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# Graft copolymers with hydrophilic and hydrophobic polyether side chains

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**Abstract**

Poly(ethylene glycol)methyl ether methacrylate (PEOMA) and oligo(propylene glycol)-4-nonylphenyl ether acrylate (OPOPhNA) were copolymerized by atom transfer radical polymerization (ATRP). *Grafting through* method was employed in the presence of CuBr/HMTETA or CuBr/PMDETA catalyst/ligand complex in anisole at 70 °C. It yielded a heterografted copolymers containing hydrophilic PEO and hydrophobic OPOPhNA side chains with polymerization degree DP = 68–315 in the presence of PMDETA and DP = 48–195 in the presence HMTETA. Moreover, higher reactivity of PEOMA than OPOPhNA ($r_{\text{methacrylate}} > r_{\text{acrylate}}$), which was observed during copolymerization, suggested the formation of copolymers with a spontaneous gradient composition starting from the grafted segment of P(PEOMA). The molecular weight distribution (MWD) was increased with DP in the range 1.2–1.6. The X-ray diffraction analysis (WAXS) indicated that larger number of PEO segments generated crystalline properties in the copolymers with amorphous OPOPhNA.


*Keywords:* Graft copolymers; Amphiphilic; Polyether grafts

## 1. Introduction

Graft copolymers with poly(ethylene oxide) (PEO) side chains, due to interesting properties such as biocompatibility, biodegradability, ionic conductivity, wettability or resistance to protein adsorption, have found a wide-range of applications in science, industry and biochemistry [1]. They can be used as conducting materials in lithium batteries technology, carriers in drug delivery systems, coating materials in biomedical implants, surface-modifying agents (membranes), hydrogels, effective dispersants and emulsifiers, stabilizers or compatibilizers in polymer blends, additives facilitating the crystal growth of inorganic salts. All these features were designed in simple way by the selection of proper monomers, which were used to build a backbone segment and side chains. The synthesis was based mostly on *grafting through* i.e. macromonomer method, which was applied for various types of polymerization, that is cationic [2], anionic [3], free radical polymerizations and its controlled systems (nitroxide-mediated polymerization – NMP [4], reversible addition-fragmentation transfer polymerization – RAFT [5], atom transfer radical polymerization – ATRP [6,7]). It supposes to be very convenient technique, because of one-pot procedure for the copolymerization of PEO macromonomer with low molecular weight comonomer or with another macromonomer, which leads to loosely or densely grafted copolymers, respectively. The well-defined PEO graft copolymers with controlled molecular weights and compositions were obtained by the anionic polymerization and by the controlled methods of radical polymerization. However, the number of references indicates that ATRP [8–10] seems to be the most commonly used method. Earlier, the PEO macromonomer was used for ATRP with several monomers that is methyl methacrylate [11], 2-hydroxyethyl methacrylate [12], and protected 2-[(trimethylsilyl)-oxy]ethyl methacrylate [13], octadecyl (meth)acrylate [14], vinylidene fluoride [15], as well as macromonomers, oligo/polymers of ε-caprolactone [16], ethylene oxide [17,18], propylene oxide [6,19], dimethylsiloxane [20], 3-hydroxybutyrate [21] functionalized by (meth)acrylate groups. Additionally, the composition of graft copolymers depends on the selected comonomer pairs resulting in a random due to the similar

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reactivity ratios of comonomers or gradient, when the reactivity of comonomer is significantly different than for PEO macromonomer.

The graft copolymers containing shorter PEO side chains ($n_{EO} = 5$) demonstrated amorphous morphology, whereas longer grafts ($n_{EO} = 23$) indicated crystalline nature. Moreover, the mechanical studies, which were based on the frequency or temperature dependencies of the real ($G'$) and imaginary ($G''$) shear moduli, presented ultra low modulus plateau in the soft gel range ($G' \leq G''$). The PEO graft copolymers can be transformed to soft rubbers ($G' \sim 10^4$ Pa at $G' > G''$) by thermal or chemical cross-linking [7,14,20].

In this paper, the ATR copolymerization of a PEO macromonomer (poly(ethylene glycol)methyl ether methacrylate; PEOMA) with a hydrophobic (oligo(propylene glycol)-4-nonylphenyl ether acrylate; OPOPhNA) via *grafting through* is described. The reactions were initiated by ethyl-2-bromo-*iso*-butyrate (EtBr*i*Bu) in the presence of copper(I) bromide complexed by HMTETA or PMDETA ligands in organic solvent. The one-pot procedure using various ratios of comonomers resulted in an amphiphilic graft copolymers with differential distribution of PEO and OPOPhNA grafts. Because of amphiphilic character, they can exhibit phase-separation of hydrophobic and hydrophilic domains in dependence on the environmental conditions (temperature, surface, and solvent). The heterografted copolymers were compared with a densely homografted P(OPOPhNA) and P(PEOMA) brush polymers, which were prepared under the same conditions. The morphology of homo- and heterografted copolymers was analyzed by wide-angle X-ray scattering (WAXS).

## 2. Experimental section

### 2.1. Materials

Oligo(propylene glycol)-4-nonylphenyl ether acrylate (OPOPhNA, $M_n \sim 419$ g/mol, $n_{PO} = 2.5$) and poly(ethylene glycol)methyl ether methacrylate (PEOMA, $M_n \sim 1100$ g/mol, $n_{EO} = 23$) were obtained from Aldrich. Antioxidant inhibitors MEHQ and BHT were removed from viscous liquid OPOPhNA by passing through an alumina column. In the case of PEOMA, which is a solid at room temperature, before polymerization it was dissolved in THF, passed through an alumina column to remove the antioxidant inhibitor, then the solvent was evaporated and the macromonomer was dried under vacuum to a constant mass. Copper(I) bromide (CuBr, Aldrich, 98%) was purified by stirring over glacial acetic acid, followed by filtration and washing the remaining solid three times with ethanol and twice with diethyl ether prior to drying under vacuum for 1 day. Anisole (Aldrich, 99.8%) was distilled and stored over molecular sieves. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Aldrich, 97%), ethyl-2-bromoisobutyrate (EtBriBu, Aldrich, 98%), dimethyl-2,6-dibromoheptanedioate (dMedBrHep, Aldrich 97%) and all other solvents were used as-received. All solvents and internal standards were used without further purification.

### 2.2. Synthesis

#### 2.2.1. Procedure for synthesis of the heterografted copolymers by ATRP (example)

PEOMA (0.91 g, 0.83 mmol) was dissolved in anisole (1.5 ml), and then OPOPhNA (0.30 g, 0.72 mmol) and PMDETA (1.6 μl, 0.0078 mmol) were added. The homogeneous solution was purged by nitrogen. After 2 h, CuBr (1.1 mg, 0.0078 mmol) was added and the mixture was purged again for 30 min at room temperature. Next, the Schlenk flask was placed in a thermostated oil bath at 70 °C. After 1 min, EtBr*i*Bu (0.6 μl, 0.0039 mmol) was added to start the reaction. During polymerization, samples were periodically removed to determine the molecular weight of the polymer by GPC and conversion by NMR. All polymerizations were stopped after 24 h by exposing the solution to air, and then mixture was diluted with chloroform and filtered through an activated (neutral) alumina column to remove the copper catalyst. The remaining unreacted PEOMA and OPOPhNA were removed by ultrafiltration in MeOH/THF (50/50 vol%) solution, and the pure graft polymer was dried under vacuum to a constant mass.

### 2.3. Characterization

The apparent molecular weights ($M_{n,GPC}$) and polydispersity indices ($M_w/M_n$) of the copolymers were determined by means of gel-permeation chromatography (GPC) in chloroform at 30 °C on a Spectra-Physics 8800 solvent delivery system. The copolymer composition was defined by $^1$H nuclear magnetic resonance (NMR) spectroscopy using a Varian 300 MHz spectrometer in chloroform-*d* at room temperature. The morphology was characterized by wide-angle X-ray diffraction (WAXS), which was carried out with diffractometer TUR M62 in the $2\theta$ range 5−50° at room temperature.

### 2.4. Characterization of (macro)monomers by NMR

$^1$H NMR OPOPhNA ($CDCl_3$) $\delta$ (ppm): 6.37, 6.09, and 5.79 (3 × 1H, CHH=CH−); 4.17−3.32 (2H, $-CH_2-CH(CH_3)-O-$); 4.50−3.60 (1H, $-CH_2-CH(CH_3)-O-$); 1.25 and 1.39 (3H, $-CH_2-CH(CH_3)-O-$); 6.75 and 6.79 (4 × 1H, aromatic −CH=CH−); 2.61 (2H, $-CH=C(CH_2-CH_2-[CH_2]_6-CH_3)-CH=$ methylene group at aromatic ring); 1.58 (2H, $-CH_2-CH_2-[CH_2]_6-CH_3$); 1.25 (6 × 2H, $-CH_2-CH_2-[CH_2]_6-CH_3$); 0.88 (3H, $-CH_2-CH_3$).

$^1$H NMR PEOMA, MW = 1100 g/mol ($CDCl_3$) $\delta$ (ppm): 6.13 and 5.58 (2H, $CH_2=C(CH_3)-$); 4.30 (2H, $-O-CH_2-CH_2-O-$), 3.42−3.75 ([4H × *n*] − 2, $-O-CH_2-CH_2-O-$); 3.38 (3H, $-O-CH_3$), 1.86 (3H, $CH_2=CCH_3$).

## 3. Results and discussion

### 3.1. Polymerization of PEOMA or OPOPhNA

Previously, the PEOMA macromonomer was homopolymerized by ATRP in organic solvents (tetrahydrofuran, 1-butanone

and anisole) using various ligands (dNbpy, PMDETA, $EHA_6$TREN, and $Me_6$TREN), which were complexed by CuBr [7,14]. In the present study, PMDETA was also used in the polymerization system at 70 °C (Table 1). The ratio of monomer to initiator 250:1 yielded copolymers containing homogeneous side chains P(PEOMA) **IA** and P(OPOPhNA) **IIA** (Scheme 1) with polymerization degree DP = 240 and 190 at 97 and 76% conversion, respectively. When the ratio was increased to 400:1, the reaction rate was reduced giving lower conversions that is 79% for P(PEOMA) **IB** and 17% for P(OPOPhNA) **IIB**. It allowed to enhance the length of P(PEOMA) (DP = 314), whereas the polymerization degree of P(OPOPhNA) was significantly lower (DP = 68) due to low reactivity of the acrylate monomer. However, it is obvious because active center concentration during polymerization of acrylate was decreased. The using of HMTETA, which is known as ligand with lower value of activation rate constant ($k_{act,HMTETA} = 0.6$ g/mol) than PMDETA ($k_{act,PMDETA} = 2.7$ g/mol) [22], the polymerization was slower. Although the lower conversions were obtained for P(PEOMA) **IC**,**D** and P(OPOPhNA) **IIC**,**D** in the system with HMTETA, it can be used for the polymerization as the alternative way leading to the graft copolymers with PEO and OPOPhNA side chains.

The apparent molecular weight determined by GPC ($M_{n,GPC}$) was significantly lower than the molecular weight calculated on the basis of NMR ($M_{n,NMR}$). The details relating to estimation of the conversion by NMR are presented in further part for the copolymerization of PEOMA and OPOPhNA in the form of Eqs. (1) or (2). The previous studies on the PEO graft copolymers showed that the theoretical values $M_{n,NMR}$ are close to the absolute molecular weight [20]. The difference between $M_{n,NMR}$ and $M_{n,GPC}$ is caused by using the linear polymer standards for the conventional GPC analysis. They have different hydrodynamic volume than the grafted copolymers with compact shape, which makes that the evaluated values are a few times lower than the absolute molecular weights. Similar observations were noticed using other molecular brushes [7]. All homografted copolymers presented monomodal molecular weight distributions. However, the polydispersity indices of P(PEOMA) were higher ($M_w/M_n = 1.3-1.7$) than that for P(OPOPhNA) in the range 1.1–1.2, which can be explained by lower conversion of the hydrophobic acrylate yielding the polymers with lower DPs and molecular weights than the hydrophilic methacrylate. The GPC traces for P(OPOPhNA) (**IIA**, **IIC**) are presented in Fig. 1 as examples for the copolymers containing homogeneous side chains, which were obtained under the same conditions with two different ligands.

### 3.2. Copolymerization of PEOMA with OPOPhNA

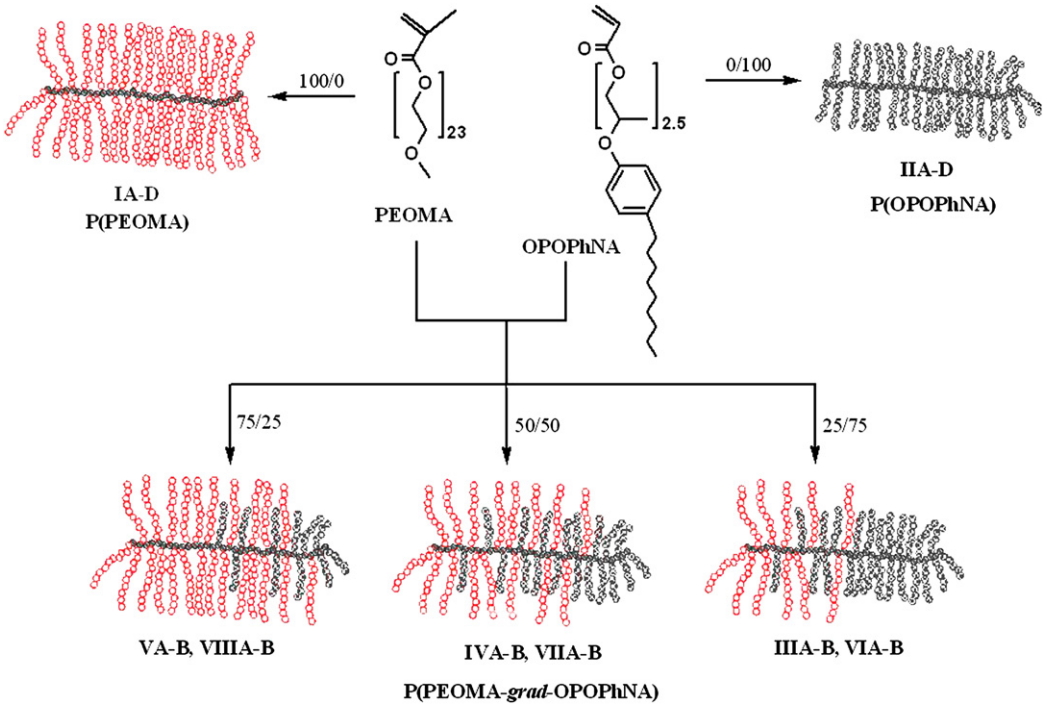
The homopolymerization conditions were also applied for the copolymerization of both monomers PEOMA and OPOPhNA with various initial ratios. The same trend, it means higher conversions in the presence of PMDETA ligand (Table 2) in comparison to HMTETA system (Table 3) were observed for the prepared copolymers. Moreover, in the case of both ligands the conversion was reduced at higher ratio of monomer/initiator and with the increase in the initial feed ratio of the hydrophobic monomer OPOPhNA. The dependence of conversion on the amount of the incorporated PEO macromonomer into the graft copolymer in the presence of PMDETA and HMTETA is presented in Fig. 2.

The progress of polymerization was monitored by $^1$H NMR, whose spectra for the representative copolymer **VIIIB** are presented in Fig. 3. It allowed to determine the conversions of both comonomers. For PEOMA, the signal of methoxy protons $-OCH_3$ (*a*, $\delta = 3.38$ ppm) in monomer and copolymer was compared with monomer signals ascribed to the vinyl proton $CH=C(CH_3)-$ (*b*, $\delta = 5.58$ ppm) as previously it was done for the other PEO graft copolymers [14,18,20]. In the case of OPOPhNA, the estimation of conversion was based on the comparison of peak integration for the signal assigned to the methine proton in the copolymer $-CH-$ (*c*, $\delta = 2.49$ ppm) with the signal of the unsaturated proton $-CH=$ (*d*, $\delta = 5.79$ ppm) belonging to the monomer. It is necessary to mention that third signal of acrylate proton at 6.10 ppm was overlapped with the vinyl proton in the methacrylate ($\delta = 6.05$ ppm). The conversions were calculated for PEOMA and OPOPhNA ($x_{PEOMA}$ and $x_{OPOPhNA}$) with Eqs. (1) and (2), respectively. Further, they were used for determination of average total conversion ($x_{av}$) for the graft copolymer (Eq. (3a)) and theoretical molecular weight $M_{n,NMR}$ (Eq. (3b)).

Table 1
Polymerization of hydrophilic PEOMA or hydrophobic OPOPhNA by ATRP at 70 °C

| Nr | Monomer | Ligand | $[M]_0/[I]_0/[CuBr]_0/[L]_0$ | NMR | | | GPC | |
|---|---|---|---|---|---|---|---|---|
| | | | | Conversion (%) | DP[a] | $M_{n,NMR}$ (g/mol) | $M_{n,GPC}$ (g/mol) | $M_w/M_n$ |
| **IA** | PEOMA | PMDETA | 250/1/2/2 | 97.0 | 242 | 266 200 | 34 700 | 1.55 |
| **IB** | | | 400/1/2/2 | 78.6 | 314 | 345 400 | 43 000 | 1.73 |
| **IC** | | HMTETA | 250/1/2/2 | 78.1 | 195 | 214 800 | 30 900 | 1.46 |
| **ID** | | | 100/1/2/2 | 95.7 | 96 | 105 600 | 12 700 | 1.31 |
| **IIA** | OPOPhNA | PMDETA | 250/1/2/2 | 76.4 | 191 | 86 900 | 18 900 | 1.17 |
| **IIB** | | | 400/1/2/2 | 17.0 | 68 | 30 900 | 4200 | 1.12 |
| **IIC** | | HMTETA | 250/1/2/2 | 48.6 | 121 | 32 800 | 11 900 | 1.13 |
| **IID** | | | 400/1/2/2 | 12.0 | 48 | 21 800 | 3500 | 1.12 |

Monomer/anisole = 1/1 (wt/vol). Reactions were stopped after 24 h.
[a] Polymerization degree of backbone containing units of PEOMA or OPOPhNA defined via conversion.




Scheme 1. Structures of PEO methacrylate, OPOPhN acrylate, and their (co)polymers.

$$x_{\mathrm{PEOMA}} = A_{(5.58)}/1/3A_{(3.38)} \quad (1)$$

$$x_{\mathrm{OPOPhNA}} = A_{(2.49)}/\left(A_{(2.49)} + A_{(5.79)}\right) \quad (2)$$

$$x_{\mathrm{av}} = [\mathrm{PEOMA}]_0 \quad x_{\mathrm{PEOMA}} + [\mathrm{OPOPhNA}]_0 \quad x_{\mathrm{OPOPhNA}} \quad (3a)$$

$$M_{\mathrm{n,NMR}} = 1100 \quad [\mathrm{PEOMA}]_0 \quad x_{\mathrm{PEOMA}} + 419 \quad [\mathrm{OPOPhNA}]_0 \quad x_{\mathrm{OPOPhNA}}/\left([\mathrm{In}]_0\right) \quad (3b)$$

where $A(\delta)$ is the integration area $A$ of signal at following chemical shift $\delta$, which ppm value is given in bracket; $[\mathrm{PEOMA}]_0$ means the initial concentration of PEO macromonomer; $[\mathrm{OPOPhNA}]_0$ means the initial concentration of acrylate comonomer; $[\mathrm{In}]_0$ is the initial concentration of initiator.

The same like for the homografted copolymers described above, the theoretical values $M_{\mathrm{n,NMR}}$ of heterografted brushes were significantly higher in comparison to apparent $M_{\mathrm{n,GPC}}$ (Tables 2 and 3). In the case of heterografted copolymers, the difference between them is larger when the number of PEO grafts in copolymer is higher. GPC chromatograms presented in Fig. 4 shows lower value of $M_{\mathrm{n,GPC}}$ for the copolymer with larger amount of PEO grafts (**VIIIB**, 75 wt.%), whereas the signals of copolymers with reduced content of the PEOMA (**IVB**, 50 wt.% and **IIIB**, 25 wt.%) are shifted to higher molecular weights. These results indicate that the molar compositions of the heterografted copolymers containing two kinds of side chains with various lengths, the PEO chains are longer than OPOPhNA grafts, make differences of their hydrodynamic volumes, which have influence on the values of $M_{\mathrm{n,GPC}}$. The similar effects were achieved for the other heterografted copolymers, which previously were synthesized by ATRP of poly(3-hydroxybutyrate) functionalized by methacrylate group with PEOMA [21]. However, all heterografted copolymers PEO/OPOPhNA displayed monomodal GPC traces with polydispersity indices $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.2-1.3$ in the presence of PMDETA and $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.2-1.6$ for HMTETA.

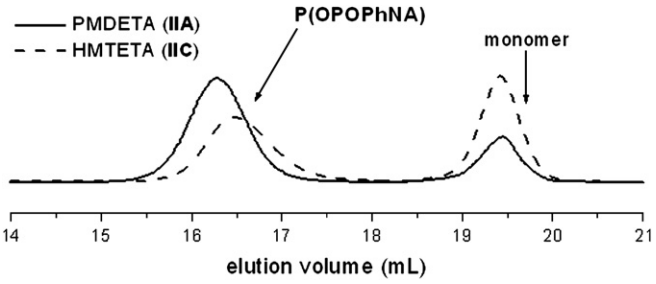



Fig. 1. GPC traces for homopolymer P(OPOPhNA) prepared in the presence of PMDETA (**IIA**) and HMTETA (**IIC**). Conditions: $[\mathrm{M}]_0/[\mathrm{EtBriBu}]_0/[\mathrm{CuBr}]_0/[\mathrm{L}]_0 = 250/1/2/2$, M/anisole = 1/1 (wt/vol), 70 °C.

The semilogarithmic kinetic plots of monomer consumption *vs* time presented in Fig. 5(a) for the copolymerization of methacrylate PEOMA with acrylate OPOPhNA in the presence of CuBr/PMDETA or CuBr/HMTETA are linear. They demonstrate the faster consumption of PEOMA than OPOPhNA, which after 12 h reached the following conversions, 52% and 24% for **IIIA** with PMDETA, whereas 38% and 16% were obtained for **VIA** using HMTETA, respectively. It suggests the formation of copolymers with a spontaneous gradient P(PEOMA-*grad*-OPOPhNA), where the PEO chains are densely grafted at the beginning of the polymer chain, in which the amount of incorporated acrylate monomer was gradually

Table 2
Copolymerization of PEOMA with OPOPhNA in the presence of PMDETA ligand at 70 °C

| Nr | PEOMA/OPOPhNA wt.% (mol.%) | $[M]_0/[I]_0/[CuBr]_0/[L]_0$ | NMR | | | | | GPC | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Conversion (%) | | | $M_{n,NMR}$ (g/mol) | DP[a] ($DP_{PEOMA}$/$DP_{OPOPhNA}$) | $M_{n,GPC}$ (g/mol) | $M_w/M_n$ |
| | | | $x_{PEOMA}$ | $x_{OPOPhNA}$ | $x_{av}$ | | | | |
| **IIIA** | 25/75 (11/89) | 250/1/2/2 | 75.0 | 40.0 | 43.8 | 63 200 | 110 (21/89) | 31 700 | 1.30 |
| **IIIB** | | 400/1/3/3 | 57.1 | 24.2 | 27.8 | 66 800 | 111 (25/86) | 31 600 | 1.27 |
| **IVA** | 50/50 (28/72) | 250/1/3/3 | 93.9 | 69.0 | 76.0 | 104 500 | 190 (66/124) | 23 100 | 1.31 |
| **IVB** | | 400/1/3/3 | 77.3 | 29.8 | 43.1 | 134 200 | 173 (87/86) | 22 800 | 1.30 |
| **VA** | 75/25 (53/47) | 250/1/3/3 | 93.1 | 65.2 | 79.9 | 170 500 | 199 (123/76) | 11 600 | 1.21 |
| **VB** | | 400/1/3/3 | 86.8 | 40.0 | 64.8 | 236 600 | 259 (184/75) | 7800 | 1.20 |
| **VC**[b] | | 400/1/3/3 | 82.4 | 45.1 | 64.9 | 230 600 | 260 (175/85) | 8600 | 1.18 |

Monomer/anisole = 1/1 (wt/vol). Reactions were stopped after 24 h.
[a] Polymerization degree of backbone containing units of PEOMA and OPOPhNA defined via conversion.
[b] Difunctional initiator dMedBrHep.

increased with the time of reaction (Scheme 1). The reactivity ratio was estimated by Jaacks method as a result of plotting kinetic data of OPOPhNA against those of PEOMA (Fig. 5(b)). It was obtained from the slope of linear dependence yielding the value $r_{OPOPhNA} = 0.35$, whereas the relative reactivity of the PEO macromonomer was evaluated by $1/r_{OPOPhNA}$, which gave $r_{PEOMA} = 2.85$. The values are similar to previously described gradient copolymers, which were obtained in ATR copolymerization of butyl acrylate, M1, and methyl methacrylate, M2 ($r_{M1} = 0.3$ and $r_{M2} = 3$) [23]. The significantly lower reactivity ratio of OPOPhNA can be explained by stiffness of the macromonomer, which combines aliphatic chain C9, benzene ring and short chain of OPO end-capped by acrylate group.

Additionally, one of the graft copolymers (**VC**) with different structure than presented in Scheme 1 for the heterografted copolymers was prepared by the copolymerization of PEOMA with OPOPhNA using difunctional initiator dMedBrHep. In consequence, the resulted graft copolymer, which is shown in Scheme 2, consisted of inner P(PEOMA) segment with short spacer corresponding to the initiator and two outer segments of P(OPOPhNA). In this case, conversions above 80% PEOMA and 40% OPOPhNA were reached. The similar values were obtained for reaction performed under the same conditions in the presence of monofunctional initiator EtBr*i*Bu (**VB**). However, higher rate of the polymerization **VC** with growing polymer chain on two initiating centers was indicated by the semilogarithmic plots, which are not linear according to Fig. 6. These results conclude the faster reaction by difunctional initiator, but significantly less controlled ATRP in comparison to the polymerization **VB**, which is linear dependence indicating first-order kinetics of reaction with monofunctional initiator.

### 3.3. Morphology of homo- and heterografted copolymers

The OPOPhNA/PEO homo- and heterografted copolymers were examined by wide-angle X-ray scattering (WAXS) to define their morphology. The X-ray diffractograms in Fig. 7 demonstrate amorphous halo at wide angles for the sample of P(OPOPhNA) **IIA**. This observation is similar to the other PEO homopolymers that is P(PEOMA) ($n_{EO} = 5$)[7] and P(PEOPhA) ($n_{EO} = 5$; where PEO chain was end-capped by phenoxy group) [18]. In the case of graft copolymers P(PEOMA-*grad*-OPOPhNA) (**VA**, **VIA**, **VIIA**), the amorphous halo from the poly(methacrylate/acrylate) backbone and P(OPOPhNA) grafts was overlapped with two reflections ($2\theta = 19.3$ and 23.5°), which corresponded to typical crystalline diffraction pattern for longer PEO chains. The PEO reflections, which are difficult to distinguish for **VIA** containing 25 wt.% PEOMA or the weak signals in the sample **VIIA** at

Table 3
Copolymerization of PEOMA with OPOPhNA in the presence of HMTETA ligand at 70 °C

| | PEOMA/OPOPhNA wt.% (mol.%) | $[M]_0/[I]_0/[CuBr]_0/[L]_0$ | NMR | | | | | GPC | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Conversion (%) | | | $M_{n,NMR}$ (g/mol) | DP[a] ($DP_{PEOMA}$/$DP_{OPOPhNA}$) | $M_{n,GPC}$ (g/mol) | $M_w/M_n$ |
| | | | $x_{PEOMA}$ | $x_{OPOPhNA}$ | $x_{av}$ | | | | |
| **VIA** | 25/75 (11/89) | 250/1/3/3 | 60.9 | 27.3 | 31.0 | 46 000 | 78 (17/61) | 15 600 | 1.21 |
| **VIB** | | 400/1/3/3 | 44.1 | 10.4 | 14.0 | 37 700 | 56 (19/37) | 16 000 | 1.18 |
| **VIIA** | 50/50 (28/72) | 250/1/3/3 | 89.2 | 43.7 | 56.5 | 104 500 | 141 (62/79) | 23 100 | 1.57 |
| **VIIB** | | 400/1/3/3 | 53.0 | 17.1 | 27.1 | 63 100 | 86 (37/49) | 18 600 | 1.30 |
| **VIIIA** | 75/25 (53/47) | 250/1/3/3 | 90.1 | 50.4 | 71.4 | 158 200 | 178 (119/59) | 17 500 | 1.60 |
| **VIIIB** | | 400/1/3/3 | 70.5 | 19.2 | 46.4 | 180 800 | 185 (149/36) | 16 100 | 1.43 |

Monomer/anisole = 1/1 (wt/vol). Reactions were stopped after 24 h.
[a] Polymerization degree of backbone containing units of PEOMA and OPOPhNA defined via conversion.

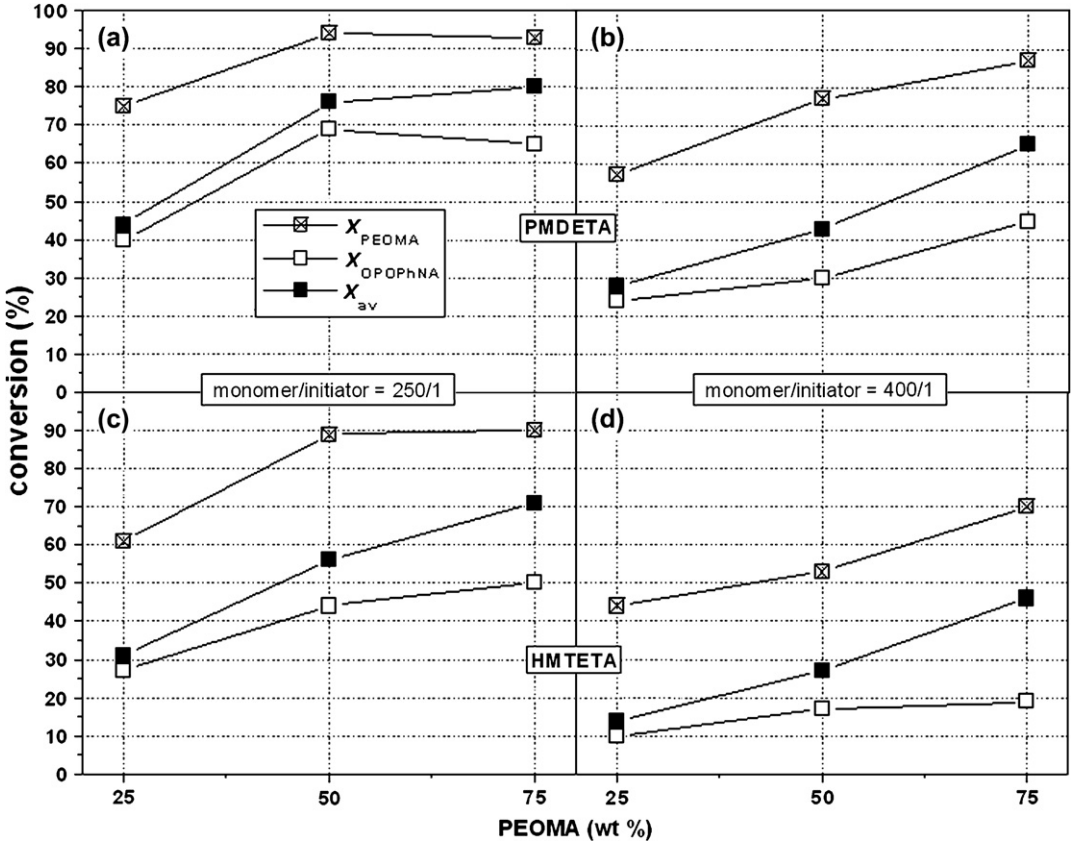



Fig. 2. Dependence of conversion on the amount of PEO macromonomer incorporated into graft copolymer in the presence of PMDETA (a, b) and HMTETA (c, d) at various ratios of monomer to initiator 250/1 (a, c) and 400/1 (b, d). Conditions are given in Tables 2 and 3.

50 wt.% PEOMA (arrows in the Fig. 7), are more intense for graft copolymer **VA** with larger amount of PEOMA (75 wt.%). The diagram for P(PEOMA) **IA** also indicates mixture of the crystalline reflections related to PEO side chains with the highest intensity and amorphous fraction of polymethacrylic main chain in the graft copolymer.

## 4. Conclusion

The amphiphilic graft copolymers containing hydrophilic/hydrophobic side chains PEO/OPOPhNA were prepared by ATRP via macromonomer method, i.e. by *grafting through.*

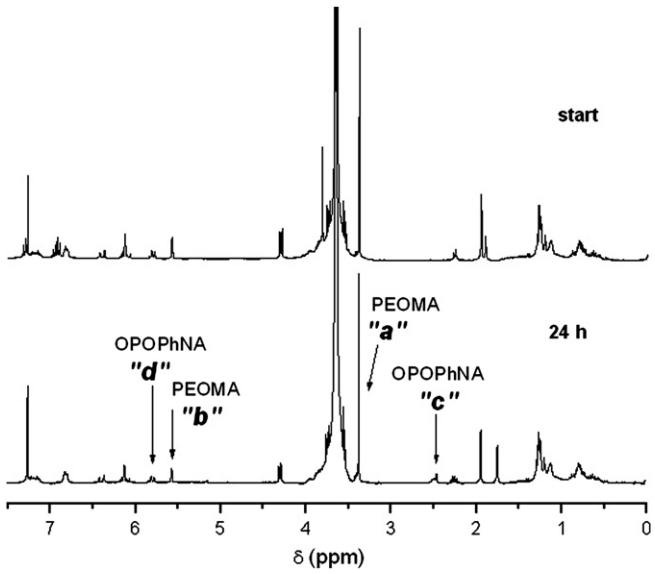



Fig. 3. $^{1}$H NMR spectra for the synthesis of heterografted copolymers **VIIIB** (PEOMA/OPOPhNA = 75/25). Conditions: $[PEOMA + OPOPhNA]_0/[EtBriBu]_0/[CuBr]_0/[L]_0 = 400/1/3/3$, M/anisole = 1/1 (wt/vol), 70 °C.

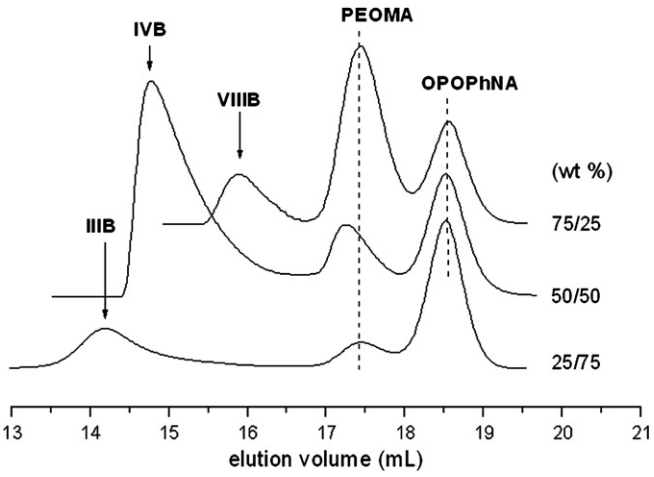



Fig. 4. GPC traces for heterografted copolymers (**IIIB**, **IVB**, **VIIIB**). Conditions are given in Tables 2 and 3.

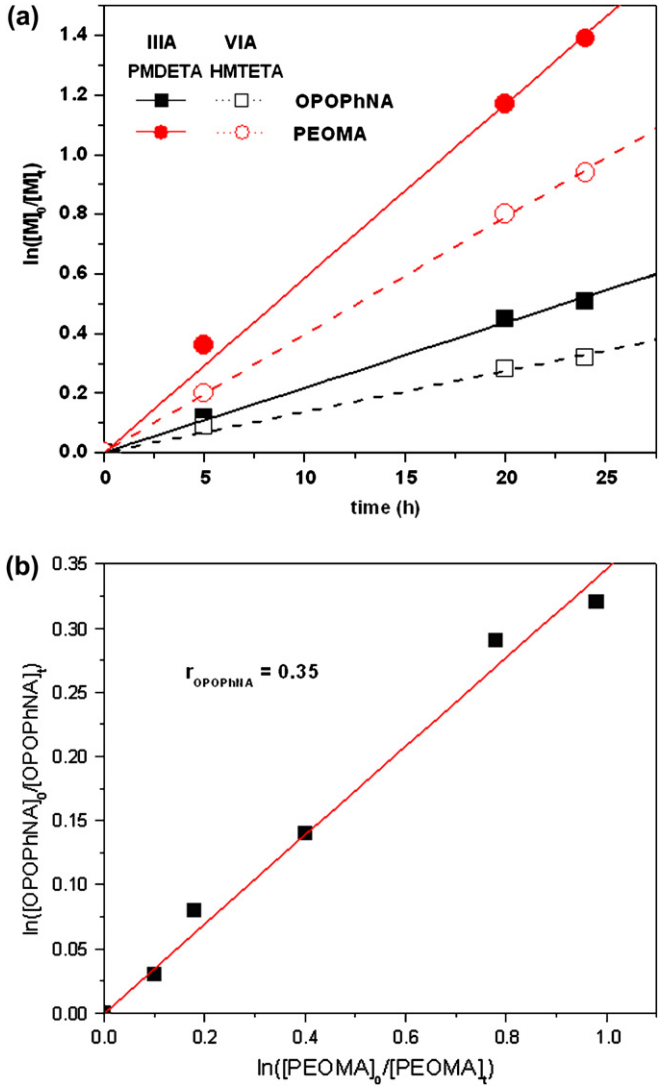
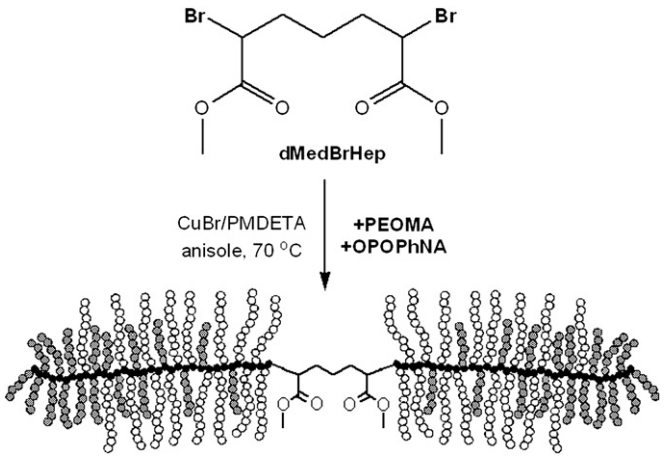



Fig. 5. Kinetic plots for the synthesis of heterografted copolymers **IIIA** and **VIA** (a) and Jaacks plot for the ATR copolymerization of PEOMA and OPOPhNA (b). Conditions: $[PEOMA + OPOPhNA]_0/[EtBriBu]_0/[CuBr]_0/[L]_0 = 250/1/3/3$, M/anisole = 1/1 (wt/vol), 70 °C.




Scheme 2. Synthesis of heterografted copolymer by difunctional initiator.

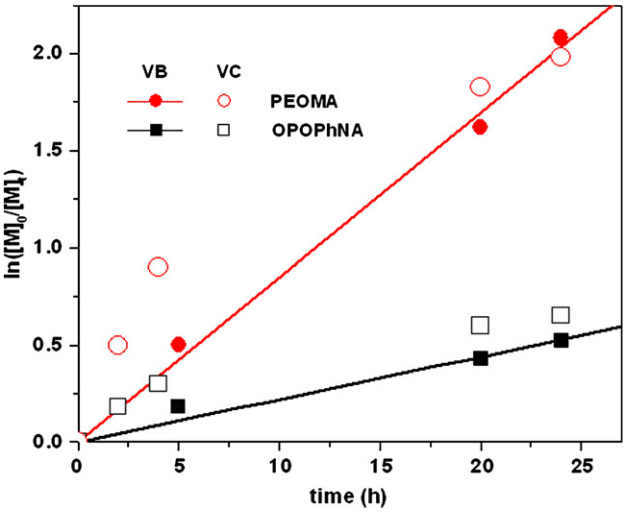



Fig. 6. Comparison of the semilogarithmic plots for copolymerizations of OPOPhNA and PEOMA initiated by mono- (**VB**) and difunctional initiator (**VC**). Conditions: $[PEOMA + OPOPhNA]_0/[In]_0/[CuBr]_0/[PMDETA]_0 = 400/1/3/3$, M/anisole = 1/1 (wt/vol), 70 °C.

The PEO methacrylate (PEOMA, $n_{EO} = 23$) and the OPOPhN acrylate (OPOPhNA, $n_{PO} = 2.5$) were copolymerized with a various ratios (25/75, 50/50 and 75/25 wt.%) using CuBr/PMDETA or CuBr/HMTETA system. Higher activity of PMDETA complex with CuBr led to higher conversions of (co)monomers in comparison to that with HMTETA. The increase in amount of the incorporated PEO macromonomer yielded the heterografted copolymers with higher polymerization degrees (DP ~ 260). It had the influence on the polydispersity indices, which were changed depending on the composition of copolymer ($M_w/M_n = 1.2–1.6$). Moreover, the homografted copolymers with PEO side segments ($DP_{PEOMA} = 95–315$) and OPOPhNA side chains ($DP_{OPOPhNA} = 50–200$) were synthesized for comparison with the heterografted copolymers containing both kinds of the grafts.

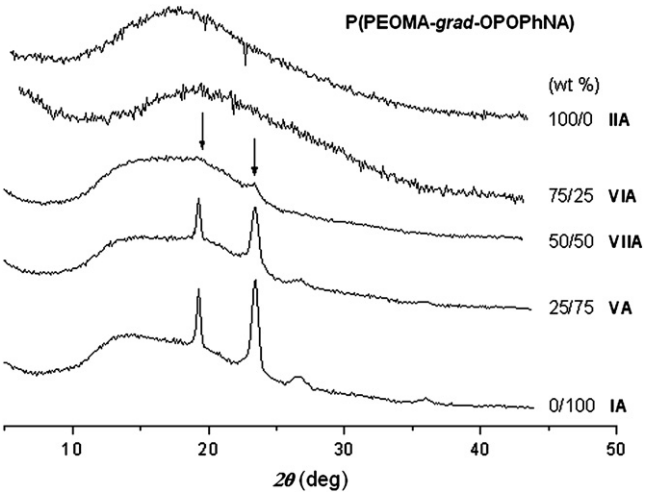



Fig. 7. Wide-angle X-ray diffractograms of P(OPOPhNA) (**IIA**), P(PEOMA-*grad*-OPOPhNA) (**VIA**, **VIIA**, **VA**) and P(PEOMA) (**IA**). Conditions are given in Tables 1–3.

The kinetic studies showed that PEOMA was polymerized faster than OPOPhNA ($r_{\text{methacrylate}} > r_{\text{acrylate}}$, $r_{\text{PEOMA}} = 2.85$, $r_{\text{OPOPhNA}} = 0.35$), which suggested the formation of copolymers with a spontaneous gradient composition. It was starting from the densely grafted segment of P(PEOMA), which was gradually changing through hetero-sequences of OPOPhNA. The analysis of morphology presented by WAXS diffraction diagram indicated that the presence of PEO segments generated crystalline properties in the graft copolymers containing amorphous fraction of OPOPhNA.

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