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Application of self seeding technique in regulating polymorphic transformations during non-isothermal bulk crystallization of polymers

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Abstract: Non-isothermal melt crystallization of trans-1,4-polyisoprene (TPIP) has been studied with the help of differential scanning calorimetry (DSC) and wide-angle x-ray diffraction. Self-seeding has been used for the controlled growth of polymorphs. Thus, self-seeding below 55° and below 71 °C has led to the exclusive crystallization of β and α polymorphs, respectively, upon non-isothermal cooling of the polymer melt. These temperatures may vary slightly with the previous thermal history and molecular characteristics of the original sample. It has been interpreted that during cooling the rate of growth (by secondary nucleation) of seeds of either polymorph remains much faster than the rate of primary nucleation of the other polymorph whose seeds are not present in the melt. As a result, the crystallizing melt becomes occupied by the spherulites of the seeded polymorph well before the other polymorph can nucleate.

Key words: Crystallization – polymorphic transformations – self-seeded crystallization – thermal analysis – trans-1,4-polyisoprene

1. Introduction

The potentiality of self-seeding technique for growing crystals of macromolecules from solutions have been established by Blundell and coworkers [1, 2]. The technique is naturally of importance for crystallization from melt also because polymers offer a wide temperature range wherein neither the crystals melt nor the nucleated melts crystallize [3]. Wunderlich's review gives a detailed account of the types of self-nucleation procedures which could be used in the crystallization of polymers [3]. It is tempting to extend the application of this technique to non-isothermal melt crystallization of polymers exhibiting polymorphism because most industrial techniques of polymer processing have to essentially deal with non-isothermal melt crystallization of polymers. Further, in the case of polymers exhibiting polymorphism it might be a frequent requirement to obtain the finished product in a particular polymorphic form; for example, in order to get maximum piezoelectric effect in polyvinylidene fluoride the articles prepared must contain the polymer in its β form. Polymorphic transformations in polymers, therefore, become an important field of study, in that it could lead to establishing certain general procedures for the stabilization of a particular polymorph in the finished product. This study was stimulated by the above ideas and trans-1,4-polyisoprene (TPIP) which is a linear hydrocarbon polymer exhibiting polymorphism was chosen for preliminary investigations. Differential scanning calorimetry and wide-angle x-ray diffraction have been used for characterizing the crystallized product.

In earlier communications on TPIP we have reported isolated single crystals and other complex growth stages of both the polymorphs from solutions [4, 5], and thermodynamic parameters and mechanism of isothermal crystallization from melt [6, 7]. The difficulty in the analysis of its crystallization data arises due to its tendency to crystallize simultaneously at moderate undercoolings in two different polymorphs: orthorhombic β [8] and monoclinic α [9, 10] form. During growth crystals of either polymorph remain exclusive to themselves [11, 12]. Based on the position of melting peaks on the temperature scale of DSC or DTA, many workers named the β and α polymorphs of TPIP as low melting (LM) and high melting (HM) forms, respectively. In a recent analysis it has been shown [13] that depending upon the crystallization conditions both low melting and high melting portions could grow during the secondary and primary crystallization of β polymorph alone.

Regarding the polymorphism behaviour: 1) TPIP can be converted exclusively in its β form by crystallizing the polymer melt well below 40 °C. The T_m versus T_c graphs of Davies and Cucarella [14] (reproduced in Fig. 3) show that DSC melting temperatures of β crystals grown at $T_c \leq 40\,^{\circ}\mathrm{C}$ will be $\leq 55\,^{\circ}\mathrm{C}$. But there is no way of crystallizing TPIP exclusively in β form having DSC melting temperatures $> 55\,^{\circ}\mathrm{C}$, because efforts to do the same by increasing T_c beyond 40 °C will lead to the growth of a mixture of both the polymorphs [6, 11, 14, 15]. 2) Both, Fig. 3 and earlier reports [6, 14] show that in order to convert a TPIP melt exclusively in its α polymorph, crystallization of the entire sample should be carried out at $T_c > 52\,^{\circ}\mathrm{C}$ which will require a temperature control for a much longer time scale [6].

From our earlier work and literature reports [3] the factors generally affecting self-seeding were identified as: the temperature to which the melt is heated, the time of residence of the melt at that temperature, the rate of cooling of the melt, and the polymorphic form of the starting material. In the present investigation a suitable combination of these factors was utilized for the growth of: 1) exclusively β polymorph with higher melting temperatures (~ 65 °C) than found in Fig. 3, and 2) exclusively α polymorph under non-isothermal conditions and in a relatively much shorter time than required for crystallization above 52 °C (as shown in ref. [6]).

2. Experimental

2.1 Material

Synthetic TPIP with $\bar{M}_w$(gpc) $= 6.4 \times 10^5$ and $\bar{M}_w/\bar{M}_n$(gpc) $= 9.4$ was kindly supplied by Polysar, Canada, in the shape of button-like chips weighing between 0.5 to 1.0 g. The polymer was used as received.

2.2 Equipments

Differential scanning calorimetry (DSC) was done on a Du pont 900 thermal analyzer. An error of ± 0.75 K is anticipated even after calibrating the instrument with benzoic acid and indium metal. The thermal scans in all cases were started from 26 °C; for the sake of brevity, however, portions relevant to only thermal transitions are shown in the figures. For x-ray analysis thin sections of ~ 1.0 mm thickness and ~ 6.0 mm diameter were cut from the supplied chips and then compression molded at room temperature. Wherever necessary these specimens of TPIP with corresponding thermal history were subjected to wide-angle x-ray diffraction using Cu-K_α radiations. The interplanar spacings, as calculated according to Bragg's law from the diffraction photographs, were compared with the reported ones [8, 9] to characterize the polymorphs.

3. Results

3.1 Self-seeding of β polymorph

The interplanar spacings measured from the x-ray diffraction photographs of the as received TPIP sample showed the presence of only β polymorph in it. Its DSC melting temperature was found to be between 52–54 °C [13]. Therefore, self seeding of β polymorph was done at 55 °C for different timings. For this, small portions (5–10 mg) of the polymer were cut with a sharp knife from the supplied chips. These samples, wrapped in thin aluminum foils, were kept in thin-walled glass fusion tubes, and immersed in a water thermostat maintained at $55 \pm 0.2\,^{\circ}\mathrm{C}$. After seeding the samples for desired periods, the fusion tubes were transferred to an ice bath. These samples were scanned after 24–36 h. Figure 1 shows the DSC scans of the seeded samples. Thin specimens of the polymer were simultaneously seeded for x-ray analysis. The interplanar spacings observed from the diffraction photographs of the seeded samples showed the presence of predominantly β polymorph.

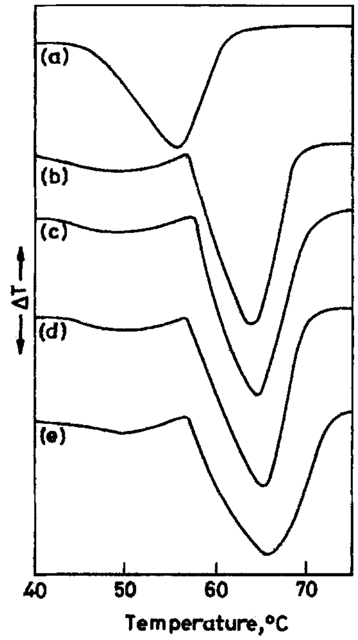

Fig. 1. DSC traces of TPIP self-seeded at 55 °C. Heating rate 10 K/min. Approximate weight of samples 5–10 mg. Seeding time: a) 0; b) 12; c) 23; d) 30 and e) 35 h

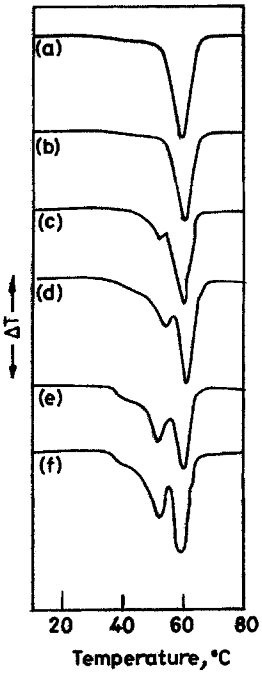

Fig. 2. DSC traces of TPIP cooled slowly (~ 7 K/hour) from: a) 70; b) 71; c) 72; d) 73; e) 74; f) 75 °C. Heating rate 10 K/min

3.2 Effect of melt temperature on the proportion of polymorphs

Some earlier workers [16, 17] have reported the effect of melt temperature on the proportion of polymorphs in the crystallized product during slow cooling of synthetic TPIP. After careful scrutiny, the results of Anandakumaran et al. [16] have been found to be an excellent demonstration of self-seeding of α form, and are worth discussing in regard to the mechanism of growth of the polymorphs in seeded crystallization. In this work we could not maintain their experimental conditions; therefore, we have reproduced their DSC traces [16] in Fig. 2 for the purpose of discussion. After slow heating of the TPIP samples to temperatures one degree apart in the range of 70–75 °C, they crystallized the samples at slow average cooling rate (~ 7 K/h). The DSC traces of the crystallized samples *a*–*f* are shown in Fig. 2. Interestingly, only α form is nucleated when the starting temperature is 70° and 71 °C. But as the starting temperature is increased the peak due to β form also appears, and gradually increases in relative size [16]. Some additional experiments done in the present analysis showed that cooling from 76 °C and above gives nearly identical thermograms like that of sample *f* in Fig. 2.

3.3 T_m versus T_c relationship and induction periods for overall crystallization of TPIP

Figure 3 is a reproduction of the graph drawn by Davies and Cucarella [14] to show the T_m versus T_c relationship in melt crystallized TPIP samples. This would enable us to ascertain the approximate range of crystallization temperatures for the non-isothermally crystallized samples of the present work.

Figure 4 has been drawn from the data of our earlier study [6] on the isothermal melt crystallization of TPIP. It shows the induction periods required for the overall crystallization of the polymer at different temperatures. By combining the cooling rates used in the non-isothermal crystallization with the data of Fig. 4, it is possible to independently evaluate the range of temperatures at which crystallization begins.

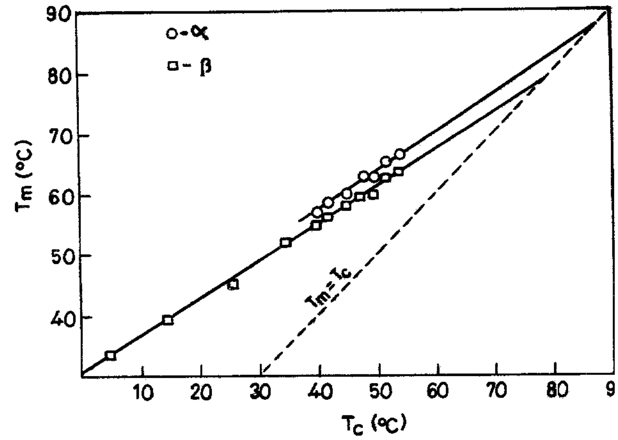

Fig. 3. Plot of melting temperature versus crystallization temperature for isothermally crystallized TPIP (reproduced from [14])

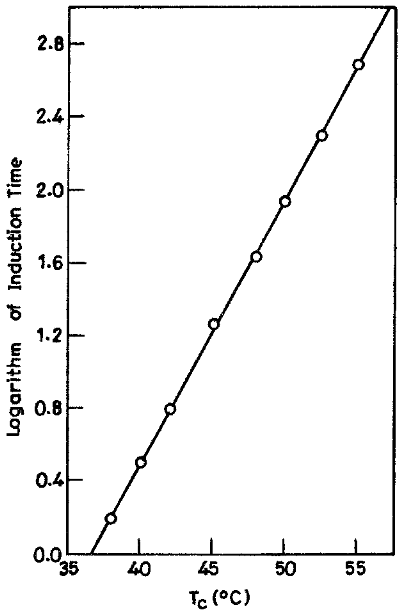

Fig. 4. Plot of logarithm of induction period versus crystallization temperature for isothermally crystallized TPIP (drawn from the data of [6])

4. Discussion

4.1 Self-seeding of β polymorph

Before we begin to scrutinize the results and merit of the experiments of Fig. 1, it is essential to discuss the results of Teitelbaum and Anoshina [18] who studied the annealing (termed as self-seeding in our work) of guttapercha (natural TPIP) by DTA. In the samples annealed at 58 °C, one major peak at 65 °C and a minor curvature in the vicinity of 52 °C was obtained. While the major peak was interpreted as due to the melting of α crystals, the minor curvature was attributed to the melting of β crystals formed during the cooling of annealed samples. In the present analysis also, despite a slight difference in annealing temperature, nearly similar DSC peaks are obtained in Fig. 1. But the interplanar spacings obtained in the x-ray diffraction photographs showed the presence of predominantly β polymorph in the samples seeded at 55 °C. Teitelbaum and Anoshina's conclusion, therefore, seem to be erroneous. The results of an earlier analysis [13] and the DSC and x-ray results of the seeded samples show that the major peaks in Fig. 1 and also in Teitelbaum and Anoshina's annealed samples correspond to chain folded β crystals formed during primary crystallization; and the curvature before the major peak must be due to the fringed micellar type crystals formed due to secondary crystallization of β polymorph during cooling and storage in the ice bath. The mechanism of crystallization in these experiments proceeds as follows.

Computations from Fig. 3 show that the melting temperature of the present TPIP sample (indicated by curve a of Fig. 1) correspond to $T_c(\beta) < 40\,°C$. Since the self-seeding is done near its melting temperature, some β nuclei of highest molecular weight are expected to survive up to a few degrees above the melting temperature indicated by curve a [3], because in dilatometric experiments last traces of β polymorph were found to exist up to 64 °C [15]. Therefore, when the sample is retained for longer durations at seeding temperature partial melting will be followed by recrystallization which will be promoted and entirely governed by the remaining active β seeds of highest molecular weight [3]. Computations from Fig. 3 also show that the melting temperatures of curves b–e of Fig. 1 correspond to $T_c(\beta)$ in the vicinity of 55 °C. It appears, therefore, that the major part of recrystallization took place at the seeding temperature itself. The dilatometric study of overall crystallization of TPIP from an unbiased melt show that at 55 °C predominantly α polymorph should grow, but only after the lapse of an induction period of ~ 500 min (Fig. 4) before the onset of crystallization [6]. But in the seeding experiments β nuclei are already available at the seeding temperature which drastically reduce the induction periods required for the onset of crystallization, and propagate growth by secondary nucleation. As a result, well before α polymorph could nucleate, the melt is mostly occupied by appreciably grown β spherulites leaving small or no scope for new nucleation of α polymorph. The difference in the thermal stability of crystals grown by and without self-seeding can be justified as follows.

It has been reported that at $T_c < 40$ °C rate of primary nucleation of β polymorph is so high that the rate of overall crystallization is determined by the formation of primary nuclei of this polymorph [11]. This high rate of nucleation of β form inhibits appreciable growth of its nuclei leading to secondary crystallization of a sizeable fraction of the material via a fringed micellar mechanism [6, 13]. Therefore, the net result of crystallization below 40 °C should be a poor level of overall crystallinity and hence poor thermal stability (curve a). On the other hand, during recrystallization at the seeding temperature there remain fewer centers of growth leading to large spherulite size, and, therefore, higher overall crystallinity and thermal stability as can be seen from the curves b–e of Fig. 1. A slight increase in the melting temperatures from curves b–e with increase in seeding time can be attributed to marginal increase in the overall crystallinity with seeding time.

Since the original TPIP had a broad molecular weight distribution it is very likely that some molecules smaller than the critical size required for crystallization at 55 °C could not have participated in the growth of β spherulites. These molecules would accumulate in the interestices [19] and crystallize during quenching to ice bath, most probably by a fringed micellar type mechanism [6, 13]. The minor curvature in curves b–e of Fig. 1 should thus be attributed to this latter crystallized material.

4.2 *Self-seeding of α polymorph*

The DSC traces of Fig. 2 show that while only α form is nucleated when the starting temperature is 70 and 71 °C, the peak due to β form also appears when the starting temperature is increased. Computations from Fig. 3 show that the temperatures of the high melting peaks of curves in Fig. 2 correspond to $T_c(\alpha)$ in the range of 42–45 °C, and temperatures of low melting peaks correspond to $T_c(\beta) < 40$ °C. Further, combined calculations from the cooling rates used in the crystallization of samples a–f of Fig. 2 ($\sim$ 7 °C/h) and the induction periods required for the onset of overall crystallization (computed from Fig. 4), show that if the melts were unbiased (unseeded) their slow cooling will initiate crystallization only after a lapse of 4 h of induction period in the vicinity of 42–46 °C.

Earlier reports [6, 11, 15] show that between 40–50 °C a mixture of both the polymorphs α and β should grow as indicated in the samples d–f of Fig. 2. But interestingly, samples a–c in that figure show the presence of only or predominantly α form. This means that the melts whereby crystallization of samples a–c took place did have a bias for the α polymorph. It may be recalled that existence of this polymorph has been reported [15] up to a temperature of 74 °C in dilatometric experiments. Therefore, it is conceivable that the TPIP melts whereby crystallization of samples a and b took place, i.e., at 70° and 71 °C, must have contained sufficient seeds of α form. As discussed in the earlier subsection for the β polymorph, during cooling, crystallization of these α seeds will proceed with accelerating rate. By the time the melt temperature comes down in the range where β form could nucleate, most of the space is occupied by α spherulites leaving no scope for new nucleation of β polymorph. Further cooling, therefore, converts the remaining melt also in α form. When the starting temperature of the melt is raised to 76 °C and above, the DSC traces of the crystallized samples showing the presence of both the polymorphs become identical to that of sample *f* of Fig. 2. This shows that all the seeds melt at 75 °C so that a mixture of both α and β polymorphs is obtained. Between 72° to 74 °C, however, the seeds melt gradually as the seeding temperature is increased. The crystallized samples c, d and e, of Fig. 2, therefore, contain increasing proportions of β form.

The experiments of Fig. 2, thus demonstrate the application of self seeding technique in melt for growing exclusively α crystals. Further, it is envisaged that if the samples are annealed at seeding temperature for longer durations, as seen in case of β polymorph, the thermal stability of the resulting α crystals will be more than that seen in Fig. 2.

5. Concluding remarks

This investigation has shown that seeds of both the polymorphs of trans-1,4-polyisoprene continue to exist up to several degrees beyond their apparent DSC melting temperatures. Therefore, self-seeding technique can be used for the exclusive growth of either polymorph from melt. 55–58 °C and 69–71 °C are found to be suitable temperature ranges for the seeding of β and α polymorphs, respectively. The starting sample for the seeding of β form must also contain only β polymorph. Such a sample can be prepared by quenching of an unseeded melt from 80° to 0 °C. Further, while quenching to low temperatures (0–10 °C) is recommended in case of melt seeded with β TPIP, slow cooling is essential for the exclusive crystallization of α seeds. Annealing for longer durations at the seeding temperature has been found to further increase the thermal stability of crystals obtained by self-seeding technique. It could be interesting to repeat the self-seeding procedure at elevated temperatures with the material already crystallized by this technique. These studies need to be suplemented by microscopic investigation, which will be taken up at a later date.

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