

Synthesis and Characterization of Butyl Acrylate-based Graft Polymers with Thermo-responsive Branching Sites *via* the Diels-Alder Reaction of Furan/Maleimide

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Abstract Thermo-responsive butyl acrylate/furfuryl methacrylate copolymer-based (PBF backbone) graft (co)polymers with dynamic covalent linkages between their backbones and side chains *via* the Diels-Alder reaction of furan/maleimide were synthesized. Atom transfer radical polymerization (ATRP) was used to synthesize graft copolymers with thermo-responsive transformation from graft copolymers to linear polymers with bimodal or wide MWD. The NMR measurements indicated that the Diels-Alder reaction and retro-Diels-Alder reaction occurred, depending on the change of the temperature, meaning that the side chains could be cleaved and reformed according to the variation of the temperature. GPC measurements demonstrated that the molecular weights of the polymers were thermo-responsive. Furthermore, three graft copolymers with various branching chains (PBF-*g*-PBA, PBF-*g*-P(BMA-*co*-MA) and PBF-*g*-PBMA) were compared to study the influence of compatibility between the backbone and the branching chain on the efficiency of Diels-Alder reaction after the cleavage of the DA linkage. The results showed that the ability of the side chains to come back to the main chain was strongly affected by the compatibility between the backbone and the side chains and the flexibility of the polymer chains.

Keywords Thermo-responsive; Furan/maleimide; ATRP; Diels-Alder; Acrylate

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INTRODUCTION

One of the most fascinating features of all living organisms is the ability to respond to external stimuli, which inspires the reasonable design of synthetic responsive polymers named as “smart polymers” that can respond to environmental stimulus (temperature, light, pH, catalyst and so on)^[1–7]. The ability of polymers to change their structures reversibly in response to external stimuli makes them capable of changing their physical/chemical properties in controllable and predictable fashion. These “smart materials” find various applications such as responsive coatings^[8], self-healing materials^[9, 10], and shape-memory materials^[4], malleable polymers^[11], reprocessible materials^[12], and erasable memories^[13].

The common method to provide a stimulus response is the introduction of specific chemical units into the materials at the molecular level^[14]. The macroscopic properties of the materials, such as mechanical strength and processability, can be adjusted by stimulus disrupting or altering of these responsive chemical units incorporated in them. Currently,

the responsiveness typically relies on the non-covalent interactions such as hydrogen-bonds^[15], metal-ligand complexation^[16] and host-guest interactions^[17]. However, the use of non-covalent reversible linkage in “smart polymers” is often limited because of their weak mechanical properties in spite of their promising responsiveness.

Reversible covalent linkages (also called as “dynamic covalent bond”) have more advantages than reversible non-covalent linkages in terms of their higher stability and higher strength, which include thermally reversible alkoxyamines^[18], photo-reversible dimerization of anthracene^[19], thermo-reversible Diels-Alder (DA) reaction^[20], reshuffling of trithiocarbonate units^[21], thermo-reversible imine chemistry^[22, 23], transesterification^[4, 12, 24] and olefin metathesis reaction^[11, 25]. Among them, thermo-reversible Diels-Alder reaction, as one kind of the “click reactions”, is a very versatile, efficient, and environment-friendly process. They can proceed under relatively mild conditions without any catalyst and have high selectivity and extraordinary tolerance towards functional groups^[26]; as a result, this kind of reaction has been utilized in many applications^[26–28]. One of the most studied examples of DA reaction is the reaction between furan and maleimide^[29]. It is an excellent candidate for the application in polymers as it has appropriate coupling (ranging from room temperature to

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80 °C) and decoupling (above 110 °C) temperatures; more importantly, this reaction does not liberate any small molecules^[29]. Besides that, the furan derivatives come from cellulose and hemicellulose, which are abundant in nature because they are important components of plants^[30, 31]. The furan/maleimide Diels-Alder linkage has been extensively used in reversible crosslinking polymers^[32], self-healing/remendable polymers^[33], polymer composites^[34], surface functionalization^[35], and polymer synthesis^[36]. The introduction of thermal-reversible Diels-Alder reaction of furan/maleimide can alter the properties of the polymers *via* simple thermal treatment without needing the external stimuli during operation^[37].

Most of the studies on the “smart polymers” have focused on the macroscopic properties such as self-healing rather than the microscopic structure changes, although the macroscopic properties originate from the reorganization or rearrangement of the microscopic structure. Recently, the reversible releasing of arms from star-like polymers utilizing the DA reaction of furan/maleimide has been studied by Urban *et al.*^[38], in which the covalent reversibility of the DA and retro-DA (rDA) process lasted up to 7 cycles, although this was only demonstrated on a small molecule scale. Syrett *et al.*^[39] synthesized poly(methyl methacrylate) with furan/maleimide thermal-reversible linkage in the middle of the molecular chain *via* atom transfer radical polymerization (ATRP) and studied its reversibility. The efficiency of 50% reformation of the DA linkage was achieved after a reheating cycle.

As we know, polymers with high molecular weight (MW) will show good performance, such as mechanical properties, but these polymers always show poor processing properties due to high melt viscosity resulting from high MW. This means that an ideal polymer should have a low MW or bimodal MW distribution in the processing stage and has high MW in the service stage. In this report, we synthesized butyl acrylate/furfuryl methacrylate copolymer-based (PBF backbone) graft (co)polymers with furan/maleimide thermo-reversible linkage between their backbones and side chains. It is expected, when the temperature rises, that the MW and MW distribution can be changed from high MW and single distribution to low MW and bimodal or broad distribution through the cleavage of thermo-reversible linkage. As a result, the graft copolymers can satisfy the “smart” requirement in the stages of processing and service. The reversibility of the synthesized samples was studied by thermo-treatment at different temperatures. The GPC and NMR measurements were used to monitor the change in the molecular weight of the graft polymer and chemical linkage with the temperature. The results showed that the reformation efficiency of DA linkage strongly depended on the miscibility between the backbone component and side chain component and the flexibility of polymer chains.

EXPERIMENTAL

General Considerations

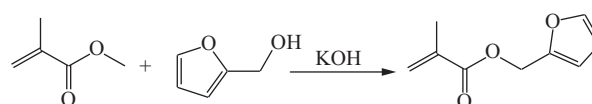
All moisture/oxygen sensitive reactions were performed using standard glove box under N₂. Furan was purchased

from the TCI and used as received, CuBr, 2,2'-bipyridyl-1,2-bromoisobutyryl bromide, *N,N,N',N'',N'''*-pentamethyldiethylene-triamine (PMDETA) and ethyl 2-bromoisobutyrate (EBIB) were purchased from Aldrich and used as received. Furfuryl alcohol, *n*-butyl methacrylate (BMA), *n*-butyl acrylate (BA), methyl acrylate (MA) and ethanolamine were commercially available reagents in chemically pure grade and vacuum distilled before used. The other commercially available reagents used in this work were in chemically pure grade and used as received unless mentioned otherwise.

NMR spectra were performed on a Bruker AV300 (400) spectrometer by using CDCl₃ as a solvent. Molecular weights (MW) and molecular weight distribution (MWD) were determined by gel permeation chromatography (GPC) on TOSOH HLC 8220 GPC at 40 °C using THF as an eluent against linear polystyrene standards. Differential scanning calorimetry (DSC, Perkin-Elmer 7 DSC instrument) was carried out in the range from –50 °C to 180 °C at a heating rate of 10 °C/min and then cooled down to –50 °C at a cooling rate of 10 °C/min under nitrogen atmosphere.

Synthesis of Furfuryl Methacrylate (FMA)

The furfuryl methacrylate was synthesized by transesterification of furfuryl alcohol and the methyl methacrylate (Scheme 1). Methyl methacrylate (120 mL, 1.13 mol), potassium hydroxide (7.2 g, 0.13 mol), furfuryl alcohol (55 mL, 0.63 mol), cyclohexane (280 mL) were put into a three-neck round-bottom flask equipped with a stir bar. Then it was heated to 110 °C, and the methanol generated was separated by a water separator. The reflux was continued for 12 h, then the flask was cooled and the mixture was poured into 300 mL of distilled water. The organic phase was collected by a separatory funnel, then washed with distilled water for three times. After that the mixture was dried with magnesium sulfate and condensed by rotary evaporator to give the crude products. The crude products were then distilled under reduced pressure, and the FMA was collected as colorless oily liquid.



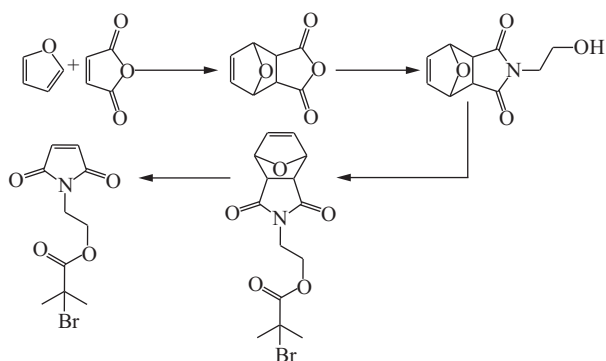
Scheme 1 Synthesis of the furfuryl methacrylate (FMA)

Synthesis of *N*-(2-(2-bromoisobutyryloxy) ethyl) Maleimide (BiBEMI)

The synthesis of *N*-[2-(2-bromoisobutyryloxy) ethyl] maleimide (BiBEMI) was according to Chen's work (Scheme 2)^[40].

Copolymerization of *n*-Butyl Acrylate (BA) and Furfuryl Methacrylate (FMA)

The copolymerization of BA and FMA was carried out under nitrogen atmosphere (Scheme 3). BA (50.0 mL, 347.28 mmol), FMA (3.4 mL, 22.17 mmol) and toluene (50 mL) were taken into a round bottom flask equipped with a stir bar, then CuBr (26.1 mg, 0.18 mmol) and PMDETA (0.18 mmol) (mixed together in 1 mL of toluene before added) were added to it. The polymerization was started by adding the initiator EBIB



Scheme 2 Synthesis of *N*-(2-(2-bromoisobutyryloxy) ethyl) maleimide (BiBEMI)

(0.25 mmol). The reaction was continued for 48 h in 80 °C oil bath. After polymerization the solution was diluted by methane chloride and passed through a short column of neutral alumina oxide to remove the catalyst. The obtained product P(BA-*co*-FMA) (PBF, for short) was precipitated by cold methanol and dried at 40 °C in vacuum.

Preparation of the Macromolecular Initiator

The macromolecular initiator was prepared by Diels-Alder reaction of PBF and BiBEMI (Scheme 3). The reaction was carried out as follows. PBF (12.14 g, containing furan group 5.50 mmol) and BiBEMI (3.21 g, 10.05 mmol) were dissolved by toluene in a two necked round bottom flask equipped with a water condenser and a stir bar. The oxygen was removed from the solution by passing nitrogen through the flask. The reaction was performed at 60 °C for 24 h under nitrogen atmosphere, and then the mixture was poured into cold methanol to precipitate the product. The crude product was dissolved-precipitated for three times to remove the BiBEMI. Finally the purified product (PBF-Br) was dried at 40 °C under vacuum.

Preparation of the Thermo-reversible Graft (Co)Polymers

The thermo-reversible graft (co)polymers were synthesized by “graft from” method (Scheme 3). Under nitrogen

atmosphere, the macromolecular initiator and CuBr were dissolved in the monomers. After the complete dissolve of macromolecular initiator, 2,2'-bipyridyl was added into the flask, and then the flask was heated to 80 °C and maintained for 1 h before exposed to the air. The catalyst was removed by passing the mixture through a short column of neutral alumina oxide. The product was precipitated by cold methanol and dried in vacuum at 40 °C.

Thermal Treatment of the Thermo-reversible Graft (Co)Polymers

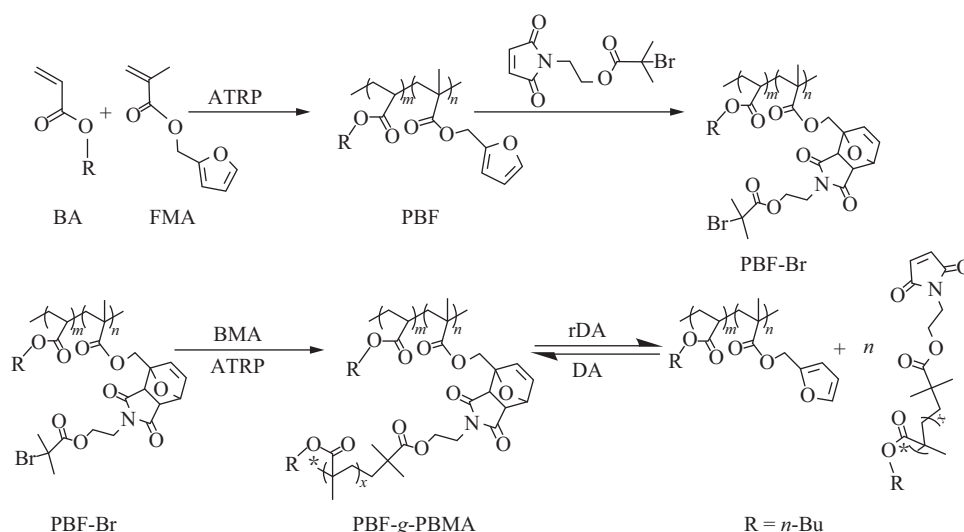
Thermo-reversible graft (co)polymers with hydroquinone (1 wt%) were dissolved in ethyl acetate, and then the solvent was volatilized to give the solid mixture, which was dried at 40 °C in vacuum. The solid mixture was then treated at different temperatures under nitrogen atmosphere. The samples were withdrawn at different time intervals for the characterization using GPC and ¹H-NMR.

RESULTS AND DISCUSSION

Synthesis of PBF-based Graft (Co)Polymers with Thermo-reversible Linkage

The synthesis of furfuryl methacrylate (FMA) monomer is illustrated in Scheme 1. It is a transesterification between furfuryl alcohol and methyl methacrylate (MMA) catalyzed by potassium hydroxide with a yield of 60%. Fig. 1 shows ¹H-NMR spectrum of the monomer. The maleimide derivative, *N*-[2-(2-bromoisobutyryloxy)ethyl]maleimide (BiBEMI), was synthesized by 4 steps as illustrated by Scheme 2. Fig. 2 shows ¹H-NMR spectrum of the resultant product.

The copolymerization of *n*-BA with FMA (6 mol%) was carried out. The resultant product P(BA-*co*-FMA) (PBF) was characterized by ¹H-NMR, GPC and DSC. Fig. 3 gives the typical ¹H-NMR spectrum of the copolymer with the corresponding assignments. The content of FMA unit in the copolymer is 6 mol%, which is close to the feed composition, suggesting that the reactivity of the FMA is roughly the same as the BA.



Scheme 3 Synthesis and rDA/DA reaction of the thermo-reversible branched polymers (PBF-g-PBMA)

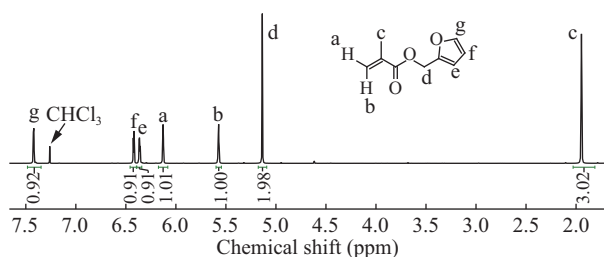


Fig. 1 ^1H -NMR spectrum of FMA in CDCl_3

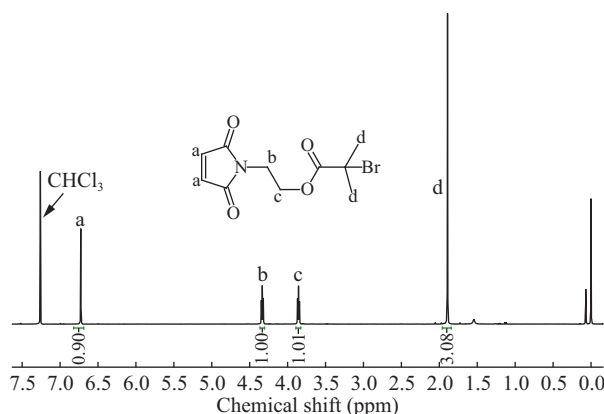


Fig. 2 ^1H -NMR spectrum of BiBEMI in CDCl_3

The glass transition temperature (T_g) of the PBF copolymer is -39°C , which is higher than that of the poly (butyl acrylate) (PBA) homopolymer (-50°C)^[41] due to the introduction of the rigid furan group. Then the macromolecular initiator (PBF-Br) was synthesized by Diels-Alder reaction of the furan groups on the PBF with the maleimide group of BiBEMI. The feed ratio of the furan group to maleimide group was 1/2 (molar ratio). After heated at 60°C for 24 h, $\sim 20\%$ of the furan group on the PBF reacted with BiBEMI, according to the ^1H -NMR (Fig. 3).

The thermo-reversible graft polymers were synthesized by “graft from” method. In order to reduce the concentration of macromolecular initiator and prevent crosslinking reaction between macromolecular initiator, monomers were used as both reactants and solvents during the synthesis of graft copolymers. After reacting for 1 h at 60°C , the viscosity of the solution obviously increased, indicating that the polymerization reaction took place. Fig. 4 shows the ^1H -NMR spectra of the resultant graft (co)polymers. After graft polymerization, there are new peaks in the ^1H -NMR spectra of the resultant graft copolymers. The PBF-g-PBMA presents a new peak at 3.8 ppm, which is ascribed to the methylene near the ester group of the BMA monomer. The PBF-g-P(BMA-co-MA) shows two new peaks at 3.8 and 3.6 ppm, respectively, which refer to the BMA monomer and the methyl group of the MA monomer.

There is no new peak in the ^1H -NMR spectra of the PBF-g-PBA, but the peak intensity at 4.0 ppm, which refers to the methylene near the ester group of the BA monomer, is increased as compared with the peak at 3.0 ppm (Diels-Alder linkage). This variation can be utilized to calculate the molecular weight of the side chains. The GPC profiles also confirmed the occurrence of graft polymerization (Fig. 5).

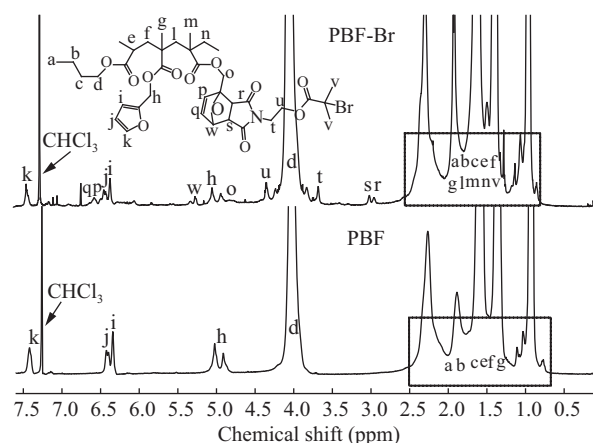


Fig. 3 ^1H -NMR spectra of PBF and PBF-Br in CDCl_3

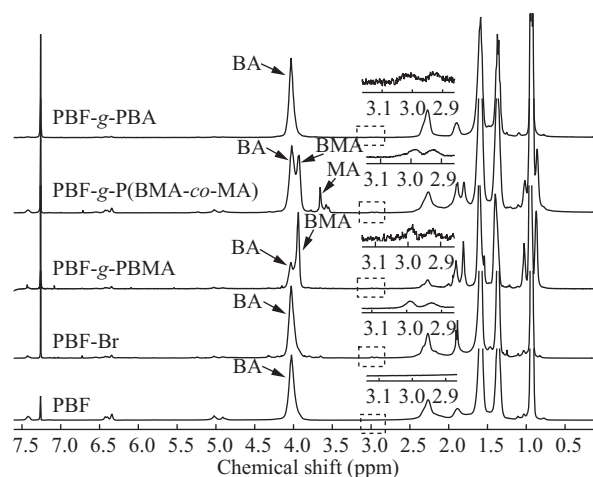


Fig. 4 ^1H -NMR spectra of thermo-reversible graft copolymers in CDCl_3

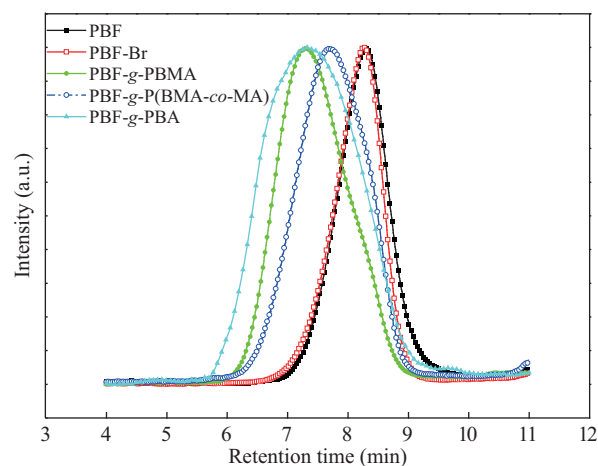


Fig. 5 GPC traces of all the polymers synthesized

Table 1 shows the molecular parameters of the obtained polymers. The molecular weights of the three graft copolymers were higher than those of PBF and PBF-Br.

DSC Analysis of PBF-based Graft (Co)Polymers with Thermo-reversible Linkage

DSC curves showed the glass transition and the retro-Diels-Alder reaction of the polymers (Fig. 6). Table 1 lists the glass

Table 1 Molecular parameters of all the polymers synthesized

Polymer	$M_n^a \times 10^{-3}$	M_w/M_n	$M_{ns}^b \times 10^{-3}$	T_g (°C)
PBF	35.6	1.61	—	−39
PBF-Br	39.7	1.46	—	−36
PBF-g-PBMA	89.4	1.78	12.2	−29, 30
PBF-g-P(BMA-co-MA)	60.9	1.82	5.4	−29
PBF-g-PBA	85.5	2.43	11.0	−39

^a The molecular weight of the backbone or the graft copolymers; ^b The molecular weight of the side chains

transition temperatures (T_g) of the polymers. The T_g of PBF is −39 °C. After reacting with the BiBEMI, the T_g of product (PBF-Br) rose to −36 °C. At the same time, two endothermic peaks appeared at 118 and 146 °C, which are corresponding to the cleavage reaction of the DA linkage^[42]. In the case of PBF-g-PBMA, besides the endothermic peak of the rDA reaction, the PBF-g-PBMA has two T_g s at −29 °C and 30 °C, respectively, which belong to the PBF backbone and the PBMA side chain. This indicates that the PBF backbone is not completely compatible with the PBMA side chain.

In contrast, the PBF-g-P(BMA-co-MA) has only one T_g at −29 °C, which indicated the good compatibility between PBF backbone and P(BMA-co-MA) side chain. In the case of PBF-g-PBA, the compositions of both the backbone and side chain of the PBF-g-PBA are almost the same, so PBF-g-PBA has just one T_g at −39 °C, which is in accordance with the PBF backbone. In addition, the endothermic peak of the rDA reaction can also be observed in the PBF-g-PBA and PBF-g-P(BMA-co-MA), which confirms the presence of DA linkage in these two polymers.

Thermo-responsive Behavior of PBF-based Graft (Co)Polymers with Thermo-reversible Linkage

The responsive ability to thermal stimuli for the thermo-reversible PBF-based graft (co)polymers was investigated. The reversibility of side chain linkage in the graft (co)polymers was monitored using GPC and ¹H-NMR measurements, when forward-reverse bonding-debonding was demonstrated at 60 and 120 °C, respectively. The efficiency of both the side chain release and reprecipitation was calculated by ¹H-NMR results, using the ratio of integrated area of the resonance peak at 3.0 ppm, related to the protons of the product of Diels-Alder reaction (r, s in the

upper, Fig. 3), against that of the resonance peak at 6.5 ppm related to the protons of furan and products of Diels-Alder reaction (i, j, p, q in the upper, Fig. 3). By this method the reaction efficiency was calculated and normalized (Supposed that the DA linkage of original sample is 100%).

For PBF-g-PBMA, an apparent change in the ¹H-NMR spectra of this copolymer can be observed after thermal treatment under different conditions, and each signal is easily identified (Fig. 7).

The resonance peak at 3.0 ppm related to the (s, r) proton of the DA adduct (Fig. 3) decreases apparently after thermal treatment at 120 °C for 1 h, and ~21.5% of the Diels-Alder linkage remains according to the results of ¹H-NMR spectra (Table 2). This indicates that retro-Diels-Alder reaction process occurred but the Diels-Alder linkage did not cleave completely under this condition. After the above sample is treated at 60 °C for 24 h, ¹H-NMR results demonstrate that about 31.4% of the Diels-Alder linkage remains at this moment. After kept at 60 °C for 48 h, approximately 44.6% of the Diels-Alder linkage is observed. This shows the reversibility of the furan/maleimide Diels-Alder linkage. The GPC traces of the PBF-g-PBMA samples treated under different conditions (different temperatures and time) confirm a significant change of the molecular weight (Fig. 8). Upon heated at 120 °C for 1 h, the GPC profile shifts to the lower molecular weight region, indicating that the side chains were released from the PBF-g-PBMA.

After being treated at 60 °C for 24 h, relatively higher molecular weight portion appears again, which is in accordance with the original PBF-g-PBMA. This indicates the partial recovery of grafting structure in the PBF-g-PBMA sample. After heat treatment at 60 °C for 48 h, the portion

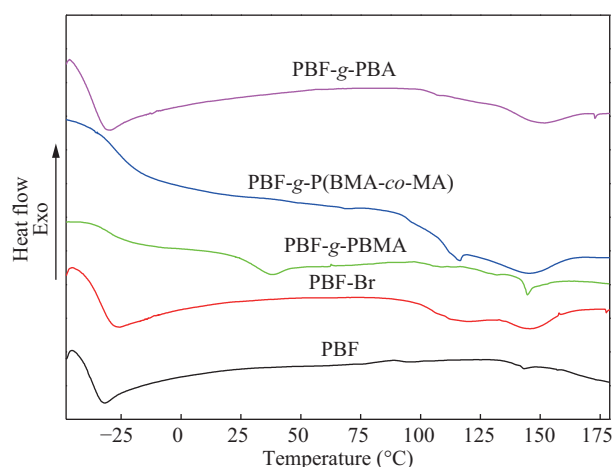
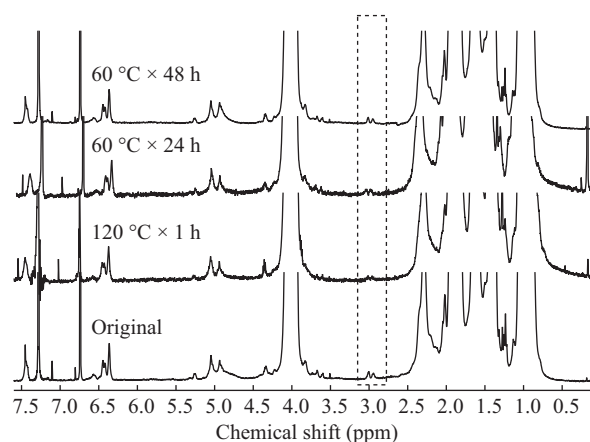
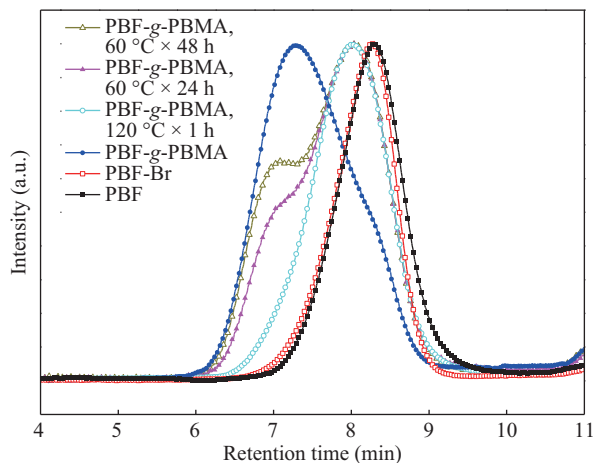
**Fig. 6** DSC curves of all the polymers synthesized**Fig. 7** ¹H-NMR spectra of the PBF-g-PBMA when heated at different temperatures in CDCl₃

Table 2 Molecular parameters of PBF-g-PBMA when heated at different temperatures

Sample	$M_n \times 10^{-3}$	M_w/M_n	DA linkage (%)
Original	89.4	1.78	100
120 °C × 1 h	47.3	1.70	21.5
60 °C × 24 h	55.2	2.02	31.4
60 °C × 48 h	60.1	2.09	44.6

**Fig. 8** GPC curves of the PBF-g-PBMA when heated at different temperatures

with higher molecular weight increases but does not return to the original state. This result means that only a part of the released side chains from the graft copolymer are re-linked to the backbone, which is in accordance with the $^1\text{H-NMR}$ characterization. The incomplete recovery of the released side chains to PBF backbone in PBF-g-PBMA is probably ascribed to the incompatibility between the PBF backbone and the PBMA side chains (two glass transition temperatures in this graft copolymer, Fig. 6). There is microphase separation (keeping covalent linking between PBF backbone and PBMA side chains) or macrophase separation (the cleavage of the covalent linking between PBF backbone and PBMA side chains) between PBA and PBMA in the PBF-g-PBMA copolymer system because of the incompatibility. When the Diels-Alder linkage between the backbone and the side chains is broken, the maleimide group at the terminal of the PBMA side chains is wrapped in the PBMA phase, and the furan group is wrapped in the PBF phase. As a result, the probability of these two groups to contact and react is dramatically reduced. So it is hard for PBF-g-PBMA to recover completely after the side chains are released by heat treatment at 120 °C.

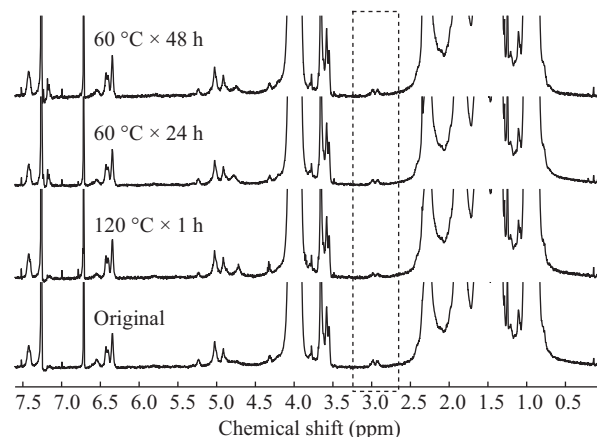
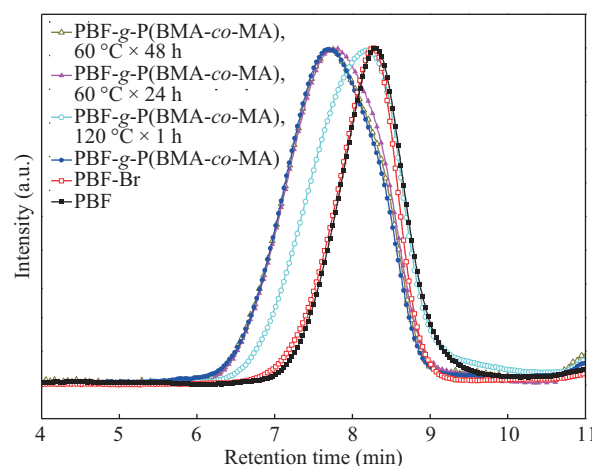
Based on the above results, PBMA side chains hereby are replaced by P(BMA-co-MA) to increase the compatibility of the side chains with PBF backbone (one glass transition temperature in this graft copolymer, Fig. 6). As shown in Fig. 9, in the case of PBF-g-P(BMA-co-MA), heat treatment at 120 °C for 1 h results in the cleavage of 31.1% Diels-Alder linkage (Table 3, calculated by the $^1\text{H-NMR}$ spectra). After the sample is heated at 60 °C for 24 h, $^1\text{H-NMR}$ analysis of the sample demonstrates that about 94.9% of the Diels-Alder linkage remains (Fig. 9). After heated at 60 °C for 48 h, approximately 100% of the Diels-Alder linkage is

Table 3 Molecular parameters of PBF-g-P(BMA-co-MA) when heated at different temperatures

Sample	$M_n \times 10^{-3}$	M_w/M_n	DA linkage (%)
Original	60.9	1.82	100
120 °C × 1 h	43.1	1.89	68.9
60 °C × 24 h	56.5	1.87	94.9
60 °C × 48 h	61.4	1.82	100

resumed, which is in accordance with the GPC results (Fig. 10). According to the previous report^[43], a healing efficiency of < 50% was found to be sufficient for significant recovery of mechanical properties. Compared to the PBF-g-PBMA, the backbone and side chains of PBF-g-P(BMA-co-MA) are compatible, meaning that after P(BMA-co-MA) side chains are released from the graft copolymer, the terminal maleimide groups of the side chains can contact well with the furan groups of PBF backbone, and the Diels-Alder reaction could proceed more easily. So the released side chains from the PBA-g-P(BMA-co-MA) can be re-linked to the backbone completely under a proper condition.

The case of PBF-g-PBA is different from those of PBF-g-PBMA and PBF-g-P(BMA-co-MA). After being heated at 120 °C for 1 h, the $^1\text{H-NMR}$ spectra showed that the

**Fig. 9** $^1\text{H-NMR}$ spectra of the PBF-g-P(BMA-co-MA) when heated at different temperatures in CDCl_3 **Fig. 10** GPC traces of the PBF-g-P(BMA-co-MA) when heated at different temperatures

resonance peak at 3.0 ppm decreased (Fig. 11). This indicated that the retro-Diels-Alder reaction occurred. The GPC traces of the polymers showed both lower molecular weight and higher molecular weight signals (wide PDI) (Fig. 12), and the average molecular weight decreased. The lower molecular weight portion can be attributed to the side chains released from the graft copolymers, and the higher molecular weight portion may be attributed to the crosslink of the polymers, which is caused by the side reactions of the furan group on the main chain^[44]. The good flexibility of PBA side chains might be the reason for more side reactions in PBF-g-PBA rather than in PBF-g-PBMA and PBF-g-P(BMA-co-MA). When the copolymer was treated at 60 °C, the average molecular weight of PBF-g-PBA increased, in which the portion with lower molecular weight decreased slightly and the portion with higher molecular weight increased obviously. This indicated that the side reactions were promoted by the heating. The ¹H-NMR spectra of the PBF-g-PBA are also different from those of PBF-g-PBMA and PBF-g-P(BMA-co-MA).

After heated at 60 °C, the resonance peak at 3.0 ppm

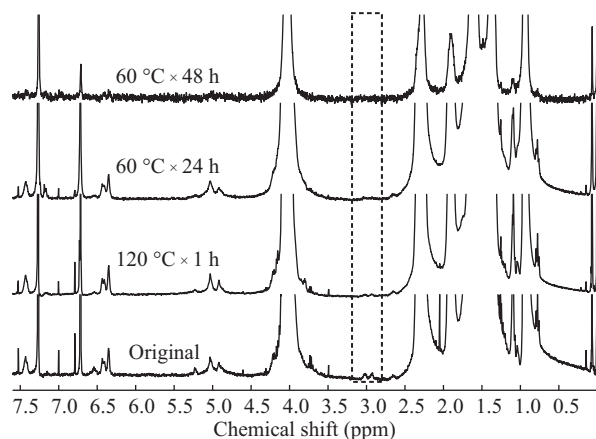


Fig. 11 ¹H-NMR spectra of the PBF-g-PBA when heated at different temperatures in CDCl₃

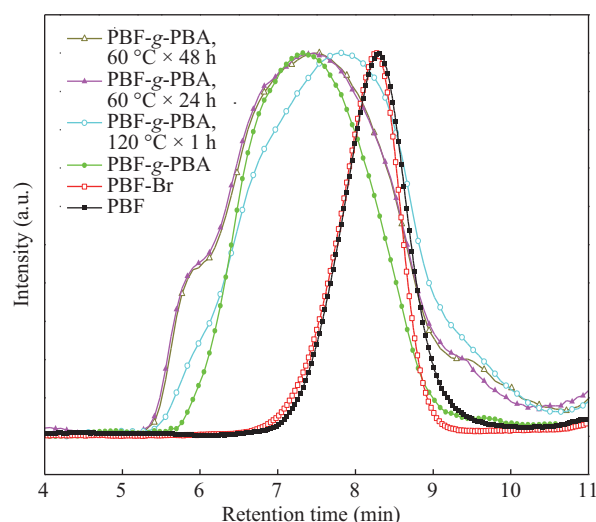


Fig. 12 GPC traces of the PBF-g-PBA when heated at different temperatures

decreased, suggesting that the ¹H-NMR characterization was affected by the crosslink reaction. As a result, the solubility of the polymers is reduced.

CONCLUSIONS

In summary, thermo-responsive graft copolymers with PBF backbone and different side chains have been successfully synthesized *via* ATRP and Diels-Alder reaction. The thermo-reversible linkage between the backbone and side chains can be broken and re-formed upon the change of the temperature, which leads to the corresponding thermo-reversible change of the molecular weights of the graft copolymers. The Diels-Alder reaction between the terminal maleimide group of side chains and the furan group on the backbone is strongly affected by the compatibility between the backbone and the side chains and the flexibility of the polymer chain. This novel thermal-responsive graft polymer affords ability to the materials that can be altered in response to heating to form the proper material composition needed.

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