

THERMOGRAVIMETRIC ANALYSIS OF AROMATIC POLYAMIDES WITH VARIOUS BENZIMIDAZOLYL CONTENTS

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Abstract

The TG analyses are given for variously meta- and/or para-linked aromatic polyamides with various benzimidazolyl (BI) contents. The TG curves of the polymers were evaluated within 600°C by use of an equation for multiple events. The TG curves of BI-substituted polymers are expressed for triple events, though the TG curves of unsubstituted polymer are expressed for double events. The amount of residue of BI-substituted polymers at 800°C is larger than that of unsubstituted polymers, perhaps because moieties concerning BI degrade at higher temperatures.

Keywords: aromatic polyamide, benzimidazolyl-substituted, meta-para linked phenylene, thermogravimetric analysis

Introduction

There are some reports [1–3] on synthesis of an aromatic polyamide substituted with a bulky group, which has better solubility than the unsubstituted one does. Their thermal stability was evaluated to be similar to that of unsubstituted one by rough TG analysis. In our previous paper [4], it is presented that the aromatic (benzimidazolyl) (BI)-substituted polyamides have better solubility and better thermal stability in comparison with those of unsubstituted one. Therein, the TG curves for the BI-substituted polyamides are complicated and not sensitive to analysis using the common isoconversional method. Recently, a more precise isoconversional method was used for complicated TG curves for poly(vinyl chloride) [5]. However, in principle, the isoconversional method is constructed on the basis of the equation on a single event.

In the present paper, the thermogravimetric results that were obtained by fitting a simple equation for triple events to the TG curves for aromatic polyamides with various BI contents, are given and discussed considering effects of the thermogravimetric behaviors on the BI contents and para-linked phenylene contents. Moreover, the validity of the new method is examined over the present work.

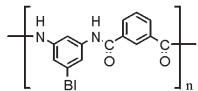
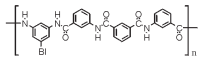
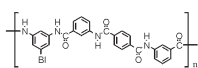
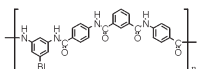
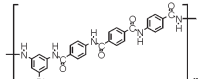
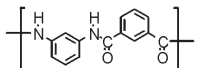
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Experimental

Materials

Two species of diamines were used for the polymerization as the diamino-monomer. One diamino-monomer was 2-(3,5-diaminophenyl)benzimidazole (DAPBI), which was synthesized as described previously [4]. Another diamino-monomers were obtained by reduction of dinitro-intermediates, which were synthesised from DAPBI and meta- or para-nitrobenzoyl chloride. The polymerization was conducted with three diamino-monomers and iso- or terephthaloyl chloride in the usual way [6]. The structure and the inherent viscosity (0.3 g dl^{-1} in N,N -dimethylacetamide at 30°C) of polymers are shown in Table 1.

Table 1 Properties and structure of the samples

Sample	Structure	BI content	Para-phenylene content	$\eta_{\text{inh}}/\text{d lg}^{-1}$
PmPIA		0.5	0	0.23
PBmPIA		0.25	0	0.13
PBmPTA		0.25	0.25	0.49
PBpPIA		0.25	0.5	0.14
PBpPTA		0.25	0.75	0.33
PIA		0	0	0.37

The content is expressed by mole per 1 mol of phenylene.

TG measurements and determination of activation energies

All TG measurements were performed using Perkin Elmer 7 series with UNIX TGA 7. A platinum TG pan was used and was flame-cleaned prior to each run. The TG data was recorded at the heating rates of 2, 5, 10 or 20°C min⁻¹ from a preheating temperature to 800°C. About 1 mg of a sample was precisely weighed.

The TG curves for the samples, not preheated, are too complicated to reflect effective information. Therefore, the samples were used for TG measurements, after heating at 200 and 400°C for 60 min. These TG curves, even TG curves for the samples preheated at 400°C, are still not single curves.

The thermal decomposition of the samples used here, proceeds essentially by the Simha type [7] of random decomposition. The random decomposition is expressed by the first-order rate equation [8]. Therefore, the TG curves obtained in this study are analyzed by use of the mass vs. temperature equation for multiple events, which is derived from the first-order rate equation and Doyle approximation [9].

$$W_i/W_{i0} = \exp[-(A\Delta E_i) \exp\{-5.33145 - 1.05178(\Delta E_i/RT)\}] \quad (1)$$

where W is the mass, A is the frequency factor, ΔE is the activation energy, R is the gas constant, and i is the number of an event. The subscript zero denotes 'the initial'. Since a TG curve expresses a relation between overall mass, W/W_0 , and temperature, T , the following equation is used.

$$W/W_0 = \sum W_i / \sum W_{i0} \quad (2)$$

By trial and error, ΔE_i ($i=1, 2, \dots$) and W_{i0} ($i=1, 2, \dots$) values are determined by fitting Eq. (2) to TG curves.

Results and discussion*TG curve analysis using Eq. (2)*

Figures 1 and 2 show the results analyzed by using Eq. (2) for the representative TG curves. The experimental TG curves within 600°C are expressed by Eq. (2) for triple events, and incompletely by Eq. (2) for double events, except the TG curve for the unsubstituted polymer. Difference in heating rate a little influences the data on events that occur at higher temperatures. They suggest the occurrence of multiple events in the range of temperature at which the BI-substituted moiety degrades. However, in the present paper, this is treated as a unique event, that is, Event 3, for simplicity and the difference in heating rate are ignored.

Meta-linked aromatic polyamides with various BI contents

Table 2 shows the data obtained from curves for meta-linked aromatic polyamides with various BI contents. The amount of residue is an extent of flame resistance. Relations between the amount of residue and the BI content depend on the preheating temperature of the samples. For the samples preheated at 200°C, PmPIA>PBmPIA>

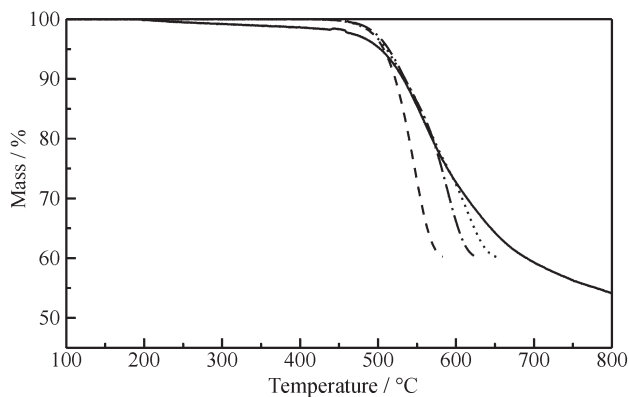


Fig. 1 TG curves fitting the equation for single event (dashed line), double events (dash-dot line) and triple events (dotted line). The solid line expresses the TG curve of PBmPIA, recorded at the heating rate of $10^{\circ}\text{C min}^{-1}$. The samples were preheated at 400°C for 60 min.

($\Delta E_1=58.8$, $\Delta E_2=63.7$) for double events,
 ($\Delta E_1=58.0$, $\Delta E_2=61.4$, $\Delta E_3=65.7$) for triple events

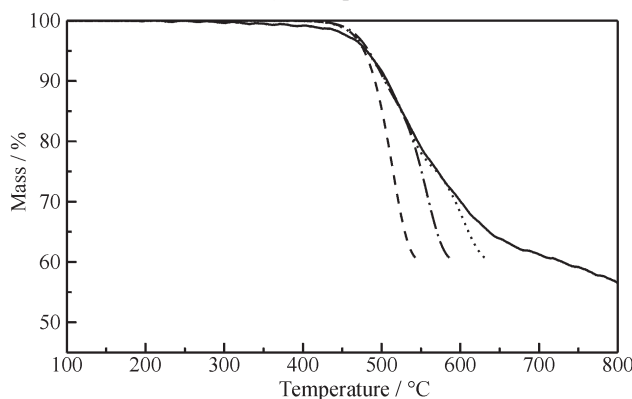


Fig. 2 Influence of heating rate. TG curves are analyzed as in Fig. 1. The solid line expresses the TG curve of the same samples except for the heating rate equal to $2^{\circ}\text{C min}^{-1}$.

($\Delta E_1=58.8$, $\Delta E_2=63.9$) for double events,
 ($\Delta E_1=58.0$, $\Delta E_2=61.8$, $\Delta E_3=67.6$) for triple events

PIA, that is, the amount of residue increases as the BI content increases. However, for the samples preheated at 400°C , $\text{PmPIA} > \text{PIA} > \text{PBmPIA}$, and this means that an event for PBmPIA occurs in the range of temperature over 400°C , and does not occur in the range of temperature between 200 and 400°C . From structural point of view, this event is presumed to be associated with oxo-1,3-phenylene-imino unit which the others are not. The $W1_0/W2_0/W3_0$ values reflect an extent of contribution of the polymer to the event. The differences in ratio between $(W2_0+W3_0)/W1_0$ for the analysis using

Table 2 Thermogravimetric parameters of aromatic meta-linked polyamides with various BI contents

Sample	Event 1		Event 2		Event 3		W_{res}	$W_{10}/W_{20}/W_{30}$
	$T_{\text{on}}/^{\circ}\text{C}$	$\Delta E/\text{kcal mol}^{-1}$	$T_{\text{on}}/^{\circ}\text{C}$	$\Delta E/\text{kcal mol}^{-1}$	$T_{\text{on}}/^{\circ}\text{C}$	$\Delta E/\text{kcal mol}^{-1}$		
PmPIA ₂₀₀	352.8 (403.8)	48.0 (52.0)	435.5 (492.5)	54.5 (59.0)	488.2 (-)	60.3 (-)	59.0	1/1.2/3.0 (1/2.0)
PBmPIA ₂₀₀	420.3 (470.6)	53.3 (55.3)	477.4 (507.8)	57.8 (60.2)	530.5 (-)	62.0 (-)	52.9	1/2.0/3.0 (1/3.0)
PIA ₂₀₀	419.1 (480.9)	53.2 (56.5)	467.2 (544.4)	57.0 (59.0)	553.4 (-)	63.8 (-)	51.4	1/1.7/4.3 (1/1.8)
PmPIA ₄₀₀	401.3 (524.2)	51.8 (61.5)	477.3 (603.7)	57.8 (67.8)	569.6 (-)	65.1 (-)	64.1	1/2.8/12.2 (1/1.9)
PBmPIA ₄₀₀	479.9 (491.0)	58.0 (58.8)	522.9 (552.0)	61.4 (63.7)	577.2 (-)	65.7 (-)	54.1	1/2.0/3.0 (1/3.0)
PIA ₄₀₀	502.7 (502.7)	59.8 (59.8)	592.4 (605.0)	66.9 (67.9)	657.7 (-)	72.0 (-)	56.7	1/0.63/0.84 (1/1.4)

T_{on} is the on-set temperature.

W_{res} is the amount of residue at 800°C.

The subscript of sample abbreviation denotes the preheating temperature.

In the parentheses, there are the data analyzed with double events. - denotes nothing.

Table 3 Thermogravimetric parameters of variously meta- and/or para-linked BI-substituted aromatic polyamides

Sample	Event 1		Event 2		Event 3		W_{res}	$W1_0/W2_0/W3_0$
	$T_{on}/^{\circ}C$	$\Delta E/kcal\ mol^{-1}$	$T_{on}/^{\circ}C$	$\Delta E/kcal\ mol^{-1}$	$T_{on}/^{\circ}C$	$\Delta E/kcal\ mol^{-1}$		
PmPIA ₂₀₀	420.3 (470.6)	53.3 (55.3)	477.4 (507.8)	57.8 (60.2)	530.5 (-)	62.0 (-)	52.9	1/2.0/3.0 (1/3.0)
PBmPTA ₂₀₀	413.5 (469.5)	52.8 (54.9)	470.8 (500.1)	57.3 (59.6)	525.3 (-)	61.6 (-)	55.0	1/2.0/3.0 (1/2.8)
PBpPIA ₂₀₀	397.2 (464.6)	51.5 (53.7)	474.4 (502.7)	57.5 (59.8)	536.7 (-)	62.5 (-)	46.7	1/1.5/3.0 (1/2.3)
PBpPTA ₂₀₀	419.1 (486.8)	53.2 (56.0)	467.2 (521.6)	57.0 (61.3)	553.4 (-)	63.8 (-)	48.1	1/1.7/4.3 (1/2.2)
PBmPIA ₄₀₀	479.9 (491.0)	58.0 (58.8)	522.9 (552.0)	61.4 (63.7)	577.2 (-)	65.7 (-)	54.1	1/2.0/3.0 (1/3.0)
PBmPTA ₄₀₀	476.1 (490.0)	57.7 (58.9)	525.4 (557.0)	61.6 (64.2)	587.3 (-)	66.5 (-)	56.4	1/2.0/3.0 (1/3.0)
PBpPIA ₄₀₀	469.7 (486.2)	57.2 (58.5)	519.1 (554.5)	61.1 (63.9)	579.8 (-)	65.9 (-)	53.2	1/1.9/3.1 (1/1.4)
PBpPTA ₄₀₀	481.1 (515.3)	58.1 (60.8)	544.4 (582.3)	63.1 (66.1)	599.9 (-)	67.5 (-)	52.0	1/1.8/3.2 (1/2.5)

Eq. (2) for triple events and W_{200}/W_{100} for the analysis using Eq. (2) for double events are given as follows: 13.1 for PmPIA, 2 for PBmPIA, and 0.07 for PIA. This suggests that as the BI contents increase, the more events are required for analysis, that is, the more complicated thermal degradation proceeds. The TG curve of the PIA sample preheated at 400°C can be almost completely expressed by Eq. (2) for double events. This is consistent with the results on thermal degradation of poly(1,3-phenylene isophthalamide), called PIA in this study, in the literature [10–11]: the thermal degradation proceeds by two different mechanisms.

Variously meta- and/or para-linked BI-substituted aromatic polyamides

The results are summarized in Table 3. TG curves of BI-substituted aromatic polyamides should be analyzed using Eq. (2) for triple events, as mentioned above. The following discussion is, therefore, conducted on the basis of the results of analysis with three events. The onset temperature, T_{on} , and ΔE values in Event 2₂₀₀ (the subscript denotes the preheating temperature of sample from here) are nearly equal to those in Event 1₄₀₀. This means that Event 1₂₀₀ occurs in the period of preheating at 400°C. The extent of contribution of Event 1₂₀₀ to Eq. (2) for PBpPIA₂₀₀ and for PBpPPTA₂₀₀ is larger than that to Eq. (2) for the others ($W_{100}/W_{200}=1/1.5$ for PBpPIA₂₀₀, 1/1.7 for PBpPPTA₂₀₀, and 1/2.0 for the others). The amount of residue for PBpPIA₂₀₀ and PBpPPTA₂₀₀ is relatively smaller ($W_{res}=46.7$ for PBpPIA₂₀₀, 48.1 for PBpPPTA₂₀₀, 55.0 for PBmPPTA₂₀₀, 52.9 for PBmPIA₂₀₀). These mean that Event 2₂₀₀ is a similar event for all samples and Event 3₂₀₀ is also a similar event for all samples. TG data on all the samples preheated at 400°C agree with each other except for the data on PBpPPTA. It is presumed that the excellent thermal stability of PBpPPTA is attributed to the good structural symmetry due to large amounts of linear links included in PBpPPTA. The good symmetry leads to the reduction of the change in the entropy in the thermal transition that causes the thermal degradation.

References

- 1 J. Preston, *Polym. Eng. Sci.*, 15 (1975) 199.
- 2 A. E. Lozano, J. Abajo, J. G. Campa and J. Preston, *Polymer*, 35 (1994) 1317.
- 3 J. A. Mikroyannidis, *Macromolecules*, 28 (1995) 5177.
- 4 H. Abematsu, M. Tsuchiya, Y. Iseri and T. Kojima, *J. Therm. Anal. Cal.*, 56 (1999) 969.
- 5 A. L. Petre, P. Budrugaec and E. Segal, *J. Therm. Anal. Cal.*, 56 (1999) 1065.
- 6 J. Preston and F. Dobinson, *Polymer Letters*, 2 (1964) 1171.
- 7 R. Simha and L. A. Wall, *J. Phys. Chem.*, 56 (1952) 707.
- 8 K. Tago, M. Tsuchiya, Y. Gondo, K. Ishimaru and T. Kojima, *J. Appl. Polym. Sci.*, 77 (2000) 1538.
- 9 C. D. Doyle, *J. Appl. Polym. Sci.*, 6 (1962) 639.
- 10 D. A. Chatfield, I. N. Einhorn, R. W. Mickelson and H. Futrell, *J. Polym. Sci.*, A1, 17 (1979) 1367.
- 11 Y. P. Khanna, E. M. Pearce, J. S. Smith, D. T. Burkitt, H. Njuguna, D. M. Hindenlang and B. D. Forman, *J. Polym. Sci. Polym. Chem. ed.*, 19 (1981) 2817.