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Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

# FAST CRYSTALLIZATION OF POLY(ETHYLENE TEREPHTHALATE)

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## Abstract

The crystallization of poly(ethylene terephthalate) (PET) was studied in the presence of nucleating agents and promoters. The effect of both by themselves and in concert was investigated using differential scanning calorimetry. The aim of this work is to find conditions of fast crystallization of PET. Sodium benzoate(SB) and Surlyn® (S) substantially increase the crystallization rate of PET at higher temperature owing to a reduction in the energy barrier towards primary nucleation, but they accelerate crystallization even more at lower temperature with an additional improvement of the molecular mobility of PET chains. Chain scission of PET caused by the reaction with the nucleating agents was proven by determination of molecular weight. The addition of S alone led to a lower reduction in molecular weight. A series of N-alkyl-*p*-toluenesulfonamides (ATSAs) were shown to effectively promote molecular motion of the PET chains, leading to an increase in crsytallization rate at lower temperature. A remarkable acceleration of crystallization of PET was attained at lower temperature when S and ATSA were added together. When the content of ATSA is low, S has the dominant influence due to its dual effect of decreasing energy barrier towards nucleation and promoting molecular motion of PET chains. A further increase of crystallization rate of PET was found only after an addition of ATSA of above 5 wt.%.

**Keywords:** crystallization, nucleation, nucleating agents, nucleating promotors, poly(ethylene terephthalate)

## Introduction

The crystallization rate of poly(ethylene terephthalate) is rather slow, as a result, the use of PET in injection molding compounds has been restricted. In the past decades, a number of additives for promoting the crystallization of PET

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were reported in the literature [1–17]. As described in our previous paper [18], to avoid confusion of nomenclatures, it is appropriate to classify additives into two kinds: nucleating agents and nucleating promoters. Nucleating agents, such as metal salts of carboxylic acid, substantially increase the rate of primary nucleation and hence the overall crystallization rate of PET in the higher temperature region, but the influence of nucleating agents is limited at lower temperature owing to the high glass transition temperature ($T_g$) of PET. However, it is particularly desired to accelerate the crystallization of PET in the lower temperature region for its use in engineering plastics. In order to achieve a fast crystallization of PET at lower temperature, nucleating promoters, such as low molecular weight organic esters, ketones, sulfoxides, nitriles or amides, have to be added to enhance molecular motion of the PET chains, and thus to promote primary nucleation of PET chains on the surface of the nucleating agents and also speed up subsequent growth. Metal salts of organic polymers containing pendant carboxyl groups are also types of nucleating agents for the crystallization of PET, but at the same time they can increase the mobility of PET chains because of their flexible chains.

In recent years, various nucleating agents and nucleating promoters were synthesized in our laboratory, and a detailed systematic study of their effect on the crystallization behavior of PET was carried out. A series of N-alkyl-*p*-toluenesulfonamides (ATSAs) with different alkyl group have been shown to be a class of nucleating promoters [18] that efficiently improve the mobility of PET chains in the supercooled state and enhance the overall crystallization rate of PET. As a continuing part of the study of series of ATSAs the crystallization behavior of PET is discussed in this paper for the case of coexistence of nucleating agents and nucleating promoters. The aim of this research is to achieve fast crystallization of PET at lower temperature. In order to distinguish the effect of nucleating agents and nucleating promoters, the influences of the nucleating agents alone on the crystallization of PET are discussed, as well as the effect of ATSAs is briefly summarized.

## Experimental

### *Materials*

Polymer: Poly(ethylene terephthalate) was a commercial product manufactured by Chinese Jinshan Petroleum Chemistry Co. It contained catalysts, stabilizers and oligomers. All these additives influence the crystallization behavior [2, 3, 19–22]. Therefore, the commercial PET was first purified before use. It was dissolved in phenol/tetrachloroethane mixture (vol.-ratio 1:1) and the solution was filtered to remove the undissolved solid particles. Then the PET was precipitated by adding methyl alcohol, leading to the formation of flocculus-like entities. This procedure was repeated twice. The resulting PET was extracted with methyl alcohol for 72 h, finally dried at 353 K in a vacuum oven for 72 h. The viscosity-average molecular weight ($\overline{M}_\eta$) of the resulting polymer was measured by solution viscosity after purification. It was 1.7 $\times 10^4$ Da.

Nucleating agents: The nucleating agents used in this work were sodium benzoate and Surlyn® 1601. Sodium benzoate was synthesized by neutralization of benzoic acid with sodium hydroxide. Reagent-grade sodium hydroxide and benzoic acid were directly used. Surlyn® 1601 was supplied by the DuPont Co. It is a sodium salt of a copolymer of ethylene/methyl methacrylic acid.

Nucleating promoters: A series of N-alkyl-*p*-toluenesulfonamides were synthesized via the Hinsberg reaction from toluene sulfonyl chloride and different alkylamines, i.e. *n*-ethylamine, *n*-octylamine, *n*-dodecylamine and *n*-hexadecylamine. Each of the products was purified by recrystallization and identified by IR measurement, melting point and chemical elementary analysis.

## *Preparation of samples*

PET/ATSA mixtures were prepared by adding a proper amount of solution of ATSA in alcohol into the PET powder to attain a predetermined content of additives. This was followed by evaporation of the alcohol while stirring the mixture, and finally the mixtures were dried under vacuum at 373 K for 72 h. The PET/SB mixtures were similarly prepared. For the PET/S mixtures, S was first ground into powder, and a predetermined amount of S powder was then mixed with a solution of PET in chloroform/trifluoroacetic acid (vol.-ratio 1:1). After the evaporation of the solvent and drying, the PET/S mixture was again crushed into a powder. According to the same procedure mentioned above, the introduction of ATSA into PET/S powder was completed by mixing the powder with the solution of ATSA in alcohol.

The series of samples, their additives and additive content are shown in Table 1. ATSAs are denoted as C2, C8, C12 and C16, respectively, according to the carbon number in alkyl group. The sample codes represent the type and content of additives in the mixtures, for example, sample C201 stands for PET/ATSA mixture containing N-ethyl-*p*-toluenesulfonamide of 1 wt.%, sample SB1 for PET/SB mixture containing sodium benzoate of 1 wt.% sample S1 for PET/S mixture containing Surlyn® of 1 wt.%, and sample S1C201 for PET/S/ATSA mixture containing Surlyn® of 1 wt.% and N-ethyl-*p*-toluenesulfonamide of 1 wt.%.

## *Determination of the molecular weight of PET*

The viscosity-average molecular weight of samples was obtained from the measurement of the solution viscosity at 298.2±0.1 K in a phenol/tetrachloroethane mixture (wt.-ratio 1:1) by using the established viscosity-molecular weight relation [23]. Experimental evidence indicated that ATSA in the samples (less than 10 wt.%) had no effect on the measurement of solution viscosity, thus ATSA was not removed from the samples before the determination of molecular weight of PET. For the PET containing S, the S was eliminated from the solution of PET in the phenol/tetrachloroethane by filtration.

**Table 1** Samples, additives and additive content

| Sample code | Additive | Additive content/wt.% | Sample code | Additive | Additive content/wt.% |
|---|---|---|---|---|---|
| PET | None | 0 | SC210 | S, C2 | 1, 10 |
| S1 | S | 1 | SC801 | S, C8 | 1, 1 |
| S5 | S | 5 | SC803 | S, C8 | 1, 3 |
| SB05 | SB | 0.5 | SC805 | S, C8 | 1, 5 |
| SB1 | SB | 1 | SC810 | S, C8 | 1, 10 |
| SB3 | SB | 3 | SC1201 | S, C12 | 1, 1 |
| C201 | C2 | 1 | SC1203 | S, C12 | 1, 3 |
| C203 | C2 | 3 | SC1205 | S, C12 | 1, 5 |
| C205 | C2 | 5 | SC1210 | S, C12 | 1, 10 |
| C207 | C2 | 7 | SC1601 | S, C16 | 1, 1 |
| C210 | C2 | 10 | SC1603 | S, C16 | 1, 3 |
| C801 | C8 | 1 | SC1605 | S, C16 | 1, 5 |
| C803 | C8 | 3 | SC1610 | S, C16 | 1, 10 |
| C805 | C8 | 5 | S5C201 | S, C2 | 5, 1 |
| C807 | C8 | 7 | S5C203 | S, C2 | 5, 3 |
| C810 | C8 | 10 | S5C205 | S, C2 | 5, 5 |
| C1201 | C12 | 1 | S5C210 | S, C2 | 5, 10 |
| C1203 | C12 | 3 | S5C801 | S, C8 | 5, 1 |
| C1205 | C12 | 5 | S5C803 | S, C8 | 5, 3 |
| C1207 | C12 | 7 | S5C805 | S, C8 | 5, 5 |
| C1210 | C12 | 10 | S5C810 | S, C8 | 5, 10 |
| C1601 | C16 | 1 | S5C1201 | S, C12 | 5, 1 |
| C1603 | C16 | 3 | S5C1203 | S, C12 | 5, 3 |
| C1605 | C16 | 5 | S5C1205 | S, C12 | 5, 5 |
| C1607 | C16 | 7 | S5C1210 | S, C12 | 5, 10 |
| C1610 | C16 | 10 | S5C1601 | S, C16 | 5, 1 |
| SC201 | S, C2 | 1, 1 | S5C1603 | S, C16 | 5, 3 |
| SC203 | S, C2 | 1, 3 | S5C1605 | S, C16 | 5, 5 |
| SC205 | S, C2 | 1, 5 | S5C1610 | S, C16 | 1, 10 |

### *IR spectroscopy*

PET was mixed with S in a Brabender plastograph at 568 K for 3 min. Thin films of PET/S mixtures were obtained by pressing samples at 533 K and quenched in methyl alcohol at 273 K. A Nicolet FTIR-5 DX Infrared Spectrophotometer was used for the IR determination.

### *Crystallization*

The crystallization of samples was studied using a DuPont 1090B 910 differential scanning calorimetry (DSC) in a nitrogen atmosphere. The sample weight was about 3 mg with an empty aluminum as reference. Calibration was conducted with standard indium.

Before performing crystallization, the sample was first melted at 563.2 K for 3.5 min to remove thermal history. It was proven that such heating treatment process was sufficient to destroy all prior crystal nuclei in the sample, by finding a constant crystallization temperature ($T_{cc}$) upon cooling sample from 563.2 K, in spite of extended heat-treatment time. The heat treatment did not decrease the molecular weight of the PET based on viscosity measurements. A higher temperature of heat treatment caused thermal degradation of the PET, while a lower temperature led to higher $T_{cc}$, indicating a part of the crystal nuclei to be left. After heat treatment, the sample was quenched in liquid nitrogen, resulting in amorphous PET.

Non-isothermal crystallization was carried out by placing the quenched sample in the DSC cell and heating at a rate of 10 K min$^{-1}$. The crystallization temperature ($T_{ch}$) was obtained along with $T_g$ from the DSC curves. The crystallization temperature ($T_{cc}$) was measured by cooling molten PET, held at 563.2 K for 3.5 min, at a cooling rate of 10 K min$^{-1}$.

Isothermal crystallization in the lower temperature region (cold crystallization) was performed by placing the quenched sample into the DSC cell at a selected temperature and holding at this temperature for the completion of crystallization. For isothermal crystallization in the higher temperature region (hot crystallization), the sample was directly melted in the DSC cell at 563.2 K for 3.5 min, then cooled quickly to a selected temperature and held until crystallization was completed. The DSC registered the rate of enthalpy change ($dH/dt$) of the samples as a function of time ($t$) at a prefixed crystallization temperature. The curve of $dH/dt$ *vs.* $t$ was integrated to determine the time for half crystallization ($t_{1/2}$).

## Results and discussion

### *Influence of nucleating agents on the crystallization of PET*

Sodium benzoate and Surlyn® are two typical nucleating agents for the crystallization of PET, their effect on the crystallization of PET is shown in Fig. 1.

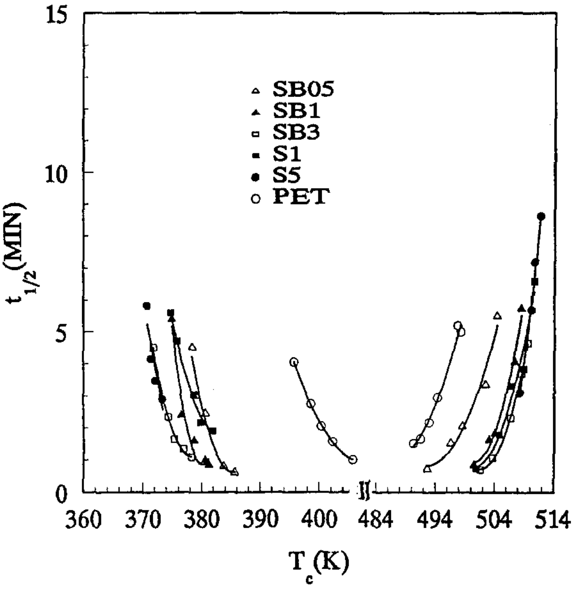


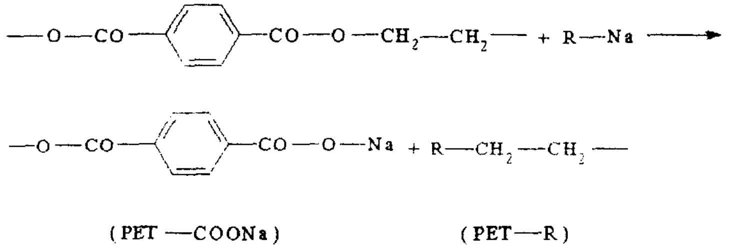
Fig. 1 Half-time of crystallization ($t_{1/2}$) of PET containing nucleating agents as a function of crystallization temperature ($T_c$)

In comparison with the crystallization of pure PET, the curves of half-time of crystallization ($t_{1/2}$) *vs.* crystallization temperature ($T_c$) for samples containing nucleating agents shift to higher temperature in the case of hot crystallization, meaning a substantial increase in the crystallization rate of PET. Usually, a small amount of nucleating agents (1 wt.%) is enough to enhance crystallization, the crystallization rate is not further increased with increasing the concentration of nucleating agents. In the case of cold crystallization, the curves of $t_{1/2}$ *vs.* $T_c$ shift even more to lower temperature due to the introduction of nucleating agents, also indicating the increase of crystallization rate. Moreover, it can be found that the increase in the concentration of nucleating agents slightly raised the crystallization rate in the lower temperature region.

In the DSC experiments, $t_{1/2}$ represents the overall crystallization rate and is determined by both rates of nucleation and linear growth. According to the classical theory of crystallization, the nucleation rate of primary nucleation is controlled by the free enthalpy ($\Delta G^*$) of crystallization of a nucleus of critical size and the free energy of activation ($\Delta G_\eta$) which governs the diffusion of macromolecular segments across the phase boundary. In the higher temperature region of crystallization, $\Delta G^*$ is the dominant factor controlling the nucleation rate. The addition of nucleating agents reduces the $\Delta G^*$, and hence increase the crystallization rate. Whereas $\Delta G_\eta$ should have the main influence on the nucleation rate in the case of cold crystallization because of the larger supercooling.

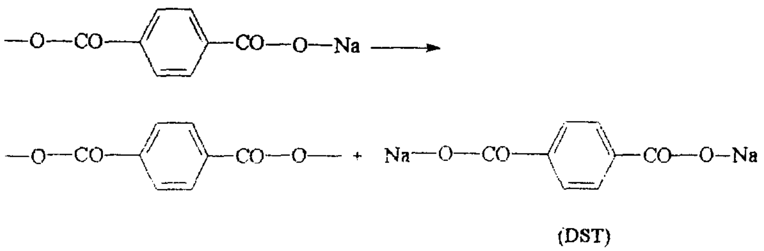
However, the evident increase of crystallization rate, that is indicated in Fig. 1 at lower temperature, must be caused by the lowering of both, $\Delta G^*$ and $\Delta G_\eta$. Because of a relatively large end-surface free energy of PET crystals, $\Delta G^*$ may not be negligible at lower temperature regardless of the larger supercooling. On the other hand, the addition of small organic molecules, such as sodium benzoate, and flexible Surlyn® can improve the molecular motion of the PET chains, and therefore lead to a reduction of $\Delta G_\eta$. Obviously, the increase in the concentration of nucleating agents will further raise the crystallization rate due to further improvement of molecular motion of the PET chains, but the further increase of crystallization rate is limited by the fact that SB may be only partially soluble in PET during the heating process and phase separation of S may take place in PET.

A new concept 'chemical nucleation' has been proposed by Legras *et al.* [24–27] to describe the mechanism of action of organic acid salts on the crystallization of PET. Organic nucleating agents do not behave as inert, heterogeneous substrates in lowering the energy barrier towards nucleation, but dissolve into PET melt and react with PET. This reaction is accompanied by chain scission of PET (Eq. 1).



(1)

where *R* can be an aromatic carboxylic acid or an aliphatic carboxylic acid (S).The resulting ionic chains-ends precipitate in the molten PET, and at longer reaction time the precipitated chain-ends react with one another to form DST with subsequent chain rebuilding (Eq. 2).



(2)

The reaction had already been verified by the study of model compounds mixed with nucleating agents, and by the determination of changes in molecular weight and by IR analysis of the reacted mixtures. The aggregated ionic chain-ends or ionic clusters form the true nucleating species for the crystallization of PET. They will lose the nucleating efficiency with the formation of DST via the exchange reaction of ionic end groups at longer reaction time or at higher reaction temperature.

In our experiments, chain scission of PET was also observed after heat treatment of the samples at 563.2 K for 3.5 min, as indicated by determination of molecular weight. The decrease of molecular weight attained with the addition of 0.5, 1.0 and 3.0 wt.% SB was 18, 28 and 41%, respectively, when compared to pure PET. Apparently, the reduction in the molecular weight is harmful to the mechanical properties of PET engineering plastics, therefore, SB can not be used in practice although it has a good nucleation efficiency. For samples of PET/S, addition of 1 and 5 wt.% S was examined. The decrease of molecular weight was found to be 17 and 6% under the same experimental condition as PET/SB. When increasing the reaction temperature and the content of S, the decrease of molecular weight was found to be less. At a higher reaction temperature, it is probable that more reaction occurs between S and PET, as is indicated by the observation of the morphology of PET/S [28]. As a result, a number of PET chains could be connected to the same chain of S, leading to the formation of comb-like structures. The latter can be soluble in phenol/tetrachloroethane, thus compensating the effect of chain scission on the molecular weight. The higher content of S may produce more comb-like structure. The formation of comb-like structure can give an explanation for less reduction of molecular weight of PET in the case of PET/S.

By means of IR spectroscopy, Legras *et al.* [24–27] identified the PET-COONa produced by reaction Eq. (1), while we confirmed the formation of PET-R. A 50 wt.% of mixture of S was made with PET at 568 K by mixing for 3 min in a Brabender plastograph. The mixture was then dissolved in phenol/tetrachloroethane, and the solution was filtered to remove insoluble S, and subsequently precipitated by the addition of methyl alcohol/water (vol.-ratio 4:1) with the elimination of DST. The IR spectra of the resulting PET is shown in Fig. 2 b, and compared with that of pure PET and S (Figs 2 a and c). Clearly, the characteristic absorption at 2910–2966 $cm^{-1}$ attributed to the ethylene stretch of pure PET shifts to 2854–2917 $cm^{-1}$, which can be identified as the ethylene stretch of pure S, this is due to the reaction of PET with S consisting of mainly ethylene groups. A detailed discussion of the reaction between S and PET, and the effect of S on the crystallization and morphology of PET will be published later [28].

### *Influence of nucleating promoters on the crystallization of PET*

The effect of various ATSAs, as a class of nucleating promoters, on the crystallization of PET has been reported [18]. Here Fig. 3 shows the efficiency of the promotion of nucleation of various ATSAs at a content of 7 wt.% in PET. For the cold crystallization, all nucleating promoters show a considerable in-

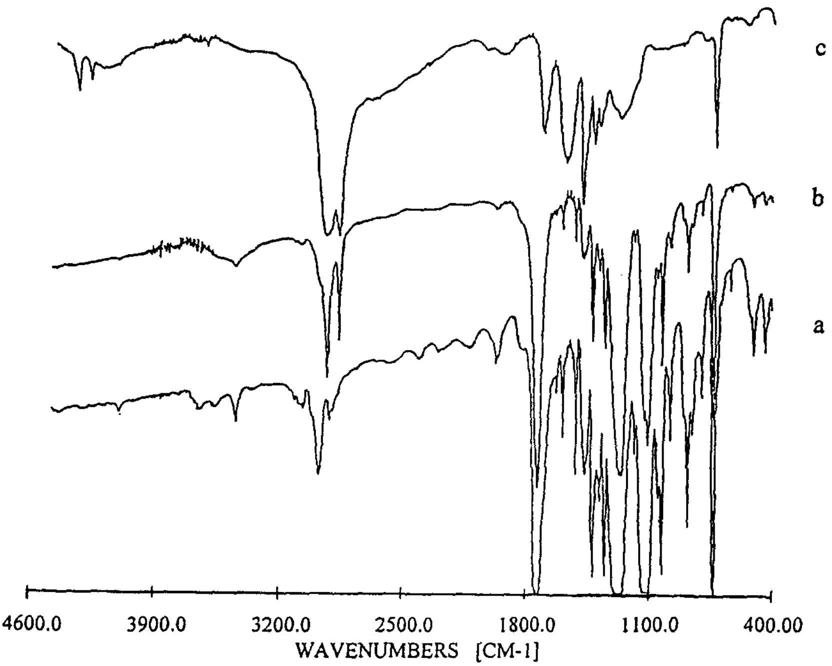


**Fig. 2** Spectra of PET and S; a. Pure PET b. PET after reaction with S c. S

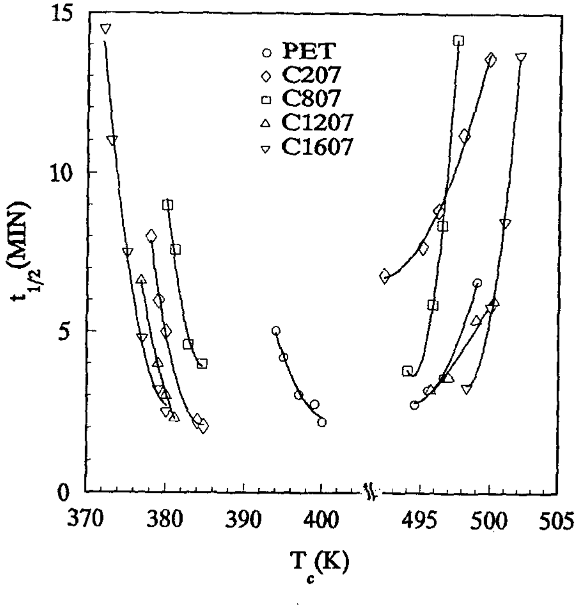


**Fig. 3** Half-time of crystallization ($t_{1/2}$) of PET containing nucleating promoters as a function of crystallization temperature ($T_c$)

crease of crystallization rate. The length of the alkyl chain has a pronounced effect on the crystallization rate. The efficiency of promoting nucleation of ATSA rises with increasing the length of alkyl chain (except for C2). Obviously the addition of ATSA enhances the molecular motion of PET chains and therefore lowers the free energy of activation for the diffusion of chain segments $\Delta G_\eta$.

For hot crystallization, the samples display a somewhat different behavior. In the case of PET/C2 and PET/C8, the curves of $t_{1/2}$ *vs.* $T_c$ shift to somewhat lower temperature, this means that the crystallization rate of PET is impeded by the addition of C2 or C8. While the $t_{1/2}$ *vs.* $T_c$ curves shift slightly to higher temperature in the case of PET/C12 and PET/C16, indicating an acceleration of the crystallization rate. It seems that there is a micro-phase separation in the mixtures of PET/C12 and PET/C16, the micro-phase of C12 or C16 in the PET matrix may act as a heterogeneous nucleus, leading to an increase of primary nucleation. In contrast, the dispersion of C2 or C8 may be quite well in the PET, so that they serve as a diluent and hinder the crystallization of PET.

The improvement of molecular motion of PET containing ATSA was proven by the measurement of the glass transition temperature. Figure 4 shows the measured values of $T_g$, which decrease almost linearly with increasing ATSA content up to 10%. Clearly ATSA behaves as a good plasticizer and substantially depresses $T_g$ of PET. Furthermore, it can be found that $T_g$ of the samples decreases with increasing length of the alkyl chains, except for C2.

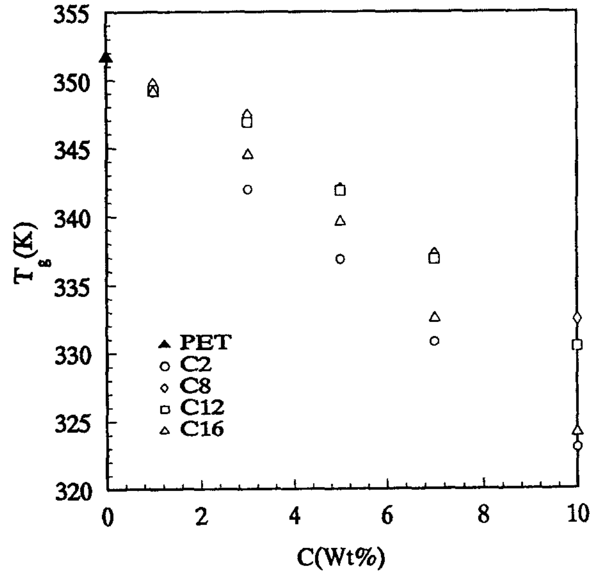


**Fig. 4** Variation of $T_g$ of PET/ATSA with the content of ATSA (C)

## *Crystallization of PET in the coexistence of nucleating agents and nucleating promoters*

The crystallization of PET in the presence of nucleating agents and promoters is shown in Fig. 5. For comparison, the influence of nucleating agents and promoters by themselves is also shown in Fig. 5. In the temperature region of cold crystallization, the nucleating promoters C2 and C16 enhance the molecular motion of PET chains and therefore increase the crystallization rate of PET, as discussed above. S has the dual effects of nucleating agent and nucleating promoter and remarkably raises the crystallization rate. The addition of 5 wt.% S enables PET to depress $T_g$ from 352 to 342 K (see below), demonstrating the improvement of the mobility of PET chains, however $T_g$ of PET can reach 338 K due to an addition of 5 wt.% C2 or C16. These experimental results indicate that the contribution of S to the increase of crystallization rate must partially come from a decrease of $\Delta G^*$, i.e. the nucleating effect of S is not negligible. When 5 wt.% of C2 or C16 was added into the PET/S mixture, the crystallization rate was further increased, undoubtedly because of added improvement of the mobility of the PET chains. In this case, the peak temperature of cold crystallization of PET was also shifted to 383 K from the 413 K of pure PET. In the case of hot crystallization, however, the nucleating efficiency of S dramatically decreased when adding 5 wt.% of C16 and S almost lost its nucleating efficiency completely when 5 wt.% of C2 was added. Probably ATSA

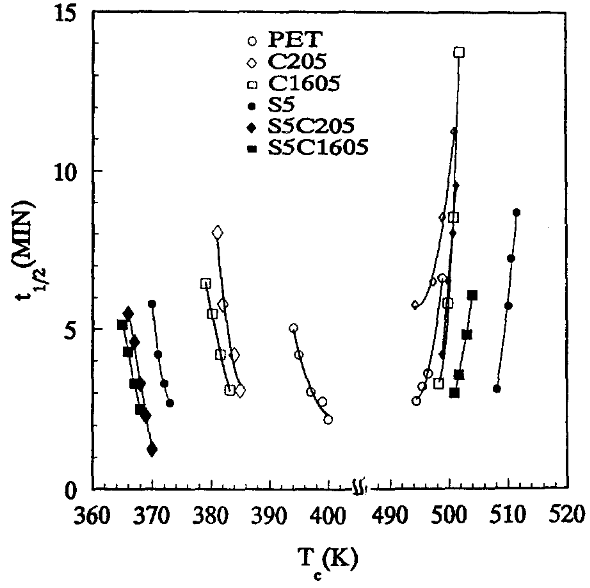


**Fig. 5** Crystallization of PET, PET/ATSA, PET/S and PET/S/ATSA; half-time of crystallization ($t_{1/2}$) *vs.* crystallization temperature ($T_c$)

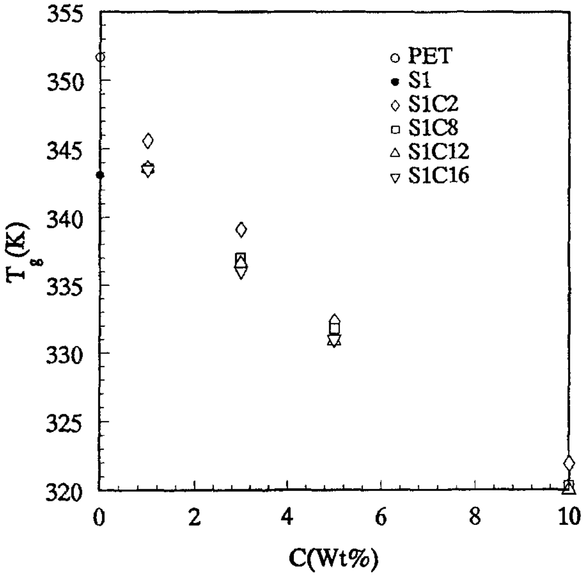


**Fig. 6a** $T_g$ of PET/S/ATSA *vs.* the content of ATSA at a content of 1 wt.% S

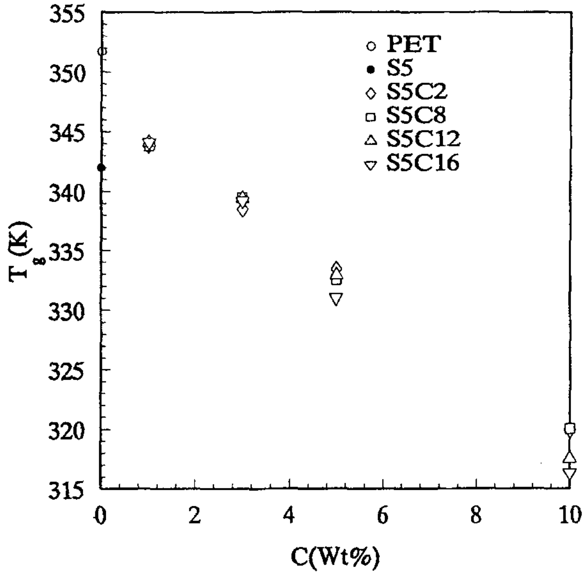


**Fig. 6b** $T_g$ of PET/S/ATSA *vs.* the content of ATSA at a content of 5 wt.% S

reacted with the ionic end groups –COONa during isothermal crystallization at higher temperature, leading to the production of sodium alkylbenzenesulfonate that is not a good nucleating agent. The dispersion of C2 in PET is better then C16, consequently, more ionic end groups –COONa can react, causing the S to lose its nucleating effect. Nevertheless, fast crystallization of PET is attained at lower temperature in the presence of nucleating agents and nucleating promoters. This is consistent with the requirement of manufacture of PET engineering plastics. When the melt of PET is injected into a mold held at a prefixed temperature, the melt is quenched to this temperature, and of course, a major part of crystallization is performed at this temperature.

In order to investigate the effect of the content of nucleating promoters, $T_g$, $T_{ch}$ and $T_{cc}$ of samples containing various amount of nucleating promoters were determined. It was reported [25] that $T_{ch}$ and $T_{cc}$ constitute an indirect measure of the crystallization rate. $T_{ch}$ corresponds to the temperature at which approximately 50% of the primary crystallization was attained. The higher $T_{ch}$, the lower is the crystallization rate. Similarly, low $T_{cc}$ corresponds to low crystallization rates. Since $T_{ch}$ and $T_{cc}$ are more easily determined, the following is discussed based on the determination of $T_{ch}$ and $T_{cc}$.

The influence of the content of nucleating promoters on the $T_g$ of PET is discussed first. As shown in Fig. 6, in the mixtures of PET/S, the existence of S depresses the $T_g$ of PET from 352 to 342–343 K, at contents of 1 and 5 wt.% S. Because of phase separation of S in PET, the increase of the content of S does not cause a further decrease of $T_g$ of PET. After the introduction of ATSA into the PET/S mixtures, $T_g$ of PET is further reduced when the content of ATSA is above 1 wt.%, as expected from the improvement of mobility of PET chains. In the case of C16, the depression of $T_g$ is somewhat little more. For the small increase in $T_g$ in both, Figs 6 a and b at the content of 1 wt.% ATSA, we have at present no explanation. On the other hand, the presence of S in the mixtures of PET/ATSA makes no difference in $T_g$ between various ATSAs, in contrast with the case of the addition of ATSAs alone.

Figure 7 shows the effect of the content of ATSA on the peak temperature of cold crystallization, $T_{ch}$. Comparing Fig. 7 with Fig. 6, it can be found that there is a minor difference between the changes of $T_{cc}$ and $T_g$ with content of ATSA, $T_{ch}$ decreases approximately parallel to the decrease of $T_g$ with the increase of content of ATSA as long as the content of ATSA is more than 3 wt.%. When the content of ATSA is less than 3 wt.%, $T_{ch}$ almost does not change, it even has a small increase. It is most likely that S is in this concentration range the dominant factor for enhancing the crystallization rate of PET due to its dual effect of decreasing $\Delta G^*$ and $\Delta G_\eta$. Therefore, ATSA of a content of at least 5 wt.% has to be added to achieve fast crystallization of PET. A further increase in the content of ATSA will, however, partially lose the mechanical properties of PET engineering plastics.

Figure 8 shows a plot of the peak temperature, $T_{cc}$, of hot crystallized samples *vs.* the content of ATSA. As mentioned above, ATSA reacts with –COONa, causing a loss of nucleating efficiency of S, and therefore, the crystallization rate of PET decreases and $T_{cc}$ shifts to lower temperature. Thermogravimetric

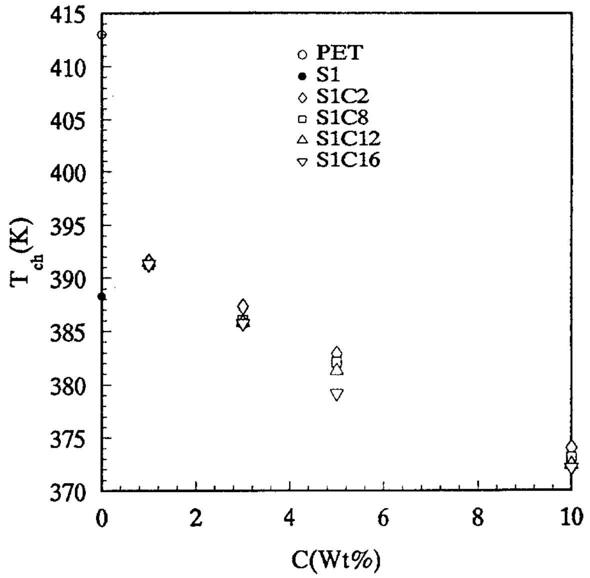


**Fig. 7a** Peak temperature of cold crystallization ($T_{ch}$) *vs.* ATSA concentration (*C*) at a content of 1 wt.% S

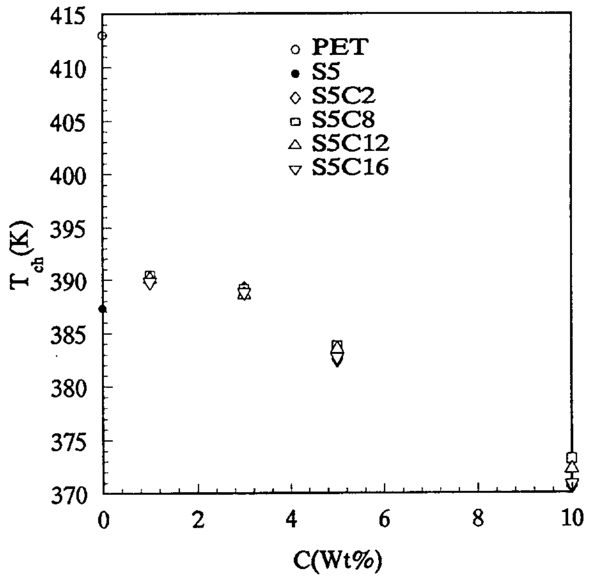


**Fig. 7b** Peak temperature of cold crystallization ($T_{ch}$) *vs.* ATSA concentration (*C*) at a content of 5 wt.% S

analysis of Surlyn® 1601 reveals that it contains only a small number of –COONa groups in the main chain, a low concentration of ATSA is, thus,

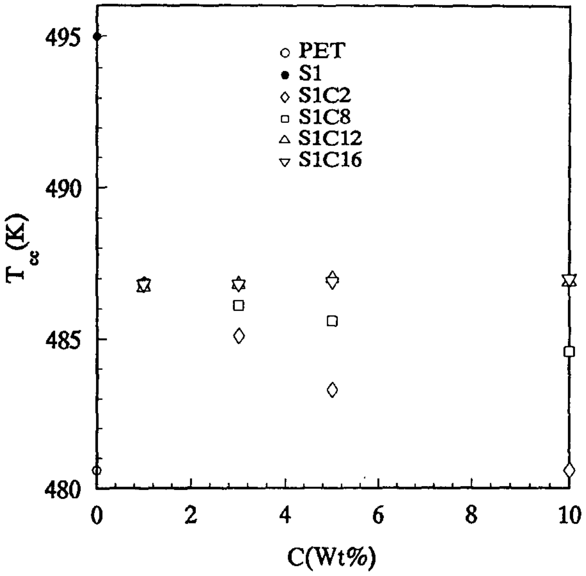


Fig. 8a Peak temperature of hot crystallization ($T_{cc}$) *vs.* ATSA concentration (*C*) at a content of 1 wt.% S

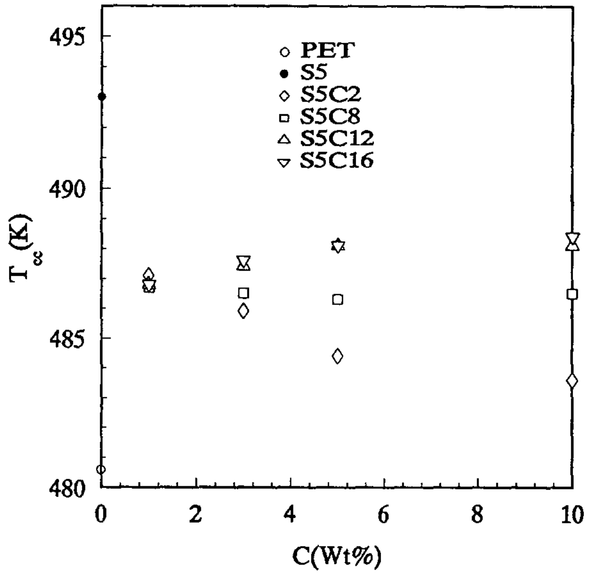


Fig. 8b Peak temperature of hot crystallization ($T_{cc}$) *vs.* ATSA concentration (*C*) at a content of 5 wt.% S

enough to react with –COONa. The remainder of C2 or C8 does not contribute to the reaction. Being dispersed in the PET, this excess acts as a diluent and hinders the crystallization. As a result, a decrease of $T_{cc}$ was found with increasing content of ATSA, while in the case of C12 or C16, a micro-phase separation occurs and thus a further increase of their content does not change $T_{cc}$ any further.

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