The Crystallization of Poly(ethylene terephthalate) and Related Copolymers[*]

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The effects of molecular weight, catalyst residues, and nucleating agents on the rates of crystallization from the melt of polymers of poly(ethylene terephthalate) and related copolymers have been studied. The influence of previous thermal and processing history has been investigated.

Poly(ethylene terephthalate), PET, is a well known commercial polymer available widely as fibre and film. Both forms are highly crystalline but crystallinity is induced by crystallization from the glassy state and is further complicated by molecular and crystallite orientation. Current interest in PET (in its crystalline, unoriented form) as a moulding material crystallized from the melt, has made necessary a detailed investigation of crystallization kinetics from the molten state.

Surprisingly there is little reported on the kinetics of crystallization of PET from the melt. Morgan and co-workers[1,2] demonstrated the importance of fusion conditions on subsequent crystallization behaviour, and the necessity of destroying previous melt thermal history by heat treating the molten polymer. Kinetic data, analyzed in the form of Avrami parameters, were presented for PET of number-average molecular weight, 17 000. They also showed the trend of decreasing rate of crystallization with increasing molecular weight up to 17 000. Processing history has also been shown to be important[3].

In view of its potential as an injection moulding material, the question of crystallization kinetics is clearly relevant to the mould temperatures and injection cycle times and may indicate possible ways of lowering these parameters by increasing the rate of crystallization at lower temperatures. Thus a study has been made of the crystallization *from the melt* of various PET samples prepared under different conditions and of a wide range of copolymer systems—both random and block. The effect of efficacious nucleating agents on the rate of crystallization has been measured. Both thermal and previous processing history have been investigated.

EXPERIMENTAL

Apparatus

A microscopical technique has been used for measuring the overall rate of crystallization. It is capable of following rapid rates of crystallization and the upper limit is estimated to be a half-life of the order of 5 s. In this work the rates of crystallization were generally too rapid for a photographic technique to be used. The recrystallization was followed by detecting the light transmitted by the sample when it was observed between crossed Nicol prisms.

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The apparatus consists essentially of two joined hot-stages insulated from each other, and held at different constant temperatures. The design of the apparatus, with some modifications, has been based on a similar one of I.C.I. Ltd, Research Department, Plastics Division. One stage (the fusion stage) is controlled at a constant temperature above the melting point of the polymer (at about 300°C for PET) while the other stage (the crystallization stage) is controlled at a temperature (the crystallization temperature, T_c) below the melting point where the rate is to be measured. The two stages are joined by a shallow channel allowing rapid transfer of the sample from the fusion to the crystallization stage. The whole assembly is mounted on a polarizing microscope such that the sample occupies the field of view when on the crystallization stage. The overall depth of the double hot-stage was too great to permit setting up of Köhler illumination using a conventional Abbé condenser. Consequently the condenser was removed and replaced by a Vickers microscope objective enabling Köhler illumination to be obtained. A cadmium sulphide photoconductive cell is mounted above the microscope eyepiece to monitor the light transmitted by the sample. The temperature of the crystallization stage is controlled by a Eurotherm stepless indicating controller with proportional/integral/derivative control. A thermocouple is used as the detector embedded in the upper metal plate of the hot-stage, and the temperature of the stage measured with a second thermocouple connected to a Honeywell Brown recorder. The measured temperature has been calibrated using simple compounds with sharp melting points. The output from the photoconductive cell is fed into a chart recorder to give a continuous record of light transmission. For a given sample viewed under constant conditions, the amount of light transmitted is proportional to the degree of crystallinity of the sample, unless a change of birefringence of the crystallites occurs on subsequent rearrangement after crystallization. In this work maximum light transmission has been taken to indicate the completion of primary crystallization. In some cases, subsequent rearrangements within the crystallites result in a slight decrease in the amount of light transmitted.

A typical recrystallization of PET is performed by placing a small amount of material between two cover slides, and inserting the sample into the fusion side of the hot stage controlled at 300°C. The sample remains on the fusion stage after melting for 0·5–1 min, and is then moved rapidly into the crystallization area at the crystallizing temperature. The half time of crystallization is determined from the half height of the trace obtained on the recorder.

Materials examined

Poly(ethylene terephthalate)—Samples were supplied by I.C.I. Fibres Ltd, Harrogate of PET of various molecular weights (intrinsic viscosity ranging from 0·65 to 1·3). The samples with high intrinsic viscosities were prepared by solid state polymerization. All of the polymers contain up to 1·5 mole % of diethylene glycol terephthalate as a co-unit from a side reaction. The polymer was made using an insoluble polycondensation catalyst. A further batch of polymer, prepared with a soluble polycondensation catalyst, was obtained. The polymers will be designated PET (S) or PET (I) respectively throughout this paper.

Random copolymers—Copolymers incorporating a sebacate co-unit in the composition range 0–30 mole % were also obtained from I.C.I. Fibres Ltd, Harrogate. The intrinsic viscosity of each of the samples was in the range 0·6–0·8.

Azelate copolymers over a similar composition range were synthesized in the laboratory. Two series of copolymers with intrinsic viscosities in the ranges 0·2–0·4 (low intrinsic viscosity) and 0·6–0·8 (high intrinsic viscosity) were obtained.

A sample of a 10 mole % copolymer from sulphonyl dibenzoic acid was prepared in the laboratory with an intrinsic viscosity of 0·7. This copolymer had a higher T_g than PET or the other copolymers.

In all samples, insoluble catalyst has been used.

Block copolymer—A sample of a block copolymer of PET (I) with 2 mole % of poly(ethylene oxide) of molecular weight 1 540 was obtained from I.C.I. Fibres Ltd, Harrogate. The intrinsic viscosity of the PET block was about 0·65.

Talc additive—Mistron Super Frost was obtained from Compounding Ingredients, Manchester, a finely divided talc with particle distribution 50% less than 1μm.

Molecular weight—Molecular weight and intrinsic viscosity have been used synonymously throughout but the two are related formally assuming the molecular weight distribution remains unchanged.

$$[\eta]=\overline{K}M_n^{\alpha}$$

where $[\eta]$ is the intrinsic viscosity (dl/g); M_n is the number average molecular weight; and K and α are constants whose value depends on the solvent–polymer pair.

The intrinsic viscosity for PET has been obtained from a relative viscosity measurement of a 1% solution in *o*-chlorophenol at 25°C. The value of intrinsic viscosity for various molecular weights, shown in *Table 1*, is from the calibration by Ravens and Ward[4].

Table 1. The variation of intrinsic viscosity with molecular weight

Intrinsic viscosity (dl/g)	Number-average molecular weight
0·64	20 000
0·76	25 000
0·89	30 000
1·12	40 000

RESULTS

The following inter-related factors which affect crystallization have been investigated: molecular weight; structure of a copolymer–whether random or block–and the effect of molecular weight; catalyst systems, nucleating action of certain residues; thermal history; alteration of the glass transition temperature, T_g, by copolymerization; and the addition of nucleating agents.

The rate data are presented graphically; the half-time of crystallization, $t_{1/2}$, being plotted against the isothermal crystallization temperature, T_c. A high rate of crystallization corresponds to a low $t_{1/2}$ and maximum rates occur at minimum $t_{1/2}$ ($t_{1/2}^{min}$).

Molecular weight

The effect of increasing molecular weight (or intrinsic viscosity) is seen in *Figure 1*. Polymers from two catalyst systems have been examined, and while the absolute rates are different (see below) the general change is to much lower rates of crystallization as the molecular weight is increased. Also there is a tendency for the curve to become narrower and for the bottom of the curve to sharpen with increasing molecular weight. The minimum $t_{1/2}$ covers a progressively narrower range of temperatures implying that greater temperature control is required for the moulding of crystalline material of high intrinsic viscosity.

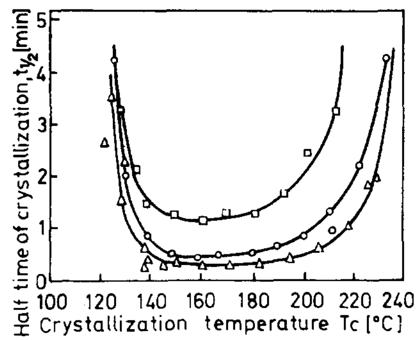


Figure 1a—The rate of crystallization of poly(ethylene terephthalate), (insoluble catalyst)–effect of molecular weight. Intrinsic viscosities (dl/g): ○, 0·93; □, 1·25; △, 0·65

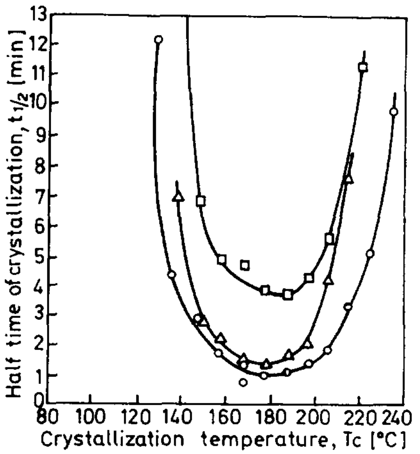


Figure 1b—The rate of crystallization of poly(ethylene terephthalate, (soluble catalyst)–effect of molecular weight. Intrinsic viscosities (dl/g): ○, 0·65; □, 1·1; △, 0·91

Copolymerization: random copolymers of other dicarboxylic acids

Figures 2 and *3* show the effect of inclusion of two different dicarboxylic acid residues in the chain replacing the terephthalate unit. *Table 2* lists the

T_g values of the various copolymers. One of these co-units has an even number of methylene links (sebacate) and the azelate contains an odd number. For the sebacate copolymers, *Figure 2*, the minimum $t_{1/2}$ increases with increasing co-unit content and the crystallization temperature of minimum $t_{1/2}$ (T_c^{min}) moves to lower temperatures in accord with the depression observed in T_g. For the lower intrinsic viscosity azelate copolymers shown in Figure 3a, again a shift to lower temperature of T_c^{min} is observed but $t_{1/2}^{min}$ is not very sensitive to changes in co-unit content of the copolymer. For the high intrinsic viscosity copolymers shown in *Figure 3b* again T_c^{min} moves to lower temperatures with increasing azelate content and concomitant shift of T_g. However $t_{1/2}^{min}$ has not moved smoothly to greater values. The odd cross-over behaviour seen is maybe an indication of poor molecular weight control (these samples were prepared from the lower intrinsic

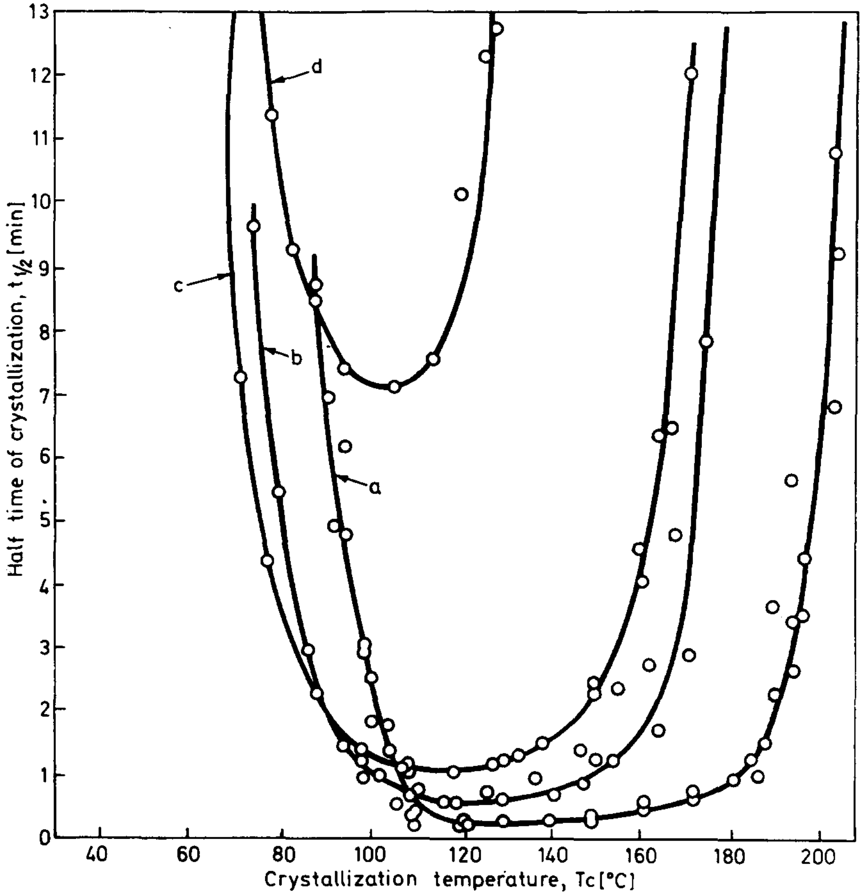


Figure 2—The rate of crystallization of ethylene terephthalate/sebacate copolymers. a, 15 mole % sebacate (I.V. 0·85); b, 25 mole % sebacate (I.V. 0·7); c, 30 mole % sebacate (I.V. 0·7); d, 35 mole % sebacate (I.V. 0·7) (I.V.–intrinsic viscosity in dl/g)

viscosity polymers by solid state polymerization) or a possible blocking non-random sequential distribution of the co-units. Nevertheless from low to high co-unit content there is an increase in $t_{1/2}^{min}$. The effect of molecular weight on the crystallization of the copolymer is similar to the homopolymer in that an increase in $t_{1/2}^{min}$ is seen and the curve becomes narrower.

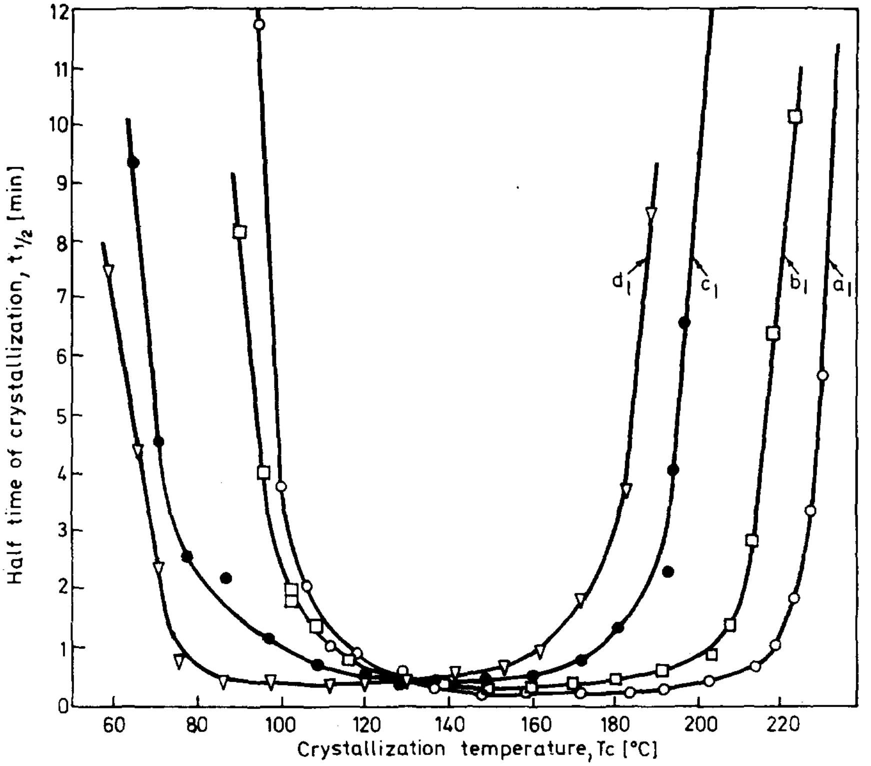


Figure 3a—The rate of crystallization of ethylene terephthalate/azelate copolymers (low intrinsic viscosity polymer).
a_1 (○), 6 mole % azelate (I.V. 0·38); b_1 (□), 11 mole % azelate (I.V. 0·28); c_1 (●), 25 mole % azelate (I.V. 0·28); d_1 (▽), 31 mole % azelate (I.V. 0·25)
(I.V.–intrinsic viscosity in dl/g)

The units described above both lead to a lowering of T_g. It is possible to select co-units where T_g is increased. In *Figure 4*, the results are shown for a copolymer with 10 mole % of sulphonyl dibenzoic acid having a T_g $\sim$80°C (quenched polymer, 10°C high then quenched PET). Like the other copolymers, T_m is depressed to a value $\sim$220°C. $t_{1/2}^{min}$ has increased as anticipated but, unlike the other copolymers described above, T_c^{min} has not decreased but lies at a higher temperature. Furthermore the curve is much narrower than for other copolymers of similar molar composition. Presumably this is a consequence of the smaller differences between T_g and T_m in this copolymer.

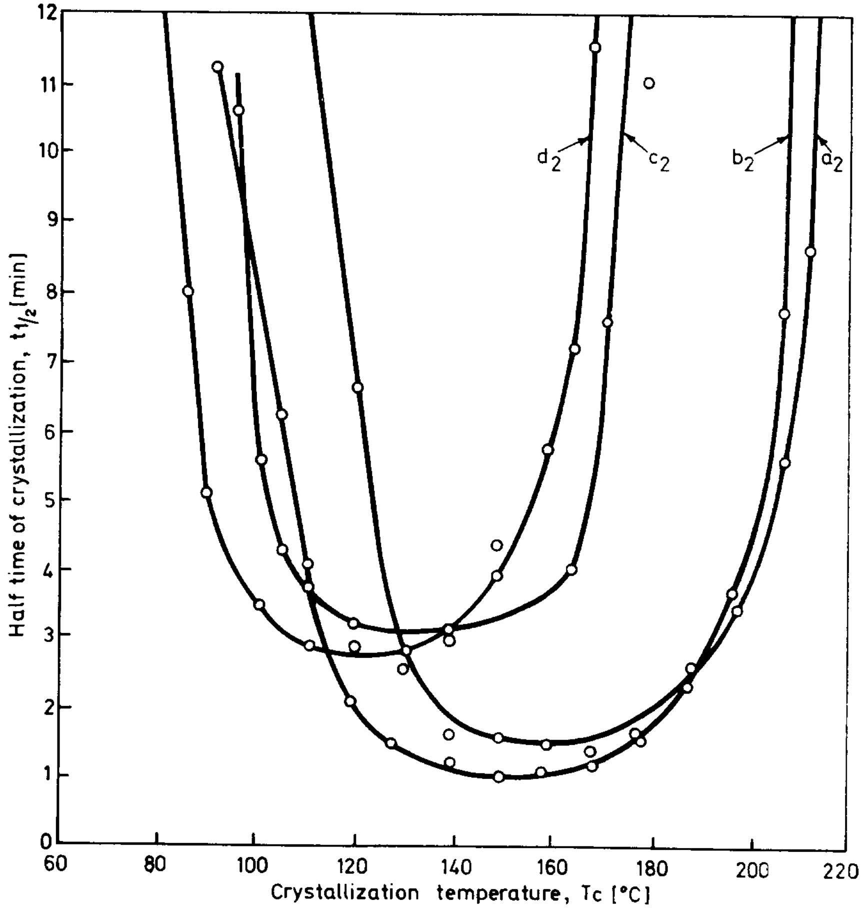


Figure 3b—The rate of crystallization of ethylene terephthalate/ azelate copolymers–(high intrinsic viscosity polymer)
a_2, 6 mole % azelate (I.V. 0·76)
b_2, 11 mole % azelate (I.V. 0·75)
c_2, 25 mole % azelate (I.V. 0·71)
d_2, 31 mole % azelate (I.V. 0·83)
(I.V.–intrinsic viscosity in dl/g)

Random copolymers of other diols

The inclusion of low molar proportions of diethylene glycol (DEG) has been examined. Commercial PET usually contains some DEG residues due to a dehydration side reaction of ethylene glycol leading to inclusion of the DEG unit in the polymer. The extent of the side reaction varies with the polymerization catalyst used and consequently we have investigated the effect, at various levels, of DEG co-units on the crystallization rate. The results for polymer of intrinsic viscosity ~0·65 are shown in *Figure 5*. As can be seen at the levels of DEG co-unit examined, there is no noticeable

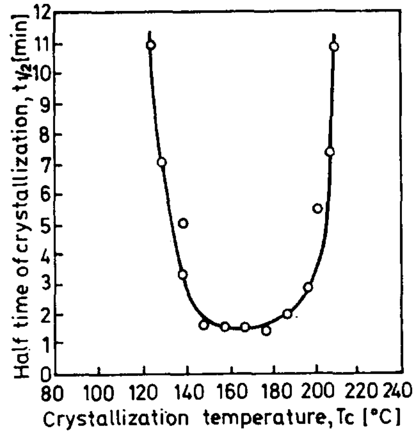


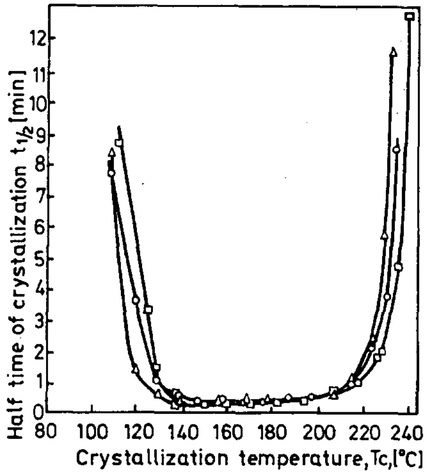
Figure 4—The rate of crystallization of ethylene terephthalate/sulphonyl dibenzoate copolymer (10% sulphonyl dibenzoate) (intrinsic viscosity=0·7 dl/g)

effect on $t_{1/2}^{min}$. There is a lowering of T_g and a shift of the curve to somewhat lower temperatures with increasing DEG content.

Block copolymer

The results for the ethylene terephthalate/oxide block copolymer (PET/PEO) are shown in *Figure 6*. The copolymer has a melting point, T_m, of ~250°C, i.e. close to PET homopolymer, but a T_g ~40°C, rather lower than PET.

Figure 5—The rate of crystallization of ethylene/diethylene glycol terephthalate copolymers. □, PET; ○, 2 mole % DEG copolymer; △, 5 mole % DEG copolymer



The crystallization curve shows a rapid increase in rate (decreasing $t_{1/2}$) with falling temperature and a wide plateau for $t_{1/2}^{min}$. It was not found possible to quench the copolymer sufficiently through the high rate part in order to examine the falling rate at low temperatures. The relative ease of crystallization was also found in other experiments. During measurement of the dynamic modulus of partially quenched samples it was observed that at temperatures immediately above T_g further crystallization took place.

No material with a higher intrinsic viscosity PET block was available for examination of the effect on crystallization rate of increasing molecular weight of the crystallizing segment.

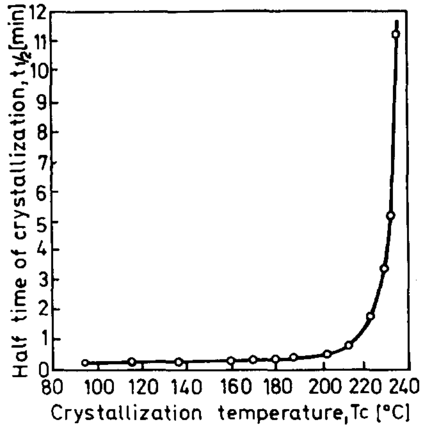


Figure 6—The rate of crystallization of ethylene terephthalate/oxide block copolymers

Nucleating agents

A number of materials in finely powdered form have been found to nucleate the crystallization of PET. An increase is observed in the overall crystallization rate and a corresponding decrease in $t_{1/2}^{min}$ is seen. *Figure 7* shows the effect of ~0·5 wt % talc, a particularly effective nucleating agent with PET (I). $t_{1/2}$ is lower for nucleated polymer over a wide range of temperature, and no apparent upturn of the curve has been found down to temperatures of ~130°C.

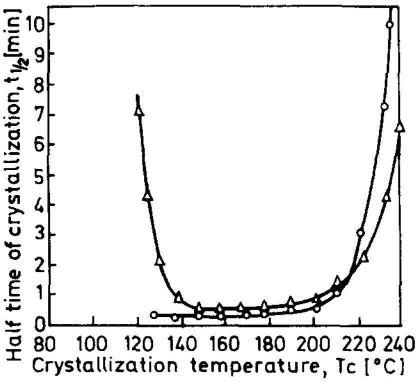
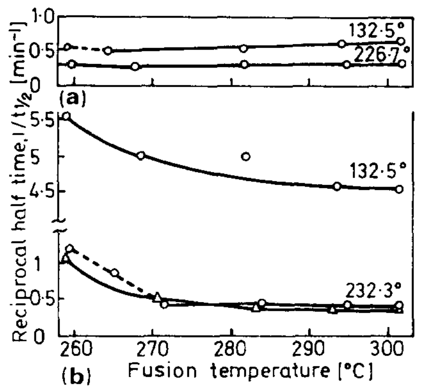


Figure 7—The rate of crystallization of poly(ethylene terephthalate)–effect of adding 0·5% talc.
△, Poly(ethylene terephthalate) (intrinsic viscosity=0·93 dl/g);
○, Poly(ethylene terephthalate)+0·5% talc (intrinsic viscosity=0·93 dl/g)

Thermal history

If previous thermal history of a polymer is not destroyed by allowing time and/or high enough temperatures in the melt for randomization of both the *inter*- and *intra*-chain configurations, the rate of crystallization will be influenced by past process history. This is shown in *Figure 8* where

PET (I) has been examined. Two crystallization temperatures, 133 and 227°C were selected and the rate of crystallization ($1/t_{1/2}$) determined after holding for 0·5–1 min in the melt at the temperature indicated. The rate falls off to a constant value for melt temperatures in excess of 270°C.



Figures 8a and 8b—The rate of crystallization of poly(ethylene terephthalate)–effect of fusion temperature at two crystallization temperatures:
(a) Poly(ethylene terephthalate) (intrinsic viscosity 0·93 dl/g);
(b) Poly(ethylene terephthalate) + 1% talc (intrinsic viscosity 0·93 dl/g)
(○, △–different samples in repeat experiments)

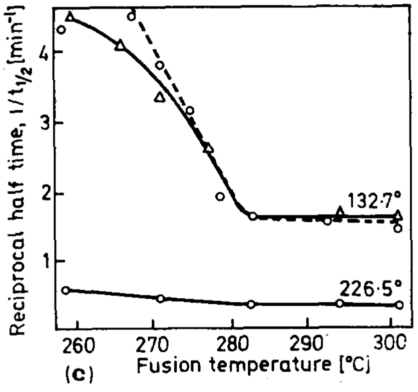


Figure 8c—The rate of crystallization of poly(ethylene terephthalate)–effect of fusion temperature at two crystallization temperatures. Poly(ethylene terephthalate) of intrinsic viscosity 0·93 dl/g after double processing; (○, △–different samples in repeat experiments)

Where polymer has had a special thermal history as in *Figure 8c* where the polymer was melted and quenched in cold water twice (once from the autoclave after preparation and subsequently after an extrusion process), the rate effects tend to be present until the melt is conditioned above 280°C. The effect is much more dramatic for crystallizations at 133°C, the T_c of importance when considering mould temperatures for injection moulding. Obviously a strong nucleating effect is induced by the double processing.

DISCUSSION

Table 2 shows the collected data for the polymers examined giving the minimum $t_{1/2}$ and the corresponding T_c. The following generalisations can be made:

1. Increasing molecular weight decreases the rate of crystallization.
2. For polymers with similar intrinsic viscosities, soluble polymerization catalyst systems give lower rates of crystallization than insoluble catalysts.

Table 2. $t_{1/2}$ for various PET polymers

Polymer	*Composition (mole %)*	*Intrinsic viscosity (dl/g)*	T_g* (°C)	$t_{1/2}^{min}$ (*minutes*)	T_c^{min} (°C)
PET (Insoluble catalyst)	–	0·65	70	0·30	160
	–	0·93	70	0·40	155
	–	1·25	70	1·15	160
PET (Soluble catalyst)	–	0·65	68	0·95	175
	–	0·91	68	1·3	175
	–	1·1	68	3·75	184
PET/DEG (Soluble catalyst)	2	0·65	68	0·40	145–180
PET/DEG	5	0·65	65	0·40	150–180
PET/Sebacate	15	0·85	28	0·30	130
	25	0·70	18	0·65	120
	30	0·70	12	1·2	115
	35	0·70	6·5	7·1	107
PET/Azelate	6	0·38	54	0·20	170
	6	0·76	54	1·45	160
	11	0·28	35	0·30	150
	11	0·75	35	1·0	150
	25	0·28	25	0·45	130
	25	0·71	25	3·1	130
	31	0·25	14	0·35	100
	31	0·83	14	2·75	122
PET/Sulphonyl Dibenzoate	10	0·70	80	1·6	160
PET/PEO block	2	–	–	0·15	95
PET+0·5 wt % talc	–	0·93	70	0·25	130

*Determined by D.T.A. on quenched amorphous samples.

3. Where random copolymerization gives a lower T_g, the rate of crystallization decreases with increasing co-unit content and also T_c^{min} the crystallization temperature at which maximum rate is observed ($t_{1/2}$ a minimum) decreases similarly.
4. Where random copolymerization gives a higher T_g, the rate of crystallization is lower but T_c^{min} increases; also the temperature range over which crystallization occurs is much narrower.
5. In a block copolymer, crystallization occurs without diminution in rate over a wider temperature range than for the homopolymer.
6. Efficacious nucleating agents increase the rate of crystallization and the maximum rate occurs over a wider range of temperature.
7. Previous history is not destroyed unless the melt is heated to at least 280°C. If material is double processed more care is required to destroy the previous history, or conversely a strong nucleating effect (enhanced rate) is observed, at lower T_c, if the melt temperature is kept below 280°C.

The two catalyst systems examined can lead to different levels of DEG co-unit in the final polymer. That the large difference in rate is not attributable to this difference has been shown by examining various DEG copolymers with the insoluble catalyst. It is concluded that the difference is due to the presence of catalyst residues from the insoluble catalyst as suggested (C. H. Baker, I.C.I. Fibres Ltd, Harrogate), which can act as nucleating centres. However, certain other nucleating agents, such as talc, have an additional effect beyond that of the catalyst residues.

The presentation of data in the form of $t_{1/2}$ does not take account of the absolute level of crystallinity finally attained in any experiment since it is not possible to derive crystallinity data from the light transmittance without elaborate calibration. Thus for copolymer crystallization, if we consider that as co-unit content is increased the degree of crystallinity attained at equilibrium decreases, then, even for the same $t_{1/2}$, the rate of increase of crystallinity must be much lower for higher co-unit copolymers. This consideration is important for the mechanical properties of copolymeric materials.

CONCLUSIONS

The rate of crystallization of PET decreases with increasing molecular weight but this can be overcome by the use of nucleating agents. The effect of increased molecular weight is less pronounced when an insoluble catalyst system is used.

Copolymerization does not increase the rate of crystallization but may lower T_c^{min} as a concomitant to the shift of T_g with copolymerization.

Thermal history can have a pronounced effect on the rate of crystallization.

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