SYNTHESIS AND RADICAL POLYMERIZATION OF CYCLOALKYL-SUBSTITUTED METHYLENEDIOXOLANES

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A number of unsaturated 4-methylene-1,3-dioxolanes were synthesized and described and their polymerization carried out in the presence of radical initiators both in mass and in solution. It has been established by data of IR and PMR spectra of the obtained polymers that the homopolymerization of the synthesized monomers proceeds both with the simultaneous participation of a methylene double bond and a dioxolane cycle with the formation of linear structural links with ketoester fragments, and only with the participation of a methylene group with the formation of links with dioxolane cycles as side groups. It has been revealed that the ratio of forming linear and cyclic structural links depends on monomer concentration and polymerization temperature. It has been established that with increase ofthe monomer concentration during polymerization in solution, the fraction of cyclic elementary links is increased, but in all cases of polymerization, the fraction of linear links prevails over the cyclic one. It has been found that with increase of the polymerization temperature, the fraction of links with the opening of the dioxolane cycle in the macrocycleis increased. The kinetics of the polymerization process was studied, and the reaction orders on monomer and initiator revealed, and the activation energy of the process was calculated. The lower value of the reaction order on monomers in comparison with polymerization of vinyl monomers was explained by availability of two various types of growing radicals in the system and their participation in the chain break reactions.

Introduction

At present, the polymerization of cyclic monomers taking place with the cycle opening, attracts special attention of researchers from both theoretical and practical points of view. This was explained as being due to the fact that such polymerization allows obtaining new polymers with unusual structural links and little accessible or practically inaccessible usual methods of the vinyl monomers polymerization [1-8]. With that consideration, we synthesized new cyclic monomer compounds from the class of methylenedioxolane compounds.

As the initial monomers for polymerization, 2-methyl-2-cyclopentyl (1), 2-methyl-2-cyclohexyl (2), 2-cyclopentylidene (3) and 2-cyclohexylidene-4-methylene-1,3-dioxolanes (4) have been used. They have been synthesized by dehydrochlorination of the corresponding chloromethyldioxolanes.

Experimental

The IR spectra were taken on device "Cary 630 FTIR" of firm Agilent Technologies (crystal ZnSe). The PMR spectra were taken on spectrometer "Fourier" (frequency – 300 MHz)

of firm "Bruker" in CCl4 solution, internal standard – hexamethyldisiloxane, the chemical shifts of signals are presented in a scale δ(ppm.). The purity of the synthesized compounds was

Synthesis of 2-methyl-2-cyclopenthyl-4-chloromethyl-1,3-dioxolane [10]

The epichlorohydrin (370 g, 4 mol) dropwise was added to a solution consisting of methylcyclopentyl ketone (224 g, 2 mol) and boron trifluoride ether (5.6 g, 0.04 mol) in constant stirring. The reaction temperature was maintained within the range of 35-40° C. After that, the reaction mixture had been stirred for another 3 hours at a room temperature. The excess of epichlorohydrin was distilled off, and then the reaction mass was distilled in a vacuum. The yield of purposeful product was 89%, B.p.=45^{0}C/2 mm.merc.c. ^{1}H-PMR–δ(ppm.) : (CDCl$_3$) 3.45-3.60 (2H, m), 3.25-4.20 (3H, m) , 1.20 (3H, s), 0.90-1.16 (9H, m).

According to a similar methodology, the corresponding 2-methyl-2-cyclohexyl, 2-cyclopentylidene and 2-cyclohexylidene-4-chloromethyl-1,3-dioxolanes were obtained from epichlorohydrin and methylcyclohexyl ketone, cyclopentanone and cyclohexanone.

Synthesis of 2-methyl-2-cyclopenthyl-4-methylene-1,3-dioxolane

The solution of 27 g (0.5 mol) of sodium methylate in DMF (100 ml) at a room temperature dropwise was added to a mixture consisting of 40.9 g (0.2 mol) of 2-methyl-2-cyclopentyl-4-chloromethyl-1,3-dioxolanes in the course of constant stirring. The mixture was stirred at the same temperature for 4 hours. Then water (150 ml) was slowly added to the reaction mixture, after which it was extracted with ester (200 ml). The organic layer was separated and dried with anhydrous MgSO$_4$ while the solvent was distilled off. The residue was distilled at a low pressure. The yield of

purposeful product (transparent liquid) –90%, B.p.=52^{0}C/10 mm.merc.c., ^{1}H-PMR– δ(ppm.) : (CDCl$_3$) 4.20-4.45 (2H, m), 3.80-4.20 (2H, m), 1.25 (3H , s), 0.92-1.16 (9H, m).

According to a similar methodology, by interaction of 4-chloromethyl-2-methyl-2-cyclohexyl, 2-chloromethyl-2-cyclopentylidene, 2-chloromethyl-2-cyclohexylidene-1,3-dioxolanes with sodium methylate, 4-methylene-2-methyl-2-cyclohexyl, 4-methylene-2-cyclopentylidene and 4-methylene-2-cyclohexylidene-1,3-dioxolanes were obtained, respectively.

Polymerization of 4-methylene-2-substituted-1,3-dioxolanes

The polymerization of synthesized monomers was carried out in sealed ampoules at 333 K. A calculated number (0,5 mol) of monomer, dry benzene (10 ml) and AIBN (0,5% from quantity of monomer) was loaded to an ampoule. Then for removal of the occluded air, the solution in the ampoules was first frozen, vacuumed for 10-15 min., and then unfrozen. This process was repeated several times. After that, the ampoule was frozen, filled with nitrogen, sealed and placed in a thermostat. The polymerization time varied depending on the type of monomer within 2-4 hours. After the specified time, the ampoule was cooled, opened and an equal quantity of solvent was added and the obtained polymer was planted in an appropriate precipitator (ester, alcohol or saturated hydrocarbon). The polymers purification was carried out by reprecipitation. The isolated polymers were dried in a vacuum at 333 K.

Results and discussion

As noted in the experimental part, 4-methylene-1,3-dioxolanes **(1-4)** were synthesized by dehydrochlorination of chloromethyldioxolanes in the presence of sodium methylate in DMF solution at a room temperature.
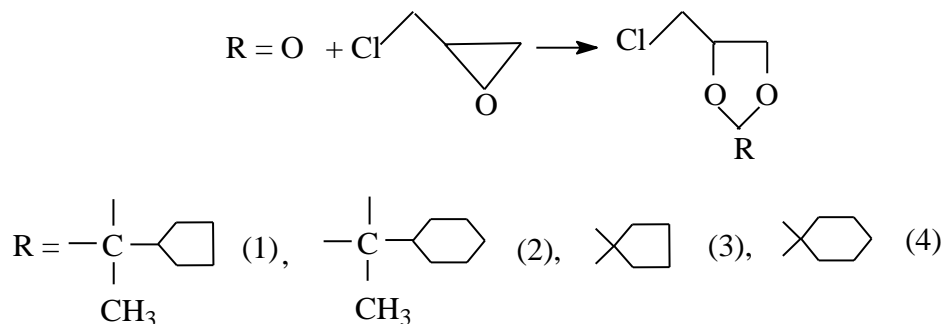
According to the data of chromatographic analysis the yields of compounds **1-4** were high (82-85%). Their structure was confirmed by data of IR and PMR spectroscopy.

In the IR spectra of compounds **1-4** there were characteristic absorption bands referring to valence vibrations of C=C bond in the field of 1645-1650 cm^{-1}. The absorption bands in the fields of 1080-1090 and 1110-1130 cm^{-1} characterized the availability of ether bond of dioxolane cycle in their molecules. In the PMR spectra of compounds **1-4** the ratio of integral intensities of the signals at δ=4.30 ppm, protons (double bond) and δ=2.80 ppm. (protons $-OCH_2$ group) was 3:1, that was possibly connected with superimposition of the signal of one proton of the methylene group on the expanded singlet of two olefin protons.

The polymerization of the synthesized monomers 1-4 was carried out in the presence of initiators AIBN (dinitrileazoisobutyric acid) and DTBP (ditertiary butyl peroxide) at various temperatures in mass and in benzene solution.

A comparison of IR spectra of the monomers and polymers derived from them showed that the main links of the macromolecular chain were linear structures formed as a result of simultaneous opening of the double bond and dioxolane cycle. Along with linear links in the chain of macromolecules, the formation of dioxolane cycle links as side groups was also observed. The availability of linear structural links in the chain of macromolecules was evidenced by the disappearance of the absorption band in the fields of 900-1000, 1640-1650 cm^{-1} (deformation and valence vibrations of vinylidene groups) available in the spectra of the initial monomers and the appearance of a new absorption band in the field of 1735 cm^{-1} that characterized the ketone group. The availability of the absorption bands in the IR spectra of the obtained polymers in the fields of 1070-1080 cm^{-1}, 1100-1120 cm^{-1} characterized ether bonds of the dioxolane cycle.

The availability of cyclic and linear structural links (cyclolinear structure)in the chain of macromolecules also confirms the data of PMR spectra, which shows that all polymers have the above-proposed structure. This is evidenced by the appearance of resonance absorptions corresponding to protons of the methylene group, which is in the vicinity of the ketone group (δ = 3.45 – 4.20 ppm.).

Thus, the data of spectral analyses of the obtained homopolymers confirm that during polymerization of monomers 1-4, the macromolecules, which consist of both linear structural links with ketoester fragments (1,5 – polymerization) and cyclic links with preservation of the dioxolane cycle (1, 2 – polymerization) are formed.

Conditions of the polymerization and some characteristics of the obtained polymers are presented in Table 1.

Also, the influence of some parameters on the flow direction of the polymerization process was studied.

Table1. Polymerizationof 2-substituted 4-methylene-1,3-dioxolanes in the various conditions.

Compounds	Initiator, mol.%	Temperature, °C	Polym. time, h	$MW^* \cdot 10^{-3}$	Yield, %	Degree of opening
1	AIBN. 5.0	60	20	4.8	28	58
		70	20	4.6	32	65
	DTBP. 5.0	110	25	4.5	53	71
	–"–	120	25	4.4	57	76
2	AIBN. 5.0	60	20	5.2	31	62
		70	20	4.8	38	66
	DTBP. 5.0	110	25	4.6	44	73
	–"–	120	25	4.5	62	78
3	AIBN. 5.0	60	20	5.4	38	81
		70	20	5.2	51	84
	DTBP. 5.0	110	25	5.0	58	88
	–"–	120	25	4.8	69	91
4	AIBN. 2.0	70	20	5.8	48	83
	DTBP. 2.0	120	25	5.2	76	92

As follows from data of Table 1, the degree of the dioxolane cycle opening depends on polymerization temperature. With temperature rise a part of links with dioxolane cycle opening is increased.

The scheme of polymerization of the synthesized monomers can be presented as follows:
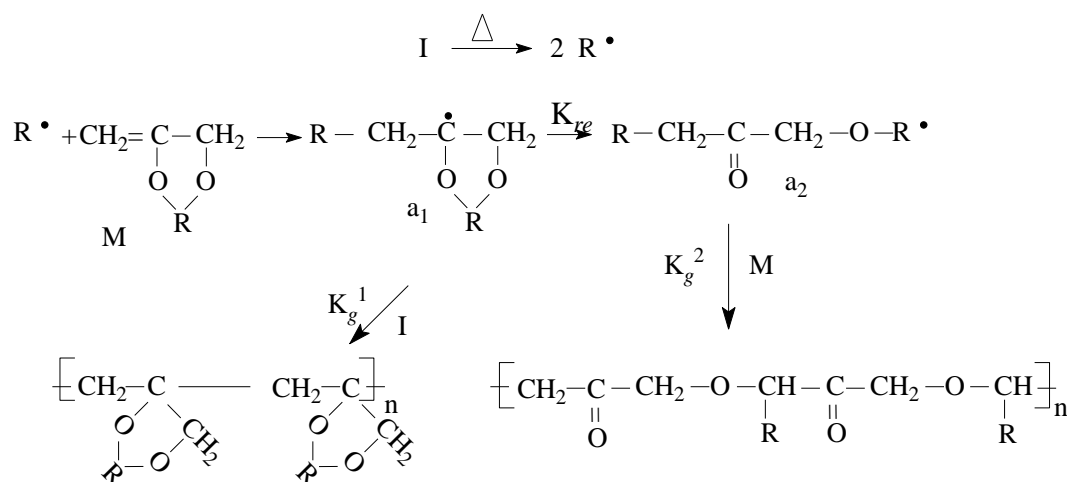
To reveal main regularities of the radical polymerization of the synthesized monomers 1-4, the kinetics of the process for monomer 1 was studied. On the basis of the data obtained for initial stages of the polymerization where almost all series of experiments had a linear dependence of conversion on time, the reaction orders for the monomer and initiator were found.

The obtained results led to the expression for total polymerization rate.

The reaction order on initiator in initiation of AIBN indicates to a bimolecular break of growing macromolecular chains. The reaction order value on monomer, less than one, is explained similarly to work [6], by availability of two different types of growing radicals in the system.

The activation energy of the polymerization corresponded to $5.84 \cdot 10^4$ J/mol.

During the polymerization of monomers 1-4 along with linear structural links in the chain of macromolecules, the formation of links containing dioxolane cycles was observed.

It follows from the kinetic polymerization scheme that the links formation rate with dioxolane cycles is expressed by the equation:

$$\frac{d[DO]}{dt} = \left(K_g^1\left[a_1^\bullet\right] + K_g^2\left[a_2^\bullet\right]\right)[M] - K_{re}\left[a_1^\bullet\right] \tag{1}$$

The monomer consumption rate is expressed by the equation:

$$-\frac{d[M]}{dt} = \left(K_g^1\left[a_1^\bullet\right] + K_g^2\left[a_2^\bullet\right]\right)[M] \tag{2}$$

Dividing equation (1) into equation (2) and substituting $a_2^{\cdot}$ value and guided by the principle of quasi-stationary process, the fraction of linear (f_l) and cyclic (f_c) structural units are expressed by equations:

$$f_c = 1 - \frac{r_{re}}{r_{re} + [M]} \qquad f_l = 1 - f_c = \frac{r_{re}}{r_{re} + [M]} \qquad \frac{1}{f_l} = 1 + \frac{[M]}{r_{re}}$$

where $r_{re} = \frac{k_{re}}{k_g^1}$.

If the polymer chains are long, the polymer composition can be estimated by determination of the molar fraction of links with dioxolane cycle f_c or the molar fraction of links with linear structure f_l. The values calculated on the basis of the obtained experimental results (according to PMR spectra) for the f_c and $f_{l\ is}$ is shown in Table 2.

Table 2. Dependence of the polymer composition on concentration of methylenedioxolane at various temperatures

T, K	[M] mol/l	f_c (mol.frac.)	f_l (mol.frac.)	$\frac{1}{f_l}$ (mol.frac)$^{-1}$	K_g^1/K_{re}	$r_{re} = \frac{K_{re}}{K_g^1}$
333	0.82	0.18	0.82	1.22	0.101	9.90
	1.64	0.25	0.75	1.33		
	3.28	0.32	0.68	1.47		
343	0.82	0.16	0.84	1.19	0.065	15.38
	1.64	0.20	0.80	1.25		
	3.28	0.26	0.74	1.35		
353	0.82	0.14	0.86	1.16	0.048	20.83
	1.64	0.22	0.82	1.22		
	3.28	0.27	0.78	1.28		

The value found for the rearrangement constants (r_{re}) means that $k_{re} > k_g^1$ and was agreed with the structure of the polymer chain. Thus, as a result of competing reactions – monomolecular rearrangement and intermolecular chain growth, the polymers containing both links with side dioxolane groups and links with linear structureare formed. The values found for r_{re} showed that the elementary links with linear structure prevail.

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TSİKLOALKİL ƏVƏZLİ METİLENDİOKSOLANLARIN SİNTEZİ VƏ RADİKAL POLİMERLƏŞMƏSİ

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Bir sıra doymamış 4-metilen-1,3-dioksolanlar sintez edilərək xarakterizə olunmuş və onların radikal inisiatorlar iştirakında kütlədə və məhlulda polimerləşməsi aparılmışdır. Alınmış polimerlərin İQ- və PMR-spektrlərinin nəticələri ilə müəyyən edilmişdir ki, sintez edilmiş monomerlərin homopolimerləşməsi həm metilen ikiqat rabitəsi və dioksolan həlqəsinin birgə iştirakı ilə ketoefir fraqmentli xətti quruluşlu manqaların, həm də yalnız metilen qrupunun iştirakı ilə yan qruplar kimi dioksolan tsiklləri saxlayan manqaların alınması ilə gedir. Müəyyən edilmişdir ki, alınan xətti və tsiklik quruluşlu elementar manqaların nisbəti monomerin qatılığından və polimerləşmə temperaturundan asılıdır. Göstərilmişdir ki, polimerləşmənin məhlulda aparıldığı halda monomerin qatılığının artırılması tsiklik quruluşlu elementar manqaların payını artırır, lakin polimerləşmənin bütün hallarında xətti quruluşlu manqaların payı tsiklik quruluşdan üstün olur. Göstərilmişdir ki, polimerləşmə temperaturunun artırılması makromolekul zəncirində dioksolan tsiklinin qırılması ilə alınan manqaların payının artmasına səbəb olur. Polimerləşmə prosesinin kinetikası öyrənilmiş, monomerə və inisiatora görə reaksiyanın tərtibi müəyyənləşdirilmiş, həmçinin

prosesin aktivləşmə enerjisi hesablanmışdır. Reaksiyanın monomerə görə tərtibinin vinil monomerlərinin polimerləşməsi ilə müqayisədə aşağı olması sistemdə iki müxtəlif tip zəncirin uzanmasını aparan radikalın olması və onların zəncirin qırılma reaksiyasında iştirakı ilə əlaqədardır.
Açar sözlər: *metilendioksolan, sintez, radikal polimerləşmə, inisiator, kinetika, tsiklin qırılması ilə polimerləşmə.*

СИНТЕЗ И РАДИКАЛЬНАЯ ПОЛИМЕРИЗАЦИЯ ЦИКЛОАЛКИЛЗАМЕЩЕННЫХ МЕТИЛЕНДИОКСОЛАНОВ

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Синтезирован и охарактеризован ряд непредельных 4-метилен-1,3-диоксоланов и проведена их полимеризация в присутствии радикальных инициаторов как в массе, так и в растворе. Данными ИК- и ПМР- спектров полученных полимеров установлено, что гомополимеризация синтезированных мономеров протекает как с одновременным участием метиленовой двойной связи и диоксоланового цикла с образованием линейных структурных звеньев с кетоэфирными фрагментами, так и только с участием метиленовой группы с образованием звеньев с диоксолановыми циклами в качестве боковых групп. Выявлено, что соотношение образующихся линейных и циклических структурных звеньев зависит от концентрации мономера и температуры полимеризации. Установлено, что с повышением концентрации мономера при проведении полимеризации в растворе доля циклических элементарных звеньев увеличивается, но во всех случаях полимеризации доля линейных звеньев преобладает над циклическими. Найдено, что с повышением температуры полимеризации доля звеньев с раскрытием диоксоланового цикла в макроцепи увеличивается. Изучена кинетика процесса полимеризации, выявлен порядок реакции по мономеру и инициатору, а также вычислена энергия активация процесса. Меньшее значение порядка реакции по мономеру по сравнению с полимеризацией виниловых мономеров объясняется наличием в системе двух разных типов растущих радикалов и участие их в реакциях обрыва цепи.
Ключевые слова: *метилендиоксолан, синтез, радикальная полимеризация, инициатор, кинетика, полимеризация с раскрытием цикла.*