

# Microphase separation behavior on the surfaces of PEG–MDI–PDMS multiblock copolymer coatings

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## Abstract

A series of poly(ethylene glycol)(PEG)–4,4′-diphenylmethanediisocyanate(MDI)–poly(dimethylsiloxane) (PDMS) multiblock copolymers were synthesized by employing two-step growth polymerization technique. Atomic force microscopy (AFM) observed nanoscopically well-organized phase-separated surfaces consisting of hydrophilic domain from PEG and MDI segments and hydrophobic domain from PDMS segments even with 50 wt.% PDMS in the copolymer, and the multiblock copolymer coatings presented a surface free energy of as low as 6–8 mN m<sup>-1</sup>.

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**Keywords:** Atomic force microscopy; Microphase separation; Multiblock copolymer; PEG–MDI–PDMS; Surface free energy

## 1. Introduction

Since the surfaces of materials have a strong influence on their performances, specifically, anti-biofouling property, biocompatibility, antithrombogenicity, etc., there have been a lot of investigations focusing on modifying the surface composition of materials using low surface free energy fluoropolymers or silicon elastomers. However, more and more experiments and practical applications have proved that the anti-biofouling property and other surface performances of the coatings depend on not only the surface free energy but also the surface microstructure [1]. Therefore, the anti-biofouling technologies are preferentially focused on designing the microphase separated surfaces of the coatings based on fluoropolymers or silicon elastomer in the recent years [2,3]. For example, Majumdar and Webster [4] synthesized a crosslinked PDMS–polyurethane coating from reactive oligomers of isophorone diisocyanate, trifunctional polycaprolactone polyol, hydroxyl functional PDMS and observed the spontaneously phase-separated surface for the coatings containing 10% PDMS, but very smooth surface for the

coatings containing 20 or 30% PDMS. Gudipati et al. [3,5] prepared an antifouling coating with in situ surface phase separation by crosslinking of hyperbranched fluoropolymers with diamino-terminated PEG or diamino-terminated PDMS.

Up to now, however, this kind of research is still very limited since fluorinated or PDMS segments can cover the whole surface very easily even at very low bulk concentration, due to their low surface energy relative to other organic components [6–12], making the control of microtopographic feature of polymer surface very difficult. In this paper, we have synthesized a series of PEG–MDI–PDMS multiblock copolymers using commercial materials by employing two-step growth polymerization approach. AFM observed nanoscopically well-organized phase-separated surfaces with an astonishing low surface free energy.

## 2. Experimental section

### 2.1. Materials

PEG ( $M_w = 200, 400, 600$  and  $1000$ , denoted as PEG200, PEG400, PEG600 and PEG1000, respectively), tetrahydrofuran (THF, spectroscopic purity) and dibutyltin dilaurate (DBTDL) were obtained from Sinopharm Group Chemical

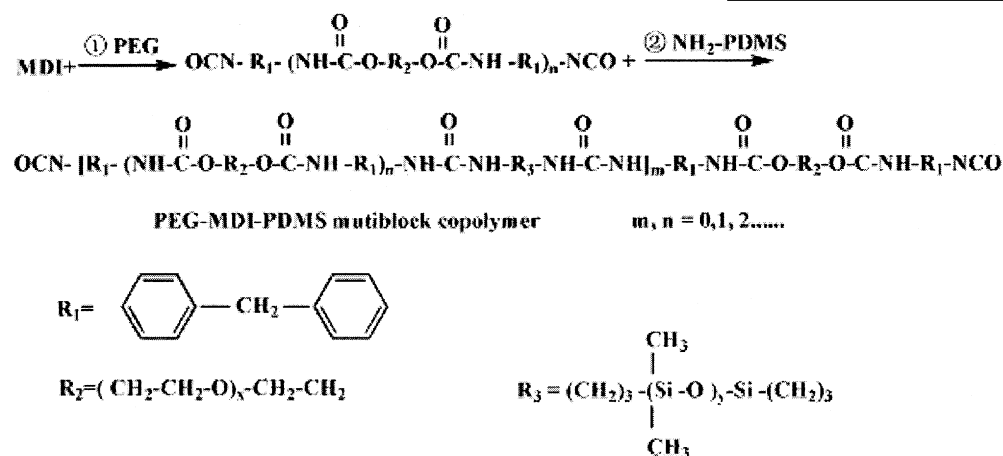
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Reagent, Co., Ltd.  $\alpha,\omega$ -Aminopropyl terminated PDMS ( $\text{NH}_2$ -PDMS,  $M_w = 2500$  g/mol) was obtained from Aldrich. MDI (>99.5%) was supplied by Bayer AG. PEG and PDMS were degassed at  $80^\circ\text{C}$  for 12 h under a vacuum of 0.1 torr before use. THF was dried over metallic sodium under reflux and distilled and others were used as received.

## 2.2. Synthesis of PEG–MDI–PDMS multiblock copolymer

The known amount of MDI and PEG (molar ratio of 2:1 for MDI to PEG) together with THF was charged into a 250 ml three-necked round bottom flask equipped with overhead agitator, heat mantle, reflux condenser, nitrogen inlet and addition funnel, and heated to  $50^\circ\text{C}$  for reaction under  $\text{N}_2$  stream for 1 h for PEG200, PEG400 and PEG600 but 6 h for PEG1000. In addition, for PEG1000, 0.05 wt.% DBTDL based on the total mass of MDI and PEG was used as the catalyst, but no catalyst was used for other PEG. The reaction was carried out until no  $-\text{OH}$  group was detected by IR and the  $-\text{NCO}$  group content in the resulted oligomer was determined by titration method. The oligomer solution was cooled to ambient temperature and dropped by a stoichiometric amount of 10 wt.% PDMS solution in THF based on the molar ratio of  $-\text{NH}_2/-\text{NCO} = 0.1\text{--}0.9$  over a period of 30 min. The mixture was stirred at room temperature for 2 h and then heated to  $50^\circ\text{C}$  to react for another 15 h. The reaction equations could be described as follows:



## 2.3. Film preparation

The films for AFM measurements were prepared with a single drop of copolymer solution in THF on freshly cleaned Si wafer. The films about 20–50  $\mu\text{m}$  thickness for other measurements were prepared by casting the copolymer solution onto clean glass disks. All these samples were dried in the following order of  $40^\circ\text{C}$  under air for 24 h, then  $60^\circ\text{C}$  under air for 24 h and finally  $80^\circ\text{C}$  under vacuum for 24 h to completely remove solvent.

## 2.4. Characterization

### 2.4.1. FTIR analysis

Fourier transform infrared analysis was performed on a Magna-IR 550 spectrometer (Nicolet Instruments, Madison, WI). The spectrum was recorded before 32 times scanning at a resolution of  $4\text{ cm}^{-1}$ .

### 2.4.2. AFM observation

The AFM observation was made on SPA 300 HV-DFM (Seiko Instruments Industry, Co., Ltd., Japan) in ultra-light-tapping mode at room temperature, using the micro-fabrication cantilevers with a spring constant of approximately  $20\text{ N m}^{-1}$ . All AFM data including the height, phase shift and the three-dimensional (3D) image as well were recorded simultaneously.

### 2.4.3. Dynamical mechanical analysis (DMA)

DMA measurements were carried out on a DMA242 (Netzsch Inc., Germany) in tensile mode. The samples were quickly cooled to  $-150^\circ\text{C}$  and equilibrated at that temperature for 3 min then heated to  $200^\circ\text{C}$  at a frequency of 1 Hz and a constant heating rate of  $3^\circ\text{C}/\text{min}$  under a nitrogen atmosphere.

### 2.4.4. X-ray photoelectron spectroscopy (XPS)

XPS was carried out on a PHI 5000C ESCA system (Perkin-Elmer Inc., USA) using an AL  $\text{K}\alpha$  X-ray source (14.0 kv and

250 W) at take-off angles of  $45^\circ$  and  $90^\circ$ , and the analyzer chamber pressure was less than  $10^{-6}$  Pa. Survey scans spectra was recorded at pass energy of 93.9 eV initially. Narrow scan spectrometer of C 1s, O 1s, N s and Si 2p were collected and peak analysis was carried out using PHI-MATLAB software.

### 2.4.5. Differential scanning calorimetry (DSC)

All experiments were performed on a DSC Q100 thermal analyzer (TA Instrument, USA) at a heating rate of 10 K/min from  $-50$  to  $200^\circ\text{C}$  in a nitrogen atmosphere.

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