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Thermogravimetry of the products in an imbalance condensation of an aromatic diamine and dichloride

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Abstract Imbalance condensation of diaminophenylbenzimidazole, DAPBI, with terephthaloyl chloride, TPC was conducted for the purpose of synthesis of macromonomers, expected to be used in syntheses of aromatic polyamides with structural regularities. The products are soluble in dimethylsulfoxide—d6, and their 1H NMR spectra indicate that all the products are carboxyl-terminated. The signal of carboxyphenyl linked to chain ends is different from that of terephthaloyl in the 1H NMR spectra. By use of the ratio of the signal intensity of the former to that of the latter, the number-average degree of polymerization, DP_{NMR} is determined. With the mole ratio in feed, DP_{NMR} of the product increases. The TG thermograms of the products are a multistage one. Each stage is classified by temperature and mass loss at an inflection point. Mass loss of each stage classified by temperature at an inflection point corresponds to mass fraction of an aromatic amide with a characteristic degree of polymerization, *DP*, and that is, the *DP* distribution of the products is roughly estimated from the TG thermograms. The *DP* distribution of macromonomers influences performance of aromatic polyamides with structural regularities, derived from the macromonomers. The convenient estimation method of *DP* distribution by TG is useful in industries of high-performance polymers. To the knowledge, such convenient technique has never reported.

Keywords Aromatic amides · Imbalance condensation · TG · Distribution of degree of polymerization

Introduction

The diamine used is 2-(3,5-diaminophenyl)benzimidazole, DAPBI, and the dichloride is terephthaloyl chloride, TPC. The products are a polymer in the condensation under 1:1 of DAPBI:TPC mole ratio in feed. They are soluble in nonionic polar solvents, such as *N*,*N*-dimethylacetamide, DMA, dimethylsulfoxide, DMSO, etc., [1, 2]. Aromatic polyamides having good solubility are industrially important, because of their ease of fabrication. Many aromatic polyamides have high performance, and, however, are difficult in solubility. Both good solubility and high performance are required for a good aramide. So, the authors thought of control of structural regularity by polycondensation of macromonomers with various regularities. Some macromonomers were synthesized by organic synthesis techniques [3–6]. However, the syntheses were very difficult because of requiring many steps.

The following theoretical equation for polycondensation suggests a single step synthesis of macromonomers.

$$DP = (r + 1)/(1 - -2rp + r) \tag{1}$$

where, *DP*, *r*, and *p* denote the degree of polymerization, the value of mole ratio in feed, the reactivity, respectively. When *p* and *r* are equal to 1 and 0.5, respectively, *DP* is equal to 3. This suggests that the chloroformyl-terminated trimer should be yielded in the condensation under DAPBI:TPC equal to 1:2. The authors conducted imbalance condensations under DAPBI:TPC equal to 2:1, 1:1.5, 1:2, and 1:3. All the products were soluble in DMSO—d_6, and, therefore, their *DP*'s were determined from their 1H NMR spectra. The TG (thermogravimetric) thermograms of all the products have some steps. Multistage thermograms like these reflect some different events. Recently, different events reflected by multistage thermograms were still

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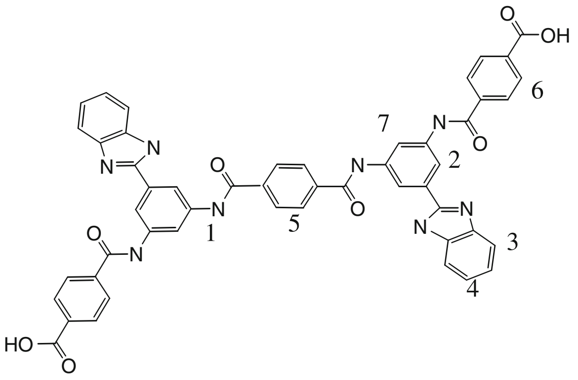


Fig. 1 The defference in structural environment of hydrogen atoms of product

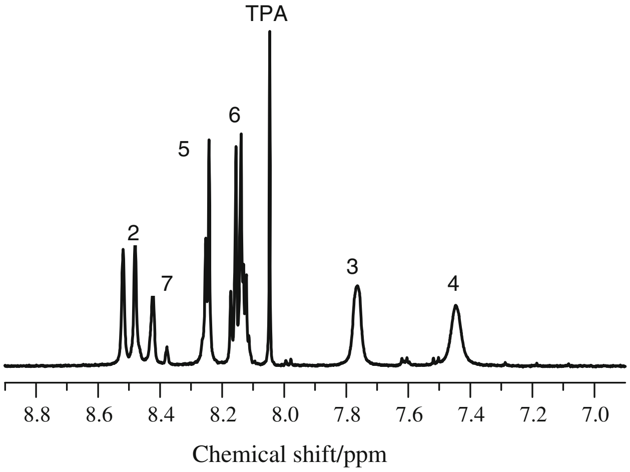


Fig. 2 A representative 1H NMR spectrum of a product (entry 2)

reported: different decomposition mechanisms for aminophosphoryl acetamide [7], alkyl chain combustion and dehydroxylation for alanine transition-metal complex [8], dehydration and decarbonation for gallium coating hydrotalcite [9], different decomposition mechanisms for copper/salen complexes [10], and existing different carbohydrates for hydrolysis lignin [11], etc. The thermograms of the products may be reflecting the *DP* distribution.

In this article, the authors discuss a TG technique for determination of the *DP* distribution by reference to the number-average *DP* determined from the 1H NMR spectra, DP_{NMR}, for the products in imbalance condensations under various mole ratios in feed. The *DP* distribution of macromonomers influences performance of aromatic polyamides with structural regularities, derived from the macromonomers. The convenient determination method of *DP* distribution by TG is useful in industries of high performance polymers. To the knowledge, such convenient technique has never reported.

Experimental

Materials

DAPBI was synthesized from 3,5-diaminobenzoyl chloride and 1,2-phenylenediamine in DMA. The product was purified by recrystalization from ethanol. The condensation was conducted by the following way: TPC dissolved in DMA was added to DAPBI dissolved in DMA. After reflux for around 1 h, the reaction mixture was poured to water. The collected precipitate was dried under reduced pressure. The details of the preparation appear in Ref. [2].

Apparatus

^{1}HNMR measurement was conducted by use of Bruker DMX500NMR spectrometer. A sample was dissolved in DMSO—d6 in a sample tube with diameter equal to 5 mm.

Table 1 Imbalance condensation of DAPBI with TPC

Entry	Ratio	DAPBI(DMA)/mmol/mL	TPC(DMA)/mmol/mL	TEA/mmol	Yield/gg^{-1}	DP	TPA/%
1	1:2.2	0.63(30.0)	1.38(15.0)	1.25	0.69	5.0	50
2	1:2.9	2.23(50.0)	6.40(20.0)	12.0	0.14	5.1	35
3	1:2.0	1.88(4.0)	3.75(4.0)	0	0.37	8.2	9
4	1:3.0	1.25(7.5)	3.75(5.0)	0	0.12	4.6	31
5	1:2.0	1.25(10.0)	2.50(6.0)	0	0.39	14.7	17
6	1:2.0	1.25(5.0)	2.50(5.0)	2.50	0.60	13.2	10
7	1:1.0	0.63(5.0)	0.63(5.0)	1.25	0.94	23.4	7
8	1:1.0	0.63(5.0)	0.63(0)	1.25	0.41	24.6	11
9	2.0:1	0.63(30.0)	0.31(7.0)	1.25	0.42	11.0	8
10	1:1.5	0.63(30.0)	0.94(20.0)	1.25	0.77	6.0	19

Yield is mass of a product/mass of monomers in feed

TEA denotes triethylamine

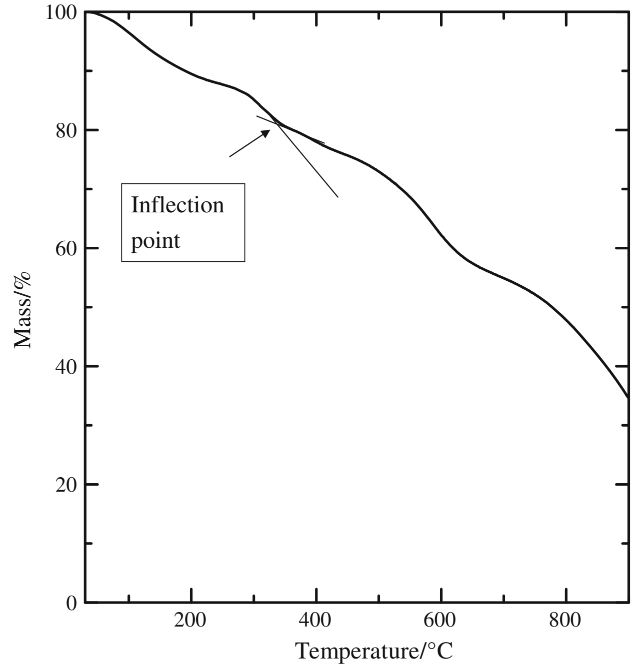


Fig. 3 A representative TG thermogram of a product (entry 8)

TG measurement was conducted by use of Perkin Elmer 7 series with UNIX TGA 7. A platinum pan was used and flame-cleaned prior to each run. The data was recorded at the heating rate of 10 °C/min. About 1 mg of samples precisely weighed. The duplicated TG runs were conducted with an error of about 10%.

Results and discussion

Table 2 Mass losses and onset temperatures determined from the TG thermograms

Entry	M_i/%	T_1/°C	M_1/%	T_2/°C	M_2/%	T3/°C	M_3/%	T_4/°C	M_4/%	M_r/%
1	3	230	14	320	25	450	12	640	47	–
2	10	220	10	310	13	420	17	610	50	–
3	6	–	–	320	18	440	16	620	60	–
4	6	230	10	320	8	450	17	620	25	34
5	10	–	–	330	6	430	16	620	40	28
6	13	240	4	–	–	440	16	620	32	29
7	11	210	8	320	6	420	17	630	25	33
8	10	210	8	320	6	420	17	630	21	29
9	6	220	5	320	6	420	16	620	32	35
10	5	220	8	320	15	450	15	640	57	–

Subscripts denote events (*i* and *r* are initial and residue, respectively)
Dashes denote unknown

Table 3 Starting temperatures of small aromatic amides

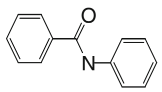
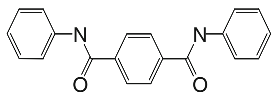
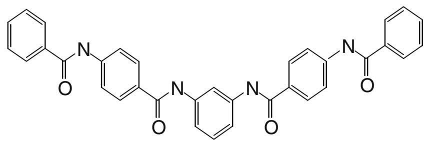
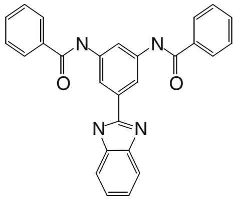
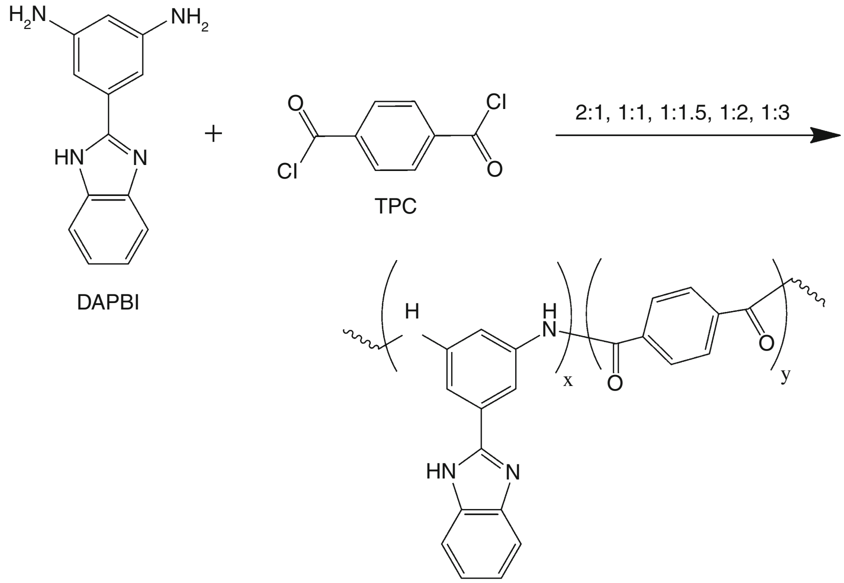
Structure	*T*s/°C
	193
	193
	193
	193

Figure 1 shows the difference in structural environment of hydrogen atoms of the products. Different seven hydrogen atoms exist. The signals of 1H NMR spectra are assigned to these hydrogen atoms as shown in Fig. 2. The signals of hydrogen atoms attached to nitrogen atoms of benzimidazole compounds in DMA are hardly assigned because of broadness of peak and ease of shifting [12]. A singlet signal at 8.05 ppm is associated with the hydrogen atoms of terephthalic acid, TPA, which was derived from TPC collected from water. The multiple signal, 5, in vicinity of 8.22–8.26 ppm is associated with the hydrogen atoms, 5, of terephthaloyls of main chain. The multiple signal, 6, in vicinity of 8.12–8.18 ppm is associated with hydrogen atoms, 6, of carboxyl-terminated phenylenes. All the products were carboxyl-terminated. Amino-terminated products were not obtained, perhaps because of its good solubility. By use of the signal intensity of terephthaloyl (signal 5), I_T, divided by that of carboxylphenyl (signal 6), I_C, the average of the numbers of phenylenes (benzene rings) included in a molecular, DP_{NMR}, is given by the following way. DP_{NMR} is a sum of the numbers of phenylenes of carboxylphenyl, N_C, terephthaloyl, N_T, and diiminophenylene, N_D. Since all the products are carboxyl-terminated, N_C, N_T, and N_D are equal to 2, $2(I_T/I_C)$, and $[2(I_T/T_C)+1]$, respectively. Accordingly, the following equation is given.

$$DP_{NMR} = 4(I_T/I_C) + 3 \tag{2}$$

The results on imbalance condensations of DAPBI with TPC are summarized in Table 1. An excess TPC exists in entries 1, 2, and 4. The smallest product is trimer with DP_{NMR} equal to three, because the functionality of

Scheme 1 The imbalance condensations of DAPBI with TPC



monomer is equal to two. It is formed in the condensation under 1:2 of mole ratio in feed. Therefore, unreactive TPC remains in the condensation under less than 1:2 of mole ratio in feed. Naturally, yield is extremely small in the reaction system including excessive TPC. The detailed discussion on yield is difficult, because exact structures of the products are undetermined. With the mole ratio in feed, DP_{NMR} of the product increases, though it is not strictly in agreement with the theory. Figure 3 shows a representative TG thermogram which has some inflection points. The thermograms of all the products are multistage like this. An inflection point was determined as the intersection point of two tangent lines drawn around the inflection point as shown in Fig. 3. An inflection point indicates onset of the following event. The mass loss between inflection points is close to the mass loss of the former event, because the former event almost offsets at an inflection point. Therefore, the authors collected temperatures and masses at inflection points. They are summarized in Table 2. The masses M_{i} and M_{r} denote initial mass loss and mass of residue, respectively. The initial mass loss may be associated with vaporization of DMA remaining in the products. The first stage may be associated with vaporization of solution of TPA in DMA, because the mass loss increases with an excess of TPC (included as TPA in the product). Perhaps it is attributed to depression of sublimation point of TPA because of dissolution in DMA. The second stage may be associated with sublimation of small aromatic amides. Table 3 shows the starting temperature of mass loss of small aromatic amides. Their thremograms are only a single stage. This suggests that the mass loss starting around 300 °C is associated with sublimation of small aromatic amides. An amide in the last line is a model of the smallest amide of the products mentioned here. Its starting temperature equal to 420 °C suggests that the third stage is also associated with sublimation. The third stage appears in the thermograms of the products with large *DP*. The third stage may consist of not only sublimation but also decomposition. The fourth stage indicates decomposition of the products. Chatfield et al. [13] and Khanna and Pearce [14] believe that hydrolytic and homolytic cleavages of the amide units occur in vicinity of 450 °C (hydrolytic) and 550 °C (homolytic) in the thermal decomposition of aromatic polyamides. The discussion mentioned above suggests that mass loss of each stage classified by temperature at an inflection point corresponds to mass fraction of an aromatic amide with a characteristic *DP*, and that is, the *DP* distribution of the products is roughly estimated from the TG thermograms Scheme 1.

Summary

The following information was obtained from this study.

(1) All the products are terminated by carboxyl and soluble in nonionic polar solvents.
(2) The number-average degree of polymerization of the products, $DP_{\mathrm{NMR},}$ is determined from the 1H NMR spectra.
(3) DP_{NMR} increases with the mole ratio in feed.
(4) The TG thermograms of the products have some inflection points at which temperatures and masses indicate a character of each stage.
(5) Mass loss of each stage classified by temperature at an inflection point corresponds to mass fraction of an aromatic amide with a characteristic *DP*, and that is, the *DP* distribution of the products is roughly estimated from the TG thermograms.

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