About the Compatibility of Polymer Components in Polymer Complexes Based on Poly(acrylamide) and Poly(vinyl alcohol)

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SUMMARY: The issue of applying the usual concepts of polymer compatibility to nonstoichiometric PVA/PAA mixtures of chemically complementary poly(vinyl alcohol) and poly(acrylamide), which form in water solution InterPC (intermolecular polymer complex) stabilyzed by H-bonds, and PAA to PVA graft copolymers (PVA-PAA$_N$) with different grafted chains number N, that are IntraPC (intramolecular polymer complexes) is discussed. PVA and PAA are compatible on molecular level. At the same time PVA/PAA mixture (50/50 W/W) is characterized by heterogeneous structure consists of InterPC with $\varphi_{char}=9g_{PVA}/g_{PAA}$ and the excess of unconnected PAA. In the case of IntraPC, yet, only PVA-PAA$_N$, where N=25, is characterized by a single glass transition temperature (Tg). At larger values of N separate PAA domains form giving rise to the corresponding Tg. These results are discussed in view of IntraPC structure peculiarities as a function of N investigated by IR spectroscopy.

Introduction

Chemically complementary polymers, which form InterPC, belong to the ultimately thermodynamically compatible polymers, because of cooperative system of intermolecular bonds formation$^{1)}$. Such polymer systems, where InterPC composition changes together with mixture component composition, form homogeneous dispersions in the bulk state with single Tg over whole composition range, which is the most unambiguous criteria of polymer compatibility. The question of applying the usual concepts of polymer compatibility to nonstoichiometric mixtures of chemically complementary polymers with composition–independent φ_{char} of their InterPC arises. The same question concerning graft copolymers based on chemically complementary polymers where certain steric obstacles exist for main and grafted chains interaction arises which is practically not yet discussed in literature.

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In this paper two types of samples have been investigated: i) nonstoichiometric (50/50) mixture of chemically complementary PVA and PAA, which according to the viscometry and high-speed sedimentation data consists of InterPC with composition $\varphi_{char}=9g_{PVA}/g_{PAA}$ and the excess of unconnected PAA$^{2)}$; ii) graft copolymers PVA-PAA$_N$ with comparable lenght and different grafted chains number N that are IntraPC.

Experimental part

The polymers used in this study all are commercial products. PAA ($\overline{M}_V = 2.72 \bullet 10^6$, 13% hydrolyzed) was obtained from "Oriana" (Ukraine). PVA ($\overline{M}_V = 4 \bullet 10^4$, 33% residual acetate groups) was from Japan. Solution blending was used with water as the solvent, and the solution concentration was 0.1 (wt/v). Mixture 50/50 in bulk state was obtained by using of freeze-dry technique.

PVA-PAA$_N$ synthesis was carried out according to Ref.$^{3)}$ PVA from "Serva" (Sweden) and acrylamide from "Reanal" (Hungary) were used. The main characteristics of graft copolymers are presented in Table 1.

Table 1. Molecular characteristics of graft copolymers samples.

Sample	$M_{PVA\text{-}PAAN} \bullet 10^{-6}$	$\overline{M}_{VPVA} \bullet 10^{-6}$	$\overline{M}_{VPAA} \bullet 10^{-6}$	N
PVA-PAA$_N$1	3.08	0.08	0.12	25
PVA-PAA$_N$2	2.49	0.08	0.06	31
PVA-PAA$_N$3	3.92	0.08	0.08	49

The length of grafted chains was determined according to Ref.$^{3)}$ The $M_{PVA\text{-}PAAN}$ and N values were determined by elemental analysis.

Structural investigations methods include wide-angle X-ray (WAXS) technique with application of DRON-2.0 apparatus and differential scanning calorimetry (DSC) technique (DuPont 1090 unit).

Results and Discussion

The WAXS curves of PVA/PAA mixture and individual components are represented in Fig. 1. PVA is characterized by partial-crystalline structure (Fig. 1, curve 1), which is typical for this polymer. The diffractogram of PAA is diffusional (Fig.1, curve 2). The amorphous character of PVA/PAA structure testifies that PVA completely loses ability to crystallize (Fig.1, curve 3). Simultaneously it is observed the considerable difference in the contours of the experimental and additive calculated diffractograms of PVA/PAA (Fig.2), which points on mixing of polymer components on the macromolecular level as a result of complex formation.

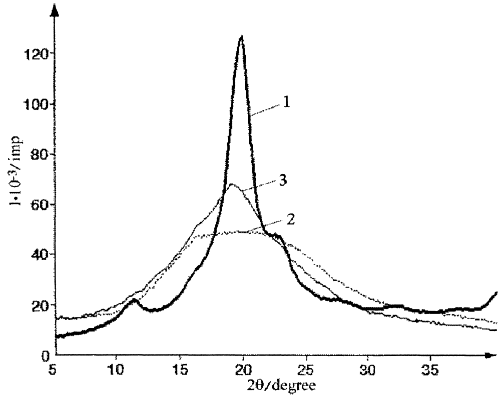


Fig. 1: Wide-angle X-ray scattering curves of PVA (1), PAA (2) and PVA/PAA (3).

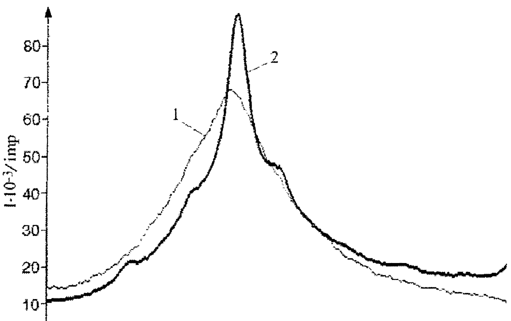


Fig. 2: Experimental (1) and additive (2) wide-angle X-ray scattering curves of PVA/PAA.

Fig.3 shows the experimental DSK-curves for all the samples and their glass transition temperature and its range ΔT_g are listed in Table 2. The temperature at the midpoint of the heat capacity transition was taken as T_g. PAA possesses by broad range of glass transition (Fig3, curve 1, Table 2). The melting point of PVA is 225,5°C, and its glass transition is disposed in relatively low temperature region (Fig.3, curve 2, Table 2). The DSC results indicate that there is single PVA/PAA T_g (Fig.3, curve 3) with broad temperature range. A broad ΔT_g may indicate that the mixture is a two-phase system. When the T_g values of both phases are close to each other a broad ΔT_g is observed. The 2-nd run of PVA/PAA after heating to 216 °C (Fig.3, curve 4) shows two glass transition temperature, id est. T_g values of the two phases are become separated: 1 - InterPC, 2 - the excess of unconnected PAA. The 3-rd run of PVA/PAA after heating to 230 °C shows the weakening of both two glass transition heat effects.

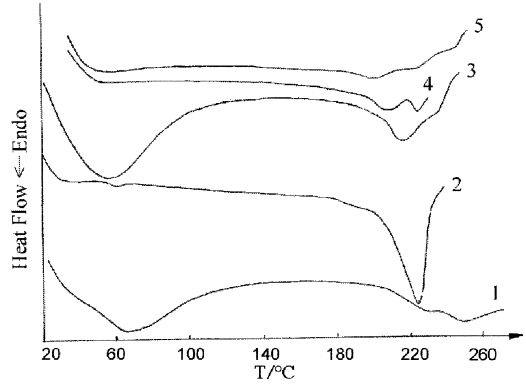


Fig. 3: DSC curves of PAA (1), PVA (2), PVA/PAA (3), 2-nd run after PVA/PAA heating to 216 °C (4), 3-rd run after PVA/PAA heating to 230 °C.

Table 2. DSC data

Sample	Tg / ^{0} C	Δ Tg / ^{0} C
PVA	58.5	8
PAA	211	21
PVA/PAA	201.5	25
PVA/PAA$^{a)}$	202	8
	223	6
PVA/PAA $^{b)}$	198	6

$^{a)}$ 2-nd run after heating to 216^0 C
$^{b)}$ 3-rd run after heating to 230^0 C

So InterPC formation in polymer mixture is attested by the appearance of a new glass transition temperature, which differs from the glass transition temperatures of the individual polymer components. At the same time DSC traces also reveal the presence of PAA domains as ascertained by the occurrence of the Tg of this polymer after heating.

PVA-PAA$_N$ samples were also investigated by WAXS method. The results of these examinations are adduced only for PVA-PAA$_N$1. For other samples similar results were observed. The amorphous character of PVA-PAA$_N$1 structure (Fig. 4, curve 3) and difference in the contours of its experimental and additive calculated WAXS curves point on intramolecular polycomplex formation.

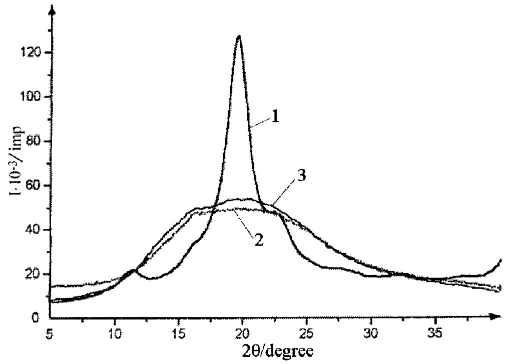


Fig. 4: Wide-angle X-ray scattering curves of PVA (1), PAA (2) and PVA-PAA$_N$1 (3).

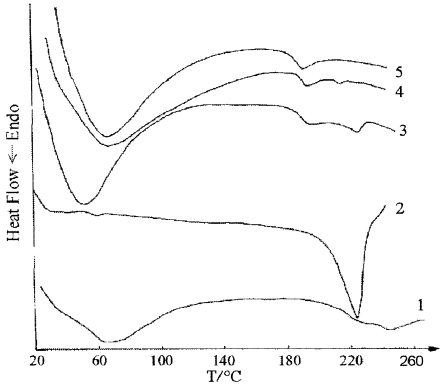


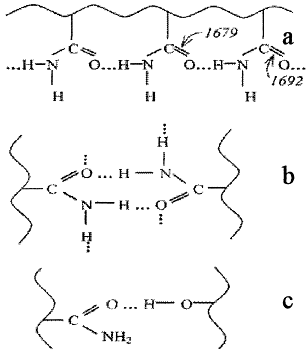
Fig. 5: DSC curves of PAA (1), PVA (2), PVA-PAA$_N$3 (3), PVA-PAA$_N$2 (4), PVA-PAA$_N$1 (5).

Table 3. DSC data.

Sample	Tg / °C	Δ Tg / °C
PVA	58.5	8
PAA	211	21
PVA-PAA$_N$1	186.5	11
PVA-PAA$_N$2	190.5	7.5
	213.5	3.5
PVA-PAA$_N$3	190	8.5
	219.5	12.5

DSC results for graft copolymers (Fig. 5, Table 3) confirm the IntraPC formation, as for all samples a new glass transition temperature is observed which clearly differs from those of pure PVA and PAA, and somewhat increases with N growth. At the same time, yet, only PVA-PAA$_N$1 where N=25 is characterized by a single Tg (Fig.5, curve 3).

Obtained DSC results are completely conformed with IR spectroscopy investigations of PVA-PAA$_N$ H-bonds structures in dependence of N. Previously set$^{3)}$ that examined copolymers structure is stabilized by hydrogen bonds systems of various types:



where a - *trans*-multimers of amide groups of PAA grafted chains; b- *cis-trans*-multimers of amide groups of PAA grafted chains; c - hydrogen bonds between main and grafted chains.

For a study of character of amide groups redistribution between the specified H-bonds structures at various N the computer processing of IR spectra in amide I and II region was carried out by spline method$^{4)}$. It was shown that the increase of grafted chains number N in PVA-PAA$_N$ results in gradual diminution of H-bonds between main and grafted chains (structure c) and magnification of H-bonds between PAA chains for a type *cis-trans*-multimers of amide groups (structure b), which defines the grafted PAA chains suppleness. As a result Tg of PAA domains occurs at more higher temperature and with greater heat effect at N growth (Fig. 5, curve 3 and 4). So in examined range of graft copolymers PVA-PAA$_N$ the value 25<N<31 is critical in that above PAA grafted chains form domains with corresponding Tg.

Conclusions

The systems of chemically complementary polymers – PVA and PAA, that in peculiar cases in a limit of applying the usual concepts of polymer compatibility form heterogeneous dispersions in the bulk state, have been examined. Nonstoichiometric mixture PVA/PAA (50/50) consists of InterPC with $\varphi_{char} = 9 g_{PVA}/g_{PAA}$ and the excess of unconnected PAA. In graft copolymers PVA-PAA$_N$ at 25<N<31 PAA grafted chains form domains with corresponding Tg.

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