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Effect of Thermal Treatments on Ferroelectric Crystalline Phase Changes in Poly (Octafluoropentyl Acrylate).

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ABSTRACT

Fluoropolymers such as Poly(vinylidene di-fluoride) and Poly(vinylidene di-fluoride)-co-Trifluoroethylene have already demonstrated their utility in thick-film based electronic applications such as in organic memory devices, sensors, transducers, etc. Our focus is to study new ferroelectric polymers which can be used either as stand-alone material or as solution blends with other fluoropolymers. In the present study, the synthesized Poly(2,2,3,3,4,4,5,5-octafluoropentyl acrylate) was solution-cast onto KBr pellets, and the changes in different crystalline phases were studied using a simple analytical tool, i.e., FTIR-Transmission spectroscopy as a function of varying thermal treatment conditions. Based on the data obtained, the relationship between crystalline phase changes and thermal conditions at below melting ($<T_m$) and above melting ($>T_m$) were established. The results obtained from this study will be helpful to researchers in identifying the ideal thermal treatment condition to obtain maximum ferroelectric crystallinity in samples for use in organic electronics.

Keywords: Fluoropolymers; As-cast film; FTIR spectroscopy; Annealing; Melt-quenching; Crystallinity.

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INTRODUCTION

Fluorinated polymers exhibit a unique combination of high mechanical and thermal stability, chemical inertness, low dielectric constants, excellent weatherability, good resistance to oxidation and very interesting surface properties.[1] Most of the fluorinated monomers exist in the gaseous phase at ambient conditions, and hence require complicated reaction conditions such as high pressure SS magnetic stirring pressure autoclave, Hastelloy autoclave, etc. for their polymerization reactions.[2] Despite such critical conditions, a few research groups have synthesized and commercialized many types of fluoropolymers such as poly(tetrafluoroethylene), polyvinylidene fluoride (PVDF), PVDF-co-chlorotrifluoroethylene, PVDF-co-trifluoroethylene, poly(hexafluoropropylene), etc.[2-6] In the case of PVDF and its copolymers, many research groups including ours have studied their ferroelectric characteristics with applications such as non-volatile memory devices, sensors, and actuators.[7-12]

PVDF exhibit at least four different crystalline phases (α , β , γ and δ), and among them, the polar β -crystalline phase is most preferred due to the favorable orientation of C-F dipoles in the PVDF backbone along the parallel direction with the net dipole moment being greater than zero. On the other hand, α -crystalline phase is the least preferred due to its non-polar nature caused by the anti-parallel orientation of C-F dipoles resulting in the net dipole moment being zero.[3] Though the as-cast PVDF film is known to exhibit a predominantly non-polar α -phase, it requires one among the many diverse methods like mechanical stretching (four times its original size in two dimensions),[3,4] application of high pressure [5] and electro-spinning [5,8] among many others to induce the ferroelectric polar β -crystalline phase suitable for various electrical and electronic applications.

Hence, it is imperative that there is an urgent need to analyze new and alternate ferroelectric materials capable of exhibiting significant β -crystalline phase even under as-cast conditions which can be developed using common and basic facilities available in research labs. Based on the literature review, we focused our attention towards acrylic fluoro monomers which when polymerized can yield a highly crosslinking film, yet containing many number of C-F dipoles in their back bone. In the present study, as-cast thick film samples of poly(2,2,3,3,4,4,5,5-octafluoropentyl acrylate), POFPA were subjected to different thermal treatments, and their crystalline phase changes were analyzed both qualitatively and quantitatively using FTIR spectroscopy technique.

EXPERIMENTAL

Poly(2,2,3,3,4,4,5,5-octafluoropentyl acrylate), POFPA was synthesized as per reported procedure.[13] The fluoro monomer and the solvents (acetone and DMF) were purchased from Sigma-Aldrich, USA. All the above chemicals were used as received without any further purification. For thermal treatment studies, as-cast thick films of POFPA were prepared from 1 wt.-% solution in DMF: Acetone (80:20) mixture on KBr pellets. The samples are treated at different temperature conditions like as-cast (AC, 40 °C), annealing (AN, 110°C), melt-quenching (MQ, 210 °C) and melt-slow cooling (MSC, 210 °C) for 24 h in vacuum in order to get samples with varying degrees of crystallinity. Unpolarized FTIR-TS was collected using Shimadzu IR Affinity-1 spectrometer with 32 scans at a resolution of 4 cm^{-1} . All the raw IR spectra were baseline corrected and used for further analysis.

RESULTS AND DISCUSSION

In order to have comprehensive interpretation of the structural changes in POFPA polymer some important vibrational bands were assigned to characteristic conformations by earlier reports [9, 14–19] and in this study we engaged all these assignments as shown in Table 1.

FTIR-TS is an effective technique widely used to identify the crystalline structures of fluoropolymers aided by the identification of varying characteristic absorptions at 542, 613, 760, 796, and 976 cm^{-1} for the α -phase; at 509, and 1279 cm^{-1} for the β -phase; and at 1232 cm^{-1} for the γ -phase.[9, 12,14, 15] Figure 1 shows the FTIR-TS of POFPA thick film samples measured at room temperature (R.T.) but prior treated under different thermal conditions like AC, AN, MQ and MSC in order to obtain the favorable crystalline phase. Among the four thermal treatment conditions, AN and MQ samples showed improved β -crystalline polar phase (1290 cm^{-1} , A_1 band) along with corresponding decrease in α -crystalline non-polar phase (604 cm^{-1}) compared to the AC and

MSC conditions. Though the qualitative data shown in Figure 1 does give some idea about the crystalline phase changes, a quantitative analysis is more preferred to confirm the same.

Table 1 List of important IR bands chosen from the relative fluoropolymers for analyzing POFPA.

Wavenumber (cm ⁻¹)	Symmetry species	Assignments ^a	Chain conformation	Reference
542, 613, 760	A2	δ (CF ₂), δ (CCC)	tg	[9, 12, 14-15]
802	-	r(CH ₂)	tttg	[15]
912	-	ν as (CC), ν (CH ₂), ω (CF ₂)		[9]
980	A2	t(CH ₂)		[16]
1074	B1	ν as (CC), ω (CH ₂), ω (CF ₂)		[9,16,17]
1172	B2	ν as (CF ₂) - r(CF ₂),		[18]
1292	A1	ν s (CF ₂), ν s(CC), δ (CCC)	tm (m > 4)	[9,16,17]
1400	B1	ω (CH ₂), ν as (CC)		[9,15,16]

^a Vibrational modes: ν_{as} , antisymmetric stretching; ν_s , symmetric stretching; δ , bending; ω , wagging; r, rocking; t, twisting.

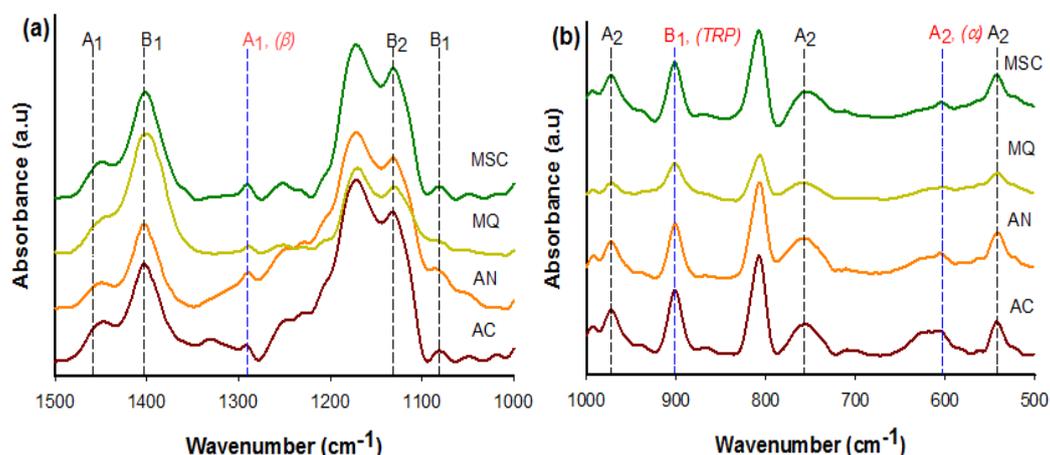


Figure 1: FTIR-TS measured at R.T. for POFPA thick films subjected to varying thermal treatment conditions: as-cast (AC), annealed (AN), melt-quenching (MQ), melt-slow cooling (MSC). (i) 1500-1000 cm⁻¹ and (ii) 1000-500 cm⁻¹.

FTIR-TS data from Figure 1 was used to quantitatively estimate the β - (1290 cm⁻¹) and α - (604 cm⁻¹) crystalline phases relative to the 902 cm⁻¹ band (internal thickness band) as shown in Figures 2 (a) and (b), respectively. In order to compensate for the varying film thickness of the samples used in our study which may result in wrongful interference in the relationship between thermal treatment conditions and crystalline phase transitions, we identified the thickness relative peak (TRP) band at 902 cm⁻¹. The ratio of crystalline absorbance/TRP is used to negate the contributions from sample thickness variations and provide information related to the changes in crystalline phase content. As shown in Figure 2 (a), the relative β -phase content increased significantly for AN and MQ samples when compared to AC sample, but declined sharply for MSC sample which reached almost to the AC condition. Figure 2 (c) also corroborates the same in a much clearer way by quantitatively comparing A_{β}/A_{α} absorbance ratio. The higher increase in β -phase content for AN sample may be attributed to the solvent effect. The DMF: Acetone mixture (80:20) used in our study may have aided in the polar interactions between the solvent and the polymer as well as the faster evaporation of acetone as co-solvent. Even though all the samples were subjected to 24 h drying under vacuum, the higher presence of residual DMF solvent in AC sample than the other samples resulted in the formation of lesser β -phase under AC condition. Compared to AC, annealing (AN) at $<T_m$ ($T_m = 165$ °C) under vacuum may have evaporated the solvents at a faster rate and caused the molecular chains to relax but oriented along the substrate direction thereby resulting in the orientation of C-F dipole perpendicular to the substrate (thermodynamically favorable state). In fact, this type of C-F dipoles orientation and the resulting β -crystalline structure in POFPA makes it

suitable for various electronic applications. The lower ratio of MSC sample is attributed to the slower cooling rate in comparison to MQ sample. When melted at 210 °C, both MQ and MSC samples are completely in liquid state and whatever the crystallization history that was present during the sample preparation would have been destroyed. However, the fast quenching from melt resulted in the crystallization of β -form, whereas the slower evaporation rate followed in MSC case resulted in the crystallization of predominantly α -form.

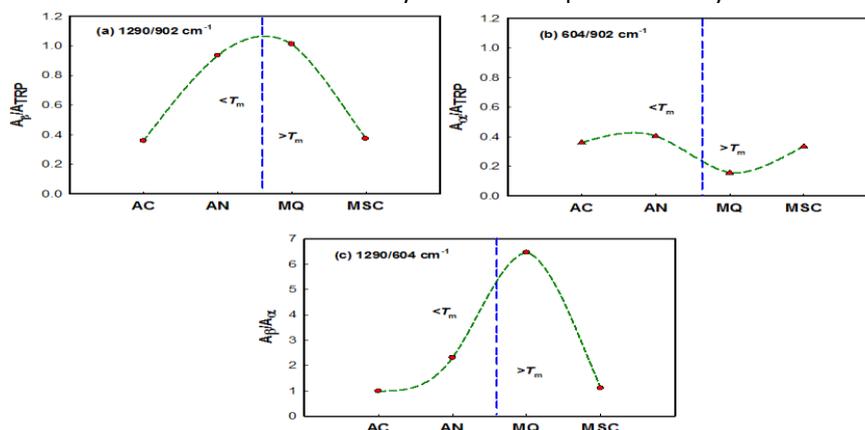


Figure 2: FTIR-TS quantitative data (extracted from Fig. 1) for peak absorbance ratio of (a) 1290/902 cm^{-1} , (b) 604/902 cm^{-1} and (c) 1290/604 cm^{-1} measured at different thermal conditions.

CONCLUSION

In this paper, the synthesized acrylic fluoropolymer, POFPA thick film samples were subjected to varying thermal treatment conditions to analyze their crystalline phase changes using FTIR transmission spectroscopy. Among the four different thermal conditions, AN and MQ were suggested to be the best condition for preparing samples with desired crystalline phase and improved crystallinity. The sample annealed at $<T_m$ showed maximum $\alpha \rightarrow \beta$ crystalline phase transition at 110 °C contributed by the annealing effect. For sample annealed at $>T_m$, the MQ 210 °C sample showed maximum $\alpha \rightarrow \beta$ crystalline phase transition due to the rapid crystallization effect caused by quenching from very high temperature. At these two conditions, the β -crystalline content is improved which is an essential requirement for polymer samples to be suitable for the fabrication of organic electronic devices without any loss in performance. The results obtained from the present study can be used for identifying the optimum temperature condition for obtaining favorably dominant crystalline phase of selected polymer samples using a very simple analytical technique, FTIR-TS.

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6. REFERENCES

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