Polymer 42 (2001) 4709–4712

polymer

www.elsevier.nl/locate/polymer

Nanocrystalline films of poly(phthalocyaninatosiloxane) and HREM studies on them

Xiao Zhou[a,b,*], Zhi-liang Xie[c], Yun-hui Wang[c]

[a] *Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China*
[b] *School of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China*
[c] *Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China*

Received 3 July 2000; received in revised form 30 October 2000; accepted 14 November 2000

Abstract

The vapor of monomer, $Si(Pc)(OH)_2$, is deposited onto the (100) face of NaCl single crystal which is heated at 350°C under a dynamic vacuum of 10^{-3} Pa. Epitaxial crystallization occurs on the substrate, and condensation polymerization takes place in situ at the same time. The resulting product is a kind of nanocrystalline film of $[Si(Pc)O]_n$ that is composed of crystalline grains with a size of about 10 nm and a lot of defect regions without thermal energy stored in them, which differs from semi-crystalline polymers. The high-resolution electron microscope observations indicate that the nanocrystalline films of the polymer have something in common compared with nano-metals. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Nanocrystalline polymer; High-resolution electron microscope; Poly(phthalocyaninatosiloxane)

1. Introduction

Great progress has been made in the past twenty years in research on nano-particles and nanostructured materials, but research mainly focused on the nano-metal, nanoglass, C_{60} and its derivatives [1–5]. In polymers, research concentrated on organic/inorganic nano-hybrids [6–10], nanocomposites [11–14], nanosphere [15], nano-particles [16], nanofiber [17] and nanopore [18]. It is difficult to find references about nanocrystalline polymers.

The usual crystalline polymer materials are semi-crystalline and belong to a system where crystalline phase and non-crystalline phase coexist. For polymer materials with high content of crystalline phase, their crystallinity may reach 80–90% or even higher. For ordinary semi-crystalline polymer, its crystallinity is nearly 50% or lower. No true parallel can be drawn between semi-crystalline polymers and nanostructured materials although around 50% of the total volume fraction of regular crystalline regions is present in the latter. That is because the size of the crystalline grains of semi-crystalline polymer is in the order of μm, and more importantantly polymers in the non-crystalline phase have a general random structure with short-range order. The latter differs from another type of random structure — 'the defect core structure' in nano-metals and inorganic nano-materials. In semi-crystalline polymers, the random structure of the non-crystalline phase is caused by the thermal energy stored in the materials. The defect core structure in nano-materials is formed by incorporating defects such as vacancies, dislocations, grain or interphase boundaries, and it is an arrangement of atoms in the neighboring crystal potential field with minimum energy and does not require any thermal energy [1]. In addition, in organic/inorganic nano-hybrids and nanocomposites of polymer/nano-particles, though particles of nano-size exist, their continuity phase is still in a rather high level of energy state and quite a lot of thermal energy is stored. Therefore, they are not very much similar to nano-metals and inorganic nano-materials in the aspect of material structure. Their properties were improved compared with their home polymers, however, the improvements are not remarkable when compared with the case of nano-metals in which there are plenty of unusual physical effects. Then a question arises: can we get a structure very much similar to that of nano-metals in polymers? In this paper we have made a preliminary trial by using poly(phthalocyaninatosiloxane), $[Si(Pc)O]_n$.

Poly(phthalocyaninatosiloxane) is formed from phthalocyaninatosilicon dihydroxide, $Si(Pc)(OH)_2$, by condensation polymerization and is a kind of rigid chain polymer. Its

---

[*] Corresponding author. Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China. Tel.: +86-10-6277-2985; fax: +86-10-6277-0304.

E-mail address: zhoux@mail.tsinghua.edu.cn (X. Zhou).

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(00)00843-0

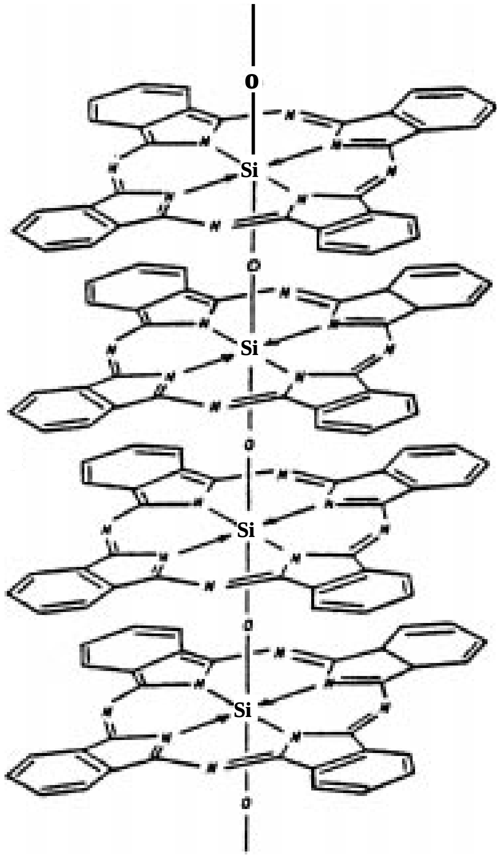

Fig. 1. Model of molecular chain of $[Si(Pc)O]_n$.

chain axis, –Si–O–Si–, is a rectilinear stick and each phthalocyanine ring (Pc ring) is perpendicular to the chain axis with an Si atom at the center (see Fig. 1). It is, therefore a rectilinear and rigid molecule in which phthalocyanine rings are parallel to each other and perpendicular to the chain axis [19]. The polymer can be prepared from its monomer crystal by solid state polymerization [20], and can also be obtained by crystallization by vapor deposition under vacuum (CVD method), in which the monomer is evaporated under vacuum and deposited onto a single crystal substrate, followed by epitaxial crystallization and condensation polymerization. In the latter case, the crystal structure in the resulting polymer film is dependent on the material and temperature of the substrate. When the vapor is deposited onto a cleaved (100) face of a NaCl single crystal which is heated at 350°C, the molecular chain will be perpendicular to the substrate in the resulting film [21]. Therefore, when we observe the specimen of the film with a high-resolution electron microscope (HREM), we can obtain the molecular image of the polymer. In the image, each of the black square blocks (actually they are not real square blocks) represent the vertical projection of the polymer chain whose shape and size are similar to those of the phthalocynine ring whose center contains a Si atom and the side length is about 1.38 nm. Such kinds of molecular images of the polymer and the likes have been reported before [19,21–26], but their crystalline grains are not in nano-size.

We have prepared the nanocrystalline film of $[Si(Pc)O]_n$ by CVD method, and have conducted analysis and investigations on its structure with a HREM.

2. Experiments

2.1. Specimen preparation

A piece of newly-cleaved NaCl single crystal was heated under dynamic vacuum of 10^{-3} Pa and the temperature rose up to 350°C. The crystal was degassed at that temperature for 2 h. Then the monomer was evaporated and deposited onto the newly-cleaved (100) face of the NaCl single crystal at the temperature (350°C) in the same vacuum system. Condensation polymerization took place in situ and epitaxial crystallization occurred on the substrate at the same time.

2.2. IR analysis of the resulting film

The composition of the resulting films was identified with a FTIR spectrometer NICLET-170SX. The films were scanned 50 times at a rate of 20 times/min.

2.3. Molecular image of the resulting film

The resulting vapor deposited films were transferred to the micro-grids coated with carbon supporting films. The morphology observation and high-resolution imaging were conducted under a transmission electron microscope JEOL JEM-200CX. The accelerating voltage was 200 kV, the filament current 200 μA, the spherical aberration coefficient 1.2 mm, the optimum defocusing −55 nm, the film exposure time 4 s and the direct magnification 2×10^5. The HREM operating process was similar to that of minimum dose system (MDS).

3. Results and discussion

3.1. Confirmation of the polymer formation

Fig. 2 is a FTIR spectrum of the resulting film mentioned above. It can be seen from the spectrum that there are no peaks at 780 and 830 cm^{-1}, which means that there is no monomer $Si(Pc)(OH)_2$ remaining in the resulting film [20]. Moreover, a peak at 910 cm^{-1} is strong and a peak at 804 cm^{-1} is weak, but the one at 911 cm^{-1} is medium and the one at 804 cm^{-1} is shoulder, it denotes that the resulting product is the polymer $[Si(Pc)O]_n$ [20].

3.2. High-resolution electron micrograph of the nanocrystalline polymer

Fig. 3 shows the high-resolution electron micrograph of

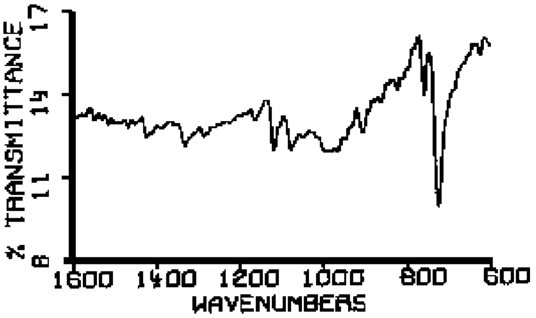

Fig. 2. FTIR spectrum of $[Si(Pc)O]_n$ polymerized and epitaxially crystallized from $Si(Pc)(OH)_2$ vapor on a newly cleaved (100) face of NaCl single crystal heated at 350°C.

the resulting film. Each of the black blocks in the figure represents a projection of the molecular chain of $[Si(Pc)O]_n$ that is perpendicular to the plane of the micrograph. Obviously, the size of each grain in the direction of a and b axis is nearly 10 nm, so the resulting film is actually nanocrystalline polymer.

3.3. A scheme of the molecular arrangement in the nanocrystalline polymer film

We can divide the film structure in Fig. 3 into two parts: nanocrystalline grain region; and defect region as shown in Fig.4. Solid blocks represent the molecular chains in the nanocrystalline grains. The black blocks denote the core part of the grains, while the gray blocks denote the remaining part of the grains in which the chain arrangement is not as perfect as that of the core part of the nanocrystalline grains. Hollow blocks represent molecules in the defect region. Square frames with full lines show the molecular chains located at clear parts in the high-resolution electron micrograph. Square frames with dotted lines show molecular chains located at not very clear parts in the micrograph. The shaded regions denote the deviated areas in nano-size. In those areas the polymer chains might be slightly tilted so that the Bragg condition is not satisfied there for molecular imaging, or they might be nanovoids.

On the whole, the resulting film is composed of grains with a size of about 10 nm and a lot of defects with the total volume fraction of each part making up about 50%. When discussed in detail, it can be seen that the polymer chains within the grains are arranged in order but a quasi-periodic array of atoms does exist [1], such as the grain C. The defect region is composed of grain boundaries and the deviated areas in nano-size. Polymer molecules in the grain boundaries are arranged as random structures basically without stored thermal energy.

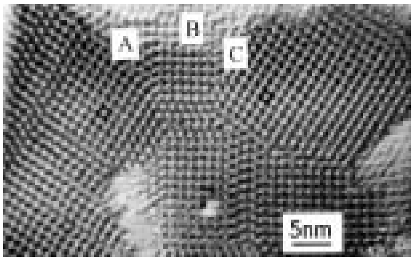

Fig. 3. HREM image of the nanocrystalline film of $[Si(Pc)O]_n$.

Wu et al. [26] showed that there are two kinds of unit-cells in the vapor deposited film of $[Si(Pc)O]_n$: the simple tetragonal unit-cell and base-centered othorhombic one. If these two kinds of unit-cells co-exist in the process of the crystal growth, stacking faults will occur. A typical situation is shown in Fig. 5 where the coexistence of the two kinds of unit-cells can clearly be seen. In actual polymer films it is sometimes easy to notice the existence of such defects as in the case of the grain boundaries of B/E and D/E marked in Fig. 4. But sometimes its existence could be recognized only by a careful study as in the case of grain boundaries of I/H and H/A marked in Fig. 4. The grain boundaries A/G and G/F are formed by a kind of edge dislocation [27], the A/B, B/C, A/E and C/E are formed by small-angle grain boundaries and the C/D is a tilt-boundary. All of them indicate that various defect nuclei concentrate on the grain boundaries. It leads to the formation of random structures far from equilibrium states and it is at low energy level.

As mentioned above, the structure of the nanocrystalline films obtained through vapor deposit/condensation polymerization, in situ and epitaxial crystallization, has many things in common with that of nano-metals prepared by vapor deposit/compact under high mechanical pressure in a vacuum chamber [28–29].

4. Conclusions

Nanocrystalline films can be obtained from monomer $Si(Pc)(OH)_2$ vapor after being deposited onto a (100) cleaved face of NaCl single crystal heated at 350°C under a vacuum. The epitaxial crystallization occurs on the substrate and the condensation polymerization takes place in situ at the same time in the direction perpendicular to the substrate surface. Such nanocrystalline films are composed of crystalline grains with a size of 10 nm and a lot of defects,

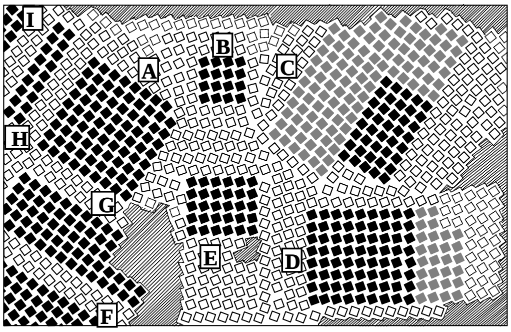

Fig. 4. A scheme of the arrangement of nanocrystalline grains, grain boundaries and nano-scale deviated areas of the $[Si(Pc)O]_n$ thin film, which are recognized in Fig. 3.

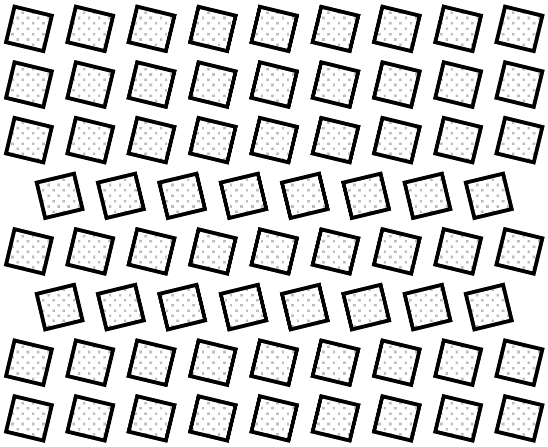

Fig. 5. A scheme of the stacking fault formed by sandwiching an orthorhombic form between the tetragonal forms.

both constituting about 50 vol%. The arrangement of polymer molecules inside nano-grains is quite orderly but dislocations also exist. Defect regions consist of grain boundaries and the deviated areas in nano-size. Such a structure of nanocrystalline polymeric films has many things in common with that of nano-metals prepared by evaporation and compacted under high mechanical pressures in a vacuum chamber.

References

[1] Gleiter H. Prog Mater Sci 1989;33:223.
[2] Edelstein AS, Cammarata RC. Nanomaterials: synthesis, properties and applications. Bristol and Philadelphia: Institute of Physics Publishing, 1998 (Parts 2, 5, and 7).
[3] Calvert P. Nature 1996;383:300.
[4] Yip S. Nature 1998;391:532.
[5] Brune H, Giovannini M, Bromann K, Kern K. Nature 1998;394:451.
[6] Kojima Y, Usuki A, Kawasumi M, Okada A, Kurauchi T, Kamigaito O. J Polym Sci, Part A: Polym Chem 1993;31:1755.
[7] Ou Y, Yang F, Yu Z-Z. J Polym Sci, Part B: Polym Phys 1998;36:789.
[8] Haraguchi K, Usami Y, Yamamura K, Matsumoto S. Polymer 1998;39:6243.
[9] Tian D, Blacher S, Jerome R. Polymer 1999;40:951.
[10] Keller TM, Son DY. In: Salamone JC, editor. Concise polymeric materials encyclopedia, Bock Raton: CRC Press, 1999. p. 677–9.
[11] Vaia RA, Sauer BB, Tse OK, Giannelis EP. J Polym Sci, Part B: Polym Phys 1997;35:59.
[12] Biswas M, Ray SS. Polymer 1998;39:6423.
[13] Neoh KG, Tan KK, Goh PL, Huang SW, Kang ET, Tan KL. Polymer 1999;40:887.
[14] Hu Q, Marand E. Polymer 1999;40:4833.
[15] Serizawa T, Chen M-Q, Akashi M. J Polym Sci, Part A: Polym Chem 1998;36:2581.
[16] Nah J-W, Jeong Y-I, Cho C-S. J Polym Sci, Part B: Polym Phys 1998;36:415.
[17] Fong H, Chun I, Reneker DH. Polymer 1999;40:4585.
[18] Tsutsui K, Tsujita Y, Yoshimizu H, Kinoshita T. Polymer 1998;39:5177.
[19] Wu J-h, Pan Z-a, Du X-l, Zhou X, Zou B-s, Zhu M. J Polym Sci, Part C: Polym Lett 1988;26:433.
[20] Dirk CW, Inabe T, Schock Jr. KF, Marks TJ. J Am Chem Soc 1983;105:1539.
[21] Zhou X, Xie Zh-l, Wang Y-h. J Chin Electr Microsc Soc 1998;17:734.
[22] Kobayashi T, Uyeda N. J Cryst Growth 1987;84:589.
[23] Kobayashi T, Uyeda N. Philos Mag B 1988;57:493.
[24] Kawase N, Kurata H, Kubono K, Isoda S, Kobayashi T. J Polym Sci, Part B: Polym Phys 1993;31:1713.
[25] Kobayashi T. Crystals growth, properties and applications. In: Freyhardt HC, Müller G, Karl N, editors. Organic crystals I: characterization, vol. 13. Berlin: Springer, 1991. p. 1–63.
[26] Wu J-h, Zou B-s, Pan Z-a, Du X-l. J Polym Sci, Part B: Polym Phys 1995;33:379.
[27] Tsuji M. In: Allen SG, Bevington JC, editors. Polymer characterization, Comprehensive polymer science. Oxford: Pergamon Press, 1989. p. 820.
[28] Wunderlich W, Ishida Y, Maurer R. Scripta Metall Mater 1990;24:403.
[29] Ping DH, Li DX, Ye HQ. J Mater Sci Lett 1995;14:1536.