

## ARTICLE

# Synthesis and analysis of thermally degradable polybutadiene containing Diels–Alder adduct

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## Abstract

The thermoreversible Diels–Alder reaction, a type of stimuli-responsive reversible organic reaction, is attractive because its direction can be easily controlled. In this study, the cross-linked Diels–Alder adduct-containing polybutadiene (DAPBD) was synthesized by the  $S_N2$  reaction of bromine-terminated polybutadiene with a furan-bismaleimide Diels–Alder adduct, and their thermodegradable behavior was analyzed by thermogravimetric analysis. DAPBD was dissociated by the retro-Diels–Alder reaction and dissolved in chlorobenzene at 132 °C to generate furan-terminated polybutadiene (FTPB) and bismaleimide that were identified by <sup>1</sup>H NMR spectroscopy. This synthetic method using premade Diels–Alder adducts is expected to enhance the thermoreversibility of the materials by significantly increasing the concentration of the Diels–Alder adduct moieties in the final DAPBD. The polymerization performed at 35 °C will help widen the scope of the use of such materials.

## KEYWORDS

cross-linked polybutadiene, Diels–Alder adduct,  $S_N2$  reaction, thermally degradable

## INTRODUCTION

Various reversible organic reactions, such as thermoreversible,<sup>1–3</sup> pH-responsive,<sup>4–6</sup> UV-responsive,<sup>7,8</sup> and chemoreversible<sup>9–11</sup> reactions, that change the direction of the reactions (forward or backward) according to a specific stimulus have been reported. Polymeric materials fabricated by reversible organic reactions have been applied in various fields such as self-healing coatings,<sup>12–16</sup> photocurable adhesives,<sup>17–19</sup> and drug delivery.<sup>16,20,21</sup> Among them, the Diels–Alder and retro-Diels–Alder reactions, the thermally reversible reaction pair involved in building or breaking a cyclic adduct, have attracted significant attention in recent years because they afford a simple method to control the structure of the polymeric materials.<sup>22–25</sup> For example, substituted cyclohexene derivatives produced by the [4 + 2] Diels–Alder reaction between a conjugated diene and a dienophile at a specific temperature can be spontaneously dissociated into the diene and the dienophile by the retro-Diels–Alder reaction at an elevated temperature.

Among the Diels–Alder reactions of various pairs of dienes and dienophiles, those between furans and maleimides are used as representative reactions to prepare

thermoreversible materials.<sup>26–31</sup> The furan moieties can be introduced along the main chain,<sup>32,33</sup> or attached as either terminal functional groups at each end of the polymer<sup>34–36</sup> or pendant groups on the main polymer chain.<sup>37–39</sup> The Diels–Alder reaction of polymers containing furan moieties with bismaleimides leads to the spontaneous fabrication of cross-linked polymers owing to the multifunctionality of furan-containing polymers and the bifunctionality of bismaleimides.

Polybutadiene (PBD) rubber, an elastomer traditionally used to manufacture tires, is often used as an additive to improve the toughness of various plastics owing to its high resistance against abrasion and cracking.<sup>40–43</sup> In particular, cross-linked polyolefin rubbers are renowned for their excellent temperature and chemical resistance and high mechanical strength.<sup>44,45</sup> However, their high stability makes the economical and eco-friendly reprocessing or recycling of the polymers and their additives difficult.

Ongoing research on the development of a new thermally reversible polymeric system based on hydroxyl-terminated polybutadiene (HTPB) in our laboratory has shown that it is necessary to increase the concentration of Diels–Alder adduct moieties in the Diels–Alder adduct-

containing polybutadiene (DAPBD) backbone. Even though the Diels–Alder reaction has been reported to proceed at a reasonable speed, the cycloadditions of furan-terminated PBDs with bismaleimides were sluggish in our laboratory at 60 °C, the typical curing temperature for most Diels–Alder reaction, or even at higher temperatures. The need to react for a long duration at an elevated temperature to construct the final polymeric structure may limit the application scope of these materials. Furthermore, the low concentration of the Diels–Alder adduct moiety obtained by the incomplete Diels–Alder reaction can considerably degrade the thermoreversible behavior of the materials. Hence, it is necessary to develop a more efficient method for increasing the concentration of Diels–Alder adduct moieties in PBD.

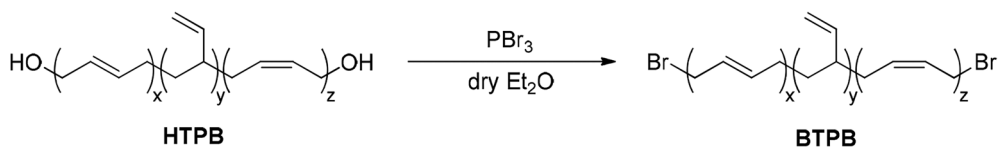
In the present study, DAPBD was synthesized, and its thermodegradable properties were thoroughly analyzed. Diels–Alder adduct moieties were introduced to the DAPBD main chains via ether linkage formed by the  $S_N2$  reaction of

bromine-terminated polybutadiene (BTPB) with the furan-bismaleimide Diels–Alder adduct (FBDA). The synthetic method to construct the Diels–Alder adduct-containing polymer by  $S_N2$  reaction of the premade Diels–Alder adduct has not been reported up to our knowledge. The resulting DAPBD is naturally cross-linked because HTPB, the precursor of BTPB, with a multiple hydroxyl functionality of 2.3 is used.

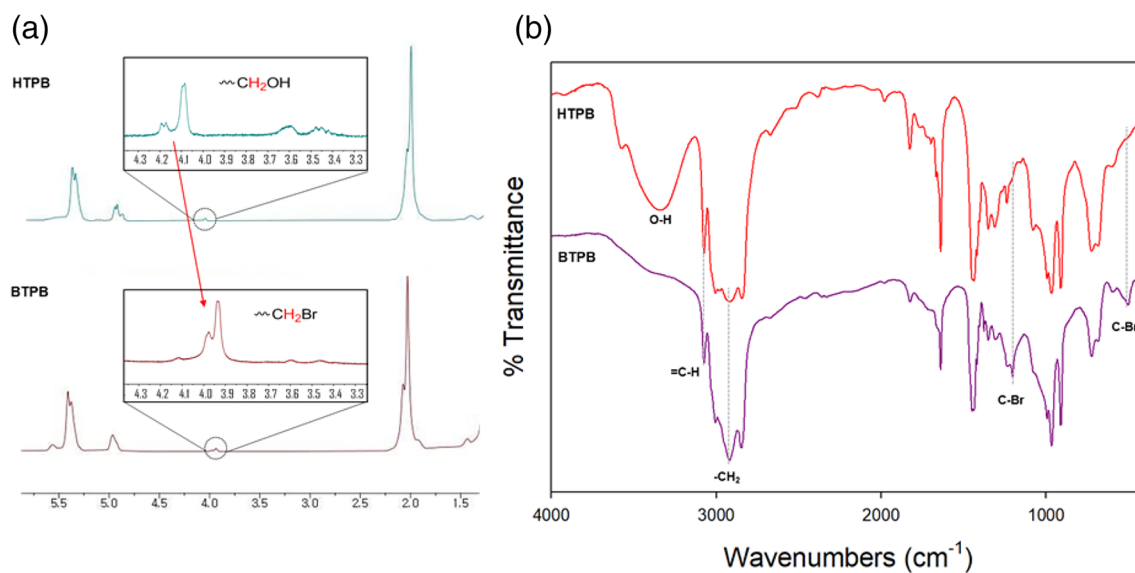
## EXPERIMENTAL

### Materials

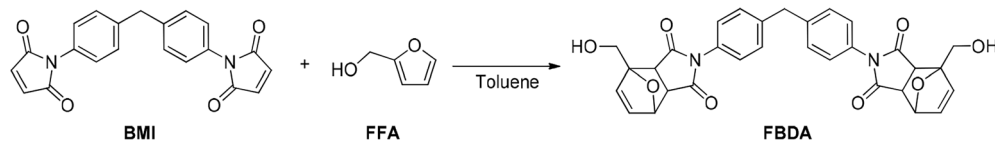
Phosphorus tribromide (98%), acetone (>99.5%), methylene chloride (>99.5%), toluene (>99.5%), diethyl ether (>99%), chloroform (>99.5%), and 4-Å molecular sieve (4–8 mesh) were purchased from Daejung Chemicals (Gyeonggi-do, Republic of Korea). 1,2,4-Trichlorobenzene (>99%), chlorobenzene (99%), chloroform-*d* (99.9%,



**SCHEME 1** Synthesis of bromine-terminated polybutadiene (BTPB) from hydroxyl-terminated polybutadiene (HTPB)



**FIGURE 1** Analysis of bromine-terminated polybutadiene (BTPB) in comparison to hydroxyl-terminated polybutadiene (HTPB): (a)  $^1\text{H}$  NMR spectra; (b) Fourier transform infrared (FTIR) spectra



**SCHEME 2** Synthesis of furan-bismaleimide Diels–Alder adduct (FBDA) via the Diels–Alder reaction

contains 0.03 vol% TMS), pyridine (>99%), and potassium *tert*-butoxide (97%) were purchased from Alfa Aesar (Ward Hill, MA, USA). Furfuryl alcohol (FFA, >98%) and 4,4'-bismaleimidodiphenylmethane (BMI, >96%) were purchased from Tokyo Chemical Industry (Tokyo, Japan). Dimethyl sulfoxide- $d_6$  (99.8%, with 0.03 vol% TMS) was purchased from Merck (Darmstadt, Germany). HTPB (0.924 meq/g of hydroxyl value,  $M_n = 2800$ ) was kindly supplied by the Republic of Korea Agency for Defense Development (ADD). Diethyl ether and toluene were dehydrated with 4-Å molecular sieves before use.

## Analytical methods

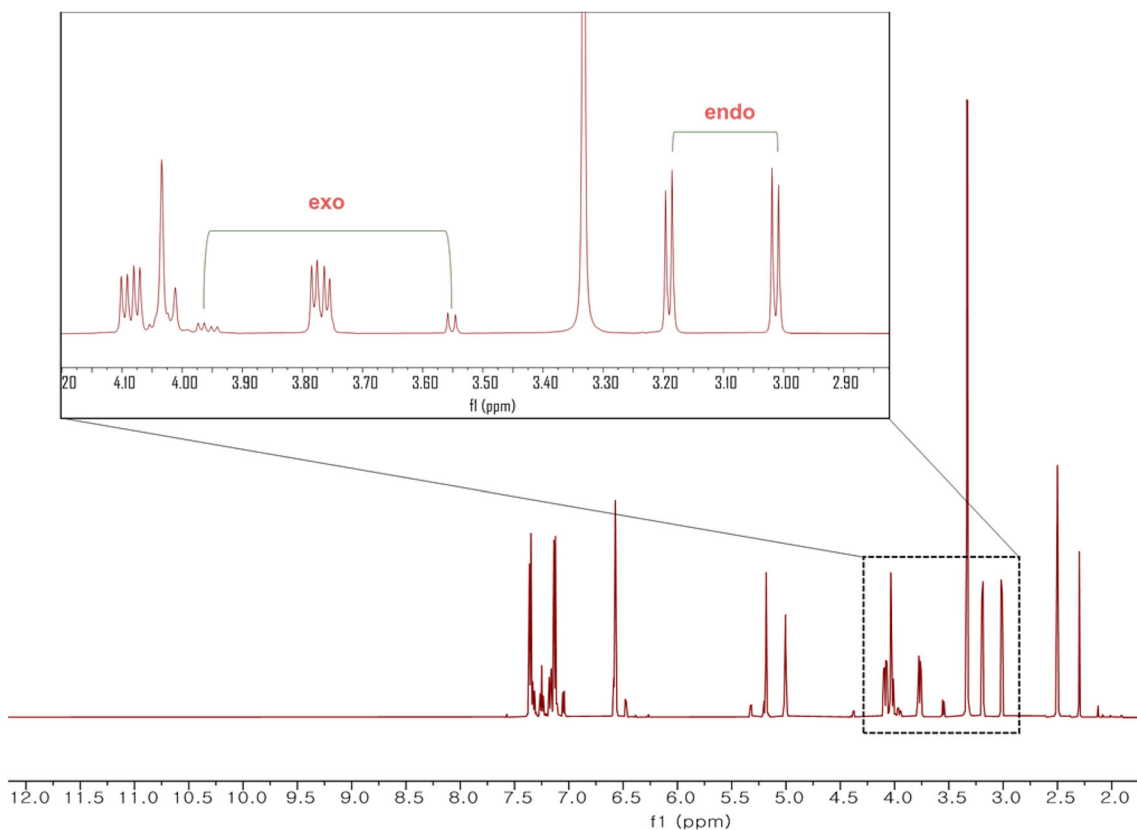
$^1\text{H}$  NMR (300 MHz) spectra were acquired on a 300-MHz spectrometer (Germini 2000; Varian, Palo Alto, CA, USA) using DMSO- $d_6$  or  $\text{CDCl}_3$  as a solvent. The chemical shifts were determined by referring to the residual solvent peaks ( $\delta_{\text{H}}$  2.50 for DMSO- $d_6$  and  $\delta_{\text{H}}$  7.26 for  $\text{CDCl}_3$ , respectively, in the  $^1\text{H}$  NMR spectra). The Fourier transform infrared (FTIR) spectra were obtained using an FTIR spectrometer (Nicolet 6700; Thermo Fischer Scientific, Waltham, MA, USA). Thermal stabilities were investigated by thermogravimetric analysis (TGA; TGA-2050, TA Instruments, New Castle, DE, USA). Thermal properties were measured by Differential scanning calorimetry (DSC, Q20; TA Instruments).

## Preparation of BTPB

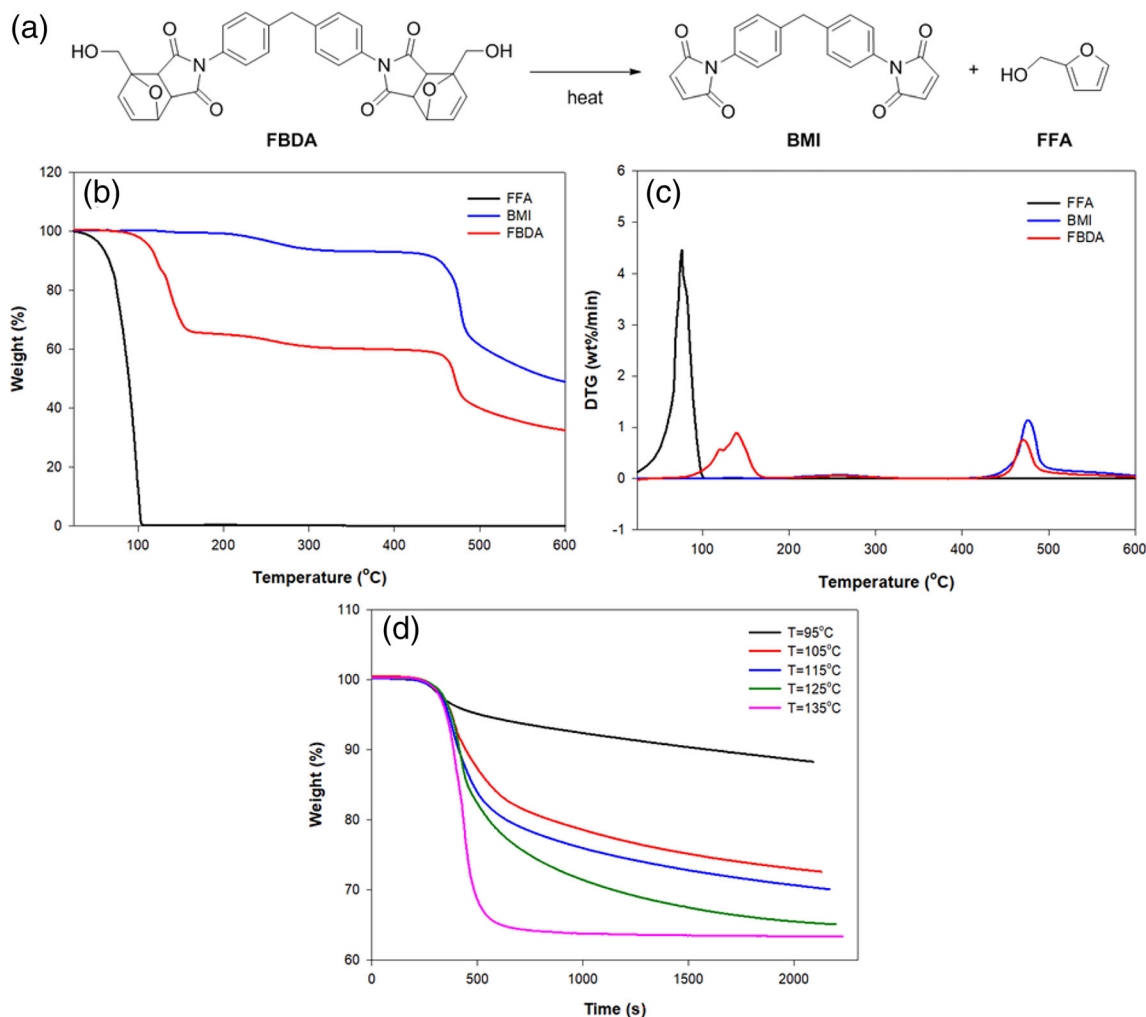
$\text{PBr}_3$  (0.45 g, 1.64 mmol) was added dropwise to a solution of HTPB (2.00 g, 0.71 mmol) in  $\text{Et}_2\text{O}$  (100 ml) at 0 °C under a  $\text{N}_2$  atmosphere. The resulting mixture was stirred for 2 days at 25 °C. Then, the solvent was evaporated under a reduced pressure. The resulting mixture was washed with acetone and then concentrated *in vacuo* to obtain BTPB (2.10 g) as a viscous liquid.

## Preparation of 2,2'-(methylenedi-4,1-phenylene)bis[3a,4,7,7a-tetrahydro-4-(hydroxymethyl)-4,7-epoxy-1H-isoindole-1,3(2H)-dione]

BMI (5.00 g, 13.95 mmol) and FFA (2.87 g, 29.30 mmol) were dissolved in toluene (50 ml) and heated for 2 days at 80 °C. The precipitate was filtered and washed with  $\text{Et}_2\text{O}$  ( $2 \times 250$  ml). The remaining solvent was removed *in vacuo* to obtain FBDA (7.49 g, 96.8%) as a yellowish powder<sup>46</sup>;  $^1\text{H}$ -NMR: (300 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$  (ppm): 7.34 (4H, m, H-8, H-8'), 7.11 (4H, m, H-9, H-9'), 6.56 (2H, d,  $J = 5.39$  Hz, H-3, H-3'), 6.55 (2H, d,  $J = 5.39$  Hz, H-2, H-2'), 5.17 (2H, d, H-1, H-1'), 4.99 (2H, s, OH), 4.06 (2H, dd,  $J = 12.58, 5.72$  Hz,  $-\text{CH}_2\text{OH}$ ), 4.02 (2H, s,  $\text{ArCH}_2\text{Ar}$ ), 3.75 (2H, dd,  $J = 12.58, 5.72$  Hz,  $-\text{CH}_2\text{OH}$ ), 3.17 (2H, d,  $J = 6.49$  Hz, H-6, H-6'), 3.00 (2H, d,  $J = 6.49$  Hz, H-7, H-7').



**FIGURE 2**  $^1\text{H}$  NMR spectrum of furan-bismaleimide Diels-Alder adduct (FBDA)



**FIGURE 3** Thermal degradation properties of furfuryl alcohol (FFA), 4,4'-bismaleimidediphenylmethane (BMI), and furan-bismaleimide Diels-Alder adduct (FBDA): (a) retro-Diels-Alder reaction scheme; (b) thermogravimetric analysis (TGA); (c) derivative TGA (DTGA); (d) TGA of FBDA at various temperatures

**TABLE 1** Extent of the retro-Diels-Alder reaction

Entry	Final temperature (°C)	Weight (%)	Retro-Diels-Alder completed (%)
1	95	88.31 ± 0.25	33.04 ± 0.71
2	105	72.61 ± 0.15	77.42 ± 0.42
3	115	70.10 ± 0.08	84.51 ± 0.23
4	125	66.09 ± 0.10	95.85 ± 0.28
5	135	64.62	100

## Preparation of DAPBD

The solution of FBDA (0.45 g, 0.82 mmol) and potassium *tert*-butoxide (0.42 g, 3.77 mmol) in Et<sub>2</sub>O (180 ml) was stirred for 1 h under a N<sub>2</sub> atmosphere. To the reaction mixture was added dropwise a solution of BTPB (2.10 g) in Et<sub>2</sub>O (20 ml). The reaction mixture was heated at 35 °C for 5 days. The solvent was evaporated under a reduced pressure. The resulting mixture was washed with acetone

and then concentrated *in vacuo* to obtain DAPBD in a quantitative yield.

## Preparation of furan-terminated polybutadiene

PBr<sub>3</sub> (0.59 g, 2.19 mmol) was added dropwise to a solution of FFA (0.64 g, 6.57 mmol) and pyridine (1.30 g, 16.43 mmol) in Et<sub>2</sub>O (25 ml) at 0 °C under a N<sub>2</sub> atmosphere. The mixture was stirred for 4 h at 25 °C. To the furfuryl bromide solution was added dropwise a solution of HTPB (2.00 g, 0.71 mmol) and potassium *tert*-butoxide (0.37 g, 3.29 mmol) in Et<sub>2</sub>O (180 ml) that was prestirred for 1 h under a N<sub>2</sub> atmosphere. Then, the reaction mixture was stirred for 2 days at 25 °C. The solvent was evaporated under a reduced pressure. The resulting mixture was washed with acetone (2 × 50 ml) and then concentrated *in vacuo* to obtain FTPB (2.08 g) as a viscous liquid.

## RESULTS AND DISCUSSION

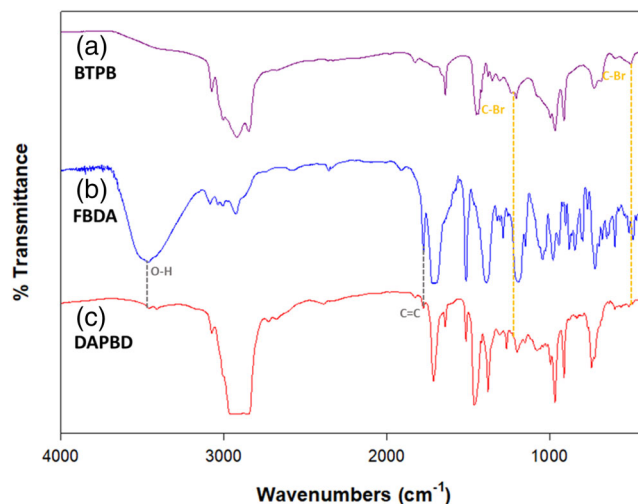
BTPB was prepared by the bromination of HTPB using 3.0 equiv. of  $\text{PBr}_3$  based on the number of hydroxyl groups in HTPB (Scheme 1). Complete disappearance of the characteristic peaks at  $\delta$  4.08–4.20 ppm corresponding to the  $\text{CH}_2$  protons adjacent to the OH group<sup>47</sup> and appearance of new peaks at  $\delta$  3.93–4.11 ppm by  $\text{CH}_2\text{Br}$  in  $^1\text{H}$  NMR spectra clearly showed the conversion of terminal hydroxyl groups to bromines (Figure 1a). Disappearance of the broad and strong peak at  $3384\text{ cm}^{-1}$  owing to O–H stretching vibration and appearance of new peaks at  $1204$  and  $501\text{ cm}^{-1}$  owing to C–Br in the IR spectra also confirmed the successful bromination (Figure 1b).

FBDA was prepared by the Diels–Alder reaction of BMI with FFA in toluene (Scheme 2). The cycloaddition was performed for 2 days at  $80\text{ }^\circ\text{C}$  to produce FBDA as a yellowish powder in 96.8% isolated yield. The synthesized FBDA was identified as a mixture of *endo*- and *exo*-adducts by  $^1\text{H}$  NMR analysis (Figure 2). The ratio of the *endo*- and *exo*-forms was calculated as 1.00:0.12 based on the peak areas at  $\delta_{\text{endo}}$  3.19 and 3.01 ppm vs. those at  $\delta_{\text{exo}}$  3.97 and 3.55 ppm, respectively.<sup>27</sup> Both isomers were used in the next polymerization as a mixture without separation.

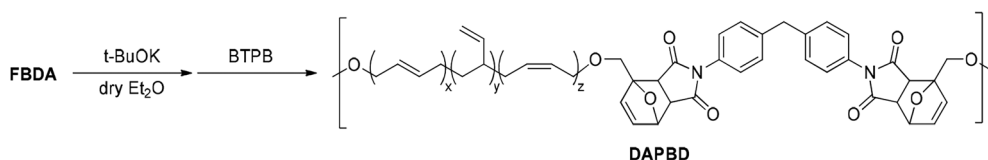
The thermal behavior of FBDA was analyzed by TGA studies of FBDA as well as of FFA and BMI, the two compounds expected to be produced in equal quantities by the retro-Diels–Alder reaction of FBDA (Figure 3a). The temperature was increased at the rate of  $20\text{ }^\circ\text{C}/\text{min}$  from the initial  $25$ – $600\text{ }^\circ\text{C}$ . The volatile FFA rapidly evaporated from the beginning and completely disappeared at  $106\text{ }^\circ\text{C}$  when the analysis was performed 5.2 mg of FFA, respectively (Figure 3b). In contrast, BMI lost only  $6.56 \pm 0.27\%$  of its original weight until the temperature reached approximately  $440\text{ }^\circ\text{C}$ . Even at  $600\text{ }^\circ\text{C}$ ,  $48.96\% \pm 0.04\%$  of BMI was retained presumably due to its homopolymerization.<sup>48</sup> The weight of FBDA began to rapidly decrease from  $95\text{ }^\circ\text{C}$  onward, the temperature at which the retro-Diels–Alder reaction begins, because the volatile FFA generated by the retro-Diels–Alder reaction of FBDA quickly evaporates at elevated temperatures. The maximum derivative temperature of FBDA was  $140\text{ }^\circ\text{C}$  (Figure 3c). The weight loss of FBDA slowed down at  $160\text{ }^\circ\text{C}$  and its weight became  $64.62\% \pm 0.01\%$  of the initial weight, the exact weight percent of the BMI moiety in FBDA. The weight loss behavior of FBDA was consistent with that of pure BMI after  $160\text{ }^\circ\text{C}$ . Hence, it can be concluded that the retro-Diels–Alder reaction was started from  $95\text{ }^\circ\text{C}$  and completed around  $160\text{ }^\circ\text{C}$  and all the released FFA quickly evaporated.

The weight loss of FBDA was investigated by performing TGA at various temperatures (Figure 3d). The temperature was increased from the initial  $25$ – $95\text{ }^\circ\text{C}$ ,  $105\text{ }^\circ\text{C}$ ,  $115\text{ }^\circ\text{C}$ ,  $125\text{ }^\circ\text{C}$ , and  $135\text{ }^\circ\text{C}$  at a rate of  $20\text{ }^\circ\text{C}/\text{min}$ . Each temperature was held for 30 min. The weight percentages of residues, the remaining FBDA and BMI, for the initial FBDA at each temperature are listed in Table 1. At  $95\text{ }^\circ\text{C}$ ,  $88.31 \pm 0.10\text{ wt}\%$  of residue was left, indicating that  $33.04 \pm 0.10\%$  of FBDA underwent the retro-Diels–Alder reaction. The percentages of FBDA that underwent the retro-Diels–Alder reaction were calculated to be  $77.42\% \pm 0.42\%$  at  $105\text{ }^\circ\text{C}$ ,  $84.51\% \pm 0.23\%$  at  $115\text{ }^\circ\text{C}$ ,  $95.85\% \pm 0.28\%$  at  $125\text{ }^\circ\text{C}$ , and  $100\%$  at  $135\text{ }^\circ\text{C}$ , based on the remaining FBDA at the corresponding temperature. The results indicate that the dissociation of the Diels–Alder adduct composed with FFA and BMI can be completed over  $135\text{ }^\circ\text{C}$ .

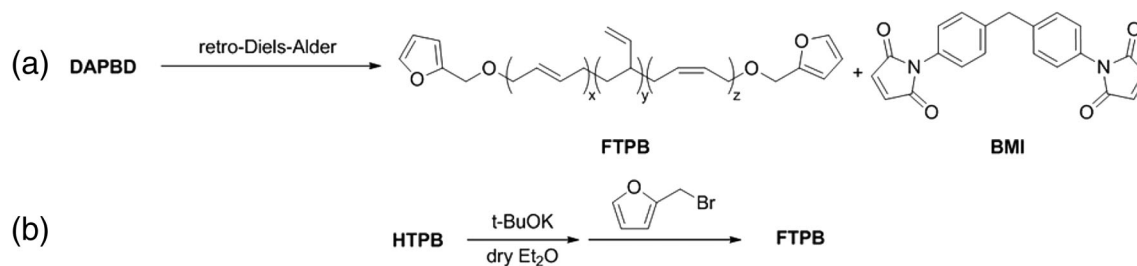
DAPBD was synthesized by the  $\text{S}_{\text{N}}2$  reaction of BTPB with FBDA using potassium *tert*-butoxide in  $\text{Et}_2\text{O}$  at  $35\text{ }^\circ\text{C}$  (Scheme 3). Disappearance of the broad O–H peak ( $3462\text{ cm}^{-1}$ ) of FBDA and the C–Br peaks ( $1204$  and  $501\text{ cm}^{-1}$ ) of BTPB clearly showed that the nucleophilic substitution proceeded successfully (Figure 4). The introduction of Diels–Alder adduct moieties was confirmed by observing the characteristic C=C peak of FBDA ( $1774\text{ cm}^{-1}$ ). The complete disappearance of C–Br and O–H bonds implies the formation of cross-linked DAPBD because HTPB with a hydroxyl



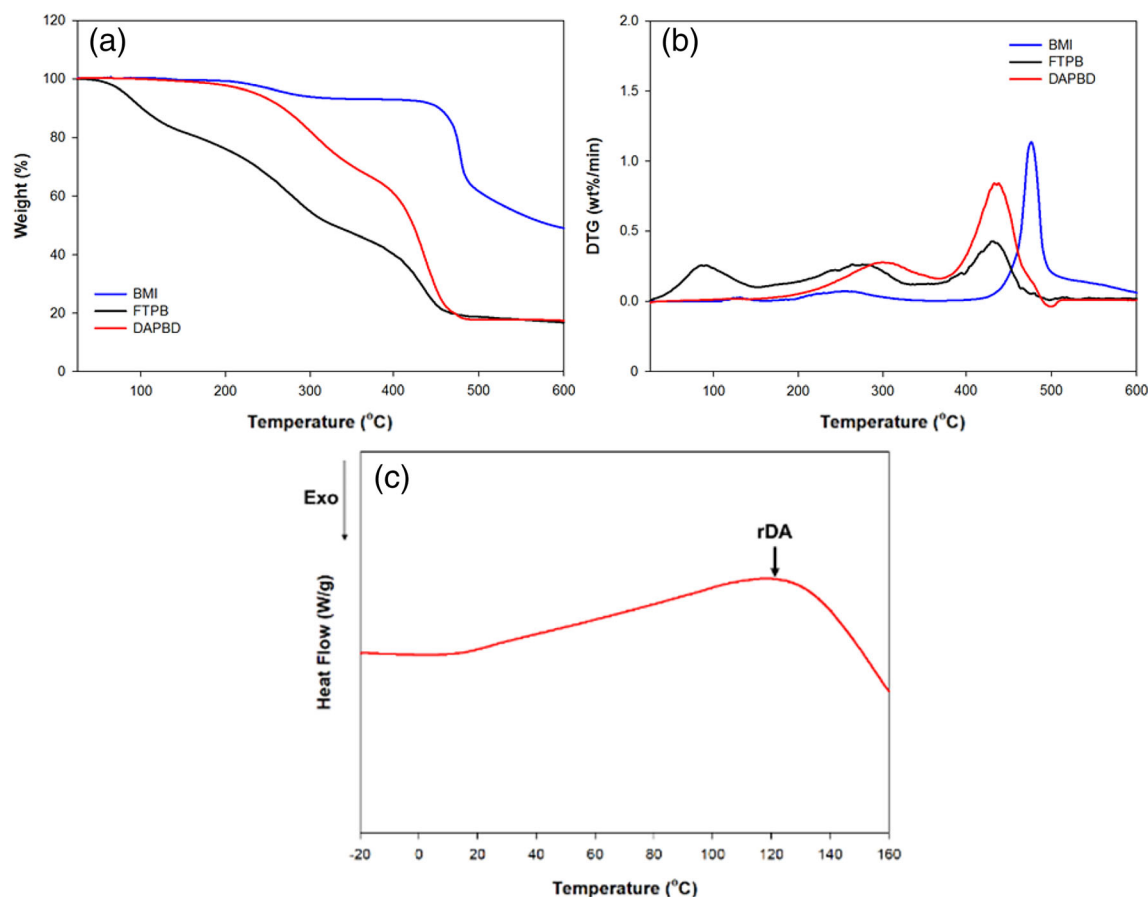
**FIGURE 4** Fourier transform infrared (FTIR) spectra of (a) bromine-terminated polybutadiene (BTPB); (b) furan-bismaleimide Diels–Alder adduct (FBDA); and (c) Diels–Alder adduct-containing polybutadiene (DAPBD)



**SCHEME 3** Synthesis of Diels–Alder adduct-containing polybutadiene (DAPBD)



**SCHEME 4** (a) Retro-Diels–Alder reaction of Diels–Alder adduct-containing polybutadiene (DAPBD); (b) synthesis of furan-terminated polybutadiene (FTPB) via  $S_N2$  reaction



**FIGURE 5** Thermal degradation of properties of, 4'-bismaleimidodiphenylmethane (BMI), furan-terminated polybutadiene (FTPB), and Diels–Alder adduct-containing polybutadiene (DAPBD): (a) thermogravimetric analysis (TGA); (b) derivative TGA (DTGA); (c) differential scanning calorimetry (DSC) thermogram of DAPBD

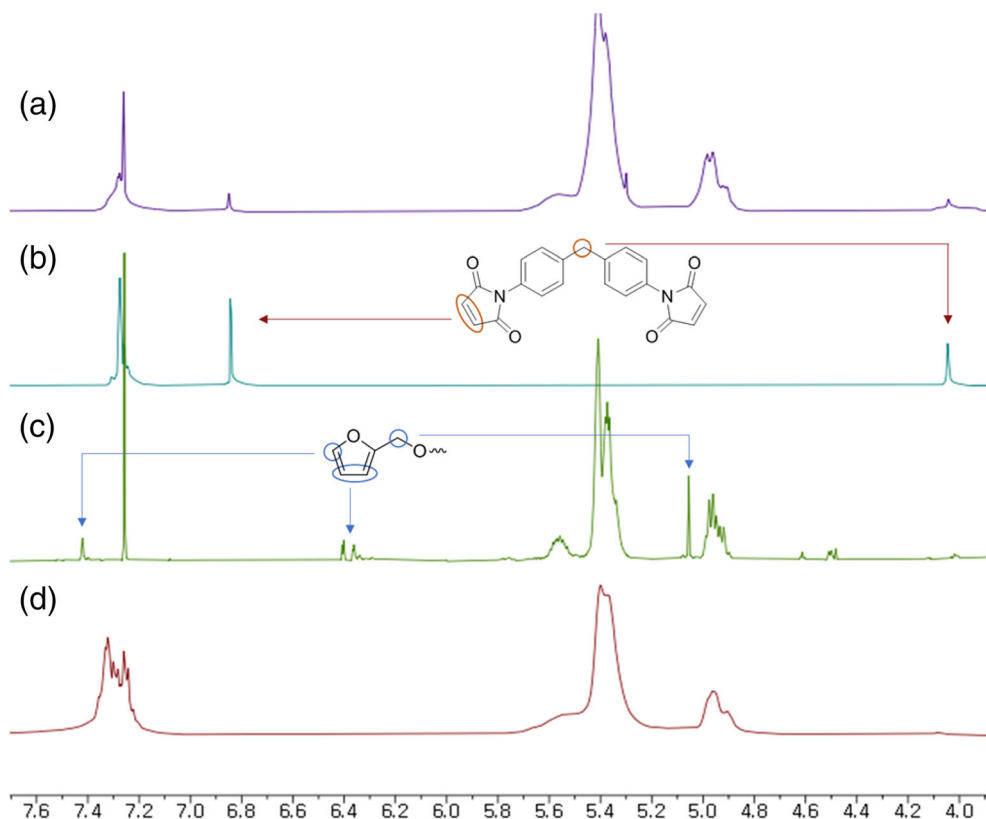
functionality of 2.3 was used. DAPBD was obtained as a rigid solid that was not soluble in any conventional solvents.

Thermal degradation of DAPBD was analyzed by TGA by increasing the temperature from 25 to 600 °C at a rate of 10 °C/min. As the retro-Diels–Alder reaction of DAPBD is expected to generate FTPB and BMI (Scheme 4a), FTPB was initially synthesized by the reaction of HTPB with furfuryl bromide prepared *in situ* by the reaction of FFA and  $PBr_3$  using potassium *tert*-butoxide (Scheme 4b).

While BMI began to lose its weight from 210 °C onward, FTPB started to lose its weight from 50 °C

onward because of the rapid cleavage and evaporation of FFA (Figure 5a,b). In contrast, the weight loss of DAPBD began at 130 °C, which clearly shows that the retro Diels–Alder reaction followed by the cleavage and evaporation of FFA begins before 130 °C. It was also confirmed by DSC analysis. The endothermic peak associated with the retro Diels–Alder reaction was observed at 122 °C (Figure 5c).

The weight of DAPBD remaining at 600 °C was  $17.47 \pm 0.03$  wt%, which was less than  $20.69\% \pm 0.57\%$ , the calculated value for the linear combination of pure



**FIGURE 6**  $^1\text{H}$  NMR spectra of (a) Diels–Alder adduct-containing polybutadiene (DAPBD) refluxed in chlorobenzene; (b) 4'-bismaleimidodiphenylmethane (BMI); (c) furan-terminated polybutadiene (FTPB); and (d) FTPB refluxed in chlorobenzene

FTPB ( $16.79 \pm 0.64\%$  wt% at  $600^\circ\text{C}$ ) and pure BMI ( $48.96\% \pm 0.04\%$  at  $600^\circ\text{C}$ ). The greater weight loss of DAPBD than the theoretical value could be explained by the slower homo-polymerization of BMI owing to the dilution effect caused by the coexistence of FTPB and HTPB produced.

To verify the production of FTPB and BMI by the retro-Diels–Alder reaction of DAPBD, the reaction was performed in chlorobenzene and 1,2,4-trichlorobenzene. DAPBD (1.0 g) was dissociated and dissolved marginally at  $160^\circ\text{C}$  and completely at  $180^\circ\text{C}$  in 20 ml of 1,2,4-trichlorobenzene. It was partially dissociated and dissolved in 20 ml of chlorobenzene at  $132^\circ\text{C}$ . The  $^1\text{H}$  NMR spectra of the dissolved compounds verified the formation of BMI by showing the peaks at  $\delta$  6.84 and 4.05 ppm (Figure 6a,b). However, the formation of FTPB was not identified because of the absence of the peaks corresponding to the furan moiety that were expected at  $\delta$  7.42, 6.40, 6.36, and 5.06 ppm (Figure 6a,c). Even though the rapid cleavage and disappearance of the furan moiety from FTPB had already been observed in TGA studies (Figure 5a), we attempted to confirm it under identical environments.

When neat FTPB was heated in chlorobenzene at  $132^\circ\text{C}$  and analyzed by  $^1\text{H}$  NMR spectra, the spontaneous removal of the peaks of furan moieties was observed (Figure 6c,d). This result clearly indicates that the retro-Diels–Alder reaction of DAPBD proceeded quantitatively to generate FTPB and BMI.

## CONCLUSION

In this study, the cross-linked DAPBD was synthesized by the  $\text{S}_{\text{N}}2$  reaction of BTPB with FBDA, and their thermodegradable behavior was analyzed by TGA. The TGA studies showed that the retro-Diels–Alder reaction of DAPBD began at  $122^\circ\text{C}$  according to the DSC study, while that of FBDA began at  $95^\circ\text{C}$ . DAPBD was partially dissociated and dissolved in chlorobenzene at  $132^\circ\text{C}$  and completely dissociated and dissolved in 1,2,4-trichlorobenzene at  $180^\circ\text{C}$ .

The synthetic method developed herein allows the construction of Diels–Alder adduct-containing PBD at  $35^\circ\text{C}$ , a notably lower temperature than that required in common methods for polymerization via Diels–Alder reactions. This result is important because high reaction temperatures can limit the use of materials in temperature-sensitive applications. More importantly, this method using premade Diels–Alder adducts can greatly increase the concentration of the Diels–Alder adduct moieties in the final PBD by providing the same effect as that obtained when the final polymerization via the Diels–Alder reaction in common methods is carried out in 100% yield. It is obvious that polymeric materials containing more Diels–Alder adduct moieties would lead to better thermodegradable and thermoreversible properties. Applications that utilize the thermally degradable property of DAPBD are currently under investigation and the results will be reported in due course.

## ACKNOWLEDGMENTS

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## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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