CHEMISTRY & CHEMICAL TECHNOLOGY

Chem. Chem. Technol., 2022,
Vol. 16, No. 1, pp. 34–41

Chemistry

TELECHELIC OLIGO(*N*-VINYLPYROLYDONE)S WITH CUMENE BASED TERMINAL GROUPS FOR BLOCK-COPOLYMER AND NANOPARTICLE OBTAINING

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https://doi.org/10.23939/chcht16.01.034

Abstract. Polymers with terminal epoxy, phosphate, fluoroalkyl groups were obtained by radical polymerization in the presence of chain transfer agents derived from isopropylbenzene. The structure of polymers was confirmed by NMR spectra and functional analysis. Polymers with functional fragment were used for synthesis of polymer-inorganic particles and copolymers with poly(2-ethyl-2-oxazoline) fragment.

Keywords: telomerization, control of kinetic and material chains, telechelic oligomers, block copolymers, nanoparticles.

1. Introduction

The creation of new functional polymers with predetermined architecture, molecular weight and structural characteristics for intended use in chemistry, biotechnology and medicine still remains an important priority for many laboratories around the world. Telechelic polymers with terminal reactive functional groups have become particularly important due to the wide range of further applications. Such polymers are used as crosslinking agents[1] and precursors to obtain linear, comb-like and star-shaped macromolecules.[2] Polymers with terminal functional groups are also used to obtain thermoplastic elastomers, surface-active emulsifiers and stabilizers of aqueous or organic dispersions, synthesis of functional macromers for surface modification.[3]

Such polymers are obtained by controlled polycondensation methods, polymeranological reactions or radical polymerization in the presence of functional chain transfer agents (telogens).[4] The main advantages of radical polymerization method are high rate, simplicity and a wide selection of functional monomers that are capable of polymerization. Polymers of complex architecture can be obtained by using the methods of controlled radical polymerization, which allow to obtain macromolecules with the required molecular weight and functionality,[5] namely: atom transfer radical polymerization (ATRP), nitroxide-mediated radical polymerization (NMRP), reversible addition-fragmentation chain transfer polymerization (RAFT). However, these methods have several significant disadvantages. The final product is contaminated with salts, which complicate the purification of the polymer. In addition, some monomers, such as unsaturated acids, cannot be used to obtain polymers and copolymers by such methods.

Telechelic oligomers with terminal functional groups can also be obtained using radical initiators or chain transfer agents with functional fragments.[6]

Wang *et al.*[7] provide an overview of methods for obtaining polymers with terminal functional OH-group *via* different methods (ionic polymerization of epoxides, synthesis based on tetrahydrofurane, synthesis with radical initiators of peroxy or azodinitrile types). The synthesis of heterotelechelic oligomers with terminal hydroxyl and carboxy groups *via* polymer-analogous transformations is shown in several works.[8-12] Polymers with biologically active fragments can also be obtained by this method.[13]

The use of chain transfer agents is a convenient and effective method of control the lengths of kinetic and material chains, *i.e.*, the rate and yield of polymerization and molecular weight distribution of macromolecules, and determines the entry into their structure of terminal functional fragments. The important advantage of using isopropylbenzene (IPB) derivatives as chain transfer agents is the high reactivity of the hydrogen atom in the isopropyl group. The activation energy is 26.5–29.5 kJ/mol for the separation of hydrogen from $Ph(CH_3)_2C–H$.[7] However, the participation of functional derivatives of IPB as chain transmitters isn't limited to the control of kinetic parameters of polymerization and

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molecular weight characteristics of the formed polymers. The presence of terminal functional fragments in the structure of oligomers provides opportunities for polymer analogous transformations by different mechanisms. Publications describing studies of telechelic oligomers with terminal functional fragments of IPB as reagents for the controlled synthesis of copolymers are absent.

We have previously shown[14] that the presence of terminal peroxide fragment in oligomer ensures its use as an oligomeric initiator for synthesis of block copolymers. The use of heterotelechelic oligomers as macroinitiators of polymerization, which contain other functional fragments in addition to the terminal peroxide group, allows to obtain new polymers with fragments of saccharides, polyethylene glycols, alcohols and lipid-like substances.[15]

Target synthesis of oligomers and copolymers with terminal functional fragments (amine, epoxy and others) and strictly defined block or comb architecture using IPB derivatives as chain transfer agents expands the range of polymeric materials and the ability to control their colloid-chemical and biological properties.[16]

The paper considers the synthesis, structural characteristics and colloid-chemical properties of surface-active telechelic polymers obtained by a radical polymerization of N-vinylpyrrolidone using of new IPB derivatives as chain transfer agents and shows the possibilities of molecular construction of functional macromolecules and nanoparticles.

2. Experimental

4-Isopropylbenzyl alcohol, epichlorohydrin, benzyltriethylammonium chloride (BTEAC), thionyl chloride, triethylamine, phosphorus oxychloride, potassium phthalimide, hydrazine hydrate, boron trifluoride etherate, *p*-toluenesulfonyl chloride, methyl *p*-toluenesulfonate (MeOTs) (Sigma-Aldrich) were used without purification. Fluoroalkyl alcohol (F-Alk): 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptan-1-ol was synthesized at the Institute of Organic Chemistry of the National Academy of Sciences of Ukraine and was used without purification. *N*-vinylpyrrolidone (NVP) (Merck) was purified by vacuum distillation. 2-Ethyl-2-oxazoline (Et-Ox) (Sigma-Aldrich) was dried for 48 h over KOH before use. 2,2′-Azobis(2-methylpropionitrile) (AIBN) (Merck) was purified by recrystallization.[17]

2-{[(4-Isopropylbenzyl)oxy]methyl}oxirane (CGE). 8.0 g (0.2 mol) of sodium hydroxide were added by portions to the solution of 15.0 g (0.1 mol) cumin alcohol and 0.1 g BTEAC in 46.0 g (0.5 mol) of epichlorohydrin at a temperature of 333–343 K. The reaction mixture was stirred for 6 h and cooled. Then 50 mL of dichloromethane was added and mixture was filtered. The resulting precipitate was distilled under vacuum. Reaction yield is 16.5 g (80 %); d_4^{20} 0.9623 g/cm^3; n_D^{20} 1.5140; MR$_\mathrm{D}$ 74.18; T_B 375-378 K/10 Pa. Found, %: C 75.32, H 8.61. $C_{13}H_{18}O_2$. Calcd. %: C 75.69; H 8.80. ^{1}H NMR (300 MHz, DMSO-d6) δ,(ppm): 7.22 (dd, J = 7.8 Hz, 4H, Ar-**H**); 4.45 (s, 2H, O-C$\mathbf{H_2}$-Ph); 3.70 (dd, J = 2.5 Hz, 1H, CH_2O glycidyl); 3.25 (dd, J = = 11.4, 6.4 Hz, 1H, CH_2-O glycidyl); 3.11 (dt, J = 6.4, 3.2 Hz, 1H, C**H** oxirane ring, rac. mixture); 2.85 (m, J = = 6.9 Hz, 1H, Ph-C**H**$(CH_3)_2$); 2.70 (t, J = 4.6 Hz, 1H, C$\mathbf{H}_2$ oxirane ring); 2.53 (dd, J = 5.0, 2.6 Hz, 2H 1H, C$\mathbf{H_2}$ oxirane ring); 1.17 (d, J = 6.9 Hz, 6H, Ph-C(C$\mathbf{H}_3)_2$).

4-Isopropylbenzyl dihydrogen phosphate (cumin phosphate, CF). Solutions of 1 g (0.007 mol) of cumin alcohol and 0.7 g (0.007 mol) of triethylamine in 3 mL dioxane were added dropwise to a solution of 5.4 g (0.035 mol) $POCl_3$ in 10 mL of dioxane (T = 273–278 K). The temperature of the reaction mixture was raised to room temperature after 3 h under stirring, and the mixture was stirred for an additional 1 h. The precipitate triethylammonium chloride was filtered off; an excess of $POCl_3$ and dioxane were distilled off under vacuum. The resulting residue was dissolved in 5 mL of dioxane, cooled to 273 K, and 2 mL of water was added under stirring for 4 h. The solvent and water were distilled off under vacuum. Reaction yield is 1.2 g (72 %); d_4^{20} 1.269 g/cm^3; n_D^{20} 1.5140; MR$_\mathrm{D}$ 57.18. Found, %: C 52.32; H 6.61. $C_{10}H_{15}O_4P$. Calcd. %: C 52.18; H 6.57). ^{1}H NMR (300 MHz, DMSO-d6), δ (ppm): 7.18 (dd, J = 8.2 Hz, 4H, Ar-**H**); 4.55 (s, 2H,-O-C$\mathbf{H_2}$-Ph); 2.24 (m, J = 7.2 Hz, 1H, Ph-C**H**$(CH_3)_2$); 1.16 (d, J = 7.2 Hz, 6H, Ph-CH(C$\mathbf{H}_3)_2$).

1-[(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptoxy)methyl]-4-isopropylbenzene (***FCE***) was synthesized through the step of obtaining intermediate dodecafluoroheptyltosylate.

A. The solution of 1.5 g (0.0044 mol) of dodecafluoroheptanol and 0.5 g (0.005 mol) of triethylamine in 10 mL of dichloromethane was added to the solution of 0.95 g (0.0044 mol) of *p*-toluenesulfochloride in 5 mL of CH_2Cl_2 under stirring (T = 273–278 K). The reaction mixture was stirred at room temperature overnight and then washed with water. The solvent was distilled off and dried under vacuum. Reaction yield is 2 g (90 %).

B. The solution of 0.85 g (0.0018 mol) of fluoroalkyl tosylate in 5 mL of THF was added to the solution of 0.3 g (0.0018 mol) of sodium 4-isopropylbenzylate in 10 mL of THF, obtained by boiling benzyl alcohol with metallic sodium for 10 h. The reaction mixture was stirred for 6 days at room temperature and 10 h at 308–313 K until tosylate was completely consumed (controlled by TLC), then cooled to room temperature and filtered. The solvent was distilled off; the resulting residue was dried under vacuum. Reaction yield is 60 %. Found, %: C 43.11; H 3.61. $C_{17}H_{16}F_{12}O$. Calcd.

%: C 43.98; H 3.47. ^{1}H NMR (300 MHz, DMSO-d6), δ (ppm): 7.67 (dd, J = 8.3 Hz, 4H, Ar-**H**), 7,18 (tt, J = 51.9, 6.6 Hz, 1H, CF$_2$**H**), 4.93 (t, J = 13.6 Hz, 2H, CF$_2$C**H**$_2$O); 4.82 (s, 2H,-O-C**H**$_2$-Ph), 2.82 (m, J = 7.2 Hz, 1H, Ph-C**H**(CH$_3$)$_2$); 1.17 (d, J = 7.1 Hz, 6H, Ph-CH(C**H**$_3$)$_2$).

Polymers with terminal functional group were synthesized by a radical polymerization of *N*-vinylpyrrolidone (1 mol/L) in propanol-2 in the presence of various chain transfer agents (0.1–0.5 mol/L). AIBN (0.1 mol/L) was used as an initiator. Polymerization was carried out in calibrated dilatometers with the volume of 15 mL with a graduation value of 0.05 mL at the temperature of 338±0.1 K. Additionally, gravimetric studies of the polymer yield were carried out after the end of the process. The polymers were purified by reprecipitation with hexane from acetone. The resulting polymer was dried under vacuum to constant weight.

Synthesis of block copolymers with the fragment of 2-ethyl-2-oxazoline (NKEO). The solution of 0.1 mL of $BF_3 \cdot OEt_2$ in 2 mL of anhydrous CH_2Cl_2 was added to the solution of 0.46 g ($1.5 \cdot 10^{-4}$ mol) of poly(2-ethyl-2-oxazoline) (Et-Ox, Mn = 3.1 kDa) and $1.5 \cdot 10^{-4}$ mol of polymer with the terminal epoxy group in 20 mL of anhydrous CH_2Cl (T = 313 K). The reaction mixture was stirred at the same temperature for 15 h. The precipitate was dried at the pressure of 0.2 kPa at the temperature of 313 K until constant weight.

IR spectra were recorded on a Specord-M80 instrument. NMR spectra were studied in deuterated solvents on a BrukerAvance DPX 300 spectrometer with an operating frequency of 300 MHz. Surface tension was measured on a PPNL-1 device. The hydrodynamic dimensions of micellar structures in an aqueous solution were measured on a DynaPro NanoStar instrument (Wyatt Technology, USA).

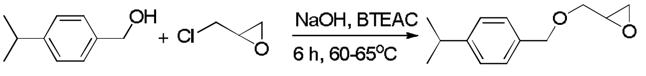
The kinetic parameters of polymerization were determined according to known methods.[18] The content of functional fragments in polymers was determined according to the methods described by Bahdasarian.[18] The molecular weight of the polymers was determined by a gel permeation chromatography using a Waters GPC/HPLC liquid chromatograph. The molecular weights of the polymers were determined using methods for measuring viscosity.[19] The phase composition of inorganic particles was investigated on a DRON-3 X-ray diffractometer.[20]

3. Results and Discussion

3.1. Synthesis of Telechelic Polymers with Terminal Functional Fragments

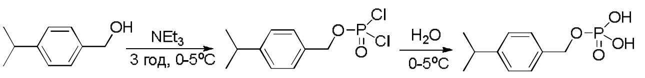
As mentioned above, IPB derivatives are effective chain transfer agents in polymerization processes. Derivatives based on cumin alcohol with epoxy, phosphate and fluoroalkyl groups were synthesized in order to obtain telechelic oligomers.

Cumin glycidyl ether (CGE) was obtained by alkylation of cumin alcohol by epichlorohydrin using powdered sodium hydroxide as a hydrogen chloride acceptor (molar ratio of reagents 1:5:3) in the presence BTEAC as a catalyst for the interphase transfer.



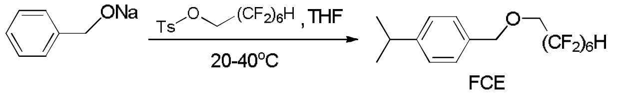
CGE

Cumin phosphate (CF) was synthesized by the reaction of cumin alcohol with phosphorus oxychloride in the presence of triethylamine, followed by hydrolysis of the intermediate acid chloride.



CF

Fluoroalkyl ether of cumin alcohol (FCE) was obtained by reacting sodium (4-isopropylphenyl) methanolate with dodecafluoroheptyl tosylate obtained from dodecafluoroheptan-1-ol with toluenesulfochloride under heating.



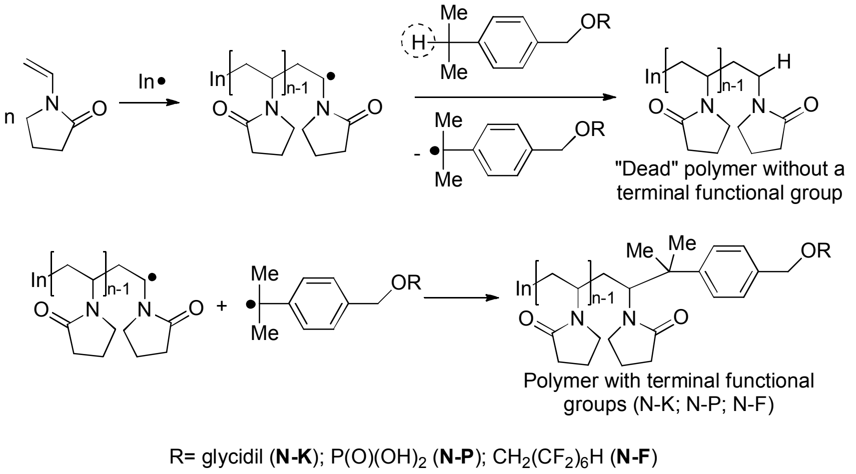
FCE

It was assumed that the use of synthesized compounds as a chain transfer allows to obtain oligomers with the appropriate terminal functional groups.

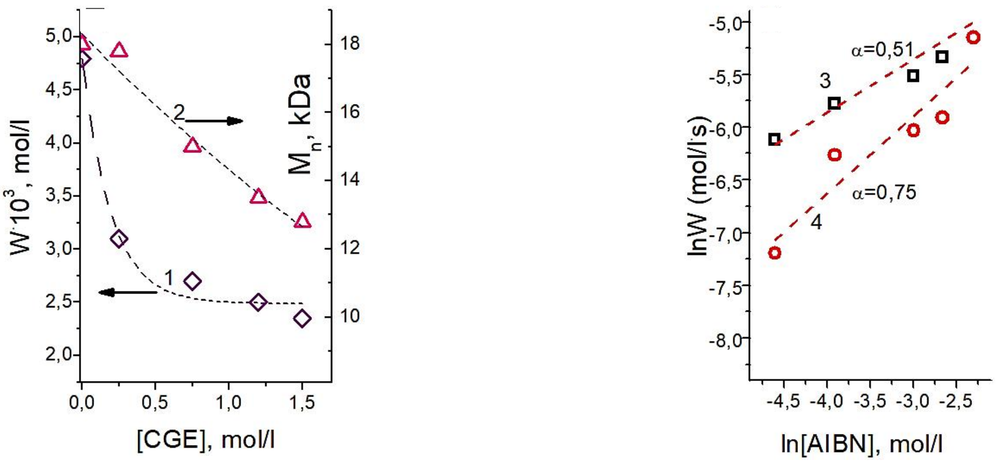
Scheme 1 shows a general scheme of the synthesis of telechelic polymers by the radical polymerization in the presence of IPB derivatives as chain transfer agents. The average numerical functionality of polymers in terms of the content of terminal functional fragments is 0.5–0.7, *i.e.*, about half of the polymer molecules contain fragments of the chain transfer agent.[21]

It was found that the content of target functional polymers depends on the synthesis conditions and, above all, on the concentration of the chain transfer agent. The increase in the chain transfer agent concentration provides the accumulation of active radicals from IPB derivatives and the increase in the part of recombination reaction with polymer radicals. This causes the accumulation in the reaction system of a low molecular weight fraction enriched in oligomers that contain the terminal functional fragments. The decrease in the polymerization rate and molecular weight of polymers (Fig. 1a, Table 1) with increasing in FCTA content in the system indicates the subordination of polymerization to known patterns of weakly inhibited polymerization[19] due to the formation of inactive radicals. These inactive radicals don't initiate polymerization, but break the growing polymer chains due to the low activation energy of the recombination reaction.

The increasing in the initiator concentration leads to the increasing in the polymerization rate (Fig. 1b). A noticeable increase in the order of polymerization of the initiator concentration indicates a significant contribution of the linear break of the polymer chains due to the transfer to the FCTA.



Scheme 1. General scheme of telechelic polymers synthesis



a)

b)

Fig. 1. NVP polymerization rate (1) and the molecular weight of the obtained polymer N-K (2) *vs.* CGE concentration ([AIBN] = 0.07 mol/L) (a) and NVP polymerization rate *vs.* concentration of AIBN without CGE (3) and 10% CGE of NVP (4). Propanol-1; 343 K; (α is order on initiator concentration)

Table 1. Kinetic characteristics of NVP polymerization in the presence of CGE and structural characteristics of polymers ([NVP] = 1 mol/L; [AIBN] = 0.07 mol/L; propanol-1; 343 K)

[CGE], mol/L	$W \cdot 10^3$, mol/(L·s)	Content of the terminal fragments, wt%	F(CGE)*	M_n, kDa	Relative transfer constant on CGE $C_{t(CGE)}$	Transfer constant on CGE k_t, L/(mol·s)**
0.21	3.11	0.65	0.56	17.8	0.006	11.9
0.72	2.72	0.78	0.57	15.0		
1.18	2.50	0.90	0.60	13.5		
1.45	2.35	0.98	0.61	12.8		

Notes: *F(CGE) is a functionality on the CGE content (average number of CGE fragments per molecule of telechelic polymer) after synthesis and after purification; ** $k_t = c_{t(CGE)} \cdot k_p$; NVP$k_p$ = 1896 L/(mol·s)[22]; M_n is the average molecular weight determined by a gel permeation chromatography.

The presence of the FCTA fragment in the polymer molecules is confirmed by ^{1}H NMR spectra. The spectra contain typical signals of NVP protons (δ, ppm: 3.49-3.13, CH_2-N; 2.77-2.37, CH_2-C=O; 2.20-1.83, CH_2-C$\underline{\mathbf{H}}_2$-CH_2), the main carbon chain (δ, ppm: 5.18-4.53, CH-N; 2.50-1.31, CH_2) and signals of FCTA fragments: 1,4-disubstituted benzene nucleus (7.67–7.18 ppm), benzyl methylene groups (4.55–4.45 ppm), gem-dimethyl groups $PhC(CH_3)_2$ (1.18–1.17 ppm) and signals of functional groups.

Different values of the integral intensities ratio of the β-CH_2 signals of the NVP ring and the aryl fragment of the FCTA indicate the incorporation of different numbers of terminal fragments of the IPB derivatives into the polymer composition. In our opinion, this is explained by the different activity of FCTA in the chain transfer reaction is caused by the different influence of the functional substituent in the aromatic ring. The FCTA activity in reactions with a polymer radical decreases in the series CGE > CF > FCE. The results of functional analysis confirm higher activity of CGE in chain transfer reactions. The values of the average molecular weights (Table 2) confirm the different activity of FCTA.

Table 2. Molecular weights and functionality of polymers with different FCTA

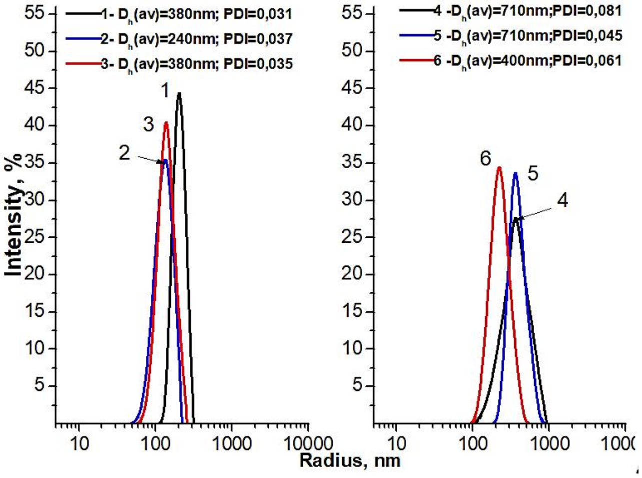
Polymer	FCTA	[FCTA], mol/L	[AIBN], mol/L	*M*, kDa	Content of the terminal fragments, wt%	F (FCTA)
N-K	CGE	0.25	0.1	12.6	0.91	0.70
N-F	FCE			30.7	-	-
N-P	CF			18.0	0.83	0.66

Table 3. Colloidal-chemical characteristics of surface-active polymers with different FCTA

Polymer	CMC·10^3, mol/L	σ_{CMC}, mN/m	σ_{min}, mN/m	S_0, A^2	$\Gamma_\infty \cdot 10^6$, mol/m^2
N-P	1.34	40.76	37.38	47	3.50
N-K	1.22	53.91	50.66	109	3.76
N-F	1.63	59.67	55.00	390	0.43

Telechelic polymers with terminal CGE and FCE fragments have a low surface activity (Table 3). In our opinion, this is due to the insignificant contribution of the hydrophobic fragment of the FCTA to the hydrophilic-hydrophobic balance of macromolecules and the formation of micel-like structures (MLS) in a solution due to the dominant effect of the hydrophilic poly(NVP) chain. The presence of the polar terminal phosphate fragment in a polymer leads to an increase in the surface activity of the telechelic polymer and promotes self-organization of molecules in the MLS (Table 3), which is typical for polymeric surfactants with polar groups.[23]

The hydrodynamic diameters of structures created by polymers with different FCTA before the CMC point (Fig. 2) are in the range of 240–400 nm and increase to 400–710 nm at concentrations above the CMC point. This indicates the impossibility of formation of stable classical polymer micelles with a compact hydrophobic core. An increase in the polydispersity of the created structures indicates the formation of aggregates with loose coils.



a) b)

Fig. 2. Hydrodynamic radius of MLS formed by polymers with terminal functional fragments: N-F (1, 4); N-K (2, 5); N-P (3, 6) before (0.5 g/100 mL) (1-3) and after (3 g/100 mL) (4-6) the CMC point

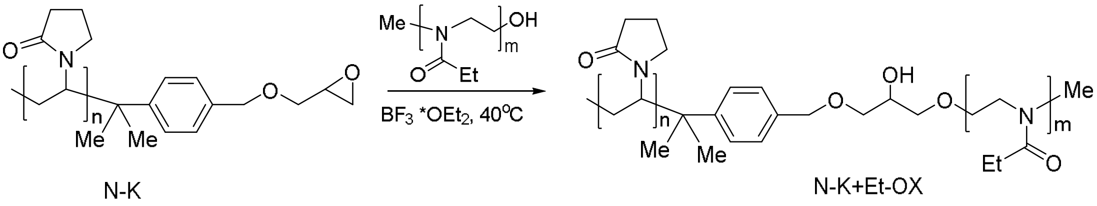
3.2. Synthesis of Block Copolymers *via* Addition Reaction

The presence of the terminal epoxide fragment of the CGE in the molecule allows the synthesis of block copolymers with a given surface activity by reactions with other functional polymers.

Thus, a block copolymer NKEO was obtained by the interaction of N-K with poly-2-ethyl-2-oxazoline (Et-Ox) containing a terminal hydroxyl group (Scheme 2).

The functional composition of the synthesized polymer is confirmed by ^{1}H NMR spectrum (Fig. 3).

The spectrum of NKEO contains characteristic signals of protons of poly(NVP) and (Et-Ox) and no signals of protons of the oxirane ring (3.25, 3.11, 2.70, 2.53 ppm). The spectrum of the copolymer contains new signals of OH-protons (3.72 ppm) and CH_2O (3.54 and 3.73 ppm), which were formed as a result of the reaction. The resulting copolymer with M_n = 12.1 kDa contains 27.7 % of [Et-Ox] block and 72.3 % of [NVP].



Scheme 2. Obtaining a block copolymer of poly(NVP) with (Et-Ox)

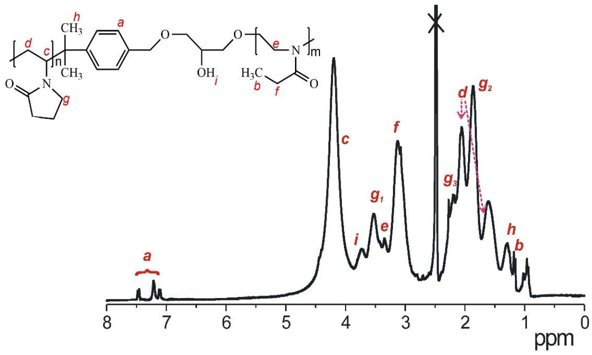
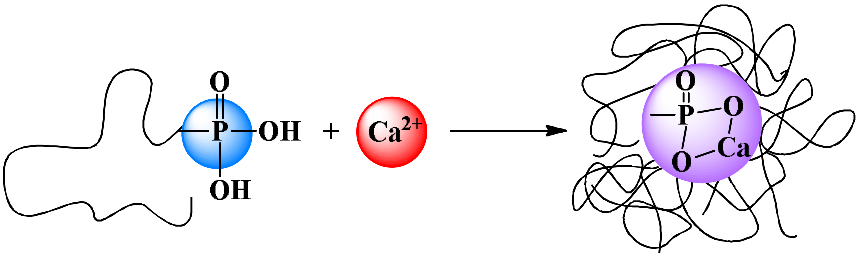


Fig. 3. ^{1}H NMR spectrum of NKEO

3.3. Synthesis of Polymer-Inorganic Particles of Calcium Phosphate

Particles of a water-insoluble polymer salt were synthesized by the reaction of poly(NVP) with a terminal phosphate group as a polymeric acid with $CaCl_2$ (Scheme 3). The presence of water-soluble poly(NVP) blocks on the surface of polymer-inorganic particles ensures the formation of dispersion with sedimentation and aggregative stability.

The differential curve (Fig. 4a (1)) of turbidimetric titration of solution N-P with $CaCl_2$ solution shows an extremum, which characterizes the formation of inorganic highly dispersed particles. The diffractogram (Fig. 4b (1)) shows diffuse maxima localized near the diffraction maxima of $Ca_3(PO_4)_2$. The shape of the curve indicates the amorphous structure of the sample and its chemical composition corresponds to $Ca_3(PO_4)_2$.



Scheme 3. Synthesis of polymer-inorganic particles of Ca^{2+} salt

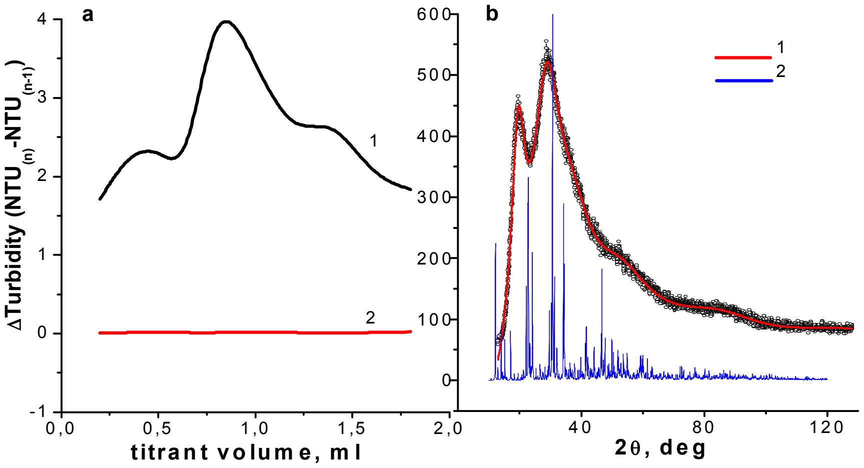


Fig. 4. Differential curves (a) of turbimetric titration of N-P with $CaCl_2$ (1) and NaCl (2); and diffractograms (b) of polymer-inorganic particles (1) and $Ca_3(PO_4)_2$ from the catalog (2)

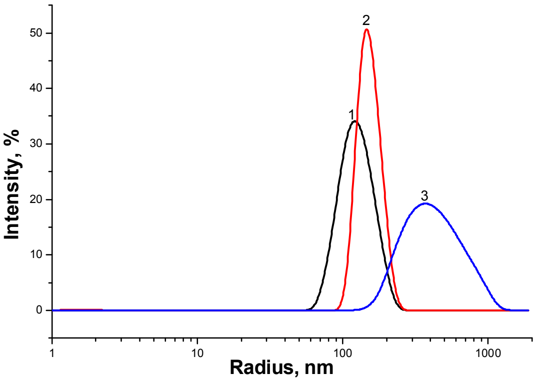


Fig. 5. Hydrodynamic radii of polymer-inorganic particles (1), MLS of polymer N-K (2) and calcium phosphate particles (3)

Dynamic light scattering results (Fig. 5) show that polymer-inorganic particles are half of the size of particles formed without a polymer. Polymer-inorganic particles have a smaller size than MLS formed by polymer molecules. This can be explained by the formation of a compact inorganic core.

4. Conclusions

The use of new derivatives of cumin alcohol with epoxy, phosphate and fluoroalkyl groups as functional chain transfer agents in the reaction of radical polymerization of N-vinylpyrrolidone has been investigated. It has been shown that the use of these compounds is a convenient tool for controlling kinetic and material chains during polymerization and allows the targeted synthesis of telechelic polymers with terminal reactive groups. Structural characteristics have been established and colloidal-chemical characteristics of new water-soluble telechelic polymers have been investigated. The ways of practical application of polymers with terminal functional fragments for the preparation of block copolymers and polymer-inorganic particles have been investigated.

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Received: July 15, 2021 / Revised: July 22, 2021 / Accepted: August 22, 2021

ТЕЛЕХЕЛАТНІ ОЛІГО(N-ВІНІЛПІРОЛІДОНИ) З КІНЦЕВИМИ ГРУПАМИ НА ОСНОВІ КУМОЛУ ДЛЯ ОТРИМАННЯ БЛОК-КОПОЛІМЕРІВ ТА НАНОЧАСТИНОК

Анотація. *Радикальною полімеризацією в присутності агентів переносу ланцюга, отриманих з ізопропілбензолу, синтезовані полімери з кінцевими епоксидними, фосфатними, фтороалкільними групами. Структура полімерів підтверджена спектрами ЯМР та функціональним аналізом. Для синтезу полімер-неорганічних частинок використовували полімери з функціональним фрагментом та кополімери з полі(2-етил-2-оксазоліновим) фрагментом.*

Ключові слова: *теломеризація, контроль кінетичних та матеріальних ланцюгів, телехелатні олігомери, блок-кополімери, наночастинки.*