

CONFINEMENT EFFECTS ON POLYMER NUCLEATION AND CRYSTALLIZATION: FROM DROPLETS TO ALUMINA NANOPORES

Rose Mary Michell¹, Iwona Blaszczyk-Lezak², Carmen Mijangos², Alejandro J. Müller^{1*}

1: Grupo de Polímeros USB, Departamento de Ciencia de los Materiales, Universidad Simón Bolívar, Apartado 89000, Caracas 1080-A, Venezuela. 2: Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva, 3, 28006 Madrid, Spain.

* e-mail: amuller@usb.ve

ABSTRACT

We review how confinement from the micron to the nanometer scale can affect nucleation and crystallization of polymers in: droplets, blends, block copolymers and infiltration into alumina nanopores. Confinement can produce fractionated crystallization or exclusive crystallization at much higher supercoolings as compared to bulk polymers, as the degree of confinement increases. For highly confined heterogeneity free micro or nano-domains, overall crystallization kinetics is dominated by nucleation and therefore becomes first order. The nucleation mechanism changes from heterogeneous nucleation for bulk polymers to surface or homogeneous nucleation for ensembles of confined and isolated heterogeneity free micro or nanodomains. Surface nucleation is more commonly found than homogenous nucleation, although this fact is not frequently recognized in the literature

Keywords: Confinement, surface nucleation, homogeneous nucleation.

RESUMEN

En este trabajo se realiza una revisión del efecto del confinamiento sobre la nucleación y cristalización de polímeros en: gotas, mezclas, copolímeros en bloque y polímeros infiltrados en plantillas nanoporosas de alúmina. El confinamiento puede producir una cristalización fraccionada o una cristalización única a subenfriamientos mucho mayores a los que exhibe el polímero en masa, a medida que aumenta el grado de confinamiento. Para micro o nano-dominios altamente confinados y aislados que están libres de heterogeneidades, la cinética de cristalización global está dominada por la nucleación y consecuentemente se transforma en una cinética de primer orden. El mecanismo de nucleación cambia de heterogeneo para polímeros en masa a superficial u homogéneo para conjuntos de micro o nano-dominios libres de heterogeneidades. La nucleación superficial ocurre mucho más frecuentemente que la nucleación homogénea, aunque este hecho no se ha reconocido lo suficiente en la literatura

Palabras Claves: Confinamiento, nucleación superficial, nucleación homogénea.

1. INTRODUCTION

Careful examination of confinement literature in the framework of our own work have lead us to postulate the following generalizations [1-4]. The nucleation of dispersed micro or nano-domains (in droplets, blends, dispersions or infiltrated templates) is a complicated process, where at least four types of situations can arise:

(1) **Heterogeneous Nucleation.** Upon cooling from the melt, the first group of domains that can crystallize are those that contain highly active heterogeneities. The nucleation occurs at low supercoolings at temperatures equivalent to those for the bulk polymer in a classic heterogeneous nucleation case. If the number of microdomains is of the same order of magnitude than the number of heterogeneities present in the bulk polymer, less active heterogeneities may trigger additional nucleation processes at higher supercoolings. This case gives rise to the so called fractionated crystallization that has been observed in many blends and block copolymers components [1-4].

(2-4) **Heterogeneity free Nucleation.** Nucleation at large supercoolings of clean droplets or microdomains.

Upon further cooling, the clean droplet population can crystallize at larger supercoolings depending on their size and interfacial characteristics. If the droplets are in contact with an external surface or interface, this surface can also induce nucleation. Therefore, even in clean droplets or microdomains, three cases must be considered at increasing supercoolings, depending on the roughness of the surface in contact with the microdomain: (a) edge nucleation, (b) surface nucleation and finally (c) classic homogeneous nucleation, at the maximum possible supercooling (taking into consideration the volume of the droplets or microdomains).

2. DISCUSSION

Additionally, the isothermal crystallization kinetics in the case of heterogeneous nucleation is that usually encountered in semi-crystalline polymers, where the Avrami index takes values of 3 to 4 (or even 2 in some cases). On the other hand, when the crystallization of heterogeneity free micro or nano-domains is considered (usually taking place at large supercoolings by surface or homogeneous nucleation), a first order crystallization kinetics (or lower) is normally obtained

(i.e., an Avrami index of 1).

Taking into account the conditions and considerations explained above, it should be readily apparent that encountering classic homogeneous nucleation, where chains spontaneously aggregate within the volume of the domains under consideration would not be common. The differences in supercooling needed for the different types of nucleation are a function of the energy barriers involved, and the largest energy barrier is that faced by polymer chains in order to nucleate homogeneously.

Although true homogeneous nucleation has been documented for some confined polymers, like poly(ethylene oxide) or polycaprolactone, there are other polymers like polyethylene (PE), where surface nucleation dominates and careful examination of the literature indicates that classic homogeneous nucleation (despite claims to the contrary, in papers where just low values of crystallization temperature have been considered instead of surface nucleation) has never been observed for the case of PE droplets, blends or block copolymers (see refs. 1-3 and references there in).

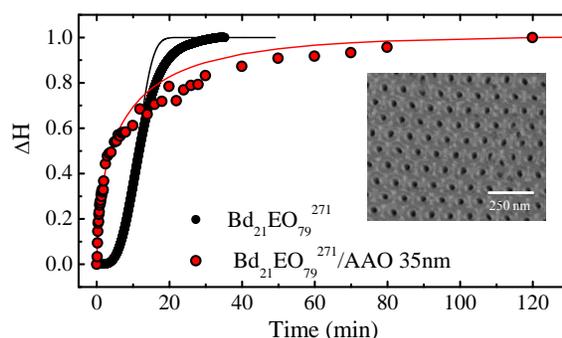


Figure 1. Variation of the relative degree of crystallinity (expressed as relative ΔH values) with time for (a) (c) $Bd_{21}-b-EO_{79}^{257}$ in the bulk ($T_c = 58$ °C) and within a 35 nm AAO template ($T_c = -4$ °C). The solid lines represent fits to the Avrami equation. The insert is a SEM micrograph showing a top view of the AAO employed.

Figure 1 is taken from a recent contribution by Michell et al. [4] where a linear diblock copolymer was infiltrated into an Alumina (AAO) template with 35 nm nanopores. The diblock copolymer was synthesized by sequential living anionic polymerization and its number average molecular weight is 257 kg/mol. It contains 79% of poly(ethylene oxide) and 21% of high 1,4 polybutadiene (PB). Its morphology consists of a percolated semi-crystalline PEO matrix with cylinders of amorphous PB. When the crystallization of the PEO block is studied in the diblock copolymer, a typical sigmoidal overall crystallization kinetics is obtained as shown in Figure 1, as expected in view of its composition. Fittings to the Avrami equation indicated that the Avrami index corresponded to instantaneously nucleated spherulites ($n=3$). After the copolymer is infiltrated in the cylindrical and isolated nanopores of the AAO template, a perfect confinement is achieved. The number of nanopores is ten orders of magnitude larger than the number of active heterogeneities present in the bulk diblock copolymer. This situation leads to statistically clean nanocylinders inside the nanopores, since the number of heterogeneities is insignificant. The PEO block of the infiltrated diblock copolymer can undergo surface or homogeneous nucleation. In this case, a classic homogeneous nucleation is most probably occurring because the crystallization temperatures observed during cooling from the melt are well correlated with those observed for PEO undergoing homogeneous nucleation taking into account the volume of the nanodomains involved in this case (details can be found in refs. 1-2, 4).

Figure 1 shows how the overall crystallization kinetics of the homogeneously nucleated PEO block infiltrated within the AAO nanopores displays a clear first order trend. In fact its Avrami index is close to 1. This was the first time that a first order crystallization kinetics was documented for a polymer component infiltrated within AAO templates. Avrami exponents obtained in other recent works have been larger than 2 indicating that ideal confinement had not been apparently obtained or that problems were encountered during the crystallization kinetics measurements.

3. REFERENCIAS

- [1]. Müller AJ, Balsamo V, Arnal ML Adv. Polym. Sci. 2005; 190: 1-63.
- [2]. Michell RM, Lorenzo AT, Müller AJ, Lin M-C, Chen H-L, Blaszczyk-Lezak I, Martín J, Mijangos C Macromolecules 2012; 45: 1517–1528.
- [3]. Müller AJ, Arnal ML, Lorenzo AT “Crystallization in Nano-Confined Polymeric Systems”. In: Piorkowska E, Rutledge G (eds.), Handbook of Polymer Crystallization; New York (USA): Wiley, 2013.
- [4]. Michell RM, Blaszczyk-Lezak I, Mijangos C, Müller AJ, Polymer 2013; 54: 4059–4077.