

Surface Immobilization of Star-Shaped Poly(ethylene oxide) on Poly(dimethylsiloxane)

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ABSTRACT: A thin layer of star-shaped poly(ethylene oxide) (PEO) (starPEO), on the polydimethylsiloxane (PDMS) membrane was prepared by a simple immobilization procedure. Photoreactive molecules were introduced on the surface of the polymeric support to achieve the formation of thin starPEO film from the materials having no functional groups. This novel technique enabled us to immobilize any kind of chemical, especially one that had no functional groups, and readily to control the amount of immobilization. The gas permeation properties of the starPEO-immobilized PDMS membranes were investigated for pure propane and propylene. The permeance of gases were found to decrease in the starPEO-immobilized PDMS membranes, although the ideal separation factors for propylene/propane were increased with the loading amount of silver ions, because of the facilitation action of silver ions in the immobilized PEO unit on the PDMS membranes, as propylene carriers. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2369–2373, 2002

Key words: star-shaped poly(ethylene oxide); surface immobilization; membrane; gas permeance

INTRODUCTION

Polymeric thin films on polymer supports are a technologically important class of materials with applications in solid-state photonics, microelectronics, biotechnology, and membranes.¹ Typical techniques for the preparation of thin polymeric film by graft polymerization, chemical modification, self-assembling, as well as Langmuir–Blodgett method, suffer from the disadvantage that a material must have a functional group to be attached to the support. Here, we introduced a simple new method to prepare polymeric films on

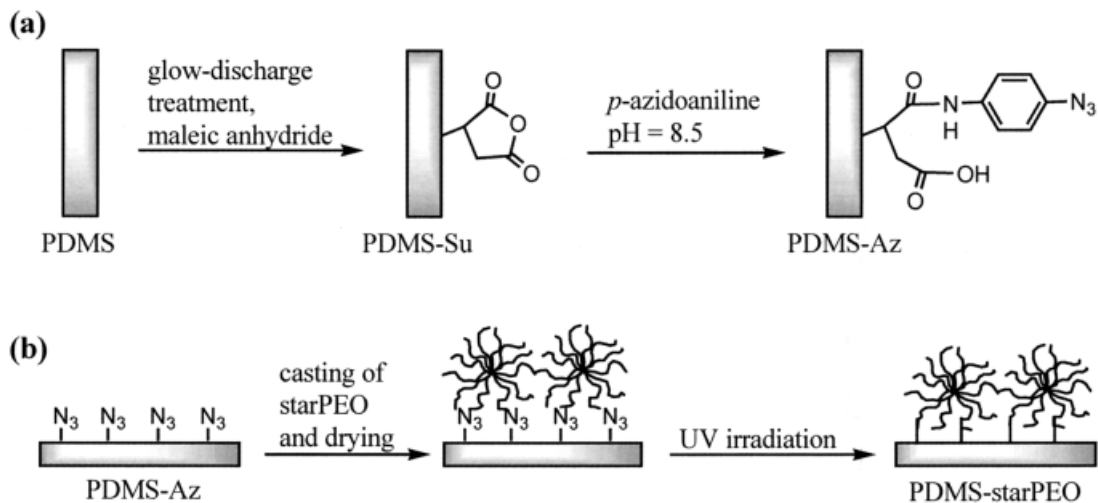
a polymeric support. Photoreactive molecules are introduced on the surface of the polymeric support to achieve formation of thin film from the materials having no functional groups. The chemistry used is general and can be extended for the immobilization of any kind of material, even those having no functional groups.

Well-controlled structural materials, such as star-shaped poly(ethylene oxide) (PEO), (starPEO), was chosen as a model for the thin film formation, because star polymers are branched polymers with several arms of approximately equal lengths joined together at one end of each chain to a central core. The discovery that PEO-attached surfaces exhibit low degrees of protein adsorption, cell adhesion, and bacterial adhesion also make this immobilization of starPEO on polymeric substrates a promising, useful approach for producing biocompatible and/or antibiotic materials.

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Scheme 1

The starPEO thin film was prepared by the method as shown in Scheme 1. StarPEO was covalently bound to the substrate surface by using the surface-induced photoreactive azidophenyl groups. To introduce an azidophenyl group on a polydimethylsiloxane (PDMS) surface, a succinic anhydride group was attached by glow-discharge treatment.² Subsequently, the succinic anhydride-modified PDMS (PDMS-Su) was immersed in an aqueous solution containing *p*-azidoaniline hydrochloride. The azido phenyl groups on the surface will react with starPEO to make the starPEO immobilized PDMS (PDMS-starPEO) by UV irradiation.

The aim of the present work was to find the preparation methods for the preparation of starPEO-immobilized polymer membranes and to investigate the effect of PEO in the permeation of gases through the membranes.

EXPERIMENTAL

Materials

Star-shaped PEO [starPEO; $M_{w, \text{star}} = 5.6 \times 10^5$, $f = 60$ arms ($M_{w, f} = 9100$); Shearwater Polymers, Inc., Huntsville, AL] and silver tetrafluoroborate (AgBF_4 ; Aldrich Chemical Co.) were used as received.

StarPEO Monolayer Film on PDMS Dense Membrane

StarPEO monolayer film was prepared by photochemical immobilization on the PDMS (model

SSPM100, Specialty Silicon Products, Inc., NY) membrane surface. The glow-discharge treatment was carried out in the presence of maleic anhydride (50 mg) by using a radio-frequency generator (R300A, $RF = 13.56$ MHz, Autoelectric, Seoul, Korea), delivering up to 50 W (0.1 Torr, 30 s). Subsequently, the PDMS-Su was immersed in the aqueous solution (pH = 8.5) containing *p*-azidoaniline hydrochloride (5 mM) at 30°C for 2 h. After the reaction, the film was taken out and washed with distilled water several times. An amount of 1.0 mL acetonitrile solution containing starPEO (1.0 wt %) was dropped on the azidophenyl-modified PDMS (PDMS-Az) and dried under N_2 atmosphere in a dark place. The film was irradiated with UV light (power = 8 W, $\lambda_{\text{max}} = 264$ nm) for 20 min and washed with distilled water in the ultrasonicator for 60 min. After drying, a certain amount of AgBF_4 ethanol solution was loaded on PDMS-starPEO and the film was dried at 35°C under N_2 atmosphere. After 12 h, the film was dried at room temperature in a vacuum oven for 1 day and stored in a vacuum before measurement.

Characterizations

The surface characterization for the modified films was carried out by using the attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectroscopy. The ATR spectra were obtained by using a KRS-5 prism with an incident angle of 45°. Tapping-mode atomic force microscopy was performed by using a Digital Instruments Nanoscope V (Santa Barbara, CA). The

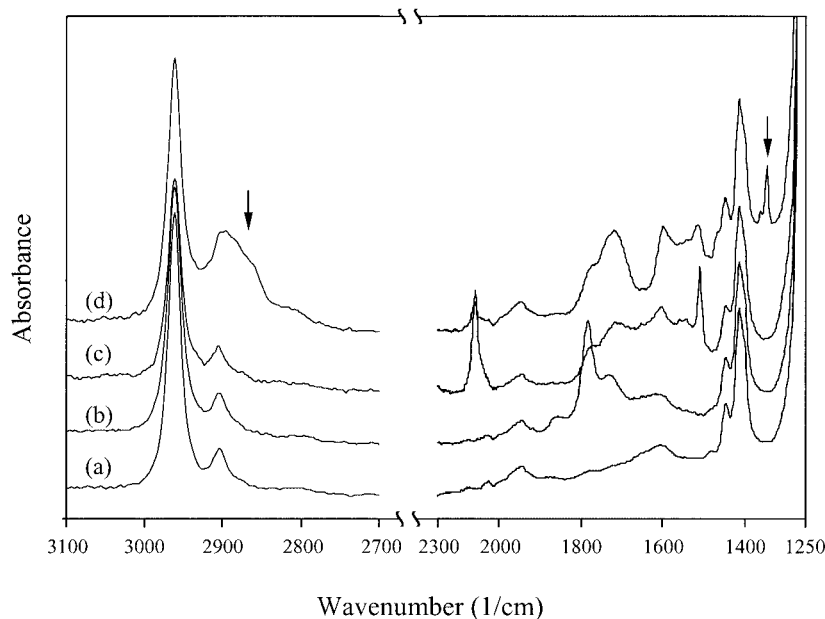


Figure 1 ATR FTIR spectra of the surface-modified PDMS films: (a) PDMS, (b) PDMS-Su, (c) PDMS-Az, and (d) PDMS-starPEO.

permeation properties of pure dry gases were measured at 23°C. All the samples were evacuated for 1 h before the gas permeation experiments. Volumetric gas flow rates were determined with a soap-bubble flow meter.

RESULTS AND DISCUSSION

Figure 1 shows the ATR FTIR spectra of a PDMS, a PDMS-Su, a PDMS-Az, and a PDMS-starPEO. After glow-discharge treatment, the new bands appeared at 1852 and 1782 cm^{-1} , which were ascribed to the asymmetric and the symmetric anhydride C=O stretching band of succinic anhydride, respectively. The band at 1728 cm^{-1} is due to the C=O stretching of the carboxyl group resulting from the ring-opening reactions of maleic anhydride on the surface [Fig. 1(b)]. After the modification with the azidophenyl group, new bands appeared at 2116 and 1509 cm^{-1} and were ascribed to the azido N≡N stretching and the aromatic C=C stretching band, respectively [Fig. 1(c)]. It is assumed that the azidophenyl groups were immobilized on the PDMS membrane surface in this condition. The characteristic bands of carboxamide groups in 1600–1700 cm^{-1} are considered to be buried because of the broadening in the range of 1500–1800 cm^{-1} frequency regions. However, it is considered that *p*-azidophe-

nylamine is fixed to the film surface in this experimental condition, because there was no detection of bands at 2116 and 1505 cm^{-1} when the films were prepared, even in different pH conditions. The azido group is well known to form the photo-initiated covalent bond by UV irradiation. The modified azidophenyl groups easily convert to phenyl nitrene group by the elimination of nitrogen from the azidophenyl group upon UV irradiation. Phenyl nitrene is a highly reactive species in a triplet state, which forms a covalent bond with neighboring atoms. In this experiment, starPEO that loaded on the PDMS film surface was introduced by the modification of azidophenyl groups upon UV irradiation, which was confirmed by IR spectrum, as shown in Fig. 1(d). The peak of the N≡N stretching band at 2116 cm^{-1} was decreased after UV irradiation. The new peaks occurred at 2887 and 1343 cm^{-1} , which were ascribed to the CH₂ symmetric stretching and CH₂ wagging band of PEO, respectively. These observations imply the introduction of starPEO on the PDMS surface. Because all starPEO were washed off from the PDMS-Su surface without the azidophenyl modification, the introduction of azido group on the PDMS surface is crucial in this procedure.

The thickness of the immobilized starPEO layer was estimated to be approximately 360 Å from the gravimetric change of membrane before

Table I Pure Gas Permeance of StarPEO-Immobilized PDMS Membranes

	Surface Roughness (nm)	EO : AgBF ₄ (mole ratio)	Q _{Propylene} (GPU) ^a	Q _{Propane} (GPU)	Selectivity ^b
PDMS	1.88	1 : 0	73	74	0.98
PDMS-Az	8.81	1 : 0	39	39	1.0
PDMS-starPEO	4.69	1 : 0	29	27	1.1
		1 : 0.7 ^c	23	19	1.2
		1 : 7.2 ^c	23	10	2.3
		1 : 36 ^c	23	5.0	4.6
		1 : 72 ^c	20	2.0	10

^a 1 GPU = 1 × 10⁻⁶ cm³ (STP) cm⁻² s⁻¹ cmHg⁻¹.

^b The ideal separation factor (= Q_{propylene}/Q_{propane}).

^c Theoretical loading mole ratio; the real mole ratio would be expected lower than these values.

and after the immobilization, which is comparable with the estimated diameter of starPEO, approximately 350 Å. The thickness was calculated from the amount of immobilized starPEO (3.9 μg/cm²) and the density of starPEO (1.08 g/cm³), under the assumption of well-distributed monolayer with no aggregates and no morphological changes. The radius of gyration $\langle R_g \rangle_{\text{star}}$ for a star polymer can be predicted by the following equation,^{3a} $\langle R_g^2 \rangle_{\text{star}}^{1/2} / \langle R_g^2 \rangle_{\text{arm}}^{1/2} = Kf^\beta$, where K and β equal 1.33 and 0.206, respectively. By using the relationship, $\langle R_g \rangle_{\text{linear}} = 0.215 M_W^{0.583} \text{ \AA}$,^{3b} $\langle R_g^2 \rangle_{\text{arm}}^{1/2} = 43.7 \text{ \AA}$. Therefore, $\langle R_g^2 \rangle_{\text{star}}^{1/2} = 135 \text{ \AA}$. If the star polymer is considered to be a sphere, the radius of a solid sphere is $(5/3)^{1/2} \langle R_g \rangle$.^{3c} Then, $\langle R_g \rangle_{\text{star}}$ would be 174 Å. The diameter assumed to be $2R_g$ is 348 Å. Although this estimation is made under the assumption of the existence of solvent and no morphological changes, the comparable order of size gives an insight into the thickness. The surface morphology was observed by TM-AFM, and the roughness was approximately 4.7 nm for the surface of PDMS-starPEO, which was half of the one for PDMS-Az, presenting the formation of a smooth layer by starPEO (results are shown in Table I).

The formation of the immobilized starPEO on polymer supports was measured by gas permeance measurements, because the permeance was affected significantly with the existence of defects. Gas permeation experiments were carried out through the starPEO-immobilized membranes with and without the impregnation of AgBF₄, and the results are shown in Table I. The 30% decrease of gas permeance, Q , was observed with the modification of the membrane surface by starPEO. It is known that PEO-containing silver salt, such as AgBF₄, became a solid polymer elec-

trolyte [i.e., silver salt dissolves in the polymer through the interaction (e.g., the oxygen in PEO) in the polymer backbone]. It is well known that silver (I) ions react reversibly with unsaturated compound such as olefins to make silver-olefin complexes but not with saturated compounds such as paraffins.⁴⁻⁶ Because of such reversible and specific reactions of silver ions with olefin molecules, silver ion can act as an olefin carrier. As shown in Table I, both propylene and propane permeances decrease with the loading amount of AgBF₄. Silver salts in ethanol solution were loaded in the range of EO : Ag = 1 : 0.7–1 : 72. Although we expected that the silver ion dissolved in ethanol would coordinate with PEO during the evaporation of ethanol but the actual mole ratio, which would depend on the evaporation condition as well as the interaction between silver ion and solvent, would be lower than the theoretical mole ratio. Therefore, excess amounts of silver salts were loaded in this experiment. A decrease of gas permeance through the polymer electrolyte films can be explained as follows: (a) the chain mobility will be reduced when silver ions coordinate with the oxygen atoms of PEO, which was confirmed by the increasing glass transition temperature of the PEO–AgBF₄ system. The reduced mobility would be due to the possibility of the role of ion as a crosslink point, whereas cations were coordinated with functional groups of the polymer.⁷ Therefore, decreasing mobility of chain would affect the gas transport behavior with increasing the loading amount of salt. (b) It is well known that there are free ions, contact ion pairs, and higher ion aggregates in a number of polymer electrolytes at higher salt concentrations.⁸⁻¹⁴ Excess amount of salts loaded would act as a barrier for the gas transport that is

shown as a significant decrease in gas permeance. However the specific and reversible interaction of silver ions with propylene molecules, silver ions can act as propylene carriers for facilitated transport in the membrane and then lead a carrier-mediated transport in addition to a normal Fickian transport, which results in propylene/propane separation. This result is similar to the previous reports.^{15,16} The membrane process using the concept of facilitated transport was considered to be an alternative for the energy-intensive cryogenic distillation processes in olefin/paraffin separation.

CONCLUSIONS

StarPEO thin layer on the PDMS support was prepared by the simple immobilization procedure. The gas permeance of PEO immobilized on the PDMS was measured. The starPEO thin layer on the PDMS membrane containing silver ions exhibited the facilitated transport of propylene. The selectivity of propylene/propane increased with the loading amount of silver ions, because of the facilitation action of the propylene carrier (i.e., silver ions dissolved in PEO unit). This novel technique enables us to immobilize any kind of polymers, especially for the one that has no functional groups, and to control readily the amount of immobilization. The starPEO-immobilized PDMS membranes have a potential for the usage of olefin/paraffin separation as well as the biocompatible materials.

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