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Fast preparation of a hydrophobic monolith by redox initiation and its application in the separation of small molecules

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\textbf{Abstract:} A novel skeleton hydrophobic polymeric monolith was prepared by redox initiation in this paper. At ambient temperature, benzoyl peroxide (BPO) and N, N-dimethyl aniline (DMA) were used as initiators; 1-Dodecene (C12) as the monomer and ethyleneglycol dimethacrylate as the crosslinking agent. The polymerization conditions were optimized in order to use for chromatographic separations. The characters of the monolith were investigated by scanning electron microscopy (SEM), fourier transform infrared spectroscopy, mercury porosimeter and nitrogen adsorption-desorption mercury porosimetry. Moreover, the prepared monolith was used as the stationary phase of high performance liquid chromatography to separate the mixture of benzenes in hydrophobic chromatography mode. Baseline separations and high column efficiencies in excess of 11,000 theoretical plates per meter were

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1. Introduction:

In recent years, monolithic stationary phase, has attracted increasing attention because of its excellent mass transfer properties and versatile surface modification compared to conventional columns packed with particles [1-2]. Basically, monolithic column are divided into two groups: rigid organic polymer-based monoliths and silica-based monoliths. The two kinds of monoliths have been used in high performance liquid chromatography (HPLC) [3-4], solid phase extraction (SPE) [5-6], and capillary electrophoresis (CE) [7-8]. The drawback of the silica-based monolith is that it is subject to an insufficient hydrolytic of the Si–O–C linkage, especially under moderately acidic or slightly alkaline conditions. Moreover, preparation of silica-based monolithic columns is not only time-consuming but also difficult to control the entire process, which leads to the problems with reproducibility. As an alternate, the organic polymeric monolith shows stability within the entire range of pH and exhibited excellent biocompatibility. However, it suffers from shrinking or swelling under the influence of temperature or organic solvents. Besides, it is difficult to prepare polymeric monoliths possessing both large through pores and multiple small pores in one step [9-12]. An alternative approach is carried out in this paper.

Hydrophobic polymeric monolithic column is an important liquid chromatography solid phase for analyzing small molecules. There are many approaches to prepare...
hydrophobic columns such as single electron transfer-living radical polymerization (SET-LRP) and atom transfer radical polymerization (ATRP) [13-14]. In situ radical polymerization has the disadvantages of slow initiation, fast increase, easy chain transfer and quick chain termination which lead a non-uniform structure [15-17], and resulting in low column efficiency, low permeability and low resolution.

The redox initiator which can reduce the activation energy of organic peroxides decomposition, is mostly used in the resin curing process. The reaction can fast occur under contact pressure and ambient temperature condition [18]. The system generally consists of peroxide in combination with reducing agent. The usually used reducing agents are N, N-dimethyl toluidine, N, N-dimethyl aniline (DMA) [19-21] and N-phenyl diethanol amine (PDEA). The benzoyl peroxide (BPO) can initiate the polymerization of vinyl monomers at ambient temperature [22]. The complex decomposes and gives free radicals or cation radicals which can then initiate radical polymerization. This curing process is mostly used in the preparation of unsaturated polyester resin, in which the linear polyester molecules are crosslinked into three-dimensional network structure. This approach has several advantages: effective control of the reaction rate, complete curing reaction, and good mechanical stability of the products. Besides, a proper accelerator can meet various process requirements. Compared to the reported references, the advantages of this method are that not time-consuming preparation and process occurring at room temperature.

In this work, a hydrophobic monolith was prepared by one-step redox initiation process. Moreover, the prepared monolith was used as HPLC hydrophobic stationary
phase to separate benzenes small molecules successfully.

2. Experimental:

2.1 Materials and instrumentation

1-Dodecene (C12) was purchased from Aladdin Co. Ltd. (Shanghai, China). Ethyleneglycol dimethacrylate (EDMA) was produced by New Jersey (USA). Cetyl alcohol, benzoyl peroxide (BPO), N, N-Dimethylaniline (DMA) and phenol, 1-naphthol, biphenyl, anthracene, triphenylamine, benzotriazole, 1-naphthylamine, 2,4-dinitrophenylhydrazine, for separated were obtained from Kermel Co. Ltd. (Tianjin, China). Potassium bromide (KBr) was bought from Skylight Optical Instrument Co. Ltd. (Tianjin, China). All of these chemicals and samples were analytical reagent grade. Triples distilled water was used for all experiments.

An Agilent Technologies (Agilent, USA) with a 1100 system which was consist of a quaternary pump with an online vacuum degasser, an autosampler with variable injection capacity ranged from 0.1 to 100 µL, and a UV detector; Agilent liquid chromatography system chemical software was used and operated under Windows XP for data acquisition and integration. Microscopic analysis was carried out using a Hitachi (Hitachi High Technologies, Tokyo, Japan) S-4300 SEM instrument. The FT-IR spectra were recorded on an FTIR-8400S IR apparatus in the region of 400-4000 cm\(^{-1}\) (SHIMADZU, Kyoto, Japan). Pore size distribution was achieved by mercury intrusion porosimetry (AutoPore II 9220 V 3.04, Micromeritics Instrument Co., Atlanta, GA). Nitrogen adsorption-desorption isotherms were measured using specific surface area analyzer (BUILDER, Beijing, China) SSA-4300 instrument.
2.2 Preparation of the monolith

The monolithic column was prepared with the optimized condition by redox initiator in stainless-steel tubes (50 mm×4.6 mm i.d.). Functional monomer C12 (0.60 mL) and cross linking agent EDMA (0.80 mL) and initiator DMA (0.03 mL) BPO (3.0 mg) were dissolved in 0.2 g melted cetyl alcohol. The mixture was surged ultrasonically and then poured into the stainless steel tube, which was sealed at both ends with close column heads. The mixture was bubbled with nitrogen for 5 min to remove gases. Then the polymerization was allowed to proceed at ambient temperature for less than 10 min. The monolith with the steel-tube was connected to the HPLC system and was washed by methanol online for 2 h at a flow rate of 1.0 mL min⁻¹ to remove all of cetyl alcohol and other soluble compounds present from the polymer rod. The polymerization scheme was given in Fig. 1.

2.3 Characterization of the monolithic column

The monoliths in the columns were pumped out and cut into small pieces followed by drying under vacuum at 60 °C overnight. Chemical groups of the monolith were detected by infrared spectra method, 1-2 mg of the dried monolith and 200 mg of dried KBr were mixed and grinded to less than 2 µm i.d., and then the powder was pressed into transparent sheet by the hydraulic press. Microstructures of the dried monolith samples were observed by scanning electron microscopy (SEM), the pieces of monoliths were snapped apart and placed on sticky copper foils, which were attached to a standard aluminum specimen stub. Then the attached monoliths were coated with about 20 nm of gold by an Eiko IB-3 sputter coating instrument (Eiko,
Tokyo, Japan). The pore size distribution was determined by mercury intrusion porosimetry and nitrogen adsorption-desorption isotherm.

The permeability of monoliths was assessed by the pressure drop of the monolithic column at different flow rates by using water and methanol as mobile phase, respectively. The values of the system pressure were measured at each flow rate without or with the monolith being connected, and the difference between the two values was calculated as the pressure drop across the monolith. According to the Darcy’s law permeability of the monolith was calculated [23].

2.4 HPLC measurements

2.4.1 Selection of the mobile phase

In order to select a suitable mobile phase for the separation of the analytes, isocratic elution with methanol and water being used as mobile phase was tested.

2.4.2 Chromatographic separation of small molecules

Chromatographic separation of small molecules was obtained by a monolithic column (50 mm × 4.6 mm i.d.). The flow rate was 1.0 mL min⁻¹, UV wavelength was set at 254 nm and the temperature was 25 °C. The injection volume of the sample was 1.0 µL. All sample solutions injected in the chromatographic system were filtered through a millipore membrane (0.22 µm) to remove particles and large aggregates. Methanol/water (75/25, v/v) was used as mobile phase.

3. Results and discussions

3.1 Optimization of polymeric conditions

In order to obtain materials with porous and uniform structure, the conditions of the
polymerization were optimized. Different compositions of polymerization mixtures were tested. The resulting polymers were qualitatively evaluated for consistency, rigidity and optical aspects. The results were summarized in Table 1.

Monomer and cross linking agent both play important roles in the preparation of the monolith. They have significant effects on not only the rigidity and porosity, but also the selectivity and column efficiency of the monolith. Three monolithic columns (column A – C in Table.1) were prepared with different volume of C12 to investigate the influence of C12 amount. Column B, D and E in Table.1 were prepared to investigate the effects of EDMA on the monolith. According to the preliminary experiments listed in Table.1, when the rate of monomer and cross linking agent was 0.6/0.8 (v/v), material with good mechanical property was obtained. SEM was used to investigate the morphology of the monoliths.

3.2 Effect of the porogen on the structure

The choice of pore-forming solvent or porogen is a tool that may be used for the control of porous properties without changing the chemical composition of the final polymer. Fig. 2 showed the effects of the content of cetyl alcohol in the polymerization mixture on pore size distribution. In general, larger pores would be obtained by using more macroporogen because of the earlier onset of phase separation. According to the visualized results, the monolithic column using 0.2 g cetyl alcohol as porogen had well-distributed pore size and submicron skeleton structure which led to high permeability and high efficiency. Based on these results the composition of the polymerization mixture chosen for further experiments was 0.60 mL of C12, 0.80 mL
of EDMA, and 0.2 g of cetyl alcohol.

The choice of porogens for the preparation of porous polymer monoliths remains an art rather than science. For example, Santora et al. carried out experiments with single solvent porogens including tetrahydrofuran, acetonitrile, toluene, chlorobenzene, hexane, methanol, dimethylformamide, and methyl-t-butyl ether, and prepared series of poly(divinylbenzene), poly(styrene-co-divinylbenzene), poly(ethylene dimethacrylate), and poly(methyl methacrylate-co-ethylene dimethacrylate) monoliths [24]. Although some of these solvents afforded polymers with a surface area as 820 m² g⁻¹, it is unlikely that they would be permeable to flow since the pores were rather small [25]. This is why not many porogens have been used and most often proven porogen mixtures are applied. It is generally accepted that good solvents serve as microporogens to provide high surface areas, while poor solvents act like macroporogens to provide good bulk flow properties. For C12-based monoliths, cetyl alcohol is a common solvent, which offered good solubility for C12 and EDTA.

Nitrogen adsorption is extensively used for determination of porous properties of monoliths in their dry state. It allows a useful estimate of expected total surface areas of porous polymeric materials and the existence of a permanent mesoporous pore space at least qualitatively [26]. We had been ascertained that monolithic column with no porogen having a surface area of 1.8 m² g⁻¹ were not suitable for the efficient separation of small molecules. When 0.2 g cetyl alcohol was used as porogen the surface area increased to 279 m² g⁻¹. Additionally, the nitrogen adsorption-desorption isotherm exhibited typical type-IV hysteresis, indicative of the presence of mesopores.
3.3 Mechanical strength and permeability

In order to characterize the mechanical performance and permeability of the monoliths, the back pressures of the monolith at different flow rates were studied. Fig. 4 showed an excellent linear and the regression factors were 0.9997 and 0.9998, that used methanol and water as mobile phase respectively, which indicated that the internal structures of the monoliths were not damaged in the range of back pressure from 13 to 90 bar. This superior flow-through property could be attributed to high cross-linking homogeneity and large pore size. Moreover, the efficiency of chromatographic separation was not affected after subjecting the high flow rates. Besides, in order to evaluate its mass transfer property, the permeability behavior, which is one of the most practical factors in designing a novel type of monolithic column, was investigated. Column permeability \( k \) reflects through-pore size and external porosity, or a domain size at a constant through-pore size/skeleton size ratio.

According to Darcy’s law, the equation is as follow:

\[
Q = -\frac{kA}{\mu} \cdot \frac{P_b - P_a}{L}
\]

Wherein, the total discharge, \( Q \) (units of volume per time, e.g., \( m^3 \cdot s^{-1} \)) is equal to the product of the permeability of the medium, \( k \) (\( m^2 \)), the cross-sectional area to flow, \( A \) (units of area, e.g., \( m^2 \)), and the pressure drop, all divided by the viscosity, \( \mu \) (Pa·s) and the length over which the pressure drop is taking place [27]. The negative sign is needed because fluid flows from high pressure to low pressure. The good permeability value of \( 8.97 \times 10^{-14} \) \( m^2 \) was calculated based on the Darcy’s law at ambient
temperature which supported the internal morphology information of Fig. 2(c). So the skeleton structure not only had good permeability and fast mass transfer, but also had higher surface which could benefit the chromatographic separation. And skeleton structure had higher column efficiency and resolution than accumulated structure. These results indicated that skeleton structure provided larger surface area and excellent permeability.

3.4 FT-IR spectra of the monolith

The FT-IR spectra of the monolith were shown in Fig. 5, in which, typical and expected bands were found. The peak at 3000 cm\(^{-1}\) was due to the stretching in C-H of aliphatic or alkenes. The clear absorption peaks at 1510 cm\(^{-1}\) and 1100 cm\(^{-1}\) were caused by the C-O-C group; The spectrum at 1725 cm\(^{-1}\) showed the presence of the -C=O of esters.

3.5 Pore size distribution of the monolith

The measurement of pore size distribution for the monoliths was carried out by mercury intrusion porosimetry. Pore size distribution determines the fraction of the total pore volume accessible to molecules of a given size and shape, which is a very important property of the monolith. The obtained result is depicted in Fig. 6. Based on Fig. 6, the total intrusion volume, median pore diameter and the porosity were 2.37 mL g\(^{-1}\), 3.5 mm and 70.5%, respectively.

3.6 Chromatographic separation of small molecules

The poly (C12-co-EDMA) monolith was used as the stationary phase of HPLC to separate small molecules. Fig. 7(a, b) showed the chromatograms, and in which two
groups of small molecular compounds distinct peaks could be observed. The retention factors \( (k) \) of each sample of the first group small molecules on the poly (C12-co-EDMA) monoliths were determined at various concentration of methanol in the mobile phase and the results were shown in Fig. 8. The elution capacity is gradually increased with the increase of the amount of methanol, but the column efficiency is not changed significantly which obtained from the calculation of theoretical plate number. This indicates that the hydrophobic interaction between the solutes and the stationary phase plays a dominating role in retaining the solutes on the monoliths. The separations of basic compounds were always suffered from peak tailing in previous reports due to non-specific adsorption on the stationary phases. However, this phenomenon was not observed on the hydrophobic organic monolithic column.

Meanwhile, some chromatographic parameters such as retention time and resolution, symmetry factor and theoretical plate number of each sample were calculated and the results were shown in Table 2, in which the theoretical plate number of biphenyl could be up to \( 10^4 \). It could be seen that the poly (C12-co-EDMA) monoliths are excellent stationary phase for separation of these analytes. Furthermore these results strongly suggested further potential of this novel monolith for an efficient downstream processing of benzenes small molecules.

**3.7 Advantages compared with other hydrophobic monoliths**

Organic polymeric monoliths, generally, are widely used as stationary phases for bio-molecule separation because efficient separation of small molecules is not easily
realized in the normal columns (4.6 mm i.d.). However, achieving good column efficiency for small molecules has been easy to obtain for capillary liquid chromatography (cLC) and capillary electrochromatography (CEC). But compared with the normal column in HPLC, both cLC and CEC methods can't achieve high throughput separation.

A series of hydrophobic interaction monolithic columns have also been prepared in a similar manner such as single electron transfer-living radical polymerization (SET-LRP) and atom transfer radical polymerization (ATRP). Nevertheless, the preparation processes of these monoliths are rather tedious and time-consuming. We have used a simple one-set approach for preparing the organic polymeric monolith, which represented a new way to prepare the organic polymeric monoliths with variety of organic monomers. In this article the polymerization was allowed to proceed at ambient temperature for less than 10 min. With the excellent hydrophobic of C12, column efficiencies in excess of 11,000 theoretical plates per meter were obtained. However, much less work has been performed with C12 as monomer in the field of monolith.

3.8 The effects of eluent linear flow velocity on the separation

The plate height (H) of the first group small molecular on the poly (C12-co-EDMA) monoliths were determined at various linear flow rate [28]. Fig. 9 shows that the van Deemter plot demonstrating effect of velocity on efficiency of monolithic column for small molecular. Fig.8 and Fig.9 were the average of seven cycle measurement results derived from succedent section 3.8 where the experimental results demonstrate a good
repeatability process. Separately, benzene was employed as the mobile phase velocity marker in this experiment according to the cited reference [29].

3.9 Repeatability and stability

A good column-to-column repeatability and monolith stability are important measure of the process. An excellent repeatability characterized by relative standard deviations (RSDs) for the retention times in the range of 1.3-2.6% was achieved on poly (C12-co-EDMA) monoliths using the same process and conditions (n=7). Furthermore, the chromatograms on the poly (C12-co-EDMA) monoliths were obtained after numerous equilibrations and separation runs involving the small molecular mixture. The results demonstrated that the preparation process had a good repeatability and the monoliths were stable.

4. Conclusion

In order to obtain a hydrophobic monolithic column with uniform structure by a simple approach, one-step redox initiation is used in the preparation of monolith in this study. A monolithic structure with hydrophobic surface properties was obtained in this study without post surface modification. The monolith had high performance in the hydrophobic separation of benzenes small molecules which was high to 11,000 plates per meter (diphenyl). The results suggested that it’s a simple, cheap and effective method to prepare hydrophobic monolith. Hence the novel method presents a promising alternative to commercially available monolithic supports.

5. Acknowledgements

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Foundation of China (No.21175031); The Applied Basic Research Program Key Basic Research Project of Hebei Province (No.11966411D); The National Major Scientific and Technological Special Project for "Significant New Drugs Development" (No.2012ZX09103-101-057); Natural Science Foundation of Hebei Province (B2012201052); The Key Project of Science and Technology of Research of College of Department of Education of Hebei Province (No.ZD2010234); The Science Foundation of Education Department of Hebei Province (No. Z2013112, CPRC003), and the Natural Science Foundation of Hebei University (No.2013-247).
References


Caption for figures and tables

**Fig. 1.** Synthesis scheme of the poly (C12-co-EDMA) monolithic column.

**Fig. 2.** Effects of varying porogen on the morphology of poly (C12-co-EDMA) monolithic columns: (a) no porogen, (b) 0.1 g cetyl alcohol, (c) 0.2 g cetyl alcohol, (d) 0.3 g cetyl alcohol.

**Fig. 3.** Nitrogen adsorption-desorption isotherm.

**Fig. 4.** Back pressures of the poly (C12-co-EDMA) monoliths at different linear flow rates. Mobile phase: 1 water, 2 methanol.

**Fig. 5.** The FT-IR spectrum of the poly (C12-co-EDMA) monolith.

**Fig. 6.** The measurement of pore size distribution for the poly (C12-co-EDMA) monolith. Pore size distribution profile measured by mercury intrusion porosimetry.

**Fig. 7.** Elution profiles of small molecules on the poly (C12-co-EDMA) monoliths.

HPLC conditions: the prepared hydrophobic monolith, 50 mm× 4.6 mm i.d.; flow rate 1.0 mL min\(^{-1}\), UV detection at 254 nm. Samples a: the analytes are 1: phenol, 2: 1-naphthol, 3: biphenyl, 4: anthracene, 5: triphenylamine; Samples b: the analytes are 1: benzotriazole, 2: 1-naphthylamine, 3: 2,4-dinitrophénylhydrazine, 4: biphenyl;

Mobile phase: methanol/water (75/25, v/v), b methanol/water (65/35, v/v).

**Fig. 8.** Relationship between \( k \) and methanol concentration on the poly (C12-co-EDMA) monolith. The retention factors \( k \) was defined as \( (t_r - t_0)/t_0 \), where \( t_r \) and \( t_0 \) represent the retention times of an analyte and an unretained compound, respectively.

**Fig. 9.** Plate height curves obtained from separations on a monolithic poly
(C12-co-EDMA) column (1 phenol, 2 1-naphthol, 3 biphenyl, 4 anthracene, 5 triphenylamine). Mobile phase: 75% (v/v) methanol in water. In general the plate heights were fitted to the van Deemter equation \( H = A + B / \mu + C\mu \).

Table 1. Qualitative comparison of polymer compositions.

Table 2. Chromatographic parameters of separation of the small molecules.
<table>
<thead>
<tr>
<th>C12 (mL)</th>
<th>EDMA (mL)</th>
<th>Cetyl alcohol (g)</th>
<th>Permeability ($\times 10^{-14}$ m$^2$)</th>
<th>Plate numbers (plates m$^{-1}$)</th>
<th>Resolution</th>
<th>Symmetry factor</th>
<th>Optical properties</th>
<th>Mechanical/physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 0.3</td>
<td>0.8</td>
<td>0.2</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>White</td>
<td>Soft, granulous</td>
</tr>
<tr>
<td>B 0.6</td>
<td>0.8</td>
<td>0.2</td>
<td>$\leq 8.97$</td>
<td>$\leq 11884$</td>
<td>$\leq 4.61$</td>
<td>$\leq 0.90$</td>
<td>White</td>
<td>Quite, hard</td>
</tr>
<tr>
<td>C 1.0</td>
<td>0.8</td>
<td>0.2</td>
<td>$\leq 0.81$</td>
<td>$\leq 1385$</td>
<td>$\leq 1.07$</td>
<td>$\leq 0.52$</td>
<td>White</td>
<td>Hard, brittle</td>
</tr>
<tr>
<td>D 0.6</td>
<td>0.5</td>
<td>0.2</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>White</td>
<td>Soft, fluffy</td>
</tr>
<tr>
<td>E 0.6</td>
<td>1.0</td>
<td>0.2</td>
<td>$\leq 1.78$</td>
<td>$\leq 1874$</td>
<td>$\leq 1.43$</td>
<td>$\leq 0.61$</td>
<td>White</td>
<td>Hard</td>
</tr>
<tr>
<td>F 0.3</td>
<td>0.5</td>
<td>0.2</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Translucent</td>
<td>Gel like</td>
</tr>
</tbody>
</table>
One equation has been used to calculate the plate number:

\[
N = \frac{5.55 (T_r/W_{0.5})^2}{L}
\]

\(N\) is the theoretical plate number per m and \(T_r\) is the retention time of the analyte in min and \(W_{0.5}\) is the peak width at half height in min and \(L\) is the length of the column.

<table>
<thead>
<tr>
<th></th>
<th>Retention time (min)</th>
<th>Resolution</th>
<th>Symmetry factor</th>
<th>Plate numbers (plates m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>1.170</td>
<td>2.84</td>
<td>0.62</td>
<td>9540</td>
</tr>
<tr>
<td>1-Naphthol</td>
<td>2.032</td>
<td>3.37</td>
<td>0.70</td>
<td>8626</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>3.735</td>
<td>2.69</td>
<td>0.78</td>
<td>11686</td>
</tr>
<tr>
<td>Anthracene</td>
<td>6.058</td>
<td>1.54</td>
<td>0.73</td>
<td>9632</td>
</tr>
<tr>
<td>Triphenylamine</td>
<td>8.442</td>
<td>___</td>
<td>0.62</td>
<td>5830</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Retention time (min)</th>
<th>Resolution</th>
<th>Symmetry factor</th>
<th>Plate numbers (plates m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzotriazole</td>
<td>1.394</td>
<td>4.61</td>
<td>0.67</td>
<td>8943</td>
</tr>
<tr>
<td>1-Naphthylamine</td>
<td>3.676</td>
<td>3.19</td>
<td>0.79</td>
<td>8222</td>
</tr>
<tr>
<td>2,4-Dinitrophényl hydrazine</td>
<td>6.921</td>
<td>1.92</td>
<td>0.82</td>
<td>8707</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>9.742</td>
<td>___</td>
<td>0.90</td>
<td>11884</td>
</tr>
</tbody>
</table>
\[
\text{CH}_3
\begin{array}{c}
\text{(CH}_2\text{)}_9\text{CH} = \text{CH}_2
\end{array} + \begin{array}{c}
\text{O-CH}_2\text{O}
\end{array}
\xrightarrow{\text{BPO;DMA}} \begin{array}{c}
\text{(CH}_2\text{)}_{11}\text{CH}_3
\end{array}
\]

80x45mm (300 x 300 DPI)
80x63mm (300 x 300 DPI)