

Synthesis, Characterization, and Amidoximation of Diaminomaleodinitrile-Functionalized Polyethylene Terephthalate Grafts for Collecting Heavy Metals from Wastewater

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ABSTRACT: Synthesis, characterization, and amidoximation of diaminomaleodinitrile-functionalized polyethylene terephthalate (PET) grafts were studied. Azobisisobutyronitrile (AIBN) was used as an initiator. Optimum conditions for grafting were as follows: monomer concentration [DAMN] = 0.5M, [AIBN] = 1.50×10^{-3} mol/L, $T = 80^\circ\text{C}$ and $t = 3$ h. Water uptake of the grafted-PET film increased with the increase of grafting yield. The imparted cyano group of the grafted polymer chains (with degree of grafting up to 83%) was converted into amidoxime group by reaction with hydroxylamine. The unique advantage of this polymer is that it contains double amidoxime groups per repeating unit and an additional diethylene spacer unit between neighboring amidoxime groups in each monomeric unit. The grafted-PET films were characterized by FTIR spectroscopy, differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). The grafted-PET films are more thermally stable than the ungrafted-PET membrane, since the grafted mem-

brane showed a single degradation pattern despite having two components. A decrease in T_g values is observed as the grafting yield of copolymers increases indicating the incorporation of polydiaminomaleodinitrile chains in amorphous copolymers with higher thermal stability. The prepared amidoximated DAMN83-g-PET was investigated for its properties in removing heavy toxic metals, such as Pb^{2+} , Cd^{2+} , Zn^{2+} , Fe^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , and Ag^{1+} from waste water. The amidoximated-film is characterized by a considerably greater binding ability with respect to heavy metals. The nature of the metal ion also has great importance in the amount binding to the polymeric material. The kinetics of the sorption/desorption process for Co^{2+} , Ni^{2+} , and Zn^{2+} are investigated. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1136–1145, 2012

Key words: graft copolymerization; polyethylene terephthalate; amidoximation; metal adsorbents

INTRODUCTION

Heavy metal ions resultants of the chemical process industries are pollutants that have received great attention of the governmental organizations since they can be absorbed by plants and animals and then concentrated in the foods. Many different natural and synthetic materials with chelating properties have been developed for use in chemical processes industries plants for preventing operational problems or contamination of the environment. Grafting of various monomers on plastic films can successfully solve the problem of preparation of polyfunctional sorbents and membranes.^{1–3} The obtained materials are convenient for waste water treatment applications, since they are able to absorb various

impurities very fast due to their chelation and/or complexation abilities through their reactive groups, such as carboxylic acid, amine, amide, nitrile, oxime groups, etc. In addition, these materials can be reused without lose of their sorption characteristics. Graft copolymerization is an attractive approach for modifying base polymers because grafting frequently results in the superposition of properties relating to backbone and side chains. Copolymerization of 2-phenyl-1,1-dicyanoethylene (PDE) with 4-fluorostyrene and pentafluorostyrene in solution with radical initiation (ABCN) at 70°C yielded random copolymers with PDE alternating units.⁴ Graft copolymerization of hydroxyethylmethacrylate (HEMA) onto polyethylene terephthalate fibers and fabric using dibenzoylperoxide as initiator and the conditions affecting on grafting yield were investigated.⁵

Preparation of polyethylene (PE) films grafted with the vinyl ether of monoethanolamine (VEMEA) using a γ -irradiation technique afforded materials of high affinity in respect to Cu (II) ions. The capacities of Ni (II) adsorption using vinyl-2-pyrrolidone

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grafted chitin from aqueous solution have been measured. The graft copolymer VP-g-Ch shows an excellent ability for Ni (II) adsorption.⁶ Metal complexes were synthesized on the basis of the copolymers of radiation grafted poly-4-vinylpyridine onto polyethylene and polytetrafluoroethylene. The formation of the complexes was carried out in solutions of the following salts: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. The introduction of metal ions depended on the degree of grafting of 4-vinylpyridine and it was found to be from 0.03 to 14.96 and from 0.11 to 34.48 mg metal ions per gram of polymer carrier for polytetrafluoroethylene and polyethylene, respectively.⁷ The newly synthesized starch graft copolymers containing aminoethyl groups was used for removing Cu (II) and Pb (II) ions in the aqueous solution by the effective complexation of amine group with Cu (II) and Pb (II) ions. The effects of various parameters such as metal ions concentration, adsorption time, adsorption temperature, and grafting percentage of the starch graft copolymers were investigated. Moreover, the adsorbed Cu (II) and Pb (II) ions can be easily desorbed by treating with HCl solution and the desorption percentage reached above 95% when desorbing with 1N HCl solution for 1 h at room temperature.⁸ Functionalized syndiotactic polystyrene polymers were prepared by the combination of metallocene catalyst and borane comonomer.⁹ Development, characterization of a microfiltration membrane catalyst containing sulfonated polystyrene grafts and esterification catalysis using functionalized membranes were reported.¹⁰ A novel strategy to synthesize graft copolymers of PS-g-PEGM with controlled branch spacing length and defined grafting sites has been investigated.¹¹ Grafting of amino functional monomer onto initiator-modified polystyrene particles was reported.¹² Synthesis and characterization of diaminomaleodinitrile (DAMN)-functionalized polystyrene grafts for application in pervaporation separation were reported.¹³ Separation of metal ions and chelating agents by nanofiltration explores the feasibility of nanofiltration for separating chelating agents from heavy metals, which would make it possible to reuse chelating agents.¹⁴ Synthesis of porous acrylonitrile/methyl acrylate copolymer beads by suspended emulsion polymerization and their adsorption properties after amidoximation revealed an excellent adsorption capacities for Hg^{2+} , Ag^+ , and Cu^{2+} , especially for Hg^{2+} , and it have good selectivity for Hg^{2+} . Also, the equilibrium was established in 10 h through adsorption kinetics study.¹⁵ Removal of uranium from mining industry feed simulant solutions using trapped amidoxime functionality within a mesoporous imprinted polymer material is successfully demonstrated.¹⁶ Chemical modification of polypropylene fibers grafted

vinyl imidazole/acrylonitrile copolymer prepared by gamma radiation. The ability of the grafted fibers and their treated forms to absorb some metal ions as Cd, Hg, and Pb from their individual and mixture solutions was evaluated.¹⁷ Adsorption efficiency of a new adsorbent towards uranium and vanadium ions was synthesized by radiation-induced graft polymerization affording a new type of fibrous adsorbent with excess amidoxime groups.¹⁸ Chemical modification of TKP through grafting has received considerable attention to impart new functional groups for different applications. Keeping this in view, graft copolymerization of acrylamide (AA) onto TKP (Tamarind kernel powder, a natural xyloglucan polysaccharide is derived from the seeds of *Tamarindus indica* Linn) was carried out in an aqueous medium using a ceric ammonium nitrate (CAN)-nitric acid initiation system. The reaction conditions were optimized for grafting with respect to the effect of the concentrations of CAN, nitric acid, TKP, AA, time, and reaction temperature. The maximum percentage grafting (%G) and percentage grafting efficiency (%GE) were found to be 231.45% and 93.66%, respectively.¹⁹ Graft reaction of acrylamide (AM) and 4-vinyl pyridine (4-VP) onto ultra-low-molecular weight poly(vinyl alcohol) by ceric (IV) ion initiation had been systematically investigated, and the graft conditions were optimized by studying the effect of monomer/initiator concentration, solvents composition, reaction time, and temperature. At optimized conditions, the maximum grafting efficiency and grafting ratio was ~ 50 and 51%, respectively.²⁰ Efficient removal of Cr^{3+} , Pb^{2+} , and Hg^{2+} ions from industrial effluents by hydrolyzed/thioamidated polyacrylonitrile fibers. The study on these modified ion exchange fibers (HTPANFs) for industrial effluents revealed that the maximum capacities of the modified PAN fibers towards Cr^{3+} , Hg^{2+} , and Pb^{2+} are 0.41, 0.05, and 0.11 mmol/g at pH 4.²¹ Preparation of amidoxime-modified polyacrylonitrile (PAN-oxime) nanofibers and their applications to metal ions adsorption have been investigated intensively due to their potential applications in many areas especially in environmental applications for removal of heavy metals ions.²² Removal of Ni(II) from synthetic solutions using new amine-containing resins based on polyacrylonitrile were investigated.²³ Radiation grafting of vinyl ether of monoethanolamine on polypropylene films for application in waste water treatment was reported.^{24,25} There are three attempts²⁶⁻²⁸ for the preparation of resins with diamidoxime units per repeating unit so far all of which completely differ from our approach. The aim of this work is to prepare DAMN-functionalized poly(ethylene terephthalate) grafts and amidoximation of grafted copolymer to investigate its properties in removing heavy toxic metals from waste water.

EXPERIMENTAL

Materials

PET film (Aldrich, average MW \sim 280,000 GPC). DAMN. The initiator, azobisisobutyronitrile (AIBN) (Merck), was recrystallized by precipitating twice from methanol and dried under vacuum oven for 2 days. All the other reagents were Merck products and they were used as received.

Characterization

FTIR spectroscopy of the grafted-PET films was recorded with a Vector 22 Fourier Transform Infrared Spectrometer (Bruker). UV-vis spectra were obtained using Shimadzu UV2401PC spectrophotometer. $^1\text{H-NMR}$ spectra were obtained by using a Varian Gemini 200 instrument at 200 MHz. Differential scanning calorimetry (DSC) were carried out on a Perkin-Elmer DSC-2 for studying the melting and glass transition temperature behavior of the copolymers. DSC measurements were performed in temperature range of 50 to 300°C at the heating rate of 10°C/min in a N_2 atmosphere. Thermal gravimetric analysis (TGA) studies on the ungrafted-, grafted-, and amidoximated-PET films were carried out using Perkin-Elmer TGA-7. Thermograms were obtained in temperature range of 20 to 700°C. The heating runs were made at a constant heating rate of 10°C/min under N_2 atmosphere.

Synthesis of graft copolymers

DAMN (0.5 mol/L) was added with 1 g of polyethylene terephthalate film in water (10 mL) and left overnight. Next, water (90 mL) and AIBN (1.5×10^{-3} mol/L in 2 mL methanol) were added to the mixture with the temperature raised to 90°C to initiate the polymerization reaction. The reaction mixture was continuously stirred for 3 h and nitrogen gas was allowed to pass through the solution. At the end, the grafted-PET film was removed and subjected to Soxhlet-extraction for 6 h with methanol and distilled water, respectively, to remove the homopolymer. At the end of the grafting procedure, homopolymer formed in the grafting medium was precipitated by the addition of excess acetone, collected and dried in an oven at 70°C. Grafting Yield (%) = [(dry wt. of grafted-PET film - dry wt. of original PET film) / dry wt. of original PET film] \times 100. Grafting efficiency (GE) was calculated as follows:

$$\text{GE (\%)} = \left[\frac{(\text{wt. of graft})}{(\text{wt. of graft} + \text{wt. of homopolymer})} \right] \times 100.$$

Amidoximation of pendant nitrile groups

The obtained graft polymer, DAMN83-g-PET, was reacted with the methanol solution of hydroxylamine hydrochloride $\text{NH}_2\text{OH}\cdot\text{HCl}$ at 80°C in the presence of triethylamine. During the amidoximation reaction, samples were taken from the reaction vessel at certain time intervals and the conversion to amidoxime structure was followed by determining the changes in CN triple bonds of polymer from respective FTIR spectra. After amidoximation reaction was completed, the amidoximated-polymer taken from reaction vessel was washed with distilled water and then dried at 40°C in a vacuum oven.

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Water absorption ratio

The film was immersed in water for 48 h in room temperature. After treatment, the excess water on the surface was removed using a filter paper. Then the wet film was weighed and dried at 70°C in the oven to a constant weight. The water absorption (Wa) ratio was calculated according to:

$$\text{Wa \%} = \left[\frac{(\text{weight of wet grafted - PET film} - \text{weight of dry grafted - PET film})}{\text{weight of dry grafted - PET film}} \right] \times 100.$$

Tensile properties

The tensile strength (σ [MPa]) and elongation (ϵ) of film samples were determined using dumbbell-shaped specimens of 50 mm long with a neck of 28 and 4 mm wide (ASTM D882). The measurements of tensile strength and elongation at break point were recorded on an "Instron" 4203 instrument at temperature of 25°C and velocity of 100 mm/min.

Metal ion uptake measurements

Sample of amidoximated grafted-PET film of known weight was soaked into 0.01M aqueous solution of the metal for 1 day until equilibrium was reached. The film was removed, dried in vacuum, and then weighed. The metal uptake, expressed in mmol/L was determined by measuring the increase in weight of the sample. The kinetics of the sorption/desorption processes of Co^{2+} , Ni^{2+} , Zn^{2+} ions were studied by photometric measurements at the wavelengths 240, 237, and 243 nm, respectively, using a Shimadzu UV2401PC spectrophotometer.

RESULTS AND DISCUSSION

Effect of polymerization time on grafting yield

Grafting of PET was carried out at various polymerization times, keeping the monomer, initiator, and temperature constant at 0.5M, 1.5×10^{-3} m/L, and 80°C, respectively. As shown in Figure 1, grafting

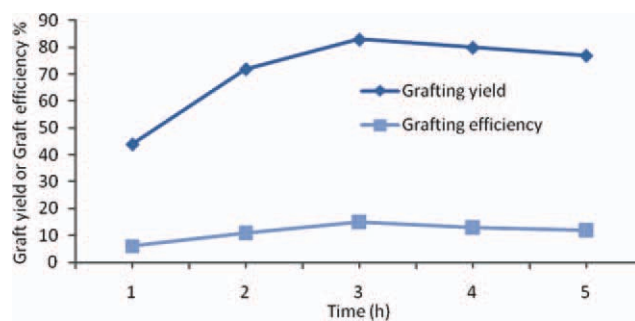


Figure 1 Effect of time on grafting yield and grafting efficiency. [AIBN] = 1.5×10^{-3} mol/L. [DAMN] = 0.5M. $T = 80^\circ\text{C}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

yield percentage first increased with increasing polymerization time; and then leveled off, reaching to a saturation grafting value of 83% at 3 h. As the polymerization time increases, the number of monomer and initiator molecules that diffuse onto polyethylene terephthalate 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 on grafting yield

The effect of temperature on graft copolymerization of DAMN onto polyethylene terephthalate was studied within the range of 50 to 90°C keeping monomer, initiator, and polymerization time constant (Fig. 2). As shown in the graph, a sharp increase in the grafting yield value of 83% was obtained and then leveled off. The enhancement in the grafting yield with increasing temperature may be attributed to the enhancement of polyethylene terephthalate

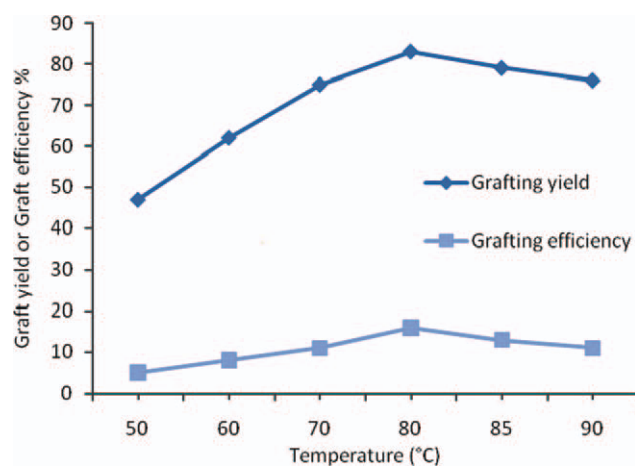


Figure 2 Effect of temperature on grafting yield and grafting efficiency. [AIBN] = 1.5×10^{-3} mol/L. [DAMN] = 0.5M. $t = 3$ h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

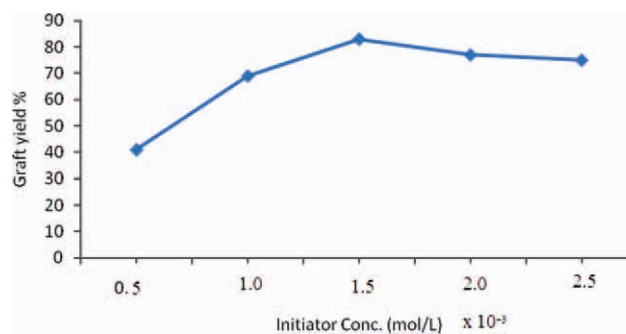


Figure 3 Effect of initiator concentration on grafting yield. mol/L. [DAMN] = 0.5M. $T = 80^\circ\text{C}$. $t = 3$ h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

swellability, an increased rate of diffusion for the initiator and monomer from the solution phase to the PET chains, an increasing number of active sites in the reaction medium and an increasing rate of initiation and propagation steps. The leveling off of the grafting yield at 80°C may be due to the increase in the formation of homopolydiaminomaleodinitrile as shown in the grafting efficiency curve in Figure 2.

Influence of initiator concentration

Figure 3 demonstrate that the graft yield increases with the increase in AIBN, concentration in the range from 0.5×10^{-3} to 1.5×10^{-3} mol/L, and then decreases with 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 PET backbone, yielding a PET radical capable of initiating grafting. However, when the initiator concentration increased to 2.5×10^{-3} mol/L, termination reactions of the graft copolymerization takes place.

Influence of the monomer concentration

The effect of DAMN monomer concentrations on the grafting yield was investigated by carrying out polymerization at six different DAMN concentrations (Fig. 4) range from 0.2 to 0.7 mol/L. The results showed that the grafting yield sharply rises with increasing DAMN concentration up from 0.2 to 0.5 mol/L, yielding 83% grafting yield, and then the grafting yield decreased with further increases in DAMN concentration. This may be attributed to the fact that when the DAMN concentration rises, the diffusion of monomer into the PET surface increases enhancing the grafting yield. The decrease in the grafting yield at higher DAMN concentrations may be due to the adsorption of monomer on the PET

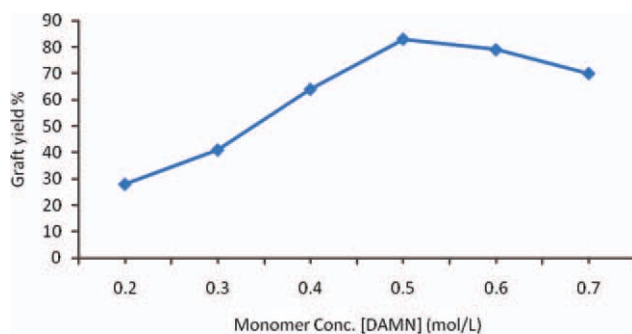
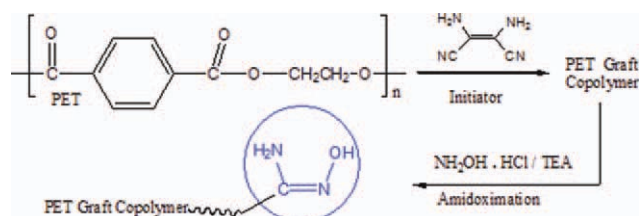


Figure 4 Effect of monomer concentration on grafting yield. [AIBN] = 1.5×10^{-3} mol/L. $T = 80^\circ\text{C}$. $t = 3$ h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

surface in excessive amounts, which prevents diffusion of the initiator molecules inside the PET resulting in lowering the graft yield. It may be also attributed to the increase of the homopolymerization rather than grafting at these high monomer concentrations.

FTIR characterization of PET grafts

Conversion of polyethylene terephthalate film into graft copolymer using DAMN as monomer in the presence of AIBN, radical initiator, and further modification into amidoxime structure are shown in



Scheme 1 Amidoximated polymer-based metal adsorbents via graft copolymerization of PET film with diamino-maleonitrile. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 1. The final step is the amidoximation of nitrile groups of grafted polymer. Nitrile groups were converted to amidoxime groups by using hydroxylamine hydrochloride in the presence of triethylamine. The unique advantage of this polymer is that it contains double amidoxime groups per repeating unit and an additional diethylene spacer unit between neighboring amidoxime groups in each monomeric unit. Grafting reaction between DAMN and PET was confirmed by FTIR (Fig. 5) spectroscopy which showed peak at 1717 and 2232 cm^{-1} assignable to (C = O) and (CN) groups, respectively. Presence of a peak assignable to CN group in the grafted-PET film indicated high efficiency of grafting process. Also, two peaks at 2917 cm^{-1} and 2849 cm^{-1}

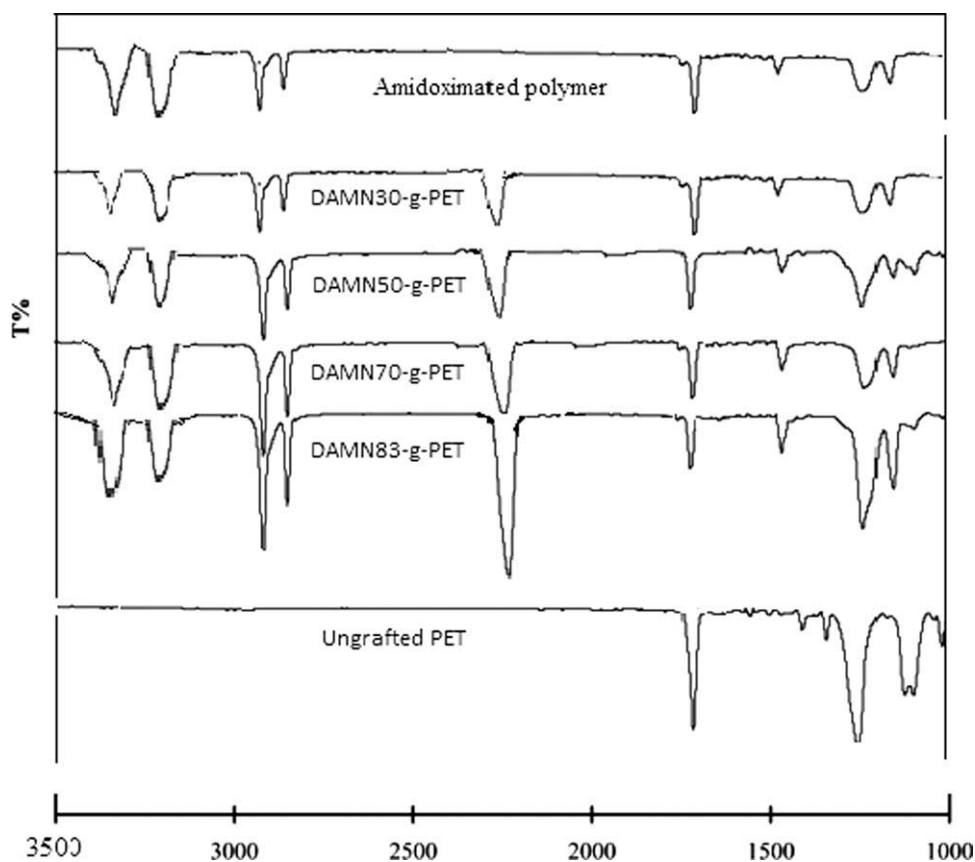


Figure 5 FTIR spectra of ungrafted-PET, DAMN-g-PET, and amidoximated DAMN83-g-PET.

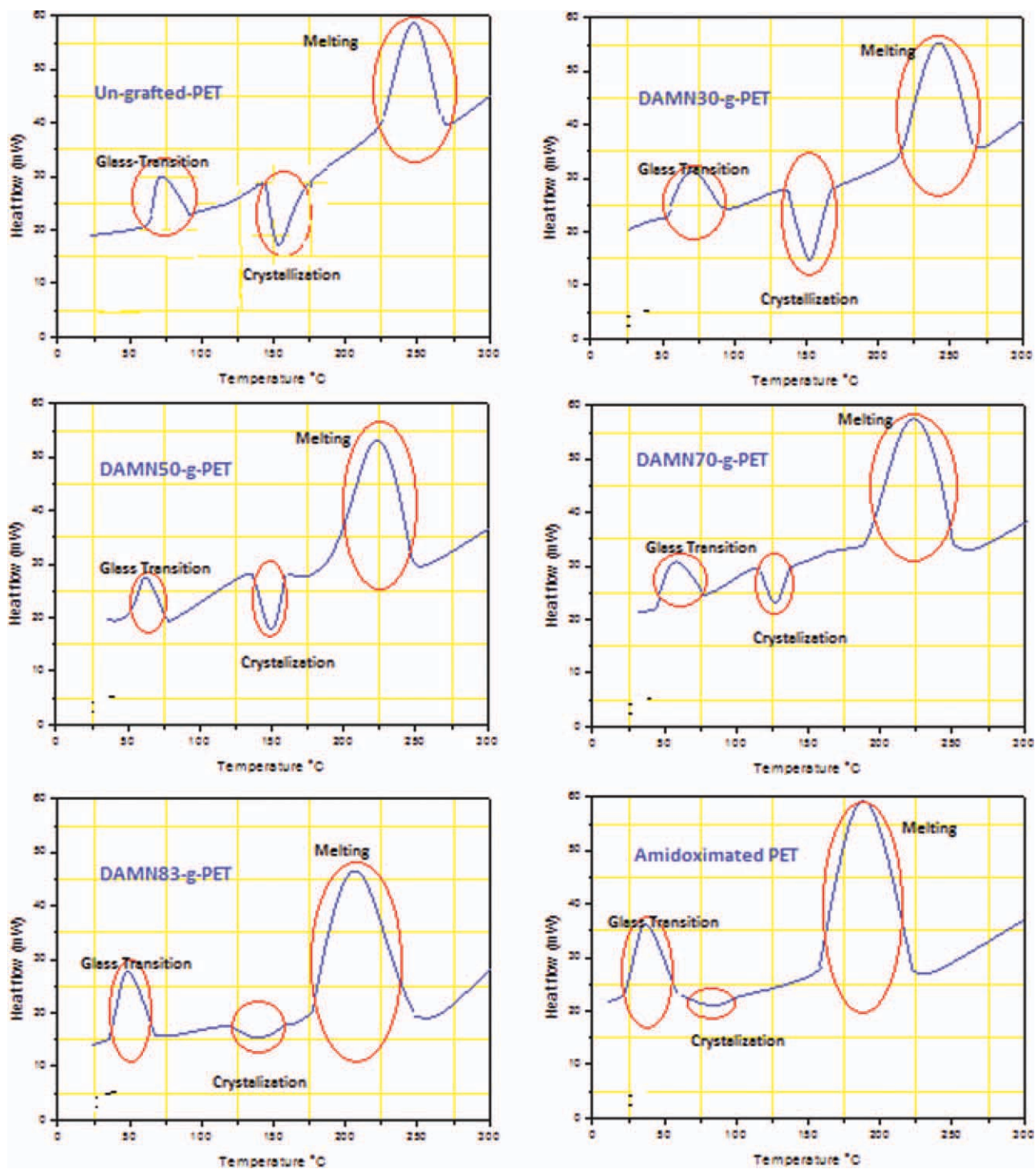


Figure 6 DSC thermograms of ungrafted PET, DAMN-g-PET, and amidoximated DAMN83-g-PET. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

assignable to CH stretching of CH_2 were found. According to Scheme 1, $\text{C}\equiv\text{N}$ groups are expected to be replaced with $\text{H}_2\text{N}-\text{C}=\text{NOH}$ groups at the end of the reaction. The bands at 3223 and 3352 cm^{-1} are assigned to antisymmetric and symmetric stretching modes of NH_2 groups, respectively, (Fig. 5). These results clearly show the disappearance of original nitrile groups in the amidoximated-polymer and formation

of amidoxime groups through the treatment with hydroxylamine under specified reaction conditions.

Thermal analysis

Melting temperature (T_m), glass transition temperature (T_g) and heat of fusion (ΔH_m) for ungrafted-PET film, grafted-PET films with various degrees of

TABLE I
Characterization of PET and DAMN-g-PET Films as Determined by Mechanical and DSC Measurements

Polymer film	Grafting yield (%)	Breaking strength (MPa)	Breaking elongation (mm)	ΔH_m (cal/g)	T_m ($^{\circ}\text{C}$)	T_g ($^{\circ}\text{C}$)
PET	–	88	0.60	4.3	246	74
DAMN ₃₀ -g-PET	30	82	0.57	4.9	241	68
DAMN ₅₀ -g-PET	50	76	0.52	5.7	229	61
DAMN ₇₀ -g-PET	70	69	0.49	6.1	218	57
DAMN ₈₃ -g-PET	83	65	0.48	6.5	204	46
Amidoximated polymer	–	63	0.46	7.1	192	39

grafting and amidoximated-polymer were taken from their DSC thermograms (Fig. 6) and are presented in Table I. The results indicated a decreasing trend of T_m as a function of increasing grafting yield. This is due to a variation of chain flexibility inherited from methylene length. It can be also observed that ΔH_m slightly increases with the increase in the degree of grafting. A decrease in T_g values is observed as the grafting yield of copolymers increases indicating the incorporation of polydiaminomaleodinitrile chains in amorphous copolymers with higher thermal stability. This might be due to an increase in their corresponding methylene length, which results in an increase in chain flexibility of the copolymer structure.

The effect of grafting on the thermal stability of the grafted-PET film was studied using thermogravimetric analysis (TGA). All the degradation temperatures were measured from the thermogram by onset extrapolation. Figure 7 shows TGA thermograms of the ungrafted and grafted PET film with grafting yield of 83%. Ungrafted-PET film showed a continuous weight loss confined to a single-step degradation pattern have significantly comparable degrada-

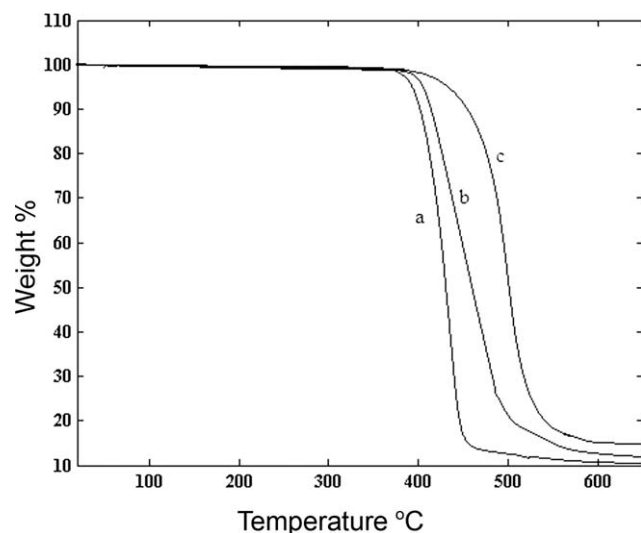


Figure 7 TGA thermograms of ungrafted PET (a), DAMN83-g-PET (b), and amidoximated DAMN83-g-PET (c).

tion temperature (T_d) at 400 $^{\circ}\text{C}$. The degradation temperature was found to vary as a result of grafting. For instance, the ungrafted-PET film recorded a degradation temperature of 400 $^{\circ}\text{C}$. This temperature increased in the grafted membrane to 423 $^{\circ}\text{C}$. These results indicate that the incorporation of polydiaminomaleodinitrile makes the PET film inalienable to thermal degradation. This means that the grafted-PET film is more thermally stable than the ungrafted PET film, since the grafted-PET film showed a single degradation pattern despite having two components. Amidoximated DAMN83-g-PET, however, shows better thermal stability with a main degradation step taking place at 450 $^{\circ}\text{C}$. This thermal stability would make the amidoximated-grafted-PET film suitable for many practical applications.

Swelling properties of PET grafts

The effect of grafting percentage on water uptake ratios for the grafted-PET films at room temperature (25 $^{\circ}\text{C}$) is shown in Figure 8 which reveals an increase in the water uptake ratios with the increase of grafting percentage. Clearly, the swelling behavior of the film depends on the amount of the grafted branches. Under the same conditions, amidoximated resultant graft copolymer shows water uptake value of 65%.

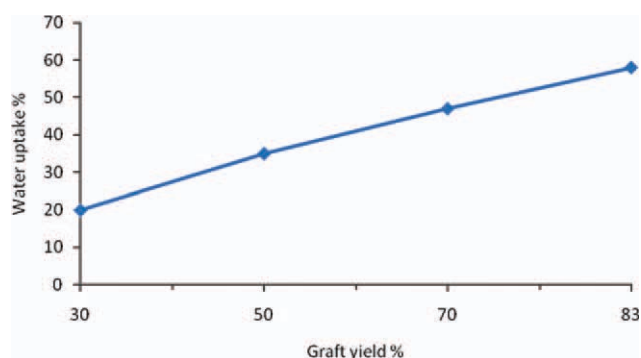


Figure 8 Water uptake ratio dependence on grafting yield. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

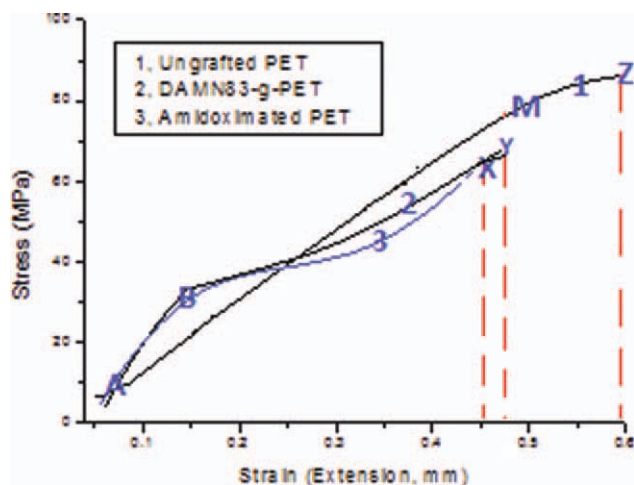


Figure 9 Typical stress/strain curve showing the linear elastic regions A-B and A-M and brittle failure point at X, Y, and Z. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Mechanical properties

Table I illustrates the effect of grafting on some mechanical properties of grafted samples. Based on the data listed in this table, one can conclude the following: Breaking strength decreased continuously with an increase in grafting yield. The behavior of elongation is the same as that of breaking strength. The grafted and amidoximated samples showed a higher decrease in breaking strength as compared with ungrafted film. The decrease in breaking strength at higher graft yield may be due to the formation of pits on the surface which probably act as weak points when film is elongated under stress. In addition, with an increase in graft yield a decrease of flexural rigidity occurs. A typical stress to strain curve is illustrated in Figure 9. The curves were recorded at 25°C. The straight line between points A and B represents the interval used by the integrated software to calculate the elastic of Young's modulus of the samples DAMN83-g-PET and amidoximated-PET. Whereas, the straight line between points A and M represents the elastic of Young's modulus of ungrafted-PET film where the true stress and true strain vary linearly, and then followed by a yield drop at the elastic limit. Points X, Y, and Z represent the break points of the samples and the approach to failure. In the case of ungrafted-PET, the mechanical behavior shown in Figure 8 is typically that of a hard and brittle material but this may be transformed to hard and strong or hard and tough through structural modification by grafting or amidoximation.

Sorption of transition metals by amidoximated DAMN83-g-PET

There is a demand for ultra-permeable polymer of good thermal and chemical stability. The study of

materials that possess voids of molecular dimensions is an area of nanoscience with technological applications.²⁹ Microporous materials are defined as solids that contain interconnected pores of less than 2 nm in size. Single tetrahedral carbon atom shared by phenyl and side chain in aminoximated DAMN83-g-PET film, besides, the formation of six-membered rings along, side chains through hydrogen bonds between amino and hydroxyl groups, make the chains nonlinear that would inhibit cofacial association and prevent structural relaxation to a dense and rigid solid (i.e., provide a site of contortion).

These polymer chains trap a considerable amount of excess free volume elements which are connected to give a micropore structure.³⁰ Thus, the maximum metal uptake is very dependent on the type of metal ion and its coordination, as well as the ionic size of the metal, all of which affect the permeability and diffusion of these metals through the porous ionic films. The latter parameter is mainly dependent on the polarity, electronic configuration, and ionic radii of these metal ions. The possibility of using the obtained materials was evaluated over several sorption/desorption cycles.

Kinetics of sorption/desorption of metal ions could not be followed by gravimetric studies because that requires removal and drying of the samples periodically, which affects the accuracy of the results. Thus, a spectrophotometric technique was applied. With this technique, it is easy to determine the desorbed/absorbed amounts of metal ions without removing and drying the samples. As the grafted film is immersed into a metal salt solution, it starts to absorb metal ion, therefore, the concentration of metal ions in solution decreases with the sorption process and this decrease was monitored using a spectrophotometer. The metal sorption increases with time and reaches a maximum after

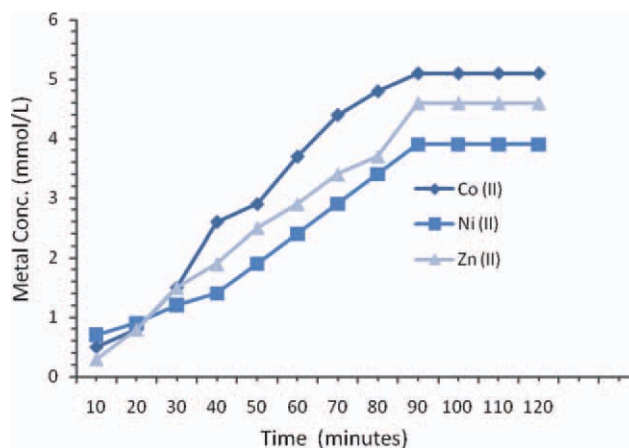


Figure 10 Kinetics of sorption process for Co, Ni, and Zn ions by amidoximated DAMN83-g-PET. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

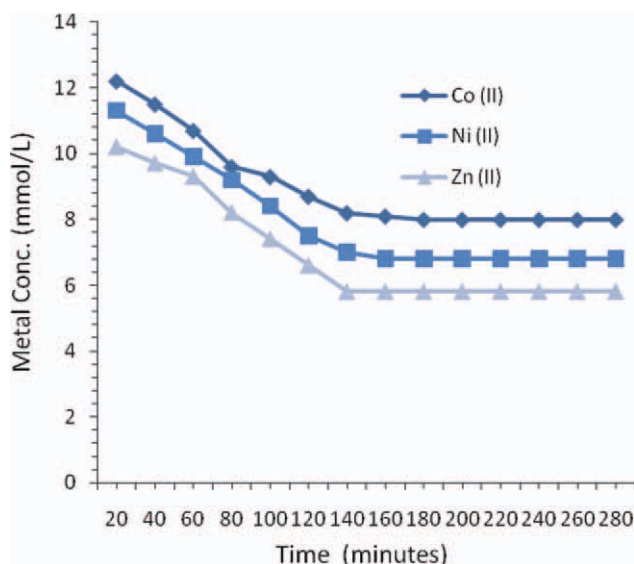


Figure 11 Kinetics of desorption process for Co, Ni, and Zn ions from amidoximated DAMN83-g-PET. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

about 2 h (Fig. 10) when the chelating sites of the film are saturated.

The maximum amount of absorbed metal salt, which was determined spectrophotometrically and expressed in mmol/L. The recovery and separation of absorbed metals can be easily carried out by treating the films with 0.01M HCl for 1.5 h. Figure 11 shows the kinetics of the desorption process for Co^{2+} , Ni^{2+} , and Zn^{2+} ions. The desorbed metal ion concentration increases in HCl solution with time and then reaches a maximum when the desorption process is complete. The regenerated films are once again effective for resorption.

The ability of the grafted films to absorb various heavy metals to evaluate the possibility of their use

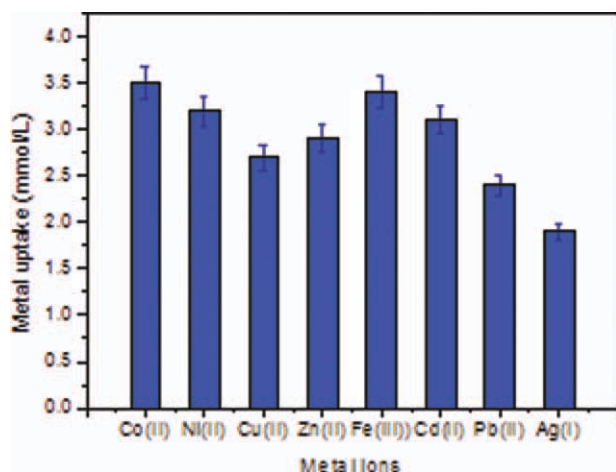


Figure 12 Sorption of different heavy metals using amidoximated DAMN83-g-PET. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in waste water treatment has been studied. A diagram showing the capacity of the grafted films for metal uptake is shown in Figure 12. It can be seen that the amidoximated-film is characterized by a considerably greater binding ability with respect to heavy metals. The nature of the metal ion also has great importance in the amount binding to the polymeric material. The affinity of metal ions to be absorbed decreases in the following series: Co^{2+} , Fe^{2+} , Ni^{2+} , Cd^{2+} , Zn^{2+} , Cu^{2+} , Pb^{2+} , and Ag^{1+} . The results pertaining to the affinity of this new adsorbent against vanadyl and uranyl ion in batch and continuous adsorption process and will be the subject of another publication.

CONCLUSIONS

AIBN, radical initiator, was used as an initiator for preparation of PET, films grafted with DAMN. Optimum conditions for grafting were found to be, monomer concentration $[\text{DAMN}] = 0.5\text{M}$, $[\text{AIBN}] = 1.50 \times 10^{-3} \text{ mol/L}$, $T = 80^\circ\text{C}$, and $t = 3 \text{ h}$. Water uptake of the grafted-PET films was found to be increasing with the increase of grafting yield. The results indicate that amidoximated product of the obtained graft copolymer, DAMN83-g-PET film, is a potentially powerful ion exchanger that can be used for heavy metals removal from waste water effluents.

References

- Kariduraganavar, M. Y.; Nagarale, R. K.; Kittur, A. A.; Kul-karni, S. S. *Desalination* 2006, 197, 225.
- Nagarale, R. K.; Gohil, G. S.; Shahi, V. K. *Adv Colloid Interface Sci* 2006, 119, 97.
- Nasef, M. M.; Hegazy, E. A. *Prog Polym Sci* 2004, 29, 499.
- Kharas, G. B.; Hanawa, E.; Hill, B. L.; Atlas, S.; Raihane, M. *J Macromol Sci Pure Appl Chem* 2009, 46, 7.
- Abdel-Bary, E. M.; Sarhan, A. A.; Abdel-Razik, H. H. *J Appl Polym Sci* 1988, 35, 439.
- José, A. R. F.; Erna, E. B.; Élcio, R. B.; Alvaro, A. A. Q. *Mater Res* 2001, 4, 53.
- Turmanova, S. C. *eXPRESS Polym Lett* 2007, 1, 585.
- Deng, K.; Jia, N.; Zhang, Y.; Yan, D.; Hou, D. *Chem J Internet (CJI)* 2006, 8, 68.
- Dong, J. Y.; Manias, E.; Chung, T. C. *Macromolecules* 2002, 35, 3439.
- Shah, T. N.; Goodwin, J. C.; Ritchie, S. M. C. *J Membr Sci* 2005, 251, 81.
- Yezi, Y.; Chunyan, H.; Pinghua, W.; Wenping, W.; Weiqi, L.; Caiyuan, P. *Polymer* 2004, 45, 4647.
- Musyanovych, A.; Hans-Jürgen, P. A. *Langmuir* 2005, 21, 2209.
- Abdel-Razik, H. H. *Chem Pap* 2008, 62, 404.
- Balanyà, T.; Labanda, J.; Llorens, J.; Sabaté, J. *J Membr Sci* 2009, 345, 31.
- Liu, X.; Chen, H.; Wang, C.; Qu, R.; Ji, C.; Sun, C.; Zhang, Y. *J Hazard. Mater* 2010, 175, 1014.
- James, D.; Venkateswaran, G.; Prasada, R. T. *Microporous Mesoporous Mater* 2009, 119, 165.
- Tahia, B. M. *J Appl Polym Sci* 2009, 111, 11.
- Kavaklı, P. A.; Seko, N.; Tamada, M.; Güven, O. *Sep Sci Technol* 2011, 39, 1631.

19. Puja, G.; Vineet, K.; Pradeep, S. J. *Appl Polym Sci* 2008, 108, 3696.
20. MinJie, G.; JianJun, X.; Zhi, F.; Zhuo, Z.; HuaiFeng, M. *J Appl Polym Sci* 2009, 113, 3954.
21. Bagheri, B.; Abdouss, M.; Aslzadeh, M. M.; Shoushtari A. M. *Iranian Polym J* 2010, 19, 911.
22. Saeed, K.; Haider, S.; Oh, T. J.; Park, S. Y. *J Membr Sci* 2008, 322, 400.
23. Arsalani, N.; Rakh, R.; Ghasemi, E.; Entezami, A. A. *Iran Polym J* 2009, 18, 623.
24. Abdel Aal, A.; Khutoryanskiy, V. V.; Nurkeeva, Z. S.; Mun, G. A. *J Mater Chem* 2002, 12, 2692.
25. Nurkeeva, Z. S.; Abdel Aal, A.; Khutoryanskiy, V. V.; Mun, G. A.; Koblanov, S. M. *Radiat Phys Chem* 2002, 65, 249.
26. Kise, H.; Sato, H. *Macromol Chem* 1985, 186, 2449.
27. Park, I. H.; Suh, J. M. *Angew Makromol Chem* 1996, 239, 121.
28. Kavakli, P. A.; Uzun, C.; Guven, O. *React Funct Polym* 2004, 61, 245.
29. Schth, F.; Sing, K.; Weitkamp, J. In *Handbook of Porous Solids*; Schth, F., Sing, K., Weitkamp, J., Eds.; Wiley-VCH: Berlin, 2002; Vol.1, p 5.
30. Srinivasan, R.; Auvil, S. R.; Burban, P. M. *J Membr Sci* 1994, 86, 67.