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A Novel Approach for the Surface Modification of Polymeric Membrane with Phospholipid Polymer

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Abstract: A new economic and convenient method to modify the surface of microporous polypropylene (PP) membranes with phospholipid polymer was given. The process included the photo-irradiated graft polymerization of N,N-dimethylaminoethyl methacrylate (DMAEMA) and the ring-opening reaction of the grafted polyDMAEMA with 2-alkyloxy-2-oxide-1,3,2-dioxo-phospholanes (AOP). Four AOPs, whose alkyloxy groups consisted of dodecyl, tetradecyl, hexadecyl and octadecyl moieties, were used to convert the grafted polyDMAEMA to phospholipid polymers. FT-IR spectra confirmed the chemical change of membrane surface. Platelets adhesion experiment indicated that PP membrane with excellent blood compatible surface could be fabricated by this method.

Keywords: Surface modification, phospholipid polymer, platelets adhesion.

Poor biocompatibility and fouling are currently major limits for common polymeric membranes in bioseparation and artificial organs. It is well known that protein in the blood stream does not foul on blood cell surface. This suggests that the blood cell membrane, mainly composed of various phospholipids, is biocompatible. With respect to suppress the fouling phenomena and to improve the biocompatibility, phospholipids were introduced on polymeric membrane surface with various methods such as graft polymerization[1], corona-discharge[2], *in-situ* polymerization[3] and blend with phospholipid polymer[4].

In this letter, we conceived a novel economic and convenient method to fabricate phospholipid-modified membranes, which is described schematically in **Figure 1**. For the phospholipid-containing monomers were very difficult to synthesize, grafted poly(N,N-dimethylaminoethyl methacrylate) (polyDMAEMA) on polypropylene micro-porous membrane was reacted with 2-alkyloxy-2-oxide-1,3,2-dioxo-phospholanes (AOP) with the improved method to generate phospholipid polymer. Additionally, the AOP used for this reaction did not require high purity and the alkyloxy-groups could be varied easily. In order to mimic the cell membrane, four AOPs, which had 12, 14, 16 and 18 carbon atoms in the alkyloxy-groups were adopted. The chemical change on membrane surface was studied by FT-IR spectroscopy. The platelet adhesion experiment was used to evaluate the blood compatibility for the modified membranes.

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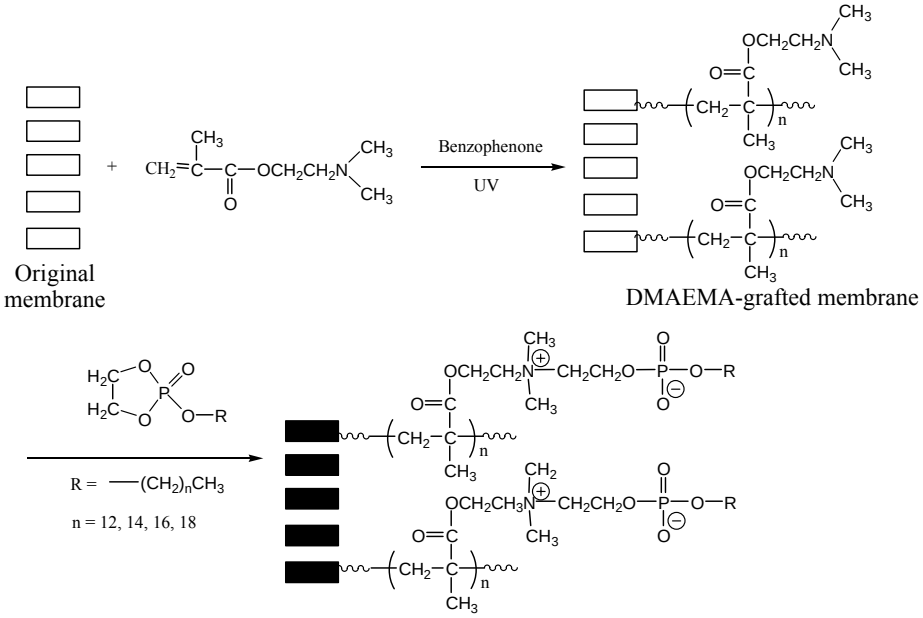
Figure 1 Schematic representative for the approach to prepare phospholipid-modified membrane



AOPs were synthesized according to the usual procedure. These raw AOPs were purified by silica gel column chromatography with a solvent mixture of methanol and chloroform. The chemical structure of AOPs was identified by FT-IR and ^{1}H-NMR spectra. IR of 2-dodecyl-2-oxo-1,3,2-dioxaphospholane (KBr, cm^{-1}): 2924, 2853, 1446, 845, 722 (-$(CH_2)_n$-, n>4), 1290 (P=O), 1030 and 930 (P-O-C); ^{1}H-NMR ($CDCl_3$, δppm) of 2-dodecyloxy-2-oxo-1,3,2-dioxaphospholane: 0.86~ 0.89 (t, 3H, -CH3), ~1.25 (s, 18H, $-CH_2CH_2(C\underline{H}_2)_9CH_3$), 1.67~1.71 (m: 2H, $-CH_2C\underline{H}_2(CH_2)_9CH_3$), 4.12~4.16 (m, 2H, $-C\underline{H}_2CH_2(CH_2)_9CH_3$), 4.33~4.46 (m, 4H, the four H atoms in the ring of 1,3,2-dioxophospholane). There were no special differences in the IR and ^{1}H-NMR spectra among different 2-alkyloxy- 2-oxo-1,3,2-dioxophospholanes except that there were 18H, 22H, 26H and 30H at ~1.26 ppm in the 1H-NMR spectra of 2-dodecyloxy-, 2-tetradecyloxy-, 2-hexadecyloxy- and 2-octadecyloxy-2-oxo-1,3,2-dioxo-phospholane, respectively.

DMAEMA-grafted polypropylene membranes were prepared according to the method of Yamada, *et al*.[5]. The DMAEMA-grafted PP membrane, acetonitrile and AOP were placed into a dried pressure-resistant flask. Then the flask was sealed and placed into an oil bath at a temperature of 60~70°C for the ring-opening reaction of AOP. When the reaction was conducted for 16 hours, the membrane was pulled out, washed with THF to remove the substance absorbed on the membrane surface thoroughly. After drying, the graft degree and the ring-opening reaction rate were calculated by weighting the membranes.

Figure 2 FT-IR spectra of the original, DMAEMA-grafted and phospholipid-modified membranes

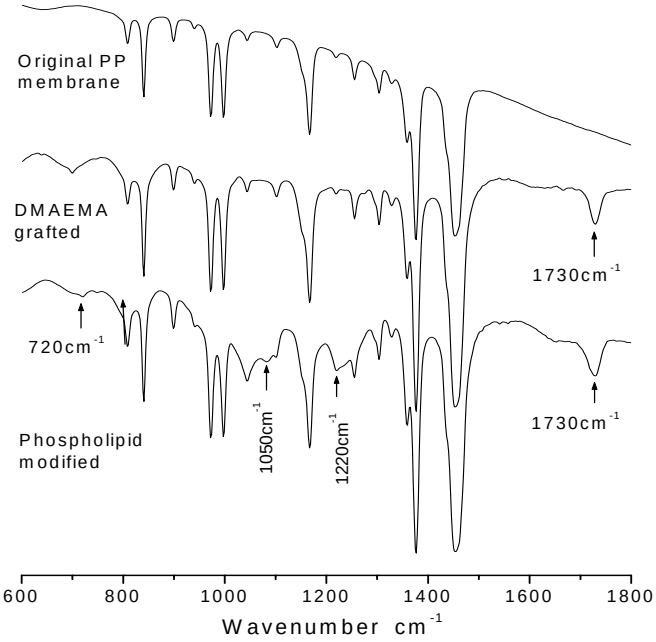
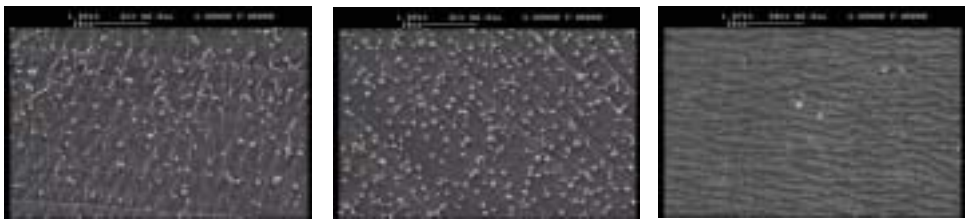
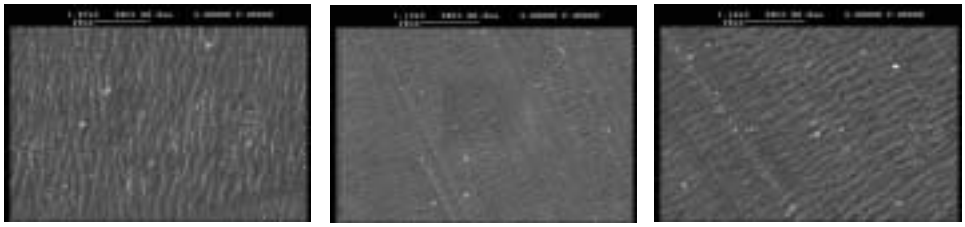


Figure 3 Platelet adhesion on virginal, polyDMAEMA-grafted and phospholipid-modified membranes. (The values in parentheses indicated the number of the carbon atom in alkyloxy groups and the graft degree, respectively)



Virginal | DMAEMA-grafted (2.37%) | Phospholipid-modified (12-, 2.05%)



Phospholipid-modified (14-, 2.65%) | Phospholipid-modified (16-, 2.63%) | Phospholipid-modified (18-, 2.43%)

The polyDMAEMA-grafted and phospholipid-modified membranes were characterized by FT-IR spectroscopy (Bruker Vector 22) with an ATR unit (KRS-5 crystal, 45º) (**Figure 2**). Compared with the original PP membrane, one vibration peak at 1730 cm^{-1} can be seen from the spectrum of the polyDMAEMA-grafted membrane, which was attributed to the stretching vibration of C=O groups in poly(DMAEMA). On the other hand, there were new adsorption peak around 1220 cm^{-1}, 1050 cm^{-1} and weak peak at 720 cm^{-1} in the spectrum of phospholipid-modified membrane, which could be attributed to the stretching vibration of P=O, P-O and the long alkyl group $-(CH_2)_{n>4}-$, respectively. As mentioned before, the stretching vibration of P=O in 2-dodecyloxy-2-oxo-1,3,2-dioxaphospholane appeared at 1290 cm^{-1}, but now its peak appeared around 1220 cm^{-1}. This change indicated that the dioxaphospholane ring in 2-dodecyloxy-2-oxo-1,3,2-dioxaphospholane was opened.

Platelet adhesion experiment was carried out to evaluate the blood compatibility of the membranes. **Figure 3** shows the SEM pictures of virginal, polyDMAEMA-grafted and phospholipid-modified PP membrane surface exposed to human platelet-rich plasma for 30 minutes. It was observed that numerous platelets were adhered on the surface of original PP membrane, and some platelets aggregated and deformed obviously. The platelets adhesion on DMAEMA-grafted PP membrane was much more serious than that on virginal PP membrane, but the platelets had less deformation and scattered evenly on the membrane surface. On the other hand, different from the virginal and polyDMAEMA-grafted membranes, platelet adhesion was suppressed on the four phospholipid-modified membranes. This result indicated that polypropylene membranes with excellent biocompatible surface could be fabricated by the approach described in this letter. Further work concerning the separation performance of the phospholipid-modified membranes has been carrying out in our lab.

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