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Surface modification of microporous polypropylene membranes by the grafting of poly(γ-stearyl-L-glutamate)

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Abstract

A polypeptide, poly(γ-stearyl-L-glutamate) (PSLG), was grafted on the surface of hydrophobic polypropylene hollow fiber membranes through the ring opening polymerization of *N*-carboxyanhydride (NCA) of γ-stearyl-L-glutamate initiated by amino groups which was generated by ammonia plasma. X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), together with water contact angle and bovium serum albumin adsorption measurements were used to characterize the modified membrane surface. The XPS and FT-IR spectra demonstrated that polypeptide was actually grafted on the membrane surface despite of the low degree of graft polymerization due to the hydroxyl groups on the membrane surface. To subject the ammonia plasma-treated membrane with γ-(aminopropyl)triethanoxysilane (γ-APS) which can react with hydroxyl groups and leave amino groups, the degree of graft polymerization could be improved. The bovium serum albumin adsorption measurement was conducted to further examine the surface properties of modified and original membranes. Potential applications of the PSLG grafted membranes are expected for enantiomer separation and/or enzyme immobilization.

Keywords: Polypropylene microporous membrane; Ammonia plasma; *N*-carboxyanhydride of γ-stearyl-L-glutamate; Graft polymerization

1. Introduction

It is well recognized that the surface chemical and physical properties play a dominant role in determining the separation characteristics of a membrane [1,2]. Therefore, there has been much interest in developing surface treatment methods to modify the chemical and physical properties of membrane materials [3–8]. In fact, surface modification of membranes is thought to be equally as important to the membrane industry as membrane material and process development. Polypropylene (PP) is one of the most important polymers widely used in various fields, while as membrane materials the existing inconveniences make it requisite to some surface modification [4,6,8]. The practical aspects of surface modification for PP membranes include: (1) the hydrophilization of membrane surface to improve antifouling property for aqueous liquid separation; (2) the fabrication of biocompatible surface for biological applications; and (3) the design of non-denaturing

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surface for the immobilization of enzymes or cell receptors. A convenient way for such modification is to graft monomers with functional groups on membrane surface. The advantage of grafting techniques compared with coating is that graft chains are chemically bonded to the membrane matrix, which means that they will not be detached from the membrane substrate when solvent permeates through the membranes. Concerning different polymeric substrates, surface modification methods are not always the same. For those polymers with functional groups in either back bonds or side chains, numerous grafting methods are suitable, while in the case of those hydrocarbon polymers with no active side chain or end-groups (for example polyethylene or polypropylene), the membranes have to be activated prior to the graft polymerization. In this procedure, plasma grafting is an effective way as well as irradiation by UV or ^{60}Co and electron beam [6,9,10]. Plasma-initiated grafting is a versatile technique for modifying membrane surface with a thin layer of grafted polymer possessing desirable properties, which can be performed in various gases without affecting the bulk properties [11,12].

Polypeptides, on the other hand, are unique among polymeric materials. High molecular weight polypeptides can be obtained by initiating the *N*-carboxyanhydride (NCA) of α-amino acids (first described by Leuchs in 1906 [13] and also known as Leuchs anhydrides) with primary amines. With the α-helical secondary structure stabilized via hydrogen bond formation as well as hydrophobic and electrostatic interactions, they are suggested as potential membranes for the enantiomer separation of amino acids [14,15]. The obtained separation factors are highly encouraging, but are generally combined with very low permeation rates. In recent years, there has been considerable interest in grafting polypeptides derived from glutamic acid on solid supports as their side chains can be modified [3,16–20]. Chemical valves (''smart'' membranes) due to the conformational change of polypeptide were prepared by grafting poly(L-glutamic acid) on porous membranes [19,20]. As suggested by Sackmann [21,22], ''hairy-rod'' polymers such as poly(γ-stearyl-L-glutamate) (PSLG) can be deposited on substrate and be further used to fabricate supported biomimetic membranes by self-assembly process. However, to avoid de-wetting (the ''hairy-rod'' polymer detached from the substrate surface) in the step of lipid self-assembly, it is better to chemically graft the ''hairy-rod'' polymer onto the support surface. It is also envisaged that membranes grafted with polypeptides having α-helical secondary structure show enantioselective behavior together with high flux. Therefore, the present study reports the preliminary results of graft polymerization of γ-stearyl-L-glutamate NCA on the surface of PP membrane initiated by the amino groups produced from plasma treatment.

2. Experimental

2.1. Materials

Microporous polypropylene hollow fiber membranes were prepared with melt-extruded/cold-stretched (MECS) method in our lab [4]. The inner and outer diameters of this hollow fiber were 240 and 290 μm, respectively, with porosity of 50% and an average pore diameter of 0.070 μm. Before use they were dipped in acetone for 24 h then dried in vacuum till constant weight. L-Glutamic acid, γ-stearyl alcohol, tertiary butyl alcohol, 98% sulfuric acid, triethylamine and γ-(aminopropyl)triethanoxysilane (γ-APS) were used as purchased. Triphosgene was purchased from Aldrich and used without further purification. Tetrahydrofuran (THF) was washed with stannous chloride solution, refluxed with sodium using benzophenone as indicators, and distilled before use. *n*-Hexane was purified by reflux with sodium–potassium alloy. All flasks for NCA synthesis were dried by heating at 150 °C under vacuum prior to use.

2.2. Ammonia plasma treatment

The plasma reactor was purchased from Peking KEEN Co. After weighed, the polypropylene membranes were fixed in the reacting chamber. The chamber was vacuumized, and then NH_3 was introduced. This process was conducted several times to insure that O_2 in the chamber was degassed. Then plasma was generated at a given pressure (5–60 Torr) and the PP membranes were exposed to plasma for a predetermined period of time. After plasma treatment, the membranes were quickly taken out of the chamber and kept into N_2 atmosphere before further modification. Amino groups produced on the membrane surface were determined by ninhydrin method [23], the calibration was performed using *n*-octylamine.

2.3. Synthesis of γ-stearyl-L-glutamate (SLG)

γ-Stearyl-L-glutamate was synthesized according to the method reported by Wasserman et al. [24]. A one liter three-necked flask filled with 20 g (0.136 mol) L-glutamic acid, 147.2 g (0.544 mol) γ-stearyl alcohol and 500 ml tertiary butyl alcohol was heated to 40 °C under vigorous stirring, then 10 ml sulfuric acid (98%) was drop wisely added whereupon the temperature increased to 50 °C. After heated to 65 °C and kept for 1 h or more, the solution turned slowly to transparent. Then the heat installation was moved away, and triethylamine (11 ml, 0.08 mol) were added followed with the addition of water and ethanol, more triethylamine (30 ml, 0.217 mol) were added under stirring. Thirty minutes later, the crude products precipitated out

which was filtered through a Buchner filter at 35 °C. The precipitate was slurried in one liter of methanol at 65°C, which was filtered through a Buchner filter to get a solid cake, then washed twice with diethyl ether and dried in a vacuum oven at 25–30 °C till constant weight. This crude product was purified by adding hot *n*-butyl alcohol–water (1:1, vol) solution and heating to 92 °C till a homogeneous system appeared, then cooling the solution to 25 °C, the precipitate was filtered followed with washing by methanol and diethyl ether alternatively. After this, the purified product was dried in a vacuum oven till constant weight to get white crystals. Yield: 42–45%. Mp: 168–170 °C. Element analysis: C, 69.25%; H, 11.09%; O, 16.11%; N, 3.45%. (Theoretical analysis: C, 69.17%; H, 11.28%; O, 16.04%; N, 3.51%.)

2.4. Synthesis of γ-stearyl-L-glutamate NCA (SLGNCA)

γ-Stearyl-L-glutamate (10 g, 0.251 mol) and THF (150 ml) was added to a flask which was fitted with a inlet for Ar gas and a condenser vented into sodium hydroxide to trap the byproduct HCl or phosgene gas. When the solution was heated to 50 °C, 1/3 of an equivalent of triphosgene was added, which would lead to a completely homogeneous solution within 3 h. Then the reaction mixture was poured into 500 ml *n*-hexane, the resulted suspension was stored at −20 °C overnight to assure complete crystallization. After filtered, the solid was redissolved and crystallized in THF or *n*-hexane, alternatively. The recrystallization step was repeated twice. Yield: 85–90%. Mp: 77–78 °C.

2.5. Grafting on the surface of ammonia-plasma pretreated PP membranes

The freshly recrystallized NCA was filtered through a filter ball, dried at vacuum. Then THF was added to the filter ball to get the monomer solution with different concentration which was then added to the bottles containing plasma-treated PP membranes. The graft polymerization lasted three days at 35 °C in N_2 atmosphere with constant vibration. After this, methanol was added to terminate the polymerization, the resulted membranes were washed several times with THF, and dried at vacuum till constant weight.

2.6. Introduction of γ-(aminopropyl)triethanoxysilane onto the surface of plasma-treated PP membranes

In this procedure, both dipping and refluxing methods were used [25]. In the dipping process, the ammonia plasma-treated PP membranes were dipped in the γ-APS solution (10 ml γ-APS: 90 ml THF) for 30 min, ultrasonically washed, then dried at vacuum. The refluxing process was similar to the dipping method except that the membranes were refluxed in γ-APS solution for 30 min. Amino groups produced on the membrane surface were also determined by ninhydrin method [23].

2.7. Characterizations

To investigate the changes of chemical structure between the unmodified original membranes and the polypeptide grafted membranes and to confirm the PSLG formed on the surface of the membrane, Fourier transform infrared spectroscopy (Bruck Vector 22 FT-IR) with an ATR unit (attenuated total reflection, KRS-5 crystal, 45°) was used.

The X-ray photoelectron spectroscopy (XPS) spectra of the samples were obtained using ESCA LAB MK-II (VG Scientific). As a phonon source, Al Kα radiation (1486.6 eV) was used, the energy scale of the spectrometer was calibrated using the lowest BE component of C_{1s} peak (E_b: 284.9 eV), and the data were collected and analyzed by a computer. In order to get more information on the bonding state of each constituent present in the superficial layer, a curve-fitting program has been applied to determine the different spectral contributions. From this treatment, the peak position, peak area, and peak width of each component are determined. Surface elemental stoichiometries were determined from peak-area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to ±10%. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries.

The static contact angle of PP membranes was measured using JY-82 system equipped with a digital camera. Measurements were carried out on both untreated and plasma-treated samples which were dried at vacuum before this measurement. Droplets of distilled water (about 82 μl) were dropped at different places and at least eight readings were taken to determine average values.

The BSA adsorption experiments were carried out by standard batch equilibrium adsorption studies at 30 °C. Carefully weighed BSA was added to the Tris–HCl buffer solution (pH = 8.0) with concentrations varied as 1.0, 2.0, 3.0, 4.0 and 5.0 mg/ml, respectively, and different membranes with the same weight were added into the BSA solutions. The mixture was incubated at 30 °C for 24 h to reach a adsorption–elution equilibrium. The amount of protein adsorbed on the membrane surface was calculated from the decreased concentration of BSA solution. The concentrations of BSA solution were determined based on the absorbance at 280 nm using a UV spectroscope.

3. Results and discussion

3.1. Treatment of PP membranes with ammonia plasma

Plasma treatment is one of the most widely used techniques for surface modification of polymeric membranes, the extent of which can be greatly effected by such factors as power, glow-discharge strength, treatment time and gas atmosphere. As the type of gas atmosphere changed, various active groups can be generated on membrane surface. In our work, PP membranes were exposed to ammonia plasma, and the representative XPS spectra for the membrane surface are shown in Fig. 1. In comparison with nascent PP membranes (Fig. 1(a)), it can be clearly seen from Fig. 1(b) that after plasma treatment, two obvious peaks, namely the peak at 533.0 eV corresponding to O_{1s} and the peak at 402.0 eV corresponding to N_{1s}, appeared. The N_{1s} peak can be designated to $-NH_2$ groups generated by ammonia plasma, while the O_{1s} peak can be ascribed to hydroxyl groups which were attributed to the residual water in ammonia and the reaction of surface radical with oxygen when the samples were taken out from the plasma reactor. To show the existence of various forms of carbon, the high-resolution spectra of PP membrane corresponding to C_{1s} were analyzed in Fig. 1(c) and (d). For the PP membranes with 10 min plasma treatment, compared with the peak at 284.6 eV assigned to bond C–C of bulk PP membranes, a new peak assigned to bond C–N (287.0 eV) and C–O appeared.

As the ammonia plasma treatment time increased, the contact angle of membrane changed accordingly (Fig. 2), which was due to the incorporation of amino and hydroxyl groups on the surface resulting in the improvement of hydrophilicity. The amino concentration measurement revealed that after 15 min of plasma treatment, about 14.52 μmol/g amino groups could be produced on membrane surface.

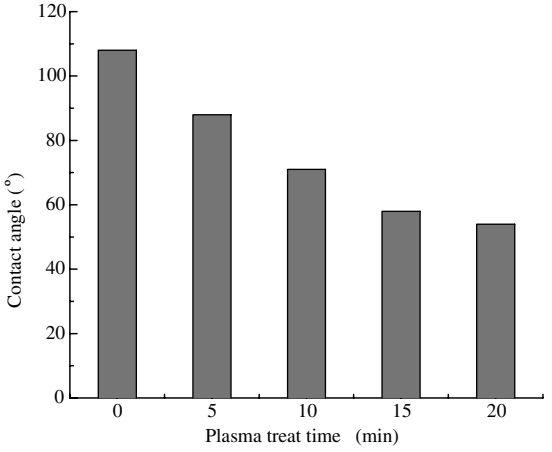


Fig. 2. The effect of plasma treatment time on the contact angle of PP membranes.

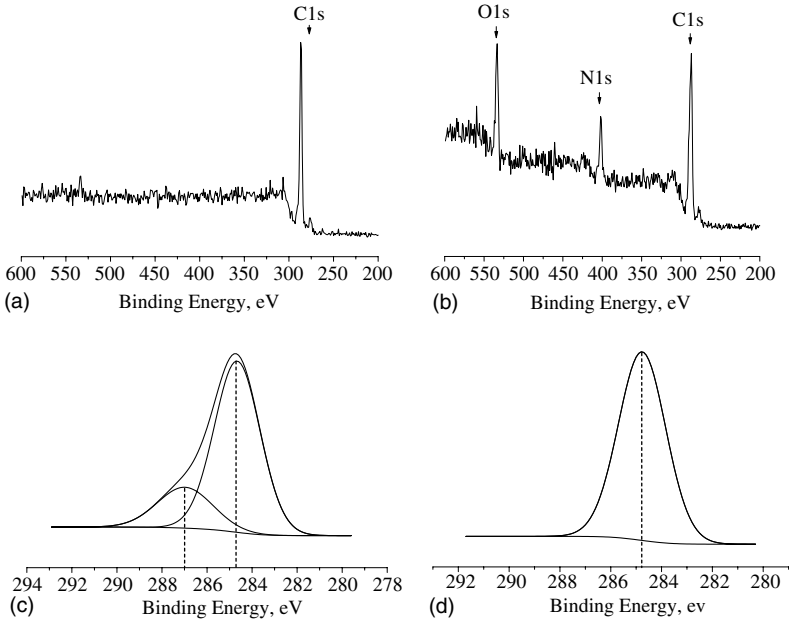


Fig. 1. XPS spectra of PP microporous membranes. (a) Nascent PP membrane, (b) ammonia plasma-treated PP membranes, (c) XPS high resolution spectrum of C_{1s} for modified PP membrane, (d) XPS high resolution spectrum of C_{1s} for unmodified PP membrane.

3.2. Graft polymerization of SLGNCA on the surface of PP membranes

NCA polymerization are usually initiated by primary amines or by a strong base such as sodium methoxide or a tertiary amine [26,27]. In our study, the surface grafting of poly(γ-stearyl-L-glutamic acid) (PSLG) was started with the amino groups introduced by ammonia plasma treatment. Fig. 3 was the XPS spectra of PP membranes before and after graft polymerization. Comparing these two spectra, it can be seen that after surface grafting, the N_{1s} peak was almost undetectable. The relative composition of PSLG-grafted PP membrane surface by XPS analysis is listed in Table 1. The data revealed that the content of N_{1s} was reduced sharply, while the content of C_{1s} increased after surface grafting, which illustrated that some structure with high content of C atom was introduced onto the membrane surface.

Sarin et al. [23] described a method to quantitatively monitor the synthesized polypeptide, which involved the reaction of free amine with ninhydrin under carefully controlled conditions and the determination of absorption at 570 nm for the resulting chromophore in solution. In our experiment, to measure the degree of graft polymerization of PSLG on the PP membrane surface, the grafted polypeptide chains was hydrolyzed in the mixture of HCl and propionic acid, and the concentration of amino acids thus obtained was determined by ninhydrin reaction mentioned above. It was found that the highest mean polymerization degree thus obtained was 4.3. For the polymerization of NCA initiated by primary amines, it is shown in Scheme 1 that the amine reacted with the NCA by nucleophilic attack on the C5 atom. After ring opening followed with the splitting of one molecule of CO_2, an amine was formed again, which would attack sequential NCAs and thus lead to chain extension. This is the so called "amine mechanism" suggested in literatures [13,28]. The key point of this mechanism is that the initiator is connected with the propagating chains, which will lead to the grafting of polymers on the substrate. In reference to our situation, there were many hydroxyl groups introduced on the membrane surface. As shown in Scheme 1, these hydroxyl groups would abstract the acidic hydrogen on the nitrogen in the NCA ring, forming an "active monomer". The active monomer would attack the C5 atom according to Scheme 1 and lead to chain extension in a similar way. This active monomer initiation usually leads to the generation of a large amount of free homopolymer. The "active monomer mechanism" competed with the "amine mechanism", resulting in the low degree of graft polymerization.

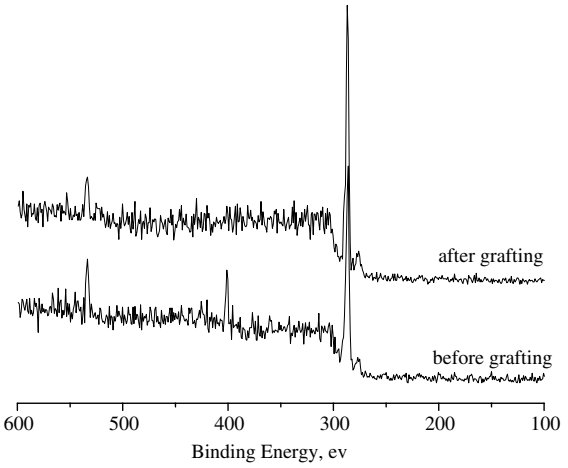


Fig. 3. The XPS spectra of PP membranes before and after graft polymerization.

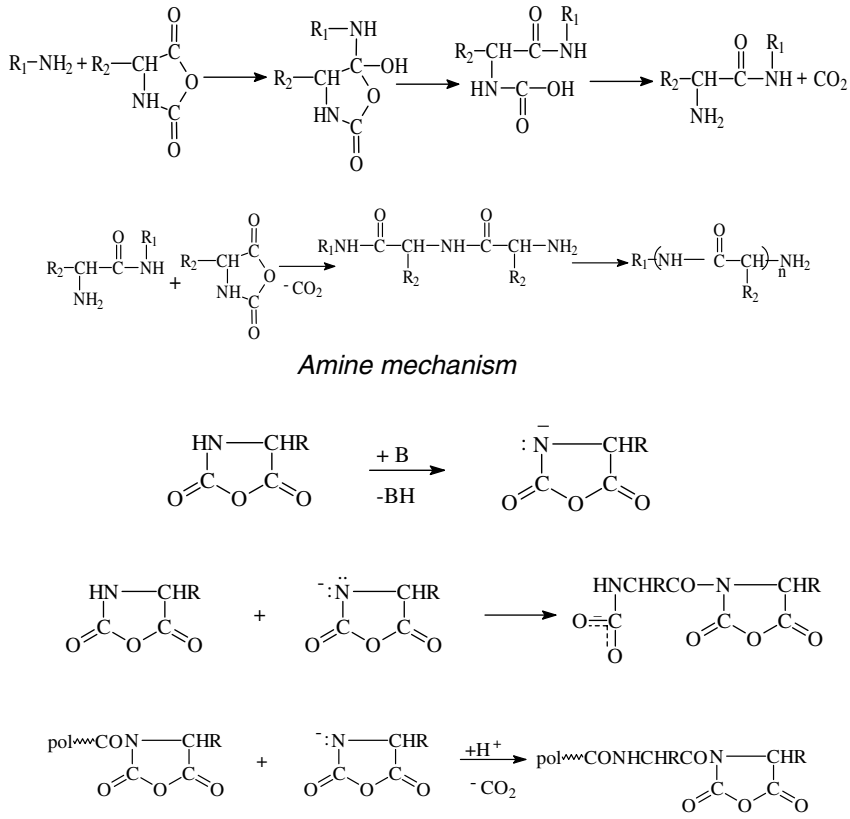
Table 1
The relative composition of PSLG-grafted PP membrane surface by XPS analysis

Content (%)	C_{1s}	N_{1s}	O_{1s}
Before grafting	81.3	11.1	7.5
After grafting	89.5	2.2	8.3

3.3. Effect of γ-APS treatment

To reduce or even eliminate the effects of hydroxyl groups, γ-APS, which would react with hydroxyl groups and introduce new amino groups to the membrane surface, was used for further modification of the ammonia plasma treated membranes. Two methods, namely dipping and refluxing method were adopted. The results of amino concentration measurement are listed in Table 2. It was found that the content of amino groups on the membrane surface treated by both of the two methods was improved greatly. For the membrane treated by 30 min refluxing, the amino group concentration was six times larger than those without γ-APS treatment, compared with the 1.6 times larger of dipping method.

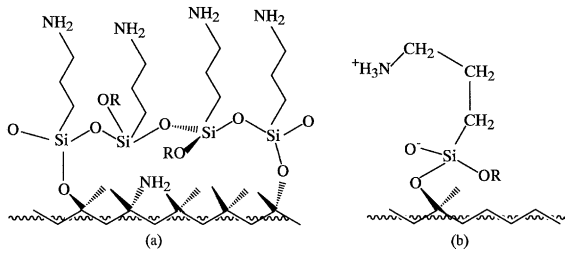
For the γ-APS treated membranes, SLGNCA was graft polymerized on the surface in the same way. The polymerization degree measurement demonstrated that after γ-APS treatment, the graft chains were lengthened and the mean polymerization degree was increased to 9.3 for dipping-treated membranes. Typically, silanes are subjected to hydrolysis during or prior to surface treatment allowing the formation of reactive silanol groups, which can condense and/or react with surface residual –OH functionality [25]. As have been reported, a vapor-phase coupling of γ-APS (refluxing method) would result in multilayer of coupling agent, sometimes even visible as a haze on the surface. While for the



Scheme 1. Mechanism for the synthesis of polypeptide from NCAs.

Table 2
The amino concentration on the membrane surface of γ-APS modified or unmodified PP membranes

Samples	Amino group concentration (μmol/g)
γ-APS treated membrane	
30 min refluxing	40.67
30 min dipping	10.61
Plasma-treated membrane	6.63



Scheme 2. Models proposed for the reaction between γ-APS and –OH groups on membrane surface. (a) Siloxane oligomer modified PP surface model, (b) model of bulk siloxane with amine hydrogen bonding.

dipping method in which the substrate membrane was immersed in the treating solutions, a monolayer of γ-APS could be introduced onto the membrane surface without the formation of polymeric globules [29]. Three models of γ-APS with substrate were suggested by Hook et al. [25], namely the interface model, surface/interface model and substrate bulk model according to the distance between APS amine and the substrate surface. For the refluxing method, the interface model dominate over the other two models, as shown in Scheme 2, the γ-APS oligomer was formed on the surface, which was detrimental to the reactivity of amino groups with NCA. For the dipping method, on the other hand, the γ-APS amines are hydrogen bonded to silanol forming in a cyclical structure, and the amines residing in the bulk and at the surface of the γ-APS coating are coupled to silicon atoms, which would greatly reduced the hydrogen group effect on the NCA polymerization, resulting in the increase of polymerization degree.

The FT-IR/ATR spectra of surface modified membranes are depicted in Fig. 4(a), and Fig. 4(b) was the corresponding spectrum of line B minus line A in Fig. 4(a). From Fig. 4(a) it can be seen that the weak absorbance at 3000–3700 cm^{-1} for original membrane was greatly improved for modified ones, which implied the existence of $–NH_2$, –OH and hydrogen bond between them. In the minus spectra the absorbance at 1640 cm^{-1} was assigned to the amide I peak and the weak peak at 1102 cm^{-1} was corresponding to the stretch vibration of Si–O band, these clearly demonstrated the changes before and after poly(γ-stearyl-L-glutamic acid) grafting. From the spectra we can conclude that the polypeptide were introduced onto PP membrane surface.

The BSA adsorption experiments were performed with different BSA concentrations. The amounts of BSA adsorbed onto different membranes were determined by subtracting the UV absorbance at 280 nm after BSA adsorption from the value before BSA adsorption. As shown in Fig. 5, for the plasma-treated PP membrane, the BSA adsorption was reduced slowly, which was consistent with other measurements since hydrophilic groups were generated on the surface. After graft polymerization, the BSA adsorption increased, but still smaller than nascent PP membranes. For the PSLG–γ-APS–PP membrane, it was surprising to see that the adsorption of BSA increased greatly, even larger than nascent PP membrane. As reported by Sigal et al. [30], non-specific protein adsorption can be discussed in terms of two limiting mechanisms: adsorption by charge–charge interaction or by hydrophobic interaction. For the PP membranes studied here, the BSA adsorption could be reduced by the contribution of the surface hydrophilicity. With the grafting of PSLG, the adsorbed BSA increased which means the decrease of surface hydrophilicity. This could be interpreted by the conformation of PSLG on the surface. It's known that polypeptide exhibits α-helix and coil conformations at different conditions. For the poly(γ-stearyl-L-glutamic acid) with long stearyl groups, Poche et al. [31] speculated that the grafted PSLG in solutions formed in α-helix conformation which was supported by the intramolecular hydrogen bonds, with the peptide main chains in the cores and γ-stearyl long side chains stretched outside. This molecular model of PSLG might be used to explain the BSA adsorption results. For the PSLG–PP membranes, the amount of adsorbed BSA increased a little, this could be ascribed to the existence of –OH groups which led to low polymerization degree. For PSLG–γ-APS–PP membrane, the polymerization degree of grafted chains increased, the stearyl long side chains stretched outside, thus greatly increased the surface hydrophobicity, resulting in the increase of BSA adsorption. It was demonstrated by Saito and coworkers [32] that high BSA adsorbed in multilayers by polymer chains grafted onto a porous hollow-fiber membrane was a promising approach to generate enantioselective membranes.

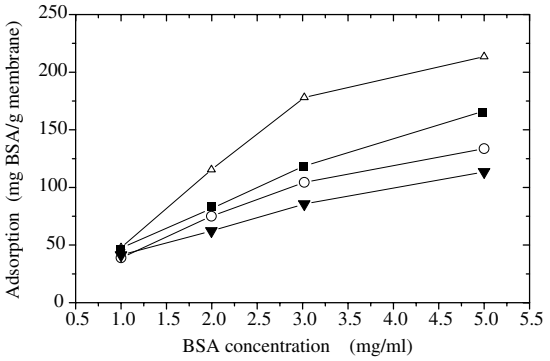


Fig. 5. BSA adsorption on different PP membranes. ■: original membrane; ▼: NH_3 plasma treated membrane; ○: PSLG grafted membrane without γ-APS treatment; △: PSLG grafted membrane with γ-APS treatment.

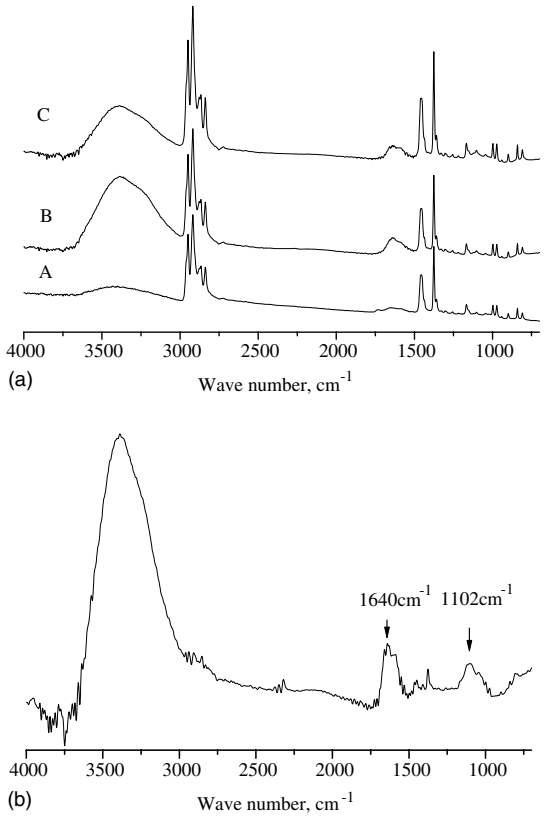


Fig. 4. (a) FT-IR/ATR spectra of the modified PP membranes. A: PSLG–PP; B: PSLG–γ-APS–PP by means of refluxing; C: PSLG–γ-APS–PP by means of dipping. (b) FT-IR/ATR difference spectrum between PSLG–γ-APS–PP and PP membranes.

4. Conclusions

Amino groups were introduced onto PP membrane surface through ammonia plasma treatment, which had successfully initiated the graft polymerization of SLGNCA, as have been demonstrated by XPS spectra. The amino acid content measurement indicated that the highest polymerization degree of grafted polymer was 4.3. The low polymerization degree might be ascribed to the existence of hydroxyl groups on the surface. This undesirable effect can be eliminated by γ-APS, a useful coupling agent containing amino groups. The XPS measurement demonstrated that γ-APS can be introduced onto the plasma-treated membrane surface by both refluxing and dipping methods, and the ATR FT-IR further illustrated that the refluxing method can produce more amino groups on the surface, while the polymerization degree of grafted polymer resulted from dipping method was much higher. Although the goal of producing PSLG-grafted PP membranes was achieved, ongoing work is required to further improve the polymerization degree of grafted polypeptide chains and to evaluate the enantioselectivity of modified membranes. This will be reported in our forthcoming paper.

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