(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
17 October 2019 (17.10.2019)

WIPO | PCT

(10) International Publication Number
WO 2019/199752 A1

(51) International Patent Classification:
C07C 57/52 (2006.01) *C08L 31/02* (2006.01)
C08F 214/20 (2006.01) *C08L 31/04* (2006.01)
C08F 214/22 (2006.01)

(21) International Application Number:
PCT/US2019/026490

(22) International Filing Date:
09 April 2019 (09.04.2019)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/655,453 10 April 2018 (10.04.2018) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:
- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) Title: FUNCTIONAL FLUOROPOLYMERS

(57) Abstract: The invention relates to novel linear, semi-crystalline, functional fluoropolymers that have been obtained by copolymerizing a fluorinated vinylic monomer and a hydrophilic (meth)acrylic comonomer bearing a halogen functionality.

FUNCTIONAL FLUOROPOLYMERS

FIELD OF THE INVENTION

[0001] The invention relates to novel linear, semi-crystalline, functional fluoropolymers that have been obtained by copolymerizing a fluorinated vinylic monomer and a hydrophilic (meth)acrylic comonomer bearing a halogen functionality. At most 10.0 weight percent of the (meth)acrylic comonomer units are present in the copolymer as single monomer units between two fluoromonomer units. The invention also relates to a process for forming the fluoromonomers/(meth)acrylic copolymer.

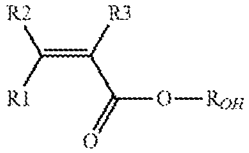
BACKGROUND OF THE RELATED ART

[0002] Fluoropolymers are traditionally used for applications requiring special properties, such as low surface energy, high resistance to chemical attack, aging resistance, and electrochemical stability. However, these advantageous properties also make fluoropolymers difficult to work with and limits their applications. For example, the lack of functional groups on the fluoropolymers makes them difficult: to adhere to substrates, to facilitate cross-linking, to provide sites for subsequent chemical modification, to be wetted by water, and to add hydrophilic characteristics. There is a need for fluorinated polymers having modified properties, such as functional groups, which can augment their properties.

[0003] However it is difficult to add functional monomer units directly into the polymerizing polymer backbone, especially in a random manner, due to the aggressive nature of the fluorine-containing free radicals. Functionality has been added by several means, such as, by direct copolymerization of a functional monomer with the fluoromonomers, and by a post-polymerization grafting mechanism, such as the grafting of maleic anhydride onto a polyvinylidene fluoride homopolymer or copolymer, as described in US 7,241,817, to form KYNAR® ADX resins available from Arkema Inc. (Pennsylvania, USA). WO 2013/110740 and US 7,351,498 further describe functionalization of a fluoropolymer by monomer grafting or by copolymerization.

[0004] US 5,415,958 discloses copolymerization of vinylidene fluoride with an unsaturated dibasic acid monoester polar monomer, to introduce carbonyl groups to the backbone of PVDF in order to improve its adhesion to different substrates.

[0005] US 8,337,725 discloses copolymerization of vinylidene fluoride with at least one hydrophilic (meth)acrylic monomer of formula:



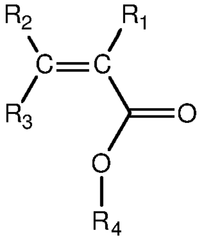
[0006] wherein each of R1, R2, R3, equal or different from each other, is independently a hydrogen atom or a C_1-C_3 hydrocarbon group, and R_{OH} is a hydrogen or a C_1-C_5 hydrocarbon moiety comprising at least one hydroxyl group.

[0007] There is a need to further improve the adhesion performance of fluorinated polymers.

[0008] The art is silent as to functional fluoropolymers obtained by copolymerizing a fluorinated vinylic monomer and a hydrophilic (meth)acrylic comonomer bearing a halogen functionality, that allow for improved adhesion to a substrate, when compared to the non-functional fluoropolymer, while maintaining good mechanical and thermal properties.

BRIEF SUMMARY OF THE INVENTION

[0009] The invention relates to a fluorinated copolymer comprising a fluorinated vinylic monomer and a halogenated monomer (1):



Monomer (1)

wherein:

R_1, R_2, and R_3 is a hydrogen or a halogen (F, Cl, Br, I), and at least one is a halogen;

R_4 is hydrogen, a C_1 to C_{16} linear, branched, aryl, or cycloalkyl group, a C_1 to C_{16} fluorinated linear, branched, aryl or cycloalkyl group, a fluorinated oligomer of hexfluoropropylene oxide, an alkali metal (lithium, sodium, potassium, rubidium, cesium), ammonium, alkylammonium, or alkylarylammonium ion.

[0010] The invention further relates to a formulation comprising the fluorinated copolymer in a solvent, and may further comprise conductive carbon additives and active material particles. Active materials for lithium ion battery cathode formulation include, but are not limited to: lithium iron phosphate (LFP), lithium nickel manganese cobalt oxide (NMC), lithium-manganese-cobalt-oxide (LCO), lithium-nickel-cobalt-aluminum oxide (NCA), lithium-manganese oxide (LMO), lithium-nickel-manganese-oxide (LNMO), and lithium manganese iron phosphate (LMFP). Active materials for anode formulation include, but are not limited to graphite, hard carbon, soft carbon, graphene, silicon, silicon monoxide (SiO), tin, or lithium titanate (LTO).

[0011] The invention further contemplates a process for preparing the fluorinated copolymer in an aqueous reaction medium, comprising:

a) forming an aqueous emulsion comprising at least one initiator, a stabilizer, at least one fluoromonomer, and a halogenated monomer (1) as defined above,

b) initiating copolymerization of said at least one fluoromonomer with said halogenated monomer (1) with stirring, under heat and super-atmospheric pressure.

[0012] The invention further relates to articles formed from the fluorinated copolymer, which benefit from the special properties of the functional copolymer. These articles find uses in applications such as for: an electrode or separator for a battery or capacitor; a hydrophilic porous membrane or hollow fiber membrane; an article coated on at least one surface with said functional fluoropolymer, impregnation of woven and unwoven fibers, and a multi-layer construction wherein said functional fluoropolymer forms a tie layer between a fluoropolymer layer and a polymer layer that is incompatible with said fluoropolymer layer.

[0013] "Copolymer" is used to mean a polymer having two or more different monomer units. "Polymer" is used to mean both homopolymer and copolymers. Polymers may be straight chain, branched, star comb, block, or any other structure. The polymers may be homogeneous, heterogeneous, and may have a gradient distribution of co-monomer units. All references cited are incorporated herein by reference. As used herein, unless otherwise described, percent shall mean weight percent. Unless otherwise stated, molecular weight is a weight average molecular weight as measured by GPC, using a polymethyl methacrylate standard. In cases where the polymer contains some cross-linking, and GPC cannot be applied due to an insoluble polymer fraction, soluble fraction/ gel fraction or soluble faction molecular weight after extraction from gel is used.

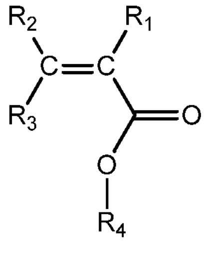
Crystallinity and melting temperature are measure by DSC as described in ASTM D3418 at heating rate of 10 C/min. Melt viscosity is measured in accordance with ASTM D3835 at 230°C expressed in k Poise @100 Sec^(-1)

DETAILED DESCRIPTION OF THE INVENTION

[0014] Fluoropolymers, particularly poly(vinylidene fluoride) (PVDF) and its copolymers, find application as the binder in electrode articles used in lithium ion batteries. As the demand for greater energy density and battery performance intensifies, the need for reduction of the binder content in the electrodes has increased. To reduce the binder content, it is paramount to increase the performance of the binder material. One key binder performance matrix is determined by an adhesion test whereby a formulated electrode is subjected to a peel test. Improved binding performance increases the potential to reduce the overall binder loading, increasing active material loading and improving battery capacity and energy density. It has been shown that copolymers of fluorinated vinylic monomers with acid-functional comonomers lead to adhesion performance improvement. These approaches have also suffered from low reaction productivity, and difficulty to supply sufficient quantities of material to a rapidly-growing market. Here, we present a new copolymer and process with vastly improved productivity.

[0015] The functional fluoropolymers provide enhanced properties compared to the fluoropolymer, such as increased adhesion and hydrophilic characteristics. The fluoropolymer of the invention may be used in applications benefiting from a functional fluoropolymer including as binders in electrode-forming compositions and separator compositions, or in forming hydrophilic membranes and hollow fibers.

[0016] The invention solves the above-cited problems by providing a fluorinated copolymer comprising a fluorinated vinylic monomer and a monomer (1):



Monomer (1)

wherein:

- R_1, R_2, and R_3 is a hydrogen or a halogen (F, Cl, Br, I), and at least one is a halogen;
- R_4 is hydrogen, a C_1 to C_{16} linear, branched, aryl, or cycloalkyl group, a C_1 to C_{16} fluorinated linear, branched, aryl or cycloalkyl group, a fluorinated oligomer of hexfluoropropylene oxide, an alkali metal (lithium, sodium, potassium, rubidium, cesium), ammonium, alkylammonium, or alkylarylammonium ion.

[0017] The fluorinated vinylic monomer is selected from the group comprising: vinylidene fluoride (VDF), tetrafluoroethylene (TFE), trifluoroethylene (TrFE), chlorotrifluoroethylene (CTFE), hexafluoropropene (HFP), vinyl fluoride (VF), hexafluoroisobutylene (HFIB), perfluorobutylethylene (PFBE), pentafluoropropene, 3,3,3-trifluoro-1-propene, 2-trifluoromethyl-3,3,3-trifluoropropene, 2,3,3,3-tetrafluoropropene, fluorinated vinyl ethers including perfluoromethyl ether (PMVE), perfluoroethylvinyl ether (PEVE), perfluoropropylvinyl ether (PPVE), perfluorobutylvinyl ether (PBVE), longer alkyl chain perfluorinated vinyl ethers, fluorinated dioxoles, partially- or per-fluorinated alpha olefins of C4 and higher, partially- or per-fluorinated cyclic alkenes of C3 and higher, and combinations thereof.

[0018] The functional copolymer according to the invention is further characterized by the following embodiments.

[0019] According to one embodiment, the fluorinated copolymer comprises up to 10 wt % of Monomer (1), preferably 0.001 to 10.0 wt%, preferably from 0.01 to 10.0wt% of Monomer (1) and 90.0 to 99.99wt% of fluorinated vinylic monomer.

[0020] According to one embodiment, the fluorinated copolymer comprises vinylidene fluoride and Monomer (1).

[0021] According to one embodiment, the fluorinated copolymer comprises vinylidene fluoride and Monomer (1), wherein R_1 is fluorine.

[0022] According to one embodiment, the fluorinated copolymer comprises vinylidene fluoride and Monomer (1), wherein R_1 is fluorine and R_4 is C_1 to C_{16} linear, branched or cycloalkyl group.

[0023] According to one embodiment, the fluorinated copolymer comprises vinylidene fluoride and Monomer (1), wherein R_1 and R_2 are fluorine and R_4 is C_1 to C_{16} linear, branched or cycloalkyl group.

[0024] According to one embodiment, the fluorinated copolymer comprises vinylidene fluoride and Monomer (1), wherein R_1, R_2 and R_3 are fluorine and R_4 is C_1 to C_{16} linear, branched or cycloalkyl group.

[0025] According to one embodiment, the fluorinated copolymer comprises vinylidene fluoride and Monomer (1), wherein R_1 is fluorine and R_4 is hydrogen or an alkali metal, ammonium, or alkylammonium.

[0026] According to one embodiment, the fluorinated copolymer comprises vinylidene fluoride and Monomer (1), wherein R_1 and R_2 are fluorine and R_4 is hydrogen or an alkali metal, ammonium, or alkylammonium.

[0027] According to one embodiment, the fluorinated copolymer comprises vinylidene fluoride and Monomer (1), wherein R_1, R_2 and R_3 are fluorine and R_4 is hydrogen or an alkali metal, ammonium, or alkylammonium.

[0028] According to one embodiment, Monomer (1) is randomly copolymerized as determined by nuclear magnetic resonance (^{19}F NMR and ^{1}H NMR) of Monomer (1).

[0029] The invention further relates to a formulation comprising the fluorinated copolymer in a solvent. The solvent is preferably chosen from: n-methylpyrrolidone (NMP), dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), triethylphosphite (TEP), acetone, tetrahydrofuran, methyl ethylketone (MEK), methyl isobutyl ketone (MiBK), ethyl acetate (EA), butyl acetate (BA), ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC) or ethyl methyl carbonate (EMC).

[0030] According to one embodiment, the formulation further comprises conductive carbon additives and active material particles in suspension in said solvent.. Such formulation is particularly suitable for forming battery electrode films, notably positive (cathode) electrode or negative (anode) electrod for a lithium ion battery. Active material for lithium ion battery cathode formulation can be selected from the group, not limiting to, lithium iron phosphate (LFP), lithium nickel manganese cobalt oxide (NMC), lithium-manganese-cobalt-oxide (LCO), lithium-nickel-cobalt-aluminum oxide (NCA), lithium-manganese oxide (LMO), lithium-nickel-manganese-oxide (LNMO) , and lithium manganese iron phosphate (LMFP). Active material for anode formulation can be from graphite, hard carbon, soft carbon, graphene, silicon, silicon monoxide (SiO), tin, or lithium titanate (LTO). The invention encompasses a battery comprising the fluorinated copolymer described herein.

[0031] The invention further contemplates a process for preparing the fluorinated copolymer in an aqueous reaction medium, comprising:

a) forming an aqueous emulsion comprising at least one initiator, a stabilizer, at least one fluorinated vinylic monomer, and a halogenated monomer (1) as defined above,

b) initiating copolymerization of said at least one fluorinated vinylic monomer with said halogenated monomer (1) with stirring, under heat and super-atmospheric pressure.

[0032] A polymerization reaction in accordance with the present invention may be carried out by charging a reactor with water (preferably deionized water), at least one fluorinated vinylic monomer, at least one halogenated Monomer (1) as defined above and optionally, one or more of a surfactant, a chain-transfer agent and/or an antifoulant. Air may be purged from the reactor prior to the introduction of the fluoromonomer. Water is added to the reactor before bringing the reactor to the desired starting temperature, but the other materials may be added before or after bringing the reactor to temperature. At least one radical initiator is added to start and maintain the polymerization reaction. Additional vinylic fluoromonomer(s) and/or additional functional monomer (Monomer 1) may be optionally added to replenish monomer that is consumed, and the other materials may be optionally added during the course of the polymerization to maintain the reaction and control the final product properties. In a typical embodiment, all monomer components will be fed at a controlled ratio (to each other) to maintain reaction pressure

Monomer (1)

[0033] The structure of Monomer (1) is detailed above.

[0034] The Monomers (1) comonomers may be used in the reactor in an amount, for example, of from about 0.001 to about 15 weight percent, preferably from about 0.01 to about 15 weight percent based on total monomer. Preferably they are used in an amount from about 0.001 to about 10 weight percent, preferably 0.01 to about 10 weight percent based on total monomer. In various embodiments, the total amount of hydrophilic monomer(s) is at least 0.001, at least 0.01, at least 0.05, at least 0.1, at least 1.0 or at least 2.0 weight percent based on total monomer. In other embodiments, the total amount of hydrophilic monomer does not exceed 13.0, 10.0, 9.0, 7.0, 6.0, 5.0 weight percent based on total monomer. The hydrophilic (meth)acrylic comonomer (Monomer (1)) may be used in solution such as in aqueous solution for convenient handling.

[0035] In one embodiment, two or more different functional acrylates was found to provide increased adhesion. While not being bound by any particular theory, it is believed that different functionalities, for example an alcohol and acid functionality, could react or crosslink to form ester groups. The two or more different functionalities preferably are present in the same terpolymer, but could also be a blend of two or more different copolymers.

Surfactants

[0036] The surfactant used in the polymerization can be any surfactant known in the art to be useful in PVDF emulsion polymerization, including perfluorinated, partially fluorinated, and non-fluorinated surfactants. In a preferred embodiment, the PVDF emulsion of the present disclosure can be fluorosurfactant free, with no fluorosurfactants being used in any part of the polymerization. Non-fluorinated surfactants useful in the PVDF polymerization could be both ionic and non-ionic in nature including, but are not limited to, 3-allyloxy-2-hydroxy-1-propane sulfonic acid salt, polyvinylphosphonic acid, polyacrylic acids, polyvinyl sulfonic acid, and salts thereof, polyethylene glycol and/or polypropylene glycol and the block copolymers thereof, alkyl phosphonates and siloxane-based surfactants.

[0037] Surfactants can also be used in combination with hydrophilic (meth)acrylic comonomer to provide further stability to the polymer emulsion. Preferred surfactants are non-fluorinated hydrocarbon surfactants, siloxane surfactants or a combination thereof. For example a hydrophilic (meth)acrylic comonomer can be used in combination with sodium dodecyl benzene sulfonate (SDDBS), sodium octyl sulfonate, sodium lauryl sulfate, ammonium lauryl sulfate, or sodium laureth sulfate, among others. In certain embodiments of the invention, no fluorosurfactant is present in the aqueous emulsion and/or no fluorosurfactant is introduced during copolymerization of the fluorinated vinylic monomer with the hydrophilic (meth)acrylic comonomer. In one embodiment, the stabilizer is a polyelectrolyte. In another embodiment, the stabilizer of the polymer emulsion is a functionalized cellulose.

Initiators

[0038] The term "initiator" and the expressions "radical initiator" and "free radical initiator" refer to a chemical that is capable of providing a source of free radicals, either induced spontaneously, or by exposure to heat or light. Examples of suitable initiators include peroxides, peroxydicarbonates and azo compounds. “Initiators” also includes redox systems useful in providing a source of free radicals. The term "radical" and the expression "free radical" refer to a chemical species that contains at least one unpaired electron.

[0039] The radical initiator is added to the reaction mixture in an amount sufficient to initiate and maintain the polymerization reaction at a desired reaction rate. The order of addition may vary according to the desired process and latex emulsion characteristics.

[0040] The radical initiator may comprise a persulfate salt, such as sodium persulfate, potassium persulfate, or ammonium persulfate. The amount of persulfate salt added to the reaction mixture (based upon the total weight of monomer added to the reaction mixture) may, for example, be from about 0.002 to about 1.0 weight percent.

[0041] The radical initiator may comprise an organic peroxide such as an alkyl, dialkyl, or diacyl peroxide, peroxydicarbonates, and peroxy esters or mixtures thereof. A preferred dialkyl peroxide is di-tert-butylperoxide (DTBP), which may be added to the reaction mixture in an amount from about 0.01 to about 5 weight percent on total monomer, and is preferably added in an amount from about 0.05 to about 2.5 weight percent on total monomer. Preferred peroxydicarbonate initiators are di-n-propyl peroxydicarbonate and diisopropyl peroxydicarbonate, which may be added to the reaction mixture in an amount from about 0.5 to about 2.5 weight percent on total monomer. Peroxy ester initiators include tert-amyl peroxypivalate, tertbutyl peroxypivalate, and succinic acid peroxide.

[0042] The radical initiator may comprise an azo initiator, such as 2,2'- azobis(2 methyl-propionamidine)dihydrochloride.

[0043] The radical initiator may comprise a redox system. By "redox system" is meant a system comprising an oxidizing agent, a reducing agent and optionally, a promoter as an electron transfer medium. Oxidizing agents include, for example, persulfate salts; peroxides, such as hydrogen peroxide; hydroperoxides such as tert-butyl hydroperoxide and cumene hydroperoxide; and oxidizing metal salts such as, for example, ferric sulfate. Reducing agents include, for example, sodium formaldehyde sulfoxylate, sodium and potassium sulfite, ascorbic acid, bisulfite, metabisulfite, and reduced metal salts. The promoter is a component of the redox system which, in different oxidation states, is capable of reacting with both the oxidant and the reducing agent, thereby accelerating the overall reaction. Promoters include, for example, transition metal salts such as ferrous sulfate. In redox systems, the oxidizing agent and the reducing agent may be utilized in an amount from about 0.01 to about 0.5 weight percent on total monomer. The optional promoter may be utilized in an amount from about 0.005 to about 0.025 weight percent on total monomer. Redox systems are described in G.S. Misra and U.D.N. Bajpai, *Prog. Polym. Sci.,* 1982, 8(1-2), pp. 61-131.

Chain-Transfer Agents

[0044] Chain-transfer agents are added to the polymerization to regulate the molecular weight of the product. They may be added to a polymerization in a single portion at the beginning of the reaction, or incrementally or continuously throughout the reaction. The amount and mode of addition of chain-transfer agent depend on the activity of the particular chain transfer agent employed, and on the desired molecular weight of the polymer product. The amount of chain-transfer agent added to the polymerization reaction is preferably from about 0.05 to about 5 weight percent, more preferably from about 0.1 to about 2 weight percent based on the total weight of monomer added to the reaction mixture.

[0045] Oxygenated compounds such as alcohols, carbonates, ketones, esters, and ethers may serve as chain-transfer agents. Examples of oxygenated compounds useful as chain-transfer agents include isopropyl alcohol, as described in U.S. Patent 4,360,652. Other classes of compounds which may serve as chain-transfer agents in the polymerization of halogen-containing monomers include, for example, halocarbons and hydrohalocarbons, such as chlorocarbons. Alkanes such as ethane and propane may also function as chain-transfer agents.

Buffering Agent

[0046] The polymerization reaction mixture may optionally contain a buffering agent to maintain a controlled pH throughout the polymerization reaction. The pH is preferably controlled within the range of from about 4 to about 8, to minimize undesirable color development in the product.

[0047] Buffering agents may comprise an organic or inorganic acid or alkali metal salt thereof, or base or salt of such organic or inorganic acid, that has at least one pK_a value and/or pK_b value in the range of from about 4 to about 10, preferably from about 4.5 to about 9.5. Preferred buffering agents in the practice of the invention include, for example, phosphate buffers and acetate buffers. A "phosphate buffer" is a salt or a mixture of salts of phosphoric acid. An "acetate buffer" is a salt of acetic acid.

[0048] Buffering agents are preferably employed where potassium persulfate is employed as the radical initiator. A preferred buffering agent for use with persulfate radical initiators is sodium acetate. A preferred amount of sodium acetate buffer is from about 50 wt.% to about 150 wt.%, based on the weight of persulfate initiator added to the reaction. In one preferred embodiment, the initiator feed comprises approximately equal weights of potassium persulfate and sodium acetate in aqueous solution.

Antifoulant

[0049] The addition of a paraffin wax or hydrocarbon oil to the reaction serves as an antifoulant to minimize or prevent polymer adhesions to the reactor components. Any long chain saturated hydrocarbon wax or oil can perform this function. The amount of oil or wax added to the reactor is an amount which serves to minimize the formation of polymer adhesions on the reactor components. The amount is generally proportional to the interior surface area of the reactor and may vary from about 1 to about 40 mg per square centimeter of reactor interior surface area. The amount of paraffin wax or hydrocarbon oil is preferably about 5 mg/cm^2 of the reactor interior surface area.

Co-Polymerization Conditions

[0050] The temperature used for polymerization may vary, for example, from 20-130 degrees Celsius, depending on the initiator system chosen. The polymerization temperature is preferably from 35-130 degrees Celsius, and most preferably from 70-125 degrees Celsius.

[0051] The pressure used for polymerization may vary from 280-20,000 kPa, depending on the capabilities of the reaction equipment, the initiator system chosen, and the monomer selection. The polymerization pressure is preferably from 2,000-11,000 kPa, and most preferably from 2,750-6,900 kPa.

[0052] The polymerization occurs under stirring or other agitation. The stirring/agitation may be constant, or may be varied to optimize process conditions during the course of the polymerization. In one embodiment, both multiple stirring speeds and multiple temperatures are used for controlling the reaction.

[0053] According to one embodiment of the process of the invention, a pressurized polymerization reactor equipped with a stirrer and heat control means is charged with water, preferably deionized water, one or more halogenated monomers (1) and at least one fluorinated vinylic monomer. The mixture may optionally contain one or more of a surfactant, a buffering agent, an antifoulant or a chain-transfer agent for molecular weight regulation of the polymer product.

[0054] Prior to introduction of the monomer or monomers, air is preferably removed from the reactor in order to obtain an oxygen-free environment for the polymerization reaction.

[0055] The order in which the polymerization components are assembled may be varied, although it is generally preferred that at least a portion of the Monomer (1) is present in the aqueous reaction medium prior to the initiation of the polymerization of the fluorinated vinylic monomer. An additional amount of Monomer (1) may be fed to the reactor during the reaction.

[0056] In one embodiment, water, initiator, Monomer (1) and optionally surfactant, antifoulant, chain transfer agent and/or buffer are charged to the reactor, and the reactor heated to the desired reaction temperature. The fluorinated vinylic monomer(s) is(are) then fed into the reactor, preferably at a rate which provides an essentially constant pressure.

[0057] Alternatively the fluorinated vinylic monomer, Monomer (1) and initiator can be fed to the reactor, along with one or more of the optional ingredients. Other variations for fluoropolymer copolymerization processes are contemplated, as known in the art.

[0058] The monomer feed is terminated when the desired weight of monomer has been fed to the reactor. Additional radical initiator is optionally added, and the reaction is allowed to react out for a suitable amount of time. The reactor pressure drops as the monomer within the reactor is consumed.

[0059] Upon completion of the copolymerization reaction, the reactor is brought to ambient temperature and the residual unreacted monomer is vented to atmospheric pressure. The aqueous reaction medium containing the copolymer is then recovered from the reactor as a latex. The latex consists of a stable mixture of the reaction components, i.e., water, Monomer (1), initiator (and/or decomposition products of the initiator) and copolymer solids.

[0060] Generally, the latex contains from about 10 to about 50 weight percent copolymer solids. The polymer in the latex may be in the form of small particles having a size range of from about 30 nm to about 800 nm.

Product Handling

[0061] The product of the copolymerization is a latex which can be used in that form, usually after filtration of solid byproducts from the polymerization process, or which can be coagulated to isolate the solids, which may then be washed and dried. For use in latex form, the latex can be stabilized by the addition of a surfactant, which may be the same as or different from the surfactant present during polymerization (if any). This later added surfactant may, for example, be an ionic or non-ionic surfactant. In one embodiment of the invention, no fluorosurfactant is added to the latex. For solid product, the latex may be coagulated mechanically or by the addition of salts or acids, and then isolated by well-known means such as by filtration. Once isolated, solid product can be purified by washing or other techniques, and it may be dried for use as a powder, which can be further processed into granules, pellets or the like.

[0062] In one embodiment, the functional copolymer according to the invention is applied to a substrate, as a latex in water or as a solvent solution, the solvent being chosen among those listed above. Optionally, a primer layer can be applied to the substrate, before the layer of functional copolymer.

[0063] In one embodiment, said substrate is porous, for example a porous membrane.

EXAMPLES

[0064] Cathode formulation and fabrication

[0065] One exemplary cathode slurry preparation procedure for laboratory scale is described here. PVDF copolymer of the invention is first dissolved in N-methylpyrrolidone (NMP) solvent, typically in 5-10wt% concentration. Conductive carbon additive, such as SuperP-Li from Timcal, is added to the binder solution, and mixed using a centrifugal planetary mixer, Thinky AR-310, for 3 repeats of 120s at 2000rpm with 1min air cooling in between. Once the conductive carbon is dispersed in the binder solution, active material such as Celcore® NMC622 (Umicore), and small amount of NMP are added to the mixture, and mixed to form a thick and uniform paste, typically 60s at 2000rpm. Then small amount of NMP is added to the paste and mixed at 60s/2000rpm to gradually reduce the slurry solids (in about 1.5% with each NMP addition) and viscosity. This dilution step is repeated multiple time until the slurry viscosity reaches proper level for coating, typically 3,000-15,000cP @1/s shear rate. A typical formulation for our laboratory cathode is active material/carbon/PVDF=97/1.5/1.5 (wt/wt/wt) on dry basis.

[0066] The cathode slurry is then cast onto aluminum foil (15μm thickness) using adjustable doctor blade on an automatic film applicator (Elcometer 4340). The wet casting is then transferred to a convection oven, and dried at 120C for 30min. After drying, the electrode is calendered using a roll mill (IRM, international roll mill), to a final density of 3.2-3.6 g/cm3, with a typical value of 3.4g/cm3. The typical areal mass loading of the dry cathode is 180-220 g/m2.

[0067] Peel strengths for cathodes were obtained via a 180° peel test using ASTM D903 with three modifications. The first modification was that the extension rate used was 50 mm/minute (peel rate of 25 mm/minute), electrodes were tested one day after fabrication, and the electrode was bonded to the alignment plate using double sided paper tape (3M Company, type 401M) with the flexible aluminum foil current collector peeled affixed in the testing grips.

[0068] NMR Analysis for % Incorporation: Samples solution was prepared at 1wt% concentration in DMSO-d6 with heating at 90C overnight. The 1H and 19F experiments were carried out using a Bruker AV III HD 500 (11.7 T) spectrometer equipped with a 5 mm TXO probe at 50°C. The peaks appearing around -160ppm in the decoupled 19F spectrum (shifted and split vs. authentic poly(methyl 2-fluoroacrylate)) were taken as indicative of the incorporated comonomer and integrated vs. total PVDF signal.

Example 1: To a 2 gallon autoclave were added 3500g of deionized water, 9.2g of low molecular weight poly(acrylic acid) (BASF CP-10S), and 0.5g of methyl 2-fluoroacrylate (MFA). The autoclave was agitated, heated to 100C and pressurized to 650psi with vinylidene fluoride. A 2.0wt% feed of potassium persulfate was started at 2.0mL/min. Upon start of pressure drop, an additional feed of MFA was started at 0.25mL/min. and pressure was maintained by additional VDF feed. Feeds were continued in this fashion, increasing MFA feed rate to moderate instantaneous VDF feed demand to maintain a range of 500-1500g/hr. MFA feed was increased in this fashion up to 1.0mL/min. All feeds were continued until a total of 1650g of VDF had been fed to the reactor, corresponding to 69.6g of MFA. Monomer feeds were stopped and the pressure was allowed to autogenously decrease for 10 minutes at which point the reactor was vented to atmospheric pressure and cooled to room temperature. Latex was discharged from the reactor and dried in a convection oven overnight. 4993g of latex was recovered with solids of 31 wt%.

Example 2: To a 2 gallon autoclave were added 3500g of deionized water, 9.2g of low molecular weight poly(acrylic acid) solution (BASF CP-10S), and 25mL of sodium 2-fluoroacrylate (SFA) as 5.25wt% solution in deionized water. The autoclave was agitated, heated to 100C and pressurized to 650psi with vinylidene fluoride. A 2.0wt% feed of potassium persulfate was started at 2.0mL/min. Upon start of pressure drop, an additional feed of SFA solution was started at 2.0mL/min. and pressure was maintained by additional VDF feed. Feeds were continued in this fashion, increasing SFA feed rate in order to moderate instantaneous VDF feed demand to maintain a range of 500-1500g/hr. SFA solution feed was increased in this fashion up to 10.0mL/min. All feeds were continued until a total of 1650g of VDF had been fed to the reactor, corresponding to 12.45g of SFA solid. Monomer feeds were stopped and the pressure was allowed to autogenously decrease for 10 minutes at which point the reactor was vented to atmospheric pressure and cooled to room temperature. Latex was discharged from the reactor and dried in a convection oven overnight. 6046g of latex was recovered with solids of 31.8wt%.

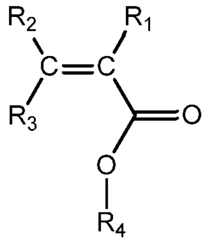
Example 3: An identical procedure as outlined in Example 1 was used except a reaction temperature of 83C was used and total of 1.15% MFA was fed vs. total VDF. Fluid latex was recovered with solids of 33.5 wt%.

Example 4: An identical procedure as outlined in Example 1 was used except a reaction temperature of 83C was used and total of 2.30% MFA was fed vs. total VDF. Fluid latex was recovered with solids of 30.5 wt%.

Example	Comonomer	Initiator Demand (ppm)	Comonomer Feed (vs. VDF total) (%)	Incorporation of comonomer into PVDF (%)	Solution Viscosity (5wt% in NMP)	Electrode Peel Strength (N/m)
HSV-900	None	~900	n/a	n/a	881	18.7
HSV-1800	None	~1500	n/a	n/a	441	22.3
Control	Acrylic Acid	12330	0.86	0.13	196	16.0
1	Methyl 2-fluoroacrylate	4177	4.25	1.1	180	33.3
2	Sodium 2-fluoroacrylate	4251	0.75	n/d	401	19.1
3	Methyl 2-fluoroacrylate	1876	1.15	n/d	311	>30
4	Methyl 2-fluoroacrylate	2737	2.30	n/d	265	>30

What is claimed is:

1. A fluorinated copolymer comprising a fluorinated vinylic monomer and a halogenated monomer (1):



Monomer (1)

wherein:

- R_1, R_2, and R_3 is a hydrogen or a halogen (F, Cl, Br, I), and at least one is a halogen;
- R_4 is hydrogen, a C_1 to C_{16} linear, branched, aryl, or cycloalkyl group, a C_1 to C_{16} fluorinated linear, branched, aryl or cycloalkyl group, a fluorinated oligomer of hexfluoropropylene oxide, an alkali metal (lithium, sodium, potassium, rubidium, cesium), ammonium, alkylammonium, or alkylarylammonium ion.

2. The copolymer of claim 1 comprising up to 10.0wt% of Monomer (1).

3. The copolymer of claim 1, wherein said fluorinated vinylic monomer is vinylidene fluoride.

4. The copolymer of claim 3, wherein R_1 is fluorine.

5. The copolymer of claim 4, wherein R_4 is C_1 to C_{16} linear, branched or cycloalkyl group.

6 The copolymer of claim 3, wherein R_1 and R_2 are fluorine and R_4 is C_1 to C_{16} linear, branched or cycloalkyl group.

7. The copolymer of claim 3, wherein R_1, R_2 and R_3 are fluorine and R_4 is C_1 to C_{16} linear, branched or cycloalkyl group.

8. The copolymer of claim 4, wherein R_4 is hydrogen or an alkali metal, ammonium, or alkylammonium.

9. The copolymer of claim 3, wherein R_1 and R_2 are fluorine and R_4 is hydrogen or an alkali metal, ammonium, or alkylammonium.

10. The copolymer of claim 3, wherein R_1, R_2 and R_3 are fluorine and R_4 is hydrogen or an alkali metal, ammonium, or alkylammonium.

11. A formulation comprising the fluorinated copolymer of any of claims 1 to 10, in a solvent.

12. The formulation of claim 11, wherein said solvent is chosen from: n-methylpyrrolidone (NMP), dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), triethylphosphite (TEP), acetone, tetrahydrofuran, methyl ethylketone (MEK), methyl isobutyl ketone (MiBK), ethyl acetate (EA), butyl acetate (BA), ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC) or ethyl methyl carbonate (EMC).

13. The formulation of claim 11 or 12 further comprising conductive carbon additives and cathode active material particles. Active material for lithium ion battery cathode formulation can be selected from the group, not limiting to : lithium iron phosphate (LFP), lithium nickel manganese cobalt oxide (NMC), lithium-manganese-cobalt-oxide (LCO), lithium-nickel-cobalt-aluminum oxide (NCA), lithium-manganese oxide (LMO), lithium-nickel-manganese-oxide (LNMO) , and lithium manganese iron phosphate (LMFP).

14. The formulation of claim 11 further comprising conductive carbon additives and anode active material particles, preferably the anode active material particles is selected from the group consisting of graphite, hard carbon, soft carbon, graphene, silicon, silicon monoxide (SiO), tin, and lithium titanate (LTO).

15. A process for preparing the fluorinated copolymer of claim 1 in an aqueous reaction medium, comprising:

a) forming an aqueous emulsion comprising at least one initiator, a stabilizer, at least one fluorinated vinylic monomer, and halogenated Monomer (1),

b) initiating copolymerization of said at least one fluorinated vinylic monomer with said halogenated Monomer (1) with stirring, under heat and super-atmospheric pressure.

16. The process of claim 15, wherein the aqueous medium is additionally comprised of at least one buffering agent.

17. The process of any one of claims 15 and 16, wherein polymerization is carried out at a temperature of from about 35 to about 130 degrees Celsius.

18. The process of any one of claims 15 to 17, wherein polymerization is carried out at a polymerization pressure of from about 2750 to about 6900 kPa.

19. The process of any one of claims 15 to 18, wherein the initiator is a persulfate or an organic peroxide.

20. An article comprising the formulation of any one of claims 11 to 13, wherein said article is a battery electrode film, notably a positive electrode for a lithium ion battery.

21. A battery comprising the fluorinated copolymer of any one of claims 1 to 10.

22. A coated substrate on which the copolymer of any one of claims 1 to 10 is applied as a latex in water or as a solvent solution.

23. A porous membrane comprising the copolymer of any one of claims 1 to 10 is applied as a latex in water or as a solvent solution.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/026490

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07C 57/52; C08F 214/20; C08F 214/22; C08L 31/02; C08L 31/04 (2019.01)

CPC - C07C 57/52; C08F 214/20; C08F 214/22; C08L 31/02; C08L 31/04 (2019.05)

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)

See Search History document

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

USPC - 428/421; 428/422; 525/199 (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2005/0170255 A1 (KOH et al) 04 August 2005 (04.08.2005) entire document	1-4, 8, 11, 12, 14-17, 21-23
Y	US 2015/0196585 A1 (RELYPSA, INC.) 16 July 2015 (16.07.2015) entire document	1-4, 8, 11, 12, 14-17, 21-23
Y	US 2014/0147726 A1 (TOYODA et al) 29 May 2014 (29.05.2014) entire document	14-17
Y	WO 2017/163756 A1 (ASAHI GLASS CO LTD) 28 September 2017 (28.09.2017) See translated document	1-4, 8, 11, 12, 14-17, 21-23

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent but published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 17 July 2019	Date of mailing of the international search report 02 AUG 2019
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/026490

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

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

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

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

3. ☒ Claims Nos.: 13, 18-20
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

This International Searching Authority found multiple inventions in this international application, as follows:
See extra sheet(s).

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

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

3. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
1-4, 8, 11, 12, 14-17, 21-23

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

Remark on Protest

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

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

☒ No protest accompanied the payment of additional search fees.

Continued from Box No. III Observations where unity of invention is lacking

Claims 1-4, 8, 11, 12, 14-17, and 21-23 have been analyzed subject to the restriction that the claims read on a fluorinated copolymer comprising a fluorinated vinylic monomer, wherein said fluorinated vinylic monomer is vinylidene flouride, and a halogenated monomer (1): wherein R1 is a halogen, wherein the halogen is fluorine, each of R2 and R3 is a hydrogen; and R4 is hydrogen.

Claims 1-3, 11, 12, 14-17, and 21-23 have been analyzed subject to the restriction that the claims read on the monomer (M1) as described in the Response to the Invitation to Pay Additional Fees in the International Application dated 27 June 2019 as further restricted to the variable definitions listed below. The claims are restricted to a fluorinated copolymer comprising a fluorinated vinylic monomer, wherein said fluorinated vinylic monomer is vinylidene flouride, and a halogenated monomer (1): wherein R1 and R2 are Hydrogen; and R3 is Fluorine; and R4 is CH3.

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees need to be paid.

Group I+: claims 1-12, 14-17, and 21-23 are drawn to fluorinated copolymers, formulations thereof, processes for preparing the fluorinated copolymer in an aqueous reaction medium, articles thereof, batteries thereof, coated substrates, and porous membranes.

The first invention of Group I+ is restricted based on the proviso that at least one is a halogen; and is restricted to a fluorinated copolymer comprising a fluorinated vinylic monomer, wherein said fluorinated vinylic monomer is vinylidene flouride, and a halogenated monomer (1): wherein R1 is a halogen, wherein the halogen is fluorine, each of R2 and R3 is a hydrogen; and R4 is hydrogen; formulations thereof; processes for preparing the fluorinated copolymer in an aqueous reaction medium; articles thereof; batteries thereof; coated substrates; and porous membranes. It is believed that claims 1-4, 8, 11, 12, 14-17, and 21-23 read on this first named invention and thus these claims will be searched without fee to the extent that they read on the above embodiment.

Applicant is invited to elect additional formula(e) for each additional compound to be searched in a specific combination by paying an additional fee for each set of election. Each additional elected formula(e) requires the selection of a single definition for each compound variable. An exemplary election would be a fluorinated copolymer comprising a fluorinated vinylic monomer, wherein said fluorinated vinylic monomer is vinylidene flouride, and a halogenated monomer (1): wherein R1 is a halogen, wherein the halogen is fluorine, each of R2 and R3 is a hydrogen; and R4 is unsubstituted C1 alkyl; formulations thereof; processes for preparing the fluorinated copolymer in an aqueous reaction medium; articles thereof; batteries thereof; coated substrates; and porous membranes. Additional formula(e) will be searched upon the payment of additional fees. Applicants must specify the claims that read on any additional elected inventions. Applicants must further indicate, if applicable, the claims which read on the first named invention if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the "+" group(s) will result in only the first claimed invention to be searched/examined.

The inventions listed in Groups I+ do not relate to a single general inventive concept under PCT Rule 13.1, because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The Groups I+ formulae do not share a significant structural element requiring the selection of alternatives for the fluorinated vinylic monomer and compound variables R1, R2, R3, R4, and accordingly these groups lack unity a priori.

Additionally, even if Groups I+ were considered to share the technical features of a fluorinated copolymer comprising a fluorinated vinylic monomer and a halogenated monomer (1); a formulation comprising the fluorinated copolymer, in a solvent; a process for preparing the fluorinated copolymer in an aqueous reaction medium, comprising: a) forming an aqueous emulsion comprising at least one initiator, a stabilizer, at least one fluorinated vinylic monomer, and halogenated Monomer (1), b) initiating copolymerization of said at least one fluorinated vinylic monomer with said halogenated Monomer (1) with stirring, under heat and super-atmospheric pressure; an article comprising the formulation, wherein said article is a battery electrode film, notably a positive electrode for a lithium ion battery; a battery comprising the fluorinated copolymer; a coated substrate on which the copolymer is applied as a latex in water or as a solvent solution; and a porous membrane comprising the copolymer is applied as a latex in water or as a solvent solution, these shared technical features do not represent a contribution over the prior art as disclosed by US 2005/0170255 A1 to Koh et al. and US 2014/0147726 A1 Zeon Corporation.

US 2005/0170255 A1 to Koh et al. teach a fluorinated copolymer (Abstract,... a fluorine-containing polymer...; Claim 9,... the structural unit L is a structural unit derived from a monomer copolymerizable with the monomer providing the structural unit K, and the structural units K and L are contained in amounts of from 0.01 to 100% by mole and from 0 to 99.99% by mole, respectively.) comprising a fluorinated vinylic monomer (Para. [0158], Also polymers having oxidation resistance and electrochemical stability can be obtained since those monomers are copolymerizable with fluoroolefins such as...vinylidene fluoride...) and a halogenated monomer having the core structure of (1) (Para. [0267], 5 g of α-fluoroacrylate: CH2=CFCOOCH2CF2CF2(OCF2CF2CF2)7OCF2CF2CF3); a formulation comprising the fluorinated copolymer, in a solvent (Para. [0207],... the non-crystalline fluorine-containing polymer (A) is in the solidified form or in the rubber-like form, a solvent may be mixed to make the polymer in the form of gel.); an article comprising the formulation (Para. [0074],... the Solvent is used and enhancement of adhesion to an electrode...), wherein said article is a battery electrode film (Paras. [0247] and [0148],...impregnating the electrode with a liquid electrolyte.... However when the fluorine-containing polymer of the present invention is used as an ion conductor forming an electrolyte, the electrolyte can have sufficient ion-conducting property.); and a battery (Claim 17, A battery produced by using the fluorine-containing polymer solid electrolyte...) comprising the fluorinated copolymer (Claims 1, 9, and 17; Para. [0158]).

US 2014/0147726 A1 Zeon Corporation teaches a process for preparing the fluorinated copolymer in an aqueous reaction medium (Paras. [0016], [0017],... the water-soluble polymer is a copolymer including 15% to 50% by weight of an ethylenically unsaturated carboxylic acid monomer unit, 30% to 80% by weight of a (meth)acrylic acid ester monomer unit, and 0.5% to 10% by weight of a fluorine-containing (meth)acrylic acid ester monomer unit.; Para. [0057],... a method for producing the water-soluble polymer...in an aqueous solvent.), comprising: a) forming an aqueous emulsion (Para. [0060],... an emulsion polymerization...) comprising at least one initiator (Para. [0258],...potassium persulfate as a polymerization initiator...), a stabilizer (Para. [0104], As the viscosity modifier, water-soluble polysaccharides are preferably used.), at least one halogenated vinylic monomer (Para. [0052],... halogen atom-containing monomers such as vinyl chloride...), and halogenated core structure of Monomer (1) (Para. [0258],... trifluoromethyl methacrylate...), b) initiating copolymerization of said at least one fluorinated vinylic monomer with said halogenated core structure of Monomer (1) with stirring, under heat and super-atmospheric pressure (Para. [0258], In a 5 MPa pressure-resistant container...polymerization initiator