

of 100 megavolts per meter or greater is applied thereacross, exhibit a dielectric constant, at room temperature, of 40 or higher at 1 kHz, and exhibit an elastic energy density, at room temperature, of 0.3 joules/cm<sup>3</sup> or higher, or any combinations thereof.

The present invention also provides a process for the preparation of polymers comprising: polymerizing a mixture of three monomers comprising at least one monomer of vinylidene-fluoride; at least one monomer selected from the group consisting of trifluoroethylene and tetrafluoroethylene; and at least one monomer selected from the group consisting of tetrafluoroethylene, vinyl fluoride, perfluoro(methyl vinyl ether), bromotrifluoroethylene, chlorofluoroethylene, chlorotrifluoroethylene, and hexafluoropropylene; stretching said polymer greater than its original length; and thereafter annealing said polymer at a temperature below its melting point, wherein said polymer exhibits an electrostrictive strain, at room temperature, of 3% or more when an electric field gradient of 100 megavolts per meter or greater is applied thereacross, exhibits a dielectric constant, at room temperature, of 40 or higher at 1 kHz, and exhibits an elastic energy density, at room temperature, of 0.3 joules/cm<sup>3</sup> or higher, or any combinations thereof.

Also provided are electrical or electromechanical devices comprising at least one layer of a polymer of the invention. Polymers include, but are not necessarily limited to, polyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene P(VDF-TrFE-CFE), polyvinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene P(VDF-TrFE-CTFE), polyvinylidene fluoride-tetrafluoroethylene-chlorotrifluoroethylene, polyvinylidene fluoride-trifluoroethylene-hexafluoropropylene, polyvinylidene fluoride-tetrafluoroethylene-hexafluoropropylene, polyvinylidene fluoride-trifluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinyl fluoride, polyvinylidene fluoride-tetrafluoroethylene-vinyl fluoride, polyvinylidene fluoride-trifluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-tetrafluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-trifluoroethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-chlorofluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinylidene chloride, and polyvinylidene fluoride-tetrafluoroethylene-vinylidene chloride

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph of electric field induced longitudinal strain as a function of the applied field amplitude for the terpolymer P(VDF-TrFE-CTFE). The terpolymer No. 49 is 72.2/17.8/10 mol %; the terpolymer No. 52 is 66/22.5/11.5 mol %; and the third embodiment of the graph is the terpolymer 58.5/31.5/10 mol %. All measurements were made at room temperature.

FIG. 2 is a graph of the field induced transverse strain as a function of the applied field amplitude for the uniaxially stretched terpolymer P(VDF-TrFE-CTFE), 63.1/25.4/11.5 mol % measured at room temperature.

FIG. 3 is a graph of the strain hysteresis loop for the terpolymer P(VDF-TrFE-CTFE), 58.5/31.5/10 mol %.

FIG. 4a and FIG. 4b are graphs of the dielectric constant and loss, respectively, as a function of temperature of the terpolymer P(VDF-TrFE-CTFE) in the frequency range from 100 Hz to 1 MHz (dielectric constant: from the top to

bottom: 100, 300, 1 k, 3 k, 10 k, 30 k, 100 k, 300 k, and 1 MHz) (dielectric loss: from the bottom to top: 100, 300, 1 k, 3 k, 10 k, 30 k, 100 k, 300 k, and 1 MHz).

FIG. 5 is a graph of the field induced longitudinal strain as a function of the applied field amplitude for the terpolymer P(VDF-TrFE-CFE), 60/36/4 mol % measured at room temperature.

#### DETAILED DESCRIPTION OF THE INVENTION

It was found that in certain classes of terpolymer systems such as P(VDF-TrFE-CTFE) (poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene)) and P(VDF-TrFE-CFE) (poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene)), an ultrahigh electric field induced strain can be achieved. In P(VDF-TrFE-CTFE), as shown in FIG. 1, a thickness strain of ~4% can be induced. If the terpolymer is mechanically stretched (4 to 5 times of the original length) and annealed afterwards at a temperature 5 to 15 degrees below the melting temperature of the polymer, a large field induced transverse strain (~3%), see FIG. 2, can be obtained. Electrostrictive strains of about 3% or above are preferred. In addition, the terpolymer has an elastic modulus at room temperature of 0.5 GPa, which results in an elastic energy density (per unit volume) ~0.4 J/cm<sup>3</sup>. Preferred elastic energy densities of terpolymers of the invention are ~0.3 J/cm<sup>3</sup> or above. Such a large strain with a very low hysteresis (see FIG. 3) is very useful for electromechanical devices.

It was also found that the P(VDF-TrFE-CTFE) terpolymer has a very high room temperature dielectric constant (c.f., FIG. 4), at 100 Hz, the room temperature dielectric constant can be more than 65, which is significantly higher than any commercial polymers. Dielectric constants of the terpolymers of the invention are preferably 40 or above.

For those applications, the composition of the terpolymer P(VDF<sub>x</sub>-TrFE<sub>y</sub>-CTFE<sub>1-x-y</sub>) should be: x is in the range of 0.55-0.75 and y in the range of 0.15-0.35.

In P(VDF-TrFE-CFE) terpolymer system, as shown in FIG. 5, there is also a large thickness strain induced electrically. In this terpolymer (60/36/4 mol %, P(VDF<sub>x</sub>-TrFE<sub>y</sub>-CFE<sub>1-x-y</sub>)), a relatively high thickness strain (~4.5%) can be induced under a field ~150 MV/m. The terpolymer also exhibits a high elastic modulus ~1 GPa which results in an elastic energy density ~1 J/cm<sup>3</sup>, much higher than those in the piezoelectric materials. For this terpolymer system, the composition range of P(VDF<sub>x</sub>-TrFE<sub>y</sub>-CFE<sub>1-x-y</sub>), x should be in the range of 0.55-0.8 and y in the range of 0.15-0.4.

The high strain and high elastic energy density discovered in the terpolymer systems here are very attractive because it is well known that polymers can withstand high elastic strains without fatigue. This is a clear advantage over any inorganic material where the fatigue at high mechanical strain is a serious problem for the electromechanical device applications.

The present invention discloses a series of terpolymer systems which preferably exhibit high electric field induced strain with high elastic energy density and also high room temperature dielectric constant. The terpolymer systems include poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene), poly(vinylidene fluoride-trifluoroethylene-vinylidene chloride), poly(vinylidene fluoride-trifluoroethylene-tetrafluoroethylene), poly(vinylidene fluoride-trifluoroethylene-vinyl fluoride), poly(vinylidene fluoride-trifluoroethylene-perfluoro(Methyl vinyl ether)), poly(vinylidene fluoride-trifluoroethylene-