

## Dual functional azo polysiloxane dyes for polyester: synthesis and application

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The purpose of this research was to design and synthesize novel functional polymeric azo dyes that not only dye the polymeric substrates, but also influence their physical handle properties. The synthesis scheme involved azo chromophores synthesis using *tert*-butyl nitrite. Single and dual azo chromophores were bonded with polysiloxane chain using carbonyldiimidazole (CDI). The synthesized molecules were applied to a polymeric polyester substrate. Due to the presence of polysiloxane chains in the molecule, the handle properties of the treated polymeric substrates were modified while the attached chromophore performed its coloration function. Molecules structures of azo polysiloxane products were elucidated by UV-Vis, MALDI-TOF mass spectroscopy, <sup>1</sup>H-NMR (500 MHz), elemental analysis. Mass spectroscopy was performed after each synthesis step to check mass difference in peaks of intermediates and products. The coupling components were applied on a polyester substrate and azo coupling reactions were carried out on the polymeric substrate itself carrying the coupling components. Azo molecules were separately synthesized for characterization. The compounds were found to be capable of altering the handle of the substrate and imparting softness even at low concentrations. The subjective evaluation of handle properties confirmed the handle modifying capability of the azo polysiloxane molecule. Two different subjective techniques were used for evaluation, namely, press method and crush method. Crush method turned out to be more reliable, as was judged by the variance among the readings taken by the subjects. Other similar dual-purpose polymeric azo dye molecules can be synthesized on the same pattern for application on other polymeric substrates.

**Keywords:** Polysiloxane, Synthesis, Azo, Carbonyldiimidazole, Polyester.

### INTRODUCTION

Handle of a fabric or any similar material describes the sum of total sensations felt when a fabric is touched by the human hand. Generation of particular handle is one major feature of textile finishing processes [1]. Handle modification refers to imparting a particular "handle or hand" to a fabric or similar material by treatment of the fabric with hand modifier compounds. When the handle of a fabric is changed in such a way that drape is enhanced and material turns silkier, the fabric is referred to have been 'softened'. The inclusion of polysiloxane molecules containing linear siloxane [-Si-O-Si-]<sub>n</sub> chains within polymeric chains of fibers accomplishes this softening process. These chains decrease the coefficient of friction between fibers and any surface in contact with them [2] thus imparting softness to the material [3]. Handle is defined by properties such as smoothness, thickness, bulkiness, extensibility, stiffness, draping character, compressibility, surface friction, and elasticity [4-6].

In this research, we evaluated the performance of

polysiloxane as a handle modifier when bonded to a chromophore. Terminal functional groups carrying polysiloxane (**4**) and (**8**) were selected to induce handle modifying property in the targeted molecules (Fig. 1). Terminal Lewis basic groups, -OH and bis-NH<sub>2</sub> on the polysiloxane chain were responsible for bonding the polysiloxane chain with the coupling component by acyl addition elimination reaction. After synthesis, coupling component compounds (**5**) and (**9**) were applied to the polyester substrate and later *tert*-butyl nitrite-assisted azo synthesis was performed on them. This resulted into mono ester of azo and amide diazo, respectively, connected with the linear polysiloxane chain. Azo synthesis involved formation of stable diazonium through diazotization by *tert*-butyl nitrite in the presence of 1,5-naphthalenedisulfonic acid. It was expected that the handle properties of the treated fabric would be modified due to the presence of polysiloxane chains in the target molecule as they would be providing fiber lubrication, while the bonded chromophore would perform the coloration function. The resulting molecule therefore functions simultaneously as a dye and as a handle modifier.

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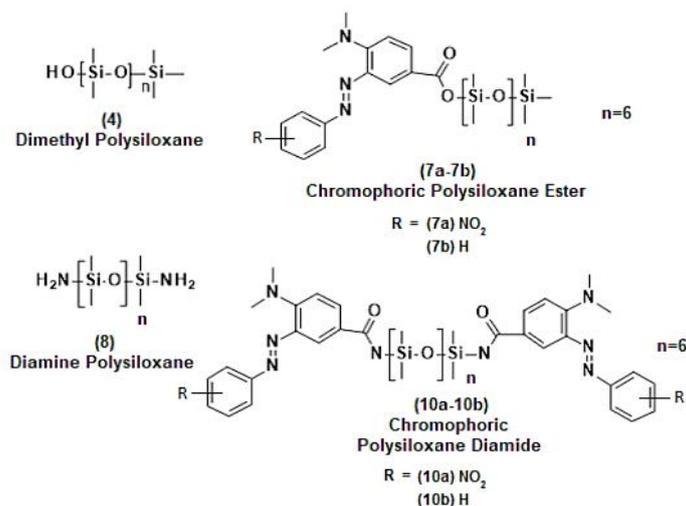


Fig. 1. Core structure of handle-modifying molecules

Subjective evaluation was used for confirming the alteration of the handle properties of the material because of the application of synthesized molecules. This technique transformed psychological perception of touch into an objective parameter by allotting it a single value. Subjective evaluation sets up a parallel between human subjective perception and mechanically measured values. AATCC (American Association of Textile Chemists and Colorists) has defined guidelines for subjective evaluation with standard conditions [7]. Similar to the molecules presented in this research work, other polymeric azo dyes with single or multiple azo chromophores connected to polymeric chains have been reported before. Two kinds of polymeric dyes are included. The first type is when the chromophore is a monomer which is polymerized. The second type has its chromophore connected to a polymeric chain. Examples include polyhydrazone [8], polystyrene azo hybrid [9] polymeric azo containing epoxy reactive group [10] and polyurethanes (PUs) disperse dyes synthesized by epichlorohydrin [11]. Monomeric heterocyclic azo-based polymers have also been reported [12]. Synthesis of these dual functional molecules and subjective evaluation of their effect on handle properties of the substrate is a novel study. It may form the basis for development of functional dyes that can simultaneously perform coloration and functional finishing jobs. Hence, production time and costs may be reduced.

## EXPERIMENTAL

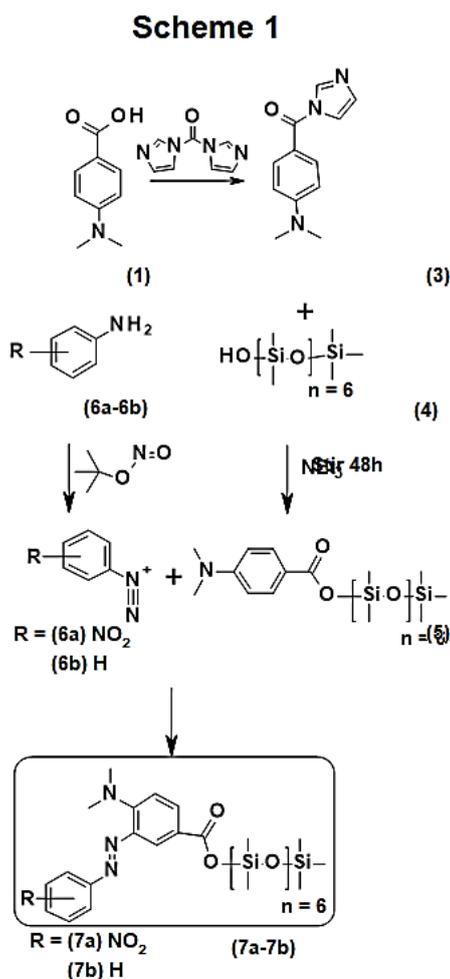
### Materials

The reagents and solvents used in the reactions and purification steps were acquired from Sigma-Aldrich chemical company, USA. Solvents used

were dried before use in reactions and purification steps and were of analytical grade. UV-Vis spectra were recorded on a Thermo Scientific evolution-300 UV-Vis spectrophotometer. <sup>1</sup>H-NMR spectra were recorded in CDCl<sub>3</sub> with Si(CH<sub>3</sub>)<sub>4</sub> as the internal standard at 500 MHz on a Bruker Avance spectrophotometer. MALDI-TOF was recorded on a Bruker MALDI mass Ultraflex III TOF 200 mass spectrometer. Thin layer chromatography (TLC) was used for monitoring the reaction completion, carried out on Merck silica gel (pre-coated) 60 F<sub>254</sub> 20 × 20 cm Al sheets. UV light of 254 and 366 nm wavelength was used to identify spots on the TLC. Reagents used in the application process - dispersing agent lycol RDN, stiffening agent arkofil, softening agent sulfosoft polysiloxane and nonionic detergent, were procured from Archroma Pakistan Ltd.

### Synthesis

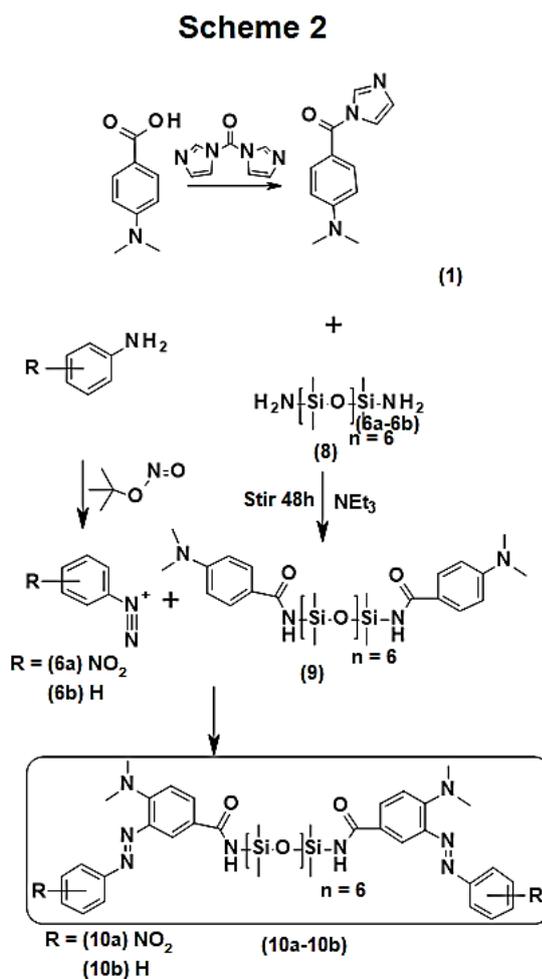
1) *Polysiloxane Coupling Components (5) and (9)*. Carbonyldiimidazole (2) (5 mmol) along with 4-N,N-dimethylamine benzoic acid (1) (5 mmol) were stirred in tetrahydrofuran THF. Stirring continued for 2 hours and then terminal hydroxypolysiloxane (4) (1.25 mmol) or terminal diaminepolysiloxane (8) (0.65 mmol) (two separate processes) was dissolved into the reaction solution. In addition, triethylamine (0.52 ml) was also added to the reaction vessel. The stirring was continued for further 48 hours. After the completion of reaction, the solvent was evaporated and the reaction mixture was put into Na<sub>2</sub>CO<sub>3</sub> solution (0.05 M). The precipitate was filtered and then washed with H<sub>2</sub>O, and extracted with dichloromethane (DCM). Finally, the extracted product was dried over Na<sub>2</sub>SO<sub>4</sub>. Subsequently, the solvent was evaporated to obtain the polysiloxane coupling components (5) or (9) (Schemes 1 and 2).



**Scheme 1.** Synthesis of polysiloxane azo dyes (**7a-7b**).

2) *Polysiloxane azo dyes (7a-7b, 10a-10b)*. In vessel A, aniline derivative (10 mmol) (**6a-6b**) was added to 1,5-naphthalenedisulfonic acid (10 mmol) in 100 ml of ethyl acetate and the solution was brought to 50 °C. Diazonium ion was synthesized by addition of *tert*-butyl nitrite (15 mmol) to the vessel A. Stirring continued for 25 min at 25 °C. In vessel B, polysiloxane coupling component (**5** or **9**) (10 mmol) was dissolved in ethanol (100 ml) and temperature was brought down to 0-5 °C. Diazonium derivative (**6a-6b**) from vessel A was transferred to the vessel B containing polysiloxane solution while pH was maintained at 5.5 with 2 % CH<sub>3</sub>COONa solution. The reaction continued for more 2.5 hours. At this point, an azo precipitate (**7a-7b, 10a-10b**) started to accumulate. This filtered product mass was washed with H<sub>2</sub>O multiple times and extracted with DCM. Finally, it was dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of DCM solvent afforded the azo polysiloxane adduct (**7a-7b, 10a-10b**). Spectroscopic details of the synthesized molecules (**7a-7b, 10a-10b**) are given below:

**(7a)** Rust colored viscous mass. Yield: 55 %; UV-Vis ( $7.27 \times 10^{-5}$  M in CDCl<sub>3</sub>) [ $\lambda_{\max}$ , nm ( $\epsilon_{\max}$ , L mol<sup>-1</sup> cm<sup>-1</sup>)]:



**Scheme 2.** Synthesis of polysiloxane azo dyes (**10a-10b**).

<sup>1</sup>cm<sup>-1</sup>]: 496.0 (42640.9); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz, 25 °C, Si(CH<sub>3</sub>)<sub>4</sub>)  $\delta$  (ppm): 0.08 (s, 9H, C<sub>1</sub>H<sub>3</sub>, C<sub>3</sub>H<sub>3</sub>, C<sub>4</sub>H<sub>3</sub>), 1.14 (s, 36H, C<sub>7,8,11,12,15,16,19,20,23,24,27,28</sub> H<sub>3</sub>), 2.91 (s, 3H, C<sub>37</sub>H<sub>3</sub>), 2.92 (s, 3H, C<sub>38</sub>H<sub>3</sub>), 7.10 (d, 1H, <sup>3</sup>J = 7.5 Hz, C<sub>34</sub>H), 7.86 (m, 3H, C<sub>33,44,48</sub>, H), 8.31 (m, 2H, C<sub>45,47</sub> H), 8.52 (d, 1H, <sup>4</sup>J = 2.0 Hz, C<sub>40</sub>H); MALDI-TOF *m/z*: 831.2 [M+H]<sup>+</sup>; Elemental analysis (%) calculated for C<sub>30</sub>H<sub>58</sub>N<sub>4</sub>O<sub>10</sub> Si<sub>7</sub>: C, 34.34; H, 7.03; N, 6.74; O, 19.24; Si, 23.65 %. Found: C, 34.37; H, 7.05; N, 6.71; O, 19.23; Si, 23.64 %.

**(7b)** Yellow colored viscous mass. Yield: 52 %; UV-Vis ( $7.27 \times 10^{-5}$  M in CDCl<sub>3</sub>) [ $\lambda_{\max}$ , nm ( $\epsilon_{\max}$ , L mol<sup>-1</sup> cm<sup>-1</sup>)]:

<sup>1</sup>cm<sup>-1</sup>]: 380.0 (8093.0); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz, 25 °C, Si(CH<sub>3</sub>)<sub>4</sub>)  $\delta$  (ppm): 0.08 (s, 9H, C<sub>1</sub>H<sub>3</sub>, C<sub>3</sub>H<sub>3</sub>, C<sub>4</sub>H<sub>3</sub>), 1.14 (s, 36H, C<sub>7,8,11,12,15,16,19,20,23,24,27,28</sub> H<sub>3</sub>), 2.93 (s, 3H, C<sub>37</sub>H<sub>3</sub>), 2.95 (s, 3H, C<sub>38</sub>H<sub>3</sub>), 6.90 (d, 1H, <sup>3</sup>J = 7.5 Hz, C<sub>34</sub>H), 7.49 (m, 1H, C<sub>46</sub>H), 7.55 (m, 2H, C<sub>45,47</sub> H), 7.77 (m, 1H, C<sub>44,48</sub> H), 7.81 (m, 1H, C<sub>33</sub>H), 8.50 (d, 1H, <sup>4</sup>J = 2.0 Hz, C<sub>40</sub>H); MALDI-TOF *m/z*: 786.1 [M+H]<sup>+</sup>; Elemental analysis (%) calculated for C<sub>30</sub>H<sub>58</sub>N<sub>3</sub>O<sub>8</sub> Si<sub>7</sub>: C, 45.82; H, 7.56; N, 5.34; O, 16.28; Si, 25.00 %. Found: C, 45.81; H, 7.57; N, 5.35; O, 16.30; Si, 23.64 %.

25.01 %.

**(10a)** Dark rust colored viscous mass. Yield: 45 %; UV-Vis ( $7.27 \times 10^{-5}$  M in  $\text{CDCl}_3$ ) [ $\lambda_{\text{max}}$ , nm ( $\epsilon_{\text{max}}$ ,  $\text{L mol}^{-1} \text{cm}^{-1}$ ): 496.0 (13755.0);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz, 25 °C,  $\text{Si}(\text{CH}_3)_4$ )  $\delta$  (ppm): 0.014 (s, 42H,  $\text{C}_{5, 6, 9, 10, 13, 14, 17, 18, 21, 22, 25, 26, 29, 30} \text{H}_3$ ), 2.98 (s, 12H,  $\text{C}_{39, 40, 39', 40'} \text{H}_3$ ), 7.03 (d, 2H,  $^3J=7.5$  Hz,  $\text{C}_{36, 36'} \text{H}$ ), 7.77 (s, 1H, NH), 7.99 (dd, 2H,  $^3J=8.0$  Hz,  $^4J=2.5$  Hz,  $\text{C}_{35, 35'} \text{H}$ ), 8.13 (m, 4H,  $\text{C}_{46, 46', 50, 50'} \text{H}$ ), 8.31 (m, 4H,  $\text{C}_{47, 47', 49, 49'} \text{H}$ ) 8.72 (d, 2H,  $^4J=2.5$  Hz,  $\text{C}_{42, 42'} \text{H}$ ); MALDI-TOF  $m/z$ : 1127.3  $[\text{M}+\text{H}]^+$ ; Elemental analysis (%) calculated for  $\text{C}_{44}\text{H}_{70}\text{N}_{10}\text{O}_{12} \text{Si}_7$ : C, 46.86; H, 6.26; N, 12.42; O, 17.03; Si, 17.43 %. Found: C, 46.88; H, 6.23; N, 12.41; O, 17.06; Si, 17.42 %.

**(10b)** Yellow colored viscous mass. Yield: 48 %; UV-Vis ( $7.27 \times 10^{-5}$  M in  $\text{CDCl}_3$ ) [ $\lambda_{\text{max}}$ , nm ( $\epsilon_{\text{max}}$ ,  $\text{L mol}^{-1} \text{cm}^{-1}$ ): 380.0 (9);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz, 25 °C,  $\text{Si}(\text{CH}_3)_4$ )  $\delta$  (ppm):  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz, 25 °C,  $\text{Si}(\text{CH}_3)_4$ )  $\delta$  (ppm): 0.014 (s, 42H  $\text{C}_{5, 6, 9, 10, 13, 14, 17, 18, 21, 22, 25, 26, 29, 30} \text{H}_3$ ), 2.98 (s, 12H,  $\text{C}_{39, 40, 39', 40'} \text{H}_3$ ), 7.02 (d, 2H,  $^3J=7.5$  Hz,  $\text{C}_{36, 36'} \text{H}$ ), 7.51 (m, 2H,  $\text{C}_{48, 48'} \text{H}$ ) 7.67 (m, 4H,  $\text{C}_{47, 47', 49, 49'} \text{H}$ ) 7.70 (s, 2H, NH), 7.89 (m, 4H,  $\text{C}_{46, 46', 50, 50'} \text{H}$ ), 7.99 (dd, 2H,  $^3J=8.0$  Hz,  $^4J=2.5$  Hz,  $\text{C}_{35, 35'} \text{H}$ ), 8.72 (d, 2H,  $^4J=2.5$  Hz,  $\text{C}_{42, 42'} \text{H}$ ); MALDI-TOF  $m/z$ : 1037.3  $[\text{M}+\text{H}]^+$ ; Elemental analysis (%) calculated for  $\text{C}_{44}\text{H}_{72}\text{N}_8\text{O}_8 \text{Si}_7$ : C, 50.93; H, 6.99; N, 10.80; O, 12.33; Si, 18.95 %. Found: C, 50.94; H, 7.01; N, 10.82; O, 12.34; Si, 18.92 %.

3) *Application Process of (5) and (9) on Polyester*: Exhaust high temperature application method was used for application of **(5)** and **(9)** coupling components on synthetic fiber fabrics. The same application method was used for both **(5)** and **(9)** molecules on polyester fabrics separately. 0.5 % compound o.w.f (on weight of fiber) was used. Before treatment, the fabric (10 g) was prewashed with nonionic detergent (2 g/L) in the presence of  $\text{Na}_2\text{CO}_3$  (2 g/L) at 75 °C for 35 min, in a liquor ratio of 1:20. The fabric was then rinsed and dried. The 10 g of polyester fabric was put in water at 65°C, in a liquor ratio of 1:20. pH was stabilized at 5.5 by  $\text{CH}_3\text{COOH}$  (10 %). 2 g/L of dispersing agent lycol RDN was dissolved in the water; 0.5 g/L (0.5 % compound o.w.f) azo polysiloxane molecule was transferred to the water. The temperature was increased from 65 to 100 °C at the rate of 5 °C/min and then further from 100 °C to 120 °C at the rate of 3 °C/min. Treatment process continued for 70 min. Temperature of the treatment vessel was reduced to 75 °C at 3 °C/min. The treated sample was rinsed and divided into smaller pieces for evaluation.

4) *Polysiloxane azo dyes (7a-7b, 10a-10b) formed inside the polyester fiber*. In vessel A, aniline

derivative (10 mmol) (**6a-6b**) was added to 1,5-naphthalenedisulfonic acid (10 mmol) in 100 ml of ethyl acetate and the solution was brought to 50 °C. Diazonium ion was synthesized by addition of *tert*-butyl nitrite (15 mmol) to the vessel A. Stirring continued for 25 min at 25 °C. In vessel B, polysiloxane coupling components (**5** or **9**)-carrying polyester (from process 3) was put in 100 ml ethanol and the temperature was brought down to 0-5 °C. Diazonium solution of aniline derivative (**6a-6b**) from vessel A was transferred to the vessel B while pH was kept stabilized at 5.5 with 2 %  $\text{CH}_3\text{COO Na}$ . Constant conditions were maintained for 2.5 hours, after which an azo compound (**7a-7b**, **10a-10b**) started to form on the surface of the polyester fibers. The sample was washed with water.

5) *Handle Evaluation Test of (7a-7b, 10a-10b)*. The treated fabric was divided into samples of  $100 \times 100$  mm size. These samples were put inside a rectangular text box. Subjects were provided with reference fabrics **A**, **B** and **C** before each evaluation and were informed of assigned values. Tests were conducted at 28 °C. The following methods were used:

#### i. Press Method

The same method was used for all samples. The subjects placed four fingers on the fabric surface inside the test box. Subjects ran their fingers along the sample linearly while applying pressure. Based upon their perception, the subjects then assigned a value between 1 and 20 (details are provided in Results and Discussion), compared to assigned values of standards **A**, **B** and **C**.

#### ii. Crush Method

Subjects were asked to place the treated sample in the palm of their hand and crush it by closing their fist. The subjects assigned a logical value between 1 and 20 (details given in Results and Discussion) compared to values given to the standards **A**, **B** and **C**.

## RESULTS AND DISCUSSION

### Synthesis

The synthesis consisted of a multiple step scheme (Schemes 1 and 2). The first step was the synthesis of coupling component. In this step, acyl addition elimination was carried out on 4-*N,N*-dimethylamino benzoic acid (**1**) with the terminal -OH and - $\text{NH}_2$  carrying polysiloxane (**4**) and (**8**) by using carbonyldiimidazole (CDI) [13]. The resultant coupling components (**5**) and (**9**) were applied to the polyester fabric substrate and then underwent electrophilic aromatic substitution with diazotised derivatives (**6a-6b**) to form the final polymeric azo dyes (**7a-7b** and **10a-10b**). Same dyes can be applied

to other polymeric substrates such as polyamide. Polyester fiber is globally the most used fiber, up to 50% of the overall synthetic fibers. Stable diazonium was formed in presence of *tert*-butyl nitrite [14] as a source of nitronium ion Lewis acid in presence of 1,5-naphthalenedisulfonic at room temperature in ethyl acetate. The structure of the azo polysiloxane can be greatly modified. Polysiloxane can be of various types, hence change in handling properties caused by these chains, can be modified as well. This can be achieved by selecting different substituents on the Si atom of the polysiloxane chain. There can be SiH(CH<sub>3</sub>), Si(CH<sub>3</sub>)<sub>2</sub>, etc. The polysiloxane itself can have different chain lengths. Alkyl substitution on the Si atom changes the polarity of the polysiloxane chain which directly relates to its resultant magnitude of softness. Hence, desired softness can be achieved.

#### Spectroscopic Analysis

We performed MALDI MS of unreacted polysiloxanes and then again after coupling component formation (**5**) and (**9**) and azo bond formation (**7a**, **7b**, **10a** and **10b**). All peaks were detected as the pseudomolecular ion peak [M+H]. MALDI spectra are given in Figs. S1-S8 (See Supplementary Section, A). We checked the difference in the masses of peaks after every reaction to confirm the formation of desired product molecule. Before esterification, the molecular ion peak of polysiloxane (**4**) was 535.2 m/z (Fig. S1) and a post-esterification compound (**5**) showed up at 682.3 m/z in MALDI-TOF (Fig. S2). This peak showed a difference of 147.1 m/z between -OH terminated polysiloxane (**4**) and modified polysiloxane (**5**). This difference confirms the

bonding of benzoic acid moiety. The difference in molecular ion peaks of compounds (**5**) and (**7a**) (Fig. S3) was found to be 148.9 m/z that confirmed the azo coupling of compound (**5**) with 4-nitroaniline (**6b**). [M+H]<sup>+</sup> for (**7a**) and (**7b**) appeared at 831.2 and 786.1 m/z, respectively.

For compound (**7b**) the difference in mass is 104.1 m/z (Fig. S4) that confirmed the azo coupling with aniline (**6a**). In the spectra of (**7a**) and (**7b**) unreacted coupling component (**5**) appeared at 682.3 m/z.

[M+H]<sup>+</sup> for (**10a**) and (**10b**) appeared at 1127.3 and 1037.3 m/z, respectively. In case of bisamine-terminated polysiloxane (**8**) (Fig. S5), the chain itself showed a peak at 535.1 m/z and a post-amide bond formation peak showed up at 829.3 m/z which confirmed the synthesis of compound (**9**) (Fig. S6). The difference of 294.2 m/z confirmed the bonding of two 4-N,N-dimethylamino benzoic s (**1**) at terminal position of the polysiloxane chain. After azo coupling reactions, molecular ion peaks of (**10a**) and (**10b**) showed up at 1127.3 m/z (Fig. S7) and 1037.3 m/z (Fig. S8), respectively. Azo coupled polysiloxane (**10a**) and (**10b**) showed differences of 298.0 m/z and 208.0 m/z, respectively, with coupling component (**9**) (Fig. S6). This confirms the azo formation at both ends of the polysiloxane chain. In the mass spectra of (**10b**) a peak was detected at 887.2 m/z (Fig. S8). This was attributed to a nitroso product. Mono and dinitroso products were detected at 858.3 m/z and 887.2 m/z in the spectra of (**10a**) (Fig. S7). This means that a nitroso byproduct was formed at both ends of the molecule, at the ortho position of the N(CH<sub>3</sub>)<sub>2</sub> on aryl rings as shown in Fig. 2. No such nitroso product was detected in the (**7a**) and (**7b**) azo molecules.

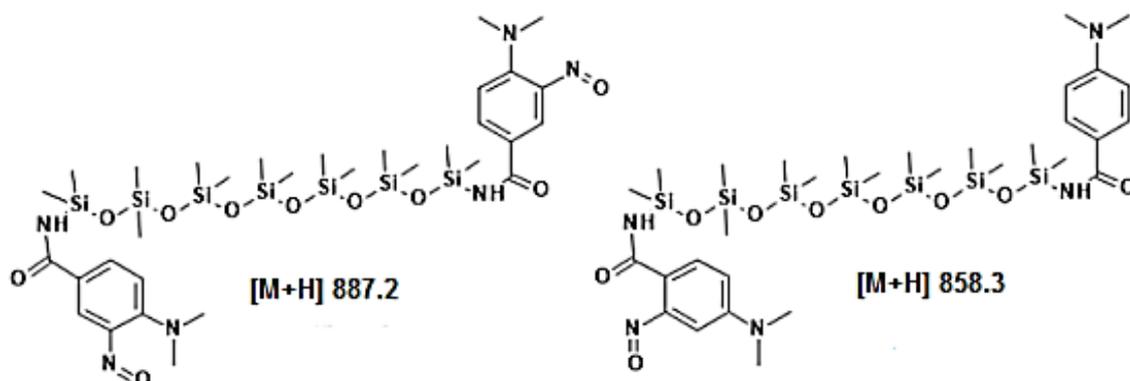


Fig. 2. Mono and dinitroso molecule

<sup>1</sup>H-NMR details are given in the spectroscopic data in the experimental section. <sup>1</sup>H-NMR spectra of (7a-7b, 10a-10b) are provided in Figures S9-S12 (see Supplementary Section B).

### Handle Properties

Subjective assessment method was used to evaluate the handle properties of the fabric containing (7a-7b) and (10a-10b). This method rated the handle-modifier molecule treated fabrics on a grading system which compares it with untreated fabric. Human subjects, designated as (P-1 to P-10), pressed their fingers against the fabric surface or crushed it inside their fists to judge the handle of the fabrics. These two approaches were called as press method and crush method [3]. The subjects gave the fabric a numerical value to the perceived handle between two extremes, i.e. fully stiffened and softener-treated fabrics of the same polymeric substrate. Values given by individual subjects for (7a-7b) and (10a-10b) are listed in Table 1. Three reference fabrics of the same polymeric structure and construction were used. One of the

reference fabrics **A** was treated with a stiffening handle modifier (arkofil; see materials section) and was given the value 1. The fabric **B** was untreated, hence was assigned the value 10. The third fabric was designated as **C** and was treated with nonionic silicone softener (sulfosoft; see materials section). Reading for **C** was pre-fixed as 20. If the fabric sample was perceived by the subject to be softer than softened reference fabric **C**, then readings beyond 20 could be recorded. Subjects were provided with reference fabrics before the test samples and the assigned values of the reference fabrics were revealed to them. Hence, the subject now had a reference scale to with two extremities at its end with untreated being the center of the scale. Subjects then assessed the samples by the above defined press method and crush method. Table 1 shows the evaluated readings. All fabrics treated with (7a-7b) and (10a-10b) showed increased softness compared to the untreated fabric **B**. Less variance was noted in the crush method values, hence it proved to be more reliable.

**Table 1.** Subjective evaluation data from the crush and the press methods on treated polyester fabric

Judge	Crush method				Press method			
	7a	7b	10a	10b	7a	7b	10a	10b
P-1	14	14	14	14	12	13	16	14
P-2	15	17	17	17	14	16	15	19
P-3	14	15	15	15	12	13	16	17
P-4	17	15	15	16	17	16	18	17
P-5	16	15	16	19	12	12	16	14
P-6	15	16	14	15	16	16	15	16
P-7	16	17	17	17	12	13	17	15
P-8	16	15	15	16	14	16	12	13
P-9	17	15	15	18	12	13	16	12
P-10	18	13	16	16	14	16	18	18
Variance	1.73	1.51	1.15	2.23	3.38	2.93	2.98	5.16

### CONCLUSIONS

The synthesis of azo polysiloxane and the study of their impact on the handle properties of treated fabrics provide a foundation for the development of functional textile dyes. We used *tert*-butyl nitrite-based stable diazonium formation method to facilitate fabric azo dye formation. These molecules can simultaneously perform the coloration and finishing functions in textile treatment processes; potentially reducing production time and costs. A series of azo-bonded polysiloxane molecules can be synthesized on a similar pattern. The resultant

handle properties were evaluated through a subjective handle evaluation model. Because of the presence of polysiloxane chains on the edge of the molecule, the handle of polymeric substrates treated with azo polysiloxane molecules was altered. This implies that bonded polysiloxane chains are responsible for dire changes in the handle of the substrate.

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