

Stimuli-responsive membranes through graft-copolymerization of acrylic acid (AAc) onto polycarbonate track etched (PCTE) membrane

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ABSTRACT

Radiation grafting of the Track Etched Membranes (TEMs) is a versatile tool for the formation of stimulus responsive membranes which change their permeation properties in response to environmental stimuli such as pH or temperature. Stimuli-responsive polymeric membranes have attracted the attention of researcher all around the world owing to their potential applications in the fields of controlled drug delivery, bio separation, water treatment, and chemical sensors. Acrylic acid (AAc), well known for its novel pH-sensitive behavior in aqueous media was successfully grafted on the surface and in the pores of polycarbonate track etched membrane (PCTE). The influence of reaction parameters such as monomer concentration, reaction time, temperature and concentration of the initiator on the grafting yield was investigated in detail. The membranes were characterized through Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) techniques. The pH-responsive behaviour of the PCTE-g-AAc membranes was studied. The PCTE-g-AAc membranes exhibit fast and reversible response to the environmental pH. Copyright © 2013 VBRI press.

Keywords: Acrylic acid; polycarbonate track etched membrane; graft copolymerization; pH-sensitive.



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Introduction

When polymer film is bombarded with swift heavy ions, it results in the formation of damaged areas in the film. These damaged areas are known as tracks. These tracks are subsequently etched to form discrete pores with a defined pore size. The membranes having the etched tracks are known as track etched membranes (TEMs) [1]. This new class of membranes of highly regular geometry has great potential to undergo modification for imparting special properties.

A variety of methods have been developed to functionalize the surface of the polymeric films to prepare stimulus responsive membranes. Stimuli-responsive membranes can vary their physical characteristics or chemical structures with changing environmental conditions such as temperature [2], electric field, magnetic field, pressure, and pH [3,-5]. Among the stimuli that can be used to control the response of a system, temperature and pH-responsive factors have drawn much attention [6]. Out of these two, pH-sensitivity is applicable factor, and it gives more choice both for the materials and applying environment as compared with thermo-sensitivity [7, 8].

Surface initiated graft copolymerization is a versatile tool for the preparation of stimulus responsive membranes [9]. Usually these stimuli-responsive membranes are prepared by chemical grafting [10, 11], radiation-induced grafting [12], photo-grafting [13, 14] and plasma-induced grafting [15, 16]. Chemical graft copolymerization is a promising technique to functionalize TEMs because polymers are grafted not only on the surface but also in the membrane pores by introducing proper treatment conditions.

Polycarbonate track etched (PCTE) membranes possess excellent morphology and many desirable physicochemical properties, such as good thermal stability, parallel cylindrical pores with diameters ranging from 10nm to 20 μm with narrow size distribution [17]. This membrane with stimuli responsive behavior is advantageous over the common membrane in terms of easily controlled pore size and quick response to external stimuli. The track etched membrane made from PC with uniform cylindrical pores had been established as a versatile candidate for sensors and component for future "lap-on-chip" systems [18]. However, until now, very few papers reported on the functionalisation of track-etched membranes by pH-responsive polymers [19].

In the present work, we report on the preparation and characterization of PCTE membranes with acrylic acid (AAc) polymer chains by using chemical graft-copolymerization method. The effect of various parameters like monomer concentration, reaction temperature, initiator concentration and the reaction time on grafting has been investigated. The effect of microstructure and the morphological characteristics of the PCTE-g-AAc were systematically investigated by employing FTIR, SEM studies. SEM studies clearly establish the switching of opening and closing of pores as a function of pH.

Experimental

Materials

PCTE membrane (Nuclepore) with pore size of 0.8 μm and 47 mm in diameter was supplied by Whatmann Co. Benzoyl Peroxide (BPO) and AAc were obtained from Sigma Aldrich and were used without further purification. All the solvents and other chemicals were of analytical grades and were used as received. Double distilled water was used as the reaction medium for graft copolymerization reaction.

Graft copolymerization procedure

The PCTE-g-AAc membranes were prepared by chemical graft copolymerization of AAc onto PCTE membranes under inert atmosphere. The reaction was carried out in Pyrex ampoules having a stop cork. PCTE membranes were immersed into the mixture of monomer concentration varying from (2-10 V/V %) and solvents in Pyrex ampoules. BPO was used as initiator. The reaction mixture was deaerated by bubbling nitrogen gas for 15-20 minutes. The reaction mixture was heated in a water bath to initiate the graft copolymerization reaction. The reaction was carried out at different temperatures varying in the range of 40°C - 80°C and for different time periods varying in the

range of 2 to 5 hours. A constant flow of nitrogen was maintained during the graft copolymerization process. After reaction, PCTE-g-AAc membranes were taken out from the monomer solution in the ampoules and washed by stirring for 24 hours with ethanol at room temperature. The washing process ensured complete removal of the unreacted monomer and the remaining homopolymers that may be occluded in the grafted membranes. The copolymers were then dried in a vacuum oven at 60°C till constant weight was obtained. The percentage of grafting (%P_g) was calculated from increase in weight of the original film. The degree of the grafting was determined by the following equation:

$$(\%P_g) = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

where W_g and W_o are the weights of the grafted and ungrafted membranes, respectively. Percentage of grafting has been determined as a function of monomer concentration, reaction temperature, initiator concentration and the reaction time respectively.

Characterization

The grafted films were characterized by various techniques. FTIR measurements on the ungrafted and grafted membranes were performed using Thermo 5700 FTIR spectrophotometer. The Surface topology of the membranes was studied by SEM performed on a LEO VP 435 instrument. A thin layer of gold was sputtered on the sample surface prior to the SEM measurement. Static water contact angles of the pristine membrane were measured at 25°C and 50% relative humidity by the sessile drop method, using a 3 μl water droplet in a telescope goniometer (contact angle instrument). The telescope with a magnification power of 23x was equipped with a protractor 1° graduation. For each sample, at least five measurements on different surface location were investigated. The angles reported were reliable to $\pm 3^\circ$. The contact angles of water droplets on PCTE and surface modified PCTE surfaces were used to determine the change in hydrophilicity of the film surface. Five measurements were recorded and an average contact angle was calculated for each material.

Swelling is an effect that is important specifically for cross-linked matter and therefore for many polymers in solvents. The swelling ability of a polymer is related to its solvents permeability and uptake, i.e., to its hydrophilicity. The swelling is believed to be a phenomenon similar to osmosis. Swelling is one of the most important parameters affecting on the characteristic properties of the grafted membrane and accordingly determining its applicability for practical use. Swelling behavior of the grafted membranes has been studied gravimetrically. PCTE-g-AAc membranes of known weight were immersed in the distilled water for 24 hours at room temperature, periodically removed from the water, blotted between filter paper to remove excess of water. Then the membranes were surface dried lightly and weighed, the percentage of swelling (%P_s) was calculated as:

$$(\%P_s) = [(W_s - W_d) / W_d] \times 100 \quad (2)$$

where W_s is the weight of swollen membrane and W_d is the weight of dry membrane. To determine the pH sensitivity, PCTE-g-AAc membranes were immersed in buffer solution of different pH values (pH=4-8.0) for known intervals of time at 37°C. The percentage of swelling (%Pg) of the grafted membranes in different pH was measured using the gravimetric method using equation 2.

Results and discussion

Parameters affecting grafted membranes

Variation of percentage of grafting with monomer concentration, temperature, reaction time and initiator concentration is represented in **Table 1**.

Table 1. Effect of monomer concentration, reaction temperature, reaction time and initiator concentration on percentage of grafting. Maximum percentage of grafting (85 %) was obtained at [AAc] = 8 % V/V, [Reaction Temperature] = 60°C, [BPO] = 0.04 M, [Reaction time] of 5 hours.

Effect of Monomer Concentration (V/V %)		Effect of Reaction Temperature (°C)		Effect of Reaction Time (hours)		Effect of Initiator Concentration (M)	
Monomer Conc.	%P _g	Reaction Temperature	%P _g	Reaction Time	%P _g	Initiator Concentration	%P _g
0	11	0	4	0	8	0	0
2	35	4	19	2	22	0.02	23
4	57	50	45	3	49	0.04	85
6	65	60	85	4	66	0.06	72
8	85	70	65	5	85	0.08	64
10	23	80	44	6	72	0.10	43

Effect of monomer concentration

It can be observed from the **Table 1**, that the grafting percentage increases smoothly with increasing monomer concentration giving maximum percentage (85%) at monomer concentration of 8% V/V AAc and then decreases with further increase in the concentration of AAc. The initial increase in grafting may be due to the reason that most of the monomer is utilized by the available free radical sites on the polymer backbone. A rapid increase of the %P_g is due to the lateral diffusion of the monomer. Moreover at the lower concentration, the extent of homopolymerization of the monomer is smaller. The grafting reaches a maximum value and thereafter decreases. This is because the number of free radical sites available on the polymer backbone becomes a limiting factor. The decrease in percentage of grafting beyond optimum monomer concentration is due to the preferential homopolymer formation.

Effect of temperature

The effect of reaction temperature on the graft polymerization was studied at temperature varying from 40°C to 80°C. It can be seen from Table 1 that an increase of temperature up to 60°C increases the percentage of grafting. This may be due to the increase of the initiation and propagation rates of graft copolymerization. Increase in the percentage grafting with increasing temperature is also due to increase in the decomposition of the initiator leading to the formation of more free radicals. But beyond 60°C, the grafting rate decreases because at higher temperatures, higher combination rates of monomer are obtained

increasing homopolymerization reactions, which results in a decreased grafting rate.

Effect of reaction time

It can be seen from **Table 1** that the percentage of grafting increases sharply with increase in the reaction time from 2 hour to 5 hours and after that it decreases smoothly. The decrease in grafting percentage after optimum time can be due to the induced decomposition of the monomer leading to decrease in active radicals required to generate active sites on polymeric back bone.

Effect of initiator concentration

Initiators are usually added to the reaction mixture to generate active sites in the polymer backbone. For this reason, BPO used as an initiator, was added in different concentrations ranging from 0.01M to 0.04 M. It is seen from Table 1 that the percentage of grafting yield slightly increases with increasing initiator concentration up to 0.04 M, after which it starts to decrease. Maximum grafting yield is 85% at this value. This indicates that this optimum concentration is sufficient to inhibit the possible homopolymerization. Above this value, ions of BPO move to the surface of PCTE and inhibit the growing macroradicals of grafted part. This is because in this system, the BPO initiator is inefficiently used. There is wastage of initiator due to its induced decomposition by the attack of propagating radicals on the initiator. This reaction can be termed as chain transfer reaction to initiator. The induced decomposition of initiator does not change the radical concentration during the polymerization, because the newly formed phenyl radical will initiate a new polymer chain. A molecule of initiator is decomposed without an increase in the number of propagating radicals or the amount of monomer being converted to graft copolymer. This results in a decrease in percentage of grafting.

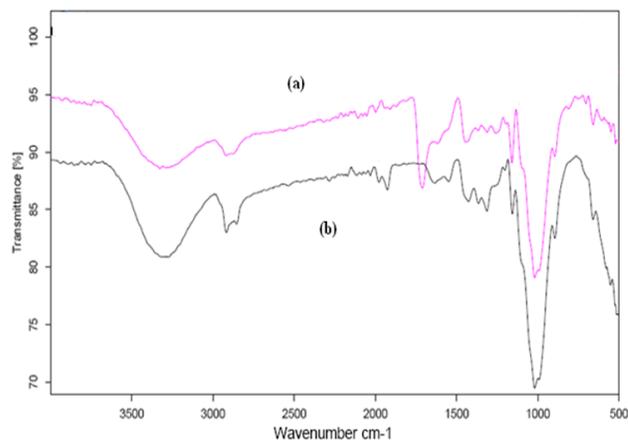


Fig. 1. FTIR spectra of (a) virgin PCTE (b) PCTE-g-AAc membrane.

FTIR spectroscopy

The chemical structure of the PCTE and the PCTE-g-AAc membranes were studied by FTIR spectroscopy. As shown in **Fig. 1**, the PCTE membrane exhibited significant peaks at 1765 cm⁻¹ (C=O) stretching) which were due to the C=O stretching vibrations of the ester group in the polycarbonate

membrane. However, comparing the spectra of the PCTE-g-AAc membrane with that of the pristine PCTE, the new absorption band appear at 1730 cm^{-1} corresponding to the ($-\text{C}=\text{O}$) carbonyl group of the acrylic acid. The absorption bands of above peaks are indicative of the existence of AAC deposited on PCTE membrane and AAC might have reacted with backbone of PCTE through graft copolymerization reaction. This band is absent in the spectra of virgin PCTE. The result indicates that the AAC has been successfully grafted on the PCTE membrane by the chemical graft copolymerization.

SEM analysis

The surface morphology of the pristine PCTE and the PCTE-g-AAc membranes with different grafting yields i.e. (18%, 45%, 85%) were studied by SEM at magnification of 1000X as shown in **Fig. 2** (a, b, c, d). The comparison of the PCTE-g-AAc with that of pristine PCTE shows clearly the change in the topography of the PCTE surface. It is clearly revealed that after grafting with AAC, the morphology of PCTE membrane changes not only on the surface but also inside the membrane, indicating that AAC monomer were grafted not only on the surface but also inside the pores of PCTE. It could be seen from the **fig.** that the pristine PCTE membrane have uniform pore geometry and cylindrical and straight pore. After grafting, the pore size decreased. Because after graft copolymerization, the entire membrane surface was covered by a thin polymer layer, indicating that the membrane surface had been evenly modified. The pristine PCTE membrane exhibits a smooth surface pattern whereas PCTE-g-AAc exhibits rough surface. The reason for the surface roughness is due to the chemical graft copolymerization of AAC onto PCTE film which opens up its matrix and shows considerable deposition of AAC on the surface of back bone polymer. It is the evidence that shows the formation of grafts on the surface. The above results show that the functional AAC chains could be successfully grafted on both the outer surface of the membrane and the inner surface of the membrane pore.

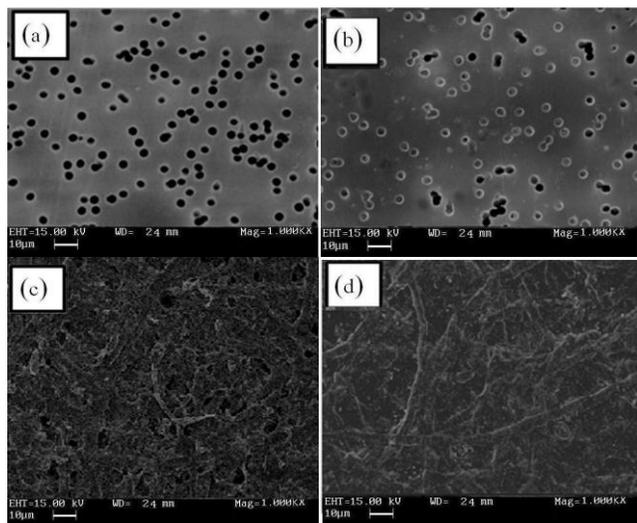


Fig. 2. SEM images (a) pristine PCTE (b) PCTE-g-AAc (18%) (c) PCTE-g-AAc (45%) (d) PCTE-g-AAc (85%) membranes

Table 2. Effect of (%P_g) on the water uptake and contact angle of the PCTE-g-AAc membranes.

Water uptake (%)		Water contact angle (°)	
%P _g	Water uptake	%P _g	(°)
18	20	Pristine	74
160	80	18%	62
210	12	85%	57

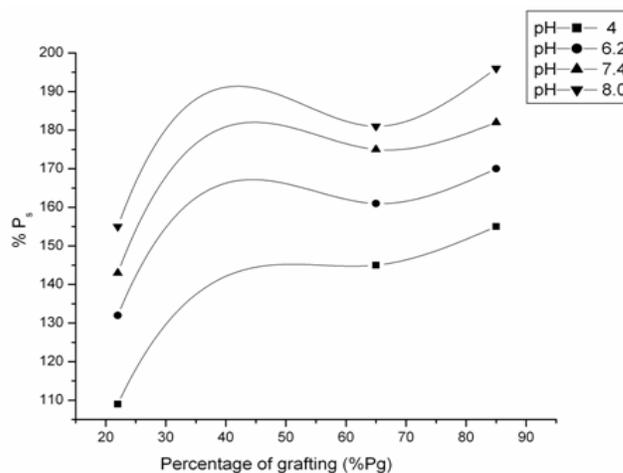


Fig. 3. pH sensitivity as a function of different percentage of grafting.

Water uptake of PCTE-g-AAc membranes

The swelling of PCTE-g-AAc increases with increase in percentage of grafting as represented in **Table 2**. The swelling rates indicate that the initial swelling process is primarily due to water penetrating into copolymer film through capillary and diffusion. Then the penetrating water is absorbed by hydrophilic groups through formation of hydrogen bonds. A higher grafted AAC content results in a greater hydrophilicity which causes a higher swelling ratio.

Water contact angle

The water contact angles on both PCTE and PCTE-g-AAc membranes were markedly different: 74° for the PCTE film surface and 57° for the PCTE grafted surface as represented in **Table 2**. The surface grafted film PCTE-g-AAc indicates the hydrophilic nature of the grafted chain of the AAC polymer side chains. The increase in the hydrophilicity is due to the presence of oxygen containing groups on the surface, such as $-\text{C}-\text{O}$, $-\text{C}=\text{O}$, $-\text{O}-\text{C}=\text{O}$, $-\text{OH}$, $-\text{OOH}$ etc and it is markedly increased by the electrostatic repulsion between the negatively charged carboxylic groups ($-\text{COO}^-$) present in the grafted chains.

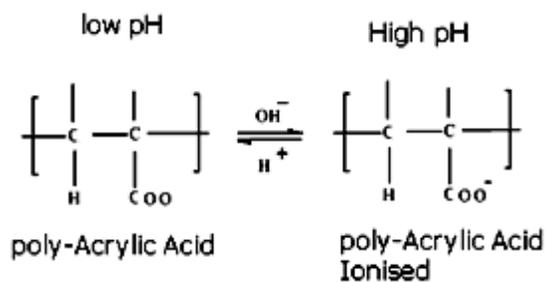
pH sensitivity as a function of percentage of grafting:

The investigation of swelling properties of the membranes is carried out in the various buffer solutions (pH= 4-8.0) at 37°C as a function of different percentage of grafting as shown in **Fig. 3**. These membranes showed significant swelling at various pH solutions. It is also evident from the figure that the swelling percentage of the films increases

with increase in the pH of the medium. The swelling of the grafted membranes also increases with the extent of percentage of grafting. Increase in the percentage of grafting implying a improved hydrophilicity is due to the presence of oxygen containing groups on the surface, such as $-C-O$, $-C=O$, $-O-C=O$, $-OH$, $-OOH$ etc.

pH responsive behaviour of PCTE-g-AAc membranes

Fig. 4 (a,b) shows the SEM images of the grafted membranes at different pH. The change in the response behavior of membranes in solution pH can be attributed to the change in conformation of graft chain on the membrane surface, especially on the pore surface and in the sub-surface region of the pores as shown in **scheme 1** [20]. Pristine PCTE is pH-independent. On the other hand, the PCTE-g-AAc membranes exhibit a pH-dependent behavior. Above a pH value of 4.8, the $-COOH$ groups of the grafted AAac polymer side chains can be ionized or dissociated into carboxylate ions and have an expanded confirmation because of the electrostatic repulsion forces between the chains [21]. The extension of the AAac polymer side chains into the pores and in the sub-surface region of the pores reduces the effective dimension of the pores (**Fig. 4a**). It results in the blocking of the pores of the PCTE-g-AAc membrane. On the other hand, at pH below 4.8, as carboxylic acid groups do not dissociate, the grafted acrylic acid chain will shrink and be precipitated on the surface of the polymer backbone (**Fig. 4b**) increasing the pore size. Such pH-responsive membranes will be useful for sensing and modulating external chemical signal, and also for drug delivery applications, as they change their chain confirmation according to the electrostatic interaction between charged groups.



Scheme 1. pH sensitivity as a function of grafting.

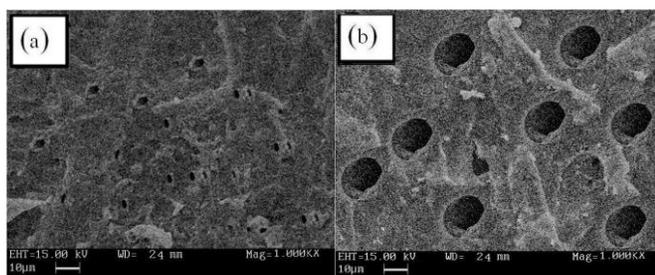


Fig. 4. SEM images of the opening and closing of the track etched membranes (a), (b).

Conclusion

The PCTE-g-AAc stimuli-responsive membranes could be prepared by chemical graft copolymerization method. The reaction parameters such as concentration of monomer, reaction temperature, initiator concentration and the reaction time are optimized to produce membranes with desired physical and chemical properties. The membrane showed good swelling behavior. The structures of Stimuli-responsive polymeric membranes were characterized by FTIR, SEM which indicates that AAac have been grafted onto PCTE. The hydrophilicity of the membranes was studied by the water contact angle. These membranes exhibited a rapid and reversible response on the solution pH in the pH range of 4-8.0. This type of work could encourage the preparation of smart membranes with pH-responsive on-off switching properties i.e. closing and opening of the pores. The present study has shown that chemical graft copolymerization is a relatively simple and effective approach to the preparation of functionalized Track Etched PC membranes with well controlled pore size, uniform surface composition, and pH responsive behavior.

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