ELSEVIER

Thermochimica Acta 388 (2002) 371–375

thermochimica acta

www.elsevier.com/locate/tca

Substituent effects on Bergman cyclopolymerization kinetics of bis-*ortho*-diynylarene (BODA) monomers by dynamic scanning calorimetry

K. Prasanna U. Perera, Hiren V. Shah, Stephen H. Foulger, D.W. Smith Jr.*

Department of Chemistry, Clemson University, Clemson, SC 29634, USA

Received 30 July 2001; received in revised form 4 October 2001; accepted 4 October 2001

Abstract

Bis-*ortho*-diynylarene (BODA) monomers polymerize thermally via the Bergman cyclization and diradical intermediates. The structure reactivity relationships of eight BODA monomers and their kinetics were studied by differential scanning calorimetry (DSC). The spacer (X = $-C(CF_3)_2$, $-C(CH_3)_2$, –O–, a bond) groups and alkyne terminal (R = Ph, $-Si(CH_3)_3$, –*iso*-propanol, pyridine, thiophene) groups were varied and the effect on polymerization rate was determined. Among the phenyl-terminated monomers, only the isopropylidene spacer group imparts a significant increase on the cure onset temperature and the activation energy. However, the terminal (R) groups play a significant role in polymerization rate of BODA monomers.

Keywords: Bergman; Cyclopolymerization; Bis-*ortho*-diynylarene; Dynamic scanning calorimetry

1. Introduction

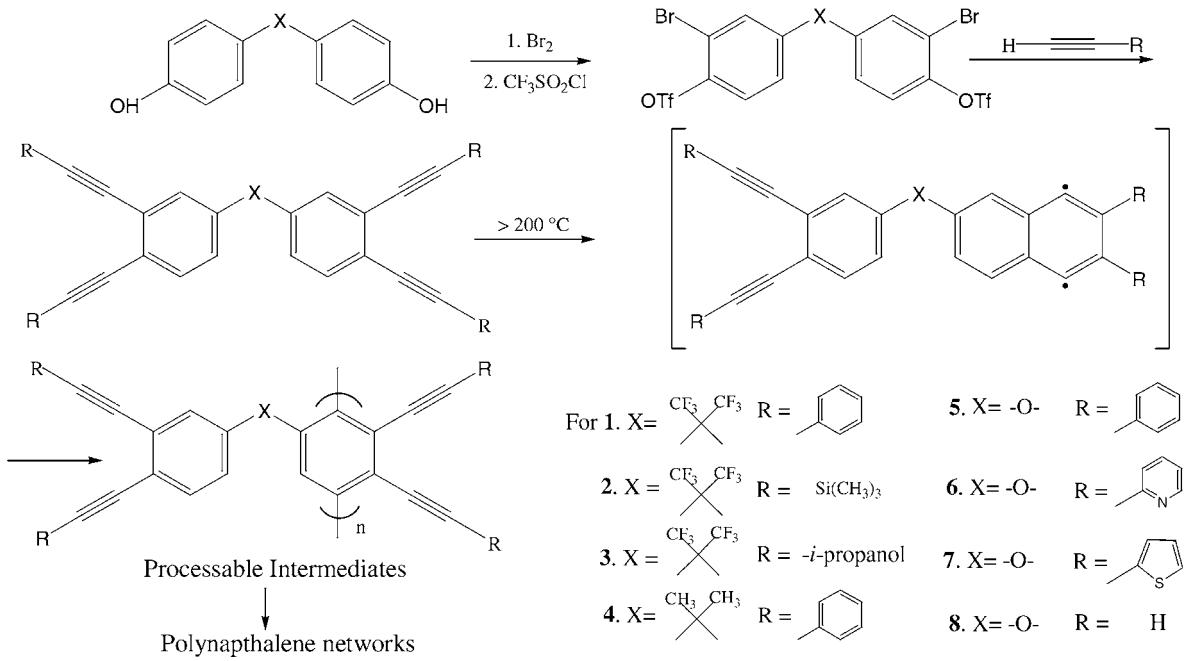
Bergman [1] cyclo-rearrangement of enediynes to form 1,4-dehydroaromatic diradicals has been extensively studied as a route for developing anti-tumor drugs [2]. The Bergman cyclization has also been established as a route to linear [3,4] and network [5–13] polynaphthalenes. As common with most high performance materials in general, linear polynaphthalenes are inherently insoluble and difficult to process [3,4]. To address the processability issue, we have developed a new class of bis-*ortho*-diynylarene (BODA) [5] compounds which form branched and therefore, soluble, reactive intermediate oligomers upon thermal polymerization (Scheme 1). BODA-derived pre-polymers can be easily solution or melt processed and subsequently cured at 450 °C providing high T_g polyarylene networks.

BODA-derived thermosets are versatile materials with excellent thermal and oxidative stability. They are potentially useful as active light emitting layers [7,8] in organic polymer-based light emitting diodes (LEDs) [7], nanocomposites [9] and as micromolded precursors to high yield electrically conductive carbon glasses for microelectromechanical system (MEMS) [10].

For many substituted aromatic diynes, Bergman cyclization kinetics has been studied by Grissom and co-workers [14,15], Kim and Russell [16], Keller and co-workers [13] and Grubbs and Kratz [17] have also described the use of calorimetry to study the thermolysis of Bergman cyclopolymerization. Our previous work focused on the cure chemistry of

* Corresponding author. Tel.: +1-8646566613.
E-mail address: dwsmith@clemson.edu (D.W. Smith Jr.).

0040-6031/02/$ – see front matter
PII: S0040-6031(02)00020-5



Scheme 1.

BODA monomers and intermediate resins where only the spacer (X) group was varied [6]. Several calorimetric kinetic techniques [6] were used to compare the polymerization rate, cure onset and activation energies. Our continuing effort is now focused on further understanding the influence offered by spacer (X) as well as the terminal group (R) for BODA polymerization [11] (Scheme 1).

In this report, we used conventional differential scanning calorimetry (DSC) to determine the reaction kinetics using *n*th order kinetics. The *n*th order kinetics allows calculating the activation energy (E_a), pre-exponential factor (Z), reaction order (n) and the rate constant (k) from a single DSC scan and the equation, $d\alpha/dt = Z\exp(-E_a/RT)(1-\alpha)^n$.

2. Experimental

The trimethyl silyl-terminated monomers were synthesized by a three-step reaction and then desilylated and coupled with aryl halides form heteroatom-terminated BODA monomers. Monomer synthesis and polymerization details are described elsewhere [5,11]. A Mettler-Toledo DSC820 was used for conventional DSC scans and the MTDSC measurements were performed using a TA Instruments 2920 DSC both equipped with a liquid nitrogen cooling accessory. For both systems, indium was used for temperature and enthalpy calibrations. For each experiment, about 8–10 mg of monomer were used. The samples were sealed in aluminum hermetic pans with a pinhole and nitrogen was used as the purge gas. All samples were equilibrated in nitrogen for about 15 min prior to each run. Since the *n*th order kinetics required a single dynamic scan, a set of three values was obtained for each monomer. These values were consistent for the activation and pre-exponential factors observed for each monomer, which illustrates the reproducible nature of the BODA polymerization under different thermal conditions. The values of T, $d\alpha/dt$ and α in the range of study were obtained from a single dynamic DSC run.

3. Results and discussion

The mechanism of BODA polymerization could be described as either step growth coupling reactions of radical intermediates or chain-type radical addition

Table 1
Selected DSC-derived data for BODA polymerization

BODA monomer			T_m peak (°C)	T_{exo} onset (°C)	Exotherm $-\Delta H$ (kJ/mol)	E_a (kJ/mol)
Number	X	R				
1	$C(CF_3)_2$	Ph	190	210	457.6	121 ± 5.4
2	$C(CF_3)_2$	TMS	147	300	350	–
3	$C(CF_3)_2$	*iso*-Propanol	90	240	438.6	–
4	$C(CH_3)_2$	Ph	147	271	324.8	142.3 ± 8.3
5	–O–	Ph	108	231	483.3	129.7 ± 12.9
6	–O–	Pyridine	202	225	308.8	127.6 ± 12.5
7	–O–	Thiophene	203	204	444.9	125.5 ± 12.1
8	–O–	H	–	109	206	–

followed by cyclization with monomer (Scheme 1). Although both mechanisms are likely to compete, the overall process appears step growth in nature [3–5].

We have conclusively shown that previously studied robust spacer groups (X = $-C(CF_3)_2$, –O–, a bond, phenyl fluorene) do not effect the rate of polymerization for phenyl-substituted BODA monomers [6]. However, when the spacer group is aliphatic, the rate is decreased dramatically. Exothermic polymerization of **1** and **4** (Scheme 1) are detected near 210 and 270 °C, respectively. The polymerization onset temperature for **4** is significantly higher than all other phenyl-substituted BODA monomers studied to date. Table 1 compares selected DSC results for monomers **1–8** (Scheme 1). Monomers **1** and **4** exhibit $-\Delta H = 112.9$ and 108.7 kJ/mol alkyne heat of polymerization, respectively. These values are typical for all BODA monomers that have been studied thus far

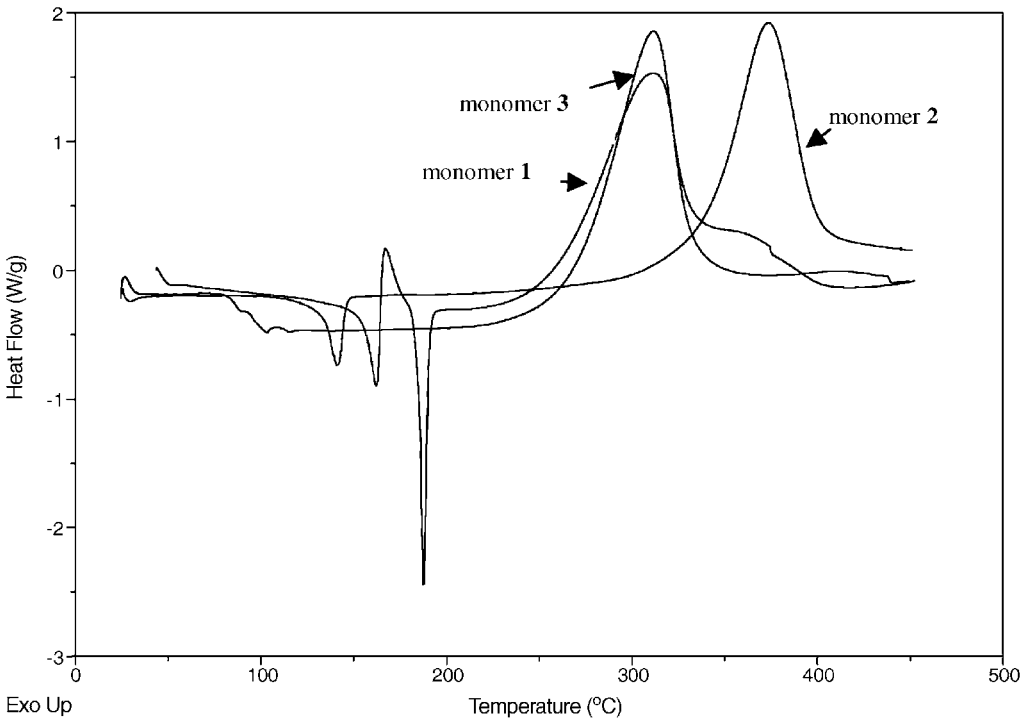


Fig. 1. DSC scans of BODA monomers (**1–3**) from ambient to 450 °C at a heating rate of 10 °C/min.

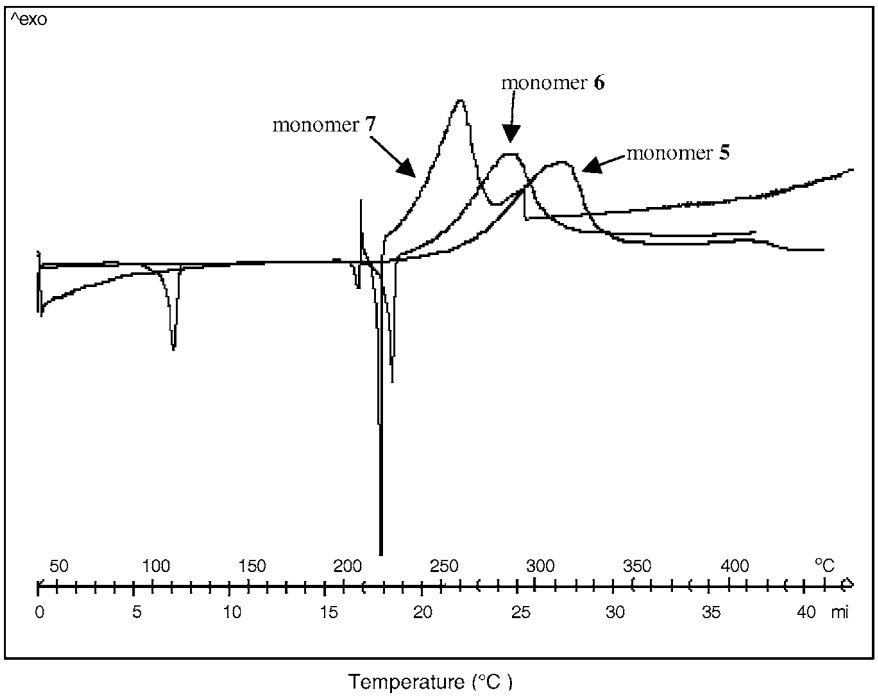


Fig. 2. DSC scan overlays of BODA monomers (**5**–**7**) from ambient to 450 °C at a heating rates of 10 °C/min.

[6]. The *n*th order model activation energy for monomer **4** ($E_a = 142$ kJ/mol) indicates a much higher value compared to monomer **1** ($E_a = 121.3$ kJ/mol) [6].

Among the phenyl-terminated BODA monomers, only monomer **4** exhibits a significant effect on the rate of the polymerization [16]. However, the major difference between previously studied BODA monomers and monomer **4** is the presence of aliphatic hydrocarbons in **4**. Aggressive phenyl radicals could abstract hydrogen atoms from the isopropyl spacer and slow the overall rate of polymerization.

We have also begun a study to probe the structure and polymerization kinetics of monomers with different terminal groups (R, Table 1). Monomers **2** and **3** exhibit much higher cure onset temperatures (300 and 240 °C, respectively) than the phenyl-terminated derivatives (Fig. 1). The cure onset temperatures of all monomers were measured as the point of intersection of the extrapolated baseline and the initial steep portion of the curve. This enhanced cure onset temperature could be a result of the steric nature offered by the terminal group or plausible self-trapping of aliphatic hydrogen atoms [12].

Monomers with oxygen spacer groups with different terminal groups, such as phenyl (**5**), pyridine (**6**) and thiophene (**7**) have also been compared (Fig. 2). Monomers **5**, **6** and **7** exhibit cure onset temperatures at 231, 225 and 204 °C, respectively and *n*th order activation energies of 129.7, 127.6 and 125.5 kJ/mol, respectively. In general, we have found that proton-terminated *ortho*-diynyl arenes are unstable at room temperature. The cure onset temperature, however, for BODA monomer **8** (X = O, R = H) was measured at 109 °C. It is known that the steric nature of the acetylene terminus—and thus the planarity of the cyclic transition state—and electronic effects of the substituents influence the rate of diradical formation in Bergman cyclization [10–12].

4. Conclusions

The structure/reactivity relationships of BODA monomers and their kinetics were studied by DSC. Among the phenyl-terminated monomers only the isopropyl spacer group imparts a significant increase

on the cure onset temperature and activation energy. Terminal (R) groups play a significant role in polymerization rate for BODA monomers studied and hetero cycle terminal groups appears to enhance the rate.

Acknowledgements

We are grateful to the National Science Foundation (CAREER Award DMR-9985160), Army Research Office and South Carolina EPSCoR for financial support and Mettler-Toledo for the donation of a DSC820 system to Clemson University. We also thank Chris Topping, Clark Ligon, and Kim Ivey (all of Clemson University) for valuable discussions and help.

References

[1] R.G. Bergman, Acc Chem. Res. 6 (1973) 25.
[2] K.C. Nicolau, W.M. Dai, Angew Chem. Int. Ed. Engl. 30 (1991) 1387.
[3] J.A. John, J.M. Tour, J. Am. Chem. Soc. 116 (1994) 5011.
[4] J.A. John, J.M. Tour, Tetrahedron 53 (1997) 15515.
[5] D.W. Smith Jr., D.A. Babb, R.V. Snelgrove, P.H. Townsend, S.J. Martin, J. Am. Chem. Soc. 120 (35) (1998) 9079.
[6] H.V. Shah, D.A. Babb, D.W. Smith Jr., Polymer 41 (2000) 4415.
[7] H. Shah, D.A. Babb, D.W. Smith Jr., Polym. Mater. Sci. Eng. 80 (1999) 199.
[8] H. Shah, K.P.U. Perera, D.W. Smith Jr., Macromolecules, submitted for publication.
[9] K.P.U. Perera, D.W. Smith Jr., Polym. Mater. Sci. Eng. 85 (2001) 366.
[10] H. Shah, S.T. Brittain, Q. Huang, S.-J. Hwu, G.M. Whitesides, D.W. Smith Jr., Chem. Mater. 11 (1999) 2623.
[11] K.P.U. Perera, D.W. Smith Jr., Polym. Preprint. 42 (2) (2001) 339.
[12] K.P.U. Perera, K.A. Abboud, D.W. Smith Jr., Macromolecules, submitted for publication.
[13] S.B. Sastri, T.M. Keller, K.M. Jones, J.P. Armistead, Macromolecules 26 (1993) 6171.
[14] J.W. Grissom, T.L. Calkins, H.A. McMillen, Y. Jiang, J. Org. Chem. 59 (1994) 5833.
[15] J.W. Grissom, T.L. Calkins, J. Org. Chem. 58 (1993) 5422.
[16] C. Kim, K.C. Russell, J. Org. Chem. 63 (13) (1998) 8229.
[17] R.H. Grubbs, D. Kratz, Chem. Ber. 126 (1993) 149.