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Complex formation between polymethacrylic acid and copolymers of adipic acid with poly(ethylene glycol) in aqueous solution

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The complex formation between polymethacrylic acid (PMAA) and the copolymers of adipic acid (AdA) with poly(ethylene glycol) (PEG) in dilute solution has been studied. The hydrophobic AdA fragments break the continuous cooperative hydrogen bonds between the polymer components in the polycomplex being however the factor that stabilizes the polycomplex (PMAA.AdA/PEG). If the AdA/PEG copolymers are of one and the same chain length the copolymer having more AdA hydrophobic fragments exhibits greater complex forming ability. © 1997 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: polycomplex; hydrophobic interactions; sequence of cooperative bonds)

INTRODUCTION

The forming reactions of interpolymer complexes (polycomplexes) with the participation of copolymers are studied less than the reactions of complex formation between homopolymers. This is valid both for interpolymer reactions between oppositely charged polyions and for interpolymer reactions with the participation of nonionogenic polymers when the complex formation is due to the existence of hydrogen bonds between the macromolecular partners. The latter case of complex formation with the participation of copolymers was first studied by Ferguson and McLeod on the base of complex formation between polyacrylic acid (PAA) and copolymers of *N*-vinylpyrrolidone (VP) with acrylamide (AAm) and styrene (St) in aqueous solution[1]. The polycomplexes were prepared in two ways: by mixing the solutions of the polymeric components, and by matrix radical polymerization of acrylic acid (AA) in aqueous solution in the presence of the above mentioned copolymers.

It was shown by the complexation between PAA and VP/AAm copolymer that the stoichiometry of the polycomplex depends on the mode of preparation. The polycomplex obtained by mixing the solutions of PAA and of VP/AAm copolymer is enriched in PAA, i.e. the polycomplex contains some amount of PAA units, unbound to the complementary VP units by a hydrogen bond. At matrix polymerization of AA in the presence of VP/AAm copolymer the polycomplex in which each PAA unit is bound to a VP unit is formed.

The complex forming reactions with the participation of copolymers have been studied in detail by Bekturov and coworkers[2–5]. As proton donor copolymers have been used copolymers of maleic anhydride (MA) with methacrylic acid (MAA), MA with acrylic acid (AA), MA with methyl monoester of itaconic acid (MMI), MAA with methyl methacrylate (MMA) and with St. Poly(ethylene glycol) (PEG) and poly(*N*-vinylpyrrolidone) (PVP) were used as proton accepting polymers. The polycomplexes containing an alternating copolymer as a component are enriched in proton accepting polymer. This could be explained by the fact that PEG or PVP units cannot form hydrogen bonds with the proton donor units (MAA, AA, MMI) of the copolymer component, due to the enlarged distance between the active groups in the copolymer chain and due to the steric hindrance caused by the bulky anhydride groups. The polycomplexes containing a random copolymer could be enriched both in proton donor and proton acceptor units. Authors find that the main difference between the polycomplexes formed by the two homopolymers and the polycomplexes formed by the participation of copolymers is that the latter are less stable. For example copolymer polycomplexes dissociate at lower content of the organic component (DMSO, DMF) in mixed solvent (water + organic solvent) than the homopolymer polycomplexes. This is in relation with the fact that the inert (non binding) monomer units in the copolymer chain break the cooperative sequence of hydrogen bonds between the macromolecular partners.

The same reason is in the fact that the polycomplexes of PAA and polymethacrylic acid (PMAA) with PEG and PVP dissociate when increasing pH of the aqueous solution[6–9]. The formed carboxylate groups from PAA and PMAA, unlike the carboxy groups, do not form hydrogen bonds with oxygen atoms of PEG and PVP, thus breaking the sequence of hydrogen bonds between the polymeric chains in the polycomplex. If the average length of the sequence with destroyed hydrogen bonds reaches some critical value the polycomplex becomes unstable[7,8].

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Table 1 Molecular weight characteristics of AdA/PEG copolymers

Copolymer	$\bar{M}_n$	$\bar{M}_W$	$\bar{M}_w/\bar{M}_n$	M_η
AdA/PEG-1	360	480	1.33	450
AdA/PEG-2	740	1010	1.36	990
AdA/PEG-3	3160	3480	1.10	3370
AdA/PEG-4	3190	3570	1.12	3430

From a study of complex formation of PEG and PVP with copolymers of AA with vinylsulfonic acid (VS) it was shown that even in the cases when the AA/VS copolymer contains 10–15 mol% units of the strong VS, the polycomplexes are destroyed[10]. The reason is the same—the dissociated VS units do not form hydrogen bonds with PEG or PVP, and this is the destabilizing factor.

The data above show that the existence of units not bound by a hydrogen bond to the homopolymer partner in the copolymer chain makes the polycomplex unstable to a certain degree.

It was proved that introducing a hydrophobic group into the PEG macromolecule considerably stabilizes its polycomplexes with PAA and PMAA in water[11–13]. The explanation is that the transfer of the hydrophobic group of monosubstituted PEG from the aqueous medium into the hydrophobic particle of the polycomplex additionally decreases the free energy of the system. There comes the question of the stability of the polycomplex where one of the polymeric partners has hydrophobic groups in its chain which are not bound by a hydrogen bond to the second partner, thus breaking the sequence of hydrogen bonds between the complex forming macromolecules.

This paper reports on complex formation between PMAA and copolymers of adipic acid (AdA) with PEG of various molecular weights in aqueous solution. Some results from the investigations were presented earlier at the Bulgarian National Symposium 'Polymers 93'[14].

EXPERIMENTAL

PMAA was prepared by radical polymerization of methacrylic acid in benzene at 60°C under N_2 with AIBN as initiator. PMAA molecular weight was 1.8×10^5 as determined viscometrically[15] at 30°C in 0.002 N HCl using the relation $[\eta] = 6.6 \times 10^{-4} M^{0.5}$, the $[\eta]$ value for the PMAA sample being 0.28 dl g^{-1}.

The copolymers of AdA with PEG were prepared by two procedures. The copolymers AdA/PEG-1 and AdA/PEG-2 were prepared by addition of ethylene oxide to AdA under argon at 160–180°C. NaOH was used as a catalyst (0.5 wt% with respect to AdA).

The copolymers AdA/PEG-3 and AdA/PEG-4 were prepared by esterification of AdA with PEG of $\bar{M}_w = 600$ and 1500 respectively, under argon at 180–200°C. *p*-Toluenesulfonic acid was used as a catalyst (0.1 wt% with respect to the mixture of the components). The initial mixture always had equimolar composition, i.e. each molecule AdA corresponded to a macromolecule of PEG of $\bar{M}_w = 600$ or 1500.

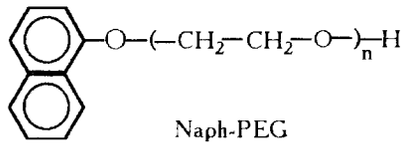
Molecular weight characteristics of the copolymers are presented in *Table 1*.

Molecular weights of the copolymers were determined by gel permeation chromatography (g.p.c.) and viscometrically.

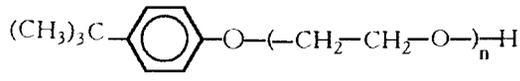
G.p.c. analyses were carried out with a Waters 244 instrument equipped with combinations of Ultrastyragel columns of 100, 100, 500 and 1000 Å in THF solution, maintained at a flow rate 1 ml min^{-1} at 45°C. RI was used for detection and the PEGs were used as calibration standards. The analysis showed no detectable content of unreacted AdA or PEG.

Molecular weights of the copolymers were determined viscometrically on an Ubbelohde viscometer as follows. In water at 25°C were determined the intrinsic viscosities $[\eta]$ of PEGs (Fluka) with $\bar{M}_W = 600$, 1000, 1500, 2000, 3000, 4000, 6000, 10 000 and 15 000. Then from the dependence of $\lg[\eta]$ on $\lg\bar{M}_w$ the parameters K and α in the Mark–Kuhn–Houwink equation were estimated. At 25°C in water the values obtained were 2.82×10^{-4} dl g^{-1} and 0.74, respectively, i.e. the dependence of $[\eta]$ on $\bar{M}_\eta$ is determined by the equation $[\eta] = 2.82 \times 10^{-4} \bar{M}_\eta^{0.74}$. Then in water at 25°C were determined $[\eta]$ for four AdA/PEG copolymers and their $\bar{M}_\eta$ values were estimated according to the above-mentioned equation. Thus the method for $\bar{M}_\eta$ determination of AdA/PEG copolymers is based on calibration by PEG of various $\bar{M}_w$. The same is valid for the g.p.c. method. The existence of a hydrophobic segment in AdA/PEG copolymer compared to the hydrophilic homopolymer PEG could change to a certain extent the hydrodynamic volume of the copolymer macromolecules and PEG calibration is not precise. But, as will be shown below, it is more important for the main purpose of the investigation to compare the molecular weights of the copolymers than their exact estimation.

Naphthyl- and *p-tert*-butylphenyl monosubstituted PEG, prepared according to the previously published method[11] have the following chemical structure:



Naph-PEG



t-ButPh-PEG

Ultraviolet (u.v.) spectra recorded on a Specord u.v. (Carl Zeiss) instrument. Differential u.v. spectra of the polycomplexes (PMAA.Naph-PEG) and (PMAA.t-ButPh-PEG) were obtained as follows. Aqueous solutions of the polycomplex was put in the basic cuvette. In another cuvette for comparison was put an aqueous solution of Naph-PEG or t-ButPh-PEG with the same concentration as in the basic cuvette. It follows that the differential u.v. spectrum, for example of the polycomplex (PMAA.Naph-PEG), is the difference between the u.v. spectrum of Naph-PEG in the polycomplex (PMAA.Naph-PEG) and the u.v. spectrum of free Naph-PEG in the solution. In the studied interval AdA/PEG copolymers are optically transparent and their presence in the solution does not influence the u.v. spectra.

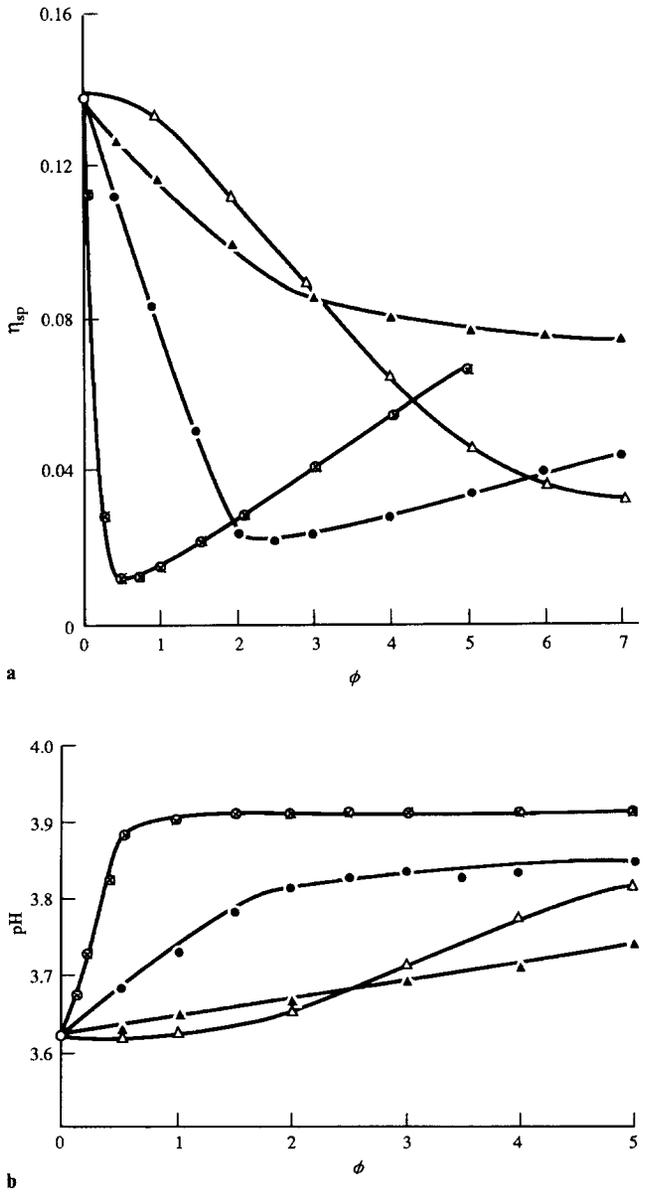
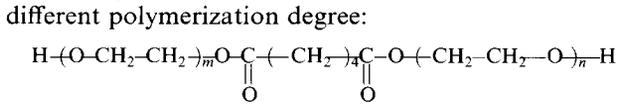


Figure 1 (a,b) Plots of η_{sp} (a) and pH (b) vs the weight ratio ϕ = [AdA/PEG]/[PMAA] for the aqueous solutions of PMAA + AdA/PEG mixtures: (△), AdA/PEG-1; (●), AdA/PEG-2; (X), AdA/PEG-3; (○), AdA/PEG-4; (▲), PEG with $\bar{M}_w = 1500$; $C_{PMAA} = 0.1$ g dl^{-1}; 25°C

Potentiometric measurements were taken on a Radelkis OP 208/1 (Hungary) apparatus equipped with combined glass electrode OP 0808 P.

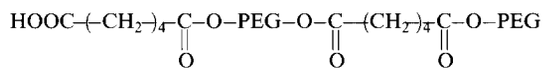
RESULTS AND DISCUSSION

First of all we should discuss the probable chemical structure of AdA/PEG copolymers. The copolymers AdA/PEG-1 and AdA/PEG-2 were prepared by the addition of ethylene oxide to diacid AdA. Therefore it is natural to assume that these copolymers are macromolecules, wherein AdA is bound to two PEG chains of different polymerization degree:



The summary average polymerization degree of the two PEG chains $\overline{DP}_n = n + m$ and is different for AdA/PEG-1 and AdA/PEG-2. $\overline{DP}_n$ can be estimated from *Table 1* presenting $\bar{M}_n$ values. For AdA/PEG-1 $\overline{DP}_n = 5$ and for AdA/PEG-2 $\overline{DP}_n = 14$.

Copolymers AdA/PEG-3 and AdA/PEG-4 were prepared via esterification of AdA by PEG macromolecules. In the case of AdA/PEG-4 PEG of $\bar{M}_w = 1500$ was used. As seen from *Table 1* the copolymer has $\bar{M}_n = 3190$. The final product from the polycondensation of the equimolar mixture does not contain detectable quantities of unreacted AdA and PEG. It could be claimed that the main product from the polycondensation of AdA with PEG of $\bar{M}_w = 1500$ is the copolymer containing two residues from AdA, bound with two PEG chains:



PEG of $\bar{M}_W = 600$ was used in the case of AdA/PEG-3. The copolymer obtained is of $\bar{M}_n = 3160$. Following the previous reasoning it could be suggested that the main product from the polycondensation of AdA with PEG of $\bar{M}_w = 600$ is a copolymer having a structure similar to AdA/PEG-4, but containing four residues from AdA, bound with four PEG chains.

The prepared copolymers of AdA with PEG, contain PEG chains as a basic structural element. It follows that the complex forming process of such copolymers with PMAA in aqueous solution should be studied by investigation methods for complex formation between PEG and the polyacids, i.e. by viscometry and pH-metry[6–8,10–12]. The utility of the mentioned methods is explained by the fact that the complex forming process between PEG and polyacids is accompanied by changes in macromolecular conformations and a considerable decrease in the viscosity of the solution due to the compact structure of the polycomplex particles. With the association of macromolecular partners, hydrogen bonds are formed between the undissociated carboxy groups of the polyacid and the oxygen atoms of PEG. It leads to a change in the acid–base equilibrium in the system and pH increases.

Figures 1a and *1b* present the dependence of the specific viscosity (η_{sp}) of the aqueous solutions of the mixtures PMAA + AdA/PEG on the weight ratio ϕ = [AdA/PEG]/[PMAA] at a constant PMAA concentration. For comparison the corresponding dependencies for PEG of $\bar{M}_w = 1500$ are also presented in the figures.

As seen from *Figure 1a*, η_{sp} of the solution of the mixtures PMAA + AdA/PEG decreases in comparison to η_{sp} of the solution of pure PMAA for all AdA/PEG copolymers. That means all copolymers are able to form polycomplexes with PMAA. AdA/PEG-3 and AdA/PEG-4 form the most stable polycomplexes. The minimum η_{sp} in these cases is reached at $\phi \approx 0.5$ and thus the complete association of the components is increased. Further increase of copolymer concentration leads to some increase of η_{sp} due to the appearance of free macromolecules of the copolymer.

The data in *Figure 1b* from pH measurements are in agreement with those obtained viscometrically: the most drastic increase in pH is in the cases when PMAA forms polycomplexes with AdA/PEG-3 and AdA/PEG-4. The limit value of pH is also reached at $\phi \approx 0.5$. That means that at $\phi \approx 0.5$ the maximum number of hydrogen bonds are formed and their complete bounding in the polycomplex has been achieved.

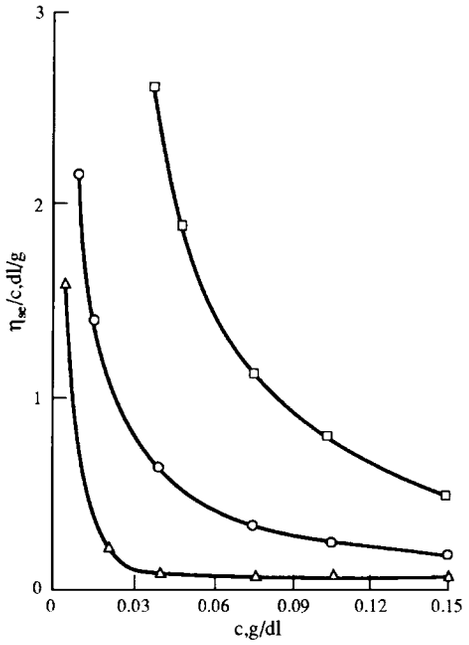


Figure 2 Plots of η_{sp}/C vs polycomplex concentration C for the polycomplexes PMAA.AdA/PEG-3 (△), PMAA.AdA/PEG-4 (○) and PMAA.PEG (□). PEG $\bar{M}_w = 3000$. The weight ratio $\phi = 0.5$; $C_{PMAA} = 0.1$ g dl^{-1}; 15°C

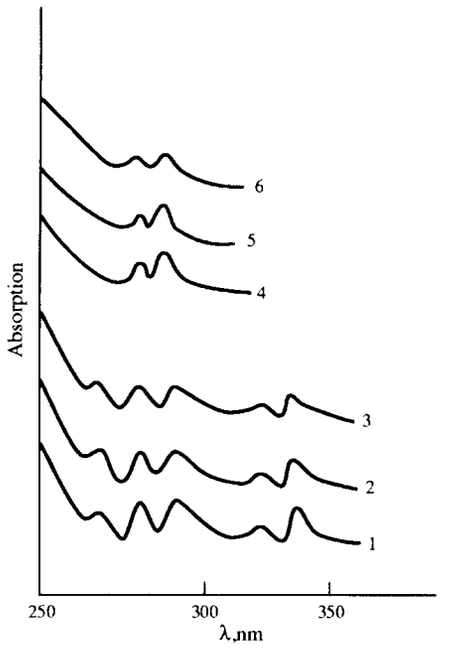


Figure 3 Differential u.v. spectra of the aqueous solutions of the polycomplexes PMAA.Naph-PEG (1), PMAA.t-ButPh-PEG (4) and of the mixtures PMAA + Naph-PEG + AdA/PEG-4 (2), PMAA + Naph-PEG + AdA/PEG-3 (3), PMAA + t-ButPh-PEG + AdA/PEG-4 (5) and PMAA + l-ButPh-PEG + AdA/PEG-3 (6). Concentration (g dl^{-1}): PMAA, 0.1; Naph-PEG, t-ButPh-PEG, AdA/PEG-3 and AdA/PEG-4, 0.05; 25°C

The comparison of the dependencies of η_{sp} and pH on ϕ for AdA/PEG-1 with $\overline{DP}_n = 5$ and those for PEG of $\bar{M}_w = 1500$ ($\overline{DP}_w = 34$) shows that the polycomplex (PMAA.AdA/PEG-1) is stronger than the polycomplex (PMAA.PEG): its η_{sp} is lower and its pH is greater, although $\overline{DP}_w$ of the PEG is seven times higher than $\overline{DP}_n$ of AdA/PEG-1. It is known that the stability of the polycomplex (PMAA.PEG) increases with the increasing polymerization degree of PEG[6,16,17]. Thus the availability of the hydrophobic fragment from AdA in AdA/PEG-1 has the same effect as the increase PEG chain length. As mentioned above, the introduction of a hydrophobic group into PEG macromolecule increases the stability of its polycomplex since during the transfer of the hydrophobic group from the aqueous medium into the hydrophobic particle of the polycomplex the isobaric–isothermal potential of the system additionally decreases[11–13]. In the case of the polycomplex (PMAA.AdA/PEG-1) the hydrophobic fragment from AdA seems to have the same role.

It is interesting to compare the stability of the polycomplexes (PMAA.AdA/PEG-3) and (PMAA.AdA/PEG-4). The copolymers AdA/PEG-3 and AdA/PEG-4 are of almost the same molecular weight, i.e. they have approximately the same total PEG chain length. The difference between AdA/PEG-3 and AdA/PEG-4 is that AdA/PEG-3 contains four AdA residues while AdA/PEG-4 has only two. The hydrocarbon chain from AdA breaks the continuous hydrogen bonds between AdA/PEG and PMAA in the polycomplex, thus destabilizing the whole polycomplex. On the other hand the hydrocarbon chain as the hydrophobic fragment should be a stabilizing factor. The comparison between the stabilities of the polycomplexes (PMAA.AdA/PEG-3) and (PMAA.AdA/PEG-4) should explain which of the above factors is of dominant importance.

As seen in *Figure 1* AdA/PEG-3 and AdA/PEG-4 form a stable complex with PMAA, and the dependencies of their η_{sp} and pH on ϕ overlap, i.e. it is impossible to determine their relative stability from the data presented in the figure.

Figure 2 presents the dependence of η_{sp} of the water solutions of the polycomplexes (PMAA.AdA/PEG-3), (PMAA.AdA/PEG-4) and the polycomplex (PMAA.-PEG) of PEG $\bar{M}_w = 3000$ on the concentration of the polycomplexes. The more stable the polycomplex is the lower the concentration is needed for its dissociation. With the dissociation of the polycomplex free PMAA occurs, polyelectrolyte effect is observed with a sharp increase of η_{sp}. As seen from *Figure 2* the polycomplex (PMAA.AdA/PEG-4) dissociates at a higher concentration than the polycomplex (PMAA.AdA/PEG-3), i.e. the latter polycomplex is more stable. The conclusion is that in spite of the fact that the hydrophobic AdA fragments break the sequence of the cooperative hydrogen bonds with PMAA, the hydrophobic interactions due to the same AdA fragments are the dominating factor in stabilizing the polycomplex. The polycomplex (PMAA.PEG) is the least stable, irrespectively to the fact PEG chain length is almost the same as those of AdA/PEG-3 and AdA/PEG-4. The reason is in the absence of the hydrophobic fragments stabilizing the polycomplex. The data presented in *Figure 2* were obtained at 15°C. The explanation is that with lowering of the temperature, the polycomplexes (PMAA.AdA/PEG) and (PMAA.PEG) become less stable and the difference in their stability is more pronounced.

The comparative stability of the polycomplexes (PMAA.AdA/PEG-3), (PMAA.AdA/PEG-4) could be relatively estimated using the reaction of intermacromolecular substitution. It was shown earlier that the complex forming reaction between PMAA and monosubstituted PEG containing a hydrophobic

chromophoric group proceeding in aqueous solution could be studied by u.v. spectroscopy[13,18,19]. This is due to the fact that u.v. spectra of the monosubstituted PEG in a polycomplex with PMAA and in free state are different. A bathochromic effect is observed when the hydrophobic chromophoric group from the monosubstituted PEG is transferred from the aqueous solution into the hydrophobic domains of the polycomplex. This fact could be used when studying the reactions of macromolecular substitution such as:

$$\text{polycomplex (PMAA.PEG}^*\text{)} + P_1 \leftrightarrow \text{polycomplex (PMAA.P}_1\text{)} + \text{PEG}^* \quad (1)$$

$$\text{polycomplex (PMAA.PEG}^*\text{)} + P_2 \leftrightarrow \text{polycomplex (PMAA.P}_2\text{)} + \text{PEG}^* \quad (2)$$

where P_1 and P_2 are macromolecules, chemically complementary PMAA, and PEG* is a monosubstituted PEG, containing a chromophoric group. If polymer P_2 forms a more stable polycomplex with PMAA than P_1, then the equilibrium (2) in comparison with equilibrium (1) will be more shifted to the right. Particularly if polymer P_1 is the copolymer AdA/PEG-4 and P_2 is AdA/PEG-3, then the relative complex forming ability of AdA/PEG-3 and AdA/PEG-4 could be determined comparing the equilibria (1) and (2).

Figure 3 presents the differential u.v. spectra of the aqueous solutions of the polycomplexes (PMAA.Naph-PEG), (PMAA.t-ButPh-PEG) and the mixtures PMAA + Naph-PEG + AdA/PEG-3, PMAA + Naph-PEG + AdA/PEG-4, PMAA + t-ButPh-PEG + AdA/PEG-3 and PMAA + t-ButPh-PEG + AdA/PEG-4. In the studied equilibrium systems (1) and (2), Naph-PEG and t-ButPh-PEG were used as PEG*s. The differential u.v. spectrum 1 of the polycomplex (PMAA-Naph-PEG) has two absorption bands at 300–350 and 250–300 nm with five local maxima at 332, 320, 287, 277 and 266 nm. U.v. differential spectra of the polycomplex (PMAA.t-ButPh-PEG) had two local adsorption maxima at 285 and 278 nm. The maxima in differential spectra 1 and 4 are characteristic of the polycomplexes (PMAA.Naph-PEG) and (PMAA.t-ButPh-PEG) respectively and might evidence the existence of the certain polycomplex in the solution. The comparison of spectra 1 and 2 shows that the introduction of the macromolecules of the copolymer AdA/PEG-4 into the solution of the polycomplex (PMAA.Naph-PEG) causes a slight decrease in the area cut but the spectrum of the polycomplex, i.e. the concentration of the polycomplex (PMAA.Naph-PEG) is slightly lowered. That means AdA/PEG-4 is a weak competitor compared to Naph-PEG in binding with PMAA, and equilibrium (1) is to a certain extent shifted to the left. As seen from the comparison of spectra 2 and 3 the introduction of the macromolecules of the copolymer AdA/PEG-3 into the solution of polycomplex (PMAA.-Naph-PEG) leads to a greater decrease in the intensity of the spectral peaks than does the introduction of AdA/PEG-4. This means equilibrium (2) is less shifted to the left than equilibrium (1). Although AdA/PEG-3 and AdA/PEG-4 are weak competitors of Naph-PEG in the complex forming reactions with PMAA, the comparison of spectra 2 and 3 prompts that AdA/PEG-3 is the stronger competitor and forms a more stable complex with PMAA than AdA/PEG-4. Such a conclusion could be drawn if t-ButPh-PEG is used instead of Naph-PEG as a PEG*. The comparison of spectra 5 and 6 shows that the addition of AdA/PEG-3 to the solution of the polycomplex (PMAA.t-ButPh-PEG) decreases more the concentration of the polycomplex (PMAA.t-ButPh-PEG) than the addition of AdA/PEG-4, and in this case the comparison of the equilibria also points to the fact that AdA/PEG-3 has a stronger complex forming ability than AdA/PEG-4. It should be noted that qualitatively and quantitatively the profile of the u.v. differential spectra of the solutions of all mixtures does not depend on the addition order of the components and does not change with time. Equilibria (1) and (2) are established in mixing process of the solutions.

Therefore, the obtained results show that breaking the sequences of the cooperative bonds between the components in the polycomplex is not always the decisive factor in destabilizing the polycomplex. In aqueous solution, particularly, hydrophobic interactions are of greater importance. The hydrophobic groups of the main polymer chain which do not participate in the cooperative bonds among the macromolecules stabilize the polycomplex. Probably the change in the free energy of the complex formation, depending on the chain length of the hydrophobic fragment in the main chain of the polymer partners, has an extreme character. Then the increase of the chain length of hydrophobic fragment will after all be the factor destabilizing the polycomplex. In practice the case is complicated by the fact that the increased chain length of the hydrophobic fragment causes a change in the hydrophilic–lipophilic balance of the macromolecules and increases the micelle forming tendencies. Then a complex will be formed between a linear polymer and the micelles, a process rather different in its characteristics from the complex formation between linear polymers.

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