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Novel Flocculants for the Natural Water Clearing Consisting Triblock Copolymers with Poly(Ethylene Oxide) and Polyacrylamide

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New high-effective flocculants containing triblock copolymers PAA-b-PEO-b-PAA (TBC) based on chemically-complementary polyacrylamide (PAA) and poly(ethylene oxide) (PEO) with the different block lengths are synthesized, characterized, tested and patented in Ukraine. Given TBCs, which are obtained by free radical block copolymerization of acrylamide with poly(ethylene glycols) of different molecular weight, are intramolecular polycomplexes (IntraPCs) with a strong interacting polymer components. It was revealed that the block copolymerization process has a matrix character because non-covalent interactions of growing PAA chains with PEO. High flocculate ability of TBC in clearing of kaolin suspensions and natural water was established.

Keywords: flocculant; intramolecular polycomplex; polyacrylamide; poly(ethylene oxide); triblock copolymer

INTRODUCTION

The problem of obtaining of high quality drinking water is a worldwide actual task. One of decisions of this important problem is flocculate clearing of natural water with application of the effective flocculants of new-generation [1]. Heterogeneous polymers such as the linear block copolymers with chemically-complementary polymer components, which formed intramolecular polycomplexes (IntraPCs) [2], are considered as one of the most perspective functional materials [3] and can potentially be used as high efficient flocculants [2,4,5]. Their structure and flocculate ability can be easily changed by the

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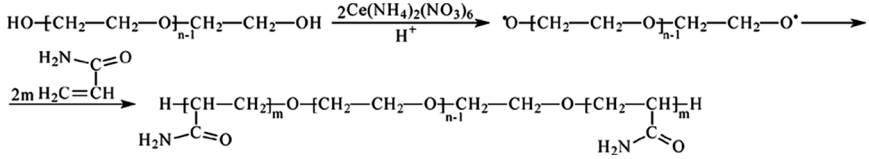
variation of the chemical nature and length of polymer components [6]. In the present work the peculiarities of synthesis, structure of flocculants, containing triblock copolymers PAA-*b*-PEO-*b*-PAA based on chemically-complementary PAA and PEO, are considered. The flocculate ability of the synthesized TBC samples in the precipitation of the model clay suspension and in the process of natural water treating in waterworks comparing with individual PAA and well known French flocculant DB 45 SSH was investigated.

EXPERIMENTAL

TBC samples were synthesized by free radical block copolymerization of acrylamide (AA) with poly(ethylene glycols) of different molecular weight: $M_{vPEG} = 1 \cdot 10^3$ (PEG1), $3 \cdot 10^3$ (PEG2), $6 \cdot 10^3$ (PEG3), $1.5 \cdot 10^4$ (PEG4), $4 \cdot 10^4$(PEG5), $1 \cdot 10^5$ (PEG6), from Germany ("Merk"), which were activated by Ce^{IV} ions and used as macroinitiators:



Block copolymerization was performed at the constant mol ratio of reacting components: $[Ce^{IV}]/[-OH] = 1$ and $[Ce^{IV}]/[AA] = 1 \cdot 10^{-3}$.

PAA sample was obtained by free radical homopolymerization of AA with application of Ce^{IV} at the same experimental conditions. The M_v of synthesized PAA sample was equaled $6.31 \cdot 10^5$. Polymerization rate and the monomer conversion in the block copolymerization and homopolymerization processes were carried out by dilatometry method [7].

Flocculative ability of the PAA-*b*-PEO-*b*-PAA samples in comparison with individual PAA on the model kaolin suspension was characterised by patented method [8]. The process of flocculation was described by 4 parameters: τ_0 – the length of the initial stage of the slow suspension precipitation (induction period); v_{rel} – the relative velocity of the fast stage of precipitation,which allows comparing the fast stages of flocculation processing or not utilizing the flocculate additives; V – the volume of precipitate formed in a fixed time (1 min) counted from the beginning of a flocculation process; D – the optical density of supernatant after a fixed time (20 min) from the beginning of a precipitation process, which characterizes the degree of water contamination. Thus, three first parameters characterize

the flocculation process while the last one – water turbidity after cleaning. Examination of new PAA-*b*-PEO-*b*-PAA flocculants was carried out on waterworks of Ukraine, which use natural water from the Desna river. Various doses of flocculation agents were introduced into the river water together with coagulation agent - predetermined optimum quantity of $Al_2(SO_4)_3$ which normally accompanies flocculants in the water treatment processes. Quality of the natural water from Desna was estimated on several parameters: turbidity, chromaticity, oxidizability and content of residual Al [9].

RESULTS AND DISCUSSION

The initiation and development of homo- and block copolymerization processes occurs on the same mechanism, therefore the comparison of kinetic parameters of both processes is possible. The results of dilatometry researches are represented in Figure 1.

It is visible, that all curves contain more or less long induction period which is connected with different time of existence of the intermediate complex formed by Ce^{IV} ions and $-OH$ groups of PEG [10].

Speed of PAA block copolymerization with the most low-molecular PEG1 sample and monomer conversion are very low, whereas the value of the induction period τ_0 is very high in comparison with PAA homopolymerization (Fig. 1, curve 1 and 2). The other picture was observed in PAA block copolymerization processes with more height-molecular PEG: $M_v > 1 \cdot 10^3$. The induction period is reduced. At the

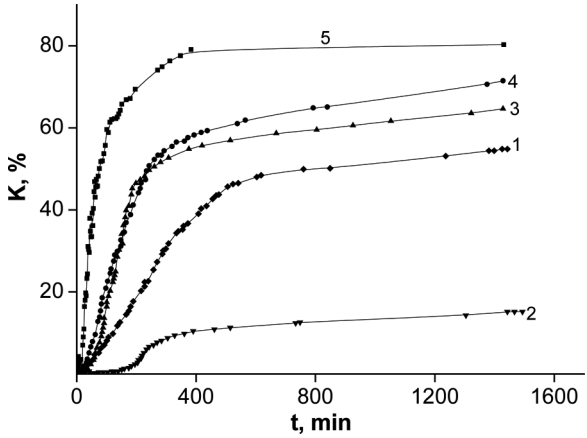


FIGURE 1 Time – conversion curves for PAA-1 and TBC-2, TBC3-3, TBC4-4, TBC5-5. T = 293 K.

TABLE 1 Kinetic Parameters of AA Copolymerization with PEO and AA Homopolymerization

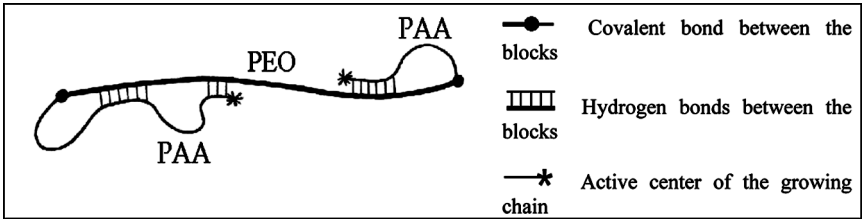
Polymer	$M_{vPEO} \cdot 10^{-4}$	τ_0^a, min	$V_r^{20} \cdot 10^{5b}$, $mol \cdot dm^{-3} \cdot c^{-1}$	$V_r^{40} \cdot 10^{5c}$, $mol \cdot dm^{-3} \cdot c^{-1}$	$V_r^{60} \cdot 10^{5d}$, $mol \cdot dm^{-3} \cdot c^{-1}$	K^e, %
PAA	–	15.5	1.6	1.2	–	40.5
TBC1	0.1	168.0	0.6 (V_r^{10})	–	–	10.9
TBC3	0.6	54.9	5.76	5.62	0.16	55.4
TBC4	1.5	31.4	4.62	4.19	0.34	57.8
TBC5	4.0	25.0	15.5	7.92	2.87	78.6

[a]Induction period.
[b]Conversion rate of block copolymerization at conversion degree of AA 20%.
[c]Conversion rate of block copolymerization at conversion degree of AA 40%.
[d]Conversion rate of block copolymerization at conversion degree of AA 60%.
[e]Monomer conversion in 420 min after beginning of polymerization.

same time the rate of polymerization and monomer conversion grow. This situation we can see in Table 1, which data are designed on the basis of kinetic curves.

It is show, that the block copolymerization speed rises at $M_{vPEG} = 4 \cdot 10^4$ on the order in comparison with AA homopolymerization, that is caused by the interaction of polymer blocks. Essential increasing of the polymerization rate and the monomer conversion in the block copolymerization process comparing with acrylamide homopolymerization carried out in the same experimental conditions, pointed out on the positive dynamic matrix effect [11]:

Schematic representation of the matrix block copolymerization process



It was shown that the block copolymerization process has a matrix character because non-covalent interactions of growing PAA chains with PEO. Thus it has been confirmed that given triblock copolymers form IntraPCs, which structures are stabilized by hydrogen bonds between the polymer blocks [12].

Molecular characteristics of TBC samples are shown in Table 2.

TABLE 2 Characterization of Triblock Copolymers

Copolymer	$M_{vPEO} \cdot 10^{-5}$	$M_{vPAA} \cdot 10^{-5}$	$M_{vTBC} \cdot 10^{-5}$	w^{a}_{PEO}, %
TBC1	0.01	–	–	–
TBC2	0.03	0.38	0.79	3.8
TBC3	0.06	0.54	1.14	5.2
TBC4	0.15	1.21	2.57	5.8
TBC5	0.40	3.18	6.76	5.9
TBC6	1.00	9.07	19.14	5.2

[a]Wt. ratio of PEO in copolymers.

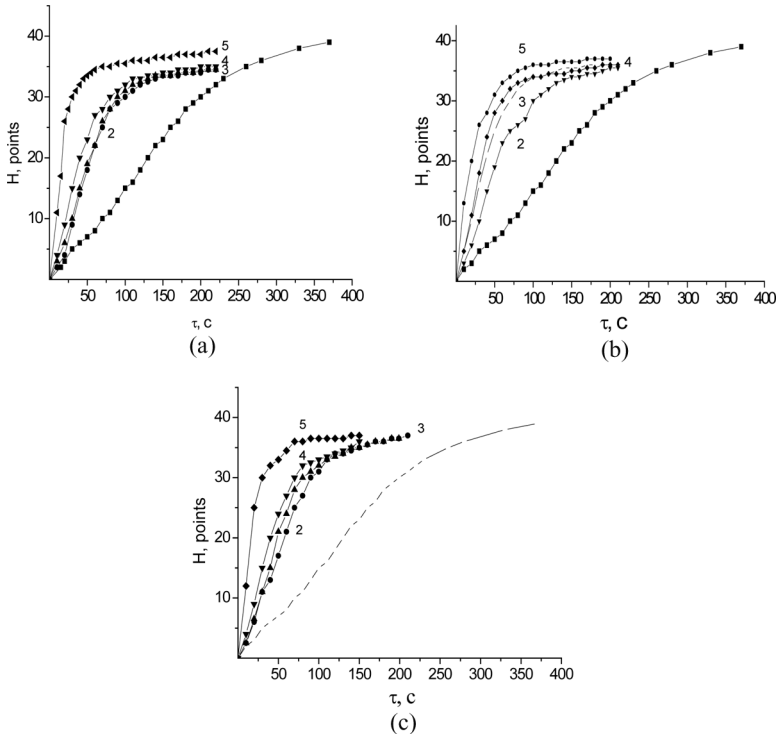


FIGURE 2 Time dependence of the height of clarified pillar for kaolin suspension ($C = 30\,kg \cdot m^3$) flocculated with TBC2 (a), TBC4 (b) and TBC5 (c) at 295 K. Flocculate concentrations: $1 \cdot 10^{-4}$–2, $5 \cdot 10^{-4}$–3, $1 \cdot 10^{-3}$–4 and $5 \cdot 10^{-3}\,kg \cdot m^{-3}$–5.

The ability of TBC samples to flocculate model kaolin suspension ($C = 30\,kg \cdot m^{-3}$, $R_{av} = 6.5\,\mu km$) for various TBC concentrations in comparison with flocculate ability of PAA are represented in Figure 2. From such dependencies of the height of clarified pillar for kaolin suspension, the parameters of the precipitation process of kaolin suspension for TBC samples and PAA were calculated. It was revealed in Table 3.

It is clear, that the TBC flocculants (in all concentration region) favorably differ from the individual PAA. TBC flocculants have higher v_{rel}, more low values of the V parameter (better flocculants form dense, but not necessary big floccules), more low induction period, because the flocculation begins at high velocity, without a stage of primary aggregation of colloid particles in comparison with individual PAA. Especially it is necessary to note, that the TBC samples in the region of the small concentration ($C < 1 \cdot 10^{-3}\ kg \cdot m^{-3}$) more effective than

TABLE 3 Parameters of the Precipitation Process of Kaolin Suspension ($C = 30\,kg \cdot m^{-3}$) for various flocculants

Flocculant	$C \cdot 10^3$, $kg \cdot m^{-3}$	V^a_{rel}	τ_0, s[b]	V, cm^3 [c]	D[d]
	0.1	2.3	53	48	1.21
	0.5	3.3	33	41	0.90
PAA	1.0	3.9	22	35	0.20
	5.0	5.2	7	24	0.03
	10.0	12.7	5	18	0.03
	0.1	3.1	11	38	0.13
	0.5	2.9	6	27	0.15
TBC2	1.0	3.7	3	23	0.09
	5.0	5.3	1	20	0.05
	10.0	9.5	3	15.5	0.041
	0.1	3.4	7	25	0.16
	0.5	3.7	2	22	0.16
TBC4	1.0	4.3	3	20	0.10
	5.0	9.1	1	15	0.02
	10.0	9.2	1	13	0
	0.1	2.7	6	28	0.19
	0.5	3.1	5	25.5	0.16
TBC5	1.0	3.6	3	23	0.21
	5.0	6.9	1	15	0.03
	10.0	14.8	1	13	0.03

[a]The relative velocity of the fast stage of precipitation.

[b]Induction period.

[c]The volume of precipitate formed in 1 min counted from the beginning of a precipitation process.

[d]The optical density of supernatant after a 20 min from the beginning of a precipitation process ($\lambda = 540$ nm).

TABLE 4 Quality of the Natural Water from Desna River Cleaned with Various Flocculants

Flocculant	Doses[a] $\cdot 10^3$ kg $\cdot$ m^{-3}			Turbidity, $\cdot 10^3$ kg $\cdot$ m^{-3}	Chromaticity, $^\circ$ Cr-Co scale	Oxidizability, $\cdot 10^3$ kg $\cdot$ m^{-3}	Residual Al, $\cdot 10^3$ kg $\cdot$ m^{-3}
	NH_3	$Al_2(SO_4)_3$	Flocculant				
–	0.1	–	–	6.9	28	5.6	0.06
	0.1	50	–	3.4	13	4.9	1.3
TBC2	0.1	50	0.05	3.8	14	5.4	2.9
TBC3	0.1	50	0.05	3.7	13	5.3	2.7
TBC5	0.1	50	0.05	3.8	13	5.3	2.6
TBC6	0.1	50	0.05	4.2	14	5.4	2.8
PAA	0.1	50	0.05	4.2	14	5.4	2.6
DB 45 SSH	0.1	50	0.05	4.5	13	5.6	2.7

[a]Dose of chlorine $1.5 \cdot 10^{-3}$ kg $\cdot$ m^{-3}

PAA are connected the smallest particles of suspension, as the optical density of supernatant (parameter D) is reduced compare with PAA. It is very important point as the real dispersions are characterized by the wide distribution on the particle sizes of a disperse phase.

The best parameters of flocculation process and degree of water clarification are observed for TBC4 sample with $M_{vPEO} = 1.5 \cdot 10^4$. The TBC4 sample at $C < 57 \cdot 10^{-3}$ kg $\cdot$ m^{-3} keeps the leadership on all parameters of clarification of modeling suspension. These data characterize this central block length of PEO in TBC as optimum, which determines the maximal flocculate ability of the given TBC. Thus, in model tests, all TBC samples worked better than individual PAA.

The following comparative test was carried out for cleaning of Desna river water at waterwork of Ukraine. The results of the quality analysis of cleaned water at optimum coagulant concentration are shown in Table 4.

In the process of water treatment on waterwork all TBC samples demonstrated the good parameters characterizing the flocculation process and quality of clarified water in comparison with the individual PAA and well-known commercial French flocculant DB 45 SSH. However the best results among the investigated samples has shown TBC3 with $M_{vPEO} = 6 \cdot 10^3$. Thus, the optimal PEO block length $M_{vPEO} = 6 \cdot 10^3$–$4 \cdot 10^4$, which provides the best parameters of the clarified water, is established. All TBC samples show the efficiency of water clarification in the region of the small concentration ($0.05 \cdot 10^{-3} - 0.1 \cdot 10^{-3}$ kg $\cdot$ m^{-3}) that is very valuable from the point of view of their practical using.

CONCLUSION

New high-effective flocculants containing triblock copolymers based on chemically-complementary PAA and PEO were obtained by free radical block copolymerization of AA with PEG of different molecular weight. The block copolymerization process has a matrix character that is caused by the interaction of polymer blocks. Thus, given tri block copolymers are the products of the matrix block copolymerization and form IntraPCs. IntraPCs contain hydrophobic areas by the means of hydrophobic interactions between non-polar bound parts of the copolymer blocks, which capable to connecting the colloidal and biological particles, organic substances from clay suspensions and natural water.

Flocculative ability of the TBC samples in comparison with individual PAA and known French flocculant DB 45 SSH on the model kaolin

suspension and during of the drinking water preparation on waterwork in dependence of PEO block length is characterised. Basing on these investigations the high efficient flocculants containing TBC with PEO and PAA for water treatment on waterworks have been created.

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