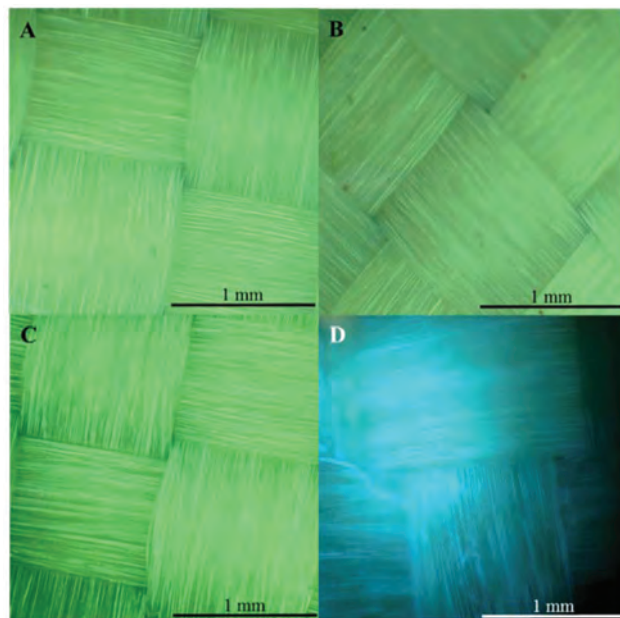

Fig. 3 Fluorescence micrographs of (a) Virgin Kevlar, (b) Kevlar coated with PPFPA-co-SSAz; (c) plain Kevlar immersed in 1-pyrenemethylamine solution; (d) Kevlar coated with pPFPA-co-SSAz that has undergone post-polymerization modification with 1-pyrenemethylamine.

Conclusions

In this work, we have adapted a versatile monomer, *p*-styrene sulfonyl azide, for use in the robust coating of inert aramid textiles. Using this approach, a variety of free radical compatible monomers are amenable to covalent grafting, along with the postpolymerization or post-grafting modification of reactive ester containing copolymers with nucleophilic substrates. The copolymers in this study were cured for 1 hour at 180 °C to ensure full crosslinking, however this curing time and high temperature are likely not necessary in all cases. All the polymers synthesized in this study except the unique case of pVBA-*co*-SSAz did not display any change in properties over several months of experimentation, demonstrating that the SSAz functionality in these polymers is highly stable and can be stored under ambient conditions. It has also been demonstrated that the curing process does not significantly damage the mechanical integrity of Kevlar.

Conflict of interest

The authors declare no competing financial interest.

Acknowledgements

Notes and references

1 H. Mera and T. Takata, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.

2 D. Zhu, B. Mobasher and S. Rajan, *J. Mater. Civ. Eng.*, 2011, **23**, 230.

3 (*a*) X.-G. Li and M.-R. Huang, *J. Appl. Polym. Sci.*, 1999, **71**, 565; (*b*) J. Brown and B. Ennis, *Text. Res. J.*, 1977, **47**, 62.

4 R. Pinto, D. Carr, M. Helliker, L. Girvan and N. Gridley, *Text. Res. J.*, 2012, **82**, 1157.

5 C. M. Welch, *Text. Res. J.*, 1988, **58**, 480.

6 J. Zimmermann, F. A. Reifler, G. Fortunato, L.-C. Gerhardt and S. Seeger, *Adv. Funct. Mater.*, 2008, **18**, 3662.

7 (*a*) V. P. Dhende, S. Samanta, D. M. Jones, I. R. Hardin and J. Locklin, *ACS Appl. Mater. Interfaces*, 2011, **3**, 2830; (*b*) B. B. Hsu and A. M. Klibanov, *Biomacromolecules*, 2010, **12**, 6; (*c*) Y. H. Kim, C. W. Nam, J. W. Choi and J. Jang, *J. Appl. Polym. Sci.*, 2003, **88**, 1567.

8 (*a*) J. R. Yeh and J. L. Teply, *J. Compos. Mater.*, 1988, **22**, 245; (*b*) J. R. Strife and K. M. Prewo, *J. Compos. Mater.*, 1979, **13**, 264; (*c*) A. Mittelman and I. Roman, *Composites*, 1990, **21**, 63.

9 B. K. Little, Y. Li, V. Cammarata, R. Broughton and G. Mills, *ACS Appl. Mater. Interfaces*, 2011, **3**, 1965.

10 H. Mahfuz, F. Clements, V. Rangari, V. Dhanak and G. Beamson, *J. Appl. Phys.*, 2009, **105**, 064307.

11 W. Chen, X.-M. Qian, X.-Q. He, Z.-Y. Liu and J.-P. Liu, *J. Appl. Polym. Sci.*, 2012, **123**, 1983.

12 (*a*) Y. Zhang, Z. Jiang, Y. Huang and Q. Li, *Fibers Polym*, 2011, **12**, 1014; (*b*) J. Luo and Y. Sun, *Ind. Eng. Chem. Res.*, 2008, **47**, 5291; (*c*) G. Fan, J. Zhao, Y. Zhang and Z. Guo, *Polym. Bull.*, 2006, **56**, 507; (*d*) G. S. Sheu and S. S. Shyu, *J. Adhes. Sci. Technol.*, 1994, **8**, 531.

13 (*a*) Y. Wu and G. C. Tesoro, *J. Appl. Polym. Sci.*, 1986, **31**, 1041; (*b*) R. Benrashid and G. C. Tesoro, *Text. Res. J.*, 1990, **60**, 334; (*c*) T. K. Lin, B. H. Kuo, S. S. Shyu and S. H. Hsiao, *J. Adhes. Sci. Technol.*, 1999, **13**, 545.

14 (*a*) J. Li and F. B. Ye, *Plast., Rubber Compos.*, 2010, **39**, 264; (*b*) T. Ai, R. Wang and W. Zhou, *Polym. Compos.*, 2007, **28**, 412.

15 G. Li, C. Zhang, Y. Wang, P. Li, Y. Yu, X. Jia, H. Liu, X. Yang, Z. Xue and S. Ryu, *Compos. Sci. Technol.*, 2008, **68**, 3208.

16 A. Akdag, H. B. Kocer, S. D. Worley, R. M. Broughton, T. R. Webb and T. H. Bray, *J. Phys. Chem. B*, 2007, **111**, 5581.

17 K. Schuh, O. Prucker and J. Rühe, *Macromolecules*, 2008, **41**, 9284.

18 G. K. Raghuraman, K. Schuh, O. Prucker and J. Rühe, *Langmuir*, 2009, **26**, 769.

19 (*a*) M. F. Sloan, W. B. Renfrow and D. S. Breslow, *Tetrahedron Lett.*, 1964, **5**, 2905–2909; (*b*) D. S. Breslow, M. F. Sloan, N. R. Newburg and W. B. Renfrow, *J. Am. Chem. Soc.*, 1969, **91**, 2273.

20 E. F. V. Scriven, *Azides and Nitrenes: Reactivity and Utility*, Academic Press, Orlando, 1984.

21 (*a*) S. K. Christensen, M. C. Chiappelli and R. C. Hayward, *Macromolecules*, 2012, **45**, 5237; (*b*) O. Prucker, C. A. Naumann, J. Rühe, W. Knoll and C. W. Frank, *J. Am. Chem. Soc.*, 1999, **121**, 8766.

22 (*a*) M. G. Moloney, W. Ebenezer and K. Awenat, *United States of America Pat*, US6699527 B1, 2004; (*b*) K. M. Awenat, P. J. Davis, M. G. Moloney and W. Ebenezer, *Chem. Commun.*, 2005, 990; (*c*) H. Wang, J.-P. Griffiths, R. G. Egdell, M. G. Moloney and J. S. Foord, *Langmuir*, 2008, **24**, 862.

23 R. Navarro, M. Pérez Perrino, O. Prucker and J. Rühe, *Langmuir*, 2013, **29**, 10932.

24 A. Blencowe and W. Hayes, *Soft Matter*, 2005, **1**, 178.

25 (*a*) L. Liu and M. Yan, *Angew. Chem., Int. Ed.*, 2006, **45**, 6207; (*b*) L.-H. Liu and M. Yan, *Acc. Chem. Res.*, 2010, **43**, 1434.

26 B. T. McVerry, M. C. Y. Wong, K. L. Marsh, J. A. T. Temple, C. Marambio-Jones, E. M. V. Hoek and R. B. Kaner, *Macromol. Rapid Commun.*, 2014, **35**, 1528.

27 (*a*) DuPont, 1992; (*b*) S. N. R. Davis and J. W. Chin, in NIST Technical Note 1746, 2012; (*c*) C. Wei, Q. Xinming, H. Xueqiu and L. Jiping, 2011 9th ICRMS, 2011.

28 R. M. Arnold, G. R. Sheppard and J. Locklin, *Macromolecules*, 2012, **45**, 5444.

29 M. Eberhardt, R. Mruk, R. Zentel and P. Théato, *Eur. Polym. J.*, 2005, **41**, 1569.

30 S. Filocamo, R. Stote, D. Ziegler and H. Gibson, *J. Mater. Res.*, 2011, **26**, 1042.

31 (*a*) A. Abu Obaid, J. M. Deitzel, J. W. Gillespie and J. Q. Zheng, *J. Compos. Mater.*, 2011, **45**, 1217; (*b*) M. Fukuda and H. Kawai, *Sen'i Gakkaishi*, 1996, **52**, 582.