

I. ADDITIVES

A. Ink Dispersants

a. Hyperbranched esters

Title: Method for the Production of Hyperbranched Water-Soluble Polyesters

Author: Jean-Francois Stumbe et al.

Assignee: BASF Aktiengesellschaft (Ludwigshafen, DE)

U.S. Patent Application: 20070293634 (December 20, 2007)

Material Patentability: Medium

Anticipated Issuing Data: Mid-2010

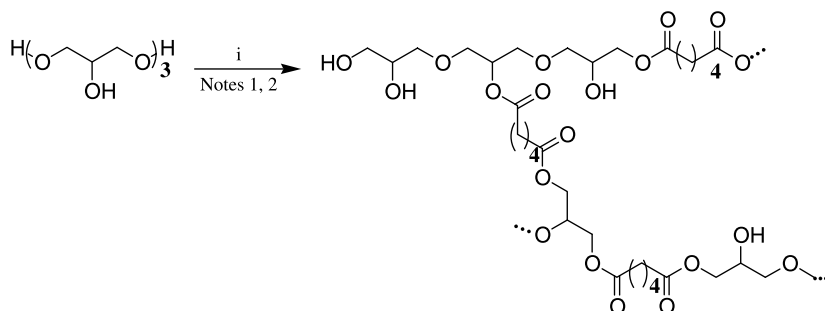
Research Focus: Preparation of nondentrimeric hyperbranched polyesters that are water-soluble or water-dispersible from dicarboxylic acids and polyether polyols.

Originality: Although dentrimeric hyperbranched polyesters have been reported in the patent literature, the agents in this application are novel.

Application: Ink dispersant

Observations: This group has developed a single-step method for preparing ester-grafted hyperbranched polymers. These materials are not dentrimeric analogs, however. Although hyperbranched ureas, carbonates, and polyesters have previously been prepared, in this application water-dispersible or soluble linear polyesters containing pendant alcohols having acid numbers from 9 to 117 were produced. The single-step method for preparing these agents entailed condensing the oligomeric glycerol with selected dicarboxylic acids in the presence of either enzyme catalyst Novozym[®]-435 or acid catalyst Fascat[®].

REACTION



i. Adipic acid, Novozym[®]-435, toluene

1. Preparation of linear hyperbranched polyester using Novozym[®]-435

Adipic acid (0.60 mol) and an oligomeric glycerol having a repeat unit of three, PG-3 (0.44 mol), were dissolved at 70°C in 80 ml of toluene and then treated with enzyme catalyst Novozym[®]-435 (14 g). The mixture was polymerized for 9 hours at 70°C at 300 mbar to remove water formed during the reaction. The mixture was then concentrated and the product isolated as a honey-like, viscous, colorless to slightly yellowish polyester. The polyester was readily soluble in water.

DERIVATIVES

A summary of water-dispersible or water-soluble linear polyesters prepared in this application containing hyperbranched alcohols and having acid numbers from 9 to 117 is provided in Table 1. Ester reactions were performed using either enzyme catalyst Novozym[®]-435 or acid catalyst Fascat[®].

TABLE 1. Physical Properties of Selected Water-Soluble or Water-Dispersible Polyesters Prepared Using Enzyme Catalyst Novozym[®]-435 or Acid Catalyst Fascat[®]

Entry	Reagents	Acid Number	M_w (Da)	M_n (Da)	Water Solubility
2	Adipic acid, PG-3, Fascat [®]	117	2220	1450	Very good
3	Adipic acid, TMPEO ^a , Novozym [®] -435	9	8000	24,000	Good
4	Adipic acid, TMPEO, Fascat [®]	50	2340	5860	Good
7	Adipic acid, PG-3, stearic acid	104	2300	3330	Dispersable
10	Phthalic anhydride, PG-3, Fascat [®]	n.d.	n.d.	n.d.	Dispersable

^aEthoxylated trishydroxymethylpropane.

NOTES

1. Additional hyperbranched polyesters based on either di-, tri-, or polycarboxylic acids or di-, tri-, or polyols are described by Bruchman et al. (1). For example, the reaction product of adipic acid, pentaerythritol and 1,4-cyclohexanedi-methanol, was prepared using di-*n*-butyltin oxide as catalyst and then post-reacted with selected diisocyanates and used as a paint additive.
2. By reacting hyperbranched polyesters with diethyl carbonate, Eipper et al. (2) prepared impact-modifying hyperbranched polyester–polycarbonates resins.
3. In an earlier investigation by the authors (3) hyperbranched polyamides were prepared by condensing adipic acid with polyamines at 150°C.
4. In related investigations hyperbranched polyureas and polycarbonates were prepared by Bruchmann et al. (4,5), respectively, while hyperbranched analogs containing ethylenically unsaturated substituents were prepared by the authors (6).

References

1. B. Bruchmann et al., U.S. Patent Application 20070213501 (September 13, 2007).
2. A. Eipper et al., U.S. Patent Application 20070244227 (October 18, 2007).
3. J.-F. Stumbe et al., U.S. Patent Application 20070191586 (August 16, 2007).
4. B. Bruchmann et al., U.S. Patent Application 20070083030 (April 12, 2007).
5. B. Bruchmann et al., U.S. Patent Application 20060093885 (February 15, 2007).
6. J.-F. Stumbe et al., U.S. Patent Application 20070027269 (February 1, 2007).

B. Ink Dispersants and Colorants

a. Azo-benzothiazole polyethers

Title: Aqueous Inks Containing Colored Polymers

Author: Jeffery H. Banning et al.

Assignee: Xerox Corporation (Rochester, NY)

Patent Application: 20060074142 (April 6, 2006)

Material Patentability: High

Anticipated Issuing Date: Mid-2008

Research Focus: Preparation of water-soluble organic ink colorants by incorporating chromophores onto oligomeric alkoxyethers.

Originality: Very versatile synthetic design for water-solubilizing ink colorants.

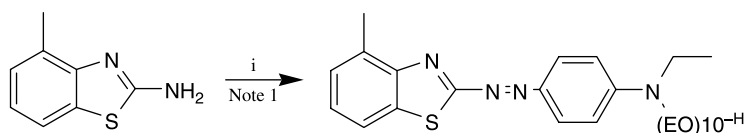
Application: Jet printing ink
Thermal ink jet process

Observations: Two separate methods were used to solubilize colorants in an aqueous medium:

- a. Graft incorporation of the colorant onto a homophilic polymer substrate
- b. Incorporation of oligomeric hydrophilic substituents directly into the colorants

The first method in this application, however, was limited to modifying alcohol-containing colorants onto polymers containing grafted succinic anhydride transesterification, and transaminated reactions were also reported. In the second method water-soluble colorants were prepared by azo coupling of colorants with alkoxyether functionalized aniline.

REACTION



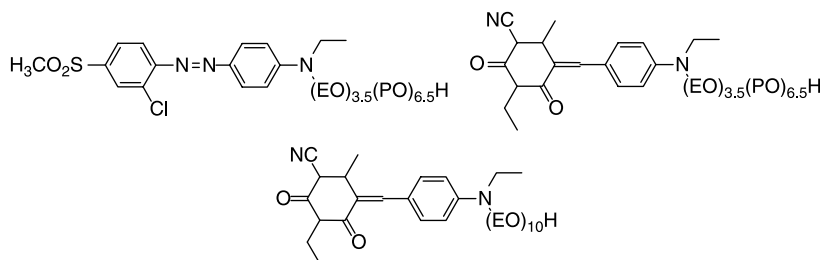
- i. Phosphoric acid, sulfuric acid, 2-ethylhexanol, 2-amino-4-methylbenzothiazole, nitrosyl sulfuric acid, sulfamic acid, POE(10)-*N*-ethyl aniline, urea, sodium hydroxide, CH₂Cl₂

EXPERIMENTAL

1. Preparation of water-soluble 4-methylbenzothiazole with alkoxyether functionalized aniline

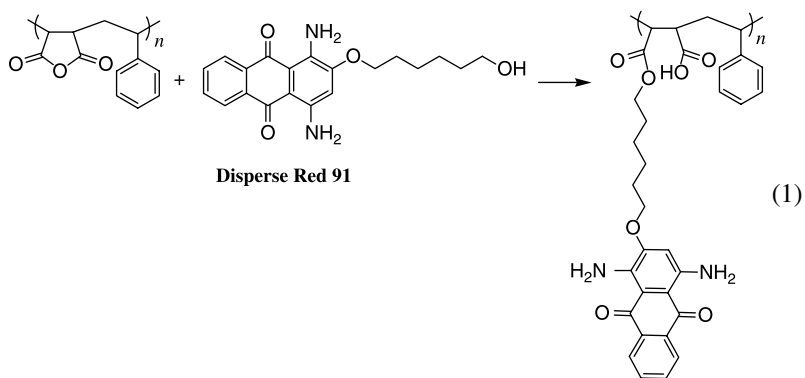
A vessel was charged with 85% H₃PO₄ (115 g), 95% H₂SO₄ (31 g), and 2 drops of 2-ethylhexanol. Stirring was then initiated and the kettle was placed in an ice/salt bath to cool the mixture to about 0°C. This mixture was then treated with 2-amino-4-methylbenzothiazole (10.2 g). A constant-pressure addition funnel was used to add nitrosyl sulfuric acid (21.7 g) dropwise over a period of about 1.5 hours and the mixture stirred an additional 90 minutes to ensure complete diazotization. Thereafter sulfamic acid (0.7 g) was added with stirring to neutralize any excess NO⁺. The diazo mixture was then slowly added over 45 minutes to a 1-liter beaker containing ice, POE(10)-*N*-ethyl aniline (36.0 g), 150 ml water, and 2.0 g of urea. The mixture was then stirred at 0°C for 2 hours followed by stirring at ambient temperature overnight. The diazo colorant was then neutralized to a pH of 7 using 50% aqueous NaOH while keeping the reaction temperature below 60°C. Following neutralization, the colorant was poured into a 1-liter separatory funnel and allowed to phase separate. The bottom water/salt layer was discarded, and the colored organic product layer was isolated and dissolved in CH₂Cl₂ and then passed through a small plug of silica gel to remove any polar impurities. The methylene chloride layer was concentrated yielding a viscous red liquid.

DERIVATIVES

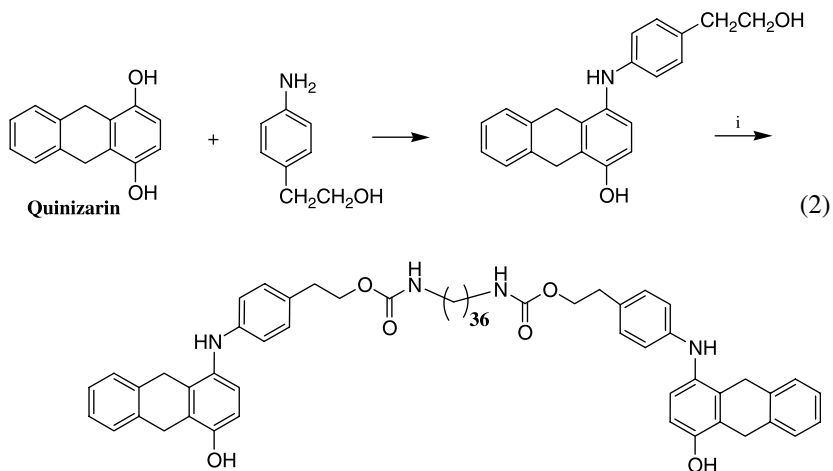


NOTES

1. An alternative method for solubilizing a colorant through chemical grafting onto a functional polymer as indicated in Eq. (1) was also described in this application.

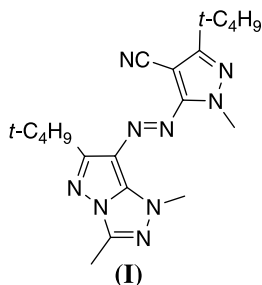


2. Additional colorant agents were previously prepared by the authors (1) and are described.
3. Beginning with quinizarin, Jaeger et al. (2) developed methods of making dimeric colorant agents as illustrated in Eq. (2).

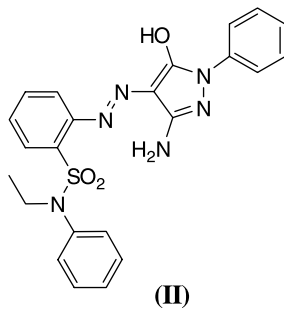


- i. 1,36-Hexatriacontane diisocyanate

4. An azo dye-colored composition, **(I)**, was prepared by Fujie et al. (3) in two synthetic steps and used as a heat-sensitive recording ink sheet.



5. A colorant containing a curable sulfonamide composition, **(II)**, was prepared by Araki (4) and used on a support as a color filter.



References

1. J.H. Banning et al., U.S. Patent Application 20070123701 (May 31, 2007) and U.S. Patent Application 20060264674 (November 23, 2006).
2. C.W. Jaeger et al., U.S. Patent Application 20060178458 (August 10, 2006).
3. Y. Fujie et al., U.S. Patent Application 20080012930 (January 17, 2008).
4. K. Araki, U.S. Patent Application 20080014536 (January 17, 2008).

C. Oil Dispersants

a. Polyacrylate amino succimides

Title: Alkyl Acrylate Copolymer VI Modifiers and Uses Thereof

Author: Sanjay Srinivansan et al.

Assignee: Afton Chemical Corporation (Richmond, VA)

Patent Application: 20080026964 (January 31, 2008)

Material Patentability: High

Anticipated Issuing Date: Mid-2010

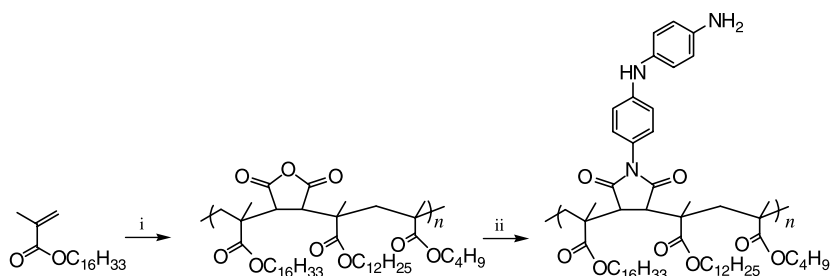
Research Focus: Preparation of polyacrylate viscosity improvers containing grafted *N*-phenyl-*p*-phenylenediamine as an antioxidant.

Originality: Departure from using oil viscosity improvers based on poly(ethylene-*co*-propylene)-*g*-succinic anhydride.

Application: Automotive oil viscosity improver

Observations: Most automotive oil viscosity improvers are based on shear stable poly(ethylene-*co*-propylene) having M_n 's < 100,000 Da. Poly(ethylene-*co*-propylene) multifunctional viscosity improvers are prepared by free radical grafting of maleic anhydride and then imidizing with *N*-phenyl-*p*-phenylenediamine. While polymethacrylate viscosity index improvers are known, attempts to prepare them having a desirable balance of antioxidantancy and high- and low-temperature viscometric shear stability have been elusive. This application has addressed that requirement.

REACTION



- i. Butyl methacrylate, lauryl methacrylate, maleic anhydride, lauryl mercaptan, 2,2'-azoisobutyronitrile
- ii. *N*-Phenyl-*p*-phenylenediamine, ethoxylated lauryl alcohol

EXPERIMENTAL

1. Preparation of anhydride

Butyl methacrylate, lauryl methacrylate, and cetyl methacrylate were combined with maleic anhydride, lauryl mercaptan, and process oil and then charged into a 2-liter reaction vessel equipped with two mixing impellers rotated at 300 rpm during the reaction. The mixture was preheated to 85°C and then treated with 2,2'-azoisobutyronitrile and heated for 4 hours at 85°C followed by 1 hour at 100°C. In some cases additional oil was added to make the product more easily pourable. Unreacted maleic anhydride and other low-molecular-weight products were removed by heating the reaction mass to 120°C while applying a vacuum. Reaction scoping results are provided in Table 1.

2. Preparation of imide

The step 1 product was dissolved in process oil at 135°C and then treated with a mixture of *N*-phenyl-*p*-phenylenediamine and ethoxylated lauryl alcohol and further heated to 160–170°C for 3 hours. The reaction mixture containing the multi-functionalized polymer reaction product was filtered where the nitrogen content was 0.36%.

REACTION SCOPING

TABLE 1. Scoping Reaction for Preparation of Step 1 Product^a

Entry	Reagents ^b						M_w (Da)	M_n (Da)
	AIBN (wt%)	LSH (wt%)	MA (wt%)	BMA (wt%)	LMA (wt%)	CMA (wt%)		
1	0.1	0.12	5.00	11.0	57.0	0.3	199,330	86,003
3	0.1	0.16	5.00	11.0	57.0	0.3	142,055	66,834
5	0.1	0.09	5.00	11.0	57.0	0.3	281,162	107,179
6	0.04	0.04	4.42	9.73	50.47	0.3	578,520	195,858

^a The viscosity index improver was prepared after reacting with *N*-phenyl-*p*-phenylenediamine.

^b AIBN = 2,2'-Azobisisobutyronitrile, BMA = butyl methacrylate, CMA = cetyl methacrylate, LMA = lauryl methacrylate, LSH = lauryl mercaptan, and MA = maleic anhydride.

TESTING

High-Frequency Reciprocating Rig

Film formation properties of lubricating fluids containing selected experimental VI improvers was determined using a high-frequency reciprocating rig (HFRR) according to the procedure outlined in SAE 2002-01-2793. Testing results are provided in Table 2.

TABLE 2. HFRR Testing Results Reflecting Film Formation Properties of Polymers in the Presence of Abrasive Contaminants^a

Carbon Black (%)	Comparative Example (%)	Imidized Entry 1 (%)
0	87	91
5	37	60
8	12	50

^aHigher results are preferred since it reflects a greater boundary film.

NOTES

1. In subsequent investigations by Loper et al. (1) and Mathur et al. (2) oil dispersant additives were prepared by reacting the step 1 product with triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, and bis-aminopropyl piperazine.
2. Vinci et al. (3) prepared automotive oil viscosity index improvers that consisted of copolymers of C₁₂-C₁₅ methacrylates with 2-ethylhexyl methacrylate and poly(ethylene-*co*-propylene) with 2-ethylhexyl methacrylate, then blended in 94.5 parts mineral oil.

3. Nanomaterials were used by Zhang et al. (4) as a replacement for polymer-based viscosity modifiers for automotive lubricants. Compared with traditional polymer-based viscosity modifiers, nanomaterials induce a more even viscosity increase across engine operating temperature ranges. In addition, nanomaterials provide a viscosity modifier that exhibits temporary shear loss that can contribute to fuel economy.

References

1. J.T. Loper et al., U.S. Patent Application 20080027181 (January 31, 2008).
2. N.C. Mathur et al., U.S. Patent Application 20080026972 (January 31, 2008).
3. J.N. Vinci et al., U.S. Patent Application 20080015131 (January 17, 2008).
4. Z. Zhang et al., U.S. Patent Application 20070293405 (December 20, 2007).

D. Oil Drilling Dispersants

a. Polymethacrylate betaines

Title: Zwitterionic Polymers Comprising Betaine-Type Units and Use of Zwitterionic Polymers in Drilling Fluids

Author: Katerina Karagianni et al.

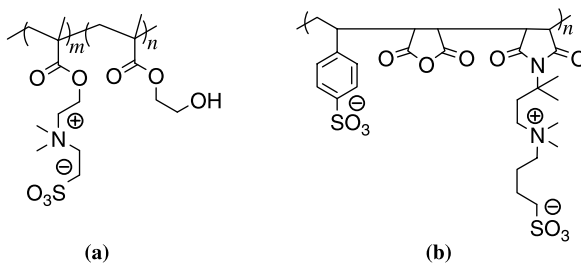
Assignee: Toyo Seikan Kaisha, Ltd. (Tokyo, JP)

Patent Application: 20080045420 (February 21, 2008)

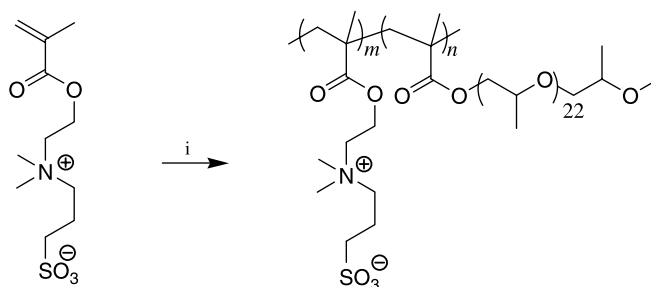
Material Patentability: Low

Anticipated Issuing Date: 2010

Observations: The current application addresses the need for mineral agent inhibitors that prevent the aggregation of argillaceous rocks and prevent the swelling of clays during subterranean drilling. While acrylamide copolymers containing sulfobetaines or phosphobetaines are effective in addressing this problem, pollution concerns limit their application. Although this application has limited novelty since both (a) *co*-methacrylates and (b) betainelike materials terpolymer have previously been prepared, the use of these materials as drilling dispersants is novel.



REACTION



- i. α -Methoxy- ω -methacrylate polyethylene glycol 1000, water, ethanol, ammonium persulfate

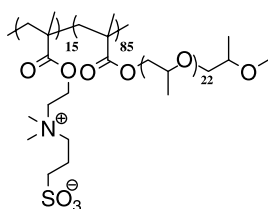
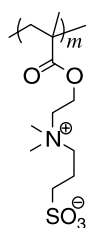
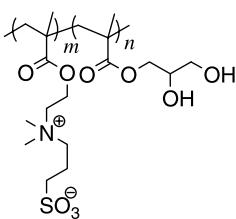
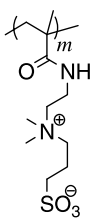
EXPERIMENTAL

1. Preparation of poly(sulfopropyl dimethyl ammonium methyl methacrylate-co- α -methoxy- ω -methacrylate-polyethylene glycol)

A reactor charged with sulfopropyl dimethyl ammonium methyl methacrylate (0.020 mol), α -methoxy- ω -methacrylate polyethylene glycol 1000 (0.009 mol), water (398 g), and ethanol (261.90 g) was heated to 78°C. The mixture was then simultaneously treated with ammonium persulfate (0.004 mol) dissolved in water (20 g) over 150 minutes, ammonium persulfate (2.5 g) dissolved in water (60 g) continuously over 120 minutes, sulfopropyl dimethyl ammonium methyl methacrylate (0.182 mol) over 120 minutes, and α -methoxy- ω -methacrylate polyethylene glycol (0.078 mol), and water (205.80 g). Thereafter the reaction was maintained at 70°C for 90 minutes and then cooled. The solution was then treated with water and ethanol removed by distillation. The product was isolated with a solids content of 27.3%, a pH of 2, a Brookfield viscosity of 36 mPa · s, and an M_w of 65,000 Da with an M_n of 8000 Da.

DERIVATIVES

TABLE 1. Selected Zwitterionic Polymers Containing Betaine-Type Units Used as Drilling Fluid Component

Entry	Repeat Unit	M_w (Da)	M_n (Da)	Brookfield Viscosity (mPa · s)
2		57,500	6500	31
4		30,000	4000	30
5		2,000,000	900,000	—
7		800,000	300,000	—

TESTING

A. Recovery Test on the Cuttings

Clay particles were used to simulate the cuttings having a size distribution between 2 and 4 mm. Sieved particles (30 g) were added to 350 ml of the test formulation containing the experimental agent. The flasks were placed in a rolling oven at 65°C for 16 hours and then cooled and the particles recovered on a 2-mm sieve. Excess experimental agent was removed using absorbant paper. The particles were then weighed and dried in an oven at 50°C until a stable weight was obtained. The particles were then reweighed and the percentage of moisture restoration calculated. High levels of restoration and low moisture contents are indicative of an inhibiting effect on clay swelling. Testing results are summarized in Table 2.

TABLE 2. Recovery Test and Extrusion Testing Results for Selected Experimental Agents^a

Entry	Dosage (%)	Moisture Content (%)	Moisture Restoration (%)	Pressure (bar)
4	1	29	99	26
4	3	33	94	35
2	1	28.7	101.4	36
Step 1 product	1	—	—	55
5	1	—	—	29
7	1	—	—	33

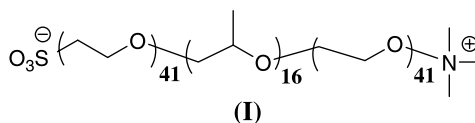
^aHigh pressures and moisture restoration with low moisture content are preferred.

B. Extrusion Test

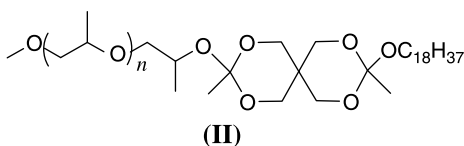
Hot rolling particles from the recovery test on the cuttings were used. Samples were extruded in a CT 15 compressometer device at a rate of 40 mm/min where the pressure necessary to extrude the particles was recorded. The harder the particles, the higher the pressure, the better the protection with regard to penetration of water, and the better the inhibiting effect on clay swelling. Testing results are provided in Table 2.

NOTES

1. Cleaning compositions comprising polyether ammonium polymers, **(I)**, were prepared by Schneiderman et al. (1) and used as a component in oil drilling compositions.



2. Oligomeric urea–formaldehyde resins prepared by Wright et al. (2) were as effective as surfactants in separating drill cuttings from oil drilling fluids.
3. Beckman et al. (3) prepared an oil drilling surfactant composition consisting of a resin blend of two 98% hydrolyzed polyvinyl alcohols where the viscosity of one of the resin components was at least 50% greater than the other.
4. Well drilling fluids having clay control properties were prepared by Hurd et al. (4) and consisted of the reaction product of tall oil and diethylenetriamine.
5. Orthoester derivatives (**II**), prepared by Funkhouser et al. (5) were effective as surfactants and used in oil drilling applications.



References

1. E. Schneiderman et al., U.S. Patent Application 20080045442 (February 21, 2008).
2. J.T. Wright et al., U.S. Patent Application 20080029460 (February 7, 2008) and U.S. Patent Application 20080017552 (January 24, 2008).
3. K.J. Beckman et al., U.S. Patent Application 20070284105 (December 13, 2007).
4. P.W. Hurd et al., U.S. Patent Application 20070167333 (July 19, 2007).
5. G.P. Funkhouser et al., U.S. Patent Application 20070066493 (March 22, 2007).

E. Fabric Additives

1. Antistatic Agents

a. Polypropylene oxide ammonium salts

Title: Polyoxyalkylene Ammonium Salts and Their Use as Antistatic Agents

Author: Patricia M. Savu et al.

Assignee: 3M Innovative Properties Company (St. Paul, MN)

Patent Application: 20080039654 (February 14, 2008)

Material Patentability: High

Anticipated Issuing Date: 2010

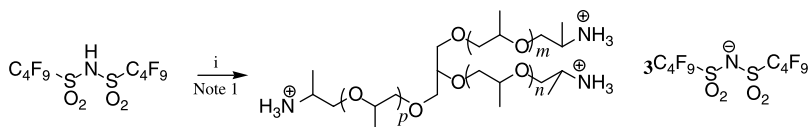
Research Focus: Preparation of biodegradable salts derived from the reaction product of polypropylene ether amines and bis(perfluorobutylsulfonyl)-imine for use as antistatic agents.

Originality: Two-year ongoing investigation.

Application: Antistatic agents for fabric and electronic devices

Observations: In fabric applications there exists a need for fluorinated antistatic agents that exhibit a balance between thermal stability, hydrophobicity, and low volatility. To address this problem antistatic agents consisting of polyether amine salts of bis(perfluorobutanesulfonylimide were prepared having low volatility, minimal corrosion characteristics, and biodegradability greater than 99%. Antistatic agents were prepared in a single step in yields exceeding 90% by condensing polyether amines with bis(perfluorobutylsulfonyl)-imine. Bis(perfluorobutylsulfonyl)imide was prepared by reacting perfluorobutylsulfonyl fluoride with triethylamine in the presence of ammonia followed by treatment with sulfuric acid.

REACTION



i. Jeffamine[®] XJT-500, water

EXPERIMENTAL

1. Preparation of antistatic agent

A reactor was charged with 96% active bis(perfluorobutylsulfonyl)imine (1.26 mol) dissolved in water (760 g) and then treated with Jeffamine[®] XJT-500 (0.66 mol) at 70°C over 30 minutes. The mixture was stirred an additional 15 minutes and the pH adjusted to 7–8. The solution was then concentrated under reduced pressure and 1042 grams of product isolated as an amber honey-like liquid.

DERIVATIVES

TABLE 1. Selected Polypropylene Ether Ammonium Salts Prepared Using Jeffamine[®] Polyether Amines and Bis(perfluoroalkylsulfonyl)imine

Entry	Jeffamine	Molecular Weight (Da)	Anion	Yield (%)
1	XJT-500	600	(C ₄ F ₉ SO ₂) ₂ N ⁻	—
2	T-406	440	(C ₄ F ₉ SO ₂) ₂ N ⁻	—
6	XJT-506	—	(CF ₃ SO ₂) ₂ N ⁻	91.7
7	XJT-500	600	(CF ₃ SO ₂) ₂ N ⁻	99.7

TESTING

TABLE 2. Concentration Effects on Surface Energy (dyn/cm) of Perfluorinated Compounds and Step 1 Product

Agent	Dosage			
	Surface Energy @ 0 ppm Treatment Level (dyn/cm)	Surface Energy @ 10 ppm Treatment Level (dyn/cm)	Surface Energy @ 100 ppm Treatment Level (dyn/cm)	Surface Energy @ 1000 ppm Treatment Level (dyn/cm)
C ₈ F ₁₇ SO ₃ K (comparison)	72	67.68	54.09	33.17
C ₄ H ₉ SO ₃ K (comparison)	72	70	67.5	53
C ₄ H ₉ SO ₂ NKSO ₂ C ₄ H ₉ (comparison)	72	61.85	41.61	34.02
Step 1 product	72	34.3	33.4	28.6

TABLE 3. Surface Resistivity for Selected Antistatic Agents Dissolved in Methylene Ketone, Then Coated onto a Sheet of Polyester film at 65°C

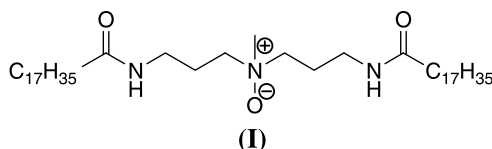
Entry	Surface Resistivity 1% MEK Solution (Ω/cm^2)	Surface Resistivity 6% MEK Solution (Ω/cm^2)
Comparative 1	1.6×10^9	1.5×10^{11}
Comparative 2	1.5×10^{12}	1.6×10^{12}
Step 1 product	8.5×10^9	3.1×10^9
Step 2 product	2.4×10^{10}	1.5×10^{11}
Step 6 product	1.6×10^9	7.8×10^9
Step 7 product	1.2×10^9	3.7×10^8

TABLE 4. Bioelimination Properties of Selected Perfluorosulfonates and Step 1 Product

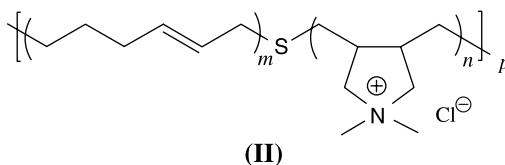
Sulfonate	Residual Sulfonate (ppm)		
	Day 1 (remaining)	Day 14 (remaining)	Day 28 (remaining)
C ₈ F ₁₇ SO ₃ ⁻	419 ± 86	309 ± 34	237 ± 25
C ₆ F ₁₇ SO ₃ ⁻	327 ± 52	61.9 ± 11.7	36.3 ± 7.7
Step 1 product	3.09 ± 1.58	0.126 ± 0.014	0.025 ± 0.02

NOTES

1. Jeffamines[®] are materials that contain polypropylene glycol, poly(ethylene oxide-*b*-propylene oxide), or poly(propylene oxide-ethylene oxide-*b*-propylene oxide), which contain an amine terminus.
2. Additional polyetheramine antistatic agents are described by the authors (1) in an earlier investigation.
3. Antistatic agents consisting of trimethylalkylammonium halides such as trimethylhexadecyl ammonium chloride were used by Iyama et al. (2) in coatings on plastic plates.
4. The antistatic agent, *N*-di-[3-(stearoylamino)propyl]-*N*-methylamine oxide, (**I**), was prepared by Baik et al. (3) and used as a fabric softer in fabric detergent compositions.



5. A block copolymer consisting of poly(ethylene-*b*-butene) oligomer and *N,N'*-dimethylpyrrolidinium chloride, (**II**), was prepared by Koroskenyi et al. (4) and used as an antistatic on polymeric finishes.



6. Polyetheresteramide antistatic agents consisting of the reaction product of undecanoic acid, hexamethylenediamine, dodecanedioic, and ethylene glycol were prepared by Linemann et al. (5) and blended with thermoplastic resins to form “breathable” polymer compositions.

References

1. P.M. Sauv et al., U.S. Patent Application 20080033078 (February 7, 2008).
2. H. Iyama et al., U.S. Patent Application 20080045636 (February 21, 2008).
3. I.S. Baik et al., U.S. Patent Application 20080039655 (February 14, 2008).
4. B. Koroskenyi et al., U.S. Patent Application 20080033115 (February 7, 2008).
5. R. Linemann et al., RE39,994 (January 1, 2008).

2. Coatings

a. Polyaromatic urethanes

Title: Polymer Compositions of Carbonyl-Hydrated Ketone-Aldehyde Resins and Polyisocyanates in Reactive Solvents

Author: Patrick Gloeckner et al.

Assignee: Degussa AG (Duesseldorf, DE)

Patent Application: 20080027156 (January 31, 2008)

Material Patentability: High

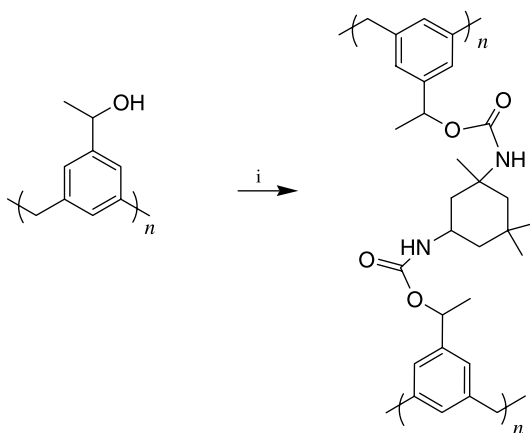
Anticipated Issuing Date: Mid-2010

Research Focus: Preparation of polyurethane coatings consisting of carbonyl-hydrogenated ketone and aldehyde resins and polyisocyanates.

Originality: Ongoing investigation in preparing Norrish I and II inactive coatings.

Application: Fabric and film coatings

Observations: A common feature of radiation curable products containing carbonyl function are Norrish type I or II degradation reactions. This group has addressed this concern by hydrogenating ketones in the base-catalyzed condensation of acetophenone and formaldehyde. In addition hydrogenated phenol-formaldehyde/mixed aldol condensation resins were also resistant to yellowing.

REACTION

- i. Isophorone diisocyanate, 2,6-bis(*tert*-butyl)-4-methylphenol, dibutyltin dilaurate, acetone

EXPERIMENTAL**1. Preparation of crosslinked polyurethane**

The hydrogenated resin of acetophenone and formaldehyde (400 g, $M_n \sim 1000$ Da) was condensed with isophorone diisocyanate (90 g) in the presence of 0.2% (on resin) 2,6-bis(*t*-butyl)-4-methylphenol and 0.1% of dibutyltin dilaurate (on resin) in 40% dilution with acetone. The mixture was refluxed until an NCO number of less than 0.1% was reached. The product was then isolated and had a melting range of from 171 to 176°C after the removal of acetone.

DERIVATIVES

Only the step 1 product was prepared.

TESTING

Resin solutions were prepared by mixing selected components illustrated in Table 1 with 1.5 wt% Darocur 1173 and then drawing down onto a glass plate using a doctor's blade. The films were then cured using a 70 W ultraviolet (UV) light mercury lamp with an optical filter at 350 nm for approximately 16 seconds.

Sample Preparation

TABLE 1. Sample preparation for Experimental Resin Compositions^a

Component	Sample A	Sample B	Sample C
UV-20 ^b (basic resin)	100	60	60
Acetophenone–formaldehyde resin (unreduced ketone)	—	40	—
Acetophenone–formaldehyde resin (reduced alcohol)			100
Tripropylene glycol diacrylate	40	64	4

^aEach material was evaluated for enhance initial drying rate, gloss, and hardness or scratch resistance.

^bUV 20 = Adduct of trimethylolpropane, isophorone diisocyanate, Terathane-650, and hydroxyethyl acrylate as a 70% strength solution in tripropylene glycol diacrylate.

TESTING

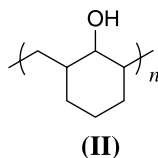
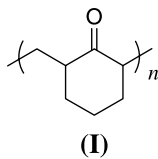
TABLE 2. Physical Properties of Resin Compositions after Sample Exposure to UV Radiation for 16 seconds

Entry	Testing ^a					Flow
	FT (μm)	EC (mm)	HK (s)	Peugeot Test	MEK Test	
A	30–37	7	115	++	> 150	Minimally
B	30–33	6	163	++	> 150	Good flow
C	30–36	6.5	192	++	> 150	Good flow

^aEC = Erichsen cupping, FT = film thickness, HK = Konig pendulum hardness, MEK test = resistance to butanone, and Peugeot test = premium-grade gasoline resistance.

NOTES

1. Cyclohexanone–formaldehyde resins, **(I)**, were previously prepared by the author (1) and used in resin compositions having enhanced hardness. Cyclohexanol–formaldehyde resins, **(II)**, were also prepared by the author (2) by hydrogenation of phenol–formaldehyde resins.



2. Baumgart et al. (3) prepared scratchproof, radiation-curable film-forming coatings by condensing siloxane tetraol, hydroxyethyl acrylate, and hexanediol diacrylate with excess hexamethylene diisocyanate catalyzed by dibutyltin dilaurate.
3. Radiation-curable liquid resin compositions were prepared by Takahashi et al. (4) consisting of the reaction product of 2,4-toluene diisocyanate, polypropylene oxide with an M_n of 2000 Da, and hydroxyethyl acrylate catalyzed by dibutyltin dilaurate. Products were used to coat optical fibers and as optical fiber ribbons.

References

1. P. Gloeckner et al., U.S. Patent Application 20060074217 (April 6, 2006).
2. P. Gloeckner et al., U.S. Patent 7,199,166 (April 3, 2007) and U.S. Patent 7,329,710 (February 12, 2008).
3. H. Baumgart et al., U.S. Patent Application 20080041273 (February 21, 2008).
4. A. Takahashi et al., U.S. Patent Application 20070191505 (August 16, 2007).

3. Hydrolysis Stabilizers

a. Polypropylene oxide aromatic amide-urethanes

Title: Macrocyclic Carbodiimides (MC-CDI) and Their Derivatives, Syntheses, and Applications of the Same

Author: Shenghong A. Dai et al.

Assignee: Great Eastern Resins Industrial Company, Ltd. (Taichung City, TW)

Patent Application: 20080161554 (2003)

Material Patentability: Very high

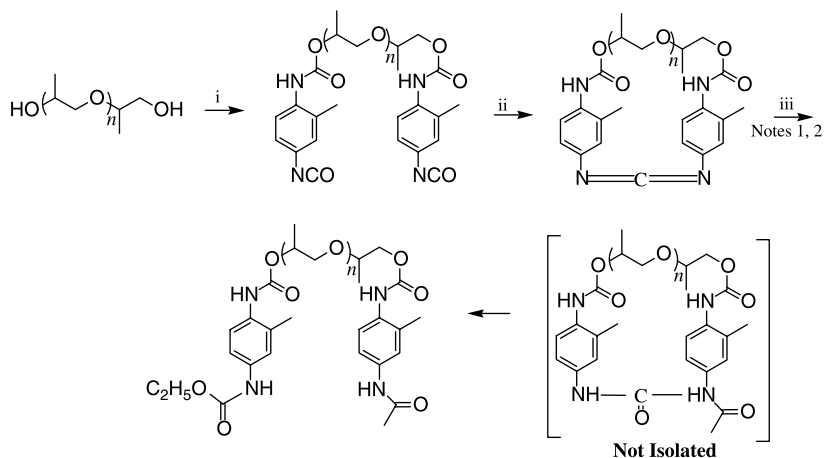
Anticipated Issuing Date: December, 2010

Research Focus: Method of preparing poly(amide-urethane) derivatives by ring-opening polymerization of macroscopic dicarbodiimides.

Originality: New and novel macrocyclic monomers and polymers.

Application: Fiber hydrolysis stabilizer

Observations: Polypropylene oxide macrocyclic carbodiimides were prepared by condensing with 2,4-toluene diisocyanate under high dilution with propylene glycol in the presence of 1,3-dimethyl-3-phospholene oxide. When the macroscopic diimide was postreacted with water and acetic acid, the urea acyclic acyl intermediate was generated. When further reacted with adipic acid or trimellitic anhydride, the corresponding poly(amide-urethane) and poly(urethane imide), respectively, were generated.

REACTION

- i. 2,4-Toluene diisocyanate
- ii. Toluene, 1,3-dimethyl-3-phospholene oxide
- iii. Acetic acid, ethanol

EXPERIMENTAL**1. Preparation of prepolymer containing isocyanate termini**

In a 250-ml three-necked flask, polypropylene glycol (0.02 mol) and 2,4-toluene diisocyanate (0.042 mol) were added and reacted under conditions provided in Table 1. When the reaction was completed, all products were isolated as transparent colorless liquids.

TABLE 1. Reaction Conditions Used in Preparing Step 1 Products^a

Reaction ID	Polypropylene Glycol (M_n)	Temperature (°C)	Reaction Time (minutes)
T2P192	192	45	50
T2P400	400	50	40
T2P700	700	50	30 (65)
T2P2000	2000	65, 70	15 (70)

^aIn all cases equimolar amounts of toluene diisocyanate and polypropylene oxide were used.

2. Preparation of macrocyclic carbodiimides

The step 1 product was diluted with 1500 ml toluene to a final concentration of 0.013 mol/L. The mixture was then treated with 1,3-dimethyl-3-phospholene oxide and heated to 90°C while the cyclization reaction was monitored by Fourier transform infrared (FTIR). When the characteristic—NCO peak was eliminated in the macrocyclic carbodiimide (2134 cm⁻¹), the reaction was stopped, concentrated, dried, and the crude product isolated. The crude product was purified by liquid column chromatography on silica gel using either ethyl acetate or ethyl acetate/*n*-hexane, 9:1, respectively, and the product isolated.

3. Preparation of macroscopic acylurea

The step 2 product was dissolved in 30 ml xylene containing acetic acid and the temperature slowly increased while monitoring the ring-opening reaction using FTIR. After heating to 140°C the solution was slowly treated with excess anhydrous ethanol. The solution was then stirred for an additional 30 minutes, concentrated, and the product isolated.

PHYSICAL PROPERTIES AND DERIVATIVES

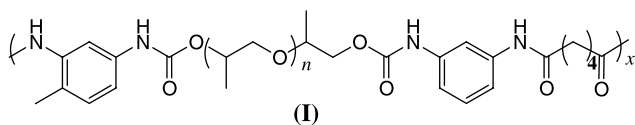
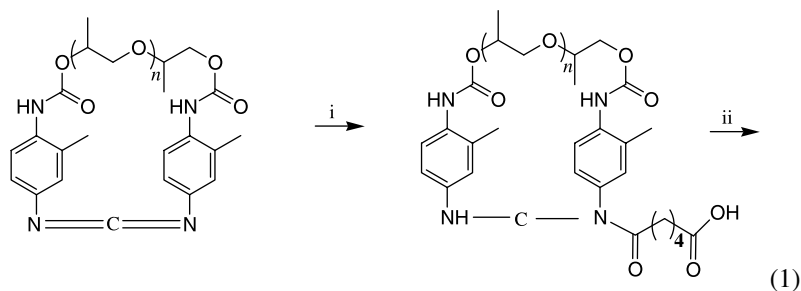
Physical properties for step 2 macrocyclic carbodiimides are provided in Table 2.

TABLE 2. Physical Properties of Step 2 Macrocyclic Carbodiimides Prepared by Ring Closure of Step 1 Product Using 1,3-Dimethyl-3-phospholene Oxide

Sample	Cyclization Time (h)	Yield (%)	Appearance	Melting Point (°C)	Polyether Segment T_g (°C)
CDI-T2P192	21	60	Faint yellow powder crystal	80.5–85.2	18.0
CDI-T2P400	18	67	Faint yellow colloid	16 and 22	6.7
CDI-T2P700	20	40	Faint yellow colloid	—	3.8
CDI-T2P2000	27	18	Faint yellow colloid	—	–49.0

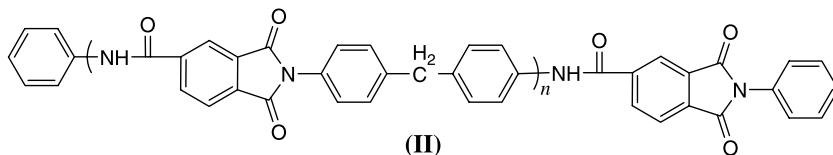
NOTES

1. Poly(amide-urethane)derivatives, **(I)**, were also prepared by reacting adipic acid with the step 2 product as illustrated in Eq. (1).



- i. Adipic acid
ii. Ethyl alcohol

2. In an earlier investigation by the authors (1) aryl *N*-acylureas were prepared and converted into polyamide-imides, **(II)**, by heating to 120°C.



3. Water-dispersible polyisocyanate compositions containing polyethylene oxide were previously prepared by the authors (2) and used as aqueous resin adhesives.
4. Imashiro et al. (3) prepared polycarbodiimides using 4,4'-dicyclohexylmethane diisocyanate terminated with moisture-resistant diisocyanates.

References

1. S.A. Dai et al., U.S. Patent Application 20070282078 (December 6, 2007).
2. S.A. Dai et al., U.S. Patent 6,838,516 (January 4, 2005).
3. Y. Imashiro et al., U.S. Patent 5,889,096 (March 308, 1999) and U.S. Patent 5,912,290 (June 15, 1999).

4. Stain Repellants

a. Polyfluorinated poly(4-vinylpyridine)

Title: Hydrophobic Fluorinated Polyelectrolyte Complex Films and Associated Methods

Author: Joseph B. Schlenoff

Assignee: Florida State University Research Foundation, Inc. (Tallahassee, FL)

Patent Application: 20070265174 (November 15, 2007)

Material Patentability: Very high

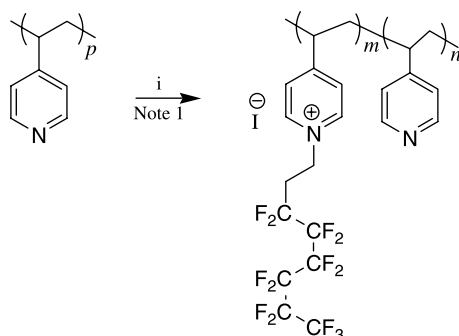
Anticipated Issuing Date: Mid-2009

Research Focus: Preparation of ultrathin films of anionic and cationic polymers.

Originality: Method for producing long-adhering chemically inert fabric modifiers.

Application: Stain repellent

Observations: Hydrophobic fluorinated pyridinium iodide ionic solvents lack sufficient adhesiveness to remain affixed to a surface whether used as a powder or thin film. To address the lack of adhesion, this group prepared multilayered elements described in U.S. Patent 5,208,111, which remain affixed when applied to supports. This strategy was used to prepare adhesives consisting of poly(4-pyridinium) cationic perfluoro polyelectrolytes, which adhered to ultrathin films of selected anionic polyelectrolytes. Amorphous complexes were also prepared by mixing solutions of polyelectrolytes bearing opposite charges. The driving force for this association or complexation of polyelectrolytes was the multiple ion pairing between oppositely charged repeat units on different molecules. In this manner ultrathin films with good mechanical adhesion were prepared having a thicknesses of 300 Å and larger.

REACTION

i. 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane, *N,N'*-dimethylformamide

EXPERIMENTAL**1. Preparation of perfluorovinylpyridinium iodide**

Poly(4-vinylpyridine) (10 mmol) having an $M_n \sim 300,000$ Da was dried and then treated with 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane (12 mmol) and the mixture reacted for 48 hours at 80°C in 50 ml *N,N'*-dimethylformamide. The solution was precipitated by pouring into ethyl acetate and then washed with petroleum ether. The material was dried under vacuum for 24 hours at 60°C and the product isolated in 90% yield.

TESTING*A. Contact Angle Testing*

Contact angle testing was performed using a dynamic contact angle analyzer with the Wilhelmy technique. This method measures the forces that are present when a sample of solid is brought into contact with a test liquid. If the forces of interaction when the geometry of the solid and the surface tension of the liquid are known, the contact angle may be calculated. The sample was initially hung on a sensitive balance and the liquid raised to contact the sample. When the solid contacts the liquid, the change in forces are detected and the balance will record this elevation as zero depth of immersion. As the solid is lowered into the liquid, the forces on the balance are recorded. Results for contact angle measurements for experimentally layered agents are provided in Table 1.

TABLE 1. Dynamic and Static Contact Angle Measurements of Selected Experimental Agents

Polyelectrolyte Multilayers ^a	Dynamic Contact Angle	Advancing Contact Angle
Blank	Advancing	20.87
Blank	Receding	17.63
(PDADMA/PSS) ₁₀ PDADMA	Advancing	61.10
(PDADMA/PSS) ₁₀ PDADMA	Receding	30.84
(PEPVP/PSS) ₁₀ PEPVP	Advancing	97.81
(PEPVP/PSS) ₁₀ PEPVP	Receding	19.10
(PDADMA/Nafion) ₁₀	Advancing	95.75
(PDADMA/Nafion) ₁₀	Receding	23.79
(PEPVP/Nafion) ₁₀ PEPVP	Advancing	114.16
	Receding	27.72

^aPDADMA = poly(diallyldimethylammonium chloride), PSS = poly(styrenesulfonic acid), PAMPS = poly(2-acrylamido-2-methyl-1-propane sulfonic acid), and PFPVP = 4-vinyl-trideca-fluoro-octyl pyridinium iodide-co-4-vinyl pyridine.

B. Thickness and Refractive Indices

Selected polyelectrolyte multilayers were prepared and their thickness and refractive indices measured using ellipsometry. Testing results are reported in Table 2.

TABLE 2. Thickness and Refractive Indices Measurements of Selected Experimental Agents

Polyelectrolyte Multilayers ^a	Refractive Index	Thickness (Å)
(PDADMA/Nafion) ₁₀	1.35	310
(PEPVP/PSS) ₁₀	1.49	441
(PDADMA/PSS) ₁₀	1.56	567
(PEPVP/Nafion) ₁₀	1.40	882

^aPDADMA = poly(diallyldimethylammonium chloride) a positively, PSS = poly(styrenesulfonic acid), PAMPS = poly(2-acrylamido-2-methyl-1-propane sulfonic acid), and PFPVP = 4-vinyl-trideca-fluoro-octyl pyridinium iodide-co-4-vinyl pyridine.

NOTES

1. Ultrathin polyelectrolyte films were also prepared using macromolecules containing polyionic charged repeat units. Amorphous complexes were formed by mixing solutions of polyelectrolytes bearing opposite charges. The driving force for association or complexation of polyelectrolytes is multiple ion pairing between oppositely charged repeat units on different molecules.
2. Bureau et al. (1) developed a method for forming a polymer film that behaved as a conductor or semiconductor on its surface by layering using electrografting.

3. Smela et al. (2) observed that some conjugated polyelectrolyte dopants caused a layering of polymer chains within a polymer. In other ionic electroactive material additives can be used for crystalline ordering. Such additives may include surfactants and/or liquid crystals.

References

1. C. Bureau et al., U.S. Patent Application 20070281148 (December 6, 2007).
2. E. Smela et al., U.S. Patent Application 20070205398 (September 6, 2007).

5. Wetting Agents

a. Polyacrylamide ionic solvents

Title: Polymerizable Sulfonate Ionic Liquids and Liquid Polymers Therefrom

Author: Holly L. Ricks-Laskoski et al.

Assignee: United States Government as Represented by Secretary of the Navy

Patent Application: 20080051605 (February 28, 2008)

Material Patentability: Very high

Anticipated Issuing Date: 2010

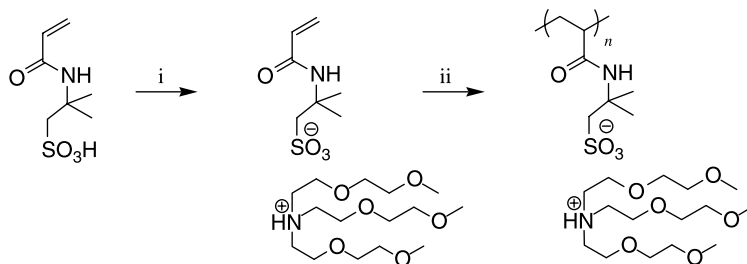
Research Focus: Preparation of liquid phase methacrylamide ionic liquid polyethers.

Originality: These agents are unreported in the patent literature.

Application: Fabric wetting agents

Observations: A high-molecular-weight liquid-phase polymeric ionic liquid having a T_g of -49°C was prepared by neutralizing tris[2-(2-methoxyethoxy)-ethyl]-amine with 2-acrylamido-2-methyl-1-propanesulfonic acid and then polymerizing with 2,2'-azobisisobutyronitrile.

Although polymeric solvents have previously been prepared, they are usually based on pyridine, imidazole, or styrene and have the physical forms of a glass or a sticky rubber. Agents in the current application are liquids. Once dissolved poly(2-acrylamido-2-methyl-1-propanesulfonic acid) oxyethylene ammonium salts, however, can be directly converted into fabrics.

REACTION

- i. Tris[2-(2-methoxyethoxy)-ethyl]amine
- ii. 2,2'-Azobisisobutyronitrile

EXPERIMENTAL**1. Preparation of 2-acrylamido-2-methyl-1-propanesulfonic acid oxyethylene ammonium salt**

Equimolar amounts of 2-acrylamido-2-methyl-1-propanesulfonic acid and freshly distilled tris[2-(2-methoxyethoxy)-ethyl]amine were mixed under an inert atmosphere and stirred for 8 hours at ambient temperature or until 2-acrylamido-2-methyl-1-propanesulfonic crystals dissolved. The monomer salt consisted of a slightly yellow viscous clear liquid. The salt monomer was used in the next step without further purification.

2. Preparation of poly(2-acrylamido-2-methyl-1-propanesulfonic acid) oxyethylene ammonium salt

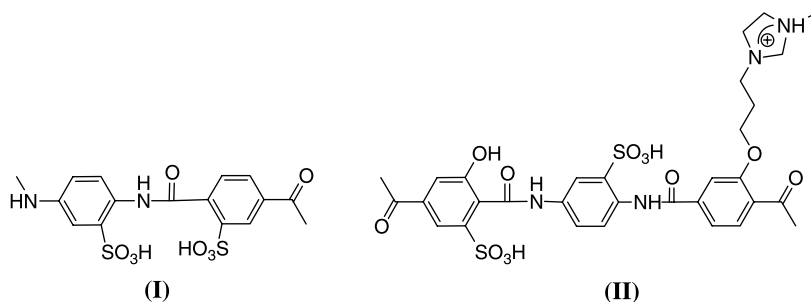
A mixture consisting of the step 1 product and 2,2'-azobisisobutyronitrile was heated to 70°C for 18 hours. The transparent amber ionic liquid polymer salt was purified by dissolving in acetone and precipitating in cold diethyl ether. The precipitate was collected by cold suction filtration and the product isolated as a tacky transparent yellow liquid that had a T_g of -49°C and an intrinsic viscosity value of 0.3.

DERIVATIVES

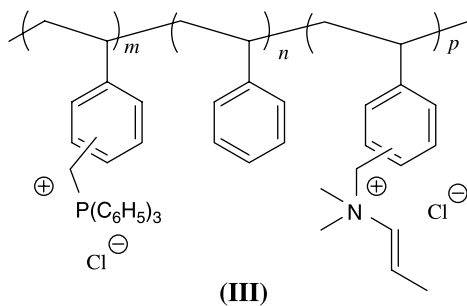
No additional derivatives prepared.

NOTES

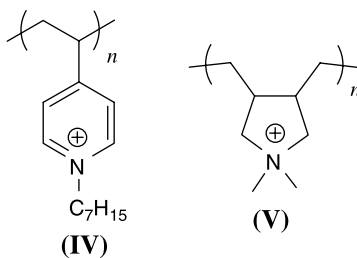
1. Monomer and polymer electrolytes containing ion-exchangeable functional groups, **(I)**, and an ionic liquid functional group, **(II)**, were prepared by Best et al. (1) and used in fuel cells.



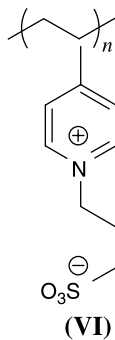
2. Giri et al. (2) prepared mixed ammonium and phosphonium polymeric ionic liquids, **(III)**, from chloromethylated polystyrene, which were useful as enhancers in chemiluminescent systems.



3. Polymeric ionic liquids, **(IV)** and **(V)**, were prepared by Schlenoff et al. (3) and used in polyelectrolyte membranes.



4. Rodrigues et al. (4) prepared polymeric ionic liquid derivatives, (VI), by condensing poly(4-vinylpyridine) with propane sultone and products used as antidyne transfer agents.



References

1. A.S. Best et al., U.S. Patent Application 20080045615 (February 21, 2008).
2. B.P. Giri et al., U.S. Patent 7,300,766 (November 27, 2007).
3. J.B. Schlenoff et al., U.S. Patent 7,223,327 (May 29, 2007).
4. K.A. Rodrigues et al., RE39,450 (December 26, 2006).

F. Paint Additives

1. Dispersants

a. Acetoacetoxylethyl polymethacrylates

Title: Monomer Compound, Process for Producing the Same, Polymer Thereof, and Water-Based Curable Composition

Author: Masami Kobata

Assignee: Kansai Paint Co., Ltd. (Amagasaki-shi, JP)

Patent Application: 20080053835 (March 6, 2008)

Material Patentability: High

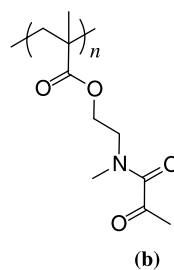
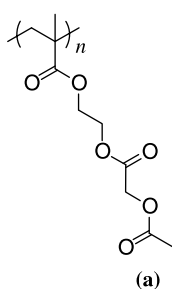
Anticipated Issuing Date: 2010

Research Focus: Enhancing the hydrolytic stability of paints using the carbonyl-containing additive poly(*N*-(2-(methacryloyloxy)ethyl)-*N*-methylpyruvamide).

Originality: This is a replacement additive for acetoacetoxylethyl-based paint Additives.

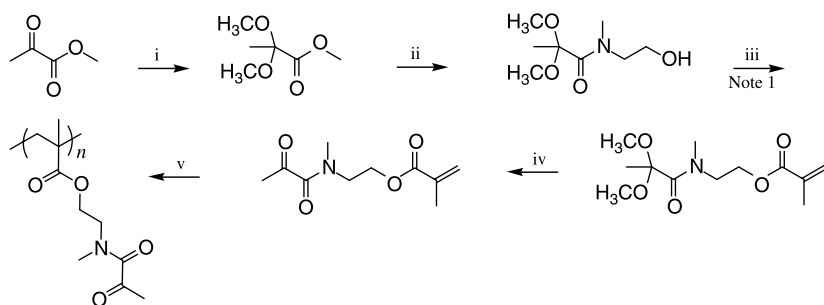
Application: Paint additive

Observations: Acetoacetoxylethyl methacrylate polymer, (a), and copolymer paint



additives are hydrolytically unstable since they undergo a retro-Claisen condensation reaction. To address this concern the hydrolytically stable poly(*N*-(2-(methacryloyloxy)ethyl)-*N*-methyl-2,2-dimethoxypropionic acid amide), (**b**), was prepared. Although these derivatives are usually prepared by condensing acrylonitrile, concentrated sulfuric acid, and a carbonyl-containing compound, a less corrosive four-step route was used. Initially a triorthoester was converted into a ketal ester followed by hydroxylalkyl amidation, esterification, and hydrolysis to the target compound.

REACTION



- i. Trimethyl orthoformate, methanol, paratoluenesulfonic acid monohydrate
- ii. *N*-Methyl-ethanolamine, methanol, sodium methoxide
- iii. Methyl methacrylate, 2,2,6,6-tetramethyl-1-piperidinyloxy intermediate, hydroquinone monomethyl ether, dioctyltin oxide, di-*t*-butyl methyl phenol
- iv. Hydrochloric acid
- v. Ethylene glycol monobutyl ether, 2,2'-azobis(2,4-dimethylvaleronitrile)

EXPERIMENTAL

1. Preparation of 2,2-dimethoxymethyl propionate

A flask was charged with methyl pyruvate (8.25 mol), trimethyl orthoformate (10 mol), methanol (1060 g), and para-toluenesulfonic acid monohydrate (0.041 mol) and then stirred at 58°C for 10 hours. It was then treated with 28% methanol solution of sodium methoxide (8 g) and concentrated. After distillation the product was isolated as a colorless transparent liquid in 98% purity having a boiling point (bp) of 80°C @ 40 mmHg.

¹H-NMR (CDCl₃): δ 3.82 (3H, s), 3.29 (6H, s), and 1.53 (3H, s)

FTIR (cm⁻¹): 3632, 2999, 2953, 2837, 1749, 1455, 1437, 1373, 1293, 1216, 1192, 1144, 1046, 976, 892, 801, 761, and 676

2. Preparation of *N*-(2-hydroxyethyl)-*N*-methyl-2,2-dimethoxypropionic acid amide

A reaction kettle was charged with the step 1 product (7.5 mol) and *N*-methyl-ethanolamine (8.25 mol) and then treated with a 28% methanol solution of sodium methoxide (0.075 mol). This mixture was heated to 70°C for 20 hours while distilling off methanol under reduced pressure. Thereafter, the mixture was treated with acetic acid (5 g) and then concentrated. After distillation 1146 g of product was isolated as a pale yellow transparent liquid with a 96% purity having a bp of 135°C @ 2 mmHg.

¹H-NMR (CDCl₃): δ 3.58–3.84 (4H, m), 2.99–3.32 (9H, m), 2.50–2.99 (1H, b), and 1.54–1.56 (3H, m)
FTIR (cm⁻¹): 3445, 2945, 2837, 1634, 1498, 1456, 1437, 1404, 1375, 1226, 1149, 1106, 1041, 892, 747, and 655

3. Preparation of *N*-(2-(methacryloyloxy)ethyl)-*N*-methyl-2,2-dimethoxypropionic acid amide

A mixture consisting of the step 2 product (0.71 mol), methyl methacrylate (3.3 mol), 2,2,6,6-tetramethyl-1-piperidinyloxy intermediate (0.23 g), hydroquinone monomethyl ether (0.23 g), and dioctyltin oxide (2.6 g) were added to a 500-ml flask equipped with a rectifying tower and stirred. The mixture was then heated to 105°C while introducing air. While maintaining the temperature at 105°C, methanol was distilled off over 12 hours during which the pressure was gradually reduced to 25 mmHg. Thereafter, the mixture was re-treated with 2,2,6,6-tetramethyl-1-piperidinyloxy intermediate (0.09 g), hydroquinone monomethyl ether (0.09 g), and di-*t*-butyl methyl phenol (0.09 g) and then distilled while introducing air. The product was isolated in 94% yield as a pale yellow transparent liquid with a 99% purity, which had a bp of 142°C @ 2 mmHg.

¹H-NMR (CDCl₃): δ 6.11 (1H, m), 5.59 (1H, m), 4.35 (2H, m), 3.68–3.90 (2H, m), 3.28 (6H, s), 3.03–3.28 (3H, m), 1.95 (3H, m), and 1.51 (3H, m)
FTIR (cm⁻¹): 3498, 2946, 2834, 1719, 1652, 1455, 1400, 1373, 1319, 1296, 1164, 1104, 1040, 945, 892, 815, 746, and 651

4. Preparation of *N*-(2-(methacryloyloxy)ethyl)-*N*-methyl-pyruvamide

A round-bottom flask was charged with the step 3 product (166 g) and 4% hydrochloric acid (495 g) and then stirred at ambient temperature for 5 hours and neutralized with a 10% aqueous NaHCO₃ solution to pH 6. This solution was then treated with 400 ml of ethyl acetate and NaCl to extract the product, the cycle being repeated four times. The organic phases were concentrated and then treated with hydroquinone monomethyl ether (0.04 g), di-*t*-butyl methyl phenol (0.04 g), and *N*-oxyl derivative (0.14 g) and distilled while introducing air. The product was isolated in 90% yield as a pale yellow transparent liquid in 96% purity having a bp of 138°C @ 3 mmHg.

¹H-NMR (CDCl₃): δ 6.11 (1H, m), 5.61 (1H, m), 4.32–4.37 (2H, m), 3.66–3.73 (2H, m), 3.05–3.09 (3H, m), 2.42 (3H, m), and 1.95 (3H, s)
FTIR (cm⁻¹): 3518, 2959, 1718, 1644, 1492, 1453, 1408, 1354, 1318, 1296, 1163, 1103, 1019, 947, 815, 745, and 656

5. Preparation of poly (*N*-(2-(methacryloyloxy)ethyl)-*N*-methyl-pyruvamide)

A 200-ml flask was charged with ethylene glycol monobutyl ether (30 g) and then heated to 85°C and treated with the step 4 product (40 g) and 2,2'-azobis(2,4-dimethylvaleronitrile) (1.5 g) over a period of 4 hours. Thereafter, a mixture of ethylene glycol monobutyl ether (30 g) and 2,2'-azobis(2,4-dimethylvaleronitrile) (0.5 g) was added over a period of 3 hours in the identical manner. After stirring an additional hour, the mixture was cooled to ambient temperature and a viscous liquid obtained. The percent solids of the liquid was 40.3% with a 98% reaction conversion.

6. Preparation of resin dispersion

Water (28 g) and polyoxyethylene phenyl ether sulfuric acid ester emulsifier (0.08 g) were added to a 300-ml flask and heated to 85°C while stirring. This solution was then treated with a mixture of the step 4 product (6.3 g), methyl methacrylate (41.6 g), styrene (14 g), butyl acrylate (23.5 g), 2-ethylhexyl acrylate (14.6 g), water (51.6 g), polyoxyethylene phenyl ether sulfuric acid ester emulsifier (6.6 g), and 0.3 g of sodium persulfate over 4 hours. Thereafter, a mixture of water (5.2 g) and ammonium persulfate (0.1 g) were added over 30 minutes and the mixture stirred for an additional 2 hours. It was then cooled to ambient temperature and a white resin isolated, which consisted of 52% solids with a polymerization conversion of 99%.

DERIVATIVES

No additional derivatives were prepared.

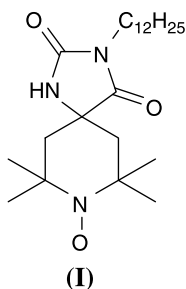
TESTING

Storage Stability

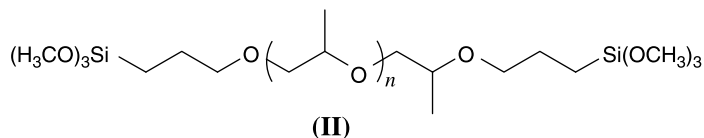
Storage stability of the resin dispersion was determined using an accelerated decomposition test at 80°C for 20 hours. The decomposition rate of *N*-methyl-pyruvamide in this dispersion after the test was less than 3%.

NOTES

1. The structure of the 2,2,6,6-tetramethyl-1-piperidinyloxy intermediate, **(I)**, provided by the author is illustrated below.



2. A curable polypropylene glycol resin containing trimethoxysilyl termini, **(II)**, having good adhesiveness and storage stability properties was prepared by Wakabayashi et al. (1) and used in water-based paint formulations.



3. Sakamoto et al. (2) prepared macromonomers consisting of poly(butyl acrylate-*b*-methyl methacrylate), which were used as paint additives to enhance adhesiveness and storage stability properties.

References

1. K. Wakabayashi et al., U.S. Patent Application 20080051547 (February 28, 2008).
2. H. Sakamoto et al., U.S. Patent Application 20080009593 (January 10, 2008).

b. Poly(4-methyl-pentene) aldehyde

Title: Functionalized Poly(4-Methyl-1-Pentene)

Author: John R. Briggs et al.

Assignee: Dow Global Technologies, Inc. (Midland, MI)

Patent Application: 20080021172 (January 24, 2008)

Material Patentability: High

Anticipated Issuing Date: Mid-2010

Research Focus: Hydroformylation of poly(4-methyl-1-pentene) terminus.

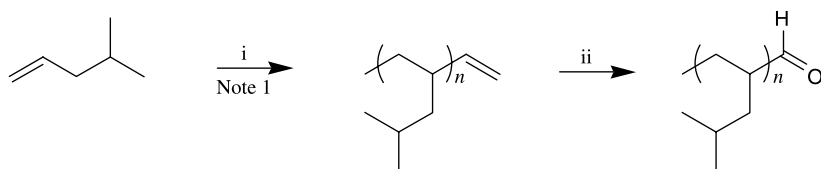
Originality: Hydroformylation of poly(4-methyl-1-pentene) is unreported in the patent literature.

Application: Paint dispersant

Observations: Although poly(4-methyl-1-pentene) was initially prepared over 40 years ago, its use has been restricted to polymer blends and paint-free additives. Copolymers of this agent are used for preparing multilayer films and film layers. The current application has developed a method using hafnium salts to prepare a polymer containing 95% chain-end unsaturation of which 80% comprises 1,2-olefinic unsaturation. This material was then hydroformylated with carbon monoxide. The hydroformylated polymer has broad applications including use in:

- a. Schiff base reactions to prepare amines
- b. Conversion to diols for use as component in polyurethanes and high-performance polycarbonates
- c. Mixed aldol condensations to generate α,β -unsaturated ketones
- d. Conversion to acids and used in making polyamides

REACTION



- i. Toluene, [*N*-(2,6-di(1-methylethyl)phenyl)amido](2,4,6-trimethylphenyl)(phenylen-2-diyl)(6-pyridin-2-diyl)methane]hafnium dimethyl, [*N*-(2,6-di(1-methylethyl)phenyl)amido](2,4,6-trimethylphenyl)(α -naphthalen-2-diyl)(6-pyridin-2-diyl)methane]hafnium dimethyl, ammonium dimethyloctadecylammonium tetrakis(pentafluorophenyl)borate, MMAO-12, PMAO-IP, Irganox[®] 1010, Irgafos[®] 168
- ii. Carbon monoxide, hydrogen, dicarbonyl acetylacetonate, tris(2,4-di-*t*-butylphenyl)phosphate, toluene

EXPERIMENTAL

1. Preparation of poly(4-methyl-1-pentene)

An autoclave was charged with 4-methyl-1-pentene (6.89 mol) and then treated with toluene solutions of [*N*-(2,6-di(1-methylethyl)phenyl)amido](2,4,6-trimethylphenyl)(phenylen-2-diyl)(6-pyridin-2-diyl)methane]hafnium dimethyl [catalyst 1] and [*N*-(2,6-di(1-methylethyl)phenyl)amido](2,4,6-trimethylphenyl)(α -naphthalen-2-diyl)(6-pyridin-2-diyl)methane]hafnium dimethyl [catalyst 2]. The amount of each catalyst was 6.0 μ mol. The mixture was then treated with 6.6 μ mol co-catalyst ammonium dimethyloctadecylammonium tetrakis(pentafluorophenyl)borate. Polymerization modifiers used were the trialkylaluminum-modified methylalumoxanes MMAO-12 and PMAO-IP. After 15 minutes of reaction time, the reactor contents are placed into a resin kettle containing 1 g of a 50/50 mixture of the antioxidant Irganox[®]-1010 and stabilizer Irgafos[®]-168. Following the reaction, the polymer was recovered by evaporating the majority of the solvent under ambient conditions and then further dried in a vacuum oven overnight at 90°C. Polymerization reaction scoping studies and physical properties of polymers are provided in Tables 1 and 2, respectively.

2. Hydroformylation process

A sample of the polymer of step 1 product was hydroformylated by reacting it with a mixture of carbon monoxide and hydrogen under 690 kPa for 4 hours catalyzed by rhodium dicarbonyl acetylacetonate (10.2 mg) and tris(2,4-di-*t*-butylphenyl)phosphite (48.2 mg) dissolved in toluene. ¹H-NMR spectrum of this polymer showed the presence of carbonyl functional groups in place of ethylenic unsaturation.

SCOPING REACTIONS

TABLE 1. Polymerization Scoping Studies for Poly(4-methyl-1-pentene) Using a Hafnium Salt Catalyst with Selected Polymerization Modifiers

Experiment	Catalyst	Polymerization Modifier	Polymerization Modifier (mmol)	Reaction Temperature (°C)	Yield (%)	Efficiency (gPP/mgHf)
1	Catalyst 1	MMAO	3.0	90	27	25
2	Catalyst 1	PMAO	0.2	100	51	48
3	Catalyst 2	MMAO	3.0	90	43	40
4	Catalyst 2	PMAO	3.0	110	46	43

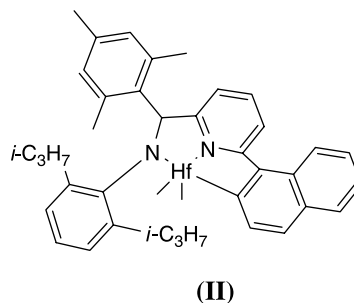
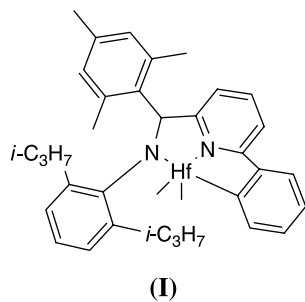
TABLE 2. Physical Properties of poly(4-methyl-1-pentene) Prepared Using Hafnium-Based Catalysts^a

Experiment	M_n (Da)	M_w (Da)	Polydispersity	T_m (°C)
1	9,320	25,000	2.68	226
2	11,200	42,600	3.8	228
3	15,900	66,440	4.18	232
4	10,000	22,500	2.25	228

^aScoping conditions are described in Table 1.

NOTES

- 4-Methyl-1-pentene polymerization catalysts are illustrated below:
 - [*N*-(2,6-di(1-methylethyl)phenyl)amido)(2,4,6-trimethylphenyl)(phenylen-2-diyl)(6-pyridin-2-diyl)methane]hafnium dimethyl, **(I)**.
 - [*N*-(2,6-di(1-methylethyl)phenyl)amido)(2,4,6-trimethylphenyl)(α -naphthalen-2-diyl)(6-pyridin-2-diyl)methane]hafnium dimethyl, **(II)**.



2. Propylene and 4-methyl-1-pentene were copolymerized by Colin et al. (1) using a Ziegler–Natta catalyst and the product characterized as having at least one fraction obtained by that had a block index greater than about 0.3 and up to about 1.0 with a polydispersity greater than 1.3.
3. Poly(ethylene-*co*-4-methyl-1-pentene) was prepared by Colin et al. (2) and used as fibers, thermoplastics, and as oil viscosity index improvers.
4. Methods for preparing and using compositions containing poly(4-methyl-1-pentene) having a controlled molecular weight distribution are described by Patel et al. (3). Methods for preparing multilayer films and film layers are also described.
5. A method for controlling the molecular weight of poly(4-methyl-1-pentene) was devised by Hustad et al. (4) and entailed limiting the monomer concentration using a precatalyst and by adding a catalytic amount of a titanium(III)-containing salt as an ethylene interceptor.

References

1. L.P.S. Colin et al., U.S. Patent Application 20070219334 (September 20, 2007).
2. L.P.S. Colin et al., U.S. Patent Application 20060199930 (September 7, 2007).
3. R.M. Patel et al., U.S. Patent Application 20070275219 (November 29, 2007).
4. P.D. Hustad et al., U.S. Patent Application 20070135575 (June 14, 2007).

G. Paint Stabilizers

1. Hydrolytically and oxidatively stable paint additives

a. Oligomeric polyaromatic esters

Title: Polyester Oligomers, Methods of Making, and Thermosetting Compositions Formed Therefrom

Author: Corrado Berti et al.

Assignee: General Electric Company, Global Research (Niskayuna, NY)

Patent Application: 20070155946 (July 5, 2007)

Material Patentability: Moderate

Anticipated Issuing Date: Mid-2009

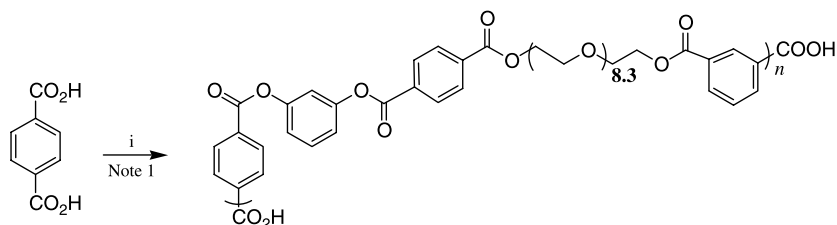
Research Focus: Preparation of hydrolytically and oxidatively stable oligomeric polyaromatic esters.

Originality: Continuation of an ongoing investigation in the development of phase-separated weatherable oligomeric esters.

Application: Exterior paint additives

Observations: Polymeric and oligomeric materials having good resistance to photo yellowing or weatherability are usually restricted to low-molecular-weight polyarylates that form a stable composition that is permanent upon crosslinking. Photostable oligomeric esters containing both noncrystalline and crystalline domains and having carboxylic acid termini were prepared in this application and then crosslinked with polyacrylates. Oligomeric esters were prepared by initially forming an ester-carbonate prepolymer and then decarboxylating the intermediate. Products were formed in quantitative yields.

REACTION



- i. Isophthalic acid, diphenyl carbonate, resorcinol, polyethylene glycol, sodium hydroxide

EXPERIMENTAL

A reaction flask was charged with terephthalic acid (12.46 g), isophthalic acid (12.46 g), diphenyl carbonate (44.07 g), resorcinol (9.63 g), polyethylene glycol (7.50 g; M_n 600), and sodium hydroxide (0.02 g) as catalyst and then heated to 170°C. The reactor was then connected to a liquid nitrogen cooled condenser and immersed in a 285°C oil bath. Phenol formed as a reaction by product was distilled and then recovered in a condenser. Carbon dioxide evolution began after 15 minutes and stopped after 2 hours while heating was continued for an additional 3 hours. Thereafter a vacuum was slowly applied to the reactor to decrease the internal pressure from atmospheric pressure to 60 mbar in approximately 10 minutes. After 30 minutes from reaching this pressure, the internal pressure was further decreased to 0.1 mbar and the reaction stopped after 15 minutes. The oligomer was then transferred to a cooling tray while still molten and allowed to cool.

REACTION SCOPING

Scoping reaction studies designed to optimize carboxylic acid content are provided in Table 1.

TABLE 1. Oligomer Scoping Reaction Studies and Physical Properties of Products Using 10–40% Excess Diacid

Entry	Catalyst ^d	Catalyst Level (ppm)	Reaction Temp. (°C)	Molar Ratio ^b		Molar Ratio		COOH End Groups (%)
				(TPA + IPA)/ (RES + PEG)	Molar Ratio ^c (DPC/ (RES + PEG)	Ratio (RES + PEG)	M_n (Da)	
1	TBT + NaH ₂ PO ₄	100	275	1.3	1.89	0.125	3900	66.1
6 ^d	C94	74	270	1.5	2.05	0.125	4700	70.7
9	NaOH	350	280	1.5	2.05	0.125	—	92.5
10	NaOH	350	280	1.5	2.05	0.625	9300	67.8

^aTBT = tetrabutyl titanate and C94 catalyst = titanium and silica-based catalyst.

^bIPA = Isophthalic acid, PEG = polyethylene glycol, RES = resorcinol, and TPA = terephthalic acid.

^cDPC = diphenyl carbonate.

^dEntry 6 represents the optimum reaction conditions for preparing the thermosetting composition.

NOTES

1. Carboxy-terminated oligomeric polyester compositions consisting of resorcinol, terephthalic isophthalic acid, diphenyl carbonate, and terephthalic acid catalyzed by titanium tetrabutoxide were prepared by Brunelle et al. (1) and used as thermosetting applications.
2. Poly(1,4-cyclohexylenedimethylene isophthalate) was prepared by Martin et al. (2) by condensing isophthalic acid and 1,4-cyclohexanedimethanol and the product used in packaging applications, textiles, sheeting, and film applications.
3. Thermoset polymeric esters consisting of neopentyl glycol, propylene glycol, trimethylol propane, adipic acid, maleic anhydride, and 2-ethyl hexanol were prepared by McAlvin et al. (3) and were used in blends containing styrene monomer. The mixture was cured by pultrusion and had improved weatherability characteristics.
4. Thermoset plastics having low permeability to fluids consisting of ethylene glycol, 4,4'-biphenol, terephthalic acid, 4-hydroxybenzoic acid, and 6-hydroxy-2-naphthoic acid were prepared by Doshi et al. (4) and used in piping and containers with high fluid barrier limits.

References

1. D.J. Brunelle et al., U.S. Patent Application 20070027290 (February 1, 2007) and U.S. Patent Application 20060116487 (June 1, 2006).
2. D.L. Martin et al., U.S. Patent 7,211,634 (May 1, 2007).
3. J.E. McAlvin et al., U.S. Patent Application 20070032608 (February 8, 2007).
4. S.R. Doshi et al., U.S. Patent Application 20080020160 (January 24, 2008).

H. Paper Additives

1. Stabilizers

a. Glyoxalated poly(vinylamide-*co*-diallyldimethylammonium chloride)

Title: Glyoxalation of Vinylamide Polymer

Author: Matthew D. Wright

Assignee: Ciba Geigy Corporation (Tarrytown, NY)

Patent Application: 20080064819 (March 13, 2008)

Material Patentability: Moderate

Anticipated Issuing Date: 2011

Research Focus: Synthesis of glyoxalated poly(vinylamide-*co*-diallyldimethylammonium chloride) by free radical polymerization.

Originality: Ongoing 4-year investigation by this group.

Application: Paper additive

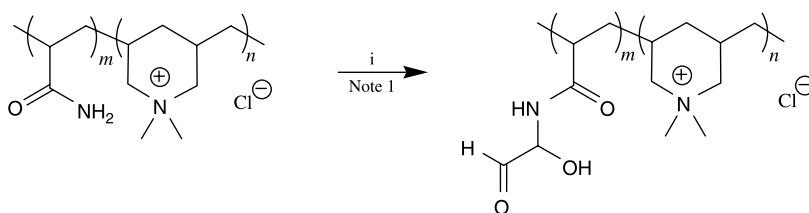
Observations: Although paper-strengthening additives have previously been prepared consisting of:

- i. Blends of polyvinylamide, polydiallyldimethylammonium chloride, and glyoxal
- ii. Glyoxalated poly(vinylamide-*co*-diallyldimethylammonium chloride) crosslinked with *N,N'*-methylene bisacrylamide
- iii. Glyoxalated poly(vinylamide-*co*-diallyldimethylammonium chloride) containing 80% vinylamide

storage stability of these consumer paper products is limited. To address this concern, glyoxalated poly(vinylamide-*co*-diallyldimethylammonium chloride) containing 91% vinyl amide was prepared in two steps and used as a storage-stable paper-strengthening additive. The method for its

preparation entailed the free radical polymerization of vinylamide and diallyldimethyl ammonium chloride and then postreacting with glyoxal in the presence of sodium hydroxide. The preparation of these cellulose reactive adducts was performed slightly below the critical micelle concentration so that the risk of gelation was minimized and the amount of incorporated glyoxal was optimized.

REACTION



i. Water, glyoxal, sodium hydroxide

EXPERIMENTAL

1. Preparation of glyoxalated poly(vinylamide-*co*-diallyldimethylammonium chloride)

An aqueous solution of poly(vinylamide-*co*-diallyldimethylammonium chloride) consisting of 91 wt% acrylamide was treated with sufficient glyoxal so that an amide/glyoxal molar ratio of 4:1, respectively, was obtained. Thereafter the mixture was treated with the dropwise addition of 5 wt% aqueous sodium hydroxide until the pH of the solution reached 9.2. Small additions of sodium hydroxide were administered as needed to maintain a constant pH of 9.2 for 30 minutes.

TESTING

Critical Micelle Concentration

To enhance the shelf life of finished paper product, the step 1 product was applied below its critical micelle concentration (CMC). Materials additized above the CMC formed insoluble gels when aged for 8 days at 73°C. The CMC ranges was determined using glyoxalated poly(vinylamide-*co*-diallyldimethyl-ammonium chloride) containing 90 wt% vinylamide and are provided in Table 1.

Tensile Strength

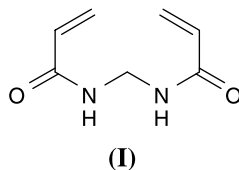
Tensile strength testing was performed using 0.05 wt% of selected experimental agents on dry cellulose. Testing results are provided in Table 1.

TABLE 1. Critical Micelle Concentration and Tensile Strength Testing Results for Glyoxalated Poly(vinylamide-*co*-diallyldimethylammonium chloride)

Entry	M_n (1×10^5 Da)	CMC Concentration Range (%)	Tensile Strength (kg/mm ²)
B	1.60×10^5	0.6–0.8	8.59
E	1.40×10^5	1.5–1.75	9.34
G	1.30×10^4	3.2–3.6	9.14
None	—	—	8.55
Comparison	1.00×10^4	—	8.99

NOTES

1. Poly(vinylamide-*co*-diallyldimethylammonium chloride) was prepared according to the method of Coscia et al. (1).
2. Blends of polyvinylamide, polydiallyldimethylammonium chloride, and glyoxal were previously prepared by Ballweber et al. (2) and used as paper fiber additives.
3. Glyoxalated poly(vinylamide-*co*-diallyldimethylammonium chloride) containing 80% vinylamide content and having a molecular weight of 1900 Da was previously prepared by Guerro et al. (3) and used as handsheet additives.
4. Glyoxalated copolymers consisting of acrylamide and diallyldimethylammonium chloride crosslinked with *N,N'*-methylene bisacrylamide, **(I)**, were prepared by Hagiopol et al. (4) and used as paper-strengthening agents.



References

1. A.S. Coscia et al., U.S. Patent 3,556,932 (January 17, 1971).
2. E.G. Ballweber et al., U.S. Patent 4,217,425 (August 12, 1980).
3. G.J. Guerro et al., U.S. Patent 4,605,702 (August 12, 1986).
4. C. Hagiopol et al., U.S. Patent Application 20050187356 (August 25, 2005).

I. Polymeric Additives

1. Anticraze agent

a. 1,2,4,5-Benzenetetracarboxylic anhydride amic acid

Title: Beta-crystalline Polypropylenes

Author: Qinggao Ma et al.

Assignee: Chemtura Corporation (Middlebury, CT)

U.S. Patent Application: 20070293609 (December 20, 2007)

Material Patentability: Moderate

Anticipated Issuing Date: Late 2009

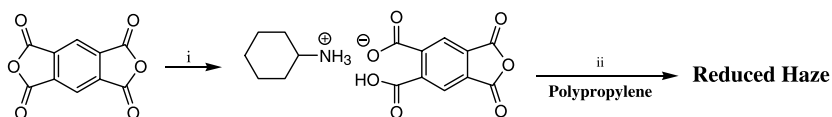
Research Focus: Preparation of high-clarity, low-craze polypropylene with improved thermal properties.

Originality: The use of imide additives to reduce haze in polypropylene is unreported in the patent literature.

Application: Preparation of transparent polypropylene films

Observations: The reaction product of 1,2,4,5-benzenetetracarboxylic anhydride and cyclohexyl amine has been determined to be effective in reducing haze for extruded polypropylene. When an amic acid intermediate was dry blended with polypropylene powder and extruded at 239°C using a small co-rotating twin-screw extruder, produced the insite generate imide reduced crystallinity associated with reduced haze.

REACTION



- i. Cyclohexylamine, xylene
- ii. Heat, propylene

EXPERIMENTAL

1. Preparation of amic acid intermediate

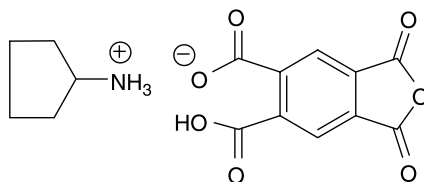
At ambient temperature a reaction flask charged with cyclohexylamine (240.69 mmol) dissolved in 50 ml of xylene was added to a second flask containing 1,2,4, 5-benzenetetracarboxylic anhydride (229.23 mmol) dissolved in 100 ml of xylene. The reaction was exothermic and a white solid then precipitated out upon mixing. Thereafter, the mixture was stirred at ambient temperature for 2 hours, filtered, and the precipitate washed with xylene. After being dried under vacuum the product was isolated as a white powder.

2. Polypropylene blending with amic acid intermediate

A mixture consisting of powdered polypropylene (59.91 g) and the step 1 product (90 mg) were tumble-mixed in a glass container for 24 hours. Thereafter the mixture (4.5 g) was compounded at 239°C using a small co-rotating twin-screw extruder. The sample required 4 minutes at a screw speed of 40 rpm to be prepared. The extruded material only had a slight haze content.

DERIVATIVES

A second amic acid derivative was prepared and is illustrated below.



TESTING

A. Optical Characterization

Transmission, clarity, and haze were measured with a haze-guard plus instrument at ambient temperature according to ASTM D-1003 protocol. Testing results are provided in Table 1.

TABLE 1. Effect of Selected Additives on Crystallinity and Haze of Extruded Polypropylene

Component	T_{cryst} (°C)	Haze (%)
None	107.2	33.5
Nucleating agent ^a	120.33	39.2
Hyperfoam HPN 68L	123.35	30.7
Cyclopentyl amic acid derivative	121.52	47.4
Cyclohexyl amic acid derivative	123.14	25.4

^a1,3:2,4-Bis(3,4-dimethylbenzylidene)sorbitol.

B. Crystallinity Determination

Crystallinity was determined using differential scanning calorimetry. About 5–10 mg of an experimental agent was heated from 25 to 200°C at a heating rate of 20°C/minute. The sample was isothermed at 200°C for 1 minute and then cooled at a cooling rate of 20°C/minute to ambient temperature. Crystallization data represents peak temperatures of exotherms in the cooling cycle and are summarized in Table 1.

NOTES

1. Jaaskelainen et al. (1) reports that polypropylene containing 3.3%, 3.7%, and 5–6% ethylene content were visbroken with Triganox 101 using a twin-screw lab extruder BF-50 and haze levels of less than five observed.
2. Stevens et al. (2) observed that the haze content of poly(ethylene-co-[isotactic]-propylene) was directly related to the monomer content and whether the material was prepared using a metallocene catalyst. Low haze values were obtained for polymers prepared using nonmetallocene catalytic agents with polymers having moderately high ethylene levels.
3. Jaaskelainen et al. (3) demonstrated that polypropylene does not strictly fractionate according to tacticity but according to the longest crystallizable sequence in the chain. It was observed that polypropylene containing random amounts of 4.5% to 12.0 mol% ethylene using temperature rising elution fractionation isolated materials had high transparency, low haze, and high gloss with crystallinity greater than 21%.

4. Trexler et al. (4) report that when unmodified polyethylene terephthalate was additized with the nucleator nylon-6,6 and passed through a single-screw extruder at 280°C, crystallization rates were 50% faster.

References

1. P. Jaaskelainen et al., U.S. Patent Application 20070287818 (December 13, 2007).
2. J.C. Stevens et al., U.S. Patent Application 20070249798 (October 25, 2007).
3. P. Jaaskelainen et al., U.S. Patent Application 20070203309 (August 30, 2007) and U.S. Patent Application 20070197743 (August 23, 2007).
4. J.W. Trexler, Jr et al., U.S. Patent 7,279,124 (October 9, 2007).

2. Polymeric Dispersants

a. Polyaromatic ester amides

Title: Preparation of Polyamide Block Copolymers

Author: David T. Williamson et al.

Assignee: E I DuPont De Nemours and Company (Wilmington, DE)

U.S. Patent Application: 20070293629 (December 20, 2007)

Material Patentability: Very high

Anticipated Issuing Date: Mid-2009

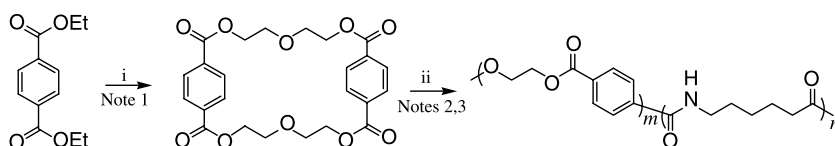
Research Focus: Method of preparing random poly(amide-*b*-ester) derivatives through depolymerization/repolymerization of cyclic polyesters then co-reacting with lactam derivatives using a nonmetallic carbene catalyst.

Originality: This method for preparing polyester amides is unreported.

Application: Polymeric dispersants

Observations: Poly(amide-*b*-ester) was prepared in two steps. Initially cyclic poly(diethyleneglycol terephthalate) was depolymerized and then repolymerized into its linear counterpart in the absence of a metallic catalyst. Once the polymerization was completed, it was co-polymerized with ϵ -caprolactam producing poly(nylon-6-*b*-diethyleneglycol terephthalate) using 1,3-di-1-adamantyl-imidazole-2-ylidene as the reaction catalyst. The copolymer had a block content of 85.8% with a molecular weight of 31,500 Da. This is the first instance in the patent literature where a nonmetallic *N*-heterocyclic carbene has been used as a catalyst in a polymerization reaction. ¹H-NMR computational methods for determining the presence of monad, diads, triads, and so forth. content was also developed.

REACTION



- i. Diethylene glycol, toluene, Novozyme 435
- ii. Caprolactam, 1,3-di-1-adamantyl-imidazole-2-ylidene, toluene

EXPERIMENTAL

1. Preparation of cyclic poly(diethyleneglycol terephthalate)

A 22-liter resin kettle was charged with 9.246 liters of toluene, diethylene glycol (2.50 mol), and dimethylterephthalate (2.50 mol) then heated to 80°C and treated with Novozyme 435. After heating and sparging the mixture for 24 hours at 80°C, toluene was distilled from the mixture at 70°C @ 50 torr. The resulting solids were divided into three equal portions and extracted with 11 liters of refluxing chloroform for 3 hours. The hot chloroform extract was then filtered to remove the enzyme catalyst and the filtrate concentrated to about 3.5 liters. The solution was then cooled to ambient temperature, refiltered, and the product isolated as a white solid in 83% yield with 99% purity.

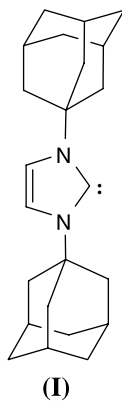
2. Preparation of poly(nylon-6-block-diethyleneglycol terephthalate)

A mixture of 1,3-di-1-adamantyl-imidazole-2-ylidene (45 mg) and caprolactam (454 mg) were heated at 230°C for 15 minutes. After cooling the number-average molecular weight was determined to be 31,500 Da with a polydispersity of 3.4 and with 86% product conversion. This material was then treated with the step 1 product (948 mg) and heated at 230°C for 30 minutes. Gas-phase chromatography (GPC) analysis indicated that the product had an M_n of 24,700 Da with a polydispersity of 3.4 and an 83% reaction conversion. The block incorporation in the polymer was 85.8%.

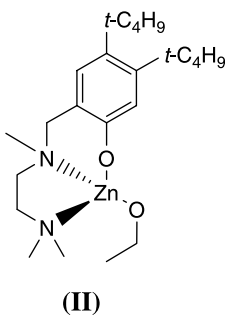
NOTES

1. The IUPAC name for the step 1 product is 3,6,9,16,19,22-hexaoxatricyclo [22.2.2.2.11,14]-triaconta-11,13,24,26,27,29-hexaene-2,10,15,23-tetrone.
2. A model reaction where both reagents and catalyst Novozyme 435 were reacted together was also performed. The model reaction product had an M_n of 17,200 Da with a polydispersity of 1.7 and had 76.3% random monomer incorporation.
3. The use of the step 2 carbene reagent catalyst, 1,3-di-1-adamantyl-imidazole-2-ylidene, (**I**), in preparing macrocyclic polyester oligomers is described by

Tam et al. (1). Ring-opening polymerization of cyclic amides using this agent are also reported by Tam et al. (2).



4. Depolymerization of macromolecular esters and repolymerization into linear polyesters is reported by Zhang et al. (3) using zinc alkoxide catalyst, (II).



References

1. W. Tam et al., U.S. Patent Application 20070252311 (November 1, 2007) and U.S. Patent Application 20060128935 (June 15, 2006).
2. W. Tam et al., U.S. Patent Application 20060100365 (May 11, 2006) and U.S. Patent Application 20060096699 (May 11, 2006).
3. D. Zhang et al., U.S. Patent Application 20070083019 (April 12, 2007).