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Graft copolymers with chemically complementary components as a special class of high-molecular-weight compounds

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Abstract. The review surveys the synthesis, bulk structures, solution behaviour and functional capabilities of graft copolymers containing chemically complementary polymer components. The influence of a system of intramolecular bonds between the main and grafted chains and between the adjacent grafted chains on the properties of graft copolymers is analysed. Such graft copolymers are shown to belong to a special class of polymer compounds referred to as intramolecular polycomplexes. The bibliography includes 204 references.

I. Introduction

Graft copolymers are considered as promising heteropolymeric functional materials. These compounds are widely used for controlling stability of disperse systems,[1–7] as compatibilisers for improving compatibility of polymer mixtures,[8–12] as matrix binders in biotechnological processes, macromolecular therapeutic systems [13–19] and paper production,[20] as semipermeable membranes,[21–23] thickeners,[24–28] film-forming coatings,[29,30] protective coatings,[31–33] lyophilising coatings,[34–40] physical gels [41] and agents of drag reduction of turbulent flow.[42–44] Such heteropolymeric systems have attracted growing interest in recent years owing to impressive progress in developing new nanoreactor catalytic processes [45,46] and nanophase technologies for the construction of composite polymeric materials, including controlled growth of metal nanoparticles in the presence of polymer matrices [47,48] and grafting of polymer chains onto the surface of inorganic nanoparticles.[49–59] The interest in graft copolymers is associated with considerable possibilities for controlling their structures and properties through variations in the chemical nature and length of polymer components and through changes in the number (density) and distribution of grafted chains.

A combination of chemically complementary (which are able to interact cooperatively) polymeric partners in the macromolecules of graft copolymers offers considerable possibilities for varying their properties and functions. Since such copolymers have features in common with intermolecular polycomplexes, they can be considered as a special class of high-molecular-weight compounds referred to as intramolecular polycomplexes. In the present review, we discuss the characteristic features of the bulk structure, solution behaviour and functional capabilities of such intramolecular polycomplexes.

In the late 1950s, Mino and Kaizerman [60,61] were among the first to perform the directed synthesis of graft copolymers. However, comprehensive and theoretically supported knowledge of the relationship between the chemical nature of polymer components and the molecular architecture of graft copolymers and the structure – properties relationship is lacking. In early studies, this problem was difficult to solve because of difficulties associated with the preparation of graft copolymers with desired structures and the lack of efficient methods for the determination of their molecular parameters. However, fundamental studies in this field are still few in number in spite of the well-developed synthetic base and modern methods for investigation of these compounds. The reason is that most attention has been focused on practical applications of graft copolymers and, hence, exclusively properties of copolymers which are of interest from a practical standpoint, have been investigated.

Nevertheless, not only the main molecular architectures (described as stars, combs and brushes) of graft copolymers [62–64] but also the major factors influencing their structures and solution behaviour were revealed. Among such factors are the chemical nature and thermodynamic compatibility of polymer components, the number (density), length and distribution of grafted chains along the main chain and the nature of the solvent and its

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selectivity (or non-selectivity) to individual polymer components.[63–69] As demonstrated below, a system of intramolecular main chain – graft and graft – graft bonds plays an important role in the structures of graft copolymers which form intramolecular polycomplexes. In addition, hydrophobic interactions between the binding regions of active groups of the polymer components, which facilitate shrinkage and association of coils, play a significant role in stabilisation of the structures of graft copolymers in an aqueous medium.

A relatively small number of publications were devoted to analysis of the properties of graft copolymers depending on the density and molecular mass of grafted chains and thermodynamic compatibility between polymer components in the last 15 years.[62–64, 70–76] The results of investigations of graft copolymers which form intramolecular polycomplexes were not analysed at all. Systematic studies of this class of polymer compounds have been carried out only for poly(vinyl alcohol)-graft-polyacrylamide (PVA-g-PAA) copolymers. Hence, in the present review emphasis is given to these graft copolymers. Published data on the synthesis, structures and properties of other graft copolymers containing chemically complementary polymer components are considered in relation to the data for PVA-g-PAA.

II. Intramolecular polycomplexes

Poly(vinyl alcohol)-graft-polyacrylamide copolymers and polysaccharide-graft-PAA copolymers were among the first graft copolymers containing chemically complementary components to be synthesised.[60, 61, 77–79] Initially, the specific rheological properties of such copolymers, in particular, significant drag reduction of turbulent flow (combined with high resistance to degradation) in dilute solutions[42, 77, 80] and high viscosity in semidilute solutions,[81] have attracted researchers' attention. Later on, yet another characteristic feature of these copolymers, *viz*., their high flocculating ability, was discovered.[5, 82, 83] It was believed that these properties are determined by a combination of the properties of polymer components involved in graft copolymers and the branched structures of copolymer macromolecules. Subsequently, graft copolymers of this type were studied over many years in parallel with copolymers containing non-interacting (incompatible) or weakly interacting polymer components without classifying them as a special group.

The possible existence of strong intramolecular interactions (hydrogen bonds), which are responsible for the properties of poly(vinyl alcohol)-graft-poly(*N*-vinylpyrrolidone) copolymers (PVA-g-PVPD) was mentioned for the first time in the study.[84] In contrast to a number of other graft copolymers, the characteristic viscosity [η] of PVA-g-PVPD in aqueous solutions decreases compared to this parameter for the starting polymer (PVA). The low value of [η] is retained over a wide temperature range. However, the addition of dimethylformamide (DMF), which facilitates destruction of H-bonds, leads to rapid swelling of the PVA-g-PVPD macromolecules.

Essentially similar effects were noted earlier.[85] The cited study was devoted to comparative investigation of the physicochemical properties of acetylcellulose-graft-PAA copolymers (AC-g-PAA) and the corresponding polymer mixtures. Actually, the solubility of the graft copolymer in aqueous solutions of acetic and formic acids, which are good solvents for both polymer components, decreases as the degree of grafting of PAA increases from 27.6% to 38.1%. Besides, the reduced viscosities of mixtures of the above-mentioned polymers are substantially lower than the calculated additive values throughout the composition range, which is unambiguously indicative of complex formation between polymers. However, the authors of the cited study have not yet interpreted these results in the context of strong interactions between AC and PAA.

Strong intramolecular interactions were revealed in the PVA-g-PVPO graft copolymers, where PVPO is poly(vinylpyridine *N*-oxide), and in mixtures of these polymers [thermodynamic studies of solvent (water) vapour sorption according to Tager's method].[86] The negative free energies of mixing and the negative values of the Flory – Huggins parameter (χ_{12}), which characterises thermodynamic affinity between polymers in a particular solvent, were observed throughout the composition range of the mixture and the graft copolymer. For the copolymers with PVPO contents of 0.39 and 0.43, the parameter χ_{12} is -1.9 and -3.8, respectively. The thermodynamic parameters of the PVA-g-PVPO copolymers also have smaller values compared to those of a mixture of the constituent polymers. From this it was concluded that compatibility between the polymer components in the graft copolymer is higher than that in their mixture.[86]

The presence of strong interactions between the main and side chains in the graft copolymers of poly(acrylic acid) (PAAc) or poly(methacrylic acid) (PMAA) onto PVA and the graft copolymers of poly(ethylene glycol) (PEG) onto PMAA was noted in the studies.[87–89] In particular, grafting of PMAA onto PVA by free-radical polymerisation in the presence of a Ce(IV) salt as an initiator was accompanied by precipitation of the copolymer[87] due to hydrogen bonding between the polymer components. In this case, the composition of the PVA-g-PMAA graft copolymer was close to equimolar. The influence of complex formation between PMAA and PEG involved in the cross-linked PMAA-g-PEG graft copolymer on hydrogel swelling and release of a drug dissolved in the hydrogel was considered.[88] It was demonstrated that hydrogen bonding hinders swelling of the hydrogel and decreases its permeability. In the presence of PEG and PMAA in an equimolar ratio, the rates of hydrogel swelling and release of the dissolved compound from the hydrogel appeared to be minimal. The complex character of association of graft copolymers based on PAAc and poly(*N*,*N*-dimethylacrylamide) (PDMAA) in solutions was noted in the study.[90] Spherical aggregates with a diameter of 150 nm, which are stabilised through both intramolecular and intermolecular H-bonds between the polymer components, were found to be formed from the PAAc-g-PDMAA molecules in an aqueous medium.

Attempts were made to analyse interactions between free and covalently bound polymer partners[91] and reveal changes in thermodynamic affinity between polymer components with increasing grafting density.[92] The thermodynamics of equilibrium complex formation between linear macromolecules and chemically complementary oligomers in dilute solutions was studied[91] for oligomers covalently end-bound to macromolecules and for mixtures of free components in solution. The polymer conformations were calculated using a general statistically mechanical approach (with a simple random walk model). The free energy of an oligomer involved in a complex was calculated using the method of generating functions. In this case, the lengths of loops, binding parts and tails were not restricted. The results of modelling of free oligomers were compared with the results obtained for oligomers covalently linked to macromolecules. Theoretical analysis provided an explanation for many experimental data, in particular, for the dependence of the part of the complex-bound oligomer links on the binding energy and the length of its chain and also for an increase in efficiency of complex formation in the presence of covalent bonds between the polymer reagents.

The influence of the grafting density on interactions between components of a binary layer of graft polymers (for amphiphilic diblock copolymers adsorbed at the liquid – liquid interface) was examined in the study.[92] The ratio of the Flory radius R_F, which characterises free isolated grafted chains in a particular solvent, to the distance D between the centres of the adjacent grafts was demonstrated to be of particular importance. The equality $D = R_F$ was considered as the overlap threshold for coils of

grafted chains. The system was shown to behave as a two-dimensional regular solution, in which the interaction parameter between components χ_{12} decreases with increasing D. Two regions in which χ_{12} decreases depending on the grafting density were revealed. In the region of D which does not reach the overlap threshold ($D > R_F$), χ_{12} decreases according to the law

$$\chi_{12} = \left(\frac{R_F}{D}\right)^2,$$

but at a high grafting density ($D < R_F$), χ_{12} changes according to the equation

$$\chi_{12} \approx \left(\frac{R_F}{D}\right)^{3/4}$$

or

$$\chi_{12} \approx \left(\frac{R_F}{D}\right)^{5/3}$$

depending on the starting theoretical premises (boundary conditions). Therefore, according to the predictions of this theory, interactions between the components of the binary layer should become weaker with increasing grafting density, the most substantial weakening occurring at $D > R_F$.[92]

It should be noted that the specific features of these copolymers were ignored in most other studies devoted to the synthesis and properties of graft copolymers containing chemically complementary polymer components, such as the above-mentioned PVA and PAA,[60, 61, 78, 93, 94] polysaccharides (dextran, starch, hydroxymethylcellulose and carboxymethylcellulose) and PAA[43, 77, 79, 81, 95–100] or poly(*N*-isopropylacrylamide) (PIPAA),[101, 102] PVA and PAAc,[89, 103] poly(ethylene oxide) (PEO) and PAA,[104] PAA,[105] the copolymer of acrylic acid (AAc) and acrylamide (AA)[106] or PIPAA,[107] chitosan and PAA [14] and, finally, PAA and PIPAA.[21, 108]

However, graft copolymers with strong intramolecular interactions serve as highly efficient flocculants,[5, 109] are used as degradation-resistant agents of drag reduction of turbulent flow [44, 110] and possess abnormally high binding ability.[88] The latter property of graft copolymers containing interacting polymer components was confirmed, in particular, by the results of the study,[111] where complex formation of individual PMAA with Cu^{2+} ions was compared with that of PMAA involved in the AC-g-PMAA graft copolymer. The constant of complex formation of the grafted chains with copper ions ($\sim 10^{6.5}$) was determined by potentiometric titration of the starting aqueous-salt solution of AC-g-PMAA ($c_{NaCl} = 0.1$ mol dm^{-3}) and of the same solution in the presence of Cu^{2+} ions (the concentration was varied from 5×10^{-5} to 5×10^{-3} mol dm^{-3}). This complex formation constant is higher than that for individual PMAA. The authors reasonably attributed the higher complex formation ability of PMAA grafted onto AC to specific conformational effects in the macromolecules of this copolymer.

Based on analysis of the data published in the literature and the results of our investigations of graft copolymers [44, 112] and intermolecular polycomplexes,[113] we hypothesised that graft copolymers containing the chemically complementary main and grafted chains belong to a special class of polymer compounds referred to as intramolecular polycomplexes.[114] This assumption was confirmed by the results of comprehensive investigation of the formation, structures, behaviour in solution and functional capabilities of the PVA-g-PAA graft copolymers depending on the grafting density and the molecular mass of the grafted chains. Further, we consider the synthesis and properties of graft copolymers which form intramolecular polycomplexes. Initially, let us determine which polymers could be assigned to the class under consideration and discuss the criteria to be used.

III. Complex formation of covalently non-bound polymeric partners as a criterion of chemical complementarity between components of graft copolymers

It is known that the spontaneous formation of intermolecular complexes through a cooperative system of bonds of a particular nature (Coulombic interactions, hydrogen bonds, donor–acceptor bonds, van der Waals contacts) is a distinguishing feature of pairs of chemically complementary polymers.[115, 116] The formation of a cooperative system of bonds causes a sharp shift of the equilibrium at the macromolecular level toward the formation of a polycomplex. The stability constant K_v of intermolecular polycomplexes increases as a power function of the number of links v (or length) in the polymer chain.[116] For cooperative interactions to occur, a particular critical chain length, which depends on the energy of a single bond, is required. In addition, the interacting macromolecules must be structurally and conformationally complementary.[115–117] The nature of the solvent is of considerable importance. The solvent molecules must neither compete with active groups of the polymers nor shield them, *i.e.*, must not hinder the formation of a network of intermolecular bonds.[116]

From the above, it can be concluded that heterogeneous block-type polymers (graft and block copolymers) containing chemically and structurally complementary polymer blocks of sufficient length can be involved in intramolecular cooperative interactions. These heterogeneous polymers belong to a class of intramolecular polycomplexes. The criterion for assigning particular graft and block copolymers to this class of compounds is spontaneous complex formation of covalently non-bound polymer components. It should be noted that the average number of units in the main chain between the adjacent grafts should be considered as the average length of the reacting blocks in graft copolymers.

Using the above criterion, it is easy to demonstrate that the assumption of chemical complementarity of a series of polymer components of graft copolymers, which was made in Section II, is justified. Actually, spontaneous complex formation between covalently non-bound polyacids (PAAc, PMAA), on the one hand, and polyalcohols (PVA), polyesters (PEO), polyamides (PAA) and polysaccharides (for example, methylcellulose, hydroxyethylcellulose or chitosan), on the other hand, was observed.[115, 118–121] Chemical complementarity between PVA and PAA was proved in our special investigations (data on complex formation between these polymers have been lacking in the literature). This was the first necessary step in studies of the PVA-g-PAA graft copolymers which form intramolecular polycomplexes.

In several studies (see, for examples, Refs 93 and 122), only selected properties of mixtures of PVA and PAA were characterised and no conclusions about the formation of intermolecular polycomplexes between these polymers were drawn. The low value of K_{AB} (0.3) for this system determined by viscosimetry is indicative of a low degree of overlapping between the molecules of the types A (PVA) and B (PAA) in dilute aqueous solutions.[93] The phase separation in the PVA–PAA–H_2O system was observed [122] at certain polymer ratios. However, this effect was not interpreted as a consequence of formation of intermolecular polycomplexes. Taking into account the above-mentioned facts, we studied the PVA–PAA system in an aqueous solution and in the bulk state by varying the molecular mass and chemical structure of the polymeric components with the use of viscosimetry, IR spectroscopy, high-speed sedimentation, gel chromatography, differential scanning calorimetry (DSC) and benzene solubilisation.[123–129] Let us briefly consider the principal results of these studies.

The formation of intermolecular polycomplexes in the PVA–PAA system at $M_{PAA} \gg M_{PVA}$ (*i.e.*, the PAA macromolecules can be considered as matrices with respect to PVA) was estab-

lished by a conventional viscosimetric method. The deviation of the ratio of the specific viscosity of mixture to the sum of specific viscosities of the individual components from unity served as the criterion for the presence of interactions between the polymers.[124] For a relatively low-molecular-weight sample of PVA ($M_v = 4 \times 10^4$), this ratio was smaller than unity, which was indicative of the formation of compact particles of intermolecular polycomplexes. For higher-molecular-weight samples of PVA ($M_v = 8 \times 10^4$ and 1.2×10^5), this ratio was larger than unity, *i.e.*, more and more friable particles of intermolecular polycomplexes appeared. Further studies of this system by high-speed sedimentation and gel chromatography demonstrated that these polycomplexes had a constant composition, which was independent of the PVA to PAA ratio in solution[124, 128] and of the molecular parameters of PVA (in the range under consideration) but decreased from $\varphi_{char} = 9$ to $\varphi_{char} = 4$ $kg_{PVA}\,(kg_{PAA})^{-1}$ (φ_{char} is the characteristic composition) as $M_{v\,PAA}$ increased from 2.72×10^6 to 4.4×10^6 (see Refs 124 and 127–129). Therefore, particles of polycomplexes contained a substantial excess of the PVA molecules. In addition, macromolecules of individual PVA and PAA were aggregated in water. These aggregates were destroyed in the process of complex formation. Taking into account this fact, a substantial excess of PVA in intermolecular polycomplexes was accounted for by interactions of the long PAA macromolecules with partially destroyed aggregates of PVA.

Interaction between the polymers through hydrogen bonding was established by IR spectroscopy.[124, 126, 127] Two of the most important regions of the IR spectra of thin films of PAA and the intermolecular polycomplex are shown in Fig. 1. The results of computer separation of overlapping bands in the Amide I and Amide II regions by the spline-function method are presented in Fig. 2. Detailed analysis of the positions and relative intensities of the bands in the spectra of the PAA film and the intermolecular polycomplexes revealed the following structures of H-bonds: a small amount of 'open' dimers of COOH groups (these groups are derived from the amide groups of PAA upon their partial hydrolysis) characterised by the band $\nu_{C=O} = 1724$ cm^{-1}; a small amount of free amide groups characterised by the Amide I band at 1707 cm^{-1}; a substantial amount of *trans*-multimers of amide groups characterised by the Amide I bands at 1692 (terminal C=O groups of *trans*-multimers) and 1679 cm^{-1} (H-bonded C=O groups of *trans* aggregates); a large amount of *cis*–*trans*-multimers of amide groups characterised by the Amide I band at 1661 cm^{-1}. In addition, the spectra of the intermolecular polycomplexes show an individual band at 1670 cm^{-1} (see Fig. 2*a*) assigned to H-bonds between PVA and PAA. With the aim of revealing changes in the structure of these polycomplexes relative to PAA, the numbers of amide groups forming one or other system of H-bonds were compared. Quantitative calculations were carried out taking into account the following facts:[127, 129] (1) similar shifts of Amide I bands of bound amide groups in the intermolecular polycomplexes and PAA relative to the band of the free amide groups; (2) the absence of substantial orientational effects in thin films of these polymers;[130] (3) the Bouguer–Lambert–Beer law

$$B_i = A_i l c_i ,$$

where B_i is the apparent integral absorption coefficient of the ith Amide I band in the IR spectrum, A_i is the true integral absorption coefficient of the absorption band, l is the film thickness and c_i is the molar concentration of amide groups, which are in the ith state, in the film.

To reduce to a minimum the effect of the difference in the film thickness along the light path and the difference in the number of acrylamide units in the films of PAA and intermolecular polycomplexes, the coefficient B_i was normalised to the apparent integral absorption coefficient B_0 of the vibration band ν_{C-H} of the methylene groups, which is proportional to the concentration of the polymer compound, and to the mole fraction of the acrylamide units in the polymer sample ($X_{n\,AA}$). The calculated $B_i/B_0X_{n\,AA}$ ratios (Table 1) are proportional to the mole fraction of the amide groups in the ith state. In addition to the above-

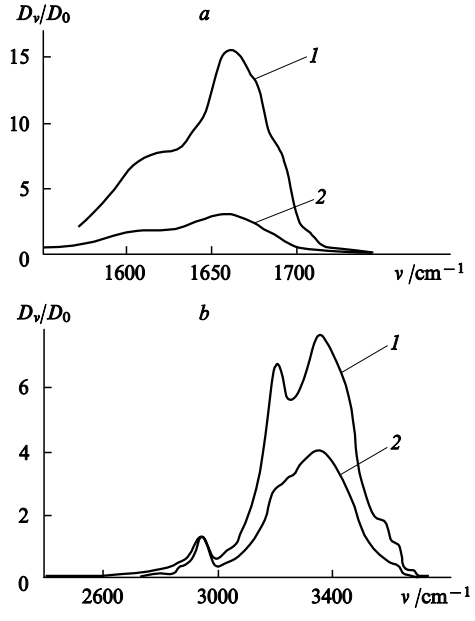


Figure 1. Reduced IR spectra of PAA films (*1*) and the PVA–PAA intermolecular polycomplex at $\varphi = \varphi_{char} = 4$ $kg_{PVA}\,(kg_{PAA})^{-1}$ (*2*) in the Amide I and Amide II regions (*a*) and in the region of C–H, N–H and O–H vibration frequencies (*b*);
D_0 is the amplitude of the band of the internal standard (C–H vibrations of the methylene groups); $T = 293$ K, $l = 7$–9 μm; $M_{v\,PAA} = 4.4 \times 10^6$, $M_{v\,PVA} = 4 \times 10^4$.

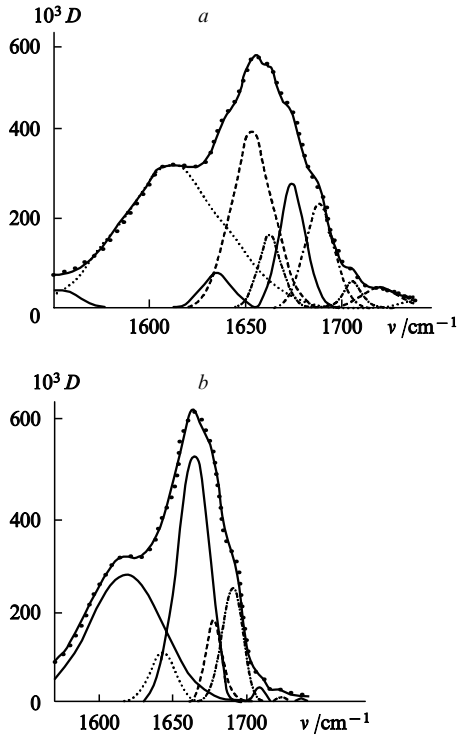


Figure 2. Results of computer processing of the IR spectra of the intermolecular complex at $\varphi = \varphi_{char}$ (*a*) and PAA (*b*) in the Amide I and Amide II regions.
Experimental (points) and calculated (solid lines) contours of overlapping bands; the contours of separated bands are presented below.

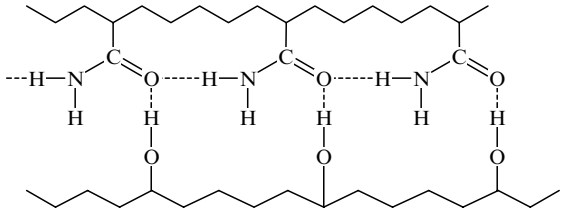
Table 1. Reduced apparent integral absorption coefficients of the Amide I absorption bands ($B_i/B_0X_{n\,PAA}$) and the effective lengths of *trans*-multimers of amide groups (β) for PAA and the PVA–PAA intermolecular polycomplex.

$B_i/B_0X_{n\,AA}$ for ν (cm^{-1})					$\beta = \frac{B_{1679}}{B_{1692}}$
1661	1670	1679	1692	1707	
Sample — PAA					
8.37	–	1.33	2.64	0.16	0.50
Sample — PVA–PAA (see [a])					
5.69	1.31	2.47	2.28	0.32	1.08

[a] $M_{v\,PAA} = 4.4 \times 10^6$ (hydrolysis degree is ~1%), $M_{v\,PVA} = 4 \times 10^4$.

mentioned parameters, Table 1 gives the effective lengths of the *trans*-multimers of amide groups (parameter β).

As can be seen from Table 1, complex formation between PAA and PVA is accompanied by destruction of a substantial amount of *cis*–*trans*-multimers of amide groups (band at ~1661 cm^{-1}), hydrogen bonding between the polymers (band at ~1670 cm^{-1}) and a slight decrease in the amount of *trans*-multimers of amide groups (band at ~1692 cm^{-1}) with a simultaneous increase in their length by a factor of more than 2. In our opinion, an increase in the rigidity of the polyacrylamide chain upon complex formation with PVA is attributable to appearance of the following sequence of H-bonds between segments of these polymers:[129]



The conclusion about interactions of PAA with PVA aggregates in solutions was completely confirmed by the results of comparative structure studies of PVA–PAA mixtures with $\varphi = \varphi_{char}$ and $\varphi = 1\ kg_{PVA}(kg_{PAA})^{-1}$ and the individual polymers in the bulk state.[123, 125, 127–129] Studies were carried out by DSC (Fig. 3). Actually, the PVA microcrystalline domains distributed in regions of the polymer component compatibility were found in the structures of polymer mixtures with a characteristic composition (curve *3′*) prepared from solutions. Evidently, the compatibility regions in the structures of intermolecular polycomplexes are attributable to the presence of segments of the polymer components linked to each other, whereas the microcrystalline regions occur due to the presence of PVA aggregates in the polycomplexes formed. In solid mixtures with composition $\varphi = 1$ (curve *4*), microregions formed by segments of excessive PAA, which was not involved in intermolecular polycomplexes, were revealed along with the above-mentioned two types of domains.[129] This is indicative of a constant composition of the polycomplex and the occurrence of disproportionation in this system (the presence of completely filled and free matrices).

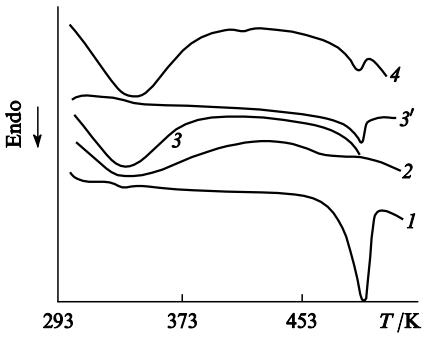


Figure 3. DSC thermograms of PVA (*1*), second scanning; PAA (*2*), first scanning; a PVA–PAA mixture at $\varphi = \varphi_{char} = 4\ kg_{PVA}(kg_{PAA})^{-1}$ (*3*), first scanning; the mixture of the same composition (*3′*), second scanning; the mixture at $\varphi = 1\ kg_{PVA}(kg_{PAA})^{-1}$ (*4*).

It was found that the stability of compact particles of intermolecular polycomplexes containing PVA with $M_v = 4 \times 10^4$ in water depends substantially on hydrophobic interactions. The volume of hydrophobic regions in the particle of the intermolecular polycomplex, which was determined by benzene solubilisation, was 408 nm^3 (see Refs 127 and 128).

The reaction of PVA with PAA in water was assigned to the known type of matrix + oligomer reactions [118, 131]

$$P_1\ (\text{matrix}) + n\,P_2 \longrightarrow$$
$$\longrightarrow \text{intermolecular polycomplex } (P_1 + n\,P_2),$$

where the PAA macromolecules act as a matrix, whereas the PVA aggregates, which are destroyed only partially, act as an oligomer (P_2). The constancy of the composition of the intermolecular complex and the existence of free matrices at $\varphi < \varphi_{char}$ are indicative of the non-uniform distribution of the oligomers between the matrices upon complex formation, *i.e.*, two levels of cooperativity take place in this reaction.[127, 128] The first level is associated with the formation of a cooperative system of H-bonds between the individual chains of the PVA aggregates and the corresponding regions of the PAA macromolecule, and the second level occurs due to interactions between the PVA aggregates onto the PAA chain (Fig. 4).

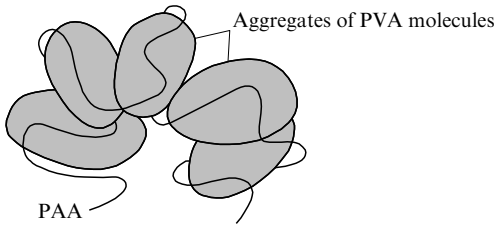


Figure 4. Schematic representation of a particle of the PVA–PAA intermolecular polycomplex.

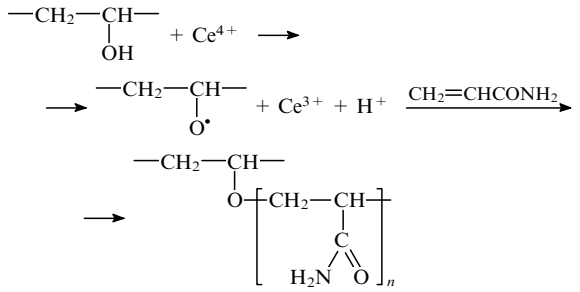
Thus, not only chemical complementarity between PVA and PAA was established but also self-assembly of small aggregates of one polymer component at the long chains of another component analogously with the known effect of self-assembly of protein globules at the chains of oppositely charged polyelectrolytes was demonstrated.[132]

IV. Matrix effects in free-radical graft copolymerisation

The synthesis of graft copolymers has been widely discussed in the literature in recent years.[72, 133–152] Let us consider the main approaches to the synthesis of graft copolymers. The first approach includes methods based on free-radical or ionic graft copolymerisation involving the transformation of the main chain into a macroinitiator as the initial step.[72, 133–145, 151] Macroinitiators can be produced with the use of redox systems involving variable-valence metals,[134–137] irradiation of chains with high-energy particles,[138–140] atom-transfer reactions [141, 142] and chemical or thermal activation of particular groups (including double

bonds) at the main chain.[141–145, 151] The second approach includes methods of polymerisation or copolymerisation involving macromonomers.[146–148] The third approach is based on the chain transfer to polymer.[149, 150] Finally, methods were developed for chemical cross-linking of the pre-formed grafts to active groups of the main chain.[152] It should be noted that many studies devoted to the kinetics and mechanisms of graft copolymerisation (see, for example, Refs 153 and 154) dealt with graft copolymers containing chemically complementary polymer components. However, the question about the possible influence of strong interactions between the main and grafted chains on the properties of these compounds has remained beyond the scope of these investigations.

At the same time, the matrix synthesis of polymers through interactions of the growing (daughter's) chain with a matrix, *viz*., a chemically complementary chain, of another chemical nature was well known.[47] Hence, it is reasonable to suggest that many processes of the synthesis of graft copolymers containing strongly interacting polymer components (in particular, graft copolymerisation) would belong to matrix processes. This aspect has received proper attention in studies of free-radical graft copolymerisation of PAA onto PVA. The PVA-g-PAA copolymers were synthesised by free-radical graft copolymerisation using a Ce(IV) salt as the initiator. The general scheme of the reaction is as follows:[129]



Until recently, the mechanism of grafting of PAA onto hydroxy-containing polymers (including PVA) was believed to be well understood.[77, 78, 81, 96, 155] This mechanism involves the formation of Ce(IV) complexes with several OH groups of the main chain as the first step [156] followed by decomposition of these complexes to form macroinitiators of free-radical graft copolymerisation.

The aim of the study [129] was to synthesise two series of graft copolymers. In each series, only one of the two major parameters responsible for the properties of graft copolymers, *viz*., the number (N) or molecular mass of the grafted chains, was varied. For this purpose, the ratio between the molar concentrations of the Ce^{4+} ions and PVA units (α) was initially varied holding the ratio (γ) between the molar concentrations of the Ce^{4+} ions and the monomer (acrylamide) constant. In a series of the PVA-g-PAA(1–3) copolymers † thus prepared, N was increased from 25 to 49 and the grafted chains in samples 1–3 had comparable molecular masses ($M_v \sim 1 \times 10^5$). In another series of the PVA-g-PAA(4–6) copolymers, N was increased from 25 to 42, and the molecular mass of the grafted chains was decreased from 3.72×10^5 to 1.63×10^5. Then the ratio γ was varied with α held constant. As a result, a series of the PVA-g-PAA(8–10) samples was prepared, in which the molecular mass of the grafted chains varied from 3.72×10^5 to 5.1×10^5 at $N = 9$.[129] In addition, the PVA-g-PAA(7) sample with $N = 4$ and $M_v = 1.12 \times 10^6$ was synthesised.[112] It should be noted that in all the copolymers synthesised, $M_{v\,PVA} = 8 \times 10^4$.

Taking into account thermodynamic affinity between PVA and PAA and the phenomenon of matrix polymerisation of monomers of the same chemical nature in the presence of complementary macromolecules of another chemical nature,[47, 155] it was hypothesised that free-radical graft copolymerisation of PAA onto PVA belongs to the category of matrix processes. This assumption was also supported by the results of the study,[157] in which the matrix effect (an increase in the growth rate of the PMAA chain by an order of magnitude) was observed in the course of grafting of PMAA onto starch granules. In order to confirm or refute this hypothesis, the kinetics of this reaction was compared with that of homopolymerisation of acrylamide performed under analogous experimental conditions.[158] The purpose was to reveal the kinetic matrix effect.[47] The kinetic parameters of the reaction, such as the time of the initial slow step (τ_0), *viz*., the initiation step, and the rates of polymerisation v_p^{20} and v_p^{60} at the conversions $K = 20\%$ and 60%, respectively, were determined by dilatometry.[158] In one series of experiments, the ratio α was increased with γ held constant (Fig. 5, Table 2). As mentioned above, this led to an increase in the grafting density in the graft copolymers [samples PVA-g-PAA(1–3)]. In another series of experiments, the ratio of α was held constant, whereas γ was decreased, the graft length being increased at constant N [samples PVA-g-PAA(8–10)]. The results of these investigations demonstrated that the rate of graft copolymerisation increases compared to the rate of homopolymerisation of acrylamide (see Table 2).[158] However, when the density of the growing daughter's chains became too high [see the data for PVA-g-PAA(3) in Table 2], the matrix effect disappeared.

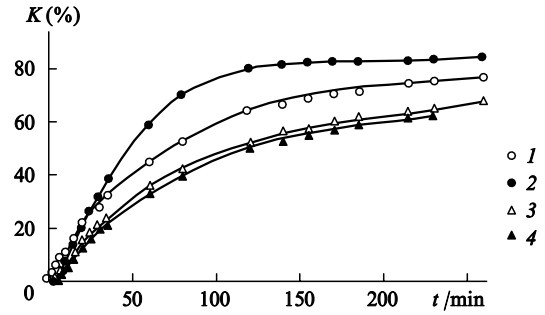


Figure 5. Plot of the monomer conversion *vs*. the reaction time of AA homopolymerisation (*1*) and graft copolymerisation of PAA onto PVA with increasing grafting density (*2–4*).
$T = 298$ K; α and γ are given in Table 2.

Table 2. Reagent ratios and the kinetic parameters for AA homopolymerisation and graft copolymerisation of PAA onto PVA.

Polymer	α (see [a])	τ_0 /min	$10^4 v_p^{20}$ (see [b])	$10^4 v_p^{60}$ (see [b])	K(%) (see [c])
PAA	1.000 [d]	8	0.95	0.48	60
PVA–PAA(1)	0.014	2	1.85	0.99	73
PVA–PAA(2)	0.027	3	1.96	1.69	82
PVA–PAA(3)	0.055	5	0.99	0.48	62

[a] For all polymers, the parameter γ was 10^{-3}. [b] In mol dm^{-3} s^{-1}. [c] The conversion after 200 min. [d] The molar ratio between Ce^{4+} and ethanol.

Therefore, not only the kinetic matrix effect was established in the synthesis of PVA-g-PAA but also its relation to the density of the growing chains was revealed. Actually, a decrease in τ_0 (compared to that for homopolymerisation of acrylamide) and a virtually twofold increase in the growth rate of the PAA chains in the graft copolymer were observed at relatively low α (< 0.055), *i.e*., in the presence of a small amount of grafted chains (small N) in the final copolymer. At $\alpha = 0.055$, the kinetic parameters of graft copolymerisation were virtually equal to those determined from the kinetic curves of homopolymerisation of acrylamide (see

† The sample numbers are given in parentheses.

Table 2). This important result can be attributable, first, to the fact that an increase in N leads to a decrease in the average length of the reacting block of the matrix (*i.e.*, the average distance between the adjacent grafted chains at the main chain), which is accessible for complex formation with the growing PAA chains, and, second, to an increase in steric hindrance to binding of grafted chains to the main chain.[158] By contrast, in the synthesis of the PVA-g-PAA(8 – 10) samples characterised by constant N and different graft lengths, the kinetic matrix effect was observed at all ratios γ and constant $\alpha = 0.014$.[158]

Investigations revealing the kinetic matrix effect and its dependence on the density of growing chains were the first step in studies of the new phenomenon, the so-called matrix graft copolymerisation. In the next step, the structural matrix effect, which is also characteristic of matrix processes, should be established.[47]

V. System of intramolecular main chain – graft and graft – graft bonds as the main factor of stabilisation of the structures of intramolecular polycomplexes

The determination of the detailed structure and the number of intermolecular bonds in intermolecular polycomplexes is of great importance for an understanding of the mechanism of complex formation of polymers at the level of single contacts between active groups. Studies devoted to these problems, most of which were carried out by IR and NMR spectroscopy, are well known (see, for example, Refs 159 – 161). The above methods allow one also to reveal the dependence of the state of these polycomplexes on different factors, in particular, on the pH of the medium [162] and temperature.[163, 164] These studies are of particular importance for polycomplexes between non-ionic polymers, in which the number of bonds is impossible to estimate by simpler methods, for example, by potentiometric titration (which can be employed in investigations of polyelectrolytes).[113, 115 – 117]

Intramolecular bonds in graft copolymers, including those containing chemically complementary components, were not studied in detail, although IR and NMR spectroscopy was used in many investigations (see Refs 14, 103, 142, 144 and 165). The aim of these investigations has been to prove the formation of graft copolymers. However, studies of systems of intramolecular bonds and changes in these systems depending on the number (density) and molecular mass (length) of grafted chains are of fundamental importance for graft copolymers, which form intramolecular polycomplexes, the more so as these systems are formed already in the course of the synthesis of these copolymers (matrix effect). Hence, considerable attention has been given to this problem in studies of the PVA-g-PAA graft copolymers. Let us briefly discuss these results.

The validity of the assignment of graft copolymers to intramolecular polycomplexes was confirmed primarily by IR spectroscopy.[114, 129, 166] The IR spectra of thin films of PVA-g-PAA(1 – 3) (which differ in N) were thoroughly analysed using computer separation of vibrational bands in the Amide I and Amide II regions by the spline-function method, and the structures of the macromolecules of the graft copolymers were demonstrated to be stabilised by an extensive hydrogen bond network, including H-bonds between the main chain and grafted chains (as in the case of the corresponding intermolecular polycomplex) and H-bonds between the units of the grafted chains (*cis* – *trans*-multimers of amide groups).[129, 166] An increase in N led to substantial changes in this hydrogen bond network (Fig. 6).[129] Actually, in the PVA-g-PAA macromolecules containing a relatively small number of grafted chains ($N \leqslant 25$), the number of main chain – graft H-bonds was large, whereas the number of graft – graft H-bonds was relatively small (see Fig. 6 *a*). As N increased from 25 to 49 in the series of the copolymers under study, steric hindrance to thermodynamic affinity between PVA and PAA became more substantial. As a result, the number of H-bonds between the main chain and the grafts decreased, whereas the number of H-bonds between the drawn together grafted chains increased (see Fig. 6 *c*). In the case of an intermediate value of N ($N = 31$), H-bonds of both types occurred (see Fig. 6 *b*), which was unambiguously established by IR spectroscopy.[129]

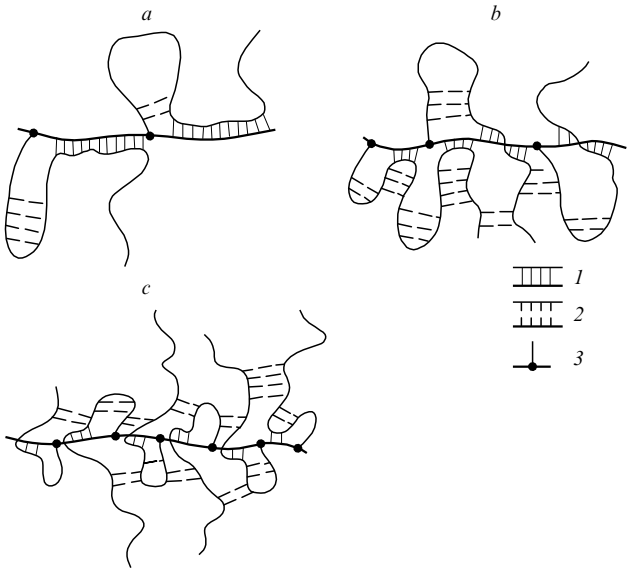


Figure 6. Redistribution of H-bonds in the PVA-g-PAA macromolecules at $N \leqslant 25$ (*a*), $N = 31$ (*b*) and $31 \leqslant N \leqslant 49$ (*c*).
(*1*) main chain – grafted chain H-bonds, (*2*) grafted chain – grafted chain H-bonds, (*3*) graft.

The influence of the molecular mass of the grafted chains on the hydrogen bond network was studied for a series of PVA-g-PAA(8 – 10) samples, in which N was held constant ($N = 9$). For this purpose, the spectra of thin films of the copolymers in the Amide I and Amide II regions were processed by the spline-function method. The spectra of these graft copolymers show all the Amide I bands which were observed in the spectra of the PVA – PAA intermolecular polycomplexes, including a band at 1670 cm^{-1} assigned to a sequence of H-bonds between PVA and PAA (see Section III).[167] Thus, it was proved that intramolecular polycomplexes are formed in macromolecules of the samples of the copolymers containing grafted chains of different lengths. It was found that the largest number of the main chain – graft H-bonds and the smallest number of the graft – graft H-bonds are characteristic of the PVA-g-PAA(9) sample containing the grafted chains with an intermediate molecular mass ($M_{v\,PAA}$ =

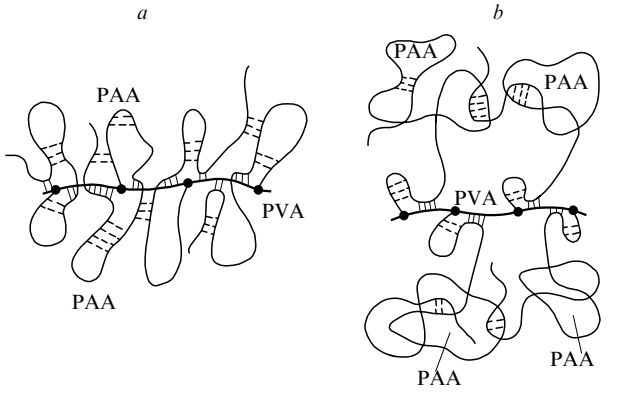


Figure 7. Scheme illustrating detachment of grafted chains from the main chain.
(*a*) $M_{v\,PAA} < M^*$, (*b*) $M_{v\,PAA} > M^*$; for notations of the elements in the scheme, see Fig. 6.

4.3×10^5). At $M_{v\,PAA} > 4.3 \times 10^5$, the hydrogen bond network in the copolymer changed as follows: the number of the main chain – graft H-bonds sharply decreased and the rigidity of the grafted chains, which was estimated from the increase in the effective length of the *trans*-multimers of amide groups, increased by a factor of more than 5. In fact, the effect of 'detachment' and stretching of the grafted chains in different directions away from the main chain was observed for polymers in which the molecular mass (length) of the grafted chains was higher than some critical value M^* (Fig. 7).[129, 167]

The above-described changes in the hydrogen bond network in PVA-g-PAA with increasing N and molecular masses of the grafted chains are reflected in all the properties of the intramolecular complexes under study.

VI. Influence of grafting density on the bulk structure and solution behaviour of intramolecular polycomplexes

The bulk structures of graft copolymers were studied in much less detail compared to their structures in solution and the structures of block copolymers. The majority of publications were devoted to graft copolymers containing thermodynamically incompatible components,[168–177] although studies of the bulk structures of graft copolymers containing chemically complementary main and grafted chains were also reported (see, for example, Ref. 25). To reveal the general and specific features of the bulk structure of PVA-g-PAA compared to the structures of other graft copolymers, let us discuss the results of the above-mentioned studies. It is known that incompatibility of components in linear block copolymers causes microphase separation to form the following regular supercrystalline structures: planar lamellas (if components are present in similar amounts), cylindrical or spherical domains, which are formed from the minor component as the percentage of the major polymer increases.[62] The state of the interface between the domains (sharp or extended) is determined by the molecular mass of the blocks. The higher the molecular mass, the higher the degree of segregation (degree of microphase separation) of the blocks and, correspondingly, the sharper the interface. The shift of the glass transition temperature of a separate microphase relative to T_g of the corresponding homopolymer is most often used as the measure of segregation of the blocks.[172, 174] A decrease in the degree of segregation of the blocks (an increase in the compatibility of the components of a block copolymer) is reflected in an increase in the shifts of T_g for the 'hard' and 'soft' microphases along the temperature scale toward each other.

In the case of star-like graft copolymers consisting of f branches, each of which is a diblock copolymer (for example, based on isoprene or butadiene as a 'soft' block and styrene or α-methylstyrene as a 'hard' block), the molecular masses of the blocks have a much lesser effect on the structure compared to the density of branches or the order of arrangement of the hard and soft blocks in the star (in the centre or at the periphery).[168–172] In particular, it was demonstrated[168–171] that the density of the branches (for f from 2 to 18) influences the structures of the star-like copolymers of isoprene (inner part of branching) and styrene (outer part of branching) with $w_{isoprene}/w_{styrene} = 0.7/0.3$ and the molecular mass of the grafted chains of $(2.3–10) \times 10^4$. Covalently non-bound branchings form a cylindrical supercrystalline structure, *viz*., long cylindrical domains of polystyrene (PS) in a polyisoprene (PIP) matrix. This structure was retained at a low density of branches ($f < 6$ and $M_n = 3.3 \times 10^4$). At higher values of f, the star structure sharply changed (both PS and PIP phases became uninterrupted). The PS blocks formed two interpenetrating tetrahedral lattices in a continuous matrix consisting of the PIP blocks. The role of the order of arrangement of the blocks in the star was considered in the study.[172] It was demonstrated that the microphases in the structures were nearly completely separated when the branched elastomeric block was located in the centre. By contrast, mixing of the components was observed when the hard block served as the branched central block.

The structures of traditional graft copolymers, in which one component serves as the main chain and another component serves as a graft, are determined not only by the density and the order of arrangement of the hard and soft blocks but also by the molecular mass of the grafted chains. This fact was supported by the results of the studies.[173–177] The authors of these studies reached the following common conclusion: the mutual mixing of the main and grafted chains increases with decreasing graft length and grafting density. Actually, irregular fractal-like microregions were observed in the structure of the PEA-g-PS graft copolymer, where PEA is poly(ethyl acrylate), at a low grafting density (on average, one grafted chain per main chain), whereas ordered lamellar microdomains were observed at a high density of rigid grafted chains (on average, three grafts per PEA chain).[173] Study of the PB-g-PS copolymer (PB is polybutadiene) by DSC revealed the effect of mutual mixing of the components (a substantial decrease in the glass transition temperature of PS in the copolymer compared to T_g of the homopolymer and a decrease in the crystallinity of PB) at a low grafting density.[174] However, this effect disappeared upon repeated heating of the sample (second scan). The glass transition temperature T_g for the PS microphase even increased (was 6–7 K higher than that of individual PS) with increasing grafting density. A substantial decrease in the difference between T_g for polydimethylsiloxane (PDMS) and PS was observed also for the PS-g-PDMS graft copolymers characterised by a low molecular mass of the grafts and low grafting density.[174] The degree of microphase separation also increased as each of these parameters increased. Analogous effects were observed for the graft copolymers of PEO onto PEA, PS, polyamide 12, copolymers of MA or MMA (MA is maleic anhydride and MMA is methyl methacrylate) and styrene and the ethylene – vinyl alcohol copolymer.[175–177] In all cases, the crystallinity of the PEO chains increased as the number of these chains grafted onto the main chain and their length increased.

X-Ray diffraction study of graft copolymers containing chemically complementary components, such as ST-g-PAA and AM-g-PAA (ST is starch and AM is amylose), revealed substantial mutual mixing of the main and grafted chains over a wide grafting-density range.[25] As a result, the main chain became uncrystallisable.

The structures of the PVA-g-PAA graft copolymers were studied by DSC[123, 129] and these results were compared with the analogous data for the individual polymers. In the case of a relatively small number of grafted chains ($N \leqslant 25$), the DSC thermograms (Fig. 8) show only one heat capacity jump, *i.e*., one glass transition (curves *1* and *2*), whose temperature $T_g = 459.5–463.5$ K (depending on the sample) was between the corresponding glass transition temperatures of PVA ($T_g = 331.5$ K) and PAA ($T_g = 464$ K). Taking into account the low PVA content in the graft copolymers (2.4 mass % –

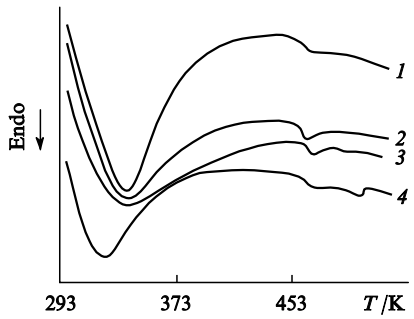


Figure 8. DSC thermograms (first scanning) for samples of PVA-g-PAA(7) (*1*), PVA-g-PAA(1) (*2*), PVA-g-PAA(2) (*3*) and PVA-g-PAA(3) (*4*).

4.0 mass %), this fact is indicative of complete compatibility of the polymer components in these samples of the copolymers and homogeneity of their structures. However, the second heat capacity jump appears in the thermograms of PVA-g-PAA at $N > 25$. This is indicative of the microphase separation in the structures of the copolymers. The height and temperature of the second heat capacity jump (second glass transition), which persisted after repeated heating–cooling cycles, increased with increasing N (see Fig. 8, curves *3* and *4*). It was established that microphase separation in the copolymers with a high grafting density is determined by the presence of compatibility regions of the polymer components along with domains formed by segments of grafted chains, which do not interact with the main chain because of steric hindrance. From the above, it can be concluded that compatibility between the main and grafted chains in graft copolymers which form intramolecular polycomplexes, is attained only for N smaller than some critical value N^* (in the series of graft copolymers under study, $N^* \approx 25$).[129]

Yet more evidence for the existence of intramolecular polycomplexes in the PVA-g-PAA(1–3) macromolecules and redistribution of hydrogen bonds with increasing N was obtained in the study of resistance of the copolymers to thermooxidative destruction by dynamic thermogravimetric analysis (DTGA). The mass-loss curves (TG curves) were processed on a computer to determine simultaneously three formally kinetic parameters of destruction steps (the total activation energy E, the reaction order n in each step and the frequency factor Z).[129, 166, 178] Three steps of thermooxidative destruction were revealed for all samples of the copolymers and for individual PVA and PAA (Fig. 9). The first step involves chemical transformations without participation of oxygen (dehydration of PVA chains, imidisation of PAA and some other conversions), as evidenced by endothermic effects in the DTA curves.

In the second step of destruction of the copolymers and PAA as well as at the end of the first step of PVA destruction, oxidation of polymer chains and accumulation of free radicals took place, which was immediately reflected in the sign of thermal effects in the DTA curves (the exothermic effect was observed instead of the endothermic effect). Bulk decomposition of the alkyl, alkoxy and peroxy radicals formed in the second step together with complete decomposition of polymer chains occurred in the final third step of destruction and was accompanied by the maximum exothermic effects.[129, 179]

The temperatures of the destruction onset (T_d) of most copolymers are intermediate between T_d for individual PVA and PAA. In the series of PVA-g-PAA(1–3) copolymers, the following changes in the parameters of destruction were observed with increasing N: a rise in the temperature of the destruction onset, an increase in the temperature ranges of the first (accompanied by the endothermic effect) and third (accompanied by the maximum endothermic effect) steps of destruction and an increase (by 92 °C) in the overall temperature range of destruction. The above-described effects are indicative of a substantial increase in resistance of graft copolymers to thermooxidative destruction with increasing number of grafted chains. Analysis of possible chemical transformations and free-radical processes in all steps of thermooxidative destruction of the polymers and the results of experimental studies of water solubility of polymer samples after thermal treatment under various conditions demonstrated that interchain cross-links, such as main chain–graft (interchain esters) and graft–graft (interchain imides) cross-links, are formed in the graft copolymers and PAA already before the onset of destruction and in its first step. Apparently, interchain cross-links formed in the PVA-g-PAA macromolecules with a low (Fig. 10 *a*) and high (Fig. 10 *b*) grafting density have different effects on further destruction. In the latter case, cross-linking between the adjacent grafted chains facilitates more substantial stabilisation of the coil as a whole. The cross-linked coil becomes poorly accessible for oxygen, and elimination of gaseous destruction products of the main and grafted chains is decelerated. This is the reason why thermal stability of the copolymers increases with increasing grafting density.[129, 179]

Interesting information was obtained in calculations of the formally kinetic parameters E, n and Z for the first step of destruction involving chemical transformations without the participation of oxygen (Table 3). In particular, for samples of the

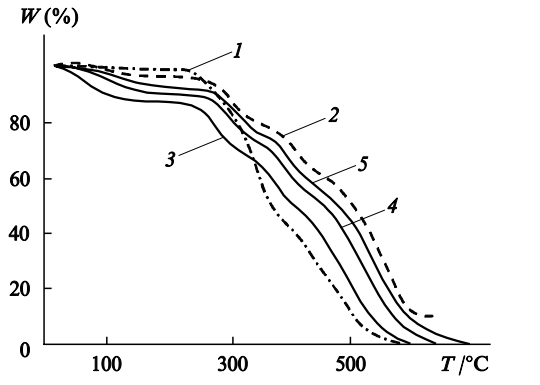


Figure 9. TG curves for PVA ($M_v = 4 \times 10^4$) (*1*), PAA ($M_v = 4.4 \times 10^6$) (*2*), PVA-g-PAA(1) (*3*), PVA-g-PAA(2) (*4*) and PVA-g-PAA(3) (*5*).

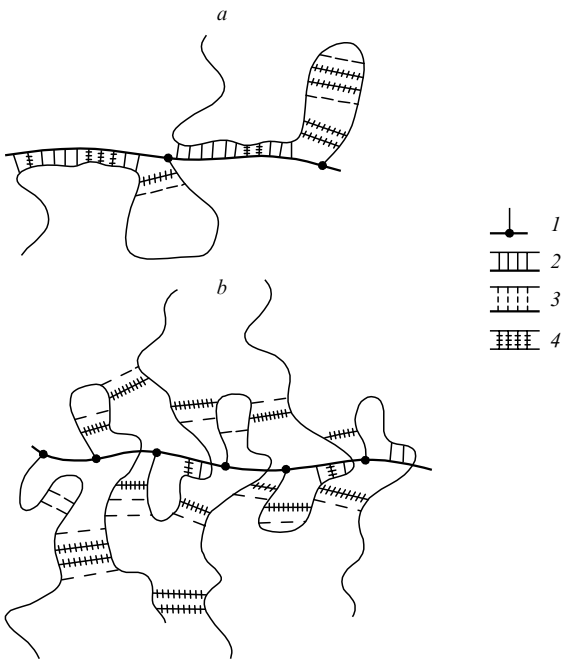


Figure 10. Schematic representation of interchain cross-links in the PVA-g-PAA macromolecules with low (*a*) and high (*b*) grafting density. (*1*) graft, (*2*) H-bonds between the main and grafted chains, (*3*) H-bonds between the units of PAA, (*4*) cross-links between the chains.

Table 3. Kinetic parameters of the first step of thermooxidative destruction of graft copolymers with different grafting densities.

Sample	E /kJ mol^{-1}	n	Z /s^{-1}	k /s^{-1} (see [a])
PVA	59.2	0.83	6.11×10^3	0.064
PAA	143.9	1.15	1.34×10^{12}	0.113
PVA-g-PAA(1)	182.2	2.36	6.9×10^{16}	0.174
PVA-g-PAA(2)	172.2	2.31	1.09×10^{15}	0.149
PVA-g-PAA(3)	139.1	1.63	6.05×10^{11}	0.140

[a] The rate constant calculated by the Arrhenius equation.

graft copolymers with $N \leqslant 25$, the parameters E, n and Z appeared to be substantially larger than the corresponding values for PAA. However, these parameters approach the corresponding parameters characteristic of PAA as N increases from 25 to 49. It is known that the parameters E and n for complex chemical processes [involving many competitive and(or) successive reactions] are integrated values. Hence, the above-mentioned substantial increase in these parameters in the first step of destruction of a PVA-g-PAA sample with a low grafting density (compared to PAA) is indicative of a specific structure in the macromolecules of these copolymers. The presence of intramolecular polycomplexes stabilised predominantly through main chain – graft H-bonds complicates chemical transformations and causes a sharp increase in the parameters E, n and Z in the first step of destruction of graft copolymers.[129, 179]

It should be noted that the results of systematic studies of thermal stability of graft copolymers and its relation to the grafting density, the molecular mass of grafted chains and thermodynamic affinity between polymer components are virtually absent from the literature. Using the results of investigations for PVA-g-PAA, we attempted to analyse the influence of not only the molecular mass of grafts and the grafting density but also of chemical complementarity between the polymer components on thermooxidative destruction of the graft copolymers. Of a few studies devoted to these problems, two investigations on thermal destruction (under an inert atmosphere) of graft copolymers containing chemically complementary components, such as ST (or AM) and PAA,[25] PVA and the AA – MMA copolymer,[103] are noteworthy. Thermal treatment of the ST-g-PAA and AM-g-PAA graft copolymers, in which only the molecular mass of the grafted chains was varied, was accompanied by several characteristic effects, such as a rise in the temperatures of the onset and completion of destruction with increasing molecular mass of PAA and an increase in thermal stability (extension of the temperature range of destruction) of graft copolymers compared to that of individual ST and AM.[25] An increase in thermal stability of the PVA-g-P(AA-co-MMA) graft copolymers compared to that of PVA was evidenced by the DTGA data obtained in the study.[103] Unfortunately, the authors of the cited studies did not report analogous results for individual PAA, which did not allow us to compare thermal stabilities of the graft copolymers and PAA. Resistance of the α-cellulose-g-PMMA graft copolymers, where PMMA is poly(methyl methacrylate), to destruction was examined by DTGA.[180] According to the results of an X-ray diffraction study, the components of these copolymers weakly interact with each other. In contrast to the above-described data, it was found that thermal stability of the α-cellulose-g-PMMA graft copolymers decreases with increasing amount of grafted PMMA. However, this fact remains to be explained.

Let us consider the change in ability of PVA-g-PAA to swell and dissolve in water depending on the number N of grafted chains. In the course of swelling and dissolution, all characteristic features of the chemical structures of the polymers, their molecular, supermolecular and macroscopic structures, the phase state and thermodynamic affinity for a particular solvent reveal themselves. The results of investigations of these properties are widely used for characterisation of the structures of graft copolymers.[21, 34, 63, 88, 104, 144] These studies are of particular importance for copolymers containing chemically complementary polymer components, because the formation of a cooperative system of bonds between these components sharply decreases accessibility of the active groups of the components for a solvent. Swelling and dissolution of films of PVA-g-PAA(1 – 3) and (for comparison) PAA in water (the thickness of the film of the copolymer was ~ 23 μm) were studied using a specially developed procedure.[181, 182] It should be noted that samples of the graft copolymers and PAA were characterised by the virtually equal amounts of hydrophilic groups (0.0141 – 0.0143 mol g^{-1}). However, the behaviour of the graft copolymers in the course of swelling and dissolution in water differs substantially from that of PAA. The PVA-g-PAA(1) sample with a low grafting density ($N = 25$) appeared to be the least hydrophilic of all the polymers under study. Among the above-mentioned three copolymers, this sample has the largest number of main chain – graft H-bonds. As N increased, the rates of swelling and dissolution of the films increased, the thickness of the polymer layer that remained undissolved (after 24 h) decreased and the degree of its swelling diminished due to a decrease in the number of H-bonds between the main and grafted chains. Therefore, thermodynamic affinity of the copolymers for water increased with increasing N.

The state of PVA-g-PAA in aqueous solutions was studied [129, 166, 183] by static light scattering. The molecular and thermodynamic parameters of the light-scattering coils were determined from the Zimm plots by the double extrapolation method. Only samples of PVA-g-PAA(2, 3) with $N \geqslant 31$, which spontaneously dissolved in water at room temperature, were examined. It was found that the PVA-g-PAA(2) and PVA-g-PAA(3) macromolecules occur as aggregates even in dilute solutions, which is attributable to low values of the second virial coefficient A_2. The latter, though it increases with increasing N (Table 4), remains close to zero, which is typical of θ solvents. This result is reasonable taking into account that PVA-g-PAA is an intramolecular polycomplex. Solubility of the copolymers in water noticeably increases with increasing N, as evidenced by an increase in A_2 and a decrease in both Z and $\langle R^2 \rangle_z^{1/2}$. Such behaviour of the graft copolymers in solutions is consistent with the above-described effect of a successive decrease in the number of main chain – graft H-bonds with increasing grafting density.

It was demonstrated [129, 183] that the grafting density influences substantially the hydrodynamic and optical characteristics of PVA-g-PAA(1 – 3) in water. Studies by viscosimetry and light scattering (by determining the depolarisation coefficients of scattered light) showed that the characteristic viscosity of solutions and the Huggins constant decrease, whereas the crossover concentration and optical anisotropy of the coils in water increase with increasing number of grafts.

Table 4. Molecular and thermodynamic characteristics of graft copolymers with different grafting densities.

$10^{-6} M_w$ (see [a])	$10^{-6} M_{w\,PVA\text{-}g\text{-}PAA}$	N	Z [b]	$10^{11} A_2$ /m^3 mol kg^{-2}	$\langle R^2 \rangle_z^{1/2}$ /nm (see [c])
Sample of PVA-g-PAA(2)					
29.07	2.49	37	12	−2.04	362
Sample of PVA-g-PAA(3)					
7.84	3.92	49	2	3.46	193

[a] The mass-average molecular mass of scattering particles. [b] Number of macromolecules in the aggregate. [c] The z-average radius of gyration of the coil.

In aqueous solutions of intermolecular polycomplexes, segregation of the bound parts of active groups of polymers through hydrophobic interactions gives rise to compact particles of the polycomplexes with developed hydrophobic regions [115, 131] or leads to phase separation of the system analogously to that observed for stoichiometric polyelectrolyte complexes.[116] Hence, it was of interest to examine this stabilisation factor in the intramolecular polycomplexes under consideration. The contribution of hydrophobic interactions to stabilisation of the structures of intramolecular polycomplexes in water was estimated by benzene solubilisation.[129, 183] The results of these studies not only confirmed that such stabilisation occurs but also demonstrated that the role of this factor substantially decreases with increasing N. Actually, the volume of hydrophobic regions in the PVA-g-PAA(1 – 3) series decreased from 794 to 98 nm^3 (per macromolecule) as N increased from 25 to 49, which correlates with

improvement of thermodynamic quality of water serving as the solvent for this series of polymers.

Therefore, a decrease in the grafting density in the PVA-g-PAA copolymers in an aqueous medium is accompanied by strong aggregation (self-assembly) of the coils of the graft copolymers to form increasingly dense and hydrophobic particles of intramolecular polycomplexes. A substantial increase in the density of aggregates with decreasing N is supported by the fact that the changes in the parameters Z and $\langle R^2 \rangle_z^{1/2}$ (see Table 4) in going from PVA-g-PAA(2) to PVA-g-PAA(3) occur at substantially different rates. Analysis of the published data demonstrated that a decrease in viscosity of aqueous solutions of the graft copolymers with increasing grafting density is typical also of other copolymers involving chemically complementary components, for example, of the dextran-g-PAA copolymer.[81, 96] However, taking into account all the above, this fact is attributable to the influence of the grafting density on complex formation between the main and grafted chains rather than to the known fact that an increase in branching leads to deterioration of thermodynamic quality of a solvent for branched macromolecules.[184, 185]

The results obtained for PVA-g-PAA provide a new insight into the fundamental principles of the state-of-the-art statistical theories of graft copolymers, which have been developed in the context of general theoretical analysis of a series of similar systems commonly referred to as polymer brushes.[62] Evidently, these theories are valid for graft copolymers containing incompatible or weakly interacting polymer components.

According to these theories, the role of the main chain (matrix) is reduced to merely a spatial factor (a 'sphere' and a 'cylinder' for star-like and comb-like graft copolymers, respectively), while the possible contributions of interactions between the main and grafted chains to the free energy are ignored. Hence, it was concluded that the state of grafted chains at a low grafting density, *i.e.*, in the absence of their overlapping, should be close to the state of an isolated chain in the same solvent.[62] As demonstrated above, an opposite situation is observed for the PVA-g-PAA graft copolymers. As the grafting density decreases, the grafted chains nestle against the main chain, which is accompanied by sharp deterioration of the quality of the solvent, segregation of hydrophobic binding regions of active groups and aggregation of macrocoils. In fact, the macrocoil as a whole undergoes collapse. However, only collapse of grafted chains is considered in the above-mentioned statistical theories.[62] This is yet another drawback restricting application of such theories to graft copolymers which form intramolecular polycomplexes. It should be noted that the effect of shrinkage of particles of intermolecular polycomplexes through strong interactions between polymeric partners (collective collapse) is well known.[47, 115–117]

Therefore, the collapse of a macrocoil as a whole, which occurs due to complex formation of the main and grafted chains, and the collapse of the main or grafted chains, which occurs due to incompatibility of the polymer components (for example, in a selective solvent), should be distinguished for graft copolymers which form intramolecular polycomplexes. Our results agree with the predictions made in the study.[92] Actually, a decrease in the grafting density leads to strengthening of thermodynamic affinity between PVA and PAA.

Investigation of the changes in the state of the PVA-g-PAA macromolecules in solution induced by factors able to destroy an H-bond network (*i.e.*, intramolecular polycomplex) is of special interest. Among these factors, the temperature[186–188] and the hydrodynamic shear field[189, 190] were examined. The complex extreme dependence $[\eta] = f(T)$ was found and the Huggins constant was demonstrated to decrease in parallel with increasing temperature. A sharp decrease in $[\eta]$ to a minimum (Fig. 11 *a*) and the corresponding sharp increase in the Huggins constant (Fig. 11 *b*) in a narrow temperature range of 303–308 K, which is virtually independent of N, are indicative of the possible conformational transition in the copolymer macromolecules. Analogous extreme temperature dependences of $[\eta]$ were observed

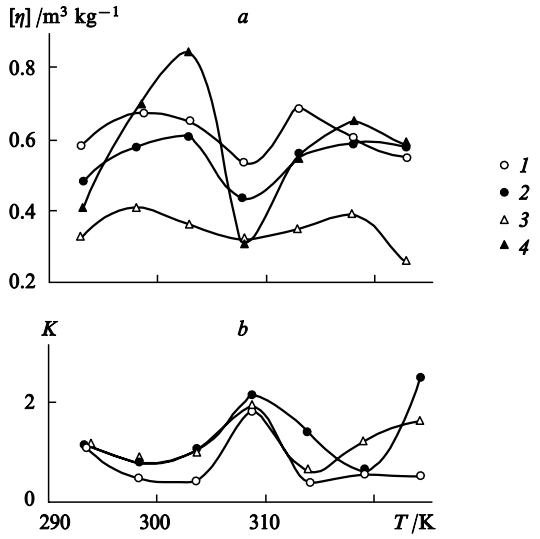


Figure 11. Temperature dependences of the characteristic viscosity (*a*) and the Huggins constant (*b*) for PVA-g-PAA(7) (*1*), PVA-g-PAA(4) (*2*), PVA-g-PAA(5) (*3*) and PVA-g-PAA(6) (*4*) (c = 0.4 kg m^{-3}).

also for a series of other graft copolymers containing chemically complementary polymer components, for example, for AC-g-PAA in acetic and formic acids,[85] DAC-g-PAA (DAC is diacetylcellulose) in formic acid [70] and PVA-g-PEO in water.[105]

The occurrence of the conformational transition in the macromolecules of PVA-g-PAA(7) (for this sample, the largest decrease in $[\eta]$ was observed) was confirmed by the results of investigations of solutions of this copolymer by quasielastic laser light scattering.[186–188] The correlation function of scattered light in a dilute solution of the graft copolymer was measured at different temperatures. The diffusion-coefficient distribution was calculated from these data using the corresponding regularisation procedure. The bimodal distribution on the diffusion coefficients was revealed (Fig. 12). Taking into account the rigid structure of coils of the copolymer, the characteristic narrow molecular-mass distribution and the criterion $\boldsymbol{q}R_g > 1$ ($\boldsymbol{q}$ is the scattering vector and R_g is the radius of gyration of macroparticles), which was maintained in the experiment, the bimodality of the distribution curves was interpreted as a sum of two exponential contributions to the normalised correlation function. The contributions are attributable to translational motion and translational-rotational motion of scattering particles,[129, 188]

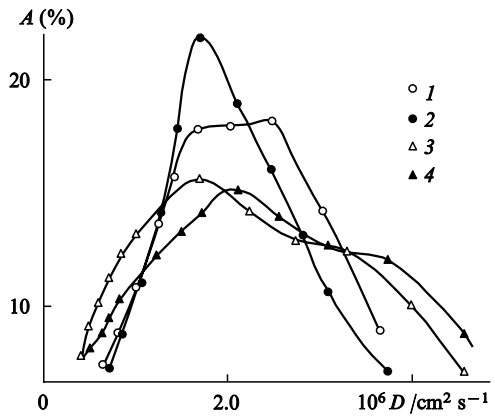


Figure 12. Distribution curves on the diffusion coefficients for PVA-g-PAA(7) at 298 (*1*), 303 (*2*), 308 (*3*) and 313 K (*4*).
A is the contribution of particles characterised by a particular diffusion coefficient to the total scattering intensity.

Table 5. Diffusion parameters of PVA-g-PAA(7) at different temperatures.

T /K	$10^{10} D_t$ /m^2 s^{-1}	$10^{-3} D_r$ /s^{-1}
298	1.8	3.5
303	1.7	2.6
308	1.7	8.2
313	2.1	7.4

$$g_1(t) = A_0(\boldsymbol{q})\exp(-\Gamma_0 t) + A_1(\boldsymbol{q})\exp(-\Gamma_1 t).$$

Here $\Gamma_0 = D_t\boldsymbol{q}^2$ and $\Gamma_1 = D_t\boldsymbol{q}^2 + 6\,D_r$ are the time constants of the exponential components of the correlation function, D_t and D_r are the effective coefficients of translational and rotational diffusion. Changes in the temperature caused the following changes in the state of the PVA-g-PAA(7) macromolecules. An increase in the temperature to $\sim$303 K led to swelling of the macrocoils due to partial cleavage of the main chain – graft H-bonds, which was accompanied by a decrease in asymmetry of the coils (increase in D_r, see Table 5) and, correspondingly, to a decrease in the contribution of the translational-rotational mode to the total scattering intensity. In the range $\sim 303 < T < 308$ K, the rupture of a large number of H-bonds led to a sharp contraction (collapse) of the coils and an increase in their asymmetry (an increase in D_r, see Table 4) because of poor solubility of PVA in water compared to PAA. This transformation was referred to as an intramolecular polycomplex $\rightleftarrows$ segregated state transition (Fig. 13).[186] A further increase in the temperature was accompanied by swelling of asymmetrical coils. The depth of conformational changes, which can be estimated as a decrease in the characteristic viscosity, was found to depend on N. The smallest changes were observed for PVA-g-PAA(6), which is characterised by the largest grafting density ($N = 42$) compared to all the other samples prepared in this experiment. This result can be attributable to substantial stretching of the main chain with a high grafting density.[62] Consequently, the ability of the main chain to be contracted on collapse is limited due to volume effects. It should be noted that no changes in [η] were observed [34] for the PVA-g-PVPD copolymer containing strongly interacting polymer components, and low viscosity persisted over a wide temperature range. Evidently, the reason is stability of intramolecular hydrogen bonding at high temperatures (in the temperature range under study).

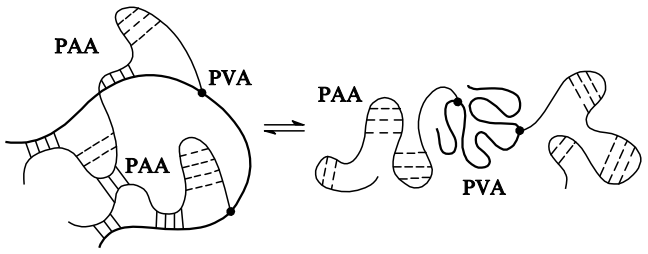


Figure 13. Scheme of the conformational transition in the PVA-g-PAA macromolecules on heating.
For notations of the elements in the scheme, see Fig. 6.

The influence of hydrodynamic shear field on the structure of PVA-g-PAA in solutions was studied on a rheo-viscometer equipped with coaxial cylinders. A non-traditional behaviour of solutions of the copolymers was observed in hydrodynamic fields.[189, 190] This is illustrated by Figs 14 and 15, which show the dependences of the effective viscosity of solutions of PVA-g-PAA(2) on the shear rate gradient and the concentration dependences of the reduced viscosity of these solutions. At relatively high

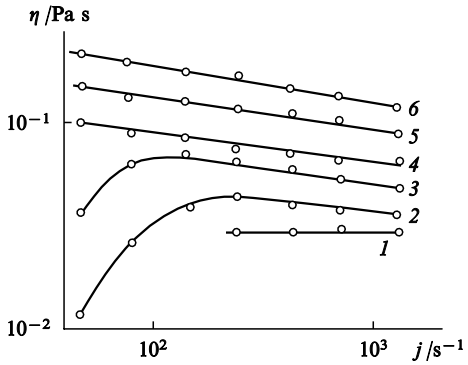


Figure 14. Plot of the effective viscosity of solutions of PVA-g-PAA(2) *vs.* the shear rate gradient.
The concentrations of the solutions /kg m^{-3}: (*1*) 0.5, (*2*) 1, (*3*) 2, (*4*) 3, (*5*) 4, (*6*) 5; $T = 298$ K.

concentrations ($c \approx 3-5$ kg m^{-3}), typical non-Newtonian flow was observed for all copolymers. At lower concentrations ($c \approx 1-3$ kg m^{-3}), the flow curves have a maximum, whose position is determined by N and c. In a dilute solution ($c \approx 0.5$ kg m^{-3}), the viscosities at small shear rate gradients j were initially low to an extent that they were beyond the sensitivity limits of the instrument. However, the viscosity of the solution sharply increased (ten – hundred times) at a critical value of j^*.[189, 190] The largest value of j^* (243 s^{-1}) is characteristic of the PVA-g-PAA(2) copolymer. According to the IR spectroscopic data, this copolymer had the largest number of main chain – graft and graft – graft bonds (see Fig. 6 *b*). It should be emphasised that all flow curves were completely reversible. A substantial reversible increase in viscosity of solutions with increasing j (negative thixotropy) indicates that the PVA-g-PAA macromolecules exhibit viscoelastic properties due to destruction of an H-bond network (destruction of the intramolecular complex) induced by the hydrodynamic field.

The critical concentration c^*, below which the intramolecular polycomplex was destroyed, was determined from the concentration dependences of the reduced viscosity of solutions of the copolymers at different j, which were calculated with the use of flow curves.[189, 190] The critical concentrations c^* in the PVA-g-PAA(1 – 3) series changed in parallel with the crossover concentration and increased from 2 to 4 kg m^{-3} with increasing grafting density. Hence, two levels of reversible destruction of PVA-g-PAA in solutions induced by the hydrodynamic shear field were revealed. At the first level, a network of pinnings is destroyed. In the second deeper level, the intramolecular polycomplexes along with primary aggregates are destroyed (Fig. 16).

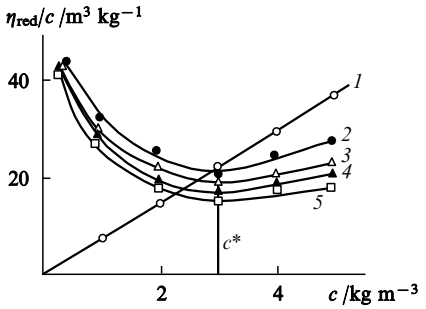


Figure 15. Concentration dependences of the reduced viscosity of solutions of PVA-g-PAA(2) at j of 49 (*1*), 146 (*2*), 437 (*3*), 729 (*4*) and 1312 (*5*) s^{-1};
η_{red} is the reduced viscosity, c and c^* are the concentration and the critical concentration of the solutions, respectively.

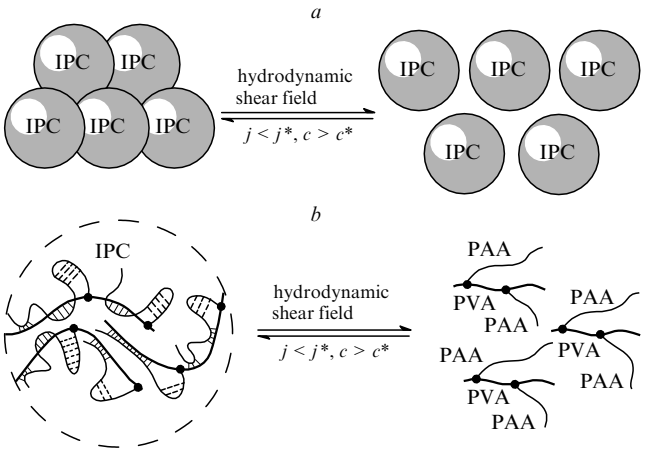


Figure 16. First (*a*) and second (*b*) levels of destruction of PVA-g-PAA structure induced by hydrodynamic shear field.
IPC is intramolecular polycomplex.
The critical values are marked with an asterisk.

Interestingly, rheological studies revealed exclusively non-Newtonian (pseudoplastic) flow for a series of other graft copolymers containing chemically complementary polymer components. These results were obtained, in particular, for the dextran-g-PAA,[81,96] ST-g-PAA, AM-g-PAA,[25] PVA-g-PMAA,[87] P(AA-co-AA)-g-PEO[106] and PAA-g-PEO copolymers.[105] However, taking into account high molecular masses of the samples under study ($\sim 2-6\times10^6$), high concentrations of the solutions used in measurements ($\sim 2-30$ kg m^{-3}) and the fact that PVA-g-PAA exhibits viscoelastic properties only in dilute solutions, the above-described result for these graft copolymers seems to be reasonable.

VII. Characteristic features of the structures and properties of intramolecular polycomplexes depending on the graft length

The molecular mass (length) of grafted chains is an important parameter, which allows one to control the structure and properties of graft copolymers. However, the role of this parameter is poorly understood. First attempts to reveal the influence of this factor on the thermodynamic properties and behaviour of graft copolymers in solutions have been made in the studies.[68,70] The 'pure' influence of the molecular mass of grafted chains is difficult to reveal because of the necessity to prepare and study samples, which should be characterised by the same grafting density and a narrow molecular-mass distribution of the grafts. This problem has attracted increasing interest in recent years because graft copolymers can be synthesised starting from macromonomers with controlled chain length. The results of the studies[148,176] devoted to the influence of the molecular mass and the grafting density of PEO on the bulk structures of PMA-g-PEO [PMA is poly(methyl acrylate)], PMMA-g-PEO and PS-g-PEO were discussed above. Among investigations of graft copolymers in solutions, several interesting systematic studies have been undertaken to reveal the role of the molecular mass and the density and distribution of hydrophobic hydrocarbon grafted chains (in comb-like copolymers with PEO[26] or with the AA – MA copolymer[27,28]) in their aggregation in an aqueous medium. Studies by static light scattering, fluorescence spectroscopy and rheology demonstrated that an increase in the concentration of solutions was accompanied by a characteristic transition from intramolecular aggregation of hydrophobic branchings to intermolecular aggregation for all the above-mentioned copolymers. This transition was shifted to lower concentrations and was attended by a sharper and sharper increase in viscosity of the solution as the length and number of neighbouring hydrophobic tails increased. In many other studies (see, for example, Ref. 31), the molecular mass and the number of grafted chains (PMMA) in graft copolymers were varied with the aim of solving single-purpose problems (in particular, for the purpose of enhancing the strength of two-component polyurethane coatings). Analogous systematic studies of the role of the molecular mass of grafted chains in graft copolymers containing chemically complementary components are few.

When studying the structure and state of the PVA-g-PAA(8 – 10) samples which are characterised by the constant number but different molecular masses of the PAA chains, in solutions, our main interest was to elucidate how the effect of 'detachment' of the grafted chains from the main chain at $M_{v\,PAA} > M^*$ (which was revealed by IR spectroscopy) is reflected in the properties of the copolymers.

The above-mentioned phenomenon was confirmed primarily by the structure studies of these copolymers by DSC.[191] The DSC thermograms of the PVA-g-PAA(8, 9) samples with $M_{v\,PAA} \leqslant 4\times10^5$ show only one heat capacity jump (Fig. 17, curves *1* and *2*), *i.e.*, these copolymers are characterised by complete compatibility of the polymer components. The DSC thermogram of the PVA-g-PAA(10) sample with $M_{v\,PAA} = 5.1\times10^5$ has already two heat capacity jumps (curve *3*), which is indicative of the microphase separation in the structure of this copolymer. One microphase ($\sim 85\%$) corresponds to regions of compatibility of the polymer components, whereas another microphase ($\sim 15\%$) corresponds to domains formed by segments of PAA, which are 'detached' from the main chain.[129,191]

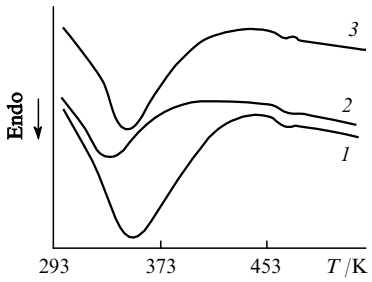


Figure 17. DSC thermograms for PVA-g-PAA(8) (*1*), PVA-g-PAA(9) (*2*) and PVA-g-PAA(10) (*3*).

Three main steps of thermooxidative destruction were revealed for these copolymers by TGA.[191] The temperatures of the onset of destruction of the copolymers were close to the analogous temperature for PAA but lower than that for PVA. The parameters of destruction changed with increasing $M_{v\,PAA}$ as follows: (1) the temperature of the onset of destruction rose; (2) the temperature of completion of destruction increased; (3) the temperature range of the first step of destruction (accompanied by the endothermic effect) became narrower; (4) the temperature range of the third step of destruction (accompanied by the maximum exothermic effect) decreased; (5) the overall temperature range of destruction decreased.

Hence, an increase in the molecular mass of the grafted chains led, on the one hand, to a slight growth of thermal stability of the copolymers (an increase in the temperature of the onset of destruction) but, on the other hand, to an increase in the rate of their complete decomposition. The latter fact is indicative of loosening of the PVA-g-PAA structure with increasing $M_{v\,PAA}$, due to which different elements of the structure become more accessible for oxygen, removal of gaseous decomposition products becomes easier and, that is why, thermooxidative destruction is accelerated. These data actually confirm the effect of 'detachment' of the grafts from the main chain. The parameters E, n and Z of the first two steps of destruction were calculated using

computer processing of the TG curves. In the first step, in which chemical processes occur without the involvement of oxygen, the parameters E, n and Z pass through a maximum for PVA-g-PAA(9) with $M_{v\,PAA} = 4.3 \times 10^5$ with increasing $M_{v\,PAA}$. This fact is in complete agreement with the maximum number of the main chain – graft H-bonds in this graft copolymer compared to those in all other samples of PVA-g-PAA under study and indicates that complicated chemical transformations occur in the first step of destruction of this copolymer.

The properties of copolymers containing grafted chains with different molecular masses were studied also by light scattering.[167] All samples of the series under consideration are water-soluble at room temperature. According to the results obtained with the use of the Zimm plots (Table 6), the thermodynamic quality of water with respect to the copolymers was improved (the parameter A_2 increased) with increasing $M_{v\,PAA}$. At the same time, the number of macromolecules in aggregates and their radius of gyration reached minimum values for PVA-g-PAA(9), which was characterised by an intermediate value of $M_{v\,PAA}$ (4.3×10^5) and existed in water in the molecular-disperse state. Two other copolymers occurred as aggregates, which differed from each other in the packing density of segments. It was demonstrated [129, 167] that loose swollen aggregates of the copolymer containing grafted chains with the highest molecular mass ($M_{v\,PAA} = 5.1 \times 10^5$) were formed due to 'detachment' of the grafted chains from the main chain and improvement of the quality of the solvent, in contrast to compact aggregates of PVA-g-PAA(8) with $M_{v\,PAA} = 3.72 \times 10^5$.

Table 6. Results obtained by light scattering for graft copolymers containing grafted chains with different molecular masses ($N = 9$).

Sample	$10^{-6} M_w$	$10^{-4} M_{w\,PVA\text{-}g\text{-}PAA}$	Z	$10^9 A_2$ (see [a])	$\langle R^2 \rangle_z^{1/2}$ /nm
PVA-g-PAA(8)	6.92	3.46	2	1.18	299
PVA-g-PAA(9)	3.81	3.81	1	1.55	253
PVA-g-PAA(10)	18.83	4.71	4	1.66	777

[a] In m^3 kmol kg^{-2}.

The depolarisation coefficients of scattered light were determined at $\theta = 0$ and $c = 0$ (θ is the scattering angle and c is the concentration of the solution), and aggregates (or macromolecules) of all samples of the copolymers in the series under consideration were demonstrated to be optically isotropic in water (the optical anisotropy is equal to zero).[129, 167] According to the results of viscometric measurements at 298 K, an increase in $M_{v\,PAA}$ in the series of PVA-g-PAA(8 – 10) leads to a successive increase in the Huggins constant, and the parameter $[\eta]$ passes through a small minimum. These results correlate qualitatively with the data obtained by static light scattering.

The results of measurements of benzene solubilisation in solutions of the copolymers were somewhat unexpected.[192] Actually, an increase in $M_{v\,PAA}$ to 4.3×10^5 did not lead to a substantial change in the amount of benzene in the bound state. However, a further increase in the molecular mass of the grafted chains to 5.1×10^5 led to a sharp increase in solubilisation. To account for this effect, the contributions to solubilisation determined, first, by dispersion interactions of benzene with hydrophobic regions (the contribution of S_d) and, second, by binding of benzene to proton-donor groups of the polymer through H-bonding (the contribution of S_H) were considered.[129, 192] Then the UV spectra of benzene in water and solutions in ethanol, PAA and the PVA-g-PAA(10) sample containing the grafted chains of maximum length were measured. These studies revealed an increase in the intensity of the characteristic absorption band of benzene at $\lambda = 260$ nm in solutions of the graft copolymer. Taking into account this fact, it was concluded that the above effect is associated with a sharp increase in the amount of H-bound benzene in swollen coils of this sample of PVA-g-PAA.

Investigation of the temperature dependence of $[\eta]$ in solutions of the above-mentioned samples of the graft copolymers demonstrated [192] that the PVA-g-PAA(10) sample, in which the grafted chains are 'detached' from the PVA chain, has the lowest temperature of the onset of conformational transition. The deepest conformational changes (a sharp decrease in $[\eta]$ in the transition region) took place in the macromolecules of the copolymer characterised by the intermediate value of $M_{v\,PAA}$ (4.3×10^5). As mentioned above, these macromolecules possessed the largest number of main chain – graft H-bonds.

VIII. Functional capabilities of intramolecular polycomplexes

It is known that intermolecular polycomplexes can adsorb various organic compounds, ions, colloidal particles and biopolymers from solutions.[115 – 117, 131, 193] Such versatility is due to the fact that these polycomplexes contain hydrophobic binding regions of the polymer components and hydrophilic cavities formed by loops of non-bound polymer units and, in addition, to the possibility of self-adjustment of the system, *i.e.*, changes in the hydrophilic – hydrophobic balance in the polycomplex particle in the course of sorption, due to which the best results can be obtained.[115, 116, 193] However, intermolecular polycomplexes have drawbacks as binding agents because of the existence of a complex formation equilibrium at the macromolecular level. Hence, these complexes can be destroyed to individual components in highly dilute solutions,[115] under the action of strong competitive agents [116] or under changes in external conditions (for example, temperature or pH of the solution).[115 – 117] In this respect, intramolecular polycomplexes, in which the interacting polymer components are additionally linked by covalent bonds, hold more promise. Due to the absence of an equilibrium at the macromolecular level, intramolecular polycomplexes are not destroyed to individual polymers even under conditions of competitive binding of the sorbed compound to just one of the components. Presently, high binding ability of intramolecular polycomplexes is used for the construction of macromolecular therapeutic systems providing prolonged action of drugs.[14, 16, 21, 88, 103]

Films of the PVA-g-PAA intramolecular polycomplex can efficiently (and selectively) adsorb phenol from water (Fig. 18). Detailed investigation of this phenomenon [194, 195] made it possible to construct highly efficient sensors for measuring phenol in natural water.

Graft copolymers containing chemically complementary polymer components are promising as flocculants. Actually, a higher flocculating ability of the graft copolymers of PAA onto oxyethylcellulose and amylopectin compared to PAA with the same molecular mass was observed in the study.[196] Later on, graft

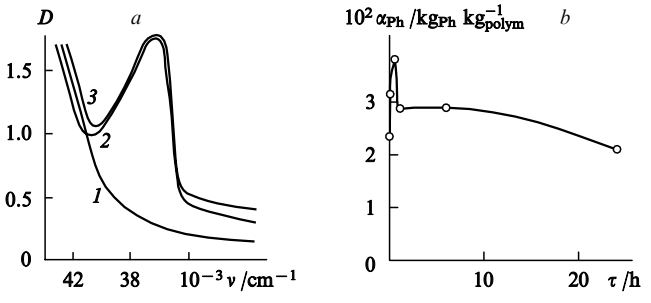


Figure 18. UV spectra (*a*) of the starting thermally treated film of PVA-g-PAA(2) (*1*) and a film kept in an aqueous solution of phenol ($c = 10$ kg m^{-3}) for 4 (*2*) and 5 (*3*) min and the change in the amount of phenol in the bound state (α_{Ph}) at $T = 293$ K calculated from the above data (*b*).

copolymers of acrylamide and acrylic acid onto water-soluble cellulose derivatives were tested and covered by patents as flocculants for clearing of water and conditioning of precipitates of waste-water treatment facilities.[5]

Numerous examples of the use of graft copolymers as flocculants were offered in the literature. In particular, graft copolymers of PAA onto polysaccharides, such as sodium alginate, starch and its components (amylose and amylopectin), were studied.[6, 7, 109, 110, 197, 198] Their flocculating ability was tested using kaolin suspensions, waste waters from the pulp-and-paper industry and waste waters obtained upon iron ore processing and in the course of concentration of 10% iron ore slurry. It was found that the copolymer of PAA grafted onto branched amylopectin is the most efficient of all the flocculants studied.[109, 110, 197] A series of samples of this copolymer containing different amounts of grafted chains with different molecular masses was studied. Unfortunately, detailed characteristics of these copolymers are lacking in the literature. However, it was noted that both a decrease in the grafting density and an increase in the graft length lead to enhancement of the flocculating effect.

Highly efficient non-ionic Unicomfloc^{intra} flocculants were developed based on the PVA-g-PAA intramolecular polycomplex for clarification of highly turbid clay suspensions [199] and preparation of drinking water at water treatment plants.[200] The effect of one sample of these flocculants in coagulative–flocculative clearing of river water is compared with that of the known Magnafloc LT-27 flocculant (Allied Colloids, UK) in Table 7. The efficiency of the individual coagulant (aluminium sulfate) and coagulant–flocculant pairs was estimated taking into account the main characteristics of the quality of water, such as turbidity, chromaticity, permanganate oxidisability and the content of residual aluminium. The advantages of the Unicomfloc^{intra} flocculants are their ability to perform complex purification of water from suspended substances of both natural and anthropogenic origin, such as phenol [201, 202] and ^{137}Cs radionuclides.[203]

Semidilute aqueous solutions of the PVA-g-PAA intramolecular polycomplex exhibit a substantial negative thixotropic effect. Thus, these solutions become thickened on slight stirring and occur in this state for several hours. As mentioned above, the reason is that a hydrodynamic field induces reversible destruction of the polycomplex. Substantial reversible thickening of solutions of the copolymers induced by a hydrodynamic shear field can serve as a basis for the development of a special type of thickening agents providing high viscosity of a solution only for a desired period of time.

Graft copolymers containing chemically complementary main and grafted chains are highly efficient agents for drag reduction of turbulent flow.[42, 44, 82, 112] For example, PVA-g-PAA samples containing a small polymer additive at $Re = 5 \times 10^3 - 5 \times 10^4$ show a drag reduction of turbulent flow $W \approx 60\%$ (Fig. 19 *a*). A somewhat higher efficiency in drag reduction of turbulent flow ($W \approx 65\% - 68\%$ at $Re = 1.4 \times 10^4$) was achieved with the use of particular samples of CMC-g-PAA (CMC is carboxymethylcellulose) and ST-g-PAA.[82] The activity of the above copolymers decreases substantially with increasing density and decreasing molecular mass of the grafted chains. It is important that solutions of these graft copolymers not only exhibit high hydrodynamic activity but are also resistant to degradation induced by turbulent flow (see Fig. 19 *b*, curve *1*), as distinguished from solutions of high-molecular-weight PEO (curve *2*) and PAA.[204] It should be noted that the time interval between two adjacent points in the curves in Fig. 19 *b* corresponds to the time during which a polymer solution was passed once through a capillary of a rheometer, and the total number of points corresponds to the number of repeated cycles of exposure of the solution to turbulent flow. Hence, resistance of solutions of PVA-g-PAA (as well as of CMC-g-PAA, ST-g-PAA and other graft copolymers, which form intramolecular polycomplexes) to degradation is determined by the fact that the macromolecules of the copolymers can rapidly and virtually completely restore their original molecular and supermolecular structures under conditions when the action of a strong hydrodynamic field is periodically interrupted. Reversibility of destruction of PVA-g-PAA in solution, which is also observed in usual rheological experiments, distinguishes these graft copolymers from PEO and PAA and is indicative of the existence of a special force, which restores the system to its original state after termination of the action of a hydrodynamic field. Undoubtedly, this is thermodynamic affinity between the main and grafted chains.

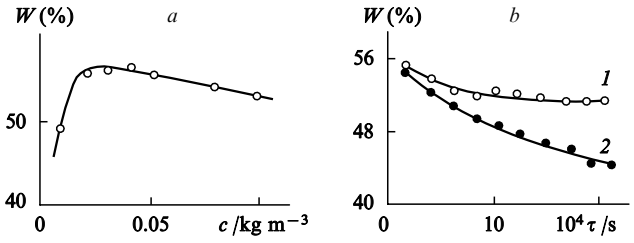


Figure 19. Drag reduction of turbulent flow *vs.* the concentration of PVA-g-PAA(7) (*a*) and the time of hydrodynamic field action of solutions of PVA-g-PAA(7) (*1*) and PEO (*2*) ($M_v = 6 \times 10^6$ at $T = 293$ K) (*b*).

Table 7. Efficiency of the clearing effect of the coagulant (aluminium sulfate) and different coagulant–flocculant pairs {a water sample from the Desna river: $T = 15$ °C, the turbidity was 4.3 mg dm^{-3}, the chromaticity was 37 deg (Cr–Co scale), the alkalinity was 3.65 mg-equiv. dm^{-3}, pH 8.2, $[NH_3] = 0.26$ mg dm^{-3}, the permanganate oxidisability was 9.1 mg dm^{-3}}.

Sample of a flocculant	Amount /mg dm^{-3} (see [a])		Turbidity /mg dm^{-3}	Chromaticity /deg (Cr–Co scale)	Oxidisability /mg dm^{-3}	c_{Al} /mg dm^{-3} (see[b])
	$Al_2(SO_4)_3$	flocculant				
–	–	–	2.5[c]	31	9.1	–
–	5	–	1.3	23	9.1	0.39
–	10	–	0.8	15	8.1	0.25
–	20	–	0.5	11	7.2	0.16
Magnafloc LT-27	5	0.1	1.3	17	7.2	0.32
	10	0.1	0.8	13	5.7	0.25
	20	0.1	0.3	9	5.0	0.15
Unicomfloc^{intra}	5	0.1	1.0	13	5.8	0.28
	10	0.1	0.5	9	5.2	0.17
	20	0.1	0	5	4.8	0.09

[a] The concentration of chlorine water was 4.8 mg dm^{-3}. [b] The concentration of residual aluminium. [c] The parameters of the starting water after clarification for 3 h.

IX. Conclusion

To summarise, graft copolymers containing chemically complementary main and grafted chains, such as PVA-g-PAA, belong to a special class of polymer compounds, which may be classified as intramolecular polycomplexes. Their structures and properties in the bulk state and solutions are determined by intramolecular H-bonds of the main chain – graft and graft – graft types. The formation of intramolecular polycomplexes occurs, evidently, already in the course of free-radical graft copolymerisation of PAA onto PVA. Hence, the synthesis of PVA-g-PAA belongs to the category of matrix processes. At a too-high density of the growing grafted chains (about three grafts per 100 units of the main chain), the matrix effect (which is reflected in an increase in the rate of graft copolymerisation compared to that of AA homopolymerisation) decreases.

An increase in the density and(or) molecular mass of the grafted chains is accompanied by redistribution of H-bonds in the PVA-g-PAA macromolecules toward a decrease in the number of main chain – graft bonds and an increase in the number of bonds between the grafted chains. As a result, the structure of graft copolymers in the bulk state retains homogeneity only up to some critical mutually dependent values of N^* and M^*. At higher N and(or) molecular masses of the grafted chains, the structures of the copolymers contain ordered microregions (domains) formed by segments of PAA along with compatibility regions of the polymer components. Due to steric hindrance (at $N > N^*$) and(or) overlapping and interactions between long grafted chains (at $M_{PAA} > M^*$) at large distances from the main chain, these PAA segments cannot realise their thermodynamic affinity for PVA, and, hence, the PAA segments form an individual microphase in the PVA-g-PAA structure. Evidently, this type of microphase separation cannot be considered as a criterion for thermodynamic incompatibility between polymer components involved in graft copolymers.

Thermodynamic affinity between the main and grafted chains is responsible for reversibility of cleavage of an H-bond network and, correspondingly, destruction of the molecular and supermolecular structure of the PVA-g-PAA macromolecules in solution induced by temperature and hydrodynamic shear field. This fact is responsible for high resistance of solutions of PVA-g-PAA and other analogous graft copolymers to degradation in turbulent flow.

Graft copolymers which form intramolecular polycomplexes composed of chemically complementary polymer components additionally linked by covalent bonds, possess high binding ability. This provides, in particular, high flocculating ability of PVA-g-PAA as well as of the known graft copolymers of PAA onto polysaccharides in clearing of various suspensions and natural water.

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