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Novel Tri-Block Copolymer of Poly (acrylic acid)-*b*-poly (2,2,3,3,4,4,4-hexafluorobutyl acrylate)-*b*-poly (acrylic acid) Prepared via Two-Step RAFT Emulsion Polymerization

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A facile method for preparing ABA tri-block functional elastomer via two-step RAFT emulsion polymerization is introduced in this work. Poly (acrylic acid)-*b*-poly (2,2,3,3,4,4,4-hexafluorobutyl acrylate)-*b*-poly (acrylic acid) (PAA-*b*-PHFBA-*b*-PAA) tri-block copolymers were synthesised and the transparent films were obtained by directly casting the synthesized latexes. Water contact angle (WCA) of the as-prepared films was dramatically improved after heat treatment at 120°C for 4h. And the films were changed from hydrophilicity to hydrophobicity. By using atomic force microscope (AFM) and X-ray photoelectron spectroscopy (XPS), the film surface structure was investigated in this work, to illustrate the mechanism of surface property variation of the films in heat treatment. Moreover, the synthesized tri-block copolymers behave as an elastomer material with a high elongation at break around 1200% and the permanent deformation below 25%.

Since reported by Rizzardo et al[1,2] in 1998, reversible addition fragmentation chain transfer (RAFT) free-radical polymerization has been fascinating researchers all over the world. However, RAFT technology has not been commercialized extensively up to now. Many researchers have tried to promote the commercialization of RAFT technology through reducing its cost, among which RAFT emulsion polymerization is considered as the most attractive one. Gilbert and co-workers have done a lot of studies[3] on emulsion RAFT polymerization, especially on theory model of emulsion RAFT polymerization.[4] The research results of Luo et al have been recognized as Luo-Tsavalas-Schork 'super swelling' theory on improving stability and molecular weight distribution on emulsion RAFT polymerization.[5] Charleux and co-workers discovered amphiphilic copolymer could form core-shell particle that could stabilize conventional ab initio emulsion polymerization, which was called polymerization induced self-assembly (PISA) method.[6] Hawkett 's team also conducted a series studies based on Charleux 's work.[7] It has been recognized that well-controlled polymerization can be conducted via PISA method with a high polymerization rate.[8, 9] As one of promising products derived from controlled/living radical polymerization (CLRP), novel thermoplastic elastomer (TPE) materials, especially ABA tri-block copolymers could be synthesized via RAFT emulsion polymerization has been interested by several groups.[10,11] For instance, the first work to synthesize triblock copolymer TPE via RAFT emulsion polymerization was conducted by Luo 's group.[12] Meanwhile, because of excellent properties, RAFT polymerization of fluorinated polymers are also interested by many researchers in recent years.[13, 14, 15] Therefore, we try to utilize double R-groups RAFT agent in emulsion RAFT polymerization as a facile route for ABA triblock copolymer. A fluoride elastomer was synthesized and analysed.

In our previous works,[16, 17] the amphiphilic di-block copolymers with well controlled molecular structure have been synthesized via RAFT emulsion polymerization, in which the reaction rate is almost equivalent to the traditional emulsion polymerization. And the copolymers with high fluorinated monomer content were successfully synthesized via a two-step synthesis protocol in a surfactant free emulsion system. For example, the poly (methacrylic acid)-*b*-poly (2,2,2-trifluoroethyl methacrylate) di-block copolymers were prepared by the newly developed surfactant free process of RAFT emulsion.

In this work, a facile method for preparing ABA tri-block functional elastomer via two-step RAFT emulsion polymerization was developed as sketched in Scheme 1. First,

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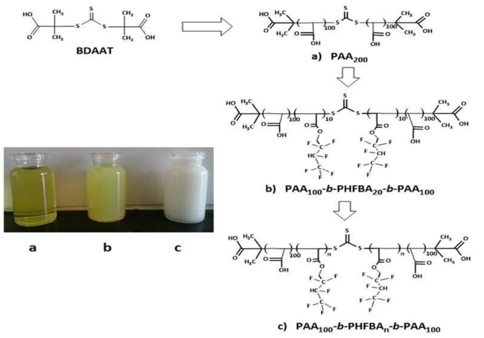
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See a macromolecular chain transfer agent (Macro-RAFT) of PAA_{200} (^1H NMR Spectrum is shown in Fig. S1) was synthesized in 1,4-dioxane by using self-synthesized RAFT agent of S, S'-bis (R, R'-dimethyl-R''-acetic acid) trithiocarbonate (BDAAT, ^1H NMR Spectrum is shown in Fig. S2)[18]. The Macro-RAFT of PAA_{100}-$PHFBA_{20}$-$PAA_{100}$was subsequently synthesized by adding the HFBA monomer into the reactor. Finally, three ABA tri-block copolymers, poly (acrylic acid)-*b*-poly (2,2,3,3,4,4,4-hexafluorobutyl acrylate)-*b*-poly (acrylic acid) (PAA-*b*-PHFBA-*b*-PAA) with various fluoride monomer content, were prepared. The detailed experimental procedures were described in Supporting Information.



Scheme. 1 Synthesis route of PAA-*b*-PHFBA-*b*-PAA tri-block copolymers via two-step emulsion polymerization.

It can be found in Table 1 that the Macro-RAFT of PAA_{100}-$PHFBA_{20}$-PAA_{100} has a narrow molecule weight distribution (PDI = 1.16) and PDI values of the three PAA-*b*-PHFBA-*b*-PAA tri-block copolymers are also relatively narrow (PDI < 1.5). That is to say, the new polymerization process developed by us was carried out under a living free-radical polymerization mechanism.[12,19,20] However, it is not a typical emulsion polymerization because a large amount of dioxane from the macro-RAFT agent was involved. Although dioxane can low polymerization rate, it can also improve the solubility of monomers, which is beneficial to the diffusion of HFBA monomer.

It is well known that narrow molecular weight distribution is good for the application of polymers as transparent material, such as transparent film.[12, 21, 22] Therefore, transparent film could be prepared easily via living free radical polymerization. It is interesting to confirm whether the synthesized PAA-*b*-PHFBA-*b*-PAA tri-block copolymers with relative narrow molecule weight distribution can form a transparent film.[23,24] As expected, the transparent films can be easily obtained by casting the synthesized PAA-*b*-PHFBA-*b*-PAA latexes at room temperature. And a typical film of Sample C with thickness of 1.5 mm is displayed in Fig. 1. The film is so clear that it is hardly to be seen when it was put on a picture. Similar to film, the newly developed PAA-*b*-PHFBA-*b*-PAA tri-block copolymers could be processed to be transparent tubes as well.

Due to the simultaneous existence of hydrophilic PAA block and hydrophobic PHFBA block in the synthesized copolymers, it is expected that hydrophilicity of the PAA-*b*-PHFBA-*b*-PAAfilm surface can be transferred under some conditions. Analysis of the hydrophilic property of film surface was performed by water contact angle(WCA) technique. The typical WCA images of Sample C before and after heat treatment at 120°C for 4h (Fig. 2) suggest the obviously improved WCA from 50° to 125°, revealing that the variation of film surface property from hydrophilicity to hydrophobicity can be induced by heat treatment. Actually, hydrophilicity of the film surface is caused by core-shell sphere morphology of the synthesized PAA-*b*-PHFBA-*b*-PAA copolymer via self-assembly effect in water, in which the hydrophilic PAA block and hydrophobic PHFBA block consist of the shell and the core, respectively[24,25]. During film formation process at room temperature, the PAA block with hydrophilic carboxylate groups was driven onto the film surface with water evaporation.[26,27,28]

Table. 1 GPC results of Macro-RAFT and ABA tri-block copolymers (GPC curves were shown in Fig. S3)

Samples[1]	Convn[2] (%)	$M_{n,\ theo}$[3] (g/mol)	$M_{n,\ exp}$[4] (g/mol)	PDI[5]
Macro-RAFT PAA_{100}-$PHFBA_{20}$-PAA_{100}	82.29%	19120	16528	1.16
S-A PAA_{100}-$PHFBA_{300}$-PAA_{100}	81.73%	85200	91200	1.33
S-B[6] PAA_{100}-$PHFBA_{400}$-PAA_{100}	88.34%	108800	113374	1.45
S-C[7] PAA_{100}-$PHFBA_{600}$-PAA_{100}	67.52%	156000	140080	1.44

1. The subscript indicates the designed numbers of monomer; 2. Convn: monomer conversion; 3. $M_{n,theo}$: designed number-average molecular weight; 4. $M_{n,\ exp}$: experimental result of number-average molecular weight; 5.PDI: experimental result of the polydispersity index(Mw/Mn); 6. 1H NMR Spectrum and transmission FTIR spectrum were shown in Fig. S4 and S5; 7. The absorbance ATR spectrum of Sample C and Sample A was shown in Fig. S6

Fig. 1 Transparent film casted directly from latex of Sample C.

How to make a hydrophobic film using the synthesized tri-block copolymer? First, the effect of hydrophobic monomer (HFBA) content is investigated. However, it is found in Fig. 3 that the content of HFBA monomer from 60 to 75 wt.% shows only weak contribution on the improvement of WCA (from 34° to 50°). It is indicated that the PAA block could be remained as matrix phase on the surface of the film, even though the content of HFBA monomer is increased to 75wt%. After heat treatment, WCA values of Sample A, Sample B, and Sample C (Fig. 3) are noticeably improved to 83°, 101°, and 125°, respectively. Theoretically, the PAA block should be the dispersed phase, if the film is at an equilibrium state and the

HFBA monomer content is much higher than the AA monomer.[29]Therefore, it is natural that WCA of the films is dramatically increased. According to the WCA results, it can be concluded that heat treatment is able to prompt the films to regain the phase equilibrium state of PHFBA as matrix phase from the un-equilibrium state of PAA as matrix phase.

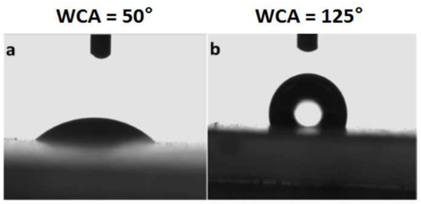


Fig. 2 WCA Photograph of Sample C film before (a) and after (b) heat treatment.

Fig. 3 WCA values before and after heat treatment of material with different content of HFBA.

In order to prove the above conclusion, AFM was used to explore the variation of surface morphology on the Sample C film before and after heat treatment. The AFM images before and after heat treatment of the Sample C film are shown in Fig.4 (a) and (b), respectively. The size of Nano-scale worm-like PAA, which is the feature of fluorine-containing polymer[30,31,32], on latex film surface was found contracted obviously after heat treatment. Comparing Fig.4 (a) and (b), it is also not difficult to find that hydrophilic PAA-rich phase (bright yellow region) reduced a lot, hydrophobic PHFBA-rich phase increased a lot after heat treatment. Therefore, the film of PAA-*b*-PHFBA-*b*-PAA tri-block copolymer could change from hydrophilic to hydrophobic[33] after heat treatment. To confirm the result of AFM, XPS was also used to measure the composition change of Sample C film surface. Considering the different in element content of PAA and PHFBA, relative amount of O and F on film surface before and after heat treatment was measured. It is clearly seen in Fig. 5that the O content was decreased while F content increased obviously after heat treatment. The XPS results perfectly confirmed the morphology change of tri-block copolymer film obtained from AFM during heat treatment. Now we can conclude that heat treatment made the film of tri-block copolymer into phase equilibrium state from PAA as matrix phase to PHFBA as matrix phase. Thus, hydrophilic film of PAA-*b*-PHFBA-*b*-PAA tri-block copolymer could change to hydrophobic after heat treatment.

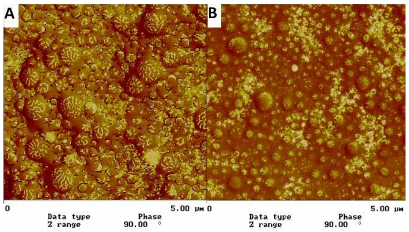


Fig. 4 AFM images of Sample C film before (A) and after (B) heat treatment.

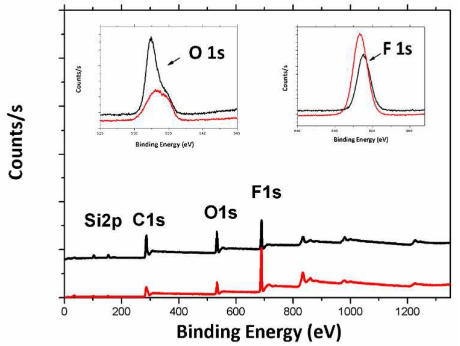


Fig. 5 XPS full-scan spectra of PAA-*b*-PHFBA-*b*-PAA tri-block copolymer film before (black line) and after (red line) heat treatment

Finally, the mechanical property of the PAA-PHFBA-PAA film was measured and the stress-strain curves are displayed in Fig. 6. For the comparison, the di-block copolymer of PAA_{200}-$PHFBA_{400}$ was synthesized, according to our previous work, whose mechanical property was also measured as show in Fig. 6 (black line). The di-block copolymer shows a brittle rupture, and the elongation at break is only 100%. However, all the synthesized tri-block copolymers in this work behave as an elastomer-like mechanical property with a large elongation at break. Meanwhile, the PAA-PHFBA-PAA tri-block copolymers are very soft materials with Shore-hardness (A) of 92, 45 and 24 for Sample A, B and C, respectively. They also have very large ultimate elongation and small permanent set. For example, the very soft Sample C with Shore-hardness A of 24 has permanent set of 25% only while its elongation at break is about 1200%. It means that more than 98% deformation could be recovered when the film was elongated until break. It indirectly indicates that all samples prepared by the newly developed two-step RAFT emulsion polymerization introduced in this paper are really tri-block copolymers.[34,35]

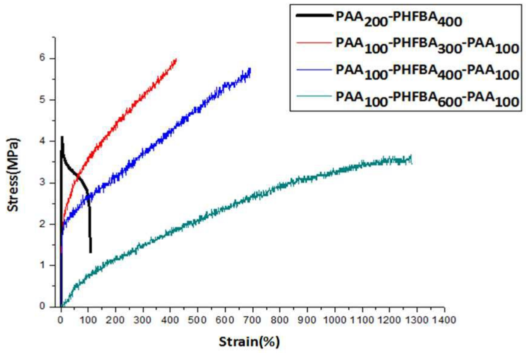


Fig. 6 Stress-strain curves of PAA_{200}-$PHFBA_{400}$di-block copolymer film and PAA-PHFBA-PAA tri-block copolymers films with different PHFBA block length.

However, tensile test cannot be used as a direct evidence for the symmetric structure of our block copolymer. Therefore, GPC results were also used as a direct evidence for molecule structure. In consideration of C-S bond is assumed in the middle of the copolymer, polymer with half molecule weight could be observed once the C-S bond is broken. It is known that solvent contained oxidizing species, such as tetrahydrofuran (THF) could lead to C-S bond breaking.[36] Hence, the copolymer was dissolved in THF and stir for different time at 60℃ to break the bond. The GPC results of Macro-RAFT are shown in Fig7.

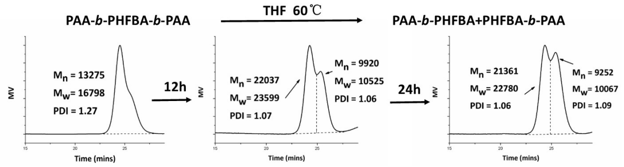


Fig. 7 GPC trace results of Macro-RAFT in THF.

Obviously, the second peak is growing up with time, and the molecule weight of degraded polymer related to the second peak happened to be half of our tri-block copolymer; therefore, the symmetric structure of our tri-block copolymer can be proved by the GPC results.

In summary, we have synthesized a novel fluoride functional tri-block copolymer of PAA-*b*-PHFBA-*b*-PAA via a newly developed two-step RAFT emulsion polymerization, which is carried out in an emulsifier-free system. The transparent film can be easily prepared by directly casting the copolymer latex at room temperature. And the film exhibits an excellent mechanical property as elastomeric material. The elongation at break is about 1200%, and the permanent set in only 25%. Adjusting the PAA/PHFBA ratio and heat treatment could control films with hydrophilic or hydrophobic surface. The novel polymers developed in this study are of great potential applications, such as transparent and elastomeric tubes in the area of medical treatments and daily uses.[37]Thenewly developed facile method of two-step RAFT emulsion polymerization could be leveraged to prepare other block polymers with different topological structure.

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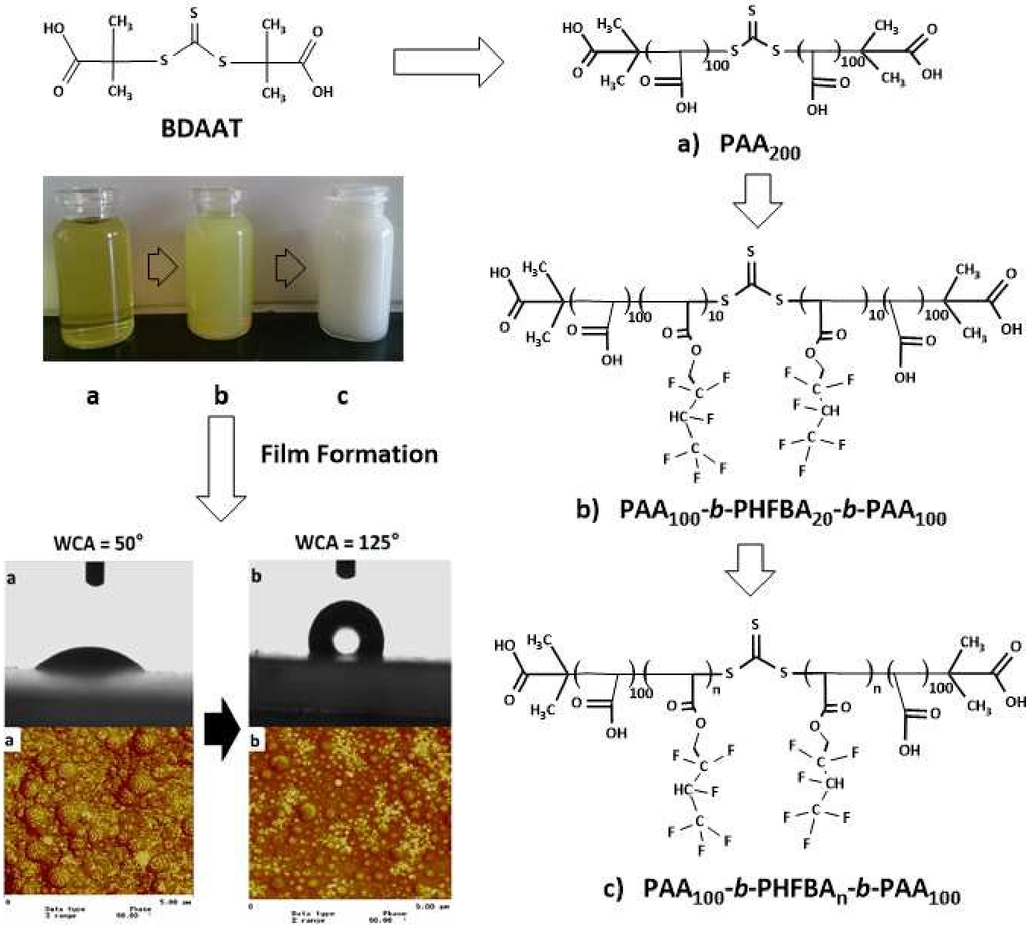
BDAAT
a) PAA200
b) PAA100-b-PHFBA20-b-PAA100
c) PAA100-b-PHFBAn-b-PAA100
a
b
c
Film Formation
WCA = 50°
WCA = 125°