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Advanced membranes containing star macromolecules with C_{60} core for intensification of propyl acetate production

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ABSTRACT

In the present work transport properties of novel polymer materials were studied in separation of quaternary mixture (*n*-propanol–acetic acid–propyl acetate–water) and binary mixture (water–acetic acid) by pervaporation that can be used in hybrid process “reaction + pervaporation” to optimize of the propyl acetate production. Physical methods are successfully used to modernize properties of polymer materials without changing the chemical structure of macromolecules. Poly(phenylene oxide) membrane was modified by novel star shaped macromolecules with fullerene C_{60} core and arms of different nature. They are twelve-arm star consisted of six nonpolar arms of polystyrene and six polar arms of poly-2-vinylpyridine that are covalently bonded to C_{60} core. The membrane structure and thermal stability were studied by SEM, DSC, and TGA. To characterize physical properties, density and contact angles were determined. Membranes modified with the star macromolecules exhibit selectivity to water. The growth of modifier content up to 5 wt% leads to increase of the membrane performance and selectivity, which provides shifting the esterification reaction equilibrium and increasing the ester yield.

1. Introduction

Membrane technologies feature prominently an important place in industrial processes of liquids and gases separation due to energy saving and environmental protection of membrane separation processes (Baker, 2012). However, new approaches to produce membranes with controlled structures and properties should be proposed to solve novel industrial problems and to optimize existing technological schemes.

Esterification of carboxylic acids and alcohols is a typical example of an equilibrium-limited reaction for ester production. After the esterification is completed, unreacted reagents and water as coproduct remain in the reactor. These facts complicate the purification of the ester by traditional methods. Recently, the pervaporation has been involved in engineering design of hybrid processes to enhance performance of chemical synthesis or technological production (Chandane et al., 2017; Penkova et al., 2013, 2015; Delgado et al., 2010; Siva Kumar and Satyanarayana, 2011; Jyoti et al., 2015; Korkmaz et al., 2011; Gómez-García et al., 2016). Combination of esterification and pervaporation is one of the most promising hybrid processes. The removal of ester or water by pervaporation during the reaction shift chemical equilibrium, thus, pervaporation is a useful technology for ester synthesis (Hasanoğlu et al., 2009; Feng and Huang, 1996; Lv et al., 2012; Zhu et al., 2013; Park, 2004).

Propyl acetate as one of the widely used industrial organic solvent in confectionery and fragrance industry (food essences and components of perfume compositions), in the manufacture of paints and varnishes

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is synthesized by esterification of *n*-propanol and acetic acid; the yield of propyl acetate usually does not exceed 70%.

$$C_3H_7OH + CH_3COOH \leftrightarrow CH_3COOC_3H_7 + H_2O$$

Besides, during the reaction the *n*-propanol and water form an azeotropic mixture ($T_b = 87.5$–$88.0\,^\circ C$, 71.8 wt% *n*-propanol) (Toikka et al., 2011; Tsvetov et al., 2015).

The task of the present work was to develop effective membrane materials for shift the chemical equilibrium and increase the yield of propyl acetate. Various methods of polymer modification are used to improve the selectivity and permeability of polymer membranes, as well as to create specific properties (Robeson, 2010; Freeman and Yampolskii, 2010). Physical methods lead to modernize the polymer properties without changing the chemical structure of macromolecules (Nasir et al., 2013). These methods include the addition of various inorganic particles to polymer and formation of different polymer blends. Change of the polymer blend composition allows improving transport properties of membranes, their mechanical properties, thermal stability, and chemical resistance. Blends based on physically modified polymers have been successfully used for the preparation of gas separation membranes (Yave et al., 2009; Wolińska-Grabczyk et al., 2017; Kubica et al., 2016; Merkel et al., 2010; Feng et al., 2013; Khosravi and Omidkhah, 2015) as well as pervaporation membranes for separating liquid mixtures (Kujawski et al., 2017; Knozowska et al., 2017; Polotskaya et al., 2010; Pulyalina et al., 2010, 2011; Shi et al., 2017; Penkova et al., 2016).

Recently, membrane composite materials consisting of the polymer matrix as film-forming component and a small amount of hybrid macromolecules with star-shaped structure as filler have been obtained without covalent bonding the fillers and the matrixes (Polotskaya et al., 2015, 2016; Vinogradova et al., 2016). In our previous work, mixed matrix membranes based on polyphenylene oxide (PPO) have been obtained by including hybrid star macromolecules composed of a twelve-arms star with six polystyrene arms and six poly(2-vinylpyridine)-*block*-poly(*tert*-butylmethacrylate) diblock copolymer arms grafted onto a fullerene C_{60} core. In pervaporation of methanol–ethylene glycol mixture these membranes showed a high affinity to methanol and a higher separation factor and flux as compared to the properties of the unmodified PPO membrane (Polotskaya et al., 2015). Similar studies on pervaporation membranes based on PPO modified by six-arm star consisting of six polystyrene arms grafted onto C_{60} core revealed also high separation capacity toward the methanol-ethylene glycol mixture (Polotskaya et al., 2016). It should be noted an appreciable influence of fullerene C_{60} core on gas transport properties of membranes composed of the star-shaped polystyrene with fullerene C_{60} core (Vinogradova et al., 2016).

The mentioned star macromolecules are formed on the fullerene C_{60} as the branching center due to its structural features and reactivity. The van der Waals diameter of the C_{60} molecule with its π-cloud is 10.18 Å (Kroto, 1987). It is known that the chemical activity of C_{60} is due to the presence of reactive C═C bonds (6–6 positions), the number of which in fullerene is 30. To one molecule, up to 60 group-addends can potentially be attached. However, it has been established (Hirsch, 1999) that in the reactions of C_{60} with nucleophilic agents, the number of additions to one C_{60} molecule varies only within the range 1–6. As a result of exhaustive nucleophilic addition, the double bonds located along the orthogonal axes of the C_{60} molecule are revealed. There are only six such bonds in the C_{60} molecule, so C_{60} has an exceptional regioselectivity in the reactions of nucleophilic addition. The maximum number of additions is 6.

Anionic polymerization methods make it possible to obtain monodisperse polymers with specified molecular weights (polymer chains of equal length). The polymerization, for example styrene, is initiated by organolithium compounds (in particular, *sec*-butyllithium) in non-polar aromatic solvents. After completion of the reaction (complete exhaustion of the monomer), the polymer chains retain the active end group —C—Li, which again can initiate polymerization if a new portion of the monomer is introduced. Such polymers with an active end group are called "living", and polymerization involving such chains is "living" (Szwarc, 1956).

The "living" anionic polymers are nucleophilic agents; therefore, in the reaction with C_{60} fullerene, the attachment of the "living" polystyrene chains (polystyryl lithium, PSLi) occurs through six C═C bonds between hexagons on a fullerene molecule, resulting in the formation of a six-arm star macromolecule with arms of equal length (regular star) (Ederle and Mathis, 1997).

After the addition of six PSLi chains on the C_{60} core, six additional C_{60}-Li groups are formed (Vinogradova et al., 2002), which after the reaction with 1,1-diphenylethylene (DPE) allows polymerization of the polar monomer (2-vinylpyridine or *tert*-butyl methacrylate) and "growing" on the C_{60} core an additional six polar polymer arms with adjustable composition and molecular weight. These factors determine the creation of complex heteroarm star-shaped macromolecules that are close in structure to "standard" macromolecules, having a composition (6 + 6) with specified molecular-weight characteristics of both non-polar and polar arms (Vinogradova et al., 2005; Lavrenko et al., 2008; Vinogradova, 2010, 2012).

In the present work, novel membranes based on PPO modified with 1, 3, and 5 wt% star macromolecules with C_{60} core (SMC_{60}) were developed to use in pervaporation separation of quaternary equilibrium mixture (*n*-propanol–acetic acid–propyl acetate–water) and binary mixture (water–acetic acid). The modifier is twelve-arm star macromolecules with arms of different nature that had not been used before as membrane component. The SMC_{60} modifier consists of a fullerene C_{60} core connected with six nonpolar arms of polystyrene (PS) and six polar arms of poly-2-vinylpyridine (P2VP) ((SMC_{60}).

When choosing SMC_{60} modifier, we took into account the its unique advantages such as thermodynamic compatibility of PS arms with the PPO matrix and the ability of P2VP arms to strong swelling in alcohol containing media (but not dissolution since the arms are covalently bound to the C_{60} center). It has been shown that these stars tend to intramolecular segregation of P2VP chains in solutions (Lavrenko et al., 2008), and this fact can influence on the membrane structure during its formation from solutions.

It is known that heteroarm star polymers, in solvents of different polarity, form unimicellar and macromicellar structures, where nonpolar arms can form a core and polar arms form a corona (or vice versa) (Tsitsilianis et al., 2000). Films prepared from similar stars with PS and P2VP arms have an ordered morphology of the "ripple" type (Lupitskyy et al., 2005). We could expect that these properties will affect the morphology and transport properties of composite membranes.

The aim of this work was to clarify the factors affecting the transport properties of membranes and to expand the application of this membrane type for pervaporation separation of the system simulating the esterification reaction of *n*-propanol and acetic acid.

2. Materials and methods

2.1. *Materials*

PPO with a molecular weight 172 000 Da and density 1.057 g cm^{-3} (Brno, Czech Republic) and fullerene C_{60} of 99.9% purity (Neo Tech Product, Research & Production Company, Russia) were used. Cellophane nonporous film (thickness 70 μm) based on cellulose hydrate (Secon, FRG) was used as support. Chloroform, n-propanol, acetic acid, and propyl acetate were purchased from Vecton (Russia). All chemicals were used without further purification.

2.2. *Synthesis of SMC_{60} macromolecules (Vinogradova, 2012)*

All reactions on the synthesis of precursor polystyryllithium (PSLi) and star macromolecules SMC_{60} were carried out in vacuum all-welded glass systems using specially purified monomers and solvents.