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NOVEL HYDROPHOBICALLY MODIFIED POLYELECTROLYTES: SYNTHESIS AND CHARACTERIZATION OF HYDROPHOBIC POLYMERS BASED ON THE ALKYL DERIVATIVES OF ACETOACETIC ESTER

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The long-chain alkyl derivatives of acetoacetic ester were synthesized for the first time by condensation and esterification reactions. The monomers modified by dodecyl and eicosan side groups were involved into Michael addition reaction with acrylic (or methacrylic) acid followed by radical polymerization. The polymers bearing hydrophobic "tail" and hydrophilic "head" were characterized by FTIR, Raman, TGA, and X-ray methods. The phase transition temperatures from the crystalline to liquid crystalline as well as from the liquid crystalline to isotropic state were determined. The conformational transition from the globular structure to coiled one was evaluated from the potentiometric titration data. The value of electrostatic Gibbs energy was calculated. It was shown by XRD that polyelectrolytes modified by eicosan groups have more ordered structure than modified by dodecyl moieties.

Introduction

The amphiphilic polymers consisting of polar and nonpolar regions are able to self-organization due to the unique capability to form stable aggregates or micelles in water [1-4]. Polymers containing amphiphilic groups are useful to model the function of active transport and ion permeable biomembranes [5], to design novel gene transfer and drug delivery system [6] as well as LB multilayers [7] and multifunctional nanoparticles [8]. Grafting of hydrophobic backbone or regulating of block size or length in the case of block copolymers controls the self-assembling properties of most amphiphilic polyelectrolytes [9]. Polyelectrolyte-surfactant complexes also belong to hydrophobically modified systems [10, 11]. Recently [12] the long-chain acrylic polymers, containing hydrophobic pendant side groups, or so-called hydrophobically modified alkali-soluble emulsion (HASE), were characterized in aqueous solution by various physico-chemical methods. It was found that HASE polymer exhibits a conformational transition from a compact hard sphere to a random coil during the process of neutralization. Laschewsky et al. [1, 13-15] comprehensively described the synthesis and characterization of zwitterionic polysoaps, which combine advantages of the behavior of bipolar ions and micellar polymers. As a result "head-type", "mid-tail type" and "tail-end type" polymer geometry was produced. The unusual low viscosities of zwitterionic polysoaps are attributed to the intramolecular aggregation of the hydrophobic side chains keeping the hydrodynamic radius small. X-ray studies reveal the formation of superstructures in the bulk. Both electrostatic attractions between positively and negatively charged

groups and hydrophobic interactions between long flexible spacers are the driving force of superstructure formation. Hydrophobically associating polyelectrolytes may be effective viscosity enhancers in high salinity media that make them useful in sewage treatment, flocculation and oil recovery processes [16, 17].

Recently [18] we have reported on synthesis and characterization of phospholipid-containing polybetaines that showed the self-aggregated structure, phase and conformational transitions in solid state and aqueous solution. In the present paper we continue the synthetic pathway of a series of hydrophobically modified polyelectrolytes and consider the structural, phase and conformational properties in dependence of various external factors.

Experimental Part

Materials. Acetoacetic ester (ethyl acetoacetate) (99%), dodecylamine (99%), 1-eicosanol (98%), acrylic acid (99.5% purity), methacrylic acid (99%), and initiator azoisobutyronitrile (AIBN) were purchased from Aldrich. Acrylic and methacrylic acids was purified by distillation under the low pressure and kept in refrigerator. Reagent grade solvents acetone, ethanol, chloroform purchased from Aldrich were used.

Monomer synthesis. Dodecylamine was dropwise added to 10 mL of acetoacetic ester (AAE) under the stirring during 3h at room temperature. After completing the reaction the mixture was additionally stirred 30 min and left overnight. The organic phase containing the key product was separated from the aqueous phase. The yield of monomer is 98%. The purity of monomers was checked by FTIR. The mixture of 1 mol of 1-eicosanol and 1 mol of NaOH

was mixed with 1 mol of AAE. It was left overnight and then washed out by water up to neutral medium. The yield of eicosanyl acetoacetate (AAEICO) was 50%. The purity of monomer was checked by elemental analysis and FTIR.

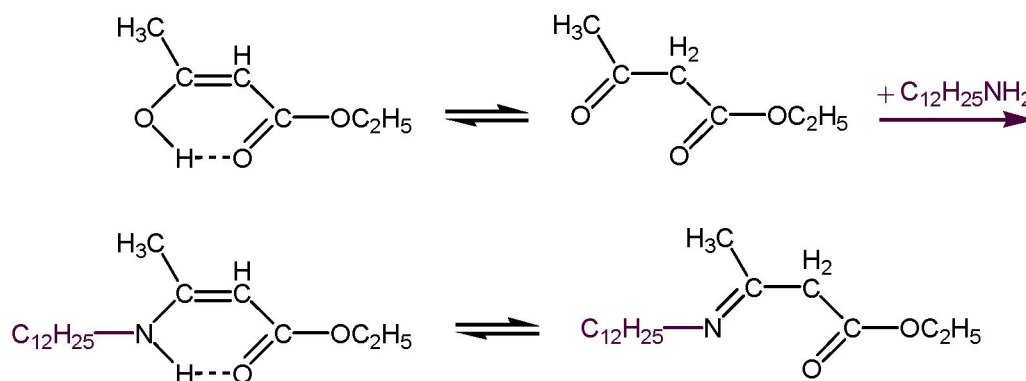
Polymer synthesis. Acrylic (or methacrylic) acid (0.8 mL, 0.5 mol) was added to CRODDA (2.2 mL, 0.5 mol), 2-3 mg of AIBN was added to monomer mixtures, and then the mixture was bubbled by nitrogen gas during 2 min and thermostated at 70 °C for 1 h. The linear polymers were purified by ultrafiltration method with the help of cellulose membrane having the pore size 2 kD. The ultrafiltrated

samples were freeze-dried. The same procedure was done with AAEICO.

Methods. FT-IR and Raman spectra were recorded using a Perkin Elmer Spectrum GX. The thermal stability of polymers was determined with Thermal Analyst, TA Instrument 2100. The temperature range was from 20 to 800 °C and the heating rate was 10 °C·min⁻¹ in nitrogen atmosphere.

Results and Discussion

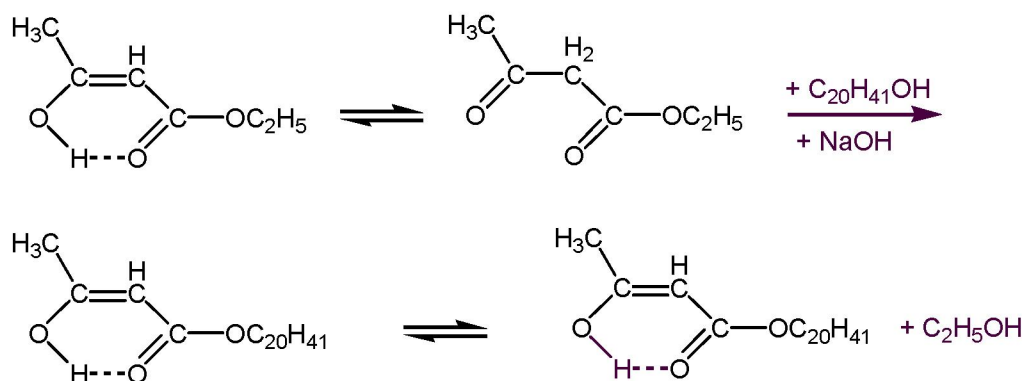
Interaction of AAE with dodecylamine (DDA) proceeds by Scheme 1 and produces ethyl 3-dodecylaminocrotonate (CRODDA).



Scheme 1. Modification of acetoacetic ester by dodecylamine via condensation reaction

Replacing of ethyl radicals by eicosan-radicals ($C_{20}H_{41}$) takes place in the course of esterification

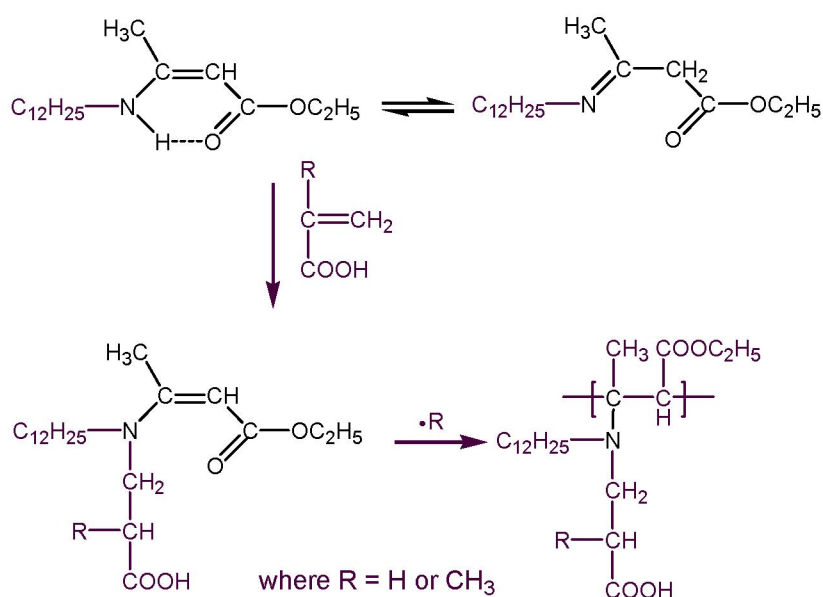
of AAE by 1-eicosanol in the presence of NaOH (Scheme 2).



Scheme 2. Modification of AAE by 1-eicosanol via esterification reaction

However both CRODDA and AAEICO, analogous to AAE and ethyl 3-aminocrotonate (CRO) [19], do not polymerize due to formation of π -conjugated keto-enol and enamine-imine tautomeric forms stabilized by intramolecular hydrogen bonds (see Schemes 1 and 2). We have shown [20,21] for the first

time that the addition of electron acceptor monomers such as acrylic and methacrylic acids to CRO breaks the intramolecular hydrogen bonds and via the Michael addition reaction produces, so called, betaine type monomers. In the case of CRODDA it is also expected that the polymerization reaction proceed



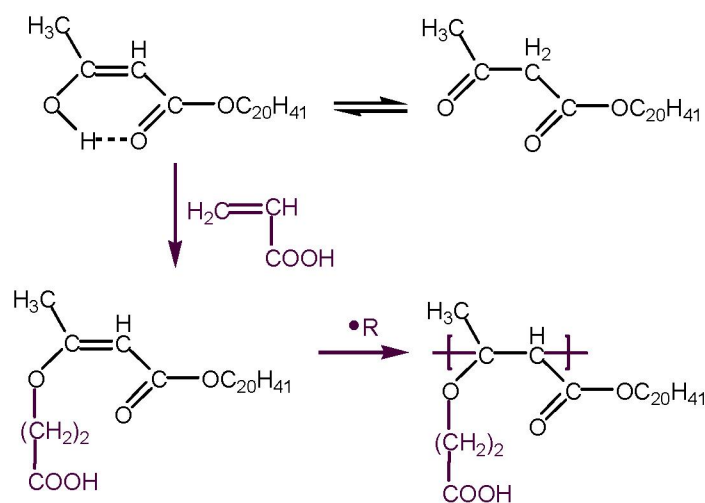
Scheme 3. Formation of CRODDA-AA (MAA) via Michael addition reaction

by the same way (Scheme 3). In the case AAEICO the Michael addition reaction followed by radical polymerization proceeds as shown in Scheme 4.

Transfer of hydrogen atoms to α -carbon atoms of unsaturated carboxylic acids from the secondary

amines in the case of CRODDA and hydroxyl groups in the case of AAEICO is responsible for the monomer and polymer formation.

The proposed structures of CRODDA-AA (or MAA) and AAEICO-AA polymers are confirmed



Scheme 4. Polymerization of AAEICO via Michael addition reaction

by FTIR and Raman spectroscopy (Figs. 1-3). Disappearance of very intensive C=C bands at 1644 cm⁻¹ confirms the involvement of double bonds into polymerization reaction. In addition, the bands of carbonyl group, symmetric, asymmetric and rocking vibrations of CH groups, symmetric and asymmetric modes of carboxylate ions are appeared (Table 1).

Thermal properties of CRODDA-AA and AAEICO derived from TGA are shown in Fig. 4. CRODDA-AA melts at 190 °C and decomposes at 420 °C. Decomposition of monomeric AAEICO takes place at 230 °C, while AAEICO-AA has two transition temperatures: the first one at 220 °C is probably connected with the melting, the second

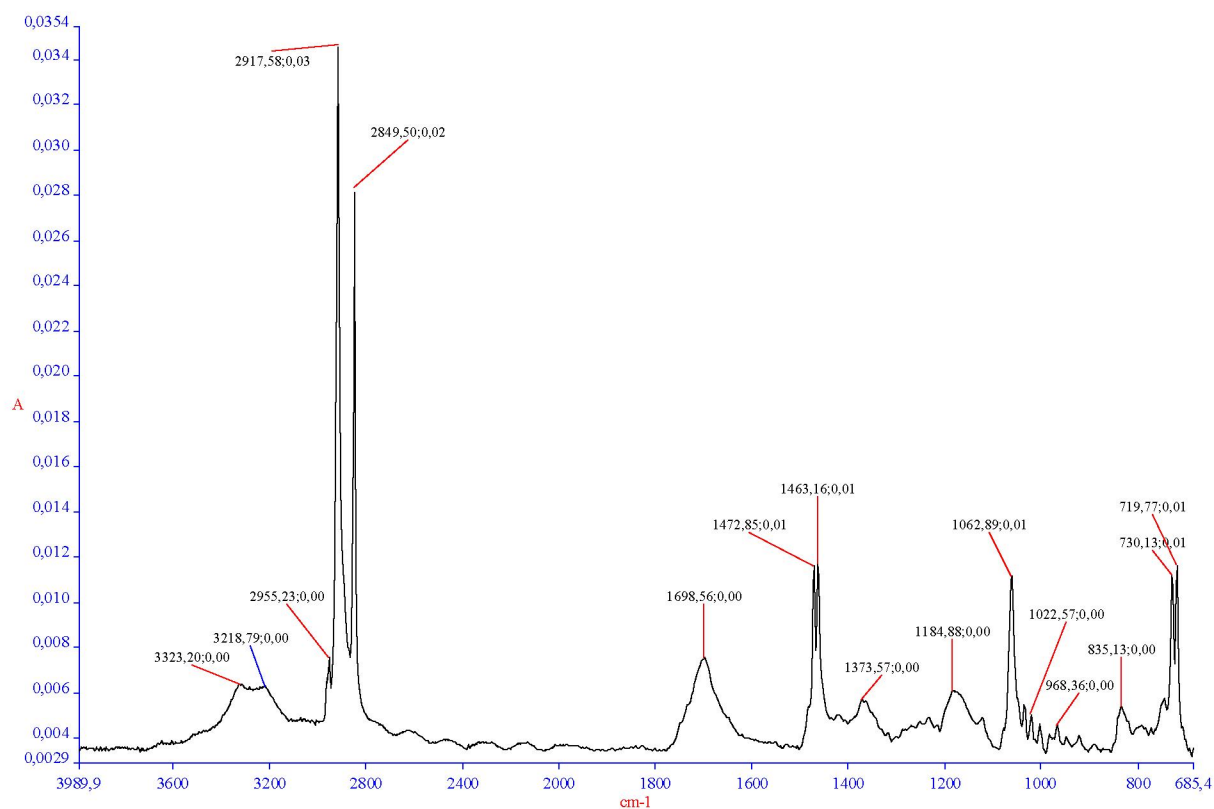


Fig. 1. IR-Fourier spectrum of AAEICO-AA

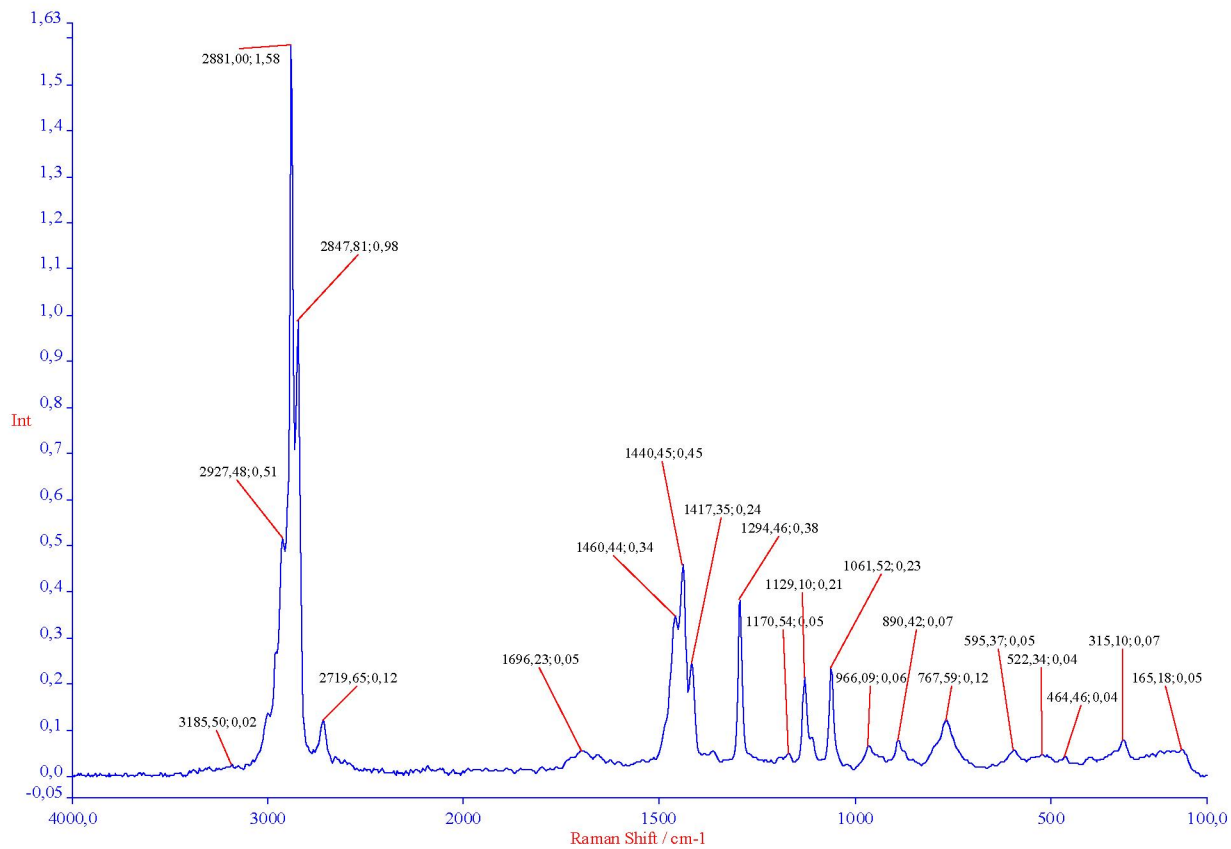


Fig. 2. Raman - Fourier spectrum of AAEICO-AA

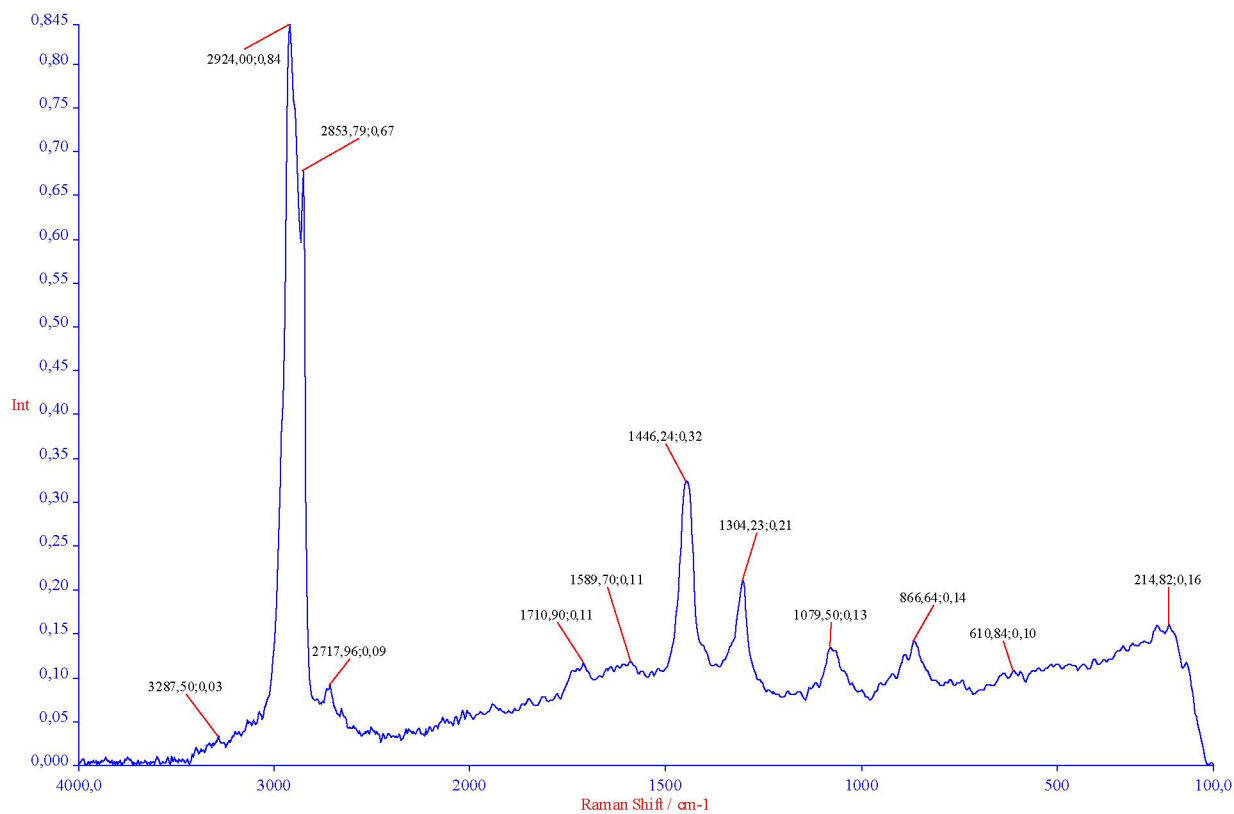


Fig. 3a. Raman - Fourier spectrum of CRODDA - AA

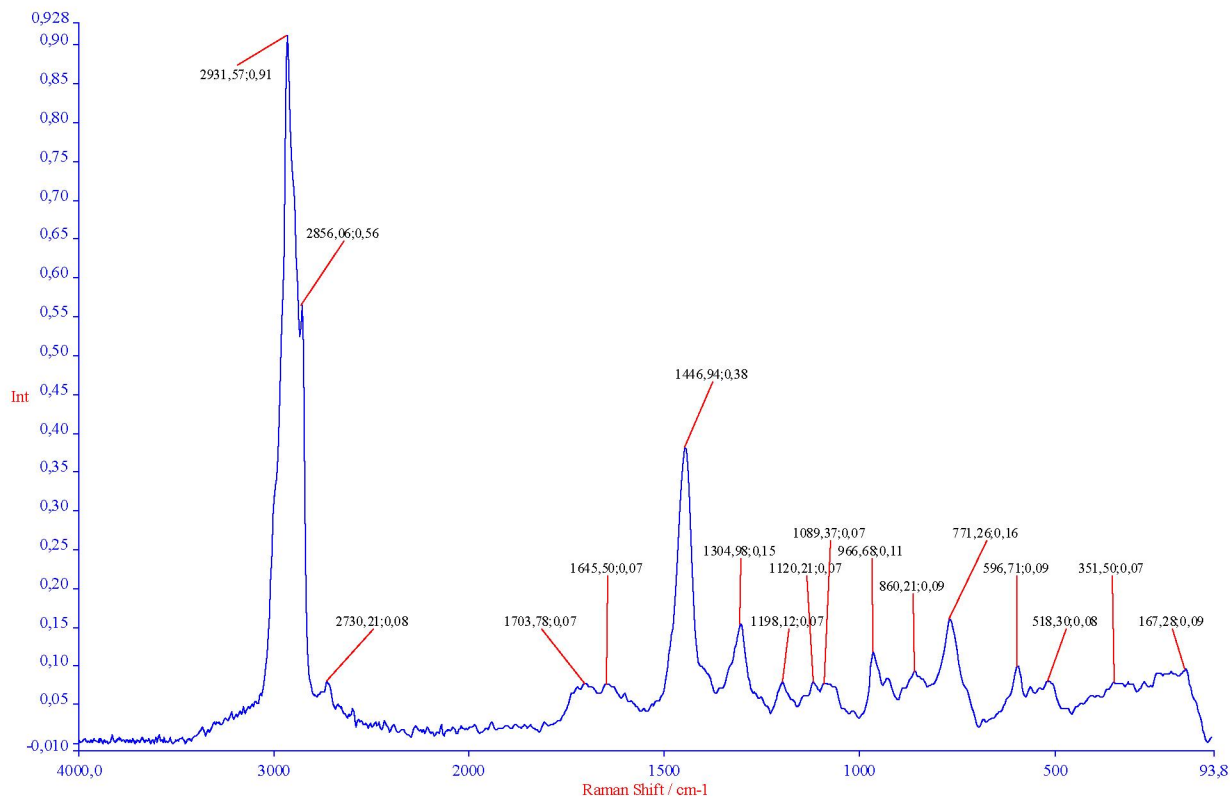


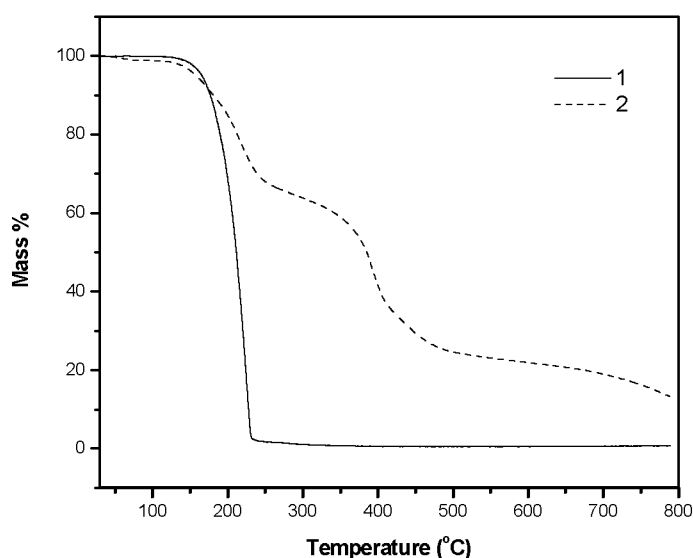
Fig. 3b. Raman - Fourier spectrum of CRODDA - MAA

Table 1. Identification of FTIR and Raman spectra of CRODDA-AA (MAA) and AAEICO-AA

Functional groups	Frequency*, cm ⁻¹					
	FTIR	Raman	FTIR	Raman	FTIR	Raman
	CRODDA-AA		CRODDA-MAA		AAEICO-AA	
v(OH)	- -	- -	- -	- -	3323 (w) 3218 (w)	- -
v(CH) _{as}	2923 (vs)	2926 (vs)	2919 (vs)	2928 (vs)	2917 (vs)	
v(CH) _s	2853 (s)	2853 (vs)	2848 (vs)	2895 (vs) 2853 (vs)	2849 (vs)	2881 (vs) 2847 (vs)
v(C=O)	1712 (vs) 1643 (vw)	1711 (w) 1650 (vw) 1608 (w)	1698 (vs) 1645 (vs)	1709 (vw) 1652 (vw) 1607 (m)	1698 (s)	1696 (vw)
v(COO ⁻) _{as}	1555 (s) 1448 (w)	1500 (vw) 1444 (m)	1512 (m) 1470 (m)	1500 (vw) 1444 (s)	1472 (s) 1463 (s)	1460 (m) 1440 (s)
v(COO ⁻) _s	1395 (m)		1388 (w) 1259 (s) 1184 (vs)		1184 (w)	1294 (s) 1129 (m)
v(COC) _{as}	1095 (w)	1080 (w)		1082 (vw)	1062 (s)	1061 (m)
ρ(CH)	721 (w)		721 (w)	759 (vw)	730 (s) 719 (s)	767 (w)

* Band intensities and vibration types: vs – very strong; s – strong; m – moderate; w – weak; vw – very weak; v – stretching, ρ – rocking, s – symmetric, as – asymmetric.

Fig. 4. TGA curves of monomeric AAEICO (1) and AAEICO-AA (2)



one at 380 °C is accounted for decomposition of polymer.

XRD spectra of CRODDA-MAA and AAEICO-AA are shown in Fig. 5. CRODDA-MAA shows only amorphous halo while both an amorphous halo and crystalline reflection appear for AAEICO-AA. A set of diffraction patterns in the

interval of $2\theta = 20-45^\circ$ is observed for AAEICO monomer with the maximum one at $2\theta = 22^\circ$. Polymeric AAEICO-AA exhibits a small diffraction peak around $2\theta = 22^\circ$ the width of which much greater than those of monomeric AAEICO. The absence of crystalline reflections for CRODDA-MAA is probably connected with low ordering of

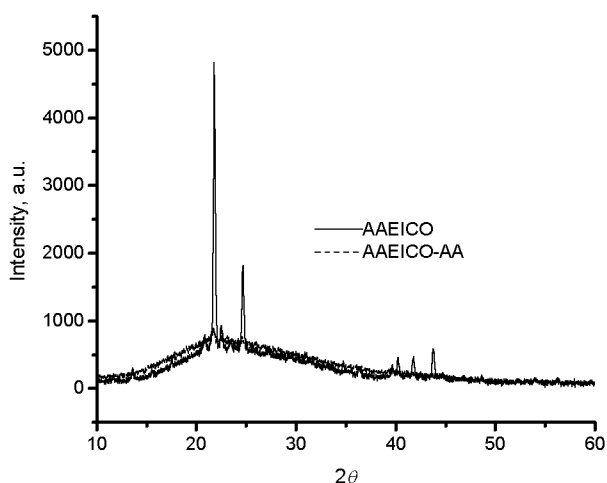


Fig. 5. XRD spectra of AAEICO and AAEICO-AA

dodecyl chains in comparison with AAEICO-AA, which has closely packed eicosan chains.

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Резюме

Этерификация және конденсация реакциялары арқылы бірінші рет ацетосірке эфирінің ұзын тізбекті алкил туындысы синтезделді. Бүйіртізбекті додецил және эйкозан топтарымен модификацияланған мономерлер Михаэльс реакциясы арқылы акрил және метакрил қышқылдарымен әрекеттесіп, соңынан радикалды полимержизацияланды. «Соңы» гидрофобты, ал «басы» гидрофильді болып келетін полимерлер ИҚ-Фурье, Раман, ТГА және рентгенді құрылымды талдау әдістемелерімен сипатталды. Додецил орынбасарлары бар полиэлектролиттерге қарағанда эйкозон топтармен модификацияланған полиэлектролиттердің құрылымы анағұрлым реттелген болып келетіндігі көрсетілді.

Резюме

Длинноцепные алкилпроизводные ацетоуксусного эфира синтезированы впервые реакцией конденсации и этерификации. Мономеры, модифицированные додецильными и эйкозановыми боковыми группами, вовлечены в реакцию Михаэля с акриловой и метакриловой кислотами и последующую радикальную полимеризацию. Полимеры, носящие гидрофобный «хвост» и гидрофильную «головку», охарактеризованы методами ИК-Фурье, Раман, ТГА и рентгеноструктурного анализа. Показано, что полиэлектролиты, модифицированные эйкозановыми группами, имеют более упорядоченную структуру, чем додецильными заместителями.

Поступила 20.11.07г.