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Feature Article

Monodisperse macromolecules – A stepping stone to understanding industrial polymers

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Dedicated to Professor Nikos Hadjichristidis in recognition of his contribution to polymer science.

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ABSTRACT

Polymers synthesized via anionic polymerization have proved important to our fundamental understanding of the processing, that is rheology and crystallisation, of bulk commodity polymers. The role of monodisperse hydrogenated polybutadienes as models for linear and branched polyethylene is examined. Systematic studies of the effects of long-chain branching, using well-defined "comb" materials have improved our understanding of how the number and length of branches affect the rheological properties and how these features impact on their crystallization behaviour. A combination of techniques including rheology, Small Angle X-ray Scattering (SAXS), and birefringence measurements have provided insight into role of linear long chains in the formation of oriented morphologies during the crystallization of hydrogenated polybutadiene blends of controlled polydispersity leading to the development of a quantitative model.

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1. Background

Polyolefins such as polyethylene and polypropylene are bulk commodity polymers which underpin billion euro industries and are extensively used in modern-day life. Despite having been produced since the 1940s, our fundamental understanding of how molecular architecture affects macroscopic behaviour, such as the mechanical properties of semi-crystalline polymers, has been limited. The predominant use of Ziegler–Natta catalysis leads to the production of polymers having very broad molecular weight distributions, and in the case of low density polyethylene (LDPE) by either free radical or Ziegler–Natta polymerization, ill-defined branching. However, the beneficial effect of this branching on polymer processing has been long-recognised in that it promotes shear-thinning, and is also associated with extensional-hardening characteristics. More recently, attention has been focussed on single-site metallocene catalysts where the molecular control is much greater [1]. In metallocene-catalysed polymerizations, ethylene can be mixed with a co-monomer to yield linear low density polyethylene (LLDPE) but unlike the previous Ziegler–Natta technology, the α-olefin co-monomer is homogeneously distributed, and the molecular weight distributions are typically much narrower with a polydispersity index of 2–3. Long-chain branches can be introduced, but again, it differs from the long-chain branching found in Ziegler–Natta catalysed LDPE in that the branches are typically far fewer and longer [2]. By improving the molecular control, improved properties such as better tear strength and transparency can be conferred to these materials as well as retaining the advantages of easier, cheaper processing. However, in order to fully exploit the latest catalyst technology, it has been advantageous to design series of polymers where the architecture, mass, polydispersity and branching characteristics are as highly controlled as possible and where the molecules can be well-characterized. This is realized through the

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use of the anionic polymerization of butadiene. These well-defined polymers are then a key ingredient in the development of models of polymer dynamics.

2. Anionic polymerization as a route to polyethylene analogues

Since its inception in the 1950s [3] "living" anionic polymerization has become one of the foremost methods for producing polymers with a low polydispersity i.e. $\overline{M}_w/\overline{M}_n < 1.1$. The procedures required for successful polymerizations are rigorous and exacting [4] but the excellent molecular mass control and the ability to produce specific architectures (Fig. 1), particularly through the use of chlorosilane chemistry, compensate for this.

The route to producing well-defined polyethylene analogues is via the anionic polymerization, and subsequent hydrogenation, of polybutadiene. Typically, the polymerization is initiated using a butyllithium initiator (BuLi). The propagation is via a Michael addition (Fig. 2) and this can either proceed via 1,4-addition or a 1,2-addition. In hydrocarbon solvents, the structure is predominantly 1,4. However, the presence of a relatively small amount of a solvating base such as tetrahydrofuran (THF) in a non-polar solvent can dramatically increase the probability of 1,2-addition. For example if [THF]:[Li] is 5:1 (initiator concentrations are typically of the order 1×10^{-3} mol, so that equates to 5 mmol THF) the percentage of 1,2-units rises to 44% whereas if the reaction proceeds solely in a hydrocarbon there is only 7% 1,2-addition. Initiator concentration, temperature and counterion can also exert an effect on the microstructure but this is far less dramatic compared to the addition of a base [5].

The hydrogenation of polybutadiene to form poly(ethylene-*co*-butene) has been accomplished using several different methods. Homogeneous catalysts such as Wilkinson's catalyst [6] or heterogeneous catalysis such as Pd on $CaCO_3$ [7] have proved effective. For branched materials, such as combs, the diimine method of Hahn [8] has been found to be particularly effective, with 100% of double bonds being saturated [9]. The full saturation of these materials is imperative for oxidative stability during high temperature testing where they could otherwise cross-link. Because there is always a significant amount of 1,2-butadiene units even when the polymerization takes place in purely hydrocarbon solvents, there are always ethyl branches present in the hydrogenated product (Fig. 3). Approximately 18 branches per 1000 carbon atoms are homogeneously distributed along the polyethylene backbone, hence the product is analogous to LLDPE. Naturally, the quantity and distribution of the ethyl branches determines the crystallization behaviour of the polymers, the melting and crystallization temperatures becoming increasingly low as the ethyl branch content rises. Ethyl branches have been shown [10] to be excluded from crystalline lamellae and as a result the lamellae are generally thinner with a greater proportion of amorphous material being present.

2.1. Linear materials

These are the simplest polybutadiene (PBd)/hydrogenated polybutadiene (HPBd) materials available. For the formation of LLDPE analogues, butadiene is polymerized in a hydrocarbon solvent using a butyllithium initiator which rapidly initiates the polymerization of butadiene (Fig. 4). The monomer is gradually consumed over a 48 h period. Because of the "living" nature of the polymerization, the reaction is only terminated when methanol is added. The molecular weight is controlled by the ratio of the monomer:initiator and because initiation is rapid compared to the propagation, the chains all have a similar degree of polymerization (DP). An ideal anionic polymerization has a Poisson distribution and $\overline{M}_w/\overline{M}_n = 1 + 1/\mathrm{DP}$. The polydispersity index ($\overline{M}_w/\overline{M}_n$) of the materials is typically <1.05 except for very low molecular mass materials where small differences in the DP have a greater effect on $\overline{M}_w/\overline{M}_n$ and for materials with a molecular mass >1,000,000 g/mol, where high viscosity can become an

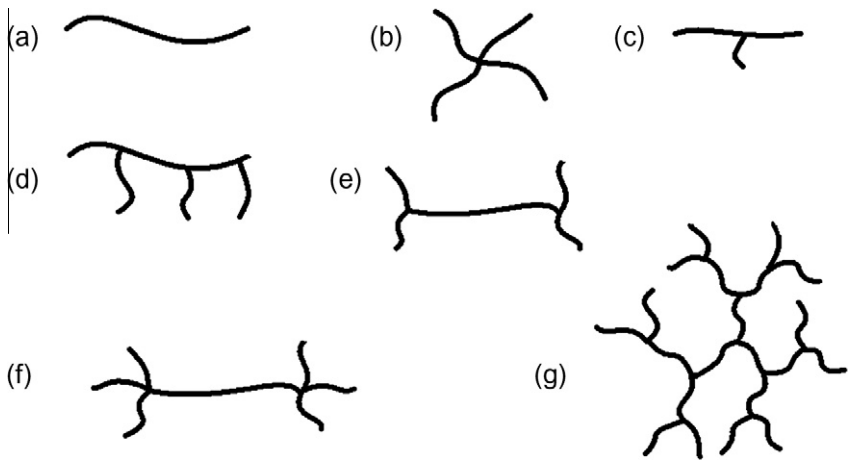

Fig. 1. Some of the different polybutadiene architectures produced using anionic polymerization and chlorosilane chemistry include (a) linear (b) symmetric star (c) asymmetric 3-armed star (d) comb (e) H-polymer (f) Super-H polymer (g) dendrimac.

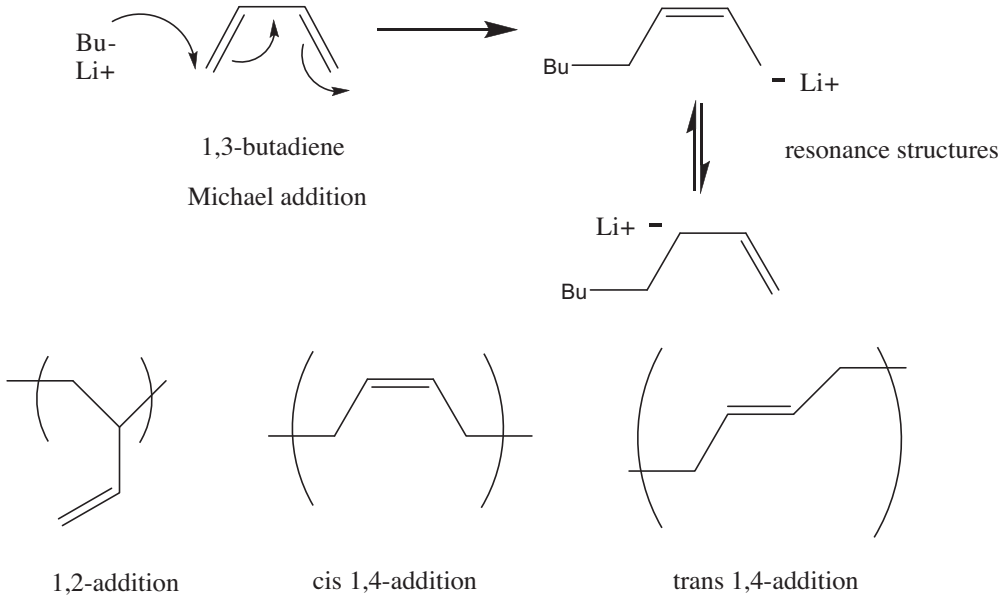

Fig. 2. Polymerization of butadiene via an anionic polymerization.

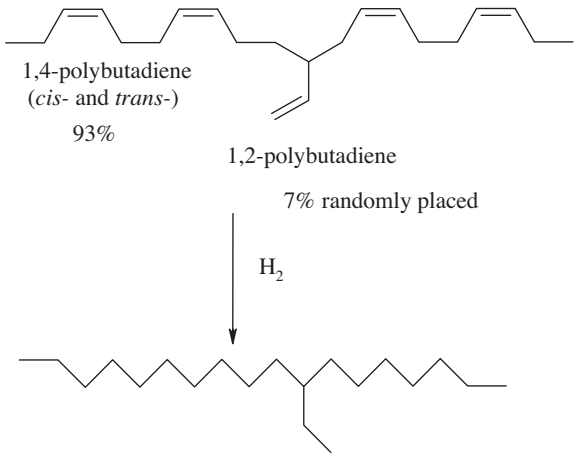

Fig. 3. Hydrogenation of polybutadiene to form an LLDPE analogue.

issue. The hydrogenation of high molecular mass materials can also prove quite difficult for the same reasons.

Theoretical models of monodisperse polymers in the melt state have been tested and refined by using the materials synthesized anionically. Narrowly distributed polymers have clearer and more striking features in both rheological and crystallization experiments. This is essential in elucidating the dominant molecular physics and also provides a rigorous test of dynamical models. This methodology can be extended to flow-induced crystallization (FIC) studies by hydrogenation of anionically synthesized polybutadienes. Although these monodisperse materials can help us to understand how polymeric materials behave during processing, our "model" materials are just models. Industrial materials typically are more akin to blends and much theoretical effort has been made to understand these. Blends can comprise mixtures of linear with branched materials but recent work has also centred on linear–linear blends.

A rich and quantitative understanding of the dynamics of entangled polymers is provided by the tube model [10,11]. In this model the complicated multi-body constraints imposed on a chain by its neighbours are simplified in a single chain problem. The key idea is that the lateral motion of chain is significantly impeded whereas motion of a chain along its own length is unopposed. Therefore a polymer chain is confined to a tube-like region, with diffusion along this tube (reptation) being the dominant relaxation mechanism. Just two material-specific parameters are required in the model: the tube diameter, a, and the entanglement time, τ_e, which is the relaxation time of a subchain of chain with length equal to the tube diameter. In the case of linear hydrogenated polybutadiene (HPBd), the material-specific parameters that affect plateau modulus and the shift parameters have been found to be dependent on the chain microstructure [12] and this could be anticipated from the chain conformation. Refinements of the model have included the effect of fluctuations of the chain contour length, which enhance relaxation at the chain ends and constraint release, whereby a neighbouring chain moves out of the way allowing some lateral motion of the tube. Constraint release is one of the principle problems of modelling polydisperse materials as the range of molecular weights leads to a wide spectrum of constraint release rates. The high molecular weight (HMW) tail in a polydisperse material dominates several phenomena that are especially pertinent to processing flows. Stretching of long chains leads to extension hardening, which stabilizes elongation dominated flows, as was shown through flow measurements and modelling by Auhl et al. [13]. The HMW tail also controls FIC [14,15].

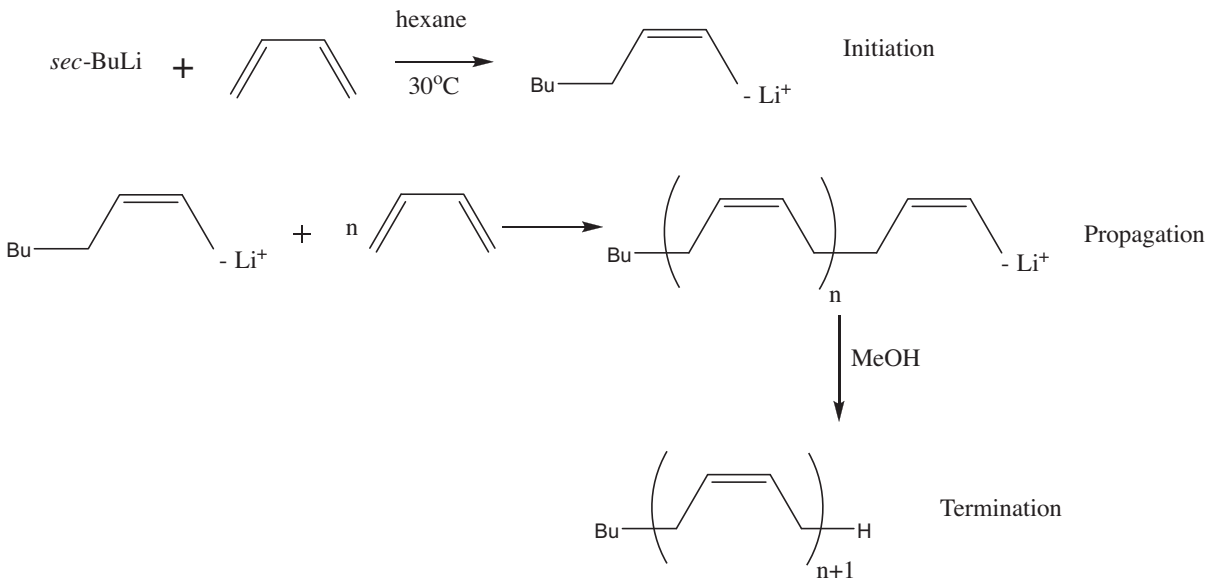

Fig. 4. Initiation, propagation and termination steps for butadiene polymerization.

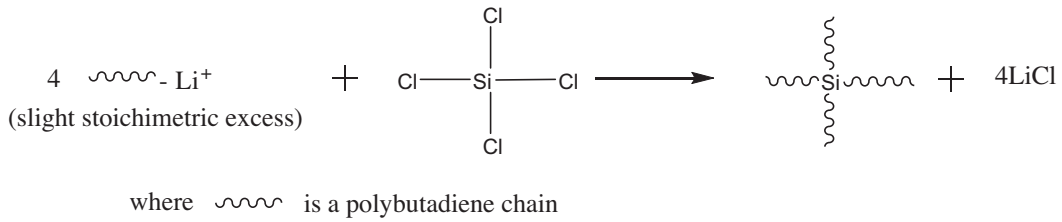

Fig. 5. Formation of a symmetric 4-armed star.

2.2. Branched materials

2.2.1. Stars

Of all the branched architectures, star polymers are probably the most straightforward to synthesise, living anionic chains reacting readily with chlorosilanes (Fig. 5). For example, Allgaier et al. [16] reacted polybutadienyllithium with a range of dendritic chlorosilanes in order to attain stars from 4 up to 64 arms. It has also been possible to achieve a star with 128 arms [17]. Highly branched 1,2-polybutadienes have been further functionalised via hydrosilylation with dichlorodimethylsilane, the addition of 1,4-polybutadienyllithium resulting in highly-branched arborescent structures [18].

It has been found, however, that the effect of the number of arms or branches is limited when it comes to its deformation and flow properties; Fetters et al. [19] examination of the melt rheology of a series of stars found that for polyisoprene stars with a functionality greater or equal to four, the viscosity is independent of the number of arms. In contrast, the zero shear viscosity is exponentially dependent on the arm molecular mass rather than the overall molecular mass of the star. In comparison, linear polymers show a power-law dependence of the zero shear viscosity on molecular weight. Thus star dynamics are much more sensitive to molecular weight that linear polymers and well-entangled stars have substantially higher viscosity than the corresponding linears. The tube model explains

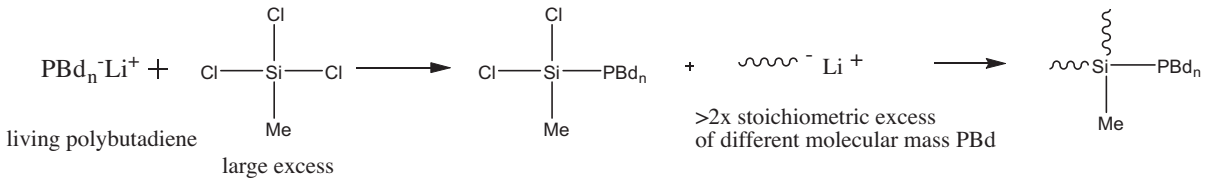

Fig. 6. Formation of an asymmetric 3-armed star. Excess trichloromethylsilane is carefully removed under vacuum before the addition of the second batch of polybutadienyllithium.

these effects by noting that reptation is impossible due to the branch point [20]. The only available relaxation mechanism is deep fluctuations of the chain end towards the branch point. This thermally activated process explains both the exponential dependence of star viscosity on arm length and its insensitivity to the number of arms. Following on from this, 3-armed stars are of special interest. A 3-armed star represents the simplest model for long-chain branching, being equivalent to an otherwise linear polymer chain having one, centrally situated branch. Frischknecht et al. [21] studied the rheology of polyisoprene asymmetric 3-armed stars, where 2 arms remained constant throughout the series of molecules but the length of the 3rd arm varied. The rheological behaviour of these star molecules was much closer to that of a symmetric star polymer than anticipated. A strong enhancement of the viscosity was seen even when the short arm was less than a single entanglement, PBd and HPBd asymmetric stars have been synthesized more recently (Fig. 6) [22]. The stress relaxation was again dependent on the arm retraction time rather than reptation of the whole molecule. The activation energy of flow was also calculated to be much higher than for linear HPBds of a similar molecular mass. For the asymmetric stars, even a relatively short 3rd arm (5000 g/mol) was found to greatly increase the zero shear viscosity and the activation energy of flow [23]. Furthermore, neutron Spin Echo measurements of 3-armed stars with labelled branch points showed that the presence of a short arm (one entanglement length) was sufficient to give it a topological confinement similar to that of a symmetric star [24]. Under non-linear shear, the difference in dynamics between linear and star polymers has recently been shown to narrow, in a way that can be predicted by the tube model [25].

2.2.2. H-polymers, super-H and pom–pom polymers

In terms of complexity of both synthesis and of rheological understanding, H-shaped polymers are the next step towards attaining polymers with multiple long-chain branches. H-polymers are the simplest structure containing a segment between branch points, i.e. with no free ends. An H-polymer can be considered to comprise a linear backbone having two long-chain branches at fixed points along the backbone, equidistant from the linear chain end. This is achieved by using a difunctional initiator from which a "crossbar" is grown having two living chain ends. The chain ends can then be capped using either trichloromethylsilane (H-polymer), tetrachlorosilane (super-H) or chlorosilanes with a functionality greater than four (pom–poms) and then a slight stoichiometric excess (with regards to the Si–Cl functionalities) of polybutadienyllithium can then be added to produce the H or super-H polymer (Fig. 7). Again, polyisoprene H-polymers were the first to be synthesised [26]. Tube modelling predicts that H-polymers should relax in a hierarchical way. First the free arms retract inwards, similarly to stars, with the cross-bar pinned by the branch points. Following on from this, repeated deep-retraction of the arms allow the branch points to move, causing the cross-bar to execute very slow longitudinal diffusion, with the same dynamics as reptation in linear polymers. Indeed, the linear rheological behavior of polyisoprene H-polymers [27] was found to combine aspects of linear polymers i.e. reptation of the entangled cross-bar sections with those of stars, namely high-frequency path-length fluctuations. Start-up of non-linear shear and extensional measurements also show strong shear thinning, shear overshoots and extension hardening, comparable to linear polymers but at much lower deformation rates. Unlike linear polymers, the maximum molecular stretch is set by the degree of branching, and this, in turn, determines the steady-state extensional viscosity in non-linear flow. The synthesis [22] and rheology [23] of HPBd H-polymers, super-H and pom–poms have been reported. These show many of the same rheological features as polyisoprene H-polymers, confirming the applicability of the tube theory to this model branched

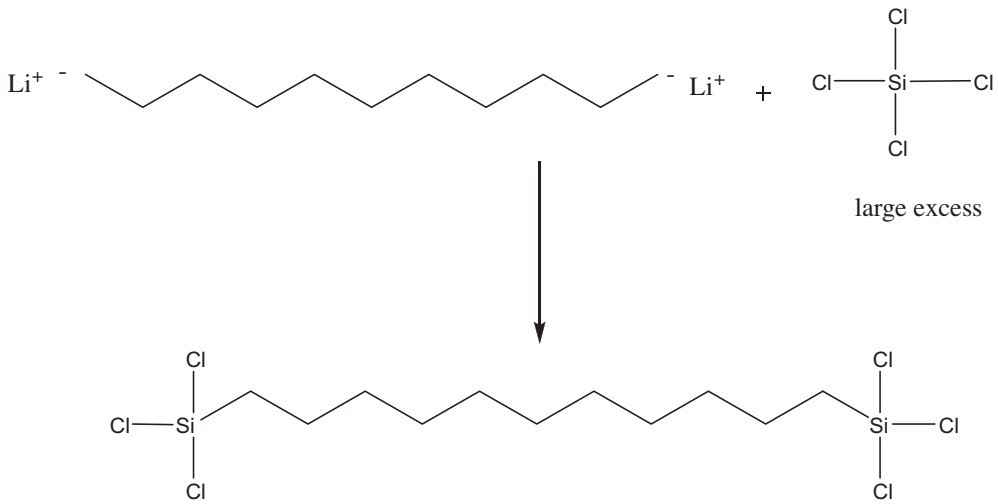

Fig. 7. By using a difunctional initiator to grow a polybutadiene chain with two living ends, the addition of a large excess of tetrachlorosilane results in a species which is capable of forming a "Super-H" polymer when further (monofunctional) polybutadienyllithium chains are added.

polyethylene. As far as we are aware there have been no reports of flow induced crystallisation in these polymers or their blends.

2.2.3. Combs

The first polybutadiene (PBd) combs were successfully synthesized in the Hadjichristidis group [22]. The method takes advantage of the chain microstructure. 1,2-Units dangling pendant from the polybutadiene backbone readily undergo a hydrosilylation reaction when reacted with chlorodimethylsilane in the presence of a platinum catalyst plus an oxygen co-catalyst in a polar solvent. The resultant chlorosilane can then be reacted with an excess of living polybutadienyllithium branches in order to create the comb molecules (Fig. 8). Either Pd on $CaCO_3$ or a Wilkinson's catalyst was used to hydrogenate the combs to the corresponding HPBds. There are several drawbacks with this method. Using a catalytic route in order to obtain a specific and limited number of sites on the backbone is not straightforward, and so some control over the number of long-chain branches is forfeited. The introduction of the catalyst and oxygen and the changing of the solvent have to be performed very carefully because even the smallest trace of water can lead to cross-linking. This method was adapted [9] in order to exert greater control over the number of branches. A limited excess of chlorosilane groups was introduced onto the backbone followed by a stoichiometric amount of polybutadienyllithium branches, the excess reactive groups then being deactivated in a further stage. This strategy allowed a series of polymers with similar backbone mass (60,000 g/mol), a similar number of branches (8) but with varying branch lengths (6000–28,000 g/mol) to be synthesized. The diimine method was employed to fully saturate the double bonds and produce analogues of long-chain branched polyethylenes.

The rheology of HPBd combs (and also the corresponding H and super-H polymers) was reported [23]. The rheological data becomes quite complex as the molecules have a greater range of relaxation times and the additional branch points along the backbone can accentuate the separation of timescales between the star-like arms and the linear-like backbone dynamics. The zero shear viscosity is higher than for comparable linear polymers as is the activation energy of flow. There may be more than one plateau region depending on the number of branches and their length. If the branches are long, then the plateau region

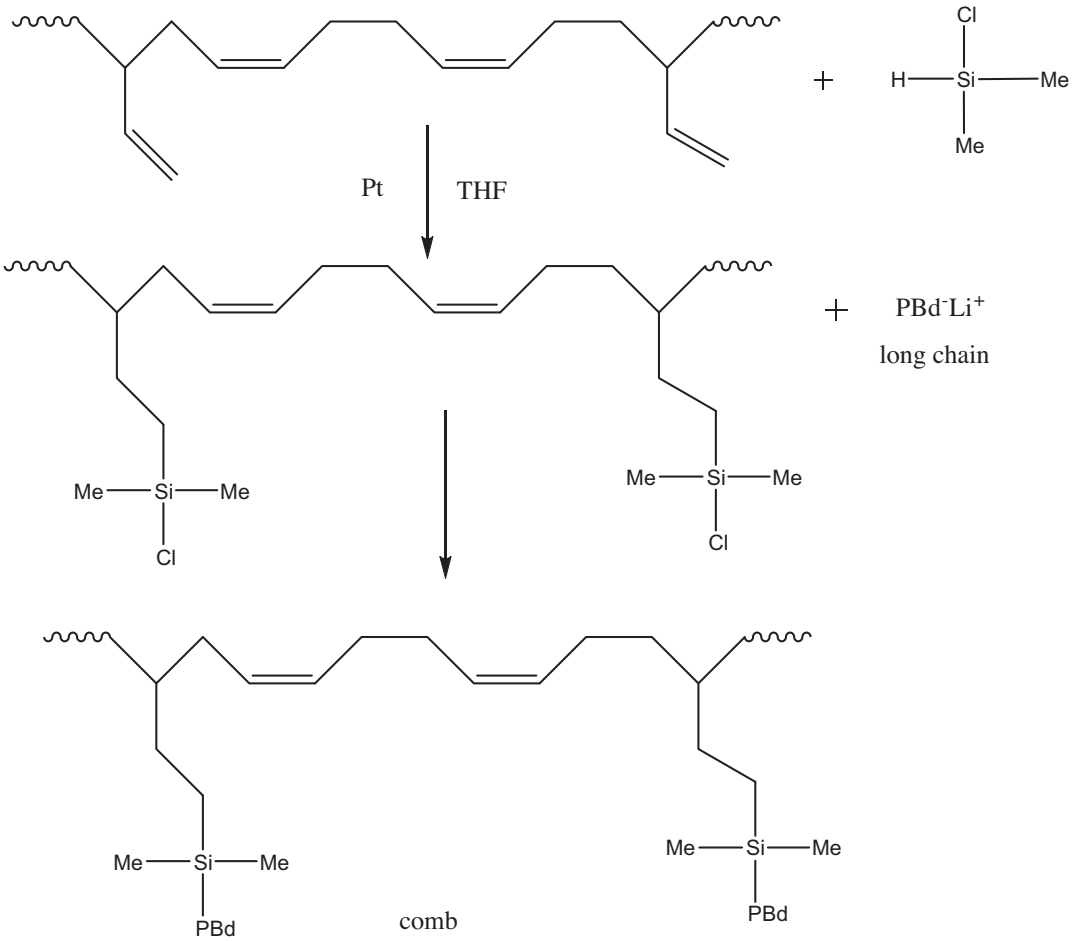

Fig. 8. Scheme briefly showing the formation of comb polymers. Polybutadiene is functionalised using chlorodimethylsilane via a Karstedt catalysed hydrosilylation reaction. The chlorosilane can then be reacted with further polybutadienyllithium chains in a similar way to stars and H/super-H polymers.

covers a relatively wide range of frequencies. The implication is that the length of the branches has more of an effect on the melt dynamics than the number of branches. The inclusion of long-chain branches was shown to promote shear-thinning even for the case of 3-armed stars. Extensional data for comb/linear blends prove that long-chain branching does indeed induce strain hardening, but this occurred only when combs were present and not for stars or linear polymers.

Applying the tube model's hierarchical relaxation scheme to combs, leads to similar dynamics to H-polymers. The free arms fluctuate at early times with star-like relaxation, crossing over to slow backbone reptation, with each branch point providing a large frictional drag. This picture has been formulated into a quantitative model for comb dynamics and validated against linear rheological measurements [28,29]. Successful comparisons with data for HPBd combs has also been made [30].

The disadvantage of the above synthesis strategy is that the branches are randomly placed along the backbone which causes two issues: firstly, there is a distribution in the number of branches per backbone [9] and secondly, the number of entanglements between branch points varies somewhat – a key parameter in the rheology of long-chain branched materials.

There have been some studies of the flow induced crystallisation of combs and their blends with linear polymers. On first inspection there are attractive features of combs in terms of their rheological properties [31]. The Rouse times of the central parts of the comb can be controlled to give a massive separation from the Rouse time of an analogous linear chain. In this way it should be possible to dose small amounts of a comb into a linear material and access long-lived stretched segments that might initiate oriented crystallisation under flow. Experimental studies of showed that combs were effective at initiating crystallisation and that they acted as nucleating agents with a linear effect on the rate of crystallisation with concentration. These studies were not without their difficulties, however, the reasons for which have now become apparent. The high viscosity (and normal forces) induced by the combs caused flow instabilities evidenced by tilting of crystals relative to the flow direction. Polymers with a narrow molecular weight distribution (MWD) are known to show melt-flow instabilities more readily than their broad MWD counterparts [31] and a significant difference between the relaxation times of the long-relaxing combs and the short relaxing linear matrix becomes prominent in these hydrogenated polybutadiene blends. In addition, combs reduce the overall degree of crystallinity making the definition of different flow regimes difficult. The combination of low crystallinity and the molecular distribution of arms blurs the boundaries of crystal orientation. Moreover, the large unoriented pom–pom, that causes the formation of the internal stretched segments, also prevents the stretched segments from approaching each other making them less effective nucleating agents.

There has been recent progress in the synthesis of comb-type materials where the branch points are fixed, their position is known and therefore the number of entanglements between branch points is known. The simplest cases are the H-polymer and super-H polymers. "Centipedes" [32] of polystyrene have been made, although these are relatively polydisperse because the synthetic route involves a condensation reaction between well-defined branched units. "Exact" PBd comb molecules having two or three evenly placed branches have been synthesized recently [33]. The methodology involves coupling together 3-armed stars where the end of one arm is "living" and coupling them together with a chlorosilane or by using 4-(dichloromethylsilyl)-diphenylethylene (DCSDPE). The addition of dichlorodimethylsilane allowed two of these stars to be coupled together to make a polybutadiene H-polymer [34]. The use of this strategy is likely to minimise the inclusion of polymeric impurities [35] but may not be enough to overcome the problems in using combs for studies of crystallisation as discussed above.

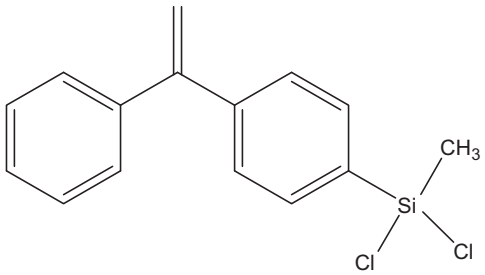

Fig. 9. 4-(Dichloromethylsilyl)-diphenylethylene: not only can the chlorosilane groups be used to introduce polybutadiene branches but the double bond of the diphenylethylene moiety can be used to initiate a further living polymerization, thus providing a building block for the formation of a dendrimac.

2.2.4. Dendrimacs

Dendrimac is a term given to dendritic type materials where macromolecules are used to build up the molecule rather than via the condensation reaction of small molecules. Second and third generation dendritic PBds have been synthesised by Orfanou et al. [36] employing DCSDPE (Fig. 9) as both a linking agent and to provide a double bond from which a further living chain could be grown on the addition of a butyllithium initiator. This method can be compared with that of Kimani and Hutchings [37] which produced a first generation PBd dendrimac via a 3-armed star where one of the branches was bromine-terminated and using a trifunctional hydroxy phenyl compound to couple the stars together via a Williamson-ether synthesis. Linear rheological measurements on dendrimacs are also consistent with the hierarchal relaxation picture. If the individual generations are sufficiently self-entangled then separate peaks in the loss modulus are predicted for each generation and this has been confirmed for 3rd generation dendrimacs [38].

3. An example of application: flow-induced crystallization of semi-crystalline polymers

Synthetic semi-crystalline polymers are ubiquitous in modern society, and worldwide consumption grows year on year. The application of plastics basically relies on the

formation of structural morphology in the processed polymers which significantly expands the range of materials' properties. There are two main morphologies: spherulites (composed of randomly oriented polymer crystals) and shish-kebabs (composed of polymer crystals with a preferred orientation). Despite the general behaviour, structure and properties of polymers being well understood, there has not been, until recently, a simple model of FIC and consequently a robust method of predicting when polymer crystal orientation will occur during processing. Most industrial processing of polyolefins take advantage of the structures introduced by FIC of polymers on an empirical basis. Whilst there is a phenomenological understanding of the polymer orientation under flow conditions there is no consensus on the exact parameters which could be used to control the formation of different structural morphologies. In fact a number of methods have been developed that use secondary flows in moulds to "improve" mechanical properties [39] and good empirical guidelines are available via finite element methods to optimise film blowing.

It is commonly accepted that two groups of parameters control the morphology of polymers during FIC: processing conditions (temperature, pressure, flow rate and duration of flow) and characteristics of the polymer (chemical composition and molecular weight distribution). While the first group of parameters can be adjusted during processing the second group is not easy to control as sometimes it may require a complete change of a synthetic route used. Certainly, if a relationship between these two groups of parameters does exist, this would significantly improve the control of structural morphologies of processed polymers rather than by using a synthetic route.

There is a general consensus that long-chain molecules play a dominating role in the formation of shish-kebab morphology in polymers crystallized under flow conditions [14,40–45]. It is actually a small fraction of long-chain molecules, present as a tail in the molecular weight distribution of industrial polymers (Fig. 10a), that controls the morphology of the polymers during FIC. This conclusion, concerning the effect of long-chain molecules is, however, based on qualitative information about the molecular weight distribution and is not related to the physical characteristics of the molecules present in the ensemble of polymers. It has been pointed out in few studies [42,45] that the relaxation times of the molecules could be one of the parameters related to the formation of oriented (shish-kebab) morphology. Unfortunately, industrial polymers do not allow this relationship to be established as their high polydispersity significantly complicates the task. The molecules present in polydisperse materials have different relaxation times and, therefore, behave differently under flow conditions. Averaged parameters available from rheology measurements [46] do not represent the appropriate characteristics relating to the formation of structural morphology at FIC as only a tiny fraction of molecules (long-chain molecules) control the process.

A number of approaches have been explored to overcome the limitations of poorly defined polydisperse materials: fractionation of polydisperse polymers followed by a preparation of binary blends with a systematic variation of

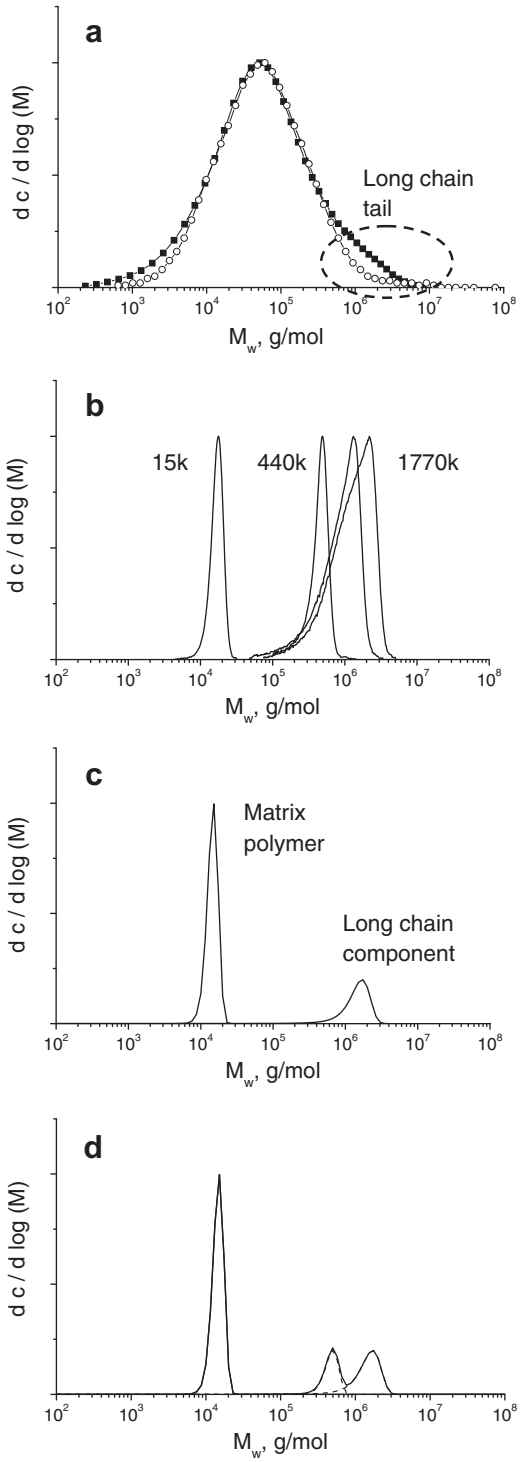

Fig. 10. Molecular weight distribution in different polymer systems: (a) polyethylene of B industrial grades (squares – high-density polyethylene, M_w = 220 kg/mol, M_w/M_n = 14, circles – low-density polyethylene, M_w = 240 kg/mol, M_w/M_n = 14), (b) hydrogenated polybutadiene of low polydispersity synthesised by anionic polymerization (M_w = 15 kg/mol, M_w/M_n = 1.1; M_w = 440 kg/mol, M_w/M_n = 1.2; M_w = 1330 kg/mol, M_w/M_n = 1.4 and M_w = 1770 kg/mol, M_w/M_n = 1.5) and a schematic of polymer blends of controlled polydispersity [bimodal blend, (c) and trimodal blend (d)]. All the curves are normalized to the peak maximum.

concentration of long chains in the blends [14]; making blends of polydisperse polymers with an ultrahigh molecular weight polymer [47]; a single stage catalyst-controlled synthesis of a bimodal polymer with high- and low-molecular-weight fractions [48] or using advantages of anionic polymerization – synthesising polymers of variable molecular weight (from 1 kg/mol to 10,000 kg/mol) with low polydispersity (Fig. 10b) and blending them in the required proportions [15,30]. The latter approach is the most versatile as it offers a wide range of flexibility in formulating a desirable molecular weight distribution in a polymer ensemble with known relaxation times. This enables polymer blends of controlled polydispersity with a wide dynamic range of relaxation times to be produced starting from the most simple variant of mixing long linear chains in a matrix of short chains (bimodal blends) of variable concentration and molecular weight simulating the effect of long-chain molecules (Fig. 10c) [15]. More elaborate blends such as trimodal blends (Fig. 10d) and multimodal blends can also be made to directly compare with industrial materials in terms of molecular weight distribution. The fact that variable molecular architectures can be synthesised via an anionic polymerization route expands its application towards an opportunity to establish the effect of molecular architectures and not only molecular weights on the structural morphology [30], e.g. branched polymers.

3.1. A model for the formation of flow-induced structural morphologies

The mechanism of formation of the shish-kebab morphology has continued to be a matter for discussion ever since it was first reported and the initial attempts to understand the underlying processes of polymer crystallization from an oriented state were made [49–52]. Subsequent studies based on the results of nucleation kinetics under flow conditions have led to a number of models based on scattering, birefringence and microscopy results [14,53–56]. Recent quantitative measurements of FIC using bimodal linear–linear blends enabled the four stages in shish-kebab formation under flow conditions to be distinguished: stretching (stage 1), nucleation (stage 2), alignment (stage 3) and fibrillation (stage 4) (Fig. 11a) [57]. There is no fundamental difference between the influence of mechanical work put into the sample either by shear flow or by extensional flow [58]. Since most data are based on shear-induced crystallization (SIC), the general term – FIC is avoided in the following text.

3.1.1. Stretching

Flow has two main effects on the structural behaviour of the polymer molecules: (1) orientation of the primitive path of the molecules along the flow direction and (2) stretching of the molecular segments along the flow at higher shear rates. While the orientation is controlled by moderate shear rates, $\dot{\gamma}$, described by disengagement time of the molecules, τ_d where $\dot{\gamma} > 1/\tau_d$, stretching is caused at higher shear rates corresponding to Rouse relaxation time of the molecules, τ_R (where $\dot{\gamma} > 1/\tau_R > 1/\tau_d$). The first observations of the shish-kebab structure led to the hypothesis that stretching of the molecules under flow conditions plays an important role in the formation of this morphology [54]. A few decades later a systematic review of the data on FIC of polymers accumulated during this period has supported the idea of stretching [43]. Finally, this hypothesis has been confirmed by direct experimental measurements using linear–linear hydrogenated polybutadiene blends of controlled polydispersity, where a direct correlation between the Rouse time of long-chain molecules, the parameter describing stretching, and threshold

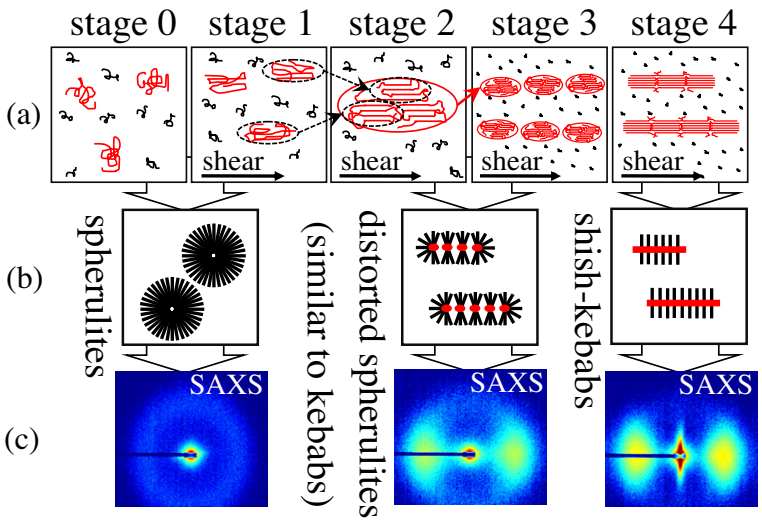

Fig. 11. A schematic diagram of the formation of shear-induced structural morphologies in polymers: a four-stage model of shish formation in the polymer melt under shear conditions combined of stretching of long-chain molecules (stage 1), nucleation (stage 2), alignment of shish nuclei (stage 3) and fibrillation (stage 4) (a); structural morphologies formed in the polymer after crystallization at different stages of the shish formation (b) and their small-angle X-ray scattering patterns (SAXS), obtained from samples after shear-induced crystallization at station ID2, ESRF, Grenoble (c). Stage 0 represents the polymer melt at quiescent conditions. The entanglements of the molecules have not been shown for clarity.

conditions for the formation of oriented shish-kebab morphology has been demonstrated [15]. These results suggest that it is not enough just to orient the molecules along the flow to create a shish morphology, stretching has also to be induced in the molecules to form the shish. Thus, stretching should be considered as the first step in the formation of shish morphology (Fig. 11a, stage 1). If, however, the molecules were to be stretched by a very short shear pulse of a duration comparable with the Rouse relaxation time of the molecules, then the molecules would relax into their original state, similar to quiescent conditions, with no signs of irreversible structural transformations. If the polymer were to be crystallized after this event a spherulitic morphology would be formed (Fig. 11b) producing a characteristic ring in a SAXS pattern (Fig. 11c) corresponding to a periodical lamellar structure with a random orientation. Thus, stretching is a necessary condition, but not a sufficient condition, for the formation of shish-kebab morphology.

3.1.2. Nucleation

Since the shish is a crystalline phase [47,59], its formation should be initiated by the formation of crystal nuclei. It has been demonstrated in a set of previous studies on shear-induced crystallization that flow can induce nucleation in polymer melts [53,60]. In accordance with classical nucleation theory [61] a stable nucleus is formed when its volume free energy exceeds its surface free energy by the value of volumetric free energy difference between the liquid and crystalline phase (ΔG). The latter is considered to be as an energy barrier which must be overcome in order for the nuclei to become stable. Under quiescent conditions $\Delta G = \Delta G_q$ is a temperature-dependent parameter, however, the polymer melt under flow conditions is supplied with additional energy which should be counted in the energy balance of the system. The effect of flow on the polymer melt can be described via an extra term (ΔG_f): $\Delta G = \Delta G_q + \Delta G_f$ [46]. This term reduces the energy barrier required for the nuclei to be stable and, therefore, increases the nucleation rate under certain thermodynamic conditions. Phenomenologically, the process of nucleation under flow conditions can be described as the following: the flow stretches polymer segments introducing conformational order into the polymer chains and also delivers one stretched segment to another until they collide and form an aggregate of stretched segments which is larger than the critical size of a stable nucleus (Fig. 11a, stage 2). These nuclei can be considered as point nuclei; however, some anisotropy should be present as they have been formed under directional conditions created by flow [62]. It would be useful to call these species shish nuclei to make them distinguishable from the general term of point nuclei used in scientific literature.

The number of stretched segments required for the formation of shish nuclei is controlled by both the critical size of the stable nucleus, which can be defined by the classical theory of nucleation [53,61], and the length of stretched segments. The latter parameter should be proportional to both the molecular weight distribution of the polymer (in particular, to the molecular weight of long chains in bimodal linear HPBd blends) and to the flow rate applied to the polymer. The number of collisions of the stretched segments during the flow controls the formation of stable shish nuclei. This is a probabilistic process, dependent on both the time of shearing (strain) and the concentration of stretched segments in the polymer ensemble. The stretched segments have to come into proximity in order to collide and, therefore, the relative distance between them should be changing (fluctuating). The changes in shape of the long-chain molecules that happen under flow conditions allow the distance between these molecules to be sufficiently small so collisions between stretched segments occur. It can be estimated that at an overlap concentration of 1770 kg/mol long-chain molecules in a bimodal linear HPBd blend (1 wt.%) fluctuations of only a radius of gyration of the molecules would be required to cause collisions of two neighbouring molecules (and, therefore, collisions of the stretched segments). However, this estimation does not exclude from consideration the possibility that the two stretched segments belong to one molecule.

The moment when the size of aggregates of stretched segments reaches the critical size of a stable nucleus should be considered as the nucleation stage (stage 2). At this stage the flow has had an irreversible effect on the polymer and after the cessation of the flow the polymer melt does not totally relax back to its original quiescent conditions as some molecules remain as crystal nuclei (unless the temperature of the melt is increased).

3.1.3. Alignment

It has to be pointed out that the effect of the flow cannot be excluded from further consideration after the shish nuclei have been formed. There is a phase boundary between the melt and the nuclei making the nuclei act as a particle surrounded by viscoelastic liquid and there have been a number of studies on the behaviour of particles in viscoelastic liquids under flow conditions that illuminate our discussion here. Adding particles to a non-linear viscoelastic fluid, such as a polymer, can considerably increase the rheological complexity of the system [63] as exemplified by particle aggregation and flow-induced alignment [64]. It was suggested in earlier studies that the alignment of the particles occurred at high shear rates such that the Weissenberg number, that is the ratio of the first normal stress difference over the shear stress, exceeded a critical value [64]. However, later studies based on quantitative measurements by small-angle light scattering suggested that the Weissenberg number is not a sufficient condition and to a first approximation the particle alignment can be strain-controlled [65]. Although, the particle alignment is not fully understood, these observations indicate that a similar effect could occur with shear-induced nuclei after their formation in the polymer melt (Fig. 11a, stage 3).

That alignment does indeed occur is supported by recent rheology measurements on shear-induced crystallization [66], which suggests that point nuclei form first and then, after reaching a saturation point, transform into another morphology corresponding to one dimensional (fibrillar) structure. Thus, following their initial formation, point nuclei require some time (strain) to align and aggregate further into a fibrillar morphology. The existence of, and differentiation between, these separate stages can also

be identified in the cross-section of solidified samples after shear-induced crystallization using a slot flow [67]. Since this geometry produces a range of shear rates across sheared samples (from wall to wall of the duct), the polymer melt experiences different flow conditions. Three distinctive layers separated by clear boundaries can be observed in these samples (Fig. 12): a spherulitic core in the centre of the sample corresponding to small shear rates followed by a transitional fine grained layer (shish nuclei) at moderate shear rates and, finally, a highly oriented layer (fibrillar morphology) at high shear rates. Thus, there is a transitional stage before the formation of fibrils (shishes) during flow.

Another substantive argument towards the stage of alignment prior to the formation of the fibrillar (shish) morphology comes from SAXS observations. Three types of scattering patterns could be registered for polymers after shear-induced crystallization (Fig. 11c): a diffraction ring indicating spherulitic morphology, two strong reflections indicating oriented lamellar stacks with the layer normal parallel to the flow and a pattern corresponding to shish-kebab morphology with a streak perpendicular to the flow direction and two oriented reflections corresponding to kebabs with layer normal parallel to the flow direction. The second type of SAXS patterns, demonstrating oriented structure, is observed in polymers after FIC at moderate flow conditions prior to the conditions when the shish-kebab morphology is formed [30,68,69]. This observation suggests that some kind of structural orientation occurs in the sheared polymers before the formation of shish morphology. The phenomenon of nuclei alignment enables the appearance of this orientation to be interpreted. In analogy with particle suspensions in viscoelastic liquids, shish nuclei, after their formation in the polymer melt, align along the flow direction forming rows of shish nuclei. After the cessation of the flow, at this stage of shearing, the aligned shish nuclei initiate secondary nucleation followed by crystal growth during crystallization. Since the crystals begin growing simultaneously along the whole row of shish nuclei, the neighbouring crystals impinge on each other from the very beginning of crystallization causing directional growth of the lamellar stacks thus producing distorted spherulites similar to kebabs (Fig. 11b). It has to be pointed out that the concentration of shish nuclei induced by flow at this stage is low [70], and/or that the shish nuclei rows are very small, and thus undetectable during the flow by means of commonly-used techniques (optical methods, rheology or structural methods such as X-ray scattering). Therefore, even if on-line SAXS measurements do not register any structural organization during the flow, the oriented morphology is detectable after the cessation of flow as the growing crystals of bulk material inherit the structural morphology of the aligned shish nuclei during the crystallization process. This structure generates SAXS patterns of the second type (Fig. 11c). The shish nuclei act in a homeopathic manner, that is leaving their imprint on the fluid whist being essentially undetectable.

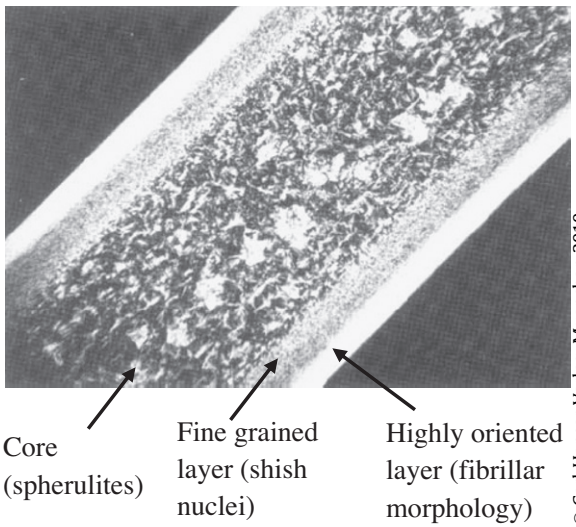

Fig. 12. A micrograph of a cross-section through a quenched sample of an industrial polypropylene after short term extrusion at 150 °C through a long duct of large aspect ratio. Shear rate at the large side wall was 68 s^{-1} for 17.6 s. From [67]

It has to be noted that the transition from stage 2 to 3 is rather tentative. Straight after the formation of the first shish nuclei in the polymer melt these nuclei tend to align under flow conditions and, therefore, stages 2 and 3 coexist together in the sheared material. Thus, time intervals of the two stages overlap and their effect on the crystallized material should be considered together (Fig. 11b). However, stage 3 occurs as a consequence of stage 2 and unless stage 2 happens, stage 3 cannot exist.

3.1.4. Fibrillation

If the shearing continues then the rows of aligned nuclei, in analogy with the suspension of particles in viscoelastic liquids [65], should accumulate into larger aggregates with the growing concentration of shish nuclei. This aggregation causes reduction of the free surface of separated nuclei making the aggregates energetically more favourable in comparison with rows of separated shish nuclei. While the particles in viscoelastic liquids after aggregation remain as separated objects, the phase boundary between aggregated shish nuclei should disappear, transforming the aggregates into single elongated objects corresponding to the formation of a fibrillar (shish) morphology (Fig. 11a, stage 4). Since the cross-section of the fibrils is larger than the shish nuclei and the total concentration of crystalline material is growing during shear, the formation of fibrillar morphology can be easily detected on-line by increasing birefringence [14,53,71] and/or by an arising streak oriented parallel to the flow in SAXS patterns [47,57,59]. It can be noted that the formation of elongated objects such as fibrils should significantly affect the rheological properties of the polymer melt [31]. A clear boundary observed between the fine grained layer (aligned shish nuclei) and the layer corresponding to highly oriented fibrillar morphology in the polymers after shear-induced crystallization in a slot flow is probably associated with a sudden change of rheological properties of the polymer melt when the fibrils (shishes) are formed [55].

After the cessation of the flow, the formed fibrils (shishes) work as nucleating agents for the rest of polymer melt

causing crystallization of kebabs (Fig. 11b). The final shish-kebab morphology can be identified by a SAXS pattern composed of two features: a streak perpendicular to the flow direction associated with the shishes and two reflections corresponding to lamellae with the layer normal parallel to the flow – kebabs (Fig. 11c) and all three of these generic SAXS patterns can be observed if an X-ray beam is scanned across the vorticity direction in a slot flow.

3.2. Mapping SIC

Following the discussion of the model for the formation of oriented structures two parameters have to be identified as responsible for the formation of the morphology indicated by stages 1 and 2 (together with stage 3) describing the stretching of the molecules and the formation of stable shish nuclei, respectively. The first parameter is associated with the Rouse time of the molecules and can be described as the minimum shear rate required for the molecules to be in a stretched state under flow conditions. This is the necessary condition for the formation of shish nuclei. Assuming that $De = \tau_R\dot{\gamma} = 1$, where De is the Deborah number [43], the minimum shear rate required for the stretching can be estimated as $\dot{\gamma}_{\min} = 1/\tau_R$. The second parameter describes the formation of stable shish nuclei. In accordance with the general concept of crystallization proposed by Willard Gibbs [72] the stability of a phase is related to the work that has to be done in order to create a critical nucleus of the new phase. Thus, the second parameter should be associated with the amount of work performed by the flow on the polymer system to build the nuclei from stretched segments of the molecules and stabilize the nuclei under certain thermodynamic conditions. It has been demonstrated that the number of nuclei increase tremendously with the amount of mechanical work applied to the system [60,70], which can be expressed as a mechanical specific work $w = \int_0^{t_s} \eta[\dot{\gamma}(t)]\dot{\gamma}^2(t)dt$, where $\eta[\dot{\gamma}(t)]$ is the viscosity and $\dot{\gamma}(t)$ is the shear rate profile experienced by the polymer during shearing. If the shear rate is constant with time then the formula can be rewritten in a more simple version $w = \eta(\dot{\gamma})\dot{\gamma}^2 t_s$ [57].

The formation of oriented morphology (stage 3) occurs straight after the formation of shish nuclei indicated by stage 2 (Fig. 11a). Coexistence of these two stages during flow makes them indistinguishable from each other. It can be assumed that the orientation can be detected straight after the formation of point nuclei and, therefore, the work parameter can also be associated with the threshold conditions for the initial orientation. In this respect it is worth analysing the formation of shish precursors, where it has been suggested that long lasting deformations under low stresses can yield the same precursors as short term deformations under high loads. Different experimental conditions (high rate or long time) can apply the same specific work and this has been used as the universal parameter to describe the formation of shish precursors [56]. This conclusion has found direct confirmation in the measurements of specific work for the onset of oriented morphology in the shear-induced polymer melts [15]. The measurements of the flow parameters for the onset of oriented morphology after shear-induced crystallization enable a diagram of parameters responsible for the formation of oriented morphology to be assembled (Fig. 13) where the shear rate associated with the onset of orientation, $\dot{\gamma}_b(t)$, is plotted versus corresponding specific work $w_b = \int_0^{t_s} \eta[\dot{\gamma}_b(t)]\dot{\gamma}_b^2(t)dt$. This diagram has shown that two parameters can be used to describe the conditions for the formation of oriented morphology: the minimum shear rate associated with the reciprocal Rouse time of the long chains present in the polymer ensemble, $\dot{\gamma}_{\min}$, and the critical specific work, w_c, which is constant at shear rates $\dot{\gamma} > \dot{\gamma}_{\min}$. These two parameters can be used to calculate flow conditions, profile of shear or extensional flow rate and time of shearing under particular thermodynamic conditions (temperature and pressure) for the formation of oriented morphology in polymers under flow. This approach has been successfully applied in the analysis of FIC in geometries resembling elements of industrial polymer processing [73].

The diagram obtained for the bimodal polymer blends shows a clear threshold at a minimum shear rate below which the formation of oriented morphology is unlikely and the specific work tends to be infinite (Fig. 13a). The

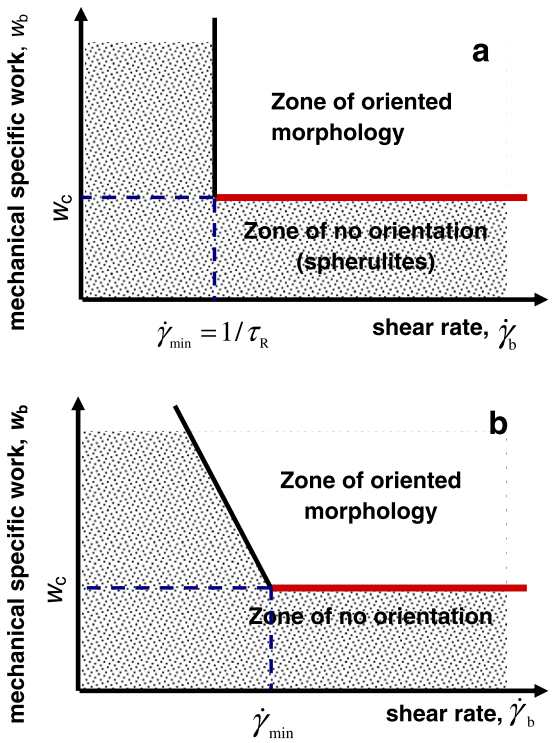

Fig. 13. Schematic diagrams of threshold conditions for the formation of oriented morphology in the melts of bimodal polymer blends of long-chain molecules in a short-chain matrix (a) and polydisperse polymers (b) under flow conditions. The solid line dividing the diagram into two zones (a zone of orientation and a zone of no orientation) corresponds to a plot of the boundary specific work required for the formation of aligned shish nuclei (stages 2 and 3 in Fig. 11), w_b, as a function of the boundary shear flow rate, $\dot{\gamma}_b$. The critical specific work, w_c, indicates the minimum amount of the specific work required for the formation of oriented nuclei at the chosen thermodynamic parameters. The minimum shear rate $\dot{\gamma}_{\min}$ indicates the flow rate below which the concentration of molecules in a stretched state decreases.

line of critical specific work should be associated with stage 2 (and stage 3) when the shish nuclei are formed. The oriented morphology caused by these nuclei, oriented along the flow direction, can be detected after crystallization. When the amount of work experienced by the polymer melt increases, the shish nuclei become more numerous and the degree of orientation of the crystallized structure increases [15,57]. At this point, stage 3 approaches stage 4 (Fig. 11a) as the high concentration of nuclei oriented in rows along the flow direction transform into fibrillar (shish) morphology and the shish can be detected during the shear flow by the observation of meridional streak in SAXS (Fig. 11c) and/or by the irreversible increase of birefringence of the sheared polymer melt [14,53,71].

Polymers of broad polydispersity exhibit SIC behaviour similar to the model blends of controlled polydispersity (Fig. 13b) [57]. There is the same constant plateau of critical specific work within the wide range of shear rates; however, the threshold for the minimum shear rate is not as well defined as for the model blends. It is still possible to identify a minimum shear rate below which the specific work required for the formation of oriented morphology is not constant. The increase of the specific work at $\dot{\gamma} < \dot{\gamma}_{\min}$ is associated with the fact that the polydisperse system has a broad and continuous molecular weight distribution and there will always be some polymers long enough to initiate shish nuclei formation even at vanishingly small shear rates. Since only longer molecules, characterized by longer relaxation times, can be stretched at lower shear rates, the increase of the specific work at shear rates below $\dot{\gamma}_{\min}$ is associated with the concentration of long-chain molecules available in the polymer ensemble for the stable nuclei formation. This increase in the work required should be related to the molecular weight distribution of the polymer. The minimum shear rate for polydisperse systems cannot be related to a Rouse time of particular molecules like in the bimodal blends, and should rather be considered as an averaged number of the ensemble of molecules present in the polymer.

3.3. Molecular structure property relations

The correlation between minimum shear rate and Rouse time observed in the bimodal blends of HPBd [15] suggests that $\dot{\gamma}_{\min}$ can be predicted for different thermodynamic conditions using relaxation times of the molecules calculated from rheological data (Fig. 14). The relaxation times of low-polydisperse hydrogenated polybutadiene in this study were calculated by the linear theory [74]. The fitting parameters were the Rouse time of a single entanglement segment, τ_e, the molecular weight between entanglements, M_e, and the plateau modulus, G_0^N. τ_e and M_e are both dependent on the specific chemistry of the polymer but not on its molecular weight. For hydrogenated polybutadiene the values obtained for τ_e and M_e are 3.137×10^{-8} s and 1.27 kg/mol, respectively. It is assumed the constraint release parameter $c_v = 0.1$. The Rouse time, τ_R, and reptation time, τ_d, were calculated by the following equations: $\tau_R = Z^2\tau_e$ and $\tau_d = 3Z^3\tau_e(1 - 3.38/\sqrt{Z} + 4.17/Z - 1.55/Z^{3/2})$, where $Z = M_w/M_e$ is the number of entanglements. The relaxation times at different temperatures were calculated by using time–temperature shift WLF parameters: $C_1 = 2.0$, $C_2 = 77$ °C and $T_{ref} = 115$ °C, which are similar to previously reported data [30,75].

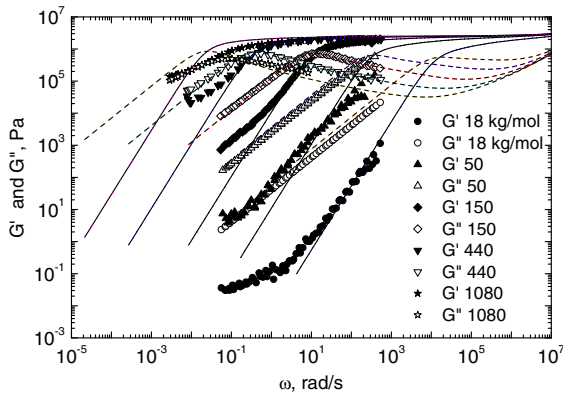

Fig. 14. Master curves of rheology data (storage modulus, G', and a loss modulus, G'', shifted to 115 °C) of a series of low-polydisperse linear hydrogenated polybutadienes (molecular weights, M_w, are indicated on the plot). Lines and dashed lines corresponding to G' and G'', respectively, represent a result of fitting by the Linear theory (Likhtman [74]).

The Rouse time demonstrates a strong dependence on molecular weight with a moderate decrease with increasing temperature (Fig. 15). It can be found that 15 kg/mol HPBd chosen as a matrix polymer for bimodal blends [15] has a very short relaxation time (<10^{-5} s) and, therefore, can be in a stretched state only at shear rates unachievable in most processes, especially those based on rheometric measurements. It is assumed that Rouse times do not change on blending because the local frictional drag experienced by a chain is unlikely to differ under these conditions. Indeed, measurements on shear-induced crystallization of polymer ensembles composed of these low molecular weight (15 kg/mol linear HPBd) polymers and their bimodal blends with intermediate molecular weight (50 and 150 kg/mol) linear HPBd did

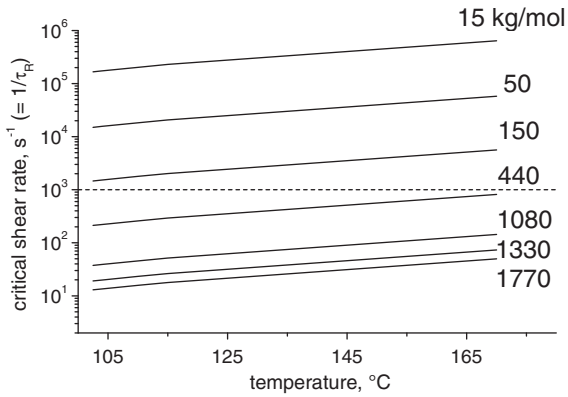

Fig. 15. Temperature dependence of reciprocal Rouse time ($\dot{\gamma}_{\min} = 1/\tau_R$) for linear hydrogenated polybutadiene of different molecular weights (indicated on the plot). The dashed line corresponds to $\dot{\gamma}_{\min} = 1000\ s^{-1}$ to indicate the limit of mechanical instruments.

not show any sign of orientation within a range of shear rates usually produced by mechanical instruments <1000 s^{-1} (Fig. 15) in the temperature range above temperature of crystallization of spherulites (around 100 °C). The first signs of orientation within this range of shear rates have been observed only for a bimodal blend with a higher molecular weight component of 440 kg/mol at 110 °C using a shear rate 400 s^{-1}. This number is consistent with the Rouse time for these molecules measured from rheology data (Fig. 15), $\dot{\gamma}_{min}$ = 1/0.0039 s = 256 s^{-1}. A further increase of the molecular weight of the long chains leads to a decrease of $\dot{\gamma}_{min}$ required for the formation of oriented morphology. It was found that 1770 kg/mol in 15 kg/mol matrix has $\dot{\gamma}_{min}$ = 16 s^{-1} [15] which is consistent with values estimated from rheology data (= $1/\tau_R$ = 18 s^{-1}). A reasonable correlation of $\dot{\gamma}_{min}$ with relaxation times has been found also for industrial polymers [57].

The data on the critical specific work accumulated for polymer blends of controlled polydispersity and industrial materials show that this parameter is dependent on temperature and molecular weight distribution and may also depend on the chemical composition of the polymer chains (Figs. 16–18). There is not enough data yet to express this dependence analytically; however, a qualitative analysis can be carried out. The bimodal blends of HPBd show that an increase of molecular weight of the long chains in the short-chain matrix at the same concentration significantly reduces the amount of specific work required for the formation of an oriented morphology (Fig. 16). For example, a slight decrease in M_w of the long-chain molecules from 1770 to 1330 g/mol caused a fivefold increase of w_c at the same temperature. Another tendency observable in these data is that w_c increases with temperature. For example, a 1080 kg/mol HPBd blend demonstrates nearly an order of magnitude difference between w_c required for the formation of oriented morphology at 110 and 112 °C. Similar indications have been found for other blends studied: in Fig. 16 the curves drawn to guide the eye show the temperature above which the orientation could not be achieved within the range of specific work values presented in the plot. It could be that the extreme temperature dependence observed is a convolution of thermodynamics, kinetics and molecular weight distribution.

The observed molecular weight dependence of w_c is also reasonable. The molecular weight dependence shows that the smaller the molecular weight the more time is required to form stable nuclei during shear. In accordance with the classical theory of nucleation the size of the nucleus is responsible for its stability. For a given set of thermodynamic conditions the same critical size is required for the formation of stable nuclei, but the number of molecules required to fill the volume of the stable nucleus, will increase with a reduction in molecular weight (controlling

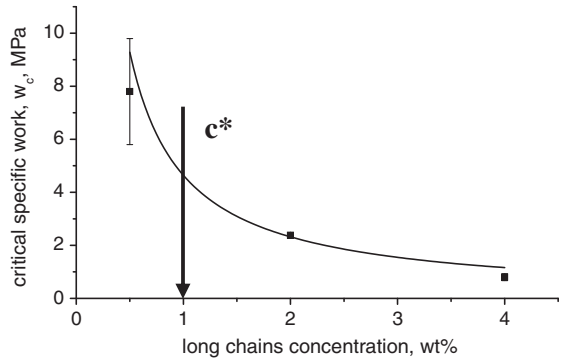

Fig. 17. Critical specific work for linear–linear HPBd blends with different concentration of long chains (1770 kg/mol) in 15 kg/mol matrix (squares) fitted with hyperbola $w_c = k/c$, where c is a concentration of long-chain molecules in the blend and k is a fitting parameter (solid line). c^* indicates overlap concentration of long-chain molecules.

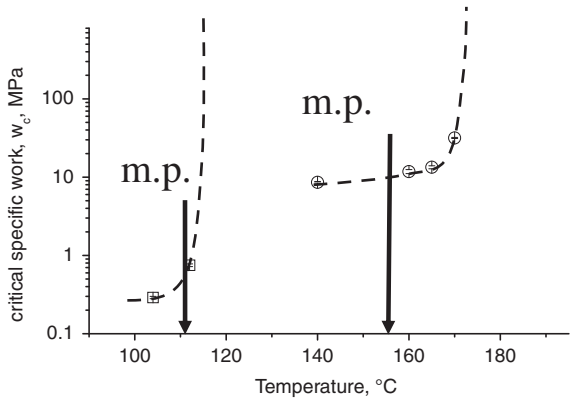

Fig. 18. Critical specific work for the formation of oriented morphology in polymers of industrial grade (square – LDPE, M_w = 240 kg/mol, M_w/M_n = 14 and circles – propylene–ethylene random copolymer, M_w = 250 kg/mol, M_w/M_n = 6). Dashed curves, demonstrating temperature dependence of the specific work for the blends, are given for guidance. Melting points of spherulites (end of melting point, m.p.) are indicated.

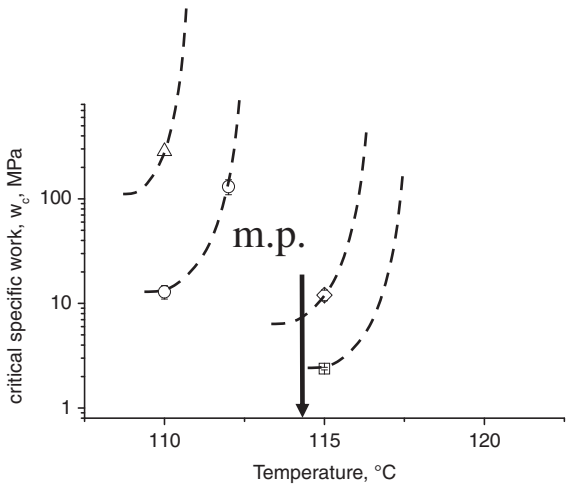

Fig. 16. Critical specific work for the formation of oriented morphology in linear–linear HPBd bimodal blends of 2 wt.% long-chain molecules in 15 kg/mol matrix (triangle – 440 kg/mol, circles – 1080 kg/mol, diamond – 1330 kg/mol and square – 1770 kg/mol. Dashed curves, demonstrating temperature dependence of the specific work for the blends, are given for guidance. The curves have an asymptotic behaviour on their high temperature side. Melting point of spherulites (end of melting point, m.p.) is indicated.

the radius of gyration). Thus, the smaller the molecules, the more are required to collide together during shear to aggregate into a nucleus of critical size because the probability of stretched segment collisions under flow conditions should be dependent on molecular weight. This increases the number of collisions required for the formation of oriented morphology and, therefore, at the same concentration of the long-chain molecules in the short-chain matrix it should increase time of shearing (and subsequently the critical specific work) required for the formation of oriented morphology. Conversely, the larger the molecular weight of the long-chain molecules in the short-chain matrix the fewer collisions of the molecules would be required to form a stable nuclei. Similar considerations can be drawn for the concentration of the long-chain molecules in the bimodal blend (Fig. 17). The increase of these molecules, directly related to the concentration of stretched segments, causes an increase in the number of collisions per unit time of shearing and, therefore, increases the probability of the formation of the shish nuclei and a decrease in the time of shearing (critical specific work). The reciprocal relation between the concentration and the critical specific work can be used as a first approximation (Fig. 17).

The temperature dependence of w_c should also be expected. The higher the temperature, the larger the critical size of the stable nucleus. Thus, at the same concentration of the long-chain molecules more collisions of stretched segments would be required at higher temperatures to form a stable nucleus. Since this process is dependent on probability, it will again increase the time of shearing and, therefore, the critical specific work required for the formation of oriented morphology. The critical specific work shows a strong dependence on temperature, especially at a range of temperatures close to or above the melting of spherulites i.e. high temperatures.

There is a dramatic increase of w_c required to produce oriented nuclei at a certain temperature (when the orientation could not be achieved within a reasonable time of shearing) associated with the molecular weight of the long chains present in the bimodal blends. The measurements of w_c shows that shish nuclei can be formed at temperatures above the melting point of spherulites. This suggests that the structural organization of shish nuclei is thermally more stable than spherulites. This effect has been reported in other studies [47,59] and the thermodynamic background for this phenomenon has been demonstrated more than a decade ago [76]. Since shish nuclei are formed by stretched segments introducing conformational order in polymer chain leading to a higher degree of crystallinity than spherulites, shish nuclei can be located between spherulites and an ideal crystal on a T–S diagram. Using a temperature-entropy diagram it was suggested that at least three temperature intervals have to be considered to describe thermal stability of polymer morphologies: temperatures above the equilibrium melting point when no crystals (including ideal crystals of 100% of crystallinity) can be formed, the temperature interval below the melting point of spherulites when sporadic nucleation can happen in the polymer melt and temperatures between the equilibrium melting point and the melting point of spherulites. The very nature of the formation of shish nuclei means that they can be stable at the latter temperature interval.

The molecular weight dependence of w_c in industrial polymers is masked by the polydispersity of the materials and, therefore, cannot be directly demonstrated. However, the temperature dependence of w_c is quite similar to the results observed for bimodal polymer blends of controlled polydispersity (Fig. 18).

4. Conclusions

Model polymers formed by anionic polymerization bring benefits of well controlled polydispersity and tailored polymer architecture and have been particularly useful in elucidating our understanding of polymer rheology and hence flow induced crystallisation. The pioneering work of Hadjichristidis [4,22,23,32,33,36,38,77,78] in this area allowed the molecular theories of polymer rheology to be refined and tested against a well defined set of materials, both linear and branched. One of the outputs of these models is the stretch relaxation or Rouse time. A logical extension of the theoretical understanding led to the design of materials and methods to test the effect of flow on crystallisation. Branched polymer show the strongest stretching effects at the lowest strains and strain rates and led to experiments designed to quantify FIC. Whilst these elegant materials clearly showed the qualitative effects, experimental problems led to quantification being elusive. The combination of model polymers and theoretical prediction lead to the identification of linear–linear blends being the system of choice. A clear set of parameters for flow induced crystallisation, based on the concept of minimum shear rate and critical work, result in a model that unifies the observed phenomena and can be used as a framework for understanding the behaviour of industrial materials.

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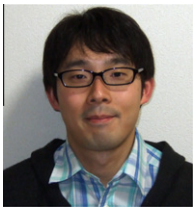

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