

High Efficient Synthesis of Hydroxyl-Terminated Polybutadiene (HTPB) based Polyurethane via Microwave Heating

YONG WEN^{a,b}, NA TENG^a, FEI LIU^a, RUOYU ZHANG^a, HAIFANG WANG^b, JING CHEN^{a,1},
JIN ZHU^a AND HAINING NA^{a*}

^a*Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, P.R. China*

^b*School of Chemical and Environmental Engineering, North University of China, Shanxi, Taiyuan 030051, P. R. China*

ABSTRACT

In this work, we establish a facile and efficient method to synthesize the polyurethanes (PUs) containing hydroxyl-terminated polybutadiene (HTPB) through microwave-assisted reactions. Comparisons of conventional heat versus microwave reactions have been made. Microwave-assisted synthesis has been found to significantly decrease the reaction time and reduce side reaction of carbon-carbon bond relative to conventional heat. Moreover, we develop a more advanced molecular design for HTPB based PU ranging from content of hard segment to types of non-planer ring structures. The Characterization of the polymers has been conducted with FT-IR, TGA, thermal and mechanical analysis. Among them, single ring contained PU shows the highest properties. In this green and promising way, we can potentially expand the application areas for HTPB based PUs with high performances.

KEYWORDS : *Polyurethanes, Microwave, HTPB, Mechanical properties*

INTRODUCTION

Polyurethane (PU), as an important class of thermoplastics, is commonly synthesized by the catalyzed polymerization of diisocyanates (or polyisocyanates) with diols (or polyols). PU possesses a wide range of properties and is

the most commonly used material for high performance engineering applications.^[1-5] Hydroxyl-terminated polybutadiene (HTPB) is an important telechelic liquid rubber, which is widely used in the binder system of composite solid propellants.^[6, 7] Up to now, the introduction

J. Polym. Mater. Vol. **35**, No. 3, 2018, 355-369

© Prints Publications Pvt. Ltd.

Correspondence author e-mail : chenjing@nimte.ac.cn (J.Chen); nahaining@nimte.ac.cn

DOI : <https://doi.org/10.32381/JPM.2018.35.03.9>

of HTPB for the fabrication of PUs has been great developed, due to its unique hydrolytic stability, resistance to acids and alkalis, low temperature flexibility, high elongation with good elastic recovery, and others.^[8-12]

HTPB based PUs is the focus of much attention because it is an important character that can be assimilated into numerous fundamental and industrial applications, including solid composite propellants in space application, coatings, adhesives and sealants.^[13-17] It is well known that the soft segment structure of HTPB based PU contains carbon-carbon double bond, which can be further reacted with other monomers to produce cross-linking and graft products. It makes PU much strong, durable or diversity to possibly improve the practical application in the future. However, due to the existence of high amount carbon-carbon double bonds (particular the cis double bonds), HTPB based PUs are easy to react with each other and thus lead to failure in synthesis. Until today, it is still a great challenge to control the polymerization process of HTPB based PUs. From many references,^[18-20] it can be noticed that majority process of the synthesis of PU is operated by conventional heating. As we know, conventional heating mainly transfer heat energy through heat conduction and simple forced thermal convection. Due to the relative low efficiency, polymerization driven by conventional heating usually needs a long time. This process requires the carbon-carbon double bond inevitably remain in the environment with rather high temperature. Consequently, the side reaction between the carbon-carbon bonds in HTPB based PUs is unexpected to happen. Therefore, there is still

need to explore an alternative and reliable strategy to produce high quality PUs with sufficient efficiency, along with the ability to easily scale up in practice.^[21-22]

As we all known, microwave radiation can transfer energy directly to the reactant (converted into molecular energy) through the dipole rotation or ion conduction, which does not depend on the heat conductivity of the reaction vessel material. Therefore it has the ability to change the energy transmission in reaction system and thus leads to high efficiency and lower by-products generating.^[23-24] Understanding the significant advantage of microwave in synthesis, we plan to utilize microwave radiation to improve the reaction rate and shorten the reaction time during the synthesis of HTPB based PU. This reaction route is expected to be helpful to weaken the cross-linking of carbon-carbon double bond under the premise of ensuring the performance, and improve the successful rate of synthesis, which has not been reported in the literature before.

In our previous work, we introduced nonplanar ring structures into the hard segment of PUs, which displayed excellent shape recoverability and mechanical properties.^[25-27] Herein, we report a simple route for the synthesis of HTPB based PU. By combination of the microwave radiation and molecular design, the feasibility of preparation process with high speed and the control of overall performances of HTPB based PU is carefully investigated. Furthermore, compared to conventional heating method used in the preparation of HTPB based PUs, this method is green, cheap and promising for functional PU fabrication.

2. EXPERIMENTAL

Materials

4,4'-methylenebis(cyclohexyl isocyanate) (HMDI, purity of 90%), 1,4-bis(hydroxymethyl)cyclohexane (cis- and trans- mixture), (CHDM, 99% purity), 3,9-bis(2-cyanoethyl)-2,4,8,10-tetraxaspiro[5.5]undecane (SPG, purity of >98%), and bis(hydroxymethyl) tricyclo [5.2.1.0^{2,6}] decanetricyclodecanedimethanol (TDM, 90% purity) were purchased from TCI (Shanghai, China). The dibutylamine (purity of 99%) and 1,4-butanediol (purity of 98%) were obtained from Aladdin (Shanghai, China). Solvents such as methanol, chloroform, formyl dimethylamine (DMF), toluene, acetone and tetrahydrofuran of an analytical grade were also from Aladdin (Shanghai, China). Hydroxyl-terminated polybutadiene (HTPB) (with number average molecular weight of 1800g/mol) was provided by Zibo Qilong Chemical Industry Co., Ltd. (China) and dried under vacuum at 80°C over 2h for further use.). Rosin glycol was homemade.

Synthesis of PUs under microwave radiation and traditional heating

The PU is synthesized by two steps, as shown in Figure 1. The hard segment was formed by the reaction of 4,4'-methylenebis (HMDI) and chain extenders bearing a different number of nonplanar rings and no ring of 1, 4-butanediol (BDO). The hard segment of PUs was controlled in the range of 38-40wt%, 47-50wt%, 57-61wt%. The basic process is as follows: HTPB was heated in vacuum oven at 80°C for 2h to remove moisture. Then 7.2g HTPB, 40mL toluene, appropriate amount of HMDI and 1 drops of DBTDL were added to a round bottom flask of 250mL. The reaction system is heated up by microwave to 70°C in 4min and then remained this temperature about 40min to complete the synthesis of prepolymer. The amount of isocyanate (NCO) in pre-polymer was determined by titration with *N,N'*-dibutylamine after synthesis. The prepolymer was then reacted with equivalent chain extender at 80°C for 55min under vigorous stirring to form HTPB based PU with a high molecular weight. Completion of synthesis of polyurethane was determined by FTIR spectroscopy, which is known as the disappearance of an isocyanate peak at 2270cm⁻¹. After synthesis,

PU was purified by 500mL methanol. The resultant precipitate was then poured into a Teflon dish, and the solvent was evaporated for 24h in an oven at 60°C. Smooth films were obtained after drying of the samples under vacuum for 24h. Then the film is cut into a dumbbell shaped strip according to the national standard after being fully dried.

Comparisons have been made with products from both conventional and microwave heating, and they appear to have similar chemical structures. The process was carried out by a similar procedure found in previous work.^[25] 7.2g HTPB, 40mL toluene, appropriate amount of HMDI and 1 drops of DBTDL were added to a round bottom flask of 250mL. The reaction system is heated up to 70°C and then remained this temperature about 1.5h to complete the synthesis of prepolymer. Then the prepolymer was reacted with equivalent chain extender at 80°C for 4h under vigorous stirring to carry out the reaction.

Characterization

Fourier transform infrared (FTIR) characterization was performed on a Thermo Nicolet 6700 Fourier transform infrared spectrometer from Thermo-Fisher Scientific (USA), scanning from 500 to 4000cm⁻¹; 32 scans were collected for each sample. Tensile testing was performed on Instron 5985 apparatus (USA) with a deformation rate of 100mm·min⁻¹, and the sample was cut into dumbbell-shaped spline with the length of 35mm and width of 2mm. All the samples were tested to calculate mean values and standard deviation. Differential scanning calorimetry (DSC) thermograms were recorded on a METTLER TOLEDO-DSC 1 instrument (Switzerland). The samples (5-7mg) were heated from -40 to 100°C at 10°C·min⁻¹. The glass transition temperature (*T_g*) of soft segment and hard segment were determined from the scan. Thermogravimetric analysis (TGA) was carried out on a METTLER TOLEDO-TGA instrument (Switzerland). The temperature range of 50-800°C was tested with a heating rate of 20°C·min⁻¹ in flowing N₂ and a sample of 3-5mg. Dynamic mechanical analysis (DMA) was conducted with DMA Q800 instrument (USA) under a tensile mode with a dynamic strain of 0.5%. The frequency and heating rate were set as 1Hz and 3°C·min⁻¹, respectively. The sample size was

12mm×4mm×0.5mm. The number-average molecular weights (M_n) and weight-average molecular weights (M_w) were measured using a HLC-8320 GPC. Dimethyl

formamide (DMF) was used as mobile phase at a flow rate of 1 mL min⁻¹.

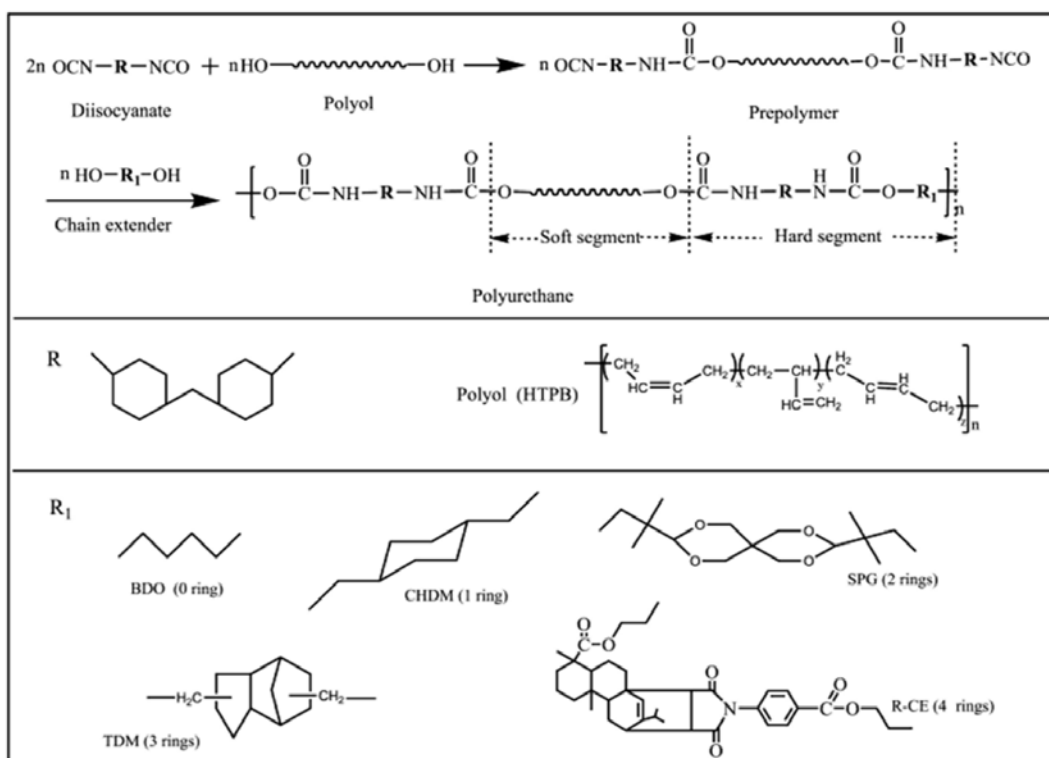


Fig. 1. Schematic diagram of PU synthesis of HTPB-based PU

RESULTS AND DISCUSSION

In the experiment, the reaction rates respectively driven by microwave radiation and conventional heating are studied with emphasis. As shown in Table 1, the heating rate between the two driven methods exists obvious difference. There shows a huge 20 times difference. As to the product, the time to finish the synthesis of prepolymer driven by microwave radiation only needs 40min. It is much faster than the reaction time of the

synthesis driven by conventional heating. Furthermore, in the stage of chain extension, the reaction rate of microwave radiation is three times faster than conventional heating. That is to say, the reaction rate of the whole process of synthesis driven by microwave radiation is obviously faster than that of conventional heating. This phenomenon is basically similar with report shown in previous literature.^[21-22] The utilization of microwave radiation provides a rapid way to improve the reaction rate of the synthesis of HTPB based PU.

TABLE 1. Comparison between microwave radiation and conventional heating

	Heating rate	Synthesis of prepolymer	Stage of chain expansion	Yield (%)	Molecular weight (M_n) $\times 10^4$
Microwave radiation	20°C/min	40min	less than 1h	65-70	1.0-1.5
Conventional heating	2°C/min	more than 1h	more than 3h	45-50	0.8-1.0

The chain composition and mechanical property are also important for HTPB based PU. As shown in Table 2, there is almost no difference with the content of hard segment in various HTPB based PUs, which are respectively synthesized by microwave radiation and conventional heating. As to the mechanical properties, the Young's modulus of PUs

synthesized by microwave radiation is somewhat lower than the PUs obtained from conventional heating, but the tensile strength and elongation is equal and even a little higher. In general, there is no large difference between the two types of PUs. Even to some extent, the PU obtained with microwave radiation shows relative high toughness.

TABLE 2. Comparison of mechanical properties of HTPB-based PU obtained by the method of microwave radiation and conventional heating (Test at 8-10°C)

Samples	-OH ^a	HS ^b (wt %)	E (MPa)	σ^d (MPa)	ϵ^e (%)
PU2	CHDM	39	12.7 \pm 0.8	9.1 \pm 0.7	1135.6 \pm 20.0
PU7	CHDM	51	99.7 \pm 4.1	18.2 \pm 1.4	518.3 \pm 8.5
PU12	CHDM	59	250.2 \pm 26.1	24.5 \pm 0.8	408.3 \pm 21.4
PU2C	CHDM	41	20.0 \pm 1.4	8.2 \pm 0.6	645.7 \pm 18.9
PU7C	CHDM	48	120.0 \pm 12.1	15.8 \pm 0.4	565.6 \pm 17.5
PU12C	CHDM	62	305.5 \pm 7.5	26.1 \pm 0.8	315.0 \pm 38.7

^aChain extender. ^bHard segment content (wt %) = $(W_{\text{diisocyanate}} + W_{\text{BDO}})/(W_{\text{HTPB}} + W_{\text{diisocyanate}} + W_{\text{BDO}})$. ^cYoung's modulus. ^dTensile strength. ^eElongation. As a control sample, the symbol "PU-C" is used to represent the HTPB based PU obtained by conventional heating.

Figure 2 further gives the infrared absorption peak of HTPB based PUs. The spectra match well with the spectra of classical polyurethane and the HTPB. For PU, the absorption peaks of carbon carbon double bonds, occurred at 966 cm^{-1} , 911 cm^{-1} and 995 cm^{-1} , which obtained by microwave radiation is stronger than the PU synthesized by conventional heating. This evidence further confirms microwave radiation driven synthesis can effectively reduce side reaction of carbon-carbon double bond.

Conversion calculation of HTPB and isocyanato is referred to our previous work [28]. Conversion of HTPB is calculated by the NCO content in prepolymer which is determined by titration with di(nbutyl) amine. Conversion of in the second step is determined by NCO peak which is located at 2270 cm^{-1} on the Fourier transform infrared spectra. The corresponded results are showed in Figure 3. Compared with traditional heating method, synthesis driven by microwave irradiation significantly promotes the rate of

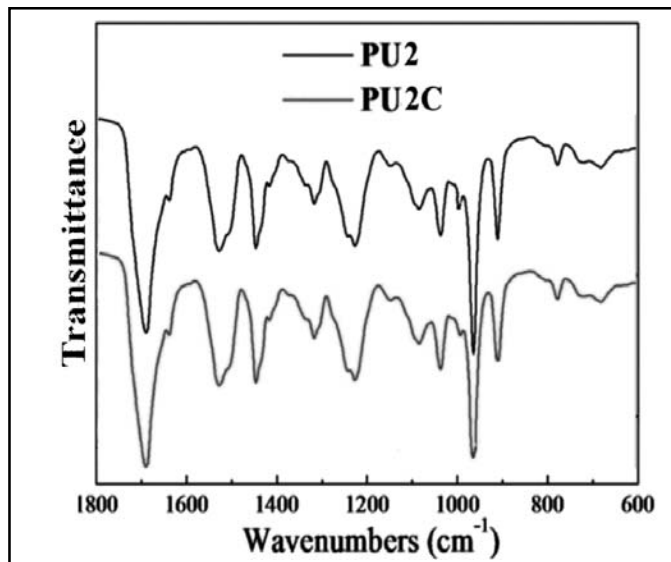


Fig. 2. The FT-IR spectra of PU2 and PU2C

polymerization especially when the reaction is closed to completion.

In summary, through the investigation of reaction rate, molecular composition and mechanical properties, the introduction of microwave radiation in the synthesis of HTPB based PU exhibits rather higher efficiency and better effect rather than conventional heating. With the use of microwave radiation in our experiment, a high efficient way to synthesize HTPB based PU is established.

Under microwave radiation, content of hard segment and type of nonplanar ring as the two important regulatory parameters are respectively introduced in synthesis. Table 3 gives the mechanical properties of PUs. With the hard segment of 40%, the introduction of non-planer ring in the molecular structure of PU produces better mechanical properties only except the rosin ring. And PU contained one

ring in its molecular structure shows the highest Young's modulus and tensile strength. Also, its elongation is over 530%. Consequently, it shows the best overall mechanical properties. After increase of the hard segment in PUs to 50% and 60%, majority nonplaner rings also show the constructive contribution to the mechanical properties of PU. The PUs with ring 1-3 all exhibit rather good overall mechanical properties. Around them, the PU with one ring in its molecular structure maintains the highest Young's modulus and tensile strength. Not only that, the elongation respectively reaches to $365.4 \pm 15.5\%$ and $250.3 \pm 10.3\%$. These results tell us, no matter how much the hard segment exists in the molecular chain of PU, the introduction of non-planer ring is very helpful to improve overall properties. Particularly, the single ring is the most suitable to initiate high Young's modulus and tensile strength of HTPB based PU. But, too large ring structure such

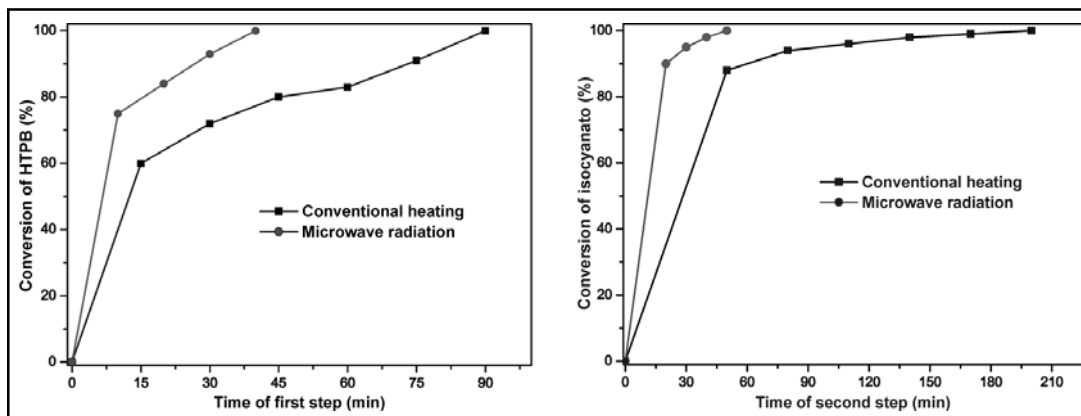


Fig. 3. Conversion speed of HTPB in the first step and conversion of isocyanato in the second step, respectively.

as rosin ring is not helpful to improve mechanical properties. In addition, the experimental data also shows that the higher content of hard segment induces larger rigidity of HTPB based PU. As shown in Table 3, with the increase of hard segment from 40% to 50% even 60% in PU, the Young's modulus obviously increases, and the elongation significantly decreases.

The TGA curves of all the PUs obtained with different content of hard segment are shown in Figure 4. It clearly shows that the PUs undergo thermal degradation in more than one stage. The thermal degradation of PUs starts at around 230-240°C and then follows with another weight loss at around 350-400°C. The above degradation observed at

TABLE 3. Composition and mechanical properties of PUs (Test at 8-10°C)

Samples	-OH ^a	HS ^b (wt %)	HBA (%)	E ^c (MPa)	σ ^d (MPa)	ε ^e (%)
1	BDO	39	58.5	26.1±0.7	9.9±0.3	605.3±11.7
2	CHDM	39	58.5	51.6±2.1	16.1±0.8	537.6±30.5
3	SPG	38	49.3	46.1±4.0	9.9±0.2	428.7±16.3
4	TDM	41	58.3	32.4±2.9	10.7±0.2	944.4±31.6
5	R-CE	37	48.5	4.3±0.4	3.6±0.1	1050±37.5
6	BDO	48	60.0	65.6±0.4	10.3±0.4	389.9±25.1
7	CHDM	48	60.9	150.7±5.9	13.7±1.1	365.4±15.5
8	SPG	49	66.3	72.1±2.2	11.5±0.5	170.8±5.9
9	TDM	48	60.3	39.7±2.0	7.7±0.4	440.3±15.1
10	R-CE	47	51.5	6.69±0.6	14.1±0.6	867.2±38.2
11	BDO	57	60.9	134.7±20.7	14.9±1.1	358.99±17.5

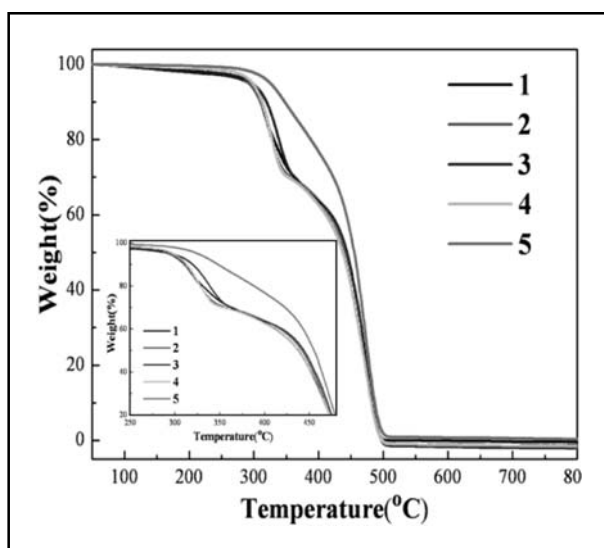
12	CHDM	59	61.6	232.4±24.4	17.9±0.4	250.3±10.3
13	SPG	58	70.7	109.3±7.9	10.7±0.4	90.7±7.8
14	TDM	59	60.7	170.1±10.5	11.1±1.8	221.9±11.7
15	R-CE	57	61.8	49.3±1.6	3.9±0.1	160.9±10.2

^aChain extender. ^bHard segment content (wt %) = $(W_{\text{diisocyanate}} + W_{\text{BDO}}) / (W_{\text{HTPB}} + W_{\text{diisocyanate}} + W_{\text{BDO}})$. ^cYoung's modulus. ^dTensile strength. ^eElongation. For example, PU1, 6, 11 indicate that the chain extender is BDO and the hard segment is 40%, 50%, 60% in turn. PU2-5 indicates that the hard segment is 40% and the chain extender is CHDM, SPG, TDM and R-CE. PU7-10 indicates that the hard segment is 50% and the chain extender is CHDM, SPG, TDM and R-CE. PU12-15 indicates that the hard segment is 60% and the chain extender is CHDM, SPG, TDM and R-CE.

similar range of temperature can be attributed to the decomposition of the labile urethane urea bonds. In fact, thermal stability of the PUs primarily depends upon the polyols and isocyanate structures. More than that, the rigidity of ring structure in chain extender can partially affect the thermal property of PU. Similar as the results shown in other research^[29-31], the change of chain extender will increase the initial decomposition temperature of polyurethane. Because of the relative stronger rigidity of rosin ring than that of BDO, CHDM, SPG, TDM in extender, it

probably leads to the increase of strong intermolecular force. As a result, it produces better thermal stability, so that RCE-based PUs exhibits higher thermal stability than other PUs.

DMA analysis is further operated to detect the other thermal properties of PUs and the results are summarized in Table 4. It is clear that all the PUs are elastic in nature with glass transition temperature (T_g) values of soft segment around -60°C . The T_g of soft segment value does not alter much with the change of the content in hard segment. There is a very



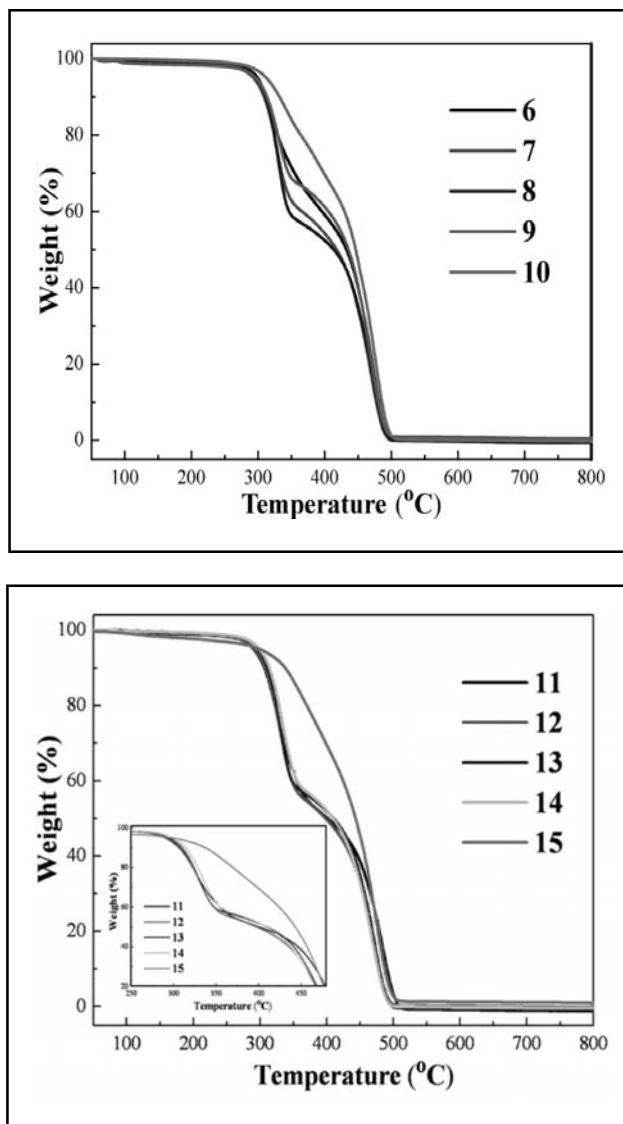


Fig. 4. TGA curves of PUs

small decrease in T_g values with increasing hard segment content in all of PUs.

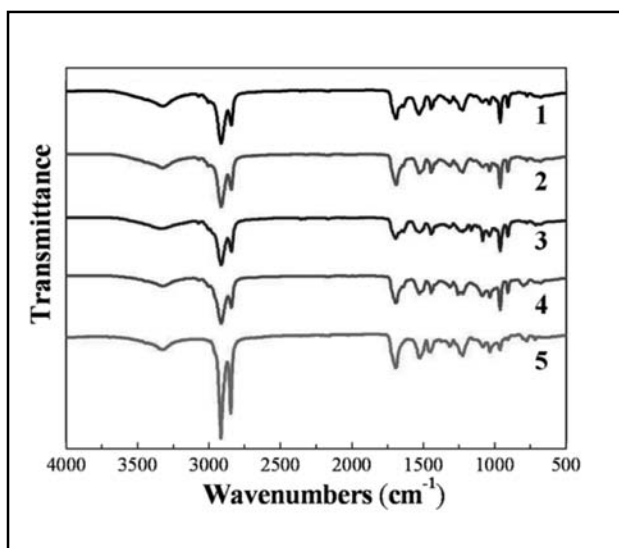
The FTIR spectra of all the PUs are shown in Figure 5. The absorptions at 3368 cm^{-1} and 1740 cm^{-1} are respectively recognized as the

groups of N–H (stretching) and $\text{C}=\text{O}$ peaks existed in PU. The absorption peaks of polybutadiene at 966 cm^{-1} for 1,4-trans, 911 cm^{-1} for 1,2-vinyl, and 724 cm^{-1} for 1,4-cis are also observed. From the FTIR spectra, no absorption

TABLE 4. Thermal properties of PUs

Samples	$T_{d5\%}^a$ (°C)	T_g^b (°C)	T_g^c (°C)
1	292.7	-57.6	34.2
2	292.7	-59.5	42.9
3	296.7	-55.9	59.6
4	298	-60.5	46.1
5	325.3	-58.7	41.9
6	299	-57.5	51.4
7	292.7	-61.3	51.8
8	295.7	-56.4	58.9
9	296.3	-61.2	54.8
10	312.3	-54.1	59.6
11	290.3	-58.7	55.2
12	293	-66.1	57.6
13	295	-57.5	59.4
14	298.7	-62.3	54.2
15	320.7	-55.8	66.1

^a Thermal decomposition temperature(5%). ^b Glass transition temperature of soft segment. ^c Glass transition temperature of hard segment.



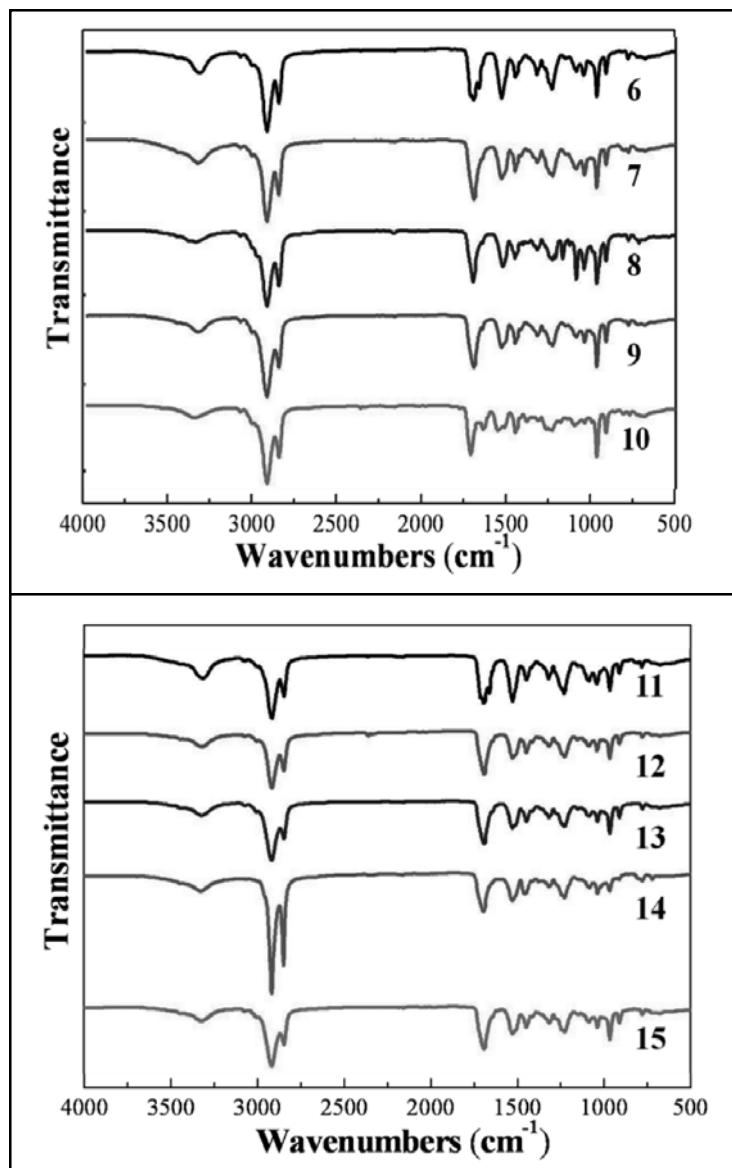


Fig. 5. The FTIR spectra of PUs

peaks of free -NCO and -OH groups are exhibited. From these results, it can be clearly distinguished that the synthesis of HTPB based PU is successful and complete. Not only the

completion level of synthesis, the degree of phase separation can be also understood by through FTIR analysis. Evidently, the hydrogen bond formed by the carbonyl group can only

be formed by the amino group in the hard segment in HTPB based PU, so the hydrogen bonded carbonyl group can represent the hard phase region. The degree of micro phase separation of hard segment and soft segment is characterized by the degree of association of hydrogen bonds (hydrogen bonding association, HBA). The greater the HBA is, the higher the degree of phase separation is.

All the spectra in the carbonyl stretching region (1670-1760 cm^{-1}) are curve fitted and resolved into two spectral components. The one at $\sim 1700\text{cm}^{-1}$ (red curve) is assigned to the hydrogen bonding between the hard segments, and the other at $\sim 1730\text{cm}^{-1}$ (blue curve) corresponded to the stretching vibration of the free carbonyl group of the hard segments. The quantitative degree of phase separation (DPS) is calculated by content of hydrogen bonded carbonyl group.^[32-33] The formula is as follows,

$$DPS = \frac{A_{1700}}{A_{1700} + A_{1730}} \times 100\%$$

where A_{1700} is the peak area at 1700cm^{-1} and A_{1730} is the peak area at 1730cm^{-1} .

With the increase of hard segment, the area of free carbonyl absorption peak (blue solid line) increases gradually and thus the degree of phase separation of all the PUs increased. Take RCE based polyurethane as an example, with the gradual increase of the content of RCE, the degree of micro-phase separation increases. RCE has an imide group and a rigid hydrophenanthrene ring, which causes stronger intermolecular and intramolecular interactions. Strong molecular interaction and stiff hydrophenanthrene ring

structure will lead to a higher solubility parameter of hard segments than that of soft segments, which intensifies the thermodynamic incompatibility and thus produces much more micro-phase separation. Similar experimental phenomenon can be also observed by someone else.^[34]

Figure 6 summarizes all the DPS of PUs with different content of hard segment and different types of non-planer ring structures. All the DPS of PU shows a trend with first increase and then decrease with the increase of number of nonplanar rings in chain extenders. That is probably because that chain extenders becomes more and more asymmetrical with increasing nonplanar rings per chain extender. The results described above has been consistent with the research reported by other researchers,^[35-41] that is, PUs based on linear, symmetrical hard segments show not only higher physical interaction between hard segments but also a higher degree of phase separation than those constructed from less symmetrical or kinked ones.

Generally, in PU, the repeat unit along the polymer chain (single chain scale) and the degree of micro-phase separation (micro-scale) are the decisive factors in controlling the final properties of polyurethane.^[42-43] On basis of the above results, it is obviously shown that the nonplanar structure is one of the key factor affecting the final property. Among all the PUs, PUs contained single ring structure (introduced by CHDM as chain extender) particularly shows the most excellent overall properties. This is because CHDM-based PUs possesses the strongest micro-phase separation. The introduction and adjustment of non-planer ring in HTPB based PU suggests a very important

way to pursue optimal degree of phase separation and excellent mechanical and thermal properties.

CONCLUSION

In summary, with use of microwave radiation, an efficient strategy to synthesize HTPB based

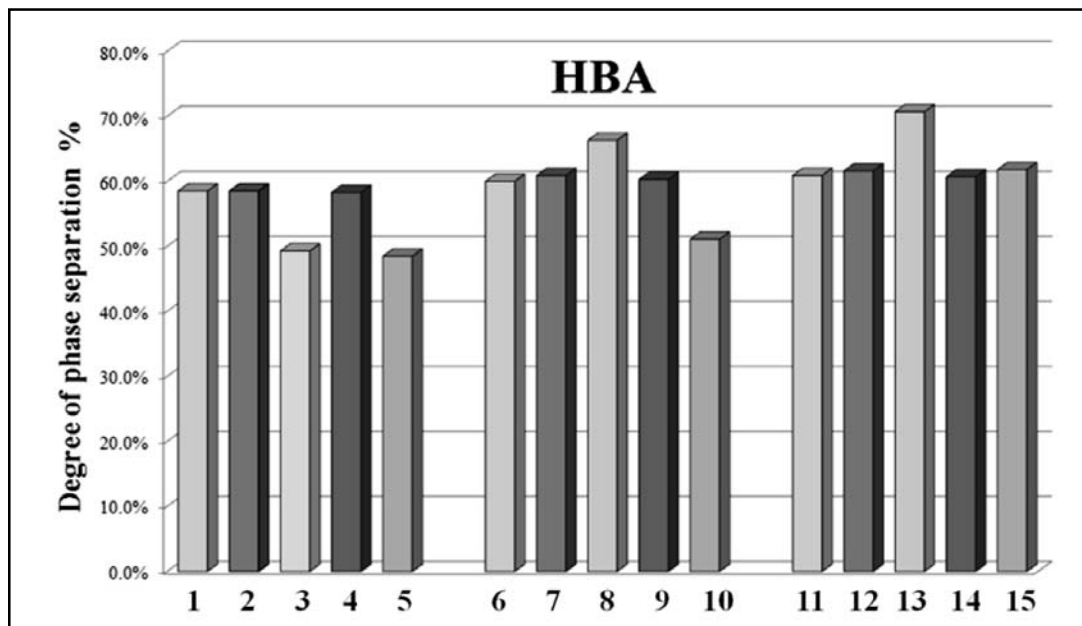


Fig. 6. Phase separation of PUs

PU is established. The application of microwave driven methods enables to achieve high efficiency and shorten the time of reaction. And side reaction of carbon-carbon bond be reduced. In order to pursue optimal properties, the content of hard segment and non-planer ring contained structure are respectively controlled in the molecular chain of HTPB based PU. With the increase of hard segment content. Degree of Phase separation DPS is found to increase, and accordingly modulus and tensile strength of the obtained PU are improved, but elongation partially decreases. Introduction of non-planer ring suggest the

other effective way to control the overall properties. Together with change of DPS, single ring provides the most effective contribution to initiate the best mechanical and thermal properties of PU. This work establishes a simple but efficient methodology to efficiently synthesize HTPB based PU and together with the ability to achieve superior performances.

Acknowledgements

This work is supported by National Key Research and Development Program of China (2017YFE0102300), OCE Project #29983 from University of Toronto (Canda), National Natural

Science Foundation of China (51503218 and 51773218), Ningbo Natural Science Foundation (2018A610034), and Youth Innovation Promotion Association CAS (2017339).

REFERENCES

1. Y. Liu, Y. Y. Wei and C. Z. Zong, *Colloid Polym. Sci.* 292 (2014) 873
2. H. L. Kim, Y. H. Lee, J. S. Kim, C. C. Park, H. Park, H. H. Chun and H. D. Kim, *J. Polym. Res.* 23 (2016) 240
3. Y. C. Chung, Y. G. Kim, J. W. Choi and B. C. Chun, *Polym. Bull.* 74(2017) 1
4. S. Misbah, *Environ. Chem. Lett.* 15(2017) 347
5. H. Y. Kim, J. W. Choi, Y. C. Chung and B. C. Chun, *Fibers Polym.* 18 (2017) 842
6. S. A. Whitmore, Z. W. Peterson and S. D. D. Eilers, *J. Propul. Power* 30(2014) 78
7. C. S. Pant, M. S. S. N. M. Santosh, S. Banerjee and P. K. Khanna, *Propell. Explos. Pyrot.* 38 (2013) 748
8. M. Abdullah, F. Gholamian and M. R. Zareiee, *J. Propul. Power* 29(2013) 1343
9. R. M. Sankar, S. Saha, K. S. Meera and T. Jana, *B. Mater. Sci.* 32(2009) 507
10. R. M. Sankar, T. K. Roy and T. Jana, *B. Mater. Sci.* 34 (2011) 745
11. R. M. Sankar, T. K. Roy and T. Jana, *J. Appl. Polym. Sci.* 114(2009) 732
12. K. P. S. Gopala, K. Ayyaswamy and S. K. Nayak, *J. Macromol. Sci. A* 50(2013) 128
13. R. Manjari, U. I. Somasundaran, V. C. Joseph and T. Sriram, *J. Appl. Polym. Sci.* 48(1993) 279
14. R. Manjari, L. P. Pandureng, U. I. Somasundaran and T. Sriram, *J. Appl. Polym. Sci.* 51(1994) 435
15. A. E. B. Sameh, A. S. Mohamed, Z. W. Tamer and E. M. Hosam, *J. Therm. Anal. Calorim.* 131 (2018) 2013
16. H. Sheikhy, M. Shahidzadeh and B. Ramezanzadeh, *Polym. Bull.* 72(2015) 755
17. D. C. Gupta, S. S. Deo, D. V. Wast, S. S. Raomore and D. H. Gholap, *J. Appl. Polym. Sci.* 55 (1995) 1151
18. D. J. Harris, R. A. Assink and M. Celina, *Macromolecules* 34 (2001) 6695
19. K. Malkappa and T. Jana, *Ind. Eng. Chem. Res.* 54 (2015) 7423
20. K. Malkappa and T. Jana, *Ind. Eng. Chem. Res.* 52(2013) 12887
21. A. Biswas, M. Appell, Z.S. Liu and H. N. Cheng, *Carbohydr. Polym.* 133(2015) 74
22. D. Q. You, H. Liang, W. Z. Mai, R. Zeng, M. Tu, J. H. Zhao and Z. G. Zha, *J. Ind. Eng. Chem.* 19 (2013) 1587
23. R. Hoogenboom and U. S. Schubert, *Macromol. Rapid Commun.* 28 (2007) 368
24. S. Sinnwell and H. Ritter, *Aust. J. Chem.* 60(2007) 729
25. L. S. Zhang, S. S. Shams, Y. P. Wei, X. Q. Liu, S. Q. Ma, R. Y. Zhang and J. Zhu, *J. Mater. Chem. A* 2 (2014) 20010
26. F. Liu, J. W. Zhang, J. G. Wang, X. Q. Liu, R. Y. Zhang, G. H. Hu, H. N. Na and J. Zhu, *J. Mater. Chem. A* 3(2015) 13637
27. W. Xu, R. Y. Zhang, W. Liu, J. Zhu, X. Dong, H. X. Guo and G. H. Hu, *Macromolecules* 49(2016) 5931
28. N. Teng, J. Y. Dai, Y. Wen, J. Chen, F. Liu, J. Zhu and H. N. Na, *J. Polym. Mater.* 35(2018) 73
29. H. K. Lee and S. W. Ko, *J. Appl. Polym. Sci.* 50(1993) 1269
30. I. Yilgor, E. Yilgor, S. Das and G. L. Wilkes, *J. Polym. Sci. Polym. Phys.* 47(2009) 471
31. S. L. Han, K. W. Ying and S. L. Hsu, *Macromolecules* 20 (1987) 2089

32. T. L. Chantawansri, Y. R. Sliozberg, J. W. Andzelm and A. J. Hsieh, *Polymer* 53(2012) 4512
33. L. Bistričić, G. Baranović, M. Leskovic and E. G. Bajsić *Eur. Polym. J.* 46 (2010) 1975
34. L. S. Zhang, Y. H. Jiang, Z. Xiong, X. Q. Liu, H. N. Na, R. Y. Zhang and J. Zhu, *J. Mater. Chem. A* 1(2013) 3263
35. D. B. Klinedinst, I. Yilgor, E. Yilgor, M. Q. Zhang and G. L. Wilkes, *Polymer* 53(2012) 5358
36. N. S. Schneider, C. S. P. Sung, R. W. Matton and J. L. Illinger, *Macromolecules* 8(1975) 62
37. K. Kojio, S. Nakashima and M. Furukawa, *Polymer* 48 (2007) 997
38. N. S. Schneider and C. S. P. Sung, *Polym. Eng. Sci.* 17(1977) 73
39. T. R. Hesketh, J. W. C. V. Bogart and S. L. Cooper, *Polym. Eng. Sci.* 20(1980) 190
40. Y. He, D. L. Xie and X. Y. Zhang, *J. Mater. Sci.* 49 (2014) 7339
41. Y. J. Li, W. X. Kang, J. O. Stoffer and B. Chu, *Macromolecules* 27 (1994) 612
42. X. Liu, T. C. Wang, J. R. Li, J. Cheng and J. Y. Zhang, *J. Polym. Res.* 22(2015) 149
43. K. K. Chee and R. J. Farris, *J. Appl. Polym. Sci.* 29(1984) 2529

Received: 03-09-2018

Accepted: 03-11-2018