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(72) Inventeurs/Inventors:
LUCHT, BRETT L., US;
EULER, WILLIAM B., US;
GREGORY, OTTO J., US

(73) Propriétaire/Owner:
THE BOARD OF GOVERNORS FOR HIGHER EDUCATION, STATE OF RHODE ISLAND AND PROVIDENCE PLANTATIONS, US

(74) Agent: BORDEN LADNER GERVAIS LLP

(54) Titre : POLYMERES THERMOCHROMES POUR ESTIMATION VISUELLE RAPIDE D'UNE TEMPERATURE
(54) Title: THERMOCHROMIC POLYMERS FOR RAPID VISUAL ASSESSMENT OF TEMPERATURE

(57) Abrégé/Abstract:
A thermochromic polymer-based temperature indicator composition which comprises a polythiophene and a carrier medium. The structure of the compound is designed such that when the composition is placed in a heat-exchange relationship with an article, the composition will exhibit a color change when a design temperature or a temperature beyond the design temperature is reached in the article.

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(71) Applicant *(for all designated States except US)*: **THE BOARD OF GOVERNORS FOR HIGHER EDUCATION, STATE OF RHODE ISLAND AND PROVIDENCE PLANTATIONS** [US/US]; 301 Promenade Street, Providence, RI 02908 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **LUCHT, Brett, L.** [US/US]; 145 Legend Rock Road, Wakefield, RI 02879 (US). **EULER, William, B.** [US/US]; 35 Flintstone Road, Narragansett, RI 02882 (US). **GREGORY, Otto, J.** [US/US]; 87 Westwind Road, Wakefield, RI 02879 (US).

(74) Agents: **STEVENS, Richard, L.** et al.; Samuels, Gauthier & Stevens, Suite 3300, 225 Franklin Street, Boston, MA 02110 (US).

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(54) Title: THERMOCHROMIC POLYMERS FOR RAPID VISUAL ASSESSMENT OF TEMPERATURE

(57) Abstract: A thermochromic polymer-based temperature indicator composition which comprises a polythiophene and a carrier medium. The structure of the compound is designed such that when the composition is placed in a heat-exchange relationship with an article, the composition will exhibit a color change when a design temperature or a temperature beyond the design temperature is reached in the article.

Thermochromic Polymers for Rapid Visual Assessment of Temperature

Background of the Invention

1. Field of the Invention

The invention relates to polythiophene-based temperature indicators.

2. Description of Relevant Art

Polythiophenes are known for their electrically conductive properties. One technique used to study polythiophenes is to analyze associated color changes when the temperature of the polythiophene is varied. Color changes provide insight into the electro-conductive properties of the polymer. There are numerous patent and literature citations which describe this work.

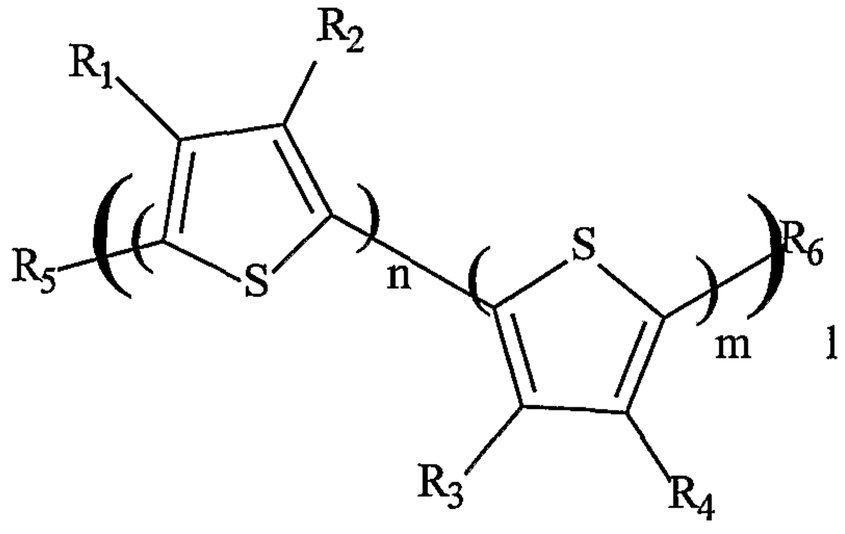
In many instances it is clearly desirable to know when an object or article reaches or has exceeded a specific temperature simply by viewing the object and noting that at least a portion of the object has exhibited a color change. Viewing includes visual observation by an individual or detection of color change by a sensor, which sensor would output a signal to be detected in any suitable manner.

As an example, in the food service industry there are hot trays and cold trays in which food is stored and/or served. If a cold tray, such as by regulation, is required to be maintained at a temperature of 38° or lower then a sensor system might be in place to signal (alarm) that the temperature is above 38°F. Alternatively, a thermometer might be used. However, in the food service industry, margins are thin, and unless required by regulation, sensing systems will not be used. There are enumerable situations where it would be desirable to provide a visual color indicator which would appear on an article if the temperature were unsafe, hot drink cups, stove tops, etcetera and/or not functioning properly, hot plates, freezers, etcetera, or if to know when desired temperatures were reached, e.g. ovens.

Brief Summary of the Invention

The present invention utilizes the color change characteristics of polythiophenes in a sensing system, which system will change color at a specific design temperature.

The polythiophene is generally of the structure:



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wherein R_1-R_6 = a hydrogen, substituted or unsubstituted alkyl radical, substituted or unsubstituted alkoxy radical, substituted or unsubstituted aryl radical, substituted or unsubstituted thioalkyl radical, substituted or unsubstituted trialkylsilyl radical, substituted or unsubstituted acyl radical, substituted or unsubstituted ester radical, substituted or unsubstituted amine radical, substituted or unsubstituted amide radical, substituted or unsubstituted heteroaryl or substituted or unsubstituted aryl radical

n is between 1 and 1000,

m is between 0 and 1000, and

l is between 1 and 1000.

The synthesized polythiophene is mixed with a carrier system or liquid medium. Depending upon the specific polythiophene used, the carrier system can be aqueous or organic. The polythiophene can be used in the carrier system as a mechanical separation, colloidial solution, or a molecular solution. Also, surfactants, anionic, cationic or non-anionic, can be used if necessary in the carrier system to ensure uniform distribution of the polythiophene in the system.

For the example described in the Background, a polythiophene is synthesized to exhibit the color change at about 38°F and maintain that color change at lower temperatures when used in a carrier system, which system is placed in heat transfer relationship with the tray (article) the temperature of which is being monitored.

Conversely, if the hot tray is to be maintained at about 180°F or higher then a polythiophene is synthesized to change color at about 180°F. The polythiophene is mixed in a carrier system, which carrier system is placed in heat exchange relationship, such as by coating, at least a portion of the tray.

In a preferred embodiment, polythiophene in an amount of 0.05 to 5.0% by weight based on the total weight of the system, preferably 0.2 to 0.8% weight, is mixed with an organic solvent. Suitable solvents include tetrahydrofuran, chloroform, methylene chloride, toluene, and N-methylpyrrolidone.

In yet another embodiment, polythiophene in an amount of 1.0-25% by weight based on the total weight of the system, preferably 7.0 to 14% weight, is dispersed in commercially available printable ink formulations, e.g. oil with resins, pigment extenders and other additives. The system can be printed using conventional methods such as ink-jet and letter press. Examples of ink formulations that polythiophene can be dispersed in can include combinations of resins such as cellulose, nitrocellulose with co-binders including polyamides, polyester amides, alkyd, epoxy acrylates, amine acrylates, polyurethanes, and polyvinyl butyral (UNI-REZ, UNI-JET, BECKOSOL, EPOTUF), suitable oils such as napthenic petroleum oils and vegetable oils, e.g. soy bean oil, and suitable pigment extenders and additives that can include organic acids and esters of organic acids such as malic acid and organic solvents such as 1,5-pentanediol, diethylene glycol, along with other alcohols and related compounds (VERTEC, SYLFAT, UNI-KYD, and ICM, DY-SOLVE lines of additives.).

In yet another embodiment of an ink formulation system, polythiophene is dispersed in an ink formulation in an amount of about 1 .0 to 25% by weight of the total system, preferably 7.0 to 14% weight. The ink formulation system can then be printed on at least a portion of a suitable substrate, e.g. a portion of paper, plastic, or ceramic food/beverage containers, a portion of packaging materials for foods and goods, labels, a portion of labels, stickers, etc., using conventional printing methods. The polythiophenes dispersed in the system can be in particulate form and have diameters in the range of between about 0.01 – 0.1 microns thereby rendering the system suitable for fine printing.

In another embodiment of the invention, the system is applied to the article as a coating on an area of the article, or the entire article, which will be visible during the expected use of the article. The coating can be applied by any technique known in the art, such as by brush, roller, spraying, etc. Accordingly, the coatings typically have a

thickness of 0.1 to 1000 microns. The carrier system can also be absorbed on a surface or both absorbed and adsorbed on a surface.

In another aspect of the invention, the system is comprised of polythiophenes that visually and reversibly change color at a prescribed temperature in the range of about -40-180 °C and are thermally stable to high temperatures in a range of about 200-300 °C. The temperature of the color change of the polythiophenes, hereinafter the thermochromic transition, and the high and low temperature colors can be tailored by chemical modification of the polythiophenes.

In synthesizing a polythiophene for a specific design temperature, eg. for the series of poly(3-alkylthiophene)s there is roughly an inverse correlation with the length of the *n*-alkane substituent and the temperature of the thermochromic transition for both the regiorandom (R_1=alkyl, R_4=alkyl, n≈0.8, m≈0.2, l=40-80, R_2,R_3,R_5,R_6=H) and regioregular (R_1=alkyl, n= 40-80, m=0, R_2,R_5,R_6=H), poly(3-*n*-alkylthiophene)s. For regiorandom polymers longer substituents such as *n*-hexadecyl have lower temperature thermochromic transitions (81 °C) than shorter chain substituents such as *n*-octyl (130 °C). The regioregular polymers have higher thermochromic transitions than the regioregular polymers but the same inverse correlation with chainlength is observed. The *n*-hexadecyl and *n*-octyl have thermochromic transition centered around 125 and 175 °C. As long as the number of thiophene units in the polymer is approximately greater than sixteen the thermochromic transitions is molecular weight independent. Oligothiophenes ($n+m+1 < 16$) have lower temperature thermochromic transitions than the polythiophenes ($n+m+1 > 16$).

Yet another aspect of the invention comprises paint, plastic or rubber composites comprised of the polythiophenes that are one color at temperatures below the thermochromic transition and are another color while above the transition. Both the low and high temperature colors and the temperature of the color change vary as a function of the substituent groups R_1, R_2, R_3, R_4, R_5, and R_6, the number of repeat units (l), and regioregularity of the repeat units (n and m).

The invention also comprises polythiophenes that can be used as pure compounds or can be incorporated into paints including polyurethanes, polysiloxanes, polyacrylates, and other related polymer-based paints and coatings with about 0.5 % polymer based pigment with retention of the thermochromic behavior. The thermochromic polymer-based pigments can be incorporated via injection molding or extrusion into many

commercially important plastics such as poly(ethylene terephthalate) (PET), polysytrene, polyethylene (HDPE and LDPE), other polyolefins, polydienes, polycarbonates, polyacrylics, polyacrylic acids, polyacrylamides, polymethacrylics, polyvinyl ethers, polyvinyl halides, poly(vinyl nitrile)s poly vinyl esters, polyesters, polysofones, polysulfonamides, polyamides, polyimines, polyimides, carbohydrates, and polymer mixtures and copolymers. The plastics retain a visually retrievable thermochromic response with pigment loadings of about 0.5 % polymer-based pigment.

The sensor system can be used as a safety feature or a thermal sensor for stoves, baking utensils or pans, radiator caps, cooling racks, paper/plastic coffee cups and lids, baby bottles, cooking utensils, cooking ware, fire safety, food packaging, instrument sterilization, novelty items, food preparation and handling equipment, warning labels, packaging film, microwave dishes, frozen food packages, beverage bottles, cable or wire coverings, motor and engine parts, breaking systems, automobile or truck tires, bathtub coatings, road signs, refrigerator cases, interior wall paint and other substrates and/or articles where a visual indication of a temperature change is important.

Brief Description of the Drawing(s)

Fig. 1 is a photograph depicting a polythiophene film of the invention on glass, hot and cold.

Fig. 2 is a graph depicting the visible spectrum of a polythiophene film of the invention as a function of temperature.

Fig. 3 is a graph depicting a plot of the wavelength of the absorption band edge at half the maximum intensity for a polythiophene as a function of temperature.

Description of the Preferred Embodiment(s)

Referring to Fig. 1, a photograph of two films is depicted, one at room temperature and one above the thermochromic transition. The films are comprised of a polythiophene wherein R_1 and R_4 are $-(CH_2)_{17}CH_3$, R_2, R_3,R_5 and R_6 are H, n is 0.8, m is 0.2, and l is between 40 and 80. The film changes color at about 60 °C.

Referring to Fig. 2, a graph of the visible spectrum of a polythiophene wherein $R_1 = R_4 = -(CH_2)_{17}CH_3$, $R_2 = R_3 = R_5 = R_6 = H$ as a function of temperature is shown. The graph displays a dramatic difference in absorption around 500 nm. At low temperature the absorbance is quite high while at high temperature the absorbance is low. This feature in the optical spectrum is responsible for the visual color change of the polythiophene.

Referring to Fig. 3, a plot of the wavelength of the absorption band edge at half

of the maximum intensity for a polythiophene as a function of temperature is shown. The inversion point for the color transition for the polythiophene wherein $R_1 = R_4 = -(CH_2)_{17}CH_3$, $R_2 = R_3 = R_5 = R_6 = H$ occurs at about 62°C while the inversion point for the color transition for the polythiophene wherein $R_1 = R_4 = -(CH_2)_{15}CH_3$, $R_2 = R_3 = R_5 = R_6 = H$ occurs at 81° C. This indicates that the temperature of the thermochromic transition can be changed by altering the substituents on the polymer backbone.

Based on the teachings of this disclosure, one skilled in the art could design a polythiophene with a predetermined thermochromic transition by investigating the systematic trends of the thermochromic transition as a function of polythiophene or oligothiophene structure. The temperature can be dropped by increasing the length of the alkyl substituent R_1 or by via the preparation of oligmers. The temperature of the thermochromic transition can be increased by preparing regioregular poly(3-alkylthiophene)s or using shorter alkylsubstituents (R_1).)

The invention will further be described with reference to following non-limiting examples.

Preparation of Poly(3-alkylthiophene)s

3-*n*-octadecylthiophene

3-*n*-octadecylthiophene was prepared as set forth in Kumda et al *Bull. Chem Soc. Jpn.* 1976, *49*, 1958-1969 and Tetrahedron 1982, *38*, 3347-3354. A dry 1000 mL 2 neck flask was charged with Mg ribbon (3.34 g, 137 mmol) under N_2 followed by addition of ~200 mL of anhydrous Et_2O. The flask was cooled in an ice bath (0° C). In a separate 500 mL flask 40 g (120 mmol) of *n*-$C_{18}H_{37}Br$ was dissolved in ~200 mL of anhydrous Et_2O under N_2. The Et_2O solution of *n*-$C_{18}H_{37}Br$ was slowly transfer into the flask containing the Mg ribbon, with sonication, stirring, and addition of I_2 to initiate Grignard. After complete addition of *n*-$C_{18}H_{37}Br$ to the Mg the reaction mixture was allowed to stir overnight to allow for complete formation of the Grignard reagent (*n*-$C_{18}H_{37}MgBr$). A dry 1000 mL 3-neck flask was charged with 0.540 g of 1,3-Bis(diphenylphosphino)propane nickel (II) chloride was added under nitrogen followed by ~100 mL of anhydrous Et_2O and 11.25 mL (120 mmol) of 3-bromothiphene. The flask was then cooled in an ice bath (0° C). The Et_2O solution of *n*-$C_{18}H_{37}MgBr$ was slowly added to the flask containing the nickel catalyst and the 3-bromothiophene to prevent the generation of excessive heat and high concentrations of *n*-$C_{18}H_{37}MgBr$ in the presence of the catalyst. The reaction mixture was allowed to stir overnight resulting in the formation of two layers. The top Et_2O layer contained the product and the second

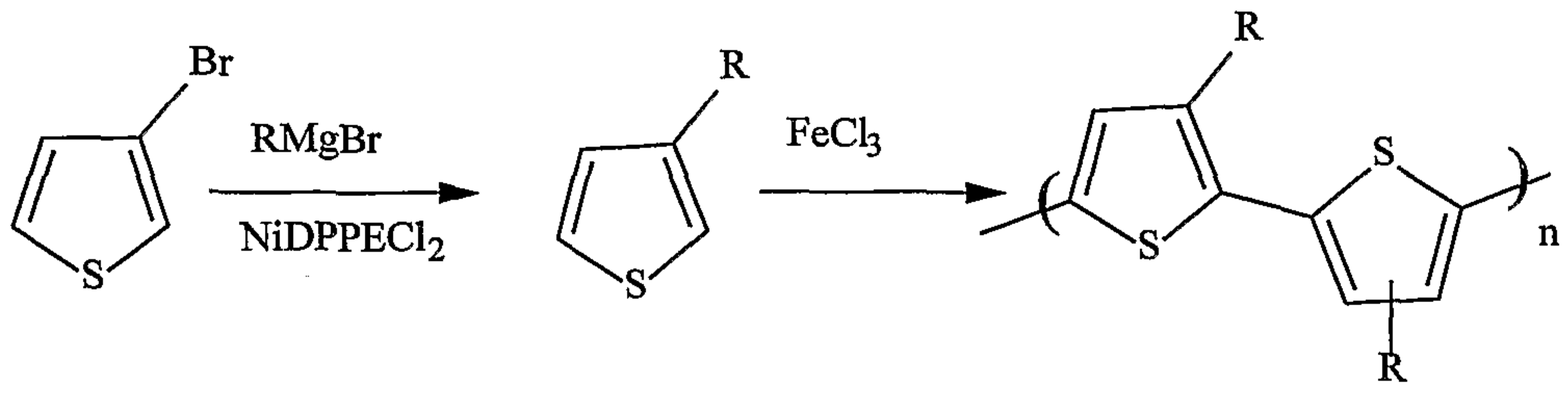
small lower dark brown oily layer contained the Ni catalyst and the Mg salts. The primary side product of the reaction was the coupling product of two equivalents of *n*-$C_{18}H_{37}MgBr$ to form $C_{36}H_{74}$, which was easily separated form the product since it had low solubility in Et_2O. The product was purified via aqueous workup followed by filtration and removal of the Et_2O by rotoevaporation to leave the impure low melting solid product. This solid was redissolved in a minimal amount of Et_2O (~ 30 mL) followed by addition of ~250 mL of MeOH and placed into low temperature freezer (-80 °C) for recrystalization. The yield of this reaction is about 80-90 %.

Poly(3-*n-ocatdecylthiophene*)

Poly(3-*n-ocatdecylthiophene*) was prepared as forth in Leclerc et. al. *Makromol. Chem.* 1989, *190*, 3105-3116. 3-ocatadecylthiophene (10 g, 30 mmol) was added to a dry 500 mL round bottom flask under N_2 and dissolved in 100 mL of $CHCl_3$. In a separate dry 500 mL flask under N_2 was added $FeCl_3$ (24.3 g, 90 mmol) and 100 mL of $CHCl_3$. The $CHCl_3$ solution of 3-ocatadecylthiophene was slowly transferred to the flask containing the $FeCl_3$ resulting in the generation of heat. The contents of the flask were stirred at RT for 24-36 h. The reaction mixture was then slowly dripped into rapidly stirring MeOH (1 L) resulting in the precipitation of the polymer. The precipitate was collected via vacuum filtration, washed with MeOH (100 mL) and redissolved in ~150 mL of $CHCl_3$ with the assistance of sonication. The solution was washed/reduced with aqueous hydrazine (2x100 mL, 0.5 M) and aqueous HCl (2x100 mL, 0.5 M). The organic layer was slowly dripped into of rapidly stirring MeOH (1 L) to reprecipitate the polymer which was collected by vacuum filtration.

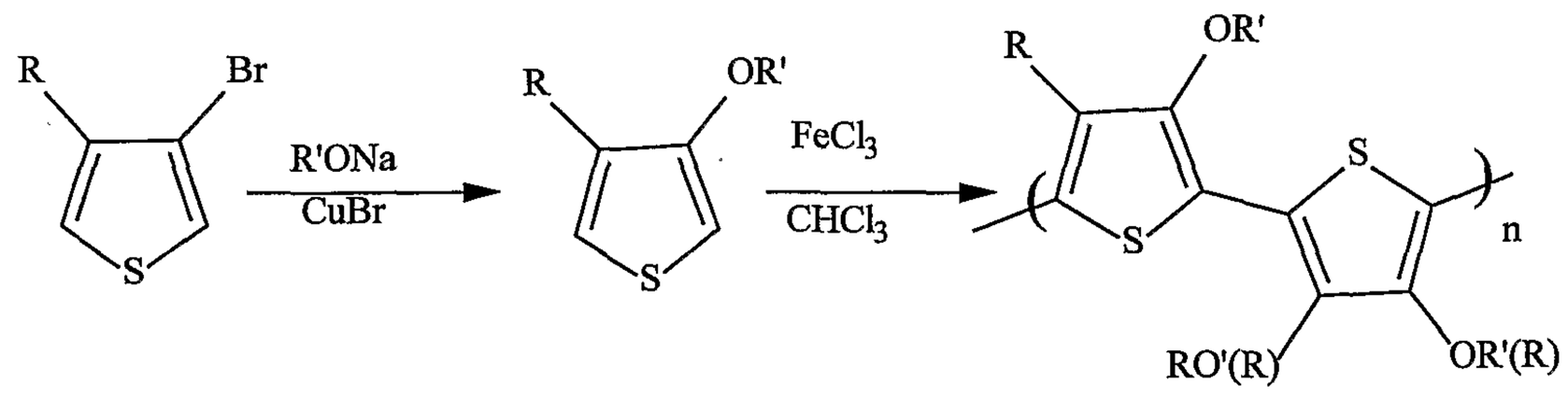
One skilled in the art would recognize that other known methods only precipitate the polymer once and reduce/purify the polymer via Sohxlet extraction with MeOH. Further, it will be apparent to one skilled in the art that the polymerization reaction can be carried out in methylene chloride as opposed to chloroform if it would be more economical or EPA acceptable.

Development of Thermochromic Paints



Scheme 1

50 mg of poly (3-octadecylthiophene) prepared via the procedure shown in Scheme 1, where R = $C_{18}C_{37}$ was dissolved in 2.0 ml of tetrahydrofuran. This deeply colored solution was added to 25 ml of Minwax fast drying polyurethane (clear semi-gloss). This provides a uniform mixture that was applied to paper, plastic, and painted metal surfaces. Upon drying (20 min) the surfaces where heated to 100°C for 1 min to remove any residual solvent from the coating and then allowed to cool to room temperature. After cooling to room temperature the "painted" surfaces are red. When the red surfaces are heated above 60-70°C the color of the surfaces changes from red to yellow. The color change is accompanied by a change in the visual transparency of the surface coating. When the red coating is opaque while when yellow the coating is translucent. This process is very similar to what is observed for the pure poly (3-octadecylthiophene). The coating adheres strongly to paper, plastic, and painted metal surfaces. Addition of blue pigments such as ultramarine blue allow adjustment of the cold and hot colors. The color can be adjusted to a gray/purple when cold and bright green when hot. The thermochromic paints can be applied in various manners including brush, sponge, roller, and airbrush.



Scheme 2

Non-regioregular 3-alkoxy-4-alkyl substituted polythiophenes for thermochromic applications have been synthesized according to Scheme 2, where R = CH_3 and R'= $C_{18}H_{37}$. These polymers can be used as a reversible thermal sensor that detects excursion through a single temperature with visual or optical detection. At temperatures below the thermochromic transition polymer films are violet, above the transition the films are orange. The temperature of the thermochromic transition can be adjusted by variation of the backbone alkyl or alkoxy substituents.

All of the polythiophene-based pigments described herein, most particularly 3-alkylpolythiophenes and 3-alkoxy-4-alkylpolythiophenes, can be incorporated into polymer based-paints such as polyurethanes and polysiloxanes or plastics and retain the

thermochromic behavior. Upon incorporation of the thermochromic polymer based pigments into plastics the materials have been determined to be viable for FDA approval.

Development of Thermochromic Plastics

Two hundred g of polypropylene was weighed into a small self-sealing bag. 1.0 g of poly(3-octadecylthiophene) was added to the polypropylene. The mixture was vigorously shaken until the poly(3-octadecylthiophene) was well dispersed in the polypropylene. The mixture was then added to the addition funnel of a BOY 22-D injection molding machine to produce polypropylene chips containing 0.5% by weight of poly(3-octadecylthiophene). When the red polypropylene chips are heated to temperatures above 60-70° C the chips turn yellow. When the chips are removed from the heat they return to the low temperature color as at a rate comparable to that of the cooling rate of the chips. The color change is accompanied by a change in transparency. The chips are significantly more transparent at high temperatures than at low temperatures.

Two hundred g of polystyrene was weighed into a small self-sealing bag. 1.0 g of poly(3-octadecylthiophene) was added to the polystyrene. The mixture was vigorously shaken until the poly(3-octadecylthiophene) was well dispersed in the polystyrene. The mixture was then added to the addition funnel of a BOY 22-D injection molding machine to produce polystyrene chips containing 0.5% by weight of poly(3-octadecylthiophene). When the red polystyrene chips are heated to temperatures above 60-70° C the chips turn yellow. When the chips are removed from the heat they return to the low temperature color as at a rate significantly slower to that of the cooling rate of the chips. The color change is accompanied by a change in transparency. The chips are significantly more transparent at high temperatures than at low temperatures.

Development of Thermochromic Coatings

12.5 mg of poly(3-octadecylthiophene) was added to a 25mL solution of poly(vinylidine fluoride) (PVDF) in THF (50 g/L of PVDF). The mixture was sonicated for 3 h to form a homogeneous solution. The solutions were solution cast onto silicon wafers and dried at 50° C to form red films. When heated above 60-70° C the PVDF films containing 1.0 % poly(3-octadecylthiophene) changed from red to yellow. When the films were allowed to cool back to room temperature the films changed back to red.

The foregoing description has been limited to a specific embodiment of the invention. It will be apparent, however, that variations and modifications can be made

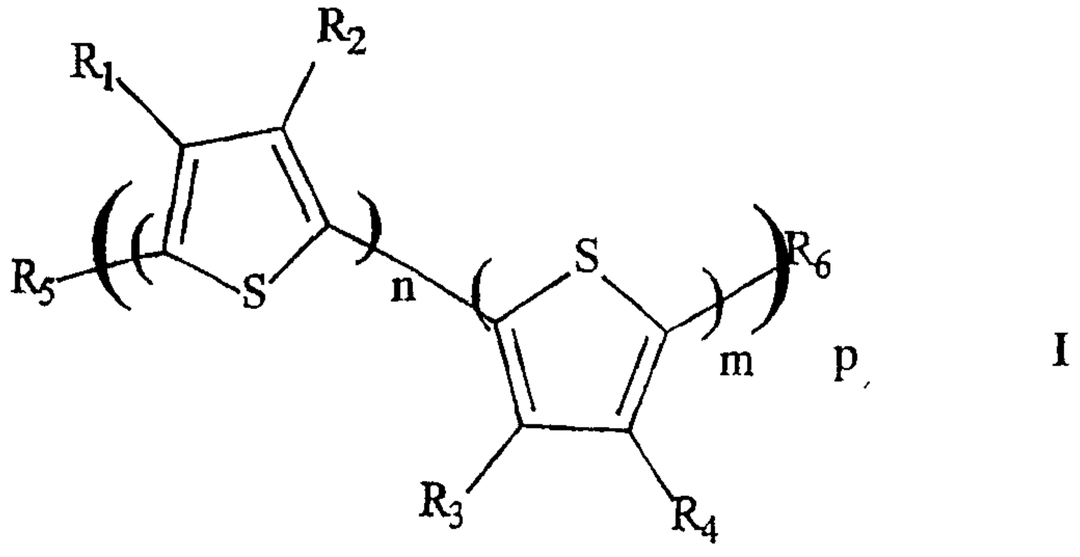
to the invention, with the attainment of some or all of the advantages of the invention. Therefore, it is the object of the appended claims to cover all such variations and modifications as come within the true spirit and scope of the invention.

Having described our invention, what we now claim is:

CLAIMS:

1. A method of detecting when an article meets or exceeds a specific temperature which comprises:

treating at least a portion of the article with a composition comprised of a carrier medium and a compound having the following structure:



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wherein R_1-R_6 = a hydrogen, substituted or unsubstituted alkyl radical, substituted or unsubstituted alkoxy radical, substituted or unsubstituted aryl radical, substituted or unsubstituted thioalkyl radical, substituted or unsubstituted trialkylsilyl radical, substituted or unsubstituted acyl radical, substituted or unsubstituted ester radical, substituted or unsubstituted amine radical, substituted or unsubstituted amide radical, substituted or unsubstituted heteroaryl or substituted or unsubstituted aryl radical

n is between 1 and 1000,

m is between 1 and 1000, and

p is between 1 and 1000; and

wherein the compound is present in the carrier medium in an amount of about 0.05 to about 25.0% by weight based on the total weight of the composition, the structure of the compound designed such that when the composition is placed in a heat-exchange relationship with the article, the composition will exhibit a color change when the specific temperature is met or exceeded in the article; and

detecting when the article has met or exceeded the specific temperature.

2. The method of claim 1 wherein treating comprises brushing.

3. The method of claim 1 wherein treating comprises rolling.

4. The method of claim 1 wherein treating comprises spraying.

5. The method of claim 1 wherein treating comprises:
admixing the composition with at least a portion of the article.

6. The method of claim 1 wherein treating comprises coating at least a portion of the article.

7. The method of claim 1 wherein treating comprises coating at least a portion of the article and admixing the composition with at least a portion of the article.

8. The method of claim 1 wherein the design temperature of the composition is in the range of between – 40 to 180°C.

9. The method of claim 8 wherein the specific temperature is 5 to 10°C below the thermochromic transition temperature and the color change ends 5 to 10°C above the thermochromic transition temperature.

10. The method of claim 9 wherein the design temperature of the composition is any selected temperature with the range.

11. The method of claim 1 wherein the medium is polyurethanes; elastomers including polysiloxanes and polydienes; polyacrylates, polyethylene terephthalate)s (PET), polysytrenes, polyolefins including polyethylenes (HDPE and LDPE) and polypropylene, polycarbonates, polyacrylics, polyacrylic acids, polyacrylamides, polymethacrylics, polyvinyl ethers, polyvinyl halides, poly(vinyl nitrile)s polyvinyl esters, polyesters, polysofones, polysulfonamides, polyamides, polyimines, polyimides, carbohydrates, or organic solvents including toluene, and N-methylpyrrolidone.

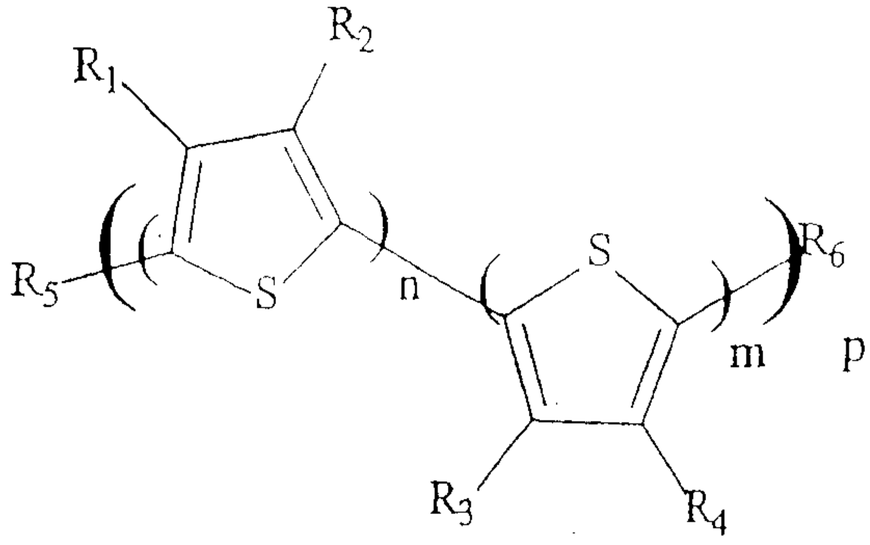
12. The method of claim 1 wherein R_1 and R_4 are $-(CH_2)_{17}CH_3$, R_2, R_3, R_5, and R_6 are H, n and m are in a ratio of 4:1, and p is between 40 and 80, the composition characterized in that a low temperature color is red, a high temperature color is yellow, and the color change of the composition occurs at about 60 °C.

13. The method of claim 1 wherein the compound is present in the medium in an

amount of about 0.5% by weight based on the total weight of the composition.

14. A thermochromic polymer-based temperature indicator composition which exhibits a color change when the composition meets or exceeds a specific temperature which comprises:

a polymeric compound comprised of the following structure:



I

wherein R_1– R_6 = a hydrogen, substituted or unsubstituted alkyl radical, substituted or unsubstituted alkoxy radical, substituted or unsubstituted aryl radical, substituted or unsubstituted thioalkyl radical, substituted or unsubstituted trialkylsilyl radical, substituted or unsubstituted acyl radical, substituted or unsubstituted ester radical, substituted or unsubstituted amine radical, substituted or unsubstituted amide radical, substituted or unsubstituted aryl radical or substituted or unsubstituted aryl radical,

n is between 1 and 1000,

m is between 1 and 1000, and

p is between 1 and 1000; and

a carrier medium, the compound present in the medium in an amount of about 0.05 to about 25.0% by weight based on the total weight of the composition, the structure of the compound designed such that when the composition is placed in a heat-exchange relationship with an article, the composition will exhibit a color change when a design temperature or a temperature beyond the design temperature is reached in the article.

15. The composition of claim 14 wherein the design temperature is in the range of between about -40 to 180°C.

16. The composition of claim 15 wherein the design temperature is 5 to 10°C below the thermochromic transition temperature and the color change ends 5 to 10°C above the thermochromic transition temperature.

17. The composition of claim 16 wherein the design temperature is any selected temperature within the range.

18. The composition of claim 14 wherein the composition is coated on at least a portion of the surface of the article.

19. The composition of claim 14 wherein the composition is admixed with at least a portion of the article.

20. The composition of claim 14 wherein the composition is coated on and admixed with at least a portion of the article.

21. The composition of claim 14 wherein the medium is polyurethanes; elastomers including polysiloxanes and polydienes; polyacrylates, poly(ethylene terephthalate)s (PET), polysytrenes, polyolefins including polyethylenes (HDPE and LDPE) and polypropylene, polycarbonates, polyacrylics, polyacrylic acids, polyacrylamides, polymethacrylics, polyvinyl ethers, polyvinyl halides, poly(vinyl nitrile)s polyvinyl esters, polyesters, polysofones, polysulfonamides, polyamides, polyimines, polyimides, carbohydrates, or organic solvents including toluene, and N-methylpyrrolidone.

22. The composition of claim 14 wherein R_1 and R_4 are $-(CH_2)_{17}CH_3$, R_2, R_3, R_5, and R_6 are H, n and m are in a ratio of 4:1, and p is between 40 and 80, the composition characterized in that a low temperature color is red, a high temperature color is yellow, and the color change of the composition occurs at about 60°C.

23. The composition of claim 14 wherein the compound is present in the medium in an amount of about 0.5% by weight based on the total weight of the composition.

24. The method of claim 1, wherein the compound is present in the medium in an amount of about 1.0 to about 25% by weight based on the total weight of the composition.

25. The method of claim 24 wherein treating comprises printing the composition on at least a portion of the article.

26. The method of claim 25 wherein treating comprises printing the composition on, coating the composition on and admixing the composition with at least a portion of the article.

27. The method of claim 24 wherein the design temperature of the composition is in the range of between – 40 to 180°C.

28. The method of claim 27 wherein the design temperature is 5 to 10°C below the thermochromic transition temperature and the color change ends 5 to 10°C above the thermochromic transition temperature.

29. The method of claim 28 wherein the design temperature of the composition is any selected temperature within the range.

30. The method of claim 24 wherein the medium is an ink formulation.

31. The method of claim 30 wherein the ink formulation comprises oils, resins, pigment extenders and additives.

32. The method of claim 24 wherein R_1 and R_4 are $-(CH_2)_{17}CH_3$, R_2, R_3, R_5, and R_6 are H, n and m are in a ratio of 4:1, and p is between 40 and 80, the composition characterized in that a low temperature color is red, a high temperature color is yellow, and the color change of the composition occurs at about 60°C.

33. The thermochromic polymer-based temperature indicator composition of claim 14, wherein the compound is present in the medium in an amount of about 1.0 to about 25% by weight based on the total weight of the composition.

34. The composition of claim 33 wherein the design temperature is in the range of between about -40 to 180°C.

35. The composition of claim 34 wherein the design temperature is 5 to 10°C below the thermochromic transition temperature and the color change ends 5 to 10°C above the thermochromic transition temperature.

36. The composition of claim 35 wherein the design temperature is any selected temperature within the range.

37. The composition of claim 33 wherein the composition is printed on at least a portion of the surface of the article.

38. The composition of claim 33 wherein the composition is printed on, admixed with and coated on at least a portion of the article.

39. The composition of claim 33 wherein the medium is an ink formulation.

40. The composition of claim 39 wherein the ink formulation comprises oils, resins, pigment extenders and additives.

41. The composition of claim 33 wherein R_1 and R_4 are $-(CH_2)_{17}CH_3$, R_2, R_3, R_5, and R_6 are H, n and m are in a ratio of 4:1, and p is between 40 and 80, the composition characterized in that a low temperature color is red, a high temperature color is yellow, and the color change of the composition occurs at about 60°C.

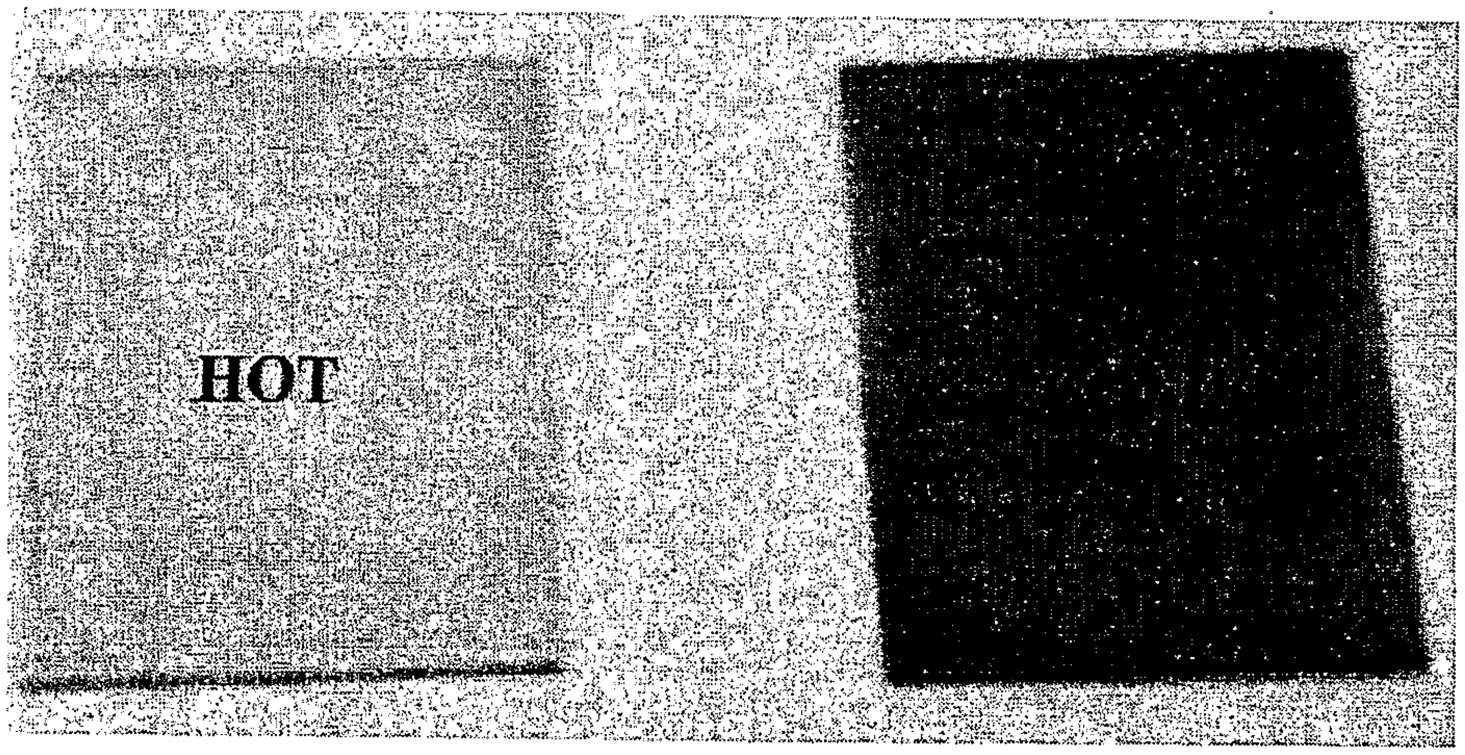


Fig. 1

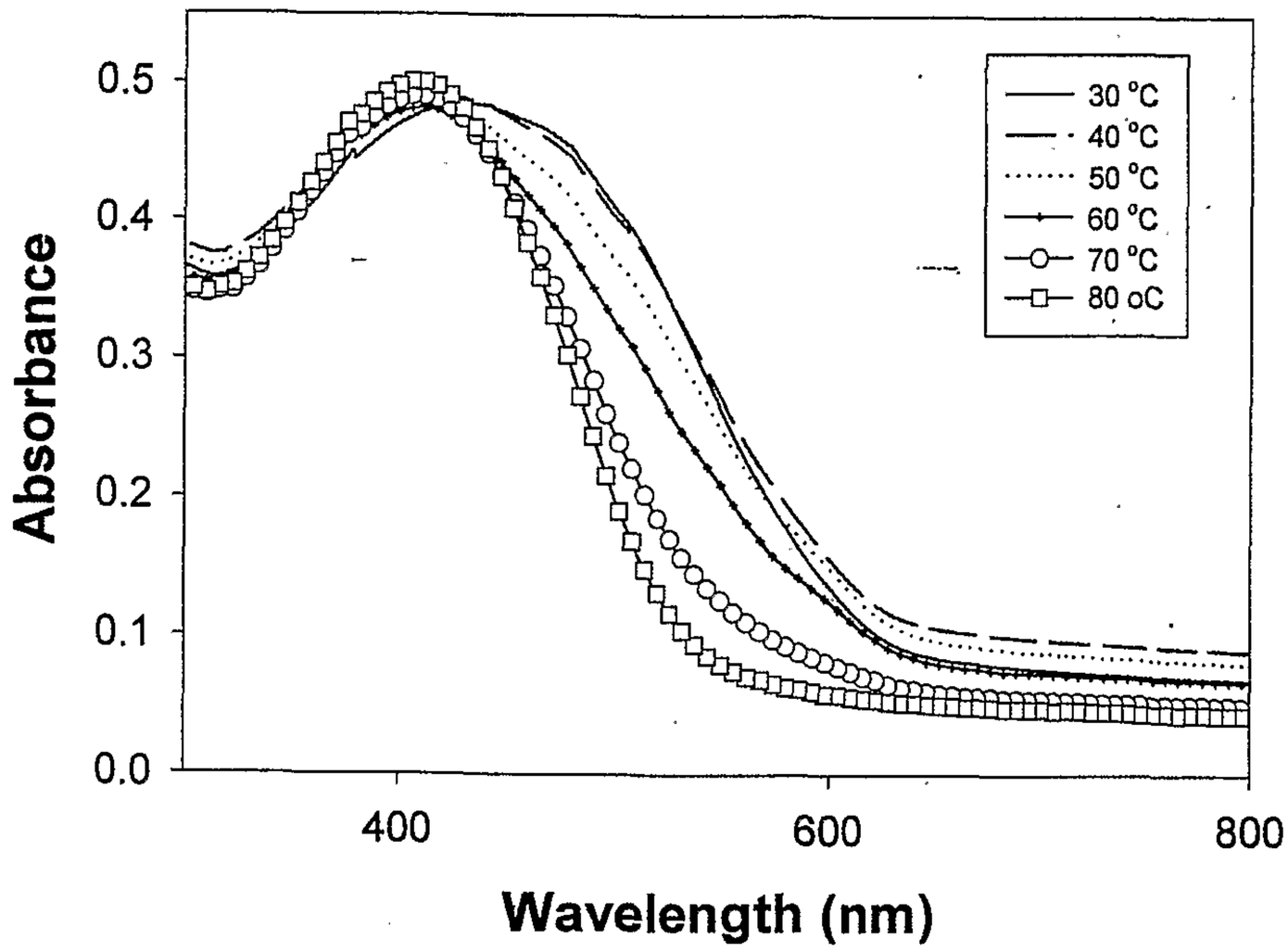

0.5
0.4
0.3
0.2
0.1
0.0
Absorbance
400
600
800
Wavelength (nm)
30 °C
40 °C
50 °C
60 °C
70 °C
80 oC

Fig.2

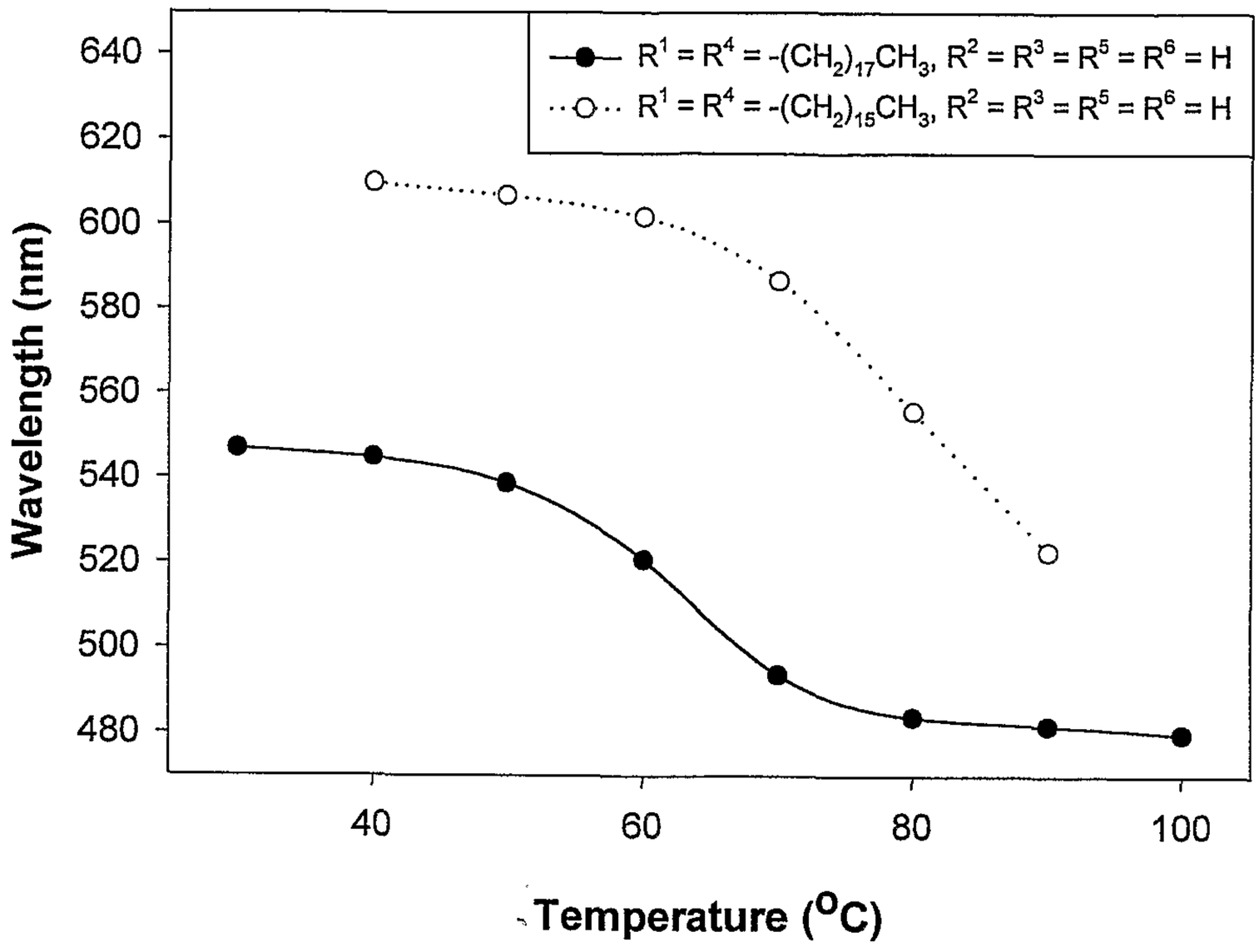

R1 = R4 = -(CH2)17CH3, R2 = R3 = R5 = R6 = H
R1 = R4 = -(CH2)15CH3, R2 = R3 = R5 = R6 = H
Wavelength (nm)
640
620
600
580
560
540
520
500
480
40
60
80
100
Temperature (°C)

Fig. 3