# Synthesis and properties of gradient copolymers of butyl methacrylate and fluorinated acrylate via RAFT miniemulsion copolymerizations

Guangfa Zhang,[1] Qinghua Zhang,[1] Qiongyan Wang,[2] Xiaoli Zhan,[1] Fengqiu Chen[1]

[1]College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, People's Republic of China
[2]Research and Development Center, Zhejiang Sucon Silicone Co., Ltd., Shaoxing 312088, People's Republic of China
Correspondence to: Q. Zhang (E-mail: qhzhang@zju.edu.cn)

**ABSTRACT:** A series of gradient fluorinated copolymers with a broad variation of the monomer units in the polymer chain were synthesized via semibatch CPDB-mediated RAFT miniemulsion polymerization technique. In the presence of RAFT agent 2-cyanoprop-2-yl dithiobenzoate (CPDB), the copolymerization of BMA and FMA in miniemulsion exhibited typical features of a controlled molecular weights and narrow polydispersities. The macromolecular structure and thermal behavior of the synthesized fluorinated copolymers were investigated in detail. The DSC analyses show that the gradient copolymers showed a unique thermal behavior with broad range of transition temperature. It was also confirmed that the fluorinated gradient copolymer exhibited obvious surface segregation structure and ultra-low surface energy between 16.8 and 20.3 mN/m. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42936.

## INTRODUCTION

Precise control of the macromolecular structure and chemical composition distribution provides a great challenge for polymer chemists and engineers.[1] In the past decade, the outstanding contribution of controlled/living radical polymerization (CRP) has provided a novel approach to design polymers with tailored architecture under relatively mild reaction conditions.[2] RAFT is one of the most efficient CRP techniques based on reversible chain transfer through the dithioester functionality of the mediated agent and it makes possible to polymerize a wide variety of monomers.[3,4] Compared to operate in bulk/solution system,[5–7] heterogeneous emulsion polymerization remains the technique of choice in many industrial applications because of the advantages of compartmentalization, environmental concerns.[8,9] The current studies are intended to apply these techniques in aqueous dispersed systems. Miniemulsion is a dispersion of critically stabilized oil droplets with diameters of 50–500 nm prepared by shearing a system containing monomers, surfactants, initiators, water and a certain kind of costabilizer.[10] Polymerization in miniemulsion does not rely on monomer transport through the water phase, but droplet nucleation is the predominant initiation mechanism.[11] Due to its unique features, miniemulsion has been proven to be the most effective way to operate RAFT polymerization in aqueous system.[12–15]

Fluorinated polymers have attracted much attention due to their unique physical and chemical properties, such as high thermal stability, excellent mechanical properties, water and oil repellent properties and low dielectric constant, which originate from the enrichment of fluorine moieties at surface layers.[16,17] Therefore, fluoropolymers are used prevalently in the textile, functional coatings and microelectronic fields.[18–20] Some new omniphobic fluorinated materials were applied in self-cleaning coating and biological materials because of the special surface wettability performance.[21–24] Fluorinated acrylate with more than eight fluorinated carbon atoms (C8) is a perfect component to prepare functional polymer materials with super low surface energy because of the low surface molecular mobility.[25–27] Unfortunately, the long perfluoroalkyl chains have been confirmed to resist degradation and bioaccumulate in human and animal tissue.[28,29] More research presently has focused on developing environmentally friendly and nontoxic alternative fluorinated materials to replace the traditional perfluoroalkyl polymers. In our previous work, a series of novel monomers containing environmental friendly short perfluoroalkyl groups and their polymers with special surface performance have been studied.[25,28,30]
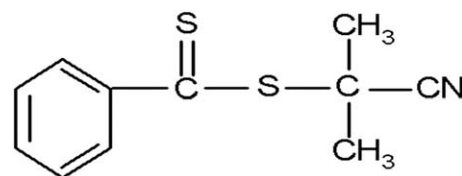
As is well known, performances of polymer materials not only rest with the monomer properties, but also rest with well-
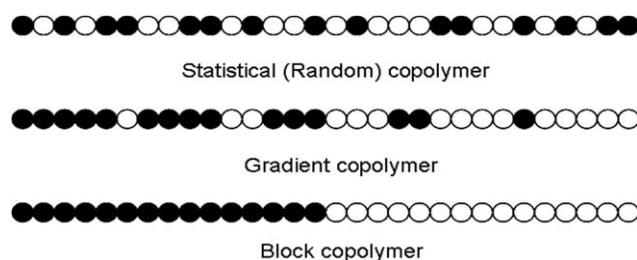
Scheme 1. Molecular structure of linear copolymer with various sequence distributions.



Scheme 2. Chemical structure of the RAFT agent CPDB.

defined microstructure and sequential composition of the macromolecule chains.[25,31,32] The special interface and surface properties of the fluorinated copolymer materials are heavily influenced by the multiscale structure and heterogeneous composition.[33–35] The advent of CRP techniques has given a new interest to development of advanced well-defined fluorinated copolymers with various architectures.[36,37]

Gradient copolymer is a novel class of polymers with a special molecular structure (Scheme 1), which exhibits a gradual change in composition from mostly one monomer to mostly another monomer along the copolymer chain backbone.[38] Such sequence distributions is very different from random and block copolymers. The molecular structure of random copolymers maintains a constant average composition along the polymer chain, and block copolymers abruptly change composition along the chain.[39,40] The gradual change in composition along the gradient copolymer chains results in less intrachain and interchain repulsion, and this should exhibit a much wider range of local environments, unique interfacial behavior and thermal properties, compared to random and diblock copolymers.[41,42] For this reason, gradient copolymers have been found to be a new effective compatibilizer for polymers blends.[43,44] In order to make a gradient copolymer with similar composition changes continuously from one end of the chain to the other, simultaneous initiation and uniform growth of all propagation chains are necessary in the polymerization process. The parallel growing of the chains in a CRP process cause a similar microstructure of all copolymer chains, so the CRP is an excellent method used to prepare gradient copolymers.[38,45–48] There are two types of typical gradient copolymers prepared by CRP. The first type can be called spontaneous gradient, which is prepared by a simultaneous copolymerization method based on the difference of the reactivity ratios between the comonomers.[49–51] The second type is tailored gradient most prepared by a semibatch technique, in which a monomer is continuously added into a polymerization mixture during the reaction process, and a majority of gradient copolymers have been made by this procedure.[38,52–55]

Gradient copolymers containing fluoropolymer segments would be particularly interesting and potentially useful, and it may be used as a compatibilizer facilitated mixing of fluoropolymers and non-fluoropolymers by modifying the interface between the two dissimilar polymers. Only few literatures reported the synthesis of fluorinated gradient copolymers so far.[56,57] In this study, copolymers of fluorinated acrylate with gradient composition along the macromolecular chains were synthesized by semibatch RAFT miniemulsion polymerization. And this CRP technique allows to control the molecular weight and to obtain gradient copolymers with various sequence distributions. The characters of P(BMA/FMA) gradient copolymers via semibatch polymerization by addition of a FMA to a reaction vessel containing the comonomers FMA and BMA were also demonstrated. Furthermore, the thermal behaviors, surface wettability associate with surface composition of the fluorinated copolymers were investigated in detail.

## EXPERIMENTAL

### Materials

Hexafluorobutyl Methacrylate (FMA, $M_n = 250$) purchased from Xeogia Fluorine-Silicone Chemical Co., Ltd. (Harbin, China) was purified by distillation under reduced pressure. Butyl methacrylate (BMA) was purified by vacuum distillation. Potassium persulfate (KPS, >99%), sodium dodecyl sulfate (SDS, surfactant), Octyl Phenol Polyethoxylate with 10 ethylene oxide units per molecules (OP-10, surfactant), and hexadecane (HD, costabilizer, Aldrich) were used as received without further purification. RAFT agent 2-cyanoprop-2-yl dithiobenzoate (CPDB) was synthesized and purified according to the literature,[58] and the structure of CPDB is shown in Scheme 2. Hydroquinone was used as received. HD and d-chloroform($CDCl_3$, 99.8%)were purchased from Aladdin and used as received. Deionized water (conductivity < 4 $\mu$s/cm) was used as received.

Table I. Preparation of Forced Gradient Copolymers by Semibatch RAFT Miniemulsion Copolymerization at 70°C

| Sample | Monomers in feeds (mol) | | Initial FMA molar fraction | Monomer fed in the second stage | Feed rate | Polymerization time (total) | Conv | $M_n$ | PDI |
|---|---|---|---|---|---|---|---|---|---|
| | FMA | BMA | | | | | | | |
| G1 | 0.005 | 0.050 | 9.1% | 0.020 mol(FMA) | 5 mmol/h | 4 h | 87 ± 2% | 25830 | 1.28 |
| G2 | 0.010 | 0.045 | 18.2% | 0.020 mol(FMA) | 6.mmol/h | 4 h | 91 ± 3% | 29120 | 1.24 |
| G3 | 0.015 | 0.045 | 25% | 0.020 mol(FMA) | 6 mmol/h | 4 h | 93 ± 2% | 31520 | 1.26 |

## Semibatch RAFT Miniemulsion Copolymerization

The tailored gradient copolymers of FMA and BMA were pre-
pared by semibatch RAFT miniemulsion copolymerization
according to the following procedure. The monomers BMA and
FMA were mixed with HD and the RAFT agent CPDB. The
mixture was then added to the aqueous phase [water, OP-10,
SDS 70:0.6:0.3 (wt/wt/wt)] under stirring. After 20 min, the
resultant emulsion was then homogenized by ultrasonication for
120 s with 60% amplitude; temperature was kept at 0°C to pre-
vent polymerization. The final miniemulsion was then moved
to a 100ml glass reactor equipped with a mechanical stirrer, a
thermometer and a reflux condenser. Before the reaction was
started, the reactor was purged with nitrogen for 60 min. KPS
was dissolved in 2 g water and added into the reactor when its
temperature reaches 70°C. Polymerization was carried out in a
nitrogen atmosphere. Simultaneously the monomer FMA was
continuously fed to the reactor according to a predetermined
rate via a syringe pump. Aliquots were periodically withdrawn
via a syringe to monitor monomer conversion by gravimetry
and composition by $^1$H-NMR. The polymerization conditions
and results are summarized in Table I.

## Characterization

Conversion of polymerization was determined gravimetrically
based on the samples taken during the process. Dried samples of
latexes were obtained from precipitation in ethanol. And the fil-
tered precipitate was washed several times with water and etha-
nol to remove emulsifiers and then dried in a vacuum oven at
50°C. Resulting product was dissolved in CDCl$_3$ and $^1$H-NMR
analysis was conducted on this solution with a Bruker 500-MHz
nuclear magnetic resonance spectrometer (Avance DMX500) at
room temperature. The compositions of the copolymers were
calculated from the characteristic proton integrals.

The molecular weight and PDI were measured using Waters
1525/2414 GPC (gel permeation chromatography) system con-
sisting of a Waters 1525 binary high-performance liquid chro-
matography pump, a Waters 717 plus autosampler, three Waters
Styragel columns (Styragel HR2, HR3, and HR4) and a Waters
2414 refractive-index detector. THF was used as the eluent with
a flow rate of 1.0 mL/min at 30°C.

Static contact angles were characterization of copolymers surface
property and measured by a CAM200 optical contact angle
meter (KSV Co., Ltd.). The static contact angles of water and
HD (each droplet volume was 2 $\mu$L) were measured. The sur-
face free energy was calculated from the static contact angles
following Owens and Wendt's equation as described in
literature.

X-ray photoelectron spectroscopy (XPS) spectra were recorded
with a VG ESCALAB MARK II spectrometer with a standard
Mg K$\alpha$ X-ray source (1253.6 eV) operating at 300W. The work-
ing pressure was $<10^{-7}$ Pa. Extended spectra (survey) were col-
lected in the range 0-1060eV (50 eV pass energy). Detailed
spectra were recorded for the following regions: C(1s), O(1s),
and F(1s) (50 eV pass energy). The standard deviation in the
BE values of the XPS line was 0.10 eV. To take into account
charging problems, the C(1s) peak was considered at 285.0 eV
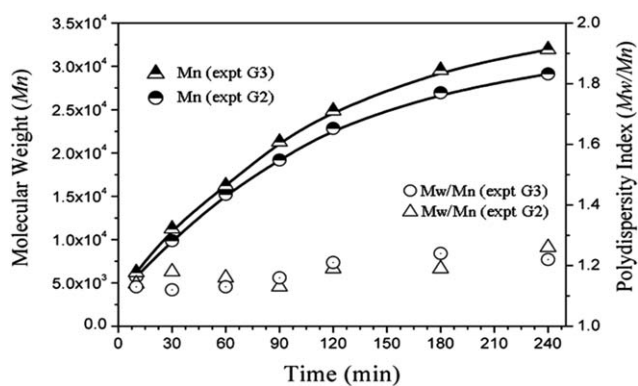and the peak BE differences were evaluated.



**Figure 1.** $M_n$ and polydispersities index as a function of reaction time
during gradient copolymerization of BMA and FMA (expt G2 and G3 in
Table I).

## RESULTS AND DISCUSSION

### Fluorinated Gradient Copolymers by Semibatch RAFT Miniemulsion Copolymerization

It is well accepted that the copolymer composition (CC) and
copolymer composition distribution (CCD) are the important
structure parameters for gradient copolymer.[38] Therefore, the
control of CC and CCD is of greatest importance. Actually,
there are two types of typical gradient copolymers including the
spontaneous gradient and forced gradient. The spontaneous gra-
dient is commonly prepared by a simultaneous copolymeriza-
tion method, and the composition of spontaneous gradient is
mainly controlled by the monomer compositions and reactivity
ratios of the comonomers. This method in practice is subject to
many restrictions. In contrast, the tailored (forced) gradient is
prepared by a semibatch technique, that is, a monomer is con-
tinuously added into the polymerization mixture during the
reaction process. A majority of gradient copolymers have been
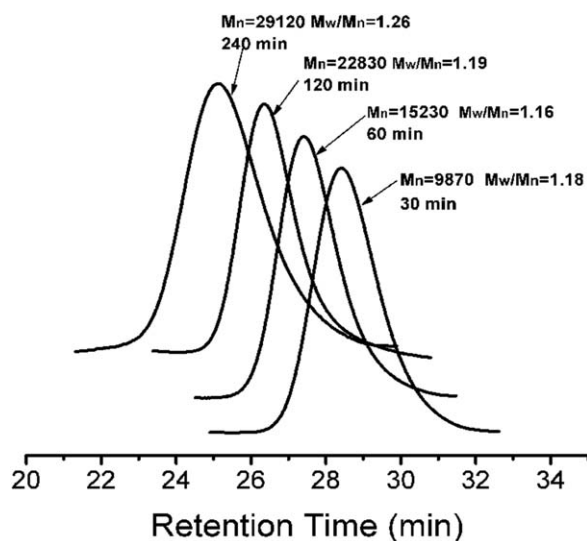made by this procedure.



**Figure 2.** Evolution of $M_n$ GPC traces for gradient copolymerization of
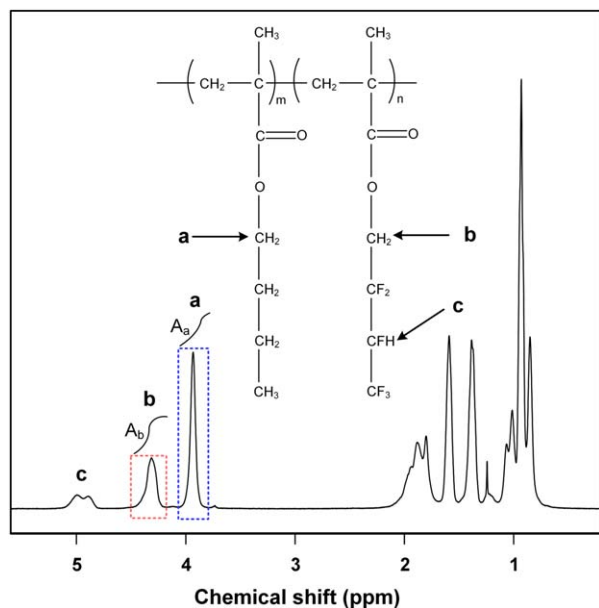BMA and FMA (expt G2 in Table I).

**Figure 3.** ^{1}H NMR spectrum of fluorinated gradient copolymer (G3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For tailored gradient copolymer, the CC is mainly regulated by the feeding rate/strategy. Basically, it has been reported that there are two types of feeding rate profiles. One type of feeding rate profiles can be calculated by the kinetic model that is trained from the batch copolymerization of the co-monomers.[52] The composition distributions commonly exactly as targeted design according to the composition control method of kinetic model. However, it would be a tedious and complex to obtain the kinetic model. Therefore, many researchers would like to control the gradient CC by a constant speed strategy since the operational feasibility and simplification. In this work, CPDB-mediated miniemulsion polymerization combined with semi-batch process of constant speed strategy was used to prepare the
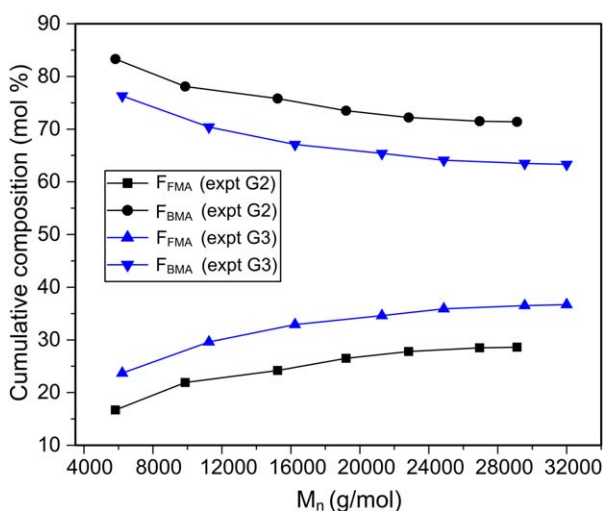


**Figure 4.** Cumulative molar composition plots of the gradient copolymers as a function of $M_n$ (expt G2 and G3 in Table I). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
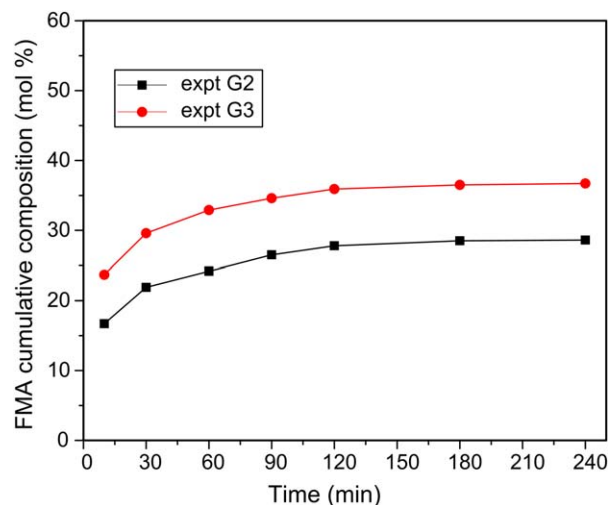


**Figure 5.** FMA cumulative mole fraction curves of the gradient copolymers as a function of reaction time (expt G2 and G3 in Table I). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

gradient copolymers that with a broad variation of the monomer units in the polymer chain. This process of polymerization is based on the semicontinuous addition of the monomer FMA during the copolymerization of FMA and BMA. The recipes and results of semibatch RAFT miniemulsion copolymerization of FMA and BMA are showed in Table I.

The gradient structure of the copolymers can be also characterized through the copolymerization kinetics. Figure 1 shows the evolution of molecular weight and polydispersity index of copolymer with time during the semibatch CPDB-mediated miniemulsion copolymerization. The copolymer molecular weights increased with time, and polydispersities stay below 1.3. In expt G2, the total conversion of the two monomers can reach $91 \pm 3\%$ in 4 h, and the resulting molecular weight gradually increased to 29,120 g/mol and a polydispersity of $M_w/M_n = 1.24$. The increase of $M_n$ with time and low polydispersity maintained throughout the reaction suggests that a controlled
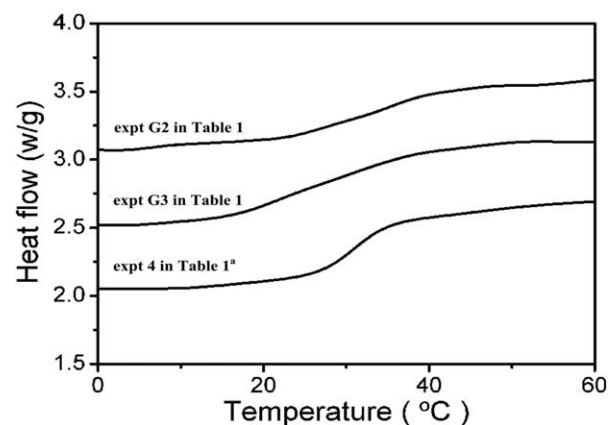


**Figure 6.** DSC heating curves for FMA/BMA copolymers with gradient and statistical composition distributions, a the DSC heating curve of statistical copolymer of FMA/BMA was included in our previous work.[59]
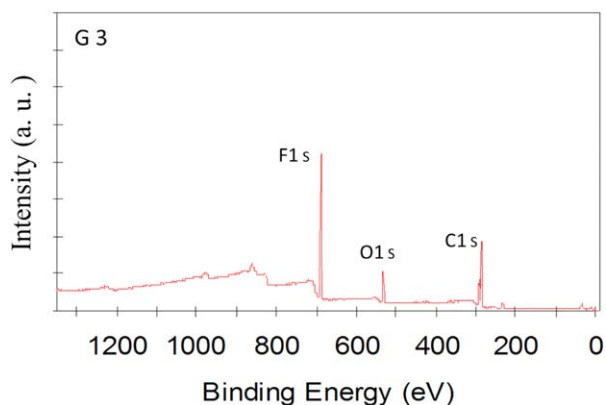
**Figure 7.** XPS survey spectrum of the fluorinated gradient copolymer (G3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymerization occurred under these semibatch conditions. GPC traces of samples taken with regular time intervals are shown in Figure 2 (expt G2). The GPC profiles of copolymer remained single modal distribution and smoothly to higher molecular weights with very low polydispersity (<1.3) during the polymerization. The low polydispersity index indicated a fast exchange between the growing and dormant polymer chains.

The chemical structure and $^1$H NMR spectrum of fluorinated gradient copolymer (take G3 as an example) is shown in Figure 3. The peak at 3.93 ppm was assigned to the proton of —OCH$_2$— in BMA, and the peak at 4.32 ppm represented the —OCH$_2$— group of FMA. The chemical shifts from 4.89 to 5.00 ppm were attributed to the proton of —CFH— in FMA. These results basically indicated that the fluorinated gradient copolymer has indeed been synthesized.

During the course of the experiment, samples were taken with regular time intervals. The corresponding copolymers were precipitated from the samples, which were used for the measurement of copolymerization kinetics and the composition evolution of gradient copolymers. The molar composition of fluorinated gradient copolymers can be calculated from the integral areas of corresponding —OCH$_2$— protons of BMA and FMA in the $^1$H NMR spectra discussed above. In this work, the cumulative compositions of FMA and BMA segments were exactly obtained from $^1$H NMR data analysis. As shown in Figure 3, $A_a$, $A_b$ were the integral areas of corresponding —OCH$_2$— protons in BMA and FMA segments, respectively. Consequently, the molar fractions of FMA (F$_{FMA}$) and BMA

(FBMA) in the gradient copolymers were determined according to the following equations:

$$F_{FM} = \frac{A_b}{A_b + A_a} \times 100\% \qquad (1)$$

$$F_{BMA} = (1 - F_{FMA}) \times 100\% \qquad (2)$$

The cumulative composition (FMA and BMA mole fraction) plots versus number-average molecular weight for CPDB-mediated gradient miniemulsion copolymerizations are shown in Figure 4 and the mole fraction of the comonomers were obtained by $^1$H-NMR analysis. Figure 4 shows an evidently increasing composition of the monomer FMA along the polymer chain from the initiator site to the end. At the same time, the comonomer BMA decreases sequentially along the polymer chain. In expt G2, for example, when the molecular weight reach 5820 g/mol at initial polymerization stage, the cumulative composition of copolymer is FMA/BMA=16.7/83.3 (mol %), then, the mole fraction of FMA in the copolymers increase with the increase of the molecular weight. As the molecular weight increase to 29120 g/mol in the end, the cumulative mole fraction of FMA increases from 16.7% to 28.6%. It is evident that the semibatch operation provided well controlled gradient copolymers. Besides, the evolution of FMA cumulative mole fractions in the gradient copolymers with reaction time is presented in the Figure 5. Take G2 for an example, it was observed that the FMA cumulative mole fractions remarkably increased from the initial polymerization stage to 120 min, and after 120 min, the FMA cumulative mole fractions slightly increased until reached a steady value. The change trend of FMA cumulative mole fractions with reaction time is well in agreement with the results presented in Figure 4. In summary, the gradient copolymers with a broad variation of the monomer units along the macromolecular chain can be prepared by semibatch polymerization with suitable conditions.

**Thermal Properties of Fluorinated Gradient Copolymers**
The gradual change in composition along the length of gradient copolymer chains can result in special thermal properties compared to random and blocks copolymers. A DSC measurement was performed to study the glass transition behaviors of the above gradient copolymers. Figure 6 shows the typical DSC heating curves of statistical copolymer and gradient copolymers. As shown in the graph, the statistical copolymer that was reported in our previous study exhibits a clear value of $T_g$ with a narrow range in 30–34°C.[59] In contrast, there were substantial differences in the temperature range with the gradient

**Table II.** The chemical atomic concentration of C, O and F in bulk and surface for the fluorinated gradient copolymers

| Copolymer films | C/% | | O/% | | F/% | |
|---|---|---|---|---|---|---|
| | Bulk[a] | Surface[b] | Bulk[a] | Surface[b] | Bulk[a] | Surface[b] |
| G1 | 69.66 ± 2.2 | 58.89 ± 1.8 | 23.22 ± 1.5 | 16.83 ± 1.2 | 7.12 ± 0.8 | 24.28 ± 1.4 |
| G2 | 65.03 ± 2.0 | 53.28 ± 2.2 | 21.67 ± 1.3 | 14.27 ± 1.5 | 13.30 ± 1.1 | 32.45 ± 1.5 |
| G3 | 61.94 ± 1.9 | 49.69 ± 2.0 | 20.64 ± 1.2 | 13.55 ± 1.4 | 17.42 ± 1.2 | 36.76 ± 1.3 |

[a] The theoretical composition of the gradient copolymer determined by $^1$H NMR.
[b] The surface composition of the gradient copolymer calculated by XPS.

**Table III.** Static contact angles and surface tension data for the fluorinated gradient copolymers

| Copolymers | FMA Content (mol %) | $\theta_{Water}$ (deg) | $\theta_{HD}$ (deg) | $\gamma_S$ (mN/m) | $\gamma_S^d$ (mN/m) | $\gamma_S^p$ (mN/m) |
|---|---|---|---|---|---|---|
| G1 | 9.1 | 98.5 ± 1.8 | 52.7 ± 1.6 | 20.3 ± 0.9 | 17.7 ± 0.5 | 2.5 ± 0.4 |
| G2 | 17.8 | 103.2 ± 2.1 | 56.3 ± 1.4 | 18.2 ± 0.8 | 16.6 ± 0.4 | 1.6 ± 0.3 |
| G3 | 24.6 | 106.4 ± 2.2 | 59.5 ± 1.7 | 16.8 ± 0.8 | 15.6 ± 0.5 | 1.2 ± 0.3 |

copolymers, which have very broad range of transition temperature. The $T_g$ values were extended to a range of temperature from 20°C to 50°C. It is difficult to estimate accurately the value of $T_g$ directly from the DSC heating curves, because the gradient copolymer exhibits a unusually broad nature of the $T_g$. And the broad $T_g$ is due to a smoothly variation of the incorporation of the comonomer units in the macromolecular structure. This nanoscale variation in the composition profile within the ordered gradient copolymer is responsible for the distinctively broad nature of the glass transition response of the gradient copolymers P(FMA/BMA.).

It is well known that the compatibility of the fluoropolymer and non-fluoropolymer is very weak, which is caused by the distinct polarities of this two dissimilar components. Meanwhile, the block copolymers can readily lead to self-assembled heterogeneous structure due to the mutual chemical incompatibility of different blocks. In other word, the block copolymers are usually subject to the strong intrachain repulsion. The composition profile of gradient copolymers was designed in a gradual change route along the chains so that the fluorinated gradient copolymers will result in less intrachain repulsion. Shiping Zhu et al, have reported that the gradient copolymers can combine the advantages of diblock copolymers and random copolymers to some extent and can show an excellent compatibility between the different polymers.[43] Moreover, Kim et al. have also reported that their synthesized gradient copolymers are effective as compatibilizers.[60] Consequently, in the present work, the resulting fluorinated gradient copolymer with tailored gradient composition profile may be expected to exhibit unique compatibility to the blend of fluoropolymers during melt processing.

**Surface Composition and Wettability of Fluorinated Gradient Copolymers**

To quantitatively analyze the surface chemical structure of the prepared gradient copolymers, XPS was exploited to examine the surface elemental compositions. As seen in Figure 7, for the XPS survey spectra of gradient copolymers G3 in Table II, it was showed the signals due to the elements constituting the repeat units: C(~294 eV), O(~532 eV) and F(~689 eV). In the XPS analysis, five random spots were tested on each sample and the reported data were the average of these five tests. The atomic composition data for the copolymer surface and the corresponding values calculated from the stoichiometric ratios of copolymer samples are summarized in Table II. It showed that the samples after annealing processes had reduced C and O concentration and a higher F contents, indicating a surface segregation of fluorinated groups with low surface energy. Take the

sample G1 in Table II as example, the carbon, oxygen and fluorine atomic percentage in bulk are about 69.66%, 23.22%, and 7.12%, while the corresponding surface atomic composition become 58.89%, 16.83%, and 24.28%, respectively. There is a higher ratio of fluorine to carbon in surface, indicating that the fluorocarbon molecule chains in gradient copolymers migrated to the surface and this enrichment of low surface energy groups should make the surface more hydrophobic.

Contact angles of liquid on the material surface are usually used to determine surface wetting performance. The static contact angles of water ($\theta_{water}$) and HD ($\theta_{HD}$) on the surface of fluorinated gradient copolymers tested by CAM 200 contact angle apparatus are described in Table III. According to the same methods reported in our previous work, the surface free energy $\gamma$ composed of dispersion component $\gamma^d$ and the polar component $\gamma^p$ could be calculated by Owensand Wendt equation. As presented in Table III, it was noticeable that all of the gradient copolymers showed very low surface free energy as 16.8~20.3 mN/m. The distinct low surface free energy in our case could be attributable to the enrichment of ─CF3 groups on the surface. The well-defined gradient structures of the fluorinated copolymers cause the obvious surface segregation of fluorinated groups, which promote the hydrophobicity of the copolymers.

## CONCLUSIONS

In this work, fluorinated gradient copolymers with a broad variation of the monomer units in the polymer chain were synthesized via a semibatch polymerization technique. The copolymers of BMA with FMA exhibited typical features of a controlled molecular weights and narrow polydispersities. The structure of gradient copolymers was confirmed by the variation of the accumulative fraction of the fluorinated monomer in copolymer chains. The result shows that the semibatch RAFT miniemulsion polymerization is an excellent method to design and prepare tailored gradient copolymers. The DSC analyses show that the gradient copolymers showed a unique thermal behavior with broad range of transition temperature. The prepared gradient copolymer exhibited obvious surface segregation structure with enrichment of fluorinated groups, which result in excellent hydrophobic property with low surface energy between 16.8 and 20.3 mN/m.

## REFERENCES

1. Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93.

2. Tasdelen, M. A.; Kahveci, M. U.; Yagci, Y. *Prog. Polym. Sci.* **2011**, *36*, 455.

3. Smith, A. E.; Xu, X.; McCormick, C. L. *Prog. Polym. Sci.* **2010**, *35*, 45.

4. Semsarilar, M.; Perrier, S. *Nat. Chem.* **2010**, *22*, 811.

5. Garnier, S.; Laschewsky, A. *Macromolecules* **2005**, *38*, 7580.

6. Shrivastava, S.; Matsuoka, H. *Langmuir* **2014**, *30*, 3957.

7. Sun, W.; He, X.; Liao, X.; Lin, S.; Huang, W.; Xie, M. *J. Appl. Polym. Sci.* **2013**, *130*, 2165.

8. Dan, M.; Huo, F.; Xiao, X.; Su, Y.; Zhang, W. *Macromolecules* **2014**, *47*, 1360.

9. Liu, G.; Qiu, Q.; Shen, W.; An, Z. *Macromolecules* **2011**, *44*, 5237.

10. Li, X.; Wang, W.; Weng, F.; Li, B.; Zhu, S. *Ind. Eng. Chem. Res.* **2014**, *53*, 7321.

11. Zhang, Q.; Zhan, X.; Chen, F. *J. Appl. Polym. Sci.* **2007**, *104*, 641.

12. Li, Z.; Chen, W.; Zhang, Z.; Zhang, L.; Cheng, Z.; Zhu, X. *Polym. Chem.* **2015**, *66*, 1937.

13. Zhan, X.; He, R.; Zhang, Q.; Chen, F. *RSC Adv.* **2014**, *44*, 51201.

14. Zhang, Q.; Wang, Q.; Luo, Z.; Zhan, X.; Chen, F. *Polym. Eng. Sci.* **2009**, *49*, 1818.

15. Qinghua, Z.; Xiaoli, Z.; Fengqiu, C.; Ying, S.; Qiongyan, W. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1585.

16. Signori, F.; Lazzari, M.; Castelvetro, V.; Chiantore, O. *Macromolecules* **2006**, *39*, 1749.

17. Iyengar, D. R.; Perutz, S. M.; Dai, C.; Ober, C. K.; Kramer, E. J. *Macromolecules* **1996**, *29*, 1229.

18. Hansen, N. M. L.; Jankova, K.; Hvilsted, S. *Eur. Polym. J.* **2007**, *43*, 255.

19. Malshe, V. C.; Sangaj, N. S. *Prog. Org. Coat.* **2005**, *53*, 207.

20. Rixens, B.; Severac, R.; Boutevin, B.; Lacroix-Desmazes, P. *Polymer* **2005**, *46*, 3579.

21. Sunny, S.; Vogel, N.; Howell, C.; Vu, T. L.; Aizenberg, J. *Adv. Funct. Mater.* **2014**, *24*, 6658.

22. Leslie, D. C.; Waterhouse, A.; Berthet, J. B.; Valentin, T. M.; Watters, A. L.; Jain, A.; Kim, P.; Hatton, B. D.; Nedder, A.; Donovan, K.; Super, E. H.; Howell, C.; Johnson, C. P.; Vu, T. L.; Bolgen, D. E.; Rifai, S.; Hansen, A. R.; Aizenberg, M.; Super, M.; Aizenberg, J.; Ingber, D. E. *Nat. Biotechnol.* **2014**, *32*, 1134.

23. Shiratori, S.; Okada, I. *Sci. Adv. Mater.* **2014**, *66*, 2406.

24. Vogel, N.; Belisle, R. A.; Hatton, B.; Wong, T.; Aizenberg, J. *Nat. Commun.* **2013**, *44*,

25. Zhang, Q.; Wang, Q.; Jiang, J.; Zhan, X.; Chen, F. *Langmuir* **2015**, *31*, 4752.

26. Matsunaga, M.; Suzuki, T.; Yamamoto, K.; Hasegawa, T. *Macromolecules* **2008**, *41*, 5780.

27. Fujimori, A.; Hayasaka, Y. *Macromolecules* **2008**, *41*, 7606.

28. Zhang, Q.; Wang, Q.; Zhan, X.; Chen, F. *Ind. Eng. Chem. Res.* **2014**, *53*, 8026.

29. Lindstrom, A. B.; Strynar, M. J.; Libelo, E. L. *Environ. Sci. Technol.* **2011**, *45*, 7954.

30. Wang, Q.; Zhang, Q.; Zhan, X.; Chen, F. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2584.

31. Nakatani, K.; Ogura, Y.; Koda, Y.; Terashima, T.; Sawamoto, M. *J. Am. Chem. Soc.* **2012**, *134*, 4373.

32. Badi, N.; Lutz, J. *Chem. Soc. Rev.* **2009**, *38*, 3383.

33. Zhao, X.; Chen, W.; Su, Y.; Zhu, W.; Peng, J.; Jiang, Z.; Kong, L.; Li, Y.; Liu, J. *J. Membr. Sci.* **2013**, *441*, 93.

34. Abrakhi, S.; Péralta, S.; Fichet, O.; Teyssié, D.; Cantin, S. *Langmuir* **2013**, *29*, 9499.

35. Chen, W.; Su, Y.; Peng, J.; Dong, Y.; Zhao, X.; Jiang, Z. *Adv. Funct. Mater.* **2011**, *21*, 1

36. Wang, H.; Zhou, H.; Chen, Y.; Zhang, C. *Colloid Polym. Sci.* **2014**, *292*, 2803.

37. Chen, J.; Li, J.; Luo, Z. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 1107.

38. Sun, X.; Luo, Y.; Wang, R.; Li, B.; Zhu, S. *AIChE J.* **2008**, *54*, 1073.

39. Phan, T. N. T.; Maiez-Tribut, S.; Pascault, J.; Bonnet, A.; Gerard, P.; Guerret, O.; Bertin, D. *Macromolecules* **2007**, *40*, 4516.

40. Vidts, K. R. M.; Dervaux, B.; Du Prez, F. E. *Polymer* **2006**, *47*, 6028.

41. Jiang, R.; Jin, Q.; Li, B.; Ding, D.; Wickham, R. A.; Shi, A. *Macromolecules* **2008**, *41*, 5457.

42. Jakubowski, W.; Juhari, A.; Best, A.; Koynov, K.; Pakula, T.; Matyjaszewski, K. *Polymer* **2008**, *49*, 1567.

43. Wang, R.; Li, W.; Luo, Y.; Li, B.; Shi, A.; Zhu, S. *Macromolecules* **2009**, *42*, 2275.

44. Kim, J.; Zhou, H.; Nguyen, S. T.; Torkelson, J. M. *Polymer* **2006**, *47*, 5799.

45. Guo, Y.; Zhang, J.; Xie, P.; Gao, X.; Luo, Y. *Polym. Chem.* **2014**, *55*, 3363.

46. Steinhauer, W.; Hoogenboom, R.; Keul, H.; Moeller, M. *Macromolecules* **2013**, *46*, 1447.

47. Chen, Y.; Zhang, Y.; Wang, Y.; Sun, C.; Zhang, C. *J. Appl. Polym. Sci.* **2013**, *127*, 1485.

48. Chen, Y.; Luo, W.; Wang, Y.; Sun, C.; Han, M.; Zhang, C. *J. Colloid. Interface Sci.* **2012**, *369*, 46.

49. Ritz, P.; Látalová, P.; Kříž, J.; Genzer, J.; Vlček, P. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1919.

50. Min, K.; Li, M.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3616.

51. Harrisson, S.; Ercole, F.; Muir, B. W. *Polym. Chem.* **2010**, *11*, 326.

52. Sun, X.; Luo, Y.; Wang, R.; Li, B.; Liu, B.; Zhu, S. *Macromolecules* **2007**, *40*, 849.

53. Min, K.; Kwon Oh, J.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1413.

54. Fu, C.; Yang, B.; Zhu, C.; Wang, S.; Zhang, Y.; Wei, Y.; Tao, L. *Polym. Chem.* **2013**, *44*, 5720.

55. Zhang, J.; Li, J.; Huang, L.; Liu, Z. *Polym. Chem.* **2013**, *44*, 4639.

56. Inoue, Y.; Watanabe, J.; Takai, M.; Yusa, S.; Ishihara, K. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6073.

57. Lobert, M.; Hoogenboom, R.; Fustin, C.; Gohy, J.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5859.

58. Le TPMG, R. E. T. S., WO, 9801478, **1998**.

59. Zhang, Q.; Zhan, X.; Chen, F. *Chem. J. Chin. Univ.* **2009**, *30*, 427.

60. Kim, J.; Mok, M. M.; Sandoval, R. W.; Woo, D. J.; Torkelson, J. M. *Macromolecules* **2006**, *39*, 6152.