production of nonwoven fabrics. PBT nonwoven materials are inherently hydrophobic in nature leading to a high degree of nonspecific protein adsorption, making the base material itself a poor platform for bioseparations. Direct hydrolysis of polyGMA grafts on PBT using acidic conditions makes the fiber surface completely hydrophilic and substantially decreases nonspecific hydrophobic protein adsorption. Each monomer unit of GMA contains an epoxy end group that can be used to covalently attach ligands via nucleophilic substitution with available amines, thiols, and hydroxyl groups. In the study by Liu et al., diethylene glycol covalently attached to the polyGMA brushes was also found to substantially eliminate protein adsorption by nonspecific hydrophobic interactions.

PolyGMA grafted nonwovens offer a convenient platform for the development of effective ion exchange membranes. Saito et al. successfully grafted polyGMA brushes to polypropylene fabrics and polyethylene hollow fibers. See K. Saito, T. Kaga, H. Yamagishi, S. Furasaki, T. Sugo, J. Okamoto, Phosphorylated hollow fibers synthesized by radiation grafting and crosslinking, J. Membr. Sci. 43 (1989) 131-141. These grafted materials were functionalized with phosphoric acid groups to develop strong cation exchange membranes to capture divalent metal cations.

In a study by Zheng et al., polyGMA was grafted to polypropylene nonwoven and functionalized with diethyl amine (DEA) to develop a weak anion exchanger. See Y. Zheng, H. Liu, P. Gurgel, R. Carbonell, Polypropylene nonwoven fabrics with conformal grafting of poly(glycidyl methacrylate) for bioseparations, J. Membr. Sci. 364 (2010) 362-371. This material achieved equilibrium binding capacities for bovine serum albumin (BSA) of 120 mg/g of membrane.

Liu et al. investigated the effects of various degrees of polyGMA grafting by UV grafting on nonwoven PBT for the capture of BSA by anion exchange. See H. Liu, Surface modified nonwoven membranes for bioseparations, Raleigh NC USA, North Carolina State Univ., PhD thesis, 2012. In that study, polyGMA grafts were converted to weak anion exchangers with DEA and challenged with BSA. It was determined that the overall protein binding capacity increased with the degree of grafting (% weight gain). The largest equilibrium binding capacity of 800 mg/g was observed at a 12% polyGMA weight gain. This investigation also showed that residence times of several hours to a full day were required to reach maximum binding, and that these binding times increased with increased grafting weight % gain. These long residence times preclude the use of these polyGMA grafted nonwoven PBT membranes for the development of high throughput, high capacity protein capture devices for downstream processing, and they are a disadvantage for the capture of any target molecule.

Accordingly, there remains a need for grafted nonwoven membranes capable of high throughput, high capacity protein capture.

SUMMARY

In one embodiment of the present disclosure, polybutylene terephthalate (PBT) nonwovens can be readily grafted with glycidyl methacrylate (GMA) or similar methacrylate polymers via a heat-induced radical polymerization to create uniform and conformal polymer brush networks around each fiber that can

be chemically modified to function as anion or cation exchangers. The use of a thermal initiation process enables grafting of polymer layers on nonwoven fabrics, monoliths or solids that prevent the transmission of UV light because of their large thickness or density, thus making UV grafting impossible. In addition, in certain embodiments, the thermal-initiated grafted nonwoven webs of the disclosure are capable of achieving binding equilibrium with a target molecule, such as a protein, much faster than comparable UV-initiated grafted nonwoven webs. Binding equilibrium is understood to mean the state at which the forward rate and the reverse rate of the binding reaction are equal. In some embodiments, affinity ligands can be covalently attached for target capture. Further, heat grafting can be used to graft various shaped webs, fibers, and monoliths with uniform, conformal grafted layers. Additionally, heat induced grafted fibers can also be used for high capacity capture of small target molecules such as metal contaminants or other charged contaminants in, biological systems, waste water or other water sources to be purified (optionally including desalinations).

In one or more embodiments, the present disclosure relates to methods for preparing a polymer grafted and functionalized nonwoven membrane. The so-formed membrane can particularly be adapted for use in separation of a target molecule. In a non-limiting example, the method can comprise: i) receiving a nonwoven web comprising a plurality of polymeric fibers; ii) grafting an acrylate or methacrylate polymer onto the plurality of polymeric fibers to form a plurality of polymer segments covalently attached thereto, thereby forming grafted polymeric fibers, the grafting step comprising: a) contacting the nonwoven web with a solution comprising a thermal free-radical initiator to allow adsorption or absorption of the thermal initiator to the fibers in the nonwoven web, b) contacting the nonwoven web with a solution comprising at least one acrylate or methacrylate monomer, and c) exposing the nonwoven web to heat to initiate polymerization of the acrylate or methacrylate monomer; and iii) functionalizing the grafted polymeric fibers to attach at least one functional group adapted for binding the target molecule to the polymer segments of the grafted polymeric fibers.

In one aspect, there is provided a method for preparing a polymer-grafted and functionalized nonwoven membrane adapted for use in capture of a target molecule, comprising:

i) receiving a nonwoven web comprising a plurality of polymeric fibers;

ii) grafting an acrylate or methacrylate polymer onto the plurality of polymeric fibers to form a plurality of polymer segments covalently attached thereto, thereby forming grafted polymeric fibers, the grafting step comprising:

   a. contacting the nonwoven web with a solution comprising a thermal free-radical initiator to allow absorption of the thermal initiator into the nonwoven web,

   b. contacting the nonwoven web with a solution comprising at least one acrylate or methacrylate monomer, and

c. exposing the nonwoven web to heat to initiate polymerization of the acrylate or methacrylate monomer; and

iii) functionalizing the grafted polymeric fibers to attach at least one functional group adapted for binding the target molecule to the polymer segments of the grafted polymeric fibers.

In further embodiments, the method can be characterized in relation to one or more of the following statements, which can be combined in any number and order.

The polymeric fibers are selected from the group consisting of polyolefins, polyesters, thermoplastic polymers, and combinations thereof.

The polymeric fibers comprise thermoplastic polymers selected from the group consisting of polyamides, polycarbonates, polyethersulfones, and combinations thereof.

The polymeric fibers are selected from the group consisting of polybutylene terephthalate (PBT), polytrimethylene terephthalate (PTT), polyethylene terephthalate (PET), polyamide 6 (PA6), polyamide 6-6 (PA6-6), and combinations thereof.

The method comprises receiving a nonwoven web comprising a plurality of polybutylene terephthalate fibers and grafting a methacrylate polymer comprising poly(glycidyl methacrylate (polyGMA).

The thermal free-radical initiator is a material configured for decomposing into radical species at a temperature at which an acrylate or methacrylate monomer polymerizes.

The polymer-grafted and functionalized nonwoven membrane is configured for reaching a binding equilibrium for the target molecule in a time of about 1 hour or less. In some embodiments, the binding equilibrium can occur in 10 minutes or less. In some embodiments, the binding equilibrium can be reached in 5 minutes or less.

In one or more embodiments, the present disclosure can further relate to a polymer-grafted and functionalized nonwoven membrane. In particular, the polymer-grafted and functionalized nonwoven membrane can be a membrane that is prepared according to the methods disclosed herein. Specifically, the polymer-grafted and functionalized nonwoven membrane can be thermally grafted so as to exhibit properties that are otherwise described herein as arising from the thermal grafting process. Said properties particularly can differentiate a thermally grafted membrane from membranes of similar materials but formed by different processes, such as UV grafting.

In another aspect, there is provided a polymer-grafted and functionalized nonwoven membrane prepared according to the method as defined herein.

In exemplary embodiments, a polymer-grafted and functionalized nonwoven membrane according to the present disclosure can comprise a nonwoven web formed of a plurality of polymeric fibers including grafted thereon a plurality of polymer segments constructed of an acrylate or methacrylate polymer, the plurality of polymer segments carrying functional groups adapted for binding to a target molecule, the plurality of polymer segments being thermally grafted to the nonwoven membrane so that the polymer- grafted and functionalized nonwoven membrane is effective for reaching a binding equilibrium for the target molecule in a time of about 1 hour or less, in some embodiments preferably 10 minutes or less and in other embodiments preferably 5 minutes or less.

Further to the above, in various embodiments, the present disclosure can also relate to methods for separating a target molecule from a solution. For example, the method can involve passing the solution with the target molecule through a polymer-grafted and functionalized nonwoven membrane as described such that at least a portion of the target molecule in the solution binds to the polymer-grafted and functionalized nonwovenmembrane.

In another aspect, there is provided a method separating a target molecule from a solution, the method comprising passing the solution with the target molecule through a polymer-grafted and functionalized nonwoven membrane as defined herein such that at least a portion of the target molecule in the solution binds to the polymer-grafted and functionalized nonwoven membrane.

Still further, the present disclosure can relate to methods for reducing the time to reaching a binding equilibrium in the separation of a target molecule from a solution. As noted above and otherwise described herein, polymer-grafted and functionalized nonwoven membranes prepared according to the present disclosure can exhibit properties that are not achieved in membranes formed by UV grafting methods. The membranes of the present disclosure thus can be particularly useful in developing highly efficient and high throughput separation methods. In an example, a method for reducing the time to reach binding equilibrium

in the separation of a target molecule from a solution can comprise passing the solution with the target molecule through a polymer-grafted and functionalized nonwoven membrane that is formed by thermal grafting of an acrylate or methacrylate polymer onto a plurality of polymeric fibers forming a nonwoven web, the so-formed polymer-grafted and functionalized nonwoven membrane being effective for reaching the binding equilibrium for the target molecule in a time of about 1 hour or less, in some embodiments preferably in 10 minutes or less, and in some embodiments preferably 5 minutes or less. The present disclosure describes a process where grafting can be carried out on nonwoven fabrics or supports of large

dimensions, thicknesses and densities that do not allow penetration of UV light, precluding the use of UV graftingtechniques.

In another aspect, there is provided a method for reducing the time to reaching a binding equilibrium in the separation of a target molecule from a solution, the method comprising passing the solution with the target molecule through a polymer-grafted and functionalized nonwoven membrane that is formed by thermal grafting of an acrylate or methacrylate polymer onto a plurality of polymeric fibers forming a nonwoven web, the so-formed polymer- grafted and functionalized nonwoven membrane being effective for reaching the binding equilibrium for the target molecule in a time of about 1 hour or less.

In another aspect, there is provided a polymer-grafted and functionalized nonwoven membrane comprising a nonwoven web formed of a plurality of polymeric fibers including grafted thereon a plurality of polymer segments constructed of an acrylate or methacrylate polymer, the plurality of polymer segments carrying functional groups adapted for binding to a target molecule, the plurality of polymer segments being thermally grafted to the nonwoven membrane so that the polymer-grafted and functionalized nonwoven membrane is effective for reaching a binding equilibrium for the target molecule in a time of about 1 hour or less.

The disclosure includes, without limitation, the following embodiments.

Embodiment 1: A method for preparing a polymer-grafted and functionalized nonwoven membrane adapted for use in capture of a target molecule, comprising: i) receiving a nonwoven web comprising a plurality of polymeric fibers; ii) grafting an acrylate or methacrylate polymer onto the plurality of polymeric fibers to form a plurality of polymer segments covalently attached thereto, thereby forming grafted polymeric fibers, the grafting step comprising: a) contacting the nonwoven web with a solution comprising a thermal free-radical initiator to allow absorption of the thermal initiator into the nonwoven web, b) contacting the nonwoven web with a solution comprising at least one acrylate or methacrylate monomer, and c) exposing the nonwoven web to heat to initiate polymerization of the acrylate or methacrylate monomer; and iii) functionalizing the grafted polymeric fibers to attach at least one functional group adapted for binding the target molecule to the polymer segments of the grafted polymeric fibers.

Embodiment 2: The method according to any preceding or subsequent embodiments, wherein the polymeric fibers are selected from the group consisting of polyolefins, polyesters, thermoplastic polymers, and combinations thereof.

Embodiment 3: The method according to any preceding or subsequent embodiments, wherein the polymeric fibers comprise thermoplastic polymers selected from the group consisting of polyamides, polycarbonates, polyethersulfones, and combinations thereof.

Embodiment 4: The method according to any preceding or subsequent embodiments, wherein the polymeric fibers are selected from the group consisting of polybutylene terephthalate (PBT), polytrimethylene terephthalate (PTT), polyethylene terephthalate (PET), polyamide 6 (PA6), polyamide 6-6 (PA6-6), and combinations thereof.

Embodiment 5: The method according to any preceding or subsequent embodiments, wherein the method comprises receiving a nonwoven web comprising a plurality of polybutylene terephthalate fibers and grafting a methacrylate polymer comprising poly(glycidyl methacrylate (polyGMA).

Embodiment 6: The method according to any preceding or subsequent embodiments, wherein the thermal free-radical initiator is a material configured for decomposing into radical species at a temperature at which an acrylate or methacrylate monomer polymerizes.

Embodiment 7: The method according to any preceding or subsequent embodiments, wherein the thermal free-radical initiator is a peroxide or an azo compound.

Embodiment 8: The method according to any preceding or subsequent embodiments, wherein the thermal free-radical initiator is selected from the group consisting of tert-amyl peroxybenzoate, 4,4- axobis(4-canovaleric acid), 1,1'-azobis(cyclohexanecarbonitrile), 2,2'-azobisisobutyronitrile (AIBN), benzoyl peroxide, 2,2-bis(tert-butylperoxy)butane, 1,1-bis(tert-butylperoxy)cyclohexane, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, 2,5-bis(tert-butylperoxy)-2,5-dimethyl-3-hexyne, bis(1-(tert-butylperoxy)-1-methylethyl)benzene, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, tert-butyl

Embodiment 20: A method of separating a target molecule from a solution, the method comprising passing the solution with the target molecule through a polymer-grafted and functionalized nonwoven membrane according to any preceding embodiment such that at least a portion of the target molecule in the solution binds to the polymer-grafted and functionalized nonwoven membrane.

Embodiment 21: A method for reducing the time to reaching a binding equilibrium in the separation of a target molecule from a solution, the method comprising passing the solution with the target molecule through a polymer-grafted and functionalized nonwoven membrane that is formed by thermal grafting of an acrylate or methacrylate polymer onto a plurality of polymeric fibers forming a nonwoven web, the so-formed polymer-grafted and functionalized nonwoven membrane being effective for reaching the binding equilibrium for the target molecule in a time of about 1 hour or less.

Embodiment 22: The method of any preceding embodiment, wherein the polymer-grafted and functionalized nonwoven membrane is effective for reaching the binding equilibrium for the target molecule in a time of about 10 minutes or less.

Embodiment 23: A polymer-grafted and functionalized nonwoven membrane comprising a nonwoven web formed of a plurality of polymeric fibers including grafted thereon a plurality of polymer segments constructed of an acrylate or methacrylate polymer, the plurality of polymer segments carrying functional groups adapted for binding to a target molecule, the plurality of polymer segments being thermally grafted to the nonwoven membrane so that the polymer-grafted and functionalized nonwoven membrane is effective for reaching a binding equilibrium for the target molecule in a time of about 1 hour or less.

These and other features, aspects, and advantages of the disclosure will be apparent from a reading of the following detailed description together with the accompanying drawings, which are briefly described below. The disclosure includes any combination of two, three, four, or more of the above-noted embodiments as well as combinations of any two, three, four, or more features or elements set forth in this disclosure, regardless of whether such features or elements are expressly combined in a specific embodiment description herein. This disclosure is intended to be read holistically such that any separable features or elements disclosed, in any of its various aspects and embodiments, should be viewed as intended to be combinable unless the context clearly dictates otherwise.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to provide an understanding of embodiments of the invention, reference is made to the appended drawings, which are not necessarily drawn to scale. The drawings are exemplary only, and should not be construed as limiting the invention.

Fig. 1 graphically illustrates heat induced grafting evaluated by % weight gain for different GMA concentrations (% v/v) and different polymerization temperatures over a range of polymerization times;

Figs. 2A-2F are SEM micrographs (4000x) of heat induced grafting onto PBT nonwovens for increasing % weight gain, wherein (A) shows PBT nonwoven prior to grafting, (B) shows PBT nonwoven