Synthesis and characterization of polyacene quinone radical polymers with high-dielectric constant

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ABSTRACT

Polyacene quinone radical polymers (PAQRs) and their hydroxyl- or alkoxyl-modified derivates (HO-PAQR and RO-PAQR) were synthesized through the solid-state heating, the solution polymerization, and the improved process (pre-polymerization before solid-state heating). PAQRs synthesized by the improved process provided the higher yields than those from the other two methods. The high-dielectric constants were achieved for the PAQRs from the solid state and the improved process, due to the high polarization resulted from the existence of large amount of polar domains, which were the aggregation of the conjugated ladder-structured macromolecules with extended regions of associated π-orbital. The HO-PAQRs or RO-PAQRs showed good blending or solving features in polymer or solvent, but they were of low dielectric constants for the groups of hydroxyl and alkoxyl destroyed the planar conjugation of the associated π-orbital, and provided the steric hindrance to the formation of regular stacks of the conjugated macromolecules, which could produce huge polarization. The molecular and the aggregated structures of PAQRs with varied chemical modifications and from varied polymerization processes were confirmed by the analysis of X-ray, IR, TG, TEM and the dielectric measurement.

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1. Introduction

In the recent three decades, electroactive polymers (EAPs), that can produce a significant change in shape or size in response to an electrical stimulation and are often utilized as electromechanical transducers, have attracted much attention from engineers and scientists from diverse disciplines, and are now on the verge of many exciting applications, such as those in the field of MEMS, energy storage and biomimetics [1–3]. EAPs can exhibit fast response speeds, low hysteresis and strain levels far above those of traditional piezoelectric materials [4,5], but a high electric field or a high-dielectric constant is required to generate a high input electric energy density which can be converted to strain energy [5,6].

As high electric field makes it costly for the equipment, polymeric materials with high-dielectric constant are desired. Since 1998, Zhang et al. have found an exceptionally high electrostrictive response (4%) in electron-irradiated poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymer with the dielectric

constant about 80 [5,7,8], and the introduction of another component (termonomer) of large and nonpolar comonomer will raise the electromechanical property further [9–12,15], as a heterogeneous material such as composites and block copolymers obtains the significantly enhanced dielectric and electromechanical effects due to interfacial polarization. Over the last two decades, the research has been focused on the composites of ceramic and polymers [6,13,14]. In 2000, an organic polymeric composite with huge-dielectric constant was found by Xu et al., which is a composite based on the copper-phthalocyanine (CuPc) oligomer and the P(VDF-TrFE) copolymer [15].

CuPc is an organic semiconductor with a high-dielectric constant and can be well blended with polymers than ceramics, so is polyacene quinone radical polymers (PAQRs) [16–18]. Till present day, the polyphthalocyanines or their derivatives are prepared, and their electronic or dielectric properties are studied, including their composite materials with high-dielectric constants to behave as an actuator, while the PAQRs have been rarely reported. It's not because they are inferior to polyphthalocyanines in performance, on the contrary, the dielectric constants of intrinsic PAQR polymers are usually much higher than those of polyphthalocyanines. It lies on the facts that PAQRs are difficult to be synthesized, chemically modified and blended uniformly into the polymer matrix. PAQRs are always prepared through the condensing process of aromatic

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hydrocarbons derivatives with acids or their derivatives such as anhydrides, amides and imides at high temperatures, as described by Pohl and Rosen [18]. As they are hardly dissolved or melted, their chemical structure is difficult to be characterized except for some solid methods. Some of their proposed structures have been brought forward that they obtain the highly aromatized structures with extended long-range electron orbital delocalization, which are termed as a certain superlative degree of conjugation, i.e., eka-conjugation, and is considered to be a key characteristic in polymers exhibiting enhanced electric properties, such as semi-conduction, high concentration of unpaired spins, and high-dielectric constant (60–300,000). On the other hand, these behaviors are of technical importance for applications using high-dielectric constant electronic materials, such as random access memories based on capacitive elements. Fundamental interest was initiated by the observation of huge-dielectric constant behavior in some high-T_c (Curie Temperature) compounds. Besides their excellent dielectric properties of solid states used in electronic fields, the electrorheological fluids of PAQRs are also widely used as smart materials for active devices that transform electrical energy into mechanical energy, Choi et al. have done a great deal of contributions to relative fields [19–21].

We chose the monomers of pyromellitic dianhydride and anthraquinone or hydroxyl-anthraquinone, through different processes to synthesize several kinds of PAQRs, aiming to achieve high yields, good blending with polymers and good electrical and dielectric performances. Our work is focused on the subjects of exploring the relation between the dielectric response and of the PAQRs and their structures of different scales, molecular and aggregating sizes.

2. Experimental section

2.1. Materials

The monomers chosen were anthraquinone (C.P.) and pyromellitic dianhydride (C.P.) from Shanghai Chemical Reagent Co. 1,8-Dihydroxyanthraquinone (90–95%) and 2-ethylhexyl bromide (A.R.) were from Acros Organics, the catalysts aluminum chloride and zinc chloride were from Zhenxin Chemical Reagent Co., Shanghai.

2.2. Synthesis

PAQRs were always synthesized by aromatic acid anhydride and condensed aromatic hydrocarbon or quinone or heterocyclic

several kinds of PAQR or its derivatives were prepared from pyromellitic dianhydride and anthraquinone by different processes described as follows.

2.2.1. Synthesis of PAQR

2.2.1.1. Dry-process (classical method of solid-state polymerization). The mixed powders of anthraquinone, pyromellitic dianhydride and zinc chloride with the molar ratio of 1:1:1 were ground fine, put in a lightly stopped 2 cm^3 glass tube, and then heated at 300–330 °C in a sand bath for 24 h. After it was cooled, the block of the product was ground fine and leached with 0.1 M HCl three times to extract ZnCl$_2$. The powders were then purified by extraction with water for 12 h, ethanol for 24 h and toluene for 24 h in a Soxhlet extractor. They were then dried at 60 °C in air for 6 h, and stored over a desiccant after cooled. The products were noted as dry-PAQR.

2.2.1.2. Wet-process (polymerization occurred in solutions). Anthraquinone, pyromellitic dianhydride and aluminum chloride with molar ratio of 1:1:2 were placed in a three-neck flask containing 160 ml of nitrobenzene and equipped with a nitrogen inlet tube and a condenser. After refluxing at 210 °C for 10 h, excess nitrobenzene was removed by distillation. The remaining solution was poured into 1 l methanol after cooling, and the precipitate was collected by vacuum filtration. After dried in air for several hours, the sample was purified by the same extraction method as described above. The products were noted as wet-PAQR.

2.2.1.3. Improved process (pre-polymerization before solid-state heating). The unpurified products of the wet-process were ground fine and leached with 0.1 M HCl twice to extract AlCl$_3$ and dried. After that they were put into the glass tube together with zinc chloride of the same molar amount, and heated at 300–330 °C for 24 h. The later treatment of purification was the same as the above two.

The features of the three synthesis methods and the structures of the products are described in Fig. 1.

2.2.2. Synthesis of HO-PAQR

The same synthesis processes and purification were done for the monomers of pyromellitic dianhydride and 1,8-dihydroxyl-anthraquinone, and the resultant products, hydroxyl-modified polyacene quinine radical polymers, were noted as HO-PAQR. Their chemical structure was proposed below.
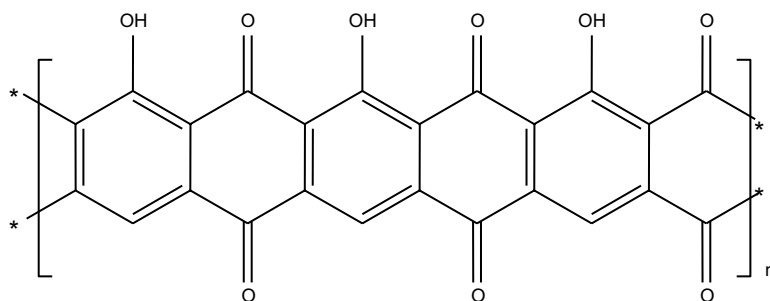
aromatics under the catalyzation of Lewis acid such as aluminum chloride or zinc chloride [18,22]. As the normal preparation of PAQR showed low yields and unsatisfying repeatability in the production and the features of the products, we tried to find a better synthesis route to assure the good dielectric constant, high yields and stability in physical and chemical properties. In the present work,

2.2.3. Synthesis of RO-PAQR

In addition, another kind of chemically modified PAQR with alkoxyl on the main chains was synthesized through the wet-process and noted as RO-PAQR. In a three-neck flask with a thermometer, a condenser and a nitrogen inlet, 5.6 g potassium hydroxide and 4 g polyethylene glycol were
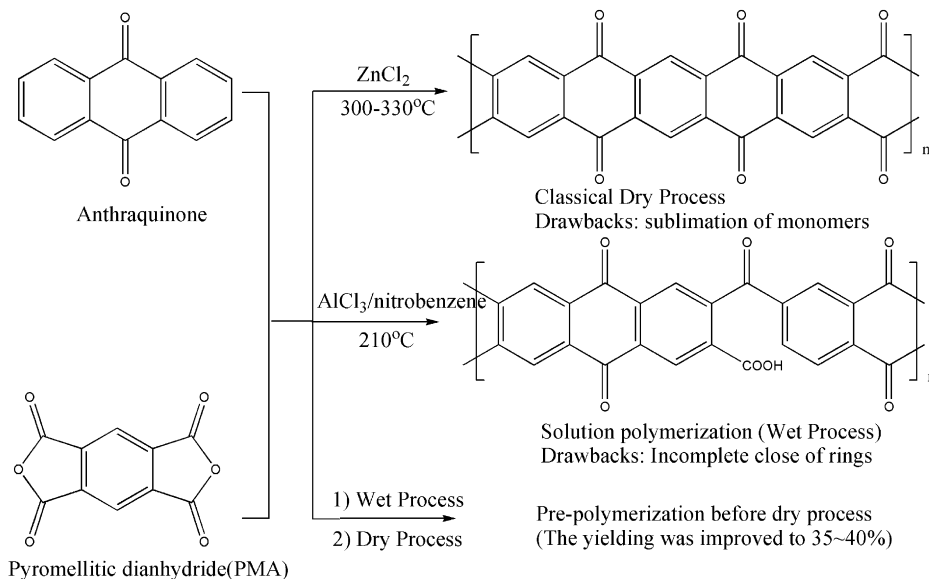
Fig. 1. The synthesis routes of dry-, wet-, and improved processes of PAQR.

dissolved in 50 ml ethanol, and then 9.6 g 1,8-dihydroxyan-thraquinone was added quickly at electromagnetic stirring. After 1,8-dihydroxyanthraquinone was dissolved and the solution turned into purple-red, 15.5 ml 2-ethylhexyl bromide was added by droplet through a drop funnel within 1 h. The reaction was maintained at 75 °C in an oil bath for 24 h till the appearance of dark-purple solids was observed. The later purification work included the distillation of the unreacted acryl bromide, rinsing with sodium hydroxide aqueous solution and extraction by ethyl ether. Alkoxy-anthraquinone thus obtained was then reacted with pyromellitic dianhydride and aluminum chloride through the wet-process as mentioned above. The final product was noted as RO-PAQR after the same purification was done. The whole procedure is described in Fig. 2.

2.2.4. Preparation of the composite film of PAQR and the polymer

The composite films of PAQR and sulfonated polyurethane (PUI) or poly(vinylidene fluoride) (PVDF) were prepared by solution casting. PAQR, in a solution of DMF with the concentration about 10 wt.%, was ground fine in a ball mill for 24 h till the average diameter of the particles reached about 400 nm, and added to the DMF solution of the polymer with the weight ratio of 20 wt.%. After fully mixed under electromagnetic stirring and ultrasonic treatment for about 1 h, the solution was poured into a copper-net, dried in a oven of 60 °C undisturbed till the solvent vaporized.

2.3. Characterization

Particle sizes of the essential PAQRs were measured by Particle Size Analyzer 90Plus BIC from Brookhaven Instrument Co., after the
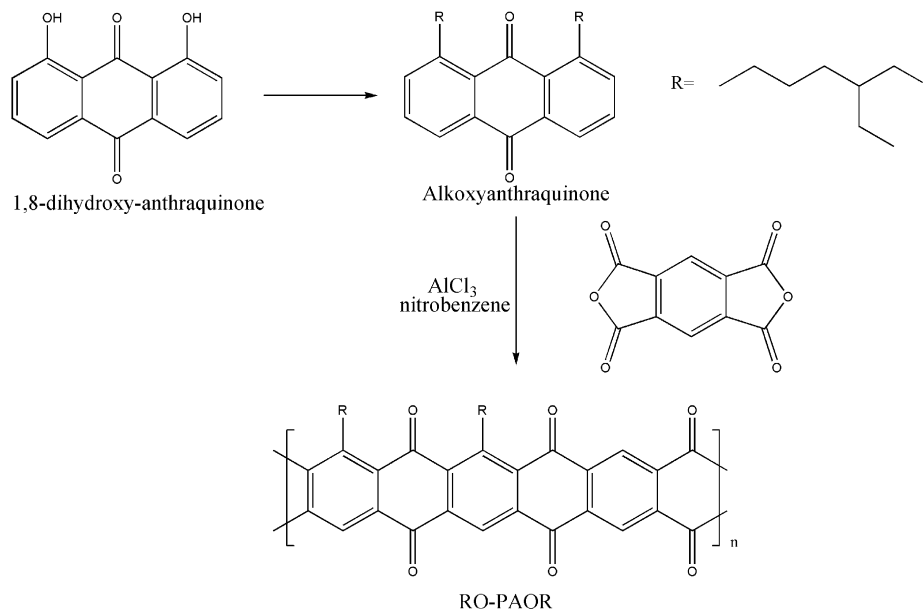

Fig. 2. The synthesis route of RO-PAQR.

PAQRs were ground in DMF solvent (10 wt.%) in a ball mill for 24 h. The thermal behavior was analyzed by TG analyzer (Perkin Elmer Pyris 1). The measurement was taken under nitrogen circumstance from 20 °C to 500 °C, and the heating rate was 20 °C/min. Samples were completely dried in a vacuum desiccator to vaporize water or solvent resident before testing. The IR spectra were taken by the Fourier transform infrared spectrophotometer of Bruker Vector-22 FT-IR with the standard laser spectrum of 632.8 nm. Samples were ground, mixed with potassium bromide and compressed to pellets for testing.

X-ray measurement was carried out by a 12-kW rotating-anode X-ray generator (Shimadzu XD-3AX) with a point focusing, and the monochromatic Cu Kα radiation (wavelength of 0.154 nm) was used. Samples tested were in powder form. Corrections of X-ray diffraction intensity were made for air scattering, background noise, polarization and absorption.

The dielectric constant was measured at room temperature by the Impedance Analyzer (HP4194A/RT) from Agilent Co. The samples were hot-pressed under 80 °C for 10 min to the thickness of about 0.3 mm, vacuum evaporated with Au electrode by an Ion Coater, Hitachi Eiko IB-3 with the area of 4.9 mm^2. The measuring voltage was 0.5 V, and the frequency was from 100 Hz to 100,000 Hz.

3. Results and discussion

Table 1 lists the yields of the products of PAQR and HO-PAQR through different processes, dry- (solid-state polymerization), wet- (solution polymerization) and the improved (pre-polymerization before dry procedure) processes. The yields of wet-process are as high as 28%, but the value will fall to 5% or even lower when we prolong the purification time to one week. As the reaction temperature in the solution is much lower than that in the dry-process and the reaction time is shorter, the polymerization degree is supposed to be low, and a large amount of oligomers of low molecular weight is produced, which will be dissolved in the solvent and get lost in the later purification. The dry-process provides a low production of about 10%, for the monomer of anthraquinone is easily sublimated around the polymerization temperature. The improved process effectively raises the yields to as high as 35–40%, which indicates that in comparison with the other two, the improved process gives a better polymerization route. That is in the first step of pre-polymerization in the solvent, most monomers are polymerized to oligomers, avoiding the sublimation of the monomers in the later high-temperature heat treatment, while in the second step of solid-state heating, the small oligomers are further polymerized and become the large molecules, so that they dissolve little in the later purification, thus provide high conversion of monomers and high yields of PAQR.

The yields of HO-PAQRs through different processes show the same trend that wet- and improved-processes provide high yields, while that of the dry-process are low. In a same synthesis process, the yields of HO-PAQR are higher than that of PAQR in the dry-process. The existence of hydroxyl group in the monomer makes the molecular weight and the polarity of monomers to increase, which induces the increase of the intermolecular forces among the monomers so the sublimation of the monomer is much less than that in the synthesis of PAQR. While in the wet-process, the monomers with hydroxyl dissolve better in the solvent as they are

polar molecules and so is the solvent, the reactants fully contact with each other and the reaction rate increases.

We find in the experiment that the products of PAQR and HO-PAQR through the improved process are similar to those from the dry-process in almost all features, like the physical out-looking, IR spectra, X-ray diffraction, TG and dielectric response, except for their yields. Based on the results, the following discussions have only been done for the PAQRs through dry- and wet-processes, which are noted as dry-PAQR and wet-PAQR respectively.

To study the difference of thermal stability between dry-PAQR and wet-PAQR, TG analysis has been done in the temperature range from room temperature to 500 °C, and the result is shown in Fig. 3. The thermal degradation of both dry-PAQR and wet-PAQR is almost the same up to 100 °C, for below that temperature, they both obtain a good thermal stability and there is no physical or chemical reactions occurring. The dry-PAQR shows a mild weight loss in accordance with the temperature going up, while the weight of the wet-PAQR lost abruptly when it is heated over 300 °C. It demonstrates that the dry-PAQR shows a better heat-stability than the wet-PAQR during the testing temperature range. It indicates that there are more active sites in the wet-PAQR that the hydrolysis occurs during heat treatment, and the polymer turns into the fractures of small-molecular weight and vaporizes at high temperatures, so the weight of the tested samples is lost. To support our assumption, we take the IR spectra of PAQR prepared from the dry- and wet-processes and show them in Fig. 4. In the spectrum of the wet-PAQR, absorption bands in the region from 1600 to 1900 cm^{-1} are due to the stretching vibrations of carbonyl from carboxylic acid (1725 cm^{-1}), anhydride (PMA, 1790 cm^{-1}), quinine (anthraquinone, 1675 cm^{-1}, a shoulder peak covered by that of carboxylic acid). We can find analogous absorption in IR spectra of the monomers. As the polymers have been carefully purified, there should be little remnants of the monomers left in the tested samples. The appearance of carboxylic acid in the wet-PAQR indicates that there occurs incomplete polymerization in the polymerizing procedure or hydrolysis during the extraction with HCl aqueous (the latter is of low possibility to occur for the HCl aqueous used which is of low concentration), which leads to the existence of anhydride end groups and the unclosed rings in the polymer chains, as drawn in Fig. 1. These carbonyl groups left in the main chain become the active spots, and by heating, they will cause chain scission and weight loss in TGA. Other absorptions observed are due to the skeletal stretching vibrations of the C–C double bonds at 1600 cm^{-1}, in-plane bending vibrations at 1000–1300 cm^{-1}, and C–H out-of-plane bending vibrations at
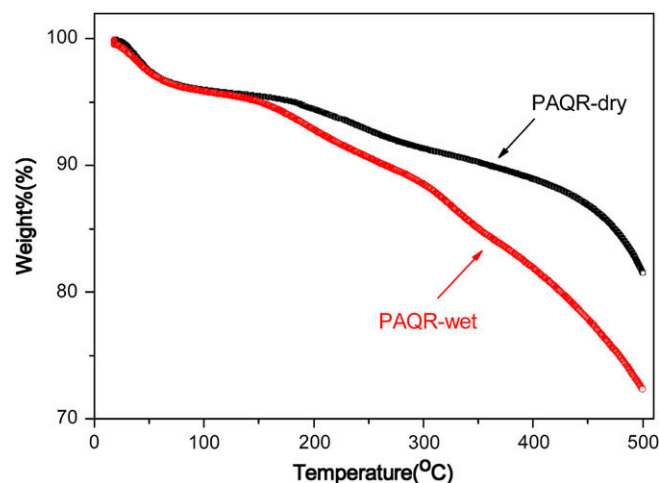
Table 1
The yields of PAQR and HO-PAQR prepared through different processes.

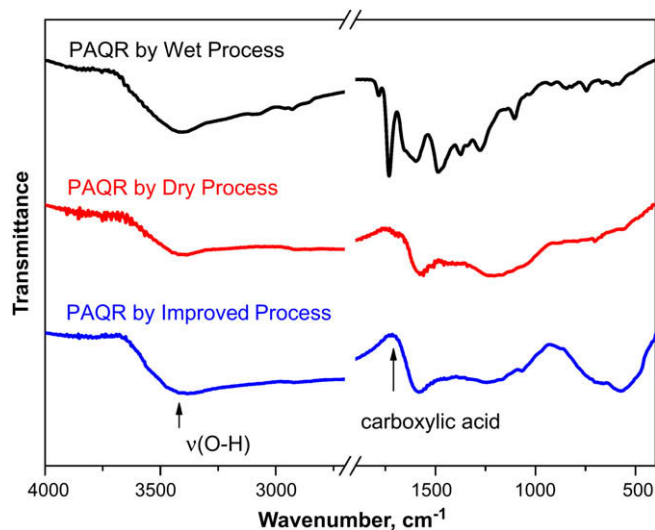|	Dry-process (%)	Wet-process (%)	Improved process (%)
PAQR	12	28	34
HO-PAQR	30	70	54

Fig. 3. The TG analysis of dry-PAQR and wet-PAQR.

Fig. 4. The IR spectra of dry-PAQR, wet-PAQR and the PAQR from the improved process.

675–900 cm^{-1}. The spectrum for the dry-PAQR shows little absorption of carbonyl stretching vibrations, only a weak peak appears around 1700 cm^{-1}, which is due to the stretching vibrations of conjugated carbonyl, the structure of quinone. It indicates that there exists little non-reacted carboxylic acid in the macromolecules of dry-PAQR, because the reaction temperature in the dry-process is high, resulting in complete polymerization of monomers, and the complete cyclization in the main chain forms the closed rings of ladder structures, so that the dry-PAQR is stable in high-temperature heat treatment, as shown in its TG measurement.

Fig. 5 describes the IR absorption of the modified RO-PAQR, one of its monomers of 1,8-dihydroxyanthraquinone, and the media production of alkoxy-anthraquinone. It can be seen from the spectra of alkoxy-anthraquinone and RO-PAQR that appeared a typical absorption peak for aryl ether vibration around 1250 cm^{-1}, which is not in the spectrum of 1,8-dihydroxy-anthraquinone, confirming the existence of alkoxyl in the media production and the final RO-PAQR. Absorption peaks around 1600 cm^{-1} are due to the skeletal vibration of benzene rings, which can be seen in all the three spectra. The stretching vibration of carbonyl appears around 1700 cm^{-1} in the spectrum of alkoxy-anthraquinone, and around 1725 cm^{-1} in that of RO-PAQR, indicating that a procedure of ring-open takes place in the quinine structure in alkoxy-anthraquinone
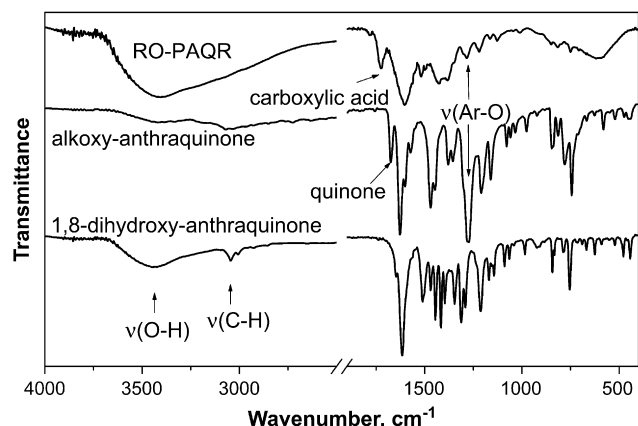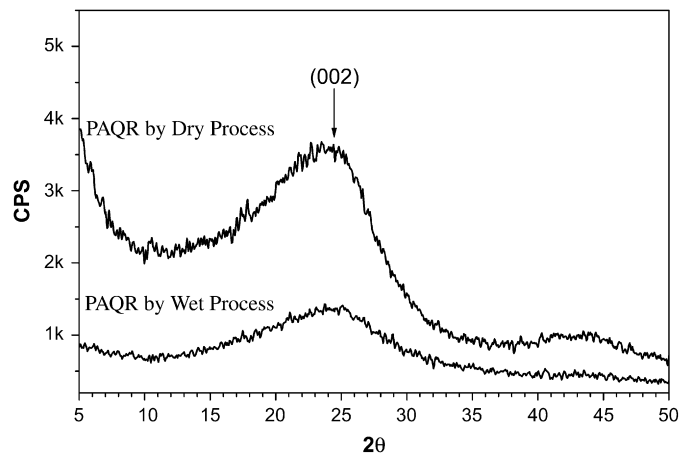
and it changes into carboxylic acid in the solution polymerization, so that it leaves carboxylic acid in the main chains or the end groups in the final RO-PAQR.

Fig. 6 shows the X-ray diffraction of the PAQRs produced through the dry- and wet-processes. The diffraction for the dry-PAQR provides a very broad diffraction peak at around 26.5° corresponding to the (002) reflection from the layer planes of 0.34 nm in distance, which is a typical peak observed from the structures of carbon or graphite. But as the (002) reflection peak is mild and broad, meaning the stacking of the graphite-like planes is not as regular as those in the natural graphite, they are in a non-graphitizing turbostratic (irregular) organization of stacks [23,24]. The intensity of (002) reflection is considered to be relevant to the crystallization degree and crystal size of graphite. As the polymerization goes on, the cyclization of high degree gets completed, forming conjugated ladder-structured polymers, then the polymers are converged into planar aromatic graphite sheet, and finally these layers stack together and become the graphite-like morphologies under high-temperature heat treatment in the solid-state dry-process, like any precursor behaves in carbonization procedure. The (002) reflection shows a higher intensity in the dry-PAQR in comparison to that in the wet-PAQR, indicating that the amount and size of graphite stacks formed in dry-process are more and larger than those formed in the wet-PAQR, for the polymerization condition, especially the heat-treat temperatures apparently affect the condensed state of the PAQR molecules, i.e., graphite-like or not.

We have measured the bulk dielectric constant and the loss of PAQR, HO-PAQR and RO-PAQR prepared through different processes, and the results are shown in Table 2. Samples have been hot-pressed at 80 °C for 20 min before testing, and the measurement is carried out at 100 Hz at room temperature. The dielectric constant of dry-PAQR has reached 10^6 at the frequency of 100 Hz, while that for the HO-PAQR by dry-process is 10^4. The behavior of high-dielectric constant in PAQR is due to a kind of colossal polarization, nomadic polarization in term, which can produce huge macroscopic polarizability. In a molecular view, within the extraordinarily long regions of associated π-orbital in PAQR, the mobile charges would move freely along extended regions of

Fig. 6. X-ray diffraction counts for the dry- and wet-PAQRs.

Fig. 5. The IR spectra of RO-PAQR and its raw and media products.

Table 2
The dielectric constant of PAQRs bulk measured at 100 Hz at r.t.

Dielectric constant/loss	Dry-process	Wet-process
PAQR	1.2×10^6/30	8.1×10^4/14
HO-PAQR	1.2×10^4/8	1400/3.5
RO-PAQR	–	80/0.6

near-zero resistance, with their domain path limited ultimately by the boundary of a planar or even stacked "huge MO polymers" [17]. The delocalized charges, arising from inherent and easily thermally excited intermolecular ionization levels of the long conjugated molecules would form a collection of highly polarizable monopoles or dipoles and thereby exhibit high bulk polarizability under the external electric field. This collection of highly field-sensitive poles would then exhibit what might be termed "hyperelectronics" polarization, leading to high-dielectric constant in macroscopic features. It is shown in Table 2 that the dielectric constant of wet-process production is lower than that of the dry-process, as the wet-process can not provide high temperature needed for complete polymerization, formation of ladder-like conjugated structure in the main chain and the later regular stacks of molecules, which we have drawn the conclusion from FT-IR and X-ray diffraction. The dielectric constant of HO-PAQR is 10^4 for dry-process and 1500 for wet-process, lower than that of PAQR respectively, and that of RO-PAQR is even much lower, 80 at 100 Hz and room temperature. It is assumed that the existence of groups of hydroxyl and alkoxyl destroys the planar conjugation of the associated π-orbital, and the steric hindrance of these large groups makes it difficult for the regular stacks of molecules, so that little polarizable poles can be accumulated to achieve macroscopic polarizability. The larger the groups, the more the conjugation destroyed and the more the steric hindrance to the polymer. Though the dielectric constant of RO-PAQR, low in PAQRs' families, is high enough when compared with other polymers whose dielectric constants are usually less than 10. In addition, RO-PAQR can be well blended with polymer matrix when its composites are prepared.

There are commonly two reasons to cause the ac-capacitors' losses, one is the conduction loss from the movement of charges, and the other is the dielectric loss due to the movement or rotation of the atoms, groups, the whole molecules, or the phase (in a heterogeneous material) in an alternating electric field, any hindrance to those movement will lead to the energy-consumption. In our case of the huge conjugated molecules, when the electric field is set or alternated, the conduction loss and the dielectric loss are much higher than the usual insulated polymers. The value of the losses is proportional to the displacement of the electrons or the size of the groups and the molecules. As the nomadic polarization is also determined by the size of the delocalized regions, the dielectric losses increase with the increase of the dielectric constants.

For a long time the organic polymers have been expected to be used in the electrostrictive applications as they obtain the supreme processability, flexibility to generate satisfying strain in electromechanical response, and good mechanical strength to sustain large stress. However, these polymers also require a high field (>70 V/μm) to generate high elastic energy densities (>0.1 J/cm^3). The elastic energy is a key parameter, measuring both the stress and strain generation capability of an actuator material. For a field-type electroactive polymer, the total elastic energy density from all the strains generated cannot exceed the input electric energy density because energy must be conserved. As a linear dielectric material, this input electric energy density is $U_E = 1/2\kappa\varepsilon_0 E^2$, where E is the applied field, ε_0 is the vacuum dielectric permittivity ($=8.85 \times 10^{-12}$ Fm^{-1}), and κ is the dielectric constant of the polymer. In order to generate a high input electric energy density which can be converted to strain energy, we need to raise the dielectric constant of polymers substantially in many practical applications. On the other hand, there have been reported on electromechanical properties of polymers that some polymeric thermoplastic elastomers, especially polyurethane elastomers, can provide high performance on field-induced strain response [25]. Hence we prepared the composites of PUI (sulfonated polyurethane) and
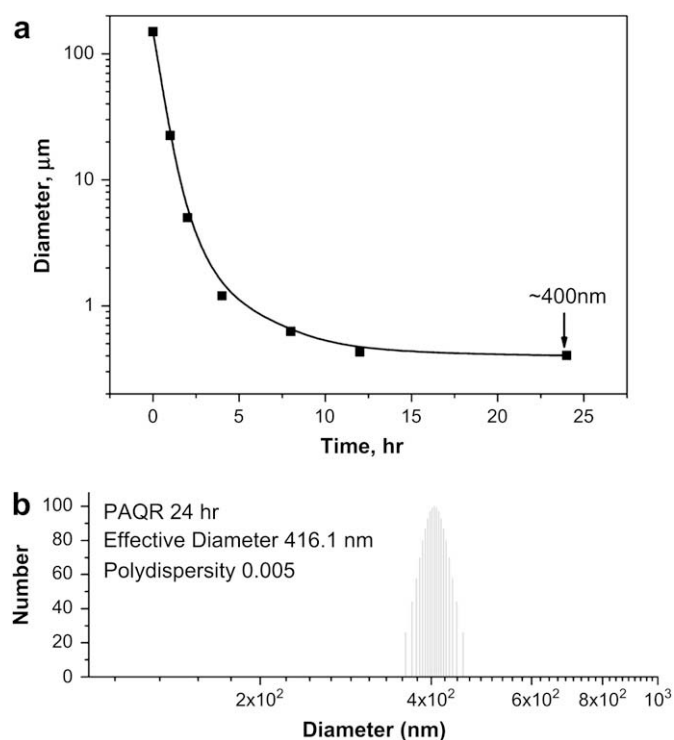

Fig. 7. (a) The average diameter of the dry-PAQR in accordance with the grinding time, and (b) the effective diameter and diameter distribution of the dry-PAQR ground after 24 h.

several kinds of PAQRs, dry-PAQR, wet-PAQR or RO-PAQR with high-dielectric constant by the method of solution casting and studied their dielectric properties.

Before its composites are prepared, dry-PAQR has been ground in a ball mill for 24 h till the average diameters of the particles achieve ca. 400 nm, tested with a Particle Size Analyzer. In Fig. 7 it shows the results of the change of the average diameter of the dry-PAQR in accordance with the grinding time (a) and the effective diameter and diameter distribution of the dry-PAQR ground after 24 h (b). The grinding is unnecessary for wet-PAQR or RO-PAQR, as they can disperse well or partly resolve in the solvent of DMF. Thus they can be blended well with the polymer matrix to make the composite films of homogeneous out-looking and good flexibility. The diameter of dry-PAQR will reach even smaller to 200 nm when we prolong the grinding time to one week, but the particles will soon aggregate to the size about 400–500 nm again, which is assumed that the state in small scale will make the surface energy or the electrostatic energy of PAQR particles very high and unstable, they have to aggregate to reduce the free energy.

The dielectric constants and losses of PUI and the composites of PAQRs and PUI prepared with the weight ratio of 45/55(PAQR/PUI) have been measured at 100 Hz at room temperature. The results have been listed in Table 3. It is clearly seen that the dielectric constants of the composites show the same trend as those of the

Table 3
The dielectric constant and loss at 100 Hz for the PUI matrix polymer and its composites with PAQRs with the weight ratio of 45/55 (PAQR/PUI).

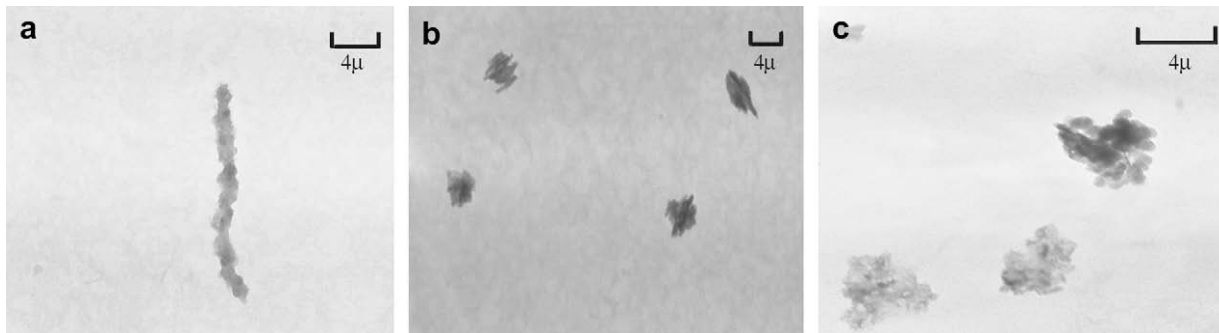|	K at 100 Hz	D at 100 Hz
PUI	78	0.6
Dry-PAQR/PUI	3.3×10^4	4.7
Wet-PAQR/PUI	2.1×10^4	13.9
Dry HO-PAQR/PUI	798	2.2
Wet HO-PAQR/PUI	80	0.7

Fig. 8. TEM photos taken for the composite film of PAQR/PVDF (20/80 w/w) of (a) dry-PAQR, (b) wet-PAQR and (c) RO-PAQR.

PAQRs through different synthesis processes. PAQRs or the composites with PAQRs from wet-process and the introduction of hydroxyl into the molecules make the dielectric constant lower than PAQRs from the dry-process and without side group on the molecules. The dielectric constant of composites is lower than that of intrinsic PAQR, but at the same time, is higher than that of the polymer matrix, especially for the composite of dry-PAQR, which makes the dielectric constant of the polymer of about 78 raise in a large scale, achieving 10^4 at 100 Hz. It is apparent that the PAQRs in the polymer matrix introduce domains of highly polarizable poles and this collection of field-sensitive poles exhibits polarization to lead to high-dielectric constant in macroscopic features. The data in Table 3 also indicates that dielectric losses of the composites of lower than the corresponding intrinsic PAQRs for the polymer matrix among the PAQRs form the insulated layers, so that the intermolecular electric conduction is reduced and the conduction loss is significantly reduced.

A lowest free energy leads to the stable aggregated structure of the particles in the polymer matrix, and the morphology results from the competition and equilibrium of the electrostatic, depolarization and elastic energies [26]. The morphologies of the micro-domains of dry-PAQR, wet-PAQR and RO-PAQR in PVDF (20 wt.%) have been observed through the TEM microscopy and the photographs are shown in Fig. 6. They declare visually the microscopic morphology of PAQRs, and show the differences among the PAQRs from different processes. The wet-PAQR (b) shows a better dispersion into the polymer matrix compared with the other two, and the particle size is of better uniformity about 2–3 μm. The aggregated morphology of the dry-PAQR is like a necklace with a long thread of beads, which is assumed that every "bead" is a polar domain, and its electric moment at the two sides of the domains joins one another by head to tail to make the domain wall without any charges, thus lowers the electrostatic energy. It verifies the huge spontaneous polarization happened in the dry-PAQR, according to the complete polymerization leading to large molecules with long range of conjugated regions. The formation of "necklace" also indicates that the micro-domain is of low charge density [27], which is due to the high electric conductivity of each "bead" that makes the charges spreading, and finally due to the highly conjugated structures. The modified RO-PAQR, though in large size, demonstrates an unclear boundary with the polymer matrix, indicating a good blending character with the polymer. It is for the good compatibility that the polymer, working as glue, sticks the molecules together so their aggregates of large size form. In our observation under TEM, we find that heating from electron collision to the surface of the sample will blur the borderline of that aggregates, showing the wrapping of polymer from the RO-PAQR. The sizes of PAQRs in Fig. 8 are not in accordance with that from the particle size analyzer, for in particle size analyzer we measure the particle size in the DMF solution with the PAQRs' mass concentration about 10%. It's concluded that the interactions between

PAQR and DMF are stronger than those between PAQR and PVDF, based on some surface-state analyses and molecular dynamics simulations performed on a model of polymer–nanoparticle composite [28].

4. Conclusions

PAQR and chemically modified HO-PAQR and RO-PAQR have been synthesized through dry-, wet-, and the improved processes. PAQRs synthesized by the improved process provide the yields of 35–40%, which is much higher than those from the other two methods. The dielectric constant of the dry-PAQR can reach 10^6 at 100 Hz and room temperature, while modified PAQRs, though obtain low dielectric constant, they perform good physical blending with the polymers.

The dielectric mechanism has been studied for the PAQRs in terms of the polymerization and the molecular and aggregated structures. PAQRs from the dry- and the improved processes obtain high-dielectric constants, due to their complete polymerization to form the cyclized molecules with extended conjugated ladder structures, and carriers (electrons) moving along them will form a collection of highly polarizable monopoles or dipoles and thereby possibly exhibit high macroscopic polarizability.

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