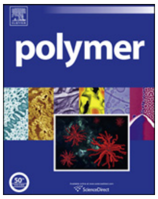
Polymer 51 (2010) 342–354

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Amphiphilic behaviour of poly(glycidol)-based macromonomers and its influence on homo-polymerisation in water and in water/benzene mixture

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ARTICLE INFO

Article history:
Received 23 July 2009
Received in revised form
24 November 2009
Accepted 25 November 2009
Available online 1 December 2009

Keywords:
Poly(glycidol)
Polymerisation of macromonomers
Micellization

ABSTRACT

The properties of amphiphilic polyether macromonomers and their behaviour during homo-polymerisation in water and in water/benzene mixture are reported. Homo-poly(glycidol) macromonomer bearing polymerisable *p*-vinyl benzyl end groups (PGl55-St) and two block poly(glycidol)-*b*-poly(glycidyl phenyl ether) macromonomers, containing polymerisable *p*-vinyl benzyl end groups attached to the hydrophobic (PGl52-*b*-PGlPhE8-St) or hydrophilic (PGlPhE9-*b*-PGl54-St) block were used for investigations. DLS measurements showed formation of micelles by all macromonomers, what is the reason for enhanced homo-polymerisation. In water the polymerisation initiated with 4,4′-azobis(4-cyanovaleric acid) was fast, while macromonomer conversion was over 90%. Introduction of benzene to the polymerisation system resulted in formation of swollen (less packed) micelles and to a decrease of the local concentration of double bonds in the micelle core. As a result the decrease of reaction rate followed by longer polymerisation time in case of PGl55-St and PGl52-*b*-PGlPhE8-St was observed. Nevertheless, their conversion remained high and varied from 95 to 10. In contrast for PGlPhE9-*b*-PGl54-St increase of polymerisation rate, accompanied by slight increase of conversion was observed for homo-polymerisation in water/benzene mixture.

1. Introduction

Branched and star-like polymers have attracted attention due to their unique properties [1–5]. Their solutions show lower viscosity in comparison to their linear counterparts. Additionally, their properties may be influenced by proper modification of functional end groups, which number is much higher in a branched molecule than in the linear chain. The properties in condensed phase are also different as the chain entanglements, which decide about the viscoelastic properties of the materials, are not likely to be formed.

Among the branched polymers a special class are regularly branched copolymer brushes. Depending on the relative length of the branch versus the polymer backbone such polymers assume a conformation that looks like a star or a brush. Generally, there are three methods which were applied to synthesize cylindrical polymer brushes: "*grafting onto*", "*grafting from*" and "*grafting through*".

In the "*grafting onto*" technique [6–8] the polymers having reactive chain ends, react and attach to another polymer backbone main chain, which bears functional groups. The advantage of this method is that both the main chain and side chain length or molecular weight distribution can be influenced (e.g. by controlled methods of polymers synthesis). However, in general only a small, usually insufficient amount of polymer reacts with the backbone due to sterical hindrance resulting in low grafting density.

The "*grafting from*" technique is based on the preparation of branched polymers by grafting of the side chains directly from the main polymer chain [9–12]. By this method well-defined polymer brushes with high and uniform grafting density can be obtained. However, the molecular weight of the side chains can only be calculated indirectly from the overall molecular weight of the brush, or if possible, by subsequent detachment of the side chains from the backbone (for example by hydrolysing the ester linkage in the brushes) [12].

The "*grafting through*" synthesis of branched polymer is based on homo-polymerisation of macromonomers bearing a polymerisable group, mainly vinyl group [13–15]. Homo-polymerisation of

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doi:10.1016/j.polymer.2009.11.056

macromonomers provides regular multi-branched comb-like polymers with a high branch density, where for example for a vinyl type macromonomer a branch is situated on every second carbon atom. Generally, both the length of branches and backbone in a comb polymer can be controlled during the synthesis. An advantage here is the use of a known macromonomer as a branch, where the molecular weight and its distribution is predicted and controlled by the method of preparation (i.e. living anionic or cationic polymerisation, group transfer polymerisation, ATRP) [15–17]. The main disadvantage of the "*grafting through*" method is the fact the macromonomers often polymerise with difficulties because of their high molecular weight as compared to lower molecular weight monomers [18]. High segment density around the propagating site is considered to prevent the propagating active site from approaching the polymerisable end group of macromonomers via the steric effect. As the result the degree of polymerisation of polymacromonomers is usually low [19–23].

It was, however, found that one feature which has great influence on both the rate of the polymerisation of macromonomers and degree of polymerisation of the polymacromonomers is the self-organization of macromonomers in the solvent. Such behaviour was observed in case of amphiphilic macromonomers, for example poly(ethylene oxide) macromonomers bearing hydrophobic polymerisable groups, where the polymerisation in water was very fast and the obtained degree of polymerisation high [24–27]. In such solvent which is a good for one part and poor or non-solvent for the second part of the molecule, micellar structures were formed. This aggregation locally concentrated and oriented hydrophobic polymerisable groups, which enhanced and accelerated their polymerisation [28–31]. This had given a new impetus to the studies of the synthesis of the brush molecules of well-defined structure.

The aim of this work was the synthesis of polymacromonomers (brushes) based on polyethers, with different properties and architecture by the "*grafting through*" method. Furthermore quantitive conversion of macromonomers, fast reaction rate and high DP of polymacromonomers were desired. Two types of macromonomers were synthesised for this studies: (i) homo-poly(glycidol) macromonomer bearing a polymerisable *p*-vinyl benzyl end group (PGl$_{55}$-St), and (ii) block poly(glycidol)-*b*-poly(glycidyl phenyl ether) macromonomers with a polymerisable *p*-vinyl benzyl end group attached to the hydrophobic (PGl$_{52}$-*b*-PGlPhE$_{8}$-St) or hydrophilic (PGlPhE$_{9}$-*b*-PGl$_{54}$-St) block. As aggregation in solution influences the polymerisation of a macromonomer the behaviour of such amphiphilic poly(glycidol)-based macromonomers in water was studied in details as first part of the work. In the second part the influence of different parameters on free radical polymerisation of obtained macromonomers in water or in water/benzene mixture was investigated.

Poly(glycidol) is a functional analogue of poly(ethylene oxide), where one of the hydrogen atoms in the chain repeating unit is replaced with a CH_2OH pendant group. Similar behaviour like that observed for PEO macromonomer was expected for homo-polymerisation in the applied polymerisation systems. Additionally each poly(glycidol) unit posses easily accessible hydroxyl groups providing possibilities for post-modification, opening a new route for more complex structures.

2. Experimental procedures

2.1. Materials

Tetrahydrofuran (THF, POCh) was dried over CaH_2 (Fluka) and refluxed over Na/K alloy. *p*-vinyl benzyl chloride (Aldrich), glycidol (2,3-epoxypropanol, Aldrich), ethyl vinyl ether (Fluka) were distilled prior to use. Glycidyl phenyl ether (Fluka) and glycidyl acetal (synthesised according to literature [32]) were purified three times by distillation over CaH_2 under inert atmosphere. α,α'-Azobis-isobutyronitrile (97%, Aldrich) and 4,4′-azobis(4-cyanovaleric acid) (98%, Aldrich) were crystallized from methanol and dried before use. 1,6-Diphenyl-1,3,5-hexatriene (DPH, Aldrich, 98%),

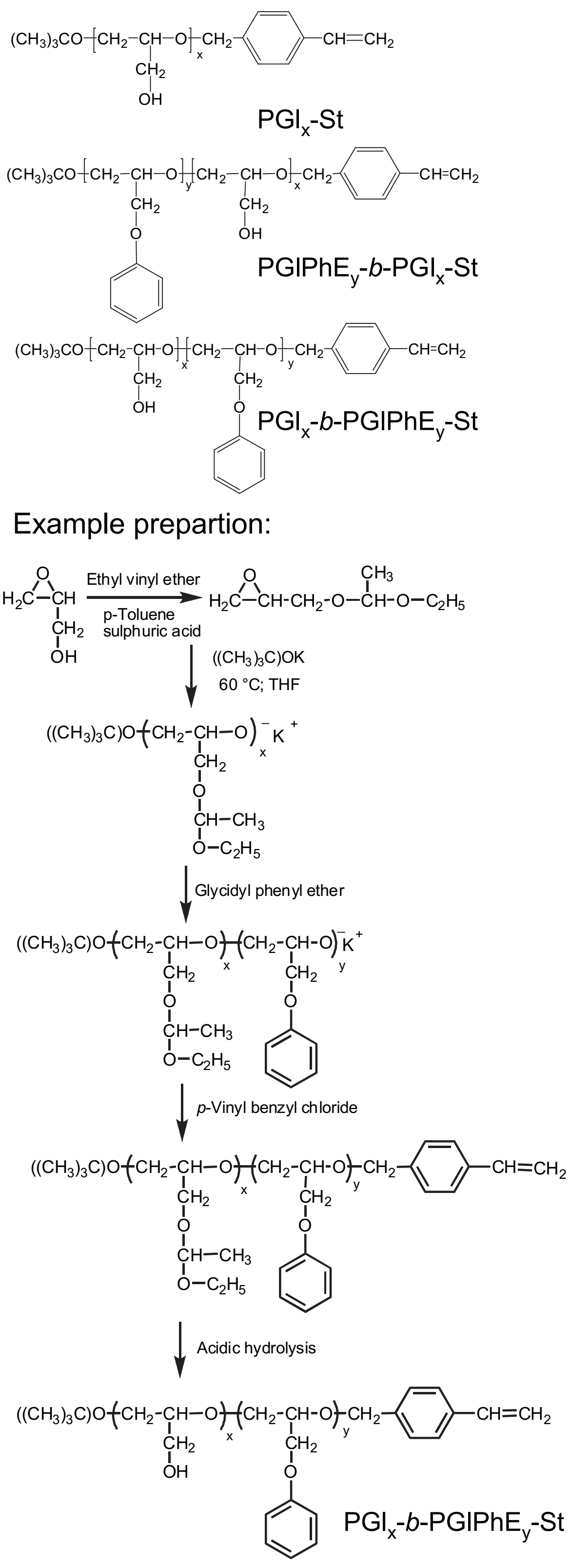

Fig. 1. Synthesis of amphiphilic macromonomers based on poly(glycidol).

potassium *tert*-butoxide (Aldrich), *p*-toluenesulfonic acid (POCh), benzene (p.a. POCh Gliwice), 2,5-dihydroxybenzoic acid (Aldrich) and oxalic acid (Fluka) were used as received.

2.2. Preparation of macromonomers

Chemical structures and synthesis conditions of polyether macromonomers used for the investigations are presented in Fig. 1. The procedure of macromonomer synthesis was described in detail in our previous work [33].

Briefly, poly(glycidol)-based macromonomers were obtained by anionic polymerisation of glycidol acetal in THF initiated with potassium *tert*-butoxide. Block macromonomers of glycidol acetal and glycidyl phenyl ether were obtained using living anionic copolymerization with sequential monomer addition. After full conversion of monomers the reactive *p*-vinyl benzyl groups were introduced into polyether chain by termination of living polymerising centre with *p*-vinyl benzyl chloride. The last step of synthesis was the removal of protecting acetal groups from poly(glycidol) (PGl) block of macromonomers under acidic conditions. The synthesised macromonomers are further denoted as PGl_x-St, PGl_x-*b*-$PGlPhE_y$-St and $PGlPhE_y$-*b*-PGl_x-St where *x* corresponds to the degree of polymerisation of PGl block and *y* to the degree of polymerisation of poly(glycidyl phenyl ether) segment.

2.3. Polymerisation of macromonomers

Conventional free radical homo-polymerisation of macromonomers was carried out in two systems: (i) in water with 4,4′-azobis(4-cyanovaleric acid) (AVA) as initiator at 60 °C; (ii) in water/benzene mixture (10:1 v/v) using 2,2′-azobis-isobutyronitrile (AIBN) as initiator at 70 °C. In order to evaluate the influence of time on macromonomer conversion samples were drawn at given times in range from 0.5 to 24 h. After removal of solvents the polymerisation product was dissolved in DMF and analysed using SEC–MALLS chromatography.

2.3.1. Polymerisation in water

The macromonomer (the amount varied from 0.25 g to 2 g) and AVA were placed in a 10 mL glass reactor, dissolved in 2 mL of bidistilled water and stirred overnight. The 10-fold molar excess of initiator in respect to the amount of reactive *p*-vinyl benzyl end groups of macromonomer was used. The air was removed from the reaction mixture by three freeze–pump–thaw cycles and the reactor was purged with nitrogen. The polymerisation was carried out in an oil bath at 60 °C for 24 h.

2.3.2. Polymerisation in water/benzene mixture

Proper amounts of AIBN were placed in a 10 mL glass reactor and dissolved in 0.2 mL of benzene. The macromonomer (amount varied from 0.25 g to 2 g) was dissolved in 2 mL of bidistilled water and added to the initiator solution. The reaction mixture was intensively stirred overnight. The 10-fold molar excess of initiator in respect to amount of reactive *p*-vinyl benzyl end group of macromonomer was used. After air was removed by three freeze–pump–thaw cycles the reaction mixture was purged with nitrogen and placed in an oil bath at 70 °C for 24 h.

2.3.3. Purification

Water-soluble polymacromonomers were purified from unreacted residue by dissolution in methanol and dialysis through a SpectraPor membrane with an exclusion limit of 50,000 g/mol. The dialysis was carried out from 5 to 7 days. Water insoluble products obtained by polymerisation of $PGlPhE_9$-*b*-PGl_{54}-St were purified from unreacted residues by precipitation from DMF solution into water.

2.4. Characterisation

DLS measurements were performed on a commercial laser light scattering spectrometer (ALV/DLS/SLS-5000) equipped with an ALV-5000EP multiple digital correlator. Laser goniometer system ALV/CGS-8F S/N 025 with a helium–neon laser (Uniphase 1145P,

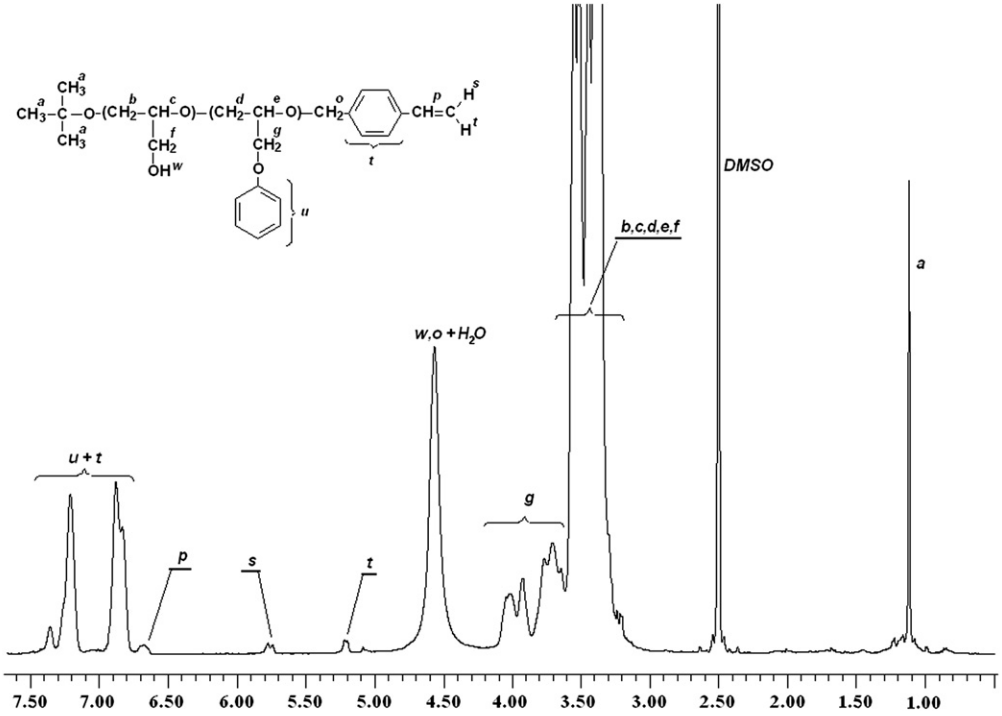

Fig. 2. Example ^1H NMR spectrum of PGl_{52}-*b*-$PGlPhE_8$-St in DMSO-d_6.

Table 1
Properties of macromonomers used for investigations.

Sample name	M_n [g/mol]		dn/dc	M_w/M_n	Degree of functionalisation[a]
	^{1}H NMR	SEC–MALLS			
PGl_{55}-St	4400	4500	0.055	1.06	0.71
PGl_{52}-*b*-$PGlPhE_8$-St	5300	5700	0.066	1.06	0.74
$PGlPhE_9$-*b*-PGl_{54}-St	5600	6000	0.065	1.05	0.72

[a] Calculated as ratio of intensity of one proton from *p*-vinyl benzyl group and intensity of one proton from *tert*-butyl initiator group.

Table 2
CMC values of macromonomers according to surface tension, UV–vis and SLS measurements.

Sample	CMC [g/L]		
	Surface tension	UV–vis	SLS
PGl_{55}-St	8.5	Not measured	9.0
PGl_{52}-*b*-$PGlPhE_8$-St	0.75	0.8	0.75
$PGlPhE_9$-*b*-PGl_{54}-St	0.6	0.6	0.6

output power of 22 mW, with $\lambda = 632.8$ nm) was used. Samples were passed through a 0.2 μm nylon membrane filter, transferred to 10 mm diameter test tube and immersed in thermostated toluene bath at 25 °C. Hydrodynamic radius measurements were performed at the scattering observation angles θ varying from 15° to 120° with 15° steps. The value of hydrodynamic radius and polydispersity index (PDI) of the micelles were obtained by cumulant analysis while R_h distributions were calculated with CONTIN.

Static light scattering (SLS) measurements were performed on a modified FICA 50 SLS apparatus equipped with a He–Ne laser (wavelength of 632 nm). For CMC measurements the aqueous solution of macromonomers in the range from 0.0044 g/L to 20 g/L were filtered using 0.1 μm nylon filters right into the 20 mm test tube, immersed in thermostated bath at 25 °C and measured. The measurements were taken at observation angles $\theta = 90°$ (determination of CMC) and at θ varying from 15° to 120° (molecular weights of micelles).

The refractive index increments (dn/dc) of macromonomers in water and in DMF were measured at 25 °C with a refractometer FICA 50.

^{1}H NMR spectra were recorded using Brucker DRX 500 (500 MHz).

Size exclusion chromatography measurements were performed in *N*,*N*-dimethylformamide (DMF) with 5 mmol/L LiBr at 45 °C using a set of PSS GRAM 10 μm columns: 10^3, 10^2 and 30 Å. All chromatograms were obtained at 1 mL/min flow. A differential refractometer Δn 1000 from WGE Dr. Bures was used as the concentration detector. The molecular weights were determined using the DAWN multi-angle laser light scattering (MALLS) detector from Wyatt Technology Corporation and their Astra software.

Surface tension measurements of the series of aqueous solutions of macromonomers in the concentration range from 0.0044 to 10 g/L were taken at 25 °C on the DSA KRUSS INSTRUMENT tensiometer.

UV–vis measurements were preformed using UV–vis Lambda 19 (Perkin–Elmer) spectrometer. Samples for measurements were prepared as follows: 25 μL of 0.4 mM DPH solution in methanol was added to the 2.5 mL of aqueous polymer solution in the concentration range from 0.0044 to 10 g/L. The final solutions, containing 1% v/v methanol and 0.004 mM of DPH, were left in the dark to equilibrate for at least 1 h but no longer than 24 h. The spectroscopic measurements were made in the wave range 300–500 nm, where the main absorption intensity peak characteristic of DPH at 356 nm was used for determination of the CMC of the polymers.

3. Results and discussion

Amphiphilic macromonomers can be prepared by sequential living anionic polymerisation of the oxiranes, glycidyl phenyl ether (GlPhE) and protected glycidol (glycidol acetal – GlAc) [33]. The polymerisation was carried out in dry THF at 60 °C using potassium *tert*-butoxide as initiator and *p*-vinyl benzyl chloride as terminating agent. Protective acetal groups were removed under acidic conditions to give a hydrophilic block of poly(glycidol). Using this procedure a variety of macromonomers with different composition was prepared. The example ^{1}H NMR spectrum of PGl_{52}-*b*-$PGlPhE_8$-St macromonomer after hydrolysis is presented in Fig. 2.

The problem which appeared during synthesis of all types of macromonomers was non-quantitive termination of living chains with *p*-vinyl benzyl chloride. As the result the functionalisation of obtained macromonomers with reactive *p*-vinyl benzyl groups was never quantitive. The obtained macromonomer functionality calculated from ^{1}H NMR spectra as a ratio of intensity of one proton from *p*-vinyl benzyl group and intensity of one proton from *tert*-butyl initiator group varied from 0.65 to 0.80.

From the synthesised macromonomers three samples with properties presented in Table 1 were chosen for the experiments described in this work.

3.1. Amphiphilic properties of macromonomers

A number of amphiphilic copolymers were shown to aggregate in the form of micelles in water [34]. The unique solution properties

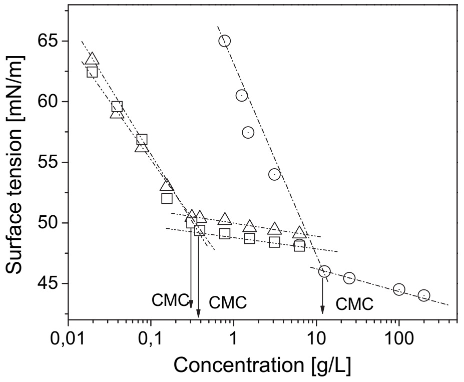

Fig. 3. CMC determined by surface tension measurements of PGl_{52}-*b*-$PGlPhE_8$-St (△), $PGlPhE_9$-*b*-PGl_{54}-St (□) and PGl_{55}-St (○) macromonomers in aqueous solution.

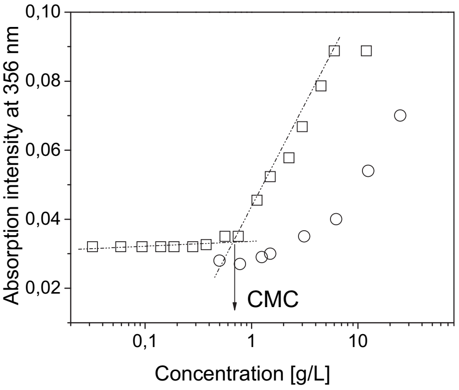

Fig. 4. CMC determined by UV–vis measurements of $PGlPhE_9$-*b*-PGl_{54}-St (□) and PGl_{55}-St (○) macromonomers.

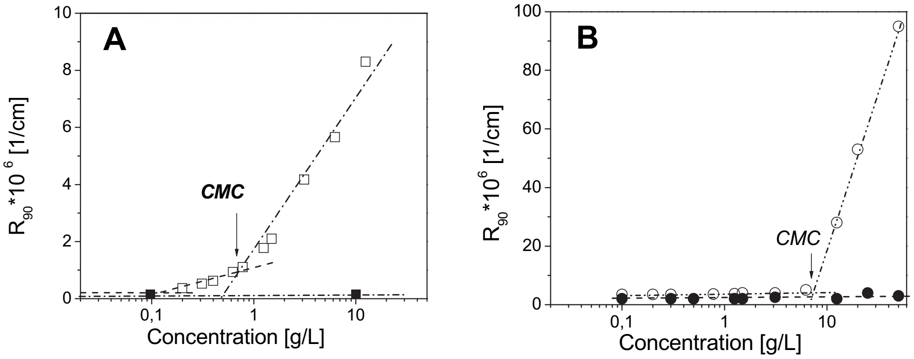

Fig. 5. CMC determined by static light scattering measurements in water (open symbols) and in DMF (closed symbols) of PGlPhE$_9$-*b*-PGl$_{54}$-St (A) and PGl$_{55}$-St (B).

of amphiphilic polymers are the consequence of their molecular structure. When a block copolymer is dissolved in a selective solvent, which is a thermodynamically good solvent for one block and a poor solvent or non-solvent for the other the copolymer chains may associate reversibly to form micellar aggregates which resemble in most of their aspects those obtained with classical low molecular weight surfactants. In case of block macromonomers of PGl$_{52}$-*b*-PGlPhE$_8$-St and PGlPhE$_9$-*b*-PGl$_{54}$-St the solubility of the blocks is different. Poly(glycidyl phenyl ether) is soluble in a wide range of solvents such as chloroform, THF, acetone, benzene, DMF, DMSO, while poly(glycidol) is a highly hydrophilic polymer soluble only in polar solvents like water, low alcohols, DMF or DMSO. Taking these into account formation of micelles by those macromonomers in water was expected. Micellization is of great influence on the polymerisation behaviour of macromonomers as it was reported by Ito et al. [24–27]. Since the self-assembly process is crucial for the polymerisation rate of macromonomers detailed studies were performed in order to estimate the critical micellization concentration of obtained macromonomers, micelle size and the aggregation number.

3.1.1. *Critical micellization concentration (CMC) measurements*

One of the parameter which is used to describe the formation of micelles is the critical micellization concentration (CMC) defined as the concentration above which micelles are spontaneously formed. Generally, by dissolution of amphiphilic macromolecules in water the polymer will initially partition into the water/air interface lowering the energy of the interface, removing the hydrophobic parts of the polymer from contacts with water. Subsequently, when the surface coverage by the solute increases and the surface free energy (surface tension) decreases the amphiphilic polymer starts aggregating into micelles. Thus, the system free energy is decreased again by decrease of the contact area of hydrophobic parts of the amphiphilic polymer with water. Excessing the CMC any further addition of amphiphilic substance will just increase the number of micelles.

Three different methods were used independently in order to estimate the CMC of poly(glycidol)-based macromonomers: Surface tension measurements, UV–vis spectroscopy, and static light scattering, where each of the techniques used different properties of the micellization process. Measurements were carried out only in pure water.

3.1.1.1. Determination of CMC by surface tension measurement. In Fig. 3 semi-logarithmic plots of the surface tension measured for aqueous solutions of macromonomers versus their concentration in water are presented.

As it can be seen with increasing macromonomer concentration the surface tension decreases almost linearly till a transition point is reached, which implied subsequent aggregation and corresponded to the CMC directly. For these materials the surface tension curves suffered a downward trend after the transition point, however decrease of the surface tension values was not so steeply as before breakpoint. Such behaviour was however already observed and was assigned to the dispersity of amphiphiles [35].

The CMC values of the three different macromonomers determined from the transition point are collected in Table 2. As was expected the values measured for block macromonomers were

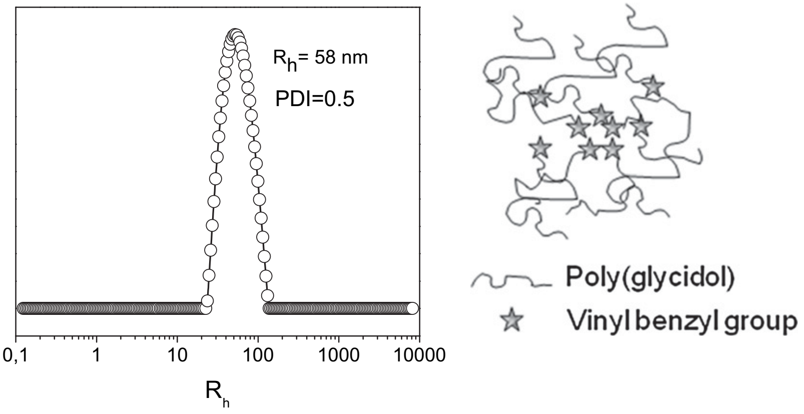

Fig. 6. R_h distribution (unweighted) at $\Theta = 90^\circ$ of PGl$_{55}$-St macromonomer in water ($C = 20$ g/L).

much lower than the one measured for homo-poly(glycidol) macro-monomer (PGl_{55}-St). It is connected with the fact that in case of PGl_{55}-St the only hydrophobic group which drives the micellization process is *p*-vinyl benzyl end group.

3.1.1.2. Determination of critical micellization concentration by UV–vis measurements. Spectroscopic techniques based either on optical absorption or on emission of light from probe molecule, are well-established for investigating a wide range of physical properties of micellar solutions [36]. The fact that micelles can solubilise relatively large amounts of sparingly water-soluble compounds has been used to determine the onset of micelles formation by measuring the change of concentration of a chosen sparingly soluble substance, possessing a convenient UV–vis absorbing chromophore. Below the CMC, the concentration of the solubilisate in the solution is the same as in aqueous solution in the absence of surfactant. Above CMC, the total amount of additives in solution increases sharply as the total micelle concentration increases because sparingly soluble substances are solubilised in the hydrophobic micelle core.

In this work the solubilisation of the dye (1,6-diphenyl-1,3,5-hexatriene, DPH) was employed in the investigation of the CMC values of macromonomers. The curves of DPH adsorption intensity at 356 nm versus log *C* of macromonomer are presented in Fig. 4 for $PGlPhE_9$-*b*-PGl_{54}-St and PGl_{55}-St. The results obtained for PGl_{52}-*b*-$PGlPhE_8$-St were corresponding well to that obtained for $PGlPhE_9$-*b*-PGl_{54}-St.

The curves obtained during UV–vis measurements of block macromonomers were sigmoidal with the district increase of the absorption above a certain value. The first inflection of the curve indicated the micelle formation and was used for the determination of the CMC. The second inflection corresponded to the complete solubilisation of the dye in hydrophobic core of formed micelles. The CMC values determined from the inflection point are collected in Table 2.

In case of PGl_{55}-St macromonomers determination of the precise value of CMC using this method was problematic. Although an increase of the concentration of the macromonomer was accompanied by the increase of the absorbance no district inflection of curve was noticed. This can be assigned to the structure of the micelles. In case of PGl_{55}-St macromonomer the only group forming the hydrophobic core is *p*-vinyl benzyl end groups. Hence, dye solubilisation is lower than in case of micelles formed by block macromonomers.

3.1.1.3. Determination of CMC by static light scattering measurements. The CMC was also determined by static light scattering experiments at 25 °C, where the Rayleigh ratio of aqueous and DMF macromonomer solution at a scattering angle of 90° was plotted against the macromonomer concentration. As can be seen in Fig. 5 micelle formation in water was proved for the macromonomers as the R_{90} parameter increased steeply with increase of concentration above that to be identified as CMC. From the other side in DMF, which is a good solvent for both blocks of macromonomers, only negligible scattering was observed indicating the molecular dissolution of macromonomers.

In case of aqueous solution of block copolymers a two step increase of R_{90} was observed. In the concentration region from 0.1 to 0.8 g/L a slight increase of R_{90} value was observed indicating probably the formation of loose aggregates and the initiation of the micellization process. However, in that region the concentration of the polymer was too low so that no well-defined micelles could be formed. Nevertheless, starting from the concentration 0.8 g/L, which was identified as CMC, the district increase of R_{90} value with increasing concentration of macromonomer indicated formation of well-organized micelles. Similar behaviour was observed for PGl_{52}-*b*-$PGlPhE_8$-St. The CMC of investigated macromonomers was summarized in Table 2.

To conclude, the CMC values of the macromonomers were well in accordance despite of the applied determination method. For the block macromonomers CMC was low and varied in the range 0.6–0.8 g/L, while macromonomers bearing *p*-vinyl benzyl end groups as the only hydrophobic group showed much higher CMC in the range 8.5–9.0 g/L. The much lower CMC values measured for block macromonomers results from the presence of poly(glycidyl phenyl) block thus from their higher hydrophobicity. As a result such macromonomers forms micelles easier.

3.1.2. Light scattering measurements of macromonomers micellization

3.1.2.1. Dynamic light scattering measurements in water. DLS technique is also a powerful tool in order to investigate the behaviour of polymers in solution. Similarly to SLS the DLS measurements confirmed formation of micelles by all studied macromonomers; however obtained results were depending on macromonomer structure.

In case of PGl_{55}-St relatively broad distribution of the hydrodynamic radii was observed as can be seen in Fig. 6. The formed structures were relatively large with the size of 58 nm. As the size of formed structures in water is relatively big (taking into account macromonomer molecular weight) PGl_{55}-St form loose, undefined aggregates with high amount of water in its structure. The hydrodynamic structure of obtained aggregates for PGl_{55}-St was proposed as presented in Fig. 6.

In case of block macromonomers monomodal distribution and much more compact micelles were formed with the hydrodynamic

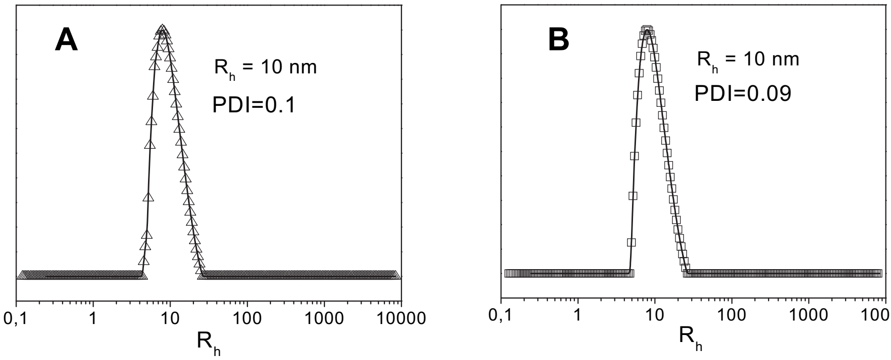

Fig. 7. R_h distribution (unweighted) at $\Theta = 90°$ of micelles formed by $PGlPhE_9$-*b*-PGl_{54}-St (A) and PGl_{52}-*b*-$PGlPhE_8$-St (B) in water ($C = 5$ g/L).

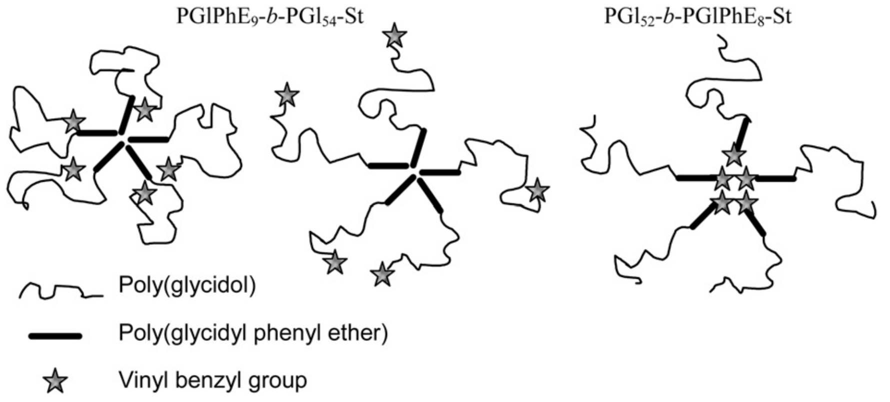

Fig. 8. Probable structure of micelles formed by block macromonomers PGlPhE$_9$-*b*-PGl$_{54}$-St and PGl$_{52}$-*b*-PGlPhE$_8$-St in water.

radius in the range of 10 nm (Fig. 7) and dispersity index of ∼0.1. The obtained micelles were stable and in the studied range the R_h was also almost independent on the macromonomer concentration (from 0.8 to 5 g/L).

Taking these data into account the micelle structure can be proposed as shown in Fig. 8. The hydrophobic core of micelles formed by PGlPhE$_9$-*b*-PGl$_{54}$-St and PGl$_{52}$-*b*-PGlPhE$_8$-St macromonomers consists of poly(glycidyl phenyl ether) and optionally *p*-vinyl benzyl groups and is surrounded by hydrophilic poly(glycidol) shell.

As the goal of the work was also studies of macromonomer polymerisation in water/benzene mixture in the next step to the water solution of micelles proper amount of benzene was added. The water/benzene ratio was kept on the level 10/1 v/v (the same as used for polymerisation experiments). Directly after addition of benzene into micelle solution in water the mixture became very turbid. For PGl$_{55}$-St after intensive stirring overnight turbidity remained almost unchanged. In contrast in case of block macromonomers decrease of solution turbidity was obtained after stirring for 24 h. As benzene is solvent for PGlPhE block and non-solvent of PGl block it migrated into micelle hydrophobic core and swollen, less compact micelles were formed.

In Fig. 9 are shown R_h distribution of micelles/aggregates in water/benzene mixture for PGl$_{52}$-*b*-PGlPhE$_8$-St and PGl$_{55}$-St. As can be seen in comparison to measurements carried out in pure water 10-times increase of R_h value of micelles was observed for PGl$_{52}$-*b*-PGlPhE$_8$-St in water/benzene mixture confirming the migration of benzene into hydrophobic micelle core. The behaviour of PGlPhE$_9$-*b*-PGl$_{54}$-St was similar to that observed for PGl$_{52}$-*b*-PGlPhE$_8$-St (data not shown).

In contrast in case of PGl$_{55}$-St R_h distribution in benzene/water mixture was very broad. However, in this macromonomer only vinyl benzyl groups are able to migrate into benzene droplets. Under the applied experimental conditions probably inhomogeneous dispersion of droplets in water was formed.

3.1.2.2. *Static light scattering measurements – number of aggregation in water.*

The aggregation number of macromonomers in micelles is very important in terms of their polymerisation process. It provides information about average number of molecules per unit and corresponds to that of the double bonds and of ω-alkyl groups of the macromonomers. Thus, from the concentration and angular extrapolations of the excess integrated scattered intensity of the copolymer samples in dilute aqueous solutions, i.e. from the Zimm plots, the apparent molecular weight of micelles were determined. Knowing the values of the refractive index increments (d*n*/d*c*) of the corresponding polymers the weight-average molecular weights (M_W) and the corresponding average association numbers could be calculated. The results obtained for block macromonomers at different concentrations are listed in Table 3. Measurements were carried out for macromonomers concentration in the solution up to 100 g/L. At higher concentrations polymer solutions were too turbid. At this concentration aggregation of micelles took place.

The investigated macromonomers showed different aggregation numbers depending on macromonomer structure. In case of PGlPhE$_9$-*b*-PGl$_{54}$-St the obtained value was lower than for the macromonomer of similar block length but opposite order of the blocks, i.e. the double bond attached to the hydrophobic block. It is likely that the differences are connected with the structures of formed micelles. As was shown in Fig. 8 in case of PGlPhE$_9$-*b*-PGl$_{54}$-

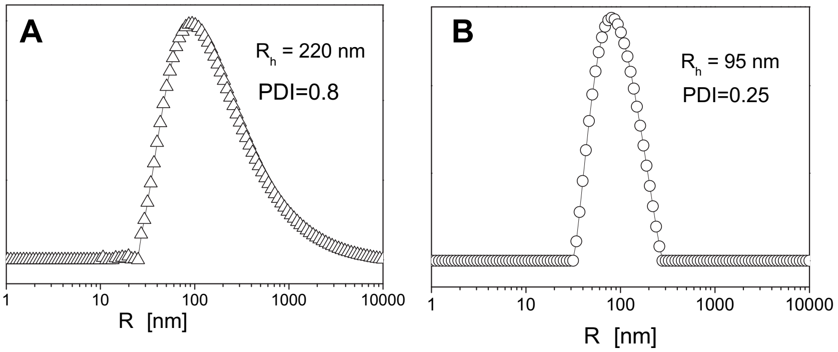

Fig. 9. R_h distribution (unweighted) at $\theta = 90°$ of PGl$_{55}$-St (A) and PGl$_{52}$-*b*-PGlPhE$_8$-St (B) in water/benzene mixture (10/1 v/v) at $C = 20$ g/L and 5 g/L, respectively.

Table 3
Properties of micelles formed in water by block macromonomers according to SLS measurements.

Sample	d*n*/d*c* in water	$C = 5$ g/L		$C = 25$ g/L		$C = 50$ g/L		$C = 100$ g/L	
		M_w	N	M_w	N	M_w	N	M_w	N
PGl_{52}-*b*-$PGlPhE_8$-St	0.134	582,000	102	702,000	123	840,000	147	860,000	151
$PGlPhE_9$-*b*-PGl_{54}-St	0.136	486,000	81	500,000	83	603,000	100	15,000,000	Aggr. of micelles

N – Average association number.
M_w – molecular weight of micelles [g/mol].

St the *p*-vinyl benzyl groups may form the core of the micelle too (flower-like micelles) increasing spatial hindrance by formation of loops. This may lead to the decrease of the amount of chains forming the micelles core. In case of $PGlPhE_9$-*b*-PGl_{54}-St also at concentration ~100 g/L aggregation of single micelles into micelles aggregates appeared.

In the next step determination of the aggregation number of micelles in water/benzene mixture was performed. Measurements were only possible for diluted polymer solutions (5 g/L) as at higher concentration the turbidity of the solution was too high. Molecular weight of micelles was found to be $M_w = 402{,}000$ g/mol ($N = 70$) and $M_w = 390{,}000$ ($N = 65$) for PGl_{52}-*b*-$PGlPhE_8$-St and $PGlPhE_9$-*b*-PGl_{54}-St, respectively. Introduction of benzene into polymer solution caused thus reduction of aggregation number of micelle. However, for calculations the refractive index increment of macromonomers in water was used, thus the result may be not fully correct.

Estimation of M_w of micelles formed by PGl_{55}-St in water or water/benzene mixture by SLS was not performed. As this polymer is a mixture of macromonomer able to aggregate and unfunctionalized poly(glycidol) the determined M_w would be the average molecular weight of micelles and soluble polymer. Additionally, turbidity of water/benzene mixture was too high.

3.2. Free radical polymerisation of macromonomers

The polymerisation of macromonomers in organic solvents usually leads to low degrees of polymerisation, slow polymerisation and low conversion [19–23]. The reason is the steric screening of the propagation centre by the branched structure formed in the polymerisation, which hampers the access of the polymerisable group to the reaction centres. However, high degrees of polymerisation were obtained when amphiphilic macromonomers consisting of poly(ethylene oxide) chains terminated with reactive double bonds were polymerised in water [24–27]. Additionally, the polymerisation of such macromonomers was fast with almost quantitative conversion of macromonomers.

Poly(glycidol)-based macromonomers form micellar structures with hydrophobic cores and hydrophilic shells. It was expected that formation of micelles by macromonomers should influence their behaviour in homo-polymerisation reactions. Thus, the free radical polymerisation of the amphiphilic poly(glycidol) macromonomers was carried out in two different polymerisation systems:

- In water using the water-soluble initiator AVA (4,4′-azobis (4-cyanovaleric acid)) ($T = 60$ °C);
- In water/benzene mixture of the volume ratio 10:1 v/v using water insoluble initiator AIBN (2,2′-azobis(isobutyronitrile) ($T = 70$ °C).

In the first system the initiator is a water-soluble compound, which has to diffuse into the hydrophobic micelle core in order to initiate polymerisation [24–27]. The second system was intended to enhance the reaction between the initiator and the reactive hydrophobic group of the macromonomer. The hydrophobic initiator (AIBN) was expected to penetrate into the hydrophobic core of the structure and to initiate the polymerisation of macromonomers in the region where the concentration of reactive groups is the highest. Since the applied initiator is water insoluble, it was introduced as benzene solution into the water reaction medium, preserving the same water to benzene volume ratio of 10/1 in all experiments. The hydrophobic solvent was also expected to penetrate the hydrophobic part of the aggregates were the polymerisable groups are concentrated, thus further increasing the polymerisation [33].

3.2.1. Detection of macromonomer conversion and molecular weight of polymacromonomers

All synthesised macromonomers are the mixture of functionalized macromonomer and non-functionalized oligomer, inert to polymerisation. The degree of functionalisation of macromonomers used for investigations varied from 71 to 74%. It has to be kept in mind that regardless of the structure the only part of macromonomers which is involved in polymerisation reaction is the *p*-vinyl benzyl group. Thus, the maximal conversion of macromonomer is equal to its degree of functionalisation.

The polymerisation of the macromonomers was monitored by ^{1}H NMR spectroscopy and SEC. In ^{1}H NMR measurements the disappearance of double bond of *p*-vinyl benzyl group was followed giving quantitative information of the polymerisation progress. In SEC measurements in all cases the polymerisation product was well separated from the mixture of non-reactive oligomer and unreacted macromonomer (Fig. 10). The conversion of macromonomers was normalized by the degree of functionalisation to give the real conversion of macromonomer in the system (Eq. (1)). For instance 70% conversion of sample PGl_{55}-St with functionality 71% refers in total to 99% of macromonomer conversion.

$$\%\,\text{Conversion} = \frac{S_{\text{pm}}}{\sum S \times \text{DF}} \cdot 100\% \qquad (1)$$

S_{pm} – peak area of polymacromonomer; ΣS – sum of all peak areas i.e. of polymacromonomer, unreacted macromonomer and non-reactive oligomer; DF – degree of functionalisation of macromonomer.

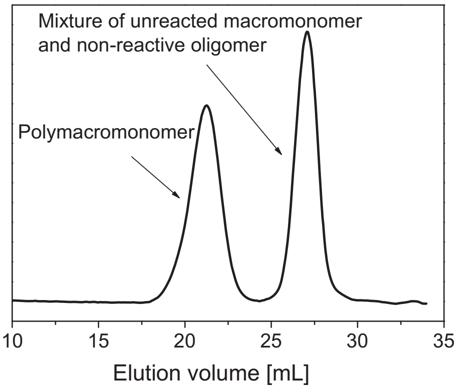

Fig. 10. SEC trace of polymacromonomer obtained from PGl_{52}-*b*-$PGlPhE_8$-St.

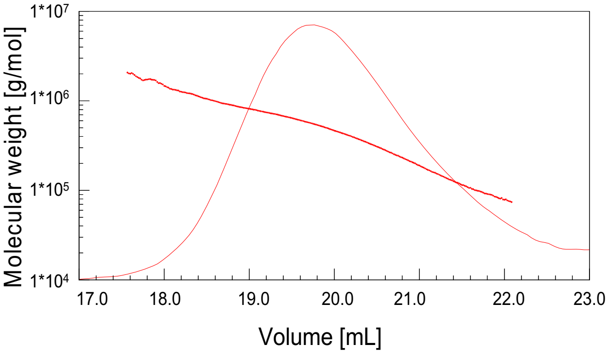

Fig. 11. Plot of molecular weight versus elution time for polymacromonomer obtained from PGl_{52}-*b*-$PGlPhE_8$-St; $M_n = 250{,}000$ g/mol.

The M_n values of polymacromonomers were determined by SEC–MALLS measurements using refractive index increments determined for macromonomers (see Table 1). The necessary condition for the correct molecular weight determination by SEC is the linearity of the molecular weight versus elution volume plot. This was well fulfilled for all synthesised polymacromonomers (Fig. 11 confirming that regardless on the structure good separation of the branched polymers was achieved on the applied columns set). Hence, it can be concluded that the obtained molecular weights of polymacromonomers are close to real values.

3.2.2. *Conversion and rate of polymerisation of macromonomers*

The conversion curves versus time obtained for poly(glycidol)-type macromonomer during polymerisation carried out in water and in water/benzene mixture are presented in Fig. 12.

As it can be seen the rate of polymerisation was strongly dependent on the macromonomer type and polymerisation system. In water maximally obtainable conversion of macromonomers varied from 90 to 99%, while the lowest value was obtained for $PGlPhE_9$-*b*-PGl_{54}-St. The rate of polymerisation was high in all cases as a constant value of conversion was reached after less than 2 h. The highest rate of polymerisation was found for macromonomers bearing polymerisable group attached to the hydrophobic block (PGl_{52}-*b*-$PGlPhE_8$-St). Already after 30 min of reaction 90% of macromonomer conversion was detected, while after 1 h conversion reached final 99%.

Such behaviour seems to be the consequence of the structure of micelles formed by macromonomers in water. The compartmentalization of the reactive groups decreases the termination rate [29–32]. As a consequence the rate of polymerisation (propagation step) increases. PGl_{52}-*b*-$PGlPhE_8$-St forms the most compact well-organized micelles with the unsaturated groups gathered in the micelle core (see Fig. 8). In case of PGl_{55}-St the formed aggregates are larger and less compact (see Fig. 6) leading to the decrease of polymerisation rate in comparison to PGl_{52}-*b*-$PGlPhE_8$-St. The lower rate of polymerisation obtained for $PGlPhE_9$-*b*-PGl_{54}-St in comparison to PGl_{52}-*b*-$PGlPhE_8$-St results from two facts: firstly the polymerisation product precipitates from water during reaction causing the interruption of the polymerisation chain; secondly although it forms compact micelles the reactive groups are concentrated at the interface of core and shell (flower-like micelles) or do not take part in the formation of the hydrophobic core at all being concentrated than in the micelle shell. As the result the local concentration of the reactive groups is lower than for PGl_{52}-*b*-$PGlPhE_8$-St macromonomer.

In case of PGl_{55}-St and PGl_{52}-*b*-$PGlPhE_8$-St macromonomers the polymerisation carried out in water/benzene mixture was slower in comparison to that carried out in pure water. For PGl_{52}-*b*-$PGlPhE_8$-St the rate of polymerisation decreased about two-times, while for PGl_{55}-St 11 h was needed to reach 95% of conversion (2 h in pure water). Nevertheless, in both cases conversion was as high as during polymerisation in pure water. The decrease of the polymerisation rate for polymerisation in water/benzene mixture is the effect of two opposite phenomena. From one side the hydrophobic initiator penetrating the hydrophobic core of the micelle structure initiated the polymerisation of macromonomers in the region where the concentration of reactive groups was the highest. However, as the initiation was introduced into the system after dissolution in benzene swollen, less compact micelles were formed. The local concentration of the double bonds in the micelle core decreased leading to the decrease of the reaction rate. Since the decomposition rate of AVA in water ($k_d = 6 \times 10^{-6}$ s^{-1}) and AIBN in benzene ($k_d = 8.3 \times 10^{-6}$ s^{-1}) was found to be only a little different from each other, this cannot be the reason of the lower rate of polymerisation in water/benzene system [24].

In contrast in case of $PGlPhE_9$-*b*-PGl_{54}-St macromonomer the formation of swollen micelles enhanced the polymerisation rate. The polymerisation rate of $PGlPhE_9$-*b*-PGl_{54}-St increased twice in comparison to polymerisation in pure water and was on the level as for PGl_{52}-*b*-$PGlPhE_8$-St. In water/benzene mixture constant conversion of this macromonomer was reached after 1 h. A slightly higher conversion (~5%) was observed in comparison to polymerisation carried out in pure water. In our opinion it is the effect of the increase of solubility of the growing radical during polymerisation. The polymacromonomer obtained for polymerisation of $PGlPhE_9$-*b*-PGl_{54}-St is completely insoluble in water, but soluble in benzene. It is thus possible that, especially at the beginning of the reaction, the presence of the co-solvent improved the solubility of the growing radical resulting in the increase of the polymerisation rate.

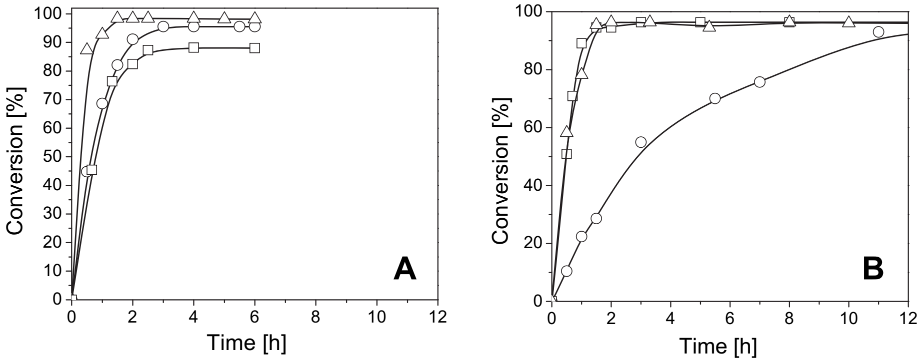

Fig. 12. Conversion of PGl_{52}-*b*-$PGlPhE_8$-St (△), $PGlPhE_9$-*b*-PGl_{54}-St (□) and PGl_{55}-St (○) in time: (A) in water using AVA ($C_{macromonomer} = 0.20$ g/mL, $T = 60$ °C); (B) in water/benzene mixture 10/1 v/v using AIBN ($C_{macromonomer} = 0.20$ g/mL, $T = 70$ °C).

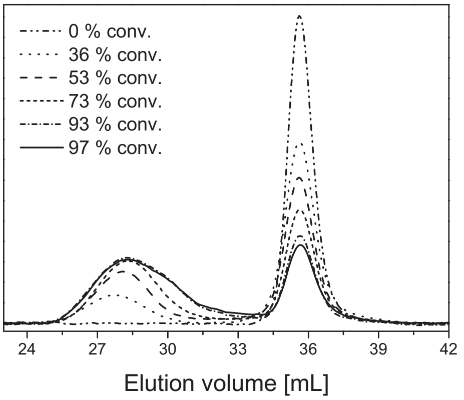

Fig. 13. SEC traces during polymerisation at different conversion of macromonomer PGl_{55}-St for polymerisation in water ($C_{macromonomer} = 0.2$ g/mL, $T = 60$ °C).

3.2.3. Influence of conversion on the molecular weight and dispersity of polymacromonomers

SEC traces of samples drawn at different time during PGl_{55}-St polymerisation are presented in Fig. 13. The data are normalized that the sum of peak areas of macromonomer and polymacromonomer remains constant. With increase of the macromonomer conversion the area of the macromonomer peak decreases, while the area of polymacromonomer peak increases. Also the increase of the polymacromonomer dispersity at higher conversions, mostly because of appearance of low molecular weight fraction in the elution volume range 30–33 mL (broadening of polymacromonomer peak) can easily be followed.

Polymerisation of macromonomers showed the typical behaviour usually observed for free radical polymerisations. Regardless of the polymerisation system or macromonomer type the molecular weight of polymacromonomers decreased with increase of the conversion of macromonomer (Fig. 14A). The decrease of the molecular weight of polymacromonomer was accompanied by an increase of the dispersity of the product (Fig. 14B). The largest increase of M_w/M_n values was observed in last phase of polymerisation, when the conversion of macromonomers exceeded 85%. It is somehow typical for free radical polymerisations, where at high conversion of reactive groups the interruption of the growing chains by e.g. chain transfer reactions becomes more privileged. Hence, the fraction of low molecular weight products increases significantly increasing the dispersity of the product and decreases its average molecular weight.

3.2.4. Influence of macromonomer concentration on the degree of polymerisation and dispersity of polymacromonomers

The influence of concentration of macromonomers during polymerisation in water and in water/benzene mixture on the degree of polymerisation (DP) of polymacromonomers and on M_w/M_n values is presented in Figs. 15 and 16. The conversion of macromonomers was only slightly dependent on its concentration in the reaction mixture and in most cases reached about 95%.

The degree of polymerisation of polymacromonomers increased with increasing initial concentration of the macromonomers in the reaction mixture regardless of the polymerisation system or macromonomer type. However, in all cases above a certain concentration (about 0.2 g/mL) DP of the polymerisation products varied only moderately with concentration of macromonomer. Additionally degrees of polymerisation of polymacromonomers are close to the aggregation numbers measured at different concentration (Table 3). In order to obtain high molecular weight polymacromonomers polymerisations were carried out at concentrations higher than suitable for SLS measurements. However, as an example the aggregation number for PGl_{52}-*b*-$PGlPhE_8$-St in water with a concentration of 0.1 g/mL was 151 and the corresponding degree of polymerisation was 140. Taking this information into account we can expect that the polymerisation proceeds mostly in micelles core. The slightly smaller PD value can be assigned to the incomplete functionalisation of the macromonomer.

In the case of PGl_{52}-*b*-$PGlPhE_8$-St and PGl_{55}-St the molecular weights of polymacromonomers obtained for polymerisation in water were higher than that obtained for polymerisation in the benzene/water mixture with the same concentration. As was already mentioned addition of benzene to the system caused a decrease of aggregation numbers of micelles for block macromonomers. Probably because of that the degree of polymerisation of PGl_{52}-*b*-$PGlPhE_8$-St decreased in water/benzene mixture, especially at higher concentrations.

The opposite effect was observed for $PGlPhE_9$-*b*-PGl_{54}-St where introduction of benzene to the polymerisation system slightly increased the DP of the polymacromonomer. As was mentioned earlier polymacromonomers obtained from $PGlPhE_9$-*b*-PGl_{54}-St are insoluble in water and precipitates from the reaction mixture during reaction. This leads to the interruption of the growing polymer chain. As the result the molecular weight of the products decreases. The introduction of benzene, which is a good solvent of that polymacromonomer, on one side decreased aggregation number of micelles but from other side enhanced the solubility of the growing radical and higher molecular weights of polymacromonomers were obtained.

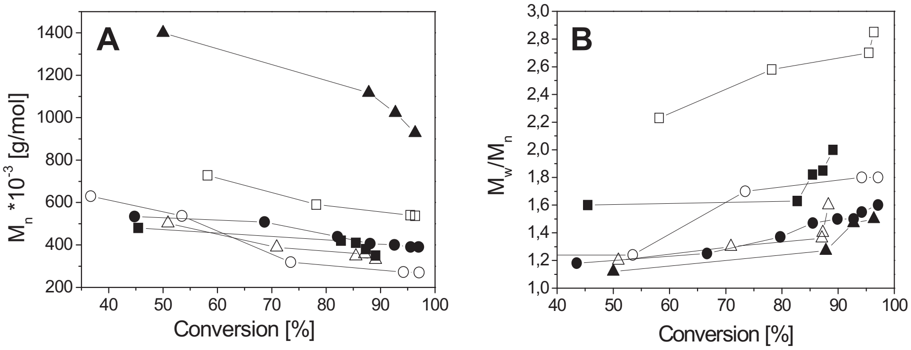

Fig. 14. Influence of conversion on the molecular weight M_n (A) and dispersity M_w/M_n (B) of polymacromonomers during polymerisation in water using AVA ($C_{macromonomer} = 0.20$ g/mL, $T = 60$ °C (open symbols)) and in water/benzene mixture 10/1 v/v using AIBN ($C_{macromonomer} = 0.20$ g/mL, $T = 70$ °C (closed symbols)) of PGl_{52}-*b*-$PGlPhE_8$-St (△), $PGlPhE_9$-*b*-PGl_{54}-St (□) and PGl_{55}-St (○).

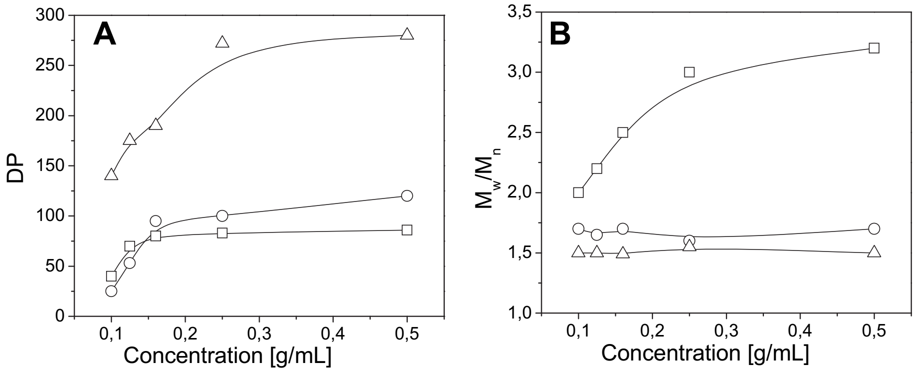

Fig. 15. Influence of macromonomer concentration on degree of polymerisation DP (A) and dispersity M_w/M_n (B) of polymacromonomer for polymerisation in water ($T = 60$ °C) for PGl_{52}-*b*-$PGlPhE_8$-St (△), $PGlPhE_9$-*b*-PGl_{54}-St (□) and PGl_{55}-St (○).

The increase of the molecular weight of the polymacromonomers with increase of macromonomer concentration during polymerisation in the mixture water/benzene was accompanied by an increase of the dispersity of the product. This may suggest that polymerisation took place in non-uniform benzene swollen micellar aggregates of different sizes. On the other side for polymerisations in water dispersity of the polymacromonomers was independent on the macromonomer concentration during polymerisation suggesting formation of relatively well-defined micelles or aggregates, of course with exclusion of the polymacromonomers obtained from $PGlPhE_9$-*b*-PGl_{54}-St, which precipitate from water during reaction.

3.2.5. *Properties of polymacromonomers*

The homo-polymerisation of macromonomers provided a series of regular polymers with comb morphology, depending on molecular weight brushes or star-like structures. The polymerisation of homo-poly(glycidol) macromonomers (PGl_{55}-St) resulted in the hydrophilic polymacromonomer with the main chain constituted of poly(styrene) substituted in *p*-position with poly(glycidol) chain. On the other side, the homo-polymerisation of block macromonomers PGl_{52}-*b*-$PGlPhE_8$-St and $PGlPhE_9$-*b*-PGl_{54}-St resulted in the core-shell structures. The properties of obtained comb structures depended not only on the chemical composition of the arms but also on the relative arrangement of the blocks in the polymer molecule, i.e. polymerisation of $PGlPhE_9$-*b*-PGl_{54}-St resulted in polymacromonomer with hydrophobic PGlPhE shell, while PGl_{52}-*b*-$PGlPhE_8$-St gave polymacromonomers with hydrophilic PGl shell, as presented in Fig. 17.

The unreacted residue was easily separated from the polymerisation product by dialysis or precipitation. Pure products with high yield were obtained by dialysis, where after 7 days complete removal of non-functionalized oligomers was observed. The efficiency of the fractionation was proved by SEC (Fig. 18).

The obtained polymacromonomers in contrast to macromonomers used for their synthesis did not show amphiphilic properties. When the hydrophilic blocks formed the shell the polymacromonomer was well soluble in water and polar solvents like methanol, but insoluble in THF or acetone. In the opposite case when short hydrophobic blocks constituted the shell the polymacromonomer remained soluble in THF, however, were completely insoluble in water. This was rather surprising as this polymacromonomer was in 75 wt-% built of hydrophilic poly(glycidol). The solubility of polymacromonomers seems to be determined by the properties of surrounding outer shell i.e. the blocks forming the outer part of the polymacromonomer. The exact composition of the macromonomer seems to be of lower importance as even short block of the poly(glycidyl phenyl ether) influenced the properties of polymacromonomer considerably.

The presence of hydroxyl groups opens, however, possibility of polymacromonomers post-modification a new synthetic approach to more sophisticated structures with new properties.

4. Summary

The properties of amphiphilic macromonomers in water and in water/benzene mixture were reported. DLS measurements showed the formation of small, compact, monodispersed micelles by the

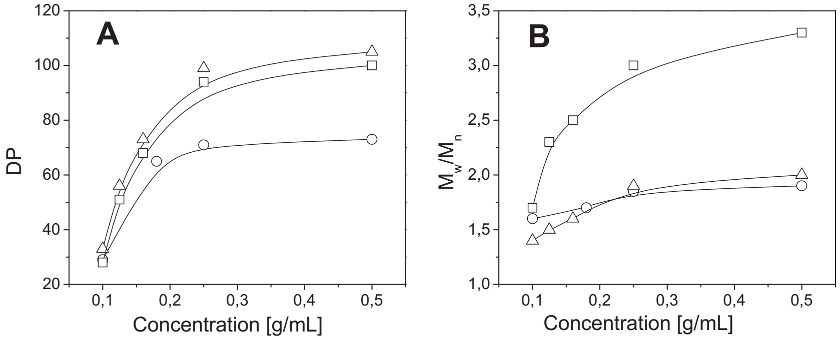

Fig. 16. Influence of macromonomer concentration on degree of polymerisation DP (A) and dispersity M_w/M_n (B) of polymacromonomer for polymerisation in water/benzene mixture 10/1 v/v ($T = 70$ °C) for PGl_{52}-*b*-$PGlPhE_8$-St (△), $PGlPhE_9$-*b*-PGl_{54}-St (□) and PGl_{55}-St (○).

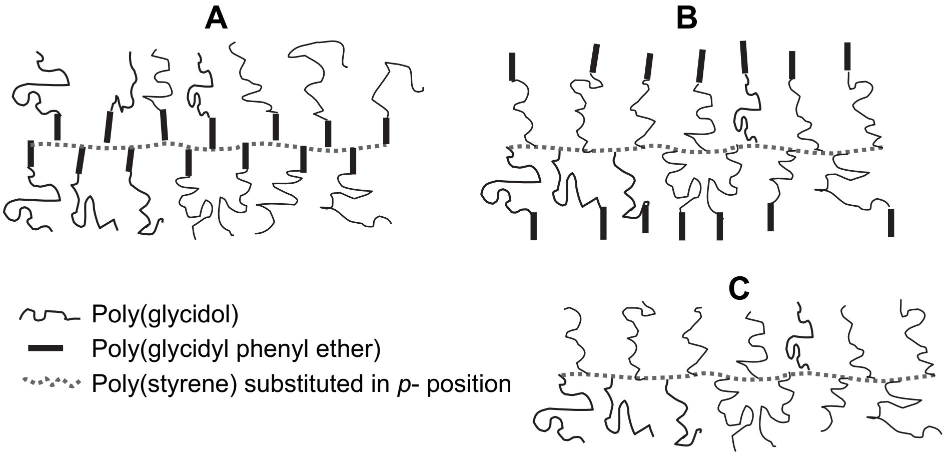

Fig. 17. Polymacromonomers obtained from: (A) PGl_{52}-*b*-$PGlPhE_8$-St, (B) $PGlPhE_9$-*b*-PGl_{54}-St, (C) PGl_{55}-St.

block macromonomers in water, while in water/benzene mixture swollen, well-defined micelles were formed. The core of the micelle was formed by poly(glycidyl phenyl ether), where poly(glycidol) formed the surrounding shell. In case of homo-macromonomer PGl_{55}-St formation of undefined, loose aggregates in both water and water/benzene mixture was observed.

Formation of micelles and aggregates significantly influenced the polymerisation of studied macromonomers in water and in water/benzene mixture (10/1 v/v). The homo-polymerisation of all investigated types of macromonomers in water initiated with AVA was fast, where after about 2 h the conversion of macromonomers reached 90–99%. The rate of polymerisation was extremely high in case of block macromonomer with polymerisable group attached to hydrophobic block. In case of polymerisation of poly(glycidol)-based macromonomers in the mixture of water/benzene initiated with AIBN the rate of polymerisation was the highest for macromonomer with polymerisable group attached to hydrophobic block. The degree of polymerisation of polymacromonomers increased with increasing initial concentration of the macromonomers in the reaction mixture regardless of the polymerisation system or macromonomer type. However, above a certain concentration (about 0.2 g/mL) DP of the products varied only moderately with macromonomer concentration.

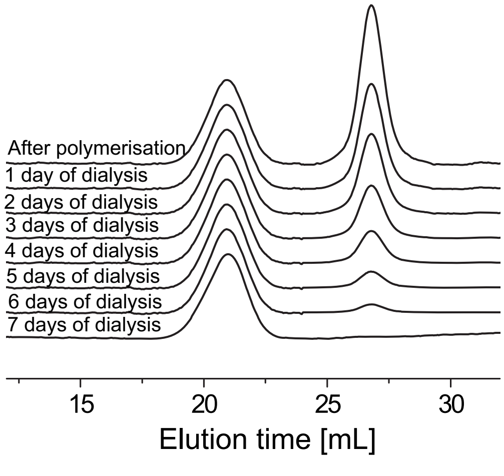

Fig. 18. Purification of polymacromonomer obtained from PGl_{52}-*b*-$PGlPhE_8$-St ($M_n = 505,000$ g/mol) by dialysis in methanol.

The homo-polymerisation of the synthesised poly(glycidol)-based macromonomers led to the mixture of densely branched macromolecules and unreacted residue due to not quantitative functionalisation. The residue was successfully removed from the polymerisation mixture by dialysis or precipitation. In that way high purity products were obtained.

Acknowledgements

The authors appreciate the support of the Polish Ministry of Scientific Research and Information Technology (grant no. 4T09A05225) and of the European Graduate College “Advanced Polymer Materials” (EGC 720) founded by Deutsche Forschungsgemeinschaft (DFG). The authors are also thankful to Prof. Dr. K.-F. Arndt (Fachrichtung Chemie und Lebensmittelchemie, TU Dresden) for the use of DLS and SLS system and Dr. V. Boyko for help in measurements.

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