

THERMAL ANALYSIS OF POLYPROPYLENE-*b*-POLYETHYLENE DIBLOCK COPOLYMERS AND CORRESPONDING BLENDS*

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ABSTRACT

Difference in thermal behavior of presumed polypropylene-*b*-polyethylene block copolymers (PP-PE) and corresponding PP+PE blends was studied. Different views in the literature were unified in our observation that faster cooling rate yielded only one exothermal peak for the blends, while slower cooling rates revealed both PP and PE exothermal peaks. Further details on when a single or double exothermal peaks would appear are discussed. Melting and crystallization temperatures for both PP and PE in blends were found to be a few degrees higher than for PP and PE in block copolymers. Thus, thermal analysis can be used to identify PP-PE block copolymers. These phenomena and the lower ΔH_f -values of PP and PE in block copolymers than the ΔH_f -values of pure homo-PP and -PE (for PE even more so) are explained in terms of restricted block movement due to covalent bond between blocks and of crystallization processes in block copolymers. The presence of block structure in the PP-PE samples studied is inferred.

In judging whether block structures were obtained in attempted block copolymer synthesis with Ziegler-Natta catalysts (e.g., polypropylene-*b*-polyethylene, PP-PE; polypropylene-*b*-ethylene propylene copolymer-*b*-polypropylene, PP-EPR-PP)^[1], resort has to be made to explore methods which can distinguish between the alleged block copolymers and the corresponding blends.

It has been known that thermal analysis could be used in distinguishing PP-PE from its counterpart PP+PE, since while two exothermal peaks appeared on cooling curves for PP-PE, blends PP+PE showed only one exothermal peak^[2-4]. Gilbert et al. reported recently, however, that both PP-PE and PP+PE yielded two exothermal peaks on thermograms^[5].

This work attempts to study experimental conditions and thermal behavior of PP-PE against the background of that of PP, PE and PP+PE, in order to elucidate the regularity of the appearance of one or two exothermal peaks and to clarify the reported discrepancy as stated above, and to ascertain whether thermal analysis could be used to differentiate between block copolymers and their corresponding blends.

It must be pointed out that, due to possible chain-transfer reactions in polymerization with Ziegler-Natta catalysts, so-called PP-PE "block copolymers" in the literature and in

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this work as well as of commercial origin are most probably impure block copolymers contaminated with block impurities (PP, PE). The very existence of the desired block structure just has to be ascertained by comparing physical behavior of the product with corresponding known blends.

EXPERIMENTAL

1. Samples

Unless specified as commercial, block copolymers and homopolymers were prepared in this Laboratory with $\text{TiCl}_3\text{-Et}_2\text{AlCl}$ catalyst at 60°C in heptane, $[\text{Ti}] = 10 \text{ mM}$, $[\text{Al}] / [\text{Ti}] = 4$, polymerization time being 60 minutes. Polymerization procedure is described elsewhere^[1]. The samples other than those described in Figure 2 were characterized as shown in Table 1.

Table 1 Characterization of samples

No.	Sample type	$[\eta]$ (dl/g)	C_3 (wt. %)
P-1 ¹⁾	Polypropylene	5.08	100
P-2		3.28	100
E-1 ²⁾	Polyethylene	1.82	—
E-2		—	—
B-1 ¹⁾	PP-PE block copolymer	4.60	69
B-2 ¹⁾		3.00	72
B-4		3.30	62
B-5		3.20	57
B-7		1.80	37

1) Commercial sample from Xiangyang Chemical Works, Beijing.

2) From Qianjing Chemical Works, Beijing.

C_3 -content of the copolymer samples was determined from measured values (180°C) of $A_{1379\text{cm}^{-1}} / A_{1459\text{cm}^{-1}}$ (Perkin-Elmer 577) using a calibration curve constructed according to Corish^[6]. $[\eta]$ values were determined with tetralin solution at 135°C .

Molded blends: Powdered PP and PE at given ratios were intermixed and compression-molded at 200°C into sheets, which were repeatedly cut and re-molded for five times.

Ground blends: Powdered PP and PE were ground in a mortar for about $\frac{1}{2}$ h.

Co-precipitation blend: PP and PE at a given ratio were dissolved at $120\text{--}130^\circ\text{C}$ in xylene and the solution was poured into a large amount of alcohol 5 minutes after dissolution. The precipitated polymer was collected and washed twice with alcohol and dried *in vacuo*.

2. Thermal analysis

Thermal analyses were performed on both DSC constructed in this Laboratory^[7] and

a Perkin-Elmer DSC-2C. On the home-made DSC, a 20-mg sample was heated at a rate of $6.5^{\circ}\text{C}/\text{min}$ under air until up to 190°C and was then cooled at a rate of 6.5, 1.7 or $0.4^{\circ}\text{C}/\text{min}$, allowing for crystallization. Sample for DSC-2C was 4 mg in size and it was heated to fusion under nitrogen at $10^{\circ}\text{C}/\text{min}$. To compare with data of Gilbert^[5], some samples were heated to 180°C after melting and maintained there for 1 h and then cooled at 40, 20, 10, 5, 2.5, 1.25 or $0.625^{\circ}\text{C}/\text{min}$, respectively. Heat of fusion, ΔH_f , values were collected on DSC-2C under nitrogen with indium as the standard.

RESULTS AND DISCUSSION

Ke^[2] and Barrall^[3] reported in their studies on thermal properties of block copolymers PP-PE and blends PP+PE that both PP-PE and PP+PE showed endothermal peaks at ca. 130 and 165°C on heating, while on cooling PP+PE blends at any ratio showed only one exothermal peak at 110°C , although PP-PE showed two peaks at 140 and 110°C respectively. Inoue also reported that PP+PE showed only one exothermal peak^[4]. The discrepancy between the thermal behavior of block copolymers and blends was attributed to a large super-cooling of PP in the blends. Recently Gilbert et al.^[5] reported the presence of two exothermal peaks for PP+PE, thus negating the use of thermal analysis as a means for distinguishing block copolymers from blends as suggested by earlier workers.

Since methods of blending and experimental conditions of previous work might not be the same, this work undertook first of all to clarify whether different methods of blending might be the cause of the reported discrepancy. It was found that, under the same heating or cooling rate of $6.5^{\circ}\text{C}/\text{min}$, blends prepared by grinding, heat-molding or co-precipitation gave the same thermal data (Table 2). On the heating thermogram, PE and PP endothermal peaks appeared at 137 ± 2 and $166 \pm 2^{\circ}\text{C}$, respectively, and on the cooling thermogram only one exothermal peak at $113\text{--}116^{\circ}\text{C}$ appeared, thus conforming the results of Ke, Barrall and Inoue.

Table 2 Thermal behavior of blends prepared in different manner¹⁾

C_3 (wt. %)	Method of blending	Endotherm ($^{\circ}\text{C}$)		Exotherm ($^{\circ}\text{C}$)	
		PE	PP	PP	PE
27	Grinding	137	167	—	
	Molding	137	164	115	
50	Grinding	135	167	116	
	Molding	139	166	114	
	Co-precipitation	135	165	113	
74	Grinding	135	168	—	
	Molding	137	168	114	

1) Rate of heating and cooling: $6.5^{\circ}\text{C}/\text{min}$.

Table 3 Effect of cooling rate on thermal behavior of PP+PE blends

C ₃ (wt.%)	Method of blending	Endotherm ¹⁾ (°C)		Rate of cooling (°C/min)	Exotherm ²⁾ (°C)	
		PE	PP		PP	PE
PE		133		6.5		109
				0.4		117
PP			169	6.5	112	
				0.4	127	
27	Grinding	135	167	6.5		116
				1.7	Shdr	119
				0.4	131	123
51	Grinding	135	167	6.5		116
				1.7	Shdr	119
				0.4	131	123.3
50	Molding	139	166	6.5		114
				0.4	130	123.3
	Co-ppion	135	168	6.5		113
				0.4	126	121
74	Grinding	135	168	6.5		113
				0.4	132	124

1) Rate of heating all at 6.5°C/min.

2) Shdr = shoulder.

It was further found, however, that cooling rate had a profound effect on the exothermogram of the blends (Table 3). When the cooling rate was lowered to 1.7°C/min, a shoulder due to PP appeared besides the PE exothermal peak; at 0.4°C/min, two peaks at 130 and 123°C due to PP and PE respectively emerged (Figure 1). Thus, the result of Gilbert was reproduced here.

To elucidate the regularities in the appearance of a single or two peaks, the effect of cooling rate was observed on crystallization of PE and PP of low and high MW and their four respective 1:1 mutual blends (Figure 2 and Table 4).

From Figure 2 it is seen that the phenomenon of super-cooling of PE and PP became progressively more pronounced with increasing cooling rate, much more so for PP than for PE. On increasing the cooling rate from 0.625°C/min to 40°C/min, the lowering of T_c was 14–15°C for PE but 29–30°C for PP. T_c was also affected by MW of the samples. While T_c of PE increased with increase in MW, the reverse was true for PP and the effect of

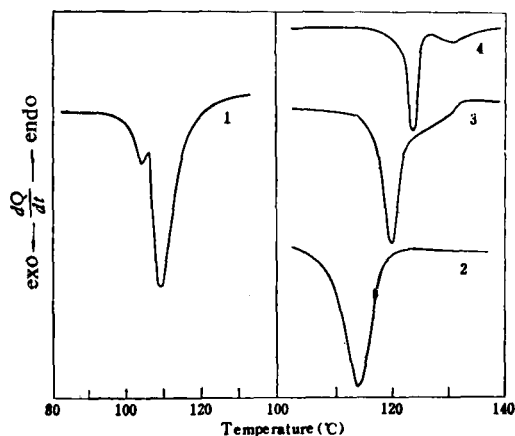


Fig. 1 Exothermal curves of PP-PE and PP+PE
 1. PP-PE, rate of cooling 6.5°C/min.
 2—4. PP+PE, rate of cooling 6.5, 1.7 and 0.4°C/min, respectively.

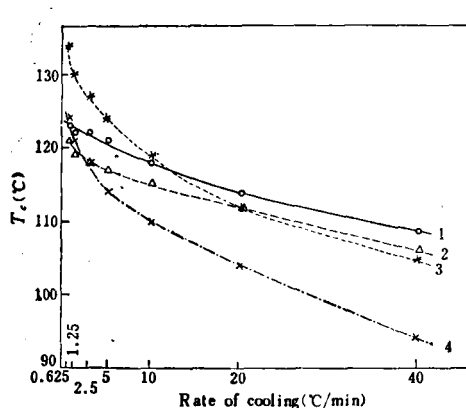


Fig. 2 T_c of PE and PP of low and high MW at various cooling rates
 1—PE_H J-1 0.2—0.4 (MI); 2—PE_L GC7260 20.0—26 (MI);
 3—PE_L 2600 11.0 (MI); 4—PP_H 1300 1.0 (MI).

MW on T_c was greater with PP than with PE.

Data in Table 4 also show the importance of the rate of cooling on the appearance of either a single or two peaks. While faster cooling rates always yielded a single exothermal peak, slower rates gave double peaks, which, according to the PE and PP components involved, appeared at the specific cooling rates determined by T_c of the components before blending as well as the annealing time at 180°C before cooling, as seen below.

It is apparent that the main factor dictating the appearance of only a single peak is supercooling, which is related to the rate of cooling. At faster cooling rates, as the result of supercooling, T_c of PP appeared below that of PE (Figure 2). At a supercooling near the T_c of PE, PE crystallites became the nucleating agent for PP melts and co-crystallization took place, giving only a single peak. This is supported by the proximity of T_c of blends that show single peak to T_c of pure PE at the same cooling rate.

Table 4 T_c of 1:1 blends of PE and PP of different MW at various cooling rates

Components ¹⁾	T_c (°C) at various cooling rates (°C/min)						
	0.625	1.25	2.5	5	10	20	40
PE _L +PP _L	128	125	122 ²⁾	117	116	—	106
	121	120	119				
PE _L +PP _H	127	123	120 ³⁾	118	115	—	104
	121	119	118				
PE _H +PP _L	126	123	122	120	117	—	107
	123	122					
PE _H +PP _H	126	123	121	118	116	111	102
	123						

1) For samples see Figure 2, L denoting low MW and H high MW.

2) Shoulder.

3) Smaller shoulder.

At slower cooling rates, PP had a higher T_c than that of PE as the result of less extent of super-cooling. Then PP had enough time to crystallize and generally two peaks appeared. However, the emergence of two exothermal peaks again depended on the difference in T_c 's of PE and PP, respectively, before blending (ΔT_c). Generally, blends with larger ΔT_c tended to give two peaks, with the crystallization of PP prior to that of PE.

The duration of annealing for removal of residual nuclei (180°C for 1 h in this work) also influenced the emergence of the second peak. Extension of the annealing to two hours usually induced the appearance of the second peak on samples that otherwise would have to yield only a single peak under higher cooling rates. This separate crystallization of PE and PP is probably due to the segregation or phase separation of the two components in the melt, favorable under a high temperature for longer times. The suggestion of segregation is supported by the following two facts. Lower MW and thus lower melt viscosity should facilitate segregation. Thus, in Table 4, blends with PE of low MW showed observable separate crystallization processes at a cooling rate of 2.5°C/min, with high MW PP exhibiting a less pronounced shoulder. Blends with PE of high MW showed the second peak at a cooling rate as slow as 0.625°C/min with PP of high MW. The second fact is that samples which once exhibited two peaks would ever show two peaks in the next cooling cycles, since the sample with phase segregation would not easily return to the original uniform state of mixing.

All the above facts point to the conclusion that since the emergence of either a single or two separate peaks depends on various samples and experimental conditions, the early assertion that the number of peaks could be used as a criterion in distinguishing between block copolymers and mechanical blends is not well founded.

In Table 5 are shown thermal data of PP-PE block copolymers both prepared in this Laboratory and of commercial origin. At both higher and slower cooling rates two exothermic peaks appeared. This is in conformity with all the previous work.

Summarizing data of Table 3 and Table 5, we conclude that for block copolymers both the melting and crystallization temperatures of either PP or PE are several degrees lower than those of the corresponding blends (Table 6). Gilbert's data^[8], when put into graphic form (not shown), lend support to this important conclusion, showing clearly the lower melting and crystallization temperatures of PP and PE in block copolymers. Thus, enough evidence is collected to show that the thermal properties of block copolymers and blends are different.

Table 5 Thermal data of PP-PE block copolymers

No.	C ₃ (wt.%)	Endotherm ¹⁾ (°C)		Rate of cooling (°C/min)	Exotherm (°C)	
		PE	PP		PP	PE
B-7	37	128	166	6.5	117	111
				0.4	127	114
B-5	57	130	165	6.5	111	109
				0.4	126	115
B-4	62	128	164	6.5	109	106
				0.4	126	115
B-2	72	122	165	6.5	110	106
				0.4	125	—

1) Rate of heating all at 6.5°C/min.

Table 6 Summary of thermal data of Table 3 and Table 5

Rate of cooling (°C/min)	Type of sample	Endotherm (°C)		Exotherm (°C)	
		PE	PP	PP	PE
6.5	Blend	133—139	166—168	—	109—116
	Block	128—130	161—165	109—117	106—111
		Δ 5—9°C	Δ 3—5°C		Δ 3—5°C
0.4	Blend	Not determined		131—136	121—124
	Block			125—127	114—115
				Δ 6—9°C	Δ 7—9°C

ΔH_f values of PP and PE in block copolymers are lower than ΔH_f of their respective homopolymeric PP and PE, with PE much more so (Table 7). The lower melting and crystallization temperatures for block copolymers than the corresponding blends is understandable in terms of the difference in ΔH_f values. The movement and hence the crystallization

of PP and PE segments in block copolymers is impeded by the covalent bond connecting the blocks, and the resulting imperfect crystalline structure leads to lower T_m and T_c and lower ΔH_f . X-ray diffraction data of this Laboratory also revealed lower PP and PE crystallinity in block copolymers than in blends of similar composition, with PE even more so^[1]. The more pronounced lowering in ΔH_f and crystallinity for PE in block copolymers is the consequence of the prior crystallization of PP in a cooling sample, which exerts greater influence on the chain movement of the late crystallizing PE than in the case of crystallization of PP in the presence of yet mobile PE chains.

Table 7 Heat of fusion of block copolymers¹⁾

No.	Type of sample	C ₃ (wt. %)	Endotherm (°C)		ΔH_f (cal/g)	
			PP	PE	PP	PE
P-2	PP	100	165		21.6	
E-2	PE	0	—	130	—	55
B-5	PP-PE	57	160.0	126.2	18.1	16.6
B-4		62	160.5	125.3	19.5	15.4
B-1		69	162.5	124.0	19.7	12.9
B-2		72	163.2	120.3	19.5	13.8

1) Rate of heating all at 5°C/min.

In summary, thermal analysis techniques based on measurement of T_c , T_m and ΔH_f (but not the number of peaks) could be used as one of the methods in distinguishing between block copolymers PP-PE and blends PP+PE. The presence of block structure in the laboratory and commercial samples studied is thus demonstrated. Results of this work infer that thermal analysis might be useful in identifying other block copolymers with crystalline or glassy segments.

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