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DESIGN OF POLYMERS OF BLOCK, COMB-LIKE AND HIGHLY BRANCHED STRUCTURES WITH PEROXIDE-CONTAINING CHAINS

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Abstract. The tailored synthesis of telechelic oligoperoxides (TO), oligoperoxide metal complexes (OMC) as well as the development of controlled radical polymerization in aqueous and hydrocarbon media initiated by them provides prospective approaches for the obtaining block, comb-like and branched polymers with the backbone and branches of various nature, polarity, length and reactivity. The polymer-precursors and final products were investigated by chemical, spectral and rheological techniques. The novel peroxide-containing copolymers were studied in the reactions of in radical polymerization heterogeneous and homogeneous media.

Key words: peroxide telogen, coordinating oligoperoxide metal complexes, controlled radical polymerization, block copolymer, comb-like copolymer, branched polymers.

1. Introduction

Until now the technique of radical polymerization for obtaining highly branched functional macromolecules is not prevailing in comparison with the methods of polycondensation and polymer analogous transformations [1-3]. This is caused firstly by the indeterminacy of structure and chain length peculiar to polymers derivable by radical polymerization techniques. Since the synthesis of telechelic oligoperoxides (TO) and oligoperoxide metal complexes (OMC) with side peroxide fragments allows controlling radical polymerization initiated by them [4, 5] it provides the realistic and very promising approach for the obtaining block, comb-like and branched polymers with the backbone and branches of predictable chain structure, length, polarity, and reactivity. The development of the tailored synthesis of new surface-active reactive block, graft and branched copolymers with peroxide-containing chains is the aim of the work.

2. Experimental

Monomers: Vinyl acetate (VA), acrylic acid (AA), styrene (St), butyl acrylate (BA), N-vinyl pyrrolidone (N-VP), 2-*tert*-butyl peroxy-5-methyl-1-hexene-3-yne (VEP) were purified using vacuum distillation; glycidyl methacrylate (GMA), Merck was used as obtained; maleic anhydride (MAN) was purified using sublimation technique.

Telogens: 1-(1-*tert*-butylperoxy-1-methylethyl)-4-isopropylbenzene (MP) was purified by vacuum distillation; 2-Isopropyl-6-(1-hydroperoxy-1-methylethyl)naphthalene (MHP) was purified by recrystallization from hexane ($O_{act} = 6.30\%$, purity - 96%) [6].

Initiators: Oligoperoxide metal complexes (OMC) were obtained by complexation reactions of VA-VEP-MAN, VA-VEP-BA-MAN with copper chloride in methanol solution under room temperature and mild stirring (polymer: $CuCl_2$ weight ratio is 1: 1) then precipitated with distilled water, filtered and dried under vacuum; 2,2'-Azobis(2methylpropionitrile) (AIBN), Merck was used as obtained.

Solvents: Ethyl acetate, dioxane, toluene, methanol, benzene were analytical grade and used without additional purification.

Sample preparation

Synthesis

All polymerization reactions were performed in glass dilatometers under argon to control reaction kinetics and product yield. Synthesis conditions are given in discussion. Obtained samples were twice reprecipitated from organic solvents and dried under vacuum. Vinyl alcohol fragments in polymer molecules were obtained by alkaline hydrolysis of VA links in methanol solution.

Sample characterization

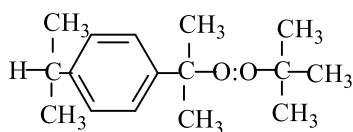
Content of peroxide-containing links. Contents of VEP and MP links were calculated from the amount of products of decomposition of peroxide groups detected on Selmi Chrom-1 gas-liquid chromatograph according to [7]. Content of MHP links was determined using iodometric technique.

Surface tension of water-ammonia solutions of polymers was measured with PPNL-1 device by the technique of excessive pressure in the vesicle.

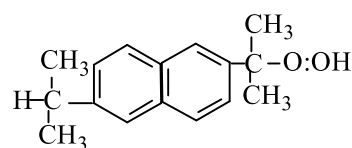
Rheology Intrinsic viscosity [3] of polymer solutions was measured with Bishoff viscosimeter, in acetone, at 298K. In case of homopolymers viscosity-average molecular weights were calculated using equation: $[\eta] = KM^\alpha$ and referred [8] K and α values.

UV-visible spectrometry was performed with SPECORD-40 (Germany).

^1H NMR spectra were recorded on 300 MHz Bruker device.



1-(1-tertbutylperoxy-1-methylethyl)-4-isopropylbenzene (MP)



2-Isopropyl-6-(1-hydroperoxy-1-methylethyl)naphthalene (MHP)

Earlier [9] we have shown that only one terminal peroxide fragment of MP or MHP is included in the polymer structure providing the availability of active radical-forming site in the molecule of polymer-precursor.

Table 1

The synthesis and characterization of polymers with terminal peroxide fragments
($[\text{AIBN}] = 10 \cdot 10^{-3}$ mole/l, 333K)

Copolymerization				W, %/h	S, %	Polymer			
Monomers	T	[T], %	Solvent			Content T in polymer, %	M_n , g/mole $\times 10^3$	f_n	
VA	MP	5	In block	5.420	68	0,16	18,0	0,13	
VA	MP	20		1.320	62	3,25	8,00	1,17	
VA	MP	30		0.390	59	3,80	6,80	1,16	
VA	MA	MP	25	Ethyl acetate	1.680	65	0,45	5,00	0,10
VA	MA	MP	33		0.480	65	4,00	4,00	0,72
VA	BA	MP	33		0.600	65	4,90	4,20	0,93
VA	MHP	7,5	In block	0.006	68	1,20	11,80	0,64	
VA	MHP	10		0.006	65	1,70	11,70	0,90	
AA	MHP	2,5	Dioxane	3.000	75	1,20	12,00	0,65	
AA	MHP	5		2.700	72	1,70	12,00	0,92	
VA	BA	MHP	5	Toluene	0.300	65	1,20	4,50	0,63

The characteristics of the kinetics of polymerization (Table 1) show that polymerization in the presence of peroxide-containing chain transfer agents occurs with feasible rate and yield and provides the obtaining telechelic oligomers. It is evident that the rate of polymerization, TO chain length and peroxide functionality are determined by the telogen nature and amount in initial reaction system as well as by the reaction conditions. One can see from the experimental data (Table 1) that MP and MHP are effective chain transfer agents possessing weakly inhibitory action, which cause the

decrease of the polymerization rate values and lowering TO molecular weight at increase of telogen concentration. Moreover, the kinetic characteristics of the polymerization, molecular weight and functionality of peroxide-containing oligomers depend on the nature and composition of monomer system.

The presence of the common absorption bands in UV-spectra of peroxide-containing telogens and oligomers with end MP or MHP fragments (Fig. 1, Fig. 2) confirms the entering active telogen residua into TO structure.

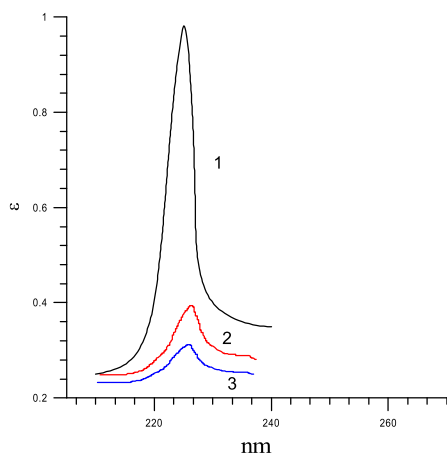


Fig. 1. Electronic spectra 1 - MP, 2 – poly VA-MP; 3 - poly VA-BA-MP

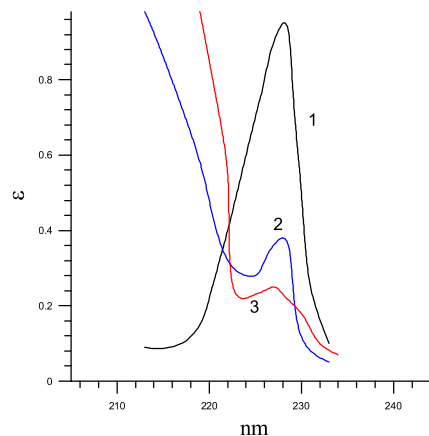


Fig. 2. Electronic spectra 1 - MHP, 2 - poly AA-MHP; 3 – poly VA-BA-MHP

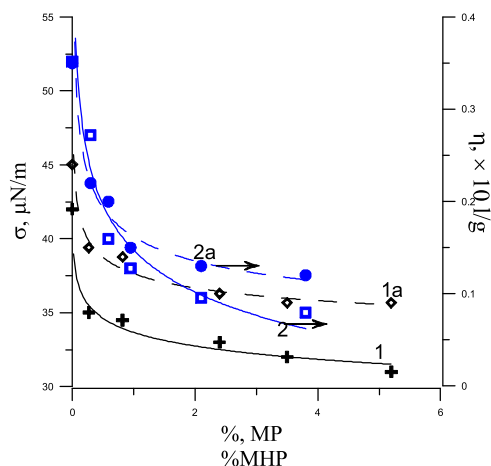


Fig. 3. Surface tension at cmc (1, 1a) and intrinsic viscosity (2, 2a) of polymers VA-MA – MP (1, 2) and AA-MHP vs. MP or MHP content

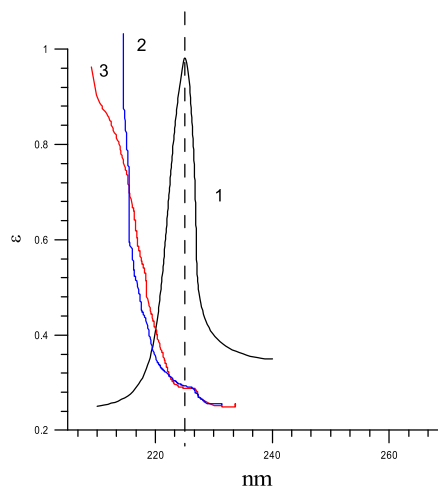


Fig. 4. Electronic spectra of block-copolymers: 1 - MP, 2 – polyvinyl alcohol - St ($M_n = 10000$ g/mole); 3 – polyvinyl alcohol - BA ($M_n = 8200$ g/mole)

The entering hydrophobic terminal residuum in oligomer molecule leads as well to enhancement of TO surface activity (Fig. 3). The TO molecules form micelle-like structures in water solutions and can solubilize water insoluble liquids. The surface activity measured at CMC witnesses the changing TO hydrophilic-hydrophobic balance as a result of entering MP or MHP fragment.

The availability of terminal peroxide-containing group in TO molecule and its controlled solubility and surface activity provide the possibility of obtaining various block-copolymers by the techniques of solution or water dispersion polymerization initiated by TO.

It is clear from the Table 2 representing the characteristics of the synthesis and properties of obtained block-copolymers that TO are active initiators of solution polymerization of various monomer systems. The initial polymer – initiators and resulting block-copolymers are of a different solubility and can be separated by dilution and precipitation in distinct solvents. The obtained block-copolymers can be composed of blocks of different polarity containing various functional fragments including peroxide groups. The variation of the synthesis conditions, nature and concentration of both initial TO-initiator and monomer mixture provides the controlling block-copolymer chain length, hydrophily and reactivity.

Table 2

The synthesis of block-copolymers and their characterization (358K, benzene, monomer:solvent 1:3)

Block-copolymerization					Block-copolymer characteristics			
Precursor	% per monomers	Monomer mixture	W, %/h	S, %	$[\eta]$, 298K, acetone $\times 10$ l/g	VEP link content, %	σ , mN/m (10% solution)	Cmc, %
VA-MP 95.5:4.5%	5.0	VA-VEP-N-VP 55:15:30	13.8	85	0.25	18	38.5	2.2
		VA-VEP-N-VP 20:35:45	4.8	75	0.15	42	32.0	1.5
	10.0	VA-VEP-N-VP 55:15:30	16.2	92	0.22	19	37.9	2.2
		VA-VEP-N-VP 20:35:45	7.8	85	0.13	40	32.2	1.7
VA-MA-MP 46:50:4.0	5.0	BA-VEP-GMA 30:55:15	21.0	98	0.10	63	-	
VA-BA-MP 25.1:70:4.9	5.0	BA-VEP-AA 35:40:25	25.4	98	0.10	50	33.5	3.0
AA-MHP 98.3:1.7	5	St	63.0	95	0.12	-	-	-
AA-MHP 98.3:1.7	10	St	144.0	98	0.10	-	-	-

The structures of block-copolymers obtained by such technique are proved by both the chemical, UV-spectral and NMR-spectral methods (Table 2, Fig. 4, 5).

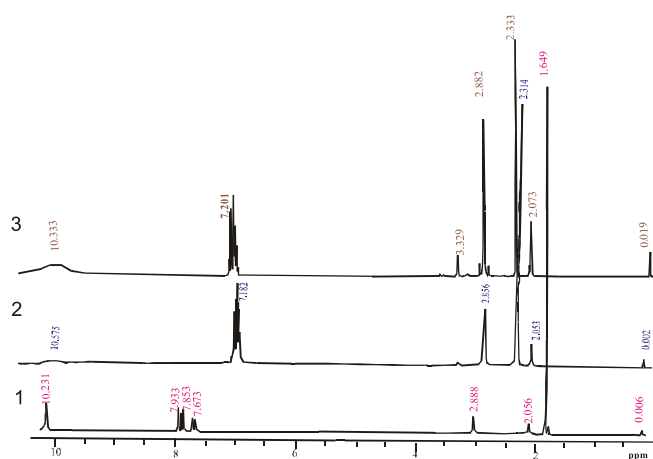
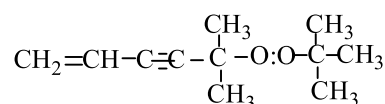


Fig. 5. NMR-spectra of initial telogen MPH, (1), TO AA-MPH (2) and poly AA – block – poly St copolymer (3)

3.2. The synthesis of macroinitiators-precursors for graft copolymerization

Macroinitiators – precursors for graft copolymerization were synthesized by copolymerization of VA with BA, MAN or AA and unsaturated peroxide of a structure:



VEP

as monomer and chain transfer agent simultaneously in hydrocarbon media and derived metal complexes on their basis as referred [10]. Earlier we have shown [5] that oligoperoxide metal complexes (OMC) are low temperature macroinitiators of radical polymerization in hydrocarbon and water dispersion media providing controlled obtaining graft copolymers of various backbone and side functional chains including groups of peroxide functionality. Some characteristics of OMC-precursors are presented in the Table 3.

Table 3

Characterization of OMC - precursors of graft- (co) polymerization

OMC, links %					[Cu ²⁺] in OMC, %	[η] (Acetone, 298 K) ×10 l/g	\bar{M}_n , g/mole	σ, 10% solution at pH=9, mN/m
VA	Vinyl alcohol	VEP	BA	MAN				
18.4	-	50.6	-	31.0	0.85	0.08	1600	33.0
22.5	-	56.7	-	20.8	0.93	-	12000	35.0
1.7	46.3	26.2	-	25.8	0.95	0.09	1800	35.0
1.6	56.1	17.8	24.5		0.35		1000	-
23.2	-	26.8	14.2	35.8	1.06	0.28	5200	30.0
10.6	-	15.8	60.1	13.5	1.25	-	14300	

It is evident from the Table 4 representing comb-like copolymer characteristics that they contain various functional groups including active ditertiary peroxide ones. One can see that obtained copolymers can be of controlled surface activity, solubility and reactivity, especially in the secondary processes of radical polymerization (Fig. 4). It is evident that grafting hydrophobic polystyrene chains to molecules of OMC-initiator leads to the enhancement of the product surface activity in water-alkaline medium, thereby

they can be used as radical-forming surfactants for the synthesis of branched polymers and colloidal particles with pre-definite shell functionality and reactivity.

The coincidence of the characteristic absorption bands peculiar to Cu²⁺ – containing fragments in the molecules of OMC and derived comb-like copolymer testifies the structural entering the OMC residual fragments into the molecule of graft-copolymer obtained as a result of polymerization initiated by OMC-precursor (Fig. 6).

Table 4

The synthesis and characterization of comb-like copolymers (358K, benzene, monomer: solvent=1:3)

(Co) polymerization					Comb-like copolymer characteristics			
Precursor-initiator	OMC, % per monomers	Monomer mixture, %	W, %/h	S, %	[η], (298K, acetone), ×10 l/g	Content of VEP links, %	σ, mN/m (10%)	Cmc, %
OMC VA-VEP-MA 20:48:32 % Cu ²⁺ =0.85%	2.5	AA-BA-VEP 90.0:5.0:5.0	0.30	60	0.095	8.0	35.0	5.0
		AA-N-VP-VEP 75.0:20.0:5.0	0.48	62	0.010	7.5	39.0	6.2
	5.0	AA-BA-VEP 90.0:5.0:5.0	0.60	65	0.090	8.6	37.0	5.2
		AA-N-VP-VEP 75.0:20.0:5.0	1.2	67	0.089	9.2	38.0	6.0

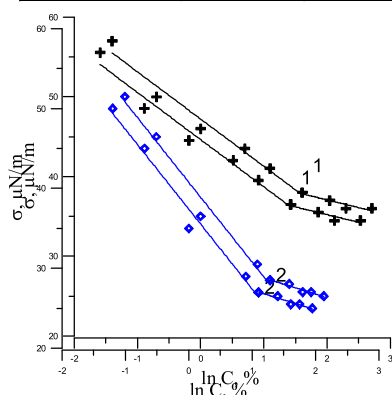


Fig. 6. Surface tension isotherms of OMC-precursor (1) and comb-like OMC-graft-poly St (2) on its basis in water-ammonium solution

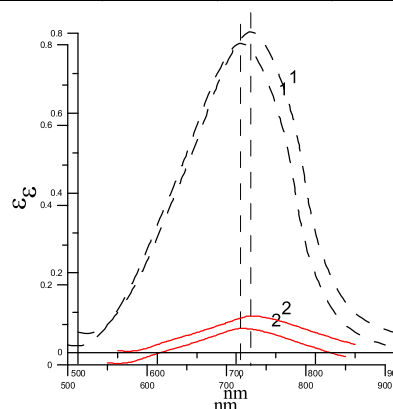


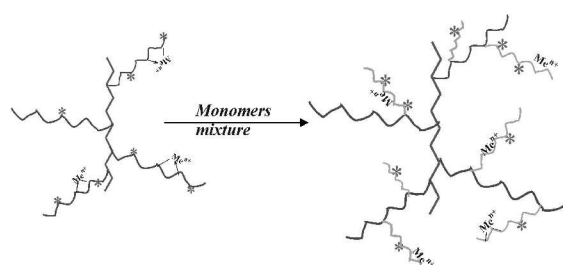
Fig. 7. UV - visible spectra of OMC (1) and OMC-graft-poly St (2) on its basis

3.3. Macroinitiators - precursors for obtaining branched copolymers

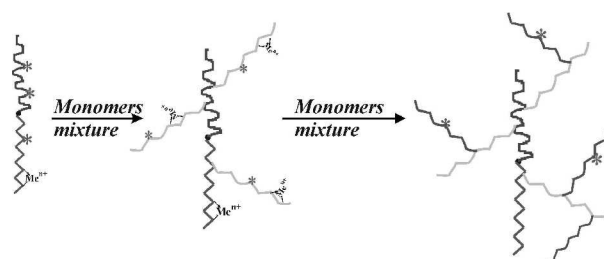
As it is clear from the scheme presented below block- and comb-like copolymers containing radical-forming ditertiary peroxide fragments in the chains are prospective macroinitiators-precursors providing obtaining branched polymers. They initiate radical polymerization in organic solutions in a wide temperature range causing the formation of branched copolymers with new branches of tailored length, functionality and reactivity (Table 5, Fig. 8, 9).

The rheological characteristics of polymer products obtained at polymerization initiated by metal complexes

on the basis of peroxide-containing macroinitiators of different degree of branching witness the formation in solution of new compact polymer structures peculiar to branched copolymers (Table 5). The changing structure and properties of obtained branched copolymers as a result of the multi-grade branching is justified as well by the appearance of the tailored adsorb ability. The combination of hydrophobic and hydrophilic peroxide-containing branches of different length in highly branched copolymers provides, their possibility to significant water absorption (Fig. 9). It is evident from the Fig. 9 that water absorption power of copolymers increases with the enhancement of the number of branched copolymer generations.



Precursor - graft-copolymer



Precursor - block-copolymer

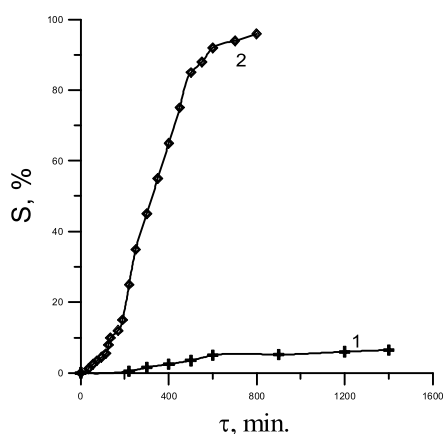


Fig. 8. St conversion vs. time polymerization initiated by comb-like copolymer OMC (VA-VEP-MA)-graft- poly (BA-VEP-AA) (1) and OMC on its basis (2) (323K, benzene, $[I] = 10\%$, St: benzene 1:3)

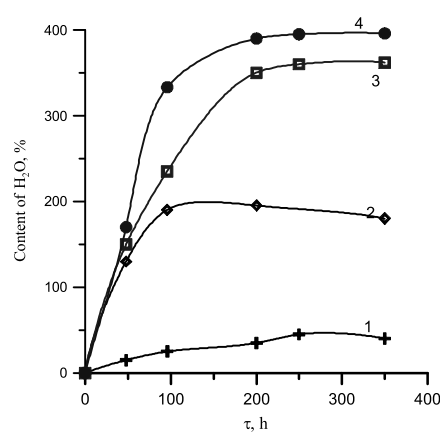
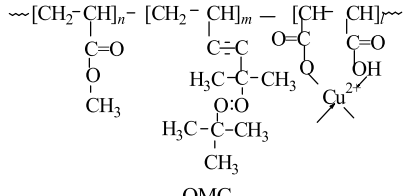
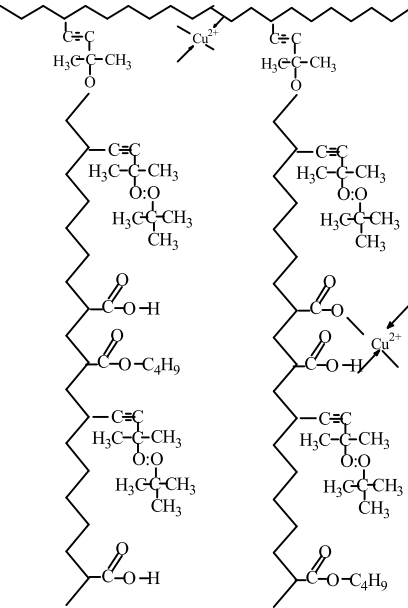
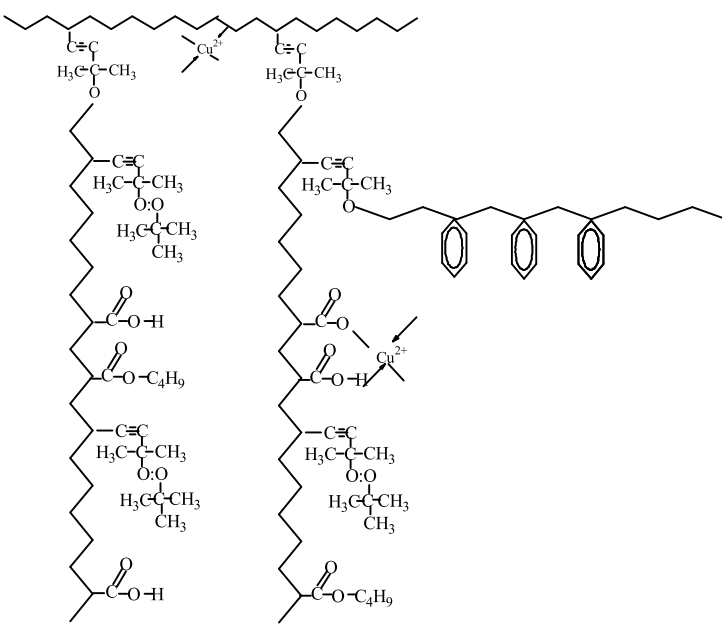


Fig. 9. Content of H₂O absorbed in composite on the basis of isoprene rubber filled with the copolymers (1:1 weight): 1 – poly (VALc-VEP-MA=20:47:33), 2 – poly (VALc-VEP-MA) - graft-poly (BA-VEP-AA=15:15:70); 3 – poly (VALc-VEP-MA) - graft-poly (BA-VEP-AA)- graft-poly (BA-AA=10:90); 4 – poly (VALc-VEP-MA) - graft-poly (BA-VEP-AA)- graft-poly (BA-AA=20:80) vs. time

Table 5

Rheological characteristics ($[\eta]$, l/g) of OMC, copolymer OMC –graft-P1 and derived copolymer OMC –graft-P1-graft – P2

	$[\eta]$, (298K, acetone), $\times 10$ l/g
 <p style="text-align: center;">OMC</p>	0.082
 <p style="text-align: center;">Poly (VA-VEP-MA)-graft-poly (BA-VEP-AA)</p>	0.090
 <p style="text-align: center;">Poly (VA-VEP-MA)-graft-poly (BA-VEP-AA)-graft-poly St</p>	0.062

4. Conclusions

The principal possibility of using the peroxide monomer or telogen as well as surface-active oligoperoxides on their basis for tailored design of reactive macromolecules of block, comb-like and branched structures with peroxide-containing chains of various nature, hydrophilily and reactivity was shown.

The kinetic study of new copolymer properties displayed that they are surface-active substances with controlled solubility, rheological characteristics, surface activity, and capability to radical forming in a wide temperature range.

The developed novel functional polymers are of a great interest for biomedical application and proposed synthesis techniques is accessible for their obtaining and controlled design.

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СИНТЕЗ ПЕРОКСИДВМІСНИХ ПОЛІМЕРІВ БЛОК-, ГРЕБЕНЕ- ПОДІБНОЇ ТА РОЗГАЛУЖЕНОЇ СТРУКТУР

Анотація. Цілеспрямований синтез телехелатних олігопероксидів (ТО), функціональних олігопероксидних металокомплексів (ОМК) та дослідження контрольованої радикальної полімеризації у водному і органічному середовищах за їх участю обумовлює перспективні підходи для одержання блок-, гребенеподібних і розгалужених полімерів з основним та боковими ланцюгами різної природи, полярності, довжини і реакційної здатності. Вихідні та кінцеві продукти були досліджені хімічними, спектральними та реологічними методами. Нові кополімери, що містять пероксидні групи, досліджували в реакціях радикальної полімеризації в гомогенному та гетерогенному середовищах.

Ключові слова: пероксидний телоген, координаційний олігопероксидний металокомплекс, контрольована радикальна полімеризація, блок-кополімер, гребене-подібний кополімер, розгалужені кополімери.