Thermal growth of organic supramolecular crystals with screw dislocations

Alexandre Dhotel · Laurent Delbreilh ·
Boulos Youssef · Jinyue Jiang · Gérard Coquerel ·
Jean-Marc Saiter · Li Tan

Abstract We report here a simple pathway to thermally assemble acene-based molecules into large crystals without modification of their chemical structures. Differential scanning calorimetry was used to characterize properly thermal events occurring during successive heating and cooling processes. More interestingly, observations by means of polarized light microscopy (POM) revealed that a spontaneous formation of screw dislocations within crystals during the isothermal treatment triggered a structural reorganization by forming large and well-defined spiral architectures. After this reorganization, new crystals showed an excellent ordering in both vertical and horizontal directions. Due to the richness in pi-electrons of acene-based molecules, we expect this work of importance to organic electronics, especially in the design of new molecular building blocks and investigation of their assembly into sophisticated supramolecular structures.

Keywords Supramolecules · Organic crystals · Phase transition · Screw dislocation · Differential scanning calorimetry (DSC) · Thermal crystallization

A. Dhotel · L. Delbreilh · B. Youssef · J.-M. Saiter
AMME—LECAP, EA4528, International Laboratory,
Institut des Matériaux de Rouen, Université et INSA de Rouen,
BP12, 76801 Saint Etienne du Rouvray Cedex, France

A. Dhotel (✉) · J. Jiang · L. Tan
AMME—A-TEAM, Department of Mechanical and Materials
Engineering, University of Nebraska, Lincoln, Nebraska 68588,
USA
e-mail: alexandredhotel@gmail.com

G. Coquerel
Equipe de cristallogenèse, Laboratoire Sciences et Méthodes
Séparatives, UPRES EA 3233, Université de Rouen, 1 rue
Lucien Tesnière, 76821 Mont Saint Aignan Cedex, France

Introduction

Supramolecular systems have received increasing interests since the early 90s for their easy configurability, structural reversibility, and processing flexibility [1–4]. In contrast to the strong interactions commonly seen in inorganic or metallic crystals, assembly of building blocks inside a supramolecule is exclusively driven by noncovalent intermolecular forces, including van der Waals interactions, hydrogen bonding, or weak electrostatic interactions [5–7]. While amphiphilic molecules are frequently chosen as the design for building blocks toward a supramolecular assembly of monolayers, bilayers, micelles, [8] and vesicles [9], flat and rod-shaped polar organic molecules have also demonstrated capabilities in delivering complex structures like liquid crystals [10]. Overall, these conventional approaches are all based on the use of highly polar molecules containing nitrogen, oxygen or fluorine atoms. As a consequence of these prerequisites, when a nonpolar molecule with engineering importance is used, lack of polar groups or atoms in its structure might give limited tunability to its solid state structure.

To aid our understanding of nonpolar molecule assembly, we chose one polyacene-based molecule and study its structural organization under a thermal treatment. Polyacenes, especially anthracene, tetracene, and pentacene, are hydrocarbon compounds that recently found important applications in organic electronic devices such as sensors and organic thin-film transistors [11–13]. Their alternating double and single bond structures lead to the formation of delocalized electrons promoting charge conduction between neighboring molecules [14, 15]. It has been found that molecular ordering is a prerequisite for efficient electronic devices and complex procedures or conditions need to be maintained before creating a uniform ordered

thin film. For instance, solution assembly is the most widely employed means in receiving supramolecules and has also been increasingly used for polyacene crystalline thin films. However, this process involves complex interplay between multiple parameters (substrate type, concentration, humidity, solvent type, assembly time, and so on) and may only produce short-range ordered materials, instead of large crystals [16–18].

We report here that one type of acene-based molecule, Ant-12 (2-dodecylanthracene, $C_{26}H_{34}$), is not only able to form supramolecular thin film through a solvent-free process but also showed the ability to undergo several crystallizations when simply cooled from the molten state. More interestingly, differential scanning calorimetry (DSC) and polarized light microscopy (POM) revealed that the high thermal energy of one of these crystallizations enables a continuous reorganization of building blocks leading to the formation of well-defined crystals or crystals with screw dislocations.

Experimental section

The chemical formula of the building block, 2-dodecyl-anthracene (named Ant-12 thereafter), is depicted in Fig. 1 and was synthesized from anthracene-2-carboxylic acid following the route described by Jiang [19].

DSC experiments were conducted on a Thermal Analysis Instruments heat flow calorimeter (DSC 2920 CE) on a 7.5 mg sample between 0 and 90 °C at a heating and cooling rate of 5 °C min^{-1}. The DSC was calibrated using indium as reference material, by matching the melting temperature and the associated enthalpy of indium. All experiments were performed under a nitrogen atmosphere.

X-ray scattering patterns were obtained on a Bruker-AXS D8 Discover diffractometer using a Cu Kα (1.544 Å) radiation. Digital data were recorded from $2\theta = 1°–9°$ at an angular resolution of 0.02° and angular velocity of 0.4° min^{-1} on an Ant-12 film prepared after heating the powder above melting temperature (105 °C). A domed hot stage was used as temperature controller to heat and cool the sample. A cooling rate of 5 °C min^{-1} was selected. Each scan was recorded 5 min after reaching the desired temperature.

Images from polarized light optical microscope (POM) were recorded on a Nikon Optiphot-2 with a Sony DXC 107AP camera. Observations were performed on thin films prepared by melting Ant-12 powder between two glass
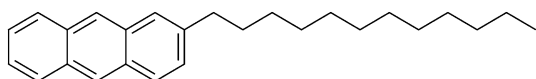

Fig. 1 Chemical formula of an Ant-12 molecule composed of a rigid aromatic ring ($C_{14}H_9$) and a soft alkyl tail ($C_{12}H_{25}$)

slides. A Mettler FP82HT hot stage connected to a Mettler FP90 central processor was used as temperature controller during observations.

Results and discussion

DSC analyses were conducted to identify the characteristic temperatures and enthalpies of transformations of Ant-12. Three exothermic events were observed upon cooling from 90 °C at 5 °C min^{-1} as shown in Fig. 2, suggesting multiple structural reorganizations. Interestingly, while the large enthalpy values (13.8 and 19.4 J g^{-1}) of the last two transitions at 59.5 and 31.8 °C (Table 1) indicate two major reorganization events from an amorphous or semi-crystalline material to oriented solid phases (S_1 and S_2), the low enthalpy value (3.6 J g^{-1}) of the first transition at 80.2 °C may suggest reorganization of an isotropic liquid via either of the two cases. Namely, at this temperature, either the hot liquid undergoes a partial crystallization that would lead to a biphasic state with coexisting liquid and solid phases or a total transformation where molecules that were originally in a totally disordered state (L) start to orient to form a transient state (TS) similar to liquid crystals [20–22]. Nonetheless, a combination of both transition types could lead to the first transition too (L–TS). The peak melting temperatures of S_2 and S_1 structures are 67.9 and 82.4 °C, respectively. Likely, the low enthalpy exothermic peak at 55 °C corresponds to the formation of S_1 crystals and the melting of TS structures is hidden by the broad S_2 and S_1 melting signals. Several heating and cooling processes revealed all these transitions totally reversible.

Polarized light microscopy was further conducted to track the cooling process. Figure 3 shows that, when cooled from the molten state to 80 °C, the material undergoes a large phase transition. Before the cooling process, Ant-12 stays as an isotropic liquid (100 °C, Fig. 3a), showing as a black background through the microscope. After cooling to 80 °C at 5 °C min^{-1} (Fig. 3b), formation of large anisotropic domains composed of a stacking of layers was observed. Bright spots indicate places where molecules tend to agglomerate. Presumably, foreign objects such as impurities coming from the substrate could act as a scaffold or nucleation site to promote the crystal formation and thus reduce their high surface energies [23–25]. Even though stacked layers suggest a high ordering in the direction normal to the substrate (Z-axis), rounded edges of these layers imply a lack of ordering in the plane parallel to the substrate (X–Y plane). The presence of a dark background at some places in Fig. 3b suggests an incomplete crystallization of the material at 80 °C.

X-ray diffraction (XRD) was also used to identify the structural modification occurring during the L–TS
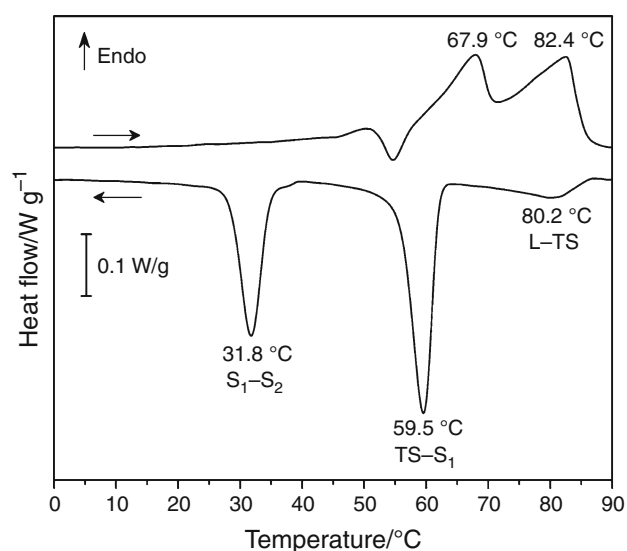
Fig. 2 DSC curves of Ant-12 showing three exothermic events upon cooling (L–TS, TS–S_1 and S_1–S_2) and two major melting processes upon heating. A rate of 5 °C min^{-1} was selected for both heating and cooling

Table 1 DSC peak temperatures and associated enthalpies of Ant-12 exothermic events when cooled from 90 to 0 °C at 5 °C min^{-1}

Exothermic event	S_1–S_2	TS–S_1	L–TS
T_p/°C	31.8	59.5	80.2
ΔH/J g^{-1}	13.8	19.4	3.6

transition. Figure 4 shows patterns recorded at 100 °C and after cooling down to 80 °C at 5 °C min^{-1}. The flat pattern exhibited at 100 °C confirms that Ant-12 forms an isotropic liquid where molecules are totally disordered [26]. After cooling down to 80 °C, a set of diffraction peaks appears. In order to ascribe these peaks, the length of our Ant-12 molecule was estimated at 2.26 nm by assuming that there are 18 consecutive carbon–carbon bonds with a length of 1.54 Å and angle of 109.5° for each bond. Therefore, a d-spacing of 2.35 nm ($2\theta = 3.8°$) indicates the molecules standing atop of each other to form lamellar structures. Each lamella being composed of a mono-molecular height layer, where molecules are fully extended and are perpendicular to the substrate. However, the pattern recorded at 80 °C also shows a minor bump at $2\theta = 3°$, corresponding to a d-spacing of 2.9 nm. This bump may originate from a secondary structure composed of a few interdigitated layers where alkyl chains of opposite directions are mixed. Unlike the crystallization process of polymeric multilayered films where layers are also at the nanometer scale, the molecular mobility inside our lamellae is not hindered by the confinement of long macromolecular chains [27–29].

The elevated temperature of the L–TS transition (80.2 °C) as well as its low enthalpy (3.6 J g^{-1}) indicate that, even if molecules formed large anisotropic domains, they should be highly mobile and thus be able to reorganize to form better-defined crystals of lower energies [23]. Indeed, Fig. 3c–e shows that, after several tens of minutes at 80 °C, Ant-12
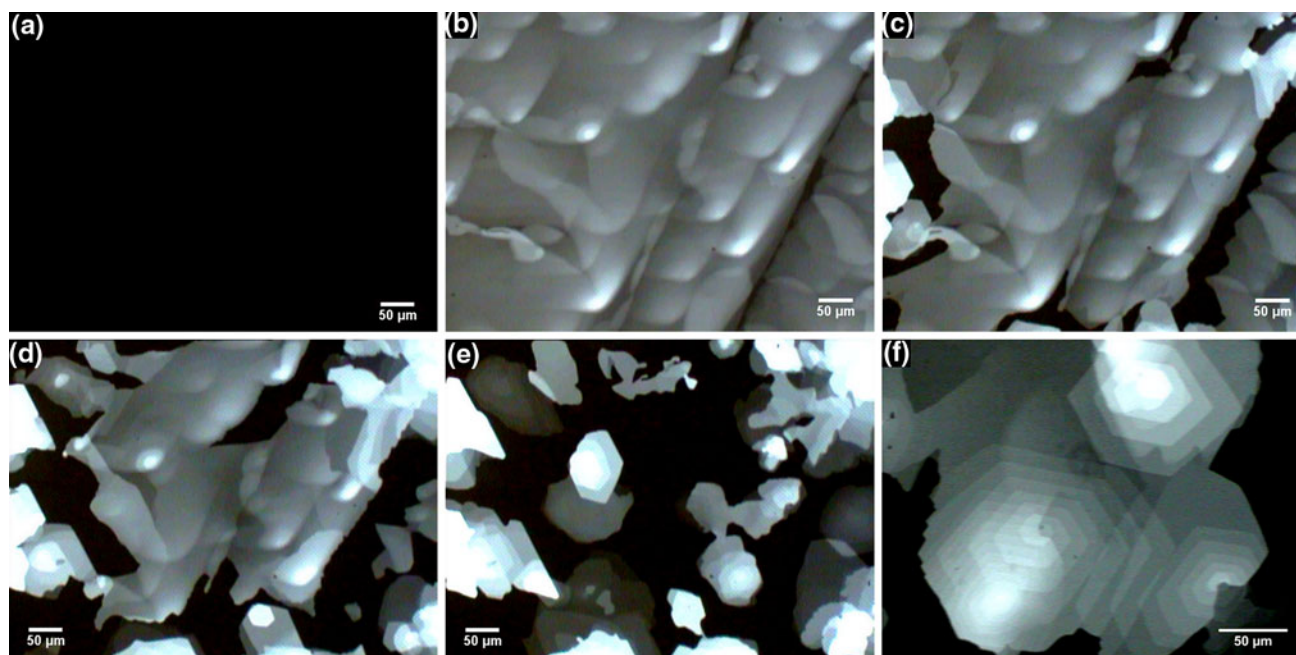

Fig. 3 Polarized light microscopy images of Ant-12 at **a** 100 °C and during the isothermal transition at 80 °C for **b** 0, **c** 10, **d** 20, **e** 30, and **f** 40 min. The cooling rate is set to 5 °C min^{-1} and remained zero after reaching the temperature of 80 °C
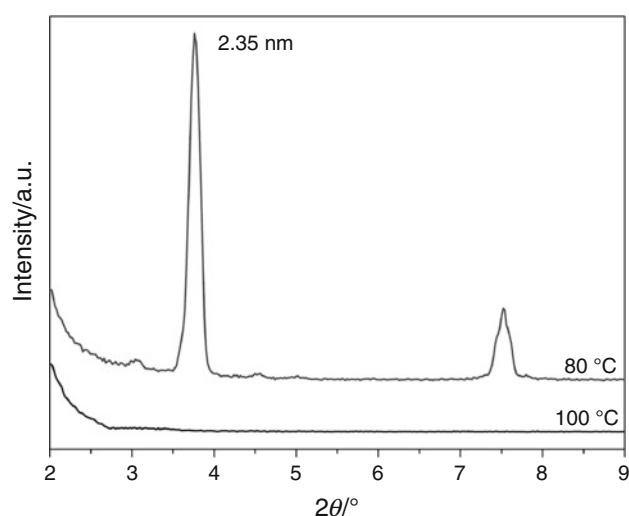
Fig. 4 XRD patterns of Ant-12. At 100 °C, the sample exhibits a flat pattern corresponding to an isotropic liquid. After cooling to 80 °C at 5 °C min^{-1}, a set of diffraction peaks shows up revealing the formation of an ordered phase

molecules reorganized to form different morphologies. Presumably, this structural reorganization is made possible by the weakness and reversibility of bonds holding molecules together. By taking into account the chemical composition of the Ant-12 molecule and especially the fact that it does not contain any polar groups, it is very likely that the building blocks within these ordered structures are only held together by van der Waals and π–π interactions. Particularly, the soft alkyl tails in Ant-12 can be packed together via van der Waals interactions and the double covalent bonds contained in the rigid polyacene head can lead them to interact through π–π interactions [19]. Such weak interactions being easily dissociated and formed, parts of the freshly formed *LT* structure can successively melt and recrystallize without degrading building blocks and give rise to a large structural reorganization over time.

Newly formed structures (*LT'*) grown over time are strongly anisotropic and exhibit straight edges suggesting a better ordering in the plane parallel to the substrate in addition to the layered stacking implying a good ordering in the three directions. One could guess that the initial cooling rate (i.e., 5 °C min^{-1}) might be too fast forcing molecules to form metastable constraint anisotropic structures (*LT*). If true, these structures that have a good Z-ordering but a poor *X*–*Y* packing will have a rather high internal energy [30]. To release this excess of energy, molecules inside *LT* structures can rearrange through a two-step process. First, *LT* structures melt to release structural strains, then newly free molecules reorganize into very well-organized structures (*LT'*) exhibiting ordering in the three directions. Finally, the film undergoes a major structural reorganization.

If the recrystallization time is further extended (40 min, Fig. 3f), large helical crystals can be observed at discrete places. Such unusual crystals have a very well-defined hexagonal shape and highly parallel straight edges between neighboring layers in all directions, highly consistent with the formation of screw dislocations. While this type of feature is often considered as defects in metal or inorganics materials, they can also be regarded as a crystal growth promoter for organic materials in specific conditions [31, 32]. In the present case, screw dislocations guide our lamellar layers to form a continuous helical ramp around the dislocation line finally forming a large helical crystal. As in pristine anthracene, the screw dislocation and the hexagonal shape may originate from the (001) basal plane of the crystal [31, 33]. We hypothesize the formation of our helical crystals as follows: free molecules previously involved in TS structures progressively agglomerate around attractive points such as impurities or defects. Over time, neighboring molecules are physically adsorbed and participate in the growth of the basal plane. As a contrast to the initial cooling ramp (i.e., 5 °C min^{-1}) leading to the formation of a lamellar structure (Fig. 3b), this isothermal treatment confers very low driving forces to the system that allows the formation of layers in the *X*–*Y* plane without further packing in the *Z*-direction [31]. Consequently, molecules start to centralize as a screw dislocation from the basal plane. Finally, the very slow growth leads to the formation of long range ordered hexagonal helical crystals with minimum surface energy [23].

Conclusions

We have shown that one type of nonpolar, acene-based molecule is not only able to form supramolecular thin film through a solvent-free process but also shows the ability to undergo several crystallizations when simply cooled from the molten state. While two of these crystallizations correspond to solid–solid transitions, one of them exhibits a very low enthalpy value corresponding to the formation of a transient state where molecules start to orient. The elevated temperature of this transition also triggers a structural reconfiguration leading to the formation of large helical crystals centered on screw dislocations. It seems that the spontaneous formation of screw dislocations is necessary for crystals to complete their growth. Finally, larger and better-defined crystals showing an excellent ordering in both vertical and horizontal directions are formed. The processing-ease of this finding makes it interesting for the creation of sophisticated supramolecular structures, as well as organic electronic devices often using acene-based nonpolar molecules.

References

1. Ling XY, Reinhoudt DN, Huskens J. From supramolecular chemistry to nanotechnology: assembly of 3D nanostructures. Pure Appl Chem. 2009;81:2225–9.

2. Dhôtel A, Li H, Fernandez-Ballester L, Delbreilh L, Youssef B, Zeng XC, Tan L. Supramolecular nanolayer reconfiguration after molecular intercalation. J Phys Chem C. 2011;115:10351–6.

3. Pensec S, Nouvel N, Guilleman A, Creton C, Boué F, Bouteiller L. Self-Assembly in solution of a reversible comb-shaped supramolecular polymer. Macromolecules. 2010;43:2526–9.

4. Yu C, Chen Z, Li H, Turner J, Zeng XC, Jin Z, Jiang J, Youssef B, Tan L. Molecularly intercalated nanoflakes: a supramolecular composite for strong energy absorption. Adv Mater. 2010;22:4455–7.

5. Lehn JM. Perspectives in supramolecular chemistry—from molecular recognition towards molecular information processing and self-organization. Angew Chem Int Ed. 1990;29:1304–16.

6. Lehn JM. Supramolecular chemistry. Science. 1993;260:1762.

7. Lehn JM. Toward complex matter: supramolecular chemistry and self-organization. Proc Natl Acad Sci USA. 2002;99:4763–6.

8. Kozlov MM, Opatowski E, Lichtenberg D. Calorimetric studies of the interactions between micelle-forming and bilayer-forming amphiphiles. J Therm Anal Calorim. 1998;51:773–782.

9. Ravoo BJ. Vesicles in supramolecular chemistry. supramolecular chemistry: from molecules to nanomaterials. 2012. doi:10.1002/9780470661345.smc032.

10. Goodby JW, Saez IM, Cowling SJ, Görtz V, Draper M, Hall AW, Sia S, Cosquer G, Lee S-E, Raynes EP. Transmission and amplification of information and properties in nanostructured liquid crystals. Angew Chem Int Ed. 2008;47:2734–54.

11. Llorente GR, Dufourg-Madec M-B, Crouch DJ, Pritchard RJ, Ogier S, Yeates SG. High performance acene-based organic thin film transistors. Chem Commun. 2009;21:3053–9.

12. Teague LC, Hamadani BH, Jurchescu OD, Subramanian S, Anthony JE, Jackson TN, Richter CA, Gundlach DJ, Kushmerick JG. Surface potential imaging of solution processable acene-based thin film transistors. Adv Mater. 2008;20:4513–4.

13. Payne MM, Parkin SR, Anthony JE, Kuo CC, Jackson TN. Organic field-effect transistors from solution-deposited functionalized acenes with mobilities as high as 1 cm^2 V^{-1} s^{-1}. J Am Chem Soc. 2005;127:4982–6.

14. Goetz KP, Li Z, Ward JW, Bougher C, Rivnay J, Smith J, Conrad BR, Parkin SR, Anthopoulos TD, Salleo A, Anthony JE, Jurchescu OD. Effect of acene length on electronic properties in 5-, 6-, and 7-ringed heteroacenes. Adv Mater. 2011;23:3696–8.

15. Martín-Lasanta A, Miguel D, García T, López-Villanueva JA, Rodríguez-Bolívar S, Gómez-Campos FM, Buñuel E, Cárdenas DJ, de Cienfuegos LÁ, Cuerva JM. Influence of the number of anchoring groups on the electronic and mechanical properties of benzene- anthracene- and pentacene-based molecular devices. ChemPhysChem. 2012;13:860–9.

16. Wo S, Headrick RL, Anthony JE. Fabrication and characterization of controllable grain boundary arrays in solution-processed small molecule organic semiconductor films. J Appl Phys. 2012;111:073711–16.

17. Takeyama Y, Maruyama S, Matsumoto Y. Growth of single-crystal phase pentacene in ionic liquids by vacuum deposition. Cryst Growth Des. 2011;11:2273–6.

18. Moser A, Flesch HG, Neuhold A, Marchl M, Ausserlechner SJ, Edler M, Griesser T, Haase A, Smilgies DM, Jakabovič J, Rese R. Crystallization of pentacene thin films on polymeric dielectrics. Synth Met. 2012;161:2595–8.

19. Jiang J, Lima OV, Pei Y, Jiang Z, Chen Z, Yu C, Wang J, Zeng XC, Forsythe E, Tan L. Self-Assembled nanolayers of conjugated silane with π–π interlocking. ACS Nano. 2010;4:3773–8.

20. Menczel J, Leslie T. Temperature calibration of an electrical compensation DSC on cooling using thermally stable high purity liquid crystals. J Therm Anal Calorim. 1993;40:914–57.

21. Hakvoort G, Hol C, van Ekeren P. DSC calibration during cooling. A survey of possible compounds. J Therm Anal Calorim. 2001;64:367–9.

22. Szilágyi A, Fetter G, Zrínyi M. Thermotropic behaviour of the complex liquid crystal system containing 8CB [4-cyano-4′-(n-octylbiphenyl)] and organic ferrofluid. J Therm Anal Calorim. 2005;82:525–6.

23. Myerson AS. Handbook of industrial crystallization. 2nd ed. Oxford: Butterworth-Heinemann; 2001.

24. Conrad BR, Gomar-Nadal E, Cullen WG, Pimpinelli A, Einstein TL, Williams ED. Effect of impurities on pentacene island nucleation. Phys Rev B. 2008;77:205325–8.

25. Kressner BE, Hudson JB. Impurity effects on heterogeneous nucleation from the vapor: selenium on glass. J Chem Phys. 1967;46:1740–5.

26. Yoshida H, Houshito Y, Mashiko K, Masaka K, Nakamura S. Thermal expansion of liquid crystalline polyesters having phenanthrene moieties: simultaneous DSC-XRD method. J Therm Anal Calorim. 2001;64:453–6.

27. Flores A, Arribas C, Fauth F, Khariwala D, Hiltner A, Baer E, Baltá-Calleja FJ, Ania F. Finite size effects in multilayered polymer systems: development of PET lamellae under physical confinement. Polymer. 2010;51:4530–9.

28. Puente Orench I, Stribeck N, Ania F, Baer E, Hiltner A, Baltá Calleja FJ. SAXS study on the crystallization of PET under physical confinement in PET/PC multilayered films. Polymer 2009;50:2680–7.

29. Arabeche K, Delbreilh L, Adhikari R, Michler GH, Hiltner A, Baer E, Saiter JM. Study of the cooperativity at the glass transition temperature in PC/PMMA multilayered films: influence of thickness reduction from macro- to nanoscale. Polymer. 2012;53:1355–61.

30. Hancock BC, Zografi G. Characteristics and significance of the amorphous state in pharmaceutical systems. J Pharm Sci. 1997;86:1–12.

31. Cuppen HM, Graswinckel WS, Meekes H. Screw dislocations on polyenes: a requirement for crystallization. Cryst Growth Des. 2004;4:1351–7.

32. Jo S, Yoshikawa H, Fujii A, Takenaga M. Surface morphologies of anthracene single crystals grown from vapor phase. Appl Surf Sci. 2006;252:3514–6.

33. AnbuSrinivasan P, Madhurambal G, Mojumdar SC. Thermal and spectral properties and induction period, interfacial energy and nucleation parameters of solution grown anthracene. J Therm Anal Calorim. 2012;108:939–48.