Progress in Polymer Science 77 (2018) 95–117

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Molecular self-assembly of one-dimensional polymer nanostructures in nanopores of anodic alumina oxide templates

Hui Wu[a,b], Yuji Higaki[b,c], Atsushi Takahara[b,c,*]

[a] College of Material Engineering, Fujian Agriculture and Forestry University, Fuzhou, Fujian 350002, China
[b] Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
[c] International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

ARTICLE INFO

Article history:
Received 11 July 2017
Received in revised form 15 October 2017
Accepted 25 October 2017
Available online 1 November 2017

Keywords:
AAO template
Crystallization
One-dimensional nanostructures
Orientation
Self-assembly

ABSTRACT

One-dimensional (1-D) polymer nanostructures have attracted much attention due to their unique properties and many potential applications in areas such as sensors, transistors, separation, storage, and photovoltaic cells. This is a review of research activities on 1-D polymer nanostructures fabricated by anodic aluminum oxide (AAO) templates. The preparation methods of polymer nanostructures by AAO templates including polymer melt infiltration, polymer solution infiltration, and chemical synthesis are introduced. According to the molecular structure of polymers, the morphology, and properties of seven types of polymers, amorphous homopolymers, amorphous–amorphous block copolymers, amorphous/amorphous polymer blends, semicrystalline homopolymers, semicrystalline/amorphous polymer blends, semicrystalline-amorphous block copolymers, and semicrystalline–semicrystalline block copolymers in nanopores are demonstrated.

Contents

Abbreviations: 1-D, one-dimensional; AAO, anodic aluminum oxide; AFM, atomic force microscopy; AIBN, 2,2′-azobis-(isobutyronitrile); APTES, 3-aminopropyltriethoxysilane; BCP, diblock copolymers; DS, dielectric spectroscopy; DSC, differential scanning calorimetry; FTIR, Fourier transform infrared spectroscopy; GI-XRD, grazing incidence X-ray diffraction; iPP, isotactic polypropylene; iPS, isotactic polystyrene; MMA, methyl methacrylate; N, the total degree of polymerization; NMR, nuclear magnetic resonance; P3ATs, poly(3-alkylthiophene)s; P3HT, poly(3-hexylthiophene); P3MT, poly(3-methylthiophene); PAA, poly(acrylic acid); PB, 1,4-polybutadiene; PBA, poly(butylene adipate); PBLG, poly(γ-benzyl-L-glutamate); PBMA, poly(*n*-butyl methacrylate); PCL, poly(ε-caprolactone); PDMS, polydimethylsiloxane; PE, polyethylene; PEDOT, poly(3,4-ethylenedioxythiophene); PEO, poly(ethylene oxide); PFPE, perfluoropolyether; PI, *cis*-1,4-polyisoprene; PMA, poly(methyl acrylate); PMAA, poly(methacrylic acid); PMAPS, poly(3-(*N*-2-methacryloyloxyethyl-*N*,*N*-dimethyl)ammonatopropanesulfonate); PMETAC, poly(2-(methacryloyloxy)ethylmethylammonium chloride); PMMA, poly(methyl methacrylate); PMPS, poly(phenylmethylsiloxane); PNIPAM, poly(*N*-isopropylacrylamide); POEGMA, poly(oligo (ethylene glycol) methyl ether methacrylate); PPO, poly(2,6-dimethylphenylene oxide); PS, polystyrene; PSPMA, poly(3-sulfopropyl methacrylate potassium salt); PTH, polythiophene; PVAc, poly(vinyl acetate); PVDF, poly(vinylidene fluoride); S, spreading coefficient; SANS, small-angle neutron scattering; SEM, scanning electron microscopy; SI-ATRP, surface-initiated atom transfer radical polymerization; sPP, syndiotactic polypropylene; sPS, syndiotactic polystyrene; T_c, crystallization temperature; TEM, transmission electron microscopy; T_g, glass transition temperature; T_m, melting point; XRD, X-ray diffraction; χ, interaction parameter.

* Corresponding author at: Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.
E-mail address: takahara@cstf.kyushu-u.ac.jp (A. Takahara).

https://doi.org/10.1016/j.progpolymsci.2017.10.004
0079-6700/© 2017 Published by Elsevier B.V.

1. Introduction

The morphology and properties of polymers in the bulk state, such as the glass transition temperature (T_g), elastic modulus, heat capacity, crystalline forms and structure, are well established [1,2]. For example, in many semicrystalline polymers without confinement, complex crystalline entities like spherulites are produced by quenching liquids into crystalline solids. Most semicrystalline polymers in the bulk state crystallize at low supercoolings via heterogeneous nucleation, which is initiated by external means such as impurities, additives, interfaces and possibly interphases. Homogeneous nucleation occurs randomly in the interior of a uniform substance, involving the spontaneous clustering of several segments with larger stable nuclei above a critical size [3].

During the past two decades, polymer nanostructures have received considerable attention due to their unique properties and many potential applications in areas such as sensors, transistors, separation, and photovoltaic cells [4–15]. The morphology depends on the geometry and dimension of nanodomains. Many efforts have been made to manipulate the structure and properties of polymers in nanoconfined dimensions. To control the properties of nanostructured materials in the development of nanotechnology, template infiltration [16], ultrathin films [17], droplets [18], nanoimprint lithographies [19], electrospinning [20], and self-assembled phase-separated block copolymers [21] have been exploited as a powerful platform to build structures of nanocylinders, nanosheets, nanospheres, nanotrenches, and nanofibers. The chain mobility, dynamics, alignment, nucleation, and crystallinity are significantly influenced by these confinements that associate with their optical, electric, and mechanic properties. Thus, polymers in confined dimensions exhibit unusual behaviors different from the bulk materials.

Among the various preparation methods developed for polymer nanostructures, template-based approaches have drawn significant attention. Martin et al. explored a general method termed template synthesis for the preparation of tubular and fibrillar micro/nanostructures, entailing the synthesis of the desired one-dimensional (1-D) materials within the pores of a nanoporous template [4]. Various porous templates, such as anodic aluminum oxide (AAO) templates [7,22], track-etched membranes [22], silicon templates [23], self-assembled block copolymers templates [24], anodic titanium oxide templates [25], patterned perfluoropolyether (PFPE) mold [26] and polydimethylsiloxane (PDMS) stamp [27] are used to make well-ordered polymeric nanostructures with controllable morphology. In particular, AAO templates, a typical self-ordered nanohole material formed by anodizing aluminum in an appropriate acidic solution [28–30], are the most commonly employed templates for the nanofabrication of various functional nanostructures in forms of nanowires, nanotubes, nanorods, nanospheres, and nanoporous films due to their unique properties and potential applications in many areas, such as molecular separation, catalysis, drug delivery, sensors, electronics, and photonics, energy generation, and storage [31,32].

AAO membranes possessing straight, rigid, separated, and monodisperse cylindrical pores are ideal templates for the preparation of nanomaterials with monodisperse diameters in the nanometer to micrometer scales. The size and shape of the features in the fabricated nanomaterials can be easily controlled by the template geometry. AAO templates are obtainable with pore diameter ranging from about 10 nm [33] up to a few hundred nm, and with pore depth from several nm to several hundred μm via an electrochemical anodization process. The thermal stability and mechanical rigidity of the inorganic alumina wall provide a strictly constrained field and avoid breakdown of the cylindrical confinement. These highly versatile AAO templates with self-organized hexagonal arrays of uniform parallel nanochannels have been intensively utilized as template systems to fabricate various 1-D functional polymeric nanomaterials. These have provided insights into polymer morphology in nanoconfinement and aid the design and fabrication of polymeric nanodevices with well-defined structure and properties. The structural order of 1-D polymer nanostructures fabricated by AAO templates (such as those discussed in Section 3) is often much greater than that in conventional polymeric nanomaterials. Nanostructured polymers exhibit certain unique properties that provide advantages over their bulk counterparts. The highly unusual anisotropic structure demonstrates the powerful geometry control capability with AAO templates, not possible using other techniques.

In this review, we aim to highlight the morphology and properties of 1-D nanostructures fabricated by AAO templates. The preparation methods of polymer nanostructures by AAO templates are presented, including polymer melt infiltration, polymer solution infiltration, and chemical synthesis. According to the molecular structure of polymers, seven types of polymers, such as amorphous homopolymers, amorphous–amorphous block copolymers, amorphous/amorphous polymer blends, semicrystalline homopolymers, semicrystalline/amorphous polymer blends, semicrystalline-amorphous block copolymers, and semicrystalline–semicrystalline block copolymers in nanopores are described in detail.

2. Methods for fabricating polymer nanostructures by AAO templates

The nanoporous AAO templates contain aligned, rigid, and separated cylindrical pores, offering unique geometry for the preparation and investigation of 1-D polymer nanomaterials with controllable shapes and morphology. Typical AAO templates with pore diameter of 300 nm, 65 nm, and 35 nm were shown in Fig. 1.