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ORIGINAL CONTRIBUTION

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Interpolymer complexes of copolymers of vinyl ether of diethylene glycol with poly(acrylic acid)

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Abstract The complex formation reactions of poly(vinyl ether of diethylene glycol) as well as vinyl ether of diethylene glycol–vinyl butyl ether copolymers with poly(acrylic acid) have been studied in aqueous and alcohol solutions. The formation of interpolymer complexes which were stabilized by hydrogen bonds was shown. The effects of molecular weight of poly(acrylic acid) and the nature of the nonionic polymer on the composition and stability of interpolymer complexes were clarified. The critical pH values of complexation were determined for different systems with various molecular weights and hydrophobic–hydrophilic balances. The stability of the interpolymer complexes formed in aqueous and alcohol solutions with respect to dimethylformamide addition was evaluated. The role of hydrophobic interactions and the presence of active groups on stability of the interpolymer complexes is discussed.

Keywords Interpolymer complexes Hydrophobic–hydrophilic balance · Critical pH · Stability

Introduction

Interpolymer complexes (IPC) stabilized by hydrogen bonds are the products of interaction between proton-donating and proton-accepting polymers in solutions. A number of studies have been performed on the subject. The general regularities of complex formation reactions, the properties of IPC as well as some perspectives of their application have been [1–5]. The complexation of poly(carboxylic acids) with various nonionic proton-accepting polymers in aqueous and organic media has been described in the literature. Usually the macromolecules of proton-accepting polymers contain oxygen or nitrogen atoms, which play the role of proton acceptors; therefore, practically all water-soluble nonionic polymers are able to form hydrogen-bonded complexes with poly(carboxylic acids). However, the influence of proton-accepting centres in nonionic polymers on the complex formation ability of polymers is has not been considered yet. Besides the question of the stability of polycomplexes in solvents of different nature requires further clarification.

Recently considerable attention has been paid to a novel class of water-soluble polymers which contain different ether pendant groups; however, this class of macromolecular compounds is represented by a limited number of polymers, for example, poly(vinyl methyl ether) [6–8], poly(methyl triethylene glycol vinyl ether) [9], poly(ethoxyethyl vinyl ether) [10], poly(vinyl ether of ethylene glycol) (PVEEG) [11, 12], poly(vinyl ether of diethylene glycol) (PVEDEG) [11, 12]. Some of the previously mentioned polymers are characterized by the presence of a lower critical solution temperature (LCST) in aqueous solutions [6–8, 10].

Our research group is interested in the study of polymers based on vinyl ethers of glycols. Earlier we demonstrated the complex formation ability of copoly(vinyl ethers of glycols) with poly(carboxylic acids) in aqueous and organic solutions [13–18, 19]. It was shown that these IPC are prospective materials for the preparation of composite polymeric films with regulated swelling properties [20].

In the present work we studied the complex formation between homopolymers and copolymers of vinyl ether of diethylene glycol and poly(acrylic acid) (PAA) in aqueous and organic solutions. It was demonstrated that the complexing ability of polymers and that the stability of the polycomplexes formed depend on the number of proton-accepting centres in the nonionic polymer and the nature of the solvent.

Experimental

Synthesis and characterization of copolymers

PVEDEG, PVEEG, poly(vinyl butyl ether) (PVBE) and copolymers of VEDEG with vinyl butyl ether (VBE) were synthesized by a γ-ray-irradiation polymerization method in mass at high degrees of conversion (more than 40%) with the help of ^{60}Co "MRX-γ-25M" at an irradiation dosage of 1 Gy/s as described in Refs. [11, 12]. The copolymers synthesized were reprecipitated several times from ethanol to diethyl ether and dried in a vacuum desiccator at 30 °C until a constant weight was achieved. The viscosity-average-molecular weights of PVEDEG and PVEEG in water were calculated according to the equations [12]

$$[\eta] = 28.9 \times 10^{-4} M^{0.40} (\text{for PVEDEG}) \ ,$$

$$[\eta] = 8.8 \times 10^{-4} M^{0.50} (\text{for PVEEG})$$

and are (85 ± 5) × 10^3 and (75 ± 5) × 10^3 g/mol, respectively.

The evaluation of number-average molecular weight of the copolymers was conducted using ebullioscopy. The composition of the copolymers was determined by ^{13}C NMR spectroscopy in dimethyl sulfoxide solutions. The spectra were recorded using a Bruker Avance 250 DPX spectrophotometer with a long delay between pulses (15 s). The applied pulse was $\pi/2$. Tetramethylsilane was used as a standard. DEPT-135 subspectra were generated for identification of chemical shifts. A typical spectrum of VEDEG–VBE is depicted in Fig. 1. The composition of the copolymers was calculated through the intensity ratio $[CH]/[CH_3]$ related to the chemical shifts of 73.53 and 13.90 ppm, respectively. The synthesis conditions as well as the composition and molecular weights of the copolymers are shown in Table 1.

PAA with molecular weights of 2 × 10^3, 25 × 10^4, 75 × 10^4 and 125 × 10^4 g/mol was purchased from Aldrich and was used without further purification.

Methods

The viscosity measurements were performed with a Ubbelohde viscometer at 25 ± 0.1 °C with a flow time of 100–120 s.

The turbidimetric titrations were carried out using a SPEKOL spectrophotometer (Germany) at room temperature at 400 nm.

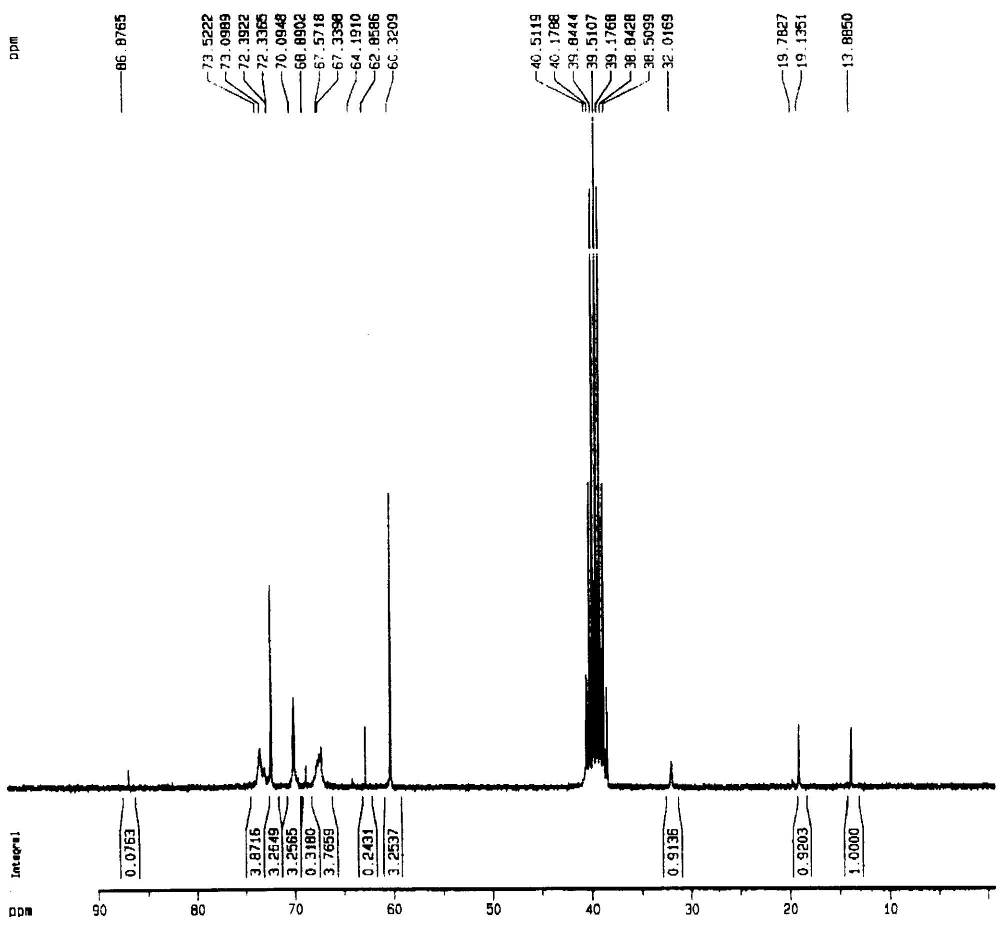

Fig. 1 ^{13}C NMR spectrum of copolymer of vinyl ether of diethylene glycol and vinyl butyl ether (*VEDEG-co-VBE*) (74:26 mol%)

Table 1 Synthesis of copolymers

Feed mixture (mol%)		Irradiation dose (kGy)	Copolymer composition (mol%)		M_n (g/mol × 10^{-3})
VEDEG	VBE		VEDEG	VBE	
90.0	10.0	39.96	91.1	8.9	27 ± 3
80.0	20.0	46.80	82.9	17.1	26 ± 3
70.0	30.0	50.40	74.3	25.7	25 ± 3
50.0	50.0	59.60	54.2	45.8	23 ± 3

The pH of the solutions was adjusted with very small amounts of 0.1 M HCl or NaOH and was determined using an EV-74 pH meter (USSR).

The samples of dry polycomplexes were obtained by mixing 0.1 M solutions of PVEDEG and PAA (1:2) in 2-propanol, centrifugation and drying in a vacuum desiccator at 30 °C until a constant weight was achieved. The IR spectra of the polycomplexes and the initial polymers were recorded using a JASCO IR-810 spectrophotometer (Japan).

Results and discussion

Complex formation of homopolymers in aqueous solutions

Recently we reported the complex formation of copolymers of VEEG with PAA [13–19]. The formation of stoichiometric IPC both in aqueous and organic solutions was observed.

Unlike PVEEG, PVEDEG possesses a higher number of proton-acceptor oxygen atoms in its pendant group. Earlier we demonstrated that nonionic polymers containing higher numbers of proton-accepting centres are characterized by a greater ability to form IPC [21] with poly(carboxylic acids). Taking into account these data we supposed that PVEDEG would also possess greater complexing ability with PAA in comparison with PVEEG. In other words, the stability of the IPC formed from PVEDEG should be higher than that of PVEEG complexes.

Turbidimetric and viscometric titration curves of PAA by PVEDEG at pH 3.0 are shown in Fig. 2. The maximum and minimum positions indicate the formation of IPC containing two carboxylic groups per PVEDEG unit. The formation of stoichiometric complexes between PAA and the majority of nonionic polymers, such as poly(ethylene oxide) (PEO), poly(vinylpyrrolidone), poly(vinylmethyl ether) and poly(vinyl alcohol), is known from the literature [3]. Probably, the formation of IPC with participation of PVEDEG occurs according to the scheme in Fig. 3.

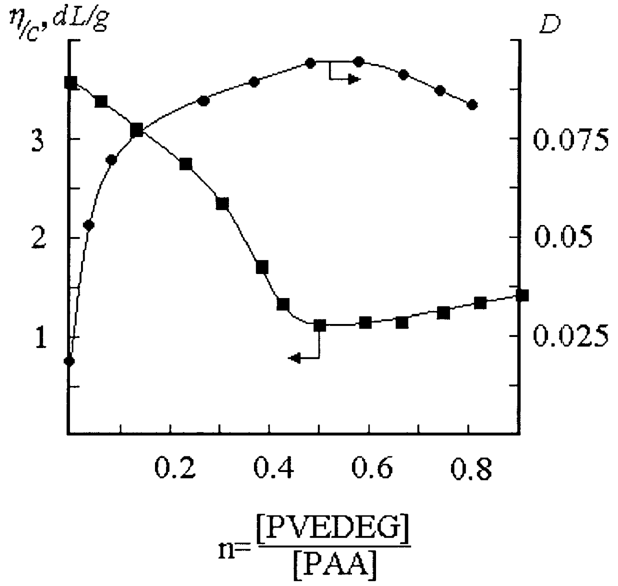

Fig. 2 Viscometric and turbidimetric titration curves of poly(acrylic acid) (*PAA*) by PVEDEG in water. [PAA] = [PVEDEG] = 0.05 M, pH 3.0

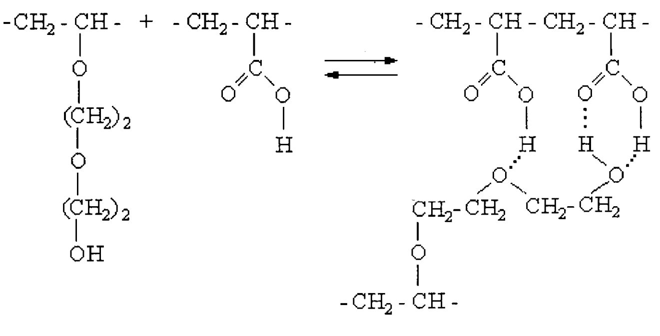

Fig. 3 Postulated complex mechanism formation

Tsuchida and Abe [3] demonstrated the existence of critical pH values for systems composed of mixtures of poly(carboxylic acids) and nonionic polymers in aqueous solutions. Below this value the formation of IPC and the appearance of a precipitate are observed. In our previous works [16–18, 21] we suggested considering the critical pH values as a criterion for the ability to form IPC for any interacting system that is composed of a poly(carboxylic acid) and a nonionic polymer. The higher the critical pH value, the greater the ability of the system to form complexes.

In the present study we determined the critical pH values for a system of PVEDEG–PAA using samples of PAA with different molecular weight. The dependence of the optical density of the mixture of the polymers on

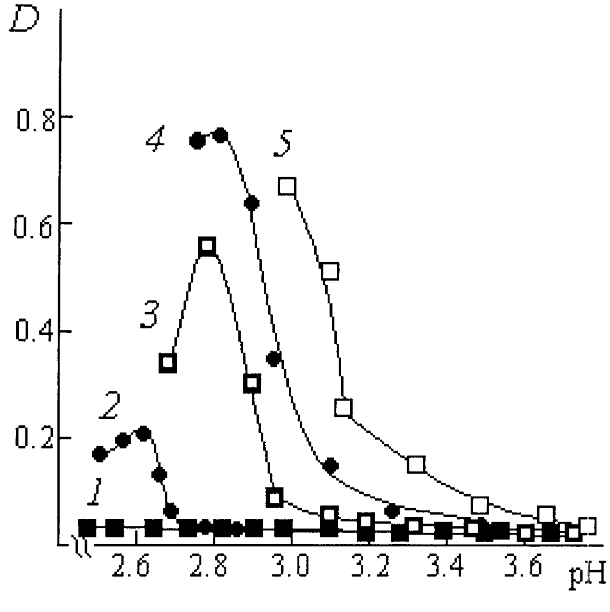

Fig. 4 Dependence of the optical density of PVEDEG–PAA (*1*, *3*–*5*) and poly(vinyl ether of ethylene glycol) (*PVEEG*)–PAA (*2*) mixtures (1:2) on pH. Molecular weight of PAA: 2,000 (*1*), 250,000 (*2*, *3*), 750,000 (*4*) and 1,250,000 (*5*). [PAA] = [PVEDEG] = [PVEEG] = 0.01 M

pH is shown in Fig. 4. It is seen that PAA with a molecular weight of 2,000 g/mol does not form polycomplexes. Kabanov and Papisov [1] reported that for the cooperative effect involved in polyacid–nonionic polymer complex formation a minimum chain length is required. Probably, the molecular weight of PAA of 2,000 g/mol is below the minimal chain length required for complexation and polycomplexes are not formed. An increase in the molecular weight of PAA in the range 250,000–1,250,000 g/mol shifts the critical pH values to a higher pH region owing to the strengthening of the ability of macromolecules to form complexes. Besides, as is seen from Fig. 4, the PVEDEG–PAA system (curve 3) is characterized by higher critical pH values than was reported for PVEEG–PAA [16, 18] (curve 2), indicating the greater complexing ability of PVEDEG in comparison with PVEEG.

Thus, the composition of IPC and the complex-forming ability of polymers strongly depends on the number of proton-accepting atoms in the nonionic polymers. An increase in the number of proton-accepting atoms in the elementary unit of the nonionic polymer as well as an increase in the molecular weight of the polymers strengthens the ability of the macromolecules to form IPC.

Effect of copolymer hydrophobicity

In aqueous solutions the IPC are formed owing to the cooperative system of hydrogen bonds and additional stabilization of a compact structure by hydrophobic interactions; therefore, the major factors that govern the complex formation reactions in aqueous solutions are the complementarity of the interacting macromolecules and their hydrophobic–hydrophilic balance.

A disturbance of the macromolecular complementarity usually affects the complex-formation processes. The complementarity of the macromolecules can be broken by ionization of the polyacid or by introduction of inactive groups into the structure of the macromolecules. Iliopoulos and Audebert [22] showed that ionization of PAA up to 10% completely prevents the complex formation with PEO. Krupers et al. [23] studied the effect of nonionic structure defects of hydroxyethyl methacrylate (HEMA) introduced into PAA on the complex formation with (PEO). They showed that increasing the number of HEMA structure defects in PAA results in a decreased degree of complexation. According to Bekturov and Bimendina [2] the IPC composed of copolymers containing inactive groups (so-called systems with broken complementarity) are less stable than the complexes of homopolymers. The stabilization of IPC by hydrophobic interactions can be considerably enhanced by hydrophobization of polyacid or nonionic polymer. Kabanov and Papisov [1] showed that poly(methacrylic acid) (PMAA) forms stronger complexes with PEO in comparison with PAA owing to the greater hydrophobicity of PMAA. Shenkov et al. [24] demonstrated that complexes of poly(propylene oxide) (PPO) with PAA possess higher stability than the complexes of PEO because of the more hydrophobic character of PPO. Recently [25, 26] it was also shown that the modification of nonionic macromolecules of poly(ether–ester)s by attachment of hydrophobic side groups promotes the complex formation with poly(carboxylic acids). Kousathana et al. [27] have shown that the considerable contribution of hydrophobic interactions to the stabilization of IPC can be achieved in the systems containing one of the polymeric components with a LCST in aqueous solutions. Earlier [14, 17] we demonstrated that the introduction of hydrophobic groups of VBE into the structure of PVEEG also leads to the formation of more stable complexes with PAA and PMAA.

In the present work we synthesized novel copolymers of VBE with VEDEG. These copolymers, VBE–VEDEG, are characterized by the presence of a LCST in aqueous solutions. This fact according to the previously mentioned work [27] indicates that these copolymers would provide a considerable contribution of hydrophobic interactions to the stabilization of IPC in the course of the complexation.

The data on turbidimetric and viscometric investigations of PAA interactions with VBE–VEDEG copolymers of different compositions are depicted in Fig. 5. It is seen that the addition of aqueous solutions of VBE–

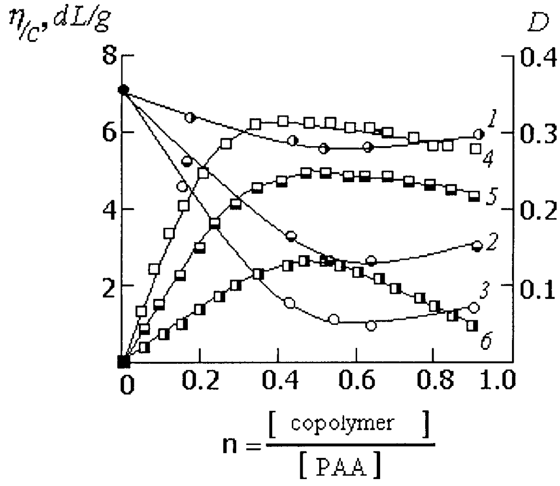

Fig. 5 Viscometric and turbidimetric tritation curves of PAA by VEDEG-*co*-VBE in water. [PAA] = [VEDEG-*co*-VBE] = 0.05 M. [VEDEG]:[VBE] (mol%) = 91:9 (*1*, *6*), 83:17 (*2*, *5*), 74:26 (*3*, *4*). pH 3.1

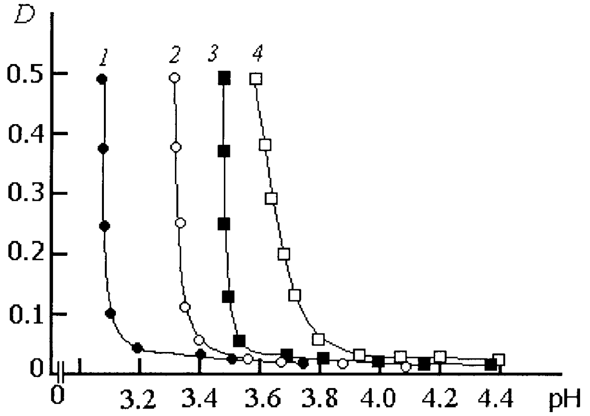

Fig. 6 Dependence of turbidity of PAA–PVEDEG (*1*) and PAA–VEDEG-*co*-VBE (*2*–*4*) solutions on pH. [PAA] = [PVEDEG] = [VEDEG-*co*-VBE] = 0.025 M. [VEDEG] = [VBE] (mol%) = 91:9 (*2*), 83:17 (*3*), 74:26 (*4*)

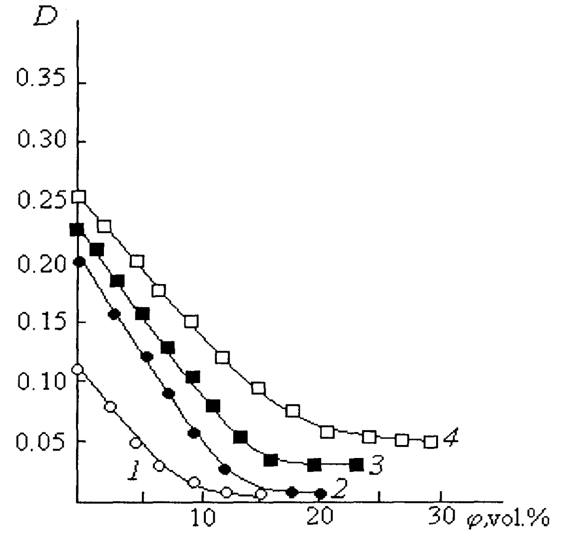

Fig. 7 Dependence of the optical density of PVEDEG–PAA (*1*) and VEDEG-*co*-VBE–PAA (*2*–*4*) mixtures (1:2) in water on addition of dimethylformamide (*DMF*). [PAA] = [VEDEG-*co*-VBE] = 0.01 M. [VEDEG]:[VBE] (mol%) = 91:9 (*2*), 83:17 (*3*), 74:26 (*4*)

VEDEG to PAA is accompanied by an increase in turbidity and a decrease in viscosity, indicating the formation of polycomplexes with more compact conformation than that of the initial macromolecules. The position of the extremes on the titration curves indicates the formation of nonstoichiometric IPC, which on average includes two monomeric units of PAA per unit of copolymers. It is seen from the viscometric curves that the more compact conformation of IPC corresponds to a higher content of VBE in the copolymer. Besides, the turbidimetric curves are also characterized by higher values of turbidity for copolymers with a higher content of VBE. Both results marginally indicate that an increase in the number of VBE units in the copolymers favours the formation of more stable complexes with PAA because of the strengthening of hydrophobic interactions. These data can be confirmed by the investigation of the effect VBE content in copolymers on the critical pH values of complexation. It is seen from the data in Fig. 6 that passing from PVEDEG to VBE–VEDEG copolymers is accompanied by a marked increase in the critical pH values. This indicates that the introduction of VBE fragments into PVEDEG macromolecules does not decrease the ability of the polymers to form complexes because of the disturbance in complementarity but increases this ability owing to the contribution of hydrophobic interactions to the IPC stabilization.

The stability of the polycomplexes formed from PAA and copolymers was also evaluated by adding the organic solvents into aqueous IPC solutions. It is seen from Fig. 7 that the addition of dimethylformamide (DMF) leads to a decrease in turbidity up to its complete disappearance caused by IPC destruction. The stability of IPC to destruction is also increased with the hydrophobization of the copolymers. Unlike the opinion of the authors of Ref. [2] in aqueous solutions the polycomplexes formed with the participation of copolymers are more stable than the IPC composed of homopolymers because of the pronounced effect of VBE groups in hydrophobic stabilization of the polycomplexes.

Complex formation in alcohol solutions and effect of inactive groups

One of the most important factors governing the interpolymer complexation is the solvent. Generally, the formation of IPC is possible when polymer–polymer interactions are stronger than polymer–solvent ones [3, 5, 28–30]. Earlier we demonstrated that the deterioration of the thermodynamic quality of a solvent favours the formation of hydrogen-bonded complexes owing to the weakening of polymer–solvent interactions [14, 18].

In the present work we studied the complex formation between PVEDEG and PAA in 2-propanol by viscometric and turbidimetric methods (Fig. 8). According to the results the composition of the IPC formed is [PVEDEG]/[PAA] = 1:2, which is in good agreement with the complexation scheme discussed before. After mixing of the initial polymer solutions the IPC was centrifuged and dried. The IR spectra of the IPC were recorded. They are characterized by the presence of bands responsible for –COOH (1,700–1,750 cm^{-1}) and C–O–C (1,050–1,100 cm^{-1}) groups, indicating the coprecipitation of both components in the IPC.

The mixing of VBE–VEDEG copolymer solutions with PAA in 2-propanol is also accompanied by the formation of IPC; however, unlike aqueous solutions the composition of the IPC strongly depends on the VBE content in the copolymers (Fig. 9). It was shown earlier [14, 17] that VBE groups do not participate in the formation of interpolymer hydrogen bonds. Moreover, in organic solvents these groups do not contribute to the hydrophobic stabilization of IPC and they enhance the polymer–solvent interactions. Hence, the presence of VBE disturbs the complementarity of the macromolecules; therefore, the composition of the polycomplexes deviates from the stoichiometry discussed. Besides, as seen from the turbidimetric data, an increase in the VBE content in the copolymers is accompanied by a decrease in the turbidity of the solutions, marginally indicating that the presence of VBE in the copolymers is unfavourable for complexation in 2-propanol, whichis probably connected with the disturbance of the macromolecular complementarity. Thus, the titration of PAA solution in 2-propanol by solutions of copolymer with relatively high contents of VBE (curve 3) and especially by homopolymer PVBE (curve 4) is not accompanied by a marked increase in the turbidity, indicating the absence of complexation.

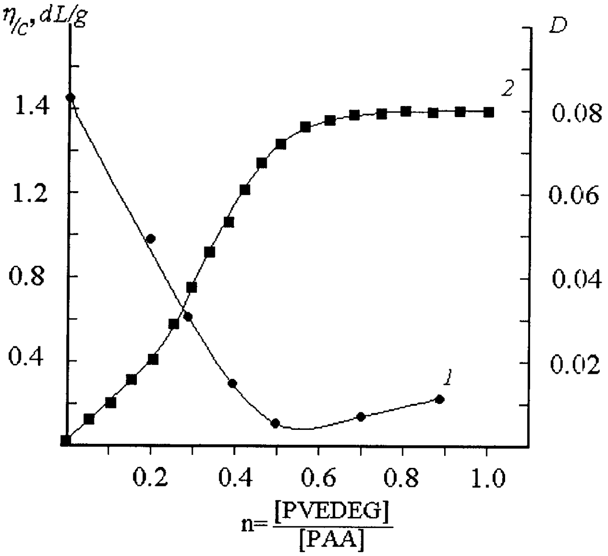

Fig. 8 Viscometric and turbidimetric titration curves of PAA by PVEDEG in 2-propanol. [PAA] = [PVEDEG] = 0.001 M

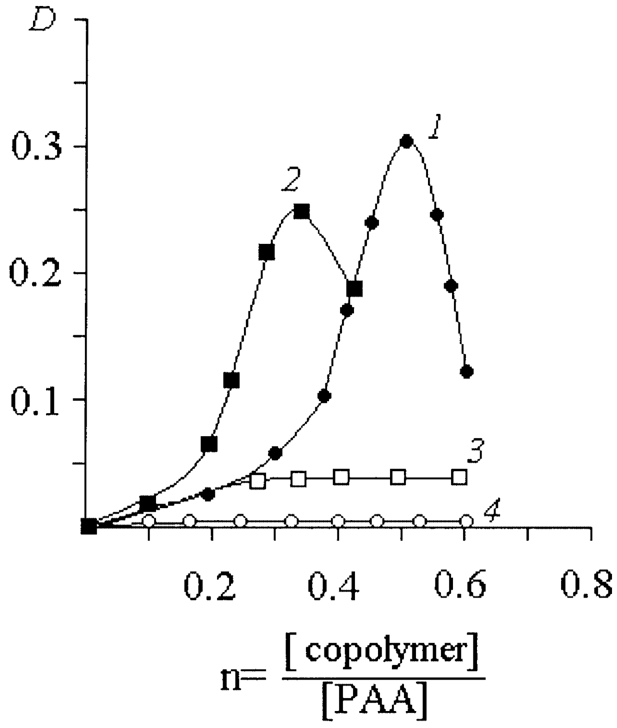

Fig. 9 Turbidimetric titration curves of PAA by PVEDEG (*1*), VEDEG-*co*-VBE (*2*, *3*) and PVBE (*4*) in 2-propanol. [PAA] = [PVEDEG] = [VEDEG-*co*-VBE] = 0.005 M. [VEDEG]:[VBE] (mol%) = 74:26 (*2*), 54:46 (*3*)

The stability of the polycomplexes formed in 2-propanol was also evaluated by adding DMF (Fig. 10). It is seen that the IPC formed by copolymers with relatively low VBE content (lower than 17 mol%) are less stable to the action of DMF in comparison with complexes of homopolymers. Thus, an increase in the VBE content in the copolymers decreases the stability of the IPC. Hence, in organic solvents the complexes formed from the copolymers are less stable than the complexes of homopolymers as was stated by Bekturov and Bimendina [2].

The comparison of the results on the stability of IPC with respect to DMF addition shows that the transition from aqueous to organic media is accompanied by a decrease in the stability of IPC for copolymers with a relatively high content of VBE (more than 17 mol.%) (Figs. 7, 10, curves 3, 4). At the same time for the

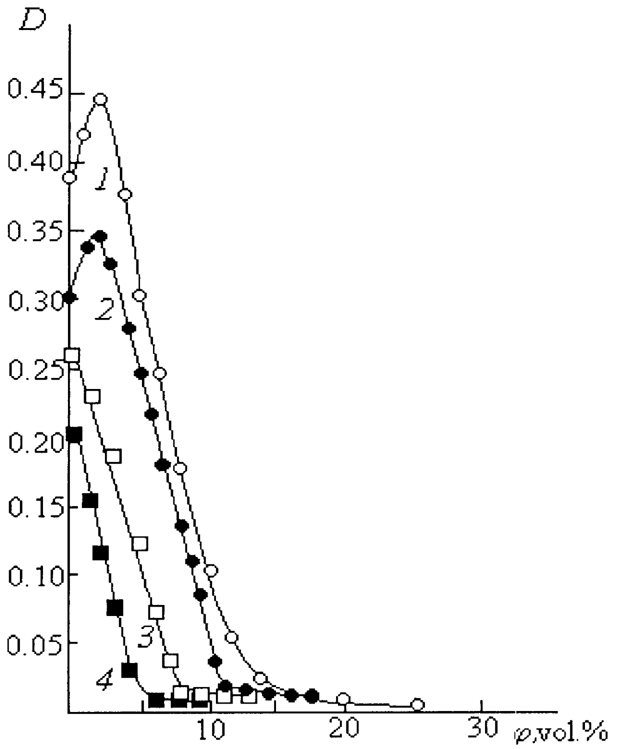

Fig. 10 Dependence of the optical density of PVEDEG–PAA (*1*) and VEDEG-*co*-VBE–PAA (*2*–*4*) mixtures (1:2) in 2-propanol on addition of DMF. [PAA] = [VEDEG-*co*-VBE] = 0.01 M. [VEDEG]:[VBE] (mol%) = 91:9 (*2*), 83:17 (*3*), 74:26 (*4*)

copolymers with a relatively low content of VBE such a transition does not influence the stability of the IPC; however, the complexes formed from PVEDEG with PAA are more stable in 2-propanol than in water (Figs. 7, 10, curve 1). These conclusions can be confirmed by the higher turbidity values for solutions of the polycomplexes in 2-propanol than in water. Probably, the transition from aqueous to organic solutions is accompanied by depressing the ionization of PAA, which increases the concentration of unionized carboxylic groups, which are able to form hydrogen bonds. This factor strengthens the complexation ability of PAA. On the other hand, the VBE units in organic solvents do not participate in hydrophobic interactions and their presence disturbs the complementarity of the macromolecules and decreases their complexing ability in organic solvents.

For copolymers with a low content of inactive VBE groups the influence of both effects (disturbance of complementarity and depression of carboxylic groups ionization upon transition from aqueous to organic solutions) is compensated. As a result the transition from aqueous to organic solutions is not accompanied by changes in the stability of the IPC. At the same time for copolymers with a high VBE content the role of hydrophobic interactions is considerable in aqueous solutions and these systems lose their stability upon transition to organic solvents (Figs. 7, 10 curves 3, 4).

Conclusions

PVEDEG as well as VBE–VEDEG copolymer form nonstoichiometric complexes with PAA in aqueous and 2-propanol solutions by hydrogen bonding because of the presence of several proton-accepting centres in their pendant group. The complexes are formed above some critical chain length of PAA only and the complex-formation ability increases with the increase in the PAA molecular weight.

Earlier the considerable role of hydrophobic interactions in the stabilization of hydrogen-bonded IPC was demonstrated by Kabanov and Papisov [1], Shenkov et al. [24], Kousathana et al. [27] and Ignatova et al. [25, 26]; however in all the works mentioned an increase in the hydrophobic contribution into the stabilization of the IPC was achieved without disturbance of the macromolecular complementarity, i.e. changes in functional group number, which are able to form hydrogen bonds (e.g. by transitions from PAA to PMAA [1], PEO to PPO [24], polyacrylamide to poly(*N*-isopropyl acrylamide) [27]). In the present work we demonstrated that the role of hydrophobic interactions in the stabilization of IPC in aqueous solutions is so considerable that even copolymers with broken complementarity can possess higher complexing ability with respect to PAA in comparison with homopolymers unlike the representations of Bekturov and Bimendina [2]. Thus, the introduction of hydrophobic VBE groups into the structure of PVEDEG intensifies the interpolymer interactions of copolymers with PAA in aqueous solutions owing to the strengthening of hydrophobic interactions. Moreover, an increase of the VBE content in VBE–VEDEG strengthens the complexing ability. For these copolymers the transition from aqueous to organic solutions is accompanied by a decrease in the stability of the IPC. However, if the role of the hydrophobic interactions in IPC stabilization is insignificant (e.g, PVEDEG–PAA) the transition from aqueous to organic media may increase the stability of polycomplexes because of the depression of the ionization of carboxylic groups.

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