Synthesis of Amphiphilic Block Copolymers and their Honeycomb Morphologies Formation

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Abstract

Amphiphilic block copolymers have been extensively studied because of the versatile synthetic approaches and the tunable morphology. In this study, block copolymers of glycidyl methacrylate (GMA) and vinyl pyrrolidone (VP) were obtained by the combination of two different free-radical polymerization mechanisms namely atom transfer radical polymerization (ATRP) and conventional free radical polymerization (CFRP). Then the polymer thin film possessing a hexagonal array of micro pores (honeycomb film) could be obtained by solution casting of amphiphilic block copolymers in high vapor solvent under a flow of moist gas.

In the first part, thermosensitive azo alky halide, difunctional initiator, was prepared . The obtained bromine ended difunctional initiator was used for ATRP of GMA monomer at room temperature in conjunction with CuBr/2, 2’-bipyridine as a catalyst. In the second part, the azo functional group of poly(glycidyl methacrylate) (PGMA) was used as a macro-initiator in FRP of VP to prepare the amphiphilic block

copolymer poly(glycidyl methacrylate-*block*-vinyl pyrrolidone) (PGMA-*b*-PVP). The objectives of this thesis are as below:

(1) The obtained bromine ended difunctional initiator was used for ATRP of GMA monomer to prepare a macro-initiator at room temperature. Molecular weight distribution of PGMA was optimized through the reaction composition or reaction condition of ATRP, including solvent, monomer/initiator ratio, catalyst and ligand concentrations. Then molecular weight, polymer dispersity index and characterized data of macro-initiators are characterized by gel permeation chromatography (GPC), Fourier transfer infrared spectroscpoy (FT-IR) and proton nuclear magnetic resonance spectrometry (^{1}H-NMR).

(2) The macro-initiator (Azo-PGMA) was used for FRP of VP monomer to synthesize poly(glycidyl methacrylate-*block*-vinyl pyrrolidone) (PGMA-*b*-PVP). Block copolymer variations of molecular weight of hydrophobic and hydrophilic parts in block copolymer were studied.

(3) Finally, a regularly porous honeycomb structured film can be prepared from the suitable solution of the amphiphilic diblock copolymer under moisture air flow. The morphology of the prepared film was observed by optical microscopy (OM) and scanning electron microscope (SEM). The diameter of the spherical pores can be controlled ranging from 2.3 μm to 0.5 μm by the amphiphilic copolymers relative molecular weight as well as by the casting conditions. We propose that most important element in the formation of order structure may be determined on the polymer to precipitate at solution/water interface.