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Cross-linked star (co)polymers containing core of C-tetraalkylcalix[4]resorcinarene

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An adapted method for synthesis of ATRP macroinitiator based on C-tetra-pentylcalix[4]resorcinarene was demonstrated. Studies on optimization the process of preparation of star-shaped acrylic polymers by ATRP controlled radical polymerization were performed.

The possibility to obtain butyl acrylate/ (hydroxyethyl) methacrylate (HEMA) copolymer in one pot synthesis initiated by octa-functionalized C-tetra-pentylcalix[4]resorcinarene macroinitiator has been shown. It was found that the polymerization process carried out at [macroinitiator]/[monomer] ratio below 1/1000 for polymeriztion time over 30 min yields to a formation of star-branched (co)polymers containing tetraalkylcalix[4]resorcinarenes core.

Key words: C-tetrapentylcalix[4]resorcinarene, ATRP polymerization, star polymers, star-branched polymers

INTRODUCTION

Star-branched polymers with nonlinear structure exhibit specific properties and therefore the subject of intensive research during last decade [1-6]. The synthesis of materials of controlled composition and architecture may be accomplished by the methods of controlled/living radical polymerization. For example, atom transfer radical polymerization (ATRP) enables the synthesis of well-defined macromolecular architectures such as block copolymers, graft copolymers and other branched structures [7,8]. Among branched macromolecules star polymers and dendrimers are those that show interesting rheological properties, due to their specific spatial architecture and existence of a large number of functional groups [9-12]. Regular star polymers consist of a core located in the center of the molecule and a different number of radiating linear chains (arms, branches) of a symmetrical structure with identical chemical composition connected to the core [2]. They are synthesized using two different approaches: "arm first" and "core first". There are two ways for the synthesis of star polymers by the use of a 'arm first" methodology [13-17]. In the first method the formation of the cross-linked core consists of the following: "living" linear polymer chain copolymerized with divinyl monomer in the presence of mono-functional macro initiator. Another method is based on direct copolymerization of macro monomer with divinyl monomer in the presence of low molecular weight initiator [18,19]. By using the "core first" approach the controlled polymerization is carried out by the initiator with a defined number of initiating groups [20-25] or by not entirely well-defined multifunctional macromolecule [26-29].

To hold a low degree of component heterogeneity star-branched polymers are required to have cores of an accurate and known structure and function. These requirements are satisfied by calix[4] resorcinarenes and their derivatives. As cyclic oligomeric precursors they are superb output fragments for construction of such architectures.

Their high functionality allows for greater variety of synthesis and modification of the polymer structures containing calixarenes fragments [30].

The *aim* of the present study was to synthesize a series of star (co)polymers of well defined predetermined structure based on suitably functionalized calix[4]resorcinarenes using ATRP polymerization technique.

EXPERIMENTAL

Materials

Triethylamine (TEA), α-bromoisobutyryl bromid (98%, Acros), 2,2'-bipyridine, cuprous chloride (CuCl), propylene glycol, dichloromethane were used as received (Acros). Tetrahydrofurane (THF) (99.5 %, Fisher) and DMSO (Fisher, 99 %) were purified by distillation over calcium hydride before use. Butyl acrylate (99%,Acros) and 2-(hydroxy-ethyl) methacrylate (HEMA) (97%, Acros) were purified to remove the stabilizers according to the following procedure: about 1% by volume deionized water was added to the liquid

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monomer, the mixture was cooled and after removing the frozen water with dissolved therein stabilizer the purified monomer was dried over magnesium sulfate. C-tetrapentylcalix[4]resorcinarene was synthesized according to the procedure described in [31] and was used without further purification.

Syntheses

Synthesis of octa-functionalized C-tetrapentylcalix[4]resorcinarene-ATRP macroinitiator. C-tetrapentylcalix[4]resorcinarene 1 mmol (0,769 g), triethylamine 24 mmol (2,43g), dry THF 12 ml and DMSO 8 ml were placed into a two-necked flask fitted with a reflux condenser and magnetic stirrer. The mixture was cooled to 0^0C and under constant agitation slowly drop wise α-bromo-isobutyryl bromide 24 mmol (5,52 g), previously dissolved in 12 ml dry THF was added. The reaction mixture was intensively agitated and purged with N_2 for 48h at room temperature. Then the reaction mixture was concentrated on a rotary evaporator. The resulting highly viscous mixture was dissolved in 100ml of dichloromethane washed with deionized water and again concentrated on a rotary evaporator. The product was precipitated in cold methanol and the resulting precipitate was filtered and dried.

Synthesis of star polymer: polymerization of butyl acrylate initiated by octa-functionalized C-tetrapentylcalix[4]resorcinarene ATRP macro-initiator. Octa–functionalized C-tetrapentylcalix[4] resorcinarene 0,1mmol (0,196 g), 2,2'-bipyridine 1,6 mmol (0,2498 g), CuCl 0,8 mmol (0,0792 g), butyl acrylate 160 mmol (22.93 ml) and propylene glycol 30,72 mmol were placed in a two-necked flask fitted with a reflux condenser and magnetic stirrer. The reaction mixture was intensively agitated and purged with N_2 for 30 min then the temperature was raised to 135^0C. The reaction was continued for 2 hours. Then the reaction mixture was cooled, 30 ml of THF was added and the resulting mixture was filtered through a column filled with neutral Al. The final product was precipitated in 40ml mixture of $MeOH/H_2O$ (v/v=80/20).

One pot synthesis of star–branched copolymers: ATRP polymerization of butyl acrylate and (hydroxyethyl) methacrylate (HEMA) initiated by octa-functionalized C-tetrapentylcalix[4] resorcin-arene macroinitiator. Octa–functionalized C-tetrapentylcalix[4]resorcinarene 0,1mmol (0,196 g), 2,2'-bipyridine 1,6 mmol (0,2498g), CuCl 0,8 mmol (0,0792g), butyl acrylate 40 mmol (5,73 ml) and propylene glycol 7,68 mmol were placed in a two-necked flask fitted with a reflux condenser and magnetic stirrer. The reaction mixture was intensively agitated and purged with N_2 for 30 min then the temperature was raised to 135^0C. The reaction was continued for 20 minutes. Then HEMA 40 mmol (4,85 ml) was added and was stirred at the same temperature for a further 20 minutes. After the completion of the second step of the polymerization process the reaction mixture was cooled, 25 ml of THF was added and the resulting mixture was filtered through a column filled with neutral Al. The finally obtained copolymer was precipitated in 40ml mixture of $MeOH/H_2O$ (v/v=80/20).

Instrumentation. ^{1}H NMR spectra were recorded on a *Bruker Avance DRX 250* (250 mHz) instrument. The samples were dissolved in deuterated solvent (dimethyl sulfoxide-d_6). Tetramethylsilane was used as an internal NMR standard.

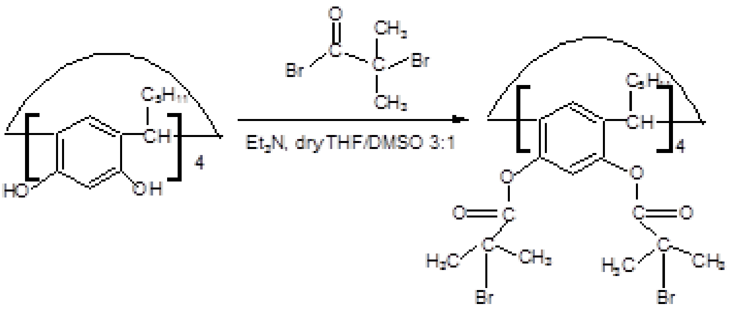
Infrared spectra of the samples were recorded on a Varian Scimitor 1000 FTIR spectrophotometer equipped with a MIRacle Attenuated Total Reflectance Attachment.

The molecular weight characteristics were determined on a chromatography line consisting of a 510 HPLC pump, a U6K universal injector, a tunable absorbance detector M 484, a differential refractive index detector M 410 (all Millipore Co., Waters Chromatography Division) and a set of three *Phenogel* columns (Phenomenex) with nominal pore sizes of 50Å, 100Å and 10000 Å. THF was used as an eluent at 40ºC and a flow rate of 1.0 ml.min^{-1}. Molecular weight characteristics were calculated using a calibration curve constructed with monodisperse poly(styrene) standards on a station for collection and processing of data through Clarity software. 1,3-dihydroxybenzene was used as an internal standard.

RESULTS AND DISCUSSIONS

Synthesis of octa-functionalized C-tetrapentylcalix[4]resorcinarene-ATRP macroinitiator. The synthesis of octa-functionalized C-tetrapentylcalix[4]resorcinarene was performed according to the methodology proposed in [32] and adapted in analogy to [33] as shown in Scheme 1.

The methodology is optimized to achieve maximum reproducibility of well defined products and to avoid the step of product purifying by column chromatography or repeated re-crystallization as described in the literature [15,24,30,32]. The methodology is optimized to achieve maximum reproducibility of well defined



Scheme 1. Synthesis of octa-functionalized C-tetrapentylcalix[4]resorcinarene

products and to avoid the step of product purifying by column chromatography or repeated recrystallization as described in the literature [15,24,30,32].

GPC, ^{1}H NMR and IR spectroscopy were used to characterize the products obtained.

In the IR spectra of both C-tetrapentylcalix[4]resorcinarene (Fig. 1a) and of the functionalized product (Fig. 1b), an oscillation band at about 3200cm^{-1} characteristic for the OH groups was not observed. A strip oscillation at about 1753 cm^{-1} was appeared which is characteristic for the C=O bond of the carbonyl group. A doublet at about 1100 cm^{-1}, characteristic for the methyl group (-CH$_3$) of the substituent was also detected. The appearance of an intense band at about 1255 cm^{-1}, which is characteristic for the (Ar) C-O-C bond is further evidence that the product was functionalized.

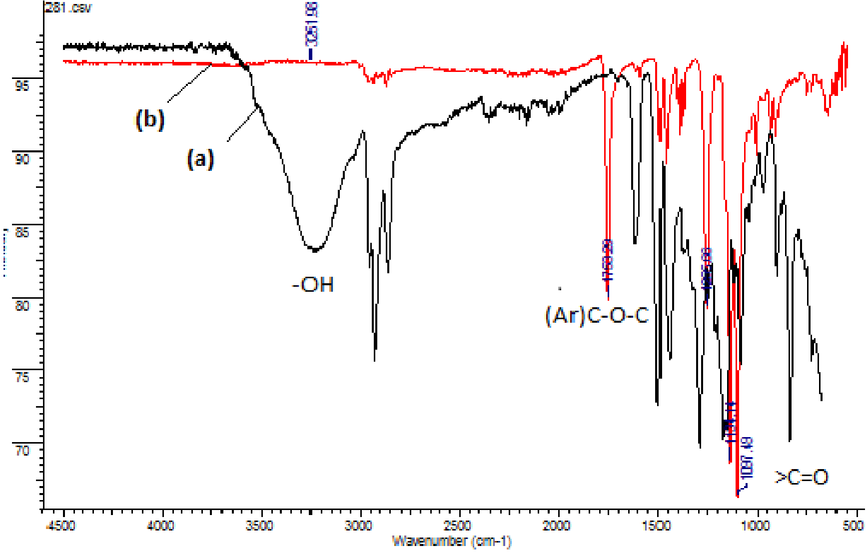


Fig. 1. IR spectra of C-tetrapentylcalix[4]resorcinarene (a) and octa-functionalized derivative (b)

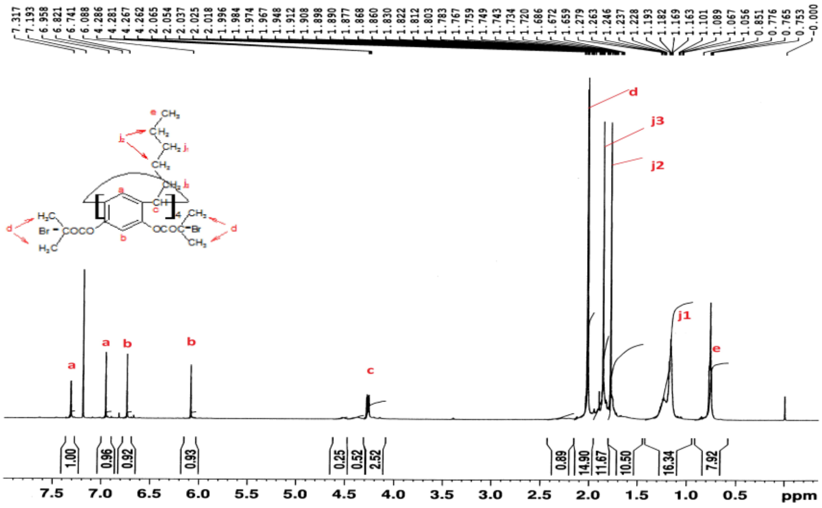


Fig. 2. ^{1}H NMR spectrum of octa-functionalized C-tetrapentylcalix[4]resorcinarene.

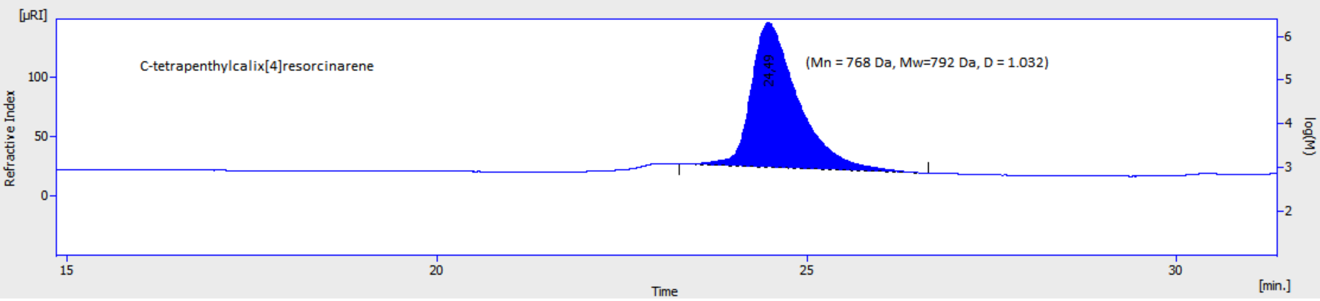


Fig. 3a.

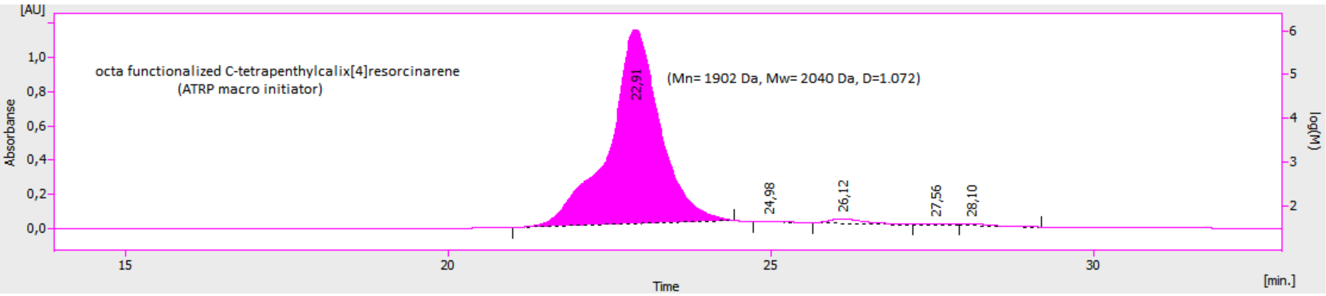


Fig. 3b.

Fig. 3. GPC traces of C-tetrapentylcalix[4]resorcinarene (a) and octa-functionalized ATRP macroinitiator (b).

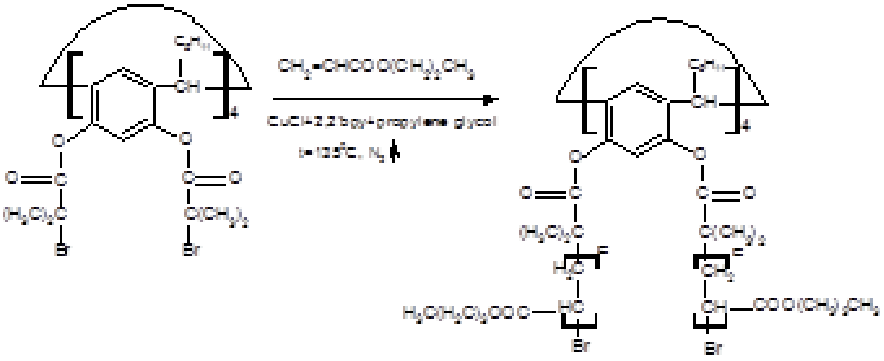
The structure of ATRP macroinitiator obtained was proved from ^{1}H NMR spectrum (Fig. 2) where signals characteristic for the protons of the expected structure are observed.

The molecular weight characteristics of the C-tetrapentylcalix[4]resorcinarene and its octa-functionalized derivative are shown in Fig. 3. The calculated from GPC traces molecular mass of the functionalized calixarene based macroinitiator of about 2000 Da (Fig. 3) corresponds to the theoretically calculated one (1960 Da).

Synthesis of star polymer: polymerization of butyl acrylate initiated by octa-functionalized C-tetra-pentylcalix[4]resorcinarene ATRP macroinitiator. The synthesis of star polymer with a core comprising octa-functionalized tetrapentylcalix[4]-resorcinarene was carried out according to the adapted methodology described in [33] as shown in Scheme 2.

The dependence of formation of star polymer of the time in ATRP polymerization of acrylate monomer initiated by octa-functionalized C-tetra-pentylcalix[4]resorcinarene was investigated. It was found that under the adopted reaction conditions almost complete conversion of the monomer was observed within about two hours. The studies were conducted at various macroinitiator/monomer ratios (1:1600; 1:1200, 1:800, 1:400). The type of reactions taking place within this time interval is determined by the data taken from the GPC eluograms.

It was found that at [In]/[M] ratio of 1/1600 (close to the value cited in [7]) polymer with a gradual increase over time molecular weight and low polydispersity was obtained.



Scheme 2. Synthesis of star polymer via ATRP of butyl acrylate initiated by octa-functionalized C-tetra-pentylcalix[4]resorcinarene macromonomer.

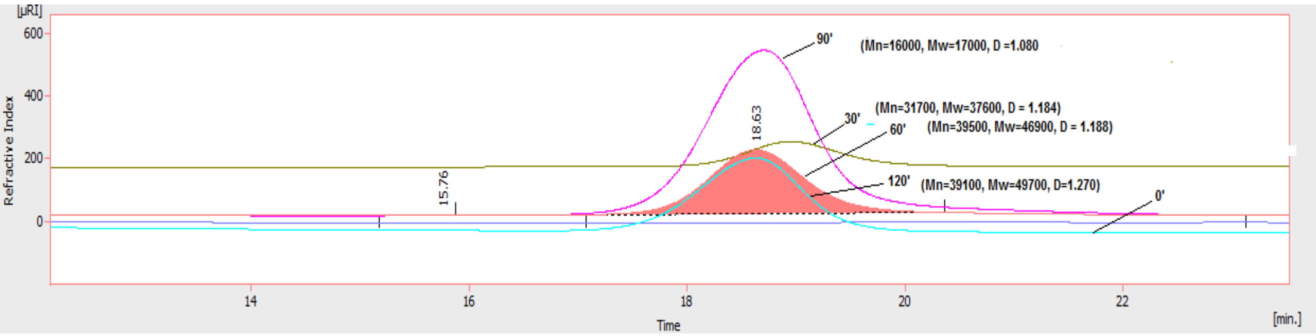


Fig. 4. GPC traces of star polymer prepared by ATRP of butyl acrylate initiated by octa-functionalized C-tetrapentylcalix[4]resorcinarene macromonomer at [macroinitiator]/ [monomer] ratio = 1/1600.

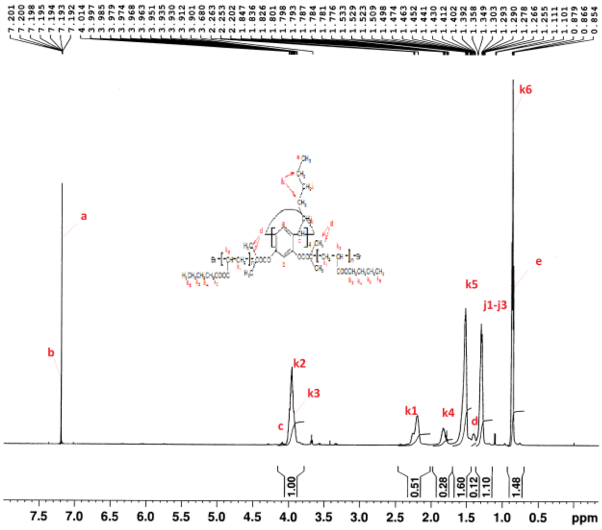


Fig. 5. ^{1}H NMR of star polymer prepared by ATRP of butyl acrylate initiated by octa-functionalized C-tetrapentylcalix[4]resorcinarene macromonomer at [macroinitiator]/ [monomer] ratio =1/1600.

The values for molecular mass of polymers synthesized at different times are marked in chromatograms shown in Figure 4. It can be seen that the star polymer with a relatively narrow molecular mass distribution and molecular mass of about 40,000 ÷ 50,000 Da was prepared at reaction time of about 60 min.

The prepared star – structure was proved by ^{1}H NMR spectroscopy. The signals characteristic for the protons of the expected structure are observed as shown in spectrum presented in Fig. 5.

There is a tendency to increase the degree of monomer conversion and to obtain a higher yield of star polymer with lower polydispersity by reducing the amount of monomer, i.e., [In]/[M] ratio. The amount of star polymer obtained against reaction time is plotted on Fig. 6.

In addition, the maximum amount of star polymer was prepared in a relatively shorter reaction time reducing the monomer content as seen from Fig. 6. When the polymerization is carried out at [In]/[M] ratio above 1/1000 the complete conversion of the monomer in selected research time interval was not occur. The optimum yield of star polymer for ATRP at [In]/[M] ratio of 1/1200 at at polymerization time of 38 min was found to be of about 64% while for polymerization at [In]/[M] ratio of 1/1600 at polymerization time of 60 min the amount of star polymer reached value of only 50%.

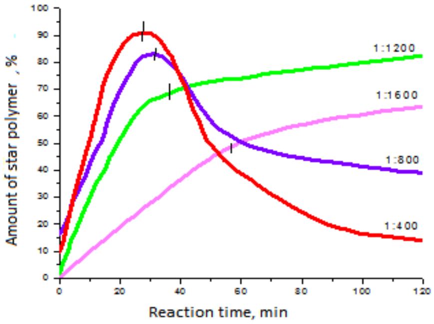


Fig. 6. Plot of the amount of star polymer against reaction time for ATRP of butyl acrylate initiated by octa-functionalized C-tetrapentylcalix[4]resorcinarene at various [In]/[M] ratios: 1/1600 (a); 1/1200 (b); 1/800 (c); 1/400 (d)

At [In]/[M] ratio up to 1:1000 the dependency of the yield of the star polymer versus the reaction time reaching a pronounced maximum at a reaction time of about 30 minutes. The almost complete monomer conversion was observed - 87.30% at [In]/[M] ratio of 1:400 and reaction time of 28 min, and 81.46% at [In]/[M] 1:800 ratio and reaction time of 32 min, respectively. The GPC traces of the reaction mixtures taken at larger reaction times showed the presence of a copolymer fraction of increased molecular weight and index of polydispersity. The amount of these polymer fractions versus reaction time was plotted in Fig. 7.

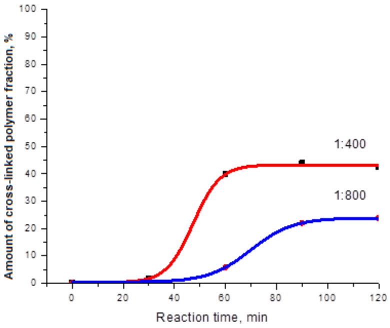


Fig.7. Plot of the amount of cross-linked polymer fraction against reaction time for ATRP of butyl acrylate initiated by octa-functionalized C-tetrapentylcalix[4]resorcinarene at [In]/[M] ratio of 1/800 (a) and 1/400 (b).

Possibly after initial almost complete monomer consumption a process of intermolecular interactions of preformed star polymer was occurred, namely coupling reactions between star macromolecules was initiated. These side effects lead to the observed decrease in the amount of star product of the desired molecular weight and polydispersity when polymerization was carried out at larger reaction times (see curves *b* and *c* shown in Fig. 6).

One pot synthesis of starcopolymer: ATRP polymerization of butyl acrylate and (hydroxyethyl) methacrylate (HEMA) initiated by . octa-functionalized C-tetrapentylcalix[4]resorcinarene macroinitiator..

Determined optimal reaction conditions for obtaining defined product at higher yield, namely the [In]/[M] ratio and polymerization time, was used in reaction of preparation of star *co*polymers by the addition of second monomer to the reaction mixture.

“One pot” synthesis was used to prepare star – branched copolymer by sequential addition of two different acrylic monomers, namely butyl acrylate and (hydroxyethyl) methacrylate **(**HEMA). The reaction course of ATRP polymerization was monitored by GPC. GPC traces of polymer obtained polymerizing butyl acrylate and the copolymer formed after the addition of second HEMA monomer are presented in Fig. 8. The two monomers were added in equimolar ratio. Each polymerization step was carried out for 20 minutes. After the first-stage of reaction – polymerization of butyl acrylate the number average molecular weight (M_n) of star homopolymer obtained was of about 15 000 Da and PDI = 1,14. At the end of the polymerization of HEMA, the second polymerization stage, the M_n was reached a value of about 21 000 Da while the polydispersity remains unchanged. Probably the reaction capability of the second monomer is less, since it established conversion rate is significantly lower (45%) for applied reaction time of 20 minutes. However, a possibility of obtaining a star-shaped (cross-linked) (co)polymers of branches of various lengths and composition by ATRP polymerization initiated with calyx resorcinarene macroinitiator is demonstrated.

CONCLUSIONS

An optimized method for synthesis of ATRP calix[4]resorcinarene macroinitiator was demonstrated and the structure of octa-functionalized C-tetrapentylcalix[4]resorcinarene prepared was proved.

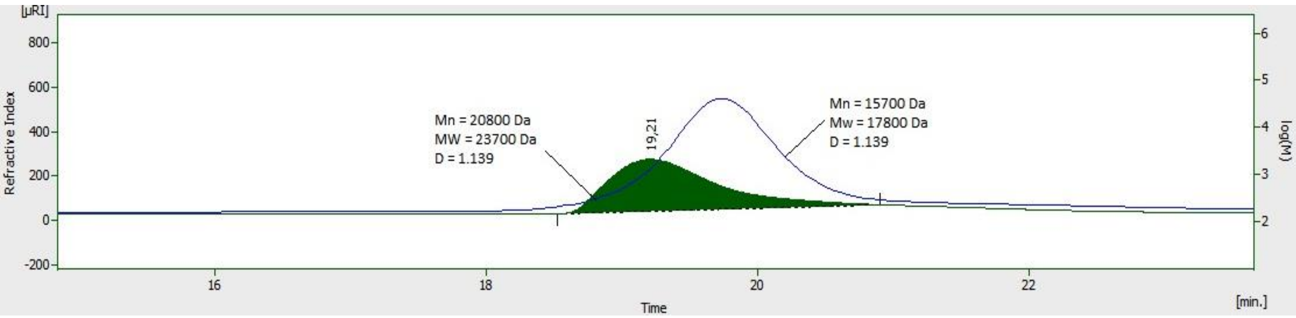


Fig. 8. GPC traces of star-branched copolymer formed via ATRP of butyl acrylate and HEMA initiated by octa-functionalized C-tetrapentylcalix[4]resorcinarene macroinitiator at macroinitiator/monomer ratios [In]/[M1]/[M2] = 1/400/400; reaction time – 60 min.

The possibility for preparation of various star–branched homo- and (co)polymers of well defined architecture via ATRP polymerization initiated by functionalized calixarene macroninitiator was established.

Butyl acrylate / (hydroxyethyl) methacrylate (HEMA) copolymer has been prepared in one pot copolymerization initiated by octa-functionalized C-tetrapentylcalix[4]resorcinarene macroinitiator.

The structure of star–branched homo- and copolymers prepared was studied by various conventional instrumental methods.

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НАПРЕЧНО СВЪРЗАНИ ЗВЕЗДОВИДНИ СЪПОЛИМЕРИ, СЪДЪРЖАЩИ ЯДРО ОТ С-ТЕТРА-АЛКИЛКАЛИКС[4]РЕЗОРЗИНАРЕНИ

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(Резюме)

По адаптирана методика е синтезиран ATRP макроинициатор на основата на С-тетрапентилкаликс[4]резорцинарен. Проведени са изследвания за оптимизиране на метода за получаване на звездовидни акрилатни полимери чрез ATRP контролирана радикалова полимеризация. Показано е, че при определени условия е възможно получаването на бутилакрилат-хидроксиеталакрилатен съполимер чрез едноетапен метод. Установено е, че при съотношения макроинциатор/мономер под 1:1000 и реакционно време над 30 минути се получават и омрежени звездовидни полимери, съдържащи С-тетраалкилкаликс[4]резорцианаренови ядра.