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

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 prepa-
ration 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 60Co “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 \((85 \pm 5) \times 10^3\) and \((75 \pm 5) \times 10^3\) 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 13C 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 π/2. Tetradeutylsilane 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],[CH3] 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 \(2 \times 10^3\), \(25 \times 10^3\), \(75 \times 10^4\) and \(125 \times 10^4\) 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.