Synthesis of Cross-Linked Polyethylene Oxide-Acetal Macrocycles for Solid Superbase Catalysts

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ABSTRACT: A novel long-chain divinyl ether of tris(diethyleneglycol)-bisacetal, has been synthesized by electrophilic addition of one molecule of diethylene glycol to two molecules of divinyl ether of diethylene glycol (DVDEG) in the presence of CF_3COOH in quantitative yield. The monomer was cationically polymerized ($BF_3{\cdot}OEt_2$, or complex $LiBF_4{\cdot}MeO(CH_2)_2OMe$) and copolymerized with DVDEG to deliver solid polymers the yields being 80–100%. The polymers represent the cross-linked polyether-polyacetal structures comprising macrocycles. The polymers were treated with 3% solution of KOH or CsOH in methanol to afford solid superbase complexes of KOH (CsOH) with cross-linked polyether-polyacetal macrocyclic networks. Preliminary tests have shown the complexes to be active catalysts for ethynylation of acetones and prototropic isomerization of methyl propargyl ethers to allenyl methyl ethers. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3363–3369, 2011

Key words: tris(diethyleneglycol)-bisacetal; cation polymerization; polymer superbases

INTRODUCTION

Solid superbase catalysts are widely used in modern chemistry and technologies.[1–5] Among their obvious advantages are high activity and recyclibility. Most of the known solid superbase catalysts are inorganic in nature and cover a rather limited range of the components combination, e.g., alkaline metals or their hydroxides, alkoxides or amides deposited on γ-Al_2O_3, SiO_2, or Si_3N_4, that, in turns, restricts their tunability and hence applications.[5] Meanwhile, organic ligands having the affinity toward alkaline metal cations may substantially extend the scope of application of superbase catalysts.

The superbase is commonly defined as a strong base complexed with an appropriate ligand which separates the alkaline metal cation from the accompanying basic anion that enhances activity of the latter.[6–9] Therefore, as the prototype of an organic superbase can be, for example, the complex of KOH with a crown ether.[10,11] However, such complexes are soluble and quite unstable stoichiometrically.[11] This article is a preliminary report on the development of a general approach to design solid superbases representing reactive polymers - cross-linked polyether-acetal macrocyclic matrix, in which alkaline metal hydroxides are incorporated. To synthesize suitable polyethylene oxide cross-linked networks involving crown-like microcycles, it would be possible to employ the polymerization of divinyl ethers of oligoethylene glycols, capable of not only cross-linking[12] but also cationic cyclopolymerization.[13,14] To attain a good permeability of solid catalytic particles it is necessary to have loose networks and large macrocycles therein. This target might be reached by polymerization of divinyl ethers of long-chain oligoethylene glycols. However, these monomers are laborious to synthesize and, particularly, purify up to grade required for polymerization.[15] To circumvent this problem we have synthesized for the first time well-defined divinyl ether having three diethylene glycol (DEG) and two acetal moieties between the divinyl groups.

RESULTS AND DISCUSSION

The synthesis of divinyl ether of tris(diethyleneglycol)-bisacetal (DVBA) was cleanly (in quantitative yield) performed by electrophilic addition of one molecule of DEG to two molecules of divinyl ether of diethylene glycol (DVDEG) in the presence of 0.5 wt % of CF_3COOH (Scheme 1).

Usually, this polyaddition reactions of such a type lead to a mixture of oligomer-homologs and the unreacted component taken in excess, i.e., in this case DVDEG. Therefore, the product obtained was

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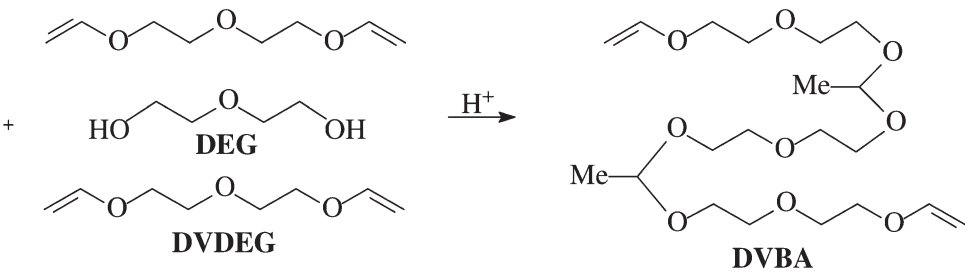


Scheme 1

scrutinized by spectral (IR, ^{1}H NMR) and gas-liquid chromatograph (GLC) methods to find out wheather we actually have the expected oligomer mixture. Surprisingly, all the analyses of the adduct have shown that we came up with the diadduct DVBA: only traces of DVDEG were detected by GLC in the neutralized (K_2CO_3) reaction mixture and no indicators of other oligomers presence were observed by IR and ^{1}H NMR spectra (see below). Besides, no DVDEG was distilled from the adduct under vacuum (40°C, 10^{-2} mmHg).

Indeed, the IR spectrum of DVBA contained no absorption band of hydroxyl groups (3600–3200 cm^{-1}), thus indicating that all DEG was consumed. A strong absorption band at 1380 cm^{-1}, which was absent in the IR spectrum of the starting compound, belonged to the CH_3 group of the acetal moiety. In the region of C—O—C band vibrations (1000-1200 cm^{-1}), the shapes of bands changed: a number of peaks at 1050, 1089, 1135 cm^{-1} typical for the acetal group appeared, whereas at 1200 cm^{-1} the strong CO band of the vinyl ether remained, all other characteristic bands of the vinyloxy group also retaining (820, 840, 960, 1620, 1635, 3100 cm^{-1}).[9,16,17]

^{1}H NMR spectrum of DVBA, a typical doublet of the acetal methyl moiety (1.28, 1.29 ppm, sharp signals), multiplet CH_2–O (3.6 ppm) and the acetal CH (CH_3) quartet (4.48–4.52 ppm) were observed, whereas the vinyl groups were typically represented by doublet of doublets (CH_2=CH) at 4.15 ppm and quartet (CH=CH) at 6.35 ppm,[9] the intensity ratio of these signals strictly corresponding to DVBA structure. In case of the expected oilgomer mixture, the spectra should contain progressions of the above signals instead of the observed pronounced sharp signals corresponding to the acetal and vinyloxy moieties of only one type.

This unexpected result of the polyaddition reaction, as depicted in Scheme 1, maybe associated with the special chemistry of the acetal moiety, which in the presence of acids is known to be easily cleaved to generate the carbocation stabilized the adjacent oxygen (Scheme 2).

Also, the acetal formation by the acid-catalyzed addition of alcohols to vinyl ethers is a reversible reaction (Scheme 3).

The combination of the above two classic processes should result in insertion of the remaining divinyl ether into the acetal moiety and further disproportionation of higher oligomers until the unimolecular adduct DVBA is formed.

DVBA was further polymerized and copolymerized with DVDEG in the presence of cationic catalysts to produce cross-linked polyethylene oxide-acetal macrocycles as possible ligands for solid KOH superbase complexes.

Our experiments have shown (Table I) that under the action of BF_3·OEt_2 or the complex $LiBF_4$·DME, a novel catalytic system for polymerization of vinyl ethers recently developed by us,[18,19] DVBA forms easily and in high yields (80–100%) insoluble cross-linked polymers (Scheme 4), capable of complexing with alkaline metal hydroxides.

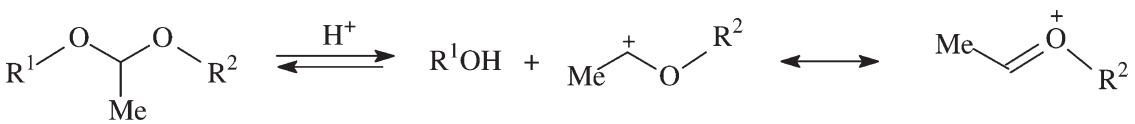
As we found early,[18] the $LiBF_4$ complexes with DME of type (A-C, Scheme 5), which were known to be formed upon dissolving the lithium salt in DME, initiated the polymerization of vinyl ethers in a mode of latent catalysts.

The mechanism of action of this catalytic system is based on the $LiBF_4$ salt thermal dissociation:

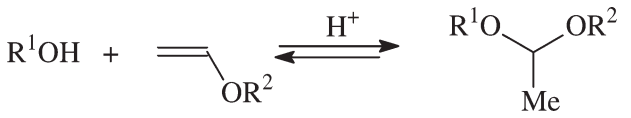
$$LiBF_4 \rightleftarrows LiF + BF_3$$

which practically does not occur at room temperature but becomes noticeable on heating.[18]

The latent (temperature-activated) catalytic system $LiBF_4$·DME seems to be more preferable for polymerization of DVBA (Table I) since it allows the



Scheme 2



Scheme 3

local polymerization to be prevented that provides for smoothly going process and stable properties of the polymers formed. The polymers synthesized do not darken and remain transparent in time, easily comminuted and, therefore, suitable for further modification.

The polymers are white powders, insoluble in common organic solvents (acetone, benzene, chloroform, ethanol), except for the polymer obtained in the presence of $BF_3{\cdot}OEt_2$, which is an elastic material, also insoluble in organic solvents. In the IR spectra of the polymers synthesized, a high background with the broad absorption bands in the region of characteristic for CH_3 (1380 cm^{-1}), C—O- bonds in ethers (1200 cm^{-1}) and acetals (1050, 1089, 1135 cm^{-1}) were observed. Only a weak remaining band of the vinyloxy group in the region 1620 cm^{-1} was discernible. The elemental composition of the polymer expectedly corresponded to that of the monomer.

Copolymerization of DVBA with DVDEG may allow one to modify the forming polyether structure (size of crown-like microcycles).

In the presence of the complex $LiBF_4{\cdot}DME$, the copolymerization of DVBA with DVDEG also proceeded efficiently (85–94% yields) [*i*-octane: toluene mixture (3 : 1), 80°C, 0.5 h] to furnish more tightly cross-linked copolymers as white powders insoluble in common organic solvents (Table II). Judging from the literature data,[13,14] we may infer that the copolymers are cross-linked by bridges **D, E** and also include the macrocyclic structures **F,G** (Scheme 6).

i-Octane as a co-solvent is known[20] to facilitate the formation of crossed-linked polymers of a higher porosity.

Since DVDEG is insoluble in *i*-octane, the reaction mixture homogeneity and the uniformity of the copolymer properties are reached by its dilution with toluene.

TABLE I
Polymerization of Divinyl Ether of Tris(Diethyleneglycol)-Bisacetal

Catalysts, wt %	T, °C	Time, h	Yield, %	Polymer appearance
$BF_3{\cdot}OEt_2$, 0.10[a]	25	0.1	100	Brown elastic material
$LiBF_4{\cdot}DME$, 0.15[a]	80	1.0	80	White powder
$LiBF_4{\cdot}DME$, 0.20	80	1.0	91	White powder
$LiBF_4{\cdot}DME$, 0.25	60	1.0	95	White powder
$LiBF_4{\cdot}DME$, 0.25	80	1.0	100	White powder

[a] In toluene (monomer : toluene 1 : 1).

In the IR spectra of the copolymers, the same moderate background with the absorption bands maxima belonging to CH_3 group (1380 cm^{-1}), C—O bond vibrations in ether and acetal moieties were detected (1200, 1050, 1089, 1135 cm^{-1}), the characteristic bands of the vinyloxy groups (1620 cm^{-1}) becoming more pronounced as compared with homopolymer of DVBA.

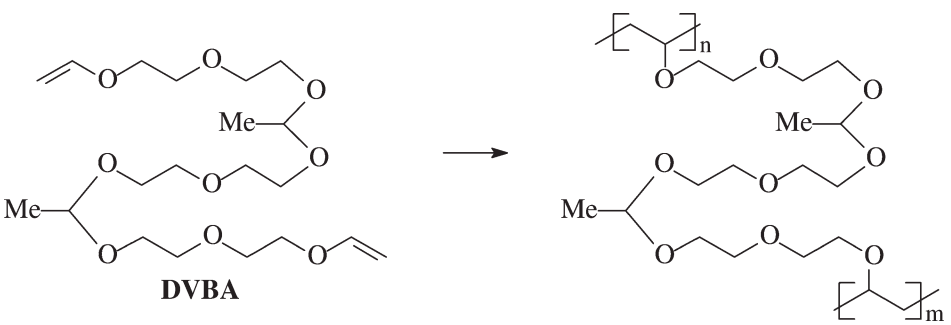
The composition of the copolymers corresponds to the comonomers ratio.

Insoluble polymer superbases (the complexes of the polymers synthesized with alkaline metal hydroxides) have been obtained by the reaction of poly-DVBA and its copolymers with methanol (ethanol) solutions of KOH or CsOH. The reaction leads to the superbases,[6–10] where alkaline metal cation is separated from anion because of the formation of complexes with polyether moieties (Scheme 7). This process is similar to the complex formation of alkaline metal cations with crown-ethers.[9,11]

In the IR spectra of polymer superbases obtained, all absorption bands maxima belonging to CH_3 group (1380 cm^{-1}), to ether and acetal moieties (1200, 1050, 1089, 1135 cm^{-1}) were remained. The new strong wide band appeared because of OH-bonds (3440 cm^{-1}).

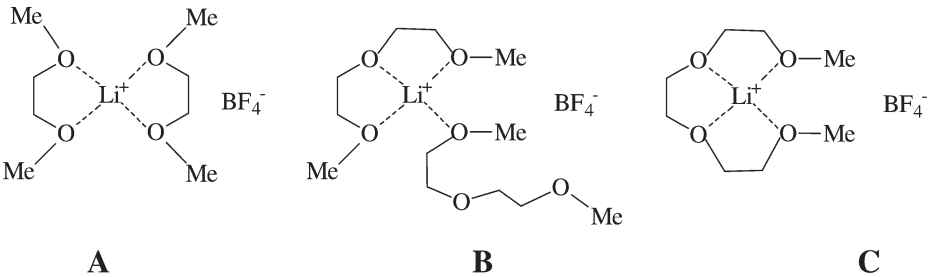
Catalytic activity of the polymer bases thus synthesized has been preliminarily evaluated using some classical bases-catalyzed reactions of acetylene such as alkynol synthesis and acetylene-allene isomerization.[21]

The polymer bases obtained show a remarkable catalytic activity in the synthesis of 2-methyl-3-butin-2-ol



DVBA

Scheme 4



Scheme 5

(MB) from acetone and acetylene (Table III, Scheme 8). MB is chosen as an important intermediate in fine organic synthesis[22,23] and an engine fuel additive enhancing its burning efficiency[24,25] as well as due to the that acetone can be produced from renewable feedstock (fermentation of starch).

When employed for the reaction in DMSO, new catalysts show the activity close to that of KOH : 93.7% and 98.0%, correspondingly. Notably, that unlike KOH, the polymer bases synthesized are easily isolated from the reaction mixture and can be used repeatedly (Table III). After the completion of the reaction (reaching the highest acetone conversion), the catalysts are used without additional treatment to continue the reaction with fresh portions of the reactants. The potassium fading out the catalyst from repeating run to run is almost negligible (3–6%, Table III) relative to its initial content indicating the complex stability.

Regeneration of the solid superbase catalysts is effected by their washing with methanol followed by treatment with methanol solution of KOH or CsOH and drying. The complete recovery of catalytic properties of the solid superbases has been proved experimentally.

The DVBA-tailored homopolymer superbases catalyze also the isomerization of methylpropargyl ether to allenyl ether (Scheme 9), the yield of the latter reaching 96%.

CONCLUSIONS

In conclusion, a conceptually new approach to the synthesis of cross-linked polyethylene oxide-acetal macrocycles with diverse size of polyethylene oxide chains and bridges has been developed. The approach comprises the cationic homopolymerization and copolymerization of originally synthesized monomer containing two acetal moieties and terminated with vinyloxy group, namely DVBA. The latter was quantitatively obtained by selective electrophilic addition of DEG to two molecules of DVDEG in the presence of trifluoroacetic acid. For the variation of sizes of the polyethylene glycol crown-like macrocycles inside the polymeric cross-linked networks, the cationic copolymerization of DVBA with DVDEG was employed. On the example of industrially important base-catalyzed reactions such as alkynyl synthesis and acetylene-allene isomerization of methyl propargyl ether, the synthesized polymers were shown to be prospective candidates for design of new solid polymer superbasic catalysts and selective absorbents of alkaline metal cations.

EXPERIMENTAL

DVDEG, a pilot product of A. E. Favorsky Irkutsk Institute of Chemistry SB RAS was washed with water, dried over K_2CO_3, and distilled twice. All characteristics of the monomer corresponded to the published data: bp 85°C (14 mmHg), n_D^{20} 1.4430.[9] DEG was purified by distillation, constants of the product matching the literature ones: bp 130°C (8 mmHg), n_D^{20} 1.4475.[26]

Lithium tetrafluoroborate ($LiFB_4$), purchased from Aldrich, was dried in vacuum (1 mmHg, 8 h) before use.

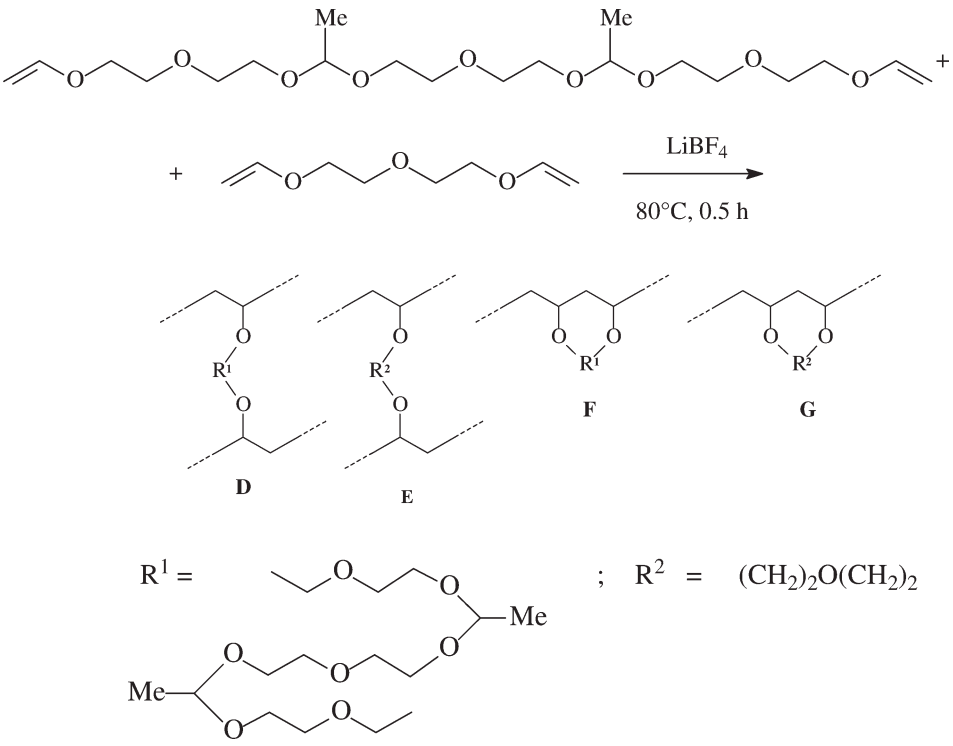
Trifluoroacetic acid (CF_3COOH) and $BF_3{\cdot}OEt_2$, both from Aldrich, were freshly distilled (72°C and 127°C, respectively).

The solvents (diethyl ether, dimethoxyethane, isooctane, methanol, toluene) were purified according to the common procedures.[27]

The monomer purity was controlled by GLC (for DVDEG), IR and ^1H NMR spectroscopy. GLC

TABLE II
Copolymerization of DVBA (M_1) and DVDEG (M_2) [80°C, 0.5 h, 0.25% $LiBF_4$, *i*-Octane : Toluene (3 : 1)]

Composition of monomer mixture, mol. pt.		*i*-Octane content relative to monomers	
M_1	M_2	mass, wt %	Yield, %
0.90	0.10	100	85
0.90	0.10	70	86
0.80	0.20	70	88
0.70	0.30	70	89
0.50	0.50	120	90
0.50	0.50	100	92
0.50	0.50	70	94



Scheme 6

analyses were performed on an Chrom-4 instrument, equipped with a heat conducting detector, 2400× 3.5 mm column, liquid phase: polyethylene glycol 20,000, 1%; solid phase: NaCl, 0.16-0.25 mm.

IR spectra were recorded on a "Bruker IFS 25" instrument in film (monomer) or KBr pellets.

^{1}H NMR spectra were obtained on a Bruker DPX 400 spectrometer at 400.1 MHz in DMSO-d_6 with HMDS as an internal standard.

Synthesis of DVBA (Scheme 1)

To a mixture of DVDEG (95 mmol, 15.00 g) and DEG (5.03 g, 47 mmol) was added dropwise CF_3COOH (0.075 g, 0.5 wt %) under stirring. The reaction was exothermic and after 10 min the temperature of the reaction mixture reached 40°C. After 2 h stirring, K_2CO_3 was added (0.12 g, 0.87 mmol) and resulted monomer (clear transparent viscous liquid, quantitative yield) was filtered and analyzed (IR- and ^{1}H NMR).

The elemental analysis of DVBA showed (%): C = 56.76, H = 9.02. Caltd. (%): C = 56.84, H = 9.08, witch was corresponding to $C_{20}H_{38}O_9$.

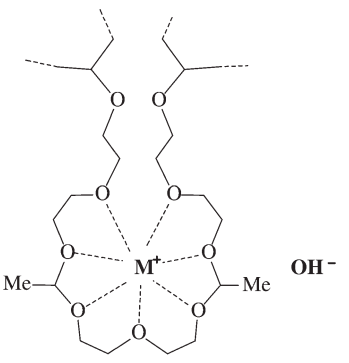
Polymerization of DVBA

Polymerization in the presence $BF_3{\cdot}OEt_2$

To a stirred solution of DVBA (2.00 g, 4.73 mmol) in toluene (2.00 mL) under argon, $BF_3{\cdot}OEt_2$ (0.02 g of 10% solution in Et_2O or 0.1 wt % relative to the monomer mass) was added at room temperature. After 10 min, the polymer formed was washed with Et_2O upon stirring and dried in vacuum up to the constant weight to give 2.00 g (yield 100%) of brown elastic material, insoluble in acetone, benzene, chloroform, ethanol (Table I).

Polymerization in the presence of complex $LiBF_4{\cdot}MeO(CH_2)_2OMe$ (a typical run)

To a stirred DVBA (6.00 g, 14.20 mmol) was added 5% solution of $LiBF_4$ (0.30 g) in dimethoxyethane (DME), 0.25 wt % relative to the monomer mass under argon at room temperature. The stirred mixture was kept at 80°C for 1 h. The colorless



M = K, Cs

Scheme 7

TABLE III
Synthesis of MB from Acetone and Acetylene in the Presence of the DVBA-DVDEG Copolymer − KOH Complex (K Contents 8.3%, Atmospheric Pressure, DMSO[a], Ambient Temperature)

Repeating run (cycle) number	C_2H_2 : acetone ratio, mol	Time, h	Acetone conversion, %	MB yield, %[b]	K lost, %
1	1.53 : 1	2	95.8	68.8	0.5
2	1.57 : 1	3	95.3	93.7	0.4
3	1.49 : 1	3	92.4	80.0	0.2
4	1.55 : 1	5	88.9	80.1	0.3
5	1.44 : 1	5	95.2	69.2	0.4
6	1.50 : 1	3	95.2	66.1	Not determined
7	1.50 : 1	5	67.3	54.6	Not determined
Reaction with KOH[c]					
1	1.55 : 1	3	100	98.0	Complete loss

[a] Swelling of copolymer complex in DMSO.
[b] Taking into account acetone conversion.
[c] KOH content corresponds to content of complex with respect to K content.

transparent solid product obtained was powdered, washed with a mixture of diethyl ether : petroleum ether (1 : 1), dried in vacuum until the constant weight (1 mmHg) to give 6.00 g (yield 100%) of the polymer as white powder, insoluble in acetone, benzene, chloroform, ethanol (some other selected results are summarized in Table I). The elemental analysis of poly-DVBA showed (%): C = 56.59, H = 8.92. Caltd. (%): C = 56.84, H = 9.08, witch was corresponding to $C_{20}H_{38}O_9$.

Copolymerization of DVBA and DVDEG (a typical run)

To the stirred mixture of DVBA (3.00 g, 7.10 mmol), DVDEG (1.10 g, 7.00 mmol), *i*-octane (6 mL) ,and toluene (2 mL) under argon at room temperature, was added 5% solution of $LiBF_4$ (0.20 g) in dimethoxyethane, 0.25 wt % relative to the monomers mass. The stirred mixture was kept at 80°C for 0.5 h. The opaque gel obtained was crushed was washed with diethyl ether: petroleum ether (1 : 1) and dried in vacuum until the constant weight (1 mmHg) to give 3.77 (yield 92%) of the polymer as white powder, insoluble in acetone, benzene, chloroform, ethanol (some other selected results are summarized in Table II). The elemental analysis of DVBA-DVDEG copolymer showed (%): C = 57.47, H = 8.92. Caltd. (%): C = 57.90, H = 9.04, witch was corresponding to $C_{28}H_{52}O_{12}$ (copolymer DVBA-DVDEG = 0.50 : 0.50).

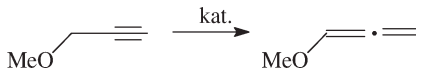
Synthesis of poly-DVDA-KOH complex (a typical run)

The powdered poly-DVBA (6.00 g, 14.20 mmol) was added to a solution of KOH (0.80 g, 14.28 mmol) in methanol (30 mL). The suspension was stirred at room temperature for 20 h; the polymer changed its color – from yellow to cream and finally to light-brown. The solvent was removed in vacuum at room temperature, the light-brown powder remained was dried in vacuum until the constant weight (1 mmHg) to give 6.80 g of the complex. The elemental analysis of complex obtained showed (%): C = 49.76, H = 8.02, K = 8.20. Caltd. (%): C = 50.19, H = 8.23, K = 8.15, witch was corresponding to $C_{20}H_{39}O_{10}K$.

Synthesis of copolymer DVDA-DVDEG-CsOH complex (a typical run)

The powdered copolymer (6.00 g, DVBA:DVDEG = 0.50 : 0.50) was added to a solution of CsOH (2.10 g, 14.00 mmol) in ethanol (50 mL). The suspension was stirred at room temperature for 20 h; the polymer changed its color – from yellow to cream and finally to light-brown. The solvent was removed in vacuum at room temperature, the light-brown powder remained was dried in vacuum until the constant weight (1 mmHg) to give 7.10 g of the complex. The elemental analysis of complex obtained showed (%): C = 45.96, H = 7.17, Cs = 18.10. Caltd. (%): C = 46.02, H = 7.32, Cs = 18.19, witch was corresponding to $C_{28}H_{53}O_{13}Cs$.

Scheme 8



Scheme 9

Synthesis of 2-methyl-3-butyn-2-ol (MB) in the presence of poly-DVBA-KOH complex (a typical run)

The copolymer DVBA : DVDEG (0.50 : 0.50)-KOH complex (1.00 g, K content 8.2%) was suspended in DMSO (50 mL). The suspension was saturated with acetylene at room temperature for 1.5 h, then to the stirred suspension acetone (1.00 g, 17.24 mmol) and toluene (0.50 g) were added (toluene was used as an internal standard for GLC analysis). After 3 h the mixture was analyzed by GLC to show the acetone conversion and the yield of MB to be 95.30% and 93.70%, respectively (some other selected results are summarized in Table III).

The same portion of the catalyst was used repeatedly. After completion of the synthesis, the reaction mixture was decanted from the solid catalyst. The latter was not washed off and not allowed to stand on air. A fresh portion (50 mL) of DMSO was added to the reaction vessel, and the above procedure was repeated. The catalyst (on seventh cycle the acetone conversion was 67.30%, and the MB yield was 54.60%) was proved to be active during seven cycles (Table III), further on the reaction was stopped.

Isomerization of methylpropargyl ether in the presence of poly-DVBA-KOH complex

A suspension of methylpropargyl ether (0.25 g, 3.60 mmol), DMSO (2.00 mL), and poly-DVBA-KOH complex (0.11 g, K content 8.2%) was heated under stirring (55–60°C) for 5 h. GLC analysis of the reaction mixture showed the ratio of methyl allenyl ether : methyl propargyl ether to be 96 : 4.

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