Influence of Plasticizers Suggests Role of Topology in Polymer Solidification at High Cooling Rates

Stefano Piccarolo, Anesh Manjaly Poulose, Alessandro Luzio

INSTM & DICGIM, Università di Palermo, Viale delle Scienze, Palermo, Italy

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ABSTRACT: Although solidification in processing determines short- and long-term properties, methods for understanding polymer crystallization mostly rely on real time experiments. Their evidences being drawn on time scales farther apart with respect to those experienced in processing. Nor significant outcomes have been so far drawn with approaches mimicking the typical processing times, the Continuous Cooling Transformation methods. Use of these techniques has indeed been limited to a heuristic interpretation of the structure developed under extreme solidification conditions without suggesting alternative routes to the understanding or even clues to the many open questions on polymer crystallization under realistic solidification conditions. If the mechanisms inferred from realtime methods cannot in principle be translated to processing conditions the oxymoron is not overcome. In this work, we compare the influence of a plasticizer on the density drop with cooling rate, and therefore on the disappearance of any long range order crystalline phases, observed after fast controlled quenching of polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). The plasticizer enhances significantly the maximum cooling rate at which PET still shows long range order crystalline phases, whereas barely modifies the situation for PBT. On the basis of a series of concurrent clues, we suggest that the complex inherent topology of macromolecular melts introduces a timescale on polymer crystallization lying in the range of the solidification conditions experienced in processing. Although melt topology is known to determine in many instances polymer solidification, all approaches so far proposed to describe the development of polymer crystallization overlook or even neglect any explicit dependence of such mechanisms on parameters like the molecular weight between entanglements. Albeit the arguments are feeble they all concur to raise several questions even on the contradictory role of nucleating agents under the extreme conditions experienced in processing. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: polymer; crystallization; plasticizer; topology; processing

INTRODUCTION

Relevance of polymer crystallization in materials science does not need to be further pointed out if one thinks that out of the overall synthetic polymers production the most important materials and materials classes are those of crystallizable polymers.

This situation has certainly given rise to a continuous interest on the understanding and gathering of relevant information whenever this was made possible by the experimental approaches. By far the most important is certainly Differential Scanning Calorimetry (DSC) able to collect, in different modes, data on crystallization and melting with characteristic times down to 10–100 s, certainly the "fastest" method if one compares with the majority of those available. A high accuracy is obtained and one can collect all sort of information related to temperature dependence of overall crystallization kinetics or identify peculiar mechanisms recently summarized in Ref. 1.

Although this work is not aiming to examine all these efforts in detail, it is clear that the time range explored is by far different with respect to processing conditions where characteristic times are of the order of 1–10 ms at least four orders of magnitude smaller. A situation encountered only on studying another dynamic process: that of glass transition. Although a significant extension to this range of cooling rates can be achieved by the fast scanning calorimeters, there are still several limitations, one of the most relevant being the unavailability of any sample on which an accurate characterization of structure or morphology could be made.

THE CONTINUOUS COOLING TRANSFORMATION APPLIED TO POLYMERS

The solidification behavior of several polymers was also investigated under conditions emulating polymer

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Correspondence to: S. Piccarolo (piccarolo@unipa.it).

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processing by a heuristic approach whereby a thin sample is solidified in a mould by a controlled continuous cooling approach very similar to that adopted in metallurgy to investigate the morphology developed in steels. In contrast to the usual approaches adopted to study crystallization, nothing is known on the evolution of the morphology during cooling but its thermal history. A suitable design of the experimental conditions[2] determining the onset of a homogeneous morphology throughout a sample that can be as thick as 0.1 mm with a surface of 20 by 20 mm. Although sample size is clearly small, it is still amenable for use of several macroscopic probes for the characterization of its overall structure, assumed to be representative of the thermal conditions experienced during cooling because the sample is homogeneous. In contrast to metallurgy, where the large heat conductivity, k, should improve thermal homogeneity, in the case of polymers its lower value implies a significant limitation on sample thickness.[2] Structure homogeneity is clearly related to homogeneity of temperature distribution across sample thickness. It is measured by the Biot number $= h \times b/k$, where h and b are the coefficient of convective heat removal by the cooling liquid sprayed onto sample surface and half film thickness respectively so that the Biot number measures the ratio of heat removed by convection by the cooling medium with respect to heat flowing by conduction within the polymer film. This simplifying approach is made possible by the assumption that the heat generation due to crystallization can be neglected,[2] another important difference with respect to metals. Although under the most drastic cooling conditions applied, the observed Biot numbers on the order or slightly larger than 0.1 imply a deviation of the temperature profile with respect to a flat distribution with time, it can however be shown that, in the case of polymers, even under such extreme conditions, the temperature profiles are parallel to each other and self similar at different times giving rise to the onset of a regular regime.[3] As a result, similarly to a propagating wave, at different positions along sample thickness the same temperature profile is experienced but at different times.

But for these heat transfer arguments, the dependence of homogeneity of the structure developed was also checked experimentally with samples of iPP (isotactic polypropylene) experiencing the disappearance of any crystallinity at cooling rates sufficiently high so that their morphology would be clearly affected by sample thickness,[2] i.e., by the onset of tiny spherulites for samples of thickness not adequate to give rise to a regular heat exchange regime which also implies thickness giving rise to values of Biot numbers much too large.

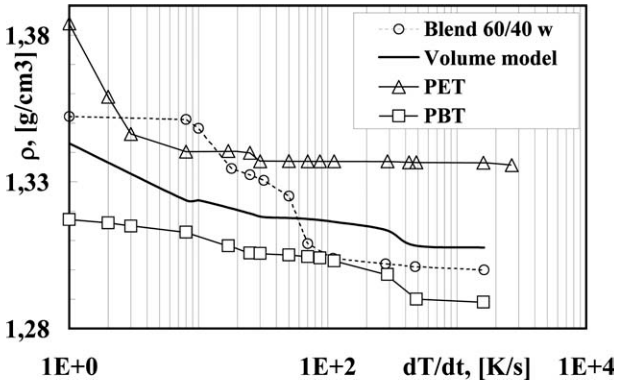

Figure 1 Solidification curve reporting the density vs cooling rate dependence for two polyesters PET and PBT in comparison to their blend with composition of 60/40 w/w, respectively. The continuous line is a prediction from a simple additive model starting from the specific volumes at the same cooling rates of pure constituents.

Advantage of producing a sizeable macroscopic sample with homogeneous structure by what since then has been called the Continuous Cooling Transformation (CCT), borrowing the term adopted in metallurgy, is that several probes can be adopted to relate the structure developed to the cooling rate adopted for sample solidification both microscopic[4] as well as bulk: wide angle X-ray diffraction (WAXD)[5] as well as small angle X-ray scattering,[6] small angle light scattering (SALS),[7] bulk mechanical properties,[8] as well by nanoindentation.[9] In addition, use of DSC was attempted, but for trivial information on transition temperatures, more subtle information related to stability issues or phase composition, especially the so-called Rigid Amorphous Phase, or their changes with time either under isothermal or scanning has been difficult to obtain due to limited reproducibility of stable calorimetric data when collected on samples significantly departed from equilibrium.

THE SOLIDIFICATION CURVE

One of the macroscopic probes adopted to determine the structure developed is sample density, once plotted versus a suitable cooling rate, it can be used to describe the nonisothermal crystallization behavior, this feature, denoted as the "solidification curve," is shown in Figure 1 for two polyesters: polybutylene terephthalate (PBT) and polyethylene terephthalate (PET). Certainly, density is not alone a probe of the structure developed especially if one recalls the complex phase composition of crystalline polymers where, but for allotropy, at least two noncrystalline phases coexist depending on their constraining to the crystalline domains. Density has the advantage that can be monitored with accuracy and reproducibility, and its measurement is accessible with limited effort making it ideally suited to represent the main feature of the polymer solidified under extreme cooling conditions.

Density has several limitations in that first of all it does not discriminate sample phase composition being necessary to collect discrete WAXD patterns to identify qualitatively the crystalline phases formed, a quantitative measurement being often difficult although possible once some hypothesis are made on the constituent phases.[5] Density can however provide useful suggestions on the thermal stability of sample's structure, its drift clearly showing that measurement temperature could not be adequate to univocally determine a characteristic of the sample, a limit overcome decreasing the temperature down to the lowest possible with the solvents adopted for the gradient column. Even so in selected cases, it was necessary to extrapolate the measurement by a suitable algorithm accounting of the fluid dynamic transient for the sample settling to the equilibrium position within the column.[2]

These observations point out that the samples produced under such extreme conditions are not in equilibrium and safe conditions for manipulation must be adopted to avoid any change in the structure formed and also to this purpose density remains a fast and efficient method for determining whether any variation has taken place.

Once the method was settled and limitations on accuracy could be assessed it was extended to the characterization of the solidification behavior of several different polymers. A collection of data of density versus cooling rate as shown in Figure 1 was thus considered as a typical feature of the solidification under conditions similar to those met in real processing but for the two other state variables determining the phase transition: orientation, through the change of entropy, and pressure.

Thus, Figure 1 represents the "solidification curve," a characteristic feature for the melt solidification of the polymer under quiescent nonisothermal conditions or, with a language borrowed from metallurgy, under a CCT. Together with discrete WAXD measurements, these data describe the same modifications occurring to the polymer structure on changing cooling rate and, when superimposed, they provide a supplementary information with respect to density alone. At sufficiently high cooling rates, a lower density plateau value is observed which, for most of the polymers studied, implies the onset of mesomorphic noncrystalline phases.[10,11] On some instances only an indirect proof for the onset of a phase with limited stability was observed as in the case of the PET where the onset of nanocrystals was inductively postulated even for samples apparently amorphous.[12] Finally, in a few situations, noticeable that of LDPE, low density polyethylene,[13] no lower density plateau was observed and therefore no critical cooling rate, Q_{cr}, could be discerned. An apparent limitation of the approach showing that for this polymer even at the largest cooling rates, on the order of 2000 K/s, crystalline phases could not be suppressed completely.

At low cooling rates, a continuous decrease of density with cooling rate is obtained related to the onset of crystalline phases whose amount decreases with cooling rate. A critical cooling rate, Q_{cr}, is observed where density suddenly falls to the level of the high cooling rate plateau. Around Q_{cr} crystalline phases disappear within a narrow range of cooling rates whereby a larger uncertainty on density determinations occurs because small modifications of cooling rate give rise to large changes of either density or WAXD pattern or even disappearance of any morphological feature which could give rise to detectable contrast in the polarized microscope[4] or to a detectable SALS pattern.[7]

The solidification curve is not only characteristic of a given polymer class,[14] it brings record of changes in molecular weight because a larger polydispersity (M_w/M_n) shifts the Q_{cr} to larger values and makes the range where Q_{cr} occurs sharper, i.e., the density falls from the value of the crystalline phases to the lower plateau density in a narrower range of cooling rates. In this context, one is clearly inclined to interpret this behavior on the basis of the larger concentration of low molecular weight chains, i.e., of chain ends, which should play an important role for crystallization at high cooling rates. The solidification curve also accounts for the presence of nucleating agents or even catalyst residues causing a clear shift to larger values of Q_{cr} and a narrower range of cooling rates where density drops and therefore all other features related to the disappearance of crystalline phases is observed.[15] Some actual figures for a few typical polymers with/without nucleating agents is reported in Table I.

Another perhaps interesting effect encountered on studying the samples produced by CCT is related to the limited thermal stability of iPP. Accelerated offline and online density measurements at temperatures well above those adopted to collect the data of Figure 1 were used to study the aging of iPP.[16] The results obtained showed that a very fast density increase takes place even on exposure to a constant temperature as low as 40°C, a drift in density often quantitatively inaccessible once comparing the timescale with respect to the method adopted, based on the settling time in a gradient column. Such transient is followed by a constant pace of density increase when plotted versus logarithm of time with the slope bearing a dependence on the structure of the initial sample before aging.[16] In any case, it is questionable that such a density increase, observed even at low temperatures, should be followed by a change

TABLE I
The Critical Cooling Rate, Q_{cr}, at Which Long Range Crystalline Phases Disappear for Several Polymer Compositions

Polymer	Additive (%, w/w)	M_w (MWD) (Da)	[η] (dL/g)	Q_{cr} (K/s)
PET	?	1.9 E4		1.8
PET	?+ PEGDME (5)	1.9 E4		∼ 50
PBT	?	1.7 E4		∼ 250
PBT	? + PEGDME (5)	1.7 E4		∼ 350
PEN	?		0.51	0.12
iPP1	Pure	4.8 E5 (6)		80
iPP3	Catalyst (∼ 0.1)	4.9 E5 (9.7)		100
iPPM7N	Catalyst + Talc (∼ 0.1 + 0.1)	3.8 E5 (5.3)		∼ 1000

PEN, polyethylene naphthalate; ?, commercial sample.

of crystallinity considering the constraining of the already crystallized material on the surrounding noncrystallized material, which limits its mobility.

Again in the two cases just discussed, as well in the case of the peculiar features of crystallization of syndiotactic polypropylene[17] or of the peculiar mechanical toughness of β nucleated iPP as a function of cooling rate,[18] one observes an isolated effort for tracing some clues on the solidification behavior at high cooling rates by the CCT method, efforts often isolated also in terms of low sophistication of the techniques adopted for characterization because interest on this technique by other teams has been very limited. Clearly less awkward morphologies being more traceable and understandable.

Initial aim of this approach was to quantitatively describe nonisothermal crystallization kinetics of polymers through an adequate model, identifying the parameters determining the best fitting with results obtained under a broad range of cooling conditions. The model identified was based on a modification of Avrami equation due to Nakamura et al.[19] adapted to account for the onset of different phases, i.e., in the case of iPP of the mesomorphic one at high cooling rates.[20] The limited physical background of the approach was clearly shown because missing of generality when transferred to the conditions met in actual processing. Although it is not in the aim of the present contribution to report the vast literature recently reviewed,[21] it is clear that polymer crystallization is more complicated than the simplifying assumptions involved in the Avrami scheme. Even more physically grounded models, based on the traditional view that a new phase forms by a multistep process whereby nucleation is followed by the growth of a crystalline phase,[22,23] cannot satisfactorily describe and account for the variety of solidification behavior encountered in polymer crystallization even restricting the observations to the influence of a temperature history alone, i.e., in the absence of any contribution of orientation or pressure.

Fortunately, the debate on polymer crystallization has found new interest in recent years once several critiques to a strong conventional view of polymer crystallization have been put forward on the occasion of an important conference on the subject,[24] and new perspectives have been discussed and elaborated in the many but certainly not enough workshops organized under the umbrella of the UE funding initiative for Cooperation in Science and Technology within the 5th and 6th framework projects.[25]

The summary of the results outlined here is not aiming to review previous work on the CCT procedure and for the details the reader is invited to consult the original works, rather one aims to show that the results so far obtained do not contribute to a significant extent to the understanding of polymer crystallization. Most of the findings are well inscribed in the traditional view and eventually make use of this to justify conjectures based on a limited set of experimental evidence.

The obvious inherent difficulties on the characterization of samples produced by the CCT procedure[26] have further limited the diffusion of the approach so that much could be done for filling the gap between samples solidified by this procedure, mimicking the conditions met in processing, and those usually adopted to study polymer crystallization where a well developed equilibrium structure is certainly preferred.

HINTS ON POLYMER CRYSTALLIZATION FROM SOLIDIFICATION UNDER EXTREME CONDITIONS

This work is a further attempt to contribute to the understanding of polymer crystallization on the basis of some observations of the solidification under nonisothermal conditions of two polyester homologues, of their blends and the influence of plasticizers.

All the multitude of results summarized in the previous paragraphs show, surprisingly, that the CCT method does not improve to a significant extent the understanding of polymer crystallization. Some specific features of the structure developed at high cooling rates was suggested on the basis of weak experimental evidence like in the case of the nanocrystalline structure present in amorphous PET and already discussed.[12] In other cases, experimental limitations related with the small size of the sample obtained from the CCT procedure to ensure its homogeneity was of prejudice for obtaining any reliable information.[26] In other cases, the limited stability of the samples, a potential source of inaccuracy, is also indicative of a clear departure from equilibrium able to eventually reveal a wealth of information on the underlying mechanisms.[16–18]

In the following one, further effort to identify relevant features on polymer crystallization, when conditions met in real processing are encountered, is described based on the same approach, i.e., on the rather fragmented experimental evidence provided by CCT complemented by the observation of the role of topology in polymers by a nonspecialist, i.e., on some of the recent literature on the subject.[27] Although the interaction between these sets, i.e., crystallization and topology, is rare in the literature only those examples useful for the discussion will be reported because a complete analysis is beyond the scope of this work.

These ideas were driven by a recent work on the crystallization of a blend of industrial interest[28] of two linear polyesters which aims at decreasing the cost of a relatively new one, PBT with a well established material more widespread and less expensive PET of limited use, however, for processing by injection moulding due to its slow crystallization rate.

In that work,[28] it was observed that by the rapid controlled cooling of a blend of PBT/PET, 60% by weight of PBT, the critical cooling rate, Q_{cr}, before an apparently amorphous phase would form does not significantly decrease, 40 K/s, with respect to the one observed on pure PBT, 400 K/s although it is definitely much larger than the critical Q_{cr} observed on pure PET, 2 K/s, as Figure 1 shows.

Although the solidification behavior at low and high cooling rates could be reconciled to some extent[28] with that of the components, in the intermediate cooling rate range the density dependence on cooling rate did not bear any resemblance with either that of PET or PBT.

If the blend were to behave as an "ideal" model where an additive behavior of the specific volumes of the two components at each temperature could be hypothesized, then the same could, in principle, be assumed at each cooling rate, and the specific volume of the blend would be given by $V_{\mathrm{blend}} = \varphi_{\mathrm{PBT}} V_{\mathrm{PET}} + \varphi_{\mathrm{PET}} V_{\mathrm{PET}}$, also reported as a continuous line in Figure 1.

Here, φ_i are the volume fractions and V_i $(=1/\rho_i)$ the specific volumes at each cooling rate for each individual constituent, eventually interpolated from empirical fits at cooling rates where that of the blend is measured.

The model is in closer agreement to the experimental data only in the extreme regions of the diagram, whereas in the intermediate cooling rate range the density dependence on cooling rate does not bear any resemblance with either that of PET or PBT, because a unique density drop is observed, i.e., in the intermediate region the model first underestimates the data and afterwards it overestimates them. The validity of the model in the high cooling rate range is reasonably explained by the complete miscibility in the molten state[29] where a lower density than the model might be related with the excess free volume of the melt generated on mixing. On the other side, at low cooling rates, the agreement with model predictions together with the observation of separate WAXD peaks[28] confirms that the two polymers do not cocrystallize because they form separate crystalline entities. On the basis of such observations, it was concluded that the density drop is nothing but the rate of the necessary demixing stage which determines the later, independent crystallization, of the two PET and PBT moieties. If this view is correct crystallization takes place immediately once the demixing of the two moieties is obtained. Because demixing implies a diffusion process on a length of the order of a crystalline stem, assuming a common value for the two moieties, the critical cooling rate, Q_{cr}, is clearly determined by chain mobility which is a feature of the homogeneous melt comprising both polymers.

On further extrapolating this view one can imagine the process to become diffusion controlled at the length scale required to demix a chain of the length of a stem, situation taking place once the limiting condition for crystallization is observed, i.e., for disappearance of any long range order, i.e., in correspondence of the common critical cooling rate, Q_{cr}, where any crystallinity disappears. Thus, the unique density drop with its characteristic critical cooling rate becomes a measure of this rate determining step.

It would certainly be wise to check such speculations by a suitable investigation on the rheological properties of the pure components as well as of the blend as close as possible to the crystallization temperature. Unfortunately, the difficulties related with the characterization of such features on a system where the experimental conditions must be very carefully chosen to avoid several competitive instances to occur are many. Just to mention the possibility that the measurement itself gives rise to a perturbation causing demixing and even crystallization under the stress necessary to be applied for the rheological characterization. Nor negligible is the possible change of molar mass distribution or even primary chemical structure due to the possibility of transesterification reactions.

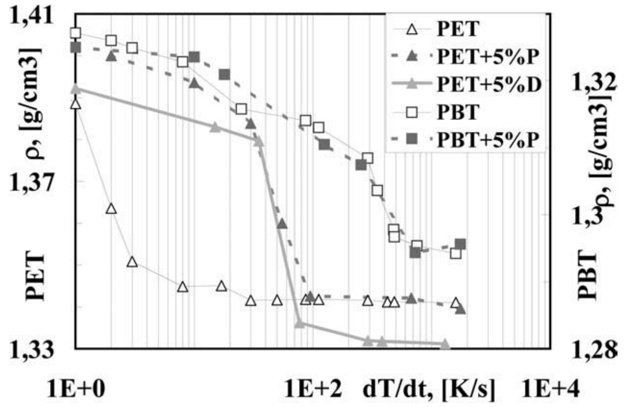

Figure 2 Solidification curves reporting the density vs cooling rate dependence for two polyesters PET and PBT whose density scales are on the left and right respectively. The influence of two plasticizers D and P, identified in the text, is also shown.

To further investigate the issue of mobility, the influence of a plasticizer on the solidification behavior of the two polyesters was studied by CCT with the experimental details reported elsewhere.[30] The two plasticizers were of different chemical structure, one bulky [Dioctyl phthalate (DOP)], the other a linear oligomer [Poly ethylene glycol di methyl ether (PEGDME) with a molar mass of ca. 1000 Da] both well known to act as plasticizers for several polyesters.[31]

A comparison of the solidification curves based on the influence of the addition of 5% (w/w) of plasticizers, D = DOP or P = PEGDME, on the two polyesters in shown in Figure 2. A clear shift of Q_{cr} moving from ca. 2 to ca. 60 K/s is observed in the case of PET, i.e., as much as one and a half order of magnitude. On the other side, in the case of PBT no significant change of Q_{cr} occurs with the addition of the same amount of plasticizer whatever its chemistry. On the other side, the difference between the two plasticizers is observed on the plateau density at cooling rates above Q_{cr} because DOP modifies the excess free volume, whereas this effect is not observed in the case of PEGDME which therefore appears to influence local mobility without a significant change on the density of the presumably amorphous phase. Clearly, these observations must be related to the chemical nature of the two plasticizers where PEGDME, being a linear oligomer, is known to significantly reduce the diffusion coefficient when blended with a long chain entangled polymer because it modifies its dynamics.[32] Unfortunately, no other specific information on the mutual compatibility with the two polyesters is available nor any information on the influence of the two plasticizers on the rheological properties of the two materials is available in the literature to our knowledge possibly for the same reasons discussed above.

IS THERE A TIMESCALE DETERMINING ONSET OF CRYSTALLIZATION?

In addition, in the case of the plasticizers one observes a clear increase of the critical cooling rate, Q_{cr}, above which long range crystalline order disappears eventually giving rise to mesomorphic or amorphous phases depending on the material or on the contrast a short range ordered phase may provide for its detection, often a subtle matter of debate as for example for PET.[33] An increase of cooling rate, i.e., a decrease of a characteristic time for disappearance of long range order is paralleled by an increase of local mobility induced either by the excess free volume produced by mixing two different moieties together or adding a small miscible molecule which apparently determine a shift on Q_{cr} of similar extent. Although, obviously, a clear cut on Q_{cr} due to the different contributions is difficult to identify due all the experimental limitations already pointed out in previous paragraphs.

Crystallization in polymers is a complex phenomenon where the mechanisms involved should not simply be those reported for simple substances, i.e., only determined by the diffusion controlled mechanisms of nucleation and growth. Even considering that this simplifying approach holds and determines crystallization one observes that the difference between primary and secondary nucleation depends only on a difference of the surface energy contribution so that nucleation becomes the rate determining step due to a difference in surface energy, a statement difficult to digest under very drastic cooling conditions.

At least three approaches interpret the nucleation in polymers, brief mention will be made inviting the reader to the original often recent papers for a full understanding. The first, due to Turnbull and Fisher[34] and then directly borrowed by Hoffman and Lauritzen[35] in what has been the most established viewpoint of polymer crystallization, accounts of a thermodynamic balance eventually determined mostly by a diffusion process at low temperatures. The second, due to Strobl,[36] suggests that the pathway followed in the growth of polymer crystallites includes an intermediate metastable phase where a thin layer with mesomorphic inner structure forms between the lateral crystal face and the melt. The first step in the growth process is an attachment of the coiled chain sequences of the melt onto the mesomorphic layer which subsequently is transformed into the crystalline state. The transitions between melt, mesomorphic layers and lamellar crystallites were described by a multiphase thermodynamic approach with the aid of a temperature-thickness phase diagram identifying two transition temperatures of the (hidden) transitions between the mesomorphic and the crystalline phase, and between the liquid and the mesomorphic phase.

An intuition of a multiple pathway toward crystallization was already advanced many years before by Rault[37] with his idea of the onset of a mesomorphic layer followed by an annealing step, embryonic with respect to the one suggested by Strobl.

Finally, the third is due to Wunderlich, recently reviewed in Ref. 1, suggests that the secondary nucleation approach is oversimplified and many other instances may take place even eventually not controlled by the secondary nucleation . This is the case of the onset of the so-called molecular nucleation where growth without secondary crystallization might explain the experimental observations. Wunderlich[1] emphasizes that "The details of each must be evaluated before a description of the thermodynamics and kinetics of crystallization is possible, an enormous task which has by now only barely begun. The tools are available for this task."

In all the approaches cited but for the last, where the complications arising on extreme solidification conditions are pointed out, the experimental background of these approaches are based on solidification conditions not much departed from equilibrium, i.e., conditions which give the possibility to follow the solidification in real time by some macroscopic method of characterization where the timescale of the experiment is above ca. 10 s, a typical value for available real time experiments.

Very interesting on this respect is the viewpoint of Lotz[38,39] in recent contributions where an apparent contradiction is emphasized between a selection rule apparently determined by the substrate where stem deposition is to take place, enforcing the traditional secondary nucleation approach, with respect to a melt whose random conformation of segments is the only established viewpoint, a situation implying that a full understanding of the steps through which a macromolecule gives rise to long range ordered crystals is far from being solved in partial agreement with Wunderlich.[1]

The reason for invoking a timescale for macromolecular crystallization to occur stands on an unstated hypothesis which has never been given sufficient evidence: the conformational rearrangement for stem deposition occurs freely without constraints whatsoever, quite hard to digest if one thinks that the stem length is of the order of 5–20 nm,[39] whereas the path distance between two entanglements is between 20 and 40 nm depending on the polymer.[40] This issue has been recently taken in consideration in Ref. 41 where the disentanglement mechanism is postulated to occur as a prerequisite for nucleation to take place. In addition, in this case, however the experimental verification was of the order of the typical timescales available for a realtime investigation, i.e., on the order of 10 s or more.

Certainly, disentanglement occurs in crystallization and it may even be pushed to such an extent that separation of different molecular weight fractions in a process called Crystaf[42] is obtained, the acronym standing for fractionation by crystallization. Again, however, the timescale of the crystallization fractionation is definitely much longer than the figure of 10 s given above.

A beautiful experiment in this context should be acknowledged: it starts from the observations of Lemstra and coworkers[43] who obtained high modulus PE fibers from very diluted solutions of ultrahigh molecular weight polyethylene, a process patented by DSM as Dyneema. Very high draw ratios can be obtained on drawing the solid precipitate although if molten the solid cannot be drawn anymore to the same extent. These results led Rastogi et al.[44] to observe the onset of a metastable melt once the disentangled solid polymer, whatever the route adopted for its development, is slowly heated. This melt will eventually crystallize much faster than the normal one obtained by fast heating above the melting point. These observations bring a striking evidence on the importance entanglements have on crystallization and on an always not sufficiently persevering investigation on the nature of a macromolecular melt in the vicinity of the transition to the solid crystalline state. An investigation to which apparently a solution was found much too preliminarily in a milestone conference proceeding with the view that macromolecular melt conformation is that of a random coil without any presumed short range order as the many unfortunately unheard contributions to that volume would concur to figure out, a conclusion mostly based on a 1979 *ab initio* modelling calculation.[45]

COMPARISON OF STEM LENGTH AND ENTANGLEMENTS DISTANCE

To interpret the feeble observations presented in this work, we deliberately overlook the general framework of understanding of the phenomena involved in crystallization and focus on the specific data of the two polymers discussed here with particular emphasis on the nature of the amorphous phase whose local mobility can eventually be influenced by a plasticizer, a small molecule, or another miscible moiety both plausibly acting as a solvent. In this context the dilution effect is postulated to take place through the notion of entanglement density determining the time scale for conformational rearrangements, a prerequisite for stem deposition.

In the literature, there are several sources of information regarding entanglement density and tube diameter for several polymers but, at least to our knowledge, not that many. A recent review recalls

TABLE II
The Ratio of Molecular Weight Between Entanglements, M_e, to That of a Stem of 50 Carbon Atoms of Each of the Polymers Listed Is Shown in the Rightmost Column

Polymer	T (K)	G_0 (MPa)	ρ (g/cm^3)	m_0	dt (nm)	M_e	M_s (min)	$(M_e/M_s)_{\mathrm{MAX}}$
PE	413	2.60	0.784	14.00	3.28	828	140.00	5.91
iPP	413	0.47	0.791	21.00	6.07	4623	630.00	7.34
iPP	298	0.48	0.852	21.00	5.19	3518	630.00	5.58
PS	413	0.2	0.969	52.50	7.65	13,309	1575.00	8.45
PA6	543	1.8	0.985	16.67	4.24	1980	500.00	3.96
PEEK	623	4	1.2	31.56	3.61	3190	946.67	3.37
PBT		??		22.60		2000	678.00	2.95
PET	548	3.1	0.989	24.25	4	1170	727.50	1.61
PC	473	2.7	1.14	31.50	3	1330	945.00	1.41

It is obtained from data reported in Refs. 46–48 are also shown here. The datum for PBT is a mere extrapolation, see text for discussion.

PA6, polyamide 6; PEEK, polyetheretherchetone.

all the relevant views related to entanglements and attempts to reconcile different methods for its measurement as well as prediction.[40] One major source of data is reported in the series of papers by Fetters et al.[46,47] where several quantities are reported including M_e and its relationship with other molecular parameters, whereas another set of data is reported in a review by Aharoni[48] on M_c, the critical molecular weight for the onset of entanglement dynamics, for a broad range of materials. Although PET is certainly among the materials listed, no mention is made of PBT, therefore for this polymer one may infer a trend on the basis of polymers with similar chemical structure or on the basis of a comparison with the parent polymer PET attributing to PBT a larger mobility due to the four methylene groups. The collection of several data on other materials which is supported by the packing model,[49] albeit criticized in a recent work,[40] mentions that M_e decreases with chain stiffness because a stiffer chain pervades a larger volume that can accommodate the same number of chains at a shorter chain length. This observation should be compared with the Kuhn length for several polymers[47] which also, for the same reason, decreases for stiffer chains.

Table II compares two relevant quantities on this respect which should determine the timescale for conformational rearrangement to take place. Such two quantities are M_e, identified as an upper limit for the chain length to be involved in a stem deposition on a growing crystalline domain, and the molecular weight of a stem, M_s. Much like in a rubber the ratio of the molecular weight between chemical crosslinks, a quantity inversely related to and often recalled as crosslink density, and Kuhn length is taken as a measure of mobility also determining its glass transition. We are implicitly making a parallel between a rubber, where the relevant quantities are the length of a Kuhn segment with respect to the distance between chemical crosslinks, to our actual situation where a stem length is compared with the distance between physical crosslinks, i.e., entanglements, an intrinsic property of an equilibrium melt. Therefore, similarly to a rubber the larger the ratio between the quantities associated with these lengths the larger the mobility and therefore the shorter the timescale for conformational rearrangement. Values for M_e where taken from all sources available and converted to M_e on the basis of the "rule" $M_c \approx 2M_e$.[40] For M_s a conservative hypothesis was made such that the stem length is ca. 50 carbon–carbon bonds in a linear all trans conformation and the molecular weight was calculated accordingly, although the scaling should not differ by more than unity.

Table II shows that the M_e/M_s ratio shows a good correlation with the critical cooling rates discussed in the previous paragraphs and reported in Table I. M_e/M_s indeed is relatively large for well know flexible chain polymers including PE, iPP, and PS, i.e., on the order of eight, although no mention is made on the influence of configuration on conformation, i.e., on flexibility which is surprising in this context. The ratio significantly decreases for polyamide 6, a relatively flexible chain polymer with strong interchain interactions due to the amide group, and polyetheretherchetone, a very rigid polymer which is however relatively free of interchain interactions and it is indeed known to crystallize. Very low values of M_e/M_s, close to unity, are obtained in the case of PET and PC (polycarbonate of Bisphenol A) which barely crystallizes giving rise to very small crystalline domains,[51] whereas finally PBT was located within the intermediate class of polymers in agreement with its crystallization behavior.

These observations help on interpreting the results shown in Figure 2 related to the influence of a plasticizer on the crystallization kinetics under processing conditions of two very similar polyesters, PET and PBT. Although they help on explaining the strong influence of the plasticizer on the Q_{cr} for PET as shown in Figure 2, the view does not improve in the case of PBT, the observations being in this case apparently in contradiction with the results of Figure 2.

Certainly, the influence of entanglements cannot be only ascribed to dilution effects because entanglement concentration is scaled with polymer volume fraction to −1.52 The different behavior of PET and PBT, if one excludes specific interactions with the plasticizer adopted in this work, should therefore come from being respectively a stiffer and a softer chain polymer respectively. Although this statement reconciles with the experimental evidence, the results account for a threshold like behavior difficult to interpret on the basis of such understanding.

One should however recall the instance for which these conclusions were drawn, it concerns the situation arising when external solidification conditions are very drastic, i.e., the driving force is so large that the limitation is not much and only on diffusivity, i.e., on the time scale for renewal of a tube conformation. The instance invoked in the case of crystallization concerns a process by which a sorting out of conformationally ordered sequences with respect to others which eventually accumulate defective conformations elsewhere of the ordered sequences. At the timescales we are thinking the process takes place without modifying the overall balance of entanglement density, indeed it is known to be unmodified with respect to the melt since the pioneering investigations on the subject.[45]

These remarks are provided here as a mere suggestion to reconsider the role of topology in polymer crystallization whose influence can determine the kinetics particularly under conditions of very drastic changes of temperature or other state variables.

If the suggestion of a threshold like behavior of mobility on the critical cooling rate for disappearance of long range crystalline order is correct than it has several implications on the role of plasticizers as well as of nucleating agents or their recipes widely used although often not fully understood.

It is clear that the early works, collected in the famous Faraday Discussions of 1979,[45] may have led to strong positions making any further discussion on polymer crystallization more difficult, one of these is certainly the idea that the time for disentanglement is much smaller than the time for selecting a stem to: (a) obtain a conformation compatible with the crystalline order and (b) aggregate on the growing embryo, what has been referred as the process of "reeling in" a chain onto the crystalline phase.

Only new methods for studying polymer crystallization can give perspectives for the understanding of polymer solidification, where the process of crystallization is dominating, under the drastic conditions met in processing. They should consider the role of the amorphous phase and its underlying structure especially in the case of semirigid chain polymers.

CONCLUSIONS

The controlled quenching procedure, also indicated as CCT, for similarity to the experimental procedure known in metallurgy, has led to several nontrivial conclusions with reference to the solidification of polymers under conditions closely mimicking those met in processing. Apart from contributing to the conventional view providing a quantitative characterization of polymer crystallization behavior under realistic solidification conditions, it also suggests interesting ideas on the complex path of the constrained macromolecule in the melt state toward the development of the crystalline morphology. They are briefly reviewed in this work, although particular emphasis is focused on the limiting conditions observed at cooling rates corresponding to the disappearance of long range order as pointed out by X-ray diffraction.

The conclusions are drawn on the basis of a series of observations obtained on the samples post mortem the most relevant being the so-called solidification curve reporting density versus cooling rate in a broad interval. At sufficiently high cooling rates, a critical value is obtained where disappearance of long range order takes place. This is characteristic not only of the polymer but also of other compositional features.

In this work, the influence of compositional parameters affecting the mobility are related to the values of critical cooling rates of two polyesters, their blend and the addition of plasticizers.

It is suggested that the drop off of density, i.e., the critical cooling rate, in the "solidification curves" is diffusion limited corresponding to a time scale limiting the extension and order of polymer crystalline domains, a characteristic time which does strongly depend on primary chemical structure.

The molecular parameter mediating such a dependence is identified with the molecular weight between entanglements, M_e, this being an upper limit for the chain length to be involved in a stem deposition on a growing crystalline domain.

On the basis of literature data on several linear polymers, the ratio between M_e and the molecular weight of a stem length, M_s, taken on average as 50 carbon atoms, is calculated. The ratio between these quantities is a characteristic of the polymer and it is in good correlation with well known limits of crystallization behavior discussed for several of the polymers so far investigated, i.e., with the critical cooling rates for disappearance of long range order.

This observation suggests that when external solidification conditions are very drastic the limitation on stem deposition is not much and only from diffusivity, i.e., on the time scale for renewal of a tube conformation but on the time for separating conformationally ordered sequences eventually accumulating defect conformations elsewhere in so doing without modifying the overall balance of entanglement density.

As a result, one observes a remarkable influence of a plasticizer on the shift of the critical cooling rate of PET, more than one order of magnitude, which however becomes negligible for PBT whose characteristic ratio, M_e/M_s, can be estimated to be at least twice suggesting a threshold like behavior between slow and fast crystallizing polymers. The former can definitely be influenced in their crystallization behavior with the addition of suitable plasticizers which may determine the possibility to be used in routes unusual for their processing.

I am indebted to all colleagues bothered on a matter sometime unwieldy and therefore without a clear answer. Most of them always had the patience to indicate a way for understanding although not always we had the strength to pursue and master the further necessary investigation.

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