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[Continued on next page]

(54) Title: SELF-ASSESSING MECHANOCHROMIC MATERIALS

(57) Abstract: A mechanochromic material includes a polymer having a backbone containing a mechanophore.

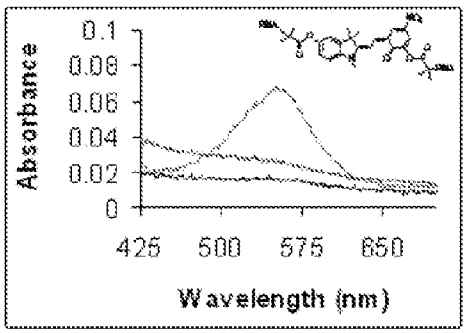

Figure 1 (a)

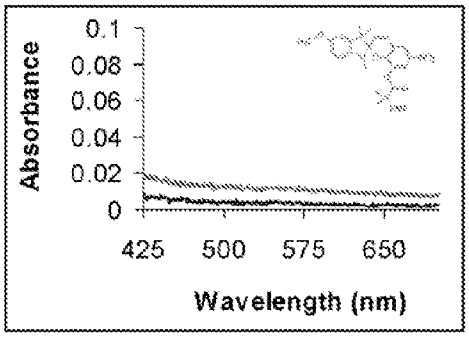

Figure 1 (b)

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GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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SELF-ASSESSING MECHANOCHROMIC MATERIALS

BACKGROUND

[01] Polymer materials are ubiquitous in everyday life and are used in various applications (medical, automobile, electronics, structural etc.). These materials experience stress through normal use, which can lead to damage and failure of the product. Having the ability to detect damage and locate areas under high stress in situ is essential to eliminating failure of the material.

[02] Several examples of self-assessing materials are known in the patent literature. The simplest incorporate a colored substance into the matrix in the form of capsules[1] or hollow fibers.[2] Initially the color is not visible, but, upon damage to the matrix, the capsules or fibers rupture and expose the colored fluid or solid. In some cases, a two part system is utilized wherein a colorless compound mixes with an activator upon the rupture of their respective containers causing a color change. The disadvantage of these systems is that the fibers and capsules need to be evenly dispersed throughout the matrix, so that the damage inducing force has a large chance of intersecting the particles.

[03] Another approach is the use of triboluminescent materials, which give off flashes of light in response to stress or damage.[3] These materials require continuous monitoring to detect when damage occurs due to the transient nature of the light flash.

[04] Smart coatings consisting of several layers of sensing materials have also been reported.[4] These are complex and require external power to accomplish many of their tasks. A diacetylene segmented copolymer is known which exhibits a shift in color when subjected to a strain.[5]

[05] In the chemistry literature, Todres outlines several organic compounds that have displayed mechanochromic properties.[6] Specifically, spiropyran has been noted to undergo a color change upon grinding;[7] however, little application exists for the small molecule alone.

[06] Weder and coworkers have incorporated cyano-substituted oligo(*p*-phenylene vinylene) derivatives into different polymer matrixes and have synthesized "self-assessing" polyurethanes, polyethylene blends, poly(ethylene terephthalate)s, and poly(ethylene terephthalate glycol)s.[8-a-e] Their approach relies on the initial formation of nanoscale aggregates of the sensor molecules in the polymer matrix. Upon deformation the cyano-substituted oligo(*p*-phenylene vinylene) sensors are transformed from excimer to monomer and a shift in the emission spectrum is observed. Most of these sensing units are not chemically incorporated into the backbone, and many exhibit only a fluorescent color change that is not visible to the naked eye. Additionally, these materials are not reversible and can only exhibit a color change once.

[07] Finally, Kim and Reneker introduced an azobenzene into a copolyamide oligomer, which was chemically incorporated into a polyurethane.[9] Upon exposing the material to tensile stress, a change in the UV spectrum at 375 nm was observed. However, no visible change was noted and the polymer had to be irradiated with UV light prior to stressing the material.

SUMMARY

[08] In a first aspect, the present invention is a mechanochromic material, comprising a polymer having a backbone containing a mechanophore.

[09] In a second aspect, the present invention is a polymer having a backbone containing a mechanophore.

[10] In a third aspect, the present invention is a method of making a polymer, comprising forming a polymer having a backbone containing a mechanophore.

BRIEF DESCRIPTION OF THE DRAWINGS

[11] Figure 1. a. UV spectrum of PMA-SP-PMA before (darkest line) and after (lightest line) sonication. The polymer returns to its original color after sitting in

ambient light (intermediate line). b. UV spectrum of end functionalized PMA-SP mechanically-inactive control before (darkest line) and after (lightest line) sonication.

[12] Figure 2. a. PMA-SP-PMA before mechanical stress has been applied. b. PMA-SP-PMA after mechanical stress has been applied, showing a pink color in the areas of highest stress.

[13] Figure 3 shows the response in mV for retention volume in mL.

[14] Figure 4 shows $M_{n\,GPC}$ in kDa versus $M_{n\,Th}$ in kDa.

[15] Figures 5 a and b show the effect of molecular weight; Figure 5 a is for low molecular weight (18 kDa) and Figure 5 b is for intermediate molecular weight (91 kDa). The top graph is before stress, and the bottom graph is after stress.

[16] Figure 6 shows the molecular weight dependence of mechanochemical activity.

[17] Figure 7 illustrates the chemical reaction of spiropyran under stress, and when subsequently exposed to light.

[18] Figures 8 a, b and c illustrate the appearance of the polymer before stress (a), after stress (b) and after 2 hours exposure to light (c).

[19] Figure 9 is a graph of the absorbance under the same three conditions.

[20] Figure 10 illustrates the control before (a) and after (b) stress. T

[21] Figure 11 illustrates the effect of the location of the mechanophore within the polymer backbone.

[22] Figure 12 illustrate the damage induced color change of the spiropyran containing polymer of the present invention, with a molecular weight of 170 kDa and 0.4 wt% spiropyran.

DETAILED DESCRIPTION

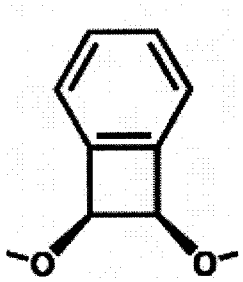
[23] The present invention includes a polymer which incorporates a chemical into the polymer backbone that signals an area under stress by causing a color change in the material. This allows for damage detection via a color change of the material and thus early repair before failure, ultimately extending the lifetime of the product.

[24] The chemical incorporated into the polymer backbone is a stress-responsive mechanophore. One mechanophore moiety is placed in the center of the polymer backbone and undergoes a structural change in response to stress. This change causes a color change of the polymer material. The color change may be a visible to the unaided eye color change.

[25] There are several advantages to this method of stress/damage detection. The damage sensing mechanophore is chemically incorporated into the polymer backbone and hence is distritbuted evenly throughout the material. Since the mechanophore is chemically incorporated, no extra processing steps are required post-polymerization and the mechanophore cannot be eliminated by everyday wear. Finally, damage can be detected visually without removing parts or using expensive detection equipment such as UV or x-ray monitors.

[26] Since our mechanophore is incorporated at the molecular level into the polymer, it is evenly dispersed throughout the matrix by default. The color change of our material is persistent over minutes to hours depending on conditions. All energy required to obtain the color change in our material is provided by the damaging force. The polymer is virtually colorless when unstressed and develops a vivid color when stressed. The appearance rather than the shift in color would be expected to be easier to detect.

[27] The mechanophore can be incorporated into different polymers, including PMMA, PS, and PVC. Examples of mechanophores include spiropyran and moiety I.

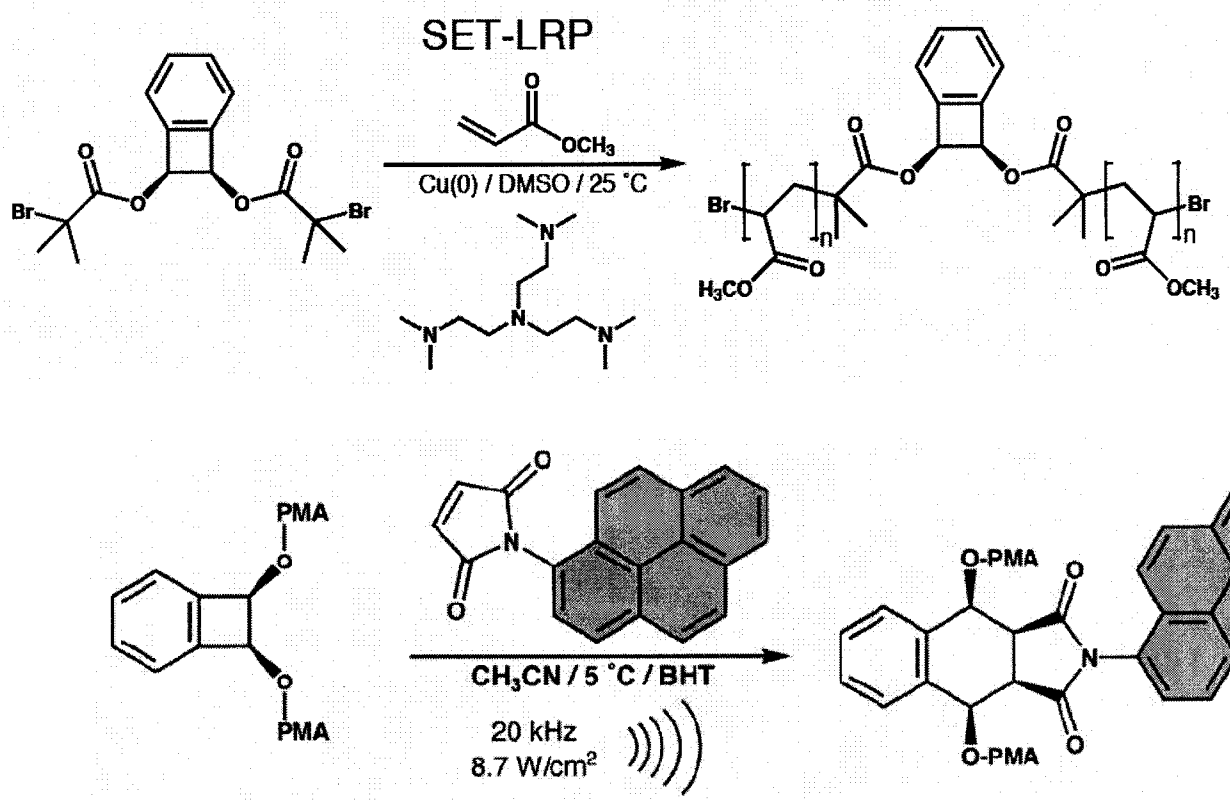


moiety I.

[28]

[29] When under stress, the force on a polymer is largest in the polymer's center. Therefore, the mechanophore is preferably positioned at or near the midpoint of the polymer backbone. The force increases with molecular weight, and therefore selective mechanochemistry may be controlled by controlling the molecular weight of the polymer. Low PDI is preferred. The threshold molecular weight for activation in a flow cell threshold is about 106 Da.

[30] Bidirectional Living Polymerization with Difunctional Mechanophore Initiator



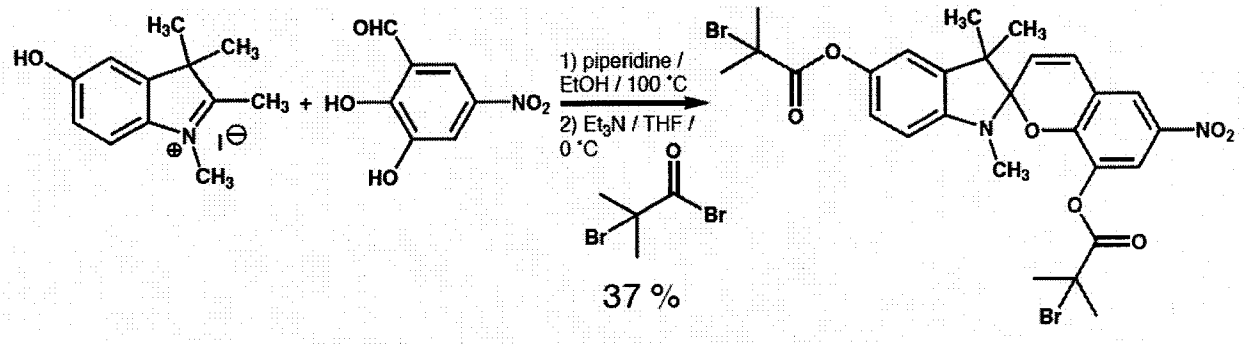
[31] Figure 3 shows the response in mV for retention volume in mL. Figure 4 shows $M_{n\,GPC}$ in kDa versus $M_{n\,Th}$ in kDa. SET-LRP is described in reference 10. The reaction scheme below shows the mechanophore reaction under stress. Figures 5 a and b show the effect of molecular weight; Figure 5 a is for low molecular weight (18 kDa) and Figure 5 b is for intermediate molecular weight (91 kDa). The top graph is before stress, and the bottom graph is after stress. Figure 6 shows the molecular weight dependence of mechanochemical activity.

[32] Color-Generating Mechanophore

[33] When incorporated into a polymethacrylate (PMA) backbone, the polymer changes color upon stretching and tearing. We analyzed the results in solution and solid state to prove that the color change is a result of the mechanochemical (stress-induced) reaction of spiropyran.

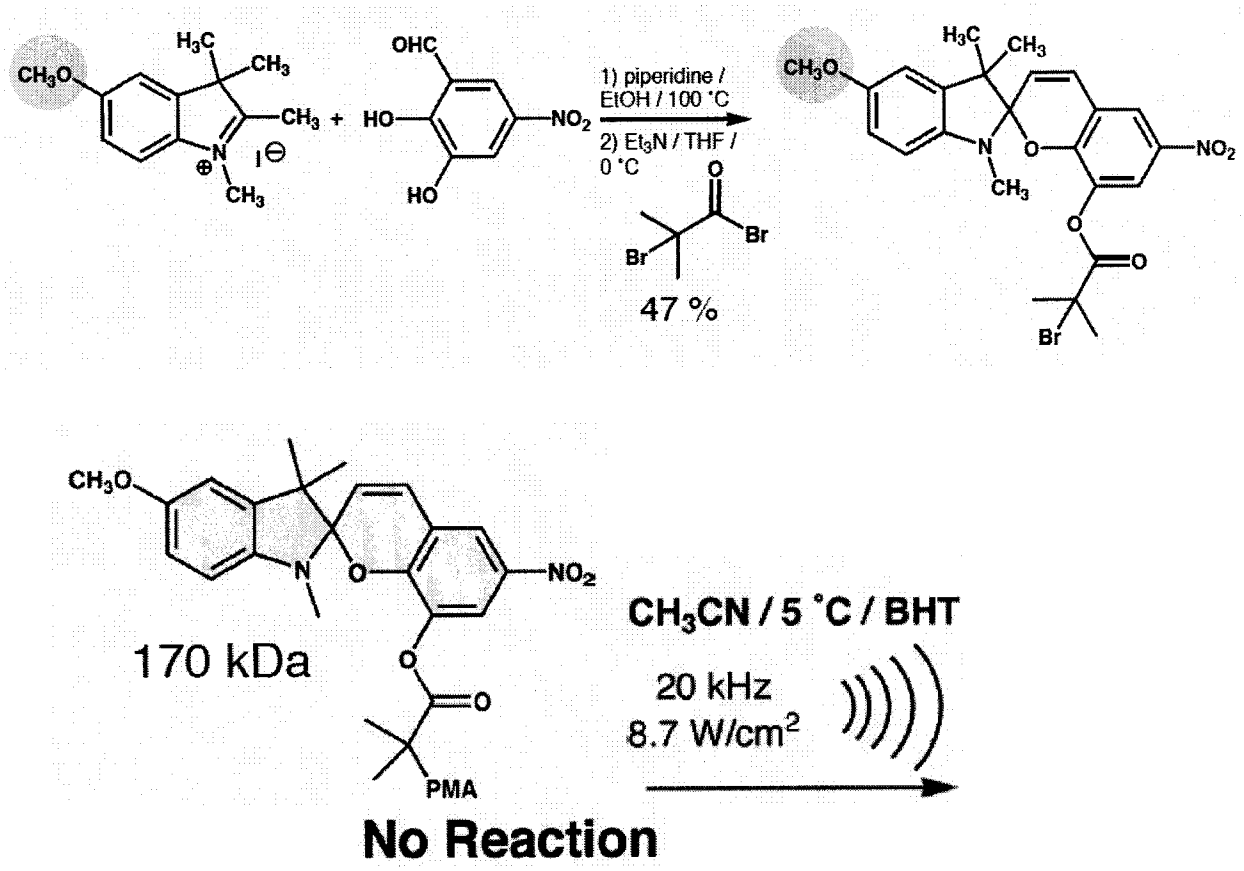
[34] Ultrasound has been used to elongate and stress polymers in solution and study the mechanochemical reactivity of compounds. The PMA polymer containing the spiropyran near the center of the polymer backbone (where mechanical forces are the greatest) was stressed using ultrasound and analyzed using a ultraviolet (UV) spectrophotometer. The results are illustrated in Figure 1. The increase in the UV absorbance of the sonicated (mechanically stressed) spiropyran polymer corresponds to the colored form of the spiropyran. A mechanically inactive spiropyran polymer (spiropyran is located at the end of the polymer chain where ultrasound does not mechanically stress the polymer) was tested and no change in the UV signal occurred. These experiments show that the color change is due to the mechanically induced structural change in the spiropyran.

[35] Studies were also carried out in the solid state. Upon stretching and tearing the spiropyran polymer, a color change was observed. The originally yellowish polymer changed to a pink color where it was under stress (Figure 2).



[36] Figure 7 illustrates the chemical reaction of spiropyran under stress, and when subsequently exposed to light. Figures 8 a, b and c illustrate the appearance of the polymer before stress (a), after stress (b) and after 2 hours exposure to light (c). Figure 9 is a graph of the absorbance under the same three conditions.

[37] The following monofunctional initiator was prepared as a control.



[38] Figure 10 illustrates the control before (a) and after (b) stress. There is no change in color. Figure 11 illustrates the effect of the location of the mechanophore within the polymer backbone. Figure 12 illustrate the damage induced color change of the spiropyran containing polymer of the present invention, with a molecular weight of 170 kDa and 0.4 wt% spiropyran.

[39] **REFERENCES**

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[41] 2. Dunleavy, M.; Haq, S. WO patent 2007003883, 2007.

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[51] (e) Kinami, M., Crenshaw, B. R., Weder, C. *Chem. Mater.* **2006**, *18*, 946.

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[53] 10. Percec *et al. JACS* **2006**.

What is claimed is:

1. A mechanochromic material, comprising a polymer having a backbone containing a mechanophore.

2. The mechanochromic material of claim 1, wherein the mechanophore is moiety I.

3. The mechanochromic material of claim 1, wherein the mechanophore is a spiropyran.

4. The mechanochromic material of any of the proceeding claims, wherein the mechanochromic material undergoes a visible change in color upon the application of stress.

5. The mechanochromic material of any of the proceeding claims, wherein the polymer is selected from the group consisting of a polymethacrylate, a polymethylmethacrylate, a polystyrene, and a polyvinyl chloride.

6. A polymer having a backbone containing a mechanophore.

7. The polymer of claim 6, wherein the mechanophore is moiety I.

8. The polymer of claim 6, wherein the mechanophore is a spiropyran.

9. The polymer of any of the proceeding claims, wherein the mechanochromic material undergoes a visible change in color upon the application of stress.

10. The polymer of any of the proceeding claims, wherein the polymer is selected from the group consisting of a polymethacrylate, a polymethylmethacrylate, a polystyrene, and a polyvinyl chloride.

11. A method of making a polymer, comprising forming a polymer having a backbone containing a mechanophore.

12. The method of claim 11, wherein the mechanophore is moiety I.

13. The method of claim 11, wherein the mechanophore is a spiropyran.

14. The method of any of the proceeding claims, wherein the mechanochromic material undergoes a visible change in color upon the application of stress.

15. The method of any of the proceeding claims, wherein the polymer is selected from the group consisting of a polymethacrylate, a polymethylmethacrylate, a polystyrene, and a polyvinyl chloride.

16. A method of monitoring stress on a structure, comprising:

forming the structure from the mechanochromic material of any of the proceeding claims;

using the structure; and

examining the mechanochromic material for a color change.

17. The method of claim 16, wherein the mechanophore is moiety I.

18. The method of claim 16, wherein the mechanophore is a spiropyran.

19. The method of any of the proceeding claims, wherein the mechanochromic material undergoes a visible change in color upon the application of stress.

20. The method of any of the proceeding claims, wherein the polymer is selected from the group consisting of a polymethacrylate, a polymethylmethacrylate, a polystyrene, and a polyvinyl chloride.

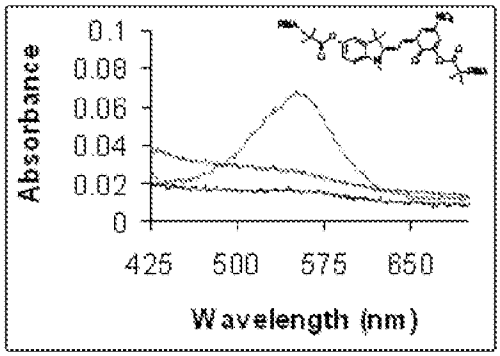

Figure 1 (a)

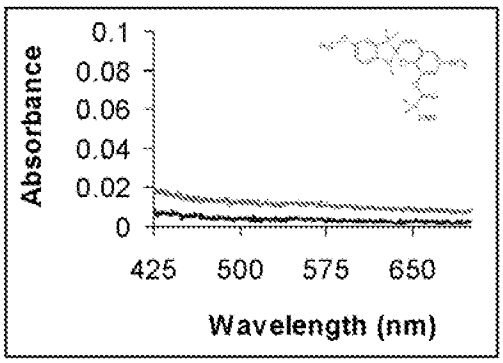

Figure 1 (b)

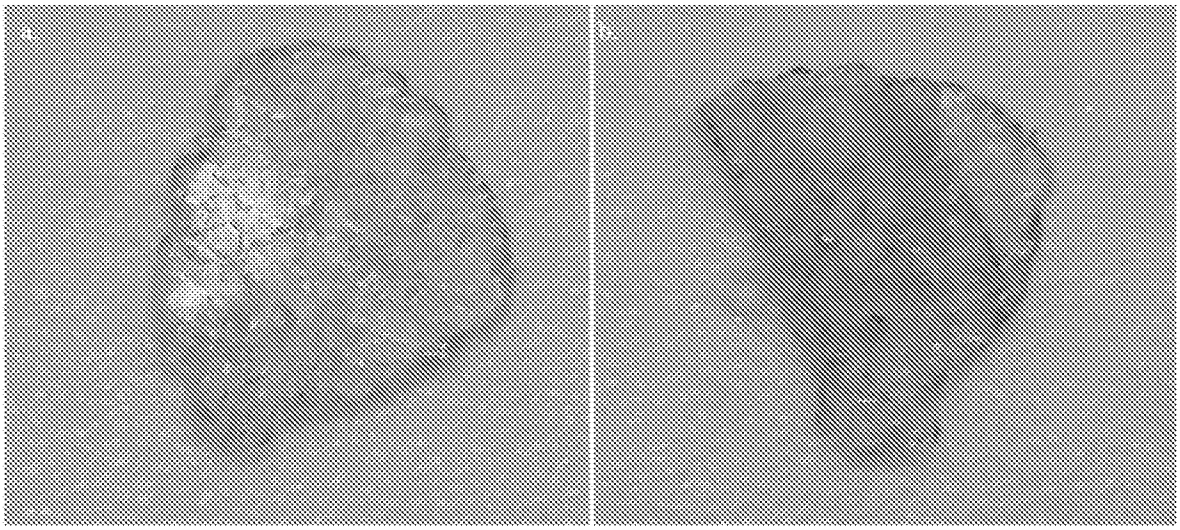

Figure 2

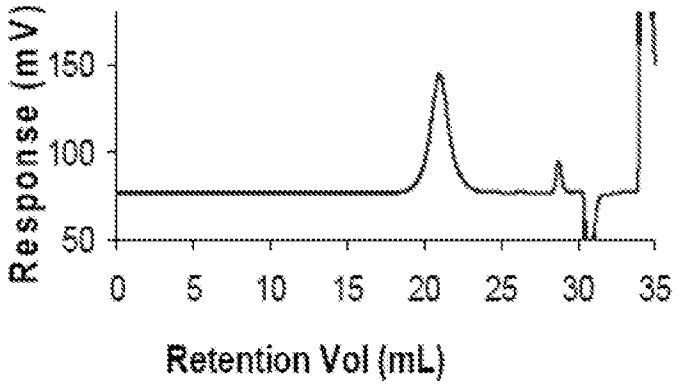

Figure 3

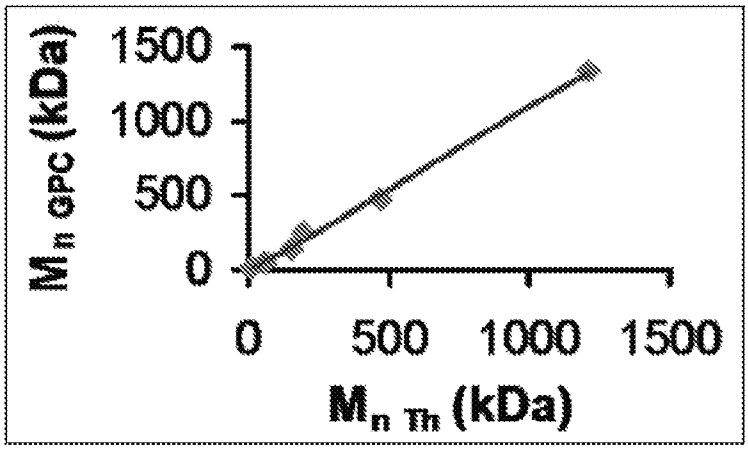

Figure 4

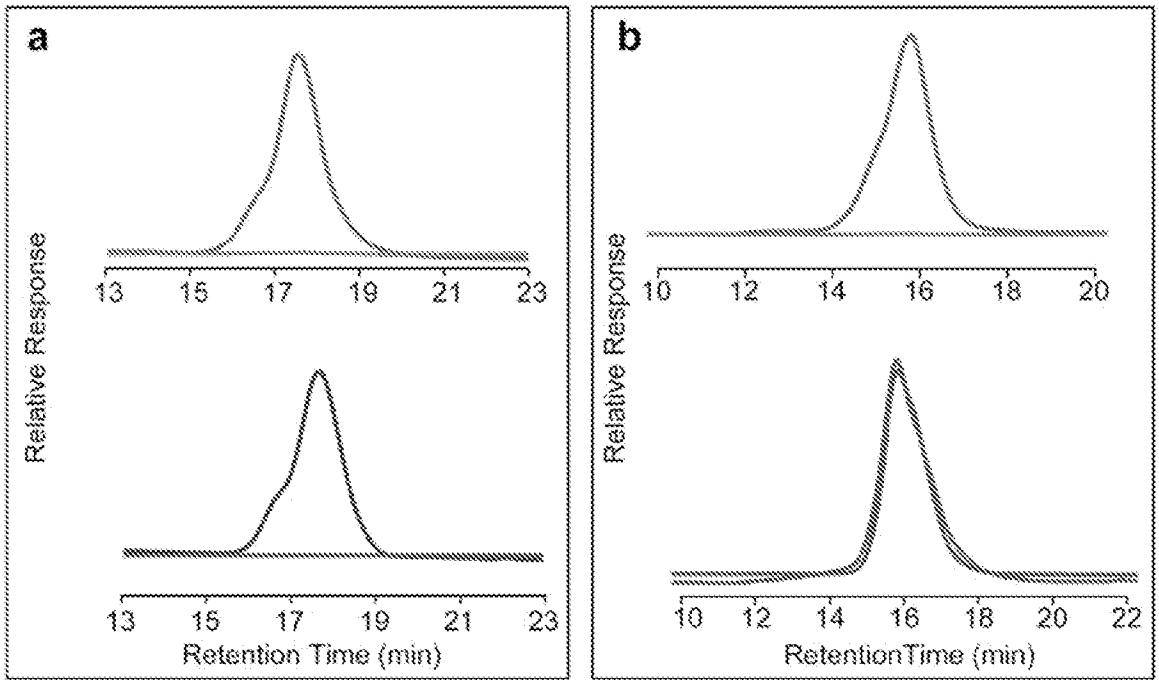
a
Relative Response
13
15
17
19
21
23
13
15
17
19
21
23
Retention Time (min)
b
Relative Response
10
12
14
16
18
20
10
12
14
16
18
20
22
RetentionTime (min)

Figure 5

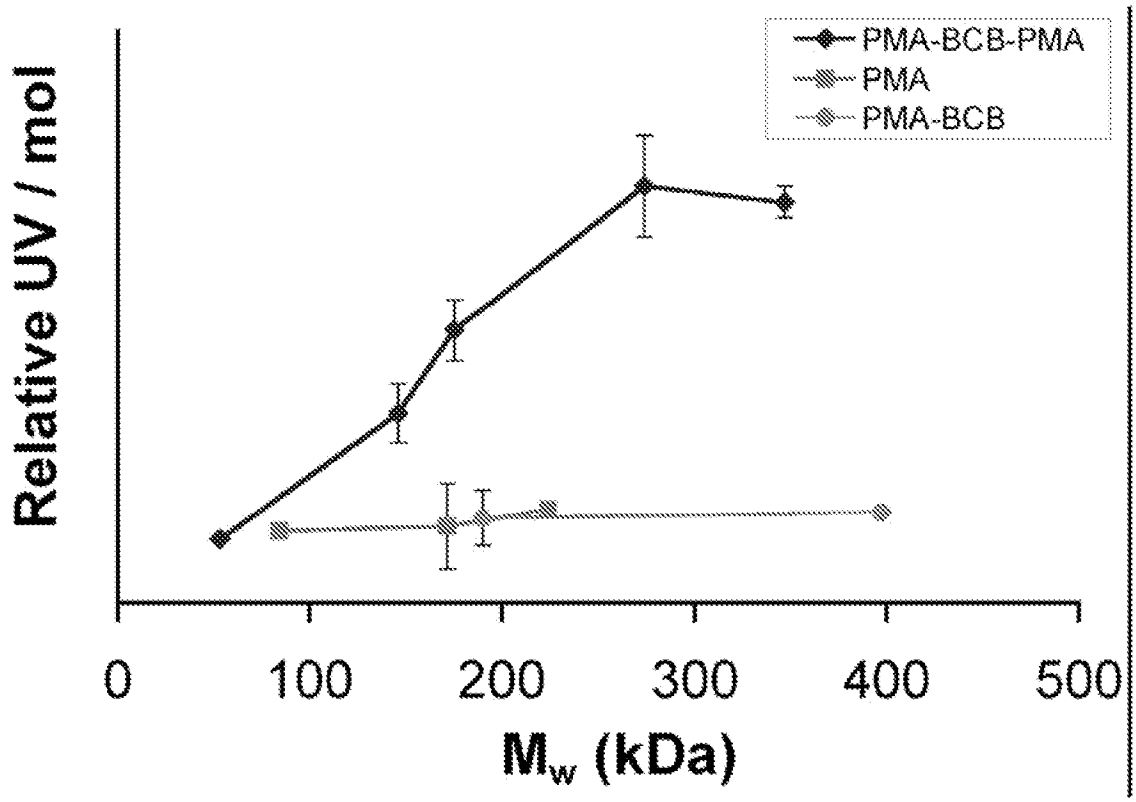
PMA-BCB-PMA
PMA
PMA-BCB
Relative UV / mol
0
100
200
300
400
500
M_w (kDa)

Figure 6

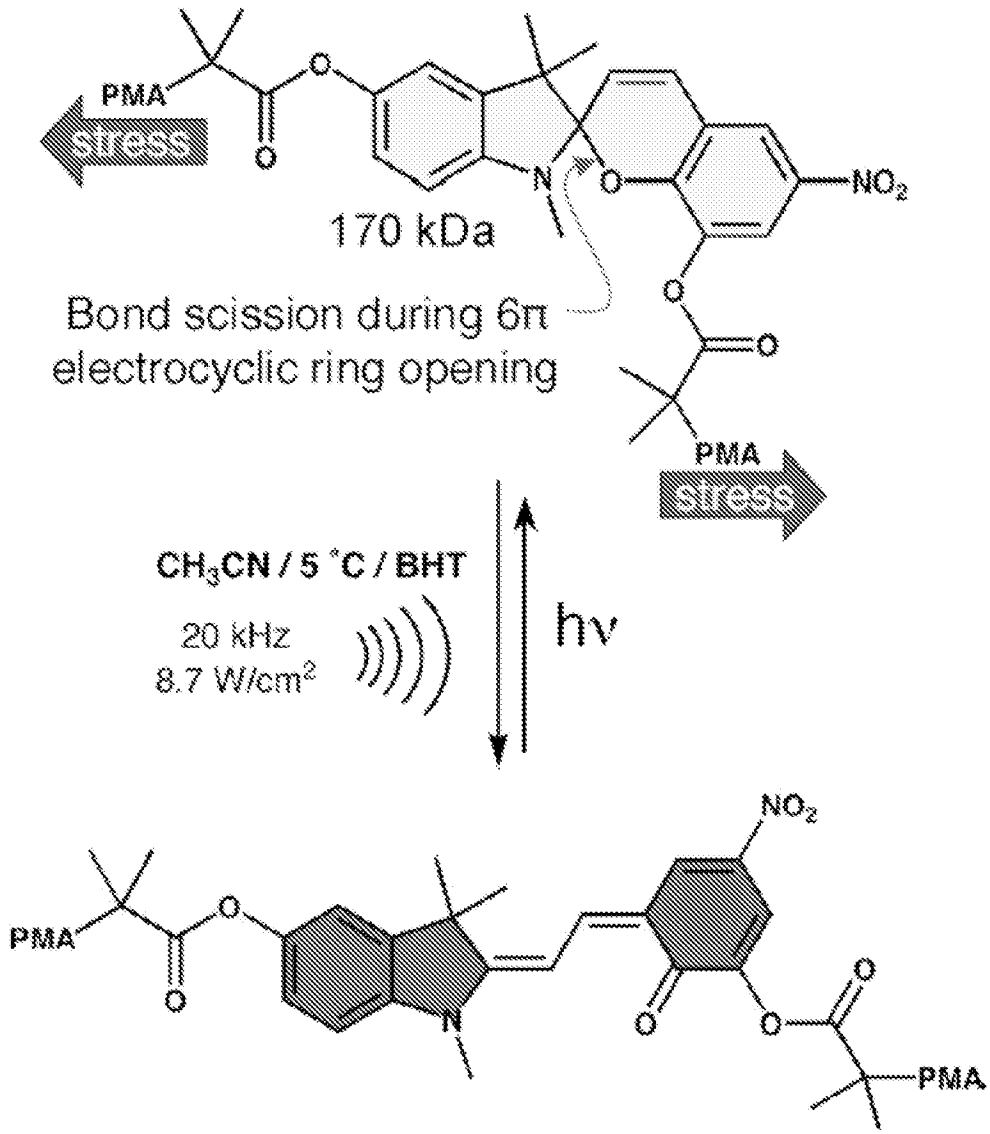
PMA
stress
170 kDa
Bond scission during 6π
electrocyclic ring opening
PMA
stress
CH3CN / 5 °C / BHT
20 kHz
8.7 W/cm2
hν
PMA
PMA

Figure 7

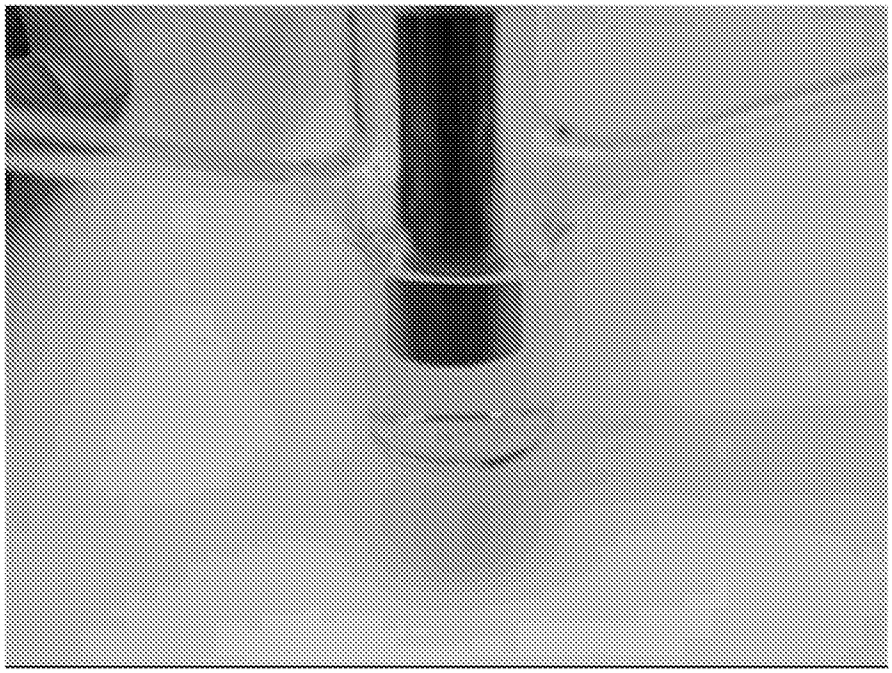

Figure 8 a (before)

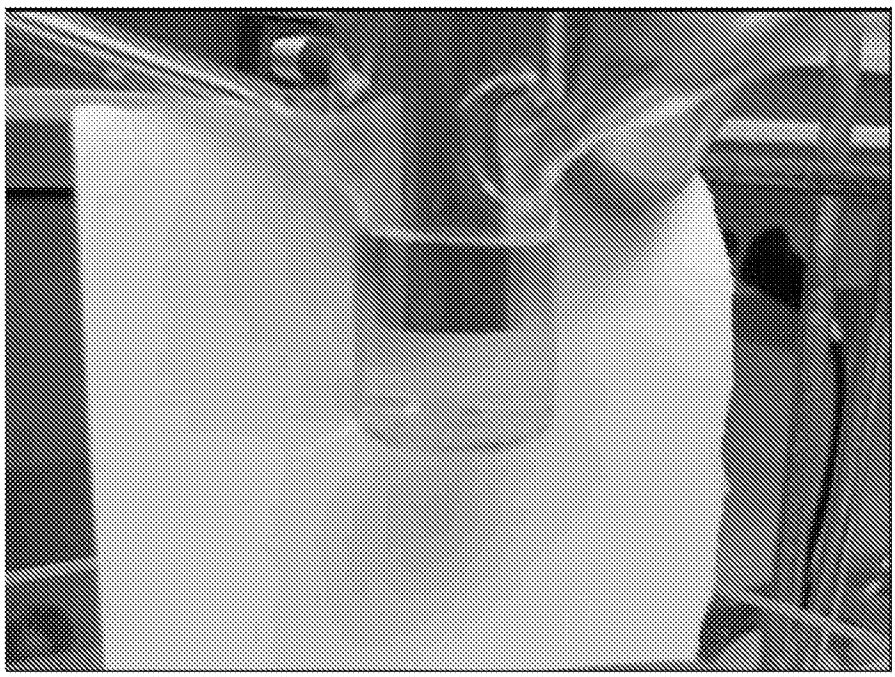

Figure 8 b (after)

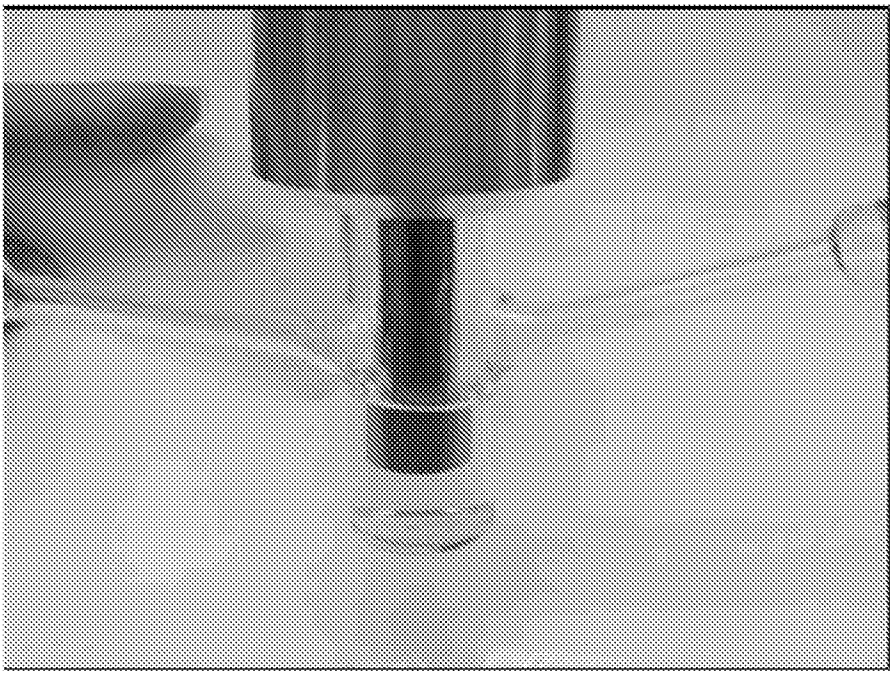

Figure 8 c (2 hours under ambient light)

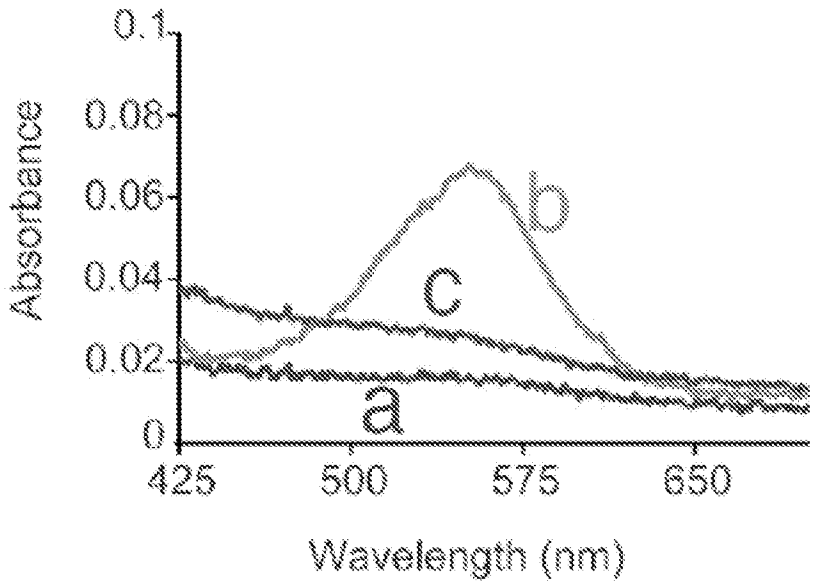

Figure 9

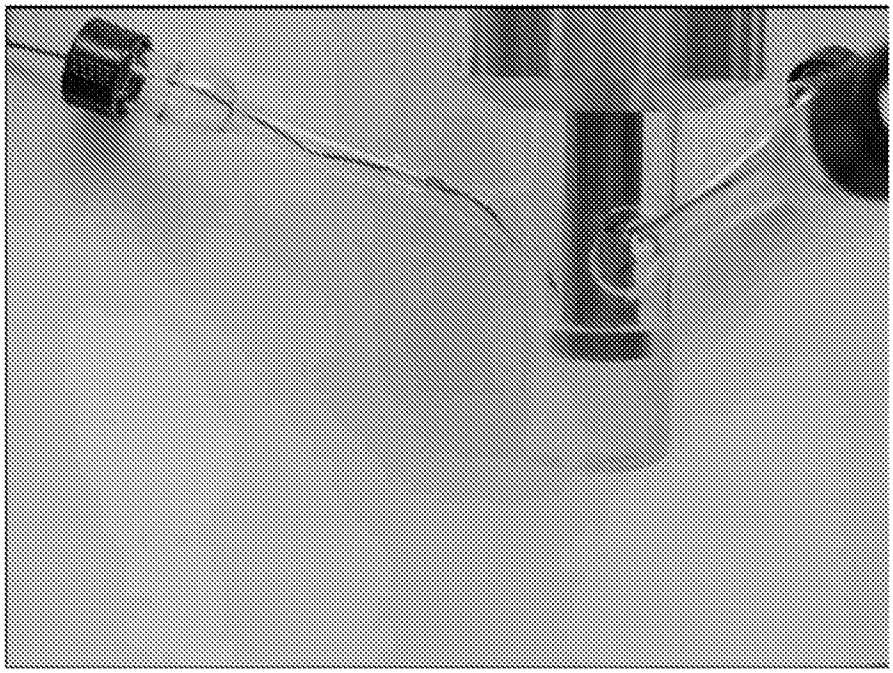

Figure 10 a (before)

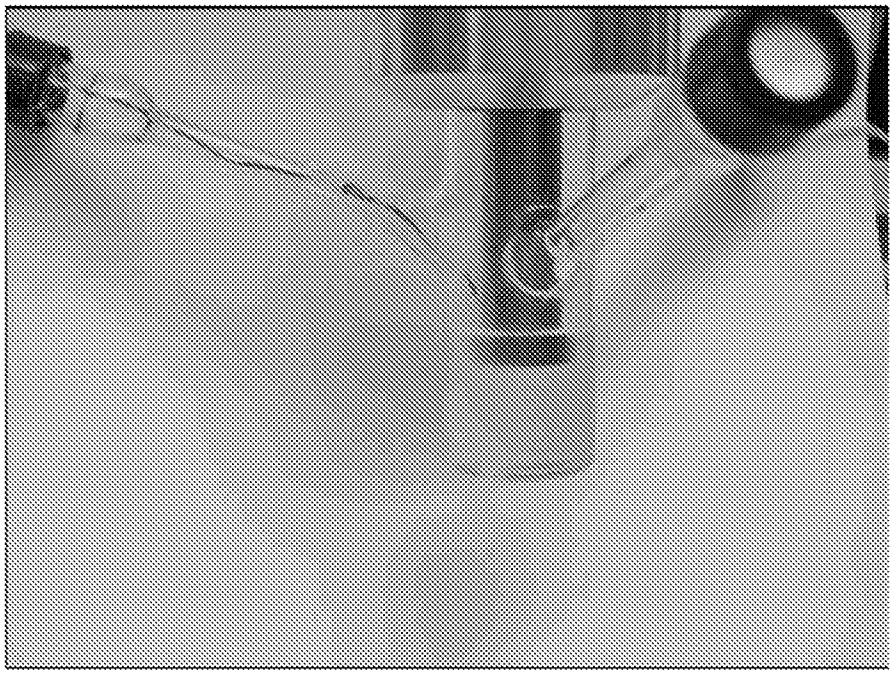

Figure 10 b (after)

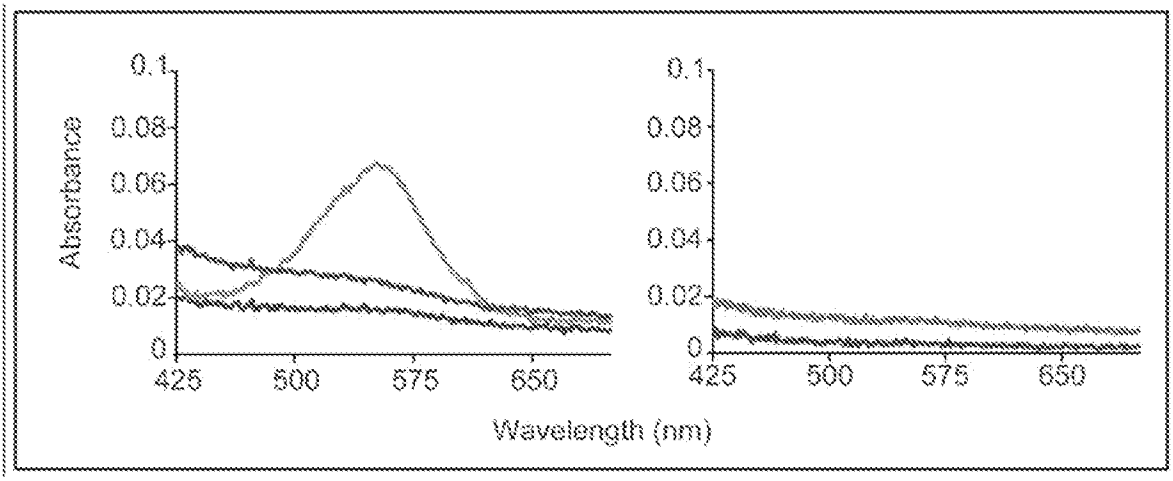

Figure 11 **Midpoint** **Terminus**

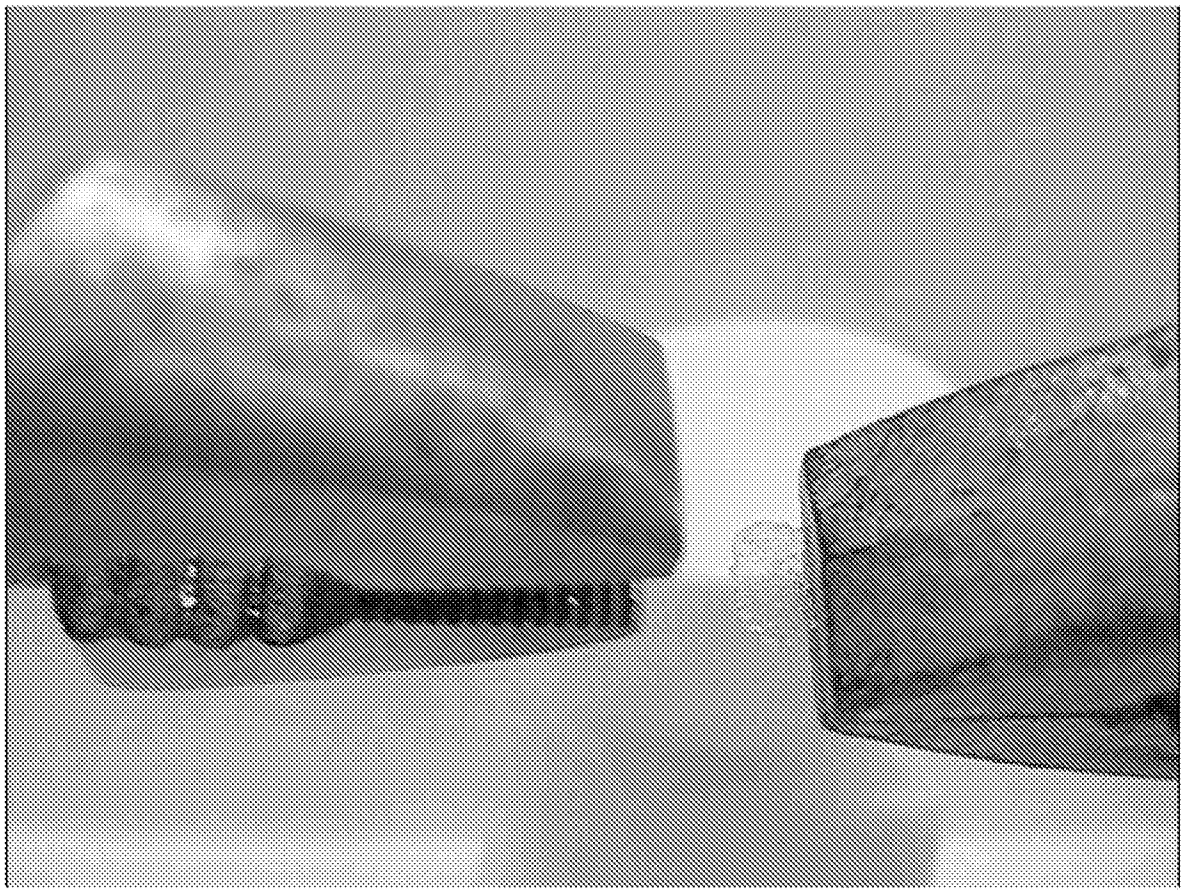

Figure 12 (170 kDa, 0.4 wt% spiropyran)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2008/071083

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F299/00 G01N31/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	C. GALIOTIS, R.J. YOUNG, D.N. BATCHELDER: "The solid state polymerization and physical properties of Bis(ethyl urethane) of 2,4-hexadiyne1,6-diol. II Resonance Raman Spectroscopy" JOURNAL OF POLYMER SCIENCE : POLYMER PHYSICS, vol. 21, 1983, pages 2483-2494, XP002496378 the whole document	1,4-6, 9-11, 14-16, 19,20
X	US 4 916 211 A (RUBNER MICHAEL F [US]) 10 April 1990 (1990-04-10) column 2, line 18 - line 56	1,4-6, 9-11, 14-16, 19,20

☐ Further documents are listed in the continuation of Box C.

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"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 September 2008	03/12/2008
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Rouault, Yannick

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2008/071083

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search reportcovers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1,4(part)-6(part), 9(part)-11(part), 14(part)-16(part), 19(part), 20(part)

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims:
1,4(part)-6(part),9(part)-11(part),
14(part)-16(part),19(part),20(pa
rt)

A polymer having a backbone containing a mechanophore

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2. claims:
2,4(part)-6(part),7,9(part)-11(part),12,
14(part)-16(part),17,19(par
t),20(part)

A polymer having a backbone wherein the mechanophore is moiety I.

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3. claims:
3,4(part)-6(part),8,9(part)-11(part),13,
14(part)-16(part),18,19(par
t),20(part)

A polymer having a backbone wherein the mechanophore is a spiropyran.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2008/071083

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4916211 A	10-04-1990	NONE	