Synthesis and Characterization of Novel Fluorosilicone Triblock Copolymers

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Abstract. Novel fluorosilicone triblock copolymers poly(2,2,3,4,4,4-hexafluorobutyl methacrylate)-block-poly(dimethylsiloxane)-block-poly(2,2,3,4,4,4-hexafluorobutyl methacrylate) (PHFBMA-b-PDMS-b-PHFBMA) were synthesized by atom transfer radical polymerization (ATRP). The optimum reaction conditions were also studied in the work. The structure and composition of the copolymers were analyzed and identified by infrared spectroscopy (IR), nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC). The effects of the fluorine and silicone content on the hydrophobic and oleophobic properties of prepared triblock copolymers were also investigated. The results showed that the prepared triblock copolymers had excellent hydrophobic and oleophobic properties.

1. Introduction
Fluorosilicone polymer combines the excellent properties of organic silicone and organic fluorine compounds, and it becomes a new hotspot in material field. It has great potential to apply in paint, textile, paper, leather finishing agent, mold dope and lubricant now [1, 2]. Recently there are many researches about the fluorosilicone polymers, most researches are focused on siloxane fluorinated polyacrylate polymers and side group type fluorosilicone polymer, but there are few researches about fluorine-silicon block copolymer [3, 4].

American scholar Jinshan Wang, Matyjiaszewski [5, 6] and Japanese scholar Sawamoto [7] proposed ATRP in 1995. Various kinds of monomers can be applied in ATRP, and the molecular weights of the obtained polymer are distributed in narrow range. It is not only an effective method for designing molecular and synthesizing model polymers, but also have low expense and easy to realize industrialization [8].

In this paper, PHFBMA-b-PDMS-b-PHFBMA were synthesized through ATRP with a series of different molecular weight prepared polydimethylsiloxane macrominitiator as raw materials. The reaction equation was shown in figure 1 The suitable catalytic system for the reaction was chose and the optimal optimal reaction condition was studied. The novel fluorosilicone triblock copolymers were obtained with clear structure, controlled molecular weight and excellent hydrophobic/oleophobic performance.
Figure 1. Synthetic scheme for the preparation of PHFBMA-b-PDMS-b-PHFBMA triblock copolymers.

2. Experimental

2.1. Materials

A series of Dichloro terminated polydimethylsiloxane (Cl-PDMS-Cl) having an average molecular weight of 1940, 2450, 3635, 5020, 6901 and 11550 g/mol respectively were produced by Shaanxi Provincial Research and Design Institute of Petroleum and Chemical Industry. 2-chloro-2-methylpropionyl chloride (CMPC, 98%) was obtained from SynAsst Chemical. 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFBMA, 98%) purchased from Lancaster was washed with 5% aqueous NaOH solution to remove the inhibitor. Cuprous chloride obtained from Tianjin chemical reagent factory was washed with glacial acetic acid and methanol. All other materials were analytical reagent and used without further purification.

2.2. Synthesis of PHFBMA-b-PDMS-b-PHFBMA Triblock Copolymers

The certain amount of Cl-PDMS-Cl, HFBMA, Cu⁺ catalyst, Catalyst ligands and 50 ml toluene were added into four-neck round-bottom flask, which was equipped with condenser, thermometer, constant pressure funnel and nitrogen conduit. The system was strictly deoxygenated by nitrogen filling time and again, and then warmed up to the specified temperature, held the temperature for reacting in a certain time. The mixture diluted with 50 ml tetrahydrofuran, through neutral alumina column to remove the catalyst, the treated liquid was precipitated in 50 ml methanol. The obtained polymer was rinsed with methanol for three times and dried to constant weight in vacuum drying box at 40 °C.

A series of different molecular weight and different fluorine content PHFBMA-b-PDMS-b-PHFBMA which came from different molecular weight Cl-PDMS-Cl and different mol HFBMA were synthesized. Consider the molecular weight of 6901 Cl-PDMS-Cl as macroinitiator, the effect of feed ratios, reaction temperature and reaction time were investigated, the kinetics of the reaction was discussed at the same time.

2.3. Characterizations and Measurements

The monomer conversion rate was determined by the weighing method: Put about 1g products into the constant weight aluminum foil tray, and then put it into a vacuum drying oven baking to constant weight (accurate to 0.1 mg). The monomer conversion rate according could calculate as follow:

$$X\% = \frac{W_2 - W_1}{W_1} \times 100\%$$

where X%-monomer conversion rate; W₂-drying to constant quality; W₁-sample quality; X₁-non volatile content; X₂-Monomer content.

The product was analyzed by VECTOR-22 infrared spectrometer with resolution of 4.0 cm⁻¹ and the average data of ten times test. ¹HNMR and ¹³CNMR spectra were measured on a Varian INOVA-400 NMR spectrometer with deuterated chloroform as the solvent. Gel permeation chromatography (GPC) was performed using THF as the eluent at a flow rate of 1 mL/min under 25 °C with a polystyrene standard as the reference. Glass transition temperature was determined by
Detla Series DSC7 under the protection of nitrogen with heating rate of 20 K/min. Static water/oil contact angle of the triblock copolymer film was measured on a telescopic goniometer (JC2000D3A). For each angle reported, at least ten sample readings from different surface locations were averaged.

3. Results and Discussion

3.1. The Optimization of Process of the PHFBMA-b-PDMS-b-PHFBMA

In the ATRP reaction, the choice of catalyst and ligand are very important because the solubility and activity of catalyst can be adjusted by forming a complex with ligand. Previous studies have suggested that using CuCl or CuBr as catalyst, 2,2 ′-bipyridine (BPY) or Schiff base as ligand can be very effective in catalyzing styrene and acrylate monomer polymerization [9-11], and amount of ligand would no longer affect polymerization rate when the number of complexing ligands is greater than 2 and [ligand]/[Cu²⁺]≥1 [12]. Therefore, the effects of different quality of catalysts and ligand on the reaction conversion rate and molecular weight distribution were investigated firstly with CuCl and CuBr as catalyst, with BPY and N-(2-pyrindinemthyl)-propylamine(PMPA) as ligand, the result was shown in figure 2a. Temperature and time were other important factors affecting the polymerization, the effects of temperature and time on the reaction conversion rate and molecular weight distribution were investigated too, and the results were shown in figures 2b and 2c.

As can be seen from figure 2a, catalyst was a major influence on ATRP. The monomer conversion rates of CuCl system were all bigger and distributions of molecular weight were smaller than that of CuBr system. It indicated that the rate of initiation was quick which was in favor of ATRP. While using CuCl as catalyst, with different ligands experimental results showed that the performance of PMPA+BPY ligand was better than PMPA and BPY, the conversion of polymerization increased rapidly with the increase of ligand just at ligand and catalyst ratio was less than or equal to 2:1 and they tended to be constant when its proportion was more than 2:1. This might be because PMPA and BPY composite ligand was easier to form coordination with catalyst which increased the solubility of the catalyst in the reaction system. The concentration of free radicals had always been to maintain a substantially constant for the reasons given above, they were the cause of the conversion rate increased and molecular weight distribution narrowed. So the copolymer was synthesized with CuCl as catalyst, with PMPA+BPY as ligand and [PMPA+BPY]/[CuCl]=2:1.

As show in figure 2b, the conversion rate was significantly increased when the temperature rises from 40 °C to 90°C, the increase extent decreased in 90 °C to 110°C. That was because in low temperature free radical formation rate slowed down, it caused the prolonged initiation process and the minor extent, molecular weight and distribution. And in higher temperature would help increase the number of the propagation and accelerate reaction rates, so as to improve the reaction degree of polymerization and molecular weight. However ATRP reaction is an equilibrium reversible reaction, increasing the temperature had a dual impact: as the heat increased the rate of the reaction increased too which was favorable to the reaction. On the other hand, because the polymerization reaction is
exothermic reaction, increasing the temperature could make equilibrium constants reduced which brought the reaction degree and molecular weight decreased. Overall however, when in a certain time the equilibrium constant was stable, the increase of conversion and molecular weight would slow, if the temperature was improved continually the side reaction might well intensify and the molecular weight distribution might become wider. So the optimal temperature was 90 °C.

As show in figure 2c, with the extension of time the conversion rate increased gradually, the molecular weight distribution became wider and the increase of the rate was small when the reaction time was more than 10 hours. It seemed likely that in longer reaction time the viscosity of the system increased gradually, the diffusion speed of monomer reduced and molecular movement stalled which caused the polymerization rate decreased. The molecular weight distribution became wider for the side reaction of chain transfer and chain termination in longer time. So the optimal reaction time was 10h.

3.2. The Preparation of the Different Molecular Weight with Different Fluorine Content PHFBMA-b-PDMS-b-PHFBMA

Under the optimum conditions, the prepared five different molecular weight Cl-PDMS-Cl were used as the raw materials and the different molecular weight PHFBMA-b-PDMS-b-PHFBMA were obtained. The results were show in table 1.

| Mn (macroinitiator) | Mn (GPC) | Mn (th) | M_w/M_n | Conversion rate | Yield (%) |
|---------------------|----------|---------|---------|----------------|-----------|
| 1950                | 7082     | 7156    | 1.12    | 90.5           | 95.1      |
| 2450                | 7601     | 7685    | 1.15    | 91.0           | 94.0      |
| 3635                | 8736     | 8824    | 1.14    | 90.2           | 94.5      |
| 5030                | 10160    | 10231   | 1.14    | 90.4           | 94.3      |
| 6901                | 12125    | 11945   | 1.15    | 90.8           | 93.3      |
| 11550               | 16657    | 16762   | 1.22    | 90.6           | 92.1      |

From the experimental results, though the molecular weight of macroinitiator was different, the yield and conversion rate of the product were very high in the optimum conditions and the theoretical results correlated well with experimental results.

4. Characterization of PHFBMA-b-PDMS-b-PHFBMA and Cl-PDMS-Cl

4.1. Infrared Spectroscopy (IR)

The IR of Cl-PDMS-Cl and PHFBMA-b-PDMS-b-PHFBMA were shown in figure 3.
Figure 3 shows that from Cl-PDMS-Cl to PHFBMA-b-PDMS-b-PHFBMA at 1740 cm\(^{-1}\) there was the carbonyl character peak develop from nothing to tender to stronger and no peak appear at 1640 cm\(^{-1}\) which was belong to C=C. At the same time, three peaks centered at 1283 cm\(^{-1}\), 1184 cm\(^{-1}\), 915 cm\(^{-1}\) corresponded to the -CF\(_3\) group, two peaks centered at 723 cm\(^{-1}\), 564 cm\(^{-1}\) belonged to -CF\(_2\)- and character peaks at 1165 cm\(^{-1}\) attributed to the C-H of Si-(CH\(_2\))\(_3\), at 1093 cm\(^{-1}\) caused by Si-O-Si and at 1260 cm\(^{-1}\), 840 cm\(^{-1}\), 798 cm\(^{-1}\) belonged to Si-CH\(_3\) remain. All of these indicate that PHFBMA-b-PDMS-b-PHFBMA was synthesized completely.

4.2. Nuclear Magnetic Resonance (NMR)
The raw material and product are characterized by NMR, figures 4a and 4b is the \(^1\)HNMR of Cl-PDMS-Cl and PHFBMA-b-PDMS-b-PHFBMA, figure 4c is the \(^{13}\)CNMR of PHFBMA-b-PDMS-b-PHFBMA.

In figure 4b, the chemical shift at 4.95ppm belonged to -CHF-, the other hydrogen atom chemical shift assignments were shown in figure 4b tagging. It also can be seen that the characteristic peaks of double bond hydrogen of CH\(_2\)=CCHCO does not appear. Likewise, \(^{13}\)CNMR in figure 4c there was no peak at 6.14 ppm which was attributed to the double bond carbon of CH\(_2\)=CCHCO, the chemical shifts at 116.54 ppm, 121.98 ppm, 119.45 ppm were caused by -CF\(_2\)-, -CHF-, -CF\(_3\) respectively and the other carbon atom chemical shift assignments were shown in figure 4c tagging. The above analysis showed that macromolecular initiator was reacted with HFBMA thoroughly and the desired product was obtained.

![Figure 4. NMR characterization.](image-url)
4.3. Gel Permeation Chromatography (GPC)
Figure 5 is the GPC of macroinitiator and fluorosilicone triblock copolymers. According to figure 5, the GPC of product was a single peak which indicates that the product was not a mixture of PHFBMA and PDMS homopolymer, because GPC curve should be more than one peak if there was a homopolymer formation. Combined with the characteristic of copolymer molecular weight and distribution, it could be confirmed that the ATRP active polymerization was achieved with Cl-PDMS-Cl as macroinitiator, and [PMPA+BPY] as catalyst.

4.4. Differential Scanning Calorimetry (DSC)
From the DSC in figure 6, it could be seen that there were two glass transition temperatures, the first was at -121.4 °C corresponding to PDMS and the second was at 51.8 °C which belong to PHFBMA. It indicates ulteriorly that the prepared copolymers were block polymers really.

Figure 5. GPC of Cl-PDMS-Cl and PHFBMA-b-PDMS-b-PHFBMA (sample: (HFBMA<sub>10</sub>DMS<sub>88</sub>HFBMA<sub>10</sub>)<sup>-</sup> Mn=11945, Mw/Mn=1.15, prepared from ClDMS<sub>88</sub>Cl, Mn=6901, Mw/Mn=1.13).

Figure 6. DSC of PHFBMA-b-PDMS-b-PHFBMA.

From IR, <sup>1</sup>HNMR, CNMR, GPC and DSC it could be concluded that the synthesized product by using Cl-PDMS-Cl as macroinitiator, HFBMA as monomer and CuCl and [PMPA+BPY] as catalyst
was fluorosilicone triblock copolymer.

5. Performance Evaluation
The PHFBMA-b-PDMS-b-PHFBMA triblock copolymers were expected to be materials with low surface energies. The triblock copolymer surface properties were also investigated through contact angle measurement, the results of water and oil contact angle were shown in figure 7, the effect of DMS and HFBMA block length on contact angles were shown in figure 8.

It could be seen from figure 8 that the water and oil contact angles toward the air-side surface of the copolymer films increased gradually with DMS block length. But when the DMS block length is above 88, the water and oil contact angles decreased. Similarly the water and oil contact angles rose with HFBMA block length. But when the HFBMA block length reaches to more than 20, the growth rate of water and oil contact angles changed little.

(a) Water contact angle  
(b) Oil contact angle

Figure 7. The triblock copolymer surface properties.

(a) The effect of DMS block length  
(b) The effect of HFBMA block length

Figure 8. The contact angle of different degree of polymerization of DMS and HFBMA.

Contact angle measurements strongly implied that the PHFBMA-b-PDMS-b-PHFBMA triblock copolymer films were hydrophobic and oleophobic.

6. Conclusions
PHFBMA-b-PDMS-b-PHFBMA triblock copolymers with designed structures were synthesized perfectly via ATRP. The optimum reaction conditions and polymerization kinetic data were studied in the work. The structure of sample was analyzed and characterized by method of IR, NMR, GPC and DSC, the results showed that the synthesized product by using Cl-PDMS-Cl as macroinitiator, HFBMA as monomer and CuCl and [PMPA+BPY] as catalyst was fluorosilicone triblock copolymers and the well-designed structure fluorosilicone triblock copolymers were obtained with narrow molar mass distributions. The effects of the fluorine and silicone content on the hydrophobic and oleophobic properties of prepared triblock copolymers were also investigated. The results showed that the
prepared triblock copolymers were hydrophobic and oleophobic.

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