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Synthesis And Characterization Of Diaminomaleonitrile Functionalized Polystyrene Grafts And Heterocyclic Crosslinked Polymer Membrane Of Microporosity

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ABSTRACT

Polystyrene (PS) was grafted in water with diaminomaleonitrile (DAMN) using azobisisobutyronitrile (AIBN) as an initiator. Variations of percentage grafting with time, temperature, monomer, initiator concentration and type of solvent were studied. It was observed that the percentage of grafting and grafting efficiency increased as time and temperature rose up to a certain value, and then they leveled off. The percentage of grafting was found to rise with increasing monomer and initiator concentrations, and then decrease. Optimum conditions for grafting were found to be maleonitrile=0.5 M, [AIBN]=1.5×10^{-3} M, T = 80°C and t=4h. The effect of the degree of grafting on the swelling of the PS graft membranes was also established. The structure properties of all membranes were investigated by contact angle measurements. The chemical structure, thermal characteristics and thermal stability of the obtained membranes were investigated by means of FTIR spectroscopy, differential scanning calorimetry (DSC) and thermal gravimetric analysis. Crosslinked PS graft membrane with degree of grafting up to 87% was found to be useful for pervaporation separation of phenol/water mixtures.

KEYWORDS

Graft copolymerization;
Polystyrene;
Pervaporation.

INTRODUCTION

Graft copolymerization is an attractive means for modifying base polymers because grafting frequently results in the superposition of properties relating to backbone and side chains.

Development and characterization of polystyrene grafts were reported[1-5].

Grafting of amino functional monomer onto initiator-modified polystyrene particles was reported[6].

The aim of this work is to prepare a heterocyclic cross-linked polymer membrane of microporosity useful for chemical separation.

EXPERIMENTAL

Materials

Polystyrene (Aldrich, average MW ca. 280,000 GPC)), diaminomaleonitrile (DAMN) and azobisisobutyronitrile (AIBN) are of analytical grade and used without further purification. The solvent toluene was dried over 5 Å molecule sieves before use.

Characterization

FTIR spectroscopy of the grafted polystyrenes were recorded with a Vector 22 Fourier transform infrared spectrometer (Bruker). Molecular masses (Mn, Mw) were determined by gel permeation chromatography (GPC) (Polymer Laboratories, PL-GPC 20) using dilute polymer solutions (10 mg/5 ml) in THF at room temperature with the rate of 1 ml/min. Differential scanning calorimetry (DSC). A Perkin-Elmer DSC-2 was used for studying the melting and glass transition temperature behavior of the copolymers. The melting studies were performed in the temperature range of 50-240ºC at the heating rate of 10ºC / min in a N_2 atmosphere. Thermal gravimetric analysis (TGA) studies on the un-grafted and grafted membranes were carried out using Perkin-Elmer TGA-7. Specimens having typical weights of 10-20 mg were used for TGA measurements. Thermograms were obtained in the temperature range of 50-700ºC. The heating runs were made at a constant heating rate of 20ºC /min under N_2 atmosphere.

Synthesis of graft copolymers

Diaminomaleonitrile(0.5mole/L) was added with AIBN (1.5×10^{-3} M) and 1gm of polystyrene in water(100 ml) with the temperature raised to 80°C to initiate the polymerization reaction. The reaction mixture was continuously stirred for 4 hours. At the end, the grafted polystyrene was first washed with methanol to remove the homopolymer, collected and dried in an oven at 60°C.

Grafting Yield (%) = [(wg - wi)/wi] × 100.

Grafting efficiency (GE) was calculated as follows:

GE (%) = [(weight of graft)/(weight of graft + weight of homopolymer)]×100

Preparation of crosslinked polystyrene graft

Five drops of triethylamine was added to a solution of polystyrene graft ($DAMN_{87}$-g-PS) (1g) in THF (75ml) and the mixture was refluxed for 8 h. The product was washed with methanol, filtered and dried in an oven at 60ºC.

Preparation of membranes

The dried polystyrene graft polymers were dissolved in THF. The membranes were made by pouring 20 ml of 4%(wt/vol) polymer/THF solution into a flat petri dish(4.8cm diameter), and the solvent was allowed to evaporate at 60ºC for 7 days.

Water absorption ratio

The substrate membrane was immersed in the water for 48 h in room temperature. After treatment, the excess water on the surface was removed using a filter paper. Then the wet membrane was weighed and dried at 70ºC in the oven to a constant weight. The water absorption ratio was calculated according to **Wa % = Ww - Wd/Wd × 100**

Where Ww is the weight of wet membrane and Wd is the weight of dry membrane.

Measurement of pervaporation flux (J)

The pervaporation flux(J) measurement of $DAMN_{87}$-g-PS crosslinked membrane was carried out according to the following conventional method. The sample membrane was used to seal the mouth of the volumetric flask containing 2,4,6 wt% phenol solutions(i.e., phenol-water mixtures), and then the volumetric flask was vacuumized at 25°C under a vacuum degree of 0.08 MPa for 1h. The value of the pervaporation flux(J) could be calculated in terms of the following formula: **J =$(G_1 - G_2)/S$ (g/m²h),** where G_1 and G_2 were the weights of the volumetric flask before and after being vacuumized, respectively. S was the area of the membrane covering the mouth of the volumetric flask.

RESULTS AND DISCUSSIONS

Effect of polymerization time on grafting

Grafting of polystyrene was carried out at various polymerization times, keeping the monomer, initiator and temperature constant at 0.5M, 1.5×10^{-3} M and 80ºC, respectively. As shown in figure 1, grafting yield percentage first rose with increasing polymerization time; and then leveled off, reaching to a saturation grafting value of 87% at 4 h. As the polymerization time increases, the number of monomer and initiator molecules that diffuse onto the polystyrene chains also increases, and this results in a higher grafting yield percentage. The leveling off of grafting may be attributed to less diffusion of the monomer as a result of the increase in the medium viscosity.

Effect of temperature

The effect of temperature on the graft copolymerization of diaminomaleonitrile onto polystyrene was studied within the range of 60-80ºC keeping monomer, initiator, and polymerization time constant (Figure 2). As shown in the graph, a sharp increase in the grafting yield value of 87% was obtained and then leveled off. The enhancement in the grafting yield with increasing temperature may be attributed to: (1) the enhancement of polystyrene swellability, (2) an increase in the mobility of the initiator and monomer, (3) an increased rate of diffusion for the initiator and monomer from the solution phase to the polystyrene chains, (4) an increased number of active sites in the reaction medium, and(5) an increased rate of initiation and propagation steps. The leveling off of the grafting yield at 80ºC was due to the increase in the formation of homopolydiaminomaleonitrile as shown in the grafting efficiency curve in figure 2.

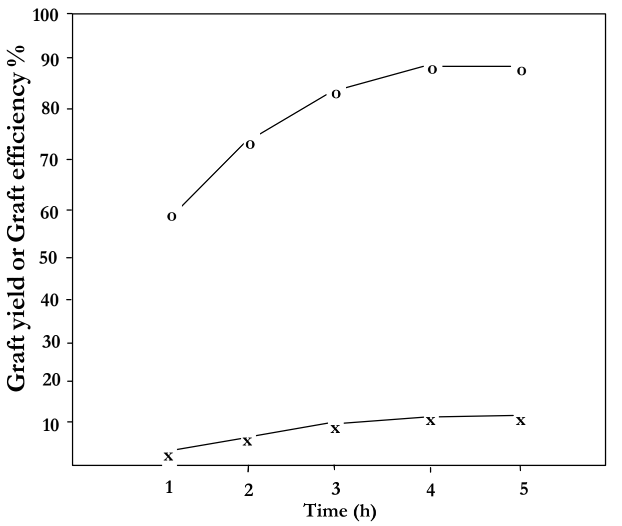

Figure 1: Effect of time on grafting yield /(o) and grafting efficiency (x). [ABIN]=1.5×10^{-3} M, [M]=0.5 M, T=80°C

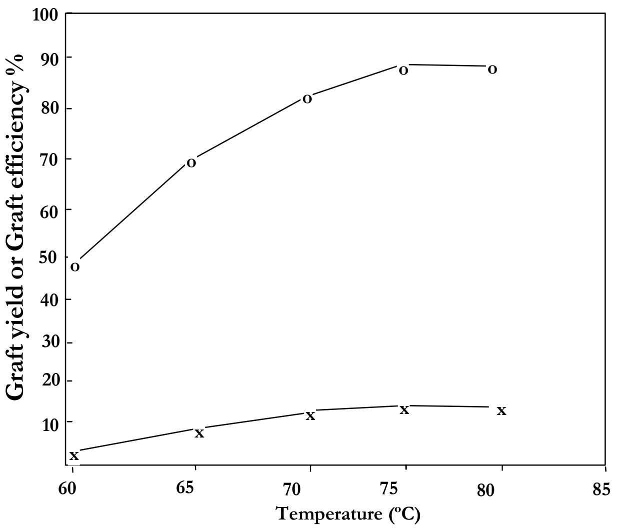

Figure 2: Effect of temperature on grafting yield and grafting efficiency. [ABIN]=1.5×10^{-3} M, [M]=0.5 M, t=4h

Influence of monomer concentration

The variation of grafting yield with the concentration of diaminomaleonitrile was investigated by carrying out polymerization at five different DAMN concentrations(Figure 3). Grafting yield sharply rises with increasing DAMN concentration up to 0.5M, yielding 87% grafting yield, and then decreases with further increases in diaminomaleonitrile concentration. As the diaminomaleonitrile concentration rises, the diffusion of monomer into the polystyrene backbone increases enhancing the grafting yield. The decrease in the grafting yield at higher DAMN concentrations may be due to the adsorption of monomer on polystyrene surface in excessive amounts, which

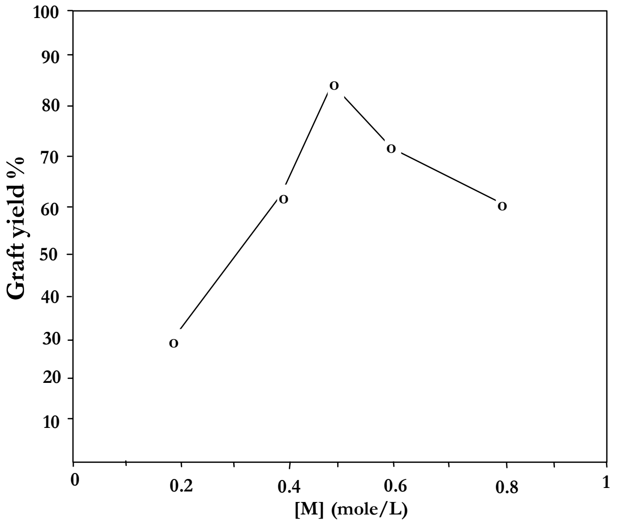

Figure 3: Effect of monomer conc. on grafting yield. [ABIN]=1.5×10^{-3} M, T=80°C, t=4h

prevents diffusion of the initiator molecules inside the polystyrene resulting in lowering the graft yield.

Influence of initiator concentration

It is shown from figure 4 that the grafting yield increases with AIBN concentration in the 0.5×10^{-3} M to 1.5×10^{-3} M range, and then decreases with any further increase in the AIBN concentration. The increase of grafting yield by increasing the AIBN concentration to a certain limit prove that free-radical species produced by the dissociation of AIBN molecules may participate essentially in the abstraction of hydrogen atoms from the polystyrene backbone, yielding a polystyrene radical capable of initiating grafting. As the initiator concentration increased above 1.5×10^{-3} M, the termination reactions of the graft copolymerization takes place.

The effect of solvents on grafting yield

The above experiments were all conducted in aqueous medium. In addition, to investigate the effect of solvents on the grafting degree, some water/organic solvents were used. The results are shown in figure 5. It is shown that the grafting yield is extremely low in alcoholic solution compared with aqueous solution. It is shown that increasing the solvent ratio in the water/solvent mixture is accompanied by a significant decrease in the graft yield. The decrease in grafting yield including solvents in the reaction medium implies that these solvents are very likely to participate in termination of the grafted growing polymer chains.

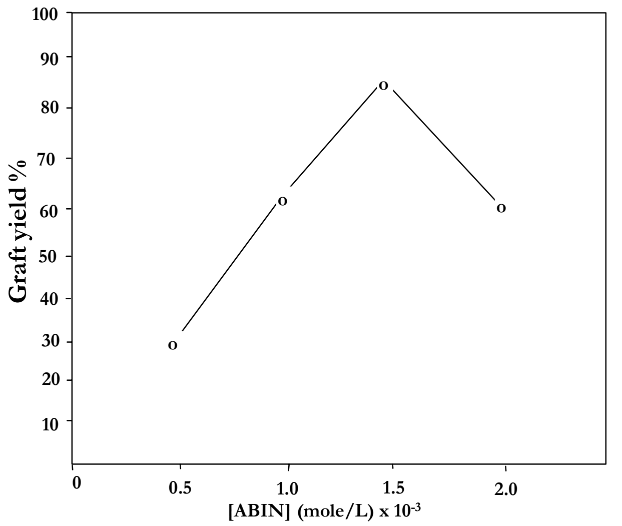

Figure 4: Effect of initiator conc. on grafting yield. [M]=1.5×10^{-3} M, T=80°C, t=4h

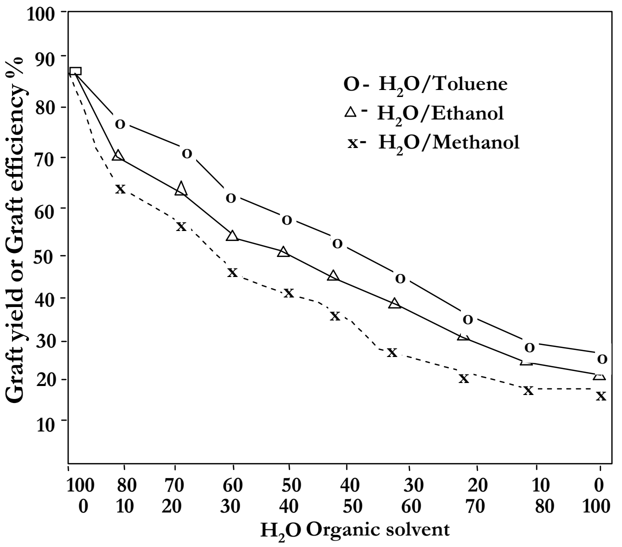

Figure 5: Effect of solvent on grafting yield. [ABIN]=1.5×10^{-3} M, [M]=0.5 M, t=4h, T=80°C

Thermal analysis

The melting temperature(T_m) and the heat of fusion(ΔH_m) for polystyrene and polystyrene grafts membranes are presented in TABLE 1. As shown from the TABLE, the melting point T_m of graft copolymers are higher than that of un-grafted polystyrene. Thus, melting point of PS increases as a result of grafting of diaminomaleonitrile. The increase in T_m with the addition of DAMN is due to the increased inter-atomic forces of the cyano and amino groups.

TABLE 1: Melting parameters of PS and DAMN-g-PS memberances as determined by DSC

Polymer membrane	graft (%)	ΔH_m (cal/g)	T_m (°C)	Tg
PS	-	4.1	237.5	100
DAMN$_{30}$-g-PS	30	4.4	246	112
DAMN $_{50}$-g-PS	50	4.9	258	119
DAMN $_{70}$-g-PS	70	5.4	276	126
DAMN $_{87}$-g-PS	87	5.8	283	139
DAMN $_{87}$-g-PS (crosslinked)	87	6.3	> 300	153

It can be also observed that ΔH_m increases with the increase in the degree of grafting indicating the incorporation of pendent polydiaminomaleonitrile chains in amorphous copolymers with higher thermal stability. As expected, the DSC results given in TABLE 1 show that the increase of DAMN content shifts Tg to higher temperature as a result of crosslinked interactions.

Thermogravimetric analysis (TGA)

The effect of grafting on the thermal stability of the un-grafted and grafted polystyrenes was studied using TGA. All the degradation temperatures were measured from the thermogram by onset extrapolation. Figure 6 shows TGA thermograms of the un-grafted PS membrane and grafted PS membranes having various degrees of grafting. Un-grafted PS membrane showed a continuous weight loss confined to a single-step degradation pattern. The degradation temperature was found to vary depending on the degree of grafting. For instance, the un-grafted PS membrane recorded a degradation temperature of 410°C. This temperature increased in the grafted membranes from 410 to 470°C with the increase in the degree of grafting from 30% to 87%. These results indicate that the incorporation of polydiaminomaleonitrile makes the PS membrane inalienable to thermal degradation due to the incorporation of some 'strong links' into the macromolecular chains. This means that the grafted PS are more thermally stable than the un-grafted PS membranes since all grafted membranes showed a single degradation pattern despite having two components. This thermal stability would make the grafted PS membranes suitable for any practical application.

FTIR characterization of polystyrene grafts and crosslinked DAMN-g-PS

The grafting reaction between diaminomaleonitrile and polystyrene was confirmed by FTIR spectroscopy . A sharp peak observed at 2228 cm^{-1}, which represents the cyano group of polystyrene graft. This peak is not observed in the spectrum of crosslinked polystyrene graft. During cross-linking, intermolecular side-chain reaction of amino groups with cyano groups forming pyrazine ring followed by intramolecular side-chain reaction forming pyrrole rings (Figure 7). This could be further supported by the presence of a sharp high intensity peak at 1624 due to C=N(heterocyclic rings) formed by cross-linking.

Molecular weights

Molecular masses of the synthesized grafts are

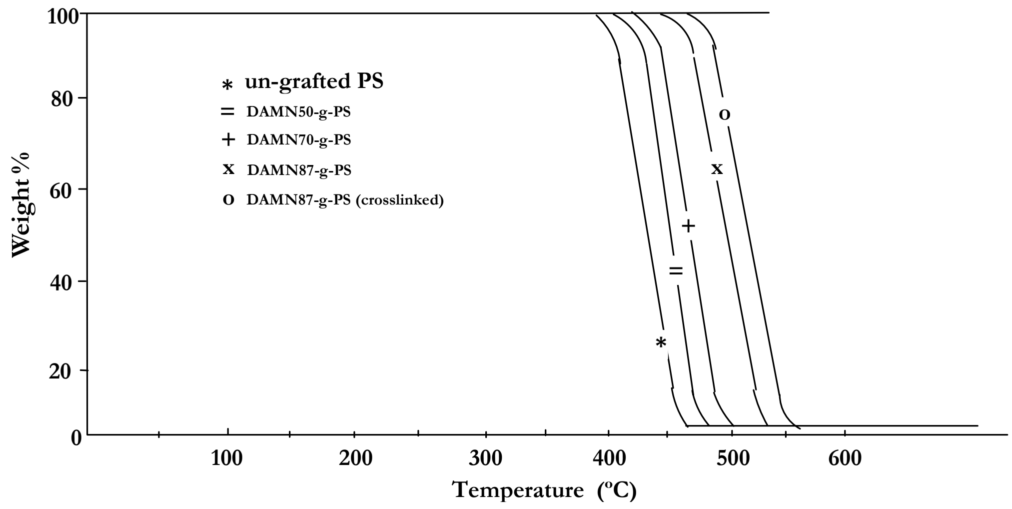

Figure 6: Typical TGA thermogram of ungrafted PS and PS grafts membranes

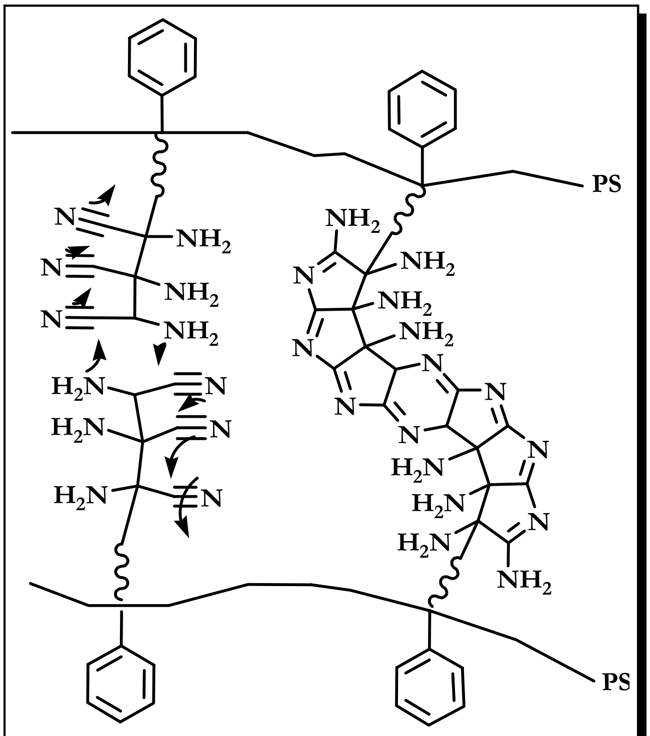

Figure 7: Schematic of the crosslinking reaction for the synthesis of the crosslinked polymer

TABLE 2: Number average molecular masses Mn and weight average molecular masses Mw of PS and copolymers

Sample	Mn (g/mol^{-1})	Mw (g/mol^{-1})
PS	78000	280000
DAMN$_{30}$-g-PS	81700	293000
DAMN$_{50}$-g-PS	83500	308000
DAMN$_{70}$-g-PS	85000	324000
DAMN$_{87}$-g-PS	90000	348000

lower when chain scission appears than when graft is synthesized. From the results shown in TABLE 2 there are longer main chains of graft (higher Mn) and there are fewer reactive sites available, which directs reaction to homopolymerisation of diaminomaleonitrile, resulting in longer graft branches. This is supported by the results of molecular masses, Mn, of polystyrene grafts.

Swelling properties of polystyrene grafts

The effect of grafting percentage on the swelling ratios for polystyrene grafts at room temperature is shown in figure 8 which reveals an increase in the swelling ratios with the increase of grafting percentage. Clearly, the swelling behavior of the membranes depends on the amount of the grafted branches. The results reflect a high degree of cross-linking in the membrane as illustrated in its low water absorbency.

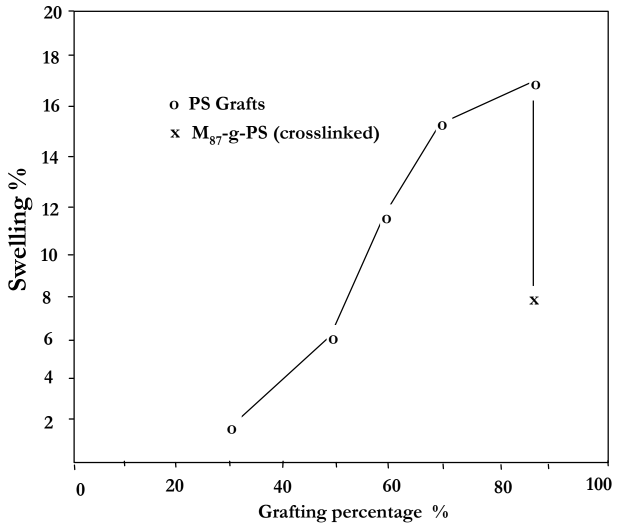

Figure 8: Swelling ratio as a function of grafting percentage

Potential application of the crosslinked polymer membrane (DAMN$_{87}$-g-PS) of microporosity

The study of materials that possess voids of molecular dimensions is an area of nanoscience with technological applications[7]. Microporous materials are defined as solids that contain interconnected pores of less than 2nm in size[8]. Covalent linkages between polymer chains can be established by the reaction of functional groups with complementary reactivity, such as an amine, -carboxylic acid or an isocynate-OH/NH_2 reaction[9].

Polymer membrane of intrinsic microporosity[10] was tested for the removal of organic compounds from aqueous solution by pervaporation. The removal of phenol from aqueous solution has also been achieved by pervaporation[8]. Pervaporation(PV) is an attractive alternative for separation of aqueous and organic mixtures of liquids having close boiling points. Pervaporation is a membrane process in which the feed is a liquid mixture and a vacuum is applied to the opposite side of the membrane to remove permeate as a vapor, which is then condensed and collected[11,12]. Accordingly, there is a demand for ultrapermeable polymer of good thermal and chemical stability. Single tetrahedral C atom shared by phenyl and heterocyclic ring in DAMN$_{87}$-g-PS crosslinked membrane, makes the chains nonlinear that would

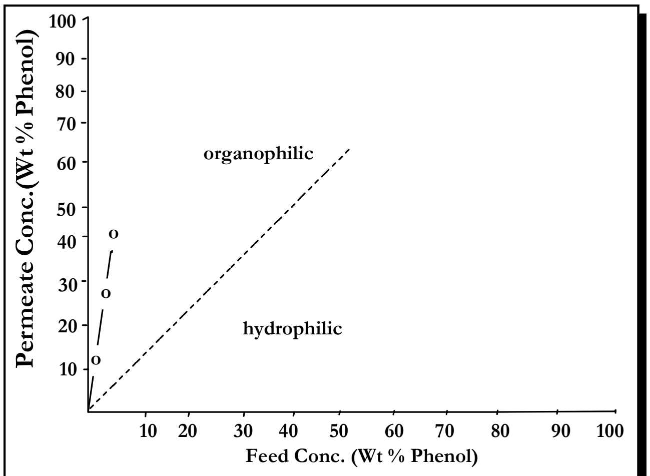

Figure 9: Pervaporation-based separation of phenol from aqueous solution using a membrane derived from crosslinked DAMN87-g-PS membrane

inhibit cofacial association and prevent structural relaxation to a dense and rigid solid(i.e. provide a site of contortion). These inflexible polymer chains trap a considerable amount of excess free volume elements are connected to give a micropore structure[13].

Pervaporation-based separation of phenol from aqueous solution using a membrane derived from crosslinked $DAMN_{87}$-g-PS membrane is illustrated in figure 9. The polymer membrane is organophilic. The permeate being enriched in the organic component(e.g. a feed of 6 wt % phenol in water gave a permeate of 42 wt % phenol which demonstrates that the membrane is selective for organic compound over water). This separation process is of environmental importance as phenols are common contaminants of wastewater streams from industrial processes.

The efficiency of separation may be expressed as a separation factor, a=(Yo/Yw)/(Xo/Xw), in which (Yo/Yw) is the weight ratio of organic compound to water in the permeate and (Xo/Xw) is the weight ratio of organic compound to water in the feed. The experimental results reveals that values of a separation factor of[12,13,14] were obtained at room temperature for feed compositions 2,4,6 wt % phenol respectively. For membranes composed of conventional high free volume polymers, some transport must occur through the dense matrix, so permeabilities are generally low and small molecules are usually more permeable than larger molecules[14,15].

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