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# Thermodynamics and Thermokinetics to Model Phase Transitions of Polymers over Extended Temperature and Pressure Ranges Under Various Hydrostatic Fluids

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## 1. Introduction

A scientific understanding of the behaviour of polymers under extreme conditions of temperature and pressure becomes inevitably of the utmost importance when the objective is to produce materials with well-defined final in-use properties and to prevent the damage of materials during on-duty conditions. The proper properties as well as the observed damages are related to the phase transitions together with intimate pattern organization of the materials.

Thermodynamic and thermokinetic issues directly result from the thermodynamic independent variables as temperature, pressure and volume that can stay constant or be scanned as a function of time. Concomitantly, these variables can be coupled with a mechanical stress, the diffusion of a solvent, and/or a chemically reactive environment. A mechanical stress can be illustrated in a chemically inert environment by an elongation and/or a shear. Diffusion is typically described by the sorption of a solvent. A chemical environment is illustrated by the presence of a reactive environment as carbon dioxide or hydrogen for example.

Challenging aspects are polymer pattern multi scale organizations, from the nanometric to the macrometric scale, and their importance regarding industrial and technological problems, as described in the state of the art in Part 2. New horizons and opportunities are at hands through pertinent approaches, including advanced *ad hoc* experimental techniques with improved modelling and simulation. Four striking illustrations, from the interactions between a solvent and a polymer to the growth patterns, are illustrated in Part 3.

## 2. Multi-length scale pattern formation with *in-situ* advanced techniques

### 2.1 Structure formation in various materials

#### 2.1.1 Broad multi-length scale organization

The development of polymer-type patterns is richly illustrated in the case of biological materials and metals.

**Pattern growth**

Among the observed morphologies which extend from polymeric to metallic materials and to biologic species, similar pattern growth is observed. Patterns extend, with a multilevel branching, from the nanometric **(Fig. 1.a-b)** to the micrometric **(Fig. 1.c-d-e)** scale structures.

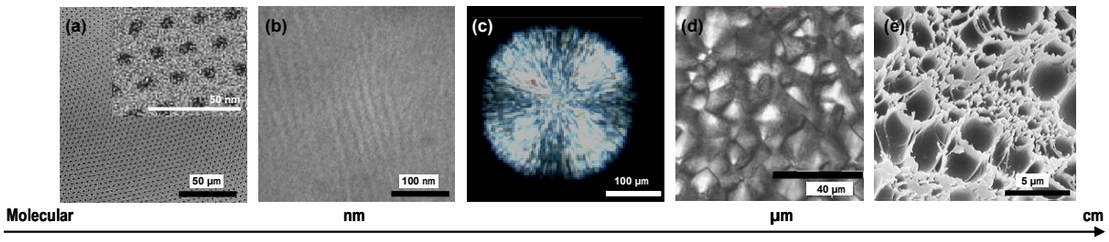



Fig. 1. Two-dimensional (2D) observations of various polymer patterns. **(a)** nanometric scale pattern of poly(ethylene-oxide) cylinders (PEO in black dots) in amphiphilic diblock copolymer $PEO_m$-*b*-$PMA(Az)_n$ (**a**, Iwamoto & Boyer, CREST-JSPS, Tokyo, Japan), **(b)** nanometric scale lamellae of an isotactic polypropylene (iPP, crystallization at 0.1 °C.min$^{-1}$, $RuCl_3$ stained) with crystalline lamella thickness of 10 nm in order of magnitude, **(c)** micrometric scale of an iPP spherulite with lamellar crystals radiating from a nucleating point (iPP, crystallization at 140 °C), **(d)** micrometric scale structure of a polyether block amide after injection moulding (**b-c-d**, Boyer, CARNOT-MINES-CEMEF, Sophia Antipolis, France), **(e)** micrometric scale cellular structure of a polystyrene damaged under carbon dioxide sorption at 317 K (**e**, Hilic & Boyer, Brite Euram POLYFOAM Project BE-4154, Clermont-Ferrand, France).

The polycrystalline features, formed by freezing an undercooled melt, are governed by dynamical processes of growth that depend on the material nature and on the thermodynamic environment. Beautiful illustrations are available in the literature. To cite a few, the rod-like eutectic structure is observed in a dual-phase pattern, namely for metallic with ceramic, and for polymeric (De Rosa et al., 2000; Park et al., 2003) systems like nanometric length scale of hexagonal structure of poly(ethylene-oxide) PEO cylinders in amphiphilic diblock copolymer $PEO_m$-*b*-$PMA(Az)_n$ with azobenzene part PMA(Az) (Tian et al., 2002). Dendritic patterns are embellished with images like snowflake ice dendrites from undercooled water (Kobayashi, 1993) and primary solidified phase in most metallic alloys (*e.g.*, steel, industrial alloys) (Trivedi & Laorchan, 1988a-b), and even dendrites in polymer blends (Ferreiro et al., 2002a) like PEO polymer dendrites formed under cooling PEO/polymethyl methacrylate PMMA blend (Gránásy et al., 2003; Okerberg et al., 2008). In the nanometric scale, immiscibility of polymer chains in block copolymers leads to microphase-separated structures with typical morphologies like hexagonally packed cylindrical structures, lamellae, spheres in centred cubic phases, double gyroid and double diamond networks (Park et al., 2003).

In polymer physics, the spherulitic crystallization **(Fig. 1.c)** represents a classic example of pattern formation. It is one of the most illustrated in the literature. Besides their importance in technical polymers, spherulitic patterns are also interesting from a biological point of view like semicrystalline amyloid spherulites associated with the Alzheimer and Kreutzfeld-Jacob diseases (Jin et al., 2003; Krebs et al., 2005). The spherulitic pattern depends on polymer chemistry (Ferreiro et al., 2002b). Stereo irregular atactic or low molecular weight compounds are considered as impurities, which are rejected by growing crystals. The openness of structure, from spherulite-like to dendrite-like, together with the coarseness of texture (a measure of the 'diameters' of crystalline fibres between which impurities become concentrated during crystal growth) was illustrated in the work of Keith & Padden (1964). These processes induce thermal and solute transport. Thus pattern formation is defined by the dynamics of the crystal/melt interface involving the interfacial energy. In the nanometric scale domain, spherulite is a cluster of locally periodic arrays of crystalline layers distributed as radial stacks of parallel crystalline lamellae separated by amorphous layers **(Fig. 1.b)**. Molecular chains through the inter-lamellar amorphous layers act as tie molecules between crystalline layers, making a confined interphase crystalline lamellae/amorphous layer.

**Cross fertilization between polymer crystallization and metal solidification**

Physical chemists and metallurgists alike are constantly confronted with materials properties related to (polymer) crystallization (*e.g.*, spherulite size distribution, lamellae spacing) or (metal) solidification (*e.g.*, grain size distribution, dendrite arm or eutectic spacing), respectively. In metal science, if accurate numerical modelling of dendritic growth remains a major challenge even with today's powerful computers, the growth kinetic theories, using accurate surface tension and/or kinetic anisotropies, are well advanced (Asta et al., 2009; Flemings, 1974). In polymer science, such approaches exist. But still insight into the physics/kinetics connection and morphologies is little known (Piorkowska et al., 2006). The most well-known growth kinetics theory is the one of Hoffman and coworkers (Hoffman, 1983) which is based on the concept of secondary nucleation; the nucleation and overall kinetics of crystallization have been also intensively studied (Avrami, 1939, 1940, 1941; Binsbergen, 1973; Haudin & Chenot, 2004).

### 2.1.2 Practical applications, importance of crystal organization

The multi-length scale and semi-crystalline structure organizations are intimately linked with the chemical, physical, mechanical integrity and failure characteristics of the materials.

**Polymers with well-defined end-used properties**

Semi-crystalline polymers gain increasing importance in manufacturing (extended to recycling) industries where the control at the nano- to micro- up to macrometric hierarchical levels of the patterns constitutes a major engineering challenge (Lo et al., 2007). The domains extend from optics, electronics, magnetic storage, isolation to biosorption, medicine, packaging, membranes and even food industry (Rousset et al., 1998; Winter et al., 2002; Park et al., 2003; Nowacki et al., 2004; Scheichl et al., 2005; Sánchez et al., 2007; Wang et al., 2010).

**Control of polymer structure in processing conditions**

Industrial polymer activities, through processes like, for instance, extrusion coating (*i.e.*, the food industry with consumption products), injection moulding (*i.e.*, the industry with

engineering parts for automotive or medicine needs) (Devisme et al., 2007; Haudin et al., 2008), deal with polymer formulation and transformation. The viscous polymer melt partially crystallizes after undergoing a complex flow history or during flow, under temperature gradients and imposed pressure (Watanabe et al., 2003; Elmoumni & Winter, 2006) resulting into a non homogeneous final macrometric structure throughout the thickness of the processed part. The final morphologies are various sizes and shapes of more or less deformed spherulites resulting from several origins: *i)* isotropic spherulites by static crystallization (Ferreiro et al., 2002a; Nowacki et al., 2004), *ii)* highly anisotropic morphologies as oriented and row-nucleated structures (*i.e.*, shish-kebabs) by specific shear stress (Janeschitz-Kriegl, 2006; Ogino et al., 2006), *iii)* transcrystalline layer (as columnar pattern in metallurgy) by surface nucleation and/or temperature gradient, and *iv)* teardrop--shaped spherulites or "comets" (spherulites with a quasi-parabolic outline) by temperature gradients (Ratajski & Janeschitz-Kriegl, 1996; Pawlak et al., 2002).

Together with the deformation path (*e.g.*, tension, compression), the morphology strongly influences the behaviour of polymers. Some models have attempted to predict the properties of spherulites through a simulation of random distributions of flat ellipsoids (crystalline lamellae) embedded in an amorphous phase described by a finite extensible rubber network (Ahzi et al., 1991; Dahoun et al., 1991; Arruda & Boyce, 1993; Bedoui et al., 2006).

Moreover by considering the high-pressure technology, the use of specific fluids plays a non negligible role in pattern control. The thermodynamic phase diagrams of fluids implies the three coordinates (pressure-volume-temperature, *PVT*, variables) representation where the fluids can be in the solid, gaseous, liquid and even supercritical state. The so-called "signature of life" water ($H_2O$) (Glasser, 2004) and the so-called "green solvent" in fact "clean safe" carbon dioxide ($CO_2$) (Glasser, 2002) can be cited. The use of $H_2O$ is encountered in injection moulding assisted with water. $CO_2$ is known as a valuable agent in polymer processing thanks to its aptitude to solubilize, to plasticize (Boyer & Grolier, 2005), to reduce viscosity, to favour polymer blending or to polymerize (Varma-Nair et al., 2003; Nalawade et al., 2006). In polymer foaming, elevated temperatures and pressures are involved as well as the addition of chemicals, mostly penetrating agents that act as blowing agents (Tomasko et al., 2003; Lee et al., 2005).

**Damage of polymer structure in on-duty conditions**

In the transport of fluids, in particular in the petroleum industry taken as an example, flexible hosepipes are used which engineering structures contain extruded thermoplastic or rubber sheaths together with reinforcing metallic armour layers. Transported fluids contain important amounts of dissolved species, which on operating temperature and pressure may influence the resistance of the engineering structures depending on the thermodynamic *T*, *P*-conditions and various phenomena as sorption/diffusion, chemical interactions (reactive fluids, *i.e.*, oxidation), mechanical (confinement) changes. The polymer damage occurs when rupture of the thermodynamic equilibrium (*i.e.*, after a sharp pressure drop) activates the blistering phenomenon, usually termed as 'explosive decompression failure' (XDF) process (Dewimille et al., 1993; Rambert et al., 2006; Boyer et al., 2007; Baudet et al., 2009). Damage is a direct result of specific interactions between semi-crystalline patterns and solvent with a preferential interaction (but not exclusive) in the amorphous phase (Klopffer & Flaconnèche, 2001).

### 2.2 Development of combined experimental procedures

The coupling of thermodynamic and kinetic effects (*i.e.*, confinement, shear flow, thermal gradient) with diffusion (*i.e.*, pressurizing sorption,) and chemical environment *(i.e.*, polar effect, oxidation), and the consideration of the nature of the polymers *(i.e.*, homopolymers, copolymers, etc.) require a broad range of indispensable *in-situ* investigations. They aim at providing well-documented thermodynamic properties and phase transitions profiles of polymers under various, coupled and extreme conditions.

#### 2.2.1 Temperature control at atmospheric pressure

Usual developed devices are based on the control of temperature, while the main concerns are high cooling rate control and shearing rate.

The kinetic data of polymer crystallization are often determined in isothermal conditions or at moderate cooling rates. The expressions are frequently interpreted using simplified forms of Avrami's theory involving thus Avrami's exponent and a temperature function, which can be derived from Hoffman-Lauritzen's equation **(**Devisme et al., 2007). However, such an interpretation cannot be extrapolated to low crystallization temperatures encountered in polymer processing, *i.e.*, to high cooling rates (Magill, 1961, 1962, 2001; Haudin et al., 2008; Boyer et al., 2011b). In front of the necessity for obtaining crystallization data at high cooling rates, different technical solutions are proposed. Specific hot stages (Ding & Spruiell, 1996; Boyer & Haudin, 2010), quenching of thin polymer films (Brucato et al., 2002), and nanocalorimetry (Schick, 2009) are the main designs.

Similarly, to generate a controlled melt shearing, various shearing devices have been proposed, for instance, home-made sliding plate (Haudin et al., 2008) and rotating parallel plate devices (*e.g.*, Linkam temperature controlled stage, Haake Mars modular advanced rheometer system). The shear-induced crystallization can be performed according to a 'long' shearing protocol as compared to the 'short-term' shearing protocol proposed by the group of Janeschitz-Kriegl (Janeschitz-Kriegl et al., 2003, 2006; Baert et al., 2006).

#### 2.2.2 Temperature-pressure-volume control

The design of devices based on the control of pressure requires breakthrough technologies. The major difficulty is to generate high pressure.

In polymer solidification, the effects of pressure can be studied through pressure–volume–temperature phase diagrams obtained during cooling at constant pressure. The effect of hydrostatic (or inert) pressure on phase transitions is to shift the equilibrium temperature to higher values, *e.g.*, the isotropic phase changes of complex compounds as illustrated in the works of Maeda et al. (2005) by high-pressure differential thermal analyzer and of Boyer et al. (2006a) by high-pressure scanning transitiometry, or the melting temperature in polymer crystallization as illustrated for polypropylene in the work of Fulchiron et al. (2001) by high-pressure dilatometry. However, classical dilatometers cannot be operated at high cooling rate without preventing the occurrence of a thermal gradient within the sample. This problem can be solved by modelling the dilatometry experiment (Fulchiron et al., 2001) or by using a miniaturized dilatometer (Van der Beek et al., 2005). Alternatively, other promising technological developments propose to couple the pressure and cooling rates as shown with an apparatus for solidification based on the confining fluid technique as described by Sorrentino et al. (2005). The coupling of pressure and shear is possible with the shear flow pressure–volume–temperature measurement system developed by Watanabe et

al. (2003). Presently, performing of *in-situ* observations of phase changes based on the optical properties of polymers (Magill, 1961, 2001) under pressure is the object of a research project developed by Boyer (Boyer et al., 2011a).
To estimate the solubility of penetrating agents in polymers, four main approaches are currently generating various techniques and methods, namely: gravimetric techniques, oscillating techniques, pressure decay methods, and flow methods. However, with many existing experimental devices, the gain in weight of the polymer is measured whereas the associated volume change is either estimated or sometimes neglected (Hilic et al., 2000; Nalawade et al., 2006; Li et al., 2008).
The determination of key thermo-mechanical parameters coupled with diffusion and chemical effects together with temperature and pressure control is not yet well established. Approaches addressing the prediction of the multifaceted thermo-diffuso-chemo-mechanical (TDCM) behaviour are being suggested. Constitutive equations are built within a thermomechanical framework, like the relation based on a rigorous thermodynamic approach (Boyer et al., 2007), and the proposed formalism based on as well rigorous mechanical approach (Rambert et al., 2006; Baudet et al., 2009).

## 3. Development and optimization of pertinent models

Modelling of polymer phase transitions with a specific thermodynamics- and thermokinetics-based approach assumes to consider the coupling between thermal, diffusion, chemical and mechanical phenomena and to develop advanced physically-based polymer laws taking into account the morphologies and associated growth. This implies a twofold decisive step, theoretical and experimental.
As regards specific industrial and technological problems, from polymer formulation to polymer damage, passing by polymer processing, the conceptualization involves largely different size scales with extensive and smart experimentation to suggest and justify suitable approximations for theoretical analyses.

### 3.1 Thermodynamics as a means to understand and prevent macro-scale changes and damages resulting from molten or solid polymer/solvent interactions

Thermodynamics is a useful and powerful means to understand and prevent polymer macro-scale changes and damages resulting from molten or solid material/solvent interactions. Two engineering examples are illustrative: foaming processes with hydrochlorofluorocarbons (HCFCs) as blowing agents in extrusion processes with a concern on safeguarding the ozone layer and the global climate system, Montreal Protocol (Dixon, 2011), and transport of petroleum fluids with in-service pipelines made of structural semi-crystalline polymers which are then exposed to explosive fluctuating fluid pressure (Dewimille et al., 1993).

**Solubility and concomitant swelling of solvent-saturated molten polymer**

In the prediction of the relevant thermo-diffuso-chemo-mechanical behaviour of polymers, sorption is the central phenomenon. Sorption is by nature complex, since the effects of fluids solubility in polymers and of the concomitant swelling of these polymers cannot be separated.
To experimentally extract reliable solubility data, the development of inventive equipments is required. In an original way, dynamic pendulum technology under pressure is used. The advanced development proposes to combine the features of the vibrating-wire viscometer

with a high pressure decay technique, the whole setup being operated under a fine control of the temperature. The limits and performances of this mechanical setup under extreme conditions, *i.e.*, pressure and environment of fluid, were theoretically assessed (Boyer et al., 2007). In the working equation of the vibrating-wire sensor (VW) **(eq. (1))**, unknowns are both the mass $m_{sol}$ of solvent absorbed in the polymer and the associated change in volume $\Delta V_{pol}$ of the polymer due to the sorption.

$$m_{sol} = \rho_g \, \Delta V_{pol} + \left[ \left( \omega_B^2 - \omega_0^2 \right) \frac{4 \, L^2 \, R^2 \, \rho_S}{\pi \, g} + \rho_g \left( V_C + V_{pol} \right) \right] \tag{1}$$

The volume of the degassed polymer is represented by $V_{pol}$ and $\rho_g$ is the density of the solvent. The other parameters are the physical characteristics of the wire, namely, $\omega_0$ and $\omega_B$ which represent the natural (angular) frequencies of the wire in vacuum and under pressure, respectively. And $L$, $R$, $\rho_s$ are, respectively, the length, the radius and the density of the wire. $V_C$ is the volume of the polymer container.

The thermodynamics of solvent-polymer interactions can be theoretically expressed with a small number of adjustable parameters. The currently used models are the 'dual-mode' model (Vieth et al., 1976), the cubic equation of state (EOS) as Peng-Robinson (Zhong & Masuoka, 1998) or Soave-Redlich-Kwong (Orbey et al., 1998) EOSs, the lattice-fluid model of Sanchez–Lacombe equation of state (SL-EOS) (Lacombe & Sanchez, 1976; Sanchez & Lacombe, 1976) with the extended equation of Doghieri-Sarti (Doghieri & Sarti, 1996; Sarti & Doghieri, 1998), and the Statistical Associating Fluid Theory (SAFT) (Prigogine et al., 1957; Beret & Prausnitz, 1975; Behme et al., 1999).

From the state of the art, the thermodynamic SL-EOS was preferably selected to theoretically estimate the change in volume of the polymer *versus* pressures and temperatures found in **eq. (1)**. In this model, phase equilibria of pure components or solutions are determined by equating chemical potentials of a component in coexisting phases. It is based on a well-defined statistical mechanical model, which extends the basic Flory-Huggins theory (Panayiotou & Sanchez, 1991). Only one binary adjustable interaction parameter $k_{12}$ has to be calculated by fitting the sorption data **eqs. (2-4)**. In the mixing rule appears the volume fraction of the solvent (index $_1$, $\phi_1$) in the polymer (index $_2$, $\phi_2$), ( $\rho_1^*$ , $p_1^*$ , $T_1^*$ ) and ( $\rho_2^*$ , $p_2^*$ , $T_2^*$ ) being the characteristic parameters of pure compounds.

$$p^* = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \phi_2 \Delta p^* \tag{2}$$

$$T^* = \frac{p^*}{\dfrac{\phi_1 \; p_1^*}{T_1^*} + \dfrac{\phi_2 p_2^*}{T_2^*}} \tag{3}$$

The parameter $\Delta p^*$ characterizes the interactions in the mixture. It is correlated with the binary adjustable parameter $k_{12}$.

$$\Delta p^* = k_{12} \sqrt{p_1^* \, p_2^*} \tag{4}$$

The mass fraction of solvent (the permeant), $\omega_1$, at the thermodynamical equilibrium is calculated with **eq. (5)**.

$$\omega_1 = \frac{\phi_1}{\phi_1 + \left(1 - \phi_1\right)\frac{\rho_2^*}{\rho_1^*}} \tag{5}$$

Coupled with the equation of DeAngelis (DeAngelis et al., 1999), the change in volume $\Delta V_{pol}$ of the polymer is accessible via **eq. (6)**:

$$\frac{\Delta V_{pol}}{V_0} = \frac{1}{\tilde{\rho}\rho^*\left(1 - \omega_1\right)}\frac{1}{\hat{\upsilon}_2^0} \tag{6}$$

$\rho^*$ and $\tilde{\rho}$ are the mixture characteristic and reduced densities, respectively. $\hat{\upsilon}_2^0$ is the specific volume of the pure polymer at fixed *T*, *P* and composition. The correlation with the model is done in conjunction with the optimization of the parameter $k_{12}$ that minimizes the *A*verage of *A*bsolute *D*eviations (*AAD*) between the experimental results and the results recalculated from the fit.

The critical comparison between the semi-experimental (or semi-theoretical) data of solubility and pure-experimental data available in the literature allows us to validate the consistency of the methodology of the calculations. The combination of coupled experimental and calculated data obtained from the vibrating-wire and theoretical analyses gives access to original solubility data that were not up to now available for high pressure in the literature. As an illustration in **Fig. 2.a-b** is given the solubility of carbon dioxide ($CO_2$) and of 1,1,1,2-tetrafluoroethane (HFC-134a) in molten polystyrene (PS). HFC-134a is significantly more soluble in PS by a factor of two compared to $CO_2$. The parameter $k_{12}$ was estimated at 0.9232, 0.9342, 0.9140 and 0.9120 for $CO_2$ sorption respectively at 338, 362, 383 and 402 K. For HFC-134a sorption, it was estimated at 0.9897 and 0.9912 at 385 and 402 K, respectively. The maximum of the polymer volume change was in $CO_2$ of 13 % at 25 MPa and 338 K, 15 % at 25 MPa and 363 K, 14 % at 43 MPa and 383 K, 13 % at 44 MPa and 403 K, and in HFC-134a of 12 % at 16 MPa and 385K, 11 % at 20 MPa and 403 K. thermodynamic behaviour of {PS-permeant} systems with temperature is comparable to a lower critical solution temperature (LCST) behaviour (Sanchez & Lacombe, 1976).

From these data, the aptitude of the thermodynamic SAFT EOS to predict the solubility of carbon dioxide and of 1,1,1,2-tetrafluoroethane (HFC-134a) in polystyrene (PS) is evaluated. The use of SAF theoretical model is rather delicate because the approach uses a reference fluid that incorporates both chain length (molecular size and shape) and molecular association. SAF Theory is then defined in terms of the residual Helmholtz energy $a^{res}$ per mole. And $a^{res}$ is represented by a sum of three intermolecular interactions, namely, segment–segment interactions, covalent chain-forming bonds among segments and site-site interactions such as hydrogen bond association. The SAFT equation satisfactorily applies for $CO_2$ dissolved in PS with a molecular mass in weight near about 1000 g.mol$^{-1}$, while it is extended to HFC-134a dissolved in PS with a low molecular mass in weight.

**Global cubic expansion coefficient of solvent saturated polymer as thermo-diffuso-chemo-mechanical parameter for preferential control of solid polymer/solvent interactions**

An essential additional information to solubility quantification, in direct relation with polymer damage by dissolved gases, is the expansion coefficient of the gas saturated polymer, *i.e.*, the mechanical cubic expansion coefficient of the polymer saturated in a solvent, $\alpha_{pol\text{-}g\text{-}int}$.

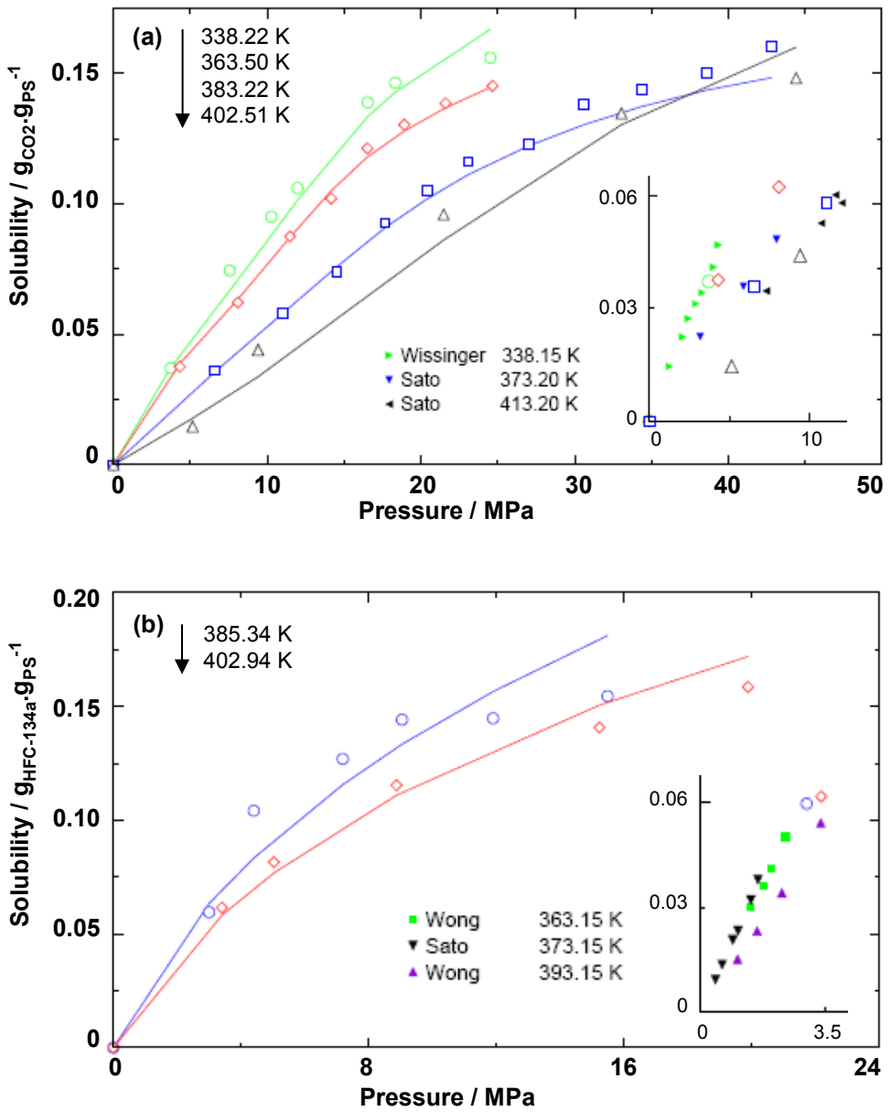



Fig. 2. Solubility of **(a)** $CO_2$ (critical pressure ($P_c$) of 7.375 MPa, critical temperature ($T_c$) of 304.13 K) and **(b)** HFC-134a ($P_c$ of 4.056 MPa, $T_c$ of 374.18 K) in PS with **(a-insert)** literature data from pressure decay measurement (Sato et al., 1996, pressure up to 20 MPa), from elongation measurement (Wissinger & Paulaitis, 1987, pressure up to 5 MPa**),** and **(b-insert)** literature data from volumetric measurement (Sato et al., 2000, pressure up to 3 MPa), from gravimetry (Wong et al., 1998, pressure up to 4 MPa**)**. The correlation of $CO_2$ and HFC-134a solubility in PS with SAFT is illustrated with solid lines.

A precise experimental methodology and a mathematical development proposed by Boyer (Boyer et al., 2006b, 2007) use the thermodynamic approach of high-pressure-controlled scanning transitiometry (*P*CST) (Grolier et al., 2004; Bessières et al., 2005). The heat resulting from the polymer/solvent interactions is measured during pressurization/depressurization runs performed under isothermal scans. Several binary polymer/fluid systems with a more or less reactive pressurizing medium have been investigated with a view to illustrate the

importance of dissociating the purely hydrostatic effect from the fluid sorption over an extended pressure range.

Taking advantage of the differential mounting of the high pressure calorimetric detector and the proper use of the thermodynamic Maxwell's relation $\left(\partial S / \partial P\right)_T = -\left(\partial V / \partial T\right)_P$, a practical expression of the global cubic expansion coefficient $\alpha_{pol\text{-}g\text{-}int}$ of the saturated polymer subjected to the compressed penetrating (permeant) solvent under isothermal conditions has been established as follows by **eq. (7)**:

$$\alpha_{pol-g-\mathrm{int}} = \frac{\left(Q_{diff,SS} - Q_{diff,pol}\right) + V_{SS,r}\,\alpha_{SS}\,T\,\Delta P}{V_{pol}\,T\,\Delta P} \tag{7}$$

$\alpha_{SS}$ is the cubic expansion coefficient of the stainless steel of which are made the cells. $V_{pol}$ and $V_{SS}$ are the volumes of the polymer sample placed in the measuring cell and of the stainless steel (reference) sample placed in the reference cell, respectively. The stainless steel sample is identical in volume to the initial polymer sample. $Q_{diff,\,pol}$ is the differential heat between the measuring cell and the reference cell. $Q_{diff,\,SS}$ is the measure of the thermodynamic asymmetry of the cells. $\Delta P$ is the variation of gas-pressure during a scan at constant temperature $T$.

Three quite different pressure transmitting fluids, as regards their impact on a given polymer, have been selected: *i)* mercury (Hg), inert fluid, with well-established thermo-mechanical coefficients inducing exclusively hydrostatic effect, *ii)* a non-polar medium nitrogen ($N_2$) qualified as "poor" solvent, and *iii)* "chemically active" carbon dioxide ($CO_2$) (Glasser, 2002; Nalawade et al., 2006). While maintaining the temperature constant, the independent thermodynamic variables $P$ or $V$ can be scanned. Optimization and reliability of the results are verified by applying fast variations of pressure ($P$ jumps), pressure scans ($P$ scans) and volume scans ($V$ scans) during pressurization and depressurization. Additionally, taking advantage of the differential arrangement of the calorimetric detector the comparative behaviour of two different polymer samples subjected to exactly the same supercritical conditions can be documented. As such, three main and original conclusions for quantifying the thermo-diffuso-chemo-mechanical behaviour of two polymers, a polyvinylidene fluoride (PVDF) and a medium density polyethylene (MDPE) with similar volume fraction of amorphous phase, can be drawn. This includes the reversibility of the solvent sorption/desorption phenomena, the role of the solvent (the permeant) state, *i.e.*, gaseous or supercritical state, the direct thermodynamic comparison of two polymers in real conditions of use.

The reversibility of the sorption/desorption phenomena is well observed when experiments are performed at the thermodynamic equilibrium, *i.e.*, at low rate volume scans. The preferential polymer/solvent interaction, when solvent is becoming a supercritical fluid, is emphasized with respect to the competition between plasticization and hydrostatic pressure effects. In the vicinity of the critical point of the solvent, a minimum of the $\alpha_{pol\text{-}g\text{-}int}$ coefficient is observed. It corresponds to the domain of pressure where plasticization due to the solvent sorption is counterbalanced by the hydrostatic effect of the solvent. The significant influence of the 'active' supercritical $CO_2$ is illustrated by more energetic interactions with PVDF than with MDPE at pressure below 30 MPa (Boyer et al., 2009). The hetero polymer/$CO_2$ interactions appear stronger than the homo interactions between molecular chains. PVDF more easily dissolves $CO_2$ than MDPE, the solubility being favoured by the presence of polar groups C-F

in the PVDF chain (Flaconnèche et al., 2001). This easiness for $CO_2$ to dissolve is observed at high pressure where the parameter $\alpha_{pol\text{-}g\text{-}int}$ is smaller for highly condensed {PVDF-$CO_2$} systems than for less condensed {MDPE-$CO_2$} system (Boyer et al., 2007).
With the objective to scrutinize the complex interplay of the coupled diffusive, chemical and mechanical parameters under extreme conditions of $P$ and $T$, thermodynamics plays a pivotal role. Precise experimental approaches are as crucial as numerical predictions for a complete understanding of polymer behaviour in interactions with a solvent.

### 3.2 Thermodynamics as a means to understand and control nanometric scale length patterns using preferential liquid-crystal polymer/solvent interactions

Thermodynamics is ideally suited to obtain specific nano-scale pattern formation, for instance 'selective decoration' of arrayed polymer structure through selected additives, by controlling simultaneously the phase diagrams of fluids and of semi-crystalline polymers.
The creation of hybrid metal-polymer composite materials, with a well-controlled structure organization at the nanometric scale, is of great practical interest (Grubbs, 2005; Hamley, 2009), notably for the new generation of microelectronic and optical devices. Inorganic nanoparticles possess unique size dependent properties, from electronic, optical to magnetic properties. Among them, noble gold nanoparticles (AuNPs) are prominent. Included into periodic structures, inorganic nanoparticles can potentially lead to new collective states stemming from precise positioning of the nanoparticles (Tapalin et al., 2009). When used as thin organic smart masks, block copolymers make ideal macromolecular templates. Especially, the unique microphase separated structure of asymmetric liquid-crystal (LC) di-block copolymer (BC), like PEO-*b*-PMA(Az), develops itself spontaneously by self assemblage to form PEO channels hexagonally packed (Tian et al., 2002; Watanabe et al., 2008). $PEO_m$-*b*-$PMA(Az)_n$ amphiphilic diblock copolymer consists of hydrophilic poly(ethylene oxide) (PEO) entity and hydrophobic poly(methacrylate) (PMA) entity bearing azobenzene mesogens (Az) in the side chains, where $m$ and $n$ denote the degrees of polymerization of PEO and of photoisomarized molecules azobenzene moieties, respectively. By varying $m$ and $n$, the size of the diameters of PEO cylinders is controlled from 5 to 10 nm while the distance between the cylinders is 10 to 30 nm. Four phase transitions during BC heating are ascribed to PEO crystal melting, PMA(Az) glass transition, liquid crystal transition from the smectic C (SmC) phase to the smectic A (SmA) phase and isotropic transition (Yoshida et al., 2004). In $PEO_{114}$-*b*-$PMA(Az)_{46}$, the temperatures of the transitions are about 311, 339, 368 and 388 K, respectively.
As such, for creating smart and noble polymer-metal hybrids possessing a structure in the nanometric domain, three original aspects are discussed. They include the initial thermodynamic polymer/pressure medium interaction, the modulation of the surface topology concomitantly with the swelling of the solvent-modified nano-phase-separated organization, the "decorative" particles distribution modulation. All the aspects have an eco-aware issue and they are characterized through a rigorous analysis of the specific interactions taking place in LC/solvent systems.

**Polymer/pressurizing fluid interactions**

The isobaric temperature-controlled scanning transitiometry (*T*CST) (Grolier et al., 2004; Bessières et al., 2005) is used to investigate the phase changes via the Clapeyron's equation while the pressure is transmitted by various fluids. The enthalpy, volume and entropy

changes are quantified *versus* the (high) pressure of either Hg, $CO_2$, or $N_2$ (Yamada et al., 2007a-b). The hydrostatic effect of "more or less chemically active" solvent $CO_2$, or $N_2$ is smaller than the hydrostatic effect of mercury. The adsorbed solvent induces smaller volume changes at the isotropic transition than the mercury pressure. This results from the low compressibility of solvent (gas) molecules compared to the free volume compressibility induced in BC. A particular behaviour is observed with "chemically active" $CO_2$ where the quadrupole-dipole interactions favour the $CO_2$ sorption into the PMA(Az) matrix during the isotropic liquid transition (Kamiya et al., 1998; Vogt et al., 2003). The hydrostatic effect by $CO_2$ overcomes above 40 MPa with a $CO_2$ desorption at higher pressures explained by the large change of molecular motions at the isotropic transition upon the disruption of π-bounds with azobenzene moieties.

**Modulation of the surface topology and swelling of the $CO_2$-modified nanometric-phase-separated organization**

Supercritical carbon dioxide ($SCCO_2$) constitutes an excellent agent of microphase separation. From *ex-situ* Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) analysis of the pattern organization, the fine control of the pressure together with the temperature at which the $CO_2$ treatment is achieved demonstrates the possibility to modulate the surface topology inversion between the copolymer phases concomitantly with the swelling of the nano-phase-separated organization. The observed phase contrast results from the coupled effect of the different elastic moduli of the two domains of the block-copolymer with chemo-diffuso phenomenology.

Remarkably, the preferential $CO_2$ affinity is associated with the thermodynamic state of $CO_2$, from liquid (9 MPa, room temperarture (r.t.)) to supercritical (9 MPa, 353 K) and then to gaseous (5 MPa, r.t.) state (Glasser, 2002). This is typically observed when annealing the copolymer for 2 hours to keep the dense periodic hexagonal honeycomb array **(Fig. 3.a-d)**. Under gaseous $CO_2$, the surface morphology of PEO cylinders is not significantly expanded **(Fig. 3.a-b)**. However, liquid $CO_2$ induces a first drastic shift at the surface with the emergence of a new surface state of PEO cylinders. This surface state inversion is attributed to domain-selective surface disorganization. PMA(Az) in the glassy smectic C (SmC) phase cannot expand. PEO cylinders dissolve favourably within liquid $CO_2$, with polar interactions, get molecular movement, expand preferentially perpendicularly to the surface substrate **(Fig. 3.c)**. By increasing temperature, liquid $CO_2$ changes to supercritical $CO_2$. The PMA(Az) domain is in the SmC phase and get potential molecular mobility. At this stage, the copolymer chains should be easily swelled. The easiness of $SCCO_2$ to dissolve within liquid PEO cylinders deals with a new drastic change of the surface topology where the absorbed $SCCO_2$ increases the diameter of the PEO nano-tubes **(Fig. 3.d)**.

The preferential $CO_2$ affinities produce porous membranes with a selective sorption in hydrophilic semicrystalline 'closed loop', *i.e.*, PEO channels (Boyer et al., 2006a). More especially, under supercritical $SCCO_2$, the PEO cylinders kept in the ordered hexagonal display exhibit the highest expansion in diameter. In the case of $PEO_{114}$-*b*-$PMA(Az)_{46}$, the exposure to $SCCO_2$ swells the PEO cylinders by 56 %, with arrays from 11.8 nm in diameter at r.t. to 18.4 nm in diameter at 353 K. The lattice of the PMA matrix, *i.e.*, periodic plane distance between PEO cylinders, slightly increases by 26 %, from 19.8 nm at r.t. to 24.9 nm at 353 K. This microphase separation is driven by disparity in free volumes between dissimilar segments of the polymer chain, as described from the entropic nature of the closed-loop miscibility gap (Lavery et al., 2006; Yamada et al., 2007a-b).

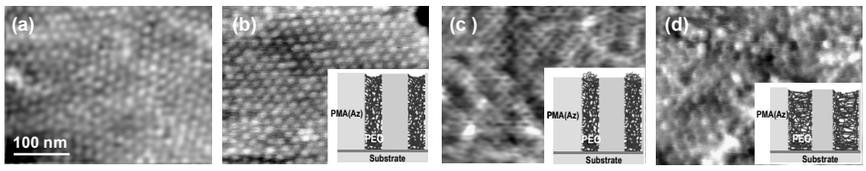



Fig. 3. Pattern control in the nanometric scale under multifaceted *T, P* and $CO_2$ constraints, 2 hrs annealed. AFM phase, tapping mode, illustrations on silicon substrate **(a)** neat $PEO_{114}$-*b*-$PMA(Az)_{46}$, PEO 'softer' than PMA(Az) appears brighter (whiter), **(b)** $GCO_2$ saturation (5 MPa, r.t.), **(c)** $LCO_2$ saturation (9 MPa, r.t.), PMA(Az) surrounding PEO becomes 'softer', **(d)** $SCCO_2$ saturation (9 MPa, 353 K), PEO becomes 'softer' while swelling. Inserts **(b-c-d)** are schematic representations of $CO_2$-induced changes of PEO cylinders. (BC film preparation before modification: 2 wt% toluene solution spin-coating, 2000 rpm, annealing at 423 K for 24 hrs in vacuum.)

**Modulation of the decorative particles distribution**

To create nano-scale hybrid of metal-polymer composites, the favourable $SCCO_2$/PEO interactions are advantageously exploited, as illustrated in **Fig. 4.a-b**. They enable a tidy pattern of hydrophilic gold nano-particles (AuNPs). AuNPs are of about 3 nm in diameter and stabilized with thiol end-functional groups (Boal & Rotello, 2000). Preferentially, the metal NPs wet one of the two copolymer domains, the PEO channels, but de-wet the other, the PMA(Az) matrix. This requires a high mobility contrast between the two copolymer domains, heightened by $CO_2$ plasticization that enhances the free volume disparity between copolymer parts. Each $SCCO_2$-swollen PEO hydrophilic hexagonal honeycomb allows the metal NPs to cluster. A two-dimensional (2D) periodic arrangement of hydrophilic AuNPs is generated in the organic PEO in turn confined into smectic C phase of PMA(Az) matrix which has potential molecular mobility. Additionally to the plasticizing action, the force of the trap is driving chemically. It is due to the hydrophilic compatibility of AuNPs in PEO cylinders by grafted polar groups (Watanabe et al., 2007).

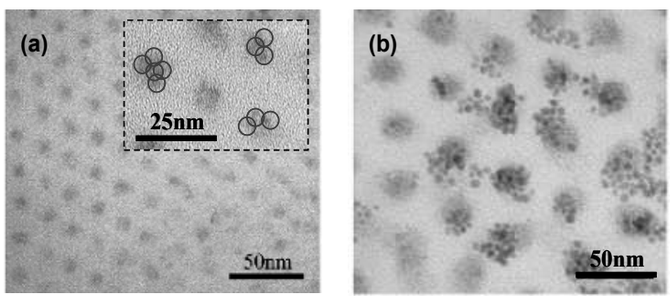



Fig. 4. Pattern control in the nanometric scale of PEO-*b*-PMA(Az) under multifaceted *T, P,* $CO_2$ constraints with AuNPs. TEM illustrations of BC on carbone coated copper grid **(a)** $PEO_{114}$-*b*-$PMA(Az)_{46}$, **(b)** $PEO_{454}$-*b*-$PMA(Az)_{155}$ doped with AuNPs under $SCCO_2$ (9 MPa, 353 K). Black spots are AuNPs wetted hexagonal PEO honeycomb, selectively. PEO is **(a)** 8.6, **(b)** 24.3 nm in diameter with a periodicity of **(a)** 17.1, **(b)** 36.6 nm. (Step 1, BC film preparation before modification: 2 wt% toluene solution solvent-casting, annealing at 423 K for 24 hrs in vacuum. Step 2, AuNPs deposition before modification: droplet of an ethanol solution of hydrophilic AuNPs (solvent in toluene of 1 %) on dried BC film, drying at r.t. for 2 hrs.)

The local affinities of AuNPs with PEO/$SCCO_2$ stabilize the thermodynamically unstable $SCCO_2$-plasticized network and keep it stable with time, which cannot be observed without the insertion of gold nano-particles mainly because of diffusion effect of the solvent (Boyer et al., **2006a)**. The mean height of AuNPs layer is about 3 nm, which is 20 times smaller than PEO cylinders with a 60 nm in length. Thus PEO channels could be considered as nano-dots receptors, schematically as a "compact core–shell model" consisting of a spherical or isotropic AuNP "core" embedded into a PEO channel "shell", consequently leading to isotropic two- and three-dimensional materials. Nicely, AuNPs clusters on PEO channel heads can be numerically expressed. The presence of, 4, 5 and 8 single Au nano-clusters for $m$ = 114, 272 and 454 is identified, respectively. It represents a linear function between the number of AuNPs on swollen PEO *versus* $SCCO_2$-swollen diameter with half of ligands of AuNPs linked with PEO polymer chain.

From this understanding, a fine thermodynamic-mechanical control over extended $T$ and $P$ ranges would provide a precious way to produce artificial and reliable nanostructured materials. $SCCO_2$-based technology guides a differential diffusion of hydrophilic AuNPs to cluster selectively along the hydrophilic PEO scaffold. As a result, a highly organized hybrid metal-polymer composite is produced. Such understanding would be the origin of a 2D nanocrystal growth.

### 3.3 Thermokinetics as a means to control macrometric length scale molecular organizations through molten to solid transitions under mechanical stress

A newly developed phenomenological model for pattern formation and growth kinetics of polymers uses thermodynamic parameters, as thermo-mechanical constraints and thermal gradient. It is a system of physically-based morphological laws-taking into account the kinetics of structure formation and similarities between polymer physics and metallurgy within the framework of Avrami's assumptions.

Polymer crystallization is a coupled phenomenon. It results from the appearance (nucleation in a more or less sporadic manner) and the development (growth) of semi-crystalline entities (*e.g.*, spherulites) (Gadomski & Luczka, 2000; Panine et al., 2008). The entities grow in all available directions until they impinge on one another. The crystallization kinetics is described in an overall manner by the fraction $\alpha(t)$ (surface fraction in two dimensions (2D) or volume fraction in three dimensions (3D)) transformed into morphological entities (disks in 2D or spheres in 3D) at each time $t$.

The introduction of an overall kinetics law for crystallization into models for polymer processing is usually based on the Avrami-Evans's (AE) theory (Avrami, 1939, 1940, 1941; Evans, 1945). To treat non-isothermal crystallization, simplifying additional assumptions have often been used, leading to analytical expressions and allowing an easy determination of the physical parameters, *e.g.*, Ozawa (1971) and Nakamura et al. (1972) approaches. To avoid such assumptions, a trend is to consider the general AE equation, either in its initial form as introduced by Zheng & Kennedy (2004), or after mathematical transformations as presented by Haudin & Chenot (2004) and recalled here after.

**General equations for quiescent crystallization**

The macroscopic mechanism for the nucleation event proposed by Avrami remains the most widely used, partly because of its firm theoretical basis leading to analytical mathematical equations. In the molten state, there exist zones, the potential nuclei, from which the crystalline phase is likely to appear. They are uniformly distributed throughout the melt,

with an initial number per unit volume (or surface) $N_0$. $N_0$ is implicitly considered as constant. The potential nuclei can only disappear during the transformation according to activation or absorption ("swallowing") processes. An activated nucleus becomes a growing entity, without time lag. Conversely, a nucleus which has been absorbed cannot be activated any longer. In the case of a complex temperature history $T(t)$, the assumption of a constant number of nuclei $N_0$ is no more valid, because $N_0 = N_0(T) = N_0(T(t))$ may be different at each temperature. Consequently, additional potential nuclei can be created in the non-transformed volume during a cooling stage. All these processes are governed by a set of differential equations (Haudin & Chenot, 2004), differential equations seeming to be most suitable for a numerical simulation (Schneider et al., 1988).

**Avrami's Equation**

Avrami's theory (Avrami, 1939, 1940, 1941) expresses the transformed volume fraction $\alpha(t)$ by the general differential equation **eq. (8)**:

$$\frac{d\alpha(t)}{dt} = (1-\alpha(t))\frac{d\tilde{\alpha}(t)}{dt} \tag{8}$$

$\tilde{\alpha}(t)$ is the "extended" transformed fraction, which, for spheres growing at a radial growth rate $G(t)$, is given by **eq. (9)**:

$$\tilde{\alpha}(t) = \frac{4\pi}{3}\int_0^t \left[\int_\tau^t G(u)du\right]^3 \frac{d\tilde{N}_a(\tau)}{d\tau}d\tau \tag{9}$$

$d\tilde{N}_a(t)/dt$ is the "extended" nucleation rate, $\frac{4\pi}{3}\left[\int_\tau^t G(u)du\right]^3$ is the volume at time $\tau$ of a sphere appearing at time $t$, and $d\tilde{N}_a(\tau)$ are spheres created per unit volume between $\tau$ and $\tau + d\tau$.

**Assumptions on Nucleation**

The number of potential nuclei decreases by activation or absorption, and increases by creation in the non-transformed volume during cooling. All these processes are governed by the following equations:

$$\frac{dN(t)}{dt} = -\frac{dN_a(t)}{dt} - \frac{dN_c(t)}{dt} + \frac{dN_g(t)}{dt} \tag{10a}$$

$$\frac{dN_a(t)}{dt} = q(t)N(t) \tag{10b}$$

$$\frac{dN_c(t)}{dt} = \frac{N(t)}{1-\alpha(t)}\frac{d\alpha(t)}{dt} \tag{10c}$$

$$\frac{dN_g(t)}{dt} = (1-\alpha(t))\frac{dN_0(T)}{dT}\frac{dT}{dt} \tag{10d}$$

$N(t), N_a(t), N_c(t), N_g(t)$ are the number of potential, activated, absorbed and generated (by cooling) nuclei per unit volume (or surface) at time *t*, respectively. *q(t)* is the activation frequency of the nuclei at time *t*. The "extended" quantities $\tilde{N}, \tilde{N}_a$ are related to the actual ones by:

$$N = (1-\alpha)\tilde{N} \tag{11a}$$

$$\frac{dN_a}{dt} = qN = (1-\alpha)\frac{d\tilde{N}_a}{dt} \tag{11b}$$

**The System of Differential Equations**

The crystallization process equations are written into a non-linear system of six, **eqs. (12, 13a, 14-17)**, or seven, **eqs. (12, 13b, 14-18)**, differential equations in 2D or 3D conditions, respectively (Haudin & Chenot, 2004):

$$\frac{dN}{dt} = -N\left(q + \frac{1}{1-\alpha}\frac{d\alpha}{dt}\right) + (1-\alpha)\frac{dN_0(T)}{dT}\frac{dT}{dt} \tag{12}$$

$$\frac{d\alpha}{dt} = 2\pi(1-\alpha)G(F\tilde{N}_a - P) \tag{13a}$$

$$\frac{d\alpha}{dt} = 4\pi(1-\alpha)G(F^2\tilde{N}_a - 2FP + Q) \tag{13b}$$

$$\frac{dN_a}{dt} = qN \tag{14}$$

$$\frac{d\tilde{N}_a}{dt} = \frac{qN}{1-\alpha} \tag{15}$$

$$\frac{dF}{dt} = G \tag{16}$$

$$\frac{dP}{dt} = F\frac{d\tilde{N}_a}{dt} = F\frac{qN}{1-\alpha} \tag{17}$$

$$\frac{dQ}{dt} = F^2\frac{d\tilde{N}_a}{dt} = F^2\frac{qN}{1-\alpha} \tag{18}$$

The initial conditions at time *t* = 0 are:

$$N(0) = N_0$$

$$\alpha(0) = N_a(0) = \tilde{N}_a(0) = F(0) = P(0) = Q(0) = 0 \tag{19}$$

*F*, *P* and *Q* are three auxiliary functions added to get a first-order ordinary differential system. The model needs three physical parameters, the initial density of potential nuclei $N_0$,

the frequency of activation $q$ of these nuclei and the growth rate $G$. In isothermal conditions, they are constant. In non-isothermal conditions, they are defined as temperature functions, *e.g.*:

$$N_0 = N_{00}\exp\left(-N_{01}(T-T_0)\right) \tag{20a}$$

$$q = q_0\exp\left(-q_1(T-T_0)\right) \tag{20b}$$

$$G = G_0\exp\left(-G_1(T-T_0)\right) \tag{20c}$$

**General equations for shear-induced crystallization**

Crystallization can occur in the form of spherulites, shish-kebabs, or both. The transformed volume fraction is written as (Haudin et al., 2008):

$$\frac{d\alpha(t)}{dt} = \frac{d\beta(t)}{dt} + \frac{d\kappa(t)}{dt} \tag{21}$$

$\beta(t)$ and $\kappa(t)$ are the thermo-dependent volume fractions transformed *versus* time into spherulites and into shish-kebabs, respectively.

**Spherulitic Morphology**

Modification of **eqs. (8)** and **(10a)** gives:

$$\frac{d\beta(t)}{dt} = (1-\alpha(t))\frac{d\tilde{\beta}(t)}{dt} \tag{22}$$

$$\frac{dN(t)}{dt} = -\frac{dN_a(t)}{dt} - \frac{dN_c(t)}{dt} + \frac{dN_g(t)}{dt} + \frac{dN_\gamma(t)}{dt} \tag{23}$$

$\beta(t)$ and $\tilde{\beta}(t)$ are the actual and extended volume fractions of spherulites, respectively. $N_\gamma(t)$ is the number of nuclei per unit volume generated by shear. Two situations are possible, *i.e.*, crystallization occurs after shear or crystallization occurs during shear.
If crystallization during shear remains negligible, the number of shear-generated nuclei is:

$$\frac{dN_\gamma}{dt} = a\dot{\gamma}(A-N_\gamma) \text{ if } a\dot{\gamma}(A-N_\gamma) \geq 0 \tag{24a}$$

$$\frac{dN_\gamma}{dt} = 0 \text{ if } a\dot{\gamma}(A-N_\gamma) \leq 0 \tag{24b}$$

$a$ and $A_1$ are material parameters, eventually thermo-dependent. As a first approximation, $A = A_1\dot{\gamma}$, with $\dot{\gamma}$ the shear rate.
If crystallization proceeds during shear, only the liquid fraction is exposed to shear and the shear rate $\dot{\gamma}'$ is becoming:

$$\dot{\gamma}' = \dot{\gamma} / (1-\alpha)^{1/3} \tag{25}$$

By defining $\tilde{N}_\gamma$ as the extended number of nuclei per unit volume generated by shear in the total volume, then:

$$\frac{d\tilde{N}_\gamma}{dt} = a\dot{\gamma}'(A_1\dot{\gamma}' - \tilde{N}_\gamma) \tag{26}$$

The number $N_\gamma$ of nuclei generated by shear in the liquid fraction is:

$$N_\gamma = (1-\alpha)\tilde{N}_\gamma \tag{27}$$

Under shear, the activation frequency of the nuclei increases. If the total frequency is the sum of a static component, $q_{st}$ , function of temperature, and of a dynamic one, $q_{flow}$ , then:

$$q = q_{st} + q_{flow} \tag{28}$$

$q_{flow}$ is given by **eq. (29)** where as a first approximation $q_2 = q_{02}\dot{\gamma}$ and $q_3$ is constant.

$$q_{flow} = q_2(1 - \exp(-q_3\dot{\gamma})) \tag{29}$$

The system of differential equations **(12, 13b, 14-18)** is finally replaced by a system taking the influence of shear into account through the additional unknown $N_\gamma$ and through the dynamic component of the activation frequency $q_{flow}$. Two cases are considered, *i.e.*, crystallization occurs after shear **(37a)** or crystallization occurs under **(37b)** shear.

$$\frac{dN}{dt} = -N\left(q + \frac{1}{1-\alpha}\frac{d\alpha}{dt}\right) + (1-\alpha)\frac{dN_0(T)}{dT}\frac{dT}{dt} + \frac{dN_\gamma}{dt} \tag{30}$$

$$\frac{d\beta}{dt} = 4\pi(1-\alpha)G(F^2\tilde{N}_a - 2FP + Q) \tag{31}$$

$$\frac{dN_a}{dt} = qN \tag{32}$$

$$\frac{d\tilde{N}_a}{dt} = \frac{qN}{1-\alpha} \tag{33}$$

$$\frac{dF}{dt} = G \tag{34}$$

$$\frac{dP}{dt} = F\frac{d\tilde{N}_a}{dt} = F\frac{qN}{1-\alpha} \tag{35}$$

$$\frac{dQ}{dt} = F^2\frac{d\tilde{N}_a}{dt} = F^2\frac{qN}{1-\alpha} \tag{36}$$

$$\frac{dN_\gamma}{dt} = a\dot{\gamma}(A_1\dot{\gamma} - N_\gamma) \tag{37a}$$

$$\frac{dN_\gamma}{dt} = a\dot{\gamma}\left((1-\alpha)^{1/3} A_1\dot{\gamma} - \frac{N_\gamma}{(1-\alpha)^{1/3}}\right) - \frac{N_\gamma}{1-\alpha}\frac{d\alpha}{dt} \tag{37b}$$

The initial conditions at time $t = 0$ are:

$$\begin{gathered} N(0) = N_0 \\ \alpha(0) = N_a(0) = \tilde{N}_a(0) = F(0) = P(0) = Q(0) = 0 \\ N_\gamma(0) = 0 \end{gathered} \tag{38}$$

**Shish-Kebab Morphology**

Firstly are introduced the notions of real and extended transformed volume fractions of shish-kebab, $\kappa$ and $\tilde{\kappa}$, respectively. Both are related by **eq. (39)**:

$$\frac{d\kappa(t)}{dt} = (1-\alpha)\frac{d\tilde{\kappa}(t)}{dt} \tag{39}$$

$\alpha(t)$ is the total transformed volume fraction for both spherulitic and oriented phases.
Shish-kebabs are modelled as cylinders with an infinite length. The growth rate $H$ is deduced from the radius evolution of the cylinder. The general balance of the number of nuclei for the oriented structure is given as:

$$\frac{dM(t)}{dt} = -\frac{dM_a(t)}{dt} - \frac{dM_c(t)}{dt} + \frac{dM_\gamma(t)}{dt} \tag{40}$$

$M(t)$, $M_a(t)$, $M_c(t)$, $M_\gamma(t)$ are the numbers of potential, activated, absorbed and generated (by shear) nuclei per unit volume, respectively. In the same way as for the spherulitic morphology, a set of differential equations can be defined where $w$ is the activation frequency of the nuclei, $b$ and $B_1$ the material parameters:

$$\begin{aligned} \frac{dM}{dt} &= -M\left(w + \frac{1}{1-\alpha}\frac{d\alpha}{dt}\right) \\ &+ b\dot{\gamma}\left((1-\alpha)^{1/3} B_1\dot{\gamma} - \frac{M}{(1-\alpha)^{1/3}}\right) - \frac{M}{1-\alpha}\frac{d\alpha}{dt} \end{aligned} \tag{41}$$

$$\frac{d\kappa}{dt} = 2\pi(1-\alpha)H(R\tilde{M}_a - S) \tag{42}$$

$$\frac{dM_a}{dt} = wM \tag{43}$$

$$\frac{d\tilde{M}_a}{dt} = \frac{wM}{1-\alpha} \tag{44}$$

$$\frac{dR}{dt} = H \tag{45}$$

$$\frac{dS}{dt} = R\frac{d\tilde{M}_a}{dt} = R\frac{wM}{1-\alpha} \tag{46}$$

*F*, *P*, *Q*, *R* and *S* are five auxiliary functions giving a first-order ordinary differential system. The initial conditions at time $t = 0$ are:

$$M(0) = M_0$$

$$\kappa(0) = M_a(0) = \tilde{M}_a(0) = R(0) = S(0) = 0 \tag{47}$$

**Inverse resolution method for a system of differential equations**

The crystallization, and especially the nucleation stage, is by nature a statistical phenomenon with large discrepancies between the sets of experimental data. The analytical extraction of the relevant crystallization parameters must be then considered as a multi-criteria optimization problem. As such the Genetic Algorithm Inverse Method is considered.
The Genetic Algorithm Inverse Method is a stochastic optimization method inspired from the Darwin theory of nature survival (Paszkowicz, 2009). In the present work, the Genetic Algorithm developed by Carroll (Carroll, "FORTRAN Genetic Algorithm Front-End Driver Code", site: *http://cuaerospace.com/ga*) is used (Smirnova et al., 2007; Haudin et al., 2008). The vector of solutions is represented by a parameter *Z*. In quiescent crystallization **(eqs. 20a-c)**, $Z = [N_{00}, N_{01}, q_0, q_1, G_0, G_1]$ with $N_{00}$, $N_{01}$, $q_0$, $q_1$, $G_0$, $G_1$ the parameters of non-isothermal crystallization for a spherulitic morphology. In shear-induced crystallization, $Z = [N_{00}, N_{01}, q_0, q_1, q_{02}, q_3, G_0, G_1, M_0, w, H, A_1, a, B_1, b]$ with ($q_{02}, q_3, A_1, a$) the parameters of shear-induced crystallization for a spherulitic morphology **(eqs. 26,29)** and ($M_0, w, H, B_1, b$) the parameters of shear-induced crystallization for an oriented, like shish-kebab, morphology **(eqs. 41,43,45,47)**.
The optimization is applied to the experimental evolution of the overall kinetics coupled with one kinetic parameter at a lower scale, the number of entities (density of nucleation $N_a(t)$). The system of differential equations is solved separately for each experimental set and gives the evolutions of $\alpha(t)$ and of the nuclei density defining a corresponding data file. The optimization function $Q_{total}$ is expressed as the sum of the mean square errors of the transformed volume fraction $Q_\alpha$ and of the number of entities $Q_{Na}$.

**Model-experiment-optimization confrontation**

The structure development parameters are identifiable by using the optical properties of the crystallizing entities. The experimental investigations and their analysis are done thanks to crossed-polarized optical microscopy (POM) (Magill, 1962, 1962, 2001) coupled with optically transparent hot stages, a home-made sliding plate shearing device and a rotating parallel plate shearing device (*e.g.*, Linkam). Data accessible directly are: *i)* the evolution of the transformed fraction $\alpha(t)$, and the number of activated nuclei $Na(t)$, *ii)* the approximate values of the initial number of potential nuclei $N_0(T)$, activation frequency $q(T)$, and growth rate $G(T)$ for isothermal conditions and their functions of temperature for non-isothermal

conditions **(eqs. 20a-c)**. The exponential temperature evolution of the three key parameters $N_0$, $q$, $G$ is possibly calculated from the values of the physical parameters obtained in three different ways: firstly, an approximate physical analysis with direct determination from the experiments *(APA)*, secondly, the use of the Genetic Algorithm method for an optimization based on several experiments (at least 5) done with the same specimen, thirdly, an optimization based on several experiments (at least 8) involving different polymer samples for which an important dispersion of the number of nuclei is observed (Haudin et al., 2008, Boyer et al., 2009). These sets of optimized temperature functions made it possible to validate the mathematical model in the 2D version, as illustrated in **Fig. 5.a-b-inserts**. The selected polymer is a polypropylene that is considered as a 'model material' because of its aptitude to crystallize with well-defined spherulitic entities in quiescent conditions.

Shear-induced crystallization, with a spherulitic morphology, gives access to the function $\mathrm{d}N_\gamma/\mathrm{dt}$ ($N_\gamma$ is the number of nuclei per unit volume generated by shear **(eq. 23)**) *versus* time and to the shear dependence of the activation frequency for different relatively low shear rates (up to 20 $s^{-1}$). A set of seven optimized parameters are identifiable: $N_{00}$, $q_0$, $G_0$ from quiescent isothermal crystallization, and ($q_{02}, q_3, A_1, a$) from isothermal shear-induced crystallization. The agreement between experiment and theory is better for higher shear rates associated with a shorter total time of crystallization. The mean square error does not exceed 12 %, the average mean square error for 5 $s^{-1}$ is equal to 6.7 %. The agreement between experiment and theory is less satisfactory for the number of spherulites, the mean square error reaches 25 %. Then, the new model is able to predict the overall crystallization kinetics under low shear with enough accuracy, when the entities are spherulitic.

Shear-induced crystallization, with both a spherulitic and an oriented morphology, is a different task. High shear rates (from 75 $s^{-1}$) enhance all the kinetics (nucleation, growth, overall kinetics) and lead to the formation of micron-size fibrillar (thread-like) structures immediately after shear, followed by the appearance of unoriented spherulitic structures at the later stages **(Fig. 6insert)**. The determination of the parameters for this double crystallization becomes a complicated task for a twofold reason: the quantitative data for both oriented and spherulitic structures are not available at high shear rate, and the double crystallization kinetics model requires to additionally determine the four parameters ($w, H, B_1, b$). So, optimization is based only on the evolution of the total transformed volume fraction **(eq. 21)**. Parameters characterizing quiescent crystallization ($N_{00}, q_0, G_0$) and shear-induced crystallization with the spherulitic morphology ($q_{02}, q_3, A_1, a$) are taken from the previous 'smooth' analysis, so that four parameters ($w, H, B_1, b$) characterizing the oriented structure have to be optimized.

**Fig. 6.** gathers the experimental and theoretical variations of the total transformed volume fraction for different shear rates. At the beginning, the experimental overall kinetics is faster than the calculated one most probably because the influence of shear rate on the activation frequency of the oriented structure is not taken into account. Since with higher shear rate thinner samples (~30 μm at 150 $s^{-1}$) are used, and since numerically the growth of entities is considered as three dimensional, the condition of 3D experiment seems not perfectly respected and the experiments give a slower evolution at the end. The mean square errors between numerical and experimental evolutions of the total transformed volume fraction do not exceed 19%.

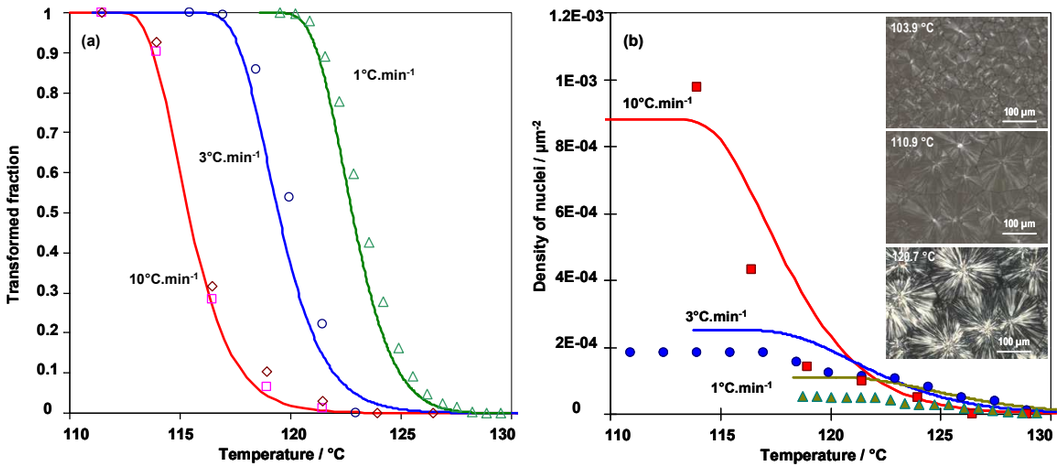



Fig. 5. Experimental (symbols) and numerically predicted (lines) of **(a)** the overall kinetics and **(b)** the number of activated nuclei *vs.* temperature at constant cooling-rate. The inserts illustrate the events at 10, 3 and 1 °C.min$^{-1}$. Sample: iPP in 2D (5 µm-thick layer).

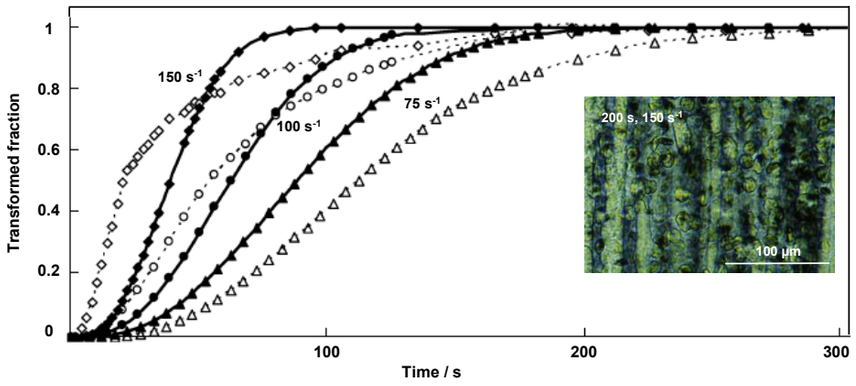



Fig. 6. Experimental (dashed-line curves) and numerically predicted (solid curves) total overall kinetics, *i.e.*, spherulitic and oriented structures, *vs.* time in constant shear, $T$ = 132 °C. The insert illustrates the event at 150 s$^{-1}$. Sample: iPP in 2-3D (~30 µm-thick layer).

The present differential system, based on the nucleation and growth phenomena of polymer crystallization, is adopted to describe the crystalline morphology evolution *versus* thermo-mechanical constraints. It has been implemented into a 3D injection-moulding software. The implementation allows us to estimate its feasibility in complex forming conditions, *i.e.*, anisothermal flow-induced crystallization, and to test the sensitivity to the accuracy of the values of the parameters determined by the Genetic Algorithm Inverse Method.

## 4. Conclusion

Fundamental understanding of the inherent links between multiscale polymer pattern and polymer behaviour/performance is firmly anchored on rigorous thermodynamics and

thermokinetics explicitly applied over extended temperature and pressure ranges, particularly under hydrostatic stress generated by pressure transmitting fluids of different physico-chemical nature.
Clearly, such an approach rests not only on the conjunction of pertinent coupled experimental techniques and of robust theoretical models, but also on the consistency and optimization of experimental and calculation procedures.
Illustration is made with selected examples like molten and solid polymers in interaction with various light molecular weight solvents, essentially gases. Data obtained allow evaluating specific thermal, chemical, mechanical behaviours coupled with sorption effect during solid to melt as well as crystallization transitions, creating smart and noble hybrid metal-polymer composites and re-visiting kinetic models taking into account similarities between polymer and metal transformations.
This work generates a solid platform for polymer science, addressing formulation, processing, long-term utilization of end-products with specific performances controlled via a clear conception of greatly different size scales, altogether with an environmental aware respect.

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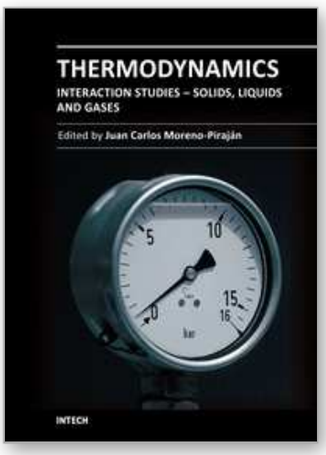
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