Properties of Poly(vinyl alcohol)-*graft*-Polyacrylamide Copolymers Depending on the Graft Length

2. Thermal Properties in the Bulk State

*Olga Demchenko,** *Tatyana Zheltonozhskaya, Jean-Michel Guenet,*[1]
Svetlana Filipchenko, Vladimir Syromyatnikov

Kiev Taras Shevchenko National University, Chemical Department, 64 Vladimirskaya Str., 01033, Kiev, Ukraine
[1] Institut Charles Sadron (CNRS-ULP) UPR 022, 6 rue Boussingault, 67083 Strasbourg Cedex, France

Summary: Thermal behavior of poly(vinyl alcohol)-*graft*-polyacrylamide copolymers (PVA-*g*-PAA), so-called intramolecular polymer-polymer complexes (intraPC), with variable $\overline{M}_{vPAA}$ and constant average number N of grafts is considered in this report. Complete compatibility of PVA and PAA through hydrogen bonding is realized in the range of the graft lengths not exceeding some critical value. The content of adsorbed and trapped water in graft copolymers reflects some features of PVA-*g*-PAA_N structure depending on the graft lengths. The first thermal decomposition region in air for copolymers begins at higher temperatures with growing $\overline{M}_{vPAA}$, but the total destruction interval reduces. Formal kinetic decomposition parameters of the first decomposition stage appear to be the largest for the PVA-*g*-PAA with the largest quantity of H-bonds between the main and graft chains. Chemical transformations in graft copolymers, PVA and PAA during thermal decomposition are discussed.

Keywords: compatibility; graft copolymer; structure; thermal analysis; thermal decomposition

Introduction

Thermal analysis methods are a powerful and effective tool to study solid-state arrangement of macromolecules and are of practical importance in many polymer applications.[1,2] The influence of the number N of grafts (in the range from 25 to ~50) on thermal behavior of PVA-*g*-PAA_N was studied in detail previously.[3,4] It was shown that in such graft copolymers the complete compatibility of PVA and PAA, determined by their interaction through H-bonds, is observed only at an N value higher than some critical value (N_{crit}≈25).[3] At the same time PVA-*g*-PAA samples became more stable to the thermal decomposition in air with growing N.[4] In

DOI: 10.1002/masy.200351317

the present report the influence of $\overline{M}_{\mathrm{vPAA}}$ (or graft length) on thermal properties of PVA-*g*-PAA is considered.

Thermal Transitions and Thermal Decomposition of PVA-*g*-PAA

Three samples of graft copolymers with a constant average number of grafts per molecule (N=9) but different molecular weight of grafts: $\overline{M}_{\mathrm{vPAA}} = 3.27 \cdot 10^5$ (PVA-*g*-PAA1), $4.3 \cdot 10^5$ (PVA-*g*-PAA2) and $5.1 \cdot 10^5$ (PVA-*g*-PAA3) were investigated. The techniques of their synthesis and characteristics are detailed in the first report.[5] For comparison, PVA with $\overline{M}_{\mathrm{v}} = 4 \cdot 10^4$ and a residual content of acetate groups of 33% (Japan) and also PAA with $\overline{M}_{\mathrm{v}} = 2.72 \cdot 10^6$ and degree of hydrolysis of acrylamide units 13% from Oriana (Ukraine), were used.

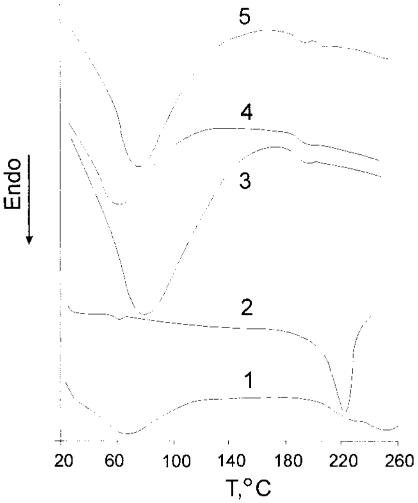


Fig. 1. DSC thermograms of *1* PAA, *2* PVA, *3* PVA-*g*-PAA1, *4* PVA-*g*-PAA2 and *5* PVA-*g*-PAA$_N$3.

Thermal transitions were studied by differential scanning calorimetry (DSC) at the heating rate 16 °C/min with a Du Pont 1090 thermal analyzer. DSC thermogram of amorphous PAA (Figure 1, curve 1) contains the endothermic peak of water evaporation, the heat capacity jump (α-relaxation transition), which corresponds to the glass transition temperature T_g (Table 1), and then a small endothermic peak, which can be attributed to the "liquid-liquid" transition (ll-transition). The last transition is well known for amorphous polymers.[6] ll-transition in PAA structure is evidently determined by the destruction of highly regular structures of hydrogen bonds, such as *cis-trans*-multimers of amide groups,[5] which are saved after α-transition. Thermogram of the semi crystalline PVA (curve 2) contains the glass transition and then the strong endothermic peak due to the crystalline phase melting (Table 1), ΔH_{melt}=83.2 J/g. Thermograms of the graft copolymers (curves 3-5) include the strong endothermic peak of water evaporation and also of the glass transition, observed practically at the same temperature (Table 1). Its value is somewhere between T_g for PVA and T_g for PAA as reflected in the compatibility of polymer components.[1,6] At the same time the thermogram of PVA-g-PAA3, having the longest graft chains (curve 5), displays the second glass transition in the region of higher temperatures.

Table 1. Glass transition temperature and temperature interval for heat capacity transition for PAA, PVA and the graft copolymers.

Polymer	T_g, °C	ΔT_g, °C
PAA	216	21
PVA	58.5	8
PVA-*g*-PAA1	188	8
PVA-*g*-PAA2	189.5	7
PVA-*g*-PAA3	186	12.5
	199	4

An analogous effect was observed when increasing the average number of grafts per molecule above some critical value ($N_{\mathrm{crit}} \approx 25$)[3] in the copolymer. It was explained with the appearance of a separate microphase formed by PAA segments which have no approach to the main chain due to higher steric hindrance. In the considered series of PVA-*g*-PAA1-3, the system of hydrogen bonds considerably changes with increasing molecular weight (length) of grafts.[5] In particular for PVA-*g*-PAA3, the effect of partial detachment of PAA graft chains from chemically complementary main chain and an increase of their rigidity are characteristic. The formation of microdomains of PAA segments, interacting far from the PVA chain, is evidently the result of described changes. Thermal decomposition of copolymers in air was compared with homopolymers PVA and PAA by differential thermogravimetric analysis[7] in the non-isothermal regime with a Q-1500D device of F.Paulik, G.Paulic, L.Erdey system. The heating rate was 2,5 °C/min. Weights of ~20 mg were used. Curves of the weight loss (TG curves), the weight loss rate (DTG) and changes in the heat flows (DTA) are shown in Figure 2.

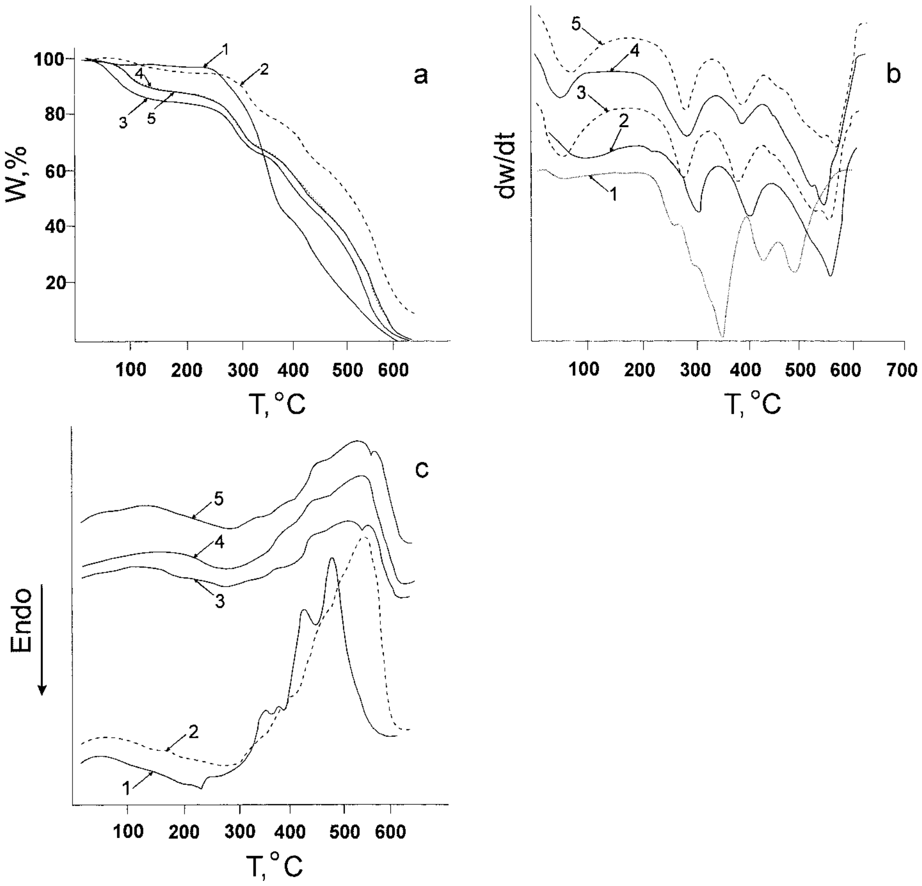


Fig. 2. TG (a), DTG (b) and DTA (c) curves for *1* PVA, *2* PAA, *3* PVA-g-PAA1, *4* PVA-*g*-PAA2 and *5* PVA-*g*-PAA3.

The first step on TG curves for the hydrophilic polymers[8] corresponds to water evaporation. Total water quantity in the polymers was determined as the weight loss before the beginning of chemical decomposition (Table 2). The amount of trapped water was taken as the weight loss occurring between 20 and 110 °C. The difference corresponded to the amount of adsorbed water (Table 2). It is seen that the quantity of trapped and absorbed water in PAA sample is much higher than in PVA. This is attributed to a higher thermodynamic affinity of water to PAA. In the PVA-*g*-PAA1-3 series the quantity of trapped water decreases (the density of segment packing grows) but the quantity of adsorbed water increases. The last result conforms to improvement of thermodynamic quality of water as a solvent with respect to the copolymer, when increasing the graft length , which was established earlier.[5]

Table 2. Thermogravimetry data of water content.

Polymer	Total water, %	Trapped water, %	Adsorbed water, %
PVA	1.6	1.0	0.6
PAA	15.0	10.0	5.0
PVA-*g*-PAA1	13.5	11.2	2.3
PVA-*g*-PAA2	10.8	7.8	3
PVA-*g*-PAA3	11.1	7.2	3.9

The thermal decomposition of all investigated samples occurs in three stages (Figure 2 a,b). But in the first decomposition stage of PVA and the third decomposition stage of graft copolymers, some substages with corresponding thermal steps appear on DTG curves (Figure 1 b) and DTA curves (Figure 2 c). The parameters of the decomposition stages are detailed in Table 3. The first decomposition stage for the copolymers begins at the temperature (T_d) that is somewhat below or reaches T_d for PVA (the least thermostable), but the temperature of their decomposition completion (T_c) lies near that for PAA.With increasing the length of grafts, the following changes of the decomposition parameters are observed: (1) T_d grows, (2) T_c increases, (3) ΔT for decomposition stage I, which is accompanied by an endothermic effect, decreases, (4) ΔT for decomposition stage III, which occurs with an intensive exothermic effect, decreases, (5) the total interval of thermal decomposition decreases. Thus, with increasing graft length, the thermostability of copolymers rises but, simultaneously, the rate of their complete degradation also increases.

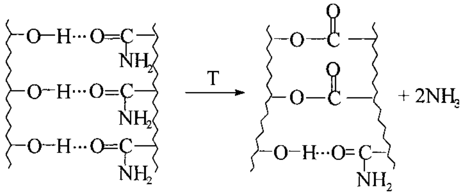
The mechanism of thermal degradation of PVA and PAA under the inert atmosphere is well known.[9-11] The degradation of PVA occurs in two stages. The first stage, which begins at ~ 200 °C, is mainly dehydration of polymer chains, accompanied by the formation of polyene structures.[9,11] The main product produced in degradation is water. Aldehydes and methyl ketones compose the main part of the other products.[9]

In the second decomposition stage, polyene chains are degraded to produce carbon and hydrocarbons. The main products forming in this stage are acetaldehyde and acetic acid.[9] PAA degradation also occurs in two stages. The main chemical process in the first stage ($T_d \approx 220$ °C) is intrachain and interchain imidization,[10] but insignificant splitting off of formaldehyde and the formation of unsaturated regions also occur. Of the volatile decomposition products, the main part is composed of: $H_2O>NH_3>CO>CO_2$.[10] In the second stage of PAA pyrolysis, carbon dioxide exceptionally forms and nitrile groups in ^{13}C NMR spectrum are detected. Note, that all chemical processes occurring in PVA and PAA thermal decomposition, are accompanied by endothermic effects. At the same, time the reactions of oxygen attachment to weak C-H bonds of organic substances or to alkyl radicals, formed in the breaking of weak chemical bonds, due to temperature, are accompanied by exothermic effects.[12] Therefore, the appearance of exothermic effect at a distinct stage (or substage) of PVA, PAA and PVA-*g*-PAA thermal decomposition means the beginning of the process of polymer oxidation. The oxygen presence increases the number of the distinct decomposition stages (Table 3) but, according to Ref.,[13] influences little T_d and T_c, which are thermochemical constants of polymers and are determined by their chemical nature. It was established that polymer oxidation proceeds by of chain reactions where alkyl, alkoxyl, peroxyl radicals and hydroperoxide compounds play the main role.[12] The oxidation rate depends on the solubility and diffusion of oxygen in the polymer bulk.[12] At the beginning of oxidation, the accumulation of radicals in macromolecules without essential change of their polymerization degree occurs.[10] When the quantity of radicals becomes quite great, the process of polymer degradation begins.[10] The discussion shows that in decomposition stage I of the polymers, which accompanied by endo effects (Table 3), the chemical transformations without oxygen participation occur. Unlike this, PVA oxidation begins still on I stage. The weight loss by PAA and PVA-g-PAA1-3 at stage I is minimal. The second stage, accompanied by a small exo effect, corresponds to the completion of chemical transformations in polymer chains and the beginning of their oxidation (accumulation of radicals). At stage III intensive degradation of macromolecules occurs, which is accompanied by the maximum (more than 50 %) weight loss and intensive exothermic effects (Table 3). Chemical transformations of PVA-g-PAA at stage I of decomposition must include the above-mentioned reactions which are characteristic of individual polymers.[9-11] However, such graft copolymers are intraPC formed by the cooperative system of hydrogen bonds. In this case it is possible to expect the formation of covalent bonds between macromolecules under the temperature influence. Similar chemical transformations in intermolecular polymer-polymer complexes are well known.[11,14]

Table 3. Characteristics of separate stages of thermal decomposition in air.

Polymer	Stage	$T_{\mathrm{in}}÷T_{\mathrm{f}}$ 1) °C	ΔT 2) °C	T_{max} 3) °C	W 4) %	Thermal effect
PVA	I	225-396	171	253	54.6	endo
				298		exo, 354
				348		exo, 382
	II	396-455	59	422	17.2	exo, 428
	III	455-574	119	488	28.2	exo, 490
PAA	I	256-344	88	302	16.5	endo
	II	344-449	105	404	21.2	exo, 404
	III	449-618	169	558	52.4	exo, 558
PVA-*g*-PAA1	I	198-332	134	278	21.6	endo
	II	332-426	94	382	23.7	exo,382
	III	426-610	184	438	54.7	exo,438
				532		exo,526
				556		exo,550
PVA-*g*-PAA2	I	221-332	111	286	18.6	endo
	II	332-438	106	394	23.7	exo,390
	III	438-617	179	446	57.7	exo,440
				526		exo,520
				548		exo,544
PVA-*g*-PAA3	I	226-335	109	290	21.0	endo
	II	335-442	107	398	23.7	exo,400
	III	442-616	174	456	55.3	exo,448
				548		exo,534
				574		exo,558

1) Initial and final temperatures.
2) Temperature interval.
3) Temperature of the maximum decomposition rate.
4) The weight loss.



They can occur before the destruction begins. Really, as it was established, PVA-g-PAA films heated at 190 °C for 30 min lost completely their solubility in water.

In order to analyze the differences in PVA-g-PAA behavior in dependence on $\overline{M}_{\mathrm{vPAA}}$ and in comparison with PAA, the formal–kinetic parameters E, n, Z and k of the two first decomposition stages, were calculated from TG and DTG curves (Table 4). With this purpose, the computer processing of experimental TG curves based on the Arrhenius equation in the matrix form and the least-squares method,[15] was carried out

Table 4. Formal kinetic parameters of two stages of thermooxidative decomposition.

Polymer	Stage number	$E^{1)}$, kJ/mol	$n^{2)}$	$Z^{3)}$, 1/s	$k^{4)}$, 1/s
PVA	I	59.2	0.83	$6.11 \cdot 10^{3}$	0.064
	II	312.0	2.03	$4.90 \cdot 10^{22}$	0.174
PAA	I	143.9	1.15	$1.34 \cdot 10^{12}$	0.113
	II	165.2	1.40	$6.13 \cdot 10^{11}$	0.110
PVA-g-PAA1	I	112.8	1.57	$5.45 \cdot 10^{9}$	0.111
	II	193.8	1.87	$4.16 \cdot 10^{14}$	0.146
PVA-g-PAA2	I	233.7	2.99	$2.52 \cdot 10^{21}$	0.365
	II	123.5	1.50	$4.05 \cdot 10^{8}$	0.085
PVA-g-PAA3	I	134.2	1.64	$4.48 \cdot 10^{11}$	0.158
	II	149.1	1.63	$4.73 \cdot 10^{10}$	0.118

1) The activation energy.
2) The order of reaction.
3) The frequency factor in the Arrhenius equation.
4) The rate constant of decomposition.

The results for stage I of the copolymer and PAA decomposition, where chemical transformations without oxygen occur, are the most interesting. Parameters E, n, Z and k with increasing $\overline{M}_{\text{vPAA}}$ go through a maximum (for PVA-g-PAA2) and then decrease. Such parameters for PVA-g-PAA2 are higher than for PAA. Note also higher n values for all copolymers compared with PAA (Table 4). It is known that for complete chemical reactions such as chemical transformations in stage I thermal decomposition, parameters E and n are effective overall values. Here n is the overall order of reaction for all reacting components (all reacting polymer groups) and E is the sum of activation energies of separate stages of the transformation.[16] This means that the E and n are the higher the more complete chemical transformations requiring large activation energies occur in the considered process. With such criterion it is possible to conclude that higher values n for copolymers are conditioned by more complete chemical reactions in PVA-g-PAA than in PAA at stage I of decomposition. At the same, time maximum values of E and n for PVA-g-PAA2, which are correlated with the largest quantity of H-bonds between the main and graft chains in the given polymer,[5] point to the strongest interaction of polymer components in the considered graft copolymer.

Conclusion

Complete compatibility of PVA and PAA through hydrogen bonding in PVA-g-PAA graft copolymers occurs only in the range of the graft lengths, not exceeding the critical value $\overline{M}_{\text{PAAcrit}} \approx 4{,}3 \cdot 10^5$ at N=9. With longer PAA graft chains, the microdomains of PAA segments form as a result of their partial detachment from the main chain. These microdomains exist together with the regions of compatibility of polymer components. That is why the microphase separation of such type cannot be used as the criterion of thermodynamic incompatibility of polymer components in studied polymer systems.

1. Sh.W. Kuo, F.Ch. Chang, *Macromolecules* 2001, *34*, 4089.
2. G.N. Smyrnova, *Izv. Vuzov:Khim. Khim. Tekhnol.* **1992**, *35*, 3.
3. O. Demchenko, N. Kutsevol, T. Zheltonozhskaya, V. Syromyatnikov, *Macromol. Symp.* **2001**, *166*, 117.
4. N. Kutsevol *"Graft copolymers based on the chemically complementary poly(vinyl alcohol) and polyacrylamide with different quantities of graft chains" Ph. D.* Dissertation, Kiev 2001, 245 p.
5. T. Zheltonozhskaya, O. Demchenko, I. Rakovich, J.-M. Guenet, V. Syromyatnikov, *Macromol. Symp.* **2003**, submitted.
6. V.A. Bershtein, V.M. Yegorov. "Differentsialnaya skaniruyushchaya kalorimetriya v fiziko-khimii *polimerov"*, Khimiya: Leningrad, 1990.
7. N.P. Prokopchuk, Izv. *Akad. Nauk. Ser. Khim. Nauk*, **1983**, *4*, 119
8. S. Rouland. *"Voda v polimerah"*, Mir: Moskva, !984.
9. Y. Tsuchiya, K. Sumi, *J. Polym. Sci,, Part A: Polym. Chem.*, **1969**, *7*, 3151.
10. W.M. Leung, D.E. Axelson, *J. Polym. Sci,, Part A: Polym. Chem.* **1987**, *25*, 1825.
11. 9. X. Lhong, K. Takegoshi, K. Hikichi, *Polymer* **1992**, *33*, 718.
12. Ye.T. Denisov. "*Okislenye i destruktsiya karbotsepnykh polimerov"*, Khimiya:Leningrad, 1990.
13. A.A. Miroshnichenko, M.S. Platitsa, V.L. Volkov, V.A. Dovbnya, *Vysokomol. Soedin.* **1988**, *A30*, 2516.
14. A.B. Zezin, V.B. Rogacheva, E.F. Razvodovsky, *Vysokomol. Soedin.* **1975**, *A17*, 2637.
15. O.V. Suberlyak, G.Yu. Uigeliy, *Dopovidy NAN Ukr.* **1998**, *11*, 150.
16. E.T. Denisov. "*Kinetika gomogennyh khimicheskikh reaktsii*", Vysshaya Shkola: Moskva, 1978.