

Polymer Chemistry

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Precise Synthesis of Thermoreversible Block Copolymers Containing Reactive Furfuryl Groups via Living Anionic Polymerization: Counteraction Effect on Block Copolymerization Behavior

Beom-Goo Kang,^a Nabendu B. Pramanik,^b Nikhil K. Singha,^b Jae-Suk Lee,^{c,*} Jimmy Mays^{a,**}

⁵ Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

The anionic block copolymerization of 4,4'-vinylphenyl-*N,N*-bis(4-*tert*-butylphenyl)benzenamine (**A**) with furfuryl isocyanate (**B**) was carried out using potassium naphthalenide (K-Naph) in tetrahydrofuran at -78 and -98 °C to prepare well-defined block copolymers containing furan groups for the formation of thermoreversible networks via Diels-Alder (DA) reaction. While no block copolymerization was observed in the absence of sodium tetraphenylborate (NaBPh₄) due to side reactions, well-defined poly(**B**-*b*-**A**-*b*-**B**) (PBAB) copolymers with controlled molecular weights ($M_n = 18,700$ – $19,500$ g/mol) and narrow molecular weight distributions ($M_w/M_n = 1.08$ – 1.17) were successfully synthesized in the presence of excess NaBPh₄. The occurrence of the undesirable side reactions during polymerization of **B** was effectively prevented by NaBPh₄, which results in the change in counteraction from K⁺ to Na⁺ for the further polymerization of **B**. The cross-linking via the DA reaction between the furan groups of PBAB and bismaleimide was proved by FT-IR and differential scanning calorimetry (DSC), and thermoreversible properties of the cross-linked polymer were subsequently investigated using DSC and solubility testing.

Introduction

The polymerization of isocyanates has been investigated by many researchers due to the fascinating properties of the polyisocyanates, resulting from their stiffness and helical conformations. Thus, polyisocyanates have been used for various applications such as chiral recognition and optical switches, and as liquid crystalline materials.^{1–11} Although polyisocyanates can be prepared readily by anionic polymerization,^{12–15} it has been difficult to synthesize well-defined polyisocyanates via living anionic polymerization because of backbiting reactions resulting in formation of trimers. To overcome this problem, we have sought efficient ways to prevent trimerization. In particular, we found that the anionic polymerization of *n*-hexyl isocyanate (HIC) can be successfully performed using sodium naphthalenide (Na-Naph) as initiator with additives such as 15-crown-5 or sodium tetraphenylborate (NaBPh₄), preventing the formation of trimers.^{16,17} In recent years, the successful living anionic polymerization of HIC has been achieved by using only low reactivity initiators such as sodium benzanilide (Na-BA) or sodium benzhydroxide (Na-BH) that serve the dual functions of controlled initiation and chain-end protection.^{18,19}

Building on the successful achievement of living anionic polymerization of HIC, we have sought to establish novel synthetic methods to prepare well-defined functional block copolymers containing HIC blocks. The anionic block copolymerization of styrene (S) and 2-vinylpyridine (2VP) with HIC was successfully carried out in the presence of NaBPh₄, which prevents side reactions during the polymerization of HIC by changing the counteraction from K⁺ to Na⁺ (Chart 1(a) and (b)).^{20,21} In these cases, the block copolymerization had to be carried out by sequential addition of the vinyl monomer as the first monomer and HIC as the second monomer due to very low reactivity of living PHIC, which generally cannot initiate polymerization of vinyl monomers. This strategy led to well-defined block copolymers such as PHIC-*b*-PS-*b*-PHIC and P2VP-

⁵⁵ *b*-PHIC, showing controlled molecular weights (M_n) and narrow molecular weight distributions (M_w/M_n).

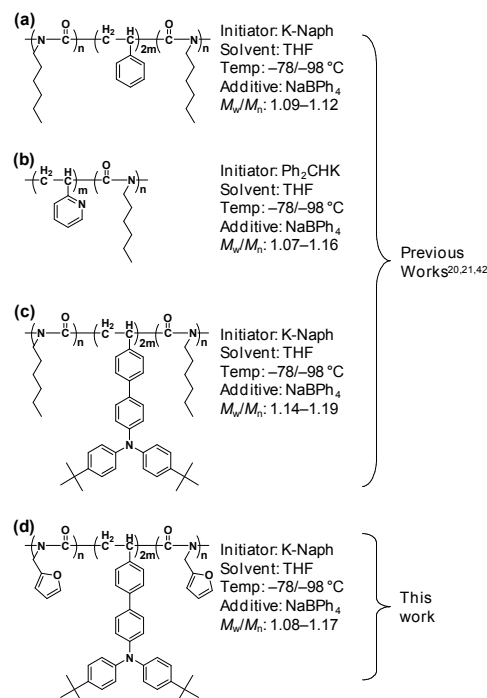


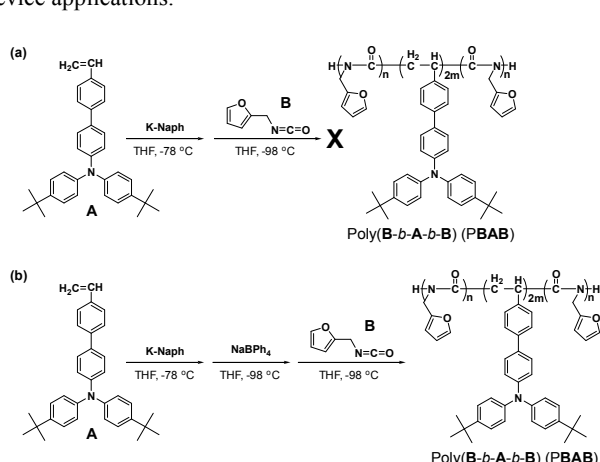
Chart 1. Summary of synthetic conditions for block copolymerization of functional vinyl monomers with isocyanate derivatives.

Recently, we succeeded in synthesizing the well-defined polyisocyanate block copolymer, poly(furfuryl isocyanate)-*b*-poly(*n*-hexyl isocyanate) (PFIC-*b*-PHIC), via living anionic polymerization.²² The PFIC block containing furan groups was

Polymer Chemistry Accepted Manuscript

functionalized via Diels-Alder (DA) reaction and self-assembly behavior of the functionalized PFIC-*b*-PHIC was subsequently investigated. From the viewpoint of post-polymerization modification of block copolymers, furan (diene) is an interesting functional group due to its utility in the DA reaction with maleimide groups (dienophile).²³⁻³³ The DA reaction is an attractive synthetic tool to enhance the versatility and applications of block copolymers. In particular, this [4+2] cycloaddition reaction between a diene and a dienophile is a thermally reversible process, and therefore cross-linked polymeric products prepared via the DA reaction can be used for self-healing applications.³⁰⁻³³

Anionic polymerization is the most powerful polymerization technique for precision synthesis of block copolymers. From the synthetic point of view, successful living anionic polymerization of functional monomers allows preparation of well-defined block copolymers with various functionalities.³⁴⁻³⁷ For example, the living character of 4,4'-vinylphenyl-*N,N*-bis(4-*tert*-butylphenyl)benzenamine (**A**) provides us with many opportunities to synthesize controlled functional block copolymers for a variety of applications.³⁸⁻⁴³ Thermally cross-linkable block copolymers, poly(4-ethynylstyrene)-*b*-poly(**A**)-*b*-poly(4-ethynylstyrene) and poly(**A**)-*b*-poly(4-ethynylstyrene), have been synthesized as an alternative hole-transporting layer to PEDOT:PSS in polymer light-emitting diodes and an active layer of the memory device. The block copolymers containing conducting and insulating components, poly(2-(2-(4-vinylphenyl)ethynyl)pyridine)-*b*-poly(**A**)-*b*-poly(2-(2-(4-vinylphenyl)ethynyl)pyridine) and PHIC-*b*-poly(**A**)-*b*-PHIC (Chart 1(c)), have also been prepared for use in polymer memory device applications.



Scheme 1. Block copolymerization of **A** with **B** using K-Naph in the (a) absence and (b) presence of NaBPh₄ in THF at -78 and -98 °C.

To the best of our knowledge, block copolymers containing reactive furan groups synthesized by anionic polymerization have not been explored yet in the formation of thermoreversible networks via the DA reaction. In this study, we report on the anionic synthesis of well-defined block copolymers containing pendent triphenylamine and furan, and formation of thermoreversible network via the DA reaction. Furfuryl isocyanate (**B**) was chosen as a co-monomer for **A** in order to introduce furan groups into the block copolymers. The block copolymerization of **A** with **B** was carried out in the presence of NaBPh₄ to successfully synthesize well-defined poly(**B**-*b*-**A**-*b*-**B**) (PBAB) (Chart 1(d)). It will be shown that addition of NaBPh₄ significantly influences anionic block copolymerization behavior

under the reaction conditions employed here. In addition, thermoreversible properties of cross-linked PBAB formed via the DA reaction with bismaleimide were investigated.

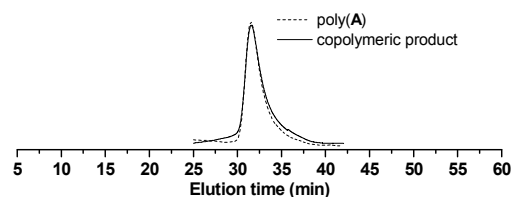


Figure 1. SEC curves of polymeric products obtained from the block copolymerization of **A** with **B** using K-Naph in the absence of NaBPh₄.

Experimental section

Materials

4,4'-Vinylphenyl-*N,N*-bis(4-*tert*-butylphenyl)benzenamine (**A**) and K-Naph were prepared based on literature methods.^{38,44} Furfuryl isocyanate (**B**, Aldrich, 97%) was dried overnight over CaH₂, distilled under reduced pressure, and finally distilled from CaH₂ on a vacuum line into ampules equipped with break-seals. Sodium tetraphenylborate (NaBPh₄, Aldrich, 99.5%) was dried under high vacuum with stirring at 80 °C for 3 days. The monomers, K-Naph and NaBPh₄ were diluted with tetrahydrofuran (THF) and divided into ampules equipped with break-seals. All ampules were stored at -30 °C before use.

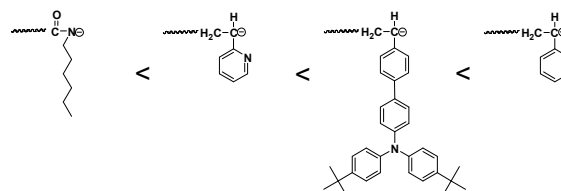


Figure 2. Nucleophilicity order of various living polymers.

Measurements

¹H NMR spectra were obtained using CDCl₃ as solvent at 25 °C (JEOL JNM-ECX400). The chemical shifts are in reference to tetramethylsilane (TMS) at 0 ppm. The polymers were analyzed by size exclusion chromatography (SEC, Waters M77251, M510) with 4 columns (HR 0.5, HR 1, HR 3, and HR 4, Waters Styragel) columns run in series; the pore sizes of the columns are 50, 100, 10³, and 10⁴ Å, respectively). The molecular weight distributions of the polymers were estimated by using SEC calibration with polystyrene standards (American Polymer Standards Corp.) using THF containing 2% triethylamine as the eluent at 40 °C. FT-IR (Perkin-Elmer, Inc., version 5.0.1 spectrometer) was used to characterize block copolymers and cross-linked polymers. The block copolymer solution in chloroform was cast over a KBr cell. The cross-linked polymer, insoluble in chloroform, was ground with KBr and then a pellet was formed under pressure. FT-IR spectra were recorded over the range of 4000–400 cm⁻¹. The thermal stability of the block copolymers was investigated using thermogravimetric analysis (TA Instruments, TGA-Q50) at a heating rate of 10 °C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analyses of block copolymers and cross-linked polymers were conducted with a TA Instruments DSC-Q20 unit at a heating rate of 20 °C/min under a nitrogen atmosphere.

Table 1. Block copolymerization of **A** with **B** using K-Naph in THF in the presence of NaBPh₄.

sample	K-Naph mmol	monomer		NaBPh ₄ mmol	block copolymer (homopolymer)		M_w/M_n^c	$f_{\text{poly(A)}}^d$
		1 st , mmol	2 nd , mmol		$M_n \times 10^{-3}$			
					calcd ^a	obsd ^b		
PBAB1	0.0710	A , 0.669	B , 1.87	0.251	15.3 (8.7)	18.7 (9.8)	1.17 (1.12)	0.23
PBAB2	0.0915	A , 1.46	B , 1.17	0.323	17.9 (14.7)	19.5 (16.4)	1.08 (1.08)	0.58

^a $M_n(\text{calcd}) = (\text{molecular weight of monomer}) \times [\text{monomer}] \times 2 / [\text{initiator}]$. ^b M_n of the block copolymer was determined by using M_n of the homopolymer and the molar ratio of each block estimated by ¹H NMR. ^c M_w/M_n was determined by using SEC calibration with PS standards using THF containing 2% triethylamine as the eluent at 40 °C. ^d Determined by ¹H NMR.

5 Block copolymerization in the absence of NaBPh₄

All block copolymerizations were conducted in an all-glass apparatus equipped with break-seals under high vacuum. The first-stage polymerization of **A** was carried out with K-Naph in THF at –78 °C for 0.5 h. After sampling poly(**A**), **B** was added to the living poly(**A**) solution at –98 °C, and the reaction was maintained at –98 °C for 0.5 h. The polymerizations were terminated with methanol and then poured into a large excess of methanol to obtain poly(**A**) and the copolymer product.

Block copolymerization in the presence of NaBPh₄

The first-stage polymerization of **A** was performed using K-Naph in THF at –78 °C for 0.5 h and NaBPh₄ was subsequently added to the living poly(**A**) solution at –98 °C after sampling a portion of the living poly(**A**). Then, addition of **B** was carried out at –98 °C and allowed to react with the living poly(**A**) solution. The reaction was maintained at –98 °C for 0.5 h. The polymerizations were terminated with methanol and then poured into a large excess of methanol to afford poly(**A**) and poly(**B-b-A-b-B**) (PBAB). The resulting block copolymer was quantitatively obtained and characterized by means of SEC and ¹H NMR. PBAB ($M_n(\text{obsd}) = 19,500 \text{ g/mol}$, $M_w/M_n = 1.08$ (Table 1, PBAB2)). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.12\text{--}2.15$ ($\text{CH}_2\text{--CH}$ and *tert*-butyl group of **A** block), 4.80 ($\text{C--CH}_2\text{--N}$ of **B** block), 6.04 ($=\text{CH--CH}=\text{}$ in furfuryl group of **B** block), 6.20 ($=\text{CH--CH}=\text{}$ in furfuryl group of **B** block), 6.32–7.39 (O--CH in furfuryl group of **B** block and phenyl group of **A** block).

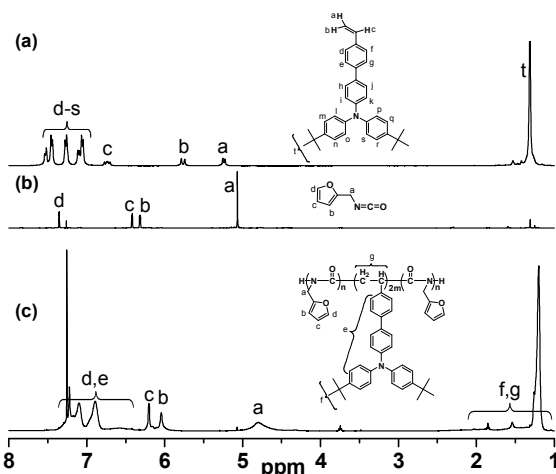


Figure 3. ¹H NMR spectra of (a) **A**, (b) **B** and (c) PBAB in CDCl₃.

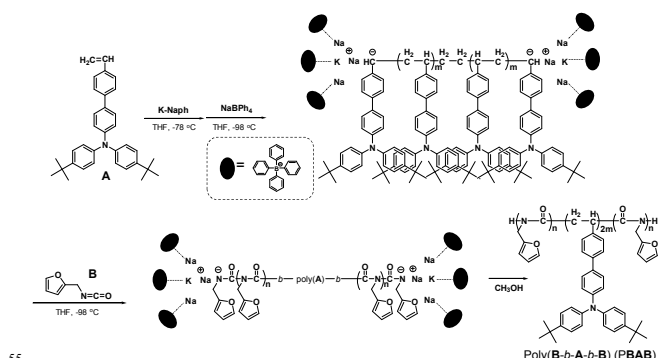
35 Cross-linking via Diels-Alder reaction

PBAB2 block copolymer and 1,1-(methylenedi-4,1-phenylene)bismaleimide (BM) were dissolved in chloroform in a 25 ml two neck round-bottom flask. The mixture was stirred at 50 °C for 24 h under a nitrogen atmosphere. The reaction mixture was then cooled to room temperature, and the solvent was removed by evaporation in a vacuum oven at 50 °C to obtain the cross-linked polymer (PBAB2-BM). The resulting cross-linked polymer was characterized by FT-IR and DSC.

Results and discussion

45 Block copolymerization

From the synthetic viewpoint, successful living anionic polymerization of **A** allows various block copolymers to be precisely synthesized via sequential anionic block copolymerization with functional monomers. Here, a functional isocyanate derivative, **B**, was selected as a co-monomer in order to prepare well-defined block copolymers containing furan groups, which can be used to form thermoreversible networks via the DA reaction.



Scheme 2. Synthetic mechanism of PBAB in the presence of NaBPh₄.

The block copolymerization was performed by sequential addition of **A** as the first monomer and **B** as the second monomer using K-Naph as initiator in THF at –78 and –98 °C (Scheme 1(a)). The polymerization solution changed to deep violet after adding **A** to the dark green K-Naph initiator solution at –78 °C. However, the deep violet color immediately disappeared when **B** was added to the living poly(**A**) solution at –98 °C. The colorless solution was maintained at –98 °C for 0.5 h. After terminating the polymerization, it was verified by SEC that no block

copolymerization occurred. The SEC curve of the final product was identical to that of the starting poly(A). As shown in Figure 1, the two curves essentially overlap. In general, the absence of second-stage polymerization reflects that the polymerization of the second monomer cannot be initiated by living polymer derived from the first monomer.⁴⁵⁻⁴⁷ However, in this case, failure of **B** to polymerize cannot be attributed to low reactivity of living poly(A) because it has been confirmed that the chain-end carbanion of poly(A) is more reactive than the amidate anion of polyisocyanate (Figure 2).^{20,21,38,42} Accordingly, it appears that an undesirable side reaction took place when **B** was added to the living poly(A) solution. As to the nature of this side reaction, we propose the direct attack of the chain-end carbanion of poly(A) on the reactive furan groups of **B**, resulting in no second-stage polymerization due to living poly(A) being terminated by **B**. The experimental observations such as immediate disappearance of the unique color of the living poly(A) solution after addition of **B**, the identical nature of the SEC curves of poly(A) and the copolymer product, and quantitative recovery of **B** after the block copolymerization support the side reaction proposed. Therefore, these findings indicate that the block copolymerization of **A** with **B** cannot be successfully carried out under the synthetic conditions employed above.

On the basis of our previous investigations on precise synthesis of block copolymers containing HIC blocks, such as PHIC-*b*-PS-*b*-PHIC, P2VP-*b*-PHIC and PHIC-*b*-poly(A)-*b*-PHIC, we decided to introduce NaBPh₄ additive prior to addition of **B** in order to prevent the termination reaction observed in the previous section. The block copolymerization was carried out by sequential addition of **A** as the first monomer and **B** as the second monomer using K-Naph as initiator in THF at -78 and -98 °C in the presence of NaBPh₄, as shown in Scheme 1(b). Excess NaBPh₄ was added to the living poly(A) solution at -98 °C after completion of the polymerization of **A**, and **B** was subsequently added to the polymerization solution at the same temperature. When **B** was added, the solution color immediately changed from deep violet to pale yellow (Figure S1 in Supporting Information). The final solution color (pale yellow) was maintained for an additional 0.5 h until termination. This change in polymerization solution color indicates that amidate anions derived from **B** were successfully formed.

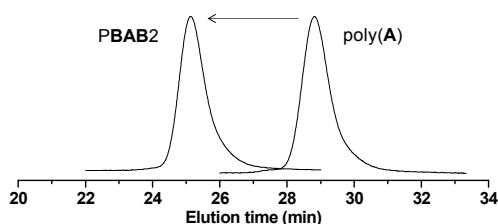
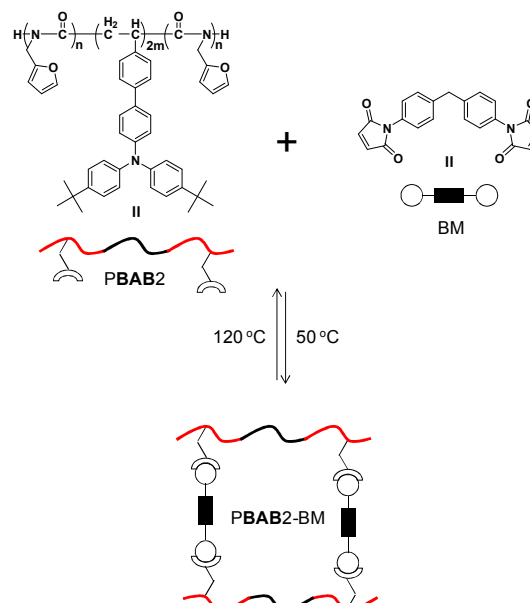


Figure 4. SEC curves of poly(A) and PBAB2.

The ¹H NMR spectra of **A**, **B** and PBAB indicate that block copolymerization of **A** with **B** was successful. Figure 3 shows the broad characteristic peaks of *tert*-butyl and phenyl groups of the **A** block and the furfuryl group of the **B** block. The peaks corresponding to the vinyl group of **A** completely disappeared after the polymerization. The characterization results shown in Figure 4 and Table 1 indicate that the desired block copolymers were obtained. Well-defined block copolymers with controlled M_n (18,700–19,500 g/mol) and narrow M_w/M_n (1.08–1.17) were quantitatively synthesized under the polymerization conditions employed. For example, the block copolymerization was successfully performed in the presence of NaBPh₄ (Table 1, PBAB2). The observed M_n (19,500 g/mol) of PBAB2 was in

good agreement with the calculated one (17,900 g/mol). In addition, the narrow SEC curve of PBAB2 was unimodal ($M_w/M_n = 1.08$) and clearly shifted from poly(A) to higher M_n region, as shown in Figure 4. These results clearly demonstrate that polymerization of **B** can be initiated by living poly(A) without undesirable side reactions, provided NaBPh₄ is added to change the counteraction from K⁺ to Na⁺, as proposed in Scheme 2. In other words, NaBPh₄ plays an important role in the successful block copolymerization of vinyl monomers with furan-containing isocyanates as well as hexyl-containing isocyanates.



Scheme 3. Synthesis of thermoreversible PBAB2-BM via DA reaction.

Cross-linking via Diels-Alder reaction

The DA reaction of PBAB2 with BM was carried out in order to prepare cross-linked polymers (PBAB2-BM), as shown in Scheme 3. In this DA reaction, it was anticipated that the furan group of PBAB2 and the maleimide group of BM would act as diene and dienophile, respectively. The reaction solution of PBAB2 and BM (1:1 molar ratio) dissolved in chloroform was stirred at 50 °C for 24 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and PBAB2-BM was isolated. It was observed that the viscosity of the reaction solution increased during the DA reaction.

The formation of PBAB2-BM was verified by FT-IR analysis (Figure 5). FT-IR spectrum of PBAB2 showed a specific peak at 1012 cm⁻¹, which is attributed to the breathing of the furan ring of PBAB2 (Figure 5(a)).²⁵ This serves as additional evidence that the reactive furan group of **B** was not attacked by the chain-end carbanion of living poly(A) in the presence of NaBPh₄, confirming that well-defined block copolymers containing furan groups were successfully synthesized under the polymerization conditions employed in this study. As shown in Figure 5(b), the peak at 1012 cm⁻¹ disappeared after the DA reaction, suggesting that the furan group of PBAB2 took part in the formation of PBAB2-BM. Furthermore, the presence of a peak at 1775 cm⁻¹, ascribed to furan-maleimide cycloadduct, supports the successful formation of PBAB2-BM via the DA reaction between furan and maleimide.²⁷⁻³⁰ The formation of PBAB2-BM was also proved by comparison of glass transition temperature (T_g) between PBAB2 and PBAB2-BM. The T_g of PBAB2-BM was estimated to be as

high as 120 °C from the second heating cycle, as shown in Figure 6(c). This is almost 30 °C higher than the T_g of PBAB2 (Figure S2 in Supporting Information). Such a large increase in T_g demonstrates that PBAB2 was cross-linked with BM, causing a reduction in chain mobility.

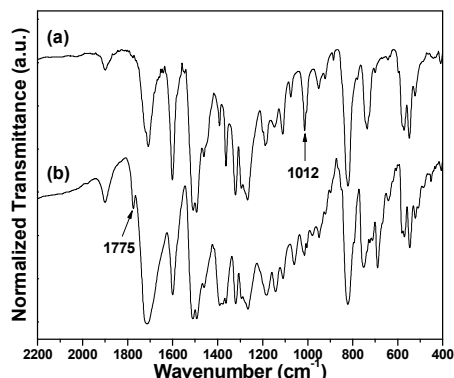


Figure 5. FT-IR spectra of (a) PBAB2 and (b) PBAB2-BM.

Thermoreversible properties of the cross-linked polymer

DSC was used to characterize the thermoreversible properties of PBAB2-BM, as shown in Figure 6. The first heating curve exhibits an intense endothermic peak at 149 °C, indicating the cleavage of PBAB2-BM via a retro-DA (rDA) reaction (Figure 6(a)). Figure 6(b) shows the cooling curve with a broad exothermic peak at 112–163 °C, which is due to the formation of covalent bonds via the DA reaction between furan and maleimide. The second heating curve shows the same curve as observed in the first heating cycle (Figure 6(c)). Therefore, the DSC results clearly show that PBAB2-BM formed via the DA reaction reported herein is thermoreversible.

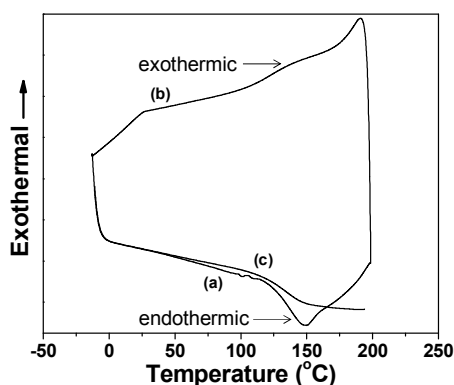


Figure 6. DSC thermograms of PBAB2-BM: (a) first heating curve, (b) cooling curve and (c) second heating curve.

In addition to DSC analysis, the thermoreversible properties of PBAB2-BM were directly observed by solubility testing. As shown in Figure 7, the solubility of PBAB2-BM was investigated in toluene at 30 and 120 °C. While PBAB2-BM cross-linked polymer was not soluble in toluene at 30 °C (Figure 7(a)), PBAB2-BM became soluble when heated at 120 °C for 10 min due to bond cleavage between furan and maleimide moieties via a rDA reaction (Figure 7(b)). When the polymer solution was again heated at 50 °C for 24 h, after the solvent was removed from the solution it was observed that the cross-linked polymer reformed via the DA reaction (Figure 7(c)). Addition of toluene again showed that the reformed PBAB2-BM was insoluble at 30 °C

(Figure 7(d)). Thus, the solubility testing results also strongly support the thermoreversible characteristics of PBAB2-BM.

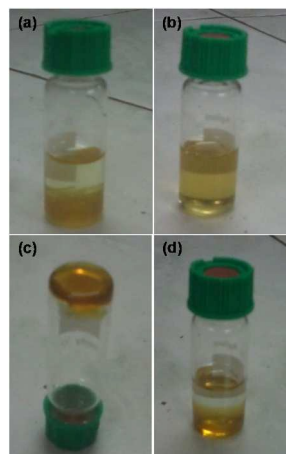


Figure 7. Solubility testing of PBAB2-BM: (a) PBAB2-BM insoluble in toluene at 30 °C, (b) PBAB2-BM soluble in toluene when heated 120 °C for 10 min, (c) PBAB2-BM reformed when soluble polymer was heated 50 °C for 24 h and (d) PBAB2-BM insoluble in toluene at 30 °C.

Conclusions

Well-defined block copolymers containing furan groups were anionically synthesized without side reactions and subsequently used for the formation of thermoreversible networks via a Diels-Alder click reaction. It was found that NaBPh₄ plays an important role in the successful synthesis of the block copolymer. This additive changes the counteraction from K⁺ to Na⁺, allowing the living anionic polymerization of B. The synthesis of a well-defined block copolymer results from the use of K⁺ and Na⁺ as the counteraction for the polymerization of A and B, respectively. The resulting block copolymer was shown to form thermoreversible networks via a Diels-Alder reaction with bismaleimide. The thermoreversible properties of the cross-linked polymer were clearly observed by use of DSC and solubility testing. For further work, it is expected from this study that different mid blocks can be introduced into triblock copolymers with furan-containing end blocks in order to create various functional block copolymers having self-healing characteristics.

Acknowledgements

This work was supported by the GIST-Caltech Research Institute Program at GIST. J.M. and B.-G.K acknowledge support by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Material Sciences and Engineering Division. N.B.P. is grateful to UGC, New Delhi, India for providing the Fellowship. N.K.S is thankful to USIEF for providing the Senior Fulbright Fellowship.

Notes and references

- (1) M. Goodman and S. Chen, *Macromolecules*, 1970, **3**, 398.
- (2) M. Goodman and S. Chen, *Macromolecules*, 1971, **4**, 3625.
- (3) S. M. Aharoni and E. K. Walsh, *Macromolecules*, 1979, **12**, 271.
- (4) M. Mtiller and R. Zentel, *Macromolecules*, 1994, **27**, 4404.
- (5) K. Maeda and Y. Okamoto, *Macromolecules*, 1998, **31**, 1046.

- (6) P. V. Shibaev, K. Tang, A. Z. Genack, V. Kopp and M. M. Green, *Macromolecules*, 2002, **35**, 3022.
- (7) G. Y. Nath, S. Samal, S.-Y. Park, C. N. Murthy and J.-S. Lee, *Macromolecules*, 2006, **39**, 5965.
- 5 (8) J.-H. Kim, M. S. Rahman, J.-S. Lee and J.-W. Park, *J. Am. Chem. Soc.*, 2007, **129**, 7756.
- (9) J.-H. Kim, M. S. Rahman, J.-S. Lee and J.-W. Park, *Macromolecules*, 2008, **41**, 3181.
- (10) P. N. Shah, J. Min, H.-J. Kim, S.-Y. Park and J.-S. Lee, *Macromolecules*, 2011, **44**, 7917.
- 10 (11) P. N. Shah, C.-G. Chae, J. Min, R. Shimada, T. Satoh, T. Kakuchi and J.-S. Lee, *Macromolecules*, 2014, **47**, 2796.
- (12) V. E. Shashoua, *J. Am. Chem. Soc.*, 1959, **81**, 3156.
- (13) Y. Okamoto, Y. Nagamura, K. Hatada, C. Khatri and M. M. Green, *Macromolecules*, 1992, **25**, 5536.
- 15 (14) C.A. Khatri, M. M. Vaidya, K. Levon, S. K. Jha and M. M. Green, *Macromolecules*, 1995, **28**, 4719.
- (15) J. Wang, R. Nomura and T. Endo, *Chem. Lett.*, 1996, **10**, 909.
- 20 (16) J.-S. Lee and S.-W. Ryu, *Macromolecules*, 1999, **32**, 2085.
- (17) Y.-D. Shin, S.-Y. Kim, J.-H. Ahn and J.-S. Lee, *Macromolecules*, 2001, **34**, 2408.
- (18) J.-H. Ahn, Y.-D. Shin, G. Y. Nath, S.-Y. Park, M. S. Rahman, S. Samal and J.-S. Lee, *J. Am. Chem. Soc.*, 2005, **127**, 4132.
- 25 (19) J. Min, P. N. Shah, J.-H. Ahn and J.-S. Lee, *Macromolecules*, 2011, **44**, 3211.
- (20) J.-H. Ahn and J.-S. Lee, *Macromol. Rapid Commun.*, 2003, **24**, 571.
- 30 (21) Y.-D. Shin, S.-H. Han, S. Samal and J.-S. Lee, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 607.
- (22) J. Min, P. N. Shah, C.-G. Chae and J.-S. Lee, *Macromol. Rapid Commun.*, 2012, **33**, 2029.
- (23) A. A. Kavitha and N. K. Singha, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 4441.
- 35 (24) A. A. Kavitha and N. K. Singha, *Macromol. Chem. Phys.*, 2007, **208**, 2569.
- (25) A. A. Kavitha and N. K. Singha, *Macromolecules*, 2010, **43**, 3193.
- 40 (26) A. Gandini, *Prog. Polym. Sci.*, 2013, **38**, 1.
- (27) Q. Tian, M. Z. Rong, M. Q. Zhang and Y. C. Yuan, *Polymer*, 2010, **51**, 1779.
- (28) C.-D. Varganici, O. Ursache, C. Gaina, V. Gaina, D. Rosu and B. C. Simionescu *Ind. Eng. Chem. Res.*, 2013, **52**, 5287.
- 45 (29) T. Engel and G. Kickelbick, *Chem. Mater.*, 2013, **25**, 149.
- (30) Y. Imai, H. Itoh, K. Naka and Y. Chujo, *Macromolecules*, 2000, **33**, 4343.
- (31) X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran and F. Wudl *Science*, 2002, **295**, 1698.
- 50 (32) X. Chen, F. Wudl, A. K. Mal, H. Shen and S. R. Nutt, *Macromolecules*, 2003, **36**, 1802.
- (33) P. Du, M. Wu, X. Liu, Z. Zheng, X. Wang, T. Joncheray and Y. Zhang, *J. Appl. Polym. Sci.*, 2014, **131**, 40234.
- (34) B.-G. Kang, N.-G. Kang and J.-S. Lee, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 5199.
- 55 (35) T. Higashihara and M. Ueda, *Macromolecules*, 2009, **42**, 8794.
- (36) Y. Kosaka, K. Kitazawa, S. Inomata and T. Ishizone, *ACS Macro Lett.*, 2013, **2**, 164.
- 60 (37) S. Tanaka, R. Goseki, T. Ishizone and A. Hirao, *Macromolecules*, 2014, **47**, 2333.
- (38) B.-G. Kang, N.-G. Kang and J.-S. Lee, *Macromolecules*, 2010, **43**, 8400.
- (39) B.-G. Kang, H. Kang, N.-G. Kang, C.-L. Lee, K. Lee and J.-S. Lee, *Polym. Chem.*, 2013, **4**, 969.
- (40) B.-G. Kang, Y.-G. Yu, N.-G. Kang and J.-S. Lee, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 4233.
- (41) B.-G. Kang, S. Song, B. Cho, N.-G. Kang, M.-J. Kim, T. Lee, J.-S. Lee, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, **52**, 2625.
- 70 (42) B.-G. Kang, J. Jang, Y. Song, M.-J. Kim, T. Lee and J.-S. Lee, *Macromolecules*, 2014, **47**, 8625.
- (43) B.-G. Kang, J. Jang, Y. Song, M.-J. Kim, T. Lee and J.-S. Lee, *Polym. Chem.*, 2015, DOI: 10.1039/c5py00381d.
- 75 (44) K. Tsuda, T. Ishizone, A. Hirao, S. Nakahama, T. Kakuchi and K. Yokota, *Macromolecules*, 1993, **26**, 6985.
- (45) T. Ishizone, N. Sueyasu, K. Sugiyama, A. Hirao and S. Nakahama, *Macromolecules*, 1993, **26**, 6976–6984.
- (46) T. Ishizone, T. Utaka, T. Ishino, A. Hirao and S. Nakahama, *Macromolecules*, 1997, **30**, 6458–6466.
- 80 (47) T. Ishizone, G. Uehara, A. Hirao, S. Nakahama and K. Tsuda, *Macromolecules*, 1998, **31**, 3764–3774.

^a Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States

E-mail: jimmy@utk.edu

^b Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India

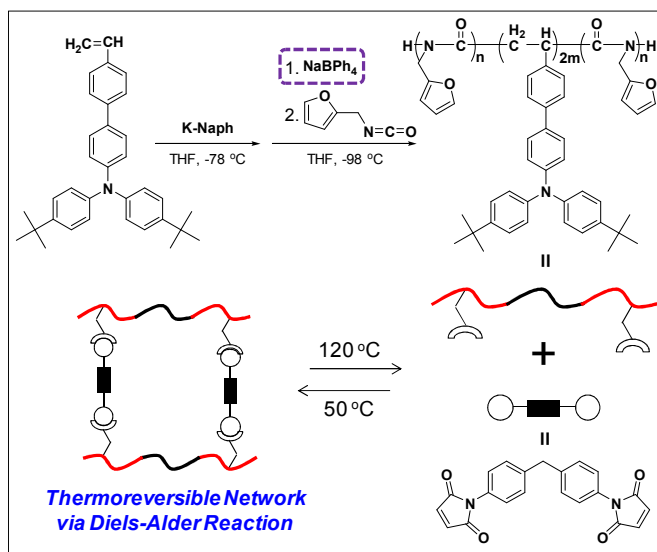
^c School of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), 123 Cheomdan-gwagiro, Buk-gu, Gwangju 500-712, Korea
E-mail: jslee@gist.ac.kr

Graphical Abstract

Title: Precise Synthesis of Thermoreversible Block Copolymers Containing Reactive Furfuryl Groups via Living Anionic Polymerization: Counteraction Effect on Block Copolymerization Behavior

Authors: Beom-Goo Kang, Nabendu B. Pramanik, Nikhil K. Singha, Jae-Suk Lee,* Jimmy Mays*

TOC graphic:



Well-defined block copolymers containing furan groups were anionically synthesized in the presence of NaBPh_4 and used for the formation of thermoreversible networks via a Diels-Alder click reaction.