Crystallization Behevior of Poly(3-dodecylthiophene)

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Abstract: The crystallization behavior of poly (3-dodecylthiophene) (P3DDT) is studied by differential scanning calorimetry (DSC) under different cooling rates. When the methods of Jeziorny, Ozawa and a new one proposed by our laboratory are applied to describe its nonisothermal crystallization behavior, the new one is confirmed to be the best and convenient. By determining kinetic parameters, the analysis of the nonisothermal crystallization behavior is performed. According to Kissinger method, the crystallization activation energy of P3DDT is also evaluated.

Keywords: Nonisothermal crystallization behavior, poly (3-dodecylthiophene).

Poly (3-dodecylthiophene), as a kind of conductive conjugated polymer, can crystallize to a certain degree due to the introduction of flexible alkyl side chain. For poly (3-alkylthiophenes) (P3ATs), having great potential applicability[1,2], it is important and necessary to study their crystallization behavior.

DSC curves are recorded when P3DDT is cooled from the molten state at the constant rate of $5.0^{\circ}C/min$, $10.0\ ^{\circ}C/min$, $15.0\ ^{\circ}C/min$ and $20.0\ ^{\circ}C/min$ under nitrogen purge, as seen in **Figure** 1. The peak position shifts to lower temperature with the increase of cooling rate, which can be explained by more energy being needed in higher degree of supercooling during crystallization. The lag effect of crystallization exothermic peak correlates with the decrease of the crystallization rate owing to the spherulite impingement in the process of secondary crystallization at the later stage.

When using Jeziorny method[3], Ozawa equation[4] and the new approach[5] to treat the experimental data obtained directly from DSC of P3DDT, linear relationship is observed only for the new approach. Accordingly, the crystallization kinetic parameters can only be easily determined from the intercepts and slopes of the plots by the new approach and are shown in **Table 1**. The results indicate that the value of F (T), which refers to the value of cooling rate which has to be chosen at unit crystallization time when the measured system amounts to a certain degree of crystallinity, increases with the increase of relative degree of crystallinity X_t. It is known from the above that high cooling rate that means high supercooled degree benefits rapid crystallization. The parameter α ,instead of n/m, equals to 0.85 approximately, which implies that difference between Avrami exponent n and Ozawa exponent m is not great.

Figure 1. DSC thermograms of P3DDT at different cooling rates
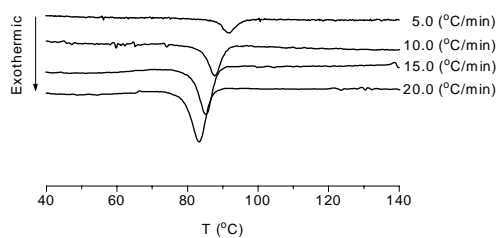
Table 1. the kinetic parameters by the new approach

X_t (%)	F (T)	α
20	9.150	0.813
40	10.294	0.833
60	11.480	0.869
80	13.281	0.892

The value of crystallization activation energy of P3DDT is estimated as 184.79 KJ/mol in the light of Kissinger method[6]. Crystallization activation energy is related to the active energy required to transport molecular segments to the crystallization surface[7], therefore, we can arrive at the conclusion that the crystallization activation energy of P3DDT should be more than the other P3ATs having shorter alkyl side chains.

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