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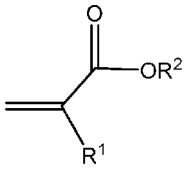
(54) Title: RHEOLOGY MODIFIERS FOR ENCAPSULATING QUANTUM DOTS



(I)

(57) Abstract: A polymer resin comprising: (a) quantum dots, (b) a compound of formula (I) (I) wherein R^1 is hydrogen or methyl and R^2 is a C_6-C_{20} aliphatic polycyclic substituent, and (c) a block or graft copolymer having Mn from 50,000 to 400,000 and comprising from 10 to 100 wt% polymerized units of styrene and from 0 to 90 wt% of a non-styrene block; wherein the non-styrene block has a van Krevelen solubility parameter from 15.0 to 17.5 $(J/cm^3)^{1/2}$.

RHEOLOGY MODIFIERS FOR ENCAPSULATING QUANTUM DOTS

FIELD OF THE INVENTION

The present invention relates to rheology modifiers useful in a process for preparing a multilayer polymer composite containing quantum dots.

BACKGROUND OF THE INVENTION

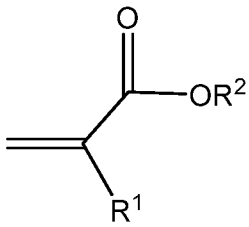
Semiconductor quantum dots (QD) provide optical absorption and emission (photoluminescence PL or electroluminescence EL) behaviors that are significantly different from those of bulk materials. As the particle size decreases, effective energy bandgap (Eg), or available energy levels, increases and creates a blue shifted PL spectrum. This spectrum tunability by the particle size dependent quantum confinement effect within the same material is a critical advantage over conventional bulk semiconductors. Because of their unique optical properties, QD have been of great interest in many display and lighting applications. Most QD have inorganic shells with a larger bandgap material to confine electron and hole pairs within the core region and prevent any surface charge states. The outer shells are then capped by organic ligands to reduce trap states of the shell that can lead to reduced quantum yield (QY). Organic ligands help QD to disperse in organic/aqueous solvents. Typical organic ligands surrounding QD have relatively long alkyl chains which provide high solubility in non-polar solvents or monomers. Unfortunately, QD are very susceptible to photo-oxidation during light absorption/conversion process. Also, moisture can have similar impacts when ligands are not compatible. QD typically are encapsulated in a polymer matrix to protect them from adverse effects of water and oxygen. For example, US2010/0084629 discloses a variety of polymers as encapsulants. However, this reference does not disclose the polymer compositions described herein.

SUMMARY OF THE INVENTION

The present invention provides a polymer resin comprising:

(a) quantum dots,

(b) a compound of formula (I)



(I)

wherein R^1 is hydrogen or methyl and R^2 is a C_6-C_{20} aliphatic polycyclic substituent, and

(c) a block or graft copolymer having M_n from 50,000 to 400,000 and comprising from 10 to 100 wt% polymerized units of styrene and from 0 to 90 wt% of a non-styrene block; wherein the non-styrene block has a van Krevelen solubility parameter from 15.0 to 17.5 $(J/cm^3)^{1/2}$.

The present invention further provides a polymer resin comprising:

(a) quantum dots,

(b) a compound of formula (I), and

(c) a homopolymer or random copolymer with M_n greater than polymer critical molecular weight, M_c and with a van Krevelen solubility parameter from 16.5 to 20.0 $(J/cm^3)^{1/2}$.

DETAILED DESCRIPTION OF THE INVENTION

Percentages are weight percentages (wt%) and temperatures are in °C, unless specified otherwise. Operations were performed at room temperature (20-25 °C), unless specified otherwise. Boiling points are measured at atmospheric pressure (ca. 101 kPa). "(Meth)acrylate" means acrylate or methacrylate. Quantum dots are well known in the art, see, e.g., US2012/0113672. Number-average molecular weight, M_n, is measured by size exclusion chromatography. A hydrocarbon

polymer is a polymer having no more than 5 wt% of elements other than hydrogen and carbon, preferably no more than 3 wt%, preferably no more than 1 wt%, percentages based on dry weight of the entire polymer.

The van Krevelen solubility parameter is described by Bicerano (Prediction of Polymer Properties, 3rd edition, Marcel Dekker, New York, 2002, Chapter 5) and tabulated in Table 5.2 ("δ_2") of the same book for a number of commercially relevant polymers. For an arbitrary polymer with known monomer chemical structure, van Krevelen-type solubility parameter can be computed using algorithms outlined in the same reference or using Materials Studio software, Synthia module (http://accelrys.com/products/collaborative-science/biovia-materials-studio/polymers-and-classical-simulation-software.html). For random copolymers, the copolymer solubility parameter can be calculated as weight-average of the solubility parameters of its comonomers.

Critical molecular weight, Mc, is calculated as described by Bicerano (Prediction of Polymer Properties, 3-rd edition, Marcel Dekker, New York, 2002, Chapters 11 and 13). For example, for polystyrene (PS), Mc = 30 kg/mol, for poly(methylmethacrylate) (PMMA), Mc = 18 kg/mol, etc. For an arbitrary polymer with known monomer chemical structure, critical molecular weight can be computed using algorithms outlined in the same reference or using Materials Studio software, Synthia module (http://accelrys.com/products/collaborative-science/biovia-materials-studio/polymers-and-classical-simulation-software.html).

In one preferred embodiment of the invention, a polymer composite made using the resin of this invention is part of a multilayer assembly which also comprises an outer layer on each side of the polymer composite. Preferably, the outer layer is an oxygen barrier which also inhibits passage of moisture. Preferably, the outer layer comprises a polymer film, preferably one comprising polyethylene terephthalate (PET), polyaryletherketones, polyimides, polyolefins, polycarbonate,

polymethyl methacrylate (PMMA), polystyrene, or a combination thereof. Preferably, the outer layer further comprises oxides or nitrides, preferably silicon oxides, titanium dioxide, aluminum oxide, silicon nitrides or a combination thereof. Preferably the oxides or nitrides are coated on the surface of the polymer film facing the QD layer. Preferably, each outer layer comprises a polymer film having a thickness from 25 to 150 microns (preferably 50 to 100 microns) and an oxide/nitride layer having a thickness from 10 to 100 nm (preferably 30 to 70 nm). In some preferred embodiments of the invention, the outer layer comprises at least two polymer film layers and/or at least two oxide/nitride layers; different layers may be of differing composition. Preferably, the outer layers have a very low oxygen transmission rate (OTR, $< 10^{-1}$ cc/m^2/day) and low water vapor transmission rate (WVTR, $< 10^{-2}$ g/m^2/day). Preferably, the polymer film in the outer layers has a Tg from 60 to 200 °C; preferably at least 90 °C, preferably at least 100 °C.

Preferably, the thickness of the polymer composite of this invention is from 10 to 500 microns, preferably at least 20 microns, preferably at least 30 microns, preferably at least 40 microns; preferably no greater than 400 microns, preferably no greater than 300 microns, preferably no greater than 200 microns, preferably no greater than 150 microns. Preferably, the thickness of each outer layer is from 20 to 100 microns, preferably from 25 to 75 microns

Preferably, the polymer composite of this invention is prepared by free radical polymerization of the resin prepared by mixing monomers, QD and other optional additives. Preferably, the resin is coated on a first outer layer prior to curing by typical methods, e.g., spin coating, slot die coating, gravure, ink jet and spray coating. Preferably, curing is initiated by exposing the resin to ultraviolet light or heat, preferably ultraviolet light, preferably in the UVA range.

Preferably, R^2 is a C_7-C_{17} aliphatic polycyclic substituent, preferably R^2 is a C_8-C_{15} aliphatic polycyclic substituent. Preferably, R^2 is a bridged polycyclic substituent; preferably a bicyclic,

tricyclic or tetracyclic substituent; preferably a bicyclic or tricyclic substituent. Preferably, R^2 is a saturated aliphatic substituent. Preferred structures for R^2 include, e.g., adamantanes, bicyclo[2,2,1]alkanes, bicyclo[2,2,2]alkanes, bicyclo[2,1,1]alkanes and tricyclodecanes (e.g., tricyclo[5,2,1,0^{26}]decane); these structures may be substituted with alkyl, alkoxy groups, hydroxy groups or (meth)acrylate esters (i.e., the compound of formula (I) may have at least two (meth)acrylate ester substituents; preferably no more than two); preferably alkyl and alkoxy groups have from one to six carbon atoms, preferably one to four. Tricyclodecanes and bicyclo[2,2,1]alkanes are especially preferred, particularly tricyclo[5,2,1,0^{26}]decane, dimethanol dimethacrylate and isobornyl acrylate. More than one compound of formula (I) may be present in the resin. Preferably, the resin comprises a compound of formula (I) having one (meth)acrylate ester substituent and a compound of formula (I) having two (meth)acrylate ester substituents; preferably in a weight ratio from 100:1 to 1:20, respectively; preferably 10:1 to 1:15.

Preferably, the polymer resin comprises from 70 to 95 wt% of the compound(s) of formula (I); preferably at least 73 wt%, preferably at least 76 wt%, preferably at least 79 wt%; preferably no more than 93 wt%, preferably no more than 91 wt%, preferably no more than 89 wt%.

Preferably, the polymer resin of this invention comprises from 0.01 to 5 wt% of quantum dots, preferably at least 0.03 wt%, preferably at least 0.05 wt%; preferably no more than 4 wt%, preferably no more than 3 wt%, preferably no more than 2 wt%. Preferably, quantum dots comprise CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, HgS, HgSe, HgTe, GaN, GaP, GaAs, InP, InAs or a combination thereof.

Preferably, ligands surrounding the inorganic part of quantum dots have non-polar components. Preferred ligands include, for example, trioctyl phosphine oxide, dodecanethiol and fatty acid salts (e.g., stearate salts, oleic acid salts).

Preferably, the block or graft copolymer is a hydrocarbon polymer. The block or graft polymer is added to the polymer resin as a rheology modifier, i.e., a thickener. Preferably, the block or graft polymer comprises at least 15 wt% styrene, preferably at least 20 wt%, preferably at least 25 wt%; preferably no more than 90 wt%, preferably no more than 80 wt%, preferably no more than 70 wt%, preferably no more than 60 wt%, preferably no more than 50 wt%, preferably no more than 45 wt%. Preferably, the block or graft polymer comprises at least 10 wt% of a non-styrene block, preferably at least 20 wt%, preferably at least 30 wt%, preferably at least 40 wt%, preferably at least 50 wt%, preferably at least 55 wt%; preferably no more than 85 wt%, preferably no more than 80 wt%, preferably no more than 75 wt%, preferably no more than 60 wt%, preferably no more than 50 wt%, preferably no more than 45 wt%. Preferably, the non-styrene monomers in the copolymer (non-styrene block) are alkenes, dienes, (meth)acrylates, siloxanes, or combinations thereof; preferably alkenes and/or dienes. Preferably, the non-styrene in the copolymer comprises polymerized units of C_2-C_8 alkenes and/or dienes, preferably C_2-C_5 alkenes and/or dienes. Preferably, the block or graft polymer is a block copolymer. Preferably, the C_2-C_8 alkenes and/or dienes are selected from ethylene, propylene, butylene, isoprene and butadiene. Preferably, M_n of the block or graft polymer is at least 60,000, preferably at least 70,000, preferably at least 80,000; preferably no more than 350,000, preferably no more than 300,000, preferably no more than 250,000.

Preferably, the non-styrene block has a van Krevelen solubility parameter less than 17.2 $(J/cm^3)^{1/2}$, preferably less than 17, preferably less than 16.5; preferably at least 15.5.

Preferably, a homopolymer or random copolymer with M_n greater than polymer critical molecular weight, M_c has a van Krevelen solubility parameter no greater than 19.5 $(J/cm^3)^{1/2}$; preferably at least 17, preferably at least 17.5, preferably at least 18.0. Preferably, M_n is at least 1.5 times M_c, preferably at least twice; preferably no more than 20 times M_c, preferably no more than ten

times. Preferred polymers having M_n greater than M_c include, e.g., those comprising polymerized units of styrene, alkenes, dienes, (meth)acrylates, siloxanes, or combinations thereof. M_c for polystyrene is 30,000 kDa.

Other additives which may be incorporated into the polymer composite of this invention include UV stabilizers, antioxidants and scattering agents to improve light extraction.

Preferred forms for the polymer composite include, e.g., films, beads, strips, rods, cubes and plates. The polymer composite is useful in many applications, including, e.g., displays, lighting and medical applications. Preferred display applications include public information displays, signage, televisions, monitors, mobile phones, tablets, laptops, automotive dashboards and watches.

EXAMPLES

SAMPLE PREPARATION FOR EXAMPLES

A) Liquid sample preparation

All QD resin samples were prepared under inert environment. Styrene-based polymers were dissolved in isobornyl acrylate by mixing at 80 °C for ~ 30 min using magnetic stirring. After all components except quantum dots were loaded to a crimp vial, the vial is degassed and mixed for 3 to 5 minutes using a dual axis planetary mixer (Thinky ARE-310). Quantum dots were pre-dispersed in isobornyl acrylate, then mixed with the other components followed by rolling for 1 hr.

B) Film sample preparation

All samples were prepared by lamination of the resin formulations between two i-Component PET barrier films. Approximately 2 mL of resin was dispensed on the bottom film and the top has applied with a gap coating bar with gap setup based on desired film thickness. Samples were cured in a Fusion UV F300S curing system with UVA ~400mJ/cm^2. The films were then cut into approximately 0.2" square pieces for Quantum Yield Measurements and 1 x 1" square pieces for photo oxidation tests. Freestanding films were also prepared by coating of the resin formulations on glass, followed by curing in a FUSION UV SYSTEMS, INC (DRS-10/12 QNH) with UVA ~400mJ/cm^2. The free-standing films were then delaminated from glass and used for O_2 permeability testing using Mocon ox-tran model 2/21 with 3% O_2 and 97% N_2 at 23 °C.

C) Characterization

Viscosity was measured by Brookfield DV-II+ viscometer. Frequency sweep and steady state flow experiments of resins were performed using a AR G2 rheometer at 20 °C. Both liquid and film photoluminescent Quantum Yield (PLQY), peak emission wavelength (PWL) and full-width half-max of the emission peak (FWHM) were measured with a Hamamatsu C9920-02G integrating sphere. Film thicknesses were determined by measurement of the cured films with a micrometer and then subtracting out the barrier film thickness. Edge ingress was determined by image analysis of 1"x1" samples aged on a bare backlight unit. Number average molecular weight (M_n) and polydispersity (PDI) of polymers were determined using a size exclusion chromatography equipped with a mixed A PLgel 20

um X 300 mm X 7.5 mm (X2 + guard) column with stabilized tetrahydrofuran at 1.0 mL/min @ 35 °C and a refractive index detector (against polystyrene standards).

D) Chemical composition description:

Polymer rheology modifier	CAS number	Chemistry	Styrene content	η in 25 wt% solution at 25 °C (Pa·s)*	Melt index at 230 °C, 5 kg, g/10 min*	Mn (kDa)	PDI	Van Krevelen Solubility Parameter of Non-Styrene Block, $(J/cm^3)^{1/2}$
Polystyrene	9003-53-6	Styrene homo	100%			139	2.85	
KRATON A1535	66070-58-4	SEBS triblock	56-60%		<1	244	1.41	15.9
KRATON G1701	68648-89-5	SEP diblock	35-39%	>50	1	149	1.18	16.4
KRATON G1652	66070-58-4	SEBS triblock	28-30%	1.8	6	85	1.19	15.9
KRATON G1650M	66070-58-4	SEBS triblock	28.8-31.6 w%	1100 – 1900 (20 w%)	<1	101		15.9
KRATON G1702	68648-89-5	SEP diblock	26-29%	50	<1	208	1.21	16.4
KRATON G1642	66070-58-4	SEBS triblock	19-23%	1.1-1.6	<1 (2.16 kg)	138	1.16	15.9
KRATON G1645	66070-58-4	SEBS triblock	12-14%		2-4.5 (2.16 kg)	186	1.32	15.9
KRATON G1750	127883-08-3	(EP)n star	0%	8.7	8 (200 °C)	489	1.26	

* Data from KRATON

SEBS: styrene-ethylene/butylene-styrene; SEP: styrene-ethylene/propylene;EP: ethylene/propylene

Chemical name	Description	CAS #
AEROSIL R104	A hydrophobic fumed silica after treated with (Octamethylcyclotetrasiloxane)	68583-49-3
AEROSIL R106	A hydrophobic fumed silica after treated with (Octamethylcyclotetrasiloxane)	68583-49-3
AEROSIL R974	A hydrophobic fumed silica after treated with Dimethyldichlorosilane	68611-44-9
AEROSIL R812S	A hydrophobic fumed silica after treated with hexamethyldisilazane	68909-20-6
CABOSIL TS720	A medium surface area fumed silica which has been surface modified with polydimethylsiloxane	67762-90-7
CABOSIL TS530	A treated, high-purity silica that has been treated with hexamethyldisilazane.	68909-20-6

EXAMPLE 1 (1001 formulation): **Comparison of fumed silica to KRATON block copolymer (styrene-ethylene/butylene-styrene triblock copolymer (SEBS))**

The KRATON block copolymer showed higher viscosity enhancement of the acrylic monomer than the inorganic fume silica. Both the KRATON block copolymer and some of the inorganic fumes silica showed compatibility with QD.

Formulation	Isobornyl acrylate + Additive (6wt%)	Viscosity (cP at 25 °C)
A1	none	8
B1	AEROSIL R104	37.3
C1	AEROSIL R106	60.6
D1	AEROSIL R974	96
E1	AEROSIL R812S	69
F1	CABOSIL TS720	64.8
G1	CABOSIL TS530	31.5
H1	KRATON G1652	145

Formulation	Isobornyl acrylate + Additive (2 wt%) + Nanoco CFQD™ quantum dot (0.175 wt%)	Quantum yield (%)
A2	none	68.1
B2	AEROSIL R104	68.8
C2	AEROSIL R106	65.7
D2	AEROSIL R974	68.3
E2	AEROSIL R812S	67.7
F2	CABOSIL TS720	70.4
G2	CABOSIL TS530	68.9
H2	KRATON G1652	69.4

EXAMPLE 2 (1031 formulation)

Comparison of KRATON to lower MW acrylate oligomers

KRATON G1652 showed higher compatibility with QDs (higher QY, lower peak wavelength, and FWHM) than the lower MW acrylate oligomers tested.

Component\formulation	A	B	C	D	E	F
Nanoco CFQD™ quantum dot	0.3	0.3	0.3	0.3	0.3	0.3
Isobornyl acrylate	55.2	55.2	55.2	59.2	59.2	77.2
Tricyclodecane dimethanol diacrylate	10	10	10	10	10	10
IRGACURE I-819	1.5	1.5	1.5	1.5	1.5	1.5
KRATON G1652 copolymer	4.5	4.5	4.5	4.5	4.5	7.5
CN9010 urethane acrylate oligomer	20	20	20	20	20	
BR-641D urethane acrylate oligomer	5				1	
CN-9014 urethane acrylate oligomer		5				
CN-309 acrylate oligomer			5			
CD9055 acrylate additive				1		
ZOCO 101 powder	2	2	2	2	2	2
TINUVIN 123	1.5	1.5	1.5	1.5	1.5	1.5

	Film thickness (um)	Film QY (%)	Peak wavelength (nm)	Full width half maximum (nm)
Formulation A	31.33	46.5	645.6	63.6
Formulation B	33.67	47.9	644.1	63.9
Formulation C	34.00	50.6	637.7	62.1
Formulation D	27.00	43.6	637.4	59.3
Formulation E	30.00	46.7	640.6	63.7
Formulation F	26.67	50.9	636.4	55.7

EXAMPLE 3 (1104 formulation)

Comparison of two KRATON block copolymers with different MW

The KRATON SEBS block copolymer, G1650, with a similar styrene composition but a higher MW (also indicated by solution viscosity in toluene and melt index) showed a higher viscosity enhancement of the acrylate-based QD resins

Thickener	Styrene content	Mn (kDa)	Solution viscosity in toluene @25 °C (cP)	Melt Index, 230 °C, 5 kg (gms/10
KRATON G1652M	29.0 – 30.8 w%	85	400 – 525 (20 w%)	5
KRATON G1650M	28.8-31.6 w%	101	1100 – 1900 (20 w%)	<1

Component\formulation	A	B	C	D	E	F	G	H	I
Isobornyl acrylate	62	63	65	67	69	62	63	66	69
Tricyclodecane dimethanol diacrylate	24	24	24	24	24	24	24	24	24
Irgacure I-819	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
KRATON G1650 copolymer	9	8	6	4	2				
KRATON G1652 copolymer						9	8	5	2
Zoco 101 powder	2	2	2	2	2	2	2	2	2
Tinuvin 123	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

	Viscosity (cP at 25 °C)
Formulation A	4820
Formulation B	1173
Formulation C	236.7
Formulation D	101
Formulation E	38.5
Formulation F	500
Formulation G	350
Formulation H	146
Formulation I	39.4

EXAMPLE 4 (0421 formulation)

Comparison of different KRATON polymers and a styrene homopolymer mixed with a single monomer

KRATON block copolymers are generally compatible with QDs in IBOA as shown by PLQY, PLmax, and FWHM.

	Isobornyl acrylate (94.825 wt%) + Additive (5 wt%) + Nanoco CFQD™ quantum dot (0.175 wt%)	Styrene content of additive	PLQY (%)	Peak wavelength (nm)	Full width half maximum (nm)
A1	None	N/A	75.3	639.89	57.41
B1	Polystyrene	100%	76.3	639.89	57.78
C1	KRATON A1535	56-60%	75.8	639.89	57.53
D1	KRATON G1701	35-39%	75	640.64	57.59
E1	KRATON G1652	28-30%	77.5	638.41	57.99
F1	KRATON G1702	26-29%	73.4	639.89	57.81
G1	KRATON G1642	19-23%	73.8	639.15	58.51
H1	KRATON G1645	12-14%	74.9	639.89	57.79
I1	KRATON G1750	0%	76.1	642.12	57.26

Comparison of different KRATON polymers and a styrene homopolymer mixed with a mixture of a monomer and a crosslinker and a single crosslinker

KRATON block copolymers with a styrene composition higher than 12% are soluble in the IBOA:SR-833 (1:1) mixture, and those with a styrene composition higher than 26% are soluble in SR-833.

	Additive (5 wt%) + Nanoco CFQD™ quantum dot (0.175 wt%)	Chemistry	Styrene content of additive	Viscosity (cP at 20 °C)	
				Isobornyl acrylate (47.41%) + tricyclodecane dimethanol diacrylate (47.41%)	Tricyclodecane dimethanol diacrylate (94.82%)
A2	None	N/A	N/A	23	146
B2	Polystyrene	Styrene homo	100%	441	2940
C2	KRATON A1535	SEBS triblock	56-60%	658	Gel (high viscosity)
D2	KRATON G1701	SEP diblock	35-39%	96	411
E2	KRATON G1652	SEBS triblock	28-30%	62	397
F2	KRATON G1702	SEP diblock	26-29%	76.5	415
G2	KRATON G1642	SEBS triblock	19-23%	63	Insoluble
H2	KRATON G1645	SEBS triblock	12-14%	68	Insoluble
I2	KRATON G1750	(EP)n star	0%	Insoluble	Insoluble

EXAMPLE 5 (0528 formulation)

Comparison of two different KRATON block copolymers in full resin/film formulation

Replacement of KRATON G1652 with KRATON A1535 with a higher MW and higher styrene content resulted in a lower loading of rheology modifier to obtain comparable resin viscosity, comparable PLQY, and a lower edge ingress of QD films aged at 60 °C and 90 RH%.

Rhoelogy modifier	Styrene content	Mn (kDa)	Melt index at 230 °C, 5 kg, g/10 min
KRATON A1535	56-60%	244	<1
KRATON G1652	28-30%	85	6

	Formulation A	Formulation B
Nanoco CFQD™ quantum dot	0.2	0.2
Isobornyl acrylate	51.3	43.8
Tricyclodecane dimethanol diacrylate	40	40
Irgacure I-819	1.5	1.5
KRATON A1535 copolymer	3.5	0
KRATON G1652 copolymer	0	11
Finex 30S-LP2 zinc oxide powder	2	2
Tinuvin 123	1.5	1.5

	Viscosity at 25 °C (cP)	PLQY
Formulation A	877	53.2
Formulation B	918	53.6

Edge ingress after 60 °C, 90% humidity chamber accelerated testing

	72hrs	168hrs	336hrs	504hrs
Formulation A	0.62	1.27	1.98	2.84
Formulation B	0.93	1.80	2.77	3.89

EXAMPLE 6

Comparison of two different KRATON block copolymers in films (barrier property)

Replacement of KRATON G1652 with KRATON A1535 with a higher MW and higher styrene content resulted in a better O_2 barrier of films which is consistent with the lower edge ingress of QD films at accelerated testing.

Materials	Formulation A	Formulation B
Isobornyl acrylate	53.0	57.0
Tricyclodecane dimethanol diacrylate	30.0	32.3
KRATON A1535	3.2	0
KRATON G1652	0	9.5
Finex 30S LP2	6.0	6.0
I-819	1.5	1.5

	O_2 permeability at 50% RH, 76 cmHg, 23 °C (3% O_2 & 97% N_2), cc/m/day/atm)
Formulation A2	0.047
Formulation B2	0.11

EXAMPLE 7

Comparison of two different KRATON block copolymers in resins (rheological property)

Materials	Formulation A	Formulation B
Isobornyl acrylate	51.4	47.6
Tricyclodecane dimethanol diacrylate	45.6	42.4
KRATON A1535	3	0
KRATON G1652	0	10

The mixture of isobornyl acrylate and tricyclodecane dimethanol diacrylate with 3% KRATON A1535 exhibits rheological simplicity at 20 °C (i.e., it obeys the "Cox-Merz rule" that the complex viscosity as a

function of frequency and the shear viscosity as a function of shear rate overlap) indicating a simple polymeric fluid (The structure and rheology of complex fluids, Oxford, New York, 1999, Chapter 1), while that with 10% KRATON G1652 does not. A simple polymeric fluid with rheological simplicity is preferred for viscosity control of resins.

3% KRATON A1535

Frequency sweep		Strain rate sweep-1		Strain rate sweep-2	
Frequency (rad/s)	Complex viscosity (Pa·s)	Rate (1/s)	Viscosity (Pa·s)	Rate (1/s)	Viscosity (Pa·s)
63.09	0.2147	0.1892	0.2108	0.1893	0.2242
39.81	0.2102	0.2383	0.2164	0.2383	0.2219
25.12	0.2081	0.3	0.2165	0.3	0.2177
15.85	0.2069	0.3776	0.2145	0.3777	0.2116
10	0.2069	0.4754	0.2169	0.4754	0.2102
6.309	0.2069	0.5986	0.2161	0.5986	0.2069
3.981	0.2073	0.7535	0.2116	0.7536	0.206
2.512	0.2071	0.9487	0.2083	0.9486	0.2058
1.585	0.2069	1.194	0.2071	1.194	0.2062
1	0.2069	1.504	0.2067	1.504	0.2059
0.6309	0.2068	1.893	0.2061	1.893	0.2045
0.3981	0.2068	2.383	0.2056	2.383	0.2059
0.2512	0.2068	3	0.2065	3	0.205
0.1585	0.2065	3.777	0.2057	3.777	0.205
0.1	0.2069	4.755	0.2056	4.755	0.2051
0.06309	0.2068	5.986	0.2055	5.986	0.2048
0.03981	0.2068	7.536	0.2054	7.536	0.2048
0.02512	0.2065	9.487	0.2054	9.487	0.2048
		11.94	0.2054	11.94	0.2048
		15.04	0.2055	15.04	0.2049
		18.93	0.2055	18.93	0.2049
		23.83	0.2056	23.83	0.2049
		30	0.2055	30	0.2049
		37.77	0.2055	37.77	0.2049
		47.55	0.2055	47.55	0.205
		59.86	0.2055	59.86	0.2051
		75.36	0.2055	75.36	0.2051
		94.87	0.2055	94.87	0.2051
		119.4	0.2055	119.4	0.205
		150.4	0.2054	150.4	0.2049
		189.3	0.2053	189.3	0.2048
		238.3	0.2051	238.3	0.2046
		300	0.2048	300	0.2044
		377.7	0.2046	377.7	0.2042
		475.5	0.2043	475.5	0.2038
		598.6	0.2037	598.6	0.2033
		600	0.2034	600	0.203

10% KRATON G1652

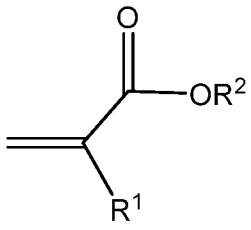
Frequency sweep		Strain rate sweep-1		Strain rate sweep-2	
Frequency (rad/s)	Complex viscosity (Pa·s)	Rate (1/s)	Viscosity (Pa·s)	Rate (1/s)	Viscosity (Pa·s)
63.09	0.3421	0.1892	0.2713	0.1894	0.306
39.81	0.3443	0.2383	0.2661	0.2383	0.2925
25.12	0.3415	0.3	0.2583	0.3	0.2892
15.85	0.3373	0.3777	0.2534	0.3777	0.274
10	0.3395	0.4755	0.2546	0.4755	0.2574
6.309	0.3389	0.5985	0.2453	0.5986	0.2359
3.981	0.3389	0.7537	0.2317	0.7536	0.2278
2.512	0.3392	0.9488	0.2244	0.9487	0.217
1.585	0.3422	1.194	0.2169	1.194	0.2102
1	0.3421	1.504	0.2085	1.504	0.2057
0.6309	0.3397	1.893	0.2074	1.893	0.2101
0.3981	0.3396	2.383	0.2055	2.383	0.2077
0.2512	0.3388	3	0.2042	3	0.204
0.1585	0.3355	3.777	0.2045	3.777	0.2065
0.1	0.3415	4.755	0.2038	4.755	0.2032
0.06309	0.3478	5.986	0.2038	5.986	0.2039
0.03981	0.3364	7.536	0.2037	7.536	0.2041
0.02512	0.3436	9.487	0.2035	9.487	0.2035
		11.94	0.2035	11.94	0.2034
		15.04	0.2035	15.04	0.2035
		18.93	0.2034	18.93	0.2034
		23.83	0.2033	23.83	0.2034
		30	0.2031	30	0.2032
		37.77	0.2028	37.77	0.2029
		47.55	0.2025	47.55	0.2026
		59.86	0.2019	59.86	0.202
		75.36	0.2011	75.36	0.2012
		94.87	0.1999	94.87	0.2
		119.4	0.1982	119.4	0.1983
		150.4	0.1959	150.4	0.1961
		189.3	0.1931	189.3	0.1933
		238.3	0.1892	238.3	0.1893
		300	0.1844	300	0.1846
		377.7	0.1789	377.7	0.1791
		475.5	0.1729	475.5	0.173
		598.6	0.1663	598.6	0.1664
		600	0.1663	600	0.1664

CLAIMS:

1. A polymer resin comprising:

(a) quantum dots,

(b) a compound of formula (I)



(I)

wherein R^1 is hydrogen or methyl and R^2 is a C_6-C_{20} aliphatic polycyclic substituent, and

(c) a block or graft copolymer having M_n from 50,000 to 400,000 and comprising from 10 to 100 wt% polymerized units of styrene and from 0 to 90 wt% of a non-styrene block; wherein the non-styrene block has a van Krevelen solubility parameter from 15.0 to 17.5 $(J/cm^3)^{1/2}$.

2. The polymer resin of claim 1 in which R^2 is a C_7-C_{17} bridged polycyclic substituent.

3. The polymer resin of claim 2 in which the block or graft copolymer is a hydrocarbon polymer which comprises at least 20 wt% polymerized units of styrene and polymerized units of alkenes, dienes or a combination thereof.

4. The polymer resin of claim 3 comprising from 70 to 95 wt% of the compound of formula (I), from 1 to 20 wt% of the block or graft copolymer, 0.01 to 5 wt% of quantum dots and from 0.3 to 5 wt% curing agents.

5. The polymer resin of claim 4 in which R^2 has a bicyclo[2,2,1]alkane or tricyclodecane ring system.

6. The polymer resin of claim 5 in which the block or graft copolymer has M_n from 60,000 to 300,000.

7. The polymer resin of claim 6 in which the block or graft copolymer has at least 20% polymerized units of styrene and no more than 80 wt% polymerized units of monomers selected from the group consisting of C_2-C_8 alkenes and C_2-C_8 dienes.

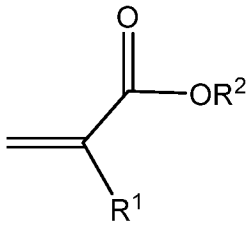
8. The polymer resin of claim 7 in which the C_2-C_8 alkenes and dienes are selected from the group consisting of ethylene, propylene, butylene, isoprene and butadiene.

9. The polymer resin of claim 8 in which the hydrocarbon polymer has M_n from 70,000 to 250,000.

10. A polymer resin comprising:

(a) quantum dots,

(b) a compound of formula (I)



(I)

and

(c) a homopolymer or random copolymer with M_n greater than polymer critical molecular weight, M_c and with a van Krevelen solubility parameter from 16.5 to 20.0 $(J/cm^3)^{1/2}$.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/032311

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/02 C08F287/00 C08F292/00 B82Y40/00 B82Y20/00
ADD.

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)
C09K C08F C08K B82Y

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 practicable, 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,P	EP 3 070 109 A1 (ROHM & HAAS ELECT MATERIALS [US]; ROHM & HAAS ELECT MATERIALS [KR]; DO) 21 September 2016 (2016-09-21) examples	1-10
X	JP 2015 028139 A (JSR CORP) 12 February 2015 (2015-02-12) example 5	1-10
X	US 2016/005932 A1 (LEE JEONG HEE [KR] ET AL) 7 January 2016 (2016-01-07) claims; examples	1-9

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

☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 July 2017	31/07/2017

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1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2017/032311

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