Crystallization phenomena in some polyester – urethanes

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A density balance has been used to measure the crystallization isotherms of poly(ethylene adipate) and copolymers which were prepared by extending the polyester with four different diisocyanates. The occurrence of extensive secondary crystallization processes precluded satisfactory interpretation in terms of the Avrami theory and further analysis could only be based on the half-time for crystallization. This parameter has the advantage that it is determined directly and is independent of any theoretical analysis. The presence of very small concentrations of diisocyanate units can have a profound effect on the rate of crystallization if they are very different structurally from the parent polyester, e.g. a molar concentration of about 5% of 2,4-tolylene diisocyanate increases the half-time by a factor of 20 whereas the same concentration of hexamethylene diisocyanate has an insignificant effect. The temperature dependence of the half-times is discussed in relation to several theories of crystallization.

INTRODUCTION

The crystallization characteristics of a polymer are of great importance in the determination of the processing conditions for obtaining a satisfactory end product. In any given process, (e.g. extrusion, injection moulding etc), there is a complex interplay between the time/temperature relation of the process on the one hand and the crystallization/temperature relation on the other. The morphology and consequently the properties of the processed polymer depend on this inter-relation. For example in the manufacture of filaments from poly(ethylene terephthalate), the as-spun fibres are amorphous and crystallinity only develops during the drawing process; on the other hand, with poly(tetramethylene terephthalate), crystallization is rapid on cooling the melt so the spun fibres are crystalline.

It is therefore of interest to know the speeds of crystallization of the polymers as this will lead to a knowledge as to whether products are likely to be crystalline and the extent to which the crystallinity may develop in the time/temperature cycles involved in the processing.

This report is concerned with a study of the rates of crystallization of those polyesters and polyesters extended via the urethane group whose melting points and glass transition properties were discussed previously[1]. The samples under examination are poly(ethylene adipate) (PEA) of different molecular weights and copolymers prepared from these by extending them by reaction with a range of diisocyanates. Since the low molecular weight starting polymer had a 'most probable' distribution of molecular weight and since only small molar fractions of diisocyanates were used, the sequence of units in the extended polymer must be very similar to that expected in a true random copolymer.

Four different isocyanates, given below, were selected so that the polyester chain would be modified in different ways. (A) Hexamethylene diisocyanate (HDI) will introduce a long thin flexible unit which should be little different sterically from the polyester chain and is about the same length as an ethylene adipate unit. (B) Diphenylmethane diisocyanate (MDI) will insert a unit which has approximately the same dimensions as an ethylene adipate unit so that the main effect will be to stiffen the chain by introducing two aromatic rings into the polyester chain. (C) 2,4-Tolylene diisocyanate (TDI) and (D) 1,5-Naphthalene diisocyanate (NDI) both introduce rigid and bulky sections and may cause kinks in an otherwise straight chain.

EXPERIMENTAL

Full details of the preparation of the polymers and a discussion of their glass transition and melting phenomena have been presented earlier[1]. It proved difficult to measure reliably the molecular weights of the extended polymers, but it is safe to say that they are all 20 000 or more. Characteristics of the copolymers used are given in *Table 1*, and in addition, some results are given below for a poly(ethylene adipate) P7 whose molecular weight 18 000 is similar to those of the extended polymers.

Many methods are now available for the measurement of rates of crystallization, but the choice was restricted by a number of considerations. It was proposed to measure a

Table 1 Characteristics of polymers used

Designation	Molecular weight of parent PEA	Molar concentration of isocyanate	T_g (°C)	T_m (obs) (°C)	ln of minimum half-time (min)
P2-HDI	3000	0.0532	−45.5	50	1.15
P2-MDI	3000	0.0532	−36.5	45	2.90
P2-NDI	3000	0.0532	−36.0	45	3.62
P1-TDI	1850	0.0847	−35.5	38	6.55
P2-TDI	3000	0.0532	−38.2	44	4.80
P3-TDI	5000	0.0338	−40.5	50	3.68
P5-TDI	8500	0.0198	−42.0	53	2.18
P7	18000	0.000	−46.0	59	1.55

large number of isotherms, some of which would continue for a long time, so the method should be self-recording and must be stable and sensitive enough to record any slow secondary crystallization. The optical method lends itself to automation but was rejected for two reasons, firstly the mode of crystallization in thin films may differ from that in bulk material and secondly because the relation between the amount of crystalline material and the intensity of the depolarized light has not been satisfactorily established, in fact it has been shown[2] that in certain cases false results are obtained.

A recording dilatometer or a recording density balance would fulfil all the requirements, and the latter was chosen in view of the availability of equipment. The equipment was conventional and similar to that used by Hartley *et al.*[3] The polymer was contained in a wire gauze basket suspended from a Stanton recording balance (100 mg full scale deflection); the volume decrease due to crystallization caused a decrease in buoyancy which was recorded as an apparent gain in weight. The crystallization bath consisted of a 1 litre beaker of silicone fluid immersed in a large thermostat tank, the temperature of which could be varied between 10° and 60°C and kept constant to better than ±0.1°C.

Initially the polymer was fused under vacuum at 80°C to remove air, and then allowed to solidify into a solid block which was cut into small pieces. About 1 g of these pieces was placed in the gauze basket and weighed in air. The sample was then transferred to a fusion tube containing silicone fluid, evacuated until free of air, and then fused by lowering the tube into a bath, normally at 80°C, for 20 min. The sample was cooled to just below its melting point in an auxiliary bath in the main thermostat to prevent raising the temperature of the crystallization bath appreciably. The basket was then quickly attached to the suspension of the balance and immersed in the crystallization bath. For measurements below 5°C, a refrigerated thermostat and a fusion bath were built within a dry-box and operated in a similar manner.

The chart obtained from the recording balance is similar in form to the familiar dilatometer plot and interpretation is generally straightforward; e.g. ref 4, page 30. One problem is to determine the origin of the recording because of the finite time needed for thermal equilibrium to be established.

If the rate of crystallization is low, then the cooling and crystallization phases are distinct and separated by a constant weight period during which nucleation and the initial stages of growth occur without changing the volume to a detectable extent. The growth process accelerates and finally slows down producing the normal sigmoid type isotherm. In such an experiment the initial weight w_0 and the starting time t_0 are readily established from the position of the commencement of the constant weight period.

However, if the crystallization is so fast that it causes significant volume changes before the cooling is complete, then it is impossible to establish the origin unambiguously; moreover, the early stages of the process will not have occurred isothermally. A further complication is that if the heat of crystallization is released very rapidly it may raise the temperature of the specimen appreciably. To obtain an indication of the magnitude of this problem, a thermocouple inserted in a specimen on one occasion showed a temperature rise of up to 3°C, and the specimen was at a higher temperature than the bath for about 6 min. As, under the conditions of this test the time for half the volume change was just under 9 mins, the seriousness of this will be appreciated. However, it must be realized that a similar effect could be present in a manufacturing process, and to this extent, the density balance measurements will be relevant.

In principle the determination of the final weight is trivial, but can be difficult in some isotherms in which slow secondary crystallization caused the weight to increase linearly with the logarithm of time, with little indication of attaining a limiting value.

Isotherms

The crystallization isotherms which were obtained showed that considerable secondary crystallization occurred in both the polyesters and the copolymers, despite a statement that it does not occur in poly(ethylene adipate)[4]. The enormous length of time generally required for the completion of the secondary process may be illustrated by some attempts to determine melting points by thermal analysis. Unless crystallization was allowed to proceed for about 50 times as long as the 'half-time', multiple melting peaks were found, implying that the isothermal crystallization was not complete and the residual amorphous material crystallized subsequently at room temperature to produce material having a lowered melting point.

In view of the large number of isotherms required and the lengthy periods of time required for the completion of secondary crystallization it was not practicable to continue more than a few until the secondary process was completed.

Analysis of isotherms

Since (with one exception) there was no discontinuity in the isotherms, the primary and secondary processes must have occurred simultaneously and it was consequently impossible to separate unambiguously the Avrami and the secondary stages for further analysis. Nevertheless it was considered worthwhile to make an initial analysis of the whole isotherm on the basis of the Avrami equation using an optimization method of Hillier[5].

The procedure was to adjust systematically the values of the exponent, the rate constant and the final buoyancy to give the smallest r.m.s. difference between the calculated (Avrami) and the observed apparent weight changes. As anticipated, the agreement was poor, the r.m.s. difference being of the order of 2.5% of the total weight change, and moreover, the differences were not random but showed systematic variations. Surprisingly, the deviations for the homopolymers were slightly larger than for the copolymers, the r.m.s. differences being 2.7 and 2.0% respectively, though it is possible that this is because the copolymers crystallized more slowly, consequently the recorded isotherms may have lacked more of the secondary process.

With the assistance of Dr Hillier these isotherms were compared with an equation he has derived[6] assuming that the primary crystallization, obeying Avrami kinetics, is followed immediately by secondary crystallization so that in the sample as a whole, primary and secondary processes take place simultaneously. Assuming that the secondary process was of the first order, it was found that the r.m.s. differences were reduced to the order of 1%. Although this is about the same magnitude as experimental errors, the residuals were again systematic and it was felt that further evidence is required before it is safe to conclude that

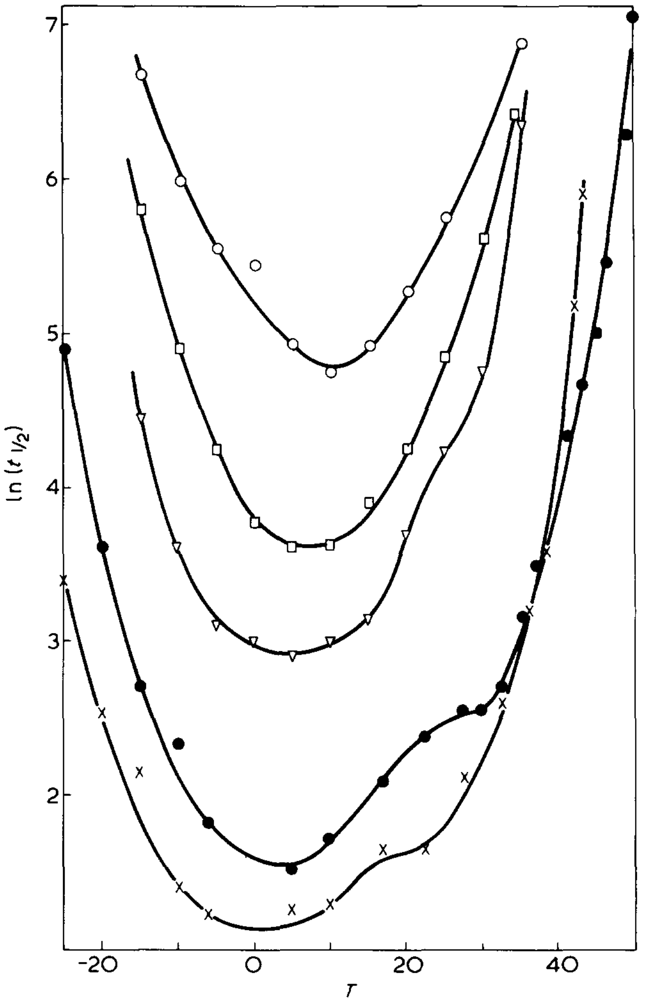

Figure 1 Half-time vs. crystallization temperature T: ○, P2-TDI; □, P2-NDI; ▽, P2-MDI; ●, P7; x, P2-HDI

crystallization of these polymers fit Hillier's theory.

Thus our experience is similar to that of Hay[7] in his attempts to analyse the crystallization of polyethylene on the basis of the Avrami and modified Avrami equations. In the literature covering polymers of very different chemical make-up, so many attempts to fit data to the Avrami equation have either failed or lead to non-integral exponents, having no mechanistic significance, that it appears that it is unusual for the crystallization process to be a simple one.

For copolymers, in which some parts of the chain are unable to enter the crystalline lattice, it is not surprising that the analysis has caused problems. Mandelkern[8] has considered the situation in which impurities are rejected from the growing crystalline regions, and there are indications that over small temperature ranges some of the polyurethane isotherms may fit his theory, but viewed as a whole the situation is very complex.

Half-times

Because of the difficulties of analysing the isotherms in detail, an initial analysis was made in terms of the 'half-time', i.e. the time required for the first half of the total volume change to take place. Even in the simple case in which the crystallization is a straightforward Avrami type process, the half-time does not uniquely define the process since it depends on both the rate constant and the Avrami exponent. In more complex cases when the Avrami process is followed by some form of secondary crystallization or when the crystallization proceeds in some other way, the half-time is even less meaningful; nevertheless it can be a useful single parameter to enable some comparison to be made of the many isotherms recorded, particularly when the differences between samples are large. It has the advantage that it is a parameter derived directly from the experimental data and is independent of any particular theoretical interpretation. Although it is difficult, because of the slow secondary crystallization, to assess the total volume change for many of the isotherms, this uncertainty is not wholly reflected in the half time since the isotherm is very steep in the vicinity of the half way stage. In contrast, the half-time is critically dependent on the assessment of the starting point of the chart, and for this reason, and also because of the non-isothermal conditions at the start, half-times of less than about 5 min cannot be precise, but nevertheless may be used to give an indication of the speed of the crystallization.

RESULTS

Homopolymers

The present results, an example of which is included in *Figure 1*, generally confirm the extensive investigations of Takayanagi[9]. The relatively small discrepancies between the two sets of data may be due to differences in distribution of molecular weight which he showed to be very significant. The shoulder on the curves has been confirmed and again shown to be associated with the morphology. In thin films crystallized at the lower temperatures, the spherulites are well developed and show negative birefringence; in the temperature range corresponding to the shoulder the spherulites are banded and at the highest temperatures they are not so well developed and their birefringence is positive.

Extended polymers

The half-times for the polymers extended with different isocyanates are shown in *Figure 1*. The molecular weight of the parent PEA for all the polymers is such that there are, on average, about 18 ethylene adipate units for each isocyanate molecule used in the preparation. Relative to high molecular weight homopolymer, the presence of the dissimilar group has increased the half-time by up to 30 times. The sample prepared using HDI is exceptional in that it apparently crystallizes faster than the homopolymer; although these rapid crystallization rates cannot be accurately determined, it may be safely concluded that the presence of HDI does not hinder crystallization. This sample is also unusual because it is the only one of the polymers studied whose spherulites are too small to be resolvable in the optical microscope. However, it does crystallize spherulitically because fracture surfaces show a particulate structure in the scanning electron microscope and it has a birefringent granular appearance when crystallized in a thin film.

The effectiveness of the other isocyanates in reducing the rate of crystallization increases in the order MDI, NDI and TDI, which is in line with their effect on the observed melting point, though the glass transition temperatures are modified in a different order. This difference in behaviour

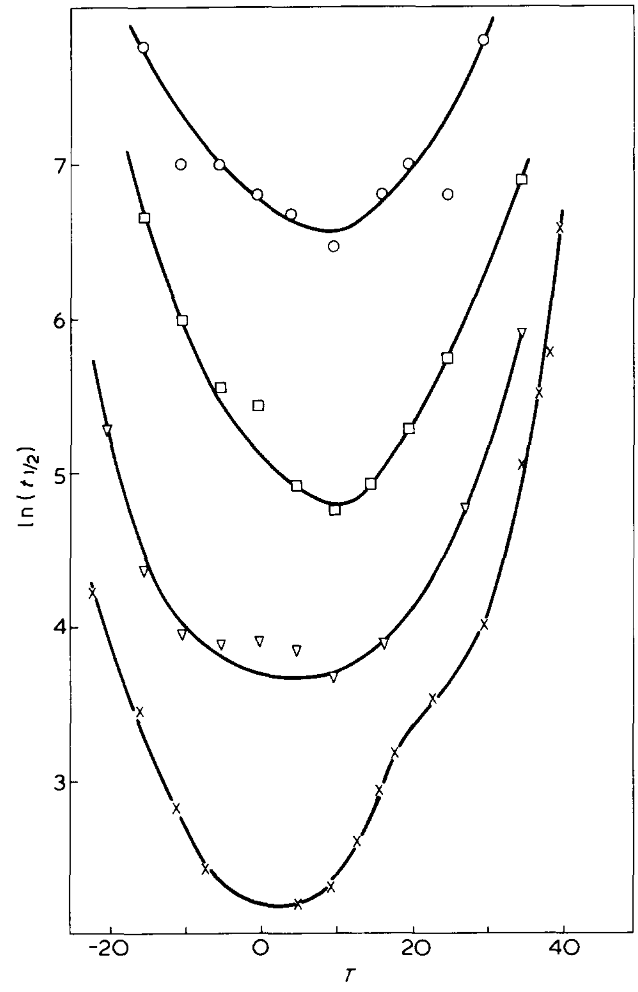

Figure 2 Half-time vs. crystallization temperature T: ○, P1-TDI; □, P2-TDI; ▽, P3-TDI; x, P5-TDI

could be anticipated because the melting point and the rate of crystallization are associated with the dispersal and the formation respectively of crystalline regions and it is natural that the same parameters will be relevant to both processes, whereas the glass transition, a feature of the amorphous content, will be affected by different factors.

The effect of varying the concentration of the non-crystallizable component is illustrated by the series of polymers extended with TDI, *Figure 2*. In the sample P5-TDI where there is only 1 unit to 50 ethylene adipate units, the half-time/temperature graph is similar in shape to that of the homopolymer, showing a shoulder on the high temperature side in the temperature range in which the spherulites are banded (though not as perfect as in PEA). As the concentration of the extender is increased, the spherulites become less and less perfect and the crystallization is slowed down until with the sample P1-TD1, in which there is 1 TDI to every 10 ethylene adipate units, the shortest half-time is about 200 times as great as for the homopolymer.

DISCUSSION

The half-time curves, *Figures 1* and *2*, for those copolymers which crystallize rapidly (P2-HDI, P5-TDI and possibly also P2-MDI) show the presence of the shoulder which is characteristic of PEA itself, and it is associated with the growth of banded spherulites, just as in the case of the parent homopolymer. Banded spherulites were also observed in the appropriate temperature range for all the copolymers studied here, but their degree of perfection varied widely, being almost perfect for P5-TDI and becoming more poorly resolved as the molar fraction of isocyanate was increased. However, their growth in a copolymer such as P1-TDI, in which it requires almost a day for visible spherulites to grow, is further evidence against early suggestions that the bands originated in cycles of alternating melting and crystallization resulting from a combination of a large heat of crystallization and a fast rate of crystallization. Nevertheless, *Figures 1* and *2* show that although banded spherulites are observed in all the polymers their presence shows itself in the half-time curves only when the crystallization is rapid.

The temperature dependence of the rate of crystallization can readily be derived from established theory; for present purposes it is conveniently expressed in the form[10]:

$$\log(1/t_{1/2}) = b_0 + b_1\frac{1}{T} + b_2\frac{1}{T}\left(\frac{T_m^0}{T_m^0 - T}\right)^2 \qquad (1)$$

where b_0, b_1, and b_2 are constants.

When this, or similar equations have been used to analyse experimental results, the measurements have frequently only been made in a small temperature range near the melting point where the last term dominates. Generally speaking, a linear relation between $\log(1/t_{1/2})$ and $T_m^2/T(T_m - T)^2$ is achieved only when a value higher than the observed melting point is used for T_m. This higher temperature is taken to be the thermodynamic melting point and the principle has been used as a means of determining the thermodynamic melting point[11].

Golike and Cobbs[10], covering a greater temperature range, applied the full equation to the analysis of their half-time data. They found that it was necessary to replace T in the second term by $(T - T_g)$ which they took to indicate that 'the crystallization rate at low temperatures is limited by a relaxation mechanism, probably segmental motion, rather than simple viscous flow'.

Kim and Mandelkern[12] have used equations similar in form to equation (1) for the analysis of overall crystallization rates, and more recently Giuliana and Sorta[13] replaced the transport term (E_D/RT) in Kim and Mandelkern's equation by the WLF relationship to obtain:

$$\log(t_{1/2}/a_T) = a + b[T_m^0/T(T_m^0 - t)] \qquad (2)$$

where a and b are constants and a_T is the WLF factor.

Both groups of workers found good agreement between their equations and experimental results reported in the literature for a number of different polymers, provided that the value of T_m^0 used in the equations was up to 20 K higher than reported values.

In an analysis of the data presented above for PEA and the extended polymers in the region between the shoulder and the melting point, it was again found that a linear relation between $\log(1/t_{1/2})$ and $T_m^2/T(T_m - T)^2$ was obtained only when a high value, frequently as high as 80°C, was assumed for T_m. Because few measurements were made in the appropriate temperature range, it was not possible to be at all precise about the required T_m, but the thermodynamic melting point for PEA was established earlier[1] as being 63°C so it is clear that this method produces temperatures which are much too high in this case.

It is unreasonable to expect these various equations to

Table 2 Fitting of half-time data for P2-NDI $T_g = -36$ in all cases

Equation	T_m^0	R.m.s. deviation
1	63	0.122
2	63	0.20
3	63	0.25
1	84	0.061
2	60	0.190
3	76	0.176

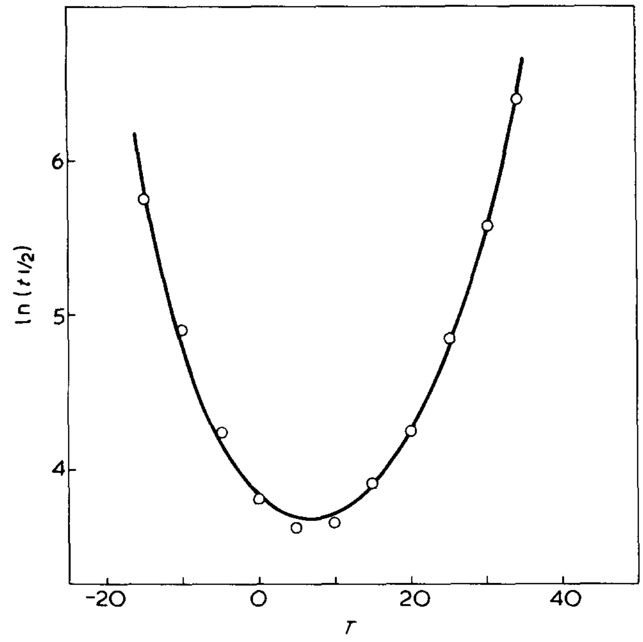

Figure 3 P2-NDI half-time vs. crystallization temperature T: ○, observed half-times; —, calculated from Golike and Cobbs' equation with $T_g = -36$°C and $T_m^0 = 84$°C

apply to the whole temperature range for poly(ethylene adipate) and some of the extended polymers because the crystallization does not follow Avrami kinetics and the mode of crystallization changes with temperature as indicated by the morphology of the spherulite and by the shoulder on the half-time curves. However, for several of the extended polymers, the temperature dependent morphology does not apparently affect the half-time curves. These curves have been fitted to the following equations (a) Golike and Cobbs (equation 1), (b) Giuliana and Sorta's modification of Kim and Mandelkern's case I (equation 2) and (c) Kim and Mandelkern's case III modified in the same way to give:

$$\log(t_{1/2}/a_T) = a + b[(T_m^0)^2/T(T_m^0 - T)^2] \qquad (3)$$

Results for all the polymers were generally similar but inspection of *Figures 1* and *2* show that the experimental data are most consistent for P2-NDI and therefore the results for this polymer will be considered. There is evidence[1] that the urethane groups are not included in the crystalline regions of the extended polymers and therefore their thermodynamic melting points, if this concept has any real meaning for a copolymer, must be the same as that of the parent polyester, viz. 63°C. Inserting this value and the measured glass transition temperature into the various equations gives the r.m.s. deviations given in the first part of *Table 2*. If, however, these temperatures are regarded as being adjustable, then it is found that the r.m.s. deviation does not vary significantly with changes in T_g, but that it is much more sensitive to changes in T_m. The conditions which give the best agreement are given in the second part of *Table 2*, and *Figure 3* illustrates the best fit achieved, using the Golike and Cobbs equation with $T_g = 36$°C and $T_m^0 = 84$°C. Whilst the numerical agreement is very satisfactory, it must be criticized on the grounds that the differences between observed and predicted half-times are systematic and that the required melting point is some 20°C higher than that determined for the homopolymer by the method of Hoffman and Weeks. This latter feature invariably appears when thermodynamic melting points are determined by means of crystallization rate data[11–13].

CONCLUSIONS

The inclusion of a non-crystalizable component in the chain of an otherwise highly crystalline polymer has generally slowed the rate of crystallization by a factor which depends on both the bulk and the concentration of the added component. However, for P2-HDI, where the isocyanate unit is very flexible and similar in shape to the ester units there may be a marginal increase in the rate, despite the fact that cocrystallization does not occur as suggested by the lowering of the observed melting point by some 6°C compared with the polyester itself. The effect of the large and rigid toluene diisocyanate, on the other hand, is dramatic as, compared with high molecular weight poly(ethylene adipate), a reduction in the rate by up to 100 times has been observed; even when only 1 in every 50 ester units was replaced by isocyanate the rate was halved. Thus, there is here a very sensitive means of controlling the rate of crystallization whilst making very small changes in the chemical constitution of the polymer.

It has been mentioned earlier that there is some connection between the effects of the presence of the isocyanate on the rate of crystallization and on the melting point. This is shown very clearly in the TDI series of polymers where there is a linear relation between melting point and the logarithm of the shortest half-time, see *Table 1*. In all the copolymers examined, the melting point has been reduced below that of the homopolymer and if this is regarded as adversely influencing the polymer properties, then for a given effect on the rate of crystallization TDI is the most efficient in that it produces a smaller lowering of the melting point than the three other isocyanates.

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