Influence of molar mass and catalysts on the kinetics of crystallization and on the orientation of poly(ethylene terephthalate)

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Poly(ethylene terephthalate) with different molar masses and different catalysts and additives (calcium acetate, manganese acetate, triphenylphosphate) was synthesized. The influence of the molar mass distribution, and of the additives used, on the rate of crystallization was studied. Also the dependence of the orientation obtained during drawing at elevated temperatures on the drawing conditions, on the average molar mass, and on the additives was investigated. It is shown that, under the same drawing conditions, an increase in molar mass leads to greater orientation. Also, at very small draw rates the orientation in the samples containing calcium acetate is greater than in those containing manganese acetate.

Keywords Poly(ethylene terephthalate); molar mass; crystallization; orientation; catalyst

INTRODUCTION

The kinetics of crystallization of commercially produced poly(ethylene terephthalate) has been studied by several authors[1,2] and the influence of the diethylene glycol content has also been determined[3]. However, in these investigations, the samples were not characterized with respect to additives such as polycondensation catalysts, and the effect of varying the molar mass was not examined. The same is true for studies of the orientation behaviour performed up to now[4]. It is generally known that, for example, calcium acetate in contrast to manganese acetate acts as a nucleating agent and that the molar mass has great influence on processing[6]. No systematic investigation of this effect has been performed however.

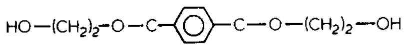
Also the effect of the molar mass is of much interest and the influence of the molar mass on the growth rate of spherulites and on the cold drawing process has already been studied by some authors[5,6]. An extension of such investigations to samples with different catalysts and additives and also to drawing processes above glass transition temperature seems necessary.

Therefore, in a series of studies we have tried to determine the influence of molar mass and that of catalysts on the crystallization and orientation behaviour of the polymer. In order to have available well characterized samples having a great variety of molar masses and additives, we have synthesized samples in the laboratory. According to previous studies[7] it is also necessary to study carefully any changes in molar mass during heat treatment in order to develop methods of preparation of the samples that which exclude thermal degradation.

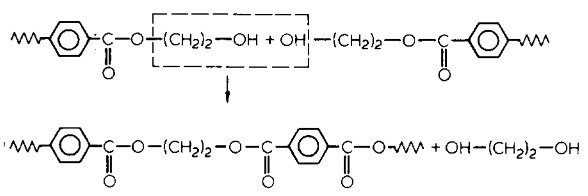
EXPERIMENTAL

Synthesis and characterization

The polymer samples were synthesized from terephthalic acid dimethylester and diethylene glycol. In the first step of the reaction from these substances bis-β-hydroxyethyl-terephthalate was obtained:



In the second step the bis-β-hydroxyethyl-terephthalate was polymerized by a condensation reaction yielding poly(ethylene terephthalate) and ethylene glycol:



Two different catalysts have been used: antimony trioxide with manganese acetate and antimony trioxide with calcium acetate. Hovenkamp[8] has shown that the first step is catalysed mainly by the manganese acetate and the calcium acetate while the second step is catalysed by the antimony trioxide. Details of the mechanism of catalysis have been described by Wolf and Herlinger *et al.*[9,10]

To get large molar masses, extremely pure materials had to be used. The terephthalic acid dimethylester was obtained from Firma Merk (No. 808 177, p.A.) and from the Nobel company. The material was purified by dissolving in methanol, filtering the solution using a heated funnel and recrystallizing under argon. The methanol was previously purified by the addition of magnesium followed by distillation. The ethylene glycol was obtained from the Riedel de Hean Company (No. 242 04, p.A) and was purified by boiling with metallic sodium for 1.5 h followed by distillation.

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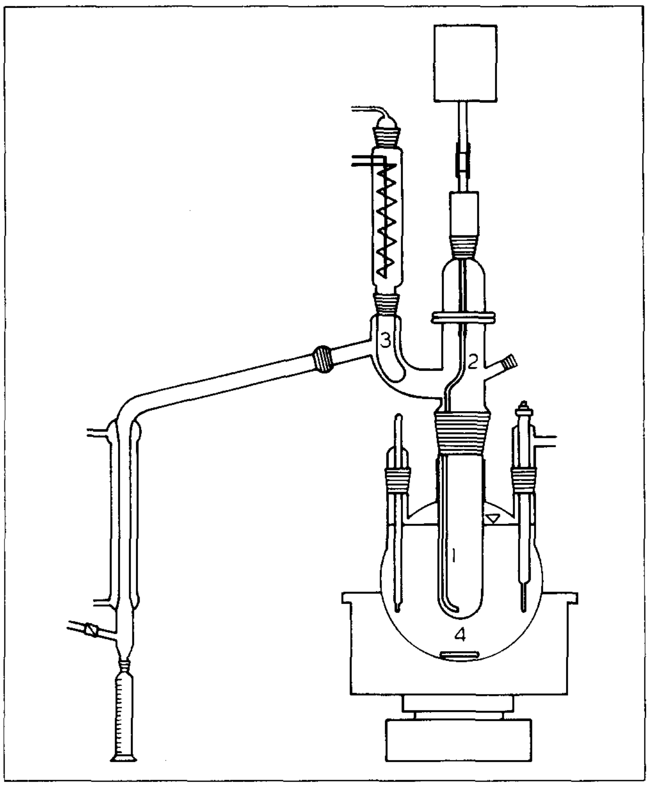

Figure 1 Polymerization apparatus, 1 = reaction tube, 2 = stirrer, 3 = partial condensor, 4 = temperature bath

As with polycondensation, the rate of reaction as well as the molar mass obtained depends on, among other things, how quickly the condensation product is removed. Accordingly, details of the polycondensation apparatus are important and are described below. The apparatus used here is based on a device developed by Buxbaum[11] and is shown in *Figure 1*. Both steps of the reaction occur without interruption in the tube. The tube is heated in a heating bath. Above the tube a partial condensor filled with methanol is kept at methanol boiling temperature. This makes it possible that during the *trans*-esterification process (first process), the material can be heated above the temperature of ethylene glycol; any ethylene glycol which evaporates off is condensed in the partial condensor while the evaporated methanol escapes. During the second process (polycondensation), the partial condensor is removed. The stirring rod 2 is bent in such a way that the polycondensating material forms a film at the wall of the tube from which the ethylene glycol formed in the reaction is quickly removed by diffusion and evaporation at 0.05 Torr. After the polycondensation reaction is complete the reaction tube has to be broken in order to get the product out of the tube.

The optimum reaction conditions were determined in a series of experiments. It was necessary to carry out the reaction in such a way that the diethylene glycol content was less than 1%. Diethylene glycol terephthalate is formed mainly from the bis-β-hydroxylethylterephthalate during the first stage, especially at the end of this stage when the concentration of the hydroxyethylterephthalate is at its highest. Therefore this stage has to be kept as short as possible. This was realized with the aid of the condenser which made it possible to raise the temperature above the boiling point of ethylene glycol without removing the ethylene glycol. In addition, other side reactions had to be minimized. Our experiments showed[12] that the best results were obtained if the temperature applied was changed as shown in *Figure 2*.

The weight average molar mass was determined by viscometry using the relation[13]

$$[\eta] = 4.68 \cdot 10^{-4} \bar{M}_w^{0.68} dl/g \tag{1}$$

Orientation and crystallization experiments

In order to perform the orientation measurements, films with a uniform thickness of 200 μ were prepared from the samples using a heating press with a special device for evacuation the space around the sample during heating and pressing. The samples were pressed for 3 min at 280°C and then quenched in ice-water. In previous investigations it was shown that under these conditions no thermal degradation took place and the molar mass after pressing was nearly the same as before pressing[14].

The samples were oriented in an Instron testing machine at temperatures between 85° and 100°C with different drawing rates and draw ratios.

The birefringences were determined by using a polarizing microscope with a rotary compensator (Ehringhaus) with calcite combination plates.

The kinetics of crystallization were determined with a 'mercury dilatometer'. The size of spherulites was observed with the aid of a polarizing microscope.

RESULTS

Weight-average molar mass as a function of polycondensation conditions

Figure 3 shows the weight-average molar mass $\bar{M}_w$ as a function of polycondensation time, for polycondensation at 270°C. The two curves refer to different catalysts. All data concerning concentration in mol % refer to the number of moles of dimethyl terephthalate. One can see that the molar mass increases with increasing polycondensation time until a constant value is reached. With manganese acetate, the polycondensation proceeds much more rapidly and the maximum value of $\bar{M}_w$ is greater than with calcium acetate.

In addition, polycondensation in the presence of triphenylphosphate (TPP) was investigated. The TPP was added to prevent thermal degradation. *Figure 4* gives the

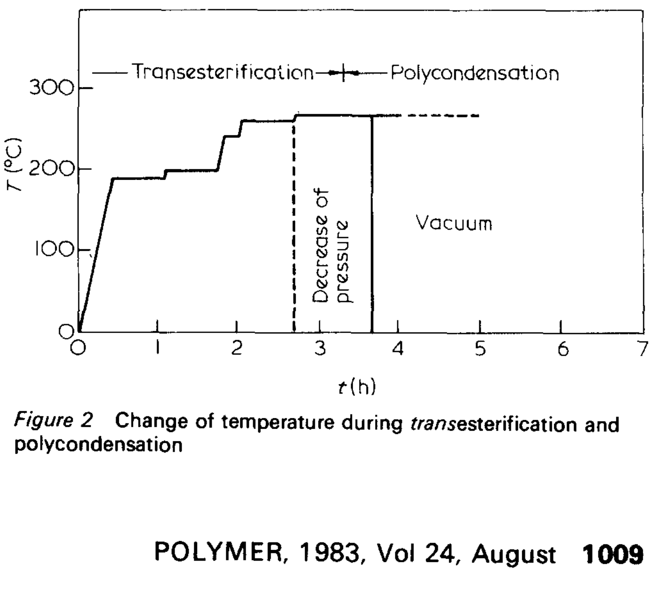

Figure 2 Change of temperature during *trans*esterification and polycondensation

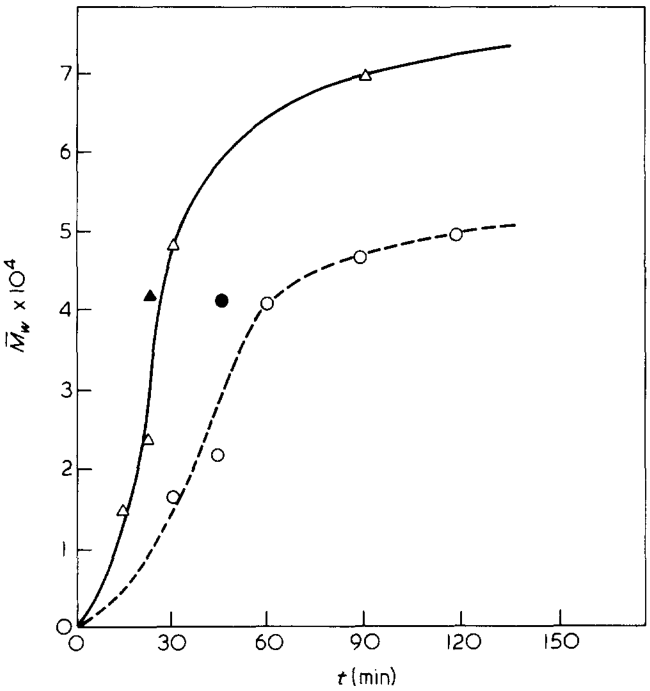

Figure 3 Weight-average molar mass as a function of polycondensation time for a polycondensation at 270°C with 0.0288 mol% Sb_2O_3 and (— O —) 0.112 mol% calcium acetate; (●) 0.224 mol% calcium acetate; (–△–) 0.112 mol% manganese acetate; (▲) 0.224 mol% manganese acetate

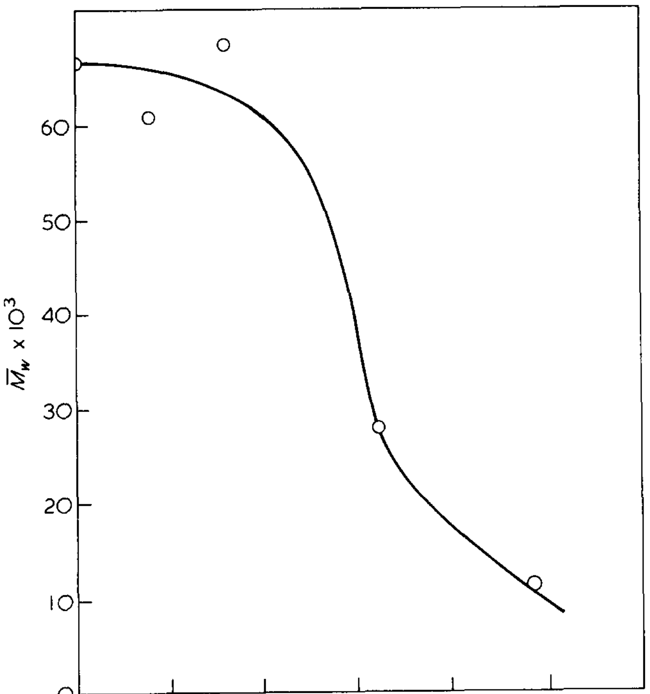

Figure 4 Weight-average molar mass $\bar{M}_w$ as a function of the triphenylphosphate content. Polycondensation at 270°C for 2 h with 0.112 mol% manganese acetate and 0.0288 mol% Sb_2O_3

weight-average molar mass as a function of triphenylphosphate content for a polycondensation at 270°C for 2 h. One can see that small amounts of TPP do not influence the molar mass which is reached, but larger amounts cause a decrease in the molar mass. That small amounts of TPP do not influence the polycondensation rate can also be seen by a comparison of *Figure 5* with the full curve in *Figure 3*.

Crystallization study

For crystallization kinetics investigations, the samples were molten at 280°C initially for 5 min in vacuum and then for 10 min under mercury in the dilatometer before they were brought to the crystallization temperature. The change of volume was registered as a function of time at constant temperature.

The dependence of the half-time of crystallization on the crystallization temperature, for some samples with different molar masses and different catalysts, is shown in *Figure 6*.

Figure 7 shows the half-time of crystallization as a function of weight-average molar mass. The two curves refer to different catalysts. One can see that with increasing molar mass the half-time of crystallization increases. This is true for both kinds of catalysts. At constant molar mass the half-time of crystallization for the sample with manganese acetate is greater than for the sample with calcium acetate.

The influence of the thermostabilizer on the crystallization rate can be deduced from *Figure 8*. For the samples with TPP the half-times of crystallization are considerably smaller than for the samples without TPP.

Crystallization rates were also determined in the temperature range above the glass transition point. The samples were molten, quenched to room temperature then brought, for differing times, to the crystallization temperature and quenched again. The density as a function of crystallization time was measured in a density gradient column. *Figure 9* shows the half-time of crystallization as a function of crystallization temperature. One can see that, again, the samples containing calcium acetate crystallize much more rapidly than those containing manganese acetate. With increasing catalyst con-

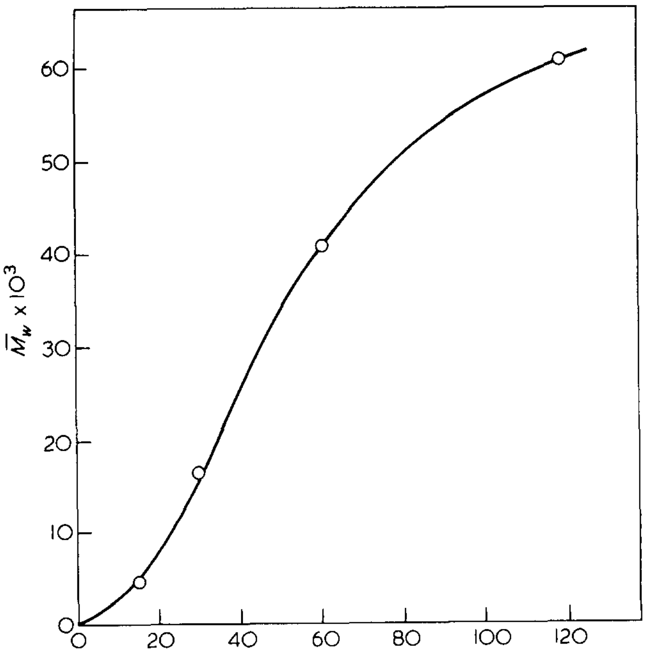

Figure 5 Weight-average molar mass M_w as a function of the polycondensation time *t* at 270°C for material with 0.122 mol% manganese acetate, 0.0288 mol% Sb_2O_3 and 0.03 mol% triphenylphosphate

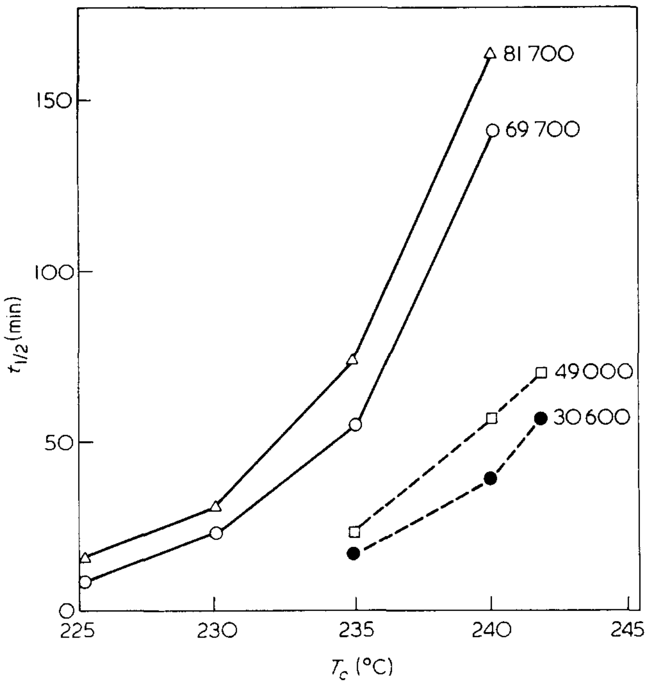

Figure 6 Half-times of crystallization $t_{1/2}$ as a function of crystallization temperature T_c. Melting conditions: 30 min at 270°C and 10 min at 280°C. The parameter is the weight average molar mass M_w. (——) = 0.0288 mol% Sb_2O_3 and 0.112 mol% manganese acetate; (– – –) = 0.0288 mol% Sb_2O_3 and 0.112 mol% calcium acetate

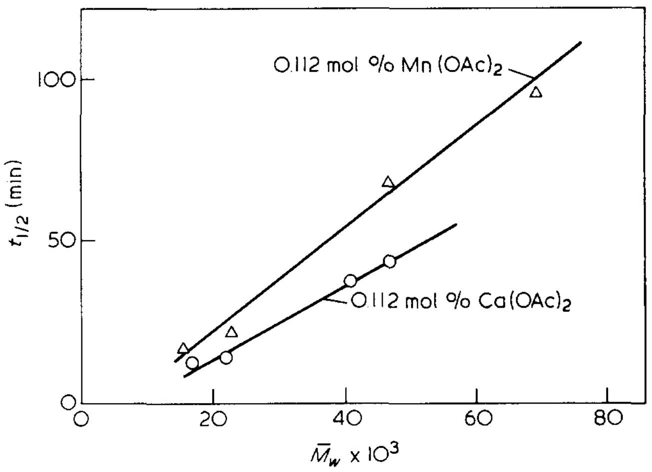

Figure 7 Half-times of crystallization at 237°C as a function of the weight average molar mass M_w. Melting conditions: 10 min 280°C. Catalyst as written on curves and in addition 0.0288 mol% Sb_2O_3

centration the half-time of crystallization decreases. A similar dependence on the catalyst concentration is also obtained at the higher crystallization temperature.

In addition to these investigations, the size of the spherulites has also been determined. The material was molten in the form of a film of thickness 50 μ, pressed and quenched at 210°C, where it crystallized. *Figure 10* shows two micrographs obtained with the polarizing microscope. One can see that the sample with manganese acetate shows large spherulites while the sample with calcium acetate shows small spherulites.

To obtain results at a lower temperature, samples were quenched from the melt to room temperature and then brought to the crystallization temperature. Some results are shown in *Figure 11*. One can see that in the sample with manganese acetate the spherulites become larger the higher the temperature of crystallization. This is in agreement with nucleation theory. Again in the sample containing calcium acetate the spherulites are much smaller than in the sample containing manganese acetate.

The microscopic results show that calcium acetate acts as a nucleating agent and that the smaller values for the half-time of crystallization observed with samples of

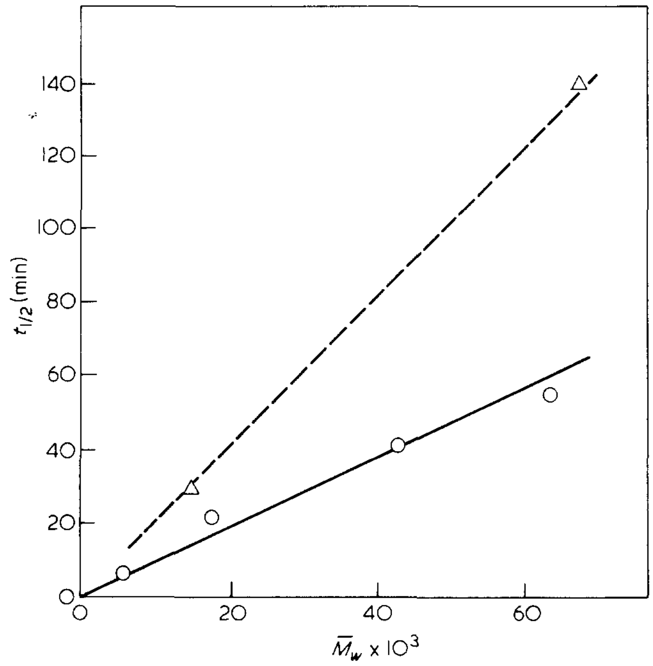

Figure 8 Half-time of crystallization $t_{1/2}$ at 240°C as a function of the weight average molar mass $\bar{M}_w$ for samples with 0.0288 mol% Sb_2O_3 and 0.112 mol% manganese acetate as catalyst: (– – –) without triphenylphosphate; (——) with 0.03 mol% triphenylphosphate

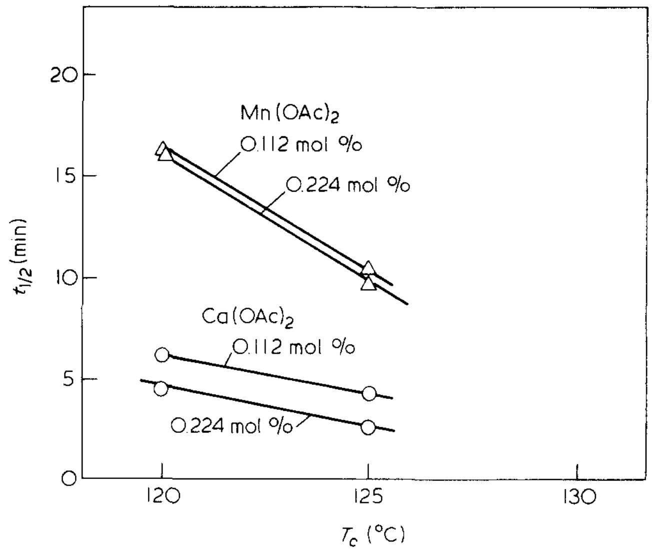

Figure 9 Half-time of crystallization $t_{1/2}$ as a function of crystallization temperature T_c after heating from the glass state. The content of manganese acetate and calcium acetate respectively is written at the curves as a parameter. The weight average molar mass is 41 000

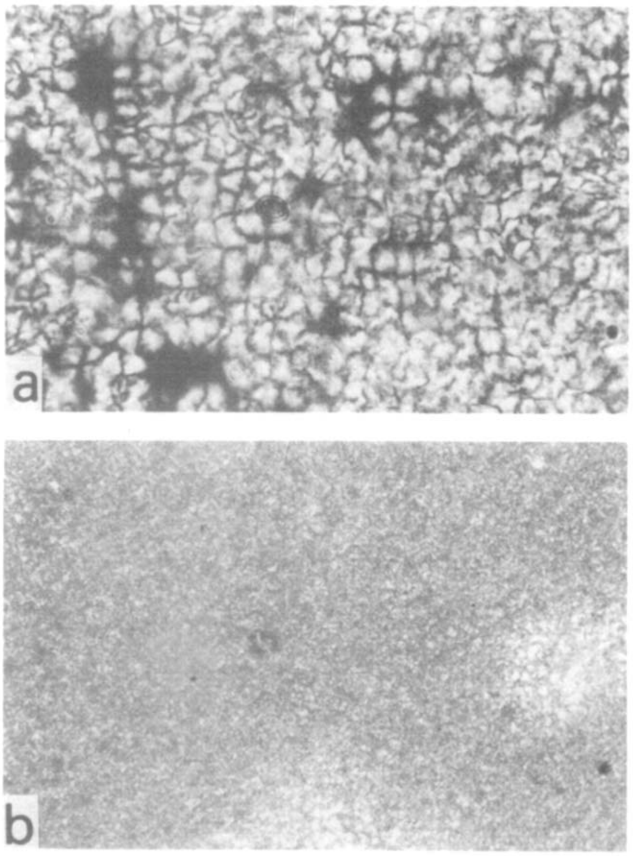

Figure 10 Micrographs obtained with the polarizing microscope from samples crystallized at 210°C after rapid cooling from the melt: (a) sample containing 0.0228 mol% Sb_2O_3 and 0.112 mol% manganese acetate; (b) sample containing 0.0228 mol% Sb_2O_3 and 0.112 mol% calcium acetate

calcium acetate are due to this nucleation effect. It has been observed also that calcium acetate was not miscible with the polymer but formed small grains which was in contrast to manganese acetate.

Study of the orientation behaviour

Figure 12 shows the birefringence obtained after drawing at 92°C with a drawing rate of 500% min^{-1} as a function of the draw ratio, λ. The parameter written on each curve is the molar mass. One can see that the birefringence obtained under the same drawing conditions is larger the higher the molar mass. For samples with a molar mass of only 14000 no orientation is obtained after drawing.

Figure 13 shows the corresponding results for a drawing rate of 5000% min^{-1}. At this large drawing rate the molar mass has almost no influence. The results obtained for the molar masses between 40800 and 60000 are approximately the same; only the birefringences of the sample with the molar mass of 21000 are smaller.

The results shown in *Figures 12* and *13* were obtained on samples synthesized with calcium acetate. For comparison, samples with manganese acetate have been investigated. The results obtained for the two different catalysts are compared with each other in *Figure 14*. Again the birefringence is plotted as a function of the draw ratio. The parameters written on the curves are the drawing rate and the drawing temperature. The molar mass was the same for all curves, namely, 40000. One can see that in the case of the small drawing rate of 400% min^{-1} the catalyst influences the orientation obtained; the birefringences for the sample with calcium acetate are larger than those for the sample with manganese acetate.

DISCUSSION

Influence of molar mass

In a previous publication[15] it has been shown that the molar mass distribution of the samples obtained in our experiments have unusually small values of $\bar{M}_w/\bar{M}_n$ lying between 1.2 and 1.8. This indicates that the value of $\bar{M}_w$ obtained by equation (1) is not correct. This equation is based on the viscosity average and the calibration for $\bar{M}_w$ is correct only for the usual molar mass distribution with $\bar{M}_w/\bar{M}_n = 2$. Therefore the true $\bar{M}_w$ values of our samples will probably be about 8% smaller than those obtained by equation (1). This, however, is not of essential importance in the following discussion.

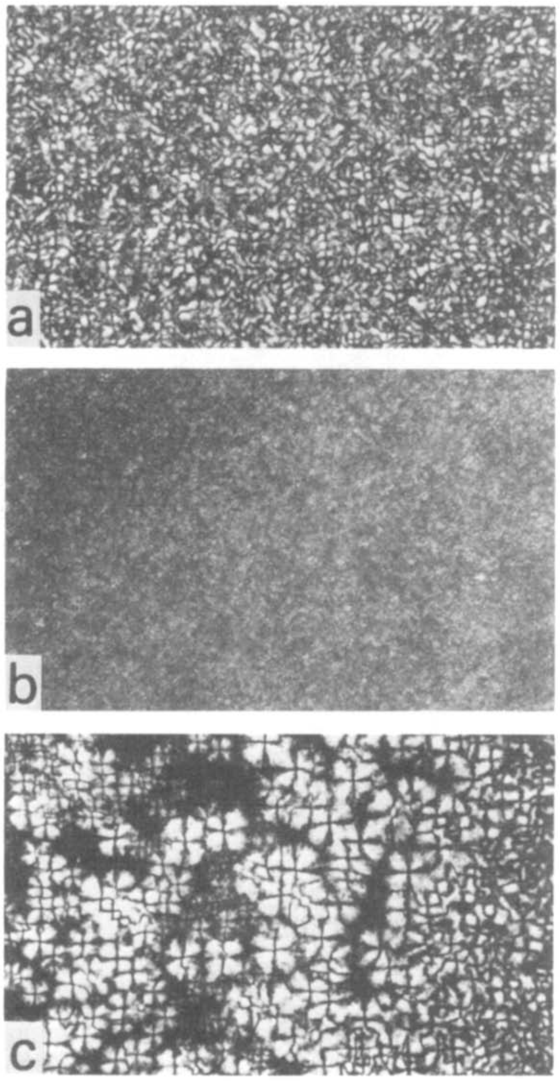

Figure 11 Micrographs obtained by the polarizing microscope from samples crystallized at different temperatures T_c coming from the glass state: (a) catalyst content: 0.0228 mol% Sb_2O_3 and 0.112 mol% manganese acetate. T_c = 130°C; (b) catalyst content: 0.0288 mol% Sb_2O_3 and 0.112 mol% calcium acetate. T_c=130°C; (c) catalyst content: 0.0228 mol% Sb_2O_3 and 0.112 mol% manganese acetate. T_c=180°C

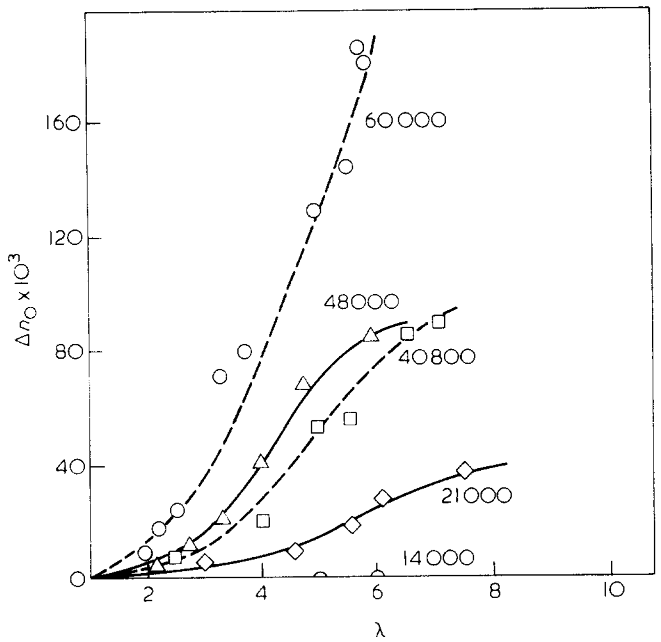

Figure 12 Birefringence Δn_0 as a function of draw ratio, λ, for samples drawn at 92°C at 400% min^{-1} with 0.0288 mol% Sb_2O_3 and 0.112 mol% calcium acetate as catalysts. The parameters written on the curves is the weight-average molar mass $\bar{M}_w$

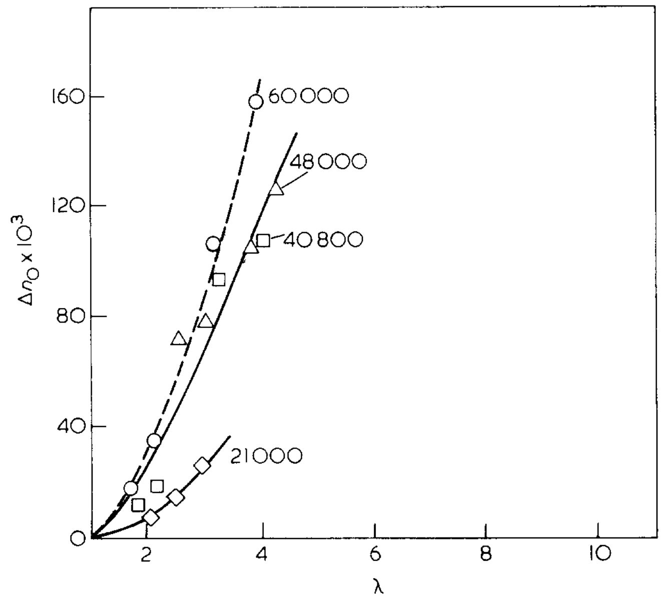

Figure 13 Birefringence Δn_0 as a function of draw ratio, λ, for samples drawn at 92°C with 5000% min^{-1} with 0.0288 mol% Sb_2O_3 and 0.112 mol% calcium acetate as catalysts. The parameters written on the curves is the weight-average molar mass $\bar{M}_w$

The decrease of crystallization rate with increasing molar mass is probably caused by the increase of viscosity and decrease in chain mobility. However, another effect should be considered: it is possible that with a larger $\bar{M}_w$ the surface morphology of the crystal lamellae changes and in turn the surface free energy σ_e changes also. Furthermore, the amount of crystal defects might also depend on $\bar{M}_w$. Both quantities would affect the free energy of nucleation and therewith the nucleation rate. Further investigations are necessary in order to decide how far these last effects are the cause of the observed results. Specifically we shall determine the degree of crystallinity and the amount of crystal defects by applying the method of Ruland which we have recently extended to poly(ethylene terephthalate)[16] and we shall also determine the long period by small-angle scattering.

It is interesting to note that the molar mass also affects the orientation obtained by drawing. The increase of orientation obtained by increasing molar mass may have in principle two causes:

(1) If the molar mass is larger, the viscosity is also higher and therefore slippage of chains becomes less important.

(2) The amount of chain entanglements increases with increasing molar mass.

Since the influence of molar mass becomes smaller when the rate of drawing increases, we can conclude that the second explanation cannot be correct. Therefore the suggested decrease in chain slipping is probably responsible for the larger orientations obtained with larger molar mass.

Influence of catalysts

There arises the question of why calcium acetate is a better nucleating agent than manganese acetate. Generally, there is no acknowledged theory from which it is possible to predict which materials act as heterogeneous

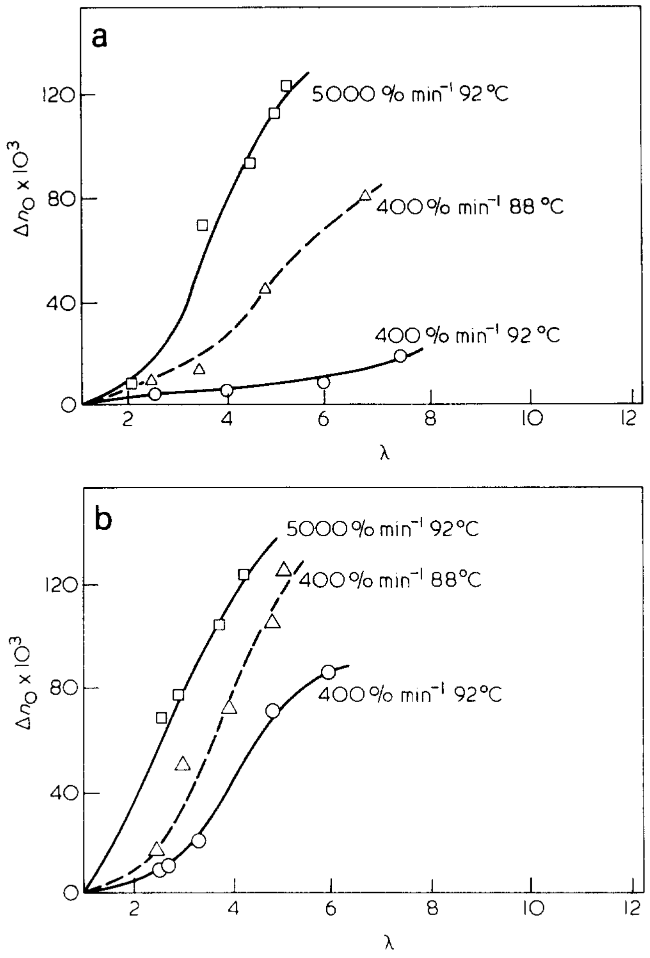

Figure 14 Birefringence Δn_0 as a function of draw ratio, λ, for samples with a weight average molar mass $\bar{M}_w$ = 48 000. The drawing rate and the drawing temperature are written as a parameter on each curve. Catalyst content: (a) 0.0288 mol% Sb_2O_3 and 0.112 mol% manganese acetate; (b) 0.0288 mol% Sb_2O_3 and 0.112 mol% calcium acetate

nuclei. We have observed that calcium acetate precipitates from the melt while manganese acetate remains soluble. We assume that this precipitation from the melt in the form of small particles is the reason for the ability of calcium acetate to act as a crystal nucleation agent.

It was surprising to us that the orientation in samples containing calcium acetate was larger than in those containing manganese acetate. We can explain this if we assume that, in addition to chain entanglements, small crystal nuclei which are formed during drawing also act as netpoints; in a polymer with calcium acetate more such nuclei will be formed than in a material with manganese acetate. Clearly, this effect occurs only at small drawing rates. For large drawing rates the effect of the chain entanglements is predominant and the improved nucleation with calcium acetate has practically no effect.

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