

Iodination of poly(ethylene glycol) by a mixture of triphenyl phosphite and iodomethane

Ūla Bernadišiūtė*,

Tomas Antanėlis,

Aušvydas Vareikis,

Ričardas Makuška

*Department of Polymer Chemistry,
Vilnius University,
Naugarduko 24,
LT-03225 Vilnius, Lithuania*

Iodination of poly(ethylene glycol) (PEG) with the molecular weight 2000 and its monomethyl ether (MPEG) by the iodinating mixture of triphenyl phosphite and iodomethane was studied in detail. The structure of the synthesized PEG (MPEG) iodides was confirmed by elemental analysis, FT-IR and ¹H NMR spectroscopy. The degree of iodination (DI) of PEG (MPEG) was determined by two independent methods based on argentometric titration and ¹H NMR spectra. Argentometric titration (the Mohr method) was found to be limited by the incomplete hydrolysis of PEG (MPEG) iodides, while the analysis based on ¹H NMR spectroscopy became accurate at a high DI only. The highest DI of PEG (MPEG) was reached carrying out the reaction of iodination in a hermetic reactor at 120 °C for 5 hours and using a double-fold excess of the iodinating mixture. The synthesized PEG (MPEG) iodides with DI 90–95 mol% could be useful for “grafting to” or even for polycondensation with diamines.

Key words: poly(ethylene glycol), iodination, PEG, Mohr method, PEGylation

INTRODUCTION

Halogen-containing compounds are useful intermediates in organic synthesis [1,2]. Halides can be employed in carbon–carbon bond forming reactions [3–5] or converted into nucleophilic organolithium compounds [6]. They have also been utilized in nucleophilic reactions for the preparation of amines and ethers [6]. Although alkyl iodides are less stable than chlorides or bromides and iodine is the most expensive of the common halogens, they are more reactive in nucleophilic substitution reactions than the other corresponding halides, and in some cases iodides are the only reactive halides [7]. The most common route to synthesize iodides is the conversion of alcohols [8,9].

Besides the well known simple “classical” iodination method [10], a search for better methods of iodination was pursued with the point to get a higher yield, to simplify the reaction course, etc. Several methods have been utilized using a variety of reagent systems, such as BF₃·Et₂O/NaI [11], P₄/I₄ [12], Cl₂SO/DMF/KI [13], MgI₂ [14], HI [15], ClSiMe₃/NaI [16], C₆H₆/hexamethylphosphoramide [17], CeCl₃·7H₂O/NaI [18], PPh₃/2,3-dichloro-5,6-dicyanobenzoquinone/RN⁺X⁻ [19], KI/BF₃·Et₂O [20], PPh₃/diethyl azodicarboxylate/LiI [21], ZrCl₄/NaI [22], I₂/petroleum ether [23]. NaI/Amberlyst 15 (strongly acidic macroporous resin with sulfonic acid functionality, which is suitable for non-aqueous catalysis) has also been used for the iodination of a variety of alcohols (except tertiary) in good yields [24]. Polymer-supported triphenylphosphine/I₂/imidazole has been adapted for the iodination of benzyl alcohols [25]. The iodination of benzyl, allyl and aliphatic alcohols by triphenylphosphine and iodine

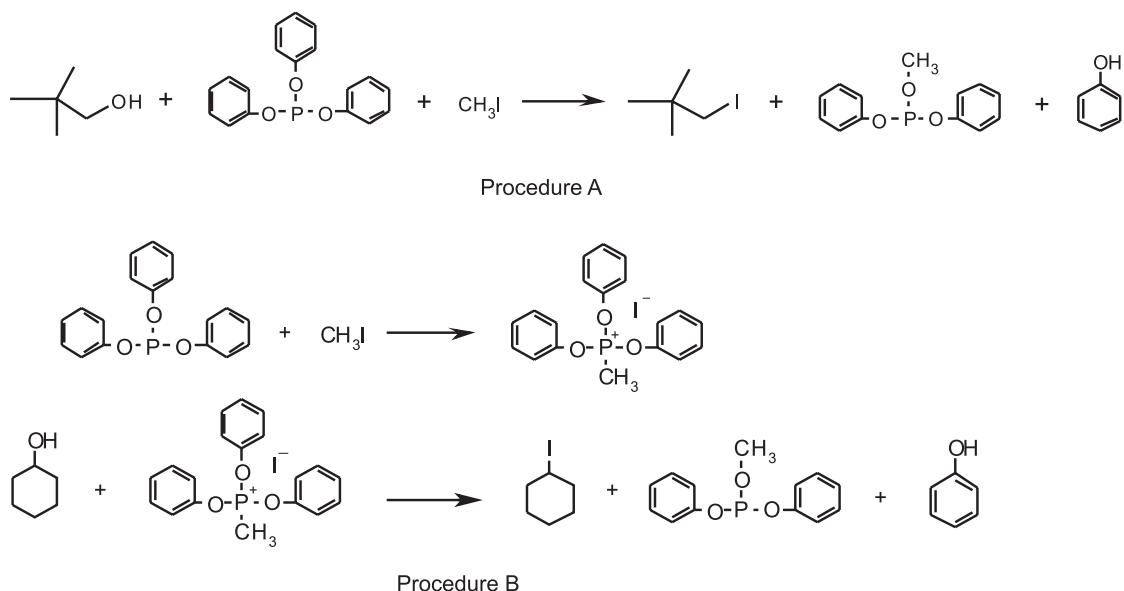
under solvent-free conditions using microwave irradiation was found to be a simple and highly chemoselective process [26].

A relatively simple method for iodination of alcohols was proposed by Rydon [27]. He reported two different procedures which were applied for low molecular weight compounds, e. g., neopentyl alcohol and cyclohexanol. Operating according to procedure A, all reactants were added at once, and the temperature of the mixture was slowly raised to 130 °C (Scheme 1). The degree of iodination of neopentyl alcohol was 64–75%. Operating according to procedure B, at first triphenyl phosphite and iodomethane were mixed in a flask, and the temperature was raised to 120 °C to get a brown viscous mixture (Scheme 1). At the second step, an alcohol was added to the oily methyltriphenoxyphosphorus iodide, the reaction mixture was shaken gently until homogenization and allowed to stand overnight at room temperature. The degree of iodination of cyclohexanol was 74–75%. Pure iodinated compounds were obtained by distillation of the crude products.

Procedure A is simpler to perform, but procedure B is preferred for sensitive alcohols and in cases where elimination of olefins is expected, e. g., using tertiary and some secondary alcohols. Procedure A is better for sterically hindered alcohols, while procedure B is especially useful for alcohols sensitive to rearrangement or alkene formation.

Although there are a lot of methods of the iodination of primary, secondary or tertiary alcohols, information related to poly(ethylene glycol) (PEG) iodination is scarce. PEGs with a narrow molecular weight distribution ($M_w / M_n = 1.05$ or less) are well defined, simple and easily synthesized polymers possessing unique properties such as solubility in polar and non-polar solvents. They can form complexes with a number of

* Corresponding author. E-mail: Ula.Bernadisiute@chf.vu.lt



Scheme 1. Synthesis of neopentyl iodide and cyclohexyl iodide using procedures A and B of the Rydon method, respectively

metals, readily adsorb to surfaces changing their properties, and render water-solubility for certain insoluble molecules [28]. Modifications of natural and synthetic polymers by PEG (PEGylation) results in block or comb copolymers which are of interest for biotechnology, biomedicine and detergency [29, 30]. However, only “activated” (containing a more reactive group than hydroxyl) PEG could be attached to surfaces or other macromolecules. “Activation” of PEG by transforming its hydroxyl groups into more reactive groups such as carboxyl, maleimide, vinyl sulphone, pyridyl disulphide, amine, chloride, bromide and iodide is known [31, 32].

In the present work, the relevance of the modified Rydon method for iodination of PEG and poly(ethylene glycol) methyl ether (MPEG) of medium molecular weight (M_r 2000) was studied for the first time. Modification of the Rydon method included the use of a hermetic flask that prevented the loss of volatile iodomethane and avoided the oxidation of the reaction species resulting in higher yields of colourless products. A discussion on the purification and analysis of iodinated PEGs and optimal iodination conditions is presented.

EXPERIMENTAL

Materials

Poly(ethylene glycol) (PEG) (M_r 2000), poly(ethylene glycol) methyl ether (MPEG) (M_r 2000), iodomethane (99%) and triphenyl phosphite (97%) were obtained from “Fluka”.

Synthesis of poly(ethylene glycol) methyl ether iodide (MPEGI) and poly(ethylene glycol) iodide (PEGI)

MPEG (20.0 g, 10 mmol), triphenyl phosphite (6.20 g, 20 mmol) and iodomethane (2.84 g, 20 mmol) or PEG (20.0 g, 10 mmol), triphenyl phosphite (12.40 g, 40 mmol) and iodomethane (5.68 g, 40 mmol) were placed into a 100 ml hermetic flask. To reduce the loss of volatile compounds, iodomethane was added at the end. The reactor was heated in an oil bath up to 60 °C and kept at this

temperature until MPEG dissolved. Then the temperature slowly (during one hour) was raised up to 120 °C, and the reaction was carried out at this temperature for 5 hours. The reaction mixture was cooled, extracted with distilled water (2×25 ml), and the aqueous extracts were neutralized with 0.5 M NaOH solution to pH \approx 7. Subsequently MPEG or PEG solution was evaporated to dryness in a vacuum oven at 50 °C for 8 h to give 20.50 g of MPEGI (yield 97.8%) or 21.20 g of PEGI (yield 95.5%).

Purification of PEGI and MPEGI

In order to purify crude PEGI and MPEGI from inorganic salts and low molecular compounds, they were dialysed against water. To purify crude PEGI and MPEGI from unreacted MPEG or PEG, they were treated with a solution of styrene-maleic anhydride (ST-MAA) copolymer.

Dialysis: 5 g of PEGI (MPEGI) was diluted with 10 ml of distilled water and dialyzed against water for 48 h using visking dialysis tubing MWCO 3.5 kDa and changing water 3 times per day. The dialysis solution was concentrated using a rotating evaporator until solid residue. Subsequently solid PEGI (MPEGI) was dried in a vacuum oven at 50 °C.

Conditioning with a ST-MAA copolymer: 2 g of PEGI, 4 g of a styrene-maleic anhydride copolymer and 40 ml of benzene were placed into a two-neck round-bottom reaction flask fitted with a condenser and thermometer. The reaction mixture in the flask was stirred for 30 min at 60 °C. The solid fraction was filtered off, and the filtrate was concentrated until solid residue using rotating evaporator. Subsequently solid PEGI was dried in a vacuum oven at 50 °C.

Spectroscopic measurements

The infrared absorption spectra were recorded with a Perkin Elmer Spectrum BX spectrometer under dry air at 20 °C by the KBr pellet method. ^1H NMR spectra of the samples dissolved in CDCl_3 were recorded on a Unity Inova Varian 300 MHz spectrometer at 29 °C.

Determination of degree of iodination of PEG (MPEG)

The degree of iodination (DI) of PEG (MPEG) was calculated according to iodine content in iodination products determined experimentally and from ^1H NMR spectra of those products. The DI (mol%) is expressed as the average number of covalently attached iodine per 100 molecules of iodinated MPEG or 50 molecules of iodinated PEG (PEG contains two hydroxyl groups in every molecule).

Iodine content was determined by argentometric titration using the Mohr method [33]. Argentometric titration of the samples was done before (gives the content of iodide anions) and after alkaline hydrolysis (gives the total content of iodine). Hydrolysis of MPEGI (PEGI) in 0.5 M NaOH solution in methanol was carried out in hermetic flasks at 80 °C. One gram of MPEGI or PEGI was dissolved in 25 ml of alkaline methanol, and the solution was kept for 3 h at the reaction temperature. The solution was cooled and titrated with an aqueous solution of 0.1 M AgNO_3 . The content of iodine I_T (%) was calculated as follows:

$$I_T = \frac{126.9 \cdot c \cdot V}{m} \cdot 100,$$

where 126.9 is the molecular weight of iodine, c is the molar concentration of AgNO_3 , V is the volume (ml) of AgNO_3 solution, and m is the weight of a sample (g).

The content of iodine I (%) covalently attached to PEG (MPEG) was calculated as follows:

$$I = I_T - I_A,$$

where I_T and I_A are the total iodine content (%) and the content of iodide anion (%), respectively.

The degree of iodination (mol.%) of PEG (MPEG) was calculated by the following equation:

$$DI = \frac{2000 \cdot I}{N \cdot (100 \cdot 126.9 - I \cdot (126.9 - 17))} \cdot 100,$$

where N is the number of hydroxyl groups per molecule ($N = 1$ for MPEG and $N = 2$ for PEG), and 17, 126.9 and 2000 are the molecular weights of the OH-group, iodine and PEG (MPEG), respectively.

The degree of iodination (mol.%) of PEG was evaluated from ^1H NMR spectra of the iodinated products. The calculation was done referring to the ratio of the signal at 3.29 ppm attributed to the iodine-bound methylene, to the broad signal at 3.66 ppm attributed to the oxymethylenes in PEG backbone (Fig. 1).

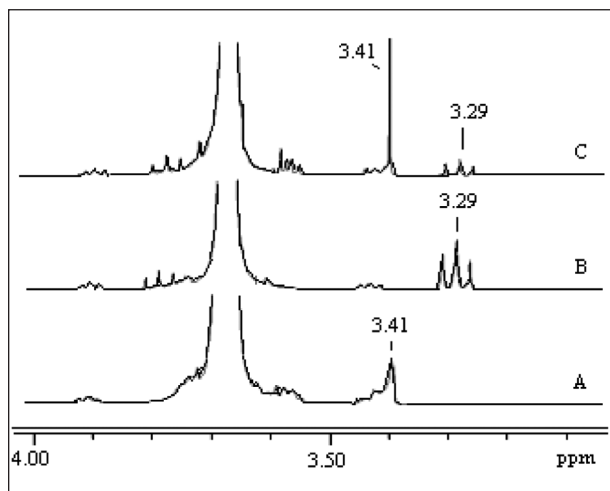


Fig. 1. Fragment of ^1H NMR spectra of MPEG (A), PEGI (B) and MPEGI (C)

The degree of iodination (mol.%) of MPEG (PEG) was calculated by the following equation:

$$DI = \frac{180 \cdot A}{2 \cdot N \cdot (A + B)} \cdot 100,$$

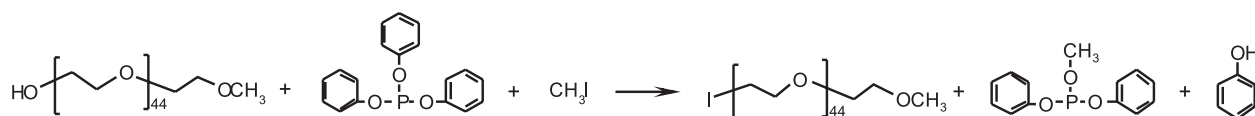
where A and B are the relative intensities of the signals of $-\text{CH}_2\text{-I}$ and $-\text{CH}_2\text{-O-}$, respectively; N is the number of hydroxyl groups per molecule ($N = 1$ for MPEG and $N = 2$ for PEG), 180 is the number of protons in MPEG (PEG), 2 is the number of protons in $-\text{CH}_2\text{-I}$.

The energy of activation of MPEG iodination was determined studying the kinetics of the reaction at 110–130 °C. The initial rate of the iodination reaction was calculated as a positive value of the analytically solved first-order derivative of the function $C_{\text{MPEGI}} = f(t)$. C_{MPEGI} after a certain duration of the reaction was calculated from the DI of the iodinated MPEG determined by Mohr's titration.

RESULTS AND DISCUSSION

Purification and identification of MPEGI (PEGI)

MPEG (PEG) iodination products contain unreacted raw materials and side products of the reaction, including phenol or phenolates and diphenyl methyl phosphates (Scheme 2). Iodination of PEG can result in two products – PEG iodide and PEG diiodide. Since oligomeric materials MPEGI and both forms of PEGI exhibit almost the same solubility as the starting materials MPEG or PEG, purification of these compounds is very complicated. Fortunately, residual MPEG (PEG) usually does not



Scheme 2. Synthesis of poly(ethylene glycol) methyl ether 2000 iodide by the Rydon method

affect successive reactions of MPEGI (PEGI) forming the ballast part of the materials. Purification of MPEGI (PEGI) from low molecular compounds was solved by simple dialysis through a semi-permeable membrane. Dialysis through a membrane with MWCO 3.5 kDa resulted in a partial loss of the target products with the molecular weight ca. 2200. The loss was quite large, usually in the range of 20 to 30%, making this procedure of purification unacceptable for routine use. DI of PEG after dialysis rose for ca. 3–6%, indicating that the low molecular fraction in crude PEGI was not large.

The purity of both crude and purified products was tested by ^1H NMR spectroscopy (Fig. 2). Crude iodinated PEG contained impurities in the form of phenol (6.82; 7.18 ppm, 5H, m, Ar-H) and triphenyl phosphite (7.20; 7.38 ppm, 5H, m, Ar-H). These data evidently demonstrated that extraction of the target product using distilled water didn't help to dispose side products of organic origin which were likely in the form of phenolates. Purification of the crude PEGI by dialysis was efficient in removing phenol or phenolates, and that was proved by disappearance of the signals at 6.82 and 7.18 ppm and by the reduction of triphenyl phosphite content. Nevertheless, even purified PEGI contains trace amounts of aromatic side products of the iodination reaction. The presence of inorganic salts in the purified PEGI is unlikely since the conductivity of the dialysis solution at the end of the process is the same as of distilled water (ca. 7 mS).

An attempt was made to remove unreacted PEG and, possibly, partially iodinated PEG by the use of an ST-MAA copolymer. The idea is based on a presumption that the hydroxyl group containing PEG molecules should form polymer-polymer complexes with the carboxyl group containing the partially hydrolyzed ST-MAA copolymer [34] which subsequently should be removed as an insoluble (gel) fraction. Conditioning of crude PEGI by a ST-MAA copolymer reduced the content of phenol but did not eliminate it (Fig. 2). Additionally, purification by the use of a ST-MAA copolymer helped to reduce the content of unreacted PEG thus increasing DI by 2 to 5%. Unfortunately, the ST-MAA copolymer left his "sign" in the

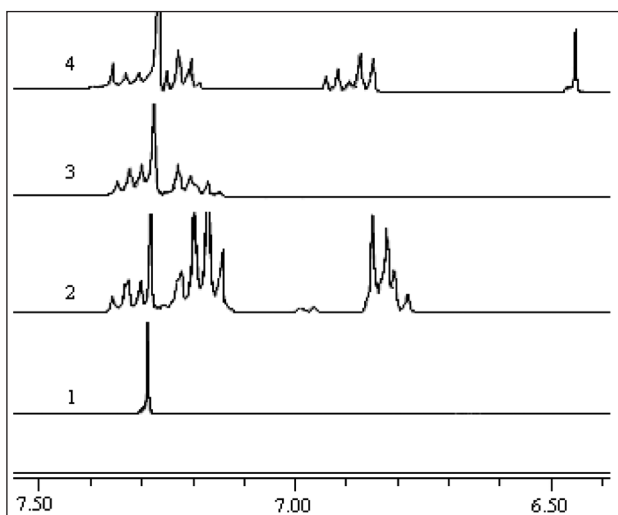


Fig. 2. Fragment of ^1H NMR spectra of PEG (1), crude PEGI (2), PEGI purified by dialysis (3) and PEGI purified using ST-MAA copolymer (4)

spectrum in the form of the signal at 6.45 ppm, which could be attributed to vinyl protons of residual monomers in the copolymer.

Determination of the DI of MPEG (PEG) by argentometric titration seems to be simple, but in fact it is not. There are three main argentometric titration methods: those of Mohr, Volhard and Fajans [35]. The Fajans method is complicated and time-consuming. The Volhard method is not suitable for the analysis of iodinated products got by the Rydon reaction since a Fe^{3+} containing indicator gives a violet-purple colour with phenolic compounds. The Mohr method is suitable, but requires hydrolysis of iodinated compounds. It was determined by us that the hydrolysis of low molecular compound 1-iodopentane was complete within 3 h, making the Mohr method the most acceptable.

Our experiments show, however, that the hydrolysis of PEGI and MPEGI is the most critical factor for the accuracy of DI determination by argentometric titration. The course of hydrolysis of PEGI in alkaline water and in methanol at two concentrations of NaOH at 80 °C is presented in Fig. 3. Hydrolysis in aqueous solutions was fast during the first 3 hours, but later it became rather slow, pointing to a very long duration of the reaction. Interestingly, hydrolysis in the solution with lower concentrations of NaOH proceeded faster. Hydrolysis of PEGI in methanolic solutions was much faster (Fig. 3) but, unfortunately, the extent of hydrolysis hardly exceeded 90%. A similar extent of hydrolysis (about 90%) was reached while carrying out the reaction of PEGI hydrolysis in aqueous 0.5 M NaOH solution under reflux. Incomplete hydrolysis of PEGI is the main drawback when adapting the Mohr method for the determination of iodine content in iodinated PEG.

The course of MPEG (PEG) iodination was followed by FT-IR and ^1H NMR spectroscopy. A wide absorption band of stretching vibrations of $-\text{OH}$ groups at 3440 cm^{-1} becomes weak and completely disappears when the extent of MPEG iodination exceeds 75%. MPEGI exhibits absorption bands of C-I stretching vibrations at 770 and 694 cm^{-1} , which is a direct evidence of the formation of an iodinated product. FT-IR analysis revealed also

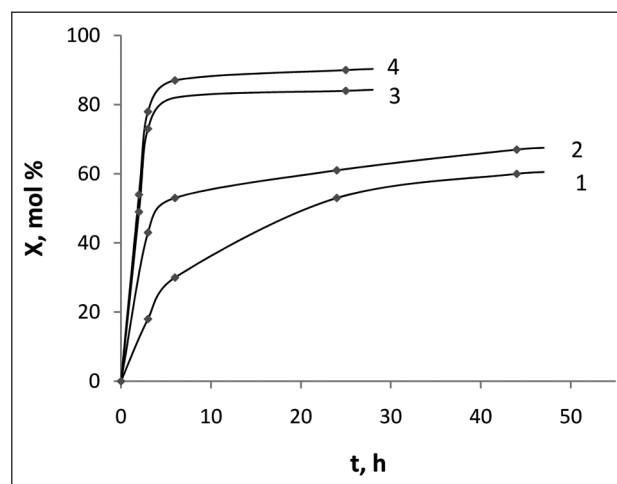


Fig. 3. Dependence of the extent of hydrolysis of PEGI on the reaction time in 1 M aqueous NaOH (1), 0.5 M aqueous NaOH (2), 1 M NaOH in methanol (3) and 0.5 M NaOH in methanol (4)

the presence of a new absorption band at 507 cm^{-1} evidencing the presence of carbon-attached iodine.

^1H NMR spectra of MPEG and of the iodinated products MPEGI and PEGI are presented in Fig. 1. A broad multiplet signal at 3.66 ppm belongs to the protons in oxyethylene groups of the backbone $-\text{[CH}_2\text{-CH}_2\text{-O]}_n$ of PEG, while a triplet signal at 3.29 ppm is attributed to the protons of $-\text{CH}_2\text{-I}$. The spectra of MPEG and MPEGI additionally contain a signal at 3.41 ppm, which evidences the presence of $\text{CH}_3\text{O-}$ groups. Although the intensity of the signal at 3.66 ppm is about a hundredfold higher than that at 3.29 ppm, moreover, the first one contains satellite signals at 3.42 and 3.91 ppm, the ratio of these signals could be used for determination of the degree of iodination with a satisfactory accuracy, if DI is sufficiently high (>50%). The DI of PEG determined from ^1H NMR spectra is usually higher by 2–5% compared to that determined by argentometric titration (Table 1). This small difference is well expected considering an incomplete hydrolysis of PEGI (MPEGI).

Table 1. Degree of iodination of PEG obtained within 3 hours of reaction

No.	[IM]* : [PEG], molar ratio	Temperature, °C	DI, mol%	
			Titration	^1H NMR
1		115	56	59
2	2:1	120	68	71
3		130	80	82
4		115	50	57
5	3:1	120	66	65
6		130	76	80
7	4:1	115	67	65
8		120	70	–

IM* – iodination mixture triphenyl phosphite : iodomethane = 1 : 1.

Table 2. Iodination of MPEG by a triphenyl phosphite and iodomethane mixture

Reaction temperature $120\text{ }^\circ\text{C}$, duration 5 h

No.	[IM]* : [MPEG], in moles	DI, mol%	q**, %	Remarks
1	2:1	29	90	Procedure according to [27]
2	3:1	37	94	
3	2:1	63	87	Diluted with biphenyl, 25 vol.%
4	3:1	67	88	
5	1:1	39	96	Modified Rydon method in optimal conditions
6	2:1	95	97	
7	3:1	93	96	

* IM – iodination mixture triphenyl phosphite : iodomethane = 1 : 1.

** q – yield of the products.

Optimization of iodination of MPEG and PEG

MPEG was iodinated trying both procedures of the Rydon method. Under standard procedures described elsewhere [27], the degree of iodination was relatively low, and the products were more or less brown (Table 2, rows 1 and 2). When several innovations were introduced (the reaction flask was hermetically capped with a rubber septum, all substances were added at once, and the reaction mixture was stirred at a given temperature) the DI substantially rose, and the products were colourless (Table 2, rows 6 and 7). An important factor is the addition order of the reagents into the reactor. Since iodomethane is very volatile, it should be added as the last compound. The temperature must be raised slowly and reach the optimal value within one hour since the formation of a complex between iodinating compounds is probably slow.

The kinetics of the reaction of MPEG iodination by an equimolar mixture of triphenyl phosphite and iodomethane was studied changing the ratio of MPEG to iodination mixture (IM), reaction temperature and the concentration of MPEG. The concentration of MPEG is varied by addition of biphenyl which is a non-polar and chemically inert compound with a high boiling temperature. The dependence of the DI of MPEG on the reaction time at different temperatures is presented in Fig. 4. Below $70\text{ }^\circ\text{C}$ the reaction is relatively slow, and at $130\text{ }^\circ\text{C}$ the main product becomes yellow-brown, i. e. is not completely discoloured by dialysis. Moreover, at a temperature ca. $130\text{ }^\circ\text{C}$, a partial fragmentation of MPEGI (or MPEG) takes place and enlarges the polydispersity of the products and lowers the DI. The partial fragmentation of iodination products obtained at the highest temperature was detected by gel-filtration: the curve contained the second small peak at a larger elution volume, suggesting a small fraction of compounds with a lower molecular weight. Naturally, the reaction of iodination should be carried out at a lower temperature, e. g., at $120\text{ }^\circ\text{C}$.

The effect of the IM to MPEG ratio is inconsistent. The ratio $[\text{IM}] : [\text{MPEG}] = 1 : 1$ is apparently insufficient, resulting in a relatively low DI in comparable conditions (Table 2, row 5). The ratio $[\text{IM}] : [\text{MPEG}] = 2 : 1$ seems to be adequate since the further increase in IM excess usually does not affect the DI. Interestingly, the energy of activation of the iodination reaction is considerably lower at a large excess of IM (Table 3). It means that the iodination of MPEG is effective at lower tem-

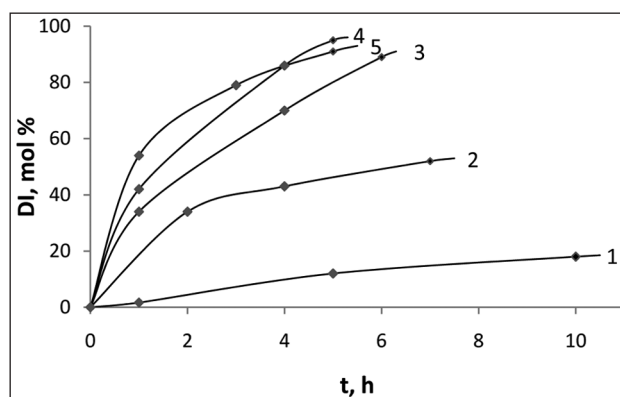


Fig. 4. Dependence of DI of MPEG on the reaction time at $70\text{ }^\circ\text{C}$ (1), $110\text{ }^\circ\text{C}$ (2), $115\text{ }^\circ\text{C}$ (3), $120\text{ }^\circ\text{C}$ (4) and $130\text{ }^\circ\text{C}$ (5). $[\text{IM}] : [\text{MPEG}] = 2 : 1$

peratures also if a significant (fourfold) excess of IM is used. Nevertheless, such conditions are not challenging since a large excess of IM demands extra efforts for the purification of iodination products.

Energy of activation of iodination reaction in a diluted solution is less (Table 3), is probably because of a lower viscosity of the reaction mixture. However, it is difficult to make profit of this phenomenon, since the dilution of the reaction mixture by biphenyl results in a decrease of DI under comparable conditions (Table 2, rows 3 and 4).

Table 3. Energy of activation of MPEG iodination at 110–130 °C

[IM] : [MPEG], molar ratio	[MPEG], mol/l	E_a , kJ/mol
2 : 1	0.383	101 ± 5
2 : 1; biphenyl	0.286	77 ± 7
4 : 1	0.356	62 ± 1

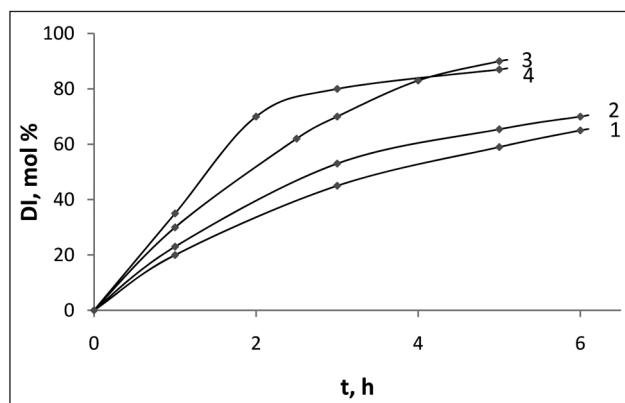


Fig. 5. Dependence of DI of PEG on the reaction time at 110 °C (1), 115 °C (2), 120 °C (3) and 130 °C (4). [IM] : [MPEG] = 2 : 1

Table 4. Iodination of PEG by the mixture of triphenyl phosphite and iodomethane.

Reaction temperature 120 °C, duration 5 hours

No.	[IM]* : [PEG], in moles	DI, mol%	q**, %
1	1 : 1	52	88
2	2 : 1	90	83
3	3 : 1	91	80

*IM – iodination mixture triphenyl phosphite : iodomethane = 1 : 1.

** q – yield of the products.

The iodination of PEG proceeds in a similar manner as that of MPEG (Fig. 5). Colourless products with the maximal DI of PEG were prepared carrying out the reaction at 120 °C for 5 hours. It should be noted, however, that the yield of the iodinated compounds separated at a high DI of PEG was noticeably lower compared to the corresponding values obtained under MPEG iodination (Table 4). The lower yield of the water-extracted product could be related to a better solubility of iodinated PEG compounds in organic phase, which increases with the degree of their iodination. Since the DI of PEG under optimal conditions of iodination reaches ca. 90%, one can assume that the products con-

tain a mixture of PEG diiodides, PEG monoiodides and the initial PEG with an obvious prevalence of the disubstituted derivative.

Thus, the optimal conditions for MPEG and PEG conversion into the corresponding iodides are specified by the molar ratio [IM] : [PEG] = 2 : 1, the reaction temperature 120 °C, and the reaction time 5 hours. The DI of MPEG was higher in the same conditions than that of PEG, but the difference was not pronounced.

CONCLUSIONS

A mixture of triphenyl phosphite and iodomethane was successfully applied for the iodination of poly(ethylene glycol) with the molecular weight of 2000 (PEG) and its monomethyl ether (MPEG). PEG iodides contain unreacted PEG and are slightly polluted by phenolates. Argentometric titration (Mohr's method) used to estimate the degree of iodination (DI) of PEG and MPEG was limited by an incomplete hydrolysis of the iodides, while an analysis based on ¹H NMR spectroscopy became accurate at a high DI only. The optimal conditions for PEG and MPEG conversion into corresponding iodides include a hermetic reactor, the reaction temperature 120 °C, the reaction time 5 hours and a two-fold excess of the iodinating mixture. PEG and MPEG iodides with the DI 90–95 mol% were synthesized; they could be useful for "grafting to" or even for polycondensation with diamines.

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Ūla Bernadišiuė, Tomas Antanėlis, Aušvydas Vareikis,
Ričardas Makuška

POLIETILENGLIKOLIO JODINIMAS TRIFENILFOSFITO IR JODOMETANO MIŠINIU

S a n t r a u k a

Ištirtas polietilenglikolio 2000 (PEG) ir jo metileterio (MPEG) jodinimas trifenilfosfito ir jodometano mišiniu. Susintetinti PEG (MPEG) jodidai ištirti elementinės analizės, FT-IR ir ¹H BMR spektroskopijos metodais. PEG (MPEG) jodinimo laipsnis (JL) buvo nustatytas dviem nepriklausomais metodais, kurie remiasi argentometriniu titravimu ir ¹H BMR spektrų analize. Argentometriniu titravimu (Moro metodas) taikymą limituoja nepilna PEG jodido hidrolizė, o ¹H BMR spektrais besiremianti analizė tampa pakankamai tiksli tik tada, kai JL didelis. Didžiausias JL pasiektas reakciją vykdant hermetiška reaktoriuje 120 °C temperatūroje 5 valandas ir esant dvigubam jodinimo mišinio pertekliui. Susintetintų PEG jodidų JL siekia 90–95 mol%, todėl jie gali būti naudojami „skiepijimo į“ reakcijoms, taip pat polikondensacijai su diaminais.