

The behaviour of honeycomb film formation from star polymers with various fluorine content



Zhou Zhang^{a,b}, Timothy C. Hughes^b, Paul A. Gurr^a, Anton Blencowe^a, Hemayet Uddin^a, Xiaojuan Hao^{b,*}, Greg G. Qiao^{a,*}

^a Department of Chemical and Biomolecular Engineering, University of Melbourne, Parkville, VIC 3010, Australia

^b Materials Science and Engineering, Commonwealth Scientific and Industrial Research Organization (CSIRO), Clayton, VIC 3168, Australia

ARTICLE INFO

Article history:

Received 23 April 2013

Received in revised form

12 June 2013

Accepted 13 June 2013

Available online 25 June 2013

Keywords:

Fluorinated star polymers

Honeycomb films

Physical properties

ABSTRACT

A series of poly(*(1H,1H*-pentafluoropropyl acrylate)-*ran*-(methyl methacrylate)) (poly(PFPA-*ran*-MMA)) star polymers with varying fluorine content were prepared *via* the core-first approach using atom-transfer radical polymerisation (ATRP). Subsequently, the star polymers were used to prepare honeycomb films on both planar and non-planar surfaces *via* the 'Breath Figures' technique using a static casting method. The fluorine content of the star polymers was observed to influence the morphology of the honeycomb structures and the formation of non-cracking honeycomb films on non-planar surfaces. Moreover, the average pore diameter of the honeycomb films was found to decrease with increasing fluorine content, as well as increasing polymer concentration in the casting solution or decreasing humidity during casting. The increasing fluorine content of the star polymers was also found to result in a decrease in their glass transition temperatures and Young's modulus values.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Highly ordered honeycomb (HC) patterned films formed *via* the 'Breath Figures' (BF) technique [1,2] are of great interest as a result of their wide range of specialised technological applications, including biosensors [3–5], membranes for purification and separation [6,7], tissue engineering [8], photonic band gap [9] and electronics [10]. The BF technique was first introduced by Rayleigh and co-workers [11], whereby water droplets were utilised as templates for polymers to form self-assembled, highly ordered HC films. Numerous (macro)molecular architectures have been used with the BF technique to obtain ordered macroporous and microporous structures, including rod-coil block copolymers [12–15], conjugated polymers [16], amphiphiles [17,18], dendronized polymers [19], star polymers [15,20,21], polyoxometalates [22], and small molecules [23]. In addition, various approaches have been established to cast HC films, including, but not limited to, computer-driven [24], dynamic [15,25–31] and static casting methods [20,21,32–34]. The advantage of the computer-driven casting system is that temperature, air velocity, relative humidity, and film thickness can be precisely and independently controlled

while the formation of HC films can be monitored using an in-line optical microscope and video recording system. In comparison, the most commonly adopted approach, known as the dynamic casting method, is a simple approach for the fabrication of HC films. However, its main drawback is the unpredictable turbulence of moist air flow, which may induce deformation of the resulting structures. This issue can be eliminated by using the static casting method, which operates without the flow of moist air, although relatively high humidities are required to form HC films.

Although HC structured films formed from numerous polymers have been reported, to date, limited studies have investigated the formation of fluorinated HC films. Fluorinated polymers have attracted significant attention as a result of their unique properties, including extremely low surface energy and high hydrophobicity, which imparts excellent water and oil repellence, and chemical and thermal stability [35–38]. Fluorinated materials have thus found applications in high performance coatings on various substrates, displaying excellent protection against corrosion, weathering, and environmental pollutants [39–42]. As a result of their biological inertness, fluorinated polymers have also been used as ophthalmic biomaterials [43,44].

Our earlier work showed that when highly dendronised star polymers with peripheral fluorinated groups were used for honeycomb structure formation, 'cylinder-like' pore structures were formed [26]. Yabu et al. [24,45] demonstrated that fluorinated HC

* Corresponding authors.

E-mail addresses: Xiaojuan.Hao@csiro.au (X. Hao), gregghq@unimelb.edu.au (G.G. Qiao).

films and their 'skin-off' pincushion structures displayed different hydrophobicities. Furthermore, they also prepared HC patterned films with submicron pore diameters *via* a computer-driven casting system [24]. These nanometre pore-sized HC patterned films were optically transparent and exhibited superhydrophobicity. Recently, we reported the formation of HC films from perfluoropolyether-based star polymers and micelles on both planar and non-planar surfaces [21]. Although these studies have highlighted the unique abilities of fluorinated polymers and their resulting HC structures, investigation of the effect of the extent of fluorination of the polymers on the formation of HC films and their physical properties have so far been limited. Our recent studies have discovered that increasing the PFFA content of a star polymer decreases its Young's modulus (E), effectively improving its ability to form non-cracking HC films on non-planar surfaces. In addition, these results indicated that E serves as a better indicator than a polymer's glass transition temperature (T_g), in terms of predicting the polymer's ability to form non-cracking HC films on non-planar surfaces [20]. Therefore, there is a need to study the influence of fluorine content in the polymer precursors on their formation of HC films in general.

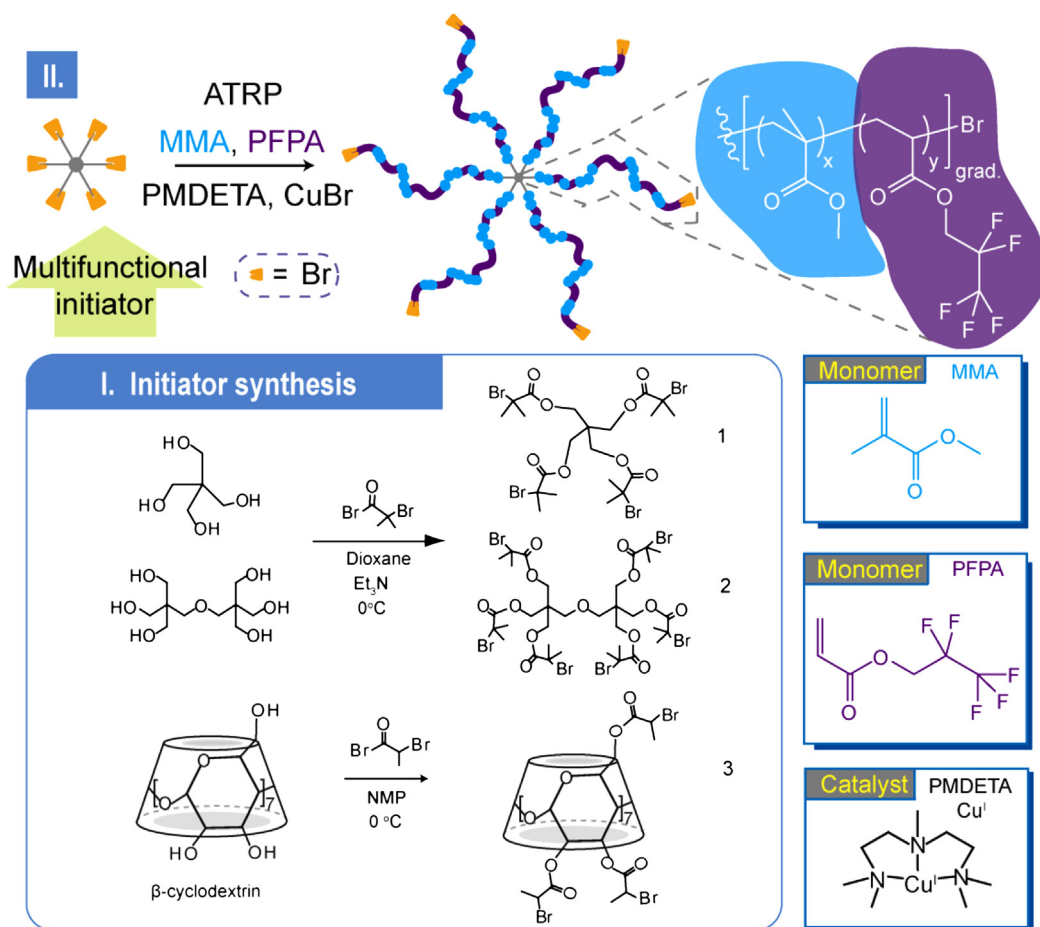
In this paper, we introduce a library of T_g tuneable fluorinated star polymers with various arm numbers (4, 6 and 21) prepared by the core-first approach and atom-transfer radical polymerisation (ATRP) of a fluorinated acrylate, pentafluoropropyl acrylate, and methyl methacrylate. The effect of star polymer composition (i.e., fluorine content) and architecture (number of arms) on the formation of HC films on both planar and non-planar surfaces, and the

physical properties of the resulting films were studied. This study also provides further experimental evidence to validate the hypothesis of the role of E in the formation of non-cracking HC films on non-planar surfaces [20].

2. Experimental

2.1. Materials

1*H*,1*H*-Pentafluoropropyl acrylate (PFFA) (Fluorochem, >97%) and activated neutral aluminium oxide (Al_2O_3) (Merck) were used as received. Methyl methacrylate (MMA) (99%) was purchased from Sigma–Aldrich, stirred with inhibitor remover (Sigma–Aldrich) for 18 h and then filtered before use. β -Cyclodextrin (β -CD) (98%), pentaerythritol ($\geq 99.9\%$), dipentaerythritol (technical grade), 2-bromo-2-methyl-propanoyl bromide (98%), copper(I) bromide (CuBr) (98%), lithium bromide (LiBr) ($\geq 99\%$), anhydrous dioxane ($\geq 99.8\%$), sodium bicarbonate (NaHCO_3), magnesium sulphate (MgSO_4) (anhydrous, $\geq 99.5\%$), *N,N,N',N'*-pentamethyldiethylenetriamine (PMDETA) (99%), and *N*-methyl-2-pyrrolidinone (NMP) (99.5%) were purchased from Sigma–Aldrich and used as received. Toluene (HPLC grade), *N,N*-dimethylformamide (DMF), dichloromethane (CH_2Cl_2) (AR grade), chloroform (CHCl_3) (AR grade), ethanol (EtOH), and methanol (MeOH) (AR grade) were purchased from Chem-Supply and used as received. Tetrahydrofuran (THF) (HPLC grade) was purchased from Burdick and Jackson. Anhydrous THF was obtained by distillation under argon from sodium benzophenone ketyl. Triethylamine (TEA)



Scheme 1. Synthesis of (i) multifunctional initiators 1, 2, and 3, and (ii) fluorinated star polymers with varying PFFA monomer content using the multifunctional initiators *via* the core-first approach and ATRP. The PFFA monomer content was controlled by varying the ratio of methyl methacrylate (MMA) to pentafluoropropyl acrylate (PFFA).

Download English Version:

<https://daneshyari.com/en/article/5181778>

Download Persian Version:

<https://daneshyari.com/article/5181778>

[Daneshyari.com](https://daneshyari.com)