



Cite this: *Polym. Chem.*, 2023, **14**, 4205

Bifunctional diazine reagent for covalent dyeing of Kevlar and inert polymer materials†

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We report a convenient bifunctional diazine reagent that is capable of photochemically modifying inert polymers, particularly those used in fibers and textiles for ballistics and blast protective gear, such as *para*-aramid and ultra-high molecular weight polyethylene (UHMWPE). The reagent's structure features a trifluoromethyl diazine group as a precursor to a carbene that binds the textile surface. On the reagent's other terminus, a benzyl bromide group acts as a site accessible for substitution reactions. As a bench-stable liquid, this bifunctional diazine can be prepared on gram-scale quantities and rapidly activates under long-wave UV light. A series of fabrics made from Kevlar, Spectra, Dyneema, etc. were functionalized with this diazine reagent, then subsequently dyed by binding nucleophilic dyes. The resulting coloration was found to be robust and colorfast with respect to water, organic solvent, and simulated laundering with detergent, and the strength of the fibers or fabrics was retained through the dyeing process, as shown through TGA and mechanical break testing. Overall, this carbene-based method provides a general, mild strategy for the covalent attachment of small molecules to textiles made from inert polymers, particularly *para*-aramids and UHMWPE, as well as nylon and fiber blends of these materials, and has potential use in next-generation protective outerwear.

Received 4th August 2023,
Accepted 27th August 2023

DOI: 10.1039/d3py00907f

rscl.li/polymers

Introduction

Lightweight, high-strength synthetic fibers made from polymers such as *para*-aramids (e.g., Kevlar® or Twaron®) or ultra-high molecular weight polyethylene (abbreviated UHMWPE, e.g., Spectra® or Dyneema®) have been implemented in a growing number of diverse applications in ropes, cables, tires, cut-resistant gloves, sportswear and athletic apparel, firefighter gear, and various types of law enforcement and military tactical gear related to ballistics and blast protection, such as vests, body armor, face masks, helmets,¹ as well as camouflage-printed flame resistant (FR) uniform fabrics,² and undergarments designed with knit and woven Kevlar components to be breathable and moisture-wicking and to protect lower extremities and soft tissues in buried blast events.³

The chemical basis of Kevlar is the *para*-aramid polymer poly(*p*-phenylene terephthalamide) (abbreviated PPTA)⁴ that is known to have a high melting point, high glass transition point, and superior thermal and chemical resistance properties.⁵ PPTA is converted to Kevlar through industrial fiber and fabric processing methods. Kevlar shows exceptional tensile strength (particularly tensile strength-to-weight ratio),⁶ Young's modulus,⁷ and stability toward thermal⁸ or mechanical degradation.⁹ Kevlar has a strong backbone of amide bonds, efficient interchain hydrogen-bonding interactions, a high degree of crystallinity, and a lack of reactive functional groups, all of which contribute to Kevlar's chemical resistance, including toward dye molecules applied with conventional methods¹⁰ and some functional coatings for use as outerwear. Traditional non-covalent dyes wash off Kevlar readily, and reactive dyes do not have sufficient electrophilic or nucleophilic sites to react and form chemical bonds.¹¹ Additionally, due to the involvement of the amide N–H groups in the hydrogen bonding networks, Kevlar does not form strong intermolecular interactions with small-molecule adsorbents. UHMWPE is also chemically inert due to its hydrocarbon structure and shows resistance to dyeing and the application of coatings. Typically, UHMWPE is processed into fibers and other structures through gel-spinning and drawing.¹² UHMWPE fibers have become ubiquitous in the fields of composite reinforcements and soft armor.¹³

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3py00907f>



Investigating new alternatives for dyeing Kevlar and other inert materials is important for developing next-generation protective outerwear that can be dyed/printed in multi-color patterns, typically in shades of green, brown, tan, and black, and suitable for camouflage in different operational environments.^{14,15} Some alternative methods for dyeing Kevlar include solution dyeing, pad dyeing, or the use of swelling agents. The drawbacks of these methods are their use of strong acids, harsh solvents, or chemical additives that raise environmental concerns for the safe treatment of effluent wastewater streams.^{11,16} Environmentally-friendly methods to dye Kevlar have emerged recently, as in the use of non-thermal plasma (NTP) as part of a pre-treatment regime with renewable materials (e.g., soybean oil, glycerol), and NTP was used as a pre-treatment in conjunction with ScCO_2 to dye Kevlar woven fabrics with disperse or cationic dyes.¹⁷ Similarly, Shim *et al.* used environmentally-friendly supercritical carbon dioxide (ScCO_2) to dye Kevlar knit fabrics through the sorption of disperse dyes.¹⁸ However, all of these methods produce Kevlar fabrics as solid colors in a limited number of monochromatic hues.

Several approaches reported derivatizing the surface of Kevlar or Kevlar composite fibers with chemical methods that introduce covalently-bound functionality, such as the use of acidic amide hydrolysis,¹⁹ *N*-silylation,²⁰ electrophilic bromination/nitration/sulfonation,²¹ and *N*-acylation.²² Yatvin *et al.* reported a significantly milder and more convenient method to covalently graft several polymers to Kevlar through C–H activation.²³ In that approach, various alkenes were first co-polymerized with a sulfonyl azide co-monomer, then the azides were thermally activated to produce electrophilic nitrene intermediates capable of insertion into the aromatic backbone of Kevlar. Aryl and diarylcarbenes have been used as reactive intermediates to functionalize and dye Kevlar fabric and other textile-related polymers, such as cotton (fabric, fibers), nylon-610 (sheet), and UHMWPE (powders).²⁴ These prior carbene-based methods are limited by their lengthy treatment times (>18 h) that are untenable for scale-up and manufacturing processes and by their use of toxic mercury-containing compounds that are unsafe for human health and the environment.

For decades, photo-crosslinking with diazirines as carbene equivalents has been used as a powerful technique in chemical biology for the identification of protein targets for small-molecule binders.²⁵ More recently, diazirines, which can be easily synthesized from ketones,^{25a} have been used in materials science for the crosslinking of unreactive polymers.²⁶ A particularly impressive demonstration of the powerful reactivity of multivalent diazirines was described by Wulff *et al.* using unfunctionalized aliphatic polymers.²⁷ Presently, we propose the use of a bifunctional, photoactivated small-molecule halogenated carbene precursor to react efficiently through covalent bond formation²⁸ with the backbone of Kevlar to provide covalently-attached electrophilic sites for the attachment of various dyes (Fig. 1). In step 1 (carbene functionalization), the bifunctional carbene precursor molecule bearing a benzyl bromide fragment (2, 4-[3-(trifluoromethyl)-3*H*-diazirin-3-yl]

benzyl bromide) covalently binds Kevlar through the carbene moiety at its first terminus. In step 2 (nucleophilic dyeing), the benzyl bromide group of 2 covalently binds weak nucleophilic dyes *via* substitution reactions.

The present carbene-based strategy has several potential advantages over existing technologies. Trifluoromethyl carbenes are more reactive than nitrenes, even though nitrenes have been used more widely for dyeing polymeric substrates.^{24c} Carbenes can also insert directly into C–H bonds.^{28a} Additionally, compared to previous carbene methods, the present method is faster (<2 h) and safer (avoids the use of hazardous mercuric compounds). Further, the present method uses a diazirine reagent that is easily prepared on gram-scale, liquid at ambient temperature and miscible with most organic solvents to facilitate convenient application to fabrics and textiles, and that is bench-stable, yet rapidly activated by long-wave UV light or heat. The diazirine carbene precursor is also more stable than a diazo precursor,^{28b,c} and it is not prone to uncontrolled decomposition that is observed with diazo compounds that can limit their effectiveness. Additionally, the reagents used in the present method are thermally stable, whereas other methods use reagents that are temperature-sensitive and can degrade non-specifically during storage or the functionalization procedures, lowering the efficiency of the dye attachment to the polymer/fiber. Overall, this diazirine method for the chemical modification of *para*-aramid (Kevlar), UHMWPE (Spectra or Dyneema), nylon (Cordura), or fiber-blend fabrics uses relatively mild conditions, does not compromise the structural integrity and mechanical strength of the fibers/fabrics, and it can be used to dye or apply other finishes or functional coating technologies (e.g., anti-wrinkle,²⁹ anti-microbial³⁰) to these high-performance textiles.

Materials and methods

Materials

Unless otherwise noted, all chemicals were obtained from commercial sources, stored at room temperature, and used as received. Diazirine-containing alcohol (3-[4-(hydroxymethyl)phenyl]-3-(trifluoromethyl)-3*H*-diazirine) (1) was purchased from TCI America and stored under argon in the dark in a refrigerator. Products were purified by flash chromatography using SiliCycle SiliaFlashP60 (230–400 mesh) silica gel. The organic base 1,8-diazabicyclo[5.4.0]undec-7-ene (abbreviated DBU) was used in these experiments with dyes that include acridine yellow G, solvent yellow 7, oil red O, 1,4-diamino anthraquinone, Texas red cadaverine, naphthazarin, quinizarin, pyridium dyes, and toluidine blue O. A multitude of synthetic and designed dyes can be used with this method, provided they contain a group capable of displacing the bromide leaving group on compound 2. The fabrics used to demonstrate the effectiveness of the diazirine-dyeing process and to verify the retention of breaking strength *via* mechanical testing consist of: Kevlar, Spectra, Dyneema, nylon Cordura, and a fiber-blend experimental fabric. A handheld UV lamp capable



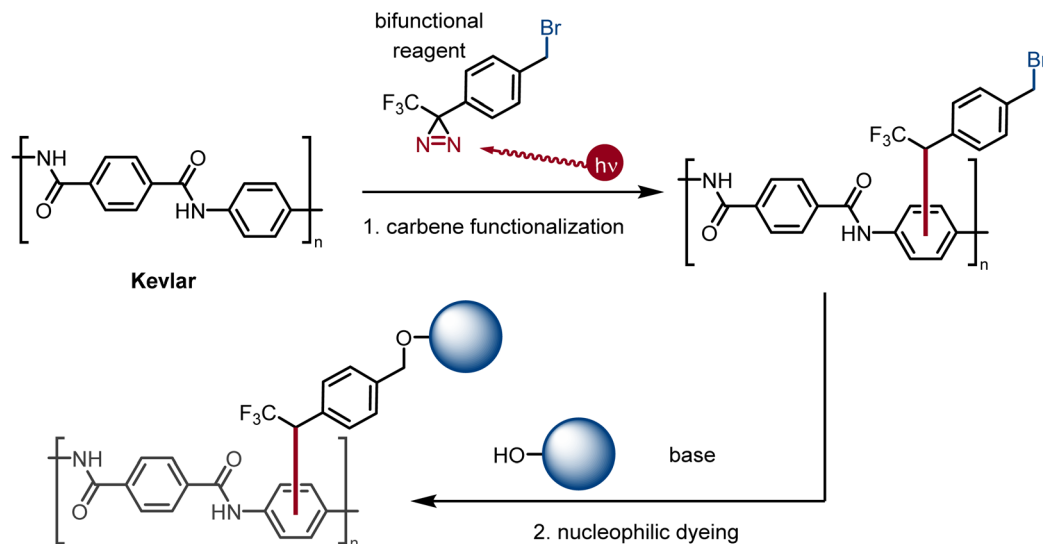


Fig. 1 General scheme for bifunctional carbene-based dyeing of inert polymers.

of producing either short-wave (254 nm) and long-wave (375 nm) light was used for the photoactivated carbene treatments.

Equipment

Nuclear magnetic resonance spectroscopy (NMR). ^1H , ^{13}C , and ^{19}F NMR spectra were obtained with a Bruker Avance-600 MHz or 500 MHz spectrometer. ^1H and ^{13}C spectra were calibrated using residual solvent as an internal reference (CHCl_3 : δ 7.26 ppm and δ 77.36 ppm, respectively; DMSO: 2.50 ppm and 39.52 ppm, respectively). Broadband ^1H decoupling was used during the collection of ^{13}C and ^{19}F NMR spectra. The following abbreviations were used to denote multiplicities: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, p = pentet, and m = multiplet.

X-ray photoelectron spectroscopy (XPS). XPS measurements were performed using a Thermo Scientific K-Alpha+ X-ray photoelectron spectrometer with a hemispherical energy analyzer and a monochromated X-ray source (Al K-alpha). Survey and high-resolution scans were collected with an X-ray spot size of 400 μm and a pass energy of 200 and 50 eV, respectively. XPS spectra were processed with the Advantage software.

Fourier-transform infrared spectroscopy (FT-IR). All of the FT-IR spectra of the diazine-dyed fabric samples were obtained on a Thermo Scientific Nicolet iS5 spectrometer (iD5 ATR, diamond).

Optical spectroscopy. Ultraviolet-visible (UV-Vis) absorption spectrometry was carried out with an Agilent Cary 5000 instrument. Total diffuse reflection measurements were performed using a PerkinElmer Lambda 1050 UV/Vis/NIR Spectrophotometer with Universal Reflectance Accessory. Photoluminescence measurements were carried out using a HORIBA Jobin Yvon Fluorolog-3 spectrofluorometer (model FL-321).

Thermogravimetric analysis (TGA). TGA measurements were carried out under nitrogen atmosphere (AirGas, ultra-high purity grade) using a TGA 550 from TA Instruments. The ramp speed was $10\text{ }^\circ\text{C min}^{-1}$, and isotherms were performed from room temperature to $900\text{ }^\circ\text{C}$. The degradation temperature (T_d) of a polymer is the temperature at which the polymer loses 10% of its initial mass.

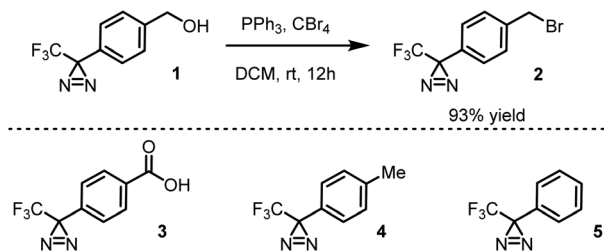
Breaking strength testing. An Instron (Model 5666) was used to determine the breaking strength and elongation properties of Kevlar, UHMWPE (Spectra or Dyneema), and the fiber-blend fabrics before or after the treatment in General procedure A. Testing was done in accordance with the international test standard ASTM D5034 titled "Breaking Strength and Elongation of Textile Fabrics (Grab Test)". A Universal Testing System (Instron Model 5500R) was used to determine the tensile strength of a Kevlar filament yarn in accordance with the international test standard ASTM D7269 ("Standard Test Methods for Tensile Testing Aramid Yarns").

4-[3-(Trifluoromethyl)-3H-diazirin-3-yl]benzyl bromide (2)

Benzyl bromide 2 was synthesized by Appel bromination of the commercially available alcohol 1.³¹ Specifically, in a 50 mL round-bottomed flask previously dried in an oven and cooled under dry nitrogen, carbon tetrabromide (1.68 g, 5.06 mmol, 1.1 equiv.) and dry dichloromethane (abbreviated DCM, 10 mL) were combined. A magnetic stir bar was added, and the flask was capped with a rubber septum. Using a needle connected to a vacuum manifold, the flask was quickly evacuated and refilled with nitrogen. This procedure was repeated a total of three times. While the solution was stirring rapidly, a solution of triphenylphosphine (1.33 g, 5.06 mmol, 1.1 equiv.) in DCM (10 mL) was added dropwise by syringe. After 30 min, alcohol 1 (1.0 g, 4.6 mmol, 1 equiv.) was added in one portion, and the reaction mixture was left to stir at rt for 12 h. At this point, the septum was removed, and the solvent was distilled



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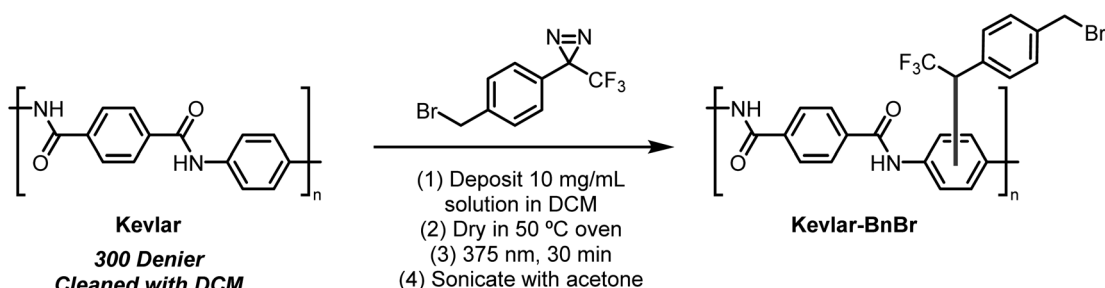


Scheme 1 Synthesis of diazirine reagent.

ditions for at least several months without noticeable decomposition. Compound **2** exhibits a broad absorbance feature in the long-wave UV range ($\lambda_{\text{max}} = 352 \text{ nm}$, $\epsilon = 270 \text{ M}^{-1} \text{ cm}^{-1}$), which decreases in intensity over 70 s of irradiation

with a handheld UV lamp (375 nm), indicating photo-activation of the diazirine (see ESI, Fig. 1†). To coordinate this reagent to Kevlar (Scheme 2), this reagent was dissolved in DCM solution (10 mg mL^{-1} concentration), deposited onto a swatch of Kevlar by soaking, then air-evaporated in a chemical fume hood. Following the evaporation of the solvent, the sample was irradiated with a handheld UV lamp for 30 min. After completion of the UV treatment, the material was extensively rinsed with DCM and acetone to remove any physisorbed organics.

X-ray photoelectron spectroscopy (XPS) was carried out to examine the elemental composition of the Kevlar surface. XPS revealed that fluorine and bromine had been incorporated in a ratio of 3 : 1, consistent with the addition of CF_3 and Br in a stoichiometric proportion (Fig. 2). For further details, see ESI, Section 2,† as a control experiment, Kevlar was treated with



Scheme 2 Coordination of brominated diazirine reagent (**2**) to Kevlar.

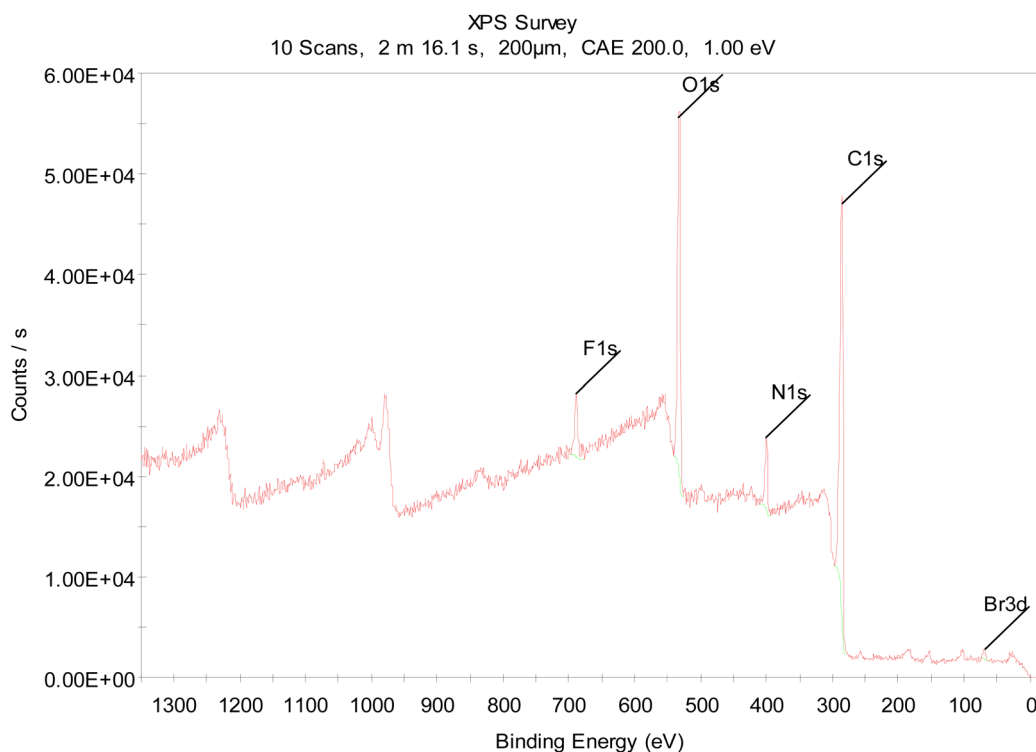


Fig. 2 XPS spectrum of Kevlar functionalized with compound **2** (see Scheme 2).



the same chemical procedure, except without UV irradiation. In this case, only trace fluorine and bromine were detected, showing that unactivated compound **1** does not bond or adsorb strongly to the Kevlar surface. Additionally, to assess

whether the covalent bonds formed with Kevlar were stable, the first, light-treated sample was subjected to Soxhlet extraction with acetone for 24 h. Although a substantial amount of the fluorine content remained, a decrease in the bromine

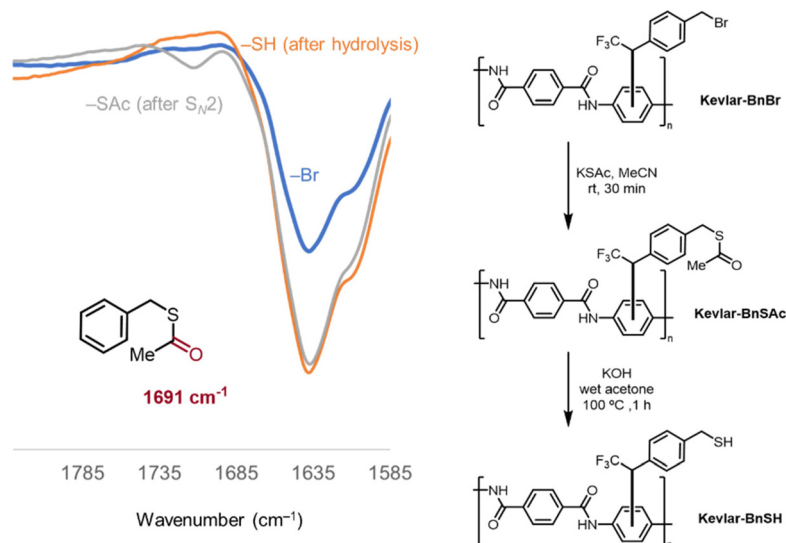


Fig. 3 IR transmission spectrum of Kevlar sample after benzyl–bromide diazine attachment (blue), thioacetate treatment (grey), and base hydrolysis of the thioester group (orange).

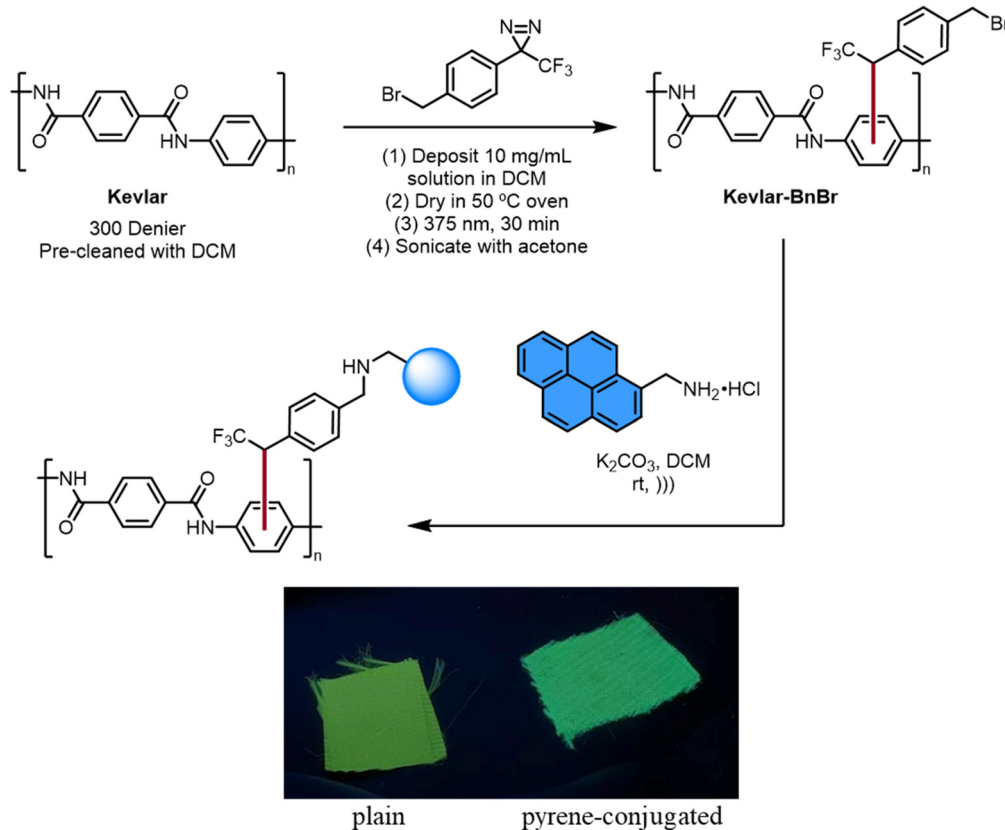


Fig. 4 Attachment of a fluorescent dye to Kevlar.



content was observed. The covalent bond of the brominated diazirine reagent **2** to the polymer appears to be fairly robust, while the benzyl bromide group may be prone to hydrolysis during prolonged exposure to solvent. Thus, in the following experiments, any subsequent functionalization was carried out within a few hours after the initial diazirine treatment.

After confirming covalent attachment of the benzyl-bromide diazirine reagent **2** to Kevlar with XPS and the solvent extraction methods, the reactivity of the bromine-containing group toward nucleophiles was tested with the diazirine coordinated to Kevlar. Specifically, a benzyl-bromide-modified Kevlar sample was prepared according to General procedure A, then treated with a potassium thioacetate (SAC) in acetonitrile solution. FT-IR spectroscopy (Fig. 3) showed the appearance of a small new signal around 1700 cm^{-1} , consistent with the carbonyl stretch of a thioester group,³⁵ in addition to the presence of the intense $\text{C}=\text{O}$ stretching peak of Kevlar^{17,36} occurring at *ca.* 1650 cm^{-1} . Upon subsequent treatment of the sample with sodium hydroxide, the thioester was hydrolyzed quantitatively, and the corresponding IR resonance at 1700 cm^{-1} disappeared (Fig. 3). This procedure verified the reactivity of the benzyl bromide group on the second terminus of the diazirine reagent to nucleophiles, without interfering with the bonding of the first terminus of the diazirine with the Kevlar surface.

This carbene method was also used to modify Kevlar with organic fluorophores through nucleophilic substitution. The photochemical treatment of General procedure A was used to attach benzyl bromide functional groups to Kevlar. A sample of functionalized Kevlar was placed in an acetonitrile solution containing 1-pyrenemethylamine and DBU. After washing the surface with various organic solvents and drying, the material exhibited bright blue fluorescence characteristic of the presence of pyrene groups, in contrast to the inherent green-yellow emission of Kevlar (Fig. 4). Photoluminescence spectra were obtained on this pyrene-modified sample, as well as control samples of plain Kevlar and Kevlar exposed to 1-pyrenemethylamine without the diazirine treatment, and the results confirmed the change in fluorescence caused by covalent attachment of the dye.

The diazirine method was used to attach various dye molecules to functionalized Kevlar. After attaching the diazirine to Kevlar through General procedure A, the Kevlar swatches functionalized with the benzyl-bromide diazirine reagent were soaked in a concentrated solution of dye in DCM or acetone solvent, with several percent of the soluble organic base DBU added to it. The sample was removed from solution, then immediately placed in a $120\text{ }^{\circ}\text{C}$ oven for 10 min. To remove excess, unreacted dye and other residual compounds, the samples were rinsed thoroughly with DCM and water, then subjected to ultrasonication in various organic solvents. The resultant samples showed visual indications of dyeing. Photographs of the dyed fabric samples, the chemical structures of the eight (8) dyes, and the total reflectance spectra of the dyed samples (and undyed Kevlar control) are provided in Fig. 5A–C.

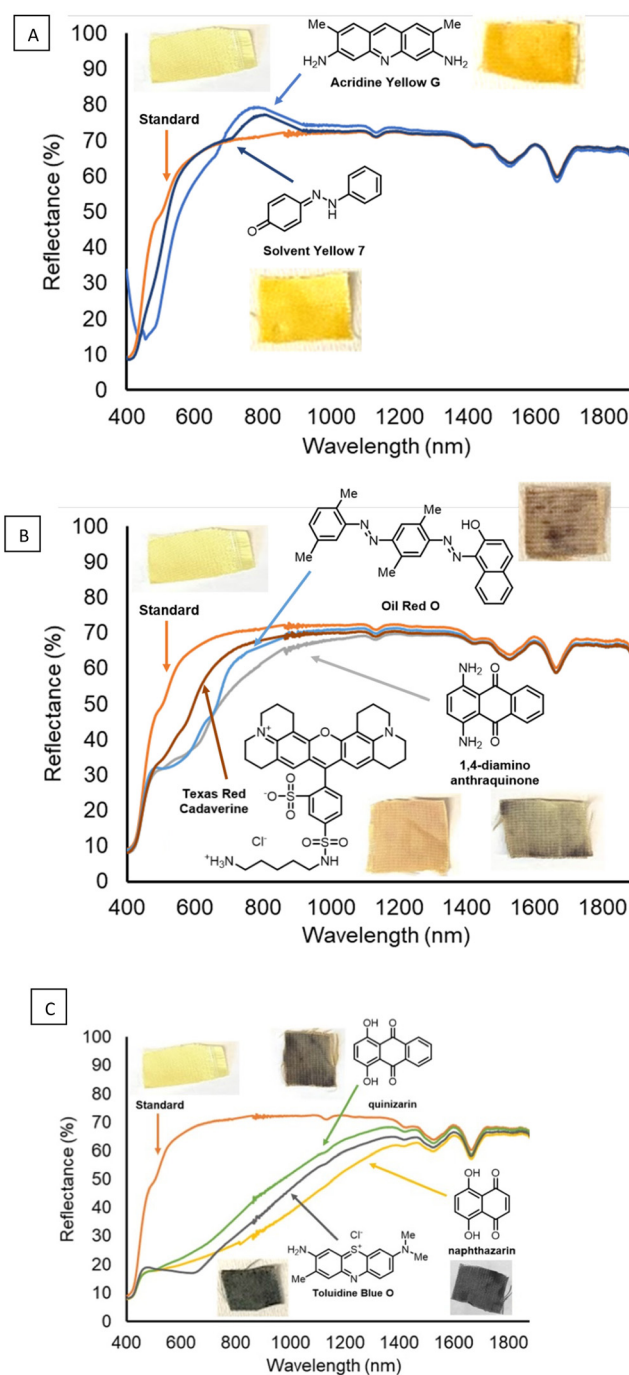


Fig. 5 (A–C) Reflectance spectra and photographs of dyed Kevlar samples, and the corresponding dye structures for each sample.

In addition to the fabric made of Kevlar mentioned above (Fig. 5A–C), a range of other ballistics-related fabrics were stained successfully through the diazirine functionalization method, followed by thermal treatment with quinizarin and DBU. Additionally, fabrics comprising UHMWPE (Spectra), nylon (Cordura), and a fiber blend experimental fabric were successfully stained a dark brown color (Fig. 6) similar to that of quinizarin-dyed Kevlar (Fig. 5C).



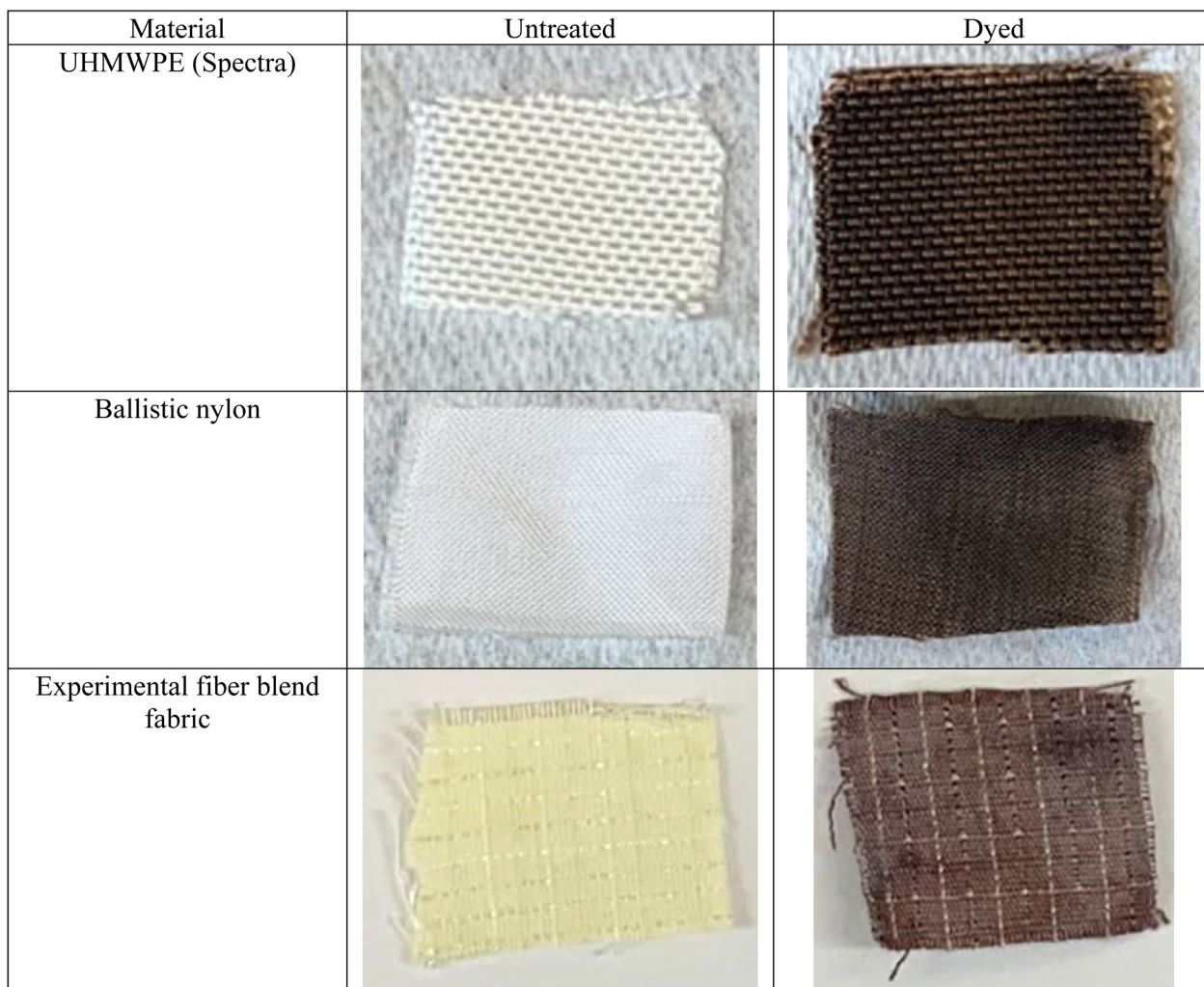


Fig. 6 UHMWPE, nylon, and fiber-blend fabrics dyed with the diazine-based method.

Colorfastness is a common measure of the ability of dyed textiles to retain color without fading or running, including during laundering. To assess the robustness of the dye attachment with the present diazine method, the colorfastness of a representative sample of dyed Kevlar was evaluated using a

simulated laundering procedure based on an international standard procedure.³⁷ The dyed Kevlar sample was subjected to an aqueous detergent mixture at elevated temperature

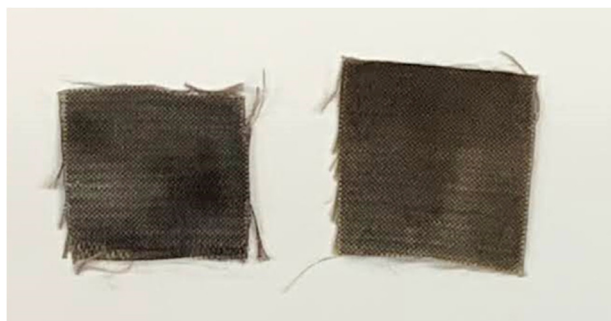


Fig. 7 Stained Kevlar sample before (left) and after (right) simulated laundering.

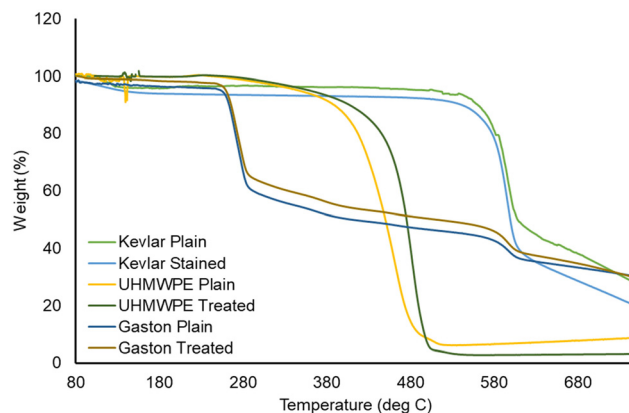


Fig. 8 Thermogravimetric analysis of three fabrics before and after carbene-based dyeing, using quinizarin as the dye component.



Table 1 Summary of tensile testing results

Sample	Diazirine treatment ^a	Direction	Max load (lbf)	Elongation (%)
Kevlar yarn		N/A	127 ($T = 21.6 \text{ gf den}^{-1}$)	N/A
Kevlar yarn	Yes	N/A	126 ($T = 21.4 \text{ gf den}^{-1}$)	N/A
Kevlar woven		Warp	571	18.0
Kevlar woven	Yes	Warp	560	18.0
Kevlar woven		Filling	846	7.9
Kevlar woven	Yes	Filling	855	7.8
Fiber blend woven		Filling	125	7.9
Fiber blend woven	Yes	Filling	127	7.9
UHMWPE woven (Spectra)		Warp	669	16.3
UHMWPE woven (Spectra)	Yes	Warp	737	16.0
UHMWPE woven (Spectra)		Fill	742	26.1
UHMWPE woven (Spectra)	Yes	Fill	740	23.9
UHMWPE knit (Dyneema)		Wales	298	184
UHMWPE knit (Dyneema)	Yes	Wales	293	191

^a Samples marked "Yes" for treatment were subjected to diazirine application according to General procedure A in the Materials and Methods.

(40 °C) with agitation (vigorous mechanical stirring), followed by rinsing with water and drying. After the simulated laundering cycle, a faint yellow color developed in the liquid phase of the wash cycle, although no noticeable fading was observed visually in the washed *versus* the unwashed fabric sample. To measure colorfastness, the total diffuse reflectance of the sample was measured before and after laundering, and the values remained virtually unchanged at 5% and 6% (at 450 nm), respectively (Fig. 7).

Most applications of *para*-aramids depend on the high tensile strength, modulus, and similar mechanical properties of the fibers. The effects of the present carbene-based dyeing method on the integrity of the fabrics or its constituent fibers was investigated using TGA measurements and mechanical break tests. The diazirine compound 2 and UV irradiation treatment were applied to Kevlar, UHMWPE, and the fiber blend experimental fabric according to General procedure A, without carrying out the subsequent dyeing step. The effect of this diazirine functionalization procedure on the thermal stability of the Kevlar fibers was evaluated using TGA, which showed (Fig. 8) that treated and untreated fabric samples decomposed at a similar temperature. This trend was observed consistently for fabrics comprising *para*-aramid (Kevlar), UHMWPE, or the fiber blend (Fig. 8).

Similarly, the breaking strength and elongation were determined for the *para*-aramid (Kevlar), UHMWPE, and fiber blend fabrics after diazirine treatment using standard test methods (in the warp and fill directions for woven fabrics, in the Wales direction for knit fabrics – see Table 1). In all cases, the stretching force tolerated by the processed samples was similar to that of the untreated textile, with some noticeable differences based on the material and the construct of the fabric being tested. Specifically, woven Kevlar, UHMWPE (Spectra), or fiber blend fabrics showed no significant change in breaking strength in either the warp or fill directions (fill direction only for the fiber blend fabric) after diazirine treatment, although Kevlar and UHMWPE (Spectra) showed significantly higher values in maximum load and per cent elongation

compared to the fiber blend fabric. Similarly, the UHMWPE (Dyneema) knit fabric showed no loss in mechanical strength resulting from the diazirine treatment, but had a substantially higher per cent elongation prior to breaking than the woven fabrics. Testing individual yarns represents a worst-case for exposure to a chemical treatment than might be expected for a fabric. A Kevlar yarn showed no significant change in breaking strength after the diazirine treatment (Table 1). Taken together with the TGA results, these results indicate there is no significant chemical or physical damage of these fibers/fabrics occurring from the diazirine treatment. Therefore, this carbene-based method can dye high performance textiles without compromising the mechanical properties of the fibers/fabrics and rendering these textiles unsuitable for their intended application(s).

Conclusions

In summary, we have developed an approach using a bifunctional diazirine intermediate for the surface modification of ballistics textiles made from high performance fibers that are generally considered difficult to dye with conventional methods. Specifically, fabrics made of *para*-aramid (Kevlar), UHMWPE (Spectra or Dyneema), nylon (Cordura), or fiber blends were functionalized to have accessible benzyl bromide groups through a relatively mild procedure that uses a bench-stable bifunctional diazirine reagent that is efficiently activated under UV irradiation. With the diazirine's first terminus covalently bonded to the fabric surface, electrophilic sites on the diazirine's second terminus are accessible to attach visible-color dyes in a robust manner. The dyed fabrics were colorfast with respect to simulated laundering, thermally stable, and retained their mechanical properties, such that the diazirine and UV treatment did not compromise the structural integrity of the fabrics or their constituent fibers. We expect that further development of bifunctional carbene reagents such as 2 will provide a convenient and general method for the incor-



poration of diverse functional groups on inert polymer surfaces, particularly applying finishes or functional coating technologies to high performance textiles used in ballistics protection.

Conflicts of interest

The authors are preparing to file a patent application based on the described method.

Acknowledgements

This research is funded in part by US Army Combat Capabilities Development Command Soldier Center (CCDC SC) in Natick, MA.

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