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Polymer 41 (2000) 5793–5797

polymer

Interpolymer complexes of some vinyl copolymers in a solution and on the boundary of two liquid phases

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

Institute of Polymer Materials and Technology, Kazakh–American University, Satpaev Str.18a, 480021 Almaty, Republic of Kazakhstan

Received 29 June 1999; received in revised form 15 September 1999; accepted 13 October 1999

Abstract

By electrochemical and spectroscopic methods the interaction of acrylic acid and vinylbutyl ether, acrylic acid and styrene, vinyl ether of monoethanol amine and styrene copolymers with some anionic (polyacrylic and polymethacrylic acids) and cationic (polyvinyl ether of monoethanol amine and poly-*N*-methyl-4-vinylethynyl piperidole-4) polymers have been investigated in a solution and on the boundary of two non-mixing liquids. The formation of interpolymer complexes with exact composition occurs. Upon realization of complexation on the liquid–liquid boundary the complex formation reaction has some time, caused obviously by diffusion of interacting macromolecules to the interface layer where the interaction takes place. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Interpolymer complexes; Boundary; Interaction

1. Introduction

It is known that the polymers containing functional groups can react with various high and low molecular weight substances and form polymer complexes [1–4]. Interpolymer complexes are usually obtained by the mixing of pre-existing complementary macromolecules in the common solvent (so called the complexes of mixing) or by the matrix polymerization.

Recently the complex formation reaction on the boundary of two non-mixing liquids, for example benzene–water, which dissolve the initial interacting components have been elaborated. These non-mixing solvents are the cross-selective ones [5] for interacting polymers and polymer complexes are formed as thin films on the boundary of the two phases [6,7].

The realization of complex formation reaction on the boundary of the two phases can be considered as a new method of obtaining polymer complexes in addition to traditional methods (the complexes of mixing or those obtained by matrix polymerization). Besides, this method of carrying out a complex formation reaction allows thin films of polyelectrolyte complexes (PEC) to be ontained in a single stage while the preparation of membranes and thin films from PEC is usually a multistage process and includes obtaining and separating of PEC as a precipitate, its dissolution in a ternary water–acetone–salt mixture, casting, removing of ingredients and sometimes thermal treatment. PEC formation reaction at the interface represents a new method of synthesis of various types of membranes or thin films and has not yet been extensively studied.

In this paper we report the results of complex formation in a solution and on the liquid–liquid interface between oppositely charged macromolecules.

2. Experimental

2.1. Materials

Copolymers of acrylic acid and vinylbutyl ether (AA/VBE), acrylic acid and styrene (AA/St), vinyl ether of monoethanol amine and styrene (VEMEA/St) were synthesized by radical polymerization in ethanol with azoisobutyronitrile ($C = 5 \times 10^{-3}$ mol/l) as the initiator. Copolymers were purified by three-fold precipitation from ethanol into diethyl ether. The composition of the copolymers was determined by element analysis and potentiometric titration. The number-average molecular weight M_n of the copolymers determined by ebullioscopy is in the range $(20–30) \times 10^3$.

Polyvinyl ether of monoethanol amine (PVEMEA) was synthesized by gamma-irradiation polymerization by means of ^{60}Co “RXM-γ-20M” at an irradiation dose of 170 rad/s

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

PII: S0032-3861(99)00767-3

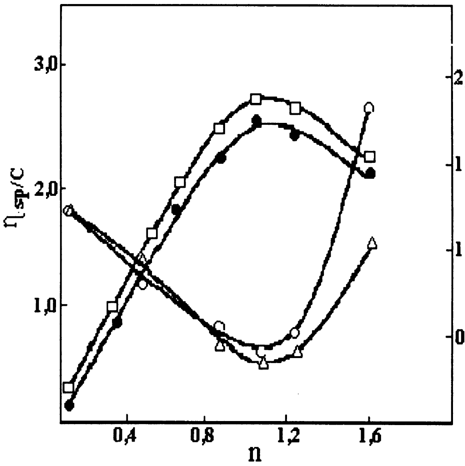


Fig. 1. Viscometric (○ ,△) and spectroturbidimetric (□, ●) titration curves for the AA/VBE–PVEMEA system. [AA]:[VBE] = 97:3 (○, ●) and 87:13 mol% (□, △).[AA/VBE] = [PVEMEA] = 5×10^{-3} mol/l; n = [AA/VBE]/[PVEMEA].

during 8 h [8]. The number-average molecular weight of PVEMEA M_n is equal to 25×10^3.

Poly-*N*-methyl-4-vinylethynil piperidole-4 (PVEP) was synthesized by the procedure described in Ref. [9]. The polymer was purified by three-fold precipitation from *N*,*N*-dimethylformamide into diethyl ether and dried under vacuum at 313 K. The viscosity-average molecular weight M_η of PVEP, determined according to the equation $[\eta] = 1.17\times10^{-4}M^{0.71}$ [10], is 70×10^3.

Poly-2-vinylpyridine (P2VP) (weight-average molecular weight $M_w = 3.4\times10^5$), sodium poly(styrenesulfonate) (SPSS) ($M_w = 3\times10^5$), poly(acrylic) (PAA) and poly(methacrylic) (PMAA) acids with viscosity-average molecular weights $M_\eta = 250\times10^3$ and 150×10^3, respectively, were purchased from "Polyscience" (USA) and used without purification.

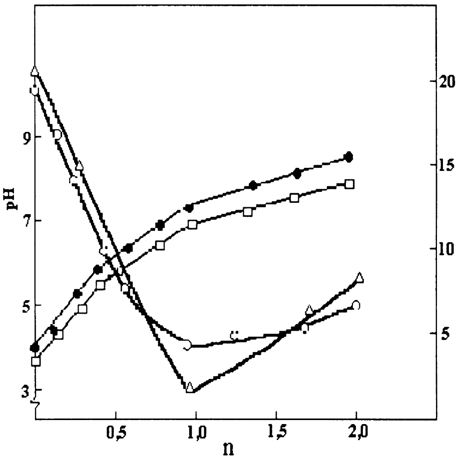
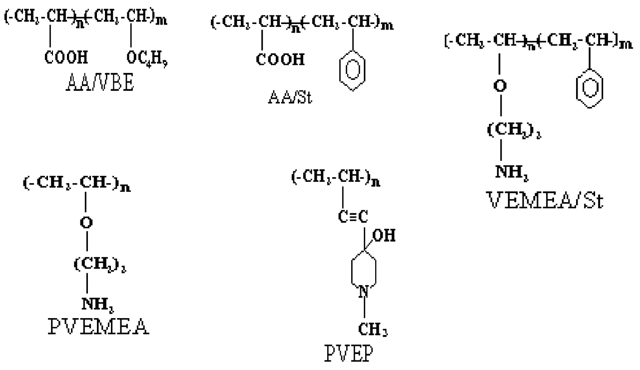


Fig. 2. Potentiometric (●, □) and conductometric (○, △) titration curves for AA/VBE–PVEP systems. [AA]:[VBE] = 97:3 (○, ●) and 87:13 mol% (□, △).[AA/VBE] = 5×10^{-3} mol/l; [PVEP] = 5×10^{-2} mol/l; n = [PVEP]/[AA/VBE].

Chemical formulae of the synthesized polymers and copolymers are given below:



Reagent-grade sodium dodecylsulfonate (SDS) and KCl were used.

2.2. Methods

Potentiometric and conductometric titrations were carried out on the pH-meter "OP-211/1" and conductometer "OK-102/1" ("Radelkis", Hungary) in a thermostated cell.

Spectroturbidimetric titrations were carried out on a "Spekol-11" spectrophotometer (Germany) at wavelengths $\lambda = 340$ and 420 nm at room temperature.

IR spectra of polymers and polyelectrolyte complexes (PEC) in solid state as well as films were obtained with a "UR-20" spectrophotometer (Germany).

Raman spectra of samples as thin films were registered with "Ramanor HG.2S" (France). The 514.5 nm line of the argon ion laser was used for excitation.

ESR spectra of Cu^{2+}-complexes were registered on the spectrometer "JEOL ME 3X ESR" (Japan) at 77 K.

The viscosity of the solutions was measured in an Ubbelohde viscometer.

Complex formation reactions on the boundary of two non-mixing liquids were performed as follows: to the aqueous solution of the water-soluble polymer component, the benzene solution of the second component was added gradually so that the surface of the aqueous solution was fully covered by the organic solvent. The formation of thin films of polyelectrolyte complex occurs immediately. The so-formed thin film is removed. After repeated removal of thin films (4–5 times) the quantity of non-reacting polymers was determined. For example, for AA/VBE-PVEMEA system the potentiometric titration of water solution of PVEMEA after the last removal of PEC film by HCl solution showed that about 20% of PVEMEA remains in solution, i.e. about 80% of this polymer forms AA/VBE–PVEMEA complex as thin film. The thickness of the films depends on the concentration of the reacting components and varies from 10 to 100 μm. PEC films are stable and swollen in water and are not soluble in ordinary organic solvents. In the free-standing state the PEC films are very fragile and are not convenient for some procedures but in

Table 1
Compositions of copolymers and polyelectrolyte complexes with their participation

Copolymer	Composition of copolymer [ionic]:[nonionic] (mol%)	The second component of PEC	Composition of PEC [anionic]/[cationic]	
			Solution	Boundary
AA/VBE	97:3	PVEMEA	1:1	
	87:13		1:1	
AA/VBE	97:3	PVEP	1:1	
	87:13		1:1	
AA/VBE	55:45	PVEMEA		1:2
VEMEA/St	15:85	PAA		1:2
VEMEA/St	27:73	PMAA		1:1
AA/St	12:88	PVEP		2:1
				1:1
VEMEA/St	27:73	SDS		
		$C = 5 \times 10^{-3}$		4:1
		$C = 5 \times 10^{-4}$		2:1
		$C = 1 \times 10^{-4}$		1:1
VEMEA/St	27:73	Cu^{2+}		1:2

the swollen state they may be used, for instance, for pervoparation purposes.

3. Results and discussion

According to the principles of physico-chemical analysis the deviation of the property—the binary mixtures composition dependencies from additivity testifies to the formation of the new compound with definite composition.

Figs. 1 and 2 represent the viscometric, spectroturbidimetric, conductimetric and potentiometric titration curves for AA/VBE–PVEMEA (Fig. 1) and AA/VBE–PVEP (Fig. 2) systems in solution. The curves show the maxima and minima as well as the points of inflection denoting the composition of the formed polyelectrolyte complex. The compositions of the PECs and some characteristics of initial polymers are summarized in Table 1.

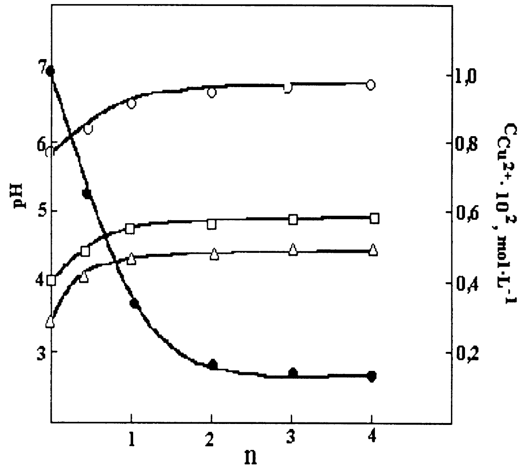
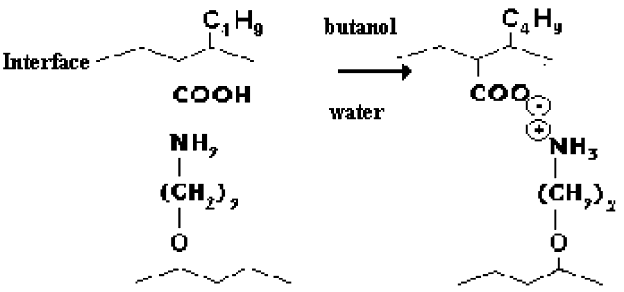


Fig. 3. Determination of the composition of complexes for the VEMEA/St–SDS (○), VEMEA/St–PMAA (□), VEMEA/St–PAA (△) and VEMEA/St–Cu^{2+} (●) systems on water–benzene boundary. $[SDS] = 1 \times 10^{-4}$; $[Cu^{2+}] = 1 \times 10^{-2}$; $[PAA] = [PMAA] = [VEMEA/St] = 5 \times 10^{-3}$ mol/l; n = [VEMEA/St]/[polyanion].

Analogous curves have been obtained at titration of different polymer systems on the boundary of two non-mixing liquids. In Fig. 3 the dependencies of pH and concentration of Cu^{2+} ions on the molar ratio of the interacting components on the water–benzene interface are represented. The composition of PECs was determined from the bends of titration curves and are given in Table 1. The composition of PECs with the participation of PVEP formed on the boundary depends on the temperature (Fig. 4 and Table 1). This may be connected to the different conformational states of PVEP macromolecules at various temperatures [10]. It was found [10] that water solutions of PVEP exhibit a lower critical solution temperature (LCST) at 298 K. Complex formation at the boundary of the two phases was carried out at $T >$ LCST (323 K) and at LCST (298 K). On raising the temperature, the PVEP macromolecules undergo a conformation transition from extended coil conformation (at 298 K) to compact coil (at 323 K) and as a result complexes richer in PVEP macromolecules are formed.

The complex formation reaction on the liquid–liquid boundary is schematically shown below:



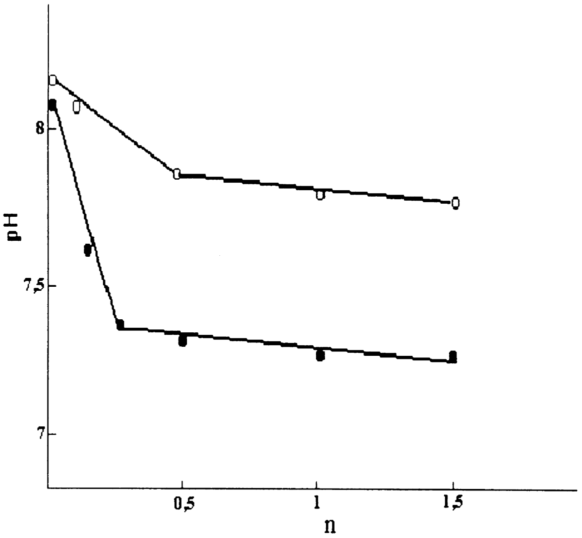


Fig. 4. Potentiometric titration curves of aqueous solution of PVEP by butanol solution of AA/VBE at $T = 298$ (○) and 323 K (■). [AA]:[VBE] = 55:45 mol%; [PVEP] = 2.4×10^{-3} mol/l; [AA/VBE] = 1.2×10^{-2} mol/l; n = [AA/VBE]/[PVEP].

Complex formation is obviously caused by the transfer of protons from carboxylic to amine groups.

IR investigations of PAA–PVEMEA complexes testify to the formation of the salt $COO^{-} \cdots NH_3^{+}$ bonds between reacting polymer components. IR spectra of AA/VBE and PVEMEA contain the characteristic absorption band of C=O groups at 1720–1710 cm^{-1}, C–O–C bond at 1128 cm^{-1} and NH_2 groups at 1576 cm^{-1}. In the IR spectra of [AA/VBE]:[PVEMEA] = 1:2 complex obtained at the boundary, the absorption band of C=O groups disappears and new absorption bands at 1563 and 3235 cm^{-1} appear. The first band is connected with the absorption of carboxylate anions (the region of absorption of COO^{-} groups is 1550–1610 cm^{-1}). The second band is identified as the absorption band of NH_3^{+} groups (the region of absorption of NH_3^{+} groups is 3150–3350 cm^{-1}). The absorption band of C–O–C groups remains unchanged. The appearance of the absorption band of COO^{-} and NH_3^{+} groups in the IR spectra of complex film thus confirms that these complexes are stabilized by salt bonds [11]. Analogous results have been obtained from FT-IR spectra of polyelectrolyte complex membranes prepared from chitosan and polyacrylic acid [12].

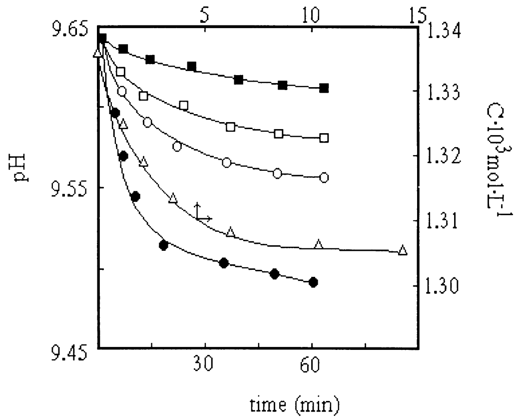


Fig. 5. Change of pH of aqueous solution of PVEMEA (■, □, ○, ●) and concentration of SPSS in water (△) with time at the addition of butanol solution of AA/VBE (■, □, ○, ●) and benzene solution of P2VP (△) at T = 288 (■), 293 (□), 298 (○, △) and 303 K (●). [AA/VBE] = 5×10^{-2}; [PVEMEA] = 1×10^{-2}; [SPSS] = 5×10^{-3}; [P2VP] = 5×10^{-2} mol/l; [AA]:[VBE] = 55:45 mol%.

Table 2
Activation energy of PEC formation process on the boundary of two phases

Interacting system	Composition of PEC	E (kJ/mol)
AA/VBE–PVEMEA	1:2	40.7
PAA–VEMEA/St	2:1	22.5
VEMEA/St–SDS	1:1	13.1
VEMEA/St–Cu^{2+}	1:2	4.4

The mechanism of PEC formation on the liquid–liquid interface is similar to the process taking place in aqueous solution. However the interface layer prevents a full mixing of the components, therefore the rate of reaction is probably controlled by diffusion of interacting macromolecules to the interface layer.

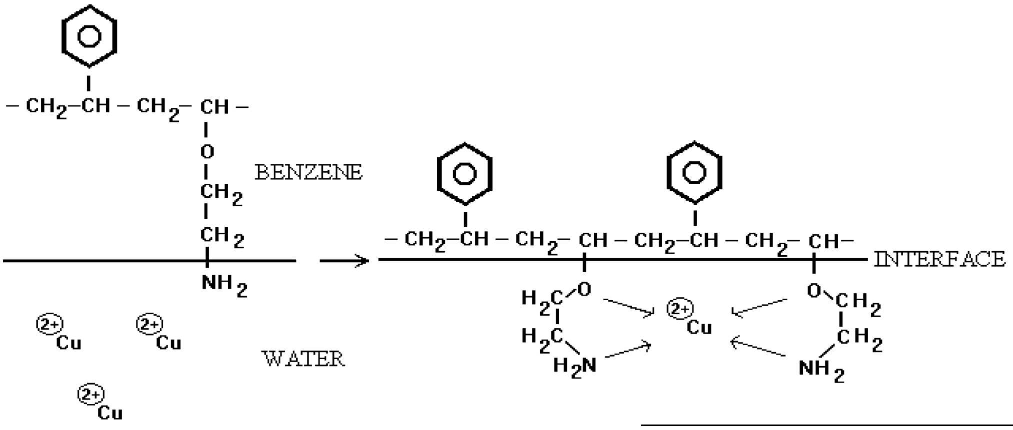
It is known that complex formation reaction in a solution is practically completed instantaneously due to the cooperative character of this process stipulated by the simultaneous rise of a great number of interchain bonds [3]. At the same time the conditions for carrying out the complex formation reaction on the boundary of two non-mixing liquids and the formation of PEC as thin films must cause some difficulties in accessing reacting groups of complementary molecules, which causes a temporary extension of the interaction. Therefore it was found to be possible to realize the complex formation reaction on the boundary for some time. In Fig. 5 the change of pH and concentration of SPSS at the time of the addition of butanol solution of AA/VBE and benzene solution of poly-2-vinylpyridine (P2VP) to aqueous solution of PVEMEA and SPSS is represented. As it is seen the complex formation reaction is completed in the first 15 min just as in a solution. The measurement of pH at various temperatures allowed calculation of the activation energy of complexation (Table 2). As it is seen from Table 2

Table 3
IR and Raman spectra of VEMEA/St copolymer and its complexes with Cu^{2+} formed at the water–benzene interface

Bond	Frequency (cm^{-1})		
	IR	Raman	IR (complex)
ν_s(C–O–C)	1090	1090	1060
ν_{as}(C–O–C)	1210	1210	1200
ν(C–N)	1325	1323	1320
δ(C–H)	1465	1466	1465
ν_s(N–H)	3315	3320	–
ν_{as}(N–H)	3387	–	3350

the complex formation reaction between VEMEA/St copolymer and Cu^{2+} ions or SDS is the most preferable, probably due to mutual access of both interacting components on the boundary as a result of the small size of the second reacting component (metal ions or surfactant molecules).

The composition of VEMEA/St–SDS complexes depends on the concentration of surfactant (Table 1) and is determined by the critical concentration of micelle formation of surfactant (CCM). At $C_{SDS} < C_{CCM}$ equimolar complexes are formed; at $C_{SDS} > C_{CCM}$ the complex particles are enriched by SDS molecules and are precipitated. Complexation of VEMEA/St with Cu^{2+} ions is accompanied by the formation of interfacial blue thin film with the maximal absorbance at $\lambda = 680$–700 nm. Table 3 presents the IR and Raman spectra of VEMEA/St–Cu^{2+} complexes. Shifting of C–O–C and N–H bands to a lower frequency region confirms the participation of oxygen and nitrogen atoms in the complexation reaction. Parameters of ESR spectra ($g_{\perp} = 2.033$, $g_{\parallel} = 2.260$, $A \parallel = 170$ Oe) suggest the participation of Cu^{2+} ions in the chelate cycle as shown below:



4. Conclusions

The interaction of some vinyl copolymers in complex formation reactions with complementary macromolecules in a solution and on the boundary of two non-mixing liquids has not been studied before. The compositions of such interpolymer complexes are determined. The complexation of the investigated copolymers is confirmed by electrochemical and spectral methods. The formation of interpolymer complexes on the boundary of two phases with exact composition can be considered as evidence of the fact that the realization of complex formation reaction on the liquid–liquid boundary is a new method of obtaining polymer complexes in addition to traditional methods. Previously the polymer complexes were usually obtained by the mixing of pre-existing complementary macromolecules in a common solvent or by matrix polymerization. At the realization of complex formation reaction on the boundary of two phases the interpolymer complexes are formed as thin films, which will probably be interesting for the separation of liquids with similar properties as well as for ultrafiltration and dialysis purposes.

Acknowledgements

This work was supported by INTAS-1746 grant.

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