Novel Synthesis of Unsaturated Pigment Anthracene Triazole Acrylate via Click Chemistry to Prepare Colored Binder for Textile Printing

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THIS WORK represents the synthesis and preparation of new unsaturated pigment, 2-anthracene triazole acrylate, via click reaction. The prepared pigment was used as a colored binder for textile printing with different fabrics types. Optimum of the prepared pigment content in the printing paste and its effect on the fastnesses properties of the prints were evaluated. This pigment contains unsaturated groups that could be co-polymerized with monomers to produce colored binders. The Measurements and Characterization of the prepared pigment (2-anthracene triazole acrylate) as particle size, particle size distribution, Glass transition temperature ($T_g$), Stiffness properties as well as its rheological properties to evaluate if this prepared pigment can be used as a colored binder in textile printing of different fabrics. The prepared pigment (2-anthracene triazole acrylate) was considered as a monomer and copolymerized with acrylic acid and butyl acrylate and characterized. From the obtained data it can be concluded that this pigments would be a part from binder chains which enhances rubbing and fastness properties of the prints fabrics.

Keywords: Emulsion polymerization, Co-polymer, Colored binder, Pigment, Textile printing, Click chemistry.

Introduction

Click Chemistry is a term that was introduced by Karl Barry Sharpless in 2001 to describe reactions that are wide in scope, high yielding, has little side products, simple reaction and purification conditions[1,2]. The copper (I) catalyzed cycloaddition of azides and alkynes (CuAAC) developed by Professors Fokin–Sharpless [3] has become good example of click reaction. Huisgen, R. was the first to understand the scope of 1, 3-dipolar cycloaddition reaction which has been widely used in organic synthesis [4]. The traditional azide alkylne Huisgen cycloaddition reaction joins an organic azide and alkyn together by heating, often to more than 100 °C for least several hours that produces a mixture of 1,4- and 1,5- disubstituted triazoles. Copper catalysts discovered by Fokin and Sharpless accelerate the reaction to minutes and at much lower temperatures. The result of this copper catalyzed reaction is mostly a 1, 4-disubstituted triazole product.

Colored binders are obtained by emulsion copolymerization of pigment particles and monomers, so that the pigment molecules will be chemically bonded with binders. This technique could improve the fastness properties of the pigments [5]. This work describes a new method of printing fabrics with pigment. The prepared pigment (2-anthracene triazole acrylate) was considered as a monomer and copolymerized with acrylic acid and butyl acrylate and characterized. Therefore the pigments would be a part from binder chains which enhances rubbing and fastness properties of the prints.

Emulsion polymerization is a versatile technique, generally utilized in industry to produce latexes for an extensive change of utilization including paints, coatings, adhesives, and binders in the textiles and paper industries [6,7]. The predominant parts of an emulsion polymerization recipe are the monomer(s), dispersing medium (usually water), surfactant and initiator. Emulsion polymerization includes the emulsification of monomers in an aqueous phase, and stabilization of the droplets by a surfactant [8-10].

With the public’s mature demand in recent times pressurized the textile industry for use of natural colorants, without any harmful effects on environment and aquatic ecosystem, and with more developed functionalities simultaneously,
new technique which saves time and energy and enhancement the final properties of the textile that consumer use. Advanced developments for the saving energy resources and their sustainable use for multifunctional clothing are gaining pace now [11-14].

The present study highlights on the preparation of new pigment, 2-anthracene triazole acrylate, via click reaction. The prepared pigment (2-anthracene triazole acrylate) was considered as a monomer and copolymerized with acrylic acid and butyl acrylate. Therefore the pigments would be a part from binder chains which enhances the textile printability as well as rubbing and all over the fastness properties of the prints. The prepared pigment was tested with different fabrics types to optimum pigment content in the printing paste This pigment contains unsaturated groups that could be co-polymerized with monomers to produce colored binders.

**Experimental**

**Chemicals:**
The chemicals used in this study include Butyl acrylate (BA, 99%, MW 128.17 g/mol, Merck Schuchardt OHG), Acrylic acid (AAc, 99.5%, MW 72.06 g/mol, Panreac Sintesis), Sodium dodecyl sulphate (SDS, 97%, MW 288.38 g/mol, Merck Schuchardt OHG, as the emulsifier), potassium persulphate/glucose as a redox initiator, (KPS, 98%, MW 270.33 g/mol, Merck Schuchardt OHG) and Glucose (95%, MW 198.17, RFCL Limited). Deionised water was used in all experiments. The monomers were distilled to remove inhibitors before use. All other chemicals were used as received.

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Chemicals used in preparation of anthracene triazole acrylate pigment include Sodium nitrite: (NaNO₂, 98%, MW 69 g/mol, Merck Schuchardt OHG), 2-aminoanthracene: (C₁₄H₁₁N₂O₂, 90%, MW 193.24 g/mol, Sigma-Aldrich Chemie GmbH), Propargyl acrylate: (98%, MW 110.11 g/mol, Sigma-Aldrich Chemie GmbH). Copper (II) Sulfate: (CuSO₄, 99.9%, MW 159.61 g/mol, Merck Schuchardt OHG), Sodium Ascorbate: (NaAsc, 99.9%, MW 198.11 g/mol, Merck Schuchardt OHG) and Tris(1-benzyl)-H-1,2,3-triazole-4-yl)methyl amine: (TBTA, 97%, MW 530.63 g/mol, Sigma-Aldrich Chemie GmbH).

Printing auxiliaries: Thickener: (Alcoprint PTP; synthetic thickener based on polyacrylic acid) was supplied by Ciba Specialty Chemicals Inc.

**Preparation:**

**Preparation of 2-azidoanthracene**

A solution of sodium nitrite (0.5 g NaNO₂/16 ml water) was added dropwise to a solution of 2-aminoanthracene (1g / 30 ml water) and 3 ml concentrated sulfuric acid at 0°C over 5 minutes. The reaction mixture was stirred at 0°C for 30 minutes, then a solution of sodium azide (0.6 g / 5 ml water) was added dropwise over 10 minutes. The solution was slowly warmed to room temperature and kept stirring for 5 h. The precipitate was isolated by filtration (Scheme 1).

**Preparation of 2-anthracene triazole acrylate pigment**

2-azidoanthracene 0.5 g and 0.3 g propargyl acrylate were placed in a 250 ml round bottom flask charged with 3:1 mixture (v/v) of DMF and water (60 ml). 0.1 g Copper (II) Sulfate, 0.2 g sodium ascorbate and 0.1g TBTA were added at room temperature. The reaction mixture was stirred for 8 hrs at room temperature. After removing the volatile solvents, the residue was treated with methanol (10 ml) and then the insoluble solid was filtered of (Scheme 2) [15].
Preparation of colored binder (micro-emulsion copolymerization of 2-anthracene triazole acrylate - butyl acrylate - acrylic acid)

The micro-emulsion co-polymerization process was carried out using mixture of BA, AAc and 2-anthracene triazole acrylate comprising 10/10/17 wt. % AAc / BA / pigment. A typical polymerization procedure was carried out in a 4-necked flask equipped with a reflux condenser, a thermometer, an addition funnel, a mechanical stirrer and N₂ gas inlet and outlet.

A solution of 2g wt. % BA, 5g wt. % SDS, 0.2g wt. % of KPS, 0.1g wt. % glucose and 57.7 ml water were charged to the reactor to prepare the pre-microemulsion. N₂ gas was bubbled through the microemulsion for 10 minutes. The flask was then heated to 70°C with mild stirring (200 rpm) for 20 minutes. Then the monomers in the addition funnel were continuously and slowly added to the polymerizing micro-emulsion through 2 hrs with mild stirring (200 rpm).

Printing
Preparation of printing pastes

The printing pastes were prepared according to the formulation given in Table 1. Ammonia, urea, diammonium phosphate and binder were mixed with water. The synthetic thickener PTP was then introduced and the paste was stirred using a high shear mixer for 10 minutes to allow full viscosity to develop. The pigment was then added to the mixture with stirring using a high shear mixer for 15 minutes. If the viscosity of the printing pastes decreases, a slight amount of the thickener is added to maintain consistent viscosity values of the pastes at 21,000 cps at rate of shear of 2.180 [16, 17].

TABLE 1. Formulation of the printing paste.

<table>
<thead>
<tr>
<th>Components</th>
<th>Weight (in grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>X</td>
</tr>
<tr>
<td>Ammonia (25 %)</td>
<td>0.5</td>
</tr>
<tr>
<td>Binder</td>
<td>15-20</td>
</tr>
<tr>
<td>Thickener (Alcoprint PTP)</td>
<td>2</td>
</tr>
<tr>
<td>Diammonium phosphate</td>
<td>0.5</td>
</tr>
<tr>
<td>Urea</td>
<td>4</td>
</tr>
<tr>
<td>Pigment</td>
<td>3-5</td>
</tr>
<tr>
<td>Total</td>
<td>100 g</td>
</tr>
</tbody>
</table>

Printing technique
All the printing pastes were applied to the fabrics using the flat screen printing technique.

Print fixation
Print fixation was done by thermofixation at 160°C for 4 minutes in an automatic thermostatic oven (Wener Mathis Co., Switzerland). Thermofixation also was done at different periods and temperature to determine the optimum condition of fixation.

Measurements and Characterization
Particle size and particle size distribution
Particle sizes of the polymerized micro-emulsion latexes were determined using a JEOL-GEM transmission electron microscope and particle size distribution was determined using Leica Qwin 500 image analyzer.

Glass transition temperature (Tg)
The Tg of the prepared binders were measured by differential scanning calorimetry (DSC) Shimadzu–50

UV/Visible spectra
The ultraviolet-visible absorbance spectrum of the prepared pigment was measured using the Shimadzu UV/V spectrophotometer.

Color strength measurements
The color strength of the printed samples expressed as K/S was evaluated by high reflectance technique [18]. Reflectance measurements of the printed fabrics were performed on Perkin – Elmer Lambda 3B, UV/V Spectrophotometer. The color strength expressed as K/S was assessed by applying the Kobelka Munk equation as follows:

\[ K/S = \frac{(1-R)^2}{2R - (1-R_o)^2/2R_o} \]

Where:

\( R, R_o \) are decimal fractions of the reflectance of the printed and unprinted fabric respectively.

K = absorption coefficient.
S = scattering coefficient.

Fastness properties
The colorfastness to rubbing (dry and wet) [19], to washing [20], to perspiration (alkaline, acidic) [21].

Color fastness to light
Color fastness to light was determined according to AATCC test method (16A–1989). The evaluation was established using the blue scale as reference of color change [22].

Stiffness properties
Stiffness of printed and unprinted samples was determined according to ASTM test method D 1388 – 96 using the cantilever apparatus [23].

Rheological properties of the printing pastes
The rheological properties of the pastes were measured using a rotary viscometer (Rheomat – 15, Zurich, Switzerland).

Results and Discussion

Effect of pigment concentration in the printing paste on properties of the prints
Table 2 shows the effect of pigment content in the printing paste on the color strength and fastness properties of the printed cotton samples, using BA-AAc commercial binder. It is evident that the color strength of the prints increases with increasing the pigment content. All prints have very good fastness to light rubbing, washing, and perspiration while the stiffness of the printed samples increases slightly with the increasing the pigment content. From the results, we can conclude that the optimum pigment content in the printing paste is 4%.

UV/Visible spectrum
The prepared 2-anthracene triazole acrylate pigment is typically yellow in color. The electronic spectrum of dilute solution of it in DMSO is shown in Figure 1. The pigment shows an absorption band in the visible region at $\lambda_{\text{max}} = 445$ nm.

Effect of monomers content ratio on the properties of micro emulsion binder
Various micro-emulsion binders were prepared by different monomers composition using, 10/10/13, 10/10/17 or 10/10/20 wt. % AAc/BA/pigment wt %. Table 14 shows the effect of monomers content ratio on the properties of microemulsion polymer. The results indicate that

<table>
<thead>
<tr>
<th>Pigment conc. (%)</th>
<th>K/S</th>
<th>Light</th>
<th>Stiffness</th>
<th>Rubbing</th>
<th>Washing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Dry</td>
<td>Wet</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alt</td>
<td>Stain</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alt</td>
<td>Stain</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alt</td>
<td>Stain</td>
</tr>
<tr>
<td>2</td>
<td>2.7</td>
<td>6</td>
<td>1420</td>
<td>3-4</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>3.8</td>
<td>6-7</td>
<td>1450</td>
<td>3-4</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>4.3</td>
<td>7</td>
<td>1490</td>
<td>3-4</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>4.4</td>
<td>7</td>
<td>1530</td>
<td>3</td>
<td>2-3</td>
</tr>
</tbody>
</table>

Fig. 1. UV/Visible spectrum of 2-anthracene triazole acrylate pigment.

the average particle size of the microemulsions was increased by increasing the pigment content. Also, all of the prepared colored binders were found to be homogeneous, compatible and stable. Table 3 shows also that the prepared colored binders have good Tg which lies between 1.9 and 3.7; enabling them to use as binders for textile pigment printing. Tg values of the prepared colored binders were increased by increasing the pigment content. This may be attributed to the presence of bulky groups restricting the mobility of polymer chains [24].

Effect of monomers content ratio on the color strength and fastness properties of the prints

On the other hand the results of Table 4 represent the effect of monomers content ratio of the colored binder on the color strength and fastness properties of pigment printed areas. The color strength increased with increasing the pigment content in the colored binder from 13% to 17% but there is no significant increase in the color strength with the increasing of the pigment content from 17% to 20%. All of the prints have very good fastness to light, washing, and perspiration. Also, all prints have good handle. From the data obtained it could be concluded that, the optimum monomer content ratio for colored binder preparation is 10/10/17 [25, 26].

Effect of the prepared binder concentration in the printing paste on properties of the pigment prints

To determine the optimum colored binder in the printing paste, five samples of cotton fabric were printed with different colored binder concentrations 18, 20, 22, 24, 26 wt % of the printing paste. As illustrated by Figure 2, the color strength of the prints increased when the colored binder content was increased in the printing paste. Also, the suitable colored binder concentration in the printing paste is 24 wt % of the paste.

TABLE 3. Effect of monomers content ratio on the properties of micro emulsion polymer.

<table>
<thead>
<tr>
<th>AAc/BA/pigment wt%</th>
<th>Average particle size (nm)</th>
<th>Tg (°C)</th>
<th>Coagulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/10/13</td>
<td>107</td>
<td>1.9</td>
<td>No</td>
</tr>
<tr>
<td>10/10/17</td>
<td>148</td>
<td>2.3</td>
<td>No</td>
</tr>
<tr>
<td>10/10/20</td>
<td>160</td>
<td>3.7</td>
<td>No</td>
</tr>
</tbody>
</table>

TABLE 4. Effect of monomers content ratio on the color strength and fastness properties of the prints.

<table>
<thead>
<tr>
<th>AAc/BA/pigment wt%</th>
<th>K/S</th>
<th>Light</th>
<th>Stiffness</th>
<th>Rubbing</th>
<th>Washing</th>
<th>Perspiration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Dry</td>
<td>Wet</td>
<td>Acidic</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alt</td>
<td>Alt</td>
<td>Alkaline</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Stain</td>
<td>Stain</td>
<td></td>
</tr>
<tr>
<td>10/10/13</td>
<td>4.7</td>
<td>8</td>
<td>1335</td>
<td>4-5</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>10/10/17</td>
<td>5.3</td>
<td>8</td>
<td>1362</td>
<td>4</td>
<td>3-4</td>
<td>5</td>
</tr>
<tr>
<td>10/10/20</td>
<td>5.4</td>
<td>7-8</td>
<td>1380</td>
<td>4</td>
<td>3-4</td>
<td>4-5</td>
</tr>
</tbody>
</table>

Fig. 2. Effect of colored binder concentration in the printing paste on the color strength of the prints.
Color strength and fastness properties of the prints using the prepared binder on different types of fabrics

Table 5 represents the color strength and the fastness’s properties of printed cotton, polyester or cotton/polyester blend fabrics using: The prepared colored binder and non-colored. From the data obtained, it is obvious that the use of colored binder enhanced the color strength and fastness properties of all fabrics types.

Conclusion

The present study involves the preparation of new pigment, 2-anthracene triazole acrylate, via click reaction. The prepared pigment was tested with different fabric types. Optimum pigment content in the printing paste and fastnesses properties of the prints were detected. The prepared pigment showed maximum UV/Visible absorption at 445 nm.

The prepared pigment, butyl acrylate and acrylic acid monomers were copolymerized to produce colored binder (pigment particles became a part of binder chains). Cotton, polyester or cotton/polyester blend fabrics were printed using the prepared colored binder. The results were compared with those produced by non colored binder. It was found that the uses of colored binder improved the color strength and fastnesses properties of all fabrics types.

**TABLE 5. Color strength and fastness properties of Pigment Print Pastes applied to cotton, polyester or cotton/polyester blend fabrics**

<table>
<thead>
<tr>
<th>Fabric type</th>
<th>Binder type</th>
<th>K/S Light</th>
<th>Rubbing</th>
<th>Washing</th>
<th>Perspiration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dry</td>
<td>Wet</td>
<td>Alt Alt Alt</td>
</tr>
<tr>
<td>Cotton</td>
<td>Non colored</td>
<td>4.3</td>
<td>7</td>
<td>3-4</td>
<td>3-4 4-5 4-5</td>
</tr>
<tr>
<td></td>
<td>Colored binder</td>
<td>5.3</td>
<td>8</td>
<td>4</td>
<td>3-4 5 5</td>
</tr>
<tr>
<td>Polyester</td>
<td>Non colored</td>
<td>4.0</td>
<td>7</td>
<td>3-4</td>
<td>3-4 4-5 4-5</td>
</tr>
<tr>
<td></td>
<td>Colored binder</td>
<td>4.7</td>
<td>8</td>
<td>4</td>
<td>3-4 5 5</td>
</tr>
<tr>
<td>Cotton/polyester</td>
<td>Non colored</td>
<td>4.1</td>
<td>7</td>
<td>3-4</td>
<td>3-4 4-5 4-5</td>
</tr>
<tr>
<td>blend 65/35%</td>
<td>Colored binder</td>
<td>5.1</td>
<td>8</td>
<td>4</td>
<td>3-4 5 5</td>
</tr>
</tbody>
</table>

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تحضير صبغات جديدة غير مشبعة 2- أنتراسين تريازول أكريليت لتحسين كيمياء النقر واستخدامها في طباعة الأقمشة

كربمة حجاج، أحمد هاشم، نجلاء الشيمي، زين محمود، فايزه قنطوش

orable صبغات جديدة غير مشبعة

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يتضمن البحث تحضير صبغات بيجمنت جديدة غير مشبعة، وذلك عن طريق تفاعل النقر. تم استخدام صبغة البيرممت المحضره كبيندر ملون لطباعة أنواع مختلفة من الأقمشة. كما اعتمدت هذه الدراسة لتطبيق النقر لتحضير الصبغة المختلفة والطريقة الجديدة كيمياء النقر في معجون الطباعة. وتأثر على خصائص ثبات الصبغات للأقمشة المطبوعة. هذه الصبغة المحضره تحتوي على مجموعات غير مشبعة يمكن بلمرتها مع مونومرات لإنتاج بيندريات ملونة. هذا وقد أجريت العديد من القياسات والتوصيفات للصبغة المحضره (2-أنتراسين تريازول أكريلات) منها على سبيل المثال حجم الجزيئات، التوزيع الحجمي لجزيئات الصبغة، درجة حرارة التحول الزجاجي (Tg)، خصائص الصلابة وكذلك الخواص الريولوجية لمسيرةها إذا كان من الممكن استخدام هذه الصبغة المحضره كبيندر ملون في طباعة الأقمشة المختلفة. وقد أوضحت النتائج أنه من الممكن اعتبار هذه الصبغة المحضره (2-أنتراسين تريازول أكريليت) كمونومر وبوليمير مع حمض الأكريليك وبيوتيل أكريليت. كما أوضحت النتائج التي تم الحصول عليها أن ملخص الصلبة للاحتكاك وخصائص ثبات الصبغة للأقمشة التي تم طباعتها في وجود هذا البيرندر الملون.