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FUSION BEHAVIOUR OF LINEAR POLYETHYLENE IN DOTRIACONTANE—A DTA STUDY

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Abstract—An additional crystalline phase has been found to form in linear polyethylene–dotriacontane blends, based on differential thermal analysis (DTA) data. The new phase is formed when blends containing linear polyethylene, at concentrations less than 34 per cent, are solidified from the melt under carefully controlled crystallization conditions. The endotherm of the new phase, as measured by the DTA, occurs at 2–5° lower than that of polyethylene. The quantity of the new crystalline phase has been found to be dependent upon polymer molecular weight, blend concentration, solidification rate and heat treatment. Blends having lower molecular weight fractions enhance the formation of the new phase. The relative amounts of the new crystalline phase and the polyethylene crystalline phase vary with the cooling rate of the blend during solidification, with the new crystalline phase predominating at slower cooling rates. Heat treatment of the solidified blend results in the merging of the polyethylene and the new crystalline phase endotherms.

INTRODUCTION

SEVERAL investigations of the compatibility and interaction of polymers and low molecular substances with crystalline polymers have been reported recently.(1–5) Parrini and Corrieri(1) have shown that compatible substances cause a decrease in crystallization rate of the pure polymer while incompatible substances cause an increase or no change. Clampitt(2) has studied the fusion process of linear-low density polyethylene blends using a differential thermal analysis (DTA) technique. He observed three DTA endothermic peaks for annealed samples of the blends and attributed the extra peaks to the formation of co-crystals. Ke(3) has studied the fusion behaviour of mixtures of branched and linear polyethylene with dotriacontane (linear hydrocarbon, $C_{32}H_{66}$) by DTA. His results indicated a progressive decrease of the melting temperature of the polymer with increasing dotriacontane concentration. Keith(4,5) has studied the morphology of fractionated linear polyethylene crystallized from solution in dotriacontane which can be considered to be a very low molecular weight polyethylene. The effect of the low molecular weight species on the crystallization of polyethylene was then studied. He observed that polyethylene exhibited unusual crystal habits in blends containing large amounts of dotriacontane.

This paper presents the results of an investigation of the interaction of linear polyethylene and dotriacontane by studying the effect of concentration, molecular weight, annealing and quenching condition on the fusion behaviour of the blends, using a differential thermal analysis technique.

EXPERIMENTAL

Polyethylene–dotriacontane blends covering the entire composition range were prepared by solution blending in *o*-xylene followed by precipitation in methanol. The precipitates were then filtered and dried in a vacuum oven. Preparation of samples for differential thermal analysis consisted of loading 2 mm DTA micro tubes with 1–2 mg samples and then heating the tubes to 193° in an aluminium

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block. An analytical thermocouple (chromel–alumel) was implanted in the centre of the melt. The sample tube with its contents was quickly removed from the aluminium heating block and cooled in a controlled manner. Depending upon the particular quenching condition desired, the sample tubes were plunged into either ice water, silicone oil at various temperatures or cooled in air. Cooling curves indicated that the samples generally solidified in less than 10 sec.

For the measurement of cooling rates, a 15 per cent polyethylene blend was used. A 2 mg sample was weighed into a 2 mm micro sample tube and heated to 193° as before. A thermocouple with cold junction at 0° was implanted in the centre of the melt and attached to a high speed x–y recorder. The sample was quenched under a particular condition and a plot of the change in mV (and hence temperature) with time was recorded as the sample cooled in the quenching medium. An assumption made here was that the rate of heat transfer is the same for blended samples of the same weight but different composition.

Annealing experiments were done in a silicone oil constant temperature bath. Each micro sample tube containing a sample and thermocouple was covered with aluminium foil to avoid contamination by the silicone oil. The tubes were placed in holes drilled in an aluminium block and the block lowered into the silicone oil so that each sample was heated uniformly.

The fusion behaviour of blends with the dotriacontane removed after the blends were quenched under a certain condition was also studied. Removal of dotriacontane from the blend was accomplished by adding *o*-xylene to a small amount of the blend in a test tube with occasional stirring at room temperature. This may also be effected by carrying out the process at a higher temperature of 50°. Polyethylene remained as a solid under these conditions while dotriacontane dissolved in *o*-xylene. The solution was removed by filtration and the remaining solid washed with *o*-xylene followed by methanol. It was then vacuum dried overnight at 60°.

All samples were run in a DuPont 900 Differential Thermal Analyser (DTA) at a heating rate of 10 ± 1°/min. The accuracy of the DTA was estimated to be ± 1° and was checked frequently with benzoic acid (melting point taken as 122°).

Hercules Hifax high density polyethylene and fractions obtained from fractionation of the whole polymer were used. The technique used in fractionating the polymer has been described already.(6) Dotriacontane ($C_{32}H_{66}$, m.p. 69–70°) from Eastman Kodak Chemicals was used as received. Dow Corning 550 silicone oil was used in the constant temperature bath.

RESULTS

Typical thermograms obtained by heating polyethylene–dotriacontane blends of different compositions in the DTA are presented in Fig. 1. These curves are similar to those obtained by Ke.(3) The samples were in powder form (vacuum dried sample of the blends); the thermograms in Fig. 1 were obtained without first melting the samples prior to making the DTA runs.

The double peak at the left of Fig. 1 corresponds to the melting of dotriacontane. The larger peak at 68° represents the actual melting of the linear hydrocarbon while the smaller one at 62° is due to the rotational transition of the *n*-paraffin chain molecules.(7,8) The positions of these two peaks remained essentially constant as the composition of the blend was varied. A plot of polyethylene melting temperature, T_m, as a function of blend composition is shown in Fig. 2.

When the 15 per cent polyethylene blend was melted at 193° and subsequently quenched in air at room temperature (26°), (a cooling rate of about 2·6°/sec), a double peak appeared in the position where a single peak would normally appear for the melting of polyethylene. The thermogram is shown in Fig. 3 together with that for the thermally untreated 15 per cent polyethylene blend for comparison. It is seen that the peak at 117° (peak I) occurs at the same temperature as the single peak produced by the untreated sample. Peak II, however, occurs at 113°. Double peaks also occurred when blends of 7·5, 15 and 25 per cent polyethylene compositions were subject to a series of different quenching conditions. The results are tabulated in Table 1. It can be seen that peaks I and II shift to higher temperatures with increasing polyethylene concentration. Closer examination of the results shows that peak I of the 15 and 25 per cent polyethylene

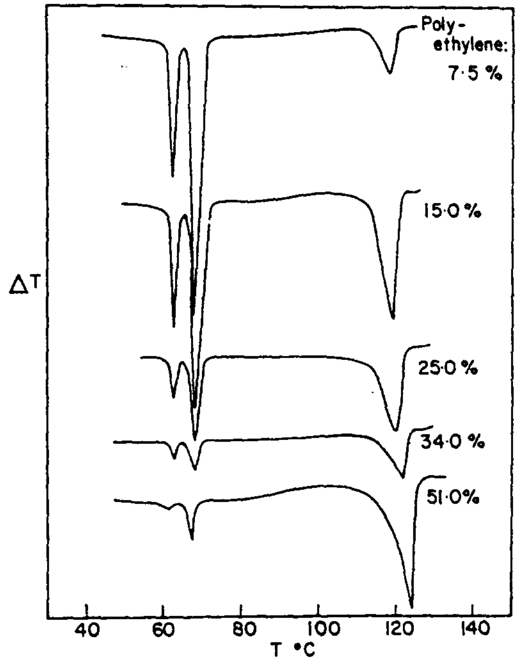

FIG. 1. Thermograms of polyethylene–dotriacontane blends.

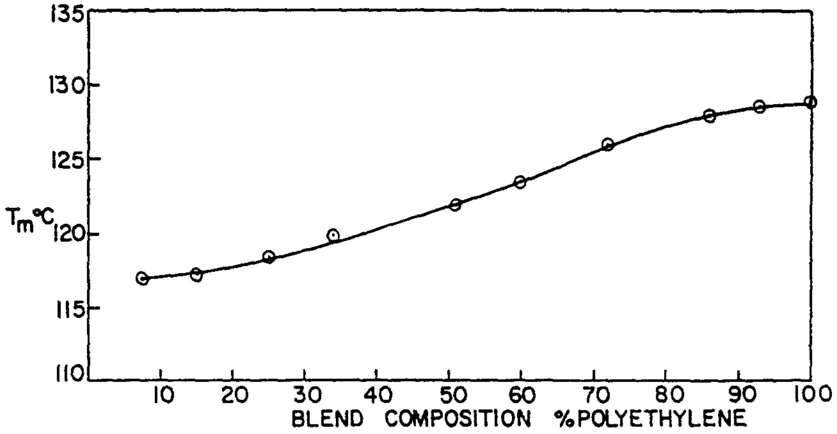

FIG. 2. Depression of polyethylene melting point by dotriacontane.

blends remains essentially at the same temperature under different quenching conditions. These peaks, however, completely disappeared when the samples were quenched in silicone oil at 110° (a cooling rate less than 0·6°/sec) leaving only peak II. The 7·5 per cent polyethylene blend still yielded a double peak under this quenching condition. Thermograms of 7·5 per cent polyethylene blended in dotriacontane obtained under different quenching conditions are presented in Fig. 4.

The results in Fig. 4 indicate that there is a change in the relative magnitudes of peaks I and II with quenching condition. A correlation was found between the relative

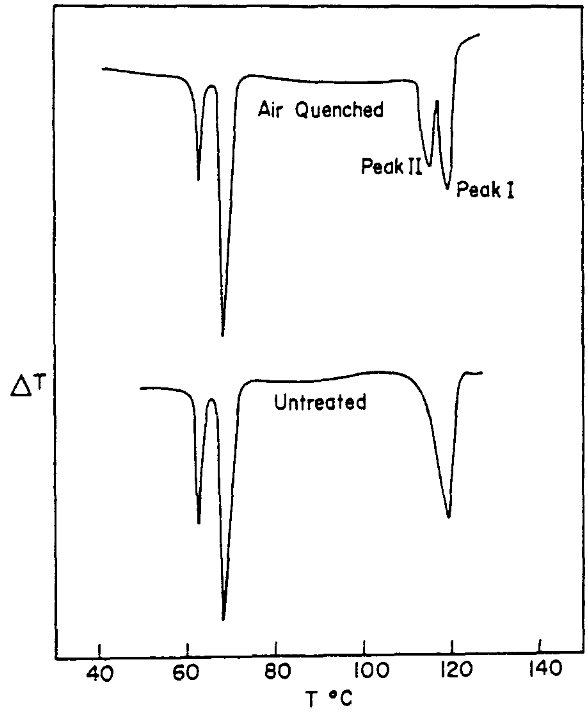

FIG. 3. Thermograms of 15 per cent polyethylene blended in dotriacontane—effect of quenching on polyethylene fusion behaviour.

magnitude of the peaks and the cooling rate of the sample in the quenching medium. In Fig. 5, the ratio of the height of peak II (h_{II}) to the sum of the heights of peaks I and II ($h_I + h_{II}$), designated as the fractional peak height, is plotted against the cooling rate. It can be seen that peak II gradually predominates at slower cooling rates. It becomes the only peak produced by the 15 and 25 per cent polyethylene blends quenched in silicone oil at 100° (less than 0·6°/sec). On the other hand, rapid quenching of the samples in ice water (47°/sec) produced predominantly peak I. Thermograms are shown in Fig. 6.

TABLE 1. PEAK TEMPERATURES OF POLYETHYLENE DOUBLET AS A FUNCTION OF QUENCHING CONDITION

Quenching condition	Cooling rate °/sec	Peak II°			Peak I°		
		7·5%PE	15%PE	25%PE	7·5%PE	15%PE	25%PE
Silicone oil 40°	27	110	111	113	115	116	118
Silicone oil 80°	11	110	111	114	115	116	118
Air at 26°	2·6	111	113	115	116	117	119
Silicone oil 100°	1·5	112	113	116	116	116	118
Silicone oil 105°	0·93	112	114	116	116	117	119
Silicone oil 110°	<0·6	114	115	117	117	—	—

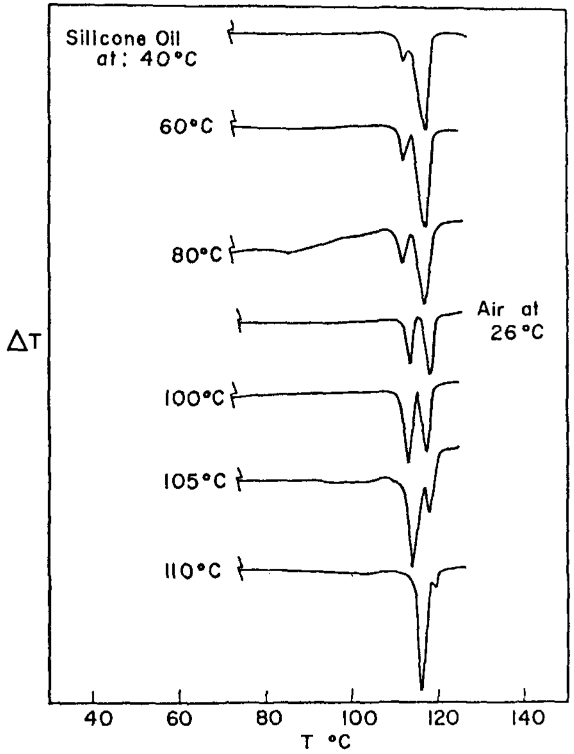

FIG. 4. Thermograms of 7·5 per cent polyethylene blended in dotriacontane—effect of quenching on peak size. (DTA peaks for dotriacontane remained essentially the same and have not been drawn.)

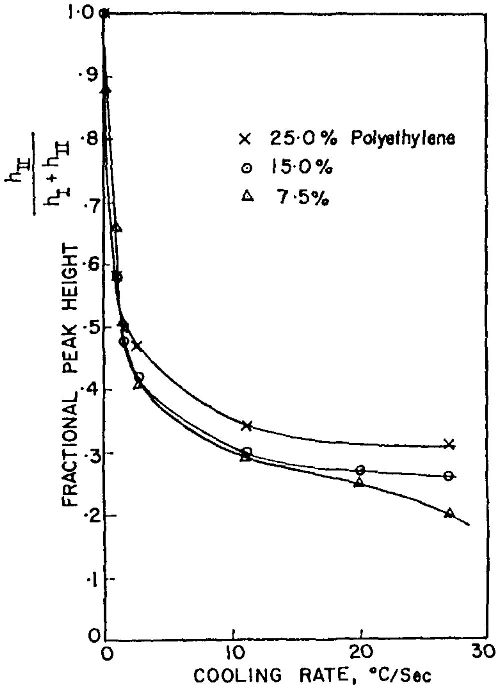

FIG. 5. Variation of fractional peak height with cooling rate.

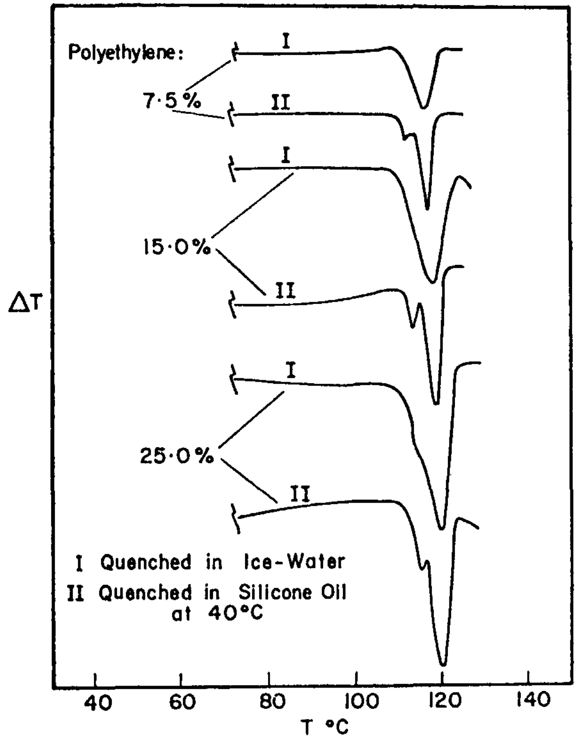

FIG. 6. Effect of composition and quenching condition on polyethylene-dotriacontane thermograms. (DTA peaks for dotriacontane remained essentially the same and have not been drawn.)

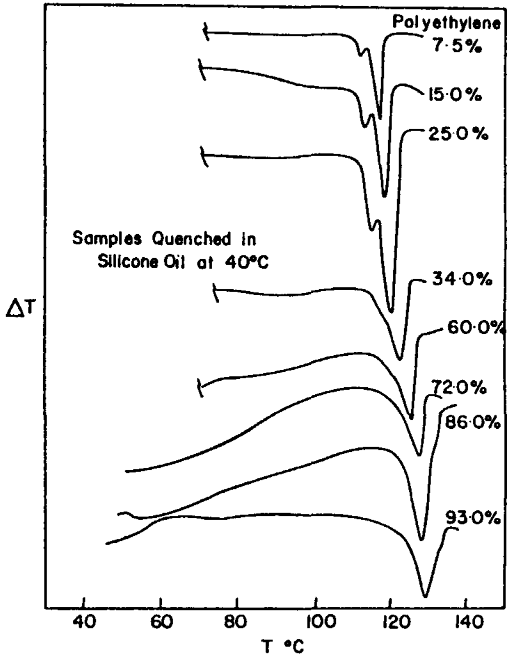

FIG. 7. Thermograms of polyethylene-dotriacontane blends—concentration dependence of the polyethylene doublet. (DTA peaks for dotriacontane remained essentially the same and and have not been drawn.)

EFFECT OF CONCENTRATION

Thermograms of blends covering the whole concentration range and quenched in silicone oil at 40° are shown in Fig. 7. It is noted that only one peak appears for the 34 per cent polyethylene blend and for all blends of higher polyethylene concentration, and that peak temperature increases with increasing polymer concentration. Similar results were obtained under two additional quenching conditions (air quenched and silicone oil at 100°) and the results are presented in Table 2.

TABLE 2. MELTING TEMPERATURE OF POLYETHYLENE AS A FUNCTION OF CONCENTRATION IN POLYETHYLENE–DOTRIACONTANE BLENDS

Composition of blend %PE	Air quenched (2·6°/sec)		Silicone oil at 40° (27°/sec)		Silicone oil at 100° (1·5°/sec)	
	Peak II°	Peak I°	Peak II°	Peak I°	Peak II°	Peak I°
7·5	111	116	110	115	112	116
15	113	117	111	116	113	116
25	115	119	113	118	116	118
34		121		121		120
51		123		122		121
60		124		124		123
72		125		126		126
86		127		126		127
93		127		127		128
100		129		128		129

EFFECT OF MOLECULAR WEIGHT

Thermograms resulting from heating in the DTA of quenched 15 per cent polyethylene blends prepared from polyethylene fractions are given in Fig. 8. It is seen that peak II persists up to a molecular weight of 51,000 and then disappears for the 140,000 molecular weight fraction, leaving peak I at 118°. Figure 8 also shows that there is a melting point depression (peak I) for the low molecular weight blends.

EFFECT OF ANNEALING

Thermograms showing the effect of annealing are presented in Fig. 9. The 15 per cent polyethylene blend was first quenched in air and then annealed at 108° (a temperature near the temperature of peak II) for various periods. The peaks are seen to broaden with increasing annealing time; after 19 hr, they merged and formed a broad fusion curve. The last thermogram in Fig. 9 shows the result of annealing a 7·5 per cent polyethylene blend (previously quenched in silicone oil at 100°) (15°/sec) at 108° for 19 hr but with the dotriacontane removed before annealing. Removal of the dotriacontane was found to be extremely difficult without affecting peak II. In many cases it resulted in its total disappearance after the washing step. It should be noted that the doublet has shifted to a higher temperature as a result of the removal of dotriacontane.

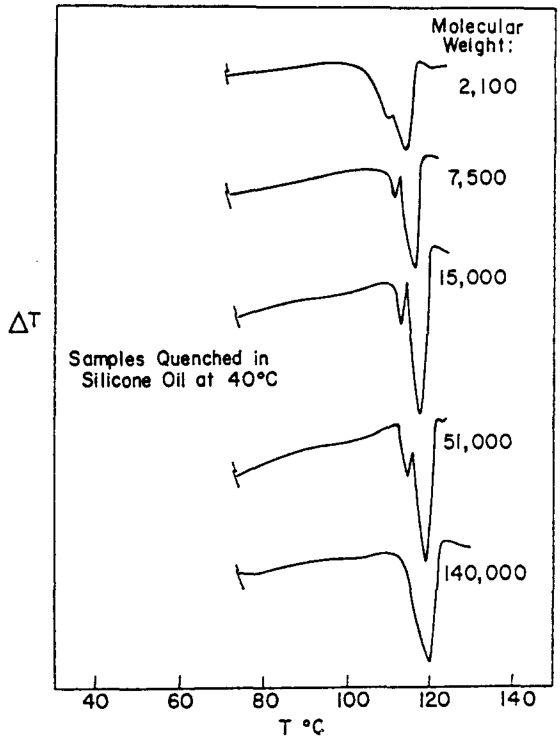

FIG. 8. Thermograms of 15 per cent polyethylene blended in dotriacontane—effect of molecular weight. (DTA peak for dotriacontane remained essentially the same and have not been drawn.)

FUSION BEHAVIOUR OF WASHED SAMPLE

Thermograms showing the fusion behaviour of the washed sample of a 7·5 per cent polyethylene blend are presented in Fig. 10. The first thermogram shows the melting of the 7·5 per cent polyethylene blend which was previously quenched in silicone oil at 100°. The second thermogram shows the melting of a sample taken from the same batch but with the dotriacontane removed by washing with *o*-xylene. The doublet has shifted to the high temperature side with peak I now appearing at 129°, the melting peak temperature of pure polyethylene under these conditions. This sample was then quenched in air and reheated. The melting process is shown in the third thermogram. It can be seen that only a single peak occurred. This would be expected for the polyethylene doublet forms only in the presence of dotriacontane. The peak temperature is 129°, the same as that for air quenched pure polyethylene.

DISCUSSION

The depression of polyethylene melting point by dotriacontane (Fig. 2) has been studied by Ke(3) who attempted a quantitative correlation with the Flory melting point depression theory.(9,10) Behaviour of this type is the manifestation of the compatibility of the two components in the blends.

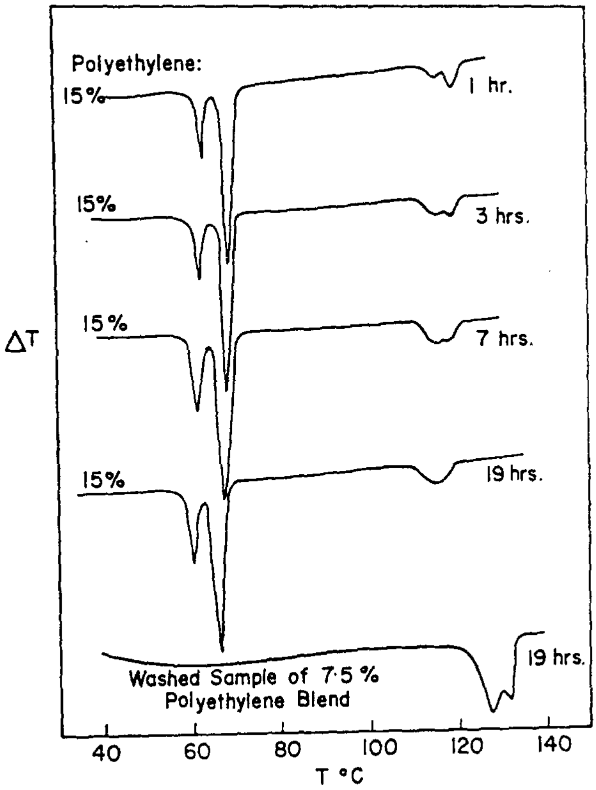

Fig. 9. Effect of annealing on polyethylene-dotriacontane thermograms.

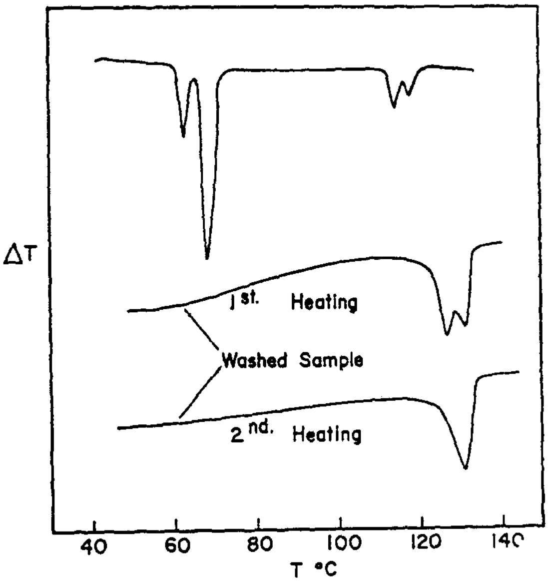

Fig. 10. Thermograms of 7·5 per cent polyethylene blended in dotriacontane—effect of washing.

The occurrence of peak II in the thermograms of polyethylene–dotriacontane blends indicates the melting of crystalline material or an enthalpy change involved in a solid–solid type of phase transition. It is considered quite unlikely that it can be due to the type of enthalpy change associated with rotational transition as in dotriacontane, or that associated with dis-orientation of oriented crystalline region such as that reported for the melting of oriented Nylon 66 monofilament.(11) Crystal–crystal transition or melting of smaller polyethylene crystallites or the melting of a distinctly different crystalline phase was considered more likely to have occurred. Under the assumption of crystal–crystal transition in the solid state, the relative magnitudes of peaks I and II should remain about the same within experimental error. However, it has been shown in Fig. 4 that the relative magnitudes of the two peaks vary with quenching condition and in extreme cases (last entry in Table 1) peak I may completely disappear. Thus experimental evidence argues strongly against the possibility of such a transition.

Hoashi and Mochizuke(12) have recently reported the appearance of multiple DTA peaks in thermograms of polyethylene samples which have been subject to various conditions of heat treatment. They found that the extra peaks which occurred at lower temperatures can be attributed to the melting of smaller, thinner or imperfectly formed crystallites. Referring to Fig. 6, it is seen that only single peaks occurred when the blends were quenched in ice water. These peaks appear at essentially the same position as peak I for the same blends quenched in silicone oil at 40°. Since crystallization of a polymer at low temperature is known to enhance the formation of small and imperfectly formed crystallites with correspondingly low melting points, then quenching of the blends in ice water should result in the predominance of peak II if this peak represents the melting of small polyethylene crystallites. The occurrence of peak I in ice water quenched samples, therefore, appears to rule out the possibility of peak II being due to the melting of small polyethylene crystallites.

The postulate that peak II is due to the melting of a distinctly different crystalline phase agrees most favourably with experimental evidence. It may be said that only a single crystalline phase was initially formed from the melt and that this first melted, giving rise to peak II and then recrystallized into a second crystal form which melted as represented by peak I. Geacintov and co-workers(13,14) have published DTA thermograms for polybutene-1 which exhibited this behaviour. However, a crystallization exotherm is clearly visible in between two melting endotherms in their work. In addition, the tendency of the two peaks to merge with increasing silicone oil temperature (decreasing cooling rate) in the present work and the change in their relative magnitudes with the cooling rate indicate that the phenomenon observed is closely associated with crystallization conditions rather than the melting process. A logical explanation, therefore, would be the formation of two crystal forms from the melt. The two peaks represent the melting of each of these crystalline phases. The variation of the relative magnitudes of the two peaks can then be interpreted as a change in the relative abundance of the two crystal forms.

The exact nature of the new crystalline phase can only be determined by further optical and electron microscopy and X-ray work. Several possibilities exist such as co-crystal formation(2) or formation of a polymorphic modification of polyethylene.(15,16) Of particular interest is the study made by Keith(4,5) on the morphology of fractioned linear polyethylene crystallized from solution in dotriacontane. He found that polyethylene crystallized in unusual radiating multilayer aggregates when blended with dotriacontane at low polyethylene concentrations. Among some of his findings are: (1) the structure of the crystals formed becomes more complex and approaches the spherulitic type as crystallization temperature decreases; (2) under the same condition, the structure of crystals formed with low molecular weight polyethylene (M = 4500) is simpler than that of crystals formed with high molecular weight polyethylene (M = 168,000); and (3) at concentration as high as 30 per cent polyethylene and above, spherulites were formed even in the low molecular weight polyethylene–dotriacontane blends.

If the assumption is made in this work that multilayer aggregates and spherulites are formed simultaneously from the melt, and if it is further assumed that peak I represents the melting of spherulites (which are more complex in structure and thus may melt at a higher temperature) and peak II represents the melting of the multilayer aggregates (simpler and probably thinner than spherulites and thus melt at a lower temperature), then some of the phenomena observed may be interpreted in the light of Keith's findings. It has been shown previously that only single peaks were observed for blends of polyethylene concentrations higher than 34 per cent. This may be explained that only spherulites are produced for blends of polyethylene concentration above 30 per cent. The variation in the relative magnitudes of the polyethylene peaks may now also be explained. Based on Keith's finding that crystal structure becomes more complex and approaches spherulitic behaviour as the crystallization temperature decreases, it can be said that the single peaks (peak I) produced in ice water quenched samples represent the fusion of the spherulites formed and the single peaks (peak II) which appeared in samples quenched in silicone oil at 110° show the melting of multilayer aggregates which were the only species formed under this condition. The decrease of the magnitude of peak II as the temperature of the silicone oil decreases can be attributed to the formation of fewer multilayer aggregates and more spherulites as the crystallization temperature decreases. The effect of molecular weight may likewise be explained. The 15 per cent polyethylene blend made of the highest molecular weight fraction (M = 140,000) has been shown to yield only a single peak under conditions comparable to blends made up of lower molecular weight species. This may indicate that spherulites were the only species formed with the highest molecular weight fraction, while both multilayer aggregates and spherulites (two peaks) were formed with lower molecular weight polyethylene fractions of the same composition.

CONCLUSIONS

Dotriacontane is compatible with linear polyethylene and this is manifested by the progressive decrease of the polyethylene melting point with increasing dotriacontane concentration. Two DTA endothermic peaks (peaks I and II) occurred during melting of polyethylene in polyethylene–dotriacontane blends having polyethylene concentrations below approximately 34 per cent under certain quenching conditions. The extra peak (peak II) was attributed to the melting of a distinctly different crystalline phase. High molecular weight polyethylene favours the formation of a single polyethylene crystalline phase in the blends while formation of two crystalline phases (peak I and II) is enhanced in blends containing lower molecular weight polyethylene species. Annealing polyethylene in the presence of dotriacontane appears to increase disorderliness in the polyethylene crystalline state as indicated by the broadening of the fusion process.

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Résumé—D'après les résultats de l'analyse thermique différentielle (ATD) un composé cristallin d'addition se forme dans les mélanges de polyéthylène linéaire et de dotriacontane. La nouvelle phase se forme lorsque des mélanges contenant moins de 34% de polyéthylène linéaire, sont cristallisés dans des conditions très soigneusement contrôlées. Le signal endothermique du à la nouvelle phase mesuré par ATD se produit de 2 à 5 degrés centigrades en-dessous de celui du polyéthylène. La quantité de la nouvelle phase cristalline dépend de la masse moléculaire du polymère, de la concentration des mélanges et la vitesse de solidification et du traitement thermique. Des mélanges contenant des fractions de faibles masses moléculaires conduisent à une formation plus abondante de la nouvelle phase. Les quantités relatives de la nouvelle phase cristalline et de la phase cristalline du polyéthylène varient avec la vitesse de refroidissement des mélanges au cours de la solidification, la nouvelle phase cristalline étant prédominante pour les faibles vitesses de refroidissement. Le traitement thermique des mélanges cristallisés se répercute sur les endothermes de fusion du polyéthylène et de la nouvelle phase cristalline.

Sommario—In base a dati tratti da analisi termiche differenziali (DTA), si è trovato che in mescole di politene-dotriacontano lineare si forma un'ulteriore fase cristallina. La nuova fase si forma quando miscele contenenti politene lineare in percentuale minore del 34%, vengono fatte solidificare in condizioni di cristallizzazione accuratamente controllate. Il punto endotermico della nuova fase avviene, come misurato mediante DTA, a 2–5° sotto a quello del polietilene. Si è trovato che la quantità della nuova fase cristallina dipende dal peso molecolare, dalla concentrazione della miscela, dalla velocità di solidificazione e dal trattamento termico. Le miscele contenenti frazioni a basso peso molecolare favoriscono la formazione della nuova fase. Le quantità relative della nuova fase cristallina e di quella del polietilene variano con la velocità di raffreddamento della miscela durante la solidificazione, con predominanza della nuova fase cristallina alle velocità di raffreddamento più basse. Il trattamento termico della miscela solidificata porta al risultato di far coincidere i punti endotermici del polietilene e della nuova fase cristallina.

Zusammenfassung—Aufgrund von Ergebnissen der Differentialthermoanalyse (DTA) wurde festgestellt, daß sich in Mischungen aus unverzweigtem Polyäthylen und Dodekatriacontan eine zusätzliche kristalline Phase ausbildet. Die neue Phase tritt auf, wenn Mischungen, die lineares Polyäthylen in Konzentrationen unter 34 Prozent enthalten, aus der Schmelze unter sorgfältig kontrollierten Kristallisationsbedingungen erstarren gelassen werden. Die Endotherme der neue Phase Liegt nach DTA Messungen 2° bis 5° tiefer als die von Polyäthylen. Es wurde gefunden, naß die Menge der neuen kristallinen Phase abhängt von Molekulargewicht, Mischungskonzentration, Erstarrungsgeschwindigkeit und Hitzebehandlung. In Mischungen, die niedermolekulare Fraktionen enthalten, tritt eine erhöhte Bildung der neuen Phase ein. Die relativen Anteile der neuen kristallinnen Phase und der kristallinen Polyäthylen Phase variieren mit der Abkühlungsgeschwindigeit der Mischung bei der Verfestigung, wobei die neue kristalline Phase bei langsamer Abkühlungsrate überwiegt. Eine Hitzebehandlung der verfestigten Mischung führt zu einer Verschmelzung der Endothermen der Polyäthylenphase und der neuen kristallinen Phase.