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Preparation and Pyroelectric Properties of Poly(pentafluorostyrene)-*r*-Poly(4-vinylaniline) Copolymer Films

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Abstract: In this study poly(pentafluorostyrene)-*ran*-poly(4-vinylaniline) (PPFS-*r*-PVA) was synthesized by solution polymerization with AIBN utilized as an initiator. The dilute THF solution of the resultant copolymer was spin-coated onto clean Ag/Si(100) substrates, and then the copolymer film was electrically poled at 85 °C for 30 min using a plane poling method with a poling voltage of 7.0 kV. The pyroelectric coefficient was determined by a digital integral method and carried out with a charge integral instrument. It was observed that the average pyroelectric coefficient of the resultant PPFS-*r*-PVA was 20.4 $\mu C/cm^2K$ in the range of 20–45 °C, and the average dielectric loss is about 0.2298 between 3.2×10^4–1.0×10^6 Hz.

Keywords: dielectric; film; poly(pentafluorostyrene)-*r*-poly(4-vinylaniline) copolymer; pyroelectric; synthesis

Introduction

In the early 1970s, poly(vinylidene fluoride) (PVDF) was discovered to be pyroelectric,[1] which lead to electro-optic, electromechanical, and biomedical applications. In particular, its piezo- and pyroelectric properties provide possibilities in many technological applications. The poly(vinylidene fluoride)-*ran*-poly(trifluoroethylene) [PVDF-*r*-PTrFE)] copolymer has been used as a ferroelectric polymer due to its good piezoelectric and pyroelectric properties,[2–4] and has attract more and more attention recently.[5–6] However, as is known, the processability of PVDF is so poor that it limits their practical applications, so methods to improve the processability, and to reform the pyroelectric properties of fluorinated polymer pyroelectric materials in general, are challenging materials research topics.

In this paper, the poly(pentafluorostyrene)-*rac*-poly(4-vinylaniline) (PPFS-*r*-PVA) copolymer was synthesized by solution polymerization, with AIBN utilized as an initiator, with the aim to improve the processability. The pyroelectric and dielectric properties of the resultant PPFS-*r*-PVA were investigated further.

Experimental Part

General Information

Pentafluorostyrene (95%, Aldrich) and 4-vinylaniline (95&, Aldrich) were used directly as received. Tetrahydrofuran (THF, Shanghai Chemical Reagent Company, Analytical Reagent) was refluxed with sodium for 24 h. Azobisisobutyronitrile (AIBN) (Merck) was recrystallized from methanol.

Synthesis of the PPFS-*r*-PVA copolymer

Pentafluorostyrene (4.4mL, 3.17×10^{-2} mol), 4-vinylaniline(3.8mL, 3.17×10^{-2} mol), and AIBN (0.1g, 1.56×10^{-3} mol) were fully dissolved in 5.0 mL of freshly dried THF in a 25 mL Schlenk flask

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equipped with a magnetic stir bar. The flask was then sealed and immersed in an oil bath at a desired temperature of 70–80 °C for a certain time. The polymerization was stopped by cooling to room temperature and exposing the reaction mixture to air. The resulting polymer was precipitated into methanol and finally freeze-dried. The conversion was 97.2% as determined by gravimetry.

Preparation of the PPFS-*r*-PVA Copolymer Film

A dilute THF solution of the resultant PPFS-*r*-PVA copolymer was spin-coated onto a cleaned Ag/Si(100) substrate at a rotation rate of 2000 rpm and the deposition took 20 s. It was then dried in a vacuum oven at ambient temperature for two days.

Thermal Poling of the PPFS-*r*-PVA Copolymer Film

Since the obtained copolymer of pentafluorostyrene and 4-vinylaniline is isotropic, a preferential dipole orientation and thus pyroelectricity were achieved by a thermal poling method. The PPFS-*r*-PVA film was electrically poled by a plane poling method at 85 °C for 30 min with a poling voltage of 7.0 kV.

Characterization

FT-IR spectra of the PPFS-*r*-PVA copolymer were recorded on PerkinElmer FTIR spectrometer. Thermogravimetric differential thermal analysis (TG-DTA) was performed using a DTA-7 under a nitrogen atmosphere at a heating rate of $10\,^{\circ}\mathrm{C} \cdot \mathrm{min}^{-1}$. Differential scanning calorimetry (DSC) measurements of the copolymer film were performed with a Perkin-Elmer DSC-7 in the temperature range from 20 to 120 °C and a heating rate of $10\,^{\circ}\mathrm{C} \cdot \mathrm{min}^{-1}$. The pyroelectric coefficients of the PPFS-*r*-PVA were determined by digital integral method and carried out with a DH-1 charge integral instrument. The pyroelectric coefficient (P) could be calculated using the following equation:[7] $P = (\delta Q \Delta N)/(\mathrm{A}(T_2 - T_1))$, missing symbol where δQ is the quantity of discharge per times, and the values of δQ fit as10^{-11} C; $DN = (\mathrm{N}_+ - \mathrm{N}\_)$, N_+, $N\_$ are the times of discharge shown in positive and negative counter, respectively; T is the temperature; A is the efficient square of the sample, which is equal to the surface area of the used electrode. The dielectric permittivity and dielectric loss of the resultant copolymer were calculated from measurements made with a HP 4192A Impedance Analyzer in the frequency range from 1000 Hz to 1000 kHz.

Results and Discussion

The FT-IR spectrum of the PPFS-*r*-PVA copolymer is shown in Figure 1. The two bands at 1122 and 1050 cm^{-1} could be attributed to the C–F stretch of the pentafluorostyrene units. In addition, the characteristic penta-peaks in the range of 3062.28–2857 cm^{-1} were attributed to the benzene ring. The occurrence of the broad band at 3434cm^{-1} was inferred to the $-\mathrm{NH}_2$ group of the 4-vinylanline units. There were no peaks corresponding to a C=C stretching at 1640 cm^{-1}, which suggests that almost all the monomer had participated in the reaction and there were no C=C bonds left in the system.

Figure 2 shows the TGA curve of the PPFS-*r*-PVA copolymer. We can see that the whole weight-loss process is observed between 376 and 467 °C. The value of the

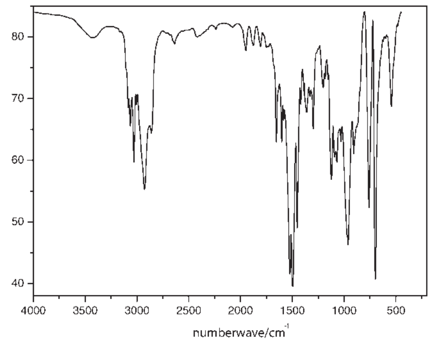

Figure 1.
The FT-IR spectra of the PPFS-*r*-PVA copolymer.

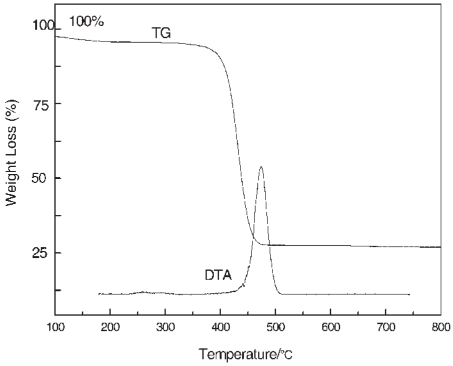

Figure 2.
TGA curve of the PPFS-*r*-PVA copolymer.

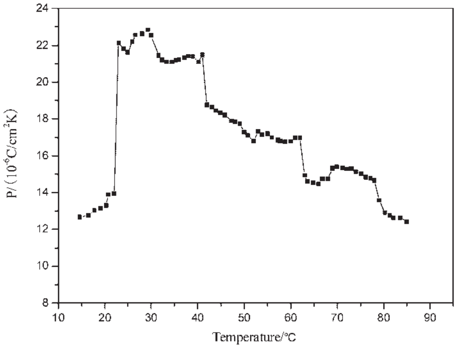

Figure 4.
Variation of the pyroelectric coefficient with temperature for the PPFS-*r*-PVA copolymer film.

maximum of the decomposition peak occurs at 434 °C, which corresponds to the temperature of maximum loss mass rate. Differential scanning calorimetry (DSC) was used to characterize phase transitions of the PPFS-*r*-PVA copolymer and the results are shown in Figure 3. Only one glass transition temperature (85 °C) was observed. It strongly suggested that the copolymerization did occur. The material was not a simple blend of two homopolymers.

The PPFS-*r*-PVA copolymer film was electrically poled by a plane poling method at 85 °Cfor 30 min with a poling voltage of 7.0 kV. The pyroelectric coefficient of the poled hybrid film versus temperature is shown in Figure 4. The multipeak can be seen in the range of 20–45 °C, and the average value of the pyroelectric coefficient is 20.4 μC/cm^{2}K. The obtained pyroelectric coefficient of the random copolymer of pentafluorostyrene and 4-vinylaniline was in the same number order as the reported values. The other properties will be further determined.

Figure 5 shows the variation of dielectric loss of the PPFS-*r*-PVA copolymer with frequency at 15 °C of the measurement temperature. The average dielectric loss is about 0.2298 between 3.2×10^4 to 1.0×10^6 Hz.

Conclusion

The random copolymer formed from pentafluorostyrene and 4-vinylaniline was

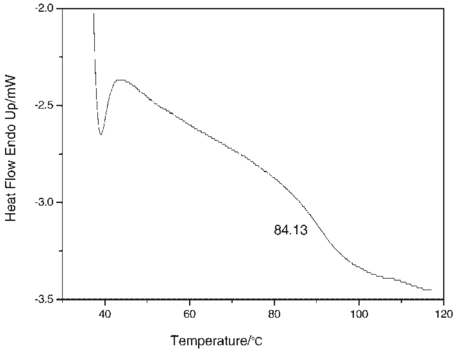

Figure 3.
DSC curve of the PPFS-*r*-PVA copolymer.

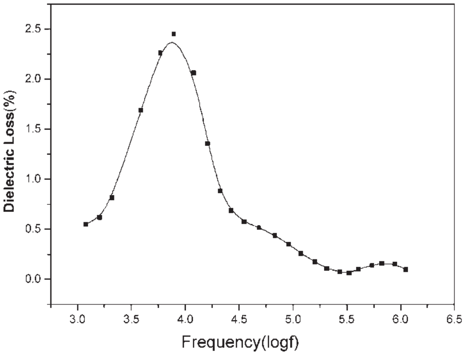

Figure 5.
Variation of the dielectric loss with Frequency for PPFS-*r*-PVA copolymer film.

synthesized in solution and AIBN was used as an initiator. The pyroelectric properties and dielectric loss of the obtained PPFS-*r*-PVA copolymer were determined. The results show that the average pyroelectric coefficient of the PPFS-*r*-PVA is 20.4 $\mu C/cm^2K$ between 20–45 °C, and the average dielectric loss is about 0.2298 between 3.2×10^4–1.0×10^6 Hz.

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