Radiation-chemical synthesis of thermosensitive copolymers based on the vinylbutyl ether and their complexing and emulsifying abilities

D.E. Zhunuspayev a, G.A. Mun a,∗, A.V. Dubolazov a, Z.S. Nurkeeva a, O. Güven b

a Kazakh National University, Department of Chemical Physics and Macromolecular Chemistry, 95a Karasai Batyr Street, Almaty, Kazakhstan
b Hacettepe University, Department of Chemistry, 06532 Beytepe, Ankara, Turkey

Available online 2 September 2007

Abstract

Novel water-soluble thermosensitive copolymers of vinyl butyl ether (VBE) with vinyl ether of ethyleneglycol (VEEG) and  N-vinylpyrrolidone (NVP) and ternary copolymers based on VBE, 2-hydroxyethylacrylate (HEA) and acrylic acid (AA) were synthesized by γ-induced radiation copolymerization. The composition of copolymers and average molecular weight of copolymers were determined using NMR 13C-spectroscopy and gel-permeation chromatography. It was shown that aqueous solutions of VBE–VEEG, VBE–NVP, VBE–HEA–AA have lower critical solution temperature (LCST) depending on copolymer composition. The complexation of copolymers with polyacrylic acid (PAA) was studied by turbidimetry method. Critical pH value of complexation (pHcrit.) was used as the criterion of complexing ability. The effect of composition and concentration of copolymers, as well as pH of medium on the formation of IPC was investigated. The effect of VBE–VEEG copolymers of different compositions on the stability of model hexane–water emulsions was studied. It was determined that the regulation of hydrophilic–hydrophobic balance of macrochains and copolymer concentration allows effectively influence on the stability of hexane–water emulsions.

© 2007 Elsevier B.V. All rights reserved.

PACS: 61.82.Pv; 64.75.Va

Keywords: VBE–VEEG; VBE–NVP; VBE–HEA–AA; Copolymer; Hydrophobic interaction; Hydrogen bonding; Emulsion stabilization

1. Introduction

Modification of polymers by copolymerizing with functional polymer chains has been a subject of fundamental and practical importance. Over the past decade in the field of new forms of medical products the new approach based on the use of polymeric thermosensitive systems, i.e. water-soluble polymers with the lower critical solution temperature (LCST) is developed [1,2]. A large number of theoretical models, which take into consideration either the hydrogen bonding interaction or the hydrophobic interaction alone are reported in the literature to explain the LCST phenomenon, for example, lattice-fluid hydrogen bond theory which predicts that both hydrogen bonding and hydrophobic interactions are essential to cause the LCST behaviour. The balance of the hydrophobic and hydrophilic groups in the polymer structure strongly determines the LCST. Therefore synthesis of amphiphilic copolymers containing both types of groups is of our interest.

Many scientific works in recent years have been dealing with materials containing N-alkylacrylamide monomer [3,4]. The reason is the LCST exhibited by polyalkylacrylamide water solutions and its crosslinked gel undergoes a reversible volume transition at the same temperature. Rather than controlling the LCST of well known thermosensitive polyalkylacrylamide by synthesis and polymerization of specific and relatively expensive monomers, we investigated the more practical copolymerization approach using readily available monomers: VEEG, NVP and HEA.
containing hydrophilic groups and VBE as comonomer with hydrophobic parts.

The addition of an ionizable comonomer introduces pH-sensitivity to the polymers [5–7]. Previous studies of acid copolymers in ionic solutions have revealed an S-shaped pH response curve for swelling and LCST. A higher LCST is observed at higher pH values, when the acid groups become deprotonated and are more hydrophilic. The final property of copolymer is thus a both pH- and thermosensitivity.

The advantage of the radiation-induced methods for the preparation of polymers compared with traditional methods lies in the purity of the materials and the possibility of carrying out the processes at low temperatures and the easy regulation of the kinetic rate of the reaction by varying the radiation parameters [8,9].

In the present study VBE–VEEG, VBE–NVP and ternary VBE–HEA–AA thermosensitive copolymers were prepared by irradiating the corresponding mixtures of monomers by γ-rays at ambient temperature. Kinetics regularities of copolymerization were determined. Complexation of copolymers with PAA in aqueous solutions was investigated. The effect of VBE–VEEG copolymers of various composition on the stability of model hexane–water emulsions was studied.

2. Experimental

VBE, VEEG, NVP and AA were purchased from “Alash Ltd.” (Kazakhstan). They were purified by distillation using refraction column (“Fisher Technology”, Germany). HEA, HCl, NaOH and hexane were purchased from “Aldrich Chemical Co.” (USA) and used without purification. PAA with weight-average molecular weight (Mw) 250,000 and 450,000 Da were purchased from “Aldrich Chemical Co.” (USA) and used without purification.

The synthesis of VBE–VEEG, VBE–NVP and VBE–HEA–AA copolymers was conducted using γ-initiated radical copolymerization with help of 60Co “MPX-γ-25M” radiation facility. The dose rate of 1.4 kGy/h was determined in accordance to the Fricke method [10]. Linear copolymers were purified by the precipitation of their alcoholic solutions in 10-fold excess of diethyl ether. The composition of copolymers was determined by 13C NMR spectroscopy in dimethylsulfoxide solutions. The spectra were recorded using a Bruker Avance 250 DPX spectrometer.

Molecular weight of copolymers and its distribution were determined using a GPC equipped with an Agilent 1100 series RI detector, quaternary pump, and three PL gel 5 μm MIXED-D columns in set. The eluent was DMF containing Bu4NBr (0.1% w/v) with a flow rate of 0.8 ml/min. The molecular weights were calibrated with polystyrene standards.

The Fourier transformed infrared (FTIR) spectra of polymers and their IPCs were recorded in KBr discs using FTIR spectrometer “Mattson Satellite 3000” (USA).

Optical density of copolymer solutions was measured with UV-2401 PC spectrophotometer (Shimadzu, Japan) at the wavelength 400 nm. The temperature was regulated with the help of thermo-electrically temperature-controlled cell positioner CPS-240A (Shimadzu, Japan).

The pH of solutions was measured with pH-meter “Ion Meter 3345” (Jenway LTD., UK) and was adjusted by addition of small amounts of 0.1 mol L⁻¹ HCl or NaOH. Emulsions were prepared by mixing 40 mL hexane and 10 mL water with addition of a certain amount of the copolymers and subsequent vigorous stirring with the rate 1100 rpm using Eurostar Power 1 Kika LABROTECHNIK (Germany) for 5 min.

The stability of emulsions was studied visually in a measuring cylinder. The amount of separated disperse phase was calculated using the following formula:

\[ H = \left( \frac{a}{V} \right) \times 100\%, \]

where \( a \) is the amount of separated disperse phase in mL and \( V \) is the total volume of the system (50 mL). The lifetime of emulsions was determined by extrapolation of the linear part of the curve in the beginning of the separation process to 100%.

3. Results and discussion

3.1. Synthesis of copolymers

The feed composition of monomer mixtures is shown in Table 1. The final composition of copolymers was determined by 13C NMR-spectroscopy and found to be enriched by hydrophilic comonomers VEEG, NVP and HEA–AA, which coincides with our former results, which showed that VBE is of low activity [11].

The conversions reached at different dose values are plotted in the Fig. 1. It shows that the conversions of the comonomers VBE and NVP, as an example of copolymerization, versus absorbed dose is increased abruptly at first and then slowly. At the initial stage of copolymerization, the viscosity of the system was comparatively low, and the diffusion of the macroradical towards monomers was easier. As the copolymerization proceeds, the viscosity is increased because of the conversion of the monomer into the copolymer, and this hinders the diffusion of the

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>IPC composition (copolymer/PAA)</th>
<th>pHcrit.</th>
</tr>
</thead>
<tbody>
<tr>
<td>VBE:VEEG</td>
<td>6:94</td>
<td>1:1</td>
</tr>
<tr>
<td></td>
<td>12:88</td>
<td>4:5</td>
</tr>
<tr>
<td></td>
<td>22:78</td>
<td>1:2</td>
</tr>
<tr>
<td>VBE:NVP</td>
<td>20:80</td>
<td>4:5</td>
</tr>
<tr>
<td></td>
<td>30:70</td>
<td>9:10</td>
</tr>
<tr>
<td></td>
<td>40:60</td>
<td>1:1</td>
</tr>
<tr>
<td>(VBE:HEA):AA</td>
<td>(30:70):10</td>
<td>3:20</td>
</tr>
<tr>
<td></td>
<td>(30:70):20</td>
<td>1:4</td>
</tr>
<tr>
<td></td>
<td>(30:70):30</td>
<td>1:4</td>
</tr>
</tbody>
</table>
macroradicals and reduces the reaction probability. It should be noted that the same conversion tendency upon absorbed dose is appeared for the rest binary and ternary copolymerizing system.

FTIR-spectra of isolated VBE-NVP copolymers are differed from spectra of PVBE and PVP and characterized by the presence of bands typical for lactam ring of PVP (1665 cm\(^{-1}\)) and ether group of PVBE (1100 cm\(^{-1}\)) which confirm the formation of VBE-NVP copolymers.

Fig. 2 demonstrates FTIR-spectra of ternary VBE–HEA–AA copolymers of different feed composition. They exhibits a rather sharp carbonyl stretching band of AA and HEA units around 1710–1725 cm\(^{-1}\). The presence of ether group of VBE monomer is confirmed by the presence of the duple peak of the C–O–C stretching vibration at 1040–1072 cm\(^{-1}\). The changes in the intensity, shape, and position of the C=O and C–O–C stretching mode are associated with different feed composition and, probably, with the interaction between VBE, HEA and AA units. It is clearly seen that an increase in AA content in feed mixture leads to lower intensity of VBE ether group available to form hydrogen bonding, and its interaction with HEA and AA units becomes significant, resulting in a large shift in AA (HEA) carbonyl absorption bands from 1721 to 1707 cm\(^{-1}\).

The spectra at 3000–3500 cm\(^{-1}\) region exhibits a broad band with low content of AA units in copolymer which includes hydrogen-bonded hydroxyl groups (self-associated) and free hydroxyl groups [12]. However, upon increase in AA content OH band is depressed resulting from the strong interaction of hydroxyl and ether groups in AA (HEA) and VBE units.

3.2. Phase behavior of copolymers in aqueous solution

The phase separation behaviour of copolymers aqueous solutions was investigated by turbidimetry as a function of temperature. Although the homopolymers of PVEEG, PVP, PHEA and PVBE do not exhibit any temperature sensitive behavior the copolymerization of VBE with other comonomers results in appearance of LCST in aqueous solutions of copolymers (Fig. 3).

An increase in the content of hydrophobic VBE units in VBE-VEEG copolymers shifts cloud points towards lower values whereas introduction of AA leads to higher values of phase separation temperature (\(T_{pc}\)) [13], i.e. that is the efficacy of hydrophobic interactions of VBE units is sufficiently depressed. It should be noted that this behavior was observed for water-soluble copolymers only, i.e. for copolymers, in which composition the content of VBE does not exceed 40 mol.%. A higher content of VBE in the copolymers makes them very hydrophobic and insoluble in water. The variation of pH of the aqueous solution of VBE–VEEG and VBE–NVP copolymers has no significant effect on its LCST.

Fig. 4 shows the dependence of solution turbidity on temperature at different pH values for compositions ([VBE]:[HEA]:[AA] (30:70):10 mol.%). It can be seen that a slight change in pH results in significant shift of cloud point of copolymer solution. The dependence of phase separation on pH is attributed to formation of intra- and inter-molecular hydrogen bonding complexes between the acid moiety of carboxylic acid and the hydroxyl groups of the HEA. It is well known that the complexation between nonionic polymers and carboxylic acids leads to hydrophobization of the whole system, thereby enhancing aggregation ability of the system. Increase in pH of the copolymer solution results in decrease of complex formation ability due to dissociation of carboxylic groups. As a consequence of these processes the LCST shifts to the higher values. Further increasing of the pH leads to growth of ionic repulsion between ionized groups and finally to complete disappearing of phase transition.

3.3. Complexation of copolymers with PAA in aqueous solutions

Earlier we report on interaction of PVEEG, PVP and PHEA and HEA–VBE copolymers with PAA in aqueous solutions which results in the formation of interpolymer complexes with the structure and stability to be depend on pH and temperature [10,14,15]. In the present study the composition of interpolymer complex (IPC) based on VBE–VEEG, VBE–NVP and ternary VBE–HEA–AA copolymers with PAA, effect of pH, polymer concentration on the interpolymer complexation with help of critical pH as criteria of complex formation ability was analyzed by turbidimetric method.

For example, Fig. 5 shows the variation of optical density of VBE–HEA–AA/PAA aqueous solutions as a function of \(n\), where \(n\) is the molar ratio of copolymer repeating units to PAA ones. Obviously blending of 0.01 mol L\(^{-1}\) aqueous solutions of PAA with ternary VBE–HEA–AA copolymer at pH 2.7 results in change of optical density of solution (\(D\)), that due to the presence of complexation. Mixture of
polymers with higher AA content is accompanied by a gradual decrease in $D$ extrema values. In the case of lower AA content in copolymer the saturation appears at around 1:4 molar ratio of copolymer on a repeating unit basis/PAA. The further increase of AA units in the feed mixture shifts extreme point to the higher content of PAA in the structure of IPC. Such behaviour specifies the formation of compact particles of polycomplexes more hydrophobic than components. However the presence of AA does not allow forming hydrogen bonds with PAA leading to lower degree of hydrophobicity and appearance of defects in the structure of polycomplexes.

Fig. 2. FTIR-spectra of VBE-HEA-AA ternary copolymers. Feed [VBE][HEA][AA] composition, mol.% = (30:70):10 (1), (30:70):20 (2), (30:70):30 (3) and (30:70):50 (4).

Fig. 3. Phase diagram of VBE-VEEG linear copolymers in aqueous solutions. Feed [VBE][VEEG] composition, mol.% = 22:78 (1), 12:88 (2) and 6:94 (3).

Table 1 represents composition of IPC based on PAA interaction with different copolymers. It is shown that for the polycrosses based on binary copolymers VBE content gradually affects the stiochiometry of IPC and its increase in the copolymer content produces higher inclusion of PAA units in the structure. That means the low activity of VBE proton-accepting ether centre in the interaction with carbonyl groups of PAA due to the steric hindrance of long butyl radical.

In the present work pH crit. values have been determined for VBE–VEEG/PAA, VBE–NVP/PAA and VBE–HEA–AA/PAA systems upon various copolymer composition and concentrations of initial components of solutions by turbidimetry [16]. An increase in polymer concentration as well as in VBE content conducts increase in pH crit. (Table 1). The same tendency for pH crit. values was observed earlier for other non-ionic polymer–PAA systems including PAA–PVEEG, PAA–PVP, PAA–PHEA [10,14,15]. However increase in AA content in ternary copolymer results in lowering of pH crit. meaning that AA units do not interact with PAA.

As a result the non-ionic copolymers can be arranged into the following series VBE–NVP > VBE–VEEG > VBE–HEA–AA depending on their ability to increase pH crit. for complexes with PAA due to the additional contribution of hydrophobic interactions. Replacement of methyl radicals by hydrophilic AA ones also results in sharp decrease in complex formation abilities of polymers.

### 3.4. Stabilization of model hexane–water emulsions by VBE–VEEG copolymers

An important property of all emulsifiers is their surface activity, i.e. ability to absorb at interfaces. An addition of VBE–VEEG copolymers to the mixture with 40 mL of hexane and 10 mL of water leads to formation of stable emulsions for a certain time. It can be clearly seen from the Table 2 that the emulsion lifetime is increased with concentration of the polymeric additive as well as with content of VBE in copolymers. The more hydrophobic copolymers stabilize emulsions more efficiently. The scheme of stabilization mechanism of emulsions by VEEG-VBE copolymer is depicted in Fig. 6.

4. Conclusion

Novel water-soluble thermosensitive VBE-VEEG, VBE-NVP and in addition pH-sensitive ternary VBE-HEA–AA copolymers were synthesized by γ-induced irradiation copolymerization. The copolymers were characterized by $^{13}$C NMR-spectroscopy and gel-permeation chromatography. Aqueous solutions of VBE-VEEG, VBE–NVP and VBE–HEA–AA copolymers have LCST, depending on copolymer composition as well as on pH.

References