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Analysis of the End Groups of Poly(methyl methacrylate)

Andrzej Stolarzewicz, Barbara Morejko-Buż, Zbigniew Grobelny, Dorota Neugebauer*

Centre of Polymer Chemistry, Polish Academy of Sciences, 41-819 Zabrze, Poland

Summary: Methyl methacrylate polymerization by potassium hydride results in macromolecules with the methyl starting group. A side-reaction occurs during the process leading to potassium methoxide. It serves as the second initiator of the polymerization and gives macromolecules with the methoxy starting group. All macromolecules possess the methine group at the chain end after protonation. Potassium alkalide K^-, $K^+(15\text{-crown-}5)_2$ produces various active centres in the initial step of the polymerization. It results in macromolecules with the methyl, ethyl, methoxy and vinyl ether starting groups. However, the majority of macromolecules are formed on the species with two active centres. The termination reaction takes place during the polymerization, therefore, not all chains have the methine end group after protonation.

Introduction

Methyl methacrylate as a polar vinyl monomer polymerizes in the presence of several anionic initiators. One group of them includes alkali metal alkoxides [1-13]. Lithium *tert*-butoxide exerts a beneficial effect on the stability of active centres, decreasing the rate of termination [6,7]. Organometallic compounds, in particular lithium alkyls, belong to another group of anionic initiators for the polymerization of methyl methacrylate [14]. "Living" process proceeds in the presence of bulky lithium alkyls [15-18], whereas in the case of smaller lithium alkyls, especially n-butyl lithium, side reactions occur [19-26]. In order to avoid such effects, a phenantrene-based lithium system [27], metalloesters [28-30] or mixed aluminium and lithium alkyls [31] were used for example as initiators.

This paper presents experimental results concerning the polymerization of methyl methacrylate by potassium hydride suspension and by potassium alkalide K^-, $K^+(15\text{-crown-}5)_2$ solution in tetrahydrofuran. Potassium hydride was used till now as the initiator of anionic polymerization of oxiranes [32-35] and β-propiolactone [36]. First information on poly(methyl methacrylate) obtained by potassium hydride were described in [37]. On the other hand, potassium alkalide with dicyclohexano-18-crown-6 in tetrahydrofuran solution was

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applied for the polymerization of methyl methacrylate [38]. The process was fast at –78 °C and even at low monomer concentration. The polymers had molecular weights of the order of 10^5 and a high polydispersity. A triad tacticity determination showed that 53 % triads were syndiotactic, 40 % heterotactic and 7 % isotactic. However, it was then reported [39,40] that the use of other alkalides containing 18-crown-6, *i.e.* K^-, K^+(18-crown-6) and Na^-, K^+(18-crown-6) results in the "living" polymerization at 20 °C. The molecular weights of the polymers ranged from 5.6×10^4 to 7.87×10^5 and M_w/M_n was relatively low and equal to 1.3 – 1.6. The tacticity of the polymers was similar to that of the previous system.

It is worth noting that the potassium alkalide solution selected for the present work is known as the most stable among others [41]. Potassium cations in this alkalide form sandwich 1 : 2 complexes with 15-crown-5 instead of the flat 1 : 1 complexes in the case of 18-crown-6 or dicyclohexano-18-crown-6.

Experimental

Materials and polymerization procedure

Methyl methacrylate (Merck) was extracted with 5% NaOH, dried over $CaSO_4$ and then over CaH_2 and distilled. Tetrahydrofuran (POCH) was purified by the standard method [41]. 18-Crown-6 (Aldrich) was dried under vacuum at 50°C for 8 h. A 35 wt.-% dispersion of potassium hydride in mineral oil (Aldrich) was diluted with hexane in a dry argon atmosphere. The system was then mixed and decanted. The operation was repeated three times followed by a three-fold washing with tetrahydrofuran. Potassium hydride was finally dried in vacuum. Sodium hydride and lithium hydride (both Aldrich) were purified in the same manner.

The polymerization was conducted at 25 °C in a 50 cm^3 thermostatted reactor equipped with a magnetic stirrer and teflon valves enabling substrates delivery and sampling under argon atmosphere. Into the reactor containing the weight amount of potassium hydride, tetrahydrofuran and then methyl methacrylate were introduced while mixing. The initial concentration of monomer was equal to 2.0 mol/dm^3, the initial amount of potassium hydride ranged from 6 g/dm^3 (0.15 mol/dm^3) to 16 g/dm^3 (0.4 mol/dm^3). The polymerization was stopped by the addition of methanol. The precipitated polymer was washed five times with methanol and then dried under vacuum to a constant mass. Potassium methoxide was obtained at 25 °C by the dropwise addition of methanol to the potassium hydride suspension in tetrahydrofuran. The process was performed as long as hydrogen was observed to evolve. Then, methyl methacrylate was introduced into the reaction mixture. The polymerization procedure was the same as by the use of potassium hydride.

0.1 mol/dm^3 K^-, $K^+(15\text{-crown-5})_2$ tetrahydrofuran solution was prepared as in [42]. The polymerization in its presence was conducted in the reactor described in [41] at –30 and +25 °C. The initial monomer concentration ranged from 0.5 to 2.0 mol/dm^3, and the initial concentration of potassium alkalide was equal to 0.04 mol/dm^3. The polymerization procedure was the same as in the case of potassium hydride.

Measurements

The number-average molecular weight, M_n, and the polydispersity, M_w/M_n, of polymers were estimated by means of gel permeation chromatography (GPC) using a Spectra-Physics 8800 solvent delivery system with 10^4, 10^3 and 500 Å "Styragel" columns in series and Shodex SF 61 refractive index detector. Polystyrene standards of low polydispersity (PL Lab) were used to generate a calibration curve. ^{13}C NMR spectra of polymers in $CDCl_3$ were recorded at 20°C on a Varian VXR 300 multinuclear pulsed spectrometer operating at the ^{13}C resonance frequency of 75 MHz. Chemical shifts were referenced to tetramethylsilane serving as an internal standard. Infra-red spectra of methyl methacrylate and poly(methyl methacrylate) were acquired on a BIO-RAD FTS-40A Fourier transform infrared spectrometer in the range of 4000-700 cm^{-1} at a resolution of 2 cm^{-1} and for an accumulated 32 scans. Samples were prepared in a form of films on KBr plates obtained after evaporating of the solvent from tetrahydorfuran solutions or as solutions in tetrahydrofuran placed into 0.066 mm cell with KBr windows. The use of the IR method to determine the concentration of methyl methacrylate during the polymerization was described in [43].

ESI-MS experiments were carried out using a Finnigan LCQ ion trap mass spectrometer (Finnigan, San Jose, CA, USA). Samples were dissolved in a methanol-chloroform mixture (1 : 9 v/v) at a concentration of 0.5 mg/mL, and introduced into the electrospray interface at a flow rate of 2 μL/min. The potential at the tip of the needle was set to 4.5 kV. The capillary temperature was adjusted to 200°C. Mass spectra were acquired in positive and negative ion modes. The ESI-MS^n experiments were performed using the Finnigan LCQ ion trap mass spectrometer with helium as a collision gas. Intensity of the parent ion was adjusted to approximately 30% of its initial abundance.

Results and discussion

A study on the first initiating system demonstrated potassium hydride to be insoluble in methyl methacrylate tetrahydrofuran solution. The reaction mixture was still heterogeneous during the polymerization.

Data presented in Table 1 show that the amount of potassium hydride does not influence the molecular weight of obtained polymers. This phenomenon remains under consideration.

Table 1. Influence of the amount of potassium hydride on the methyl methacrylate polymerization in tetrahydrofuran. Initial concentration of the monomer 2 mol/dm^3. Temperature 25°C.

No.	Initial amount of potassium hydride, in mol/dm^3	Molecular weight of polymer, M_n (GPC)	Polydispersity of polymer, M_w/M_n (GPC)	Reaction time,[a] t [min]
1.	0.15	32 000	3.5	100
2.	0.2	24 000	3.7	90
3.	0.3	30 000	2.9	40
4.	0.4	26 000	3.5	25

[a] for 95% monomer conversion.

A series of GPC measurements were performed during the polymerization. Two fractions of the polymer were found to form at the beginning of the process; one with a high molecular weight and the second with a low molecular weight (Fig. 1a). Differences between them diminished gradually (Fig. 1b) and finally the almost unimodal molecular weight distribution was observed in the chromatogram (Fig. 1c). Thus, two kinds of initiating species were expected to exist in the reaction mixture.

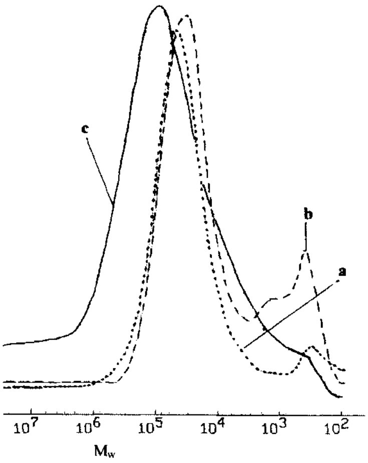


Fig. 1. GPC curves of poly(methyl methacrylate) obtained after 1h (a), 2h (b) and at the end of polymerization (c). Initial concentration of monomer 2 mol/dm^3. Initial amount of potassium hydride 0.2 mol/dm^3. Temperature 25°C.

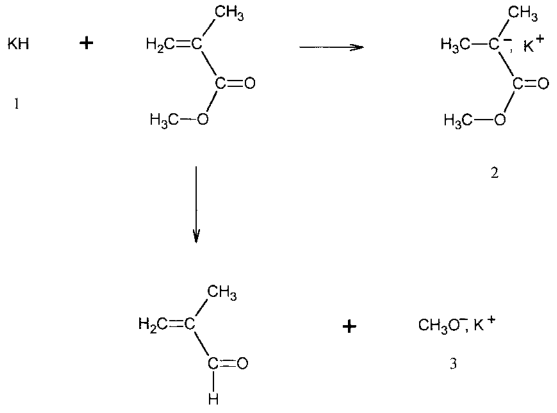
As mentioned, side reactions may occur in the anionic polymerization of methyl methacrylate because the initiator attacks not only the vinyl group but also the carbonyl group of the monomer. For instance, lithium methoxide and *tert*-butyl isopropenyl ketone were products of the side reaction when *tert*-butyl lithium was used as the initiator [44]. The alkoxide was found to be inactive in further processes. The second reaction product was incorporated into a part of macromolecules leading to "dormant" vinyl ketone terminated chain ends. However, some of them added methyl methacrylate after a certain time.

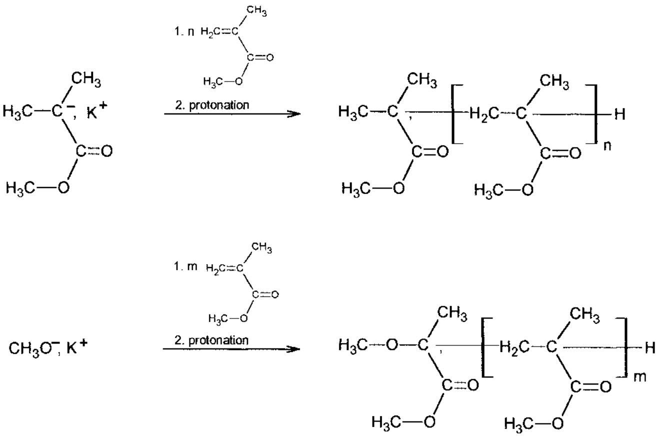
On the other hand, it was known that the reactivity of alkali metal alkoxides possessing ethereal oxygen atom increase with the size of counter-ion, *i.e.* in the order $Li^+ < Na^+ < K^+$ [2]. ESI-MS experiments were carried out to check if potassium methoxide, *i.e.* the presumable in this work side reaction product could become the second initiator of the polymerization [37]. The ESI mass spectrum in positive-ion mode of poly(methyl methacrylate) revealed the presence of sodium and potassium adduct ions, with the sodium adducts of higher intensity. The same repeating unit of 100 Da equal to the molecular weight of methyl methacrylate and the same residual mass of 32 Da were calculated for both main sets of adduct ions. Therefore, in contrast to the literature data, it was assumed that the macromolecules possessed the methoxy starting group, *i.e.* that situated at the beginning of the polymer backbone, (31 Da) and the methine proton at the chain end (1 Da).

Potassium methoxide was then used as the initiator of methyl methacrylate polymerization. The reaction occurred slower than in the presence of potassium hydride and a model polymer with the molecular weight equal to 2000 Da was obtained. In this case the polymer possessed exclusively the methoxy starting group. Its ESI mass spectrum showed a set of sodium adduct ions situated at the same m/z as it was found for the polymer obtained by potassium hydride. In ^{13}C NMR spectra of the model polymer a signal at 59.1 ppm was assigned to the carbon of $\underline{C}H_3OCH_2$ group. The similar signal was found in the ^{13}C NMR spectrum of the polymer prepared by potassium hydride.

The set of major peaks corresponding to a peak-to-peak mass increment of 100 Da was also observed in the ESI mass spectrum in negative-ion mode of the studied polymer. However, the residual mass of 2 Da indicated that these peaks represent macromolecules of a type different from those found in positive-ion mode. Analysis of their structure led to the conclusion that the methyl group was the starting group in this case. This was formed as the result of hydrogen addition (1 Da) to the methylene group of methyl methacrylate. The methine proton (1 Da) was present in the chain end after protonation of the reaction mixture.

It means that two kinds of macromolecules were formed in the studied polymerization (Scheme 1).





Scheme 1

The initiation by potassium hydride resulted in macromolecules with the methyl starting group. Potassium methoxide obtained in the side reaction gave only the low molecular fraction consisting of macromolecules with the methoxy starting group. All macromolecules possessed the methine group at the chain end. It is worth to emphasise that this polymer differs in the structure from that obtained by *tert*-butyl lithium [44]. In the latter case using the MALDI-TOF technique it was clearly shown that all macromolecules possessed the same starting group but various end groups. The vinyl compound formed in the side reaction became a co-monomer causing further dissimilarity in the polymer structure.

Sodium hydride and lithium hydride were also proved as possible initiators of the methyl methacrylate polymerization. However, they turned out to be practically inactive. Only small amounts of oligomers were found in the reaction mixture after 24 h. That was in a good agreement with the earlier statement [45] that the reactivity of potassium hydride in various processes is much higher than of sodium hydride or lithium hydride.

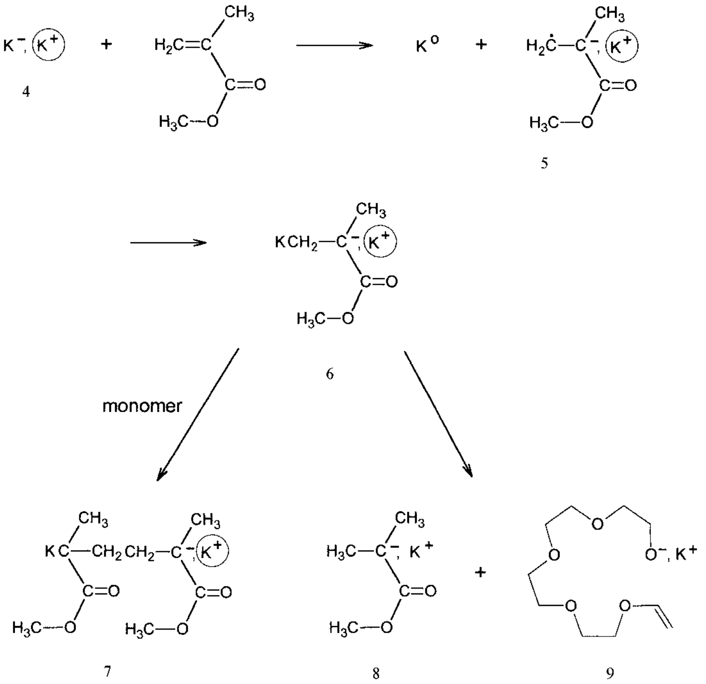
In the second series of experiments methyl methacrylate was polymerized by K^-, $K^+(15\text{-crown-}5)_2$ **4**. In contrast to the system containing potassium hydride the reaction mixture was homogeneous. Chromatographic analysis of the gas phase showed the presence of methane. Benzyl methyl ether was found by GC-MS in the liquid phase after quenching with benzyl bromide. The polymerization was very fast. The monomer was not observed in the solution after 30 s. The values of molecular weights of polymers obtained and the values of M_w/M_n are presented in Table 2. Because of the rapid polymerization it was not possible to determine changes in the molecular weight distribution during the process.

Table 2. Influence of the initial monomer concentration on the methyl methacrylate polymerization by potassium alkalide in tetrahydrofuran solution. Initial concentration of K^-, $K^+(15\text{-crown-5})_2$ = 0.04 mol/dm^3. The reaction time <30 s.

No.	Initial monomer concentration, mol/dm^3	Temperature, °C	Molecular weight of polymer, M_n (GPC)	Polydispersity of polymer, M_w/M_n (GPC)
1.	0.5	-30	3 300	2.1
2.	1.0	25	11 300	2.4
3.	2.0	25	25 000	3.0

The analysis of ^{13}C NMR spectra of the polymer with the low molecular weight (the sample 1 in Table 2) revealed carbon atom signals of the methoxy group at 59.1 ppm and the methyl group connected with the CH_2 group at 15.1 and 23.9 ppm, respectively. Weak signals characteristic for the vinyl ether group was presented at 86.5 and 151.7 ppm, as it was previously observed for poly(methyloxirane) obtained by **4** [46]. The signal at 27.8 ppm was assigned to two CH_2 groups connected mutually. A comparison of the intensity of all signals shows that the most of macromolecules possess the CH_2-CH_2 group. Signals of the carbon atoms of the methine group as well as of the ketone group were identified at 54.4 and 192.2 ppm, respectively. Thus, it appeared that macromolecules with the methyl, ethyl, methoxy and vinyl ether starting groups, as well as with the CH_2-CH_2 group in the chain, were formed during the polymerization.

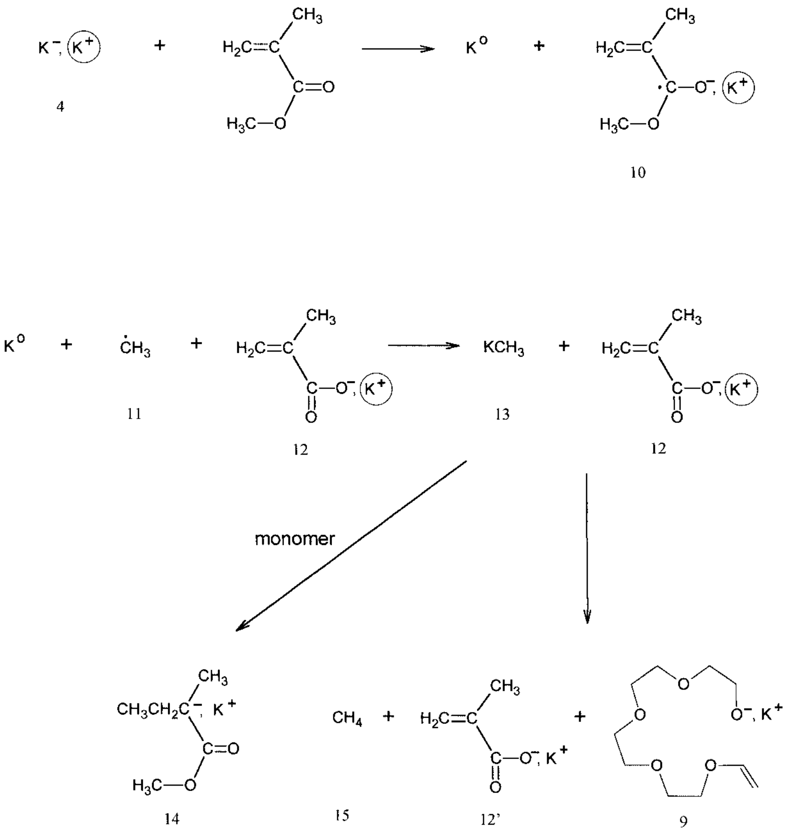
Basing on these results it was proposed that three reactions occurred in the initial step of the process. In the first one the electron is transferred from K^- of **4** to the double bond of the monomer (Scheme 2).



Scheme 2

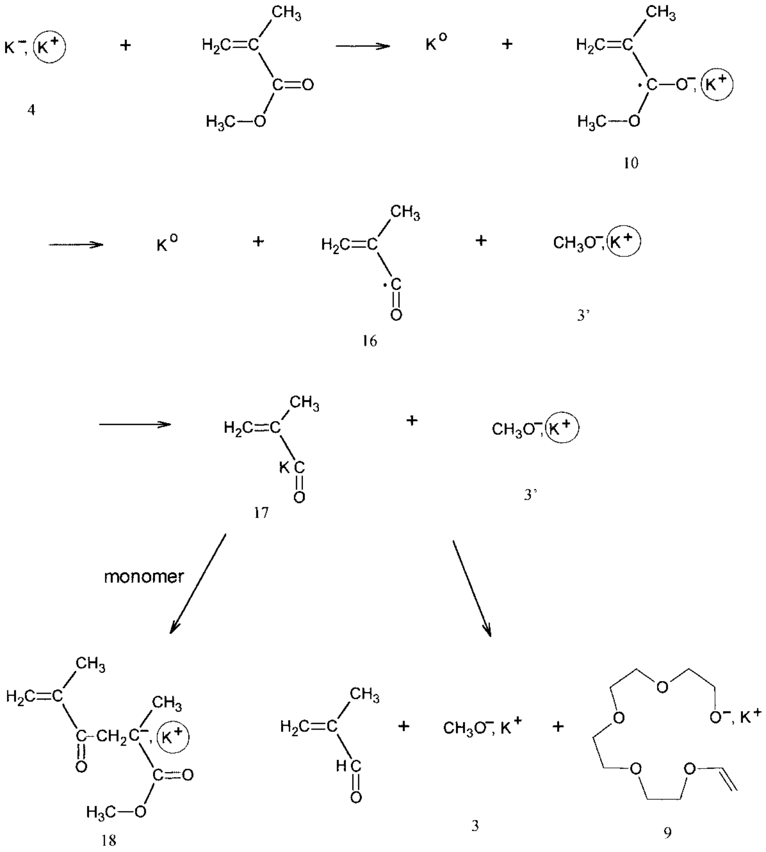
The radical anion **5** formed in this reaction recombines with K^0 giving the compound **6** with two active centres. In the first one the enolate anion possesses the potassium cation complexed by two crown molecules as the counter ion. The addition of the monomer molecule to the organometallic active centre results in a dimer **7** with the irregular head-to-head linkage. In the side reaction **6** reacts with crown ether giving new polymerization initiators, *i.e.* **8** and **9**. The crown ring opening under the influence of organometallic compounds was already described in the literature [47,48].

The transfer of the electron from K^- occurs also to the carbonyl group of methyl methacrylate. It results in the radical anion **10**, which can decompose in two ways (Scheme 3 and 4). The methyl radical **11** and the potassium salt **12** are the products formed via homolytic alkyl-oxygen bond cleavage of **10**. The former recombines with K^0 to methylpotassium **13**. It reacts then with the monomer or crown ether. The alkyl-oxygen bond cleavage in aliphatic esters by Na^-, K^+(18-crown-6) tetrahydrofuran solution was earlier described in [49]. That reaction resulted in the formation of an alkane and a salt of carboxylic acid.



Scheme 3

The decomposition of **10** can occur also via elimination of potassium methoxide **3'**. The radical **16** formed in this reaction recombines with K^0 giving the organometallic compound **17** which may then react with methyl methacrylate or crown ether.



Scheme 4

The same carbon-oxygen bond cleavage was earlier observed in the reaction of K^-, K^+(18-crown-6) with aromatic esters [50].

It is worth noting that in the present work potassium anions were assumed to react in two steps with the two electron transfer. That mechanism was recently clearly proved by Perrin [51] for reactions of potassium anions.

It seems that several compounds formed in the studied system, *e.g.* **3**, **6**, **8**, **9** and **13** are the real initiators of methyl methacrylate polymerization by **4**. They are incorporated into the macromolecules as the starting groups or as the group initiating the chain growth on two active centres. The experimental results show that **6** is the main initiating species. Unfortunately, attempts made to explain the role of the other side reaction products, also with the use of ESI-MS technique, were unsuccessful.

The presence of the ketone group in the polymer confirms the results of the work [52] concerning termination of the growing chain. It was found in that work that the primary mode of chain termination is associated with a unimolecular back-bitting reaction of the ester enolate anion with the penultimate ester group to form a six-membered ring, β-keto ester group at the chain end. Therefore, in the studied by us process only a part of macromolecules has the methine group at the chain end after protonation.

Conclusions

Two kinds of macromolecules, *i.e.* with the methoxy and the methyl starting group are obtained in the heterogeneous polymerization of methyl methacrylate by potassium hydride. The methine group is presented at the chain end after protonation. The selected potassium alkalide produces various active centres in the initial step of the polymerization in the homogeneous system. It results in macromolecules with the methyl, ethyl, methoxy and vinyl ether starting groups. However, the polymer chains are mainly formed on the species **6** possessing two active centres. The termination reaction excludes definitively the "living" character of the studied process.

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