ELSEVIER

European Polymer Journal 39 (2003) 327–331

EUROPEAN POLYMER JOURNAL

www.elsevier.com/locate/europolj

Grafting on crosslinked polymer beads by ATRP from polymer supported N-chlorosulfonamides

B. Filiz Senkal, Niyazi Bicak *

Department of Chemistry, Istanbul Technical University, Maslak, 80626 Istanbul, Turkey

Received 24 January 2002; received in revised form 14 June 2002; accepted 1 August 2002

Abstract

Grafting of methyl methacrylate (MMA) and ethyl acrylate (EA) monomers from immobilized N-chlorosulfonamide (NCSA) groups on crosslinked polystyrene-based beads have been achieved by copper mediated atom transfer radical polymerisation (ATRP) methodology. The initiation takes place via NCSA groups on the polymer, created by chlorination of crosslinked polystyrene sulfonamides. Using CuBr and hexacishexyl triethylenetetramine ligand for MMA and EA grafting showed a first order kinetics for each monomers.

Polymers with 3.18 mmol g^{-1} of NCSA groups have a progressive mass increase in accordance with increasing MMA graft polymerisation up to 380.0% grafting obtained after 6 h.

By the method presented, grafting of MMA and EA have been successfully achieved with negligible amounts of free polymer formation (6.2%) in the solution. Hence grafting by ATRP through polymer supported NCSA is superior to the common radical grafting methods which are yielding free polymers simultaneously.

The method provides an efficient procedure in preparing core-shell type of polymers, with retention of the bead shapes.

Keywords: Atom transfer radical polymerisation; Grafting; N-chlorosulfonamide

1. Introduction

Incorporation of polymer chains on solid particles, in general, is a very tedious process. Two common techniques so called "grafting onto" and "grafting from", have limited success in most cases [1].

The "grafting from" by radical initiation is most common and involves the use of anchored initiation sites on the solid surface. This method suffers from formation of significant amounts of free polymer as a side reaction due to radical fragments detached from the surface. Various intriguing approaches [2,3] including radiation induced grafting via hydroperoxy groups on solid polymers [4] have been reported to eliminate or suppress the free polymer formation.

One of the successful methods is to use polymer supported chain transfer agents in combination with a common azo initiator as a radical source [5]. However, in those methods free polymer formation seems to be inevitable due to other side reactions such as chain transfer etc.

Controlled living radical polymerisation techniques emerged in recent years offer potential use in surface grafting [6]. The atom transfer radical polymerisation (ATRP) technique, for instance, provides chain growing mostly on the solid surface, provided that the initiator function is covalently bound to the surface. An interesting aspect of this approach is controlled chain growth from TEMPO group on polystyrene support [7] to prepare new functional polymer beads.

Hallensleben's group reported a general method for controlling chain growth on silica or synthetic polymer

* Corresponding author. Tel.: +90-212-285-3221; fax: +90-212-285-6386.

E-mail address: bicak@itu.edu.tr (N. Bicak).

0014-3057/02/$ - see front matter
PII: S0014-3057(02)00224-0

particles which are pre-modified with haloalkyl functions [8,9]. Modified silicone surfaces have also been used to initiate grafting of acrylamide monomers by metal mediated ATRP [10].

Recently, bromo-*t*-butyl ester of Wang resin has been used as initiator in copper mediated ATRP grafting of methyl methacrylate (MMA) homo and copolymer blocks. The grafted polymers detached by selective ester hydrolysis from the bead surfaces have shown moderate polydispersities [11].

In those examples the halo alkyl functions are linked to the substrate with a hydrolysable ester linkage. The resulting graft chains have been detached from the surface and shown to be in relatively narrow polydispersity (i.e. 1.4–1.6). In a similar study some acrylate polymers have been grafted from chloromethyl groups on crosslinked polystyrene beads [12].

These reports imply that ATRP technique can be employed even in heterogeneous conditions successfully and grafting from solid particles can be attained with moderate or acceptable polydispersities. But more important is that ATRP is expected to eliminate free polymer formation during the graft polymerization and provide a relatively easy pathway to core-shell type of polymers.

Alkyl halides are common initiators studied in copper mediated ATRP. In our recent study [13], we have described possibility of the ATRP initiation through N-chlorosulfonamides (NCSAs) together with CuBr complex.

In this work, this analogy has been extended to polymer supported NCSA groups, to prepare graft chains on crosslinked bead polymers. For this purpose, sulfonamide groups on polystyrene beads (crosslinked with 10% divinyl benzene) have been chlorinated and feasibility of grafting from the NCSA initiator groups have been studied.

2. Experimental

2.1. Materials

Cuprous bromide was freshly prepared from $CuSO_4 \cdot 5H_2O$ (E. Merck) by the procedure as described before [13].

Methyl methacrylate (Fluka), ethyl acrylate (Fluka), styrene (Fluka), DVB (divinyl benzene) (Fluka) monomers were distilled before use. Dibenzoyl peroxide (Fluka), household bleaching liquor (with 15.0% active chlorine) and all the other chemicals were used as purchased.

2.2. Preparation of chlorosulfonated beads

This was prepared by suspension copolymerization of styrene with 10% of divinyl benzene in toluene solution using gam-arabic as suspension stabilizer in continous phase, water. Subsequent reaction of 420–590 μ size of fraction with chlorosulfonic acid gave the chlorosulfonated polystyrene in spherical beads form as described before [14].

Analysis of the chlorosulfonation degree was carried out by boiling 0.25 g of the polymer sample in 20 ml 10% NaOH solution for 4 h. After filtration and neutralization with HNO_3 solution (5 M) the chloride content of the solution was determined by the mercuric thiocyanate method [15]. The chloride analysis gave 4.0 mmol g^{-1} chlorosulfonation.

2.3. Sulfamidation with propylamine

This was performed by portionwise addition of 10 g chlorosulfonated resin to the stirred solution of 12 ml (0.145 mol) propyl amine in 2-methyl pyrrolidone at 0 °C. Then the mixture was transferred to a continuous shaker and shaken for 10 h at room temperature. The mixture was filtered, washed with water (3 × 200 ml) and 20 ml alcohol. Vacuum dried sample weighed 11 g.

2.4. Determination of the sulfonamide content

The sulfonamide content was determined by neutralization with KOH. Thus 0.5 g of polymer sample was left in contact with a methanolic solution (15 ml) of 1.5 g KOH for 24 h at room temperature.

The mixture was filtered and 5 ml of the filtrate was diluted to 25 ml with distilled water. This solution was titrated with 0.4 M HCl solution 20.8 ml of acid consumption indicates 3.64 mmol sulfonamide per gram of the polymer.

2.5. Chlorination with bleaching liquor

For chlorination of the sulfonamide nitrogen 10 g of the bead polymer was soaked into 80 ml of commercial bleaching liquor with 15% active chlorine content and left to stand over three days in a refrigerator. The beads were filtered and washed with 2 l of cold water. After washing with 40 ml alcohol and 25 ml ether the product was dried under open air to avoid decomposition under vacuum. Yield 11.2 g.

2.6. Determination of chlorine content

The chlorine content of the product was determined iodometrically by a modified procedure given for low molecular weight NCSAs [16] as follows: 0.2 g polymer sample was added to 10 ml CCl_4 in a bottle. Then exactly 0.4 g KI in 15 ml distilled water and 5 ml acetic acid were added rapidly and the bottle was closed tightly. The mixture was stirred for 24 h at room

temperature. The iodine liberated was directly titrated with 0.1 M $Na_2S_2O_3$ solution. 6.36 ml of thiosulfate consumption, relative to the blanck corresponds to 3.18 mmol N-chloro group per gram of the polymer sample.

2.7. Preparation of the ligand

The ligand used was prepared by alkylation of triethylene tetramine with hexyl bromide as described before [17]. The resulting viscous liquid product forms organo-soluble complex with copper ions.

2.8. Grafting "from" beads

Graft polymerizations of MMA and ethyl acrylate (EA) were achieved through N-chloro sulfonamide initiation sites on the crosslinked bead polymer.

A typical procedure is as follows:

0.14 g (0.97 mmol) CuBr, 0.63 g (0.97 mmol) of the ligand and 10 ml (0.097 mol) MMA in an under nitrogen were successively put in a three necked flask equipped with a reflux condenser and a nitrogen inlet. While stirring under nitrogen flow 0.5 g. Polymer sample was added to the flask and the mixture was heated to 90 °C for 1.5 h. At the end of the reaction period the reaction content was poured into 20 ml acetic acid to obtain colorless product. The mixture was filtered and washed with excess of water (300 ml) and alcohol (20 ml). Vacuum dried sample weighed 1.24 g. This experiment was repeated for different reaction periods to observe a progressive mass increase in grafting. Percentages of grafting were assigned based on mass increase and plotted as a function of time. To inspect any probable free polymer formation half of the above filtrates were added to 40 ml methanol, to precipitate the linear PMMA. Minute amount (0.62 g) of free polymer was obtained only for 6 h in the MMA polymerization.

3. Results and discussion

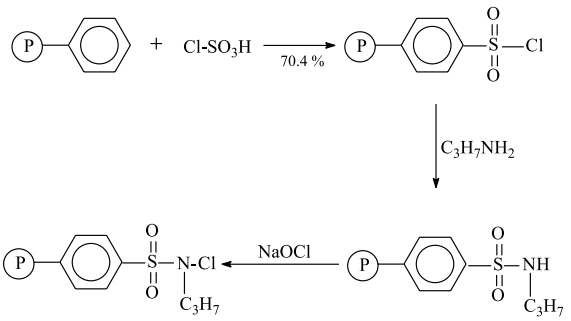
In this work core–shell type of polymers with polyacrylate ester shells were obtained by ATRP method.

Graft polymerizations of MMA and EA were achieved from NCSA groups on styrene-DVB (10%) beads.

The NCSA groups were created by three steps condensation of crosslinked styrene–divinyl benzene beads (420–590 μm size) as depicted in Scheme 1.

Chloride analysis (4.0 mmol g^{-1}) of the first step product corresponds to 70.4% of chlorosulfonation of the styrene units.

The second, sulfamidation step is achieved by treating with excess propylamine and yields 3.64 mmol sulfonamide per gram of the polymer. This implies almost quantitative (99.6%) conversion in this step.



Scheme 1.

Chlorination with commercial bleaching liquor (with 15% active chlorine content) yields NCSA product.

Content of NCSA groups (3.18 mmol g^{-1}) indicates a 98% conversion of the sulfonamide groups.

Graft polymerization of MMA and EA can be achieved from the NCSA initiator groups on the spherical beads.

Although polymerizations are heterogeneous in nature they proceed with progressive mass increases at 90 °C (Figs. 1–3).

In the polymerizations [CuBr]/[L] ratio was chosen as 1/1. But NCSA group content was kept higher (NCSA/CuBr 2.9/1) to attain reasonable grafting rates. MMA grafting is reasonably fast in comparison to EA grafting (Scheme 2).

The grafting degree (assigned by mass increase) reaches to 380.0% for 6 h of reaction period in MMA grafting. Although grafting with EA is somewhat slow, 160.0% of grafting can be attained for 44 h reactions.

In both cases $\log[M_0]/[M]$ versus time plots indicate almost linear relationships which imply possible controlled chain growings, where $[M_0]$ and $[M]$ are initial

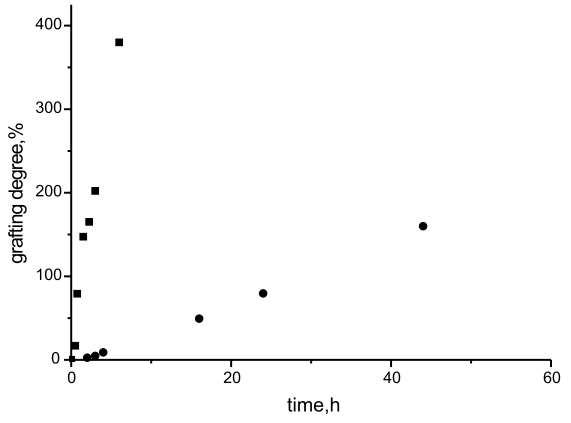


Fig. 1. Percentage grafting versus time plots for MMA (■) and EA (●) polymerizations at 90 °C [NCSA]/L/[monomer]: 2.9/1/1/100.

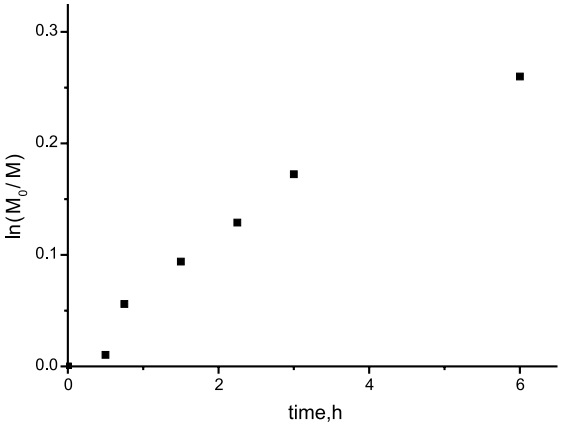


Fig. 2. Semilog–first order kinetic plots for MMA polymerization (the conditions are the same as indicated in Fig. 1).

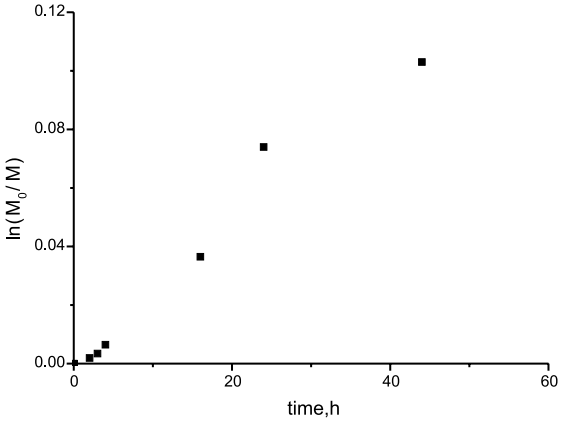


Fig. 3. Semilog–first order kinetic plots for EA polymerization (the conditions are the same as indicated in Fig. 2).

and final monomer contents in the experiments. The later one was obtained by differentiating accumulated grafts on the beads from initial monomer content. First order rate constants of grafting have been found $k = 1.23 \times 10^{-5}$ s^{-1} and $k = 7.0 \times 10^{-7}$ s^{-1} (with appreciable correlation factors 0.978 and 0.985) for MMA and EA respectively (with [NCSA]/CuBr/L = 2.9/1/1 ratio).

FT-IR spectra (Fig. 4) of the resulting graft beads represent strong C=O stretching vibrations at about 1740 cm^{-1}, which indicate incorporation of the polyacrylate ester chains. Absence of these peaks in the spectra of the prepolymer is clear cut evidence for the graft structures.

Unfortunately we are unable to predict molecular weight distributions of the graft chains. Because, the sulfonamide linkage is known to be highly stable to acid and base hydrolyses [18]. Owing to this fact detaching

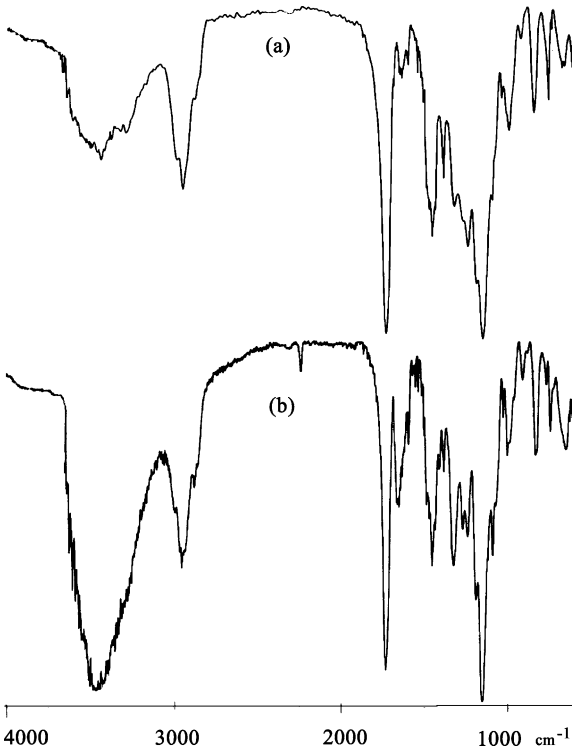
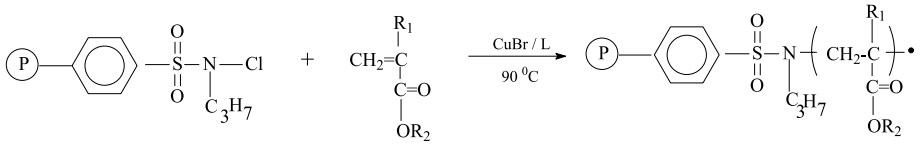


Fig. 4. FT-IR spectra of the bead polymer with MMA grafts (a) and its post-copolymerization product with acrylonitrile (b).



a) R_1 : CH_3 , R_2 : CH_3

b) R_1 : H , R_2 : C_2H_5

Scheme 2.

from the crosslinked core by hydrolysis is impossible without destruction of the graft chains.

We expected that some of NCSA groups remained unreacted due to heterogeneity of the reaction. But a qualitative analysis of the graft samples obtained for a 24 h reaction by KI + acetic acid solution gives no indication of the presence of unreacted NCSA groups. That means there is not residual NCSA groups practically after the polymerizations.

Most probably non-efficient portion of NCSA groups might be turned into sulfonamide form.

In our previous study, the initiation efficiency of *N*-chloro, *N*-propyl, *p*-toluene sulfonamide was found between 0.2 and 0.3 in MMA polymerization [13]. By assuming an equal efficiency in the supported NCSA groups here, 380.0% graft corresponds to 38 mmol MMA repeating units per gram of the starting beads. With an average 25% of initiation efficiency, $3.18 \times 25\% \cong 0.8$ mmol g^{-1} NCS must be involved in the initiation of MMA grafting. Ratio of the two yields an average 47.5 repeating units per initiation site, which is quite satisfactory to create brush structures on the spherical bead polymers.

This is in accordance with the previous reports indicating narrow molecular weight distributions of graft polymers from silica supports [19].

It is important to note that we have observed only 6.2% homopolymer after 6 h of reaction for MMA polymerization, which means chain transfers to the monomers are negligible.

Perhaps this is the most important aspect of the grafting by ATRP. Because almost all the other radical graft techniques yield free polymers inevitably. In another words grafting by ATRP method is very useful to avoid free polymer formation.

Another important aspect of the grafting procedure is of course, living nature of the chain ends of MMA and EA grafts. To inspect re-initiation ability of the chain ends, 0.5 g graft polymer samples were simply heated at 70 °C for 4 h in 5 ml of acrylonitrile monomer, together with the ligand and CuBr (0.5 mmol of each).

Washed and dried samples give 12% and 9% mass increases respectively for MMA and EA grafted samples. Low yields might be due to low copolymerisation tendency of acrylonitrile with acrylic ester monomers.

Their IR spectra (Fig. 4) exhibits characteristic C≡N stretching vibrations at 2250 cm^{-1}. This observation reveals incorporation of additional polyacrylonitrile blocks into the graft structures.

This evidence can be ascribed to activity of at least, some portions of chain ends of the grafts.

In conclusion grafting from polymer supported NCSA groups can be achieved efficiently. Although polydispersities of the graft chains are ambiguous the copper mediated ATRP can be successively applied to prepare core–shell type of spherical bead polymers and there is no need to sacrify most of monomers in non-desired free polymer formation.

References

[1] Zhao B, Brittain WJ. Prog Polym Sci 2000;25:677.
[2] Prueker O, Rühe. J Macromol 1998;31:592.
[3] Prueker O, Rühe. J Macromol 1998;31:602.
[4] Kwon OH, Nho YC, Jin JH, Lee MJ, Lee YM. J Appl Polym Sci 1999;72:659.
[5] Sreedhar MK, Anirudhan TS. J Appl Polym Sci 2000;75:1261.
[6] Kihara NC, Kanno T, Fukutomi. J Polym Sci Chem 1997;35:1443.
[7] Hodges JC, Harikrishnan LS, AultJustus S. J Comb Chem 2000;2:80.
[8] Böttcher H, Hallensleben ML, Nuss S, Wurm H. Polym Bull 2000;44:223.
[9] Böttcher H, Hallensleben ML, Janke R, Klüppel M, Müller M, Nuss S, et al. In: Yağcí Y, Mishra MK, Nuyken O, Ito K, Wnek G, editors. Tailored polymers and applications. New York: M. Decker; 2000. p. 219–32.
[10] Ejaz M, Ohno K, Tsujii Y, Fukuda T. Macromolecules 2000;33:2870.
[11] Angot S, Ayres N, Bon SAF, Haddleton DM. Macromolecules 2001;34:768.
[12] Wu T, Efimenko K, Genzer. J Macromol 2001;34:684.
[13] Senkal BF, Hzal G, Biçak N. J Polym Sci, Polym Chem, Part A 2001;39:2691.
[14] Bíçak N, Senkal BF. J Polym Sci, Polym Chem, Part A 1997;35:2857.
[15] Basset J, Denney RC, Jeffery GH, Mendham J, editors. Vogel's textbook of quantitative inorganic chemistry. 4th ed. London: Longman; 1978. p. 754–5.
[16] Suter CM. In: The organic chemistry of sulfur. John Wiley and Sons Inc; 1944. p. 613.
[17] Acar M, Bcak N. Macromolecules, submitted for publication.
[18] Synder HR, Heckert RE. J Am Chem Soc 1952;74:2006.
[19] Paik HJ, Kickelbick G, Matyjaszewski K. Polym Prepr, Div Polym Chem ACS 1999:40;434–5.