

GRZEGORZ ŁAPIENIS

Centre of Molecular and Macromolecular Studies
 Polish Academy of Sciences
 ul. Sienkiewicza 112, 90-363 Lodz, Poland
 e-mail: lapienis@bilbo.cbmm.lodz.pl

Influence of some reaction parameters on the synthesis of the first generation of stars with arms composed of poly(oxyethylene glycol)

Summary — The syntheses of the multiarm stars resulting from the reaction of oligoalcohols with diepoxides have been studied. MPEG 550, 750, and 2000 [MPEG = monomethyl ether of poly(oxyethylene glycol)] as precursors of arms and diglycidyl ethers of ethylene (DGEG) or neopentyl glycol (DGNG) as the core forming diepoxides were used. The increase in M_n , polydispersity (MWD) and the number of arms (f) in stars with the increase in the concentration of reagents and $[\text{diepoxide}]_0/[\text{MPEG}]_0$ ratio, and the decrease in temperature were observed. The final content of unreacted MPEG lowers with increasing concentration of reagents, proportion of the alkoxide groups in the initiator ($[\text{RO}^-]/[\text{RO}^- + \text{ROH}]$), length of MPEG chain, and $[\text{diepoxide}]_0/[\text{MPEG}]_0$ ratio and also with decreasing reaction temperature.

Key words: star polymers, diepoxides, poly(oxyethylene glycol), anionic polymerization, number of arms, molecular weight, polydispersity, NMR.

WPLYW NIEKTÓRYCH PARAMETRÓW REAKCJI NA SYNTEZĘ PIERWSZEJ GENERACJI GWIAZD O RAMIONACH ZBUDOWANYCH Z GLIKOLU POLIOKSYETYLENOWEGO

Streszczenie — Praca dotyczy syntezy polimerów gwiazdzistych o ramionach zbudowanych z monometylowych eterów glikolu polioksyetylenowego (MPEG) o różnych ciężarach cząsteczkowych (MPEG 550, 750 oraz 2000) i o rdzeniu na podstawie diepoksydów, mianowicie diglicydowych eterów glikolu etylenowego (DGEG) bądź neopentylowego (DGNG). Zbadano wpływ różnych warunków syntezy na jej przebieg (rys. 1 i 2) oraz na charakterystykę powstających produktów (tabela 1). Stwierdzono, że na zmniejszenie zawartości nieprzereagowanego MPEG w końcowej mieszaninie reakcyjnej wpływa obniżenie temperatury, wzrost długości łańcucha tego prekursora i wyjściowego stosunku $[\text{diepoksyd}]_0/[\text{MPEG}]_0$ a także zwiększenie stężenia reagentów oraz alkoholu (RO^-) w inicjatorze ($\text{RO}^- + \text{ROH}$) (rys. 3). Obniżenie temperatury jak również zwiększenie stężenia reagentów i stosunku $[\text{diepoksyd}]_0/[\text{MPEG}]_0$ powoduje wzrost M_n , polidispersyjności (MWD) oraz liczby ramion (f) otrzymywanych polimerów gwiazdzistych (rys. 4—6).

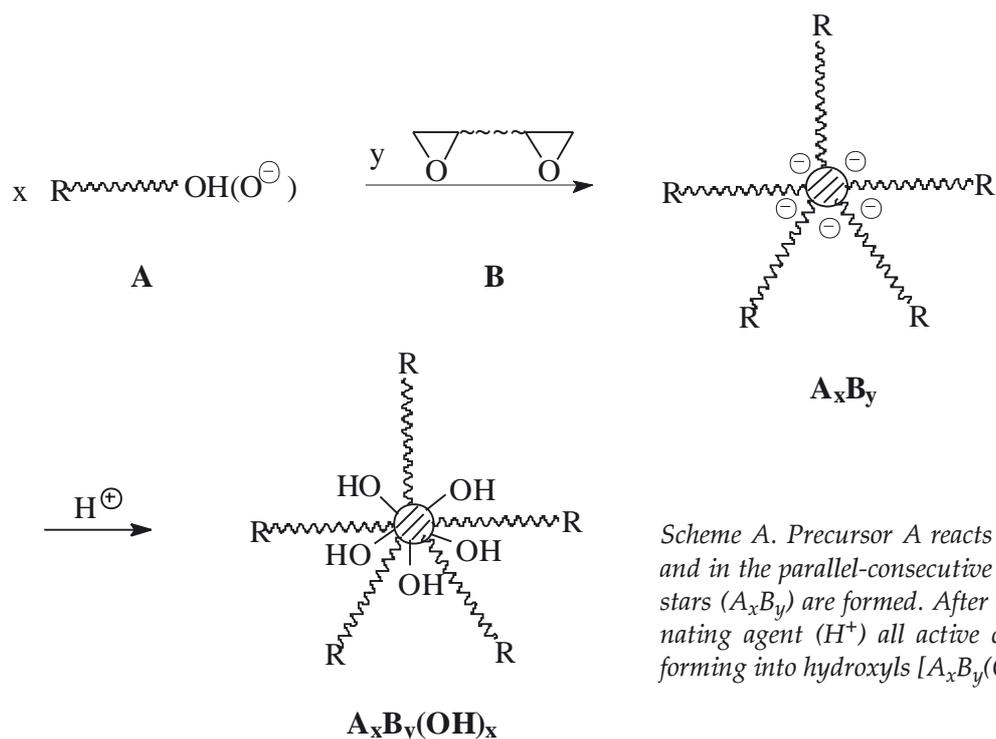
Słowa kluczowe: polimery gwiazdziste, diepoksydy, glikol polioksyetylenowy, polimeryzacja anionowa, liczba ramion, ciężar cząsteczkowy, polidispersyjność, NMR.

In the previously published papers of this series the synthetic method and the analyses of the star-shaped polymers were described in detail [1—5]. Application of the scanning electron microscopy method with the triple detection (TriSEC[®]) allowed determination of the branching index (g) and eventually of the number of arms (f). Homostars having one and/or two generations of poly(ethylene oxide) (PEOX) arms and core formed of diglycidyl ethers of ethylene glycol (DGEG) or neopentyl glycol (DGNG) were characterized in this way [1—4]. The same procedure was applied in the characterization of the heteroarm stars built of polyglycidol (PGL) — first generation of arms and PEOX — second generation [5].

Recently the demarcation line between soluble stars and insoluble products, produced in the reaction of

monomethyl ether of poly(oxyethylene glycol) (MPEG) and diglycidyl ether of neopentyl glycol (used as diepoxide), as a function of M_n of MPEG and $[\text{diepoxide}]_0/[\text{MPEG}]_0$ ratio was determined and the conditions of a quantitative conversion of both precursors (for MPEG having $M_n \geq 2000$) into stars have been found [6].

Previously star polymers with a large number of PEOX arms and cores having different structures — *e.g.* built of divinylbenzene (DVB) [7, 8], hyperbranched polyglycerol [9], crosslinked polyurethane [10], fullerene [11, 12], polyamidoamine (PAMAM) [13, 14], polyether [15] or carbosilane [16] — were obtained. More information about the syntheses of star-shaped polymers containing PEOX arms was given in the previous paper [4].



Scheme A. Precursor A reacts with diepoxide B and in the parallel-consecutive reactions the first stars (A_xB_y) are formed. After addition of terminating agent (H^+) all active centers are transforming into hydroxyls [$A_xB_y(OH)_x$]

The present paper is devoted to the analyses of the influence of different reaction parameters, namely a length of precursor, [diepoxide]₀/[MPEG]₀ ratio, concentration of reagents, and the temperature on the formation of stars containing MPEG arms. Diglycidyl ethers of ethylene (DGEG) and of neopentyl glycol (DGNG) were used as diepoxides (Scheme A).

EXPERIMENTAL

Materials

Commercial MPEG 550 (Fluka), 750 (Aldrich), and 2000 (Sigma) (usually contaminated with PEG) were purified as described previously [17].

The procedure of purification of Argon, THF, NaH (Fluka), and diglycidyl ethers of ethylene (DGEG) and of neopentyl glycol (DGNG) (both Aldrich technical products, purity ~50 %) was described previously too [4].

Syntheses of star-shaped polymers

Commercial MPEG 550, 750, and 2000, used as the precursors of arms, were converted, at least partially, into their alkoxide anions. Syntheses were carried out in THF solvent (concentration 50–60 wt. %) at 50 °C or 70 °C. The proportion of the alkoxide groups (RO^-) in the initiator, *i.e.* $[RO^-]/[RO^- + ROH]$, was usually equal to ~50 % (in some experiments approached 100 %; *e.g.* Table 1, entries 2, 3, 5, and 12).

The progress of the reaction was followed by 1H NMR and SEC. Small samples of the reaction mixtures were taken off at various stages of reaction and active centers were deactivated by addition of 5 % acetic

acid solution in methanol. Samples $A_xB_y(OH)_x$ (Scheme A) were characterized by 1H NMR and SEC chromatography after removal of all volatile products.

The method of the synthesis of star-shaped polymers was reported previously [1–5]. One typical example (for MPEG 550) is nevertheless given below, for completeness of the present paper. Similar procedures were applied in the syntheses with MPEG 750 and 2000 used as precursors.

Example

2.66 g of the purified MPEG 550 ($4.84 \cdot 10^{-3}$ mole) and 75.8 mg of NaH ($3.16 \cdot 10^{-3}$ mole) were placed together in a vacuum glass ampoule closed with Rotaflo[®] stopcock and attached to the high vacuum line. The ampoule was evacuated and ~4.5 mL of THF was distilled in. Then the ampoule was heated at ~60 °C for a few hours until all NaH reacted [until no gas evolution (H_2) and no solid NaH were observed]; $[RO^-]/[RO^- + ROH] = 65.3 \%$. To this reaction mixture 1.17 g of DGNG ($5.42 \cdot 10^{-3}$ mole) was added ($[DGNG]_0/[active\ centers]_0 = 1.12$, where $[active\ centers] = [-O^-] + [-OH]$; concentration of reagents = 48.9 wt. %). During this operation dry Ar was passing through the ampoule. Then the reaction mixture was kept at 50 °C for 140 h. From time to time small samples were taken from the reaction mixture for the determination of the presence of epoxy groups (1H NMR) and the overall progress of reaction (1H NMR and SEC). Finally the resulting product was terminated with CH_3COOH and was purified by ultrafiltration in water (Table 1, entry 10).

Purification of the products

Some products were purified by ultrafiltration in water with Amicon Ultrafiltration Stirred Cell (200 mL),

using membrane with a molecular weight equal to 1000 cut off (Diaflo[®] ultrafiltration membranes).

Methods of testing

— The ¹H NMR spectra were recorded in CDCl₃ using a Bruker AC-200 apparatus operating at 200 MHz. The primary -OH (-OH in precursor A) and the secondary -OH (-OH on the core of stars, *i.e.* in A_xB_y, Scheme A) were determined in the form of their trifluoroacetic esters ...-CH₂OC(O)CF₃ (~4.50 ppm δ) and ...>CHOC(O)CF₃ (~5.30 ppm δ), respectively, converted with trifluoroacetic anhydride, according to the procedure described earlier [17].

— Mentioned previously SEC chromatography was carried out using a chromatograph composed of LKB 2150 HPLC pump or Knauer K-501 HPLC pump with LDC RI detector and Viscotek T60A dual detector [right angle laser light scattering at λ = 670 nm (RALLS) and differential viscometer]. Detectors were connected in parallel. Three Suprema columns (30 + 100 + 3000 Å; 8 · 300 mm; Polymer Service Standard) were used in a series. Aqueous solution of NaN₃ (0.1 %) was used as a mobile phase at the flow rate of 1.0 mL · min⁻¹. The samples (concentration of polymers: ~ 5 mg · mL⁻¹) were filtered through 0.2 μm pore size membrane filters. Injection volumes of the samples solutions were 100 μL. Calibration was performed with two standards of linear PEOX, delivered by Viscotek, with narrow ($M_n = 22\,300$; $M_w = 23\,200$) and broad ($M_n = 31\,500$; $M_w = 97\,900$) molecular weight distribution (MWD); TriSEC[®] software (Viscotek) was used to treat the data. The whole procedure of calculation based on RALLS and viscosity numbers [η] measurements is given in one of the recently published papers, where a large part of Viscotek manual is quoted [18].

— The number of arms (*f*) was determined in a similar way as in earlier papers of this series, namely by comparing M_n of the stars with M_n of the arm precursors or from the contraction factor of radii of gyration (*g*), determined by TriSEC[®] [4, 5].

RESULTS AND DISCUSSION

Star polymers were synthesized using arms precursors of different M_n (MPEG 550, 750, and 2000) and various [diepoxide]₀/[arm]₀ ratios (range: 0.76—3.44).

From ¹H NMR spectra a concentration of epoxy groups present in the reaction mixture — allowing determination of the progress of the reaction and the content of primary and secondary hydroxyl groups — was determined, as it was previously described [4]. Reaction of stars formation was carried out until no more epoxide groups were detected. At that moment some amount of unreacted precursor (MPEG) was still present in the reaction mixture. This presence at the end of the reaction was always observed for MPEG 550 and 750 and also in

many experiments when MPEG 2000 was used as a precursor.

Influence of [diepoxide]₀/[MPEG]₀ ratio on the final content of unreacted precursor

For all reactions the content of unreacted MPEG in the reaction mixture at the end of the reaction (no epoxy groups were observed) is decreasing with increasing [diepoxide]₀/[MPEG]₀ ratio. Both diepoxides — DGEG and DGNG — gave the similar results.

In Figure 1 the dependence of the content of -CH₂OH groups (unreacted MPEG 550) in the reaction mixture at the end of the reaction at 70 °C, on [diepoxide]₀/[MPEG 550]₀ ratio is given. Both regression lines for DGEG and DGNG are close each to other. The vertical dotted line corresponds to [diepoxide]₀/[MPEG 550]₀ ratio — that is a border of formation of soluble stars [6]. Beyond this value only insoluble products were obtained. Arrows pointing to ~10 % and ~13 % indicate the lowest theoretical amounts of unreacted -CH₂OH end groups present in the reaction mixture at the end of reaction. Thus, there is almost the same proportion (close to the lowest theoretical value) of the unreacted MPEG 550 for a given starting [diepoxide]₀/[MPEG 550]₀ ratio, which does not depend on the nature of diepoxide used. Similar dependence was observed for MPEG 750.

The crossing points of the regression lines (for the experimental data) with the abscissa determine the conditions of the complete conversion of a precursor — dis-

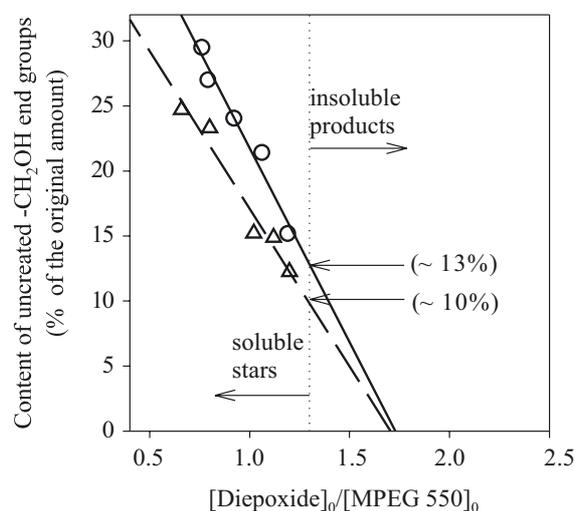


Fig. 1. Content of -CH₂OH groups (unreacted MPEG 550) in the reaction mixture (at the end of the reaction) vs. [diepoxide]₀/[MPEG 550]₀ ratio for DGEG (o) and DGNG (Δ). Reaction conditions: THF, concentration of reagents ~50 wt. %; temp. 70 °C. The vertical line corresponds to the ratio of [diepoxide]₀/[MPEG 550]₀ = ~1.3, responsible for the insoluble products formation (determined from demarcation line [6]). Theoretical lowest amounts of unreacted -CH₂OH end groups (unreacted MPEG 550) — ~10 and ~13 % — are shown for the respective diepoxides

appearance of $-\text{CH}_2\text{OH}$ end groups. It is equal to ~ 1.7 for MPEG 550 and to ~ 2.1 for MPEG 750 (not shown in the Fig. 1). These values are situated in the area of insoluble products formation. Thus, it means that complete conversion of starting compounds (MPEG and diepoxide) is not practically possible for both MPEG 550 and 750 for the applied conditions of reaction, that was confirmed experimentally.

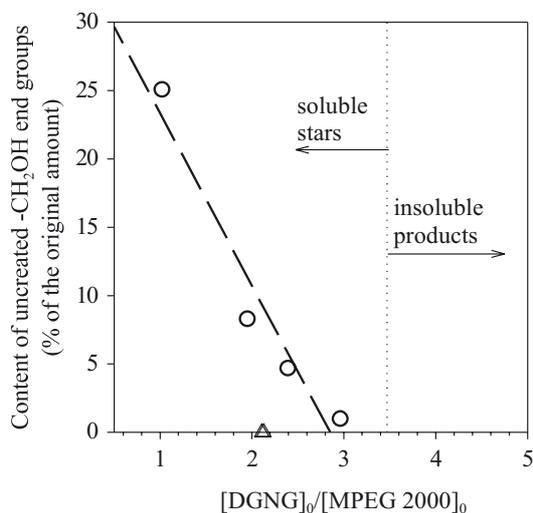


Fig. 2. Content of the $-\text{CH}_2\text{OH}$ groups (unreacted MPEG 2000) in the reaction mixture (at the end of the reaction) vs. $[\text{DGNG}]_0/[\text{MPEG 2000}]_0$ ratio. Reaction conditions: (o) THF, concentration of reagents ~ 50 wt. %; temp. 70°C . The vertical dotted line shows the ratio $[\text{diepoxide}]_0/[\text{MPEG 2000}]_0 = \sim 3.5$, responsible for insoluble products formation (determined from demarcation line [6]). In this plot entries 2 and 3 from Table 1 point (Δ) (concentration of reagents ≤ 37 wt. %), not included for calculation of the regression line, with complete conversion of both reagents [6] are also given

In Figure 2 the dependence of the content of $-\text{CH}_2\text{OH}$ groups (unreacted MPEG) in the reaction mixture at the end of the reaction at 70°C on $[\text{DGNG}]_0/[\text{MPEG 2000}]_0$ ratio is given. The vertical dotted line gives the $[\text{DGNG}]_0/[\text{MPEG 2000}]_0$ ratio equal to ~ 3.5 that corresponds to conditions of insoluble product formation for this precursor.

The regression line is crossing the abscissa at value ~ 2.9 , i.e. in the area of soluble product formation. Thus, for MPEG 2000 it is possible to get the quantitative conversion of precursor (even theoretically).

Influence of the concentration of reagents and the proportion of the alkoxide groups (RO^-) in the initiator ($\text{RO}^- + \text{ROH}$)

The content of unreacted $-\text{CH}_2\text{OH}$ groups in the reaction mixture decreases with the increasing concentration of both reagents (the sum of $[\text{MPEG 550}]_0$ and $[\text{DGNG}]_0$) (Fig. 3). But even for the reaction in bulk not complete

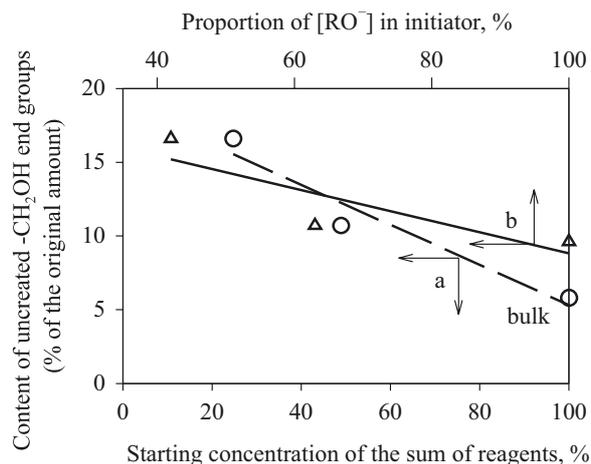


Fig. 3. Content of $-\text{CH}_2\text{OH}$ groups (unreacted MPEG 550) in the reaction mixture (at the end of the reaction) vs. starting concentration of the sum of reagents ($[\text{MPEG 550}]_0 + [\text{DGNG}]_0$) and vs. the proportion of alkoxide anions in the initiator $[\text{RO}^-]/[\text{RO}^- + \text{ROH}]$. Reaction conditions for plot (a): (o) $[\text{DGNG}]_0/[\text{MPEG 550}]_0 = 1.12$, $[\text{RO}^-] = 65.3\%$, temp. 50°C (Table 1, entries 9—11) and for plot (b): (Δ) $[\text{DGNG}]_0/[\text{MPEG 550}]_0 = 1.12$, THF, concentration of reagents ~ 46 — 49 wt. %, temp. 50°C (Table 1, entries 10, 12, and 13)

disappearance of precursor was observed. The ratio of $[\text{DGNG}]_0/[\text{MPEG 550}]_0$ and the content of the alkoxide groups in the initiator ($[\text{RO}^-]/[\text{RO}^- + \text{ROH}]$) were constant and equal to 1.12 and 65.3 %, respectively. It was observed that with four times increasing concentrations of reagents (Table 1, entries 9—11) the reaction time decreases, e.g. from 411 h for the reaction carried out in THF (concentration: 24.7 wt. %) to 35 h for the reaction in bulk.

The increase in the ratio $[\text{RO}^-]/([\text{RO}^-] + [\text{ROH}])$ leads to decreasing content of the unreacted MPEG (Fig. 3) and time needed to complete the reaction (e.g. from 195 to 65 h, Table 1, entries 13 and 12, respectively). However, even for $[\text{ROH}]/[\text{RO}^-] = 0$ (100 % of RO^- groups) the complete conversion of MPEG 550 could not be reached. In this series of experiments the ratio of $[\text{DGNG}]_0/[\text{MPEG 550}]_0 = 1.12$ and the concentration of reagents equal to ~ 46.0 wt. % were kept constant and only the proportion of alkoxide anions (RO^-) in the initiator ($\text{RO}^- + \text{ROH}$) varied from 42.2 to 100 %.

Influence of the temperature

The decrease in temperature caused the increase in M_n of the formed stars and did not influence considerably the final content of unreacted MPEG. Thus, for $[\text{RO}^-] = 47.3\%$ and $[\text{DGEG}]_0/[\text{MPEG 550}]_0$ ratios equal to 0.76 (70°C) and 0.79 (50°C), M_n of products were equal to 12 900 and 18 700, respectively; while the final contents of MPEG in these experiments were practically the same — 29.5 and 27.0 % of the MPEG used, respectively (Table 1, entries 7 and 8).

Some properties of the stars prepared

Characteristic parameters of several stars derived from MPEG 550 and 2000 and prepared by the method described above, are summarized in Table 1. M_n , M_w , MWD , $[\eta]$, branching indexes (g and g' , determined by TriSEC[®] from radii of gyration and viscosity numbers), and finally the average number of arms (f) calculated from M_n and g (for stars with regular and random distributed arms), are given. In the last column the concentrations of reagents and the proportion of the alkoxide groups present in the initiator are reported.

It should be mentioned that in described reaction a variety of macromolecules, containing different numbers of arms, is formed. Therefore, the obtained stars have a broad distribution of the number of arms, built of polydispersed MPEG. The length of arms influence also the process of star's formation and their final structure.

The methods of calculation of the number of arms were described previously [4, 5]. Stars obtained in this work could be consider as "copolymers" built of linear polyoxyethylene glycol arms and crosslinked (or branched) core. For example, the stars derived from MPEG 2000 (Table 1, entries 2 and 3), obtained in the reaction with the complete conversion of both reagents [6], contain ~82 wt. % MPEG and ~18 wt. % core. On the other hand the stars derived from MPEG 550 have larger core,

namely ~24 wt. % (Table 1, entries 7, 8) or even ~33 wt. % (Table 1, entries 9—13). The structures of stars with longer arms (MPEG 2000) are more homogeneous than of that one having shorter arms (MPEG 550). That probably could be a reason that the numbers of arms, determined from M_n and g (reg.) (in stars derived from MPEG 2000) are almost equal (Table 1, entries 1—5). On the other hand in the stars derived from MPEG 550 the numbers of arms, calculated from M_n , are: (1) close to the values determined from g (ran.) (in case of DGEG used as diepoxide, Table 1, entries 7, 8) or (2) situated between f values determined from g (reg.) and g (ran.) (for DGNG, Table 1, entries 9, 10, 12, 13).

Thus, the length of precursor substantially influences the number of arms (as it is shown in Figure 6) and additionally rules the structure and homogeneity of the resulted stars.

Reported values of $g' \leq 1$ confirm additionally more compact structure of the resulted stars in comparison to linear poly(oxyethylene oxide) (PEOX) — e.g. $[\eta] = 0.686$ was determined for PEOX standard ($M_n = 50\ 000$).

Higher molecular weights (and the average number of arms) were obtained for higher $[\text{diepoxide}]_0/[\text{MPEG}]_0$ ratio. In Figure 4 the appropriate data for MPEG 550 and 2000 are shown. Points are rather scattered but the relationship is unambiguous and similar to that one observed by Lutz [19] and Rempp [20], in the

Table 1. Characterization of star-shaped polymers^{a)}

No. a),b)	[DGNG] ₀ / [MPEG] ₀	Determined (TriSEC)						f calculated from			Concentration, % ^{c)}
		M_n	M_w	D_M	$[\eta]$, dL/g	g	g'	M_n	g (reg.)	g (ran.)	
1 ^{d)}	1.02	20 600	34 800	1.69	0.136	0.311	0.435	8.7	8.3	15.0	50.2 (70.8)
2 ^{e)}	2.10	37 500	68 300	1.82	0.163	0.218	0.316	14.8	13.0	24.4	37.2 (100)
3 ^{e)}	2.10	23 000	32 300	1.40	0.155	0.313	0.415	9.1	8.9	16.1	19.1 (100)
4 ^{d)}	1.95	46 000	87 800	1.91	0.133	0.148	0.230	19.0	19.6	37.5	42.5 (59.7)
5 ^{d)}	2.39	71 500	126 100	1.76	0.121	0.095	0.166	28.8	30.9	60.1	49.7 (100)
6 ^{f)}	3.44	252 100	1 531 000	6.07	0.176	0.050	0.102	92.0	59.3	117.0	60.4 (70.8)
7	0.76 ^{g)}	12 900	16 500	1.28	0.096	0.306	0.405	18.3	9.1	16.5	51.5 (47.3)
8	0.79 ^{g)}	18 700	23 700	1.27	0.088	0.211	0.302	24.9	13.5	25.4	51.5 (47.3)
9	1.12	50 700	84 600	1.67	0.086	0.075	0.140	61.8	39.3	77.0	100 (65.3)
10	1.12	33 300	44 900	1.35	0.072	0.097	0.171	40.6	30.3	58.9	48.9 (65.3)
11	1.12	18 400	20 400	1.11	0.042	0.100	0.170	21.9	29.3	57.0	24.7 (65.3)
12	1.12	30 900	35 000	1.13	0.070	0.104	0.181	38.1	28.2	54.7	46.0 (100)
13	1.12	33 000	41 000	1.24	0.082	0.119	0.199	39.3	24.5	47.4	46.0 (42.2)
14	1.19	54 900	141 800	2.58	0.118	0.098	0.168	68.2	30.0	58.2	59.0 (47.3)
15	1.18	27 500	48 400	1.76	0.061	0.080	—	25.8	36.8	71.9	54.4 (56.9)
16	1.29	21 900	64 100	2.93	0.045	0.107	—	20.5	27.3	53.0	54.9 (56.9)

^{a)} For meanings of the symbols — see text.

^{b)} Polymerization carried out in THF.

^{b)} MPEG 2000, temp. 70 °C (entries 1—6); MPEG 550, temp. 70 °C (entry 7); MPEG 550, temp. 50 °C (entries 8—14); MPEG 750, temp. 50 °C (entry 15) and temp. 70 °C (entry 16).

^{c)} Concentration of the sum of reagents ($[\text{MPEG}]_0$ and $[\text{diepoxide}]_0$). In brackets the proportion of alkoxide groups $[\text{RO}^-]$ in the initiator ($[\text{RO}^-]/[\text{RO}^- + \text{ROH}]$), %.

^{d)} Some amount of unreacted MPEG 2000 was present in the reaction mixture at the end of reaction: 25.1 % (entry 1), 15.8 % (entry 4), and 7.1 % (entry 5).

^{e)} Complete conversion of both reagents (from Ref. [6]).

^{f)} After 71 h of heating (20.6 % of epoxy groups were present). After 120 h insoluble product was formed.

^{g)} $[\text{DGEG}]_0/[\text{MPEG 550}]_0$.

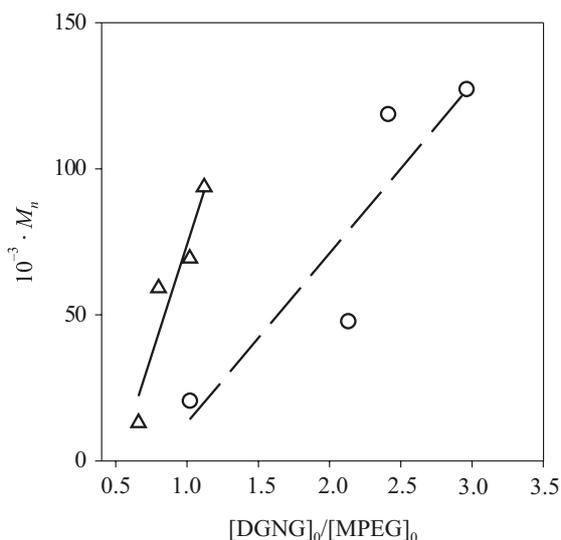


Fig. 4. M_n of star polymers vs. $[\text{diepoxide}]_0/[\text{MPEG}]_0$ ratio at temp. 70 °C (concentration of reagents ~50 wt. %); (Δ) — MPEG 550, (o) — MPEG 2000

syntheses of stars from living polystyrene (PS) with DVB, and by Matyjaszewski [21] in the reaction of poly(*t*-butyl acrylate) with DVB. MWD value and also the number of arms increase considerably for the stars obtained with all precursors if $[\text{diepoxide}]_0/[\text{MPEG}]_0$ ratio is close to the condition of insoluble products formation (Table 1, entries 6 and 14). For example, the analysis of the reaction mixture after 71 h of heating at 70 °C (Table 1 entry 6) disclosed that still 20.6 % of epoxy groups was present and no precursor (MPEG 2000) was detected by $^1\text{H NMR}$. Further heating converted this soluble star into an insoluble product (after 120 h of heating).

In Figure 5 it is shown, that the number of arms (f_n) increases from 21.9 to 61.8 when concentration of the sum of reagents ($[\text{MPEG 550}]_0$ and $[\text{DGNG}]_0$) changes from 24.7 to 100 wt. % (bulk) (Table 1, entries 9—11). These data agree with the similar observation, reported by Rempp, for the star formation from living PS and DVB [20].

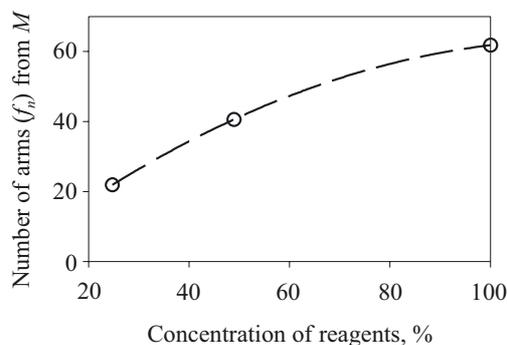


Fig. 5. Number of arms (f_n) vs. starting concentration of the sum of reagents ($[\text{MPEG 550}]_0 + [\text{DGNG}]_0$) at temp. 50 °C; $[\text{RO}^-] = 65.3\%$, Table 1, entries 9—11)

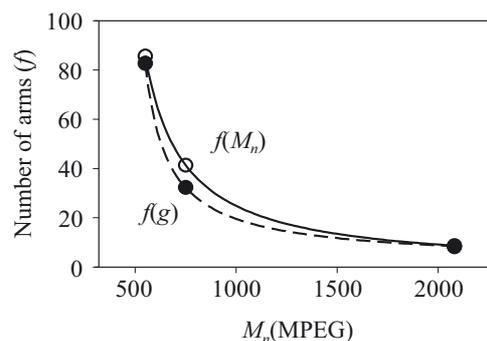


Fig. 6. Number of arms (f) vs. M_n of precursor (MPEG 550, 750, and 2000) calculated from M_n of stars [$f(M_n)$] and from parameter g [$f(g)$]. $[\text{DGNG}]_0/[\text{MPEG}]_0$ was equal to: 1.02 (MPEG 550), 0.93 (MPEG 750), and 1.02 (MPEG 2000). Reaction conditions: THF, concentration of reagents ~50 wt. %, $[\text{RO}^-] = 52\text{--}70\%$, temp. 70 °C

Similar relationship was observed for MPEG 2000 used as a precursor. The increase in the concentration of reagents from 19.1 to 37.2 wt. % resulted in an increase in M_n of the final stars from 23 000 to 37 500 and number of arms from 9.1 to 14.8 (Table 1, entries 2 and 3).

In Figure 6 the dependence of the number of arms on M_n of MPEG is shown. Number of arms, calculated from M_n of stars and from the contraction parameter g [4], increases when M_n of MPEG decreases from 2000 to 550. This dependence was given for experiments carried out at 70 °C and for almost identical ratios of $[\text{DGNG}]_0/[\text{MPEG}]_0$ (from 0.93 to 1.02). The reported relationship is similar to that observed previously by Lutz [19] and Rempp [20] for the polystyrene/divinylbenzene system.

CONCLUSION

The effects of length of a precursor, $[\text{diepoxide}]_0/[\text{MPEG}]_0$ ratio, concentration of reagents, and temperature on the formation of the multiarm stars resulting from the reactions of oligoalcohols with diepoxides were studied. The number of arms (f), determined from M_n of stars and from branching index g , decreases with the increase in the length of precursor. The increase in M_n of stars was observed for the decrease in temperature of the reaction and for increase in $[\text{diepoxide}]_0/[\text{MPEG}]_0$ ratio, the overall concentration of reagents, and the length of a precursor. The final content of the unreacted precursor (MPEG) in the reaction mixture was lower for higher: $[\text{diepoxide}]_0/[\text{MPEG}]_0$ ratio, proportion of alkoxide anions in the initiator ($[\text{RO}^-]/[\text{RO}^-] + [\text{ROH}]$), concentration of reagents, and the length of a precursor. The increase in $[\text{diepoxide}]_0/[\text{MPEG}]_0$ ratio and the overall concentration of reagents lead to higher polydispersity (MWD value) of the resulted star polymers. On the other hand the change of the proportion of alkoxide anions has no pronounced influence on M_n and f of stars. In some Figures (e.g. 3, 5, and 6) there are shown only three experimental points, but reported relationships seem to be

correct, because the ranges of the given values placed on abscissa are rather broad — usually the highest value is ~4 times higher than the lowest one. The change of temperature did not influence considerably the final content of unreacted MPEG.

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