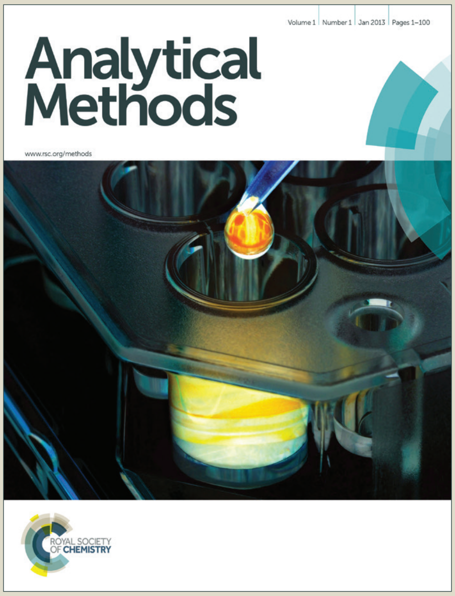
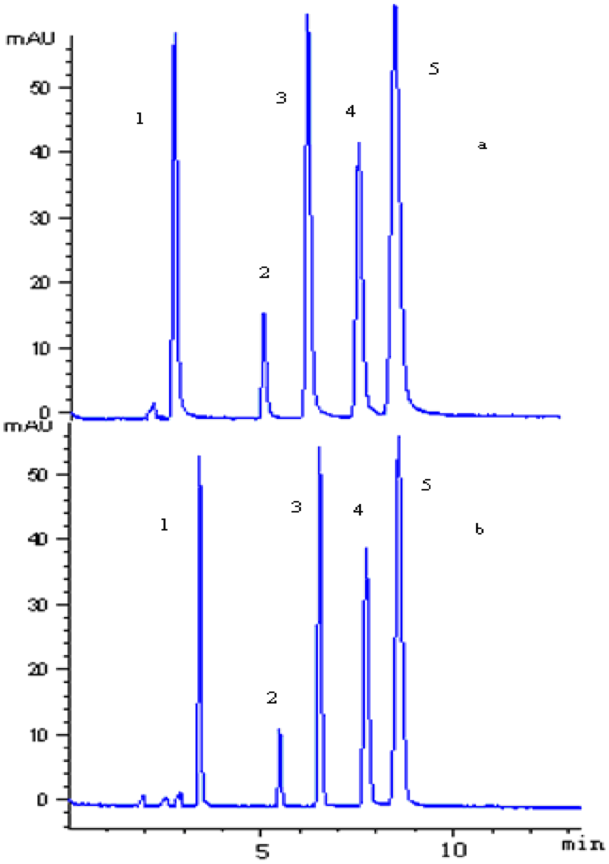


A graphical and textual abstract for the contents pages

Comparison on the reversible addition-fragmentation chain transfer polymerization of lauryl methacrylate monolithic column for capillary electrochromatography



Doping a novel controlled/"living" radical to the polymerization of lauryl methacrylate monolithic column for improving column efficiency

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Abstract

The preparation of auryl methacrylate (LMA) monolithic column for CEC by reversible addition-fragmentation chain transfer polymerization has been investigated. The s,s-2 (a, a-methyl-a″-acetic acid) 3-thiocarbonate (TTC1) was synthesized and added into the LMA monolithic column preparation as a chain transfer agent. At the same time, the preparation was compared with LMA -based monolith columns thermally polymerized without TTC1. The SEM and pore size measure showed that reversible addition-fragmentation chain transfer polymerization had more uniform polymer particle pore size, relatively narrower pore size distribution and larger surface area. The two kinds of monoliths had median pore diameters comprised 703 nm and 950 nm with pore volume of 13.22 cm^3/g and 8.31 cm^3/g, respectively. The influences of TTC1 amount and porogenic solvent composition on the physical and electrochromatographic properties of the LMA-based monolithic columns were also evaluated by capillary electrochromatography (CEC). Under the optimum conditions, H_{min} value of 7.39 μm for naphthalene was achieved. The relative standard deviations (RSDs) of column-to-column (n=9), run-to-run (n=5) and day-to-day (n=3) reproducibility were lower than 4.8 %.

Keywords: Capillary electrochromatography/ Lauryl methacrylate/ Reversible addition-fragmentation chain transfer polymerization/ Monolithic column

1 Introduction

Monolithic materials have been widely studied as stationary phase in high

-performance liquid chromatography (HPLC) and capillary electrochromatography (CEC) since the introduction of these materials in the early 1990s by Svec and Frechet.[1, 2] In recent years, the development of the monolithic column has attracted great attention in the field of micro-separation.[3, 4] The organic polymer monolith has advantages, such as chemical stability and easy preparation with different monomers, which has shown considerable application potential to the analytical field.[5-7] The methacrylate monolithic column is a type of organic polymer monolith, which is usually prepared through in situ polymerization of a mixture composed of functional monomers, cross linkers, initiators and porogenic solvents.[8-13] Currently, many technologies are applied to the monolithic columns preparation. The traditional free-radical polymerization is one of common approaches to the monolithic columns preparation. [14-16] As we know, the traditional free-radical polymerization reaction could not easily control the polymerization rate and phase separation in polymer-based monolithic column fabrication. These drawbacks could cause a large variation in polymer molecular weight and the formation of a heterogeneous polymer structure.[17] Therefore, it is important that a novel method is applied to create a more uniform polymer in the process of the polymerization reaction.

Living radical polymerization has been widely used for the commercial production of high molar mass polymers.[18] The emergence of techniques for implementing reversible deactivation radical polymerization serves to impart living characteristics to the process and has provided a new set of tools for polymer chemists that allow control over the polymerization process whilst retaining much of the versatility of conventional radical polymerization.[19] Living radical polymerization methods could be potential alternatives to overcome some of the above mentioned drawbacks of the traditional free-radical polymerization reaction. The living radical methods were proven to be a versatile and robust approach to preparing well-defined organic polymers.[20] The termination and controlled reaction was established by an equilibration between active and dormant species in the controlled/living radical polymerization. The polymerization techniques have attracted attention, including nitroxidemediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT). [21-23]

RAFT polymerization is a promising living radical method for synthesizing well-defined graft polymers.[24, 25] The RAFT polymerization has more advantages than other living radical polymerization techniques, including the ability to polymerize in the controlled manner of a wide range of monomers and the relatively easy reaction conditions.[26, 27] Importantly, the RAFT polymerization process allows linear increases in molar mass, therefore, the majority of the growing block polymers reaches the point of becoming incompatible in the polymerizing monomer medium and microphase separation over a small time interval, thereby resulting in a homogeneous cross-linked, mechanically robust and nanostructured composite.[28] Nowadays, some reports have showed that the RAFT techniques have been used to prepare monolithic columns. [29, 30]

In this study, TTC1 was initially prepared as a chain transfer agent and the TTC1 was then added into the LMA-based monolithic column preparation for CEC using 2， 2-azobisisobutyronitrile (AIBN) as thermal initiator. The influence of the porogenic solvent composition on the morphological properties and eletrochromatographic behaviors of the prepared monoliths were evaluated by CEC. The TTC1 amount was also investigated in the preparation process. The benzene and benzene homologues were investigated to determine the column efficiency of the prepared monolithic column. Compared to the preparation of LMA monoliths thermally initiated using AIBN without TTC1, the prepared monolithic column showed higher column efficiency and separation performance.

2 Experimental

2.1 Chemicals and materials

2-Acrylamide-2-methylpro panesulfonic acid (AMPS), ethylene dimethacryate (EDMA), 3-(trimethoxysily)propylmeth-acrylate (γ-MAPS), LMA, cyclohexanol and 1, 4-butanediol were purchased from Alfa Aesar (Alfa Aesar, China). AIBN, acetonitrile (ACN), concentrated hydrochloric acid, sodium dihydrogen phosphate (NaH_2PO_4), trichlormethane and methanol (HPLC grade) were obtained from Sinopharm Chemical Reagents (Shanghai, China). Petroleum ether, acetone, carbon bisulfide and tetrabutyl ammonium bromide (TBAB) were supplied by Chen Hua Chemical Reagent (Tianjin, China). Thiourea, benzene, methylbenzene, ethylbenzene and naphthalene were supplied by Sinopharm Chemical Reagents (Shanghai, China). A fused-silica capillary of 100 μm *id* was obtained from Yongnian Optic Fiber Plant (HeBei, China). Water was purified by a Milli-Q purification system (Millipore, Bedford, MA).

2.2 Apparatus

CEC experiments were performed on a HP^{3D} CE instrument (Agilent Technologies, Waldbronn, Germany) system equipped with a diode array detector (DAD), and connected to an external nitrogen pressure source. The cassette holding the capillary column was kept at 25 ºC. Data acquisition and analysis were performed with Agilent CE ChemStation. SEM photographs of monolithic materials were taken with a scanning electron microscope (Philips, Eindhoven, Netherlands). FT-IR spectra were recorded on a Nicolet 360 smart (Nicolet, USA). Elemental analysis was measured by Vario EL (Elmentar). AutoPore IV 9520 was used to measure the pore size (micromeritics, USA).

2.3 Pre-treatment of the silica capillary

According to the literature, [14] prior to the preparation of the monolithic column, the silica capillary was treated for vinyl group modification by the following procedure. The capillary was rinsed with 0.1 mol/L NaOH for 2 h, water for 30 min, 0.1 mol/L HCl for 2 h and water for another 30 min, respectively. Subsequently flushing with methanol for 60 min, it was dried by nitrogen gas. γ-MAPS was dissolved in methanol (50%, v/v) and pumped into capillary by a syringe, then the capillary was sealed with rubber. The reaction was performed at 60 ºC for 24 h in a water bath. The capillary was washed with methanol for 30 min and dried under nitrogen. Thus, the inner wall of the capillary was modified by a layer of γ-MAPS, which could supply sufficient sites for subsequent attachment of column to the wall during the following preparation.

2.4 Preparation of chain transfer agent

According to the literature, [31] TTC1 was synthesized by following procedure: carbon disulfide (2.74 g), acetone (5.23 g), chloroform (10.75 g), TBAB (0.229 g) and petroleum ether (20 mL) were added into a 100 mL three-necked flask with the dropping funnel and condensing tube under nitrogen. Sodium hydroxide (50%) (201.6 g) was added drop wise over 90 min; the stirring reaction was kept below 25 ºC for over 12 hours. When the reaction was completed, 90 mL of water was added to dissolve solid and 30 mL concentrated hydrochloric acid (6 mol/L) was used to adjust the pH < 4. The stirring reaction was kept for 30 min under nitrogen again. The yellow solid was obtained after filtration with plenty of washing and recrystallized with ethanol. The reaction route is showed in Fig. 1.

2.5 Preparation of LMA-based monolithic columns

The polymerization mixtures consisting of suitable amounts of LMA (240 μL), EDMA (160 μL) as monomers, AMPS (2 mg) supporting EOF, a ternary mixture composed of water (20 μL), cyclohexanol (440 μL), 1, 4-butanediol (140 μL) as porogenic solvent and AIBN (4 mg) containing different amount of TTC1 as initiator were ultrasonicated for 10 min to obtain a homogeneous solution and then purged with nitrogen for 10 min. The deaerated mixture was filled into the modified capillary (33 cm) to a total length of 25 cm by syringe injection. After both ends sealed with rubber stoppers, the capillary was submerged into a bath of water at 60 ºC for 20 h. The resulted column was flushed with methanol for 2 h using a HPLC pump to remove pore-forming solvent and unreacted monomers. The detection window was burned with a flame torch at the adjacent to the monolithic material.

2.6 Evaluation of LMA-based monolithic column

Prior to experiment, phosphate buffers (pH 9.2) were prepared by adding sodium hydroxide to sodium dihydrogen phosphate. All buffers were filtered with a 0.22 μm membrane filter. Standard solutions and running buffers were degassed by ultrasonication for 10 min. Each monolithic column was placed in the instrument and equilibrated with the mobile phase by applying a stepwise increase in voltage up to 25 kV and 8 bar pressure at the both ends of the column, until a stable baseline was observed. The separations were performed at 20 kV with the column kept at 25 ºC. A test mixture containing thiourea, phenol, benzene, methyl benzene and naphthalene was used to evaluate the CEC performance of columns using a mobile phase consisting of 65 % (ACN w/w), 10 mM buffer at pH 9.2. The sample solution was injected electrokinetically at 10 kV for 6 s. Detection was performed at 214 nm.

3 Result and discussion

3.1 Structural characterization of the TTC1

The chemical structure of TTC1 was confirmed by FT-IR spectroscopy (Fig. 2). The peak at 3423.84 cm^{-1} was evident as hydroxyl group and the peak at 1703.52 cm^{-1} was carbonyl group. In addition, the peaks at 1286.32 cm^{-1} and 1066.06 cm^{-1} confirmed the presence of carbon-sulfur bond (C-S-C) and carbon-sulfur double bond (C=S), respectively. Other peaks were also labeled in Fig. 2. In fact, the FT-IR data were very similar to the data of TTC1 in the literature.[32] The chemical structure of TTC1 was confirmed with C: 31.220; H: 4.282; S: 26.206 and O: 17.471 by elemental anaylsis.

3.2 Mechanism of Polymerization

The mechanism of RAFT polymerization was involved in a reversible addition fragmentation sequence. The transfer of S=C(S)-S-moiety between active and dormant chains serves to maintain the living character of the polymerization (Fig. 3). The S=C(S)-S-moiety was confirmed by infrared spectrogram for evidence of this mechanism. Fig. 3 shows that the S=C(S)-S-end group was retained in the polymeric product. TTCl was doped into the RAFT polymerization as a chain transfer agent. The effectiveness of TTC1 was attributed to its high transfer constants which could ensure a rapid rate of exchange between dormant and living chains. The S=C(S)-S-end group of TTC1 was crucial to the success of the RAFT process. It not only could activate the C=S double bond toward radical addition, but also was a good free radical leaving group.

3.3 Optimization of preparation for monolithic columns

3.3.1 Effect of porogenic solvent composition

As we know, the ratio of porogenic solvent composition could not only affect the monolithic column structure, but also relate to performance of monolithic columns in the process of preparation. Therefore, it was necessary to optimize the porogenic solvent composition in the process of preparation for the LMA-based monolithic columns. Based on our previous experiment, firstly, the polymerization temperature was selected at 60 ºC, then 4.0 mg AIBN (1.0 wt % with respect to the monomers) and 2.0 mg AMPS (0.5 wt % with respect to the monomers) were selected. Secondly, the water content (2.0 %, v/v) was fixed and the proportion of monomers to pore-forming solvents was 40:60 (v/v). Then, a series of LMA-based monolithic columns were prepared by changing the percentage of 1, 4-butanediol in the polymerization mixture. The different compositions were listed in Table 1. Table 1 indicates that with the increase of the 1, 4-butanediol content, the progressive rise in the flow velocity was obtained and the retention factor $k_{napthalene}$ calculated from the equation $k = (t_r\text{-}t_0)/t_0$ was reduced, where t_r and t_0 are the retention time of naphthalene and thiourea. The results were in agreement with the reported literature.[33] It was a reasonable explanation that the polarity of the polymerization mixture and pore size increased with an increase of 1, 4-butanediol percentage. The column efficiency was also examined by measuring the minimum plate height (H_{min}) of naphthalene. The experimental result also showed that the monolithic column with liquid pump flushing was difficulty with 1, 4-butanediol less than 12% (v/v). At the same time, we found that when the content of 1, 4-butanediol was 14.0%, H_{min} achieved the best level in the CEC experiment. It was a reasonable explanation that the pore size increased gradually with an increase of 1, 4-butanediol percentage. The behavior has been reported by other literatures.[34]

3.3.2 Effect of TTC1 amount

As we know, the polymerization reaction rate and uniformity play important roles for the homogeneities and sizes of pores and globules in the preparation of monolithic column. Therefore, the TTC1 was added into the polymerization reaction. Different proportions of TCC1 and AIBN were investigated in our experiment. The initial polymerization reaction was chosen as follows: the proportions of monomers to pore-forming solvents were 40:60 (v/v), and the optimal content of 1, 4-butanediol (14%, v/v) was found in the previous section. The TTC1 amount in the polymerization mixture was optimized by varying its amount to compare the AIBN in Table 2. The temperature was kept at 60 ºC for 20 h. Table 2 shows different amounts of TTC1 which is doped to the 1 wt% AIBN as initiator exhibited different H_{min} values for naphthalene. With an increase of TTC1 amount in the polymerization reaction, the H_{min} values of naphthalene were clearly improved. However, when TTC1 amount was double to AIBN content, the H_{min} values were stable. The retention behavior was also examined along this series. The results showed that flow rates and *k* values had little changes with the increase of TTC1 amount in the polymerization reaction.

3.4 Evaluation of monolithic column

3.4.1 Morphology and column efficiency

In order to investigate the difference of the only AIBN and the AIBN containing TTC1 as initiator, SEM pictures and CEC performance of monoliths have been performed. SEM pictures of the optimal monolithic beds show a significant difference (Fig. 4). Fig. 4B exhibits more uniform polymer pore particle size, relatively narrower pore size distribution and larger surface area than that of Fig. 4A. The porous properties of the rigid monolithic phases were further investigated using mercury intrusion porosimetry. As shown on Fig.5, The two kinds of monoliths had a median pore diameter comprised 703 nm and 950 nm with pore volume of 13.22 cm^3/g and

8.31 cm^3/g, respectively. The monolithic column using AIBN containing TTC1 as initiator had a very narrow size distribution. At the same time, under the same separation conditions, the monolithic column using AIBN containing TTC1 as initiator has better efficiency values. The behaviors indicate the presence of higher number of microspores and larger surface area in the globule structure of the monolithic columns thermally polymerized with AIBN containing TTC1 as initiator. The Fig.6 indicates that two type monolithic columns have different column efficiency, it may conclude that LMA-based monolithic columns thermally initiated using AIBN containing TTC1 have advantages over those using the only AIBN as initiator.

3.4.2 Monolithic column repeatability and stability

In order to evaluate repeatability and stability of the resulting columns, the monolithic columns were prepared under the optimal polymerization reaction conditions, and several electrochromatographic parameters were determined by CEC. The reproducibility of column production was assessed by the relative standard deviation (RSD, %) from column-to-column (n = 3) and batch-to-batch (n = 3) using thiourea and benzene homologous series as a model system. The results are listed in Table 3. As seen from Table 3, satisfactory reproducibilities were obtained for all tested parameters. Run-to-Run repeatability (n = 5) and column-to-column (n = 9) stability were achieved with RSDs<1.7% and RSDs<4.0% in the studied electrochromatographic parameters, respectively. The electrochromatographic behaviors of the prepared monolithic column using AIBN containing TTC1 was consistent with those by conventional preparation method for column.

4 Concluding remarks

As a chain transfer agent, TTC1 was synthesized and added into the polymerization reaction of LMA-based monolithic columns. The influences of TTC1 amount and porogenic solvent composition were investigated. The experimental results showed that the possibility of a fine-tuning of porous and electrochromatographic properties of monolithic columns were achieved by adjusting the 1, 4-butanediol content and TTC1 amount. Under optimum conditions of preparation for monolithic columns, H_{min} value of 7.39 μm for naphthalene was achieved. The produced monolithic columns also exhibited good repeatability and **s**tability. A comparison of the CEC performance with LMA-based columns thermally polymerized using AIBN without TTC1 as initiator was also carried out. The LMA-based monolithic columns initiated with AIBN containing TTC1 had better H_{min} value and much higher permeability than those polymerized using AIBN without TTC1 as initiator. Thus, the TTC1 added to the polymerization reaction could offer an attractive way to prepare the monolithic columns.

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Lists of figures and tables

Table 1. Electrochromatographic properties of monolithic columns initiated by AIBN at different 1, 4-butanediol percentages

[a] CEC condition: mobile phase, ACN/phosphate buffer=65/35(v/v); 10 mmol/L phosphate buffer pH 7.0; supplement pressure: 8 bar; sample injection ,10 kV/6s; applied voltage: 20 kV; detection wavelength: 214 nm

Table 2. Electrochromatographic properties of monolithic columns initiated by AIBN with different TTC1 amount

[a] CEC condition: the same as table 1

Table 3. Reproducibility of EOF, retention factor, and efficiency on column

[a] CEC condition: the same as table 1

Fig.1. The synthetic route of RAFT regent TTC1

Fig.2. FT-IR spectrum of RAFT regent TTC1

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Fig.4. SEM photographs of LMA-based monolithic columns at 14.0 wt% of 1, 4-butanediol percentages in the polymerization mixture. Part A initiated by AIBN, Part B initiated by AIBN with TTC1.

Fig.5. Differential pore size distribution profile of a porous monolith with TTC1 and Non- TTC1

Fig.6. Electrochromatogram of five compounds with LMA-based monolithic column (a) AIBN as initiator; (b) AIBN and TTC1 as initiator

[a] CEC condition: mobile phase, ACN/phosphate buffer=65/35(v/v); 10 mmol/L phosphate buffer pH 7.0; supplement pressure: 8 bar; sample injection ,10 kV/6s; applied voltage: 20 kV; detection wavelength: 214 nm. Solute: 1 thiourea; 2 phenol; 3 benzene; 4 methyl benzene; 5 naphthalene.

Table 1

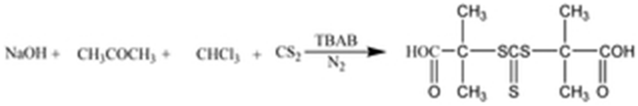
Monolithic column	Monomer/AIBN	Cyclohexanol/1,4-butanediol/water.	$u^{b)}$ (mm/s)	$K_{naphthalene}$	$H_{min}^{c)}$ (μm)
1	400：4.0	460：120：20	0.22	3.34	20.1
2	400：4.0	440：140：20	0.35	2.54	16.9
3	400：4.0	420：160：20	0.50	2.20	21.2
4	400：4.0	400：180：20	0.54	2.01	34.9
5	400：4.0	380：200：20	0.68	1.79	43.9

Table 2

Monolithic column	Monomer/ RAFT/AIBN	Cyclohexanol/1,4-butanediol/water.	$u^{b)}$ (mm/s)	$K_{naphthalene}$	$H_{min}^{c)}$ (μm)
1	400：0：4.0	440：140：20	0.35	2.54	16.9
2	400：4.0：4.0	440：140：20	0.32	3.46	11.0
3	400：6.0：4.0	440：140：20	0.30	3.47	9.85
4	400：8.0：4.0	440：140：20	0.28	3.52	7.39
5	400：10.0：4.0	440：140：20	0.27	3.53	7.37
6	400：12.0：4.0	440：140：20	0.29	3.49	9.73

Table 3

	EOF (%RSD)	Retention factors (%RSD)		Capillary efficiency (%RSD)	
		thiourea	naphthalene	thiourea	naphthalene
Column-to-column (n =9)	2.8	3.3	4.0	3.8	3.7
Run-to-run (n = 5)	1.6	1.7	1.8	3.2	3.2
Day-to-day (n = 3)	2.6	2.5	2.8	4.6	4.8



The synthetic route of RAFT regent TTC1
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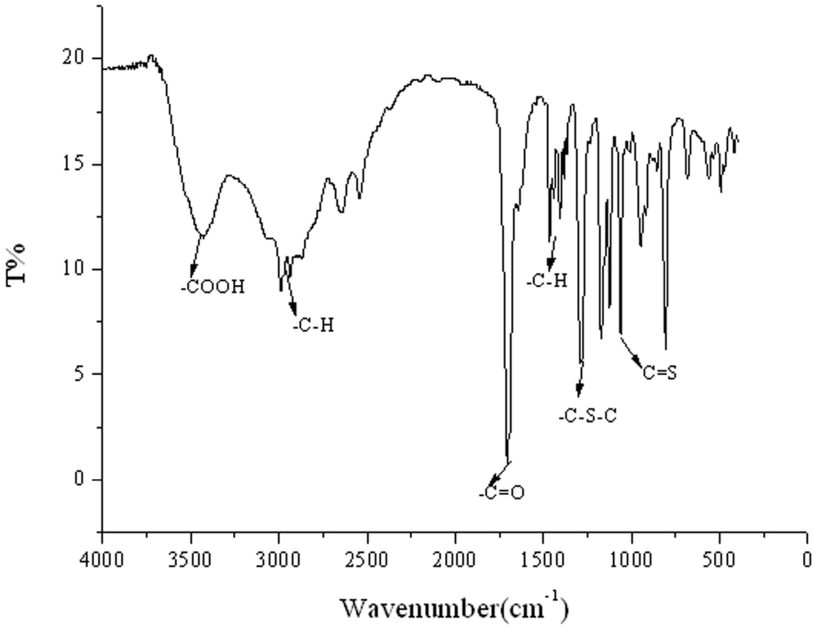

FT-IR spectrum of RAFT regent TTC1
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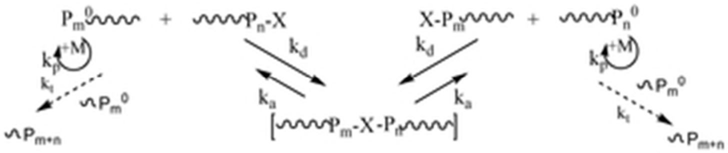

The mechanism of RAFT regent TTC1 polymerization
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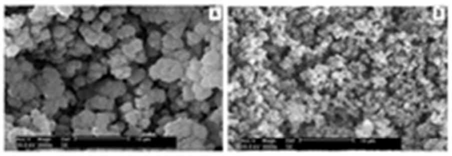

SEM photographs of LMA-based monolithic columns at 14.0 wt% of 1, 4-butanediol percentages in the polymerization mixture. Part A initiated by AIBN, Part B initiated by AIBN with TTC1.

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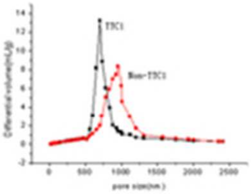

Differential pore size distribution profile of a porous monolith with TTC1 and Non- TTC1
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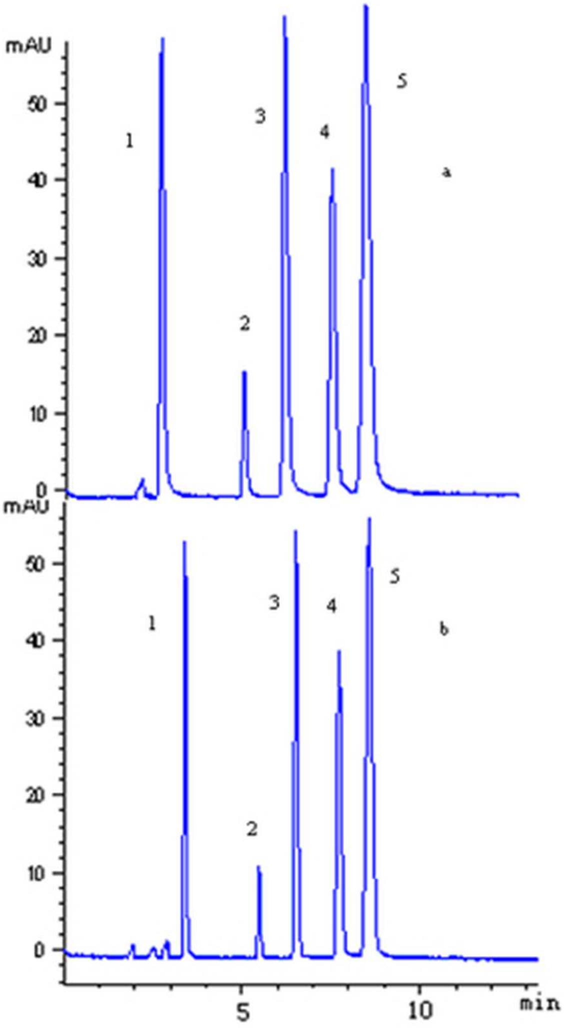

Electrochromatogram of five compounds with LMA-based monolithic column (a) AIBN as initiator; (b) AIBN and TTC1 as initiator
25x44mm (300 x 300 DPI)