

Thermal Characteristics of Energetic Polymers Based on Tetrahydrofuran and Oxetane Derivatives

YING-LING LIU,¹ GING-HO HSIUE,^{1*} and YIE-SHUN CHIU²

¹Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan, Republic of China, and ²Chung-San Institute of Science and Technology, Lungtan, Taoyuan, Taiwan, Republic of China

SYNOPSIS

Thermal characteristics and decomposition behaviors of energetic polymers based on oxetane derivatives, 3,3'-bis(azidomethyl)oxetane (BAMO), 3-azidomethyl-3'-methyloxetane (AMMO), 3-nitratomethyl-3'-methyloxetane (NMMO), and 3,3'-bis(ethoxymethyl)oxetane (BEMO), were studied by means of differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA). These polymers were found to exhibit low glass transition and large decomposition enthalpies which were brought about by the attached azide ($-\text{N}_3$) and nitrate ($-\text{ONO}_2$) groups. The decomposition enthalpies depended on the types and contents of the energetic substituents. The NMMO-based polymers exhibited relatively higher decomposition enthalpies and less thermal stability than the others. Furthermore, the thermal stability of the polymers was further improved by partial curing treatment. These results reveal that these polymers are potentially useful for application in energetic propellant binders. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Recently the developments of new propellants have attracted a lot of attention especially in the aspects of high energy content, low smoke production, low damage, and high-temperature sensitivity.¹⁻⁸ To meet the above requirements, some efforts such as replacing the traditional aluminum fuel with a highly energetic boron fuel, using nitrate esters as an energetic plasticizer, and developing new energetic oxidizers, have been done. These developments made the traditional propellant binder hydroxy-terminated polybutadiene (HTPB) incompatible with the new compositions of the propellants. Since the binder plays a major role in the performance of the propellants, searching for a new generation binder is thus a matter of urgency.

The development of new propellant compositions indicates that high energy would be a major requirement for the new binder. Additionally other characteristics, such as compatibility with nitrate ester plasticizer, low glass transition temperature, capac-

ity of processing, high load-bearing capacity, and good mechanical property, are also necessary for this application. Glycidyl azide polymer (GAP) was first reported to possess the aforementioned properties for the new generation binder.¹⁻⁹

Azide ($-\text{N}_3$) group was covalently incorporated into GAP to make it energetic. However, some critical limitations still exist for GAP as a binder. One particular limitation is that GAP is in liquid state under ambient condition.¹⁻⁴ On the other hand, oxetane-based polymers, which have low glass transition temperature, satisfactory compatibility with new nitroester plasticizer, and capability using as a thermal plastic elastomer (TPE) system, were outstanding in the developments of new propellant binders.⁸⁻²² The versatility in chemical modification on oxetane derivatives also leads to various types of oxetane polymers with different properties.¹⁰⁻²² This further demonstrates high potential of the oxetane-based polymers to improve the physical properties of the binder systems, thereby enhancing its performance and stability.

Since Mitsch¹⁰ first reported that polyoxetane was suitable to serve as propellant binders, there have been more than 20 oxetane derivatives and their corresponding polymers reported.¹¹⁻¹⁷ Among

* To whom correspondence should be addressed.

these, those which contain specific energetic groups are particularly of interest. Investigation on synthesis and characterization of these energetic oxetane-derivatives based polymers have been studied systematically.¹¹⁻²² Homopolymers, random copolymers, and block copolymers based on several oxetane derivatives, i.e., 3,3-bis(azidomethyl)oxetane (BAMO), 3-azidomethyl-3'-methyloxetane (AMMO), 3-nitratomethyl-3'-methyloxetane (NMMO), and 3,3'-bis(ethoxymethyl)oxetane (BEMO), have been synthesized to develop novel polymeric binders for propellants in our previous studies.²⁰⁻²² Under meticulous synthesis design, these polymers are thermoplastic and curable upon heating. This further confirms the high applicability of these oxetane-based polymers in propellant binders.

According to the literature^{1-5,23-27} thermal properties of binder materials are important to the performance of the propellants. Therefore, in this study, investigation on the thermal characteristics of the oxetane-based polymers was performed to provide better understanding for their application in the propellant binders. Glass transition temperatures (T_g 's), thermal and temporal stability, decomposition behavior, and decomposition enthalpies of the polymers were studied by means of differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA). Furthermore, the effect of energetic groups and their contents on the thermal properties of the polymers were also discussed.

EXPERIMENTAL

Materials

All of the polymers utilized in this work were synthesized in our laboratory. The preparation of BAMO-, NMMO-, and AMMO-based polymers has been reported.^{21,22} For the sake of comparison, BEMO-based polymers were also prepared in this research through the reported technique.^{20,22} Four types of polymers were used, i.e., homopolymers poly-A, block copolymers poly-A-block-B-block-A, random block copolymers poly-(A-co-B)-block-B-block-(A-co-B), and random copolymers poly-A-co-B, where A denotes oxetane derivatives and B denotes tetrahydrofuran (THF). The chemical structures and the abbreviations of the homopolymers are summarized in Table I.

Partial cured samples were obtained from the interaction of the hydroxy-terminated polymers (1 g) with a bifunctional chemical agent 3,3'-dimethyl-biphenyl-4,4'-diisocyanate [$\text{OCN}_2\text{C}_6\text{H}_3(\text{CH}_3)_2$]

Table I Chemical Structure of the Analyzed Polymers

Polymer	Repeating Unit Structure
Poly(THF)	$\left[\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \right]_n$
Poly(BAMO)	$\left[\begin{array}{c} \text{CN}_2\text{N}_3 \\ \\ \text{OCH}_2\text{CCCH}_2 \\ \\ \text{CH}_2\text{N}_3 \end{array} \right]_n$
Poly(AMMO)	$\left[\begin{array}{c} \text{CH}_2\text{N}_3 \\ \\ \text{OCH}_2\text{CCH}_2 \\ \\ \text{CH}_3 \end{array} \right]_n$
Poly(NMMO)	$\left[\begin{array}{c} \text{CH}_2\text{ONO}_2 \\ \\ \text{OCH}_2\text{CCH}_2 \\ \\ \text{CH}_3 \end{array} \right]_n$
Poly(BEMO)	$\left[\begin{array}{c} \text{CH}_2\text{OC}_2\text{H}_5 \\ \\ \text{OCH}_2\text{CCH}_2 \\ \\ \text{CH}_2\text{OC}_2\text{H}_5 \end{array} \right]_n$

$\text{C}_6\text{H}_3(\text{CH}_3)\text{NCO}$, DMPI 0.06 g] and pentaerythritol [$\text{C}(\text{CH}_2\text{OH})_4$, 0.02 g] as a curing agent.²⁸ This reaction was performed by heating the reactant mixtures at 100°C for 0.5 h.

Measurements

DSC analysis was performed by a Seiko DSC 5200 at a heating rate of 10°C/min under nitrogen atmosphere. TGA thermograms were taken through a DuPont 951 thermogravimetric analyzer under nitrogen atmosphere. The heating rate was also maintained at 10°C/min.

RESULTS AND DISCUSSION

The typical DSC thermograms of the block copolymers are shown in Figure 1. First, two distinct glass transition temperatures (T_g) were found in all of the block copolymers. The first one originates from the poly-THF segments, and the other one from the poly-oxetane-derivative segments. Also, endothermic peaks were found in all of the curves. The

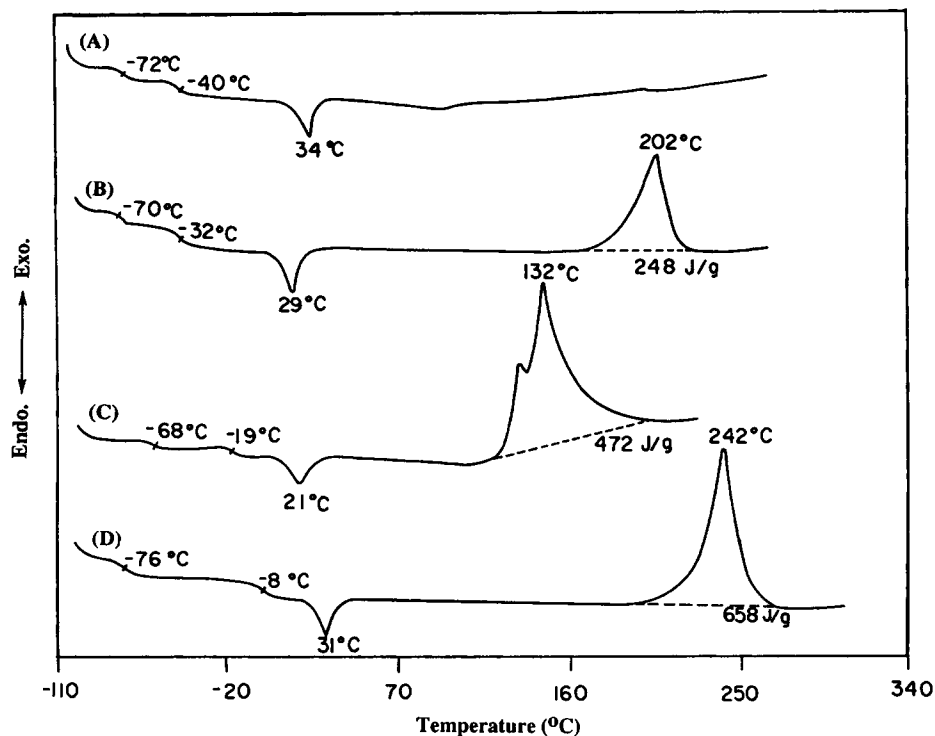


Figure 1 DSC thermograms of triblock copolymers based on THF and (a) BEMO, (b) AMMO, (c) NMMO, and (d) BAMO.

peaks were assigned from the melting behavior of the poly-THF segments.²² The melting temperature varies with the molecular weights of the polymers or on the other hand, with the molecular weights of the poly-THF segments. Furthermore, in the higher temperature region, a large exothermic peak was observed for all of the block copolymers except for BEMO-based ones. The absence of the exothermic peak in the DSC heating scan of BEMO-based polymers could be explained easily from the chemical structure. The substituents in BEMO, ethoxymethyl, however, are not as thermally sensitive as the other two substituents, i.e., azidomethyl and nitratomethyl, in AMMO, BAMO, and NMMO. Therefore, BEMO would not produce a specific exothermic peak from the substituent decomposing during the DSC heating scan.

The DSC thermograms of the random copolymers are shown in Figure 2. This figure indicated the presence of only one T_g and no endothermic peaks at temperatures higher than T_g . This implies that the crystalline morphology of poly-THF was destroyed while copolymerizing with oxetane derivatives. Furthermore, a large exothermic peak was also found while the random copolymers contained energetic substituent groups.

The glass transition temperatures of some analyzed polymers are summarized in Table II. The

substituents exerted a significant influence on the T_g 's of the oxetane-derivative homopolymers. Poly-BEMO has the lowest T_g , and poly-BAMO has the highest one among these homopolymers. For block copolymers, two T_g 's coming from the respective segments both show a shifting toward a higher temperature. Poly-THF segments show that a higher T_g is reasonable since it is linking to harder segments. However, poly-oxetane-derivative segments show a higher T_g than that of the respective homopolymers. This suggests that the block linkage had a negative effect on polymer chain motion. The high molecular weights should be a reasonable factor to derive such an effect. On the other hand, the observation of two T_g 's in the block copolymers also reveals the existence of phase separation in the microstructure. A physical crosslinking model can be applied to these polymers. In our previous work,²¹ the physical crosslinking characteristic of poly-BAMO-block-THF-block-BAMO has been examined. Moreover, the T_g 's of random copolymers of oxetane derivatives with THF are also shown in Table II. All of the T_g 's of random copolymers fell in the temperature region between their respective T_g 's of homopolymers. As expected, the T_g 's were found to depend on the monomer composition of the polymers. However, they do not give a good linear relationship to the monomer compositions. In

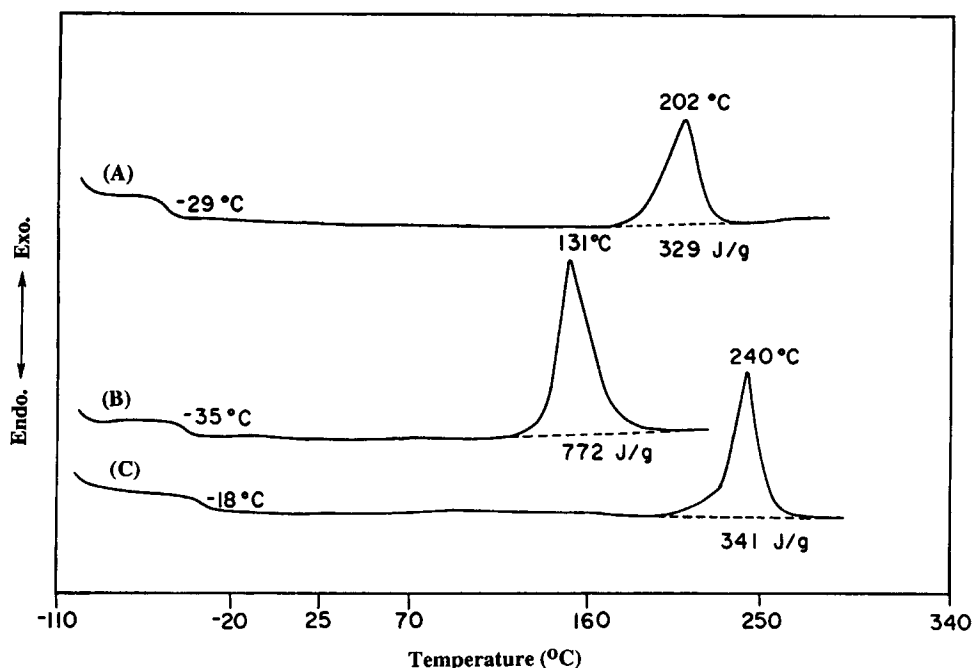


Figure 2 DSC thermograms of random copolymers based on THF and (a) AMMO, (b) NMMO, and (c) BAMO.

propellant binder applications, the required T_g of oxetane-based polymers is lower than -40°C . However, most of the energetic oxetane homopolymers exhibit T_g 's higher than -40°C . Therefore, formation of copolymers, either block or random type, with a low T_g polymer, for example, poly-THF, is a convenient and efficient approach of lowering the T_g 's of the oxetane-based polymers.

From Figures 1 and 2, exothermic peaks were found in the DSC thermograms of energetic group attached polymers. Since BEMO-based polymers did not give such a peak as well as the others, this exothermic behavior could be attributed to the decomposition of the energetic groups of the polymers. The corresponding decomposition enthalpies are summarized in Table III. As found in this

table, the decomposition enthalpies were highly dependent on the type and contents of the energetic groups. Poly-NMMO shows the largest decomposition enthalpy, 1104 J/g, implying that nitrate groups are more energetic than azido groups. The narrow peaks might indicate that the thermal decomposition of these energetic groups in the polymers is highly sensitive to the temperature variation. This was also revealed from the TGA thermograms (Fig. 4). The polymers did not give notable weight loss before the decomposition temperature. While the temperature was up to the decomposition temperatures of the polymers, a rapid decomposition appeared as the drastic weight loss occurred. Furthermore, the decomposition enthalpy of poly-BAMO doubled that of poly-

Table II Glass Transition (T_g) and Decomposition Temperatures (T_d) of the Random and Block Copolymers Based on THF and Oxetane Derivatives

Oxetane Derivatives	T_g 's of Random Copolymers ($^\circ\text{C}$)	T_g 's of Block Copolymers ($^\circ\text{C}$)	T_d of Polymers ($^\circ\text{C}$)	T_d of Monomers ($^\circ\text{C}$)	
THF	-75	—	—	—	
BAMO	-23	-76	-8	242	160
AMMO	-41	-70	-32	202	139
NMMO	-28	-68	-19	132	113
BEMO	-44	-72	-40	—	—

Table III Thermal Characteristics of Polymers Based on THF and Oxetane Derivatives

Polymer Types ^a	Oxetane Derivatives	\bar{M}_w	Mol. Ratio of THF/Oxetane in Copolymers	Decomposition Enthalpies (J/g)
I	NMMO	12110	0/100	1104
II	NMMO	14320	91/9	200
II	NMMO	15260	65/35	472
II	NMMO	40660	88/12	247
III	NMMO	12190	35/65	840
III	NMMO	5420	48/52	772
I	AMMO	3746	0/100	459
II	AMMO	25030	68/32	218
II	AMMO	29645	81/19	141
II	AMMO	32640	88/12	103
III	AMMO	6672	28/72	389
III	AMMO	5421	38/62	367
I	BAMO	4548	0/100	914
II	BAMO	12673	50/50	658
II	BAMO	25920	68/32	504
II	BAMO	55676	90/10	205
IV	BAMO	1425	81/19	341
IV	BAMO	2104	84/16	298
I	BEMO	8937	0/100	—
II	BEMO	14603	53/47	—
II	BEMO	29440	70/30	—
II	BEMO	68760	90/10	—

^a (I) Homopolymer, (II) poly-A-block-B-block-A triblock copolymer, (III) poly-A-co-B random copolymer, (IV) poly-(A-co-B)-block-B-block-(A-co-B) random-block copolymer. A, oxetane derivatives; B, THF.

AMMO. This is quite reasonable since BAMO contains two units of energetic azide group, and AMMO contains only one in each repeating unit of the polymers. From these results, the decomposition of the energetic azide groups seems to be only dependent on the contents of the energetic groups. Thus, further information was derived from Figure 3. The curves were obtained from plotting decomposition enthalpies vs. energetic group contents. The three linear curves revealed that the decomposition enthalpies are only dependent on the energetic group contents of the polymers, and are almost independent on the copolymer types. Therefore, the exothermic enthalpy was derived entirely from the decomposition of the energetic groups.

In addition to the decomposition enthalpies, the decomposition temperatures were also obtained from the DSC thermograms (see Table II, column 5). Polymers based on the same energetic monomers have almost the same decomposition temperature. Polymers based on NMMO, in spite of giving a largest decomposition enthalpy, are de-

composing at the lowest temperature among these polymers. Interestingly, BAMO- and AMMO-based polymers exhibited different decomposition temperatures, despite the fact that these two kinds of polymers contain the same energetic substituent azide group. BAMO monomer decomposes at around 160°C, and its corresponding polymers at 242°C. On the other hand, AMMO monomer decomposes at around 139°C, and its corresponding polymers at 202°C. This would imply that the thermal stability of the azide group is dependent on its chemical surroundings. For BAMO- and AMMO-based polymers, introducing another azide substituent also yields a positive effect toward enhancing the thermal stability of the azide groups.

The decomposition temperatures of the energetic groups and the thermal stability of the polymers were further studied by TGA technique. Typical TGA thermograms of block copolymers based on THF and oxetane derivatives are shown in Figure 4. Two stages of weight loss were found in BAMO- and AMMO-based polymers [Fig. 4(a) and (b)]. The first stage

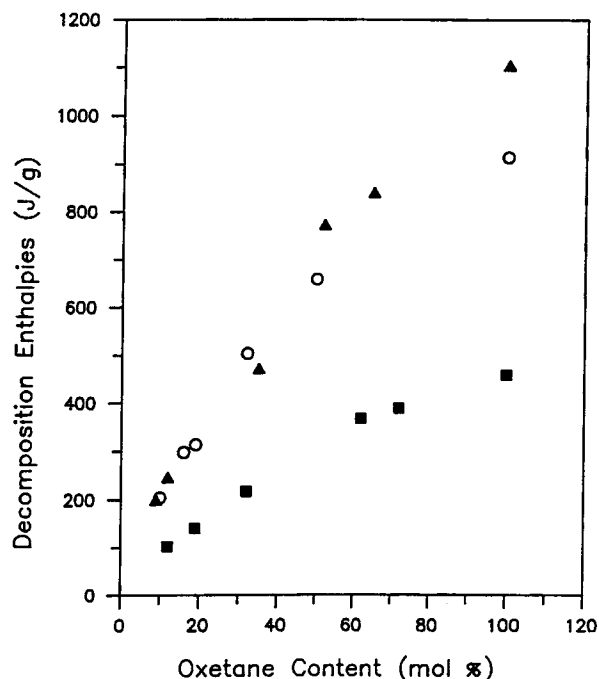


Figure 3 Plots of decomposition enthalpies vs. energetic group contents of the polymers containing energetic oxetane derivatives (▲) NMMO, (○) BAMO, and (■) AMMO.

of weight loss occurred at 242 and 202°C for BAMO- and AMMO-based polymers, respectively. These two temperatures are almost the same as the decomposition temperatures of the azide groups read from DSC analysis. The percentages of the weight loss also matched with the weight loss from the decomposition of the azide groups. Therefore, the thermal decomposition behaviors of the azide groups could be monitored by TGA tracing. The decomposition of the polymer backbones appeared as the second-stage weight loss occurred at 60°C higher than the first-stage weight loss. Furthermore, BEMO-based polymers, which do not contain any energetic substituents, did not show a two-stage weight loss during the heating process [Fig. 4(c)]. The large weight loss at 308°C should be a result of the decomposition of the polymer backbones. From the above results and discussion, these polymers based on THF and oxetane derivatives (BAMO, AMMO, and BEMO) have excellent thermal properties compatible to those of the propellant binders.⁸⁻²²

On the other hand, a notable weight loss was found at around 131°C for NMMO-based polymers. This temperature of 131°C also matches the exothermic temperature in DSC analysis. Thus, the weight loss could be reasonably assigned as the decomposition of the nitrato groups of NMMO

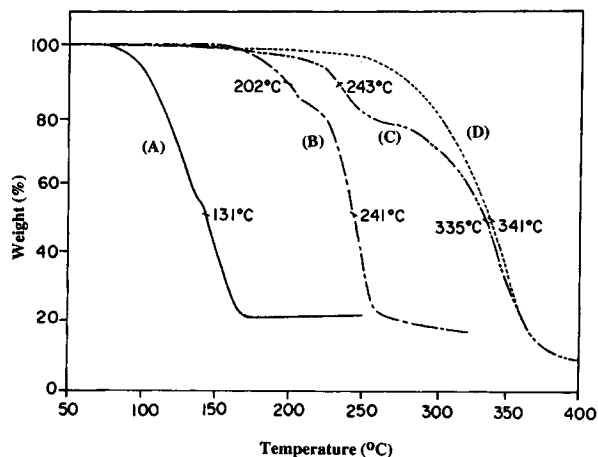


Figure 4 TGA thermograms of triblock copolymers based on THF and (a) NMMO, (b) AMMO, (c) BAMO, and (d) BEMO.

repeating units. However, the NMMO-based polymers did not show a clear two-stage weight loss in TGA analysis as well as azide-containing polymers. The experimental results indicated that THF/NMMO triblock copolymer is not as thermally stable as the other THF/oxetane derivatives-based copolymers. This is uncommon since these polymers contain similar repeating units and backbones. Thus, a reasonable explanation was given as follows. Owing to the large decomposition enthalpy of nitrato groups, the decomposition of nitrato groups would produce much heat at the decomposition temperature. Consequently, the polymer backbone linkages were broken to cause the decomposition of the polymers. The above statements were supported by the absence of two-stage weight loss in TGA thermograms of NMMO-

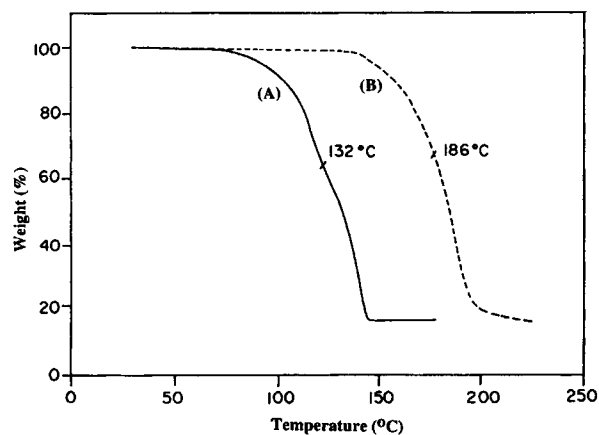


Figure 5 TGA thermograms of poly-NMMO homopolymer (a) before and (b) after curing.

based polymers. Furthermore, a partial crosslinking NMMO/BAMO triblock copolymer exhibited a one-stage weight loss at 204°C in TGA analysis.²¹ This further confirms the aforementioned remarks. The NMMO/BAMO decomposed at 204°C, which was substantially lower than the decomposition temperature (242°C) of BAMO-based polymers. This result implied that the decomposition of the poly-BAMO segment was induced by the decomposition of poly-NMMO segment before 242°C. The large decomposition enthalpy of the nitrate groups in the poly-NMMO segment caused the decomposition of the polymer chains, thereby producing a one-stage weight loss. On the other hand, the weight loss temperature was much higher than that of poly-NMMO (132°C from this study). The enhancement in thermal stability of this NMMO-based polymer was contributing from its partial crosslinking structure.

The enhancing effect of crosslinking on the thermal stability of the polymers was further studied in this work. A partial curing poly-NMMO was obtained from the reaction of hydroxyl-terminated poly-NMMO with a diisocyanate agent DMPI and pentaerythritol. TGA thermograms of poly-NMMO before and after curing are shown in Figure 5. Notably, the weight loss temperature of the polymer was raised from 132 to 186°C by partially curing the polymer. Indeed, the thermal stability of the NMMO-based polymers was effectively enhanced.

CONCLUSION

Thermal characteristics of various types of polymers based on some oxetane derivatives—BAMO, BEMO, NMMO, and AMMO—were studied. Those polymers exhibited one or two low glass transition temperatures for homopolymers/random copolymers and block copolymers, respectively. T_g 's of the copolymers were adjustable by altering the monomer type and/or monomer composition in the copolymers. The BAMO- and AMMO-based polymers exhibited decomposition temperatures at higher than 200°C. Their decomposition processes are two stage, one is for the decomposition of azide groups, the other is for that of polymer backbones. Furthermore, the NMMO-based polymers exhibited a highest decomposition energy (1104 J/g for homopolymer). The decomposition enthalpies were dependent on the energetic group contents of the polymers and not on the copolymer types. TGA thermograms revealed that the high decomposition enthalpies of

NMMO-based polymers brought about the decomposition of the polymer backbones at the first weight loss temperature, i.e., decomposition temperature of nitrate groups. This decomposition subsequently led to a relatively poor thermal stability for NMMO-based polymers. Additionally, thermal stability of the polymers could be further improved by partial curing. It is concluded that these polymers are potentially useful for application as novel energetic propellant binders.

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