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Synthesis of Fullerene–Polyphenylene Oxide Membranes for Separating Aqueous-Organic Mixtures

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Abstract—Homogeneous fullerene–polyphenylene oxide membranes containing up to 2 wt % C_{60} are synthesized and characterized by the density, electrical resistivity, and contact angle with water and ethanol. The effect of fullerene additive on the transport characteristics of the membranes in pervaporation of water mixtures with ethanol and ethyl acetate is studied.

Membrane processes find steadily growing use for purification, concentration, and fractionation of liquid and vapor mixtures. Pervaporation (separation of binary and multicomponent mixtures by evaporation through a membrane) appears to be an efficient process in those cases when the use of conventional methods such as distillation and rectification is impractical or inadvisable (for example, separation of azeotropic mixtures and substances with close physicochemical properties). In pervaporation under reduced pressure, the driving force of transmembrane transport is the pressure gradient controlling the fluxes across the membrane. It is commonly accepted that the model "dissolution–diffusion" most adequately reproduces the mechanism of this process [1–4].

The selectivity and efficiency of pervaporation is controlled by such factors as the structure, chemical nature, and composition of the membrane material. The spectrum of commercial pervaporation membranes is rather limited. Therefore, searching for novel high-performance membranes is, without question, of significant scientific and practical interest. In this relation, membranes based on hybrid polymeric materials containing various ultradispersed and nano particles show promise for advanced membrane processes. It is obvious that of primary interest are polymeric composites containing highly physicochemically active substances. In this study we examined thin-film membrabes based on poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) modified with fullerene C_{60}.

The modification yields PPO–C_{60} donor–acceptor complex. Rheological and hydrodynamic study of its solutions revealed that the donor–acceptor bond is strong enough to remain stable upon dilution, despite small decrease in the intrinsic viscosity and broken symmetry of the PPO molecule [5]. It was demonstrated by TGA–MS and differential calorimetry that modification with fullerene improves the heat resistance of PPO [6]. Biryulin *et al*. [7] studied photoluminescence spectra of C_{60}–PPO films. Molecular complexes were found in the films containing up to 2 wt % C_{60}, while in the 4% C_{60}–PPO films, the major part of fullerene molecules is free.

Only a few publications are devoted to properties of fullerene-containing membranes based on poly(trimethylsilylpropyne), polystyrene, and Martimide [8–10]. It was demonstrated in our previous studies that the presence of fullerene strongly affects the transport characteristics of polystyrene and PPO in gas separation to enrich air with oxygen, increasing the selectivity and decreasing the permeability [11, 12]. In this study we examined the effect of modification with C_{60} on physical and pervaporation characteristics of homogeneous PPO membranes. The transport properties of the membranes were studied in separating aqueous-organic systems with ethyl acetate and ethanol.

EXPERIMENTAL

In the study we used PPO with MW 178 000. Fullerene containing more than 98% of C_{60} (Ioffe Physicotechnical Institute, Russian Academy of Sciences) was dried by heating to 100°C in a vacuum. Composites C_{60}–PPO containing up to 2 wt % C_{60} were prepared by mixing toluene solutions of the components.

Membranes 50–80 μm thick were produced by removal of toluene at 40°C from the mixed solution poured onto cellophane. The density ρ of the membranes was determined at 25°C in the sucrose solution by the flotation method. The free volume v_f was estimated by Eq. (1):

$$v_f = v_{sp} - 1.3v_w, \qquad (1)$$

where $v_{sp} = 1/\rho$ is the specific volume and v_w, van der Waals volume determined by the Bondi method. The contribution of C_{60} to the occupied volume and molecular weight of PPO monomeric unit was taken into account in estimating v_w of the C_{60}–PPO composites.

Dielectric measurements were carried out in a hermetically sealed glass cell using chrome-plated brass contact electrodes at 0.1 kHz in a vacuum. Contact angles of the membrane surface with water and ethanol were determined by the Wilhelmy method on a KRUSS contact angle measuring system with computer-controlled sample immersion rate and data processing.

The pervaporation experiments were conducted using a laboratory cell with an effective membrane area of 14.8 cm^2 with stirring of the feed mixture at 50°C over the membrane at a residual pressure under the membrane of 0.2 mbar. The compositions of the feed mixture and permeate were determined refractometrically or chromatographically. The partition factor α was estimated as

$$\alpha = (X_A/X_B)/(Y_A/Y_B), \qquad (2)$$

where Y_A and Y_B are the weight fractions of A and B in the initial (feed) mixture and X_A and X_B, in the permeate. The transport characteristics were determined to within 5%.

The equilibrium swellability (sorption) was determined gravimetrically. The equilibrium sorption S was estimated by Eq. (3):

$$S = (m_s - m_0) \times 100/m_0 \qquad (3)$$

where m_s and m_0 are the weights of the swollen and dry membrane, respectively.

The formation of C_{60}–PPO donor–acceptor complex imparts typical brown color to the modified PPO membranes; the color intensity depends on the percentage of C_{60}. We examined some physical characteristics of the C_{60}–PPO membranes, which are relevant to understanding the features of the transport of small molecules across homogeneous membranes. In particular, we have determined the distribution of C_{60} in PPO films (from the dielcometric measurements) and also the density of the films and contact angles.

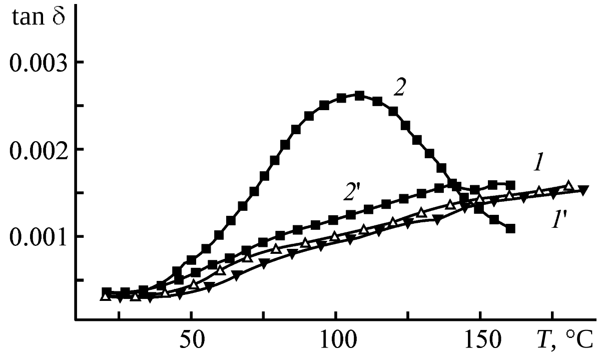

Fig. 1. Dielectric loss tangent tan δ as a function of the temperature T: (*1, 1'*) PPO and (*2, 2'*) 2% C_{60}–PPO. (*1, 2*) Before heating and (*1', 2'*) after heating to 150°C without air access. Frequency 0.1 kHz.

Figure 1 shows the temperature dependences of the dielectric loss tangent tan δ of the initial PPO and 2% C_{60}–PPO membranes. At room temperature PPO occurs in the glassy state, demonstrating no dielectric relaxation range up to 180°C (Fig. 1, curve *1*). In the case of the C_{60}–PPO membranes we found a relaxation range at 80 to 120°C. Since $\tan\delta_{max}$ is observed only in the presence of C_{60}, it may be suggested that the occurrence of the relaxation range is associated with the mobility of the kinetic units of fullerene. Heat treatment of the C_{60}–PPO membrane suppresses the relaxation transition, and the temperature dependence of tan δ becomes similar to that of PPO.

It is known from the literature that fullerenes in solutions can form clusters [13]. It may be suggested that, as in the C_{60}–polystyrene system [12], the observed relaxation transition is associated with the mobility of the dipoles of fullerene clusters. However, in the C_{60}–PPO composite, the intensity of this transition is lower by an order of magnitude than that in the system with polystyrene, suggesting that only a small fraction of fullerene molecules in PPO films exist in the form of clusters. This is supported also by the lack of the $\tan\delta_{max}$ peak in the heat-treated sample (Fig. 1, curve *2'*). In preparing the composite films from solutions, the most of C_{60} molecules are more regularly distributed throughout the PPO film thanks to donor–acceptor interaction of C_{60} with the lone pair of the oxygen atom of PPO in addition to the interac-

Table 1. Selected physical characteristics of membranes

Polymer	$\log \rho_v^*$	Density, g cm^{-3}	Free volume, cm^3 g^{-1}	Contact angle, deg	
				water	ethanol
PPO	15.15	1.057	0.181	91.2	20.2
1% C_{60}–PPO	–	1.093	0.150	–	–
2% C_{60}–PPO	16.48	1.120	0.128	94.4	17.9

* (ρ_v) Electrical resistivity.

tion of the phenyl ring with the π system of C_{60}. The fullerene molecules associated with PPO are capable of strong intermolecular interactions resulting in physical cross-linking of the PPO chains via fullerene bridges, which is reflected in considerable increase in the dielectric permittivity of the C_{60}–PPO composites (Table 1) and also can increase the density.

Introduction of foreign particles into polymer systems may result in both compaction and loosening of the polymer structure. To elucidate the effect of C_{60}, we measured the density of PPO films with various C_{60} content and estimated their free volume. Table 1 shows that addition of C_{60} increases the density of PPO, i.e., the PPO globules becomes more compact, and the free volume of the fullerene-containing composites decreases, thus reflecting the intercomponent interactions.

The contact angle is a parameter most commonly used to characterize the surface tension of solids [14]. We determined the contact angles of PPO and C_{60}–PPO membranes with water and ethanol using the Wilhelmy technique (Table 1). The results show that PPO is a hydrophobic polymer (contact angle with water is above 90°). Addition of C_{60} increases the contact angle, i.e., the hydrophobicity. Inversely, the PPO surface is readily wetted with ethanol, and addition of C_{60} decreases the contact angle with ethanol. These results appeared to be significant for interpretation of the effect of C_{60} on the sorption and pervaporation characteristics of PPO membranes.

Table 2. Equilibrium sorption *S* and interaction parameters of membrane materials with components of liquid mixtures

Solvent	*S*, wt %		Interaction parameter χ	
	PPO	2% C_{60}–PPO	PPO	2% C_{60}–PPO
Ethyl acetate	23	26	1.22	1.13
Ethanol	13	15	1.45	1.34
Water	0	0	–	–

In pervaporation, polymeric membranes operate as molecular sieves, but having active sites capable of dipole–dipole, ion–dipole interactions or hydrogen bonding with components of a liquid mixture to be separated [15]. The mass transfer depends to a considerable extent on the affinity of the membrane material for components of the mixture [2, 4]. Quantitatively, this affinity is characterized by the Flory–Huggins interaction factor χ (as known, χ directly characterizes the solubility of a polymer in a given solvent [16]). In the case of equilibrium sorption and a one-component solvent, χ can be estimated by Eq. (4) [17]:

$$\chi = \frac{-\ln \varphi_i - \varphi_p}{\varphi_p^2}, \tag{4}$$

where φ_i and φ_p are the volume fractions of the solvent and polymer, respectively.

Therefore, the fraction of the solvent in the polymer phase increases with decreasing χ, i.e., the lower χ, the better sorption. Equation (4) can be used for estimating parameters of interaction in binary solvents also on the condition that these parameters are composition-independent [17]. To estimate the interaction parameter, we studied the sorption of ethyl acetate, ethanol, and water vapors on the homogeneous membranes. The results obtained after establishment of the equilibrium show (Table 2) that the affinity of the PPO and C_{60}–PPO membranes for the solvent decreases in the order ethyl acetate > ethanol >> water (water appears to be absolutely inert solvent with respect to the polymers studied). The C_{60}-modified membranes better sorb both ethyl acetate and ethanol.

Pervaporation of aqueous-alcoholic mixtures represents a classical task for this membrane separation technique [18–20]. We studied the effect of C_{60} on the pervaporation characteristics of PPO membranes in pervaporation of the H_2O–EtOH mixture. Figure 2 shows the dependences of the EtOH concentration in the permeate and selectivity on the EtOH concentration in the feed mixture in pervaporation of the H_2O–EtOH mixture through PPO and C_{60}–PPO membranes. The trend of the concentration dependence for pervaporation differs significantly from the equilibrium liquid–vapor diagram in the system water–ethanol (Fig. 2a). In pervaporation, at any concentration of the feed mixture, a water-enriched permeate is formed, i.e., the membranes in hand are selective with respect to water. Addition of C_{60} decreases the alcohol concentration in the permeate, i.e., the selectivity increases (Fig. 2b). This fact can be attributed to decreasing free volume of PPO with addition of C_{60} (Table 1), which could cause a decrease in the size of the transport channels in the modified PPO membranes, and, therefore, an increase in the selectivity with respect to water.

Figure 3 shows the permeability Jl as a function of the ethanol concentration in the initial mixture in pervaporation of the water–ethanol mixture. Since the penetrant flux J is inversely proportional to the membrane thickness l, which varied from 50 to 80 μm for different samples, we used the product Jl, to compare transport characteristics of the homogeneous membranes (the use of this product was demonstrated to be more correct [21]. As seen from Fig. 3, addition of C_{60} increases the penetrant flux across the membrane. Furthermore, increasing concentration of less penetrating component, ethanol, in the initial mixture also increases the permeability of the membranes, which seems to be surprising. This fact can be attributed to the specific sorption features of the investigated membranes with respect to water and ethanol.

Figure 4 shows the dependence of the equilibrium sorption on the EtOH concentration in the water–ethanol mixture for PPO and 2% C_{60}–PPO membranes. As seen, all the membranes studied are inert with respect to water, but readily sorb ethanol. Therefore, even small amounts of ethanol in water initiate swelling of PPO. In this case, addition of C_{60} increases the sorption capacity, which is consistent with data of Table 2 demonstrating that, in ethanol, the interaction parameter and contact angle of fullerene-containing membranes decrease. This is responsible for the fact that, with increasing EtOH concentration in water, the sorption on C_{60}–PPO composite increases to a larger extent than for PPO.

To interpret the observed preferential transport of water in pervaporation of water–ethanol mixtures through hydrophobic PPO-based membranes, we sug-

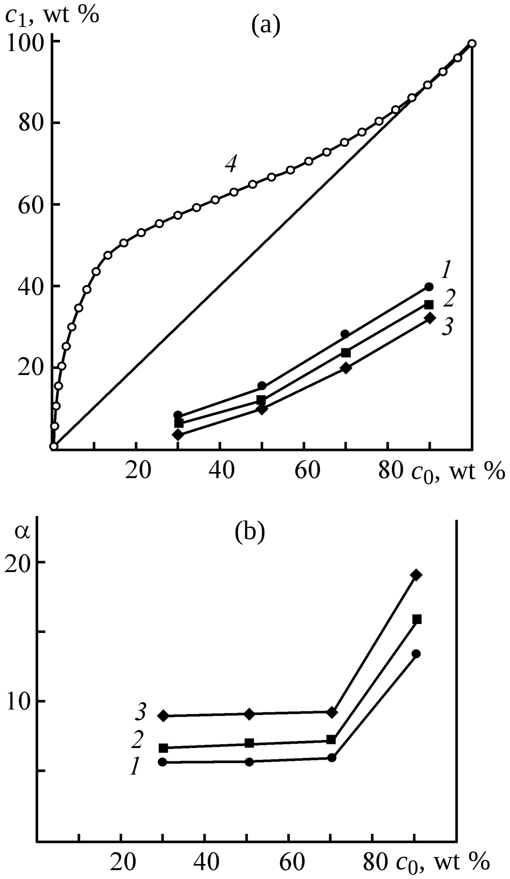

Fig. 2. (a) Ethanol concentration in the permeate c_1 and (b) partition factor α H_2O/EtOH as functions of the ethanol concentration in the initial mixture c_0 in pervaporation of the water–ethanol mixture: (*1*) PPO, (*2*) 1% C_{60}–PPO, (*3*) 2% C_{60}–PPO, and (*4*) liquid–vapor equilibrium curve at 50°C.

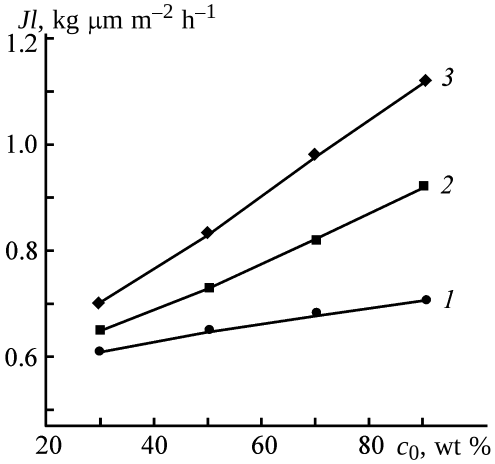

Fig. 3. Permeability Jl as a function of the ethanol concentration in the initial mixture c_0 in separating water–ethanol mixture by pervaporation on (*1*) PPO, (*2*) 1% C_{60}–PPO, and (*3*) 2% C_{60}–PPO membranes.

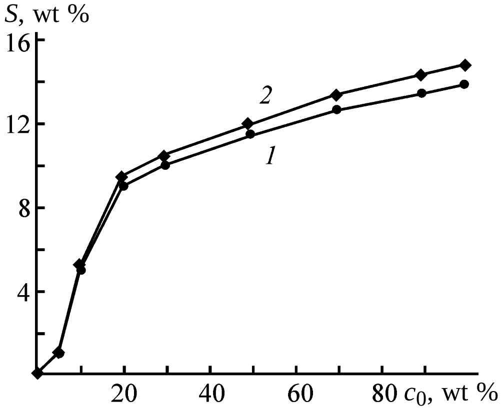

Fig. 4. Equilibrium sorption *S* as a function of the ethanol concentration in the water–ethanol mixture c_0 for (*1*) PPO and (*2*) 2% C_{60}–PPO membranes.

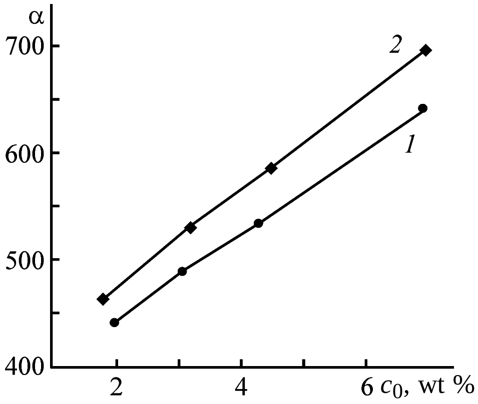

Fig. 5. Partition factor α for the pair ethyl acetate–water as a function of the ethyl acetate concentration in the initial mixture c_0 in pervaporation of the mixture water–ethyl acetate on (*1*) PPO and (*2*) 2% C_{60}–PPO membranes.

gested the following mechanism. Initially only ethanol molecules are involved in the sorption through interaction with the lone electron pair of the oxygen atom of the PPO backbone with formation of hydrogen bonds; in such a way ethanol molecules are retained in the membrane phase, creating transport channels. Thanks to a considerable affinity for ethanol, water penetrates these channels whose size is well comparable with the kinetic diameter of the water molecule, the penetrability of water being higher because of smaller size of its molecules as compared to ethanol. Increasing ethanol concentration as a swelling agent in the feed mixture weakens the intra- and intermolecular interactions in the PPO membrane, i.e., placticizes the membrane, favoring increase in the permeate flux across the membrane. The sorption data confirm the increase in the degree of plasticization of the PPO matrix as well as of the number of mass-transfer channels with increasing ethanol concentration in water. These transformations result in increasing penetrability of water and selectivity, the tendency being more clearly pronounced for C_{60}–PPO membranes.

In studying pervaporation in the system water–ethyl acetate, the primary attention was paid to separation of ethyl acetate from homogeneous water-rich mixtures (<7 wt % ethyl acetate). The reason is that the phase separation in this system occurs over a wide composition range, and the homogeneity ranges are found at an ethyl acetate concentration below 7 and above 97 wt %. We studied the transport characteristics of PPO and C_{60}–PPO membranes in pervaporation of dilute aqueous ethyl acetate solutions. For all the membranes studied we obtained high selectivity with respect to ethyl acetate (Fig. 5), which can be attributed to hydrophobic nature of PPO. After formation of the transport channels as a result of sorption and swelling of the membrane in ethyl acetate, penetration of water into these channels is hindered because of high activity coefficients of the components, which results in phase separation in the mixture at an ethyl acetate concentration above 7 wt %. Figure 5 shows that addition of C_{60} further increases the selectivity. At the same time, addition of C_{60} only slightly changes the flux across the membranes: from 0.48 to 0.52 $kg\,m^{-2}\,h^{-1}$ on passing from PPO to 2% C_{60}–PPO in pervaporation of 7% aqueous ethyl acetate. This can be a resultant of two oppositely directed factors: decreasing free volume, on the one hand, and increasing swellability of fullerene-containing membranes in ethyl acetate, on the other hand. Note, as a conclusion, that data on pervaporation of aqueous ethyl acetate solutions in combination with those on the system water–ethanol are important for developing a process for synthesis of ethyl acetate using pervaporation.

CONCLUSIONS

(1) Homogeneous PPO membranes modified with up to 2 wt % C_{60} demonstrate higher electrical resistivity and density as compared to unmodified membranes. Also the modification strongly affects the contact angle with water and ethanol.

(2) In pervaporation of water–ethanol mixture through fullerene-modified membranes, both the selectivity with respect to water and permeability increase with increasing ethanol concentration in the initial mixture. Modification of PPO membranes with fullerene makes them more organophilic (swellability in ethanol increases with increasing fullerene content). Increasing fullerene concentration increases both the

sorption capacity of the modified membranes and their efficiency in pervaporation of water–ethanol mixtures.

(3) PPO-based membranes demonstrate high selectivity with respect to ethyl acetate in pervaporation of water-rich mixtures; the selectivity grows with increasing C_{60} content.

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