Crystallization and melting behavior of polyvinylidene fluoride in confined space of nanotubes

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Abstract: Homopolymer poly (vinylidene fluoride) (PVDF) thin films were fabricated via high pressure process and then PVDF film was melt into porous anodic aluminum oxide (AAO) templates to form hollow nanotubes and isothermally crystal at a certain temperature. Scanning electron microscopy (SEM) and Transmission Electron Microscope (TEM) is used to observed the microstructure of nanotubes. To explore the influence of nanopores on the crystallization and melting of PVDF, differential scanning calorimetry (DSC) is used. It turns out that crystal phase is restrained in the nanotubes and mainly exists and at high temperature within relatively large nanopores and the bulk. As for phase, the increase of isothermal crystallization temperature results in the increase of melting temperature.

1. Introduction

Poly(vinylidene fluoride) (PVDF) has remarkable chemical, electrical and mechanical properties. There are many important usages of PVDF membranes such as gas separation, water treatment, medical applications, fuel cell membranes.1-5 As a semi-crystalline polymer, PVDF has at least four different polymorphs referred to as the α, β and γ phases and δ phases. The α phase is the most common phase, whose unit cell contains two molecular chains with tga+tg- conformation. The unit cell is monoclinic with a=0.496nm, b=0.964nm, c=0.462nm. The β phase has attracted tremendous interest in recent years due to its pyro- and piezo-electric properties. The polar β phase has all trans zigzag conformation (tttt) with a=0.847nm, b=0.490nm, c=0.256 nm. The γ phase was first observed by Gianotti et al. and frequently formed at relatively higher temperatures. It has orthorhombic unit cell with a=0.496nm, b=0.967nm, c=0.920nm. In general, crystallization of neat PVDF from melt leads to the formation of α and γ form depending on crystallization temperature. Crystallization at low temperatures, e.g. lower than 150 °C, only α crystals form. Melt crystallization of PVDF at temperatures above 158 °C is complicated. Normally, a mixture of α and γ phase is detected. In this
case, two kinds of $\gamma$ phase forms can be produced. One $\gamma$ phase forms directly from melt with higher growth rate. The other $\gamma$ phase forms through solid state transition from $\alpha$ phase. The $\gamma$ phase transited from $\alpha$ phase is most frequently called $\gamma'$ phase. The $\alpha$, $\gamma$ and $\gamma'$ phases produce three distinct melting peaks in the DSC thermogram of heating scan.

2. Materials and Methods
Poly(vinylidene fluoride) (PVDF) (Mw=530000) was purchased from Sigma-Aldrich Cop. The AAO membranes with pore diameter of 30 nm, 60 nm, 100 nm and 200 nm were bought from Whatman International Ltd. The AAO membranes were infiltrated with PVDF by means of melt infiltration method. A piece of PVDF film was placed on the surface of the AAO template at 200 °C in the vacuum oven, above the melting temperature of PVDF. After 48 hours infiltration of the PVDF, the samples were then cooled to room temperature at 1 °C/min and finally cleaned with the aid of a blade to avoid any remaining PVDF on the AAO template surface. Thus, prepared samples were subsequently melt-recrystallized isothermally at 150 °C, 155 °C, 158 °C and 160 °C for different times or during the cooling process at 10 °C/min. The isothermal crystallization times were 6h, 24h, 48h, and 7 days, respectively. The phase transition and crystallization behavior of the PVDF in nanopores of AAO membrane were characterized by calorimetric measurements conducted in a TA Instruments Q2000 differential scanning calorimeter (DSC).

For structure characterization of the PVDF formed in the nanopores, the AAO membranes were removed after crystallization of PVDF by placing into 40 wt% aqueous potassium hydroxide solution for 24 h and thereafter the suspension was centrifuged. Suspensions of PVDF formed in the nanopores in ethanol were then prepared. The suspension was dropped either on copper for TEM study or on silicon wafer for scanning electron microscopy observation.

Scanning electron microscopy (SEM) micrographs were recorded with a JEOL JSM 6300 F. Prior to the SEM investigations, the template surfaces or PVDF nanotubes on silicon wafer were covered by platinum.

3. Results & Discussion

![Fig. 1. (a) the morphology of blank AAO template, (b) the morphology of PVDF melted into AAO, (c) the morphology after the removal of the connected layer, (d) and (e) the morphology of PVDF nanotubes.](image)
Figure 1 (a) shows the AAO template and (b) shows the morphology of the polymer film before the bonding layer treatment on the template. Figure 1 (c) shows the surface morphology after DMF treatment of the connected layer. In Fig. 1 (d) and 1 (e), PVDF nanotubes with hollow morphology were respectively expressed by SEM and TEM. It is obvious that the PVDF nanotube is 10nm in thickness.

In order to study the crystallization and melting behavior of PVDF and PVDF nanotubes, we observed the change of melting peak under different isothermal crystallization conditions. As shown in Fig. 2 (a), under the condition of isothermal crystallization at 150 and 155 °C, there are two endothermic melting peaks of $\alpha$ type crystals. This is due to recrystallization of $\alpha$ type crystals. With the increase of temperature, this recrystallization behavior disappeared. When the crystallization temperature of the bulk material is 158 °C and 160 °C, the melting values of the two peaks 167 °C and 172 °C appear respectively. These peaks are thought to represent $\gamma$ type crystals. However, in Figures 2 (c), 2 (d), 2 (e) and 2 (f), it can be seen that with the increase of isothermal crystallization temperature, the melting temperature of $\alpha$ type increases gradually. When the crystallization temperature increases, it is more difficult for the sample to form crystal nuclei, so that the number of crystal nuclei decreases, the size of the crystal increases, so the melting point gradually increases. Only when the isothermal crystallization temperature is 160°C and the pore size of alumina is 200 nm, $\gamma$ type crystallization appears. However, when the pore size is less than 200nm, no $\gamma$ type crystals appear at any crystallization temperature. Taking these two facts into account, we hypothesize that the diameter of the holes in the template influences the formation of $\gamma$ and $\gamma'$ type crystallization, and that with the increase of crystallization temperature and pore diameter, the $\gamma$ type and $\gamma'$ type crystallization gradually appear.

Subsequently, the melting peaks of isothermal crystallization of bulk PVDF and PVDF nanotubes at 160°C, 158°C, 155°C and 150°C were studied. With the increase of isothermal crystallization temperature, the temperature of endothermic melting peak increases gradually. The results show that at 150°C and 155°C, the melting peak of 200nm and 100nm is higher than that of the bulk, while the melting peak of 100nm, 60nm and 20nm is lower than that of the bulk. Besides, it is found that the slope of the bulk sample is higher than that of the confinement condition. We speculate that PVDF is more prone to hetero-nucleation in the pore due to the role of template, which leads to the formation of crystals more easily. However, as the pore decreases, the confining effect increases and the crystal cannot grow further. Therefore, the melting peak value is higher than the bulk in the case of small confinement effect, and lower than the bulk in the case of strong confinement effect. Subsequently, we
extrapolated the melting point to get the equilibrium melting point. It can be seen from the data that the value of equilibrium melting point decreases gradually with the strengthening of the confinement effect, which further indicates that the crystal cannot grow further under the confinement effect.

![Graph showing crystallization behavior](image)

Fig. 3 Crystallization behavior of bulk PVDF and PVDF nanotubes with pore sizes of 200nm, 100nm, 60nm and 30nm

Two crystallization peaks appear in bulk PVDF, 135°C and 70°C respectively. The crystallization peak at 135°C is very strong and the crystallization peak at 70°C is very weak. The crystallization peak at 200nm has widened relative to the bulk and shifted to 131°C. In addition, the weak exothermic process appears at 69°C, which is a little stronger than the bulk. As the pore size of AAO decreases to less than 100nm, the crystallization peak at high temperature disappears. Meanwhile, the crystallization peak at low temperature shifts to a lower temperature and gradually becomes wider and stronger. When the pore size of AAO is 30nm, the crystallization peak is transferred to 55°C. The above data indicate that the crystallization behavior is obviously different under the confinement condition with the decrease of pore size.

4. Conclusions

In this paper, the melt recrystallization behavior of polyvinylidene fluoride (PVDF) in different nanometer restricted pore sizes was studied. By preparing PVDF into anodic alumina (AAO) template, removing the surface connecting layer, the independent polymer nanotubes were obtained. The morphology was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Crystallization and melting behavior were studied by differential calorimetry (DSC).

In anodic alumina templates with different pore sizes, PVDF was melted to form hollow nanotubes. As the pore size decreases, the γ crystal type is limited and only exists under the condition of relatively high temperature and large pore size. For the α type, the normal type is not restricted, and the equilibrium melting point decreases with the decrease of the pore size. In large pore size, the melting peak of the polymer is more dependent on temperature, while in small pore size, the dependence is relatively small.

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