ELSEVIER

Polymer 42 (2001) 2985–2989

polymer

www.elsevier.nl/locate/polymer

Properties of polyelectrolyte complex membranes based on some weak polyelectrolytes

G.T. Zhumadilova, A.D. Gazizov, L.A. Bimendina*, S.E. Kudaibergenov

Institute of Polymer Materials and Technology, Satpaev Str. 18a, 480013, Almaty, Republic of Kazakhstan

Received 28 March 2000; received in revised form 31 May 2000; accepted 9 June 2000

Abstract

Membranes derived from the polyelectrolyte complexes of polyvinyl ether of monoethanol amine and poly-*N*-methyl-4-vinylethynyl piperidinol-4 with polyacrylic acid and copolymers of acrylic acid and vinylbutyl ether have been prepared and their swelling properties were studied as a function of copolymer composition, solvent composition, pH, ionic strength and temperature. The permeability of polyelectrolyte complex membranes with respect to urea has been also considered. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyelectrolyte complexes; Membranes; Permeability

1. Introduction

Design and fabrication of polyelectrolyte complex membranes (PCM) and thin films for separation processes is of great interest [1,2]. Michaels and coworkers [3] have shown the possibility of using of PCM derived from sodium polystyrene sulfonate and polyvinylbenzyl trimethylammonium chloride for desalination of sea water, dialysis, ultrafiltration and purification of aqueous solutions containing colloids, micro- and macroparticles. Last years PCMs based on chitosan and polycarboxylic acids have been used for pervaporation of water–organic mixtures [4–6]. The permeability of PCM with respect to urea and bovine serum albumin has been studied by authors [7]. Earlier we have studied the formation of interpolyelectrolyte complexes between polyacrboxylic acids and co(polymers) of acrylic acid with some cationic polymers in aqueous solution and in the boundary of two liquid phases [8]. The preparation of interpolymer membranes and thin films from these polyelectrolyte pairs would be useful to apply them for separation processes.

In the present communication we have shown that swellable PCM films can be fabricated from the preformed polyelectrolyte complex films by thermal processing and they are sensitive to change of environment, and are able to exhibit self-permeability with respect to urea.

2. Experimental

Synthetic procedure and characteristics of polyacrylic acid (PAA), copolymers of acrylic acid and vinylbutyl ether (AA-VBE), containing 3, 13, 40 and 45 mol% of vinylbutyl ether fragments (abbreviated as CP-3, CP-13, CP-40 and CP-45), polyvinyl ether of monoethanol amine (PVEMEA), poly-*N*-methyl-4-vinylethynylpiperidinol-4 (PVEP) used in this study were described in previous work [8].

The PCM films have been fabricated from the polyelectrolyte complexes (PEC). The compositions of [PAA]: [PVEMEA] = 1:1, [CP-3]:[PVEMEA] = 1:1, [CP-13]:[PVEMEA] = 1:1, [CP-40]:[PVEMEA] = 1:1, [CP-45]:[PVEMEA] = 1:1, [PAA]:[PVEP] = 1:1, [CP-13]:[PVEP] = 1:1 mol/mol were preliminary determined from the maximums (or minimums) and bending points of viscometric, potentiometric, conductimetric and spectroturbidimetric titration curves in aqueous solution [8]. PEC solutions were prepared as follows [9]: equimolar amounts of PAA and PVEMEA or AA-VBE and PVEMEA ($C = 5 \times 10^{-3}$ mol/l) were dissolved in water containing 5 wt% of formic acid. According to this procedure [9] PEC particles remain in solution and do not precipitate due to suppression of ionization of poly(carboxylic acids). Then PEC solutions have been poured on polyethylene matrix, the solvent was evaporated at room temperature, the dried films were then vacuumed and exposed at 140–150°C during 1.5 h. After they were washed by distilled water up to

---

* Corresponding author.

E-mail address: ipmt-kau@usa.net (L.A. Bimendina).

PII: S0032-3861(00)00442-0

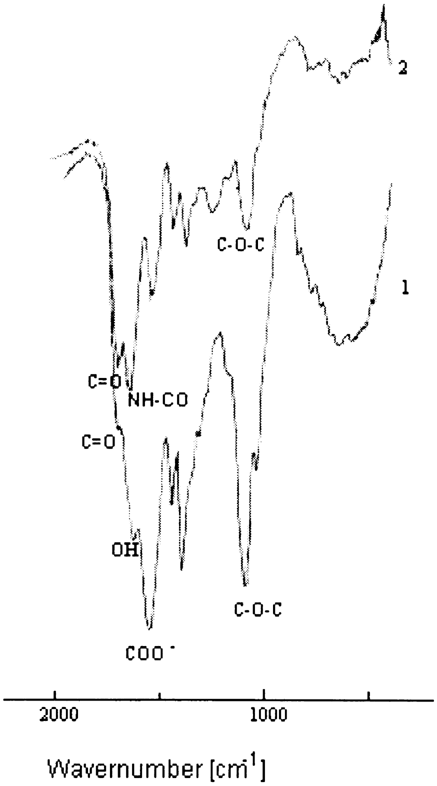


Fig. 1. FT/IR-spectra of [PAA]:[PVEMEA] = 1:1 complex film formed from 5 wt% water solution of formic acid (1) and the same film after heating at 145°C during 1.5 h (2).

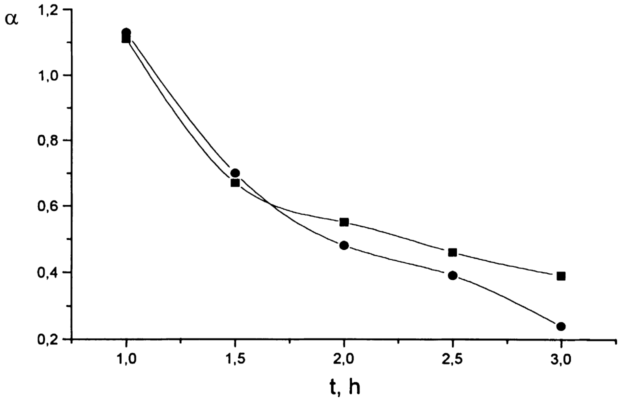


Fig. 2. Dependence of swelling degree α of AA-VBE/PVEMEA films on the time of thermal processing. ● — CP-3; □ — CP-13.

neutral pH values. As a result the transparent and good swelling in water membranes were obtained. The degree of swelling α of membranes was determined by gravimetric method: $a = (m - m_0)/m$ (where m_0 and m are the weights of dry and swollen in water membranes, respectively). The content of water in membranes in percentage expressed as $W = 100(m - m_0)/m_0$ is equal to 35–40%.

For studying of the influence of pH, ionic strength and temperature on the properties of membranes the equilibrium swollen samples with diameter 10 mm were placed into thermostated cell containing buffer solutions. The diameter of films d_0 and d_t was measured by means of cathetometer "V-630" (Russia) (where d_0 is the initial diameter of equilibrium swollen sample, d_t is the change of the diameter of membrane at definite time t) and the relative change of film's diameter expressed as $d_t/\mathbf{d}_0$ was measured in dependence of pH.

Permeability of PEC membranes with respect to urea was measured in two-chamber glass cell divided by membrane. One of the chamber contained the aqueous solution of urea (0.6 g/l), another — the distilled water. The concentration of urea was determined spectrophotometrically by means of spectrophotometer "Spekol-11" (Germany) at $\lambda = 420$ nm at room temperature by color reaction of urea with p-dimethylaminobenzaldehyde [10]. Permeability constant P was calculated by the formulae:

$$P = 2.303 \log(C_0/\Delta C)V/2At$$

where C_0 is the initial concentration of urea (g/l), $\Delta C = C_0 - C_t$ is the difference of urea concentration (g/l) in chambers 1 and 2 (where C_t is the concentration of urea at definite time t (min)), A the membrane area (cm^2), V the volume of chamber (cm^3).

IR spectra of samples were recorded on a JASCO FT/IR-5300 spectrophotometer with KBr pellets. The band resolution is 4 cm^{-1}.

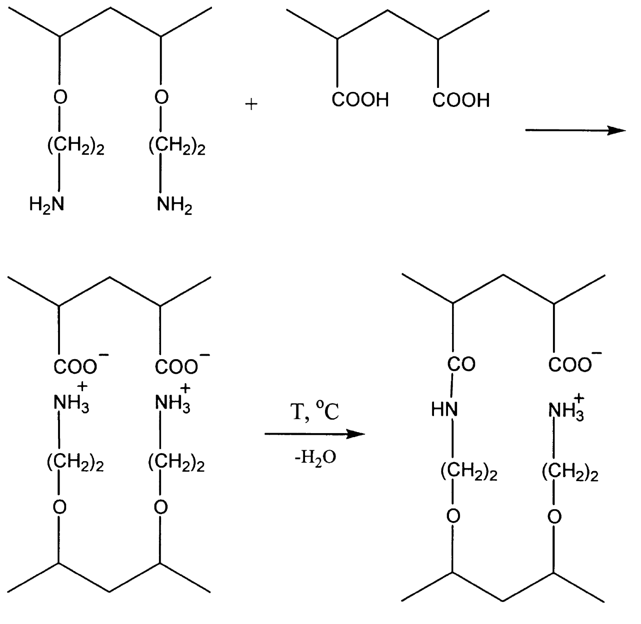
Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out with the help of a SEIKO TG/DTA 220 thermal analyzer at a heating rate 20°C/min under nitrogen atmosphere. DSC traces were obtained using SEIKO DSC 120 thermal analyzer at a heating and cooling rate 10°C/min under argon atmosphere.

The viscosity of PEC was measured in an Ubbelohde viscometer at 298 ± 0.1 K. pH of the solutions was controlled by means of the pH/Conductivity Meter "Mettler Toledo MPC 227" (Sweden). Ionic strength of solutions was adjusted by neutral salt KCl.

3. Results and discussion

IR-spectra of PAA, PVEMEA and [PAA]:[PVEMEA] = 1:1 complexes have been compared. IR-spectra of PAA and PVEMEA contain the characteristic band of C=O group at 1720–1710 cm^{-1}, C–O–C bond at 1128 cm^{-1} and NH$_2$ groups at 1576 cm^{-1}. IR-spectra of PAA/PVEMEA complex has a new bands at $\nu = 1564$ and 2950 cm^{-1}. The first band is concerned to absorption of carboxylate-anions, the second one can be identified as absorption band of NH_3^+ groups. Thus the appearance of absorption bands of COO^- and NH_3^+ groups confirms that these complexes are stabilized by ionic $COO^- \cdots NH_3^+$ bonds.

Fig. 1 presents FT/IR spectra of PAA/PVEMEA membranes before and after thermal treatment. It is seen that the untreated PCM contains the intensive band of carboxylate anions at 1563 cm^{-1} as a result of proton transfer from carboxylic groups to primary amine moieties. The band at 1631 cm^{-1} is probably belongs to bending vibrations of OH groups from the carboxylic groups. The unresolved shoulder at 1710 cm^{-1} is related to C=O groups of PAA. The thermal treatment of PAA/PVEMEA membrane leads to appearance of new peak at 1653 that is characteristic for amide bonds. The characteristic peak of C=O is located at 1716 cm^{-1}. It should be noted that for both treated and untreated membranes the band of C–O–C group at 1093 cm^{-1} practically does not change that excludes the participation of ether groups in formation of hydrogen bonds. One can conclude from IR spectra that during the thermal treatment some part of salt bridges NH_3^+ ^-OOC of PEC membranes is converted into NH–CO amide bonds due to dehydratation of intermolecular salt bonds. The formation of covalent amide bonds was shown for PAA–polyethylenimine [11] and PAA–chitosan [6] complex membranes. The gradually decreasing of the swelling degree of membranes with increasing of time exposition confirms the enhancement of covalent bonds formation (Fig. 2). The formation of covalent amide bonds for polyelectrolyte pairs PAA and PVEMEA can be represented by the scheme shown below:



Complex formation in PVEP-CP-3 (CP-13) systems is also caused by ionic bonds followed by the formation of covalent bonds in the course of thermal processing.

One of the characteristic band of PVEP that is very sensitive to complexation process and so-called “Bohlman” band appears at 2800 cm^{-1} [12]. Its appearance is connected with the availability of *trans* fragments between the free axial lone electron pairs of the nitrogen atom and axial CH-bonds in the alfa-position in relation to the nitrogen atom of heterocycle. The protonization of nitrogen atoms during the complexation leads to the disappearance of Bohlman bands owing to the disturbance of electron interactions in this fragment. Thus the binding of protons from the carboxylic groups to nitrogen atoms of PVEP should change the position and intensity of the Bohlman bands. The appearance of a new band at 2720 cm^{-1} reflects the protonization of tertiary amine groups of PVEP. The transfer of protons from the carboxylic groups of PAA and acrylic acid–vinylbutyl ether copolymers to nitrogen atoms of PVEP also leads to the appearance of asymmetric vibration signals of carboxylate anions at 1570 cm^{-1}.

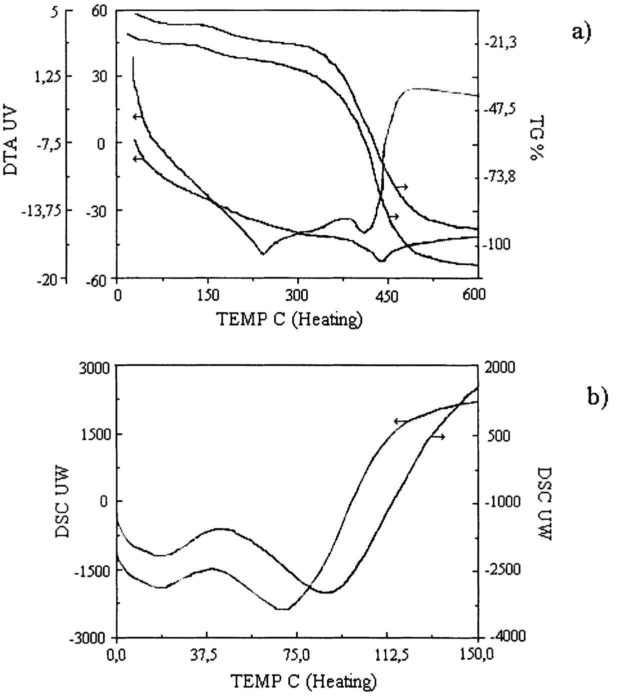


Fig. 3. TG, DTA (a) and DSC (b) data of PCMs consisting of PAA/PVEMEA and CP-45/PVEMEA.

TG, DTA and DSC data of PEC membrane consisting of PAA/PVEMEA and CP-45/PVEMEA are shown in Fig. 3. PEC membranes are stable and decompose at 420–440°C. The peak at 235°C probably reflects the melting point of composite film PAA/PVEMEA. The DSC traces of the same membranes have two minimum’s at 17.2 and 84.6°C for PAA/PVEMEA and at 20.2 and 69.8°C for CP-45/PVEMEA. The low temperature peaks is attributed to glass transition temperatures T_g of PVEMEA involved into complexation, higher temperature peaks is also the glass transition temperatures of PAA and CP-45 involved into complexation. The lower value of T_g for CP-45/PVEMEA in comparison with PAA/PVEMEA may be connected with the influence of bulky butyl radicals that disturbs the complementarity of macromolecular chains.

The swelling behavior of PCMs was studied as a function of the content of hydrophobic groups, pH and in water–methanol mixture. When the content of vinylbutyl ether in

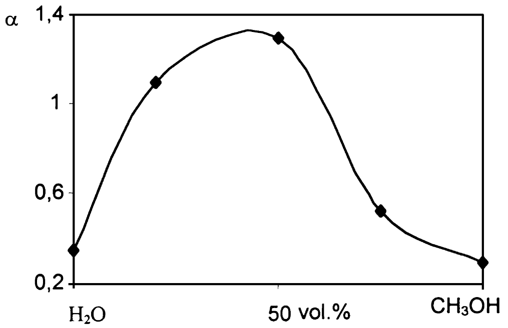


Fig. 4. Dependence of swelling degree α of [CP-13]:[PVEP] = 1:1 complex film on composition of water–ethanol mixture.

copolymers is 45 mol% the equilibrium swelling degree of PEC membranes decreases in water but increases in methanol. This is connected with strengthening of hydrophobic interactions in aqueous solution that shrink the membrane and preferentially solvation of hydrophobic groups by methanol that expands it.

The dependence of swelling degree of PEC membrane CP-13/PVEP on composition of water–methanol mixture discovers the maximum (Fig. 4). The mixed solvent corresponding to maximal swelling may be thermodynamically best solvent for this system due to the change of solvent quality with respect to hydrophilic and hydrophobic parts of membranes.

The stability of membranes with respect to pH is important characteristic of PEC membranes. The studied membranes are stable at the interval of pH 2.5–10.5. Fig. 5 represents the dependencies of d_t/d_0 values for CP-13/PVEP films on pH at different temperatures. Minimum swelling degree corresponding to pH ≅ 6.5 is due to Coulombic attractions between long sequences of acidic and basic groups of polyelectrolytes. While the considerable swelling of membrane at pH < 6.5 and pH > 6.5 is accounted for electrostatic repulsion between positively and negatively charged groups of polyelectrolytes in acidic and basic regions, respectively. The isoelectric point of PCM where the macromolecule is electroneutral is arranged at pH ≅ 6.5. To check this point the separate viscometric experiments were performed. As seen from Fig. 6, the solution of PEC, from which PCM was fabricated, show a minimum viscosity at pH ≅ 6.5. From these results one can conclude that both PEC solution and PCM behave the same properties with respect to external pH. Earlier we have shown [13] that the stoichiometric PEC solution consisting of sodium salt of PAA and poly[2-(*N*,*N*-diethyl-*N*-methylamino)ethyl acrylate] exhibits amphoteric behavior. Amphoteric character of PCM derived from chitosan and PAA was also demonstrated by authors [6].

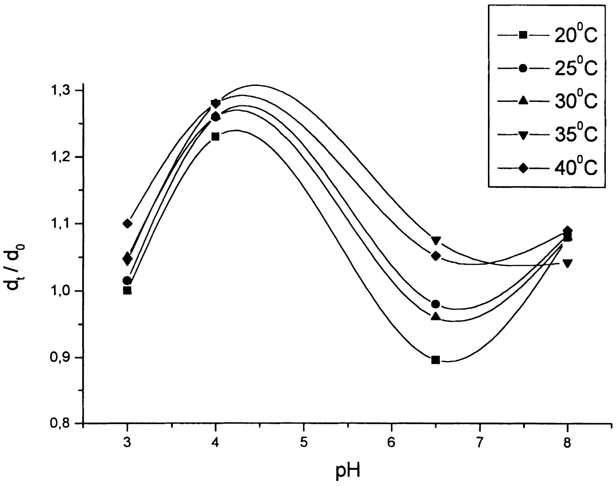


Fig. 5. Dependence of d_t/d_0 values of [CP-13]:[PVEP] = 1:1 complex films on pH.

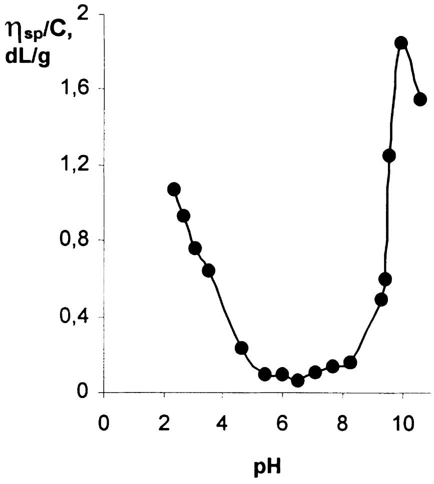


Fig. 6. Dependence of the reduced viscosity of [CP-13]:[PVEP] = 1:1 complexes on pH.

Temperature factor enhances the swelling degree of PEC membrane in 15–30°C region but the further increasing of temperature leads to contraction of membrane and decreasing of swelling degree. The latter is probably connected with enhancement of hydrophobic interactions with temperature. Increasing of ionic strength of solutions causes the increasing of swelling degree of PEC membranes that is obviously connected with partial destruction of interionic bonds as a result of screening of charged macromolecules by low molecular weight ions.

Semi-permeable properties of membranes have been checked with respect to urea transport through the membranes on the basis of PAA/PVEP and CP-13/PVEP complexes. Fig. 7 shows the change of concentration of urea with time during the dialysis experiments. The permeability constant of urea ($P \cdot 10^3$ cm/min) was determined from the slope of the linearized curves in coordinates $2.303 \log(C_0/\Delta C) - t$. The permeability constants are equal to 3.4 for PAA/PVEP and 2.3 for CP-13/PVEP. The decrease of permeability constant in the case of CP-13/PVEP is probably connected with more hydrophobic character of membranes due to the presence of bulky butyl radicals.

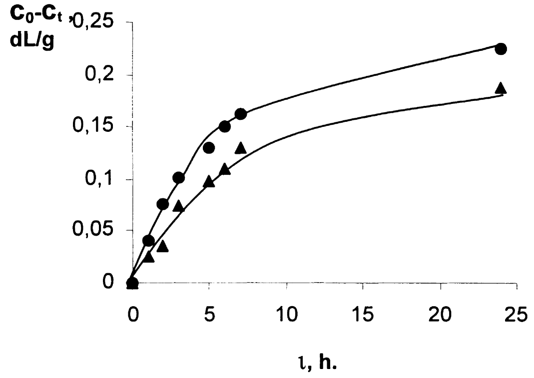


Fig. 7. Dependence c_0–c_t values of PCM films on time. ● — PAA/PVEP; □ — CP-13/PVEP.

4. Conclusions

Equimolar polyelectrolyte complex membranes have been prepared from various pairs of weak polyelectrolytes. Thermal treatment of membranes as follows from the IR spectroscopic data leads to formation of covalent amide bonds. As a result of thermal processing the transparent and swellable in water PCMs are formed. The swelling behavior of PCMs changes as a function of pH, ionic strength, temperature and solvent quality. Comparison of swelling and solution properties of PCMs and PEC, respectively, in dependence of pH shows that they behave amphoteric character. Membranes exhibit semi-permeability with respect to urea.

Acknowledgements

The authors would like to thank INTAS-1746 Grant for financial support.

References

[1] Bungay PM, Lonsdale HK, Pinho MN, editors. Synthetic membranes: science, engineering and applications, NATO ASI Series, vol. 181. Boston, MA: Reidel, 1983.
[2] Khamzamulina RE, Bekturov EA. Membranes on the basis of interpolymer complexes. Proceedings of the Institute of Chemical Sciences Republic of Kazakhstan, 1991. p. 75–131.
[3] Bixler HJ, Michaels AS. Polyelectrolyte complexes. Encyclopedia of polymer science and technology, vol. 10, 1969. p. 765.
[4] Ageev EP, Kotova SL, Skorikova EE, Zezin AB. Vysokomol Soedin Ser A 1996;38:323.
[5] Ageev EP, Vikhoreva GA, Galbraikh LS, Matushkina NN, Chaika EM, Yaminskii IV. Vysokomol Soedin Ser A 1998;40:1198.
[6] Nam SY, Lee YM. J Membr Sci 1997;135:161.
[7] Shieh JJ, Huang RYM. J Membr Sci 1997;127:185.
[8] Gazizov AD, Zhumadilova GT, Bimendina LA, Kudaibergenov SE. Polymer 2000;41:5793.
[9] Kaljuzhnaya RI, Rudman AR, Vengerova NA, Razvodovskii EF, El'tsefon BS, Zezin AB. Vysokomol Soedin Ser A 1975;17:2787.
[10] Watt G, Chrisp J. Anal Chem 1954;26:452.
[11] Zezin AB, Rogacheva VB, Komarov VS, Razvodovskii EF. Vysokomol Soedin Ser A 1975;17:2637.
[12] Kudaibergenov SE, Nurkeeva ZS, Sigitov VB, Akimbekova KZh, Ushanov VZh. Macromol Chem Phys 1997;198:183.
[13] Koetz J, Philipp B, Kudaibergenov SE, Sigitov VB, Bekturov EA. Colloid Polym Sci 1988;266:906.