pH indicator for real-time monitoring of meat freshness in smart packaging application

BACKGROUND ART

Technical Field

[0001] The present disclosure relates to pH indicators including dyes chemically bound to block co-polymers (monomer 2; the block co-polymers are derived from monomer 2).

Description of Related Art

[0002] Consumers' demands for fresh and safe food products have continuously been increasing in recent years. The current practice is the use of "use-by" dates that are incorporated into food packaging. Freshness of food can significantly be affected by improper treatment of food during distribution or by the differences in end-user's handling practice. Therefore, uniformly given "use-by" date is not always accurate to indicate freshness of the food. In addition, meat-based food products have relatively short shelf-life, even when it is properly handled or stored. Thus, there is a need to develop technologies that monitor a food quality in real-time and display freshness in a visible way.

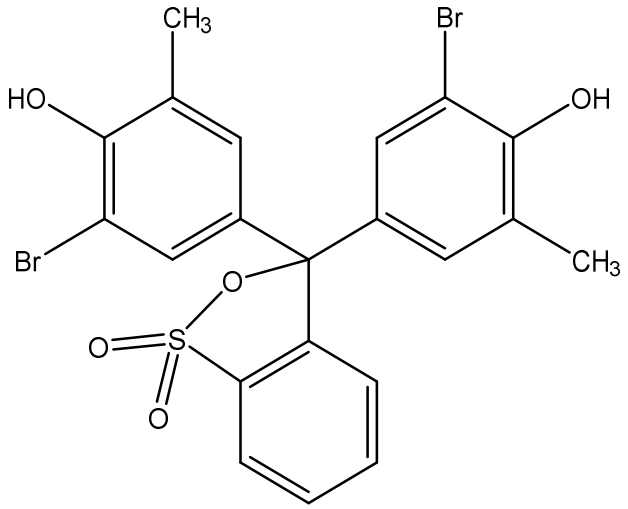
BRIEF SUMMARY

[0003] The following summary presents a simplified summary in order to provide a basic understanding of some aspects of the devices discussed herein. This summary is not an extensive overview of the devices discussed herein. It is not intended to

identify critical elements or to delineate the scope of such devices. Its sole purpose is to present some concepts in a simplified form as a prelude to the more detailed description that is presented later.

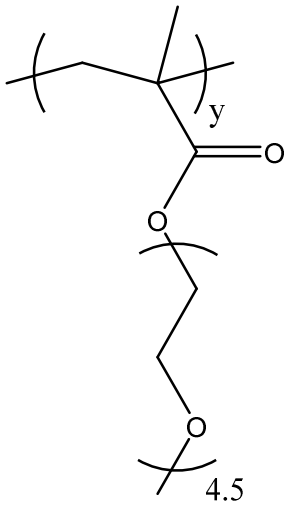
[0004] In accordance with one aspect of the present disclosure, a food package of the present disclosure includes a label including a pH indicator. The pH indicator includes a dye chemically bound to a block co-polymer (monomer 2).

[0005] In accordance with one aspect of the present disclosure, the dye is bromocresol purple. The dye includes a chemical structure of Formula (A),

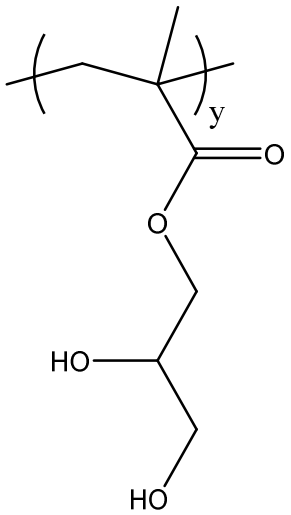


Bromocresol purple (BCP) … Formula (A).

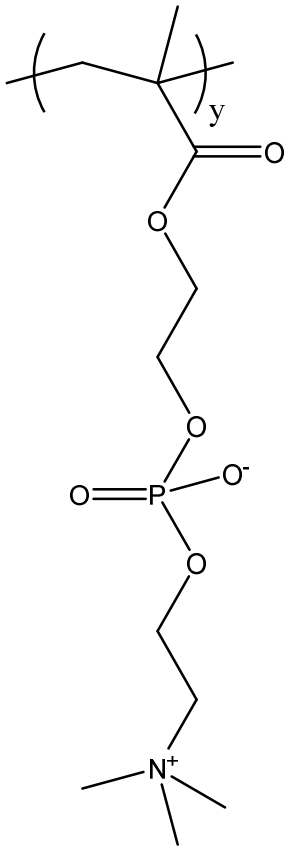
The block co-polymer (monomer 2) includes a chemical structure of Formula (B), Formula (C), Formula (D), or Formula (E),



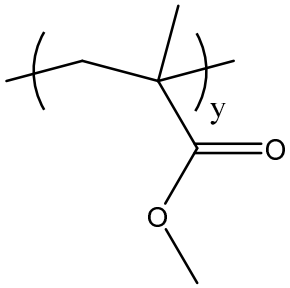
Polyethylene glycol monomethacrylate (PEGMA) …Formula (B);



Glyceryl monomethacrylate (GLMMA) …Formula (C);



2-Methacryloyloxyethyl phosphorylcholine (MPC) …Formula (D);

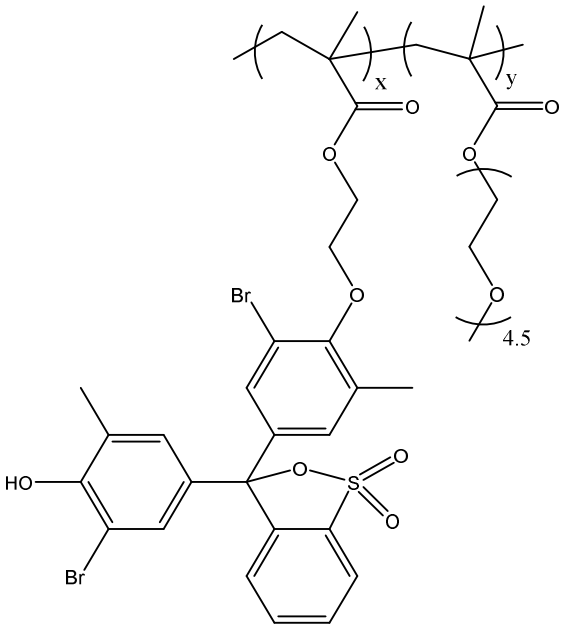


Methyl Methacrylate Monomer(MMA) …Formula (E). y is an integer representing a number of repeating units in block co-polymer and $1 < y < 3$.

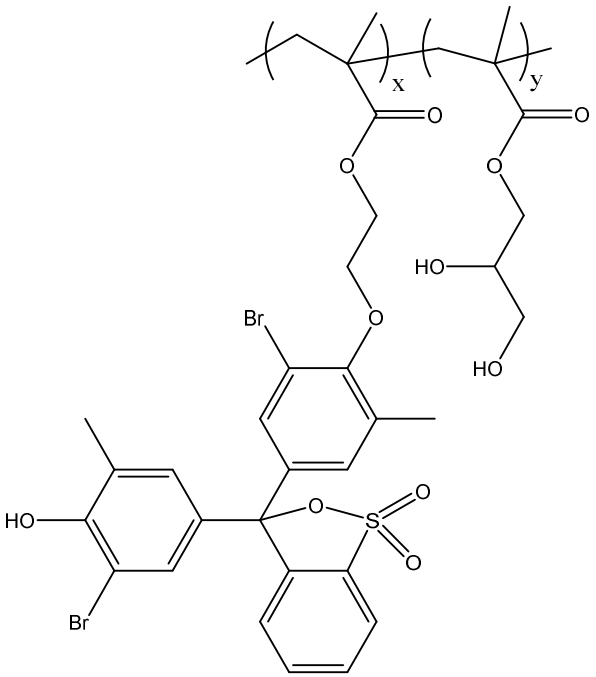
[0006] In accordance with one aspect of the present disclosure, the block co-polymer (monomer 2) is hydrophilic. A hydrophilicity degree of the block co-polymer affects a performance of the pH indicator. Each of the block co-polymer

includes Formula (B), (C), (D), or (E) that has different hydrophilicity degree which is indicated by water contact angle value. A water contact angle of the block co-polymer is 0° or more and 44° or less.

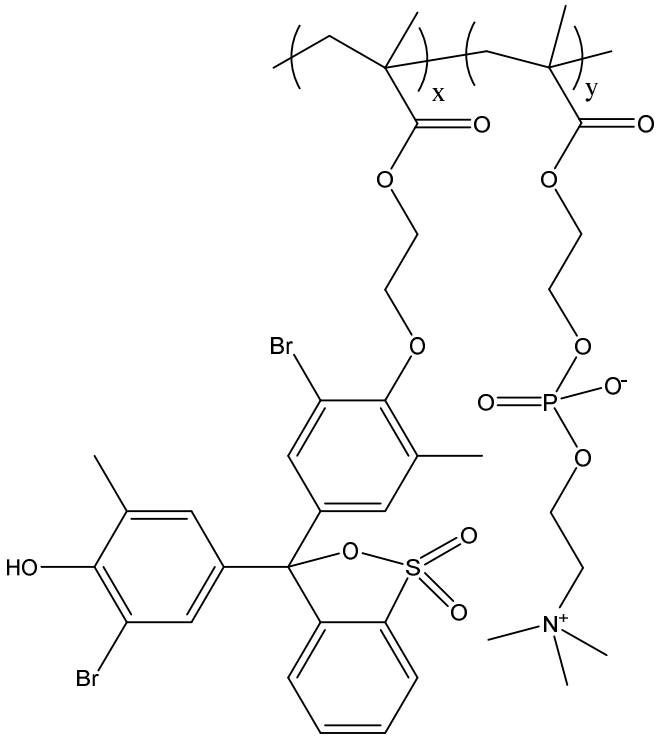
[0007] In accordance with one aspect of the present disclosure, the pH indicator includes a chemical structure of Formula (F), Formular (G), Formula (H), or Formula (I),



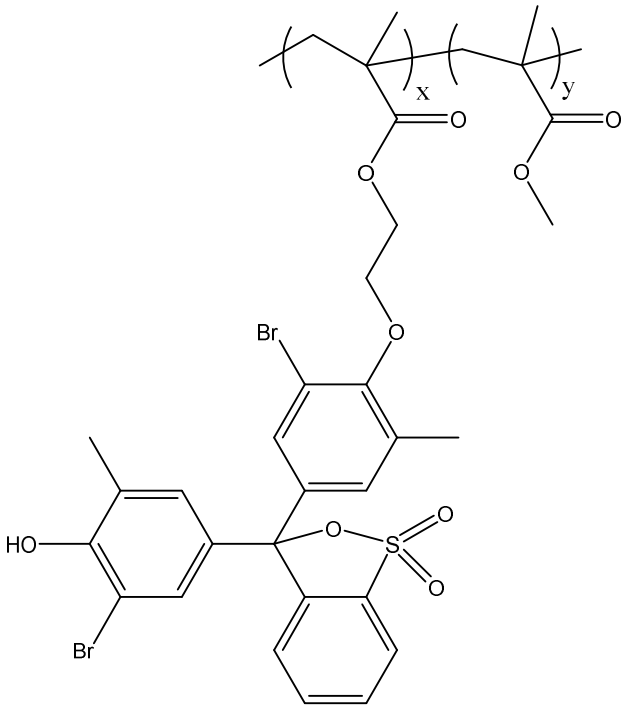
Polyethylene glycol monomethacrylate/2-Bromocresol purple Methacrylate(PGMA/2-BCPMA) …Formula (F);



Glyceryl monomethacrylate/2-Bromocresol purple Methacrylate (GLMMA/2-BCPMA) …Formula (G);



2-Methacryloyloxyethyl phosphorylcholine/2-Bromocresol purple Methacrylate (MPC/2-BCPMA) …Formula (H);



Methyl Methacrylate Monomer/2-Bromocresol purple Methacrylate (MMA/2-BCPMA) …Formula (I). x and y are an integer representing a number of repeating units in the dye chemically bound to the block co-polymer, respectively, $1 < x < 13$, $1 < y < 3$.

[0008] In accordance with one aspect of the present disclosure, the dye chemically bound to the block co-polymer (i.e., BCP binding polymer) is immobilized (e.g., dropped, soaked, immersed, sprayed, attached, included, placed, etc.) on a substrate. The substrate includes one or more of a filter paper, a fabric, a non-woven fabric, a porous silicon, and a porous ceramic. The food package further includes a first film. In accordance with one aspect of the present disclosure, the label further includes a substrate that includes the pH indicator, a second film having a surface area larger than a surface area of the substrate when viewed in a direction perpendicular to the surface of the substrate, and a breathable

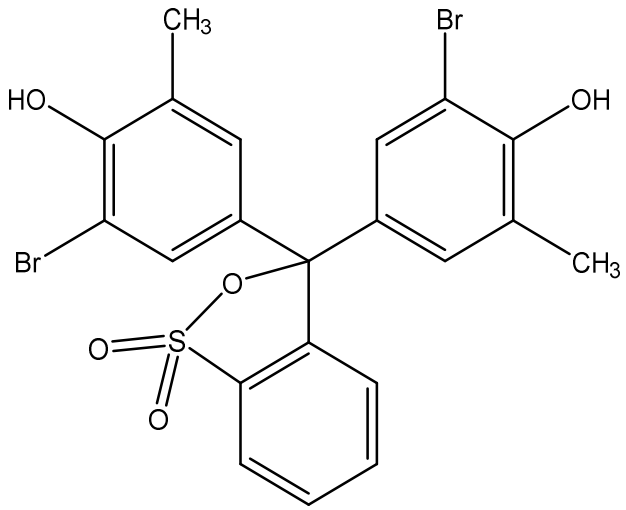
polymer sheet between the substrate and the first film, the breathable polymer having a surface area smaller than the surface area of the film and larger than a surface are of the substrate when viewed in a direction perpendicular to the surface of the substrate. The second film includes a first adhesive at an outer peripheral on a surface facing the first film, the adhesive airtight seals the substrate between the second film and the breathable polymer sheet. The breathable polymer sheet includes a second adhesive on a surface facing the first film. The breathable polymer sheet is attached to the first film with the second adhesive.

[0009] In accordance with one aspect of the present disclosure, the food package further includes a first film. The label further includes a substrate that includes the pH indicator, a second film having a surface area larger than the surface area of the substrate when viewed in a direction perpendicular to the surface of the substrate, and a third film that includes a breathable polymer sheet between the substrate and the first film. The third film has a surface area larger than the second film. The breathable polymer has a surface area smaller than the surface area of the second film and larger than a surface are of the substrate when viewed in a direction perpendicular to the surface of the substrate. The second film includes an adhesive at an outer peripheral on a surface facing the third film, the adhesive airtight seals the substrate between the second film and the third film over the breathable polymer between the second film and the third film. The food package

includes a breathable film, and the label is attached on the breathable film. The food package includes a film that includes a breathable portion, and the label is attached on the breathable portion of the film.

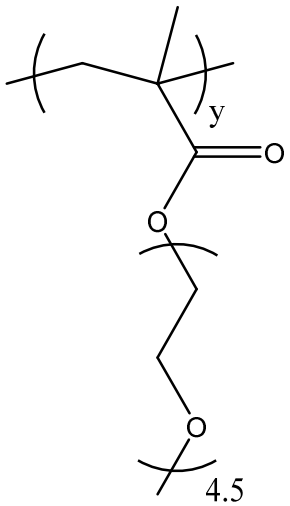
[0010] In accordance with one aspect of the present disclosure, a method for monitoring freshness of a food contained inside a package includes providing a first film wrapping a food, and providing a label attached on an outer surface of the first film. The label includes a pH indicator. The pH indicator includes a dye chemically bound to a block co-polymer. The method further includes monitoring a color of the pH indicator.

[0011] In accordance with one aspect of the present disclosure, a method for manufacturing a food package for monitoring freshness of a food in the food package includes providing a first film, providing a substrate comprising a dye chemically bound to a block co-polymer, providing a second film covering the substrate and airtight sealing the substrate with the second film on the first film. In accordance with one aspect of the present disclosure, the dye is bromocresol purple. The dye includes a chemical structure of Formula (A),

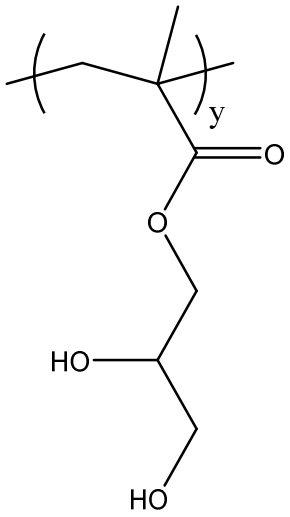


Bromocresol purple (5′ ,5″ -dibromo-o-cresolsulfophthalein) (BCP) … Formula (A).

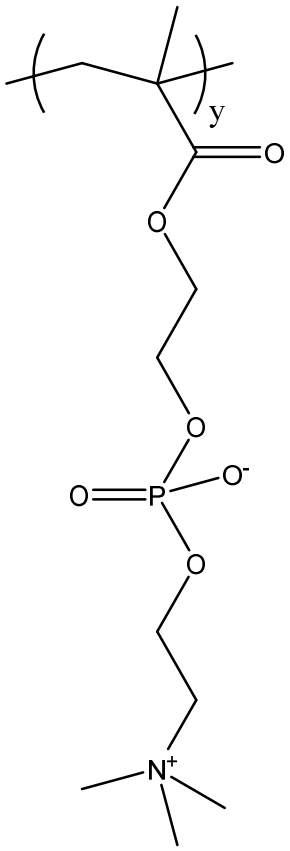
The block co-polymer includes a chemical structure of Formula (B), Formula (C), Formula (D), or Formula (E),



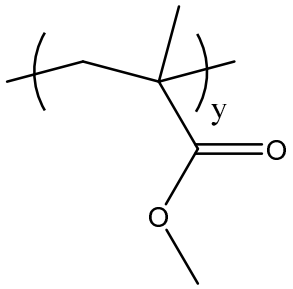
Polyethylene glycol monomethacrylate (PEGMA) …Formula (B);



Glyceryl monomethacrylate (GLMMA) …Formula (C);



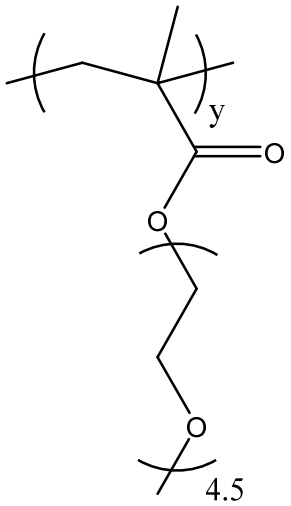
2-Methacryloyloxyethyl phosphorylcholine (MPC) …Formula (D);



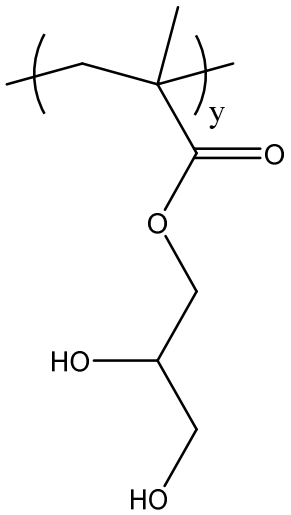
Methyl Methacrylate Monomer(MMA) …Formula (E).

y is an integer representing a number of repeating units in block co-polymer and $1 < y < 3$.

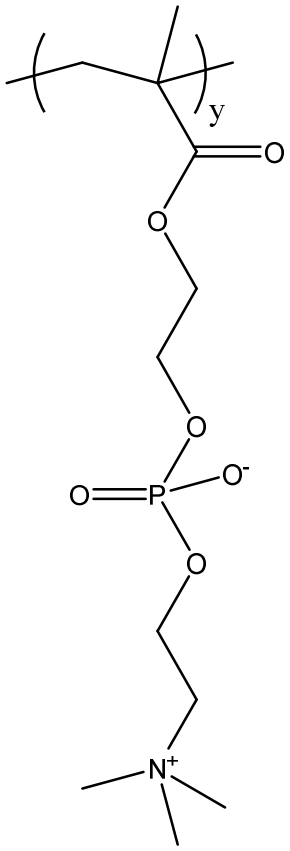
The block co-polymer is hydrophilic. The second film has a surface area larger than a surface area of the substrate when viewed in a direction perpendicular to the surface of the substrate. The method further includes providing a first adhesive at an outer periphery of the second film on a surface facing the first film, and providing a breathable polymer sheet between the substrate and the first film, the breathable polymer sheet includes a second adhesive on a surface facing the first film. The second adhesive attaches the second film to a surface of the first film covering the substrate in between the second film and the first film. The providing the substrate includes providing the dye chemically bound to the block co-polymer by chemically binding bromocresol purple to a block copolymer that includes a chemical structure of Formula (B), Formula (C), Formula (D), or Formula (E),



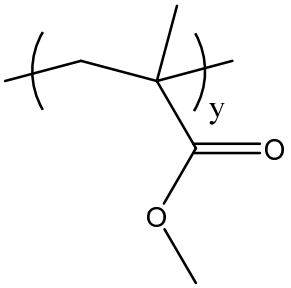
Polyethylene glycol monomethacrylate (PEGMA) …Formula (B);



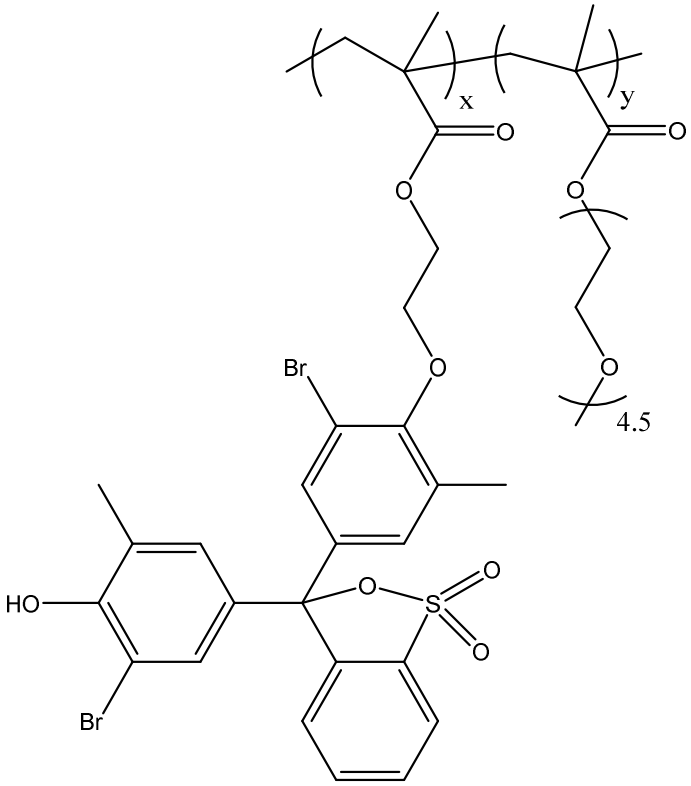
Glyceryl monomethacrylate (GLMMA) …Formula (C);



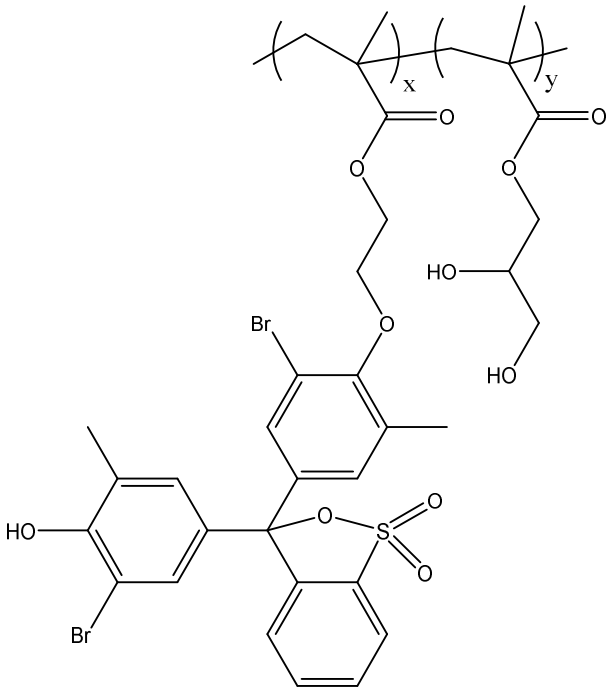
2-Methacryloyloxyethyl phosphorylcholine (MPC) …Formula (D);



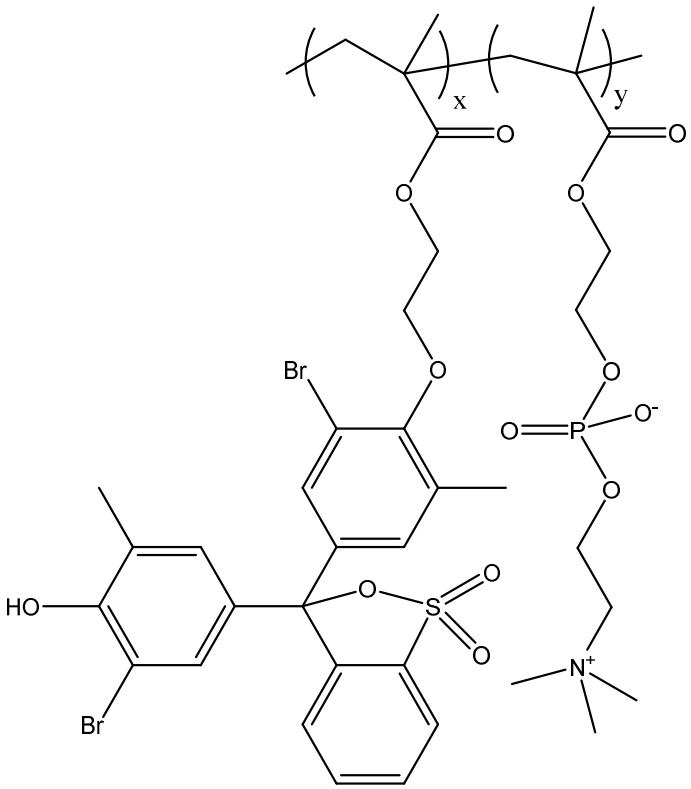
Methyl Methacrylate Monomer(MMA) …Formula (E), to make the dye chemically bound to the block co-polymer having a chemical structure of Formula (F), Formula (G), Formula (H), or Formula (I),



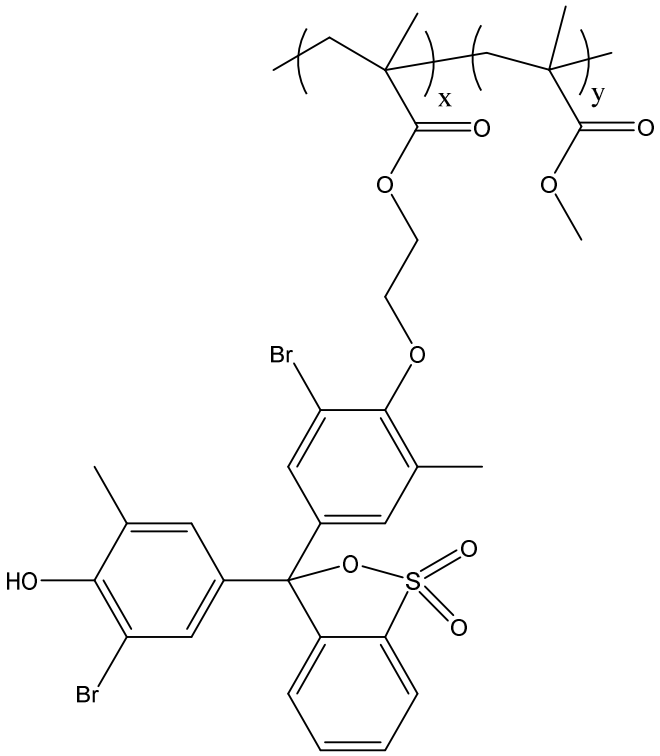
Formula (F);



Formula (G);



Formula (H);



Formula (I),

x and y are an integer representing a number of repeating units in the dye chemically bound to the block co-polymer, respectively, $1 < x < 13$, $1 < y < 3$.

[0012] The method further includes preparing a substrate by immobilizing the dye chemically bound to the block co-polymer on one or more of a substrate base material including a filter paper, a fabric, a non-woven fabric, a porous silicon, and a porous ceramic; drying the substrate at a temperature between 45˚C and 55˚C more preferably at a temperature 50 ˚C; wrapping a food by a first film;; airtight sealing the substrate with the second film on a surface of the first film, the second film having a surface area larger than a surface area of the substrate when viewed in a direction perpendicular to the surface of the substrate.

[0013]The method further includes the airtight sealed substrate in an RFID tag including an RFID chip exposed to the substrate. When the colour changes indicating the level of spoilage on the indicator, a reader scans the indicator, recognizes the colour, and enters the colour (*i.e.*, the level of spoilage) into the tag, the reader transmits energy to the tag which gives power enough for the chip and antenna to relay information (*i.e.*, the level of spoilage) back to the reader. The reader then transmits the information back to an RFID computer program for interpretation.

Brief Description of the Drawings

[0014] FIG. 1 is a synthesis route of 2-BCPMA in one embodiment

of the present disclosure.

FIG. 2 is a synthesis route of BCP bound to a polymer indicator in one embodiment of the present disclosure.

FIG. 3 is a photograph showing the appearance of BCP bound to a polymer indicators (i.e., BCP binding polymer) in one embodiment of the present disclosure.

FIG. 4 is a photograph showing colour response of BCP control and BCP binding polymers towards volatile ammonia in one embodiment of the present disclosure.

FIG. 5 is a chart showing colour response of BCP control and Samples F-I towards spoilt chicken breast.

FIG. 6 is a photograph showing a plastic container and 200g chicken breast test setup in one embodiment of the present disclosure.

FIG. 7 is a chart showing colour response of BCP control and Sample F towards spoilt chicken breast in one embodiment of the present disclosure with the setup shown in FIG. 6.

FIG. 8 is a schematic view showing experimental setups and results in one embodiment of the present disclosure.

FIG. 9 is a chart showing water contact angles of co-polymers of samples F, G, H, and I in one embodiment of the present disclosure.

FIG. 10 is an explanatory view of a colourimeter used to analyze the colour changing degree in one embodiment of the present disclosure.

FIG. 11 is a graph showing the lightness of Samples F, G, and H measured by the colourimeter in one embodiment of the

present disclosure.

FIG. 12 is a schematic view of a BCP binding polymer immobilized on a substrate in one embodiment of the present disclosure.

FIG. 13 is a schematic view of a process of BCP binding polymer immobilizing on a substrate, drying, and airtight sealing in a film in one embodiment of the present disclosure.

FIG. 14 is a schematic view of a label in one embodiment of the present disclosure.

FIG. 15 is a schematic view of a label placed on a food package in one embodiment of the present disclosure.

FIG. 16 is a schematic view of a pH indicator included in an RFID tag in one embodiment of the present disclosure.

FIG. 17 is a schematic view of another embodiment of packaging the substrate of the present disclosure.

FIG. 18 is a schematic view of another embodiment of packaging the substrate of the present disclosure.

[Detailed Description]

[0015] To develop an indicator for determining the freshness of meat, it is helpful to understand the mechanism of meat spoilage. Tissue from different meat products are all composed of proteins, lipids, carbohydrates, inorganic matters and moisture. Thus, they have similar spoilage mechanisms. Microbial growth is one of the main causes of meat spoilage. The microbes that can cause food (e.g., meat, poultry, fish, seafood etc.) spoilage comes from pseudomonads. Direct contact

between a probe to detect pseudomonads and target microbes can cause sampling errors. Therefore, it is more desirable to target gaseous by-products in the package.

[0016] Under normal packing conditions, metabolites of the microbes, such as glucose, lactic acid, CO_2, O_2, volatile nitrogen compounds, and biogenic amines, are formed within the sealed food package. These metabolites can be used as parameters to detect spoilage of meats by indicators that can recognize these metabolites in the package.

[0017] Among volatile nitrogen compounds from microbial metabolism of protein, the most commonly found forms are ammonia, dimethylamine (DMA), and trimethylamine (TMA), known as total volatile basic nitrogen (TVB-N). TVB-N can be detected with an appropriate pH indicating sensor. Solely synthetic chemical dye with the potential harmful influence to human health is not an ideal material for food packaging.

[0018] In order to eliminate the risk of dye migration to food, the inventors of the present disclosure developed a dye chemically bound to a polymer material (i.e., BCP binding polymer).

[0019] Chemicals

Bromocresol purple (BCP) was obtained from SIGMA-ALDRICH®. (Dye content 90%, SIGMA-ALDRICH®). All chemicals used were of reagent grade (supplied by Sigma-Aldrich®) and used as supplied without purification.

[0020] Polymer Indicator

Bromocresol purple (BCP) binding polymer indicator

Four BCP binding polymer indicators were synthesized via living radical polymerization shown in FIGs. 1 and 2. GLMMA, MPC, and MMA were synthesized/isolated by the same method with the different ratio of the 2-BCPMA and Monomer 2 as shown in Table 1.

[0021] Description of synthesizing reaction

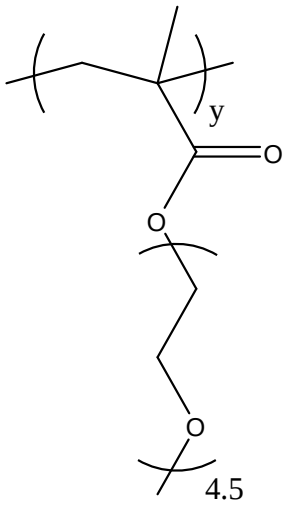
Methacrylic acid (MAA) (6.5 ml, 0.077 mol, 1 eq) with a molar mass of 86.09 g/mol and 2-Bromoethanol (8.0 ml, 0.113 mol, 1.5 eq) were reacted in the presence of 4-dimethylaminopyridine (DMAP) (1.10 g, 0.009 mol, 0.12 eq) and dicyclohexylcarbodiimide (DCC) (18.56 g, 0.090 mol, 1.2 eq) in dichloromethane (DCM) (160 ml) for 2 days to isolate 2-Bromoethyl metacrylate (BEMA). BEMA (2.01 g, 0.01 mol, 1 eq) with a molar mass of 193.04 g/mol and Bromocresol purple (5.60 g, 0.01 mol, 1 eq) with a molar mass of 540.22 g/mol were reacted in the presence of K_2CO_3 (20.78 g, 0.15 mol, 14.5 eq) , Tetrabutylammonium Iodide (BNI) (0.39 g, 0.001 mol, 0.1 eq) in N,N–dimethylformamide (DMF) (46 ml) at 40˚C for 3.5 hours and 80˚C for 2.5 hours to synthesize 2–Bromocresol purple methacrylate (2-BCPMA). 2-BCPMA 5333 mM and PEGMA 2667 mM were reacted in the presence of CP-I 80 mM, BNI 160 mM, and 2,2'-azobis(2,4–dimethylvaleronitrile) (V65) 400 mM at 70˚C for 23 hours in 70wt% DMF to isolate PEGMA/2-BCPMA.

[0022] The incorporation ratio of BCP binding polymer indicator is shown in Table 1 below. The final polymer indicators were solid dark red rough powder as shown in FIG. 3.

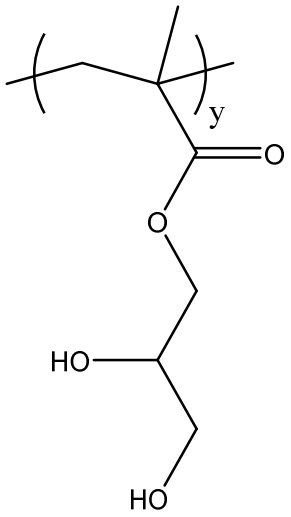
Table 1: Incorporation ratio of BCP binding polymer indicator

Sample	2-BCPMA/ monomer2/ CPI/ BNI/ V65 (mM)	Monomer 2	Incorporation ratio of 2-BCPMA : monomer 2	Wt% of 2-BCPMA (%)
F	5333/ 2667/ 80/ 160/ 400	PEGMA	2.73 : 1	86
G	2000/ 6000/ 80/ 160/ 400	GLMMA	1 : 2.96	58
H	2000/ 6000/ 80/ 160/ 400	MPC	1 : 1.62	58
I	6000/ 2000/ 80/ 160/ 400	MMA	13.64 : 1	99

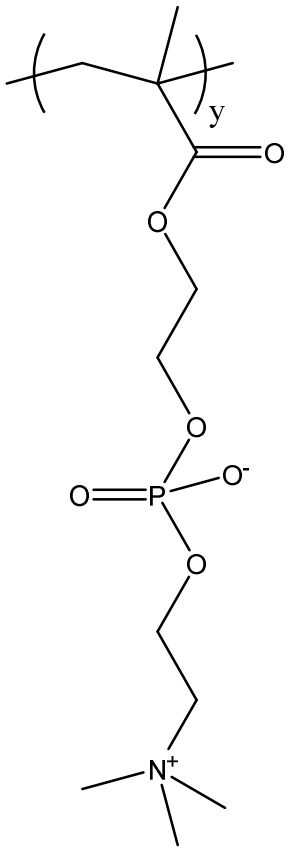
[0023] Chemical Formulae of monomer 2 bound to BCP to synthesize Samples (i.e., Polymers) F-I are as follows: Polyethylene glycol monomethacrylate (PEGMA)-Formula (B); Glyceryl monomethacrylate (GLMMA)-Formula (C); 2-Methacryloyloxyethyl phosphorylcholine (MPC)-Formula (D); Methyl Methacrylate Monomer(MMA)-Formula (E).



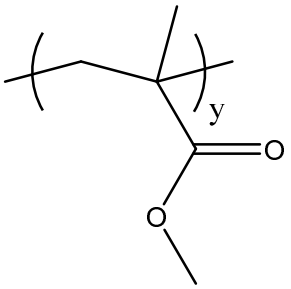
Polyethylene glycol monomethacrylate (PEGMA) …Formula (B);



Glyceryl monomethacrylate (GLMMA) …Formula (C);



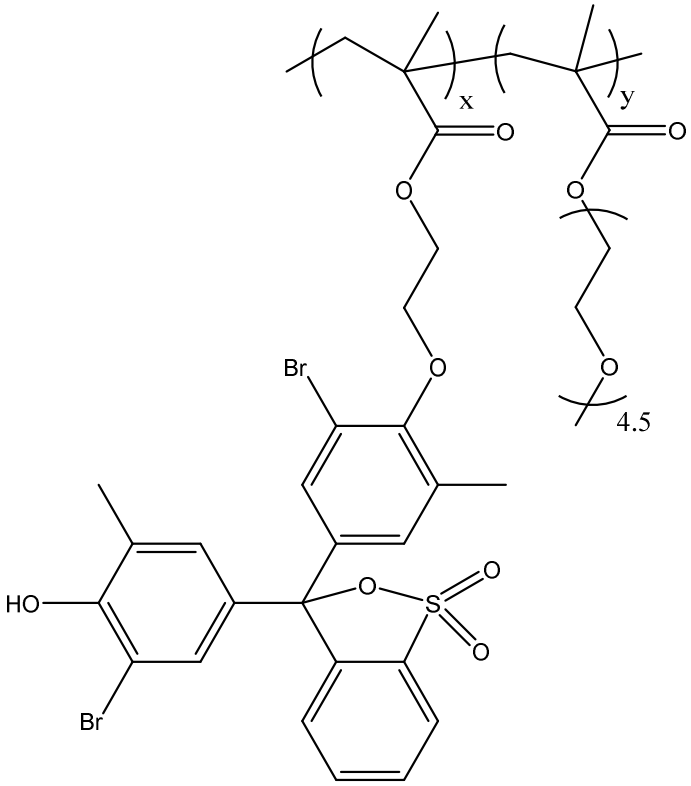
2-Methacryloyloxyethyl phosphorylcholine (MPC) …Formula (D);



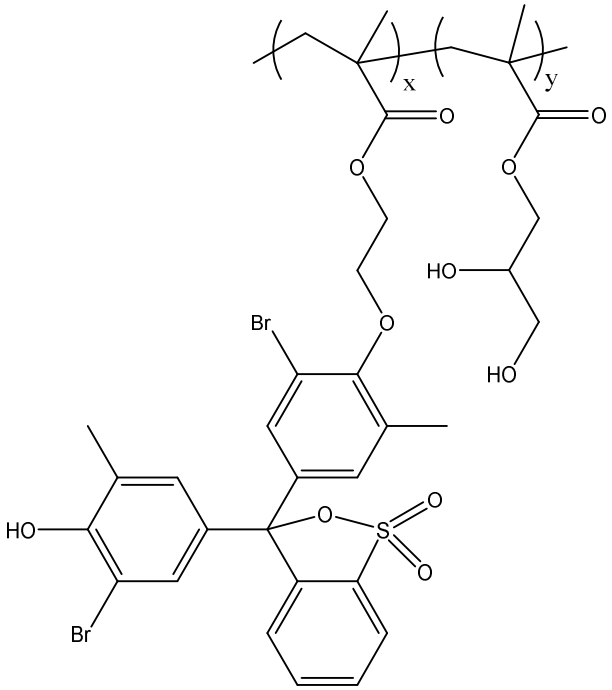
Methyl Methacrylate Monomer(MMA) …Formula (E).

y is an integer representing a number of repeating units in block co-polymer and $1 < y < 3$.

[0024] Chemical Formulae of the synthesized Bromocresol purple (BCP) binding polymer indicator are as follows: Polyethylene glycol monomethacrylate/2-Bromocresol purple Methacrylate(PGMA/2-BCPMA)-Formula (F)(Sample F), Glyceryl monomethacrylate/2-Bromocresol purple Methacrylate -Formula (G)(Sample G), 2-Methacryloyloxyethyl phosphorylcholine/2-Bromocresol purple Methacrylate (MPC/2-BCPMA)-Formula (H)(Sample H), Methyl Methacrylate Monomer/2-Bromocresol purple Methacrylate (MMA/2-BCPMA)-Formula (I)(Sample I).

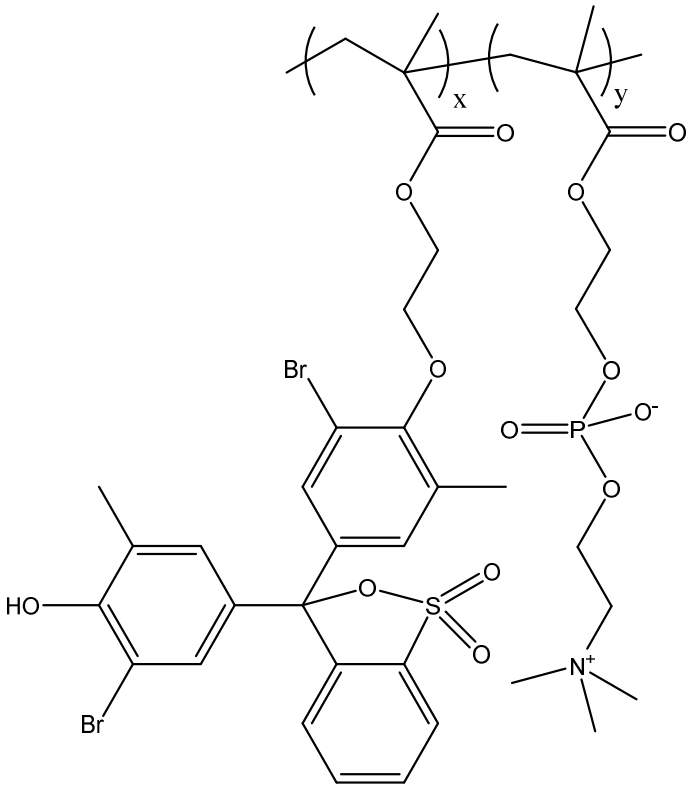


Polyethylene glycol monomethacrylate/2-Bromocresol purple Methacrylate(PGMA/2-BCPMA) …Formula (F);

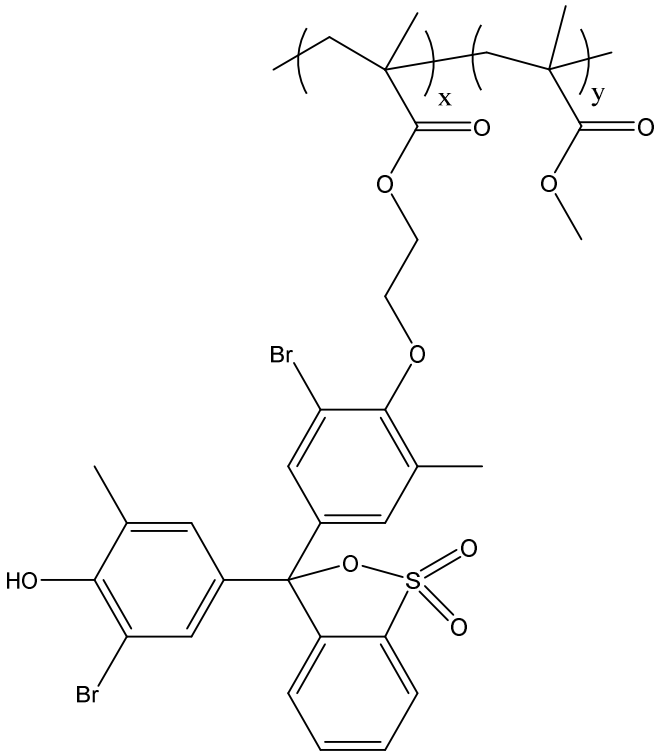


Glyceryl monomethacrylate/2-Bromocresol purple Methacrylate

(GLMMA/2-BCPMA) …Formula (G);



2-Methacryloyloxyethyl phosphorylcholine/2-Bromocresol purple Methacrylate (MPC/2-BCPMA)…Formula (H);



Methyl Methacrylate Monomer/2-Bromocresol purple Methacrylate (MMA/2-BCPMA) …Formula (I).

x and y are an integer representing a number of repeating units in the dye chemically bound to the block co-polymer, respectively, $1 < x < 13$, $1 < y < 3$.

[0025] Preparation of sensors and polymer indicators

Preparation of BCP binding polymer indicator

The mol of BCP for the BCP control and BCP binding polymer indicators were standardized to be 10^{-6} mol by using incorporation ratio (referring to Table 1).

Example calculation for Sample F

1. Amount of BCPMA (using incorporation ratio)

$$\frac{2.73}{2.73+1}\ x\ 100\% = 73.2\%\ of\ BCPMA\ in\ sample\ F$$

2. In order to obtain 10^{-6} mol of BCP moiety, we need

$$\frac{10^{-6}}{73.2\%} = 1.37\ x\ 10^{-6}$$

3. Mass of Sample F to obtain 10^{-6} of BCP moiety

= no. of mol x molar mass of sample F

$$= 1.37\ x\ 10^{-6}\ x\ 4285 = 0.00585\ g$$

[0026] Table 2: Calculated amount standardized to be 10^{-6} mol

Sample	Name	Amount (g)	Amount (mg)
Control	BCP	0.0005402	0.54
F	P((2-BCPMA)-r-PEGMA)	0.00585	5.85
G	P(2-BCPMA)-r-GLMMA)	0.01823	18.2
H	P(2-BCPMA)-r-MPC)	0.03249	32.5
I	P(2-BCPMA)-r-MMA)	0.004719	4.72

[0027] Based on the calculated amount of BCP and BCP binding polymer indicators as shown in Table 2, Samples F-I and BCP control were dissolved in 600 µL of methanol. Sample F-I and BCP control were immobilized (e.g., dropped, soaked, immersed, sprayed, attached, included, placed, etc.) on a filter paper, respectively (filter paper, 5A, ADVANTEC®). The substrates were then dried at 50˚C, for example, in an oven, by a dryer, or in a desiccator, until it is dried. The temperature can be deviated between 48˚C to 55˚C.

[0028] Colour response of sensor and polymer towards ammonia

vapor

Colour response of BCP and BCP binding polymer indicators towards volatile ammonia

Response of sensor & polymer indicator toward volatile ammonia in term of their colour change was performed. Each of the filter paper with Samples F, G, H, I or BCP immobilized and dried was placed in a 500 ml glass bottle. 30% ammonium hydroxide solution was added dropwise to each glass bottle. As shown in FIG. 4, the colour of the filters were all changed distinctively when a 1st drop of ammonium hydroxide was added. The colour change is recorded in Table 3. Therefore, it was confirmed that Samples F-I are suitable as sensors for monitoring ammonia generated by microbial in food packaging.

Table 3: Colour response of BCP and BCP binding polymer indicators towards volatile ammonia

Sample	Name	Color before adding NH_3OH	Color after adding NH_3OH
Control	BCP	Yellow	Purple
F	P((2-BCPMA)-r-PEGMA)	Orange	Green
G	P(2-BCPMA)-r-GLMMA)	Intense Orange	Dark Green
H	P(2-BCPMA)-r-MPC)	Intense Orange	Dark Green
I	P(2-BCPMA)-r-MMA)	Orange	Green

Preparation of chicken breast Samples

[0029] Colour response of BCP and BCP binding polymer indicators towards chicken breast spoilage

Referring to FIG. 5, the preparation of colour response testing of BCP binding polymer indicators of the present disclosure using chicken breast samples is explained. Fresh

chicken breast meat was purchased, and within 30 mins at temperature 20 ˚C, transported to the lab. The temperature of the meat was kept between 20 ˚C and 24 ˚C. Each meat portion around 100 g was placed in a plastic bottle with a volume of 500 ml and a meat portion around 200 g was placed in a plastic container with a volume of 500 ml. BCP sensors (i.e., the filter immobilizing BCP binding polymers (Samples F, G, H, I and control BCP)) were placed on the wall of the plastic bottle and the plastic container, respectively. The plastic bottle/plastic container was closed tightly and sealed with a parafilm (roll size: 4 in. x 125 ft). They were placed in room temperature (25˚C). The temperature can be deviated between 23˚C and 28˚C. Colour changes of the BCP sensors were observed at 0 hour, 21 hour, 25 hour, 30 hour, 45 hour, 48 hour.

[0030] The tests were performed in plastic bottles and plastic containers and all the BCP controls and BCP binding polymers were bound in close proximity with the chicken breast samples inside the plastic bottle, in order to detect the increase of volatile amine generated by spoilt chicken breast. The BCP sensors were monitored periodically. Out of 4 Samples (Samples F-I), only Samples F, G and H showed colour changes. Samples F and H showed significant colour changes from orange to green at 21 hours, the colour changes remained and intensified to dark green colour even after 48 hours. Whereas Sample G polymer only showed significant colour changes from orange to green at 25 hour. Similarly, the colour changes remained and intensified to dark green colour even after 48 hours. The results for Samples

F-H are shown in FIG. 5. The significant colour response shown on Sample F, G and Sample H is due to hydrophilic PEGMA, hydrophilic GLMMA and ionic MPC, respectively.

[0031] The rate of colour response time is as follows: Polymer H=F(21h)>Polymer G (25h).

A few experimental trials by using different containers and different amounts of chicken breast were conducted. The conditions and colour changes results were summarized in the Table 4 below.

[0032] Experiment trial using BCP binding polymers was conducted. The filter paper with Sample F was placed on a petri dish or a plastic bottle with a piece of chicken meat for 24 hours at 25˚C to observe the colour change. The observation is shown in Table 4.

Table 4: Trial experiments with varied conditions and amounts of meat

Experiment trial using BCP binding polymers

Exp. Trial	Container	Condition	Amount of meat	Conc. of BCP in polymer	Color changes
1st	Petridish	Less airtight	~60 g	10^{-6}	Yes
2nd	Petridish	Less airtight	~60 g	10^{-6}	No
3rd	Plastic bottle	More airtight	~ 100 g	10^{-6}	Yes

Experiment trial using BCP dye

Exp. Trial	Container	Condition	Amount of meat	Conc. of BCP in polymer	Colour changes
1st	Petridish	Less airtight	~60 g	Min: 10^{-6} Max: 12×10^{-5}	No
2nd	Plastic bottle	More airtight	~ 100 g	Min: 10^{-6} Max: 32×10^{-6}	Yes Even at min. conc.

From Table 4 above, it can be concluded that the colour changes are greatly affected by the amount of ammonia gas produced and the amount of ammonia gas escaped.

[0033] In order to mimic how the packaged chicken breast sold in a store, the test condition was changed to use a plastic container with a volume of 500 ml(less airtight) with chicken breast meant amount of up to 200 g were tested on BCP control and Sample F as shown in FIG. 6. Other conditions are the same as the conditions explained above. The test results are shown in FIG. 7. The colour changes observed in Sample F at 21 hours from orange to green. The colour changes remained and intensified even at 52 hours.

[0034] Colour response of BCP binding polymers towards chicken breast spoilage

<Hydrophobicity of co-polymer affects the colour changing performance>

The testing results shown in FIG. 5 used the standardized BCP amount of 10^{-6} mol. Due to the standardization of BCP amount to 10^{-6} mol, the only varied factor is on the monomer 2. The experimental setup and result is shown in FIG. 8. Referring to FIG. 5, colour changes showed significantly on Sample F, G and

Sample H. Rate of colour response time was Polymer H=F(21h)>Polymer G (25h). Spoilt chicken breast emits ammonia gas which is polar compound. BCP binding polymers are immobilized onto the filter paper. The filter paper is made of cellulose (polar). Since the polar compounds of the BCP binding polymers are attracted to the polar materials of the filter, the hydrophilic polymers (Sample F, G) have better affinity towards the filter paper which is polar. In addition, due to polarity of ammonia gas, BCP binding polymers have more stable reaction and affinity towards the ammonia gas. The affinity is due to the molecular structure of both hydrophilic polymers and ammonia compound which make them capable of hydrogen bonding.

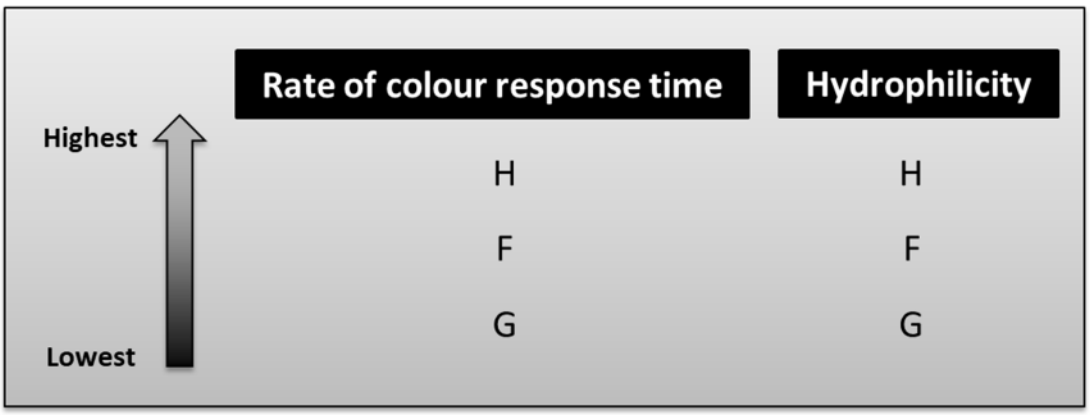
[0035] Likewise, Sample H is synthesized from ionic MPC. Ionic polymer is generally more attracted towards polar ammonia gas which has dipole moment. Polar ammonia gas has dipole moment whereby they have oppositely charged moieties in the same chemical compound. The positively charged moiety of ionic MPC can be attracted by the negatively charged moiety of a polar ammonia gas and vice versa.

[0036] All the possible reasons mentioned above may make Samples F, G and H more stable than the polymer I. Thus, colour changes shown on Samples F, G and H. The colour changes also remained and intensified when the ammonia source (spoilt chicken breast) is retained. In order to support the hypothesis of the inventors of the present disclosure, water contact angle value for Sample F-H was identified.

[0037] Water Contact Angle

Water contact angle values of co-polymers were obtained from literature search. The literature value of each co-polymers' water contact angle is shown in FIG. 9. These water contact angles support the hypothesis of the inventors of the present disclosure. Binding hydrophilic structure to BCP resulted in good colour performance on the spoilt chicken breast. The water contact angle value range of hydrophilic co-polymer is from 0° to 44°.

Table 5: Hydrophilicity and Rate of Colour Response Time

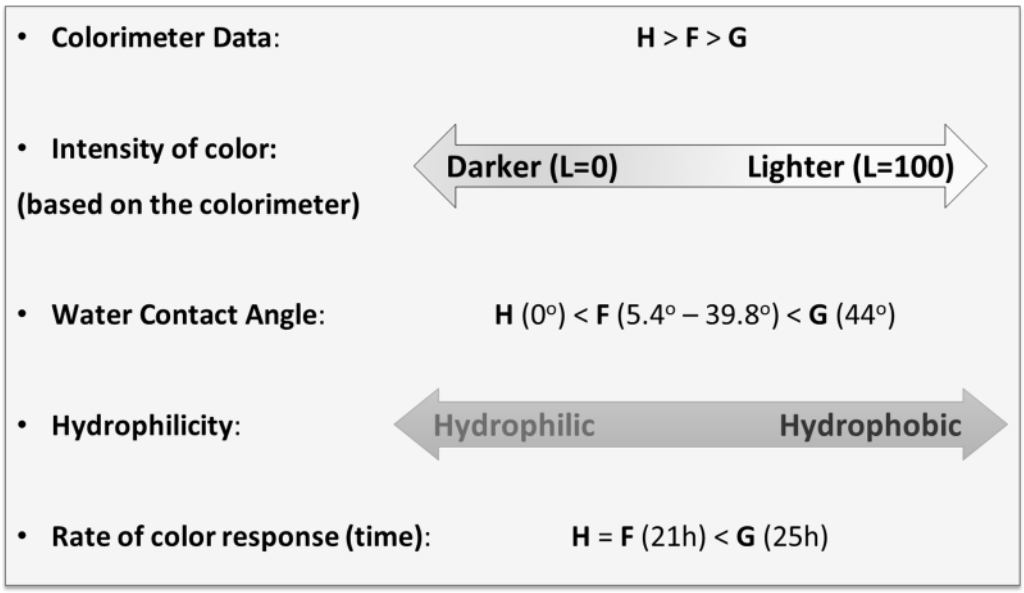


[0038] Colourimeter

As shown in FIG. 5 and Table 6, the colour changes indicating the spoilage of chicken breast were observed on Samples (Polymers) F, G and H. Colourimeter (CR-400 KONICA MINOLTA®) was used to get the image analysis on the colour changing degree. As shown in FIG. 10, colourimeter is a sophisticated colour instrument that is able to assign numerical values to help quantify, control and define colour. The value L* indicates lightness of the colour. In other words, as the value L* becomes smaller, the color becomes darker.

[0039] The colour changes of Samples (Polymers) F, G and H were measured with the numerical values in terms of the lightness. The results are shown in FIG. 11. As shown in FIG. 11, the degrees of the colours were increased from 21 hours toward 48 hours from the time the sample (e.g., meat) was placed in the setting as shown in FIGs 5 and 8. In other words, the colour becomes darker from 21 hours toward 48 hours from the time the sample (e.g., meat) was placed in the setting as shown in FIGs 5 and 8. The colourimetric data supports the hypothesis of the inventors of the present disclosure that higher hydrophilicity of the BCP binding polymers shows higher colour intensity. Qualitatively, the more hydrophilic the BCP binding polymer is, the higher the intensity of the colour performance of the BCP binding polymers on the spoilt chicken breast is.

Table 6:Colorimeter Data, Intensity of color, Water Contact Angle, Hydropholicity and Rate of color response time



[0040] Colour response of the BCP binding polymers (Sample F-I) were tested for monitoring chicken breast freshness quality. As shown in FIG. 9 and Table 6, the water contact angle literature value of the BCP binding polymers support the hypothesis of the inventors of the present disclosure that the hydrophilicity of the BCP binding polymer is proportional to the demonstrated colour performance on the spoilt chicken breast. Qualitatively, the more hydrophilic the BCP binding polymer (smaller water contact angle) is, the better colour performance on the spoilt chicken breast is. The water contact angle value range of hydrophilic co-polymer: 0˚– 44˚

[0041] Label Construction

Referring now to FIGs. 12-16, constructions of the pH indicator and labels 10 for food packaging including the pH indicator of one embodiment of the present disclosure are explained below.

[0042] The BCP binding polymer of the present disclosure is used to prepare the pH indicator discussed above. The pH indicator includes a dye, such as bromocresol purple, chemically bound to a hydrophilic block co-polymer, such as Samples (Polymers) F, G, and H. As shown in FIGs. 12 and 13, the synthesized dye 12 is immobilized to a substrate 11 and dried in an oven at around 50˚C for about 30 minutes. The temperature for drying was kept between 48 ˚C and 55 ˚C. The drying time was between 30 minutes and 40 minutes. The material for the substrate includes one or more of a filter paper, a fabric, a non-woven fabric, a porous silicon, and a porous ceramic. The dried substrate 11 is sealed in a PE plastic or a

breathable but non-leaking film 14.

[0043] As shown in FIGs. 14 - 16, the label 10 of one embodiment of the present disclosure can include a breathable film 13 in the back of the label 10 facing the food 20 and a breathable or a non-breathable film 14 on the front surface opposite from the food 20. The substrate 11 immobilizing the BCP binding polymer (pH indicator) 12 can be placed in between the films. The breathable film 15 side of the label is attached to an outer surface of a breathable film 21 including a food 20 in a package. The breathable film 15 side of the label is attached to a breathable portion of a non-breathable film including a food 20 in a package 30. The label can be incorporated in a part of the film 21 that includes a food 20 in a package, and the breathable film 15 side of the label 10 is in directly exposed to the food in the package.

[0044] In one embodiment of the present disclosure, the pH indicator 12 including the dye chemically bound to a block co-polymer of the present disclosure is incorporated in the label 10 with a Radio-frequency identification (RFID) chip 16, a barcode tag, or a QR code tag. The freshness of the food (e.g., meat, fish, poultry, etc.) indicated by the colour change of the pH indicator can be read by a colourimeter and recorded along with the use-by-date recorded in the RFID chip, the barcode tag, or the QR code tag read by a RFID reader, barcode reader, or a QR code reader. This way, the freshness monitoring can be done remotely. When the colour changes indicating the level of spoilage on the indicator, a reader scans the

indicator, recognizes the colour, and enters the colour (*i.e.*, the level of spoilage) into the tag, the reader transmits energy to the tag which gives power enough for the chip and antenna to relay information (*i.e.*, the level of spoilage) back to the reader. The reader then transmits the information back to an RFID computer program for interpretation.

[0045] The pH indicator of the present disclosure including a dye chemically bound to a block co-polymer is highly sensitive to the ammonia as an indicator of food rot. The dye (Bromocresol purple (BCP) is chemically bound to a block co-polymer (BCP binding polymer) with different hydrophilicity. The BCP binding polymer with higher hydrophilicity has better colour intensity suitable for a pH indicator. Because of the high sensitivity and the high colour intensity, the whole process of food rot from fresh to rotten of the food can be identified in a phased manner. Because of the high colour intensity, the degree of food rot can be detected in naked eye without another device or pretreatment. Moreover, in one embodiment of the present disclosure, the BCP binding polymer is immobilized to a substrate and dried. The dried substrate is sealed in a breathable but non-leaking films. Therefore, the BCP binding polymer does not leak to the food in the container. In one embodiment of the present disclosure, the dried substrate with the BCP binding polymer is incorporated into a label with an RFID chip, a barcode tag, or a QR code tag. In this embodiment, the freshness monitoring can be done remotely.

CLAIMS

What is claimed is:

1. A food package comprising:

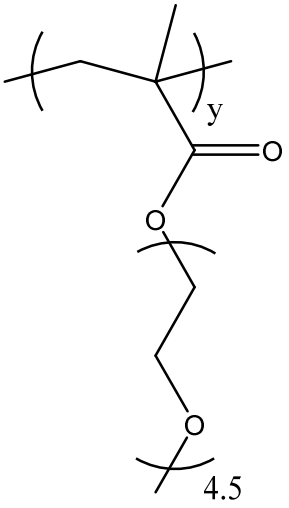
a label comprising a pH indicator:

the pH indicator comprising:

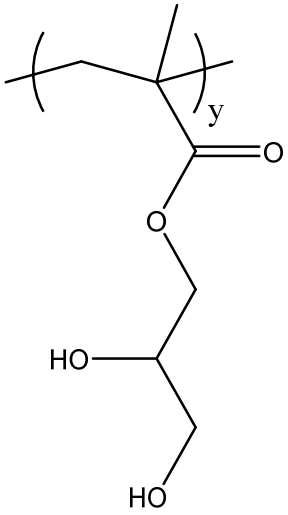
a dye chemically bound to a block co-polymer.

2. The food package according to claim 1, wherein the dye is bromocresol purple.

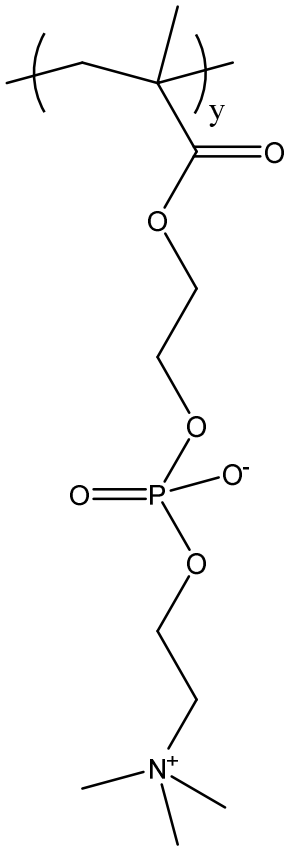
3. The food package according to claim 1 or 2, wherein the block co-polymer comprises a chemical structure of Formula (B), Formula (C), Formula (D), or Formula (E):

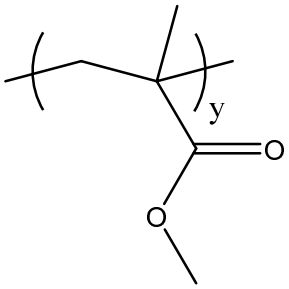


Formula (B);



Formula (C);





Formula (D); Formula (E),

wherein y is an integer representing a number of repeating units in block co-polymer

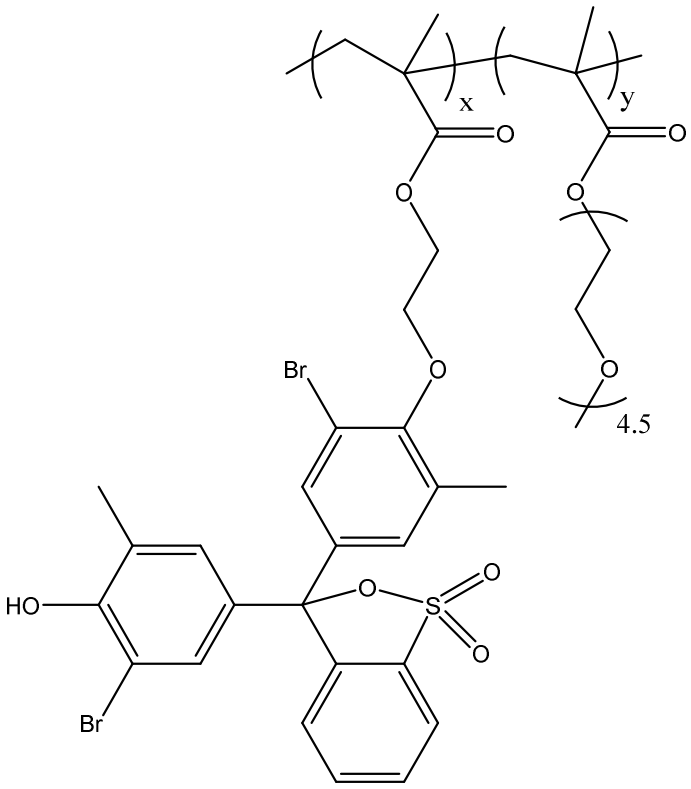
4. The food package according to any one of claims 1 to 3, wherein the block co-polymer is hydrophilic, and preferably each of the block co-polymer comprising Formula (B), (C), (D), and (E) has different hydrophilicity degree which is indicated by water contact angle value.

5. The food package according to any one of claims 1 to 4, wherein a hydrophilicity degree of the block co-polymer affects a performance of the pH indicator.

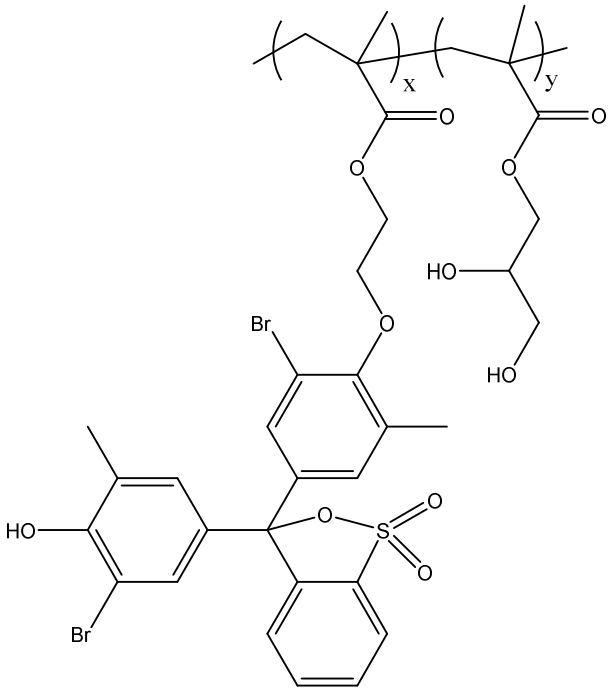
6. The food package according to any one of claims 1 to 5, wherein a water contact angle of the block co-polymer is 0° or

more and 44° or less.

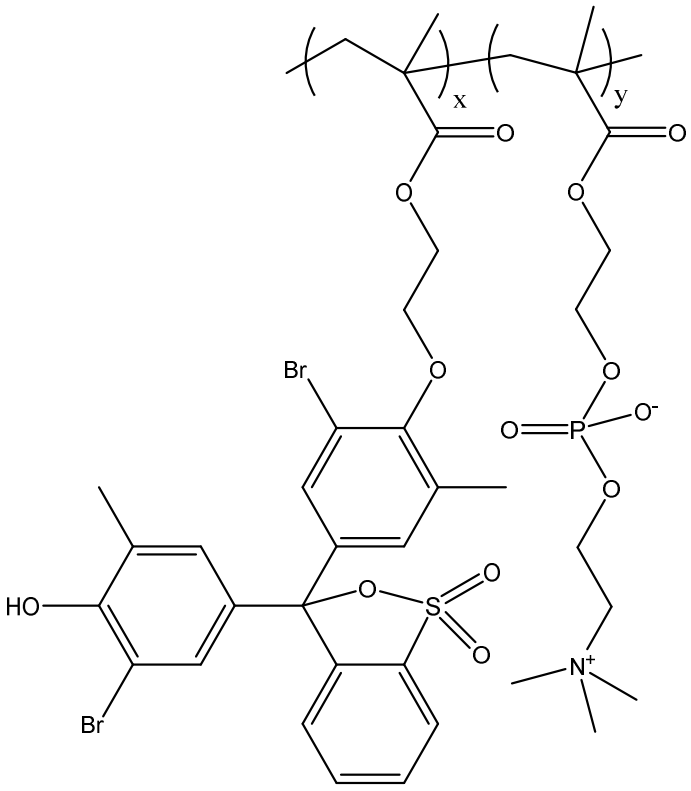
7. The food package according to any one of claims 1 to 6, wherein the pH indicator comprises a chemical structure of Formula (F), Formular (G), Formula (H), or Formula (I):



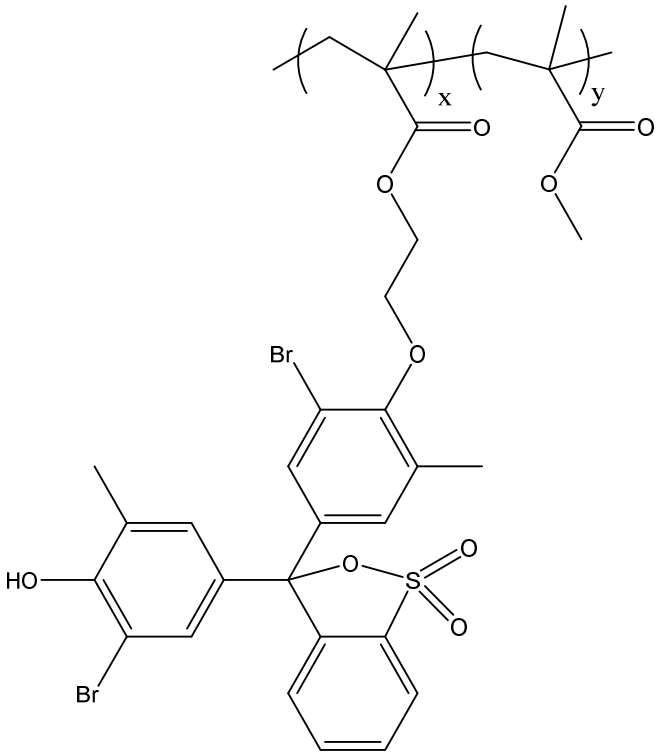
Formula (F);



Formula (G);



Formula (H);



Formula (I),

wherein x and y are an integer representing a number of repeating units in the dye chemically bound to the block co-polymer, respectively, $1 < x < 13$, $1 < y < 3$.

8. The food package according to any one of claims 1 to 7, wherein the dye chemically bound to the block co-polymer is immobilized on a substrate, and the substrate comprises one or more of a filter paper, a fabric, a non-woven fabric, a porous silicon, and a porous ceramic.

9. The food package according to any one of claims 1 to 8,

wherein the food package further comprises a first film configured to wrap a food,

the label further comprises:

a substrate comprises the pH indicator;

a second film having a surface area larger than a

surface area of the substrate when viewed in a direction perpendicular to the surface of the substrate; and

a breathable polymer sheet between the substrate and the first film, the breathable polymer having a surface area smaller than the surface area of the film and larger than a surface are of the substrate when viewed in a direction perpendicular to the surface of the substrate,

wherein the second film comprises a first adhesive at an outer peripheral on a surface facing the first film, the adhesive airtight seals the substrate between the second film and the breathable polymer sheet between the second film and the breathable polymer sheet, and

the breathable polymer sheet comprises a second adhesive on a surface facing the first film, the breathable polymer sheet is attached to the first film with the second adhesive.

10. The food package according to any one of claims 1 to 8,

wherein the food package further comprises a first film configured to wrap a food,

the label further comprises:

a substrate comprises the pH indicator;

a second film having a surface area larger than a surface area of the substrate when viewed in a direction perpendicular to the surface of the substrate; and

a third film comprises a breathable polymer sheet between the substrate and the first film, the third film having a surface area larger than the second film, the breathable polymer having a surface area smaller than the surface area of

the second film and larger than a surface area of the substrate when viewed in a direction perpendicular to the surface of the substrate,

wherein the second film comprises an adhesive at an outer peripheral on a surface facing the third film, the adhesive airtight seals the substrate between the second film and the third film over the breathable polymer between the second film and the third film.

11. The food package according to any one of claims 1 to 10, wherein the food package comprises a breathable film and the label is attached on the breathable film.

12. The food package according to any one of claims 1 to 10, wherein the food package comprises a film that comprises a breathable portion, and the label is attached on the breathable portion of the film.

13. A method for monitoring freshness of a food contained inside a package comprising:

attaching a label on an outer surface of a first film configured to wrap a food, the label comprising a pH indicator, the pH indicator comprising a dye chemically bound to a block co-polymer; and

monitoring a color of the pH indicator.

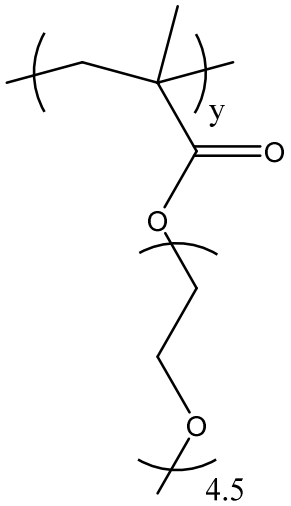
14. A method for manufacturing a food package for monitoring freshness of a food in the food package comprising:

providing a substrate on a first film configured to wrap a food, the substrate comprising a dye chemically bound to a block co-polymer;

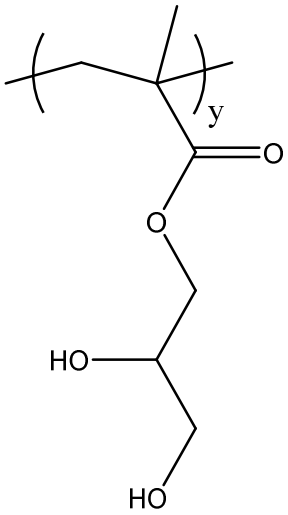
covering the substrate with a second film and airtight sealing the substrate with the second film on the first film.

15. The method according to claim 13 or 14, wherein the dye is bromocresol purple.

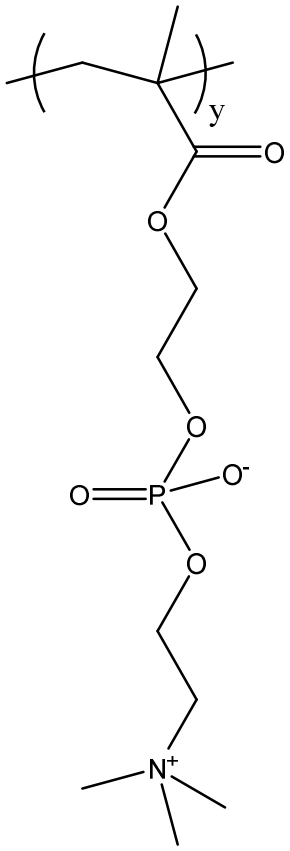
16. The method according to claim 14 or 15, wherein the block co-polymer comprises a chemical structure of Formula (B), Formula (C), Formula (D), or Formula (E):

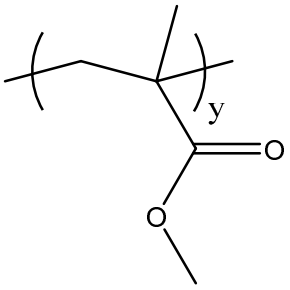


Formula (B);



Formula (C);





Formula (D); Formula (E),

wherein y is an integer representing a number of repeating units in block co-polymer and 1 < y < 3.

17. The method according to any one of claims 14 to 16, wherein the block co-polymer is hydrophilic.

18. The method according to any one of claims 14 to 17,

wherein the second film has a surface area larger than a surface area of the substrate when viewed in a direction perpendicular to the surface of the substrate,

the method further comprises:

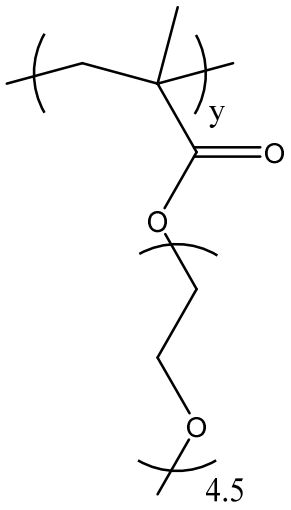
providing a first adhesive at an outer periphery of the second film on a surface facing the first film, and

providing a breathable polymer sheet between the

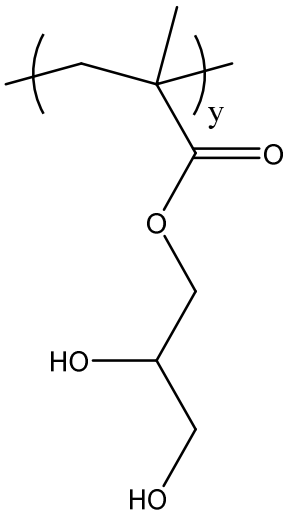
substrate and the first film, the breathable polymer sheet comprises a second adhesive on a surface facing the first film, the second adhesive attaches the second film to a surface of the first film covering the substrate in between the second film and the surface of the first film.

19. The method according to any one of claims 14 to 18, wherein the providing the substrate comprising the dye chemically bound to the block co-polymer comprising:

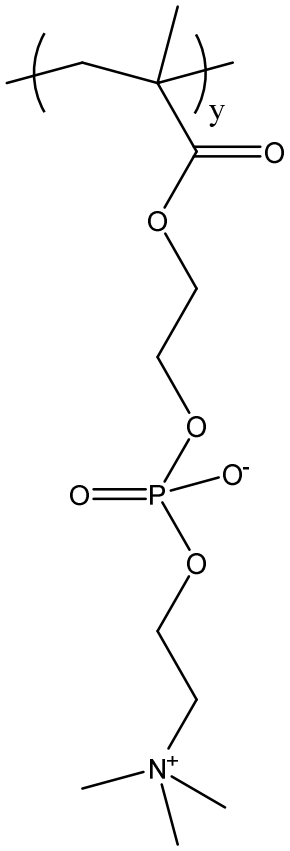
chemically binding bromocresol purple to a block copolymer comprises a chemical structure of Formula (B), Formula (C), Formula (D), or Formula (E):

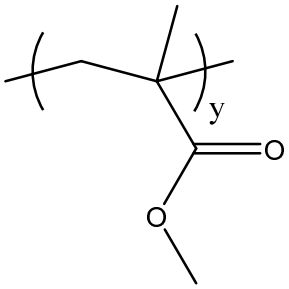


Formula (B);

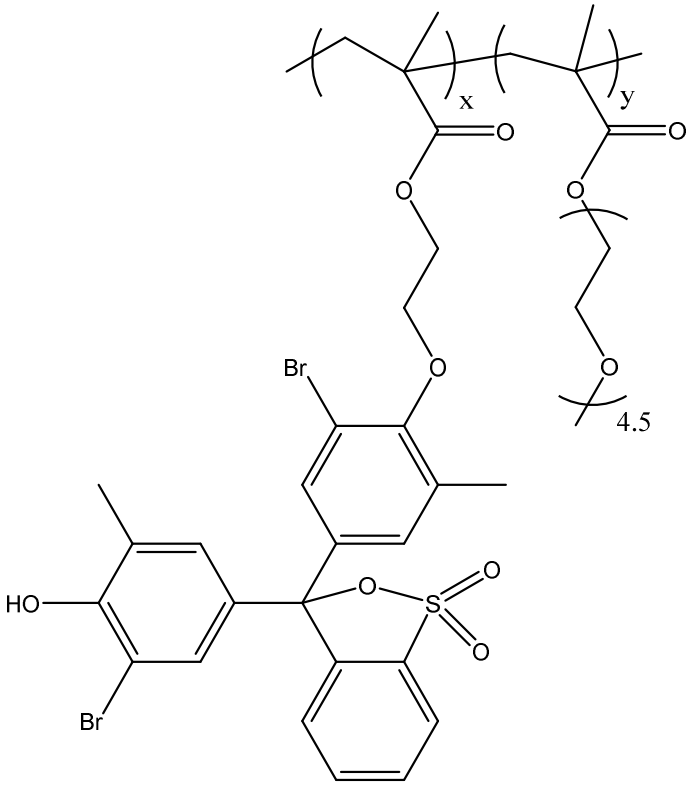


Formula (C);

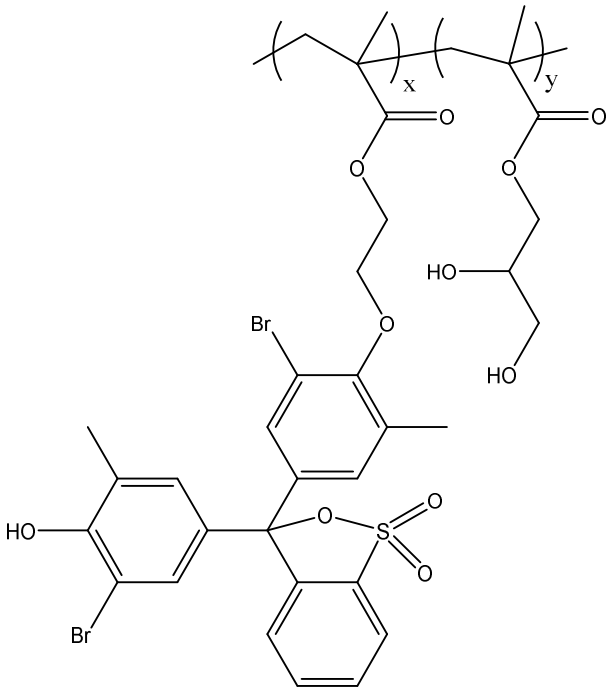




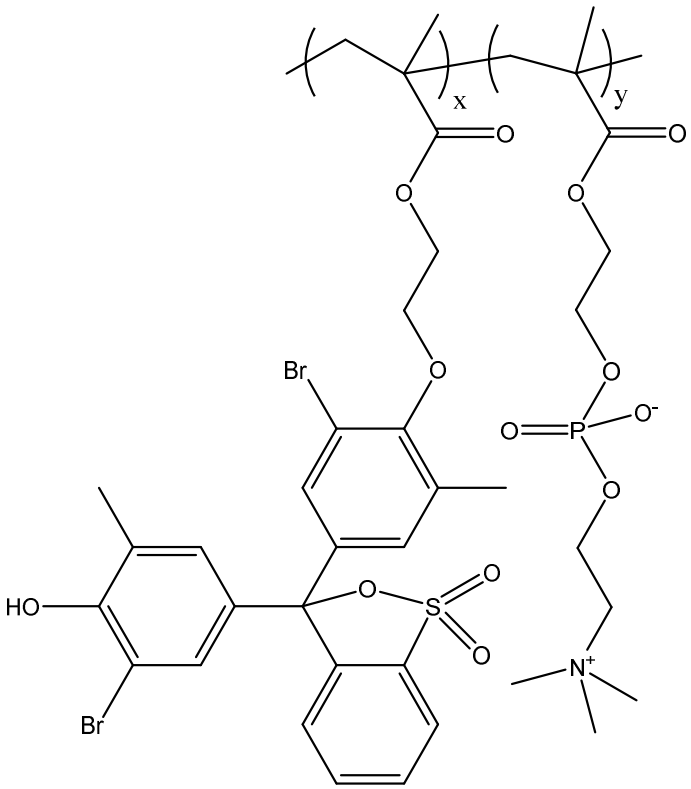
Formula (D); Formula (E), to make the dye chemically bound to the block co-polymer having a chemical structure of Formula (F), Formula (G), Formula (H), or Formula (I):



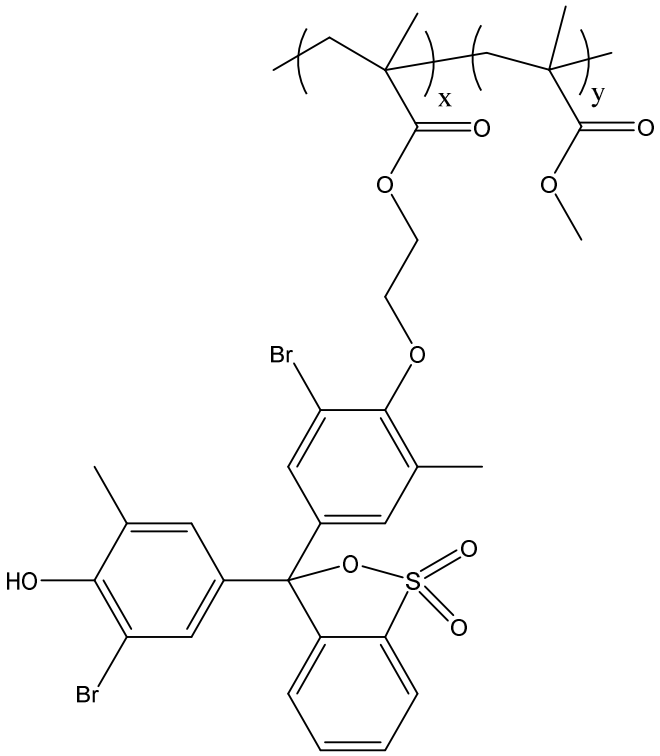
Formula (F);



Formula (G);



Formula (H);



Formula (I),

wherein x and y are an integer representing a number of repeating units in the dye chemically bound to the block co-polymer, respectively, $1 < x < 13$, $1 < y < 3$,

preparing the substrate by immobilizing the dye chemically bound to the block co-polymer on one or more of a substrate base material comprising one or more of a filter paper, a fabric, a non-woven fabric, a porous silicon, and a porous ceramic;

drying the substrate at a temperature between 48 and 55 ˚C, more preferably at a temperature of 50 ˚C;

wrapping a food by a first film; and

airtight sealing the substrate with the second film on a surface of the first film, the second film having a surface area larger than a surface area of the substrate when viewed in a direction perpendicular to the surface of the substrate.

20. The method according to any one of claims 14 or 19, wherein the method further comprises:

providing the substrate in an RFID tag comprising an RFID chip;

scanning the colour changes indicating a level of spoilage on the indicator, recognizing the colour, and entering the colour as data into the tag by a reader;

transmitting energy from the reader to the tag which powers the chip and antenna enough to relay information back to the reader;

transmitting the information back to an RFID computer program for interpretation.