The Effect of Block Copolymer and its Ionomer on the Crystallization Behaviour of Poly(ethylene terephthalate)

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A B S T R A C T

Poly (ethylene terephthalate) (PET) was blended with poly (styrene-*b*-tertiary butyl acrylate) (P(St-*b*-*t*BA)) and poly(styrene-*b*-acrylic K+) (P(St-*b*-AK+)) ionomer with level of block copolymer varying between 2 and 10 wt% which were prepared by atom transfer radical polymerization (ATRP). All the samples were prepared by the solution blending in phenol/tetrachloroethane (60/40 percent by weight) as solvent at 50ºC. The crystallization and melting behaviour of the sample were then studied by differential scanning calorimetry (DSC). The result showed that crystallization rate of PET was accelerated by the block copolymer as well as by its ionomer which was similar to that of a nucleating agent. The acceleration of PET crystallization rate was more pronounced by the increasing level of block copolymer. The melting temperature observed from the DSC analysis showed perturbation of crystal growth as reflected by the broadening of the melting endotherm and lowering of melting temperatures due to the presence of the specific interactions.

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INTRODUCTION

Poly (ethylene terephthalate) (PET) has been widely used in industrial film, fibres, and engineering plastics because of its excellent thermal and mechanical properties and high chemical resistance [1-2]. Historically, it has not been considered for application involving high speed processing such as injection mouldings because it crystallizes very slowly from the melts [3]. Over the past few decades, a great deal of effort was devoted to the discovery of nucleating agent or crystallization promoters to accelerate the crystallization rate of PET [4-10].

Blends of PET with PMMA were reported to accelerate the crystallization significantly in 85/15 wt% blend [11]. PET with a liquid crystalline polymer at

several compositions was studied by Mercier et al. [12]. They reported that heat of fusion (ΔH_f) was found to increase with increasing LCP content. The introduction of second comonomeric unit, either by copolymerization of comonomer mixture or by reactive blending of a mixture of homopolymer decreases the melting temperature, crystallinity, and the crystallization rate of PET [13-15]. However, a small amount of certain comonomeric unit has been reported to increase the crystallization rate [3, 16-18]. The rate of enhancement was due to the formation of activated surfaces to facilitate crystallization. The formation of activated surfaces and ionic group located at the end of the polymer chain were found to be capable of accelerating the crystallization of PET [19]. On the basis of the above findings, it was postulated that the specific interaction (ionic nature) might induce similar rate enhancement upon crystallization kinetics of semi-crystalline/ionomeric blend. Therefore, efforts have been made to understand the relationship between the crystallization and melting behaviour of PET blended with block copolymer and its ionomer.

In the present study, we report the melting and crystallization behaviour of commercial PET blended with poly(styrene-*b-tert* butyl acrylate) and their ionomer which were prepared by atom transfer radical polymerization (ATRP). The objective of this investigation is to elucidate the effect of composition and block copolymer and its ionomer segment on the PET crystallization rate.

EXPERIMENTAL

Materials
The materials used in this investigation were styrene, *tert*-butyl acrylate, copper (I) bromide, N,N,N′,N′′,N′′′-pentamethyldiethylenetriamine (PMDETA) and 1-bromoethyl benzene obtained from Sigma-Aldrich. PET was obtained commercially from Samyang Co., Korea, with number average molecular weight of 1.96×10^3 and weight average molecular weight of 3.64×10^3.

Synthesis of the Amphiphilic Block Copolymer
The block copolymer studied in this work has been prepared via (ATRP) [20]. Short polystyrene block
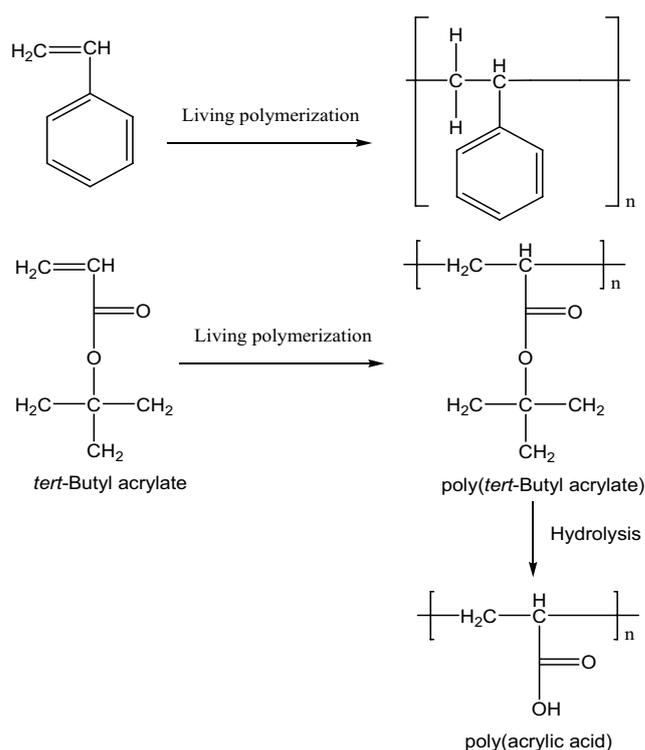
Scheme I. Schematic representation for the preparation of poly (styrene-*b-tert* butyl acrylate and its acrylic acid.

and molar fraction of *tert*-butyl acrylate above 50 mol% were targeted to obtain amphiphilic block copolymer [21]. Subsequent hydrolysis of the ester group was carried out by dissolving the block copolymer in dioxane and adding a three-fold molar excess of concentrated HCl (based on the number of moles of ester groups). The polymers were then precipitated in water, filtered, and dried under vacuum. Structures of the amphiphilic block copolymers are given in Scheme I. The number average molecular weight of synthesized polymer was determined by a vapour pressure osmometer (OSMOMAT 070) with toluene as solvent and the value was found to be 10000 and 7200 g/mol for poly (styrene-*b-tert* butyl acrylate) and poly (styrene *b-*acrylic acid), respectively. The potassium salt of acrylic acid copolymer was prepared by reaction of 20 mol% of poly (styrene-*b-*acrylic acid) with potassium hydroxide.

Blending Method
The solution blends of the different compositions used were prepared by dissolving PET with block copolymer and its ionomer of desired weight ratios in

Table 1. Summary of cooling crystallization behaviours of various blends of PET and block copolymer (P(St-*b*-tBA)) and block ionomer (P(St-*b*-AK⁺)).

Composition	Primary onset temperature(ºC)	Secondary onset temperature(ºC)	T_{c1} (ºC)	T_{c2} (ºC)	ΔT_{c1} (ºC)	ΔT_{c2} (ºC)	ΔH_{c1} (J/g)	ΔH_{c2} (J/g)	ΔT_1 (ºC)	ΔT_2 (ºC)
PET/PSt-*b*-*tert* butyl acrylate (100/0)	203	-	189	-	19	-	41.1	-	66	-
98/2	206	-	197	-	15	-	40	-	49	-
96/4	204	-	196	-	13	-	36	-	47	-
94/6	205	-	193	-	14	-	33	-	55	-
92/8	206	-	196	-	14	-	34	-	57	-
90/10	204	-	195	-	12	-	34	-	49	-
PET/PSt-*b*-poly acryl-K⁺ (98/2)	200	169	191	163	14	6	24	1.2	50	31
96/4	201	170	192	164	13	7	28	1.6	48	29
94/6	202	175	194	169	12	8	24	2.3	51	30
92/8	208	179	201	173	15	10	28	3.8	41	28
90/10	199	173	190	165	14	11	26	9.0	56	39

a mixed solvent ratio of 60/40 wt% phenol/tetra-chloroethane. These solutions were then stirred at 50ºC for 5 h and added dropwise to a large excess of cold methanol at 0ºC. The precipitate was filtered and washed with methanol in order to remove the phenol/tetrachloroethane solvent completely. The final product was dried in vacuum at 70ºC. The different compositions of PET with block copolymer and its ionomer prepared are given in Table 1. The pure PET was also subjected to identical processing in the phenol/tetrachloroethane solvent in order to nullify the effects of thermal history.

DSC Analysis
DSC measurement was carried out in a Dupont 2910 thermal analysis system. All the samples were heated to 290ºC at a heating rate of 10ºC/min under nitrogen atmosphere, held for 4 min to destroy anisotropy and then cooled at the rate of 10ºC/min to 30ºC. The crystallization and melting behaviour of the whole blend was obtained from the heating and cooling scans. T_m was considered to be the maximum of the endothermic melting peak from the heating scans and T_c the maximum of the exothermic peak of the crystallization from cooling scans. The heat of crystallization (ΔH_c) and heat of melting (ΔT_m) were determined from the areas of crystallization and melting peaks respectively. The (ΔH_c) and (ΔT_m) are referred to the whole blends. All the results are average of three samples.

RESULTS AND DISCUSSION

Influence of Block Copolymer of Poly (styrene-*b*-tert*-butyl acrylate) on PET
The cooling and heating scans of the PET/poly (styrene-*b*-tert* butyl acrylate) blends are given in Figures 1 and 3, respectively. Both crystallization and melting parameters are incorporated in Tables 1 and 2 respectively. It is evident that there is an endothermic
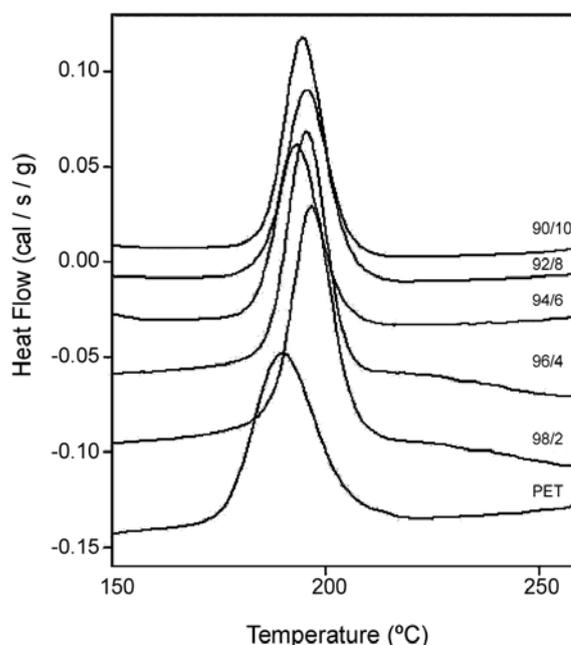
Figure 1. DSC Thermograms of the crystallization peaks of PET/P(St-*b*-tBA) blend with different compositions.
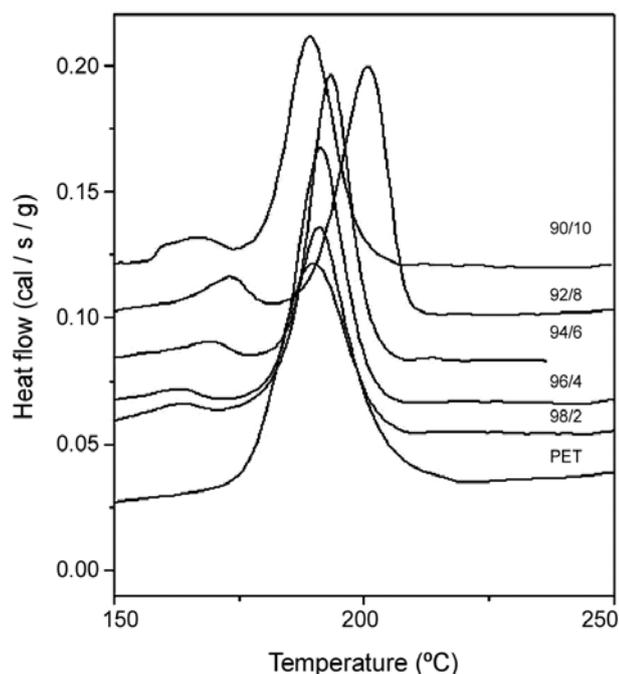
Figure 2. DSC thermograms of the crystallization peak of PET and PET blends with 2 to 10 wt% of P(St-*b*-AK⁺).

represent the results in the modification of the nucleation process. Changes in growth rate may be due to the partial miscibility of the block copolymer or an ester interchange reaction at the elevated melting temperature as reported by Legras et al. [22]. Changes in the crystallization peak width (ΔT_c) and the heat of crystallization (ΔH_c) are related to the overall crystallization rate and extent of crystallization, respectively. ΔT_c and ΔH_c for the blends are lower than those of pure PET and the value of ΔT_c of the blend is 4 to 7°C lower than that of pure PET.

In the programmed cooling, the crystallization temperature reflects the overall crystallization rates attributed to the combined effect of nucleation and growth [3]. Thus the degree of supercooling ($\Delta T = T_m - T_c$) is a measure of polymer crystallizability which means that smaller the ΔT, the higher would be the overall crystallization rate. The ΔT values for the blend composition are reduced by 9 to 19°C, compared to that of pure PET (66°C). These results again indicate that the overall crystallization of the blend is higher than that of PET.

The melting behaviours of the blends are given in Table 2. Two melting temperatures (primary and secondary melting (T_{m1} and T_{m2}) are noted for PET/block copolymer. Primary and secondary melting temperatures of the blends are lower than those of pure PET in the all five compositions. The onset temperature of melting and melting peak width (T_m) is related to the least stable and distributed crystallites,

melting peak and a distinct exothermic crystallization peak in all the heating/cooling scans. The crystallization onset temperature and crystallization peak temperature (T_c) for all the blend compositions are higher than those of pure PET. The blend composition of 98/2 wt% exhibits higher crystallization onset temperature and crystallization peak temperature (T_c). The shifts in crystallization onset temperatures and T_c

Table 2. Summary of melting behaviours of various blends of PET with block copolymer (P(St-*b*-tBA)) and block ionomer (P(St-*b*-AK⁺)).

Composition	Primary onset temperature (°C)	Secondary onset temperature (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_{m1} (J/g)	ΔH_{m2} (J/g)
PET/PSt-*b*-*tert* butyl acrylate (100/0)	243	-	255	-	37.5	-
98/2	231	185	246	196	32.6	1.5
96/4	224	179	243	195	31.0	2.5
94/6	233	177	248	196	26.0	3.0
92/8	239	178	253	200	28.0	3.9
90/10	228	179	244	196	27.0	4.5
PET/PSt-*b*-poly acryl-K⁺ (98/2)	221	181	241	194	22.0	4.7
96/4	221	175	240	193	23.7	5.8
94/6	231	178	245	199	24.3	6.9
92/8	221	184	242	201	25.0	8.1
90/10	231	173	246	204	24.4	9.0

Figure 3. DSC Heating scans of PET blends contained 2 to 10 wt% of P(St-*b*-tBA).
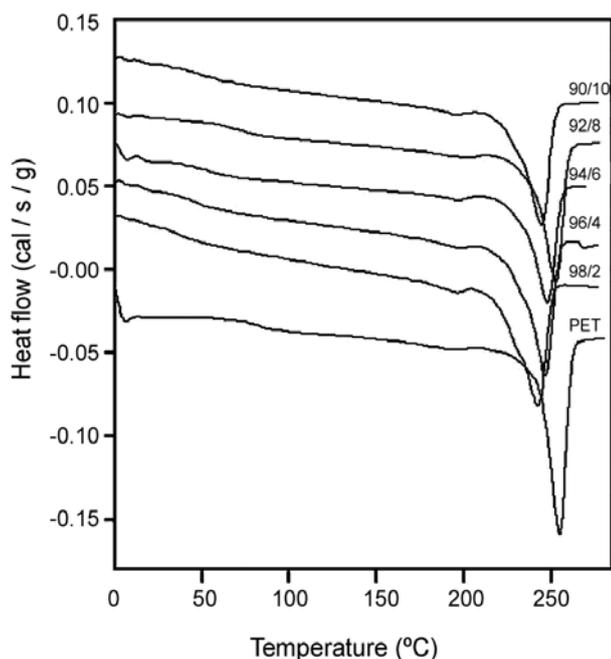

Figure 4. DSC Heating scans of PET and PET blends contained 2 to 10 wt% of P(St-*b*-AK$^+$).

respectively [23]. Among the blends, 92/8 wt% ratio of PET/block copolymer exhibits the maximum primary and secondary melting at 253°C and 200°C, respectively. These results indicate that PET crystallites in the blends are less perfect when compared to that of pure PET.

Effect of Block Ionomer on PET

DSC cooling and heating scans for PET and its blend with 2-10 wt% of poly (styrene-*b*-acrylic K$^+$) ionomer are given in Figures 2 and 4, respectively. It is clear from the figure that for the blends, there are two endothermic melting peaks in all heating scans and also two exothermic crystallization peaks in all cooling scans. The melting parameter determined from heating scans for all the blends are given in Table 2. The melting temperatures of the block copolymer as well as the ionomer containing blends are lower than those of the melting temperature of pure PET. This is an indication of the least stable and distributed PET crystallites data which would change when blending with 2-10 wt% of block copolymer and its ionomer [13,15,18]. The melting temperatures of block ionomer show a comparatively lower value than that of block copolymer in the blend systems. It is
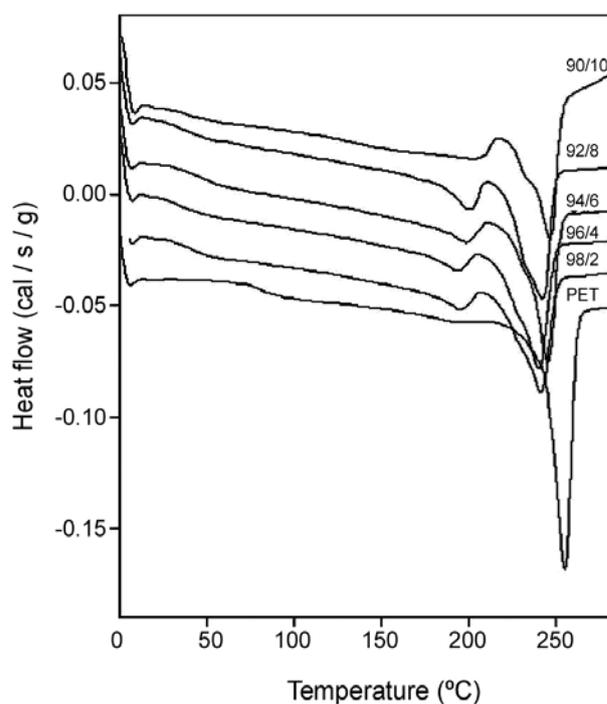
generally found that the melting enthalpy based on the multiple endotherms is lower for the blends relative to that of pure PET. This behaviour may be associated with the presence of specific interaction between polymer chains through ester interchange which decreases the crystallizability of the PET in the blends [24,25]. Moreover, the value of broadening of melting endotherm ($T_m - T_{onset}$) for 94/6 and 90/10 wt% blend compositions is found to be lower than that of other blend compositions and with respect to that of pure PET. This phenomenon further indicates the presence of specific interaction which decreases the crystallizability of the blend system, even though the polymer chain has higher mobility at higher T_c. On the basis of these results, it is interesting to note that the specific interaction enhances the crystallization rate of the semi-crystalline component, at the same time it reduces the crystallizability of that component in the blend. This is possibly due to the nucleation densities induced by the presence of specific interaction which are too high, and therefore the crystallites grow very fast simultaneously, though in a chaotic manner, leaving little space for further crystal growth and thus giving rise to overall lowering of bulk crystallinity [26].

The effect of block segment composition on the crystallization parameters of cooling PET/block ionomer blends are shown in Table 1. The crystallization peak temperature (T_c) denotes the temperature at which a maximum crystallization rate occurs. In PET/ block ionomer there are two crystallization temperatures, one at a temperature lower than the crystallization of pure PET (secondary crystallization) and another at higher temperature region than that found in pure PET (primary crystallization). All these crystallization temperatures are increased with increasing the level of block ionomer part in the blend up to 8 wt%. The term secondary crystallization is used to describe the effect that enhances the crystallinity following the event of primary crystallization [27]. Presence of secondary crystallization may be due to the interaction of PET chains with block copolymer segments. The crystallization shows a clear increase of 12ºC compared to that of pure PET (189ºC). This shift in crystallization temperature represents the modification of nucleation process.

In addition there have been several experimental indications that the ionic groups are located at the end of the polymer chains acting as nucleating sites and accelerating the crystallization rate of polymers [19-21]. The maximum crystallization temperature is obtained for blend containing block ionomer, compared to that of block copolymer containing PET. On the basis of the above findings it is postulated that more effective nucleating sites are formed in the modified blend (ionomer) which could explain the enhanced crystallization rate as compared to that of the block copolymer/PET blends.

The crystallization rate of PET with block copolymer and block ionomer is given in Figure 5. It is clear from the Figure that all the blend compositions show higher crystallization rates than that of pure PET. In PET/P(St-*b*-tBA) blends, of 98/2 (wt%) composition exhibits the higher crystallization rate whereas in PET/ (P(St-*b*-A K$^+$), of 92/8 wt % blend system the highest crystallization rate is observed. In other words 2 wt% P(St-*b*-tBA) accelerates the PET crystallization rate 2.1 times whereas, 8 wt% P (St-*b*-A K$^+$) in the blend accelerates the primary and secondary crystallizations at a rate of 1.9 and 0.2 times, respectively. It is also shown from the figure that the crystallization rate values of the block ionomer increases with
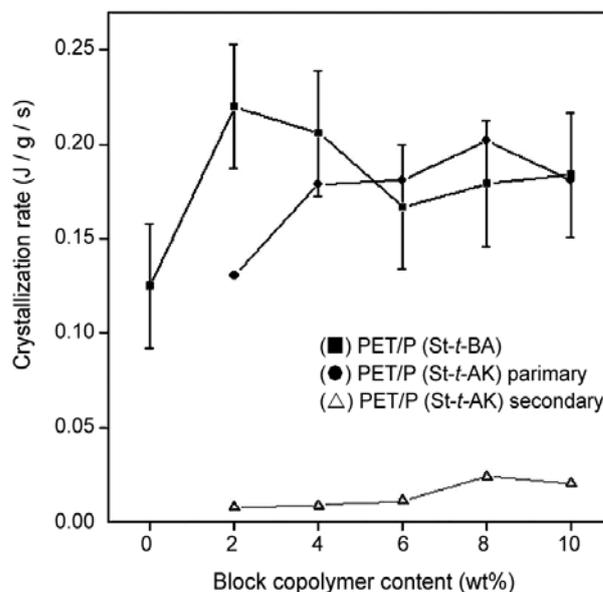

Figure 5. Crystallization rate of PET and its blends with P(St-*b*-tBA) and (P(St-*b*-AK$^+$) contained different block copolymer contents (with error bar).

increase in concentration of ionomer content up to 8 wt%.

CONCLUSION

The block copolymer and their ionomers were prepared by ATRP technique to study the effect of these polymer systems on the PET crystallization rate with special emphasis on the composition of blends. The results of the study have clearly indicated that both the copolymer and ionomer accelerate the rate of PET crystallization. It is confirmed that block ionomer is more effective than block copolymer to accelerate nucleation and crystallization, because the ionic groups located at the end of the polymer chain act as nucleation sites by accelerating the crystallization rate of polymers. It is well known that the crystallization behaviour of the polymer may be improved in a blend due to the presence of other components. The block ionomer in the blend has exhibited two crystallization temperatures and there has been multiple endotherms observed in both block copolymer and block ionomer blends with PET. The 98/2 wt% P(St-*b*-tBA) and 92/8 wt% P(St-*b*-A K$^+$) blends have exhibited the most significant acceleration rates in PET crystalliza-

tion over the copolymer content varied from 2 to 10 wt%.

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