Organogelators and Polymer Crystallisation

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Summary: The specific impact of low molecular weight organic gels on polymer crystallisation is examined. Conventional nucleating agents (NA) influence the polyolefins crystallisation and improve their mechanical properties, via an epitaxial mechanism. In the particular case where the pair NA/polymer form a gel at intermediate temperatures on cooling, optical properties (clarity) are significantly improved. This improvement is linked with the ability of organic gels to develop 3-D fibrillar network. The fibres morphology offers a large specific area, thus produces a high density of nuclei, homogeneously dispersed. Gelling organic molecules are certainly a promising route towards the design of efficient additives in polymer processing.

Keywords: crystallization; DBS; DSC; gels; nucleating agents; polymer; TEM

Introduction

Polymer crystallisation is a phase transition that involves two successive steps: nucleation and growth of the crystals. The nucleation can be homogeneous or heterogeneous. The linear growth rate (G) as well as the onset of heterogeneous crystallisation depends on the nature of the polymer chain and on the degree of supercooling. For a given polymer at a given temperature, G cannot be significantly modified. On the contrary, heterogeneous nucleation can be notably altered. Two fundamentally different procedures have been devised to enhance the nucleation density (number of nuclei per unit volume).

The first procedure, self-seeding[1] takes advantage of the intrinsic polydispersity of polymers [large domain of melting temperatures]. The polymer crystals are nearly but not completely molten, the more stable remaining crystal residues (thus the thickest and more perfect lamellae) are used as seeds (nuclei) in a subsequent cooling. The second procedure, induced heterogeneous nucleation, consists in adding a controlled quantity (normally less than 1%) of a foreign substance suitable as a crystallisation substrate called nucleating agent (NA). NAs have been known since the middle of the last century[2,3] but their mode of action via epitaxial crystallisation was recognised only later.[4]

Both nucleating procedures result in a reduction of the spherulite average size. However, certain NAs may also favour the growth of a metastable phase.[5,6] Optimal self-seeding produces spherulite sizes up two orders of magnitude smaller than those obtained for the best NAs.

In practice, this size reduction has diverse and important effects. For isothermal crystallisation, the half-crystallisation time is reduced, for non-isothermal crystallisation (as in a DSC cooling run) the crystallisation temperature is increased, and thus industrial processes are accelerated.

Mechanical and optical properties of thermoplastics strongly depend on the spherulite size.[6] Small spherulites improve flexural modulus, rigidity, heat distortion temperatures while, at the same time, impact properties deteriorate in general. The optical properties benefit also from the size reduction, haze is reduced and clarity improved. In practice, the aim is to produce transparent films of semi-crystalline polymers.

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Here, the conventional NA, the means to investigate and evaluate their influence on polymer crystallisation, the benefits linked to gelling agents named clarifying agents (CA) are presented. We show that looking for gelling additives is a clever route to design new polymer additives of any type (anti-oxidant, anti-acids, light stabilizer, processing stabilizer etc.); indeed, NA are only one group of the many additives introduced in industrial polymer processing.

Conventional Nucleating Agents

The very first works, mentioned above,[2,3] aimed at understanding the mechanism at the root of the efficacy of the thousands of NA that had been discovered empirically. For this purpose, polyethylene (PE) and isotactic polypropylene in its alpha phase (αiPP), the two major crystalline polyolefins that represent over 64% of the world production of thermoplastics were the selected polymer matrix. These very first attempts did not provide any unified view. Moreover one of the authors explicitly ruled out the epitaxial mechanism shown later to be the active one.[4]

The conventional NAs belong to four main groups: salts of aromatic or aliphatic acids, aromatic pigments, hydrazones from aromatic aldehydes, and phylosilicates. At first sight, these compounds have hardly anything in common: they have different chemical nature, and they crystallise in many very different crystallographic systems. The chain conformations and unit cell symmetries of PE and α iPP crystals seem also to have nothing in common (PE: planar zig-zag, orthorhombic unit cell; α iPP: 3_1 helix, monoclinic unit cell).

Yet, most of the NAs, in particular, the salts of aromatic acids have similar organisation, a sandwich structure with a regular alternation of polar layers and aromatic apolar layers. The easy cleavage planes of the NAs crystals run between two apolar layers. These planes are lined up by rows of benzene rings (BR) bearing or not various substituents. The distance between the furrows depends on the nature and position of the substituents borne by the BR.

In fact, during crystallisation, PE chains or prominent methyl rows of iPP can lie down in the furrows defined by the rows of BR. For epitaxial growth of PE on substrates, it was established that the inter-chains distance determines the PE contact plane interacting with substrates.[7] The similarity between the 0.5 nm inter-chains distance in the PE $\underline{bc}$ plane and the same 0.5 nm along the diagonal of the lozenge methyl pattern of the $\underline{ac}$ plane of iPP, explains that some substrates are able to induce the epitaxial growth for both PE and iPP despite their above mentioned difference in crystalline structure.[8]

Thus, *NAs act via a physical nucleation process, an epitaxial mechanism*, a mechanism that is governed by geometrical matching between the polymer and the NA in the contact planes.[4] Moreover, for non-polar regular polyolefins, van der Waals interactions are the only potential interactions. The situation is somewhat different for polar polymers such as polyesters for which chemical interactions can play a role.[9]

Investigation Methods and Efficiency Scale

The epitaxial requirement being established above, procedures have to be designed to prove that a given compound is an efficient NA or a potential NA. A compound can be an efficient NA if, and only if, minute crystallites can be grown and finely dispersed in the polymer matrix. Most of these compounds are molecular crystals. Therefore, large surfaces formed at the polymer/NA interface ensure a high density of uniformly dispersed nuclei. We use a three steps procedure, described hereafter, to investigate NAs.

The first test is a visual test in optical microscopy. Epitaxial crystallisation results in a well known and easy to observe trans-crystallisation. Trans-crystallisation results from spatial limitation of the 3D growth of polymer spherulites resulting from the high density of nuclei at the polymer/NA interface. The crystalline chains oriented orthogonal to the interface form a thin highly birefringent layer, easy to observe in polarised optical microscopy (Figure 1). The larger the trans-crystallised zone, the more efficient is the NA.

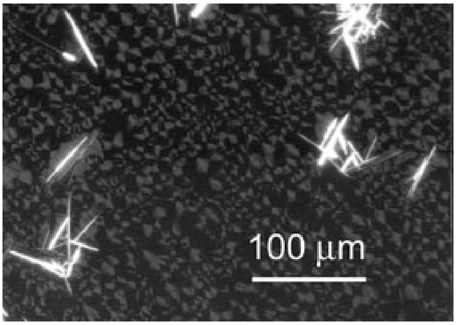

Figure 1.
Illustration of the nucleating effect of nucleating agents. The NA crystals (bright) were deposited on a thin film of the polymer. After melting and recrystallisation, preferred nucleation induces a so-called transcrystalline layer stemming from the NA particles edges.

As already mentioned, epitaxial interactions are a prerequisite for polyolefins NAs but are not sufficient. A lack of chemical compatibility between polymer and NA results in the formation of exceedingly large molecular crystals in the polymer matrix. This in turn, results in limited interfaces detrimental to create uniformly dispersed nuclei.

Secondly, before using any further sophisticated investigation of NAs, it is safe to control the influence of the NA candidates on the crystallisation temperatures. For a long time, the reduction of crystallisation half time in isothermal crystallisation and/or the increase of crystallisation temperature (T_C) for non-isothermal crystallisation were the criteria to evaluate the NAs. These methods compare the T_C of a nucleated polymer to T_{C0} of the non-nucleated one named here the blank polymer. They do not compare the nucleated polymer to the best possible nucleation that is attainable by optimal self-seeding that results in a crystallisation at T_{Cmax}. Seeds produced by self-seeding (the polymer residues from the most stable lamellae) are finely dispersed in the molten polymer, and of course are fully compatible on both geometrical and chemical grounds. Therefore, we have designed an efficiency scale method that compares the polymer nucleated by a given NA at concentration C to both ends of the full nucleation domain, the blank polymer and the ideally self-seeded one.[10] The efficiency coefficient is defined as:

$$\mathrm{E} = 100((T_C - T_{C0})/(T_{C\max} - T_{C0}))$$

This simple, convenient and reliable efficiency scale defines a semi-quantitative scale ($T_{Cmax} - T_{C0}$ must be determined for each sample), has significant advantages and helps classify the NA with a reliable method. Some examples of the results for an iPP (molecular weight 378 000, polydispersity 5,2) are reported in Table 1. The crystallisation temperatures are measured with a differential scanning calorimeter (DSC) following a precise procedure defined elsewhere.[10] From Table 1, it is obvious that some chemicals cannot be described as NAs.

Moreover, with the Avrami and Ozawa equations and employing the variation of G

Table 1.
Efficiency coefficients determined for the above mentioned iPP sample.

Nucleating Agent	C%	T_C (°C)	E%
Self-seeded Polymer	X	137.4	100
Phthaloyl Glycine	1	129.8	72
4-Biphenyl Carboxylic Acid*	2	128.8	66
2-Naphtoic Acid*	1	127.8	62
Thymine*	1	125.3	50
N,N′ Dicyclohexyl Terephthalamide Acid	1	123.7	43
1,3:2,4-Dibenzylidene Glucitol (DBS)*,+	0,4	123.2	41
Isonicotinic Acid*	1	123	39
Sodium Benzoate*	1	121.2	31
4-tertio-Butyl Benzoic Acid*	1	120.7	29
2-Hydroxy 3-Naphtoic Acid*	1	116	7
Blank Polymer	0	112.5	0

* NA patented before our work.

\+ Best known as 1,3:2,4-dibenzylidene sorbitol; sorbitol is the common name for glucitol. Sorbitol will used here due to its extensive use.

with temperature, this efficiency scale can also be correlated to nucleation density and to more telling spherulite size. In principle, the spherulite size can be measured from optical microscopy, but the method is limited by the wavelength of visible light while the DSC method just described allows to estimate sizes down to 0.1 μm.

Third, investigating the NAs' effects on polymers implies to characterise the polymer phase obtained and the determination of the NA/polymer crystallographic relations. EM is the most appropriate tool to study interfaces both in the real and reciprocal space. Usually EM diffraction patterns are employed to determine both the nature of the phase and the epitaxial relationships. In some particular cases, such as iPP, the α and β phases have distinct morphologies, the quadrite for the α phase and many screw dislocations for the β phase spherulites that can be distinguished in a simple bright field image (Figure 2).

Gelling Nucleating Agents, Clarifying Agents

In polymer processing, 1,3:2,4-dibenzylidene sorbitol (DBS) and its derivatives are considered as excellent NAs. This claim is obviously questioned by the results of Table 1. At the regular concentration used in practice (0.4%), DBS ranks in the centre of our scale. This indicates that the spherulite size is not the unique criterion to take into consideration. As a matter of fact, DBS belongs to a specific class of NA named clarifying agents. Certainly, CAs increase T_Cs. But, by definition, their main contribution is to improve the optical properties i.e. reduce the haze and improve clarity.

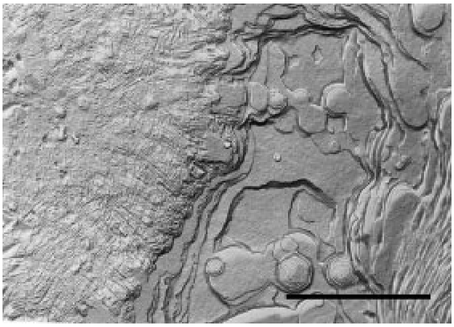

Figure 2.
Surface of a bulk sample of isotactic polypropylene, (first chemically etched to highlight the morphological features. This area displays the edges of two spherulites. On the left, the α form, with its characteristic cross-hatched lamellar structure, induced by a homoepitaxy specific to this crystal phase. On the right, the β form, which displays hexagonal screw dislocations, a means to multiply the number of lamellae during spherulite growth.

DBS is a bi-substituted sorbitol acetal patented by Japan Chemical as gelling agent, the first patented member of a whole family of substituted DBS. DBS and the related mono- and tri-benzylidene sorbitols are produced by acetalysation of glucitol (sorbitol) by benzaldehyde. Numerous derivatives with diverse substituents on different positions of the benzene rings have been introduced later on. The (1,3:2,4-bis-(p-methylbenzylidene) sorbitol) (p-DMDBS) patented by Milliken under the trade name Millad®3988 is to our knowledge the best CA.

As mentioned above, DBS is a gelling agent with unique features. It forms a gel at extremely low concentrations in almost every solvent (polar solvents like esters or non-polar solvents like alkanes) except in water (see illustration in Figure 3b). The gel formation depends upon the type of solvent and the DBS concentration in the solvent. In general more or less transparent isles of "microgel" appear first; for appropriate concentrations the merging isles take up the whole volume of the system and the gel is formed. The gel aspect depends on the solvent and the concentration, for instance, they are very transparent for ester derivatives.

As numerous gelling agents, (like 12-hydroxystearic acid[11] or steroid derivatives[12]) DBS is a chiral amphiphilic molecule. In highly diluted solutions, the DBS molecule adopts a butterfly conformation. The non-polar benzene wings spread outside the modified sorbitol polar core (Figure 3a). The two non-reacted OH-groups from the central core are involved in hydrogen bonds. This molecular architecture is essential to build up stable gel networks. Indeed, a 3-D fibrillar network of nearly infinitely long fibres is formed in the

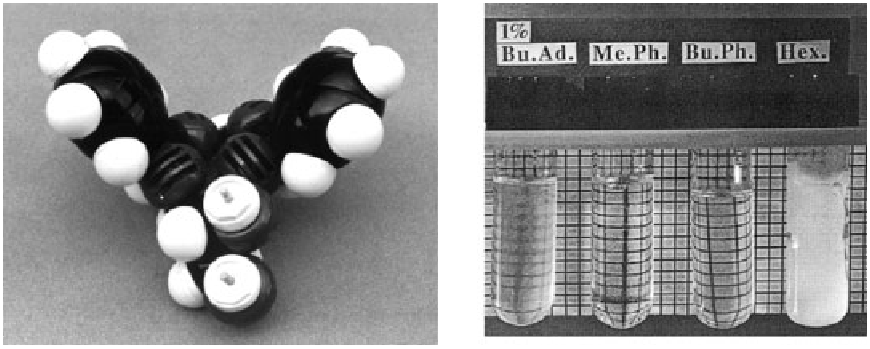

Figure 3.
Left: Molecular model of dibenzylidene sorbitol. The polar part with its two hydrogen atoms involved in hydrogen bonds are in front, the benzylidene-substituted parts in the back. Right: Illustration of the impact of the nature of the solvent on the clarity of DBS gel, (from left to right:butyl adipate, methylphthalate, butylphthalate, hexane). Note that DBS/hexane gel is already turbid at this 1% concentration of DBS.

gel as can be seen in a bright field EM image of a DBS xerogel prepared directly on the microscope grid (Figure 4).[13] The fibrillar morphology has been observed later, directly in samples of DBS/polypropylene glycol by using a staining technique.[14]

All the dibenzylidene sorbitols and xylitols —substituted or not by methyl and ethyl groups— that we have investigated produce, at intermediate concentrations and in various solvents, the same 3-D fibrillar network with some minor differences in the flexibility of the fibres (Figure 4). Xylitol and sorbitol have exactly the same sequences of configurations of the asymmetric carbons along their core that ends up with identical conformation. They differ only by the length of their central core (C6 for sorbitol, C5 for xylitol). All the other dibenzylidenes synthesised from the hexols do not gel. This confirms, if necessary, the crucial influence of the conformation of the amphiphilic molecule to build up self-assembled structures. Although DBS fibres often merge together in bundles, some individual proto-fibres with an average diameter in the range of 10 nm can be observed. The twist along the fibres is linked to the chirality of the molecule.

DBS, like most of the gelling molecules does not yield large single crystals needed to solve the crystalline structure. Therefore, we had to rely on tricks to demonstrate that DBS is able to induce epitaxial crystallisation of polyolefins (Figure 5). First, we have used the known polymer decoration

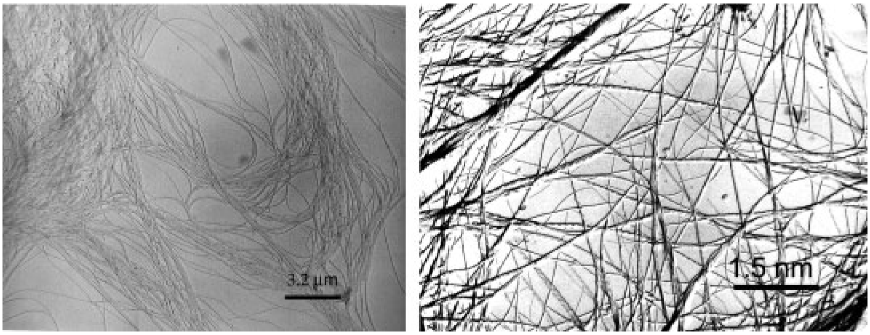

Figure 4.
Electron micrographs of Xerogel fibres of DBS (left) and di-ethylDBS (right). The gel is prepared on the microscope grid from a tetrahydrofuran solution, later gelled by addition of benzene. (The sample is Pt/C shadowed). **(Incomplete Figure corrected after initial online publication)**

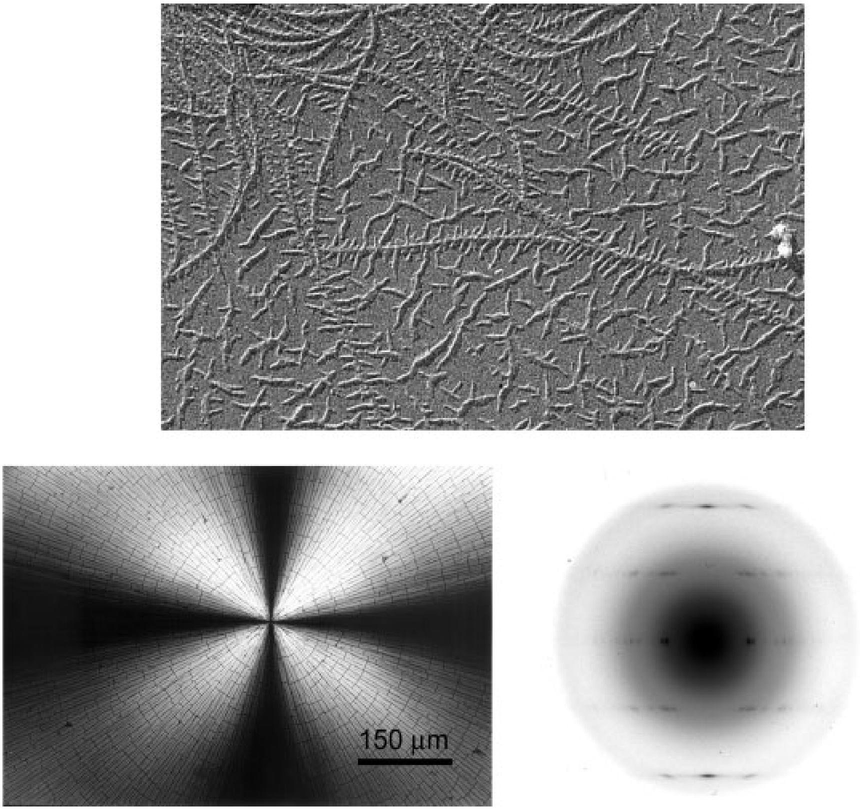

Figure 5.
Upper part: Electron micrograph of DBS fibres decorated by vaporised PE (see text); lower left: Optical micrograph of a DBS spherulite previously partially molten near 210 °C then cooled to room temperature. Lower right: Electron microscopy diffraction pattern of PE oriented on partially molten DBS spherulite, a small area preserving local orientation of DBS was selected. (DBS was dissolved before EM diffraction; c^*PE vertical). **(Incomplete Figure corrected after initial online publication)**

method.[15] A polymer, in this case PE, is deposited by vacuum cracking on the DBS fibres. The PE lamellae formed by condensation of PE are randomly oriented on non-interacting substrates and are preferentially oriented in the case of epitaxial growth. In Figure 5a, all the PE lamellae nucleated on DBS fibres grow at right angle to the PE/DBS interface, whereas the PE lamellae grown on the glass slide used as support for DBS fibres are oriented at random. A second proof of the PE/DBS epitaxial relationships was collected on a partially molten DBS spherulite (Figure 5b). This partial melting preserves locally a uniform orientation of the DBS molecules. Again, PE was deposited under vacuum on the sample and was subsequently dissolved for EM observations. Figure 5c shows that the PE diffraction pattern obtained on a spatially limited zone of a DBS spherulite is a fibre pattern. The angular dispersion of the spots is negligible, indicating a unique orientation of the PE *c* axis. The orienting effect of DBS on PE crystal growth is thus revealed.

At this point, we are able to describe the scenario of polymer crystallisation in presence of DBS. When the high temperature homogeneous melt DBS/polymer is cooled down, first the *DBS eggregates and constructs a 3-D homogeneous fibrillar network*. As the temperature is further reduced, the DBS fibres crystallise and then nucleate the polymer crystallisation. This intermediate gel phase has the exceptional advantage to

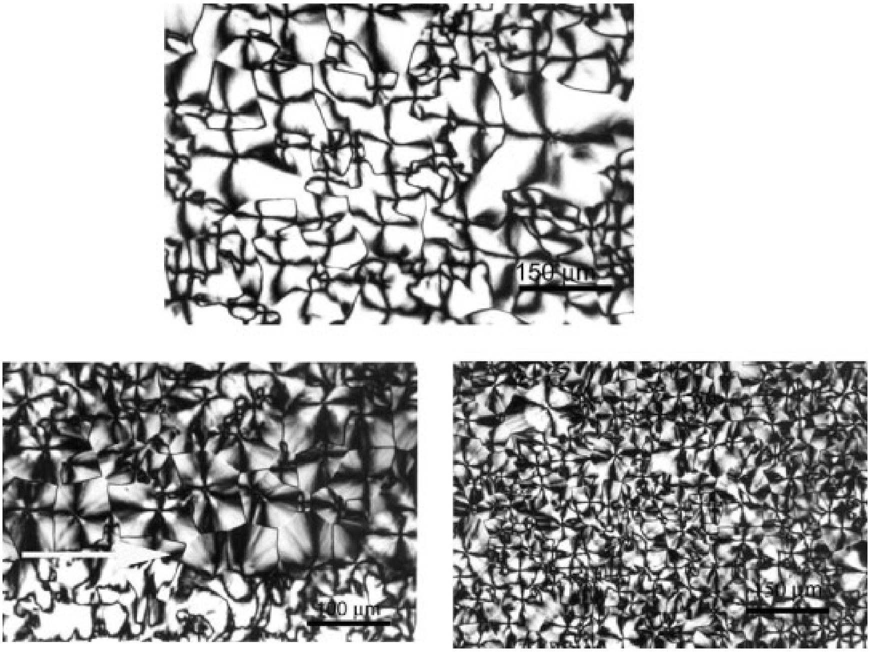

Figure 6.
Optical micrograph, scenario of POE/DBS mixture crystallisation when cooled from homogeneous melt. Upper part: purely mesomorphic phase; lower left: intermediate state as the crystallisation progress (the upper part of the picture is already crystallised while the lower part is still in the mesomorphic phase, the white arrow indicates the transition line); lower right: the whole sample has crystallised.

produce a large number of seeds (nuclei) uniformly distributed in the whole polymer matrix. To some extent the *foreign additive mimics the self-seeding process*. Fibres of 10 nm create a DBS/polymer interface as large as *400 m^2 per gram of DBS*, giving rise to a significant number of nuclei. Another, and not the least, advantage of the fibres formation is to limit light scattering at the DBS/polymer interface. The individual fibres diameter is smaller than the wavelength of visible light. Only bunches of fibres scatter visible light and are detrimental to optical properties. In fact, the optimal optical effect of DBS on haze is obtained for a 0.25% of DBS in iPP, 0.25% is most likely the onset of DBS aggregation in the melt.

The scenario of polymer/DBS crystallisation has been checked, on a poly(oxyethylene) (POE)/DBS blend. This blend is selected for practical reasons, namely its low transition temperatures. Mixtures of DBS with POE (Mn = 6000) molten at about 60 °C are observed, in cross-polar optical microscopy during cooling to room temperature. Figure 6 shows the sequence of appearance of the different phases: first, a fluid mesomorphic texture characteristic of gel phases, then a stiff phase followed immediately by the onset of crystallisation.

The kinetics of formation of the DBS gels were also examined by rheological measurements in a Couette geometry for three different esters, namely di-methyl phthalate (MePht), di-butyl phthalate and di-butyl adipate. The gel phase growth after quenching from the homogeneous melt is always very fast: typically a 0.5% DBS solution in MePht gels at 27 °C in nearly 150s.[16] The gel times depend on solvent and concentration (C) but are unchanged from 27–40 °C; they decrease with the C following a −4.5 power law. The 60s isochronal creep compliance and the storage modulus at 0.5 Hz varies with concentration with strong power law coefficients, −4 and 4 respectively.

Due to their industrial importance, the binary systems DBS/polymer or like molecules have been extensively studied. In this short paper we simply recall some complementary but significant results. The onset of gel formation has been characterised by a gel concentration range rather than by a gel point for DBS/poly(propylene oxide).[17] A monotectic phase diagram of p-DMDBS/iPP[18] was established and the development of organised structures for sheared melts was followed in real time by X-ray scattering.[19]

Owing to their unique activity as CA, the concept of self-assembling or butterfly-shaped molecules has been taken up again to design potential NA or better CA. A butterfly shaped molecule has been invented by Asahi Denka Kogyo[20] while tectonics based upon barbiturates and 2,4, 6-triaminopyrimidines[21] and 1,3,5-benzenetrisamides derivatives[22] have been proposed and patented. To the best of our knowledge, however they have not superseded DBS-like molecules to improve optical properties.

Concluding Remarks

Epitaxial growth is the fundamental mechanism of interaction between polyolefins and nucleating agents. These nucleating agents can be best evaluated via an efficiency scale related to the temperature of crystallisation measured by DSC. We have demonstrated that the intermediate gel phase, such as the one formed in polymer/DBS (or similar derivatives) mixtures are essential to design high performing clarifying agents. Such molecules self-organise into nano-scale fibrils, they develop intermolecular forces, hydrogen bonding and π-interactions. During processing, such molecules promote the epitaxial growth of polymer crystals while the intermediate gel phase ensures a homogeneous dispersion of nuclei in the polymer. These molecules improve the mechanical and optical properties of polymers.

However, due to their cost, DBS derivatives are mainly used when outstanding optical properties are essential. These derivatives are compatible with most co-additives, including nucleating agents. Therefore, in practice they are used in connection with more common and less expensive nucleating agents. These nucleating agents can be molecular crystals or polymers (such as isotactic poly(vinylcyclohexane) for iPP).[23] Of course, the ideal situation would be to design a cheap clarifying agent with the highest possible gain in crystallisation temperature measured for the best nucleating agents.

Finally, physical gels must be considered as a very relevant process in the development of many classes of polymer/additive pairs towards high performances.

[1] D.J. Blundell, A. Keller, A.J. Kovacs, *Polymer Lett.* **1966**, *4*, 481.

[2] H.N. Beck, *J. Appl. Polym. Sci.* **1967**, *11*, 673.

[3] F.L. Binsbergen, B.G.M. De Lange, *Polymer* **1970**, *11*, 309.

[4] J.C. Wittmann, B. Lotz, *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1837.

[5] C. Mathieu, A. Thierry, J.C. Wittmann, B. Lotz, *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 2504.

[6] K. Friedrich, *Prog. Coll. Polym. Sci.* **1978**, *64*, 103.

[7] J.C. Wittmann, B. Lotz, *Polymer* **1989**, *30*, 27.

[8] B. Lotz, J.C. Wittmann, *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 1079.

[9] R. Legras, J.P. Mercier, E. Nield, *Nature* **1983**, *304*, 432.

[10] B. Fillon, J.C. Wittmann, B. Lotz, A. Thierry, *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31*, 1383;B. Fillon, B. Lotz, A. Thierry, J.C. Wittmann, *ibid.* **1993**, *31*, 1395.

[11] T. Tachibana, T. Mori, K. Hori, *Bull. Chem. Sci. Jap.* **1981**, *54*, 73.

[12] P. Terech, R. Ramasseul, F. Volino, *J. Colloid Interface Sci.* **1983**, *91*, 280.

[13] A. Thierry, C. Straupé, B. Lotz, J.C. Wittmann, *Polym. Commun.* **1990**, *31*, 299.

[14] D.J. Mercurio, R.J. Spontak, *J. Phys. Chem. B* **2001**, *105*, 2091.

[15] J.C. Wittmann, B. Lotz, *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 205.

[16] G. McKenna, F. Kern, S.J. Candau, J.C. Wittmann, A. Thierry, *ACS Polym. Prep.* **1991**, *32*, 455.

[17] M. Dumitras, Chr. Friedrich, *J. Rheol.* **2004**, *48*, 1135.

[18] M. Kristiansen, M. Werner, T. Tervoort, P. Smith, M. Blomenhofer, H.W. Schmidt, *Macromolecules* **2003**, *36*, 5150.

[19] A. Nogales, G.R. Mitchell, *Polymer* **2005**, *46*, 5615.

[20] S. Yoshimoto, T. Ueda, K. Yamanaka, A. Kawaguchi, E. Tobita, T. Haruna, *Polymer* **2001**, *42*, 9627.

[21] T. Bauer, R. Thomann, R. Mülhaupt, *Macromolecules* **1998**, *31*, 7651.

[22] M. Blomenhofer, S. Ganzleben, D. Hanft, H.W. Schmidt, M. Kristiansen, P. Smith, K. Stoll, D. Mäder, K. Hoffmann, *Macromolecules* **2005**, *38*, 3688.

[23] D. Alcazar, JrJ. Ruan, A. Thierry, B. Lotz, *Macromolecules* **2006**, *39*, 2832.