

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
13 September 2007 (13.09.2007)

PCT

(10) International Publication Number  
**WO 2007/102984 A1**

(51) International Patent Classification:

C08F 299/00 (2006.01) C08F 220/38 (2006.01)  
C08F 220/22 (2006.01) C08F 220/34 (2006.01)

(21) International Application Number:

PCT/US2007/004426

(22) International Filing Date:

20 February 2007 (20.02.2007)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

60/743,431 8 March 2006 (08.03.2006) US

(71) Applicant (for all designated States except US): **3M INNOVATIVE PROPERTIES COMPANY** [US/US];  
3M Center, Post Office Box 33427, Saint Paul, Minnesota  
55133-3427 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **MARX, Ryan E.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **NELSON, James M.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **PINNOW, Matthew J.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **SCHMID, Matthew J.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **DAMS, Rudolf J.** [BE/BE]; Hermeslaan 7, B-1831 Diegem (BE). **DE WITTE, Johan E.** [BE/BE]; Hermeslaan 7, B-1831 Diegem (BE).

(74) Agents: **GEISE, C. Michael** et al.; 3M Center, Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, 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
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CONTROLLED ARCHITECTURE MATERIALS

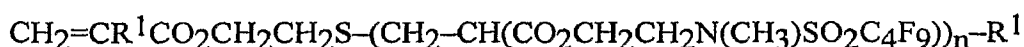
(57) Abstract: A block copolymer; a method of reducing the surface tension of a liquid comprising adding to said liquid less than 10 wt % of a surface active agent derived from the block copolymer; a method for modifying the surface chemistry of a polymeric substrate comprising adding less than 10 wt % of a surface active agent derived from the block copolymer; a polymerized foam composition made from a mixture containing one or more of monomers, oligomers, and polymers, the mixture comprising less than 10 wt % of a surface active agent derived from the block copolymer and an article comprising the polymerized foam. A block copolymer comprising at least one block having a quaternary ammonium ion.

WO 2007/102984 A1

## CONTROLLED ARCHITECTURE MATERIALS

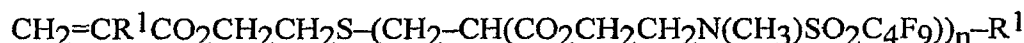
### SUMMARY

In one aspect, the present invention relates to a block copolymer comprising at least one  
 5 block comprising a fluorinated macromonomer ("OLIGOC4") having the general formula:



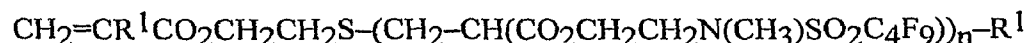
wherein each  $\text{R}^1$  is independently selected from the group consisting of H, an alkyl, an alkyloxy, a  
 halogen, a phenyl, a benzyl, a benzoyl, a hydroxyl, a carboxyl, an amine, an amide, a sulfide, a  
 sulfoxide, a sulfate, a phosphate, a phosphate ester, a nitroxide, a thioester, and a carbonyl;  
 10 and n is selected from 1 to 25.

In another aspect, the present invention relates to a block copolymer comprising at least one  
 block having a quaternary ammonium ion and at least one block comprising a fluorinated  
 macromonomer having the general formula:



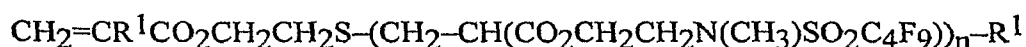
wherein each  $\text{R}^1$  is independently selected from the group consisting of H, an alkyl, an alkyloxy, a  
 15 halogen, a phenyl, a benzyl, a benzoyl, a hydroxyl, a carboxyl, an amine, an amide, a sulfide, a  
 sulfoxide, a sulfate, a phosphate, a phosphate ester, a nitroxide, a thioester, and a carbonyl;  
 and n is selected from 1 to 25.

In yet another aspect, the present invention relates to a method of reducing the surface  
 20 tension of a liquid comprising adding to a liquid a surface active agent in an amount of from 0.0025  
 to 10 % by weight of the surface active agent, based on the total weight of the liquid and surface  
 active agent, wherein the surface active agent is derived from a block copolymer comprising at least  
 one block comprising a fluorinated macromonomer having the general formula:



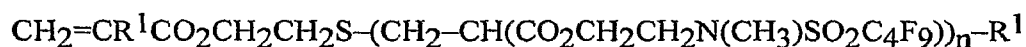
wherein each  $\text{R}^1$  is independently selected from the group consisting of H, an alkyl, an alkyloxy, a  
 25 halogen, a phenyl, a benzyl, a benzoyl, a hydroxyl, a carboxyl, an amine, an amide, a sulfide, a  
 sulfoxide, a sulfate, a phosphate, a phosphate ester, a nitroxide, a thioester, and a carbonyl;  
 and n is selected from 1 to 25.

In a further aspect, the present invention relates to a method for modifying the surface chemistry of a polymeric substrate comprising adding to a polymer a surface active agent in an amount of from 0.1 to 10% by weight of the surface active agent, based on the total weight of the polymer and surface active agent, wherein the surface active agent comprises a block copolymer comprising at least one block comprising a fluorinated macromonomer having the general formula:



wherein each  $\text{R}^1$  is independently selected from the group consisting of H, an alkyl, an alkyloxy, a halogen, a phenyl, a benzyl, a benzoyl, a hydroxyl, a carboxyl, an amine, an amide, a sulfide, a sulfoxide, a sulfate, a phosphate, a phosphate ester, a nitroxide, a thioester, and a carbonyl; and  $n$  is selected from 1 to 25.

Another aspect of the present invention relates to a polymerized foam composition made from a mixture containing one or more of monomers, oligomers, and polymers, the mixture comprising from 0.1 to 10 wt% of a surface active agent derived from a block copolymer comprising at least one block comprising a fluorinated macromonomer having the general formula:



wherein each  $\text{R}^1$  is independently selected from the group consisting of H, an alkyl, an alkyloxy, a halogen, a phenyl, a benzyl, a benzoyl, a hydroxyl, a carboxyl, an amine, an amide, a sulfide, a sulfoxide, a sulfate, a phosphate, a phosphate ester, a nitroxide, a thioester, and a carbonyl; and  $n$  is selected from 1 to 25.

In another aspect, the present invention relates to an article comprising the polymerized foam composition. An example of an article is a pressure sensitive adhesive tape.

In yet another aspect, the present invention relates to a block copolymer comprising at least one block having a  $-\text{CO}_2\text{CH}_2\text{CH}_2\text{S}-(\text{CH}_2-\text{CH}(\text{CO}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{SO}_2\text{C}_4\text{F}_9))_n-\text{R}^1$  group, wherein the block copolymer is a comb-like block copolymer and wherein each  $\text{R}^1$  is independently selected from the group consisting of H, an alkyl, an alkyloxy, a halogen, a phenyl, a benzyl, a benzoyl, a hydroxyl, a carboxyl, an amine, an amide, a sulfide, a sulfoxide, a sulfate, a phosphate, a phosphate ester, a nitroxide, a thioester, and a carbonyl; and  $n$  is selected from 1 to 25.

For purposes of the present invention, the following terms used in this description are defined as follows:

"block" refers to a portion of a block copolymer, comprising many monomeric units, that has at least one feature which is not present in the adjacent block or blocks;

"Block copolymer" means a polymer having at least two compositionally discrete segments, for example a di-block copolymer, a tri-block copolymer, a random block copolymer, a graft-block copolymer, a star-branched block copolymer or a hyper-branched block copolymer;

"Random block copolymer" means a copolymer having at least two distinct blocks wherein at least one block comprises a random arrangement of at least two types of monomer units;

"Di-block copolymers" and "Tri-block copolymers" means a polymer in which all the neighboring monomer units (except at the transition point) are of the same identity, *for example*, -AB is a di-block copolymer comprised of an A block and a B block that are compositionally different and ABC is a tri-block copolymer comprised of A, B, and C blocks, each compositionally different;

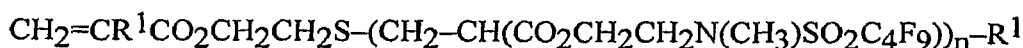
"Graft-block copolymer" means a polymer consisting of a side-chain polymers grafted onto a main chain. The side chain polymer can be any polymer different in composition from the main chain copolymer;

"Star-branched block copolymer" or "Hyper-branched block copolymer" means a polymer consisting of several linear block chains linked together at one end of each chain by a single branch or junction point, also known as a radial block copolymer;

"End functionalized" means a polymer chain terminated with a functional group on at least one chain end.

## DETAILED DESCRIPTION

The block copolymers of the present invention comprise at least one block comprising a fluorinated macromonomer having the general formula:

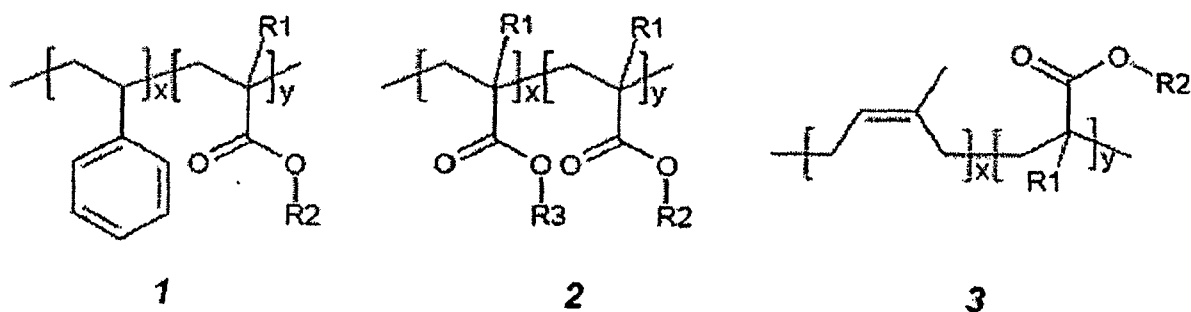


wherein each  $\text{R}^1$  is independently selected from the group consisting of H, a C1 to C4 alkyl, and a functional group derived from an initiator;

and n is selected from 1 to 25.

By "group derived from an initiator" it is meant a group, such as an alkyl radical, an alkoxy radical, a halogen, or another organic or inorganic group that is used to initiate the oligomerization of the  $-(CH_2-CH(CO_2CH_2CH_2N(CH_3)SO_2C_4F_9))_n-$  segment in the preparation of the macromonomer.

In some embodiments, specific structures illustrating the block copolymers described herein may be illustrated by the following fluorinated copolymer structures:



wherein each  $R^1$  is independently as described above,  $R^2$  is  $-CH_2CH_2S-(CH_2-CH(CO_2CH_2CH_2NMESO_2C_4F_9))_n-R^1$ , and  $R^3$  is an alkyl or aryl substituent.

Block copolymers according to the present invention can be synthesized using any suitable living polymerization technique, including living anionic or living radical methods.

The block copolymers described in this invention have many potential applications as a result of their unique chemical structure, morphology, and molecular topology. The block copolymers described herein are fluorinated materials, typically having very low surface energies. The block copolymers may function effectively as surface modifiers, surfactants, compatibilizers, rheology modifiers, or other polymer additives. Because these materials can contain a block of a non-fluorinated material, it is possible to tailor the solubility of the block copolymers described herein in a variety of polymers and solvents, thus improving the dispersibility either of the block copolymers themselves, or some other additive to the polymer or solvent (that is, wherein the block copolymer acts as a dispersing agent for the other additive in the polymer or solvent).

In other embodiments, block copolymers of the present invention may form ordered morphologies at the molecular level. Such ordered morphology block copolymers could be applied

for a variety of applications related to nano-engineering, including the functions of dispersion, encapsulation, transport, delivery, and separation.

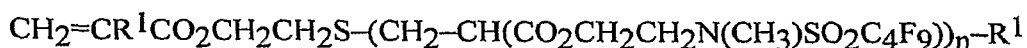
Furthermore, block copolymers produced from the macromonomer described herein may possess a higher concentration of fluorine atoms per side chain than, for instance, similar block  
5 copolymers produced from the monomer 2-(N-methylperfluorobutanesulfonamido) ethyl methacrylate (MeFBSEMA). The higher concentration of fluorine atoms may enhance the repellant (oil, water) properties of block copolymers and materials containing block copolymers described herein over block copolymers and materials containing block copolymers produced from the monomer MeFBSEMA.

10 Furthermore, in some embodiments, the fluorinated macromonomer described herein may be incorporated into a block copolymer composition containing other inexpensive, readily available hydrocarbon monomers, such as methacrylate monomers. Such block copolymers may display substantially improved oil and water repellency over the same compositions of free radically  
15 polymerized polymers (that is, copolymers of the fluorinated macromonomer and a hydrocarbon monomer, that is not a block copolymer). In some embodiments, block copolymer compositions according to the present invention can provide nearly the same level of surface energy reduction as fluoromethacrylate homopolymers, where the block copolymers described herein incorporate levels of fluorinated macromonomer as low as 10 to 20% by weight.

20 In yet further embodiments, the block copolymers of the present invention provide utility in surface activity and surface modification applications, even where the overall block copolymer has very low fluorine content, for instance, less than 50% by weight, less than 30% by weight, less than 20% by weight, or even less than 10% by weight, based on the weight of the block copolymer.

The block copolymers according to the present invention include di-block copolymers, as well as those having more complex molecular architectures, such as, for instance, triblock,  
25 multiblock, star, graft, and comb-like architectures. Materials where at least one of the blocks constitutes a copolymer of multiple monomers, for instance the fluorinated macromonomer described herein, are also within the scope of this invention. Some embodiments of block copolymers include di-block copolymers, tri-block copolymers, random block copolymers, graft-block copolymers, star-branched copolymers or hyper-branched copolymers. Additionally, block  
30 copolymers may be end functionalized (that is, have end functional groups).

Some embodiments of the present invention comprise block copolymers comprising at least one block having a quaternary ammonium ion and at least one block comprising a fluorinated macromonomer ("OLIGOC4") having the general formula:



wherein each  $\text{R}^1$  is independently selected from the group consisting of H, a C1 to C4 alkyl, and a functional group derived from an initiator; and n is selected from 1 to 25.

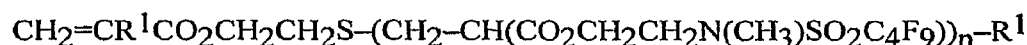
In some embodiments of the present invention, the block copolymers comprising OLIGOC4 can modify the surfaces of polymeric substrates and plastics when a small amount is blended into the substrate. When a block copolymer of the present invention is added into a polymeric material or plastic using standard compounding processes (for example melt extrusion), the resulting surface properties of the plastic can be modified. This can potentially provide unique surface attributes to the substrate including: antifouling, scratch resistance, lubrication, printability, and others. The amount of fluorinated polymer added to a substrate is preferably less than 10 wt %, more preferably less than 5 wt %, and most preferably less than 1 wt %.

Useful thermoplastic elastomeric polymeric resins for substrates include, for example, polybutadiene, polyisobutylene, ethylene-propylene copolymers, ethylene-propylene-diene terpolymers, sulfonated ethylene-propylene-diene terpolymers, polychloroprene, poly(2,3-dimethylbutadiene), poly(butadiene-co-pentadiene), chlorosulfonated polyethylenes, polysulfide elastomers, block copolymers, made up of segments of glassy or crystalline blocks such as polystyrene, poly(vinyltoluene), poly(t-butylstyrene), polyester and the like and the elastomeric blocks such as polybutadiene, polyisoprene, ethylene-propylene copolymers, ethylene-butylene copolymers, polyether ester and the like as for example the copolymers in poly(styrene-butadiene-styrene) block copolymer manufactured by Shell Chemical Company under the trade name of "KRATON". Copolymers and/or mixtures of these aforementioned polymers can also be used

Useful polymeric resins for substrates also include fluoropolymers, that is, at least partially fluorinated polymers. Useful fluoropolymers include, for example, those that are preparable (for example, by free-radical polymerization) from monomers comprising chlorotrifluoroethylene, 2-chloropentafluoropropene, 3-chloropentafluoropropene, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene, 1-hydropentafluoropropene, 2-hydropentafluoropropene, 1,1-dichlorofluoroethylene, dichlorodifluoroethylene, hexafluoropropylene, vinyl fluoride, a

perfluorinated vinyl ether (for example, a perfluoro(alkoxy vinyl ether) such as  $\text{CF}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$ , or a perfluoro(alkyl vinyl ether) such as perfluoro(methyl vinyl ether) or perfluoro(propyl vinyl ether)), cure site monomers such as for example nitrile containing monomers (for example,  $\text{CF}_2=\text{CFO}(\text{CF}_2)_L\text{CN}$ ,  $\text{CF}_2=\text{CFO}[\text{CF}_2\text{CF}(\text{CF}_3)\text{O}]_q(\text{CF}_2\text{O})_y\text{CF}(\text{CF}_3)\text{CN}$ ,  $\text{CF}_2=\text{CF}[\text{OCF}_2\text{CF}(\text{CF}_3)]_r\text{O}(\text{CF}_2)_t\text{CN}$ , or  $\text{CF}_2=\text{CFO}(\text{CF}_2)_u\text{OCF}(\text{CF}_3)\text{CN}$  where  $L = 2-12$ ;  $q = 0-4$ ;  $r = 1-2$ ;  $y = 0-6$ ;  $t = 1-4$ ; and  $u = 2-6$ ), bromine containing monomers (for example,  $\text{Z-R}_f\text{-O}_x\text{-CF}=\text{CF}_2$ , wherein  $\text{Z}$  is  $\text{Br}$  or  $\text{I}$ ,  $\text{R}_f$  is a substituted or unsubstituted  $\text{C}_1\text{-C}_{12}$  fluoroalkylene, which may be perfluorinated and may contain one or more ether oxygen atoms, and  $x$  is 0 or 1); or a combination thereof, optionally in combination with additional non-fluorinated monomers such as, for example, ethylene or propylene. Specific examples of such fluoropolymers include polyvinylidene fluoride; terpolymers of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride; copolymers of tetrafluoroethylene, hexafluoropropylene, perfluoropropyl vinyl ether, and vinylidene fluoride; tetrafluoroethylene-hexafluoropropylene copolymers; tetrafluoroethylene-perfluoro(alkyl vinyl ether) copolymers (for example, tetrafluoroethylene-perfluoro(propyl vinyl ether)); and combinations thereof.

In some embodiments, the present invention may provide a method for stabilizing cellular polymeric membranes when a block copolymer comprising a fluorinated macromonomer having the general formula:



wherein each  $\text{R}^1$  is independently selected from the group consisting of  $\text{H}$ , a  $\text{C}_1$  to  $\text{C}_4$  alkyl, and a functional group derived from an initiator; and  $n$  is selected from 1 to 25, is added into various monomeric and/or polymeric systems (for example, curable acrylic monomer/polymer mixtures including froths that comprise gas and polymerizable material). For instance, the block copolymer may be added in an amount less than 10 wt%, less than 5 wt %, or even less than 1 wt % of a surface-active agent derived from a block copolymer of the present invention. These materials provide for and control the formation of a large number of small cells or voids in the membrane, which leads simultaneously to the formation of a cellular membrane with low density and an opaque, uniform appearance. The properties and methods of making cellular pressure-sensitive adhesive (PSA) membranes of this type are described in U.S. Pat. No. 4,415,615 (Esmay). Cellular



PSA membranes or foam tapes can be made not only by forming a cellular polymeric membrane that has PSA properties, but also by applying a layer of PSA to at least one major surface of a cellular polymeric membrane.

Block copolymers according to the present invention may be formed by sequentially  
5 polymerizing different monomers. Useful methods for forming block copolymers include, for example, anionic, cationic, coordination, and free radical polymerization methods.

In multi-component compositions the block copolymers of the present invention may interact with fillers through functional moieties. For instance, the block copolymers of the present invention may be useful as a dispersing agent in a composition comprising a host polymer, a filler,  
10 and a block copolymer according to the present invention. Suitable host polymers include, for instance, any of a number of thermoplastic polymers and thermoplastic elastomeric polymers, which may be fluorinated or non-fluorinated.

Useful thermoplastic polymer resins include polylactones such as, for example, poly(pivalolactone) and poly(caprolactone); polyurethanes such as, for example, those derived from  
15 reaction of diisocyanates such as 1,5-naphthalene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 2,4-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, 4,4'-diphenylisopropylidene diisocyanate, 3,3'-dimethyl-4,4'-diphenyl diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl diisocyanate, dianisidine diisocyanate,  
20 toluidine diisocyanate, hexamethylene diisocyanate, or 4,4'-diisocyanatodiphenylmethane with linear long-chain diols such as poly(tetramethylene adipate), poly(ethylene adipate), poly(1,4-butylene adipate), poly(ethylene succinate), poly(2,3-butylenesuccinate), polyether diols and the like; polycarbonates such as poly(methane bis(4-phenyl) carbonate), poly(1,1-ether bis(4-phenyl) carbonate), poly(diphenylmethane bis(4-phenyl)carbonate), poly(1,1-cyclohexane bis(4-phenyl)carbonate), or poly(2,2-(bis(4-hydroxyphenyl) propane) carbonate; polysulfones; polyether  
25 ether ketones; polyamides such as, for example, poly(4-aminobutyric acid), poly(hexamethylene adipamide), poly(6-aminohexanoic acid), poly(m-xylylene adipamide), poly(p-xylylene sebacamide), poly(metaphenylene isophthalamide), and poly(p-phenylene terephthalamide); polyesters such as, for example, poly(ethylene azelate), poly(ethylene-1,5-naphthalate),  
30 poly(ethylene-2,6-naphthalate), poly(1,4-cyclohexane dimethylene terephthalate), poly(ethylene

oxybenzoate), poly(para-hydroxy-benzoate), poly(1,4-cyclohexylidene-dimethylene terephthalate) (cis), poly(1,4-cyclohexylidene-dimethylene terephthalate) (trans), polyethylene terephthalate, and polybutylene terephthalate; poly(arylene oxides) such as, for example, poly(2,6-dimethyl-1,4-phenylene oxide) and poly(2,6-diphenyl-1,1-phenylene oxide); poly(arylene sulfides) such as, for example, polyphenylene sulfide; polyetherimides; vinyl polymers and their copolymers such as, for example, polyvinyl acetate, polyvinyl alcohol, polyvinyl chloride, polyvinyl butyral, polyvinylidene chloride, and ethylene-vinyl acetate copolymers; acrylic polymers such as, for example, poly(ethyl acrylate), poly(n-butyl acrylate), poly(methyl methacrylate), poly(ethyl methacrylate), poly(n-butyl methacrylate), poly(n-propyl methacrylate), polyacrylamide, polyacrylonitrile, polyacrylic acid, ethylene-ethyl acrylate copolymers, ethylene-acrylic acid copolymers; acrylonitrile copolymers (for example, poly(acrylonitrile-co-butadiene-co-styrene) and poly(styrene-co-acrylonitrile)); styrenic polymers such as, for example, polystyrene, poly(styrene-co maleic anhydride) polymers and their derivatives, methyl methacrylate-styrene copolymers, and methacrylated butadiene-styrene copolymers; polyolefins such as, for example, polyethylene, polybutylene, polypropylene, chlorinated low density polyethylene, poly(4-methyl-1-pentene); ionomers; poly(epichlorohydrins); polysulfones such as, for example, the reaction product of the sodium salt of 2,2-bis(4-hydroxyphenyl) propane and 4,4'-dichlorodiphenyl sulfone; furan resins such as, for example, poly(furan); cellulose ester plastics such as, for example, cellulose acetate, cellulose acetate butyrate, and cellulose propionate; protein plastics; polyarylene ethers such as, for example, polyphenylene oxide; polyimides; polyvinylidene halides; polycarbonates; aromatic polyketones; polyacetals; polysulfonates; polyester ionomers; and polyolefin ionomers. Copolymers and/or combinations or blends of these aforementioned polymers can also be used.

Useful thermoplastic elastomeric polymeric resins include, for example, polybutadiene, polyisobutylene, ethylene-propylene copolymers, ethylene-propylene-diene terpolymers, sulfonated ethylene-propylene-diene terpolymers, polychloroprene, poly(2,3-dimethylbutadiene), poly(butadiene-co-pentadiene), chlorosulfonated polyethylenes, polysulfide elastomers, block copolymers, made up of segments of glassy or crystalline blocks such as polystyrene, poly(vinyltoluene), poly(t-butylstyrene), polyester and the like and the elastomeric blocks such as polybutadiene, polyisoprene, ethylene-propylene copolymers, ethylene-butylene copolymers, polyether ester and the like as for example the copolymers in poly(styrene-butadiene-styrene) block

copolymer manufactured by Shell Chemical Company under the trade name of "KRATON".

Copolymers and/or combinations or blends of these aforementioned polymers can also be used

Useful polymeric resins also include fluoropolymers, that is, at least partially fluorinated polymers. Useful fluoropolymers include, for example, those that are preparable (for example, by free-radical polymerization) from monomers comprising chlorotrifluoroethylene, 2-chloropentafluoropropene, 3-chloropentafluoropropene, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene, 1-hydropentafluoropropene, 2-hydropentafluoropropene, 1,1-dichlorofluoroethylene, dichlorodifluoroethylene, hexafluoropropylene, vinyl fluoride, a perfluorinated vinyl ether (for example, a perfluoro(alkoxy vinyl ether) such as  $\text{CF}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$ , or a perfluoro(alkyl vinyl ether) such as perfluoro(methyl vinyl ether) or perfluoro(propyl vinyl ether)), cure site monomers such as for example nitrile containing monomers (for example,  $\text{CF}_2=\text{CFO}(\text{CF}_2)_L\text{CN}$ ,  $\text{CF}_2=\text{CFO}[\text{CF}_2\text{CF}(\text{CF}_3)\text{O}]_q(\text{CF}_2\text{O})_y\text{CF}(\text{CF}_3)\text{CN}$ ,  $\text{CF}_2=\text{CF}[\text{OCF}_2\text{CF}(\text{CF}_3)]_r\text{O}(\text{CF}_2)_t\text{CN}$ , or  $\text{CF}_2=\text{CFO}(\text{CF}_2)_u\text{OCF}(\text{CF}_3)\text{CN}$  where  $L = 2-12$ ;  $q = 0-4$ ;  $r = 1-2$ ;  $y = 0-6$ ;  $t = 1-4$ ; and  $u = 2-6$ ), bromine containing monomers (for example,  $\text{Z-R}_f\text{-O}_x\text{-CF}=\text{CF}_2$ , wherein Z is Br or I,  $\text{R}_f$  is a substituted or unsubstituted  $\text{C}_1\text{-C}_{12}$  fluoroalkylene, which may be perfluorinated and may contain one or more ether oxygen atoms, and x is 0 or 1); or a combination thereof, optionally in combination with additional non-fluorinated monomers such as, for example, ethylene or propylene. Specific examples of such fluoropolymers include polyvinylidene fluoride; terpolymers of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride; copolymers of tetrafluoroethylene, hexafluoropropylene, perfluoropropyl vinyl ether, and vinylidene fluoride; tetrafluoroethylene-hexafluoropropylene copolymers; tetrafluoroethylene-perfluoro(alkyl vinyl ether) copolymers (for example, tetrafluoroethylene-perfluoro(propyl vinyl ether)); and combinations thereof.

Useful commercially available thermoplastic fluoropolymers include, for example, those marketed by Dyneon LLC under the trade designations "THV" (for example, "THV 220", "THV 400G", "THV 500G", "THV 815", and "THV 610X"), "PVDF", "PFA", "HTE", "ETFE", and "FEP"; those marketed by Atochem North America, Philadelphia, Pennsylvania under the trade designation "KYNAR" (for example, "KYNAR 740"); those marketed by Ausimont, USA, Morristown, New Jersey under the trade designations "HYLAR" (for example, "HYLAR 700") and "HALAR ECTFE".

Suitable fillers include, for instance, carbon black, carbon nanotubes, clay, and any conventional filler or additive utilized, for instance, in melt processing compositions. In particular, fillers may also include pigments, carbon fibers, hindered amine light stabilizers, anti-block agents, glass fibers, aluminum oxide, silica, mica, cellulosic materials, or one or more polymers with reactive or polar groups. Examples of polymers with reactive or polar groups include, but are not limited to, polyamides, polyimides, functional polyolefins, polyesters, polyacrylates and methacrylates.

In one embodiment, the filler is a cellulosic material. Cellulosic materials are commonly utilized in melt processable compositions to impart specific physical characteristics to the finished composition. Cellulosic materials generally include natural or wood materials having various aspect ratios, chemical compositions, densities, and physical characteristics. Non-limiting examples of cellulosic materials include wood flour, wood fibers, sawdust, wood shavings, newsprint, paper, flax, hemp, rice hulls, kenaf, jute, sisal, peanut shells. Combinations of cellulosic materials, or cellulosic materials with other interfering components, may also be used in the melt processable composition.

The block copolymers of the present invention may also be used as part of a composition for melt processing. Non-limiting examples of melt processes amenable to this invention include methods such as extrusion, injection molding, batch mixing and rotomolding.

The block copolymers of the present invention may also be suitable for use as a polymer processing aid or as a coupling agent improve the melt processability of polymer composite systems containing conventionally known fluoropolymer, particularly fluoroplastic and fluoroelastomeric processing aids. In particular, the present invention may improve the melt processability of compositions containing fillers, particularly interfering components that may have a strong interfacial tension with host polymers. The block copolymers may enable a significant reduction in the interfacial tension between the host polymer and the fillers, thus resulting in an improved efficacy of the block copolymer either as a polymer processing aid or as an additive to improve the performance of a fluoropolymer processing aid. The resulting processed material may exhibit a significant reduction in melt fracture as well as improved physical characteristics such as water uptake, flexural modulus, or tensile strength.

The block copolymers of the present invention may comprise functional blocks, typically having one or more polar moieties such as, for example, acids (for example,  $-\text{CO}_2\text{H}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{PO}_3\text{H}$ );  $-\text{OH}$ ;  $-\text{SH}$ ; primary, secondary, or tertiary amines; ammonium; N-substituted or unsubstituted amides and lactams; N-substituted or unsubstituted thioamides and thiolactams; anhydrides; linear or cyclic ethers and polyethers; isocyanates; cyanates; nitriles; carbamates; ureas; thioureas; heterocyclic amines (for example, pyridine or imidazole)). Useful monomers that may be used to introduce such groups include, for example, acids (for example, acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, and including methacrylic acid functionality formed via the acid catalyzed deprotection of t-butyl methacrylate monomeric units as described in U.S. patent application publication No. U.S. 2004/0024130 A 1 (Nelson et al.)); acrylates and methacrylates (for example, 2-hydroxyethyl acrylate), acrylamide and methacrylamide, N-substituted and N,N disubstituted acrylamides (for example, N-t-butyl-acrylamide, N,N-(dimethylamino)ethyl-acrylamide, N,N-dimethyl-acrylamide, N,Ndimethyl-methacrylamide), N-ethyl-acrylamide, N-hydroxyethyl-acrylamide, N-octyl-acrylamide, N-t-butyl-acrylamide, N,N-dimethyl-acrylamide, N,N-diethyl-acrylamide, and N-ethyl-N-dihydroxyethyl-acrylamide), aliphatic amines (for example, 3-dimethylaminopropyl amine, N,N-dimethylethylenediamine); and heterocyclic monomers (for example, 2-vinylpyridine, 4-vinylpyridine, 2-(2-aminoethyl)pyridine, 1-(2-aminoethyl)pyrrolidine, 3-aminoquinuclidine, N-vinylpyrrolidone, and N-vinylcaprolactam).

Other suitable blocks may have one or more hydrophobic moieties such as, for example, aliphatic and aromatic hydrocarbon moieties such as those having at least 4, 8, 12, or even 18 carbon atoms; fluorinated aliphatic and/or fluorinated aromatic hydrocarbon moieties, such as for example, those having at least 4, 8, 12, or even 18 carbon atoms; and silicone moieties. Non-limiting example of useful monomers for introducing such blocks include: hydrocarbon olefins such as ethylene, propylene, isoprene, styrene, and butadiene; cyclic siloxanes such as decamethylcyclopentasiloxane and decamethyltetrasiloxane; fluorinated olefins such as tetrafluoroethylene, hexafluoropropylene, trifluoroethylene, difluoroethylene, and chlorofluoroethylene; nonfluorinated alkyl acrylates and methacrylates such as butyl acrylate, isooctyl methacrylate lauryl acrylate, stearyl acrylate; fluorinated acrylates such as perfluoroalkylsulfonamidoalkyl acrylates and methacrylates having the formula  $\text{H}_2\text{C}=\text{C}(\text{R}_2)\text{C}(\text{O})\text{O}-$

X-N(R)SO<sub>2</sub>R<sub>f</sub> wherein: R<sub>f</sub> is C<sub>6</sub>F<sub>13</sub>, -C<sub>4</sub>F<sub>9</sub>, or -C<sub>3</sub>F<sub>7</sub>; R is hydrogen, C1 to C10 alkyl, or C6-C10 aryl; and X is a divalent connecting group.

The block copolymers according to the present invention may also have blocks selected from the group consisting of vinyl aromatics, styrenics, dienes, vinyl pyridines, acrylates, methacrylates, epoxides, oxiranes, cyclic sulfides, lactones, lactides, cyclic carbonates, lactams, cyclosiloxanes, acrylonitrile, [n]metallocenophanes, fluorinated acrylates, fluorinated methacrylates and anionically-polymerizable polar monomers.

Other non-limiting examples of useful block copolymers having functional moieties include poly(OLIGOC4-block-methacrylic acid)), poly(OLIGOC4-block-t-butyl methacrylate), poly(styrene-block-t-butyl methacrylate-block- OLIGOC4), poly(styrene-block-methacrylic anhydride-block-OLIGOC4), poly(styrene-block- methacrylic acidblock-OLIGOC4), poly(styrene-block-(methacrylic anhydride-co-methacrylic acid)-block-OLIGOC4)), poly(styrene-block-(methacrylic anhydride-co-methacrylic acid-co-OLIGOC4)), poly(styrene-block-(t-butyl methacrylate-co-OLIGOC4)), poly(styrene-block-isoprene-block-t-butyl methacrylate-block- OLIGOC4), poly(styrene-isoprene-block-methacrylic anhydride-block-OLIGOC4), poly(styrene-isoprene-block-methacrylic acid-block-OLIGOC4), poly(styrene-block-isoprene-block-(methacrylic anhydride-co-methacrylic acid)-block-OLIGOC4), poly(styrene-block-isoprene-block-(methacrylic anhydride-comethacrylic acid-co-OLIGOC4)), poly(styrene-block-isoprene-block-(t-butyl methacrylateco-OLIGOC4)), poly(OLIGOC4-block-methacrylic anhydride), poly(OLIGOC4-block-(methacrylic acid-co-methacrylic anhydride)), poly(styrene-block-(t-butyl methacrylateco-OLIGOC4)), and hydrogenated forms of poly(butadiene-block- OLIGOC4), and poly(butadiene-block-methacrylic acid-block-OLIGOC4).

## EXAMPLES

### Film Preparation

To form the films, each material to be analyzed was placed between 0.051 mm thick untreated polyester liners, which in turn were placed between 2 aluminum plates (3.2 mm thick each) to form a stack. Two shims (1 mm thick each) were placed to either side of the stack such that upon pressing the assembled stack the mixture would not come into contact with either shim. Each stack was placed in a heated hydraulic press available under the trade designation "WABASH MPI

MODEL G30H-15-LP" from Wabash MPI (Wabash IN). Both the top and bottom press plates were heated at 193 °C. The stack was pressed for 1 minute at 1500 psi (10 MPa). The hot stack was then moved to a low-pressure water-cooled press for 30 seconds to cool the stack. The stack was disassembled and the liners were removed from both sides of the film disc that resulted from pressing the mixture.

### Injection Molding

2" x 4" plaques were injection molded at 180 °C and 70 psi using a Mini-Jector Injection Molder Model 45 (available from Mini-Jector Machinery Corp, Newbury, OH).

### Test Methods

#### Molecular Weight and Polydispersity

The average molecular weight and polydispersity of a sample was determined by Gel Permeation Chromatography (GPC) analysis. Approximately 25 mg of a sample was dissolved in 10 milliliters (mL) of tetrahydrofuran (THF) to form a mixture. The mixture was filtered using a 0.2 micron polytetrafluoroethylene (PTFE) syringe filter. Then about 150 microliters (μL) of the filtered solution was injected into a Plgel-Mixed B column (available from Polymer Laboratories, Amherst, MA) that was part of a GPC system also having a Waters® 717 Autosampler and a Waters® 590 Pump (available from Waters Corporation, Milford, MA). The system operated at room temperature, with a THF eluent that moved at a flow rate of approximately 0.95mL/min. An Erma ERC-7525A Refractive Index Detector (available from JM Science Inc. Grand Island, NY) was used to detect changes in concentration. Number average molecular weight (Mn) and polydispersity index (PDI) calculations were based on a calibration mode that used narrow polydispersity polystyrene controls ranging in molecular weight from 580 to  $7.5 \times 10^6$ . The actual calculations were made with PL Caliber® software available from Polymer Laboratories, Amherst, MA.

#### Block Concentration

The concentration of different blocks in a block copolymer was determined by Nuclear Magnetic Resonance (NMR) spectroscopy analysis. A sample was dissolved in deuterated chloroform to a concentration of about 10 weight % and placed in a Unity® 500 MHz NMR Spectrometer available from Varian Inc., Palo Alto, California. Block concentrations were calculated from relative areas of characteristic block component spectra.

### Surface Chemistry Modification (Water Repellency)

The water repellency of composite samples was measured using a water/isopropyl alcohol test and is expressed in terms of a water repellency rating using a scale of 0 to 10. Composite materials that are resistant to water only are given a rating of 0, whereas composite materials resistant to isopropyl alcohol (the most penetrating of the test solutions) are given a rating of 10. Intermediate values are determined by the use of other water/isopropyl alcohol mixtures, in which percentage amounts of water and isopropyl alcohol are each multiples of 10. The repellency rating corresponds to the amount of isopropyl alcohol in the most penetrating mixture that does not penetrate or wet the composite samples after 10 seconds contact. Thus, a rating of 2 reflects that the most penetrating mixture that does not penetrate or wet the composite sample after 10 seconds of contact contains 20% isopropyl alcohol and 80% water.

### Material Description

Material	Description
Isoprene	Available from Aldrich Chemical Co., Milwaukee, WI
OLIGOC4	CH <sub>2</sub> =C(CH <sub>3</sub> )CO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> S-(CH <sub>2</sub> CH-(CO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N(CH <sub>3</sub> )SO <sub>2</sub> C <sub>4</sub> F <sub>9</sub> )) <sub>n</sub> -H synthesized by reaction of methacrylic anhydride and HOCH <sub>2</sub> CH <sub>2</sub> S-(CH <sub>2</sub> CH-(CO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N(CH <sub>3</sub> )SO <sub>2</sub> C <sub>4</sub> F <sub>9</sub> )) <sub>n</sub> -H, the OLIGOC4 having a value for n of from 1 to 8 and a weight average molecular weight Mw of about 1900 to 3500. Synthesized according to the methods described in U.S. Patent No. 5,276,175 (Dams et al.).
Cyclohexane	Available from Aldrich Chemical Co., Milwaukee, WI



Sec-butyl lithium	Available from Aldrich Chemical Co., Milwaukee, WI (1.4 Molar in cyclohexane)
Toluene	Available from Brenntag Great Lakes, St. Paul, MN
High density polyethylene (HDPE)	BH-53-35H Fortiflex ®, a high density polyethylene, commercially available from BP Amoco, Houston, TX
$\alpha$ -Methyl styrene (AMS)	Available from Aldrich Chemical Co., Milwaukee, WI

### Examples 1a–1d

Synthesis of P(I-*b*-OLIGOC4) block copolymer via continuous polymerization:

The P(I-*b*-OLIGOC4) block copolymer was synthesized by sequential anionic polymerization using a stirred tubular reactor (STR) according to the methods outlined in U.S. Patent 6,969,491. The polymerization was quenched with isopropanol. Table 1 details the experimental conditions, temperature profile and polymer analytical data for the P(I-*b*-OLIGOC4) block copolymer respectively. Flow rates were varied as in Table 1 to produce Examples 1a–1d, shown in Table 2.

TABLE 1

Reagent	Entry Zone	Flow Rates (g/min)			
		Example 1a	Example 1b	Example 1c	Example 1d
BuLi (3.8% in cyclohexane)	1	1.9	1.9	1.9	1.5
Toluene	1	15.4	15.4	15.4	15.4
Isoprene (I)	1	17.5	17.5	17.5	17.5
THF	1	2.0	2.0	2.0	2.0
AMS	3	1.0	1.0	1.0	1.0
OLIGOC4 (32% solution in toluene)	4	4.3	10.7	21.4	8.0

The temperature profile in each zone was, by zone, T1 (10°C); T2 (70°C); T3 (15°C); T4 (0°C); T5 (0°C).

The Polymer analytical data for the P(I-*b*-OLIGOC4) block copolymer is shown below. 1,2-polyisoprene, 1,4- polyisoprene, 3,4- polyisoprene, and OLIGOC4 are incorporated into the block copolymer, OLIGOC4 monomer is residual monomer in the block copolymer:

TABLE 2

Example	1,2 PI mole %	1,4 PI mole %	3,4 PI mole %	OLIGOC4 polymer mole %	OLIGOC4 monomer mole %	Mn (x 10 <sup>4</sup> )	PDI
Example 1a	7.1	39.9	52.6	0.4	0.0	1.48	2.49
Example 1b	7.2	38.2	53.0	1.5	0.0	1.50	2.40
Example 1c	6.8	38.2	52.3	2.4	0.3	1.33	2.70
Example 1d	8.1	35.3	55.6	1.0	0.0	2.10	2.30

#### Examples 2a-2b and Comparative Examples 1a-1b.

High density polyethylene (HDPE) was compounded with P(I-*b*-OLIGOC4) using a 19 mm, 15:1 L:D, Haake Rheocord Twin Screw Extruder (commercially available from Haake Inc., Newington, NH) equipped with a conical counter-rotating screw and an Accurate open helix dry material feeder (commercially available from Accurate Co. Whitewater, WI). The extrusion parameters were controlled and experimental data recorded using a Haake RC 9000 control data computerized software (commercially available for Haake Inc., Newington, NH). Materials were extruded through a standard 0.05 cm diameter, 4-strand die (commercially available from Haake Inc., Newington, NH).

HDPE was first pre-dried in a vacuum oven for 16 hr at 80°C (ca. 1 mmHg). Oligomeric additive samples were cryogenically ground prior to compounding. HDPE/additives were then dry mixed in a plastic bag until a relatively uniform mixture was achieved. The material was flood fed into the extruder and was processed at 180 °C.

Injection molded plaques were prepared as described above (Injection Molding), for CE-1a and Ex-2b, as shown in Table 3. For Ex-2b, HDPE was compounded with P(I-*b*-OLIGOC4) produced from Example 1a. CE-1a was prepared as in Ex-2b, without the P(I-*b*-OLIGOC4). Pressed films were also prepared as described above (Film Preparation), for CE-1b and Ex-2a, as shown in

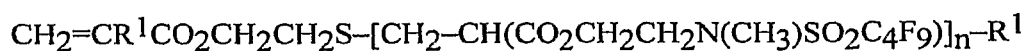
Table 3. For Ex 2-a, HDPE was compounded with P(I-*b*-OLIGOC4) produced from Example 1a. CE-1b was prepared as in Ex-2a, without the P(I-*b*-OLIGOC4).

TABLE 3

Example	Resin	Additive	Resin:Additive (wt%)	Molding method	Result: Water Repellency Test
CE-1a	HDPE	None	100:0	Injection molded	0
CE-1b	HDPE	None	100:0	Pressed Film	0
EX-2a	HDPE	P(I- <i>b</i> -OLIGOC4) (Example 1a)	95:5	Pressed Film	2
EX-2b	HDPE	P(I- <i>b</i> -OLIGOC4) (Example 1a)	95:5	Injection molded	2

We claim:

1. A block copolymer comprising at least one block comprising a fluorinated macromonomer having the general formula:



wherein each  $\text{R}^1$  is independently selected from the group consisting of H, an alkyl, an alkyloxy, a halogen, a phenyl, a benzyl, a benzoyl, a hydroxyl, a carboxyl, an amine, an amide, a sulfide, a sulfoxide, a sulfate, a phosphate, a phosphate ester, a nitroxide, a thioester, and a carbonyl; and  $n$  is selected from 1 to 25.

2. The composition of claim 1 wherein the block copolymer is a star-branched block copolymer.

3. The composition of claim 1 wherein the block copolymer is di- or tri- block copolymer having AB, ABA, or ABC architecture.

4. The composition of claim 1 wherein at least one of the blocks is a random copolymer of at least two monomeric species.

5. The composition of claim 1 wherein at least one of the blocks comprises a monomer that is selected from the group consisting of vinyl aromatics, styrenics, dienes, vinyl-pyridines, acrylates, methacrylates, epoxides, oxiranes, cyclic sulfides, lactones, lactides, cyclic carbonates, lactams, cyclosiloxanes, acrylonitrile,  $[n]$ metallocenophanes, fluorinated acrylates, fluorinated methacrylates, and anionically-polymerizable polar monomers.

6. The composition of claim 1 wherein at least one of the blocks comprises a hydrogenated polydiene block.

7. The composition of claim 1 wherein the block copolymer contains at least three blocks wherein each block is selected from the group consisting of a hydrophilic block, a lipophilic block, and a fluorophilic block.

8. The composition of claim 1 having at least one block comprising a functional group selected from the group consisting of an acid, an anhydride, and a combination thereof.

5 9. The composition of claim 1 wherein the block copolymer is end-functionalized with a single reactive group.

10. The composition of claim 1 wherein at least one block comprises a quaternary ammonium ion.

10 11. A method of reducing the surface tension of a liquid comprising adding to a liquid a surface active agent in an amount of from 0.0025 to 10 % by weight of the surface active agent, based on the total weight of the liquid and surface active agent, wherein the surface active agent comprises the block copolymer of claim 1.

15 12. The method of claim 11, wherein the liquid is in the form of a froth comprising a gas and a polymerizable monomer.

20 13. A method for modifying the surface chemistry of a polymeric substrate comprising adding to a polymer a surface active agent in an amount of from 0.1 to 10% by weight of the surface active agent, based on the total weight of the polymer and surface active agent, wherein the surface active agent comprises the block copolymer of claim 1.

25 14. A polymerized foam composition made from a mixture containing one or more of monomers, oligomers, and polymers, the mixture comprising from 0.1 to 10% by weight of a surface active agent, based on the total weight of the mixture, wherein the surface active agent comprises the block copolymer of claim 1.

30 15. An article comprising the polymerized foam composition of claim 14.

16. The article of claim 15 wherein the article is a pressure sensitive adhesive tape.

17. A block copolymer comprising at least one block having a  $-\text{CO}_2\text{CH}_2\text{CH}_2\text{S}-[\text{CH}_2-\text{CH}(\text{CO}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{SO}_2\text{C}_4\text{F}_9)]_n-\text{R}^1$  group, wherein the block copolymer is a comb-like block copolymer and wherein each  $\text{R}^1$  is independently selected from the group consisting of H, an alkyl, an alkyloxy, a halogen, a phenyl, a benzyl, a benzoyl, hydroxyl, carboxyl, amine, amide, sulfide, sulfoxide, sulfate, phosphate, nitroxide, thioester, carbonyl; and n is selected from 1 to 25.

## INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/US2007/004426****A. CLASSIFICATION OF SUBJECT MATTER***C08F 299/00(2006.01)i, C08F 220/22(2006.01)i, C08F 220/38(2006.01)i, C08F 220/34(2006.01)i*

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)

IPC 8: C08, C07C,

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

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

eKIPASS, Registry(STN)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5276175 A(Rudolf J. Dams, et al.) 04 January 1994 see whole document.	1-17
A	US 5211854 A(Wen P. Liao, et al.) 18 May 1993 see whole document.	1-17
A	EP 1 216 275A(3M Innovative Properties Company) 26 June 2002 see whole document.	1-17
A	US 6,441, 114 B1(Rechard L. Peloquin, et al.) 27 August 2002 see whole document.	1-17
A	US 6783850 B2(Youichi Takizawa et al.) 31 August 2004 see whole document.	1-17

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

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

25 JULY 2007 (25.07.2007)

Date of mailing of the international search report

**25 JULY 2007 (25.07.2007)**

Name and mailing address of the ISA/KR

Korean Intellectual Property Office  
920 Dunsan-dong, Seo-gu, Daejeon 302-701,  
Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

SHIN Gwi Im

Telephone No. 82-42-481-8392



**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/US2007/004426**

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US5276175A	04.01.1994	BR9205842A	02.08.1994
		CA2105301AA	03.10.1992
		DE69204831C0	19.10.1995
		DE69204831T2	28.03.1996
		EP00578651B1	13.09.1995
		EP578651A1	19.01.1994
		JP06506239	14.07.1994
		JP3242920B2	25.12.2001
		KR100214322B1	02.08.1999
		KR1019940700572	22.02.1994
		US5453540A	26.09.1995
		W09217635A1	15.10.1992
US05211854	18.05.1993	CA2061714AA	26.10.1992
		CA2061714C	20.01.2004
		US5211854A	18.05.1993
		US5298566A	29.03.1994
		US5374336A	20.12.1994
		US5385676A	31.01.1995
		US5387318A	07.02.1995
		US5415740A	16.05.1995
		US5532308A	02.07.1996
EP01216275A1	26.06.2002	DE60010490C0	09.06.2004
		DE60010490T2	14.04.2005
		EP01216275B1	06.05.2004
		EP1216275A1	26.06.2002
		JP15510439	18.03.2003
		KR1020020039353	25.05.2002
		TW227722B	11.02.2005
		US2003220388A1	27.11.2003
		US6391807B1	21.05.2002
		US7084168BB	01.08.2006
		W00123472A1	05.04.2001
US06441114	27.08.2002	AU200013257A1	02.01.2001
		US20020115808A1	22.08.2002
		W00077117A1	21.12.2000



**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/US2007/004426**

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US06783850	31.08.2004	CN1434844A	06.08.2003
		CN1737074A	22.02.2006
		JP13181589	03.07.2001
		JP2001181589A2	03.07.2001
		KR1020020075385	04.10.2002
		KR1020070007974	16.01.2007
		TW249562B	21.02.2006
		US20030008140A1	09.01.2003
		US493206S1	20.07.2004
		US6783850BB	31.08.2004
		W0200146328A1	28.06.2001