

제4암모늄기의 곁가지를 가지는 폴리프로필렌에서 등온결정화속도

Guangtian Liu^{*,**,*†}

^{*}Hebei Key Laboratory of Applied Chemistry, Yanshan University

^{**}Institute of Environmental and Chemistry Engineering, Yanshan University

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Isothermal Crystallization Kinetics of Quaternary Ammonium Group Grafted Polypropylene

Guangtian Liu^{*,**,*†}

^{*}Hebei Key Laboratory of Applied Chemistry, Yanshan University, Qinhuangdao, 066004, People's Republic of China

^{**}Institute of Environmental and Chemistry Engineering, Yanshan University, Qinhuangdao, 066004, People's Republic of China

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Abstract: In this paper, the isothermal crystallization kinetics of a functional PP (FPP) with different grafting yields (GY)-methacryloxyethyltrimethyl ammonium chloride (DMC) grafted PP were investigated by differential scanning calorimetry (DSC). The results showed that the crystallization rate of FPP (GY=4.83%) was the highest for all of the studied samples. Furthermore, for the FPP with different GY, the value of $t_{1/2}$ became longer with increasing the grafting yield (GY). The possible explanation was that the quaternary ammonium groups introduced affected the crystallization process of the FPP in two opposite directions, i.e. promoting the nucleation and hindering the transport of the chain molecules towards the growing nuclei. Polarized optical micrographs showed that the DMC chains acted as nucleating agents, which accelerated the nucleation. In addition, the results showed the FPP had lower nucleation free energy than the PP. This study would be useful for designing the processing parameters of the grafted samples.

Keywords: crystallization, kinetics, methacryloxyethyltrimethyl ammonium, grafted, polypropylene.

Introduction

Owing to its outstanding mechanical properties and cost-effectiveness, polypropylene (PP) is one of the most widely used polyolefins in a number of industrial and technological fields. However, its applications can be limited, especially in dyeing, painting, adhesion or blending with other polar polymers, because of its hydrophobic nature and lack of polar sites. Modification of PP through a grafting technique with a polar monomer is considered to be one of the main routes to overcome these problems.¹ A large number of reports on grafting polar monomers onto PP have been published, using conventional solution, melt and solid-state grafting processes, where polar vinyl monomers, such as maleic anhydride (MAH), methyl methacrylate (MMA) and acrylic acid (AA),²⁻⁶ were used; the backbone molecular architecture of PP was not changed significantly.

It is well known that the microstructure and crystallinity of polymeric materials strongly affects their physical properties, so the crystallization behaviors of polymeric materials as well as their relations with the mechanical properties are of practical interest.⁷⁻¹¹ In this paper, the isothermal crystallization kinetics of a novel functional PP (FPP), i.e. methacryloxyethyltrimethyl ammonium chloride (DMC) grafted PP was investigated by differential scanning calorimetry (DSC). The results showed that the half crystallization time of FPP ($t_{1/2}$) was much smaller than that of the pure isotactic PP (iPP) in isothermal crystallization. The $t_{1/2}$ increased as the grafting yield (GY) increased. The reasons are discussed about the differences in crystallization behaviors for the grafted PP with different GY.

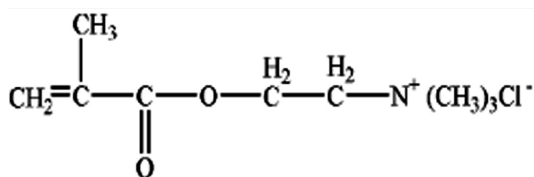
Experimental

Materials. Commercial isotactic PP (iPP) (PPH-XD-425, MFR=47.6 g/10 min) was provided by Jinjiang Petrochemical Co. Ltd. (China); methacryloxyethyltrimethyl ammonium chloride (DMC) grafted PP with grafting yield (GY) of 4.83,

[†]To whom correspondence should be addressed.

E-mail: gtl@desire@163.com

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Scheme 1. Schematic structures of methacryloxyethyltrimethyl ammonium chloride (DMC).

6.27, 7.07% were self-prepared.¹² Methacryloxyethyltrimethyl ammonium chloride (DMC), was used as a grafting monomer, with the schematic structure shown in Scheme 1.

Isothermal Crystallization Kinetics. The crystallization behaviors were investigated by using a Perkin-Elmer DSC-7 thermal analyzer (U.S.A). Before the data gathering, all samples were heated to 220 °C and held in the molten state for 5 min to eliminate the influence of thermal history. All operations were carried out under nitrogen environment. Samples weights were about 7 mg. In the isothermal crystallization

experiments, the sample melts were subsequently quenched to the crystallization temperatures at a rate of 40 °C/min. The exotherms were recorded at selected crystallization temperatures: 120, 122, 124, and 126 °C.

Morphology. The morphologies of the PPs in thin films were studied by using an optical polarizing microscope (type 59-XA, Yongheng Optical Instrument Co., China) with a Mettler FP-90 automatic hot-stage thermal controller (Shanghai Juling control equipment Co., China). The samples were sandwiched between microscope cover slips, melted at 200 °C for 5 min in a separate hot stage, and then rapidly moved to another hot stage which was equipped with the microscope and set to the crystallization temperature (e.g. 126 °C).

Results and Discussion

Isothermal Crystallization Kinetics. The isothermal crystallization kinetics of a material can be analyzed by evaluating

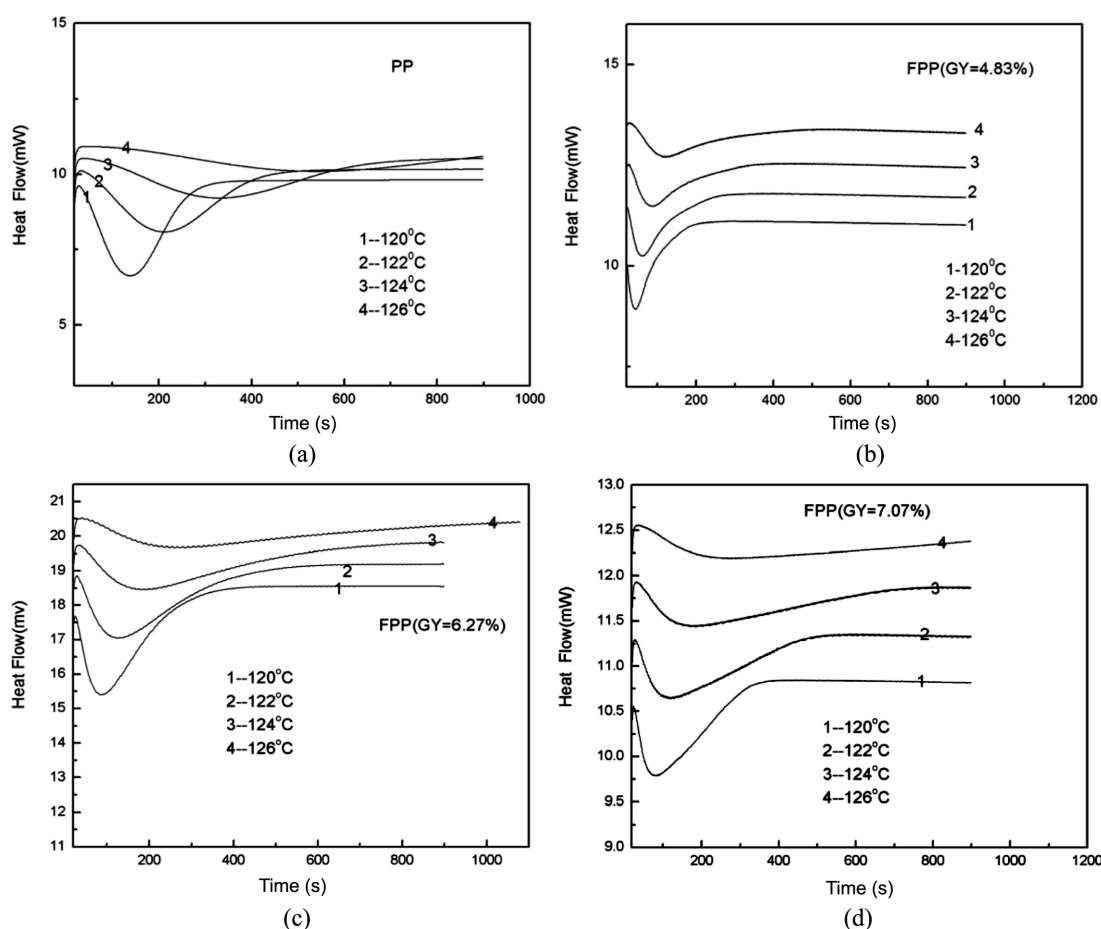


Figure 1. Isotherms crystallization of pure PP and FPP at different crystallization temperatures: (a) pure PP; (b) FPP ($\text{GY}_{\text{FPP}}=4.83\%$); (c) FPP ($\text{GY}_{\text{FPP}}=6.27\%$); (d) FPP ($\text{GY}_{\text{FPP}}=7.07\%$).

its degree of crystalline conversion as a function of time at a constant temperature. The variation of the crystallinity is related to the ratio of the heat generated at time t (Q_t) to the heat generated at infinite time (Q_∞) according to eq. (1).^{13,14}

$$X(t) = Q_t/Q_\infty = \int_0^t (dH/dt)dt / \int_0^\infty (dH/dt)dt \quad (1)$$

where dH/dt is the rate of heat evolution. The development of relative crystallinity can be analyzed using the Avrami eq. (2).^{15,16}

$$C(t) = X(t)/X(\infty) = 1 - \exp(-k_n t^n) \quad (2)$$

where n is a constant whose value depends on the mechanism of nucleation and on the form of crystal growth, $C(t)$ is the relative crystallinity at time t , and k_n is a constant containing the nucleation and the growth parameters. The crystallization half-time, $t_{1/2}$, defined as the time to a relative crystallinity of 50%, can be obtained:

$$t_{1/2} = \left(\frac{\ln 2}{k_n} \right)^{1/n} \quad (3)$$

Eq. (2) can be changed to

$$\ln(1 - C(t)) = -k_n t^n \quad (4)$$

or

$$\log[-\ln(1 - C(t))] = n \log t + \log k_n \quad (5)$$

By plotting the left side in eq. (5) vs. $\log t$, we should get a straight line. The n (the slope of the straight line) and K (the intersection) values can be obtained.

In order to analyze the effect of temperature on the crystallization, the isotherms crystallization of pure PP and FPP at different crystallization temperatures are graphically presented in Figure 1. As can be seen, the time to reach the maximum degree of crystalline order in pure PP and FPP increased as the crystallization temperature increased. The FPP reached the maximum degree of crystalline order earlier than pure PP, which was manifested more at high crystallization temper-

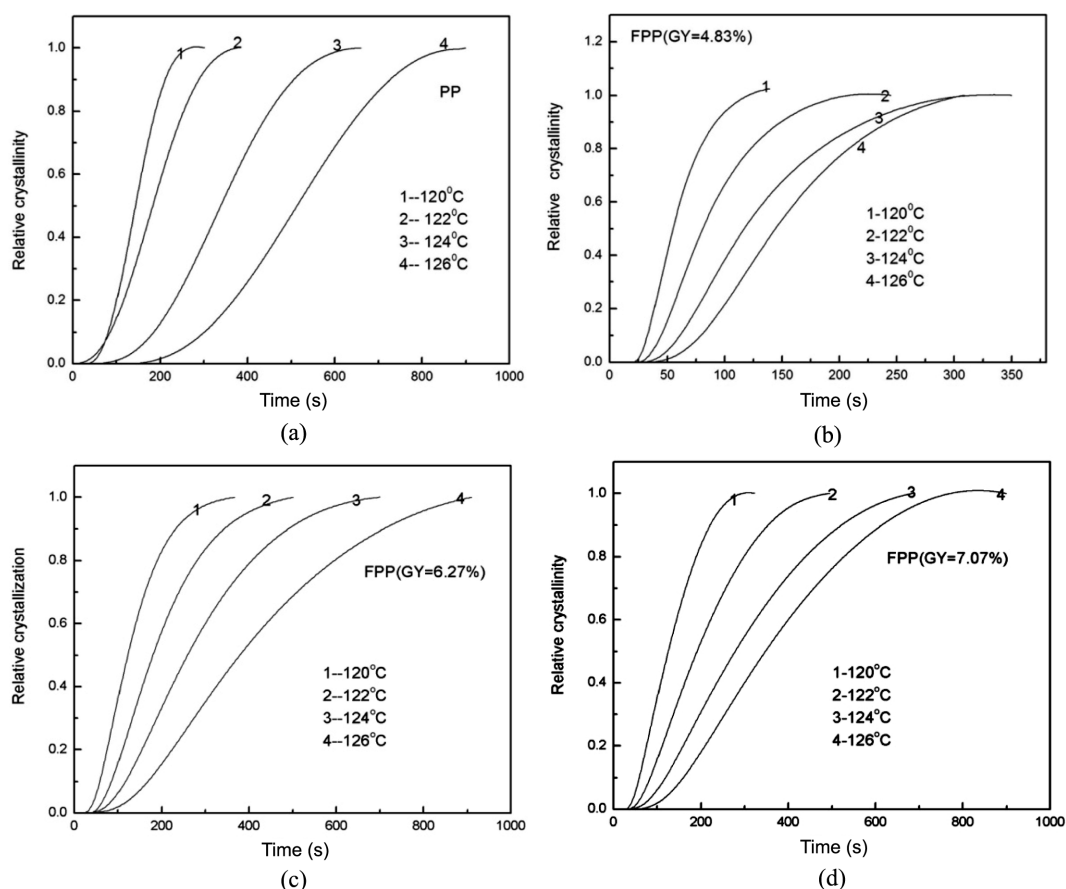


Figure 2. Development of relative crystallinity with time for isothermal crystallization for pure PP and FPP: (a) pure PP; (b) FPP ($GY_{FPP}=4.83\%$); (c) FPP ($GY_{FPP}=6.27\%$); (d) FPP ($GY_{FPP}=7.07\%$).

atures. As explained later, this is ascribed to the differences in the crystallization processes for pure PP and FPP. Crystallization of FPP proceeded mainly via heterogeneous nucleation while that of pure PP proceeded both by heterogeneous and homogeneous nucleation mechanisms. Since homogeneous nucleation starts spontaneously by chain aggregation below the melting point,^{13,17} it requires a longer time, whereas heterogeneous nuclei form simultaneously as soon as the sample reaches the crystallization temperature. Homogeneous nucleation, therefore, requires more time at higher crystallization temperatures. Thus, the time to reach the maximum degree of crystalline order in pure PP was longer than that in FPP. Crystallization continued until the time after which no further heat flow was observed. The relative amount of crystallinity for pure PP and FPP are plotted in Figure 2 for four crystallization temperatures. Figure 3 also shows that FPP (4.83%) crystallizes faster than pure PP.

Plots of $\log[-\ln(1-C(t))]$ vs. $\log t$ are shown in Figure 3.

There are good linearities of $\log[-\ln(1-C(t))]$ vs. $\log t$ over a wide relative crystallinity range. It is clear that the Avrami equation was effective for analyzing the experimental data of the isothermal crystallization kinetics. The values of $\log k$, n , and $t_{1/2}$, obtained from Figure 3 are listed in Table 1. With crystallization temperature increasing, $t_{1/2}$ of all samples increased. The values of $t_{1/2}$ obtained from the experimental data in Figure 1 are also given in Table 1. They are consistent with those calculated from eq. (3), indicating the validity of the Avrami equation in this study. Furthermore, in the FPP samples of different grafting yield, the value of $t_{1/2}$ became longer with increasing of grafting yield; the crystallization rate of FPP (GY=4.83%) was the highest in the studied samples. It means the introduction of quaternary ammonium groups contributed to the acceleration of crystallization. A possible explanation is that the nucleation was increased because the ionic interactions in FPP may lead to higher crystallization rates, but the ionic interactions between quaternary ammonium cations may result

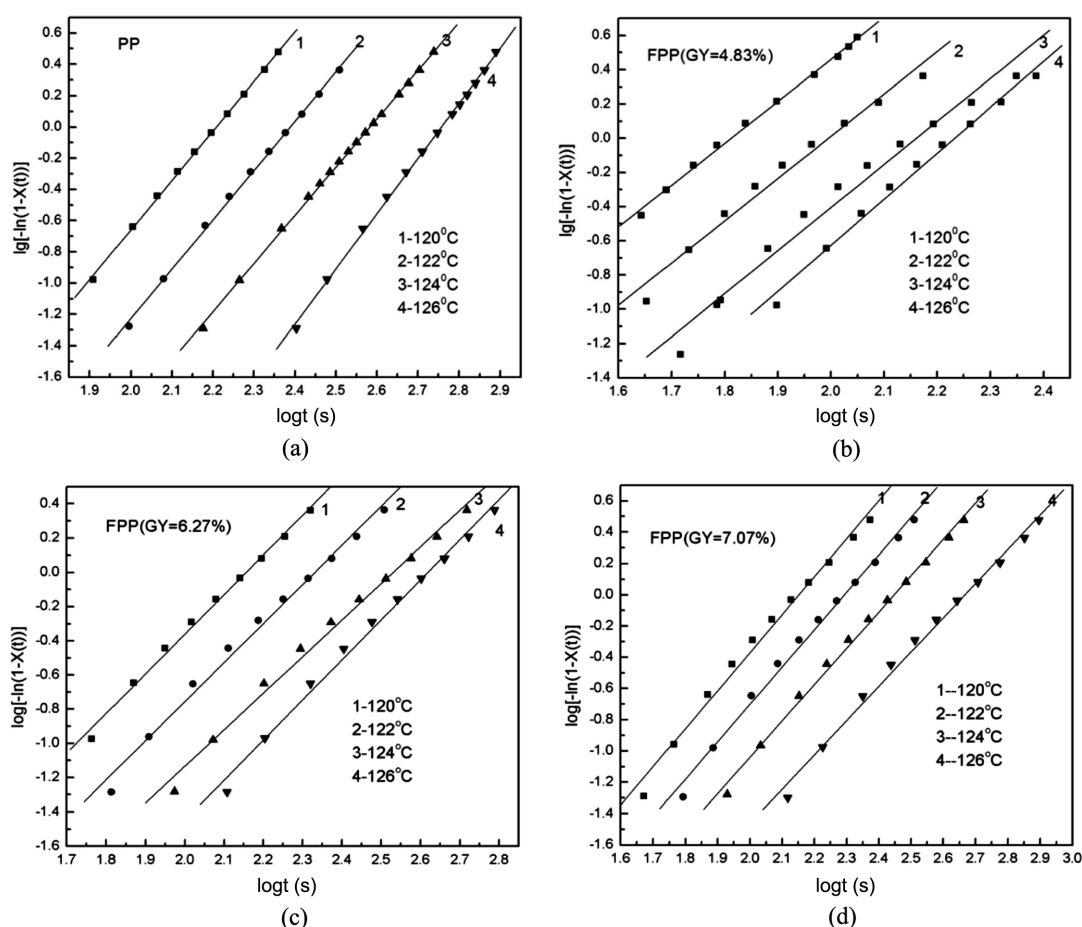


Figure 3. Avrami plots for isothermal crystallization of pure PP and FPP at various crystallization temperatures: (a) pure PP; (b) FPP (GY_{FPP}=4.83%); (c) FPP (GY_{FPP}=6.27%); (d) FPP (GY_{FPP}=7.07%).

Table 1. Various Parameters of Pure PP and FPP from the Avrami Equation

Sample (the grafting yield (GY))	T (°C)	n	$\log k$	$t_{1/2}^a$ (experiment) (s)	$t_{1/2}^b$ (calculated) (s)
GY=0%	120	3.172	-7.004	142.98	143.25
	122	3.156	-7.538	183.00	218.30
	124	3.087	-7.974	339.00	340.39
	126	3.533	-9.742	514.02	515.13
GY=4.83%	120	2.454	-4.446	55.02	55.55
	122	2.471	-4.929	81.00	85.46
	124	2.517	-5.438	117.00	124.64
	126	2.690	-6.005	144.00	149.49
GY=6.27%	120	2.431	-5.233	118.75	121.70
	122	2.390	-5.481	170.83	167.68
	124	2.320	-5.682	250.98	240.05
	126	2.250	-5.845	342.03	334.55
GY=7.07%	120	2.300	-4.997	124.98	127.18
	122	2.284	-5.323	190.98	182.69
	124	2.137	-5.407	278.00	285.72
	126	2.342	-6.132	348.00	355.11

^aObtained from experimental data. ^bCalculated from eq. (3).

in a decrease of chain diffusion at the same time. In other words, the quaternary ammonium groups introduced have effects on the crystallization process of the FPP in two opposite directions¹²: (1) the quaternary ammonium groups promoted the nucleation (2) the quaternary ammonium groups hindered the transport of the chain molecules towards the growing nuclei. The action of these two effects changes with crystallization temperature to a different degree. With increasing the temperature, the ionic interaction decreases and molecular motion increases. In this study, small amounts of incorporated DMC appear to have little effect on the chain regularity and these DMC chains acted as nucleating agents during the crystallization process;¹⁸ therefore, the crystallization rate of FPP (GY=4.83%) was higher than that of pure PP or those of the higher grafting yield samples. However, with amounts of DMC increasing, the strengths of the electrostatic interactions between quaternary ammonium cations became stronger, which might result in electrostatic cross-links; chain diffusion and mobility of the crystallizable segments would diminish, and thus the crystallization process was slowed for the FPP (GY=6.27% and 7.07%).

The n , depending on the mechanism of nucleation and crys-

tal growth, should have different integer values. However, non-integer values of the Avrami exponent were obtained for all the samples from the experimental data, ranging from 2.30 to 3.17 and from 2.25 to 3.53 at the crystallization temperature, 120 °C and 126 °C, respectively. The deviation is likely attributable to complex nucleation modes, the change in material density and secondary crystallization processes. Moreover, some experimental errors in the determination of the zero point of crystallization could also lead to non-integer value of n . The variation of n can be neglected within the error range in this study. The n values of FPP were different from those of pure PP. A significantly decrease in the Avrami exponent means the introduction of cationic group in FPP influences the mechanism of nucleation (heterogeneous nucleation) and the growth of the iPP spherulites, the possible reason is attributed to differences in the number of existing heterogeneous nuclei; in addition, electrostatic interaction between quaternary ammonium cations might affect the crystal growth mode, which need further studies.

We analyzed the rate of crystallization, expressed by reciprocal half-times, $1/t_{1/2}$, in terms of Hoffman's theory. Accordingly, the rate of crystallization at which crystallinity develops

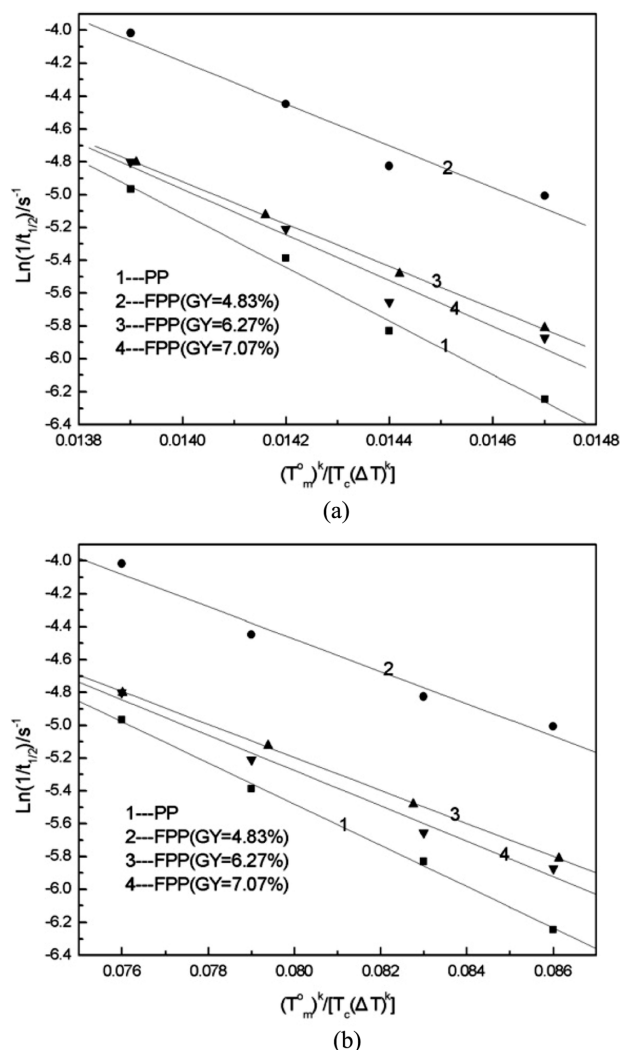


Figure 4. Plots of $\ln(1/t_{1/2})$ vs. $(T_m^0)^K/[T_c(\Delta T)^K]$: (a) $k=1$; (b) $k=2$.

from the melt, follows an Arrhenius-like relationship. The corresponding activation energy is comprised of two contributions, one from the transport of the chain molecules towards the growing nuclei and another from nucleation. Since it is difficult to separate these two contributions precisely, we used eq. (6):¹⁹

$$\ln(1/t_{1/2}) = A - B_K (T_m^0)^K / [T_c(\Delta T)^K] \quad (6)$$

where T_m^0 represents the equilibrium melting temperature ($T_m^0 = 481.15$ K); $\Delta T = T_m^0 - T_c$, the undercooling of the system; K ($K=1$ or 2) represents different crystallization model parameters, and A is a constant; B_K depends on the free energy of the interface (σ) and the exothermic heat of crystallization (ΔH_m^0):¹⁹

Table 2. Values of B_K for Pure PP and Different FPP Samples

Samples (the grafting yield (GY))	B_{K1}	B_{K2}
GY=0	1635.29	125.57
GY=4.83%	1275.59	98.34
GY=6.27%	1288.25	100.59
GY=7.07%	1391.47	107.74

$$B_K \propto (\sigma)^{K+1} / (\Delta H_m^0)^K \quad (7)$$

From eq. (6), plots of $\ln(1/t_{1/2})$ vs. $(T_m^0)^K/[T_c(\Delta T)^K]$ should give straight lines with slope B_K (when $K=1$ or 2 , B_{K1} or B_{K2} are obtained) (Figure 4). The relevant quantities, calculated from the slopes, are listed in Table 2. It is worth mentioning that the coefficients B_{K1} of pure PP was higher than that of FPP. This is because the FPP have lower nucleation free energies and nucleate more readily.

Morphologies. The polarized optical micrographs of pure PP and FPP are shown in Figure 5 during the isothermal crystallization process for 15 min at 126 °C. The FPP showed the number of effective nuclei in the FPP increased, and the spherulite size correspondingly decreased, which indicates that the DMC chains functioned as nucleating agents; the quaternary ammonium groups accelerated the nucleation.

In addition, it is well known that the change of chain mobility in polymer backbones can affect significantly the nucleation and crystal growth rates. The influence of chain mobility change of the PPs with different DMC contents on the crystallization rates may be discussed by incorporating the glass transition and equilibrium melting temperatures of the FPPs. This study need to discuss in detail further.

Conclusions

In this paper, we investigated the isothermal crystallization kinetics of DMC grafted PP using DSC. The Avrami equation was used to analyze the isothermal crystallization of the samples. The crystallization rate of the FPP was higher than those of pure PP. From the calculated results, DMC acted as a heterogeneous nucleation agent during the crystallization of FPP and accelerated the crystallization rate. Furthermore, for the FPP with different grafting yields, the value of $t_{1/2}$ became longer with increasing of the grafting yield.

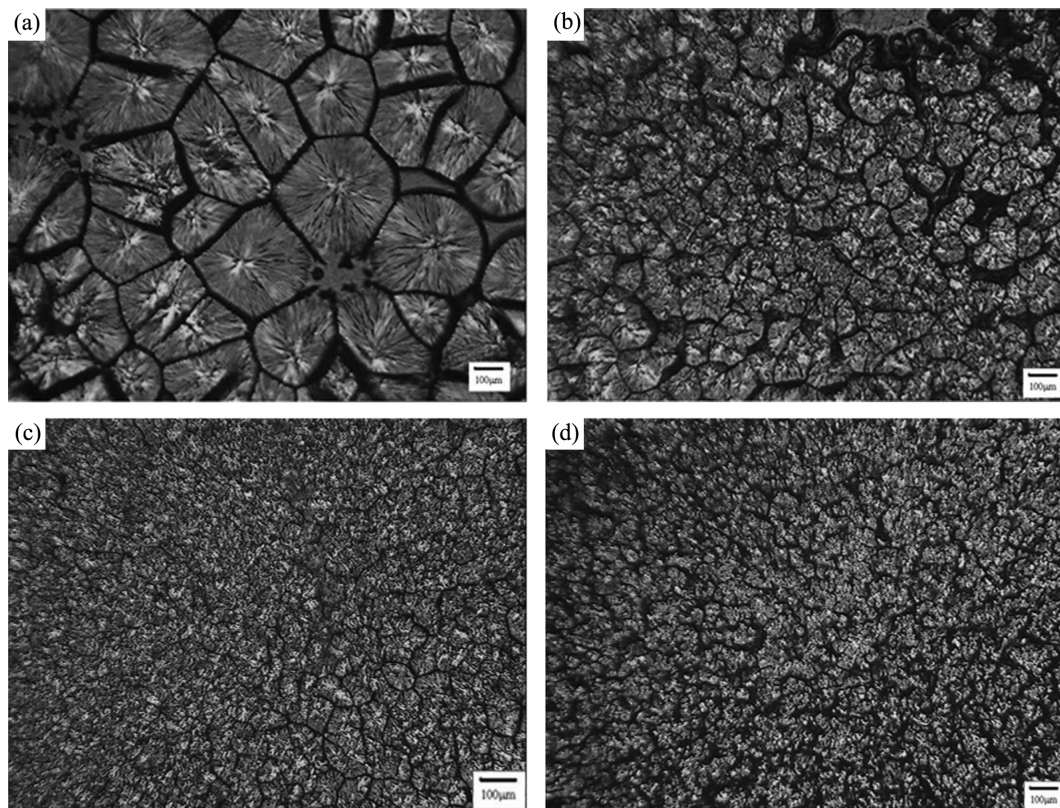


Figure 5. Polarized micrographs of pure PP and FPP at 126 °C: (a) pure PP; (b) FPP ($GY_{FPP}=4.83\%$); (c) FPP ($GY_{FPP}=6.27\%$); (d) FPP ($GY_{FPP}=7.07\%$).

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