Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information for

Bifunctional Diazirine Reagent for Covalent Dyeing of Kevlar and Inert Polymer Materials

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1. Absorbance Spectroscopy

Diazirines bearing aryl substituents typically exhibit a broad absorption in the long-wave UV, and as expected, reagent **2** as a solution in DCM displays a medium-intensity absorption with maximum at 352 nm. Upon irradiation with a handheld UV lamp, the solution noticeably develops small bubbles over time, and the characteristic absorbance decreases in intensity. Some diazirines are known to isomerize to the diazo form upon irradiation, which usually has slight color and is associated with an absorbance above 400 nm. However, under the current conditions, diazo species are not formed or are unable to accumulate to a significant extent.

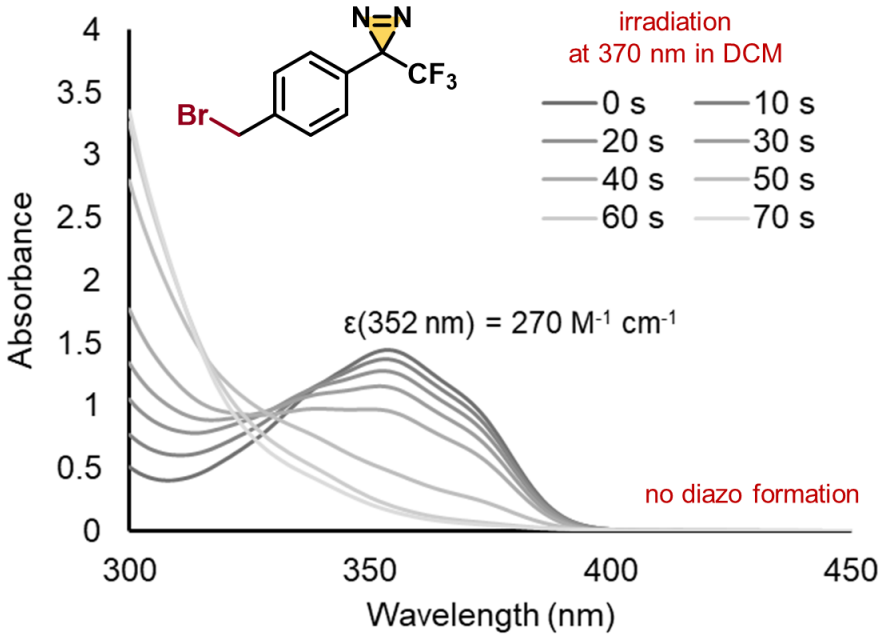
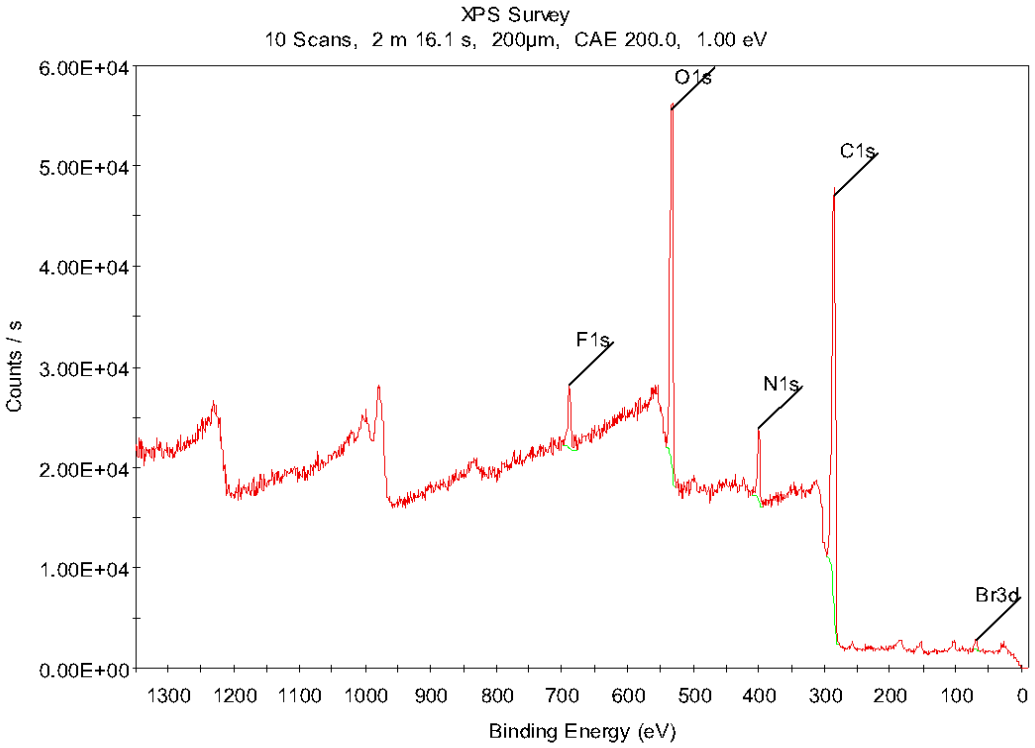


Figure 1. Absorbance spectra of diazirine **2** in DCM upon irradiation by 370 nm lamp.

2. X-Ray Photoelectron and IR Spectroscopy

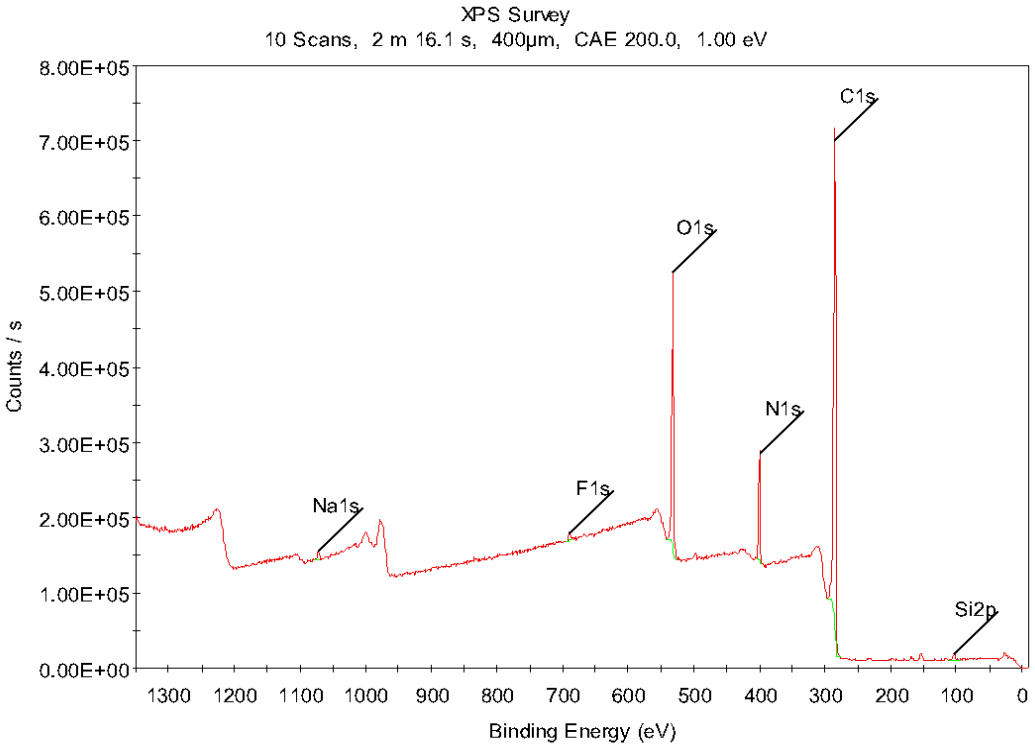
X-ray photoelectron spectroscopy (XPS) was performed to provide evidence for the covalent incorporation of benzyl bromide groups upon treatment of Kevlar with diazirine **2**. In the treated sample **Kevlar-BnBr**, observation of surface fluorine and bromine in a 3:1 ratio was consistent with incorporation of the depicted chemical group (Figure 2).



	Kevlar (Theory)	Kevlar	Kevlar-BnBr
C	78	73	70.6
N	11	5	5.1
O	11	22	21.9
F			1.9
Br			0.6

Figure 2. XPS spectrum of **Kevlar-BnBr** and elemental composition.

In contrast, when the same treatment was performed but without UV irradiation, minimal incorporation of the benzyl bromide groups was observed (<0.04% Br content), showing that the diazirine is likely not being physically adsorbed or retained within the fibers and that a photochemical process is essential (Figure 3).

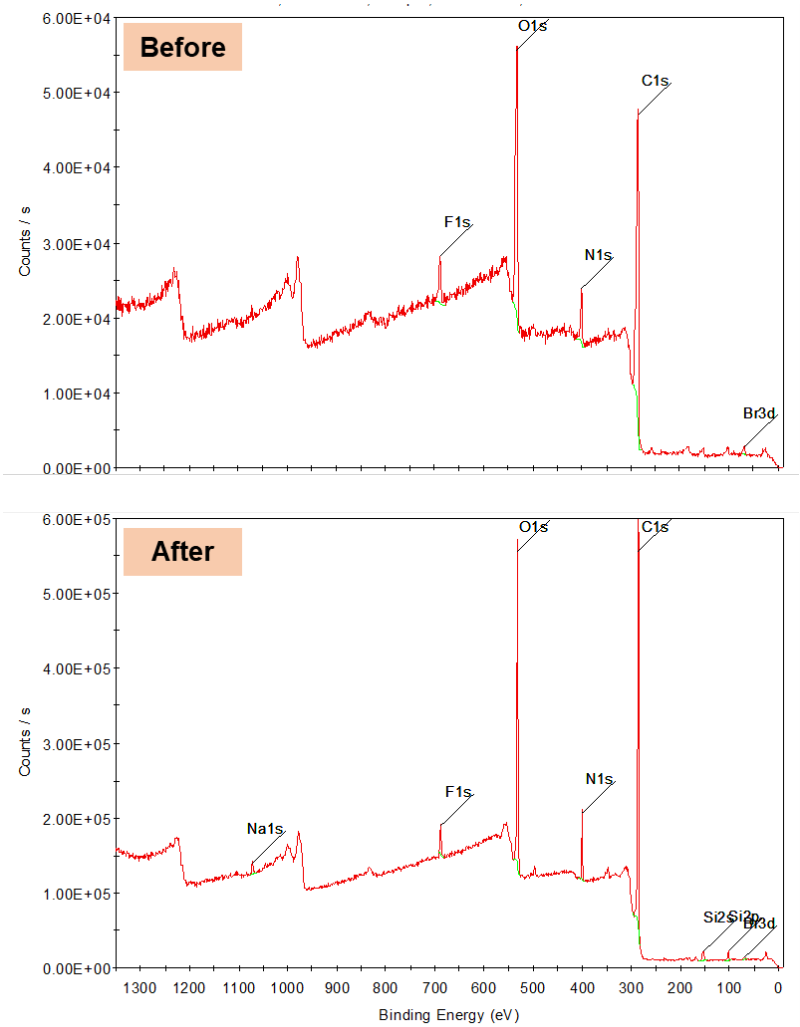


	Kevlar	"Dark Sample"	Kevlar-BnBr
C	73	73.9	70.6
N	5	8.8	5.1
O	22	17.2	21.9
F		0.16	1.9
Br		0.04	0.6

Figure 3. XPS spectrum of a control sample (no UV irradiation) and its elemental composition.

To evaluate the robustness of the benzyl bromide attachment, a functionalized sample of **Kevlar-BnBr** was subjected to Soxhlet extraction with acetone for 24 h (Figure 4). Only a minimal

decrease in the fluorine content was observed, although the bromine content had decreased to 0.13%, suggesting that the linkage to the Kevlar is stable, but the benzyl bromide may be labile to hydrolysis.



	Kevlar	Kevlar-BnBr	After Extraction
C	73	70.6	71.0
N	5	5.1	6.3
O	22	21.9	21.4
F		1.9	1.3
Br		0.6	0.13

Figure 4. XPS spectra of **Kevlar-BnBr** before and after Soxhlet extraction with acetone.

3. Comparison of Dye Retention With and Without Diazirine Treatment

Control studies were performed to show that diazirine-based functionalization improves dye retention. A sample of Kevlar was treated with dye according to General Procedure B, but without pre-treatment by diazirine according to General Procedure A. Although a small amount of color was retained, it is visually apparent that the carbene treatment greatly improved dye incorporation.

Figure 5. Comparison of plain Kevlar (left), Kevlar with dye treatment (center), Kevlar with diazirine treatment then dye treatment (right).

4. FTIR and Spectral Reflectance of Alternative Dyed para-Aramid or UHMWPE Fabrics

To explore the potential use of Kevlar and UHMWPE as lightweight replacement options for nylon (Cordura) tactical fabrics used as outerwear in military and law enforcement applications (e.g., armor plate carriers, etc.), a series of low-denier yarn fabrics made of Kevlar or UHMWPE were woven and dyed specific shades that match different terrains or surroundings. These fabrics are evaluated using FTIR-ATR spectroscopy to identify specific chemical structures, and with spectral reflectance measurements to determine the suitability of these fabrics in mimicking background reflectance in different operational environments, an important consideration for effective camouflage.[14]

MATERIALS AND METHODS

Fabrics. The para-aramid fabrics in this study were made using K159 or KM2+ yarns (DuPont Co.). A 300 D plain weave fabric made with K159 Kevlar yarns (JPS Industries, Anderson, SC) was used either undyed or dyed to the color/shade tan 499 using a pigment dyeing process with a full-width commercial pad dyeing process (Royal Carolina Corp., Greensboro, NC, USA or Heathcoat Fabrics Ltd, Westexe, UK). A plain weave 400 D Kevlar fabric solution dyed black, and a 3×1 twill Kevlar fabric with the feel of heavy denim was made using 600 D Kevlar yarns and dyed black (Wilson College of Textiles, North Carolina State University, Raleigh NC). A 600 D Kevlar (KM2+) plain weave fabric with 100% tightness (JPS Industries, Anderson SC) was scoured but not dyed, and used as a Kevlar standard. A 300 D, plain weave UHMWPE fabric was made using 3GX19-300 Diamond Fiber Dyneema (Royal DSM N.V.) and dyed tan 499 (UPN Co, Daegu, South Korea). Spectra 955 (180 D, 55 × 55 thread count, plain weave by Honeywell International Inc.) was also evaluated and compared to a standard FTIR spectrum of UHMWPE (Loretex Corp) stored in the OMNIC library.

Equipment. The commercial fabrics, dyed or undyed, were used with no further sample preparation. The FT-IR spectra of all of these fabric samples comprising para-aramid (Kevlar), UHMWPE (Spectra or Dyneema), and nylon were carried out using a diamond tip ATR attached to a Nicolet 6700 FT-IR spectrometer (Thermo Electron Corporation) equipped with a KBr beam-splitter and a DTGS-TEG detector from 400 – 4000 cm^{-1} in ambient conditions. The FTIR spectra were evaluated for bands and compared to a stored library of standard FTIR spectra using OMINC software (Thermo-Fisher). Fabric samples were visually evaluated for shade (data not shown), and Spectral Reflectance was measured using a Varian Cary 5000 spectrophotometer and/or HunterLab Pro spectrophotometer.

RESULTS

Figure 6 displays representative FTIR data of Kevlar and UHMWPE fabrics, and Table 1 lists all of the observed FTIR band for all of the commercial dyed Kevlar and UHMWPE fabrics. All of the Kevlar fabrics showed the three (3) main peaks characteristic of para-aramids. Specifically, a large peak at ca. 3300 cm^{-1} (−NH− stretching frequency), an intense peak at 1650 cm^{-1} (−C=0 stretching), and a peak 1540 cm^{-1} (−NH− stretching frequency), as reported previously for oxy-fluorinated Kevlar[36] and Kevlar dyed with NTP after a pre-treatment with soybean oil.[17a,b] In those respective cases, some additional characteristic peaks appeared at ca. 1300–1063 cm^{-1} (assigned to −C−N stretching and −N−H−, and −C−C− vibrations) or at 1513 cm^{-1} (assigned to amide II), 1305 (assigned to C−N stretching), and 1017 and 820 (assigned to C−H of aromatic rings). In the current experimental results (see Table 1), peaks also appeared for the different fabrics in the range ca 1248 – 610 cm^{-1}. In contradistinction to Kevlar, the UHMWPE fabrics made of Spectra 955 or Dyneema dyed Tan 499, which were visibly white and tan, respectively, showed intense peaks observed at ca. 2900/2800, 1470/1460, and 730/715 cm^{-1}, and minor small peaks at ca. 1730, 1200, and 1150 cm^{-1}. FTIR results, appear to determine more information regarding the molecular groups of the underlying polymer (PPTA or UHMWPE) than of the dye molecule.

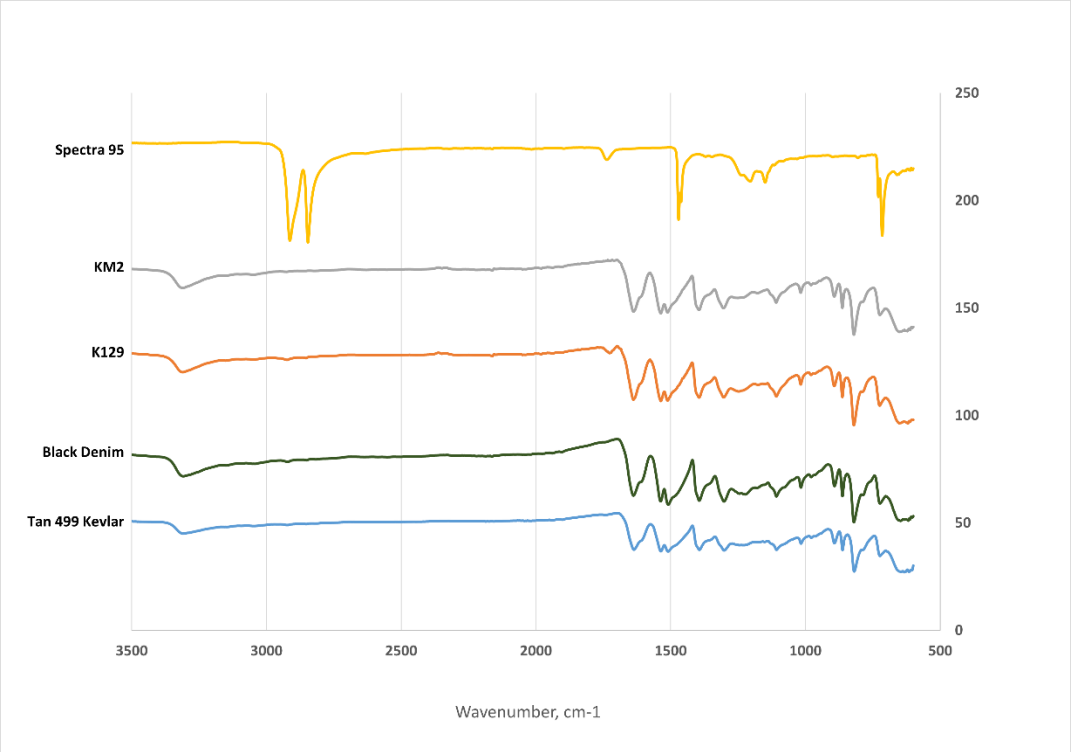


Figure 6. FTIR-ATR data showing peaks characteristics of UHMWPE (Spectra 955) and Kevlar for various fabrics, yarn types, and with or without dyeing.

Table 1. FTIR-ATR spectra of para-aramid (Kevlar) fabrics varying yarn type, fabric construct, the presence of dye, and the dye color, and UHMWPE (Spectra 955 and TAN 499 Dyneema) fabrics.

Undyed Kevlar K159	Undyed Kevlar KM2	Black Kevlar 3×1 twill	Tan 499 Kevlar K159 300d	Spectra 955	Tan 499 Dyneema
3305	**3302**	**3309**	3310	**2913**	**2913**
3044	**3044**			**2846**	**2846**
2924		**2921**		**1738**	**1736**
1637	**1637**	**1637**	1636	**1471**	**1471**
1536	**1536**	**1537**	1536	**1462**	**1462**
1509	**1507**	**1509**	1510	**1205**	
1393	**1393**	**1393**	1394	**1150**	**1148**
1302	**1301**	**1302**	1302	**729**	**730**
1248	**1223**	**1223**		**715**	**716**
1107	**1107**	**1107**	1107		
1017	**1016**	**1016**	1016		
978	**978**	**978**			
892	**891**	**892**	892		
862	**862**	**862**	862		
819	**820**	**820**	819		

787	786			
722	722	723	724	
637	634	646	633	
616	610	611	616	

Vis-nIR %reflectance was measured for Kevlar (black or Tan 499) and Dyneema (Tan 499). Black and Tan 499 Nylon. These colors/shades are typical of many environmental backgrounds, whose reflectance camouflage tries to match (see Figures 1 and 2 in Burkinshaw et al. 1996 and references therein). The data in Table 2 highlight the differences observed in %Reflectance that occur with different dye molecules, dye colors, and fabric substrates. Most notably, the sample of Tan 499 Dyneema has in general over the wavelength region examined a significantly higher %Reflectance of this sample of Tan 499 Dyneema compared to this Tan 499 Kevlar sample.

Table 2. Vis-nIR %(spectral reflectance) of Black Kevlar and Tan 499 Kevlar, UHMWPE, or Nylon fabrics.

Wavelength (nm)	Black Kevlar 400d	Tan 499 Kevlar 300d	Tan 499 Dyneema	Tan 499 Nylon 600 D
600	6.3	14.3	19.0	18.9
620	6.4	14.9	17.7	17.9
640	6.4	15.3	18.9	18.2
660	6.7	15.7	36.3	24.9
680	8.1	16.2	62.2	30.6
700	11.3	16.6	76.0	32.4
720	14.8	17.1	79.4	36.1
740	17.3	17.5	80.1	40.6
760	17.5	17.9	80.1	42.9
780	17.1	18.2	80.5	43.7
800	19.0	18.6	80.5	43.9
820	24.5	18.9	80.5	44.2
840	34.4	19.2	80.3	44.4
860	46.3	19.4	80.5	44.9