Macromol. Symp. **2005**, *222,* 135-142

Structural Transitions in Triblock Copolymers Based on Poly(ethylene oxide) and Polyacrylamide under the Temperature Influence

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Summary: Thermal transitions in the bulk structure of triblock copolymers (PAA-*b*-PEO-*b*-PAA) based on polyacrylamide and poly(ethylene oxide) with varying molecular weight (length) of PEO block comparing with the structures of individual polymers and polymer mixtures were investigated. A lot of effects, such as the melting temperature depression, decreasing of the crystallinity degree of PEO and also appearance of the microphase separation in amorphous regions of the polymer mixtures and the triblock copolymers were found. Such investigations pointed to a strong intramolecular interaction of the polymer blocks in the triblock copolymers that is confirmed by the results of IR spectroscopy. It was shown that PEO and PAA blocks formed the system of H-bonds with participant of *trans*-multimers of amide groups.

Keywords: block copolymer; crystallinity degree; hydrogen bonds; intramolecular polycomplex; microphase separation

Introduction

Graft and block copolymers with a strong interacting polymer components, which was called as intramolecular polycomplexes (IntraPC), are of great interest last years.[1] The main element of self-regulation of such systems is the thermodynamic affinity between polymer components. In present there are relatively many researches devoted to peculiarities of the bulk structures and state in solution of IntraPCs formed in the graft copolymers.[2,3] But the complex formation of chemically complementary polymers in linear block copolymers is not practically investigated. In the present work a thermal transitions in the bulk structure of triblock copolymers (TBC) based on polyacrylamide and poly(ethylene oxide) (PAA-*b*-PEO-*b*-PAA), which are capable to interact with each other were studied.

DOI: 10.1002/masy.200550416

Triblock copolymers in the bulk state

In order to establish the role of the central block length three PEO samples from "Merk" (Germany) with $M_{vPEO}=3\cdot10^3$; $4\cdot10^4$ and $1\cdot10^5$ were used in the synthesis of TBCs. Synthesis was carried out in aqueous solution according to the method of graft copolymerization of PAA onto poly(vinyl alcohol) with application of Ce (IV) salt, as the initiator.[4] The ratio between Ce (IV) and PEO concentrations was 2 $mol_{Ce\ (IV)}/mol_{PEO}$. TBC were precipitated by acetone and freeze dried. The sample of individual PAA, with $M_{PAA}=6.3\cdot10^5$, was synthesized in the same experimental conditions. TBC molecular characteristics calculated from the elemental analysis data are shown in Table 1.

Table 1. Parameters of the triblock copolymers.

Polymer	$M_{v\ PEO}\cdot10^4$	$M_{v\ PAA}\cdot10^5$	$M_{v\ PAA\text{-}b\text{-}PEO\text{-}b\text{-}PAA}\cdot10^6$	n [1)]
PAA-*b*-PEO-*b*-PAA1	0.3	0.38	0.08	7.9
PAA-*b*-PEO-*b*-PAA2	4	3.18	0.68	4.9
PAA-*b*-PEO-*b*-PAA3	10	9.07	1.91	5.6

[1)] The ratio of base-mol_{PAA}/base-mol_{PEO} in the copolymer macromolecules.

It is seen, that the PAA block length increase in TBC samples.

Thermal transitions in the TBC bulk structure comparing with individual polymers and mixtures of the same polymers were studied by differential scanning calorimetry (DSC) at the heating rate 16 °C/min with a Du Pont 1090 thermal analyzer. The liquid nitrogen cooled the carefully dried polymer samples placed in the opened capsules and then the heat flow-temperature curves in two heating-cooling cycles were measured. The sapphire crystal was used as standard. The heat capacity-temperature DSC thermograms calculated from these data are shown in Figures 1, 2.

DSC thermograms of amorphous PAA (Figure 1, a) contain the intense endothermic peak of water evaporation and one glass transition. On the DSC thermograms of crystalline PEO (Figure 1 b, c) only melting peaks are revealed. The temperature (T_m) and enthalpy (ΔH_m) of the melting transition increases with growth M_{PEO} but reduces in the 2-nd runs (Table 2).

DSC thermograms of the triblock copolymers with relatively shot PEO blocks ($M_{vPEO}\leq4\cdot10^4$) do not contain any melting transitions for PEO (Figure 1, e, f). A weak melting peak appears only in the thermogram of PAA-*b*-PEO-*b*-PAA3 with the longest PEO block (Figure 1, g). The ΔH_m value for this melting transition (Table 2) is much lesser than that one for melting process in individual PEO2. This fact testifies to much lesser crystallinity of the PEO block in the copolymer comparing with individual PEO. Moreover, the T_m value found for the given copolymer essentially reduces in comparison with analogous value for PEO2 (Table 2), that is the phenomenon of the melting point depression takes place. It is known that above-mentioned effects namely: the melting point depression and decreasing of the crystallinity degree of a polymer in a polymer mixture are conditioned by strong interaction of polymer components in the amorphous regions of a bulk structure.[5]

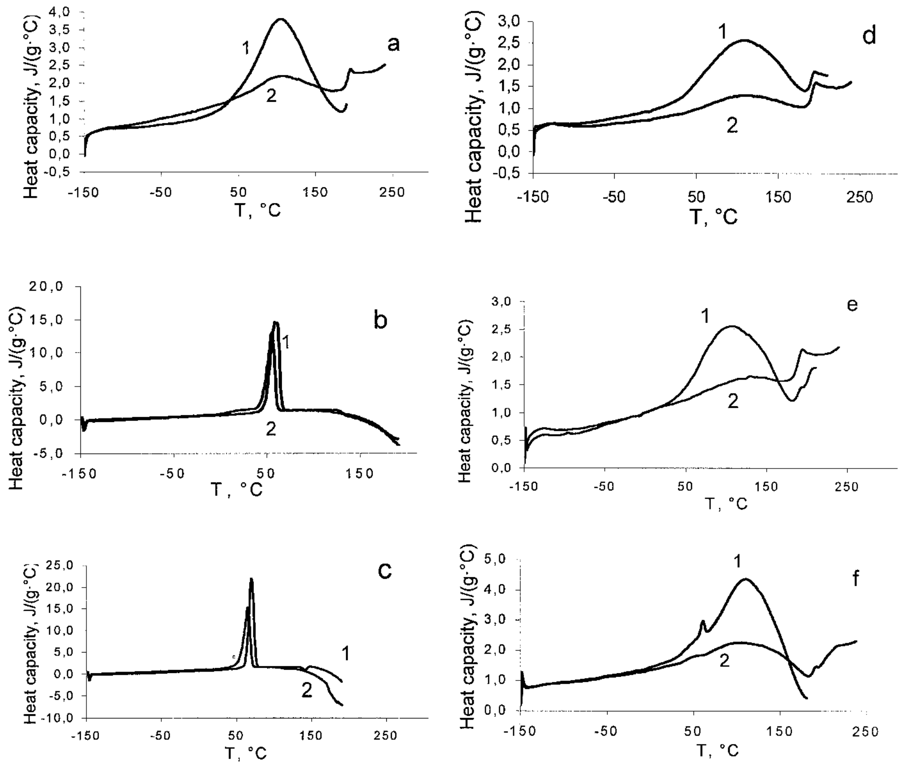


Figure 1. DSC thermograms of PAA –a, PEO1 –b, PEO3 –c, PAA-*b*-PEO-*b*-PAA1 – d, PAA-*b*-PEO-*b*-PAA2 –e, PAA-*b*-PEO-*b*-PAA3 –f. 1-st run (1) and 2-nd run (2).

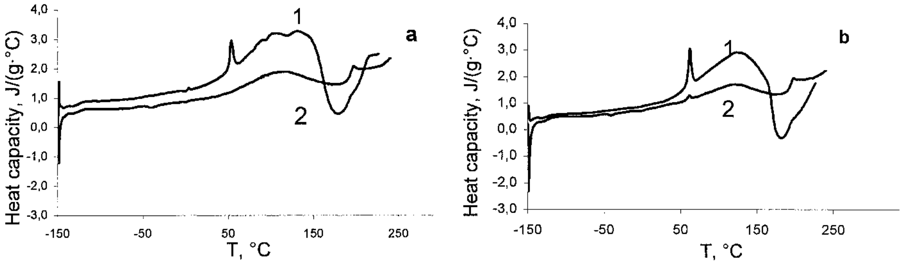


Figure 2. DSC thermograms of polymer blend of PAA+PEO1 –a and polymer blend PAA+PEO2 – b. 1-st run (1) and 2-nd run (2).

Table 2. Parameters of structural transitions in PAA, PEO and PAA-*b*-PEO-*b*-PAA.

Polymer	Cycle (run)	T_g, °C	ΔT_g, °C	ΔC_p1), J/g·°C	T_m, °C	ΔT_m, °C	ΔH_m, J/g	X_c2), %
PAA	2-nd	190.9	8.0	0.55	-	-	-	-
PEO1	1-st	-	-	-	58.0	78.0	157.6	80
	2-nd	-	-	-	55.0	105.1	141.1	72
PEO2	1-st	-	-	-	70.0	101.0	172.3	88
	2-nd	-	-	-	65.0	100.0	156.3	79
PAA-*b*-PEO-*b*-PAA1	2-nd	190.8	9.0	0.55	-	-	-	-
PAA-*b*-PEO-*b*-PAA2	1-st	187.2	9.3	0.24	-	-	-	-
		202.0	8.5	0.34				
	2-nd	188.0	12.3	0.57	-	-	-	-
PAA-*b*-PEO-*b*-PAA3	1-st	-	-	-	60.9	24.0	73,2	37
	2-nd	187.0	6.6	0.33	56.1	30.0	22.5	11
		204.6	20.8	0.72				

1) The heat capacity jump

2) The degree of crystallinity. $X_c = \Delta H_m/\Delta H^\circ_m$, where ΔH°_m is the melting enthalpy of 100% crystalline polymer (196.8 J/g).[6]

It allows to conclude that the PAA and PEO blocks strongly interact with each other in the triblock copolymers. Comparative analysis of the parameters T_g and ΔT_g and ΔC_p, which characterize thermal transitions in the amorphous regions of the triblock copolymers and individual PAA, confirms such conclusion.

Really, DSC thermograms for PAA-*b*-PEO-*b*-PAA2 and 3 samples (Figure 1, f, g) demonstrate by contrast with thermogram of the 1-st copolymer sample (Figure 1, e) two glass transitions. The T_g value of the first of them is lower than that of individual PAA (Table 2) but the T_g of the second glass transition is higher. Thus, a microphase separation in the amorphous regions of the structure of both considered copolymers occurs. Analogous situation was observed in the bulk structure of the PAA to poly(vinyl alcohol) graft copolymers (forming IntraPC) since some critical values of the number and molecular weight

of the grafts.[1] Such sort of microphase separation was attributed to existence in the amorphous areas of the graft copolymer structure side by side with the regions of full compatibility of polymer components also domains formed by PAA segments only which do not contact with the main chain. Basing on these data one can suppose that appearance of the microphase separation in the triblock copolymer amorphous regions is connected not with lengthening of the PEO block (that can only intensify the cooperative interactions between different blocks), but mainly with corresponding growth of the PAA block length (Table 1).
Similar but more weak effects observe for two bulk polymer mixtures having the same polymer rations as in corresponding triblock copolymers (Figure 2, Table 3). These mixtures were obtained by freeze drying of the mixture of aqueous solutions.

Table 3. Parameters of structural transitions in PAA + PEO blends.

Polymer	Cycle (run)	T_g, °C	ΔT_g, °C	ΔC_p, J/g·°C	T_m, °C	ΔT_m, °C	ΔH_m, J/g	X_c, %
PAA+PEO1	1-st	189.5	9.2	0.58	53.4	25.0	160.1	81
		208.5	11.8	1.00				
	2-nd	193.0	9.0	0.62	-	-	-	-
PAA+PEO2	1-st	191.9	9.1	0.68	62.3	29.0	146.9	75
		-	-	-				
	2-nd	193.3	8.0	0.61	60.9	19	12.9	7

Really, the depression of T_m values of PEO in both mixtures and lowering of X_c (in the PAA+PEO2 mixture) comparing with such parameter in individual PEO are displayed in the 1-st heating cycle (1-st run). Additionally, two glass transitions are revealed in the 1-st run for both polymer mixtures (Figure 2 a, b; curves 1). Compatibility of the polymers essentially grows after heating of their mixtures higher than T_g. Such conclusion is confirmed by practically full absence of the PEO melting peaks and appearance only one glass transition in the 2-nd runs for both polymer mixtures (Figure 2 a, b; curves 2; Table 2).
Interaction between PEO and PAA blocks in TBC was studied by IR spectroscopy. IR spectra of thin films of individual polymers and two TBC samples, were recorded with the use of FTIR Micolett Nissan – 450 (USA) spectrometer. The examples of spectra are shown in the Figure 3.

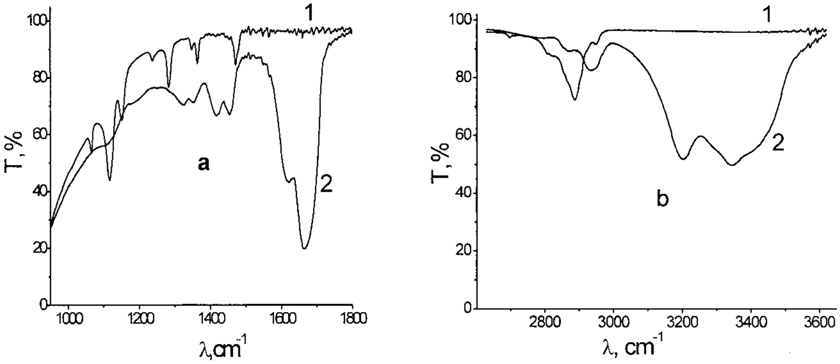


Figure 3. IR spectra of PEO2 –*1* and PAA-*b*-PEO-*b*-PAA2 –*2* films in the most important regions (a, b). T=293 K.

Formation of the H-bond system between polymer blocks is proved first of all by the low-frequency displacement (in 23 cm^{-1}) of the $\nu_{C\text{-}O\text{-}C}$ vibration band of PEO in TBC comparing with the same band in the spectrum of individual PEO ($\nu_{C\text{-}O\text{-}C}$ 1113 cm^{-1}). In order to establish the changes in the H-bond system between amide groups of PAA in TBCs (in comparison with individual PAA) under influence of the central PEO block the computer dividing of the overlapping amide I bands using the spline-functional method was carried out.[7] One examples is shown in Figure 4.

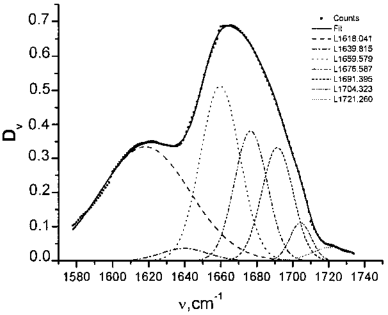


Figure 4. Computer processing of IR spectra of PAA-*b*-PEO-*b*-PAA2 in the amide I and amide II region. Experimental (···) and calculated (—) vibration band contours. The separate amide I bands are shown also.

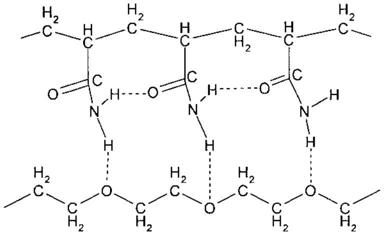
Using only two overlapping bands in the amide I and amide II region it can not be correctly process these areas of spectra. Therefore, all bands of PAA which were well known and described earlier were introduced into a computer.[8] Then the integral absorption coefficients of separate amide I bands were used to calculate their contributions (α_i) in the common carbonyl absorption (Table 4).

Table 4. Contributions of the apparent integral absorption coefficients of separate amide I bands in common $\nu_{C=O}$ absorption.

Polymer	α — %				β 1)= B_{1676}/B_{1691}
	ν~1660 cm^{-1}	ν~1676 cm^{-1}	ν~1691 cm^{-1}	ν~1704 cm^{-1}	
PAA	47.6	23.7	24.8	4.0	0.95
PAA-*b*-PEO-*b*-PAA2	45.9	29.4	19.1	5.7	1.54
PAA-*b*-PEO-*b*-PAA3	45.3	26.7	22.9	5.1	1.17

1)The effective length of *trans*-multimers of amide groups

Note, that the band near 1660 cm^{-1} is attributed to *cis-trans*-multimers of amide groups.[8] Two bands at 1676 cm^{-1} and 1691 cm^{-1} belong to terminal and inside (H-bond) amide groups of *trans*-multimers. Finally, the band at 1704 cm^{-1} points on existence of free amide groups. Basing on the data of Table 4, it can be conclude that there are relatively lesser of *cis-trans* and also *trans*-structures of H-bound amide growps in the TBC samples under study comparing with individual PAA. At the same time the effective length of *trans*-multimers of amide groups in the TBC samples, in comparison with PAA, grows. Increasing of rigidity of PAA chains in TBCs can be explained by a participation of *trans*-multimers of the PAA amide groups in the formation of H-bond system between PEO and PAA blocks, as in the case of intermolecular complex formation between PAA and poly(vinil alcohol):[9]



Conclusion

Thus, triblock copolymers based on PEO and PAA are intramolecular polycomplexes, stabilized by the system of H-bond between PEO and PAA blocks. Intramolecular complex formation is reflected in the practically full absence of PEO crystalline domains in the block copolymer structure and also in the specific microphase separation in amorphous domains.

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