

Competitive Hydrogen Bonding Mechanisms Underlying Phase Behavior of Triple Poly(*N*-vinyl pyrrolidone)–Poly(ethylene glycol)–Poly(methacrylic acid-*co*-ethylacrylate) Blends

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ABSTRACT: Differential scanning calorimetry (DSC) of triple blends of high molecular weight poly(*N*-vinyl pyrrolidone) (PVP) with oligomeric poly(ethylene glycol) (PEG) of molecular weight 400 g/mol and copolymer of methacrylic acid with ethylacrylate (PMAA-*co*-EA) demonstrates partial miscibility of polymer components, which is due to formation of interpolymer hydrogen bonds (reversible crosslinking). Because both PVP and PMAA-*co*-EA are amorphous polymers and PEG exhibits crystalline phase, the DSC examination is informative on the phase state of PEG in the triple blends and reveals a strong competition between PEG and PMAA-*co*-EA for interaction with PVP. The hydrogen bonding in the triple PVP-PEG-PMAA-*co*-EA blends has been established with FTIR Spectroscopy. To evaluate the relative strengths of hydrogen bonded complexes in PVP-

PEG-PMAA-*co*-EA blends, quantum-chemical calculations were performed. According to this analysis, the energy of H-bonding has been found to diminish in the order: PVP-PMAA-*co*-EA-PEG(OH) > PVP-(OH)PEG(OH)-PVP > PVP-H₂O > PVP-PEG(OH) > PMAA-*co*-EA-PEG(-O-) > PVP-PMAA-*co*-EA > PMAA-*co*-EA-PEG(OH). Thus, most stable complexes are the triple PVP-PMAA-*co*-EA-PEG(OH) complex and the complex wherein comparatively short PEG chains form simultaneously two hydrogen bonds to PVP carbonyl groups through both terminal OH-groups, acting as H-bonding crosslinks between longer PVP backbones. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3017–3036, 2007

Key words: polymer blends; interpolymer complexes; phase state; hydrogen bonding; competitive interaction

INTRODUCTION

On a macroscopic scale, physical properties of polymer materials are a function of their phase state. In turn, the phase state is often a complex and concealed function of the structure and molecular interaction. From the practical point of view, knowledge of the structure–property relationship is of considerable importance for rational design of new materials with tailored performance properties. As a rule, polymers are not miscible.^{1,2} Existence of specific favorable interactions between different polymer components allows mixing on a molecular scale. One such favorable interaction is hydrogen bonding that has been reported for many polymer blends.^{3–7} Although a considerable amount of research work has been performed on the contribution of hydrogen bonding to the phase behavior of polymer blends,^{8–13} there is lack of mechanistic

understanding of effects of hydrogen bonding on the phase state of polymer blends.

Polymers containing ternary amide groups, such as poly(*N*-vinyl pyrrolidone) (PVP) are potentially good proton acceptors because of the basic nature of the functional groups.¹⁴ PVP is reported to form strong H-bonded complexes with polymers bearing proton donating functional groups in the repeat units of their backbones, such as carboxyl groups in polyacrylic and polymethacrylic acids (PAA, PMA)^{15,16} and hydroxyl groups in poly(vinyl alcohol) (PVA).¹⁷ As H-bonding groups are located in monomer units of backbones, due to the balance between the gain in enthalpy and the loss in entropy, the first hydrogen bond appearing between the chains of complementary polymers initiates the process of cooperative binding, which resembles a fast zip formation and leads to a ladder-like structure between two macromolecules. Even though PVP and PMA are hydrophilic, water-soluble polymers, the ladder-like PVP-PMA complex is insoluble in water.¹⁸ In this way, the formation of insoluble, ladder-like product due to favorable interaction of two complementary soluble polymers may be regarded as interchain crosslinking. Because every junction of the

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ladder-like network represents a sequence of numerous hydrogen bonds, it is of no surprise that the ladder-like network is strong and cannot be destroyed because of material interaction with a solvent.

Both PVP and high molecular weight poly(ethylene glycol) (PEG) contain only electron-donating functional groups in their repeating units. For this reason PEG, like PVP, is capable of forming ladder-like interpolymer complexes with carboxyl groups of polyacids.¹⁹ A competitive hydrogen bonding in triple PMA–PVP–PEG system was studied by Papisov et al.^{20–22} Adding PVP to interpolymer complex of PMA with PEG ranging in molecular weight from 3000 to 40,000 g/mol in aqueous solution led to the replacement of PEG in the complex by the PVP. The implication of this fact is that amide groups of PVP form with PMA carboxyls much stronger hydrogen bonds than the oxygen atoms in PEG oxyethylene units.

At room temperature PVP is immiscible with PEG of molecular weight 1000 g/mol and higher.²³ However, PVP is easily soluble in liquid low molecular weight fractions of PEG (100–600 g/mol).^{24,25} The PVP solubility is due to hydrogen bonding between terminal proton-donating hydroxyl groups at the ends of PEG short chains and complementary electron-donating carbonyl groups in longer PVP macromolecules.²⁶ Forming simultaneously two hydrogen bonds through both terminal OH groups, short-chain PEG acts as a reversible and labile crosslinker of PVP.²⁷ Characteristic feature of the PVP–PEG network complex is its nonequimolar stoichiometry that is independent of the composition of PVP–PEG blends in wide concentration range from 20 to 80 wt % PEG.^{26,27} In the stoichiometric PVP–PEG complex either of the five PVP units is crosslinked with another PVP unit by hydrogen bonding through telechelic short PEG chain.

The ladder-like crosslinking leads to appreciable increase in cohesion and decrease in free volume. In contrast, if the reactive functional groups are located at the ends of comparatively short and flexible chains of crosslinking polymer, the crosslinks formed are of appreciable length and flexibility. This type of crosslinking is accompanied with an increase of both cohesion and free volume^{26,28} and is referred to as “carcass-like.” While mechanism of the ladder-like crosslinking is cooperative,²⁹ the interaction of carcass-like crosslinker (short chain PEG) with film-forming polymer (PVP) is rather typical of low molecular weight ligands.²⁷

PVP blends with oligomeric PEG are unique in demonstrating rubber-like elasticity²⁸ and pressure-sensitive adhesion^{30,31} in very narrow range of PEG content (around 36 wt % PEG). In this concentration range the PVP–PEG stoichiometric complex is fully formed and provides specific balance between high

cohesion energy and large free volume, the factors that are responsible for adhesive behavior of polymer materials at a molecular level.²⁶ The PVP–PEG adhesive blends have found use as skin contact adhesives in transdermal therapeutic systems,²⁶ nevertheless their applications are restricted by solubility in aqueous media. The solubility of PVP–PEG complex in water is a consequence of carcass-like type of crosslinking that results in much looser network than the ladder-like crosslinking of hydrophilic polymers by hydrogen bonding. To make PVP–PEG adhesives insoluble but swellable, in this work we have combined the carcass-like and ladder-like types of PVP crosslinking. With this purpose, a carboxyl-containing polymer has been added to PVP–PEG blend. While mechanical, adhesive, and gel properties of triple PVP–PEG based blends are considered elsewhere,³² in the present article we focus on the phase behavior of ternary PVP–PEG–polyacid blends that is affected by competitive hydrogen bonding of reactive functional groups of three involved polymers.

Every component of hydrophilic adhesive polymer blends has a special mission to provide tailored performance properties of the composition. Thus, the term “film-forming” polymer (FFP) relates to a hydrophilic polymer that is present in the composition in the greatest amount. The terms “noncovalent crosslinker,” “ladder-like” (LLC) or “carcass-like” crosslinker (CLC) refer to the polymers that are complementary with respect to the FFP but the amount of which in blend is less compared with that of the FFP.

MATERIALS AND METHODS

PVP (Kollidon K-90), $M_w = 1,000,000$ g/mol, glass transition temperature $T_g = 178^\circ\text{C}$ (BASF, Germany), and PEG of molecular weight 400 g/mol, $T_g = -70^\circ\text{C}$ (Carbowax Sentry NF, Union Carbide) were employed in this work as FFP and CLC, respectively. Both polymers are hygroscopic and the degree of their hydration, evaluated by the weight loss under drying at 105°C , is taken into account to prepare physical blends containing from 20 to 41 wt % of PEG-400. Depending on the relative humidity (RH) of the surrounding atmosphere, PVP degree of hydration ranged from 6 to 8 wt %, while the PEG contained less sorbed water (0–1 wt %). As LLC we employed a copolymer of methacrylic acid with ethylacrylate (PMAA-co-EA, mole ratio 1 : 1, molecular weight 250,000 g/mol), which is available from Rohm America as Eudragit L-100-55. All the polymers were used as received.

The ternary PVP–PEG–PMAA-co-EA blends were prepared by casting-drying method from ethanol solutions. Required amount of PVP was first dissolved in ethanol mixture with PEG-400 under vigorous

stirring (600–700 rpm) using a Cole-Parmer (USA) laboratory mixer (model 50,002-25). Stirring rate was then increased to 900–1000 rpm and the PMAA-co-EA was slowly added. The total concentration of polymers in ethanol averaged 20 wt %. This solution was then kept stirred for 1 h until homogeneous solution was obtained. The homogeneous solution was cast onto a polyethylene terephthalate (PET) casting sheet PEBAX-600. Films were dried overnight at ambient conditions. Upon drying, the PVP-PEG adhesive films were covered by the second sheet of the PEBAX-600 release liner.

In the differential scanning calorimetry (DSC) apparatus the samples were first quench cooled with liquid nitrogen from ambient temperature to -150°C , subjected to isothermal annealing at this temperature and then heated up to 220°C at a rate of $20^{\circ}\text{C}/\text{min}$. The DSC heating traces were obtained with a Mettler TA 4000/DSC 30 thermoanalyzer, calibrated with indium and gallium. Heats of the PEG melting peaks were computed by constructing linear baselines from the peak onset to completion and numerically integrated with appropriate software supplied by Mettler. All reported values are the average of replicate experiments varying less than 1–2%. In the DSC measurements the samples of 5–15 mg in weight were sealed in standard aluminum pans supplied with pierced lids so that absorbed moisture could evaporate upon heating. An argon purge (50 mL/min) was used to avoid moisture condensation at the sensor.

The weight fractions of crystalline PEG in the blends with amorphous PVP and PMAA-co-EA, w_{crPEG} , have been calculated as the ratios of appropriate heats of melting, H_m , of blended PEG to the reference values for unblended PEG, taking into account the weight fraction of absorbed water, $w_{\text{H}_2\text{O}}$:

$$w_{\text{crPEG}} = \frac{\Delta H_m(\text{blend})}{\Delta H_m \text{ PEG} (1 - w_{\text{H}_2\text{O}})} \quad (1)$$

The ΔH_m reference value of unblended crystalline PEG-400 was 113.6 J/g .

The content of absorbed water in the blends was determined gravimetrically by the termination of weight loss upon drying in vacuum. In addition, the content of water was also measured by weighing the samples before and after DSC scans using a Mettler Analytical Balance, AE 240, with an accuracy of 0.01 mg. Weight loss of the sample after scanning was compared to the amount of desorbed water evaluated from the enthalpy change associated with water evaporation from the sample by DSC.

FTIR spectra of the blends and parent polymers were recorded using a Bruker IFS-113v spectrometer (Germany) with a resolution of 1 cm^{-1} . Four hundred scans were done for each spectrum. Films used as specimens

were cast on Si plates from 5–20% ethanol solutions followed by drying at ambient temperature. The thickness of dry films was 10–15 μm . The spectra were treated using GRAMS program (Microsoft). Quantum chemical calculations were performed with complete optimization of geometric parameters by means of minimization of energy within the frameworks of Chem Office 2004 using MOPAK, DFT, and GAUSSIAN programs.³³

RESULTS AND DISCUSSION

Phase behavior

Thermal transitions of unblended polymers

Thermal transitions featured for dry unblended PVP, PMAA-co-EA, and PEG-400 are illustrated in Figure 1. Heating scan of unblended PVP reveals a broad symmetric endotherm of water thermodesorption at 116°C followed by a heat capacity jump at the glass transition ($T_g = 178^{\circ}\text{C}$, $\Delta C_p = 0.27 \text{ J/g K}$). The amount of water sorbed with PVP, determined as a ratio of water thermodesorption enthalpy to the reference value of bulk water vaporization heat, is found to be 7.3 wt %. This value is in close agreement with the loss in the sample weight after scanning (6.6 wt %). Immediate rescanning of the specimen using the same heating program shows neither endotherm nor weight loss, while the temperature of PVP glass transition remains practically intact (Fig. 1). No freezing water is detected under PVP hydration even if 20% water sorption is attained.

In contrast to PVP, the PMAA-co-EA contains only 2 wt % of absorbed water. DSC thermogram of dry PMAA-co-EA, shown in Figure 1, displays $T_g = 132^{\circ}\text{C}$ and $\Delta C_p = 0.19 \text{ J/g K}$. It is worthy of note that the T_g value of PMAA-co-EA depends on ionization degree of carboxyl groups. With the increase of the content of methacrylate anions, the T_g tends to decrease, while

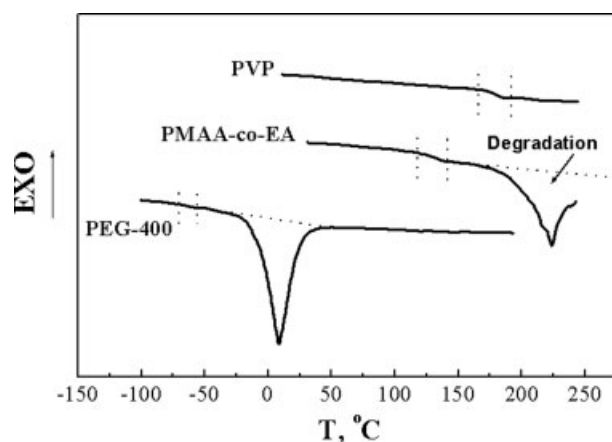


Figure 1 DSC heating thermograms of unblended PVP, PMAA-co-EA, and PEG-400.

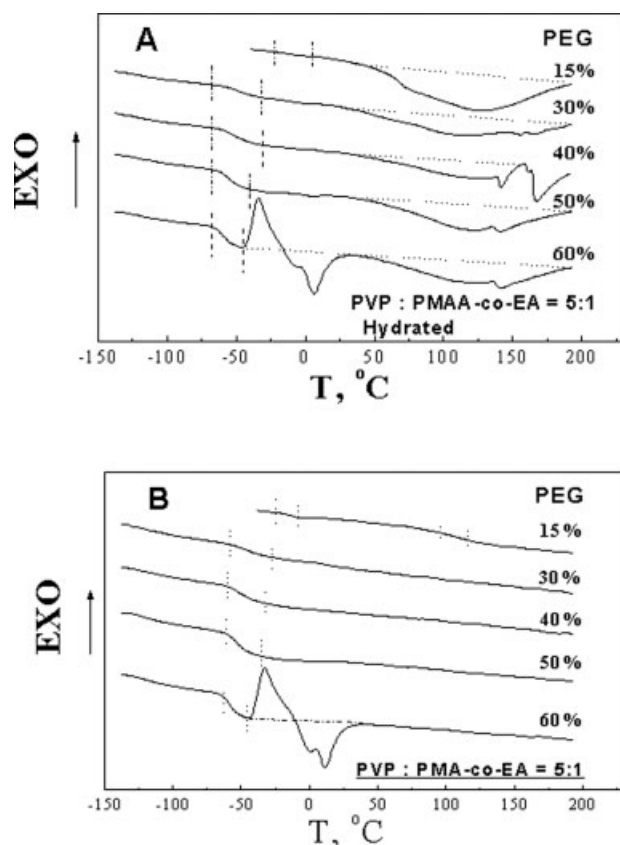


Figure 2 DSC heating thermograms of triple PVP-PEG-PMAA-*co*-EA blends containing different amounts of PEG-400. [PVP] : [PMAA-*co*-EA] = 5 : 1. (A) Hydrated blends, absorbing 4 ± 1 wt % of water; (B) Dry blends (second scans).

the content of absorbed water increases. At temperatures above 150°C the PMAA-*co*-EA exhibits thermal decomposition.

The DSC heating curve of unblended dry PEG reveals $T_g = -67^{\circ}\text{C}$, $\Delta C_p = 0.11$ J/g K, and endotherm of melting at 9°C (melting heat $\Delta H_m = 113.6$ J/g). Following its exposure to water vapor at RH = 50%, PEG-400 displays glass transition at -70°C , $\Delta C_p = 0.32$ J/g K, and PEG fusion endotherm at $T_m = 8^{\circ}\text{C}$, $\Delta H_m = 112.4$ J/g. The PEG is nearly six times less hydrated than PVP, and the broad peak of water desorption is shifted to 127°C . As the content of sorbed water increases to 11.3%, ΔC_p achieves the value 1.17 J/g K and the glass transition in PEG becomes more conspicuous ($T_g = -71^{\circ}\text{C}$). Again, no freezing water is found if the PEG hydration is as high as 17 wt %, corresponding to maximum content of bound water reported to be 2.7 water molecules per PEG unit.^{34,35}

Phase state of triple blends as a function of PEG content

Effect of PEG content on DSC curves of triple PVP-PMAA-*co*-EA-PEG blends is presented in Figure 2.

The ratio between FFP (PVP) and LLC (PMAA-*co*-EA) concentrations is fixed at 5 : 1. With the rise of PEG content, T_g decreases smoothly as is shown in Figure 3. This finding implies that PEG-400 acts as a good plasticizer for PVP-PMAA-*co*-EA mixture. In hydrated blends, endotherms of water thermo-desorption at high PEG concentration (40% and more) have bimodal character, implying the occurrence of at least two types of absorbed water, comparatively loosely and strongly bound water. Similar effect was earlier observed for binary PVP-PEG blends.³⁶

Dry PVP-PMAA-*co*-EA blend with 15% of PEG-400 in Figure 2(B) shows two glass transitions at $T_g = -14$ and 106°C . These T_g values are untypical of parent polymers and imply that both phases in triple blend are due to partial miscibility between PVP and PMAA-*co*-EA. Existence of a single T_g for the systems containing 30% PEG and higher is an evidence in favor of PVP miscibility with PMAA-*co*-EA. In this way, PEG-400 facilitates PVP-PMAA-*co*-EA miscibility. Taking into consideration that the miscibility of polymers results most often from specific interaction between them,³ we can suppose that PEG-400 acts most probably as a helper in PVP-PMAA-*co*-EA interaction.

Characteristic feature of the blends containing 60% PEG and greater is the presence of PEG cold crystallization exotherm at -34°C , coupled with symmetric high-temperature endotherm of PEG melting at 8°C (Fig. 2). Using eq. (1) allows us to evaluate the content of PEG-400 associated with PVP and PMAA-*co*-EA within amorphous phase, and determine the fraction of PEG-400 bound into interpolymer complex with both amorphous polymers. In the blends containing 60 wt % of PEG and 3% of absorbed water, the amount of bound PEG has been found to be 36.5%,

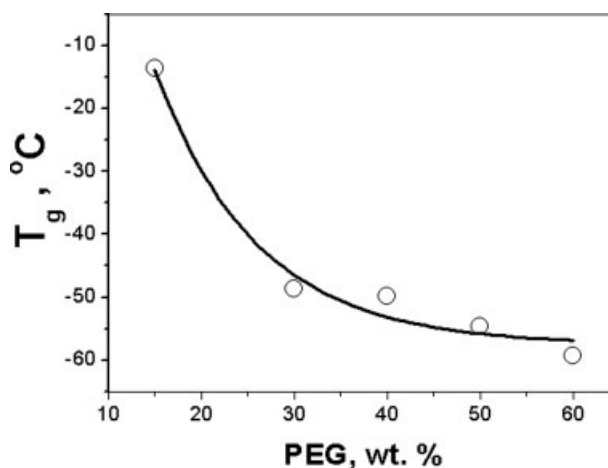


Figure 3 Relationship of T_g to the concentration of PEG-400 in PVP-PEG-PMAA-*co*-EA triple blends. [PVP] : [PMAA-*co*-EA] = 5 : 1.

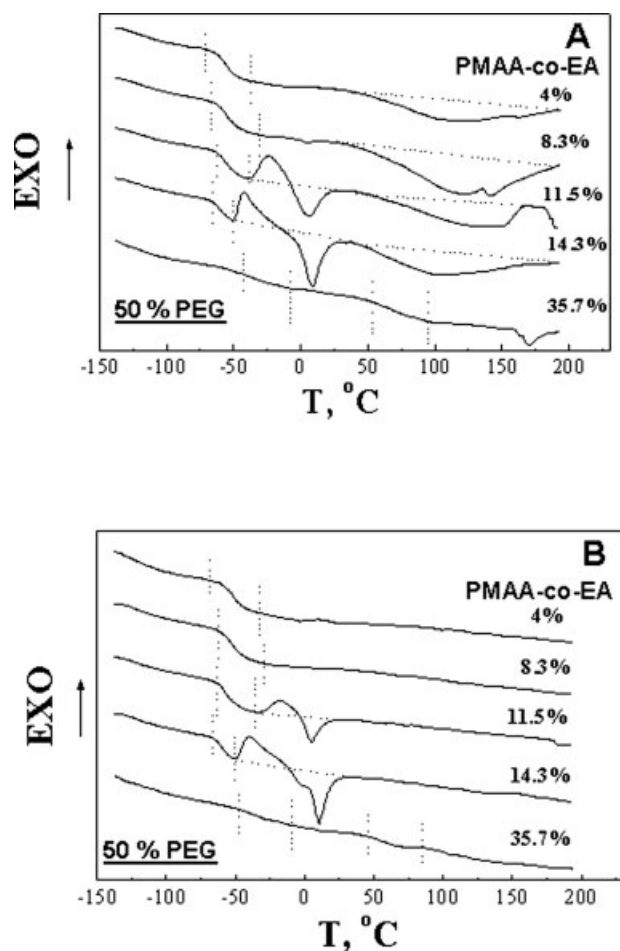


Figure 4 DSC heating thermograms of triple PVP-PEG-PMMA-co-EA blends containing different amounts of PMMA-co-EA and 50 wt % PEG-400. (A) Hydrated blends containing 3 wt % of absorbed water, (B) dry blends.

while in the dry blend this amount is 38.6%. Thus, absorbed water behaves as a competitor to PEG-400 in the process of hydrogen bonding with amorphous polymers. Similar effect was earlier established for dry and hydrated binary PVP-PEG blends.³⁷

In aqueous media, the PVP-PEG-PMMA-co-EA blends are capable of absorbing great amounts of water.³² Under ambient conditions (room temperature and RH = 50–80%), the binary PVP-PEG blends contain 6–11% of absorbed water,³⁶ whereas triple PVP-PEG-PMMA-co-EA blends, loaded even with a small amount of LLC, are appreciably drier (2–3 wt % of water). In this connection the pertinent question is: What is the maximum amount of water that may be dissolved in the system without formation of separate phase of freezing water? As DSC thermograms of supermoistened PVP-PEG-PMMA-co-EA blends containing 50 wt % of water have shown, the solubility of water in the blends averages 34.2 ± 1.5 wt % regardless the PEG content.

Phase state of triple blends as a function of PMMA-co-EA concentration

We consider now the effect of LLC, PMMA-co-EA, on the phase state of PVP-PEG system. It is pertinent to note once more that binary PVP-PEG system is a single phase and involves reversible crosslinking of PVP macromolecules via hydrogen bonding through terminal OH groups of short chain PEG.^{26,27} As follows from the data in Figure 4, the blends containing less than 30 wt % of PMMA-co-EA possess the single glass transition and are miscible. However, the PVP-PEG blend with 35.7% PMMA-co-EA demonstrates two T_g s of -38 and 55°C . Both T_g values are untypical of parent components (compare with Fig. 1) and composition-dependent, implying that they relate to mixed phases and that the system is partially compatible. Based on the results of phase state investigation of binary PVP-PEG blends,^{26,27} the lower- T_g phase can be logically related to PVP-PEG-PMMA-co-EA complex, whereas the upper- T_g phase corresponds most likely to the phase enriched with PMMA-co-EA. Further increase in the PMMA-co-EA concentration leads to rapid growth of upper T_g value.

In the blends containing less than 9 wt % of PMMA-co-EA all the PEG is associated with PVP in amorphous phase and unavailable for crystallization. This fact is readily explained since in binary PVP blends with PEG-400 the crystalline phase arises as PEG content achieves 45–50 wt %.^{26,27} Most surprising feature of the DSC traces shown in Figure 4 is that the endotherm of PEG melting appears in the range between 10 and 30 wt % of PMMA-co-EA and vanishes as its amount becomes as high as 36%. Weight fractions of bound (noncrystallizable) PEG in dry and hydrated blends containing various amounts of PMMA-co-EA are listed in Table I. As follows from these data, even very small amount of absorbed water ($\sim 2\%$) lowers appreciably the PEG binding degree.

Thus, the analysis of PEG melting endotherms in DSC traces of ternary PVP-PEG-PMMA-co-PEA blends provides information about the state of CLC (PEG) in the blends. The increase in LLC content leads to

TABLE I
Effects of PMMA-co-EA Content and Absorbed Water on the Amount of Noncrystalline PEG-400 Associated with Amorphous Polymers in PVP-PMMA-co-EA Blends Containing 50 wt % PEG-400

PMMA-co-EA wt %	Hydrated blends		
	wt % H ₂ O	Bound PEG wt %	Dry blends
8.3	3.5	50.0	50.0
11.5	2.0	40.1	45.2
14.3	1.9	34.9	36.9
28	2.1	30.4	–
35.7	0.5	50.0	50.0

the appearance of crystallizable (unbound) PEG due to partial replacement of PEG in PVP-PEG complex by the LLC (PMAA-co-EA). On the basis of this observation we are able to propose that the carboxyl groups of PMAA-co-EA form with PVP carbonyls stronger hydrogen bonds than the bonds with PEG-400. This conclusion confirms the observations reported earlier by Papisov et al.²⁰⁻²² At higher LLC concentrations, all PEG becomes associated with PMAA-co-EA. This allows us to characterize the PVP-PEG-PMAA-co-EA blends as a system with strong favorable and competing interactions between components of the blend.

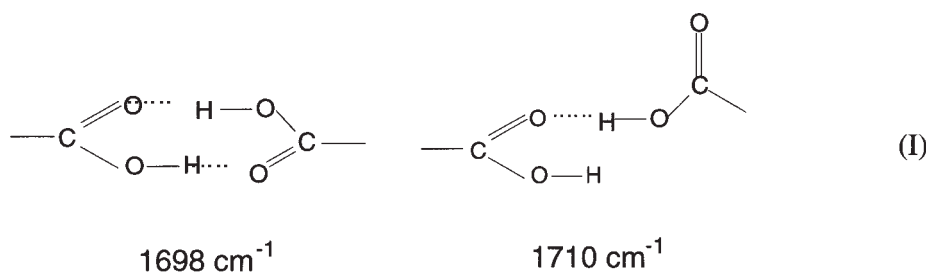
Observed mechanism of competitive hydrogen bonding, that is evident from the data of the phase behavior of PVP-PEG-PMAA-co-EA system, is also in good agreement with the values of Flory-Huggins pair interaction parameters, χ , which were recently determined from isotherms of water vapor sorption by triple PVP-PEG-400-poly(acrylic acid) (PAA) blends.³⁸ Large negative values of the χ parameter correspond to strong exothermic bonding between relevant functional groups. The magnitudes of the pair interaction parameters in the PVP-PEG-PAA blends were found to increase in the order: $\chi_{PAA-PEG} = -7.37 < \chi_{PVP-PAA} = -1.81 < \chi_{PVP-PEG} = -0.23 < \chi_{PAA-H_2O} = 0.08 < \chi_{PEG-H_2O} = 0.4 < \chi_{PVP-H_2O} = 0.84$.³⁸ The pair interaction parameters provide integral measure of interaction strength. Thus, largest negative χ value found for PAA-PEG interaction is most likely due to a great amount of proton-accepting functional groups in PEG molecule (oxygen atoms in oxyethylene repeat units and terminal hydroxyl groups). To compare the relative strengths of individual hydrogen bonds in PVP-PEG-PMAA-co-EA blends, the FTIR spectra were obtained and quantum-chemical calculations were performed.

FTIR spectroscopy characterization of hydrogen bonds in PVP-PEG-PMAA-co-EA system

FTIR spectrum of triple blend as compared to the spectra of unblended polymers

The data of FTIR Spectroscopy provide unambiguous identification of interacting functional groups in complementary macromolecules. The formation of hydrogen bonds between functional groups is manifested in the IR spectra by the shift of their characteristic frequencies toward lower wavenumbers. The bands of vibrations of the carbonyl bond in amide group of PVP and carboxyl group of PMAA-co-EA in the IR absorption spectra are observed in the region of 1720–1650 cm^{-1} , and the bands of hydroxyl groups at the ends of PEG short chains fall within the range of 3600–3200 cm^{-1} . FTIR spectra of PVP and PMAA-co-EA in the region of carbonyl group stretching vibration along with the spectrum of PVP-PEG-PMAA-co-EA film are presented in Figure 5. In PVP spectrum (a) the band at 1661 cm^{-1} (see Table II) relates to the association of carbonyl groups with water.^{39,40} In the spectrum of PVP-PEG-PMAA-co-EA blend, this band splits into three separate modes at 1650, 1660, and 1675 cm^{-1} . While the latter two may be assigned to the C=O stretch in native and loosely associated states, the shoulder at 1650 cm^{-1} corresponds, most likely, to the hydrogen bond between PVP carbonyl and PMAA-co-EA carboxyl groups.

In the PMAA-co-EA spectrum [Fig. 5(b)] there exist two bands relating to carboxyl groups: at 1710 cm^{-1} (monomeric form) and 1698 cm^{-1} (associated form, Table II).⁴¹ Referring the band at 1710 cm^{-1} to carboxyl group of MMA monomer unit doesn't mean that the group is free from association. It can be associated with the same group but without formation of cyclic dimers.



The broad band at 2600 cm^{-141} in the PMAA-co-EA spectrum confirms the presence of eight-membered cyclic dimers of carboxyl groups. The carboxyl group, which is absolutely free from association, can have an absorption peak at 1730 cm^{-1} , but it is impossible to identify the peak among highly overlapping bands in this region. Deconvolution of the broad peak at 1734 cm^{-1} results in no less than six

highly overlapping bands. The presence of several bands in this region can't exclude the possibility of association of MMA carboxyl groups with EA ester groups in copolymer. We performed theoretical analysis of stretching vibration of RC(O)OR_1 esters as described in,⁴² where R is Me, Et, Pr, R_1 is Et, Pr, Bu. The $\nu_{\text{C=O}}$ band position in esters spectra was shown to depend on stretching angle of $-\text{C}-\text{O}-\text{R}_1$

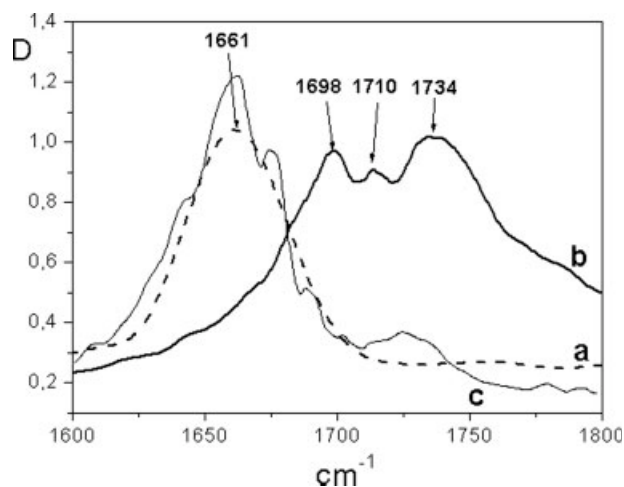


Figure 5 FTIR Spectra of PVP (a), PMAA-co-EA (b), and PVP (42%) – PEG (50%) blend with 8% of PMAA-co-EA (c) in the region of carbonyl and carboxyl groups stretching vibration.

group. As stretching angle changes from 115° to 127° C=O band shifts from 1745 to 1730 cm^{-1} with no change of field force at the given molecular location. Since conformation analysis of $-\text{C}-\text{O}-\text{R}_1$ stretching angles shows nearly free rotation around $-\text{C}-\text{O}-$ bond, it is believed that side groups with different stretching angles $-\text{C}-\text{O}-\text{Et}$ can exist in EA. In this case, a broad band at $1730\text{--}1735\text{ cm}^{-1}$ is observed in vibration spectrum.

Quantum-chemical simulation described in this article shows that oxygen atoms of ester group in acrylates can associate also with PEG terminal $-\text{OH}$ group and MAA carboxyl group. However, the formation energy for such hydrogen bonds doesn't exceed 5–8% relative to the association energy between carboxyl groups or that of carboxyl group with amide- or PEG OH groups. Experimental evidence of preferable association of PEG terminal $-\text{OH}$ groups with amide or carboxyl groups compared to the association of the

TABLE II
Positions and Assignations of Bands in FTIR Spectra of PVP (1), PMAA-co-EA (2), and PVP-PEG-PMAA-co-EA Blend (3) in the Region of Carbonyl Group Stretching Vibrations

Band assignment	PVP (a)	PMAAEA (b)	PVP-PEG-PMAAEA (c)
$-\text{C}(\text{O})\text{OC}_2\text{H}_5$	–	1734s^*	1733w
$-\text{C}(\text{O})\text{OH}$	–	1710s 1698s	1709w 1697i 1683i (1675i) (1675i)
$-\text{C}(\text{O})\text{NR}_2$	1661s	–	1660s 1650sh

s, strong intensity; w, weak intensity; i, intermediate intensity; sh, shoulder.

same groups with ester ones is evidenced also by the spectra in Figure 6. In Figure 6 the curve (a) corresponds to IR-Fourier spectrum of a film representing the blend of polybutylacrylate (PBA, 90%), sodium polymethacrylate (SPMA, 5%) and polyoctylacrylamide (POAA, 5%). Curve (b) shows the spectrum of the same film with addition of 10% PEG-400. Comparison of the spectra shows that addition of 10% PEG doesn't affect appreciably neither the position of a maximum nor the shape of stretching vibration band of ester group in PBA (1734 cm^{-1}) but the bands of amide group and carboxylate-anion split and shift in maximum. So, in our opinion, referring the band of 1710 cm^{-1} to partly associated carboxyl group is a fairly reasonable supposition.

In the spectrum of PVP-PEG-PMAA-co-EA blend (Fig. 5) the bands relating to the carboxyl groups (1709 and 1697 cm^{-1}) gain in intensity contrary to a low content of the PMAA-co-EA in the blend (8 wt %). Specific feature of the blend spectrum [Fig. 5(c)] is a presence of new band at 1683 cm^{-1} , which is most likely due to hydrogen bonding between carboxyl group of PMAA-co-EA and carbonyl group of PVP. Notice that the band at 1675 cm^{-1} , which was earlier assigned to an associate of PVP carbonyl group with water, may also belong to the hydrogen bond between PMAA-co-EA carboxyl group and the carbonyl group of PVP (Table II). In this way, the occurrence of two forms of the PVP-PMAA-co-EA hydrogen bond must not be ruled out. Weak broad band at 1725 cm^{-1} in the spectrum in Figure 5(c) corresponds to stretching vibration $\nu_{\text{C}=\text{O}}$ in EA units associated with OH-groups in PEG. Since the content of ester groups in the blend is much less than that of terminal $-\text{OH}$ groups in PEG, association between

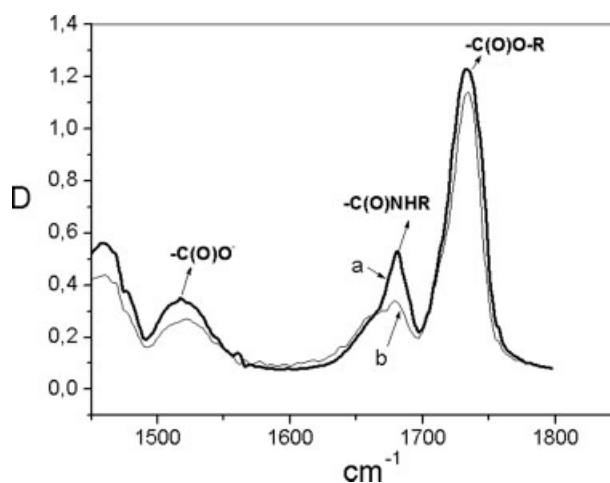


Figure 6 Comparison of IR spectra of polymer blends: Curve (a): the blend of polybutylacrylate PBA (90%), sodium polymethacrylate SPMA (5%), and polyoctylacrylamide POAA (5%); Curve (b): 90% of the same blend plus 10 wt % of PEG-400.

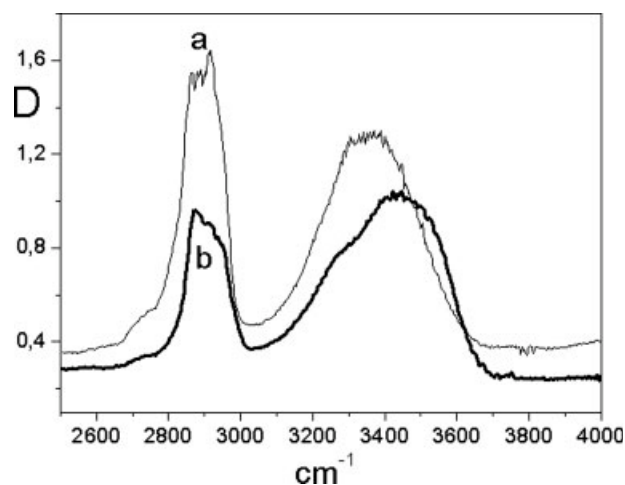


Figure 7 Comparison of FTIR spectra of unblended PEG-400 (a) and triple blend of 42 wt % of PVP with 50 wt % PEG and 8 wt % of PMAAA-co-EA (b) in the region of hydroxyl group stretching vibrations.

—C=O groups in EA and —OH groups in PEG is quite possible.

Thus, the data presented in Table II and Figure 5 provide direct spectral evidences of the participation of PVP carbonyl groups and carboxyl groups of PMAA-co-EA in hydrogen bonding. At the same time, the presence of the band at 1734–1733 cm^{-1} , assigned to carbonyl groups of ethyl acrylate units,⁴³ in the spectra of unblended PMAA-co-EA and triple PVP-PEG-PMAA-co-EA blend (Fig. 5, Table II) implies that ethylacrylate (EA) groups of PMAA-co-EA are not involved into interaction with PVP and PEG.

Interaction of PEG-400 in triple blends

Figures 7 and 8 are informative on the role of PEG-400 in hydrogen bonding with PVP and PMAA-co-EA in triple blend. A wide band at 3380 cm^{-1} [Fig. 7(a)] suggests a high degree of self-association of terminal hydroxyl groups in unblended PEG.⁴³ This association results in a toothed shape of the wide band in the range of 1100 cm^{-1} [Fig. 8(a)], implying a large variety of the conformational states of C—O—C groups in self-associated PEG-400.⁴⁴

Mixing PEG-400 with PVP and PMAA-co-EA and hydrogen bonding through PEG terminal hydroxyl groups, leads to the shift of ν_{OH} from 3380 to 3420 cm^{-1} [Fig. 7(b)]. This shift signifies weakened hydrogen bonding of terminal PEG hydroxyl groups in the blend as compared to PEG self-associates.⁴³ A shoulder at 3300 cm^{-1} in the spectrum of PVP-PEG-PMAA-co-EA blend [Fig. 7(b)] is an indication that PEG OH-groups also form comparatively stronger H-bonds with the components of triple blend. Flattening of the wide band at 1100 cm^{-1} in the blend spectrum [Fig. 8(b)] is an evidence in favor of rearrangement of PEG oxyethy-

lene units in the complex, which is accompanied with straightening of PEG chains.

Binary blends of PEG-400 with PVP and PMAA-co-EA

Because the major components of our triple polymer system are PVP and PEG-400, it is pertinent to compare the FTIR spectra in Figures 7(b) and 8(b) with the spectra of binary PVP-PEG blends, which have been described in detail in earlier publications of our group.^{44,45} As has been shown in these works, mixing PVP with PEG-400 results in the shift of the band related to PVP carbonyl group stretching vibrations from 1679 to 1655 cm^{-1} and the corresponding shift of PEG terminal hydroxyls vibrations from 3455 to 3332 cm^{-1} . This effect is indicative of strong H-bond formation between these groups. Note that^{44,45} dehydrated PVP was employed. In present work we deal with PVP containing equilibrium amount of absorbed water (6–7 wt %) and, for this reason, the band of carbonyl group vibrations lie at 1661 cm^{-1} , indicating the association of PVP carbonyl groups with water. For the system PVP-poly(vinyl phenol) (PVPh), similar shift of the PVP carbonyl group vibrations from 1682 to 1655 cm^{-1} has been earlier observed,⁴⁶ which is the result of strong hydrogen bonding between PVP carbonyls and OH-groups of PVPh.

In full agreement with the spectral data of the present work obtained for ternary PVP-PEG-PMAA-co-EA blends (Figs. 7 and 8), the binary PVP-PEG-400 system reveals reorientation of PEG chains whereby the terminal PEG hydroxyl groups become no longer self-associated or bound with the oxyethylene units of neighboring chains.^{44,45} Differential FTIR spectrum of the PVP-PEG blend in the region of PVP carbonyl

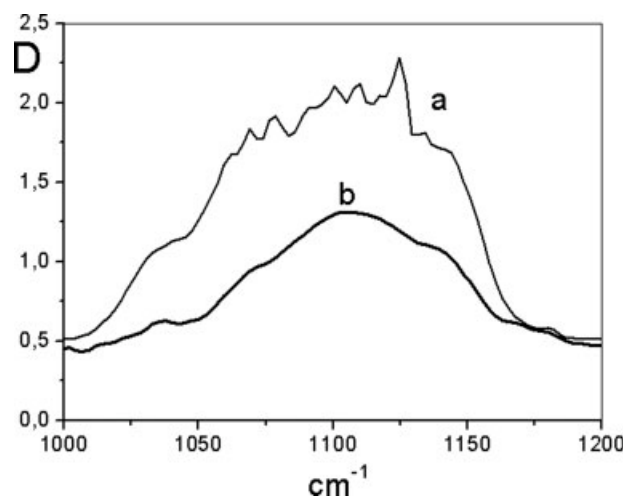


Figure 8 FTIR spectra of PEG-400 (a) and triple blend of PVP (42 wt %) with 50 wt % PEG and 8 wt % of PMAAA-co-EA in the region of C—O—C groups stretching and bending vibrations.

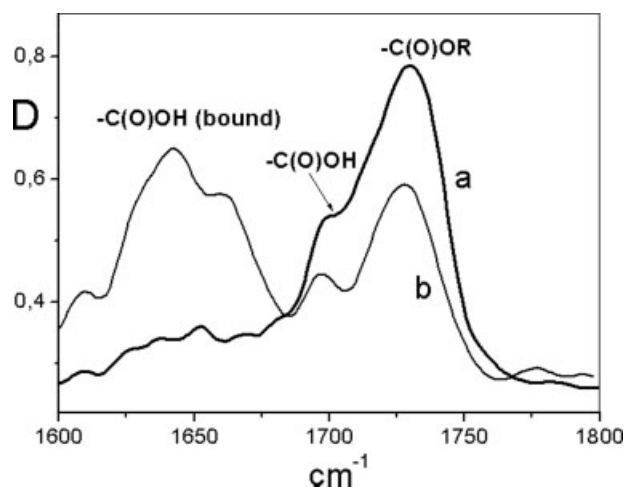


Figure 9 FTIR spectra in the region of carbonyl group vibrations of binary PMAA-co-EA blends with 50 (a) and 95 wt % (b) of PEG-400. Curves are obtained by deconvolution of experimental spectra (Fourier Self-Deconvolution by Gaussian).

group stretching vibration demonstrates the bands at 1716, 1680, and 1650 cm^{-1} , which can be respectively, assigned to the free, comparatively loosely, and strongly bound with PEG OH-groups the PVP carbonyls.⁴⁵ The loosely bound mode of 1680 cm^{-1} relates most likely to the PEG chains forming with PVP carbonyl groups only single H-bond through one terminal hydroxyl group. The strongly bound mode at 1650 cm^{-1} corresponds to H-bonds formed by PEG chain through both terminal OH groups. As both end groups of PEG short chain are involved into hydrogen bonding with PVP carbonyl groups, the PEG chain acts as a nonpermanent crosslinker of longer PVP macromolecules.

To appreciate the contribution of PMAA-co-EA into hydrogen bonding between PVP and PEG-400, we now consider FTIR spectra of binary PEG-PMAA-co-EA and PVP-PMAA-co-EA blends. Figure 9 demonstrates the effect of composition on the spectra of PEG-PMAA-co-EA blends in the region of PMAA-co-EA carbonyl group stretching vibrations. In 50 : 50 mixture, the most intensive band at 1725 cm^{-1} [Fig. 9(a)] relates to the carbonyl group in EA units.⁴¹ In the spectrum of unblended PMAA-co-EA [Fig. 5(b)], this band appears at 1734 cm^{-1} (Table II). Consequently, the shift of EA band from 1734 to 1725 cm^{-1} is a result of hydrogen bonding between EA carbonyls and terminal hydroxyl groups of PEG-400. The band at 1698 cm^{-1} , which is also typical for PMAA-co-EA spectrum [Fig. 5(b); Table II], corresponds to the self-association of carboxyl groups.⁴¹ The bands in the region 1690–1540 cm^{-1} are due to hydrogen bonding with OH-groups of PEG-400 because the oxyethylene units of the PEG are incapable of forming H-bonds with PMAA carboxyl groups. Their positions and especially intensities depend appreciably on the com-

position of PMAA-co-EA-PEG blend (Fig. 9). While in 50:50 blend spectrum [Fig. 9(a)] the bands at 1670 and 1655 cm^{-1} have comparatively low intensity, in the spectrum of 95 : 5 PEG-PMAA-co-EA blend [Fig. 9(b)] the bands at 1660 and 1645 cm^{-1} possess intensities that become comparable with that of EA units. Evidently at small content of high molecular weight glassy polymer, there is increase in number of hydrogen bonds that are formed between carbonyl groups of PMAA-co-EA and terminal hydroxyl groups of PEG short chains.

Figure 10 characterizes the state of PEG oxyethylene units upon mixing PEG-400 with PMAA-co-EA. When 5 wt % of PMAA-co-EA is added to PEG, the IR spectrum of the blend reveals splitting of the bands within wide spectral range of 1050 and 1150 cm^{-1} [Fig. 10(a,b)]. This splitting suggests the existence of a wide variety of the conformations of PEG chains.⁴⁴ In the blend enriched with PMAA-co-EA [Fig. 10(c)], the flattened spectrum in the region of C—O—C vibrations indicates that the set of PEG chain conformations becomes more uniform. Similar effect has been also observed for triple PVP-PEG-PMAA-co-EA blends (Fig. 8). Taking into consideration that PEG mixing with PVP leaves IR spectrum in this range unaffected,⁴⁴ we conclude that observed effect is due to interaction of PEG oxyethylene units with carboxyl groups of PMAA-co-EA.

The spectra in Figure 11 are informative of the interaction of OH-groups in PEG-PMAA-co-EA blends. The band at 3380 cm^{-1} in the spectrum of unblended PEG-400 [Fig. 11(a)] relates to stretching vibrations of self-associated terminal hydroxyl groups. As 5 wt % of carboxyl containing PMAA-co-EA is added to PEG [Fig. 11(b)], this band shifts to 3430 cm^{-1} implying partial disintegration of OH-group self-associates. The

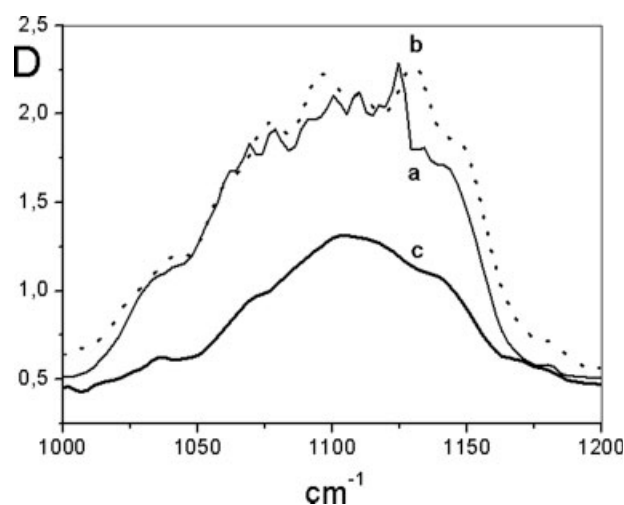


Figure 10 Comparison of IR spectra of PEG-400 (a) and its blends with 5 wt % (b) and 95 wt % of PMAA-co-EA (c) in the region of C—O—C bond vibrations.

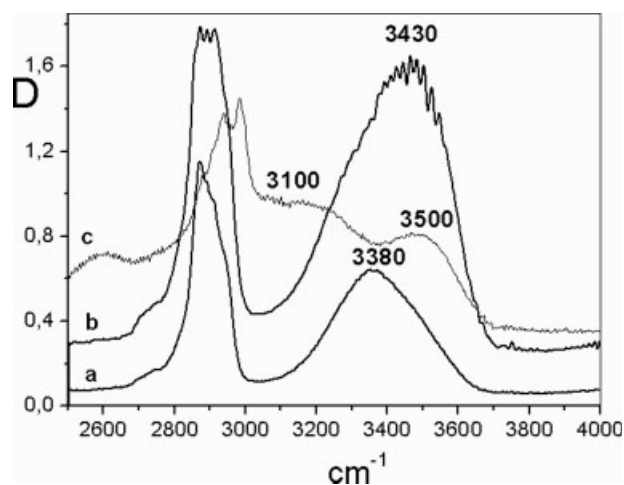


Figure 11 IR spectra of PEG-400 (a) and its blends with 5 wt % (b) and 95 wt % of PMAA-co-EA (c) in the region of OH-group stretching vibrations.

spectrum of the blend overloaded with PMAA-co-EA [Fig. 11(c)] corresponds to the spectrum of pure PMAA-co-EA. The implication of these data is that carboxyl groups of PMAA-co-EA interact mainly with C—O—C groups in PEG chains and this interaction causes the release of PEG terminal hydroxyls from self-associates featured for unblended PEG.

Interaction between PVP and PMAA-co-EA

Since vibration bands of carbonyl groups in PVP and PMAA-co-EA appear within the same region of the spectrum, between 1640 and 1750 cm^{-1} , their assignment is a challenging problem. With this purpose in Figure 12 we compare FTIR spectra of binary PVP-PMAA-co-EA blends containing 5 and 95 wt % of PMAA-co-EA. Adding 5 wt % of PMAA-co-EA to PVP results in the shift of 1661 cm^{-1} band, featured for the carbonyl in unblended PVP [Fig. 5(a)], to 1653 cm^{-1} [Fig. 12(a)]. Because in the spectrum of unblended PVP all the carbonyl groups are associated with absorbed water, this shift implies that hydrogen bonding between PVP and carboxyl groups of PMAA-co-EA is stronger than the bonding of PVP with water.

Adding 5 wt % of PVP to PMAA-co-EA is accompanied with marked change of FTIR spectrum. The band at 1733 cm^{-1} [Fig. 12(b)] relates to carbonyl vibrations in EA units. In the spectrum of unblended PMAA-co-EA this band is observed at 1734 cm^{-1} [Fig. 5(b)]. The bands at 1698 and 1710 cm^{-1} in the spectrum of pure PMAA-co-EA [Fig. 5(b)], which correspond to dimeric and monomeric forms of carboxyl groups (Table II), shift to 1702 and 1720 cm^{-1} , respectively, [Fig. 12(b)]. The change in relative intensities of these bands [compare Figs. 12(b) and 5(b)] demonstrates that in PMAA-co-EA blend with 5% of PVP the amount of unassoci-

ated carboxyl groups is increased through partial dissociation of dimer. The band at 1686 cm^{-1} [Fig. 12(b)] is most likely due to the shift of 1661 cm^{-1} band of hydrated PVP carbonyls [Fig. 5(a)], showing that mixing PMAA-co-EA with hygroscopic PVP causes the appearance of PVP carbonyl groups, which are free of H-bonding with water. The wide band of hydrated carbonyl groups at 1661 cm^{-1} in PVP spectrum [Fig. 5(a)] in the blend overloaded with PMAA-co-EA [Fig. 12(b)] degenerates into three small peaks at 1656, 1666, and 1673 cm^{-1} , implying the existence of a range of H-bonded complexes of PVP carbonyl groups with water. And finally, the band at 1647 cm^{-1} signifies strong hydrogen bonding of PVP carbonyl groups with the carboxyl groups of PMAA-co-EA.

Thus, FTIR spectra presented in this section (Figs. 5–12) reveal the formation of following types of strong hydrogen bonds in ternary PVP-PEG-PMAA-co-EA mixture. The carbonyl groups of PVP form H-bonds with the carboxyl groups of PMAA-co-EA and are also involved into H-bonding to PEG terminal hydroxyls, giving the bonds of various strength. Besides PVP, the OH-groups at the ends of PEG chains form H-bonds to the carbonyl groups of EA units and carboxyl groups in PMAA-co-EA, and are also involved into self-association with hydroxyl groups and oxyethylene units of neighboring PEG chains. And finally, apart from hydrogen bonding with PVP and PEG, the carboxyl groups of PMAA-co-EA yield self-associates. What is more interesting is that in equilibrium state (room temperature and RH = 50–70%), the PVP-PEG-PMAA-co-EA blends contain 2–3 wt % of absorbed water that is completely associated with polymer components. Consequently, all the polymers in the PVP-PEG-PMAA-co-EA blends are capable of forming H-bonded complexes both directly to one another and

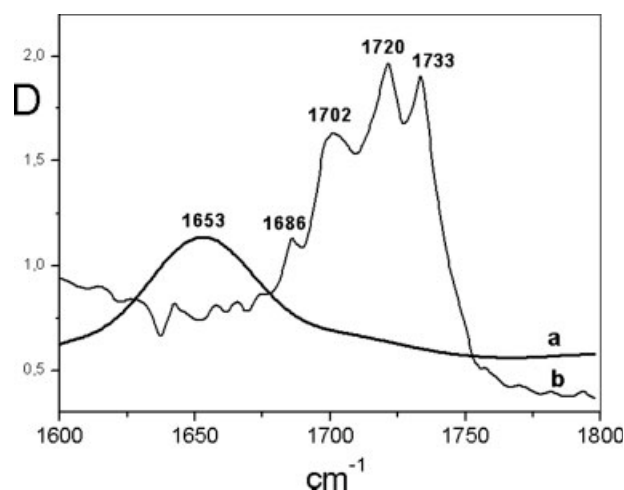


Figure 12 Effect of PVP-PMAA-co-EA blend composition on FTIR spectra in the region of carbonyl group stretching vibrations. (a) 95 wt % PVP, 5 wt % PMAA-co-EA, (b) 5 wt % PVP, 95 wt % PMAA-co-EA.

through molecules of absorbed water. Such complexes are not binary but involve three and even four components. In addition, the types of H-bonded complexes depend on the blend composition implying the existence of chemical equilibrium between competing mechanisms of hydrogen bonding. In turn, the competition between different types of hydrogen bonding governs the phase behavior and physical properties of composite material.

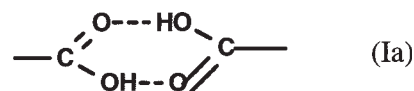
Quantum chemical evaluation of competitive hydrogen bonding in the system PVP-PEG-PMAA-co-EA

Self-association of hydroxyl and carboxyl groups in unblended components

To evaluate the competition in hydrogen bonding between reactive functional groups of PVP, PEG, and PMAA-co-EA in triple blends containing absorbed water, we should take into account the energies of formation of different types of hydrogen-bonded structures, which exist in the blends based on the data of FTIR Spectroscopy. With this purpose we have performed quantum chemical calculations of the energy of formation for more than 110 complexes of various types. The results of the calculations are presented in Table III and are arranged in order of diminishing magnitudes of the formation energy.

The polymers and low molecular weight substances bearing hydroxyl and carboxyl groups in their molecules have a tendency to form self-associates.⁴ For the complex (interassociate) to be formed, the gain in its formation energy must cover the amount of energy expended to break the self-associate. The formation energy of linear self-associate between two molecules of water has been found to be 22.934 kJ/mol. Cyclic dimer of water molecules is characterized with the energy of formation of 22.279 kJ/mol. Inclusion of third water molecule into linear and cyclic self-associate increases the formation energy of trimer to 44.833 and 64.469 kJ/mol, respectively. Linear self-associate involving four water molecules demonstrates the energy of formation of 70.360 kJ/mol, whereas the formation energy of cyclic tetramer is as high as 94.654 kJ/mol (Table III). Linear pentamer of water molecules possesses the energy of self-association of 77.058 kJ/mol. Starting with hexamers, the energy of formation of linear and cyclic self-associates begins to decrease gradually. Thus, the formation energy of linear water hexamer is 54.428 kJ/mol. Since the triple blends under our consideration contain not more than 3 wt % of absorbed water, and taking into account that free water appear in the blends under very high hydration degree (more than 34 wt %, see Results and discussion), the formation of water clusters including more than three water molecules is unlikely in our case.

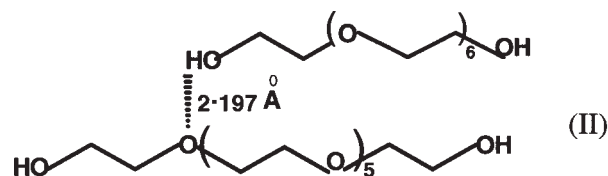
From a variety of carboxyl group dimers, the most energetically favorable (26.447 kJ/mol) is the structure:



IR spectra of such self-associates are well described.⁴¹ Aside from the shift of the band relating to carbonyl group stretching vibrations from 1700 to 1680 cm^{-1} , these cyclic self-associates demonstrate two wide bands in the region of 2600–2400 cm^{-1} . However, in the spectrum of triple PVP-PEG-PMAA-co-EA blend [Fig. 6(b)] there are no bands in this region. Thus, dimerization of PMAA-co-EA carboxyl groups in triple blend is hardly possible most likely due to comparatively low content of such groups in the blend.

Macromolecule of PEG-400 ($\text{HO}—[\text{CH}_2—\text{CH}_2—\text{O}]_n—\text{H}$) is composed of nine oxyethylene units and the PEG chain length is a crucial factor controlling the density of H-bonded network in PVP-PEG binary blends.^{27,47} In turn, the number of monomer units in PEG macromolecule (n) affects the results of quantum chemical calculations. In the present work our calculations has been performed for $n = 7$. Following increase in the number of monomer units up to $n = 8$ and 9 complicates essentially the calculations, but exerts comparatively negligible effect on the magnitudes of the energy of self-associate and complex formation. For this reason, all the values reported below relate to $n = 7$.

In contrast to PMAA-co-EA and water, PEG is a major component of triple PVP-PEG-PMAA-co-EA blends and its self-associates involving three and four macromolecules can not be ignored. Among such self-associates, the most energetically favorable (21.940 kJ/mol, Table III) is the structure (II), wherein the proton of PEG terminal hydroxyl group interacts with the next to last oxygen atom of neighboring PEG chain:



If PEG terminal hydroxyl interacts with central oxygen atoms of neighboring PEG chain, the formation energy of such self-associates decreases to 18.492 kJ/mol at the same length of hydrogen bond as in the structure (II). Approximately the same value of the energy of formation (18.401 kJ/mol) demonstrates the structure (III), involving cyclic self-association of PEG terminal hydroxyl groups:

TABLE III
Schematic Structures and the Energies of Formation of Hydrogen-Bonded Complexes
in the System PVP-PEG-PMAA-co-EA-H₂O

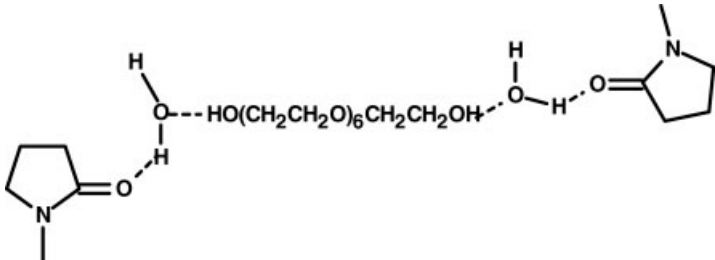
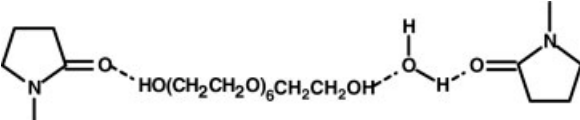
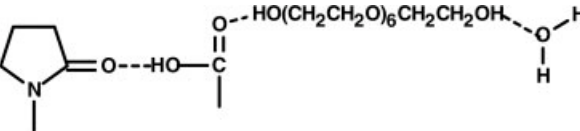
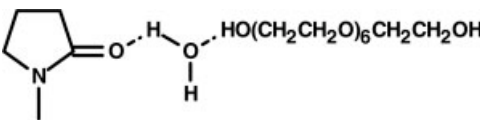
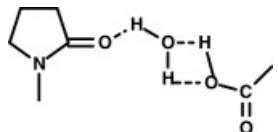
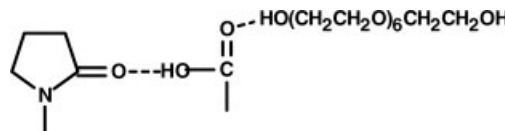
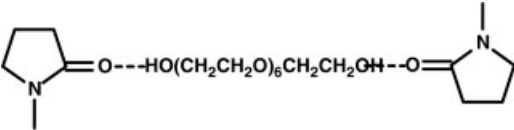
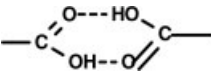
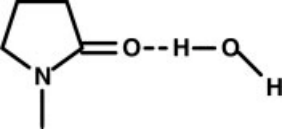
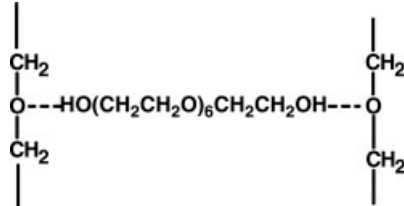
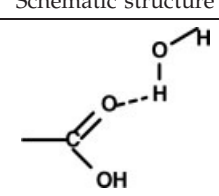
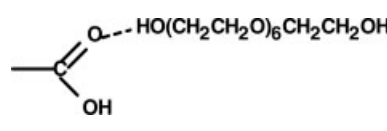
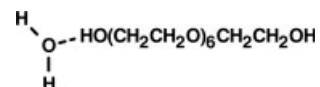
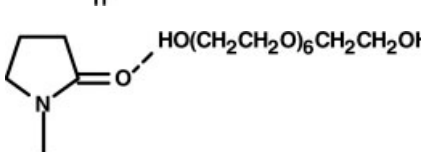
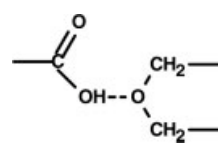
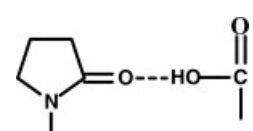
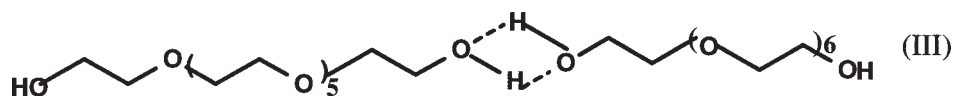
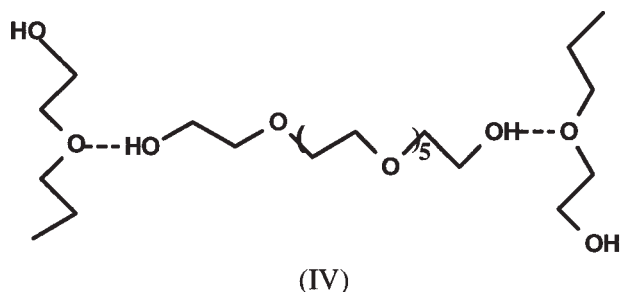
Complex	Schematic structure	$-\Delta E$ (kJ/mol)
PVP-H ₂ O-PEG-H ₂ O-PVP		79.399
PVP-PEG-H ₂ O-PVP		78.932
PVP-PMAA-co-EA-PEG-H ₂ O		66.026
PVP-H ₂ O-PEG		50.135
PVP-H ₂ O-PMAA-co-EA		44.097
PVP-PMAA-co-EA-PEG		40.72
PVP-PEG-PVP		33.705
PMAA-co-EA-PMAA-co-EA		26.477
PVP-H ₂ O		26.384
PEG-PEG		24.567

TABLE III Continued

Complex	Schematic structure	$-\Delta E$ (kJ/mol)
PMAA-co-EA-H ₂ O		22.605
PMAA-co-EA-PEG (OH)		23.475
PEG-H ₂ O		20.352
PVP-PEG		20.291
PMAA-co-EA-PEG(COC)		18.492
PVP-PMAA-co-EA		14.687



Among PEG self-associates, which are made up of three macromolecules, the structure (IV) provides the greatest gain in energy under formation (24.576 kJ/mol):



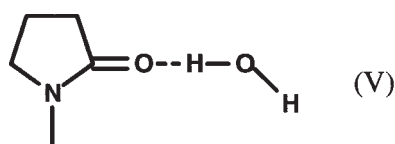
However, the attempts to include four macromolecules of PEG into self-associate result in the decrease of magnitude of the formation energy to 4.030 kJ/mol.

Bearing in mind reported peculiarities of PEG self-association, we nevertheless have to take into our consideration that, according to the above presented FTIR data, the interaction of PMAA-co-EA carboxyl groups with oxyethylene units of PEG chains inhibits the formation of PEG self-associates.

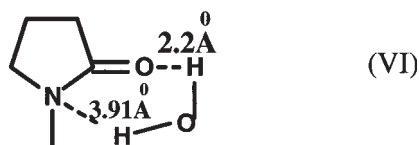
H-bonded complexes of polymer components with water

PVP is the most hygroscopic component of PVP-PEG-PMAA-co-EA blends. Arrangement of water molecules associated with repeating units of PVP within the first hydrate shell has been recently studied thoroughly in our group.⁴⁸ The results of calculations presented in Table III are in good agreements with earlier data.

Among all associates of PVP monomer units with water, the most energetically favorable (26.384 kJ/mol) is the complex based on hydrogen bond formed between oxygen atom of PVP carbonyl group and a proton of water (V):

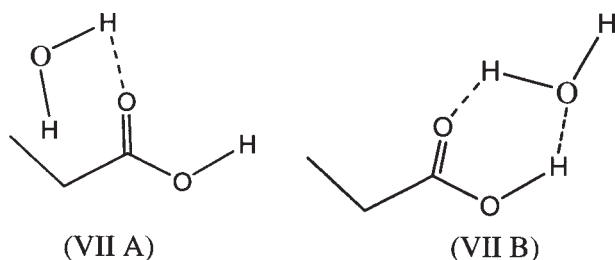


The complex of structure (VI), wherein both protons of water molecule form H-bonds with oxygen and nitrogen atoms of amide group in pyrrolidone ring is also real:

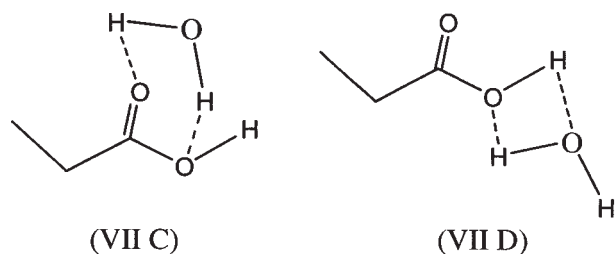


However, the energy of this complex formation (23.843 kJ/mol) is appreciably lower, and the hydrogen bond between the oxygen atom of carbonyl and water proton is much longer than in the complex (V) (3.91 instead of 2.64 Å). The complex involving only single H-bond between water proton and nitrogen atom in pyrrolidone ring is less stable (13.667 kJ/mol) and the length of hydrogen bond has been found to be 2.68 Å. Association of PVP unit with two and three water molecules leads to the decrease of complex stability. In this way, in the PVP–water system the most favorable are the complexes of 1 : 1 stoichiometry.

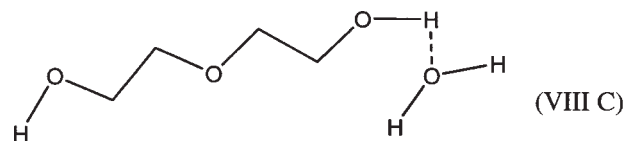
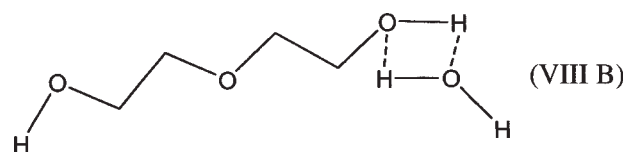
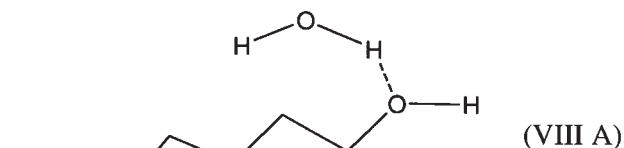
Among four hydrates of PMAA-*co*-EA carboxyl group, the most stable are the structures VII A and VII B (22.605 and 22.470 kJ/mol, respectively).



The structures VII C (18.431 kJ/mol) and VII D (16.679 kJ/mol) are less favorable:



As is well known, the water molecules associated with oligomers of ethylene glycol are mainly arranged at terminal hydroxyl groups.⁴⁹ For the sake of simplicity, the PEG chain is designated in schemes VIII and further by diethylene glycol, although the results of calculations relate always to heptamer of ethylene glycol. Among three PEG associates with water (VIII A–C) the complex VIII A is most energetically favorable (20.352 kJ/mol).

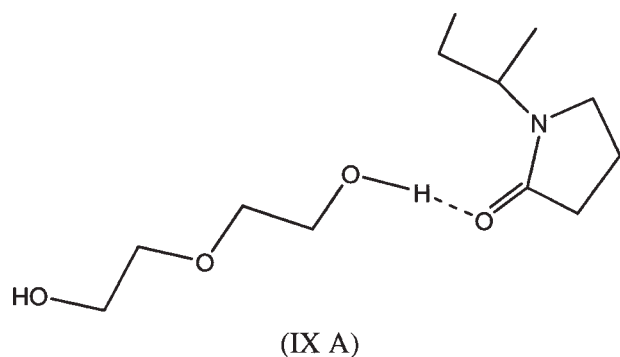


Other two structures (VIII B and C) are significantly less stable (14.233 and 13.900 kJ/mol). Hydrogen bonding of water proton to the oxygen atom in oxyethylene units in the middle of PEG chain leads to the complex that is much less stable (4.742 kJ/mol) and provides no competition to the hydroxyl groups at the chain ends.

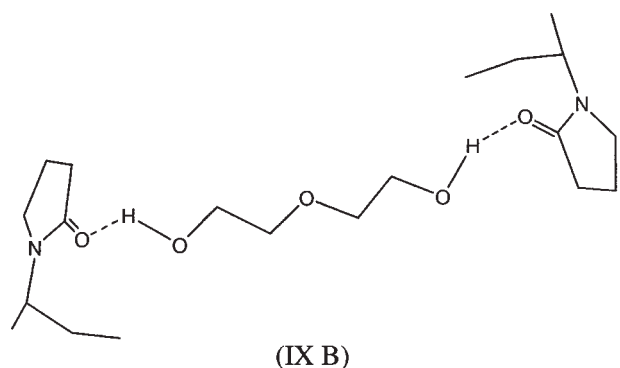
By this means from three polymers employed in present study the most energetically strong are the hydrates of PVP and the least stable are the associates of PEG with water. The hydrates of the carboxyl group in PMAA-*co*-EA are intermediate in the strength between PVP–water and PEG–H₂O complexes.

Pair complexes of polymer components

As follows from the data presented in Table III, hydrogen bonding of the oxygen atom in PVP carbonyl group to the proton of hydroxyl group at the end of PEG short chain (structure IX A) is characterized with the energy of complex formation of 20.291 kJ/mol.

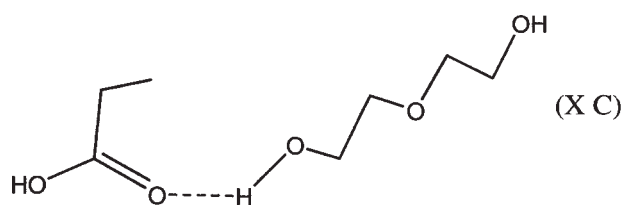
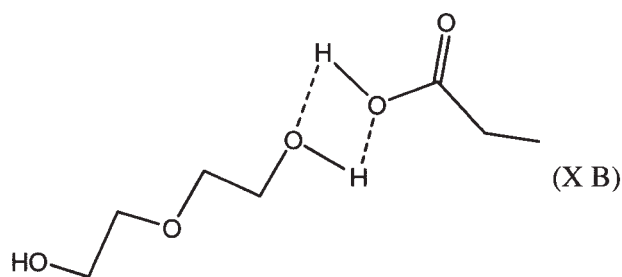
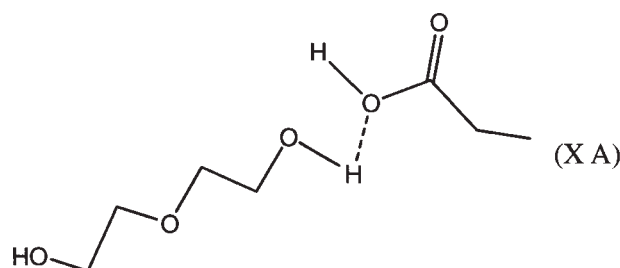


In this way, the strength of PVP-PEG complex is appreciably lower than the energy of PVP association with water (26.384 kJ/mol). However, as both hydroxyl groups at the opposite ends of the PEG chain are involved into hydrogen bonding to the PVP carbonyl groups, acting as a crosslink between PVP units (IX B), the formation energy of such network complex is much greater (33.705 kJ/mol).



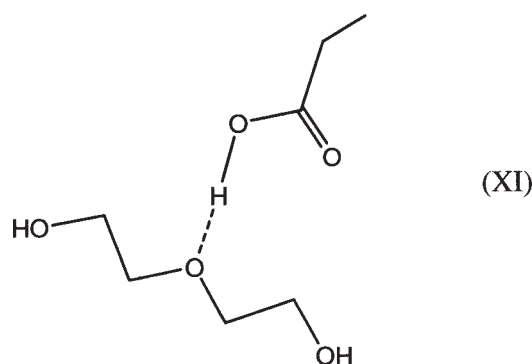
The energy of complex formation between oxygen atom of PVP carbonyl and the proton of carboxyl group in PMAA-co-EA has been found to be 14.687 kJ/mol (Table III). In this way, the hydrogen bonding between PVP and PMAA-co-EA is less favorable than the PVP-PEG interaction. Hydrogen bonding of the proton in PMAA-co-EA carboxyl group to the nitrogen atom of PVP amide group is further unfavorable (10.305 kJ/mol).

Among the complexes of the PMAA-co-EA carboxyl group with terminal hydroxyl groups in PEG short chains (X A, B, and C), the most energetically favorable are the structures X A and X B (24.056 and 23.271 kJ/mol), in which the OH-group of the carboxyl in PMAA-co-EA is bonded to the OH group of the PEG by single or two hydrogen bonds.



The hydrogen bonding through the oxygen atom of carbonyl in PMAA-co-EA carboxyl group (IX C) is energetically unfavorable (4.356 kJ/mol).

Alternative mechanism of specific interaction between the carboxyl group of PMAA-co-EA and PEG is the hydrogen bonding through the oxygen atom of oxyethylene units (-C-O-C-) in the PEG chains (XI):

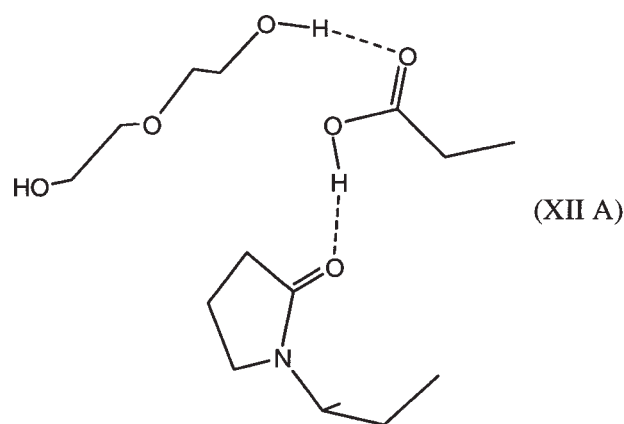


Although this type of the PMAA-co-EA interaction with PEG is less favorable (16.450 kJ/mol) as compared to the pair complexes outlined by the structures X A and B, this mechanism is nevertheless of great importance in triple PVP-PEG-PMMA-co-EA blends because every PEG-400 macromolecule contains seven oxyethylene units in the middle of chain. The contributions of different mechanisms of PEG-PMAA-co-EA complex formation and the amount of reactive groups in PEG molecules are supposed to be responsible for enormously large negative magnitude of the PEG-PAA pair interaction parameter ($\chi_{\text{PAA-PEG}} = -7.37$) evaluated as discussed above from the isotherms of water vapor sorption by triple PAA-PEG-PVP blends.³⁸ The formation of such type of structures in ternary PVP-PEG-PMMA-co-EA blends has been shown by FTIR spectroscopy from the analysis of the spectra presented in Figure 9.

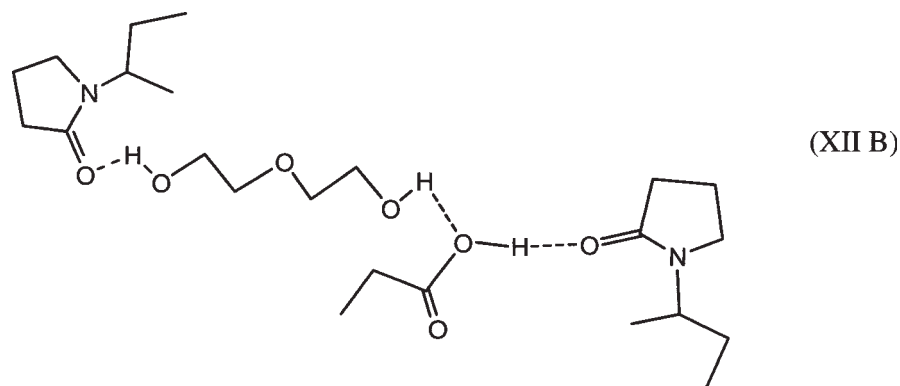
Triple PVP-PEG-PMAA-co-EA complex

The data of quantum chemical calculations presented in previous sections of this article allow us to arrange the strength of hydrogen bonded pair complexes formed in the triple PVP-PEG-PMAA-co-EA blend in the following pattern: PVP-PEG > PMAA-co-EA-PEG > PVP-PMAA-co-EA. However, according to the values of pair interaction parameters,³⁸ not only does the interaction of carboxyl groups of PAA with PEG, but the PVP-PAA interaction also ($\chi_{\text{PVP-PAA}} = -1.81$) is stronger than the strength of PVP-PEG complexes ($\chi_{\text{PVP-PEG}} = -0.23$). To bring the results of calculations and experiment into better agreement, we have to consider the allowance for the formation of triple PVP-PEG-PMAA-co-EA complex.

As quantum chemical calculations have shown, the triple PVP-PMAA-co-EA-PEG complex (XII A) reveals much higher value of the formation energy (40.172 kJ/mol) than the corresponding values of relevant pair PVP-PMAA-co-EA (14.687 kJ/mol), PVP-PEG (20.291 kJ/mol) and PMAA-co-EA-PEG (24.056 kJ/mol) complexes.

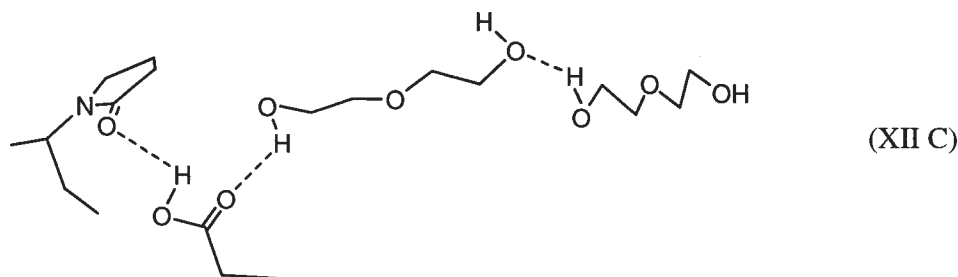


If two PEG chains, assembled into linear self-associate through terminal OH-groups, are bonded to the carbonyl group of PVP through the carboxyl group of PMMA-co-EA as is shown in structure XII B, the stability of such triple complex occurs to be significantly improved (46.881 kJ/mol):



Involvement of the carboxyl group as an intermediate link into the structure of crosslinked PVP-PEG-PVP complex increases further the energy of such complex formation from 33.705 to 60.871 kJ/mol (XII C):

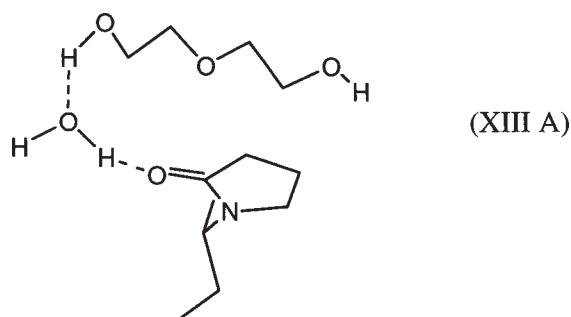
Thus, established reinforcement of the PVP-PEG complexes by means of the inclusion of carboxyl group of PMAA-co-EA between the PVP carbonyl and the hydroxyl group of PEG may account for the increase in the value of PVP-PMAA-co-EA interaction parameter.



Effect of water on the formation energy of H-bonded complexes

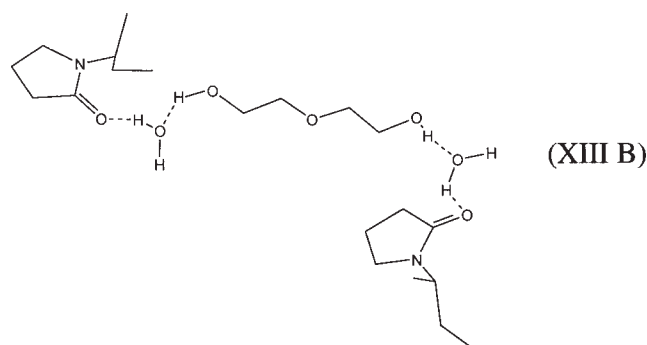
As has been earlier observed from the molecular dynamics of binary PVP blends with PEG-400, absorbed water facilitates the process of PVP-PEG complex formation.^{50,51} As the data of FTIR spectroscopy have shown in the present and earlier studies,^{44,45} water is strongly bound with most hygroscopic component of the blends, PVP,³⁶ and H-bonding of PEG to PVP proceeds most likely through the molecules of water in PVP hydrates. Bound water affects markedly the phase state^{36,37,47} and physical properties of PVP-PEG blends.^{28,30,31} In this connection the investigation of the effect of water molecules associated with polymer components in PVP-PEG-PMMA-co-EA blend on the toughness of H-bonded complexes is of undoubted interest.

The calculated energy of PVP-PEG complex formation as indicated above is 20.291 kJ/mol. However, as a molecule of bonded water is located between the carbonyl group of PVP and terminal hydroxyl group of PEG (XIII A), the strength of H-bond complex becomes as high as 50.135 kJ/mol.



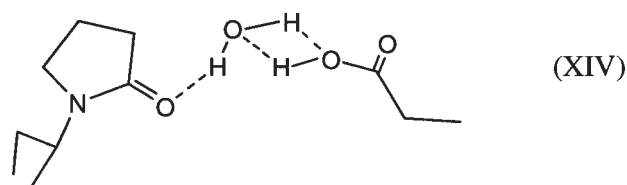
The evaluated strength of PVP-H₂O-PEG complex (XIII A) implies that the water bound by PVP must be considered as a helper in the complex formation with PEG rather than competitor to PEG terminal OH groups for hydrogen bonding with PVP. PVP is always hydrated. The complex formation of PVP of different degrees of hydration with various low and high molecular weight compounds and drugs is a subject of numerous studies reviewed by Kirsh and Buehler in their books.^{14,24} Despite appreciable difference in the amount of water absorbed by the PVP, various authors report reproducible results. The significance of this fact is that the PVP hydrates behave as individual polymer and not as the blends of PVP with water. In this way, intervening role of water associated with PVP within the first hydrate shell is most likely a specific feature characteristic of not only PVP interaction with PEG but of a variety of other systems.

Incorporation of water molecule, bound with carbonyl groups of two neighboring PVP chains, results in structure of hydrogen bonded network complex, outlined in IX B, gives the structure XIII B, which possesses the free formation energy of 79.399 kJ/mol:

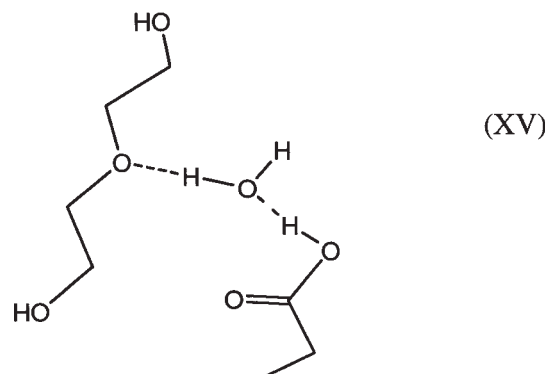


The PVP-H₂O-PEG-H₂O-PVP network complex XIII B is strongest among the variety of the structures provided by competitive hydrogen bonding in PVP-PEG-PMMA-co-EA system.

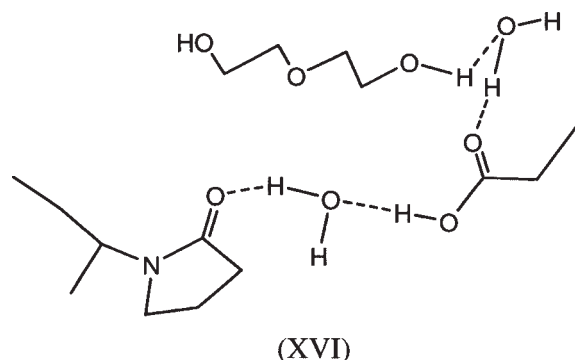
As is seen from Table III, the strength of PVP complex with carboxyl group of PMMA-co-EA is 14.687 kJ/mol. However, the incorporation of water molecule between the carbonyl group of the PVP and carboxyl group of the PMMA-co-EA leads to the increase of the complex formation energy to 44.097 kJ/mol (XIV):



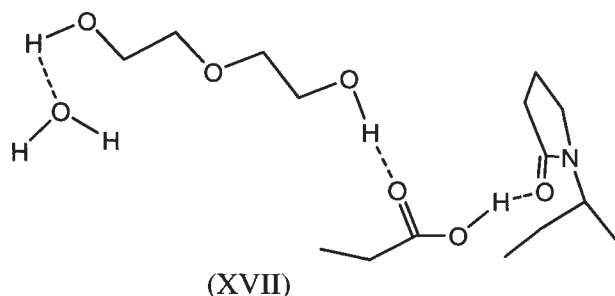
While the complexes of PVP with PEG and PMMA-co-EA are strengthened by incorporation of water molecule between the reactive functional groups of polymer components, this is not the case for PEG-PMMA-co-EA complexes. Arrangement of the molecule of water between OH group of PEG and carboxyl group of PMMA-co-EA causes the drop of the free energy of complex formation from 24.056 (structure X A) to 2.699 kJ/mol. At the same time, participation of water molecule in hydrogen bonding between the proton of PMMA-co-EA carboxyl group and the oxygen atom in PEG oxyethylene units makes the formation of the complex (XV) much more favorable (50.103 kJ/mol):



The triple PVP–PMAA-*co*-EA–PEG complex (XII A, $-\Delta E = 40.172$ kJ/mol) becomes looser ($-\Delta E = 11.732$ kJ/mol) if two water molecules are placed between the functional groups of polymers forming PVP–H₂O–PMAA-*co*-EA–H₂O–PEG complex (XVI):



The formation of PVP–H₂O–PMAA-*co*-EA–PEG complex has been found to be energetically unfavorable (0.911 kJ/mol). In contrast, bonding of water molecule to the free hydroxyl group at the end of PEG chain, involved into hydrogen bonding to the carboxyl group of PMAA-*co*-EA and PVP, makes H₂O–PEG–PMAA-*co*-EA–PVP complex (structure XVII) much more stable (66.026 kJ/mol) than the triple PVP–PMAA-*co*-EA–PEG complex ($-\Delta E = 40.172$ kJ/mol):



As concluded from FTIR spectra of PVP–PEG–PMAA-*co*-EA–H₂O systems [Fig. 12(a), section 2.4],

the interaction of protons of PMAA-*co*-EA carboxyl groups with PVP is stronger than the PVP–water interaction. However, the data of quantum chemical calculations presented in Table III reveal the opposite. Actually, the gain in energy of PVP–PMAA-*co*-EA complex formation has been found to be 14.687 kJ/mol, whereas that for PVP–H₂O association is 26.384 kJ/mol. The implication of this fact is that the triple complexes of PVP–PMAA-*co*-EA–PEG–H₂O (66.026 kJ/mol), PVP–H₂O–PMAA-*co*-EA (44.097 kJ/mol), and PVP–PMAA-*co*-EA–PEG (40.172 kJ/mol) are really formed in blends.

Structural and electronic characteristics of hydrogen bonded interpolymer complexes in the system PVP–PEG–PMAA-*co*-EA are presented in Table IV. Hydrogen bonding is accompanied with the change in bond lengths, valent angles, and significant polarization of the atoms forming H-bonds. As follows from the data presented in Tables III and IV, the major factor describing the strength of hydrogen bonds is not the bond length, but the energy of complex formation and atom polarization.

Equilibrium between different mechanisms of hydrogen bonding and phase behavior of PVP–PEG–PMAA-*co*-EA–H₂O system

The competitive interaction signifies the existence of equilibrium between different mechanisms of hydrogen bonding. The change in blend composition shifts the equilibrium accordingly, making the specific type of interaction prevailing in particular concentration range. In binary blends of hydrated PVP with PEG-400, the structures of network (XIII B) and uncrosslinked (XIII A) PVP–PEG complexes involving bound water are predominant. As a result, the PEG is bonded to PVP in amorphous phase and inaccessible for crystallization (Fig. 4). In comparatively dry PVP–PEG blends the PVP–PEG–PVP (IX B) and PVP–H₂O–PEG–PVP (Table III) complexes are formed, which are also strong enough. Adding PMAA-*co*-EA leads to the

TABLE IV
Structural and Electronic Features of the Components of PVP–PEG–PMAA-*co*-EA–H₂O System and Some H-Bonded Complexes

System	ΔE (kJ/mol)	Bond lengths (Å)			Valent angles (°)		Atom charges				
		O...H	C=O	–O–H	N(C)CO	HOH(O)	N	C=	=O	H	O
PVP	–	–	1.240	–	126.0	–	–0.335	+0.307	–0.354	–	–
PEG	–	–	–	0.965	–	107.4	–	–	–	+0.197	–0.320
PMAA- <i>co</i> -EA	–	–	1.234	0.971	–	109.7	–	+0.304	–0.361	+0.242	–0.321
H ₂ O	–	–	–	0.961	–	103.5	–	–	–	+0.191	–0.338
PVP–H ₂ O	26,384	2.199	1.244	0.963	124.9	104.2	–0.337	+0.323	–0.394	+0.205	–0.411
PVP–PEG–PVP	33,705	2.15(a)	1.243	0.967	126.1	106.6	–0.325	+0.313	–0.378	+0.224	–0.352
		2.16(b)	1.243	0.968	125.8	106.3	–0.334	+0.318	–0.383	+0.227	–0.357
PVP–PMAA- <i>co</i> -EA–PEG	40,172	2.09(a)	1.244	0.978	125.7	110.5	–0.332	+0.323	–0.395	+0.276	–0.318
		2.15(b)	1.238	0.968	128.9	106.3	–0.160	+0.320	–0.408	+0.231	–0.353

appearance in amorphous phase of the stable PVP-PMAA-co-EA-PEG (XII A) and PVP-PMAA-co-EA-PEG-H₂O (XVII) complexes.

A vulnerable feature of the triple PVP-PMAA-co-EA-PEG complex is that its formation requires strictly defined ratio of the concentrations of polymer components. With the increase in PMAA-co-EA content (and corresponding decrease in PVP concentration, Fig. 4) the probability of the formation of triple complex decreases because of the lack of PVP, which is a most powerful hydrogen bonding component in the blend. As a result, the total gain in energy at the expense of hydrogen bonding between PEG and PMAA-co-EA becomes comparable with the strength of both PMAA and PEG self-associates (Table III). Occurrence of crystalline phase in PVP blends with 50% of PEG-400, containing from 10 to 20 wt % PMAA-co-EA, is a sign in favor of PEG self-association. The formation of PEG self-associates in ternary blends has been clearly established by FTIR spectroscopy corresponding to the band at 3380 cm⁻¹ in the spectrum presented in Figure 10. Further increase in PMAA-co-EA content shifts the equilibrium toward the formation of less stable PMAA-co-EA complex and disappearance of crystallizing PEG self-associates. However, the existence of two different T_g s for the blend containing 37% PMAA-co-EA and 50% PEG (Fig. 4) is an evidence that the self-association of the carboxyl groups of PMAA-co-EA leads to the formation of amorphous PMAA-co-EA phase. The occurrence of the carboxyl group self-associates of PMAA-co-EA in the PVP-PEG-PMAA-co-EA blends has been earlier established by the presence of 1698 cm⁻¹ band in FTIR spectrum [see Fig. 5(b) and Table II].

CONCLUSIONS

Partially miscible PVP-PEG-PMAA-co-EA blends demonstrate very strong competitive hydrogen bonding between PVP carbonyl groups, carboxyl groups of PMAA-co-EA, terminal hydroxyl groups, and oxyethylene units of PEG short chains, while ethyl acrylate monomer units of PMAA-co-EA do not contribute appreciably to interpolymer hydrogen bonding. The equilibrium between different mechanisms of hydrogen bonding makes possible the formation of triple and four-component complexes, involving all three polymers and absorbed water. As a result, the strength of hydrogen bonded complexes in PVP-PEG-PMAA-co-EA-H₂O system diminishes in the order: PVP-H₂O-PEG-H₂O-PVP > PVP-H₂O-PEG-PVP >> PVP-PMAA-co-EA-PEG-H₂O >> PVP-H₂O-PEG >> PVP-H₂O-PMAA-co-EA > PVP-PMAA-co-EA-PEG >> PVP-PEG-PVP > PMAA-co-EA self-associates > PVP-H₂O > PEG self-associates > PMAA-co-EA-H₂O > PMAA-co-EA-PEG(OH) > PEG-H₂O > PVP-

PEG > PMAA-co-EA-PEG(C—O—C) > PVP-PMAA-co-EA. As is obvious from these data, the most stable complexes in the PVP-PEG-PMAA-co-EA-H₂O system are formed owing to the participation of PVP and the water molecules associated with the PVP monomer units in the first hydrate shell. The competitive hydrogen bonding governs the phase state of triple polymer blends.

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