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Short Communication

Graft copolymerization of acrylamide onto xanthan gum

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Abstract

The graft copolymerization of acrylamide onto xanthan gum initiated by the Fe^{2+}/BrO_3^- redox system in aqueous medium was studied gravimetrically under a nitrogen atmosphere. The effect of Fe^{2+}, BrO_3^-, H^+, acrylamide and xanthan gum on graft copolymerization was studied by determining the grafting parameters, i.e. grafting ratio, efficiency, conversion and add on. Homopolymer too has been separated out. An increase in grafting parameters was observed with increase in ferrous ion concentration (4×10^{-3} mol dm^{-3} to 5.0×10^{-3} mol dm^{-3}) while with increasing bromate ion concentration, grafting ratio, efficiency, add on and conversion were found to decrease. It was observed that grafting takes place efficiently when acrylamide concentration and temperature were 4.0×10^{-3} mol dm^{-3} and 35°C, respectively. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Acrylamide; Xanthan gum; Graft copolymerization

1. Introduction

Xanthan gum is extensively used in the petroleum industry for enhanced oil recovery because it is a drag reducing agent with good shear stability. But it faces a tough competition from synthetic polymers such as polyacrylamide which are better drag reducing agents although they lack good shear stability. Studies have shown that graft copolymers formed between acrylamide and other polysaccharides, e.g. guar gum, carboxymethyl cellulose give the good drag reducing effectiveness of polyacrylamide and shear stability of polysaccharides (Deshmukh, Sudhakar, & Singh, 1991; Kanan, 1998; Prasad, Mark, & Fai, 1995; Singh and Jain, 1991). Therefore, in this paper, studies were carried out to graft acrylamide onto xanthan gum. The change of thermal stability before and after grafting polyacrylamide onto xanthan gum was also investigated.

2. Experimental

Acrylamide (E. Merck) was recrystallised twice from methanol and dried in vacuum. Ferrous sulphate (AR BDH), potassium bromate (E. Merck) and xanthan gum (Sigma) were used as such.

3. Graft copolymerization

For each experiment a xanthan gum solution was prepared by slow addition of the calculated amount of gum in a constant temperature reactor containing triple distilled water. The calculated amount of acrylamide, ferrous sulphate, sulphuric acid were added in the reactor. A known amount of bromate solution was added to initiate the reaction. The reaction was performed under continuous flow of nitrogen gas. After the desired time interval the reaction was stopped by letting air into the reactor. The grafted sample was precipitated by pouring the reaction mixture into methanol/water mixture. After leaving overnight the precipitate was filtered dried and weighed. To the filtrate a small amount of hydroquinone was added and was concentrated by distillation under reduced pressure. This concentrated filtrate was poured into the pure methanol to precipitate the homopolymer.

Grafting parameters were calculated according to Fanta's (1973) definition

$$\text{Grafting ratio (\%G)} = \frac{\text{Polymer in graft}}{\text{Weight of substrate}} \times 100$$

$$\text{Efficiency (\%E)} = \frac{\text{Polymer in graft}}{\text{Total weight of polymer formed}} \times 100$$

$$\text{Add on (\%A)} = \frac{\text{Polymer in graft}}{\text{Total weight of grafted sample}} \times 100$$

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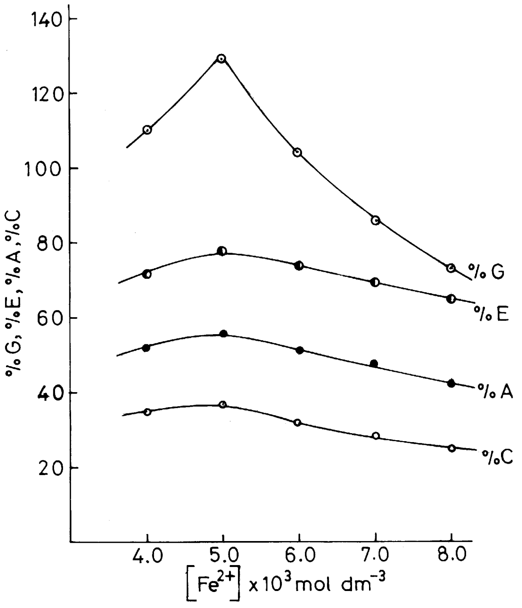

Fig. 1. Effect of ferrous ion concentration on grafting parameters: $[BrO_3^-] = 4.0 \times 10^{-3}$ mol dm^{-3}; $[H^+] = 1.8 \times 10^{-3}$ mol dm^{-3}; $[ACM] = 4.0 \times 10^{-2}$ mol dm^{-3}; Time = 120 min; Temp. = 35°C; $[XOH] = 65.0 \times 10^{-2}$ g dm^{-3}. %A = Add on, %C = Conversion, %E = Efficiency, %G = Grafting ratio.

$$\text{Conversion (\%C)} = \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100$$

$$\text{Homopolymer (\%H)} = 100 - \text{\%Efficiency}.$$

4. Results and discussion

4.1. Effect of ferrous ion concentration on grafting parameters

The effect of the ferrous ion concentration on grafting reaction was studied by varying the concentration of ferrous ion from 4×10^{-3} to 8×10^{-3} mol dm^{-3} (Fig. 1). There was increase in grafting ratio, efficiency, add on, and conversion as the concentration was increased to 5×10^{-3} mol dm^{-3} but thereafter these parameters decreased. Increase in grafting ratio with increasing ferrous ion concentration up to a certain value may be attributed to an increase in the concentration of free radicals produced by Fe^{2+}/BrO_3^- redox pair resulting in the production of xanthan gum radicals at a faster rate. The decrease in grafting ratio beyond the optimum concentration of ferrous ions may be attributed to the inhibiting effect of the excess of ferric ions produced by the oxidation of ferrous ions. The premature termination of growing grafted chains was also observed by Morin and Rogovin (1976) and Mishra, Dogra, Kaur, and Jassal (1979) during the graft copolymerization initiated with H_2O_2/Fe^{2+} system beyond a certain concentration of ferrous ions.

Table 1
Effect of bromate ion concentration $[BrO_3^-]$ on grafting parameters: $[Fe^{2+}] = 5.0 \times 10^{-3}$ mol dm^{-3}; $[H^+] = 1.8 \times 10^{-3}$ mol dm^{-3}; $[XOH] = 65.0 \times 10^{-2}$ g dm^{-3}; $[ACM] = 4.0 \times 10^{-2}$ mol dm^{-3}; Time = 120 min; Temp. = 35°C

S. no.	$[BrO_3^-] \times 10^3$ mol dm^{-3}	%E	%A	%C	%H	%G
1	2.0	84.9	59.0	39.2	15.1	145.6
2	3.0	79.0	57.0	38.4	21.0	132.7
3	4.0	78.0	56.3	37.8	22.0	129.1
4	5.0	74.2	54.2	36.4	25.8	118.2
5	6.0	58.8	45.5	32.4	41.2	83.4

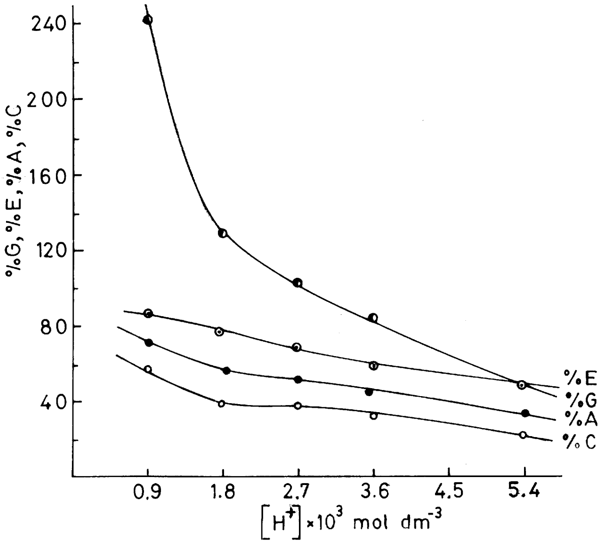

Fig. 2. Effect of hydrogen ion concentration on grafting parameters: $[Fe^{2+}] = 5.0 \times 10^{-3}$ mol dm^{-3}; $[BrO_3^-] = 4.0 \times 10^{-3}$ mol dm^{-3}; $[ACM] = 4.0 \times 10^{-2}$ mol dm^{-3}; Time = 120 min; Temp. = 35°C; $[XOH] = 65.0 \times 10^{-2}$ g dm^{-3}. %A = Add on, %C = Conversion, %E = Efficiency, %G = Grafting ratio.

4.2. Effect of bromate ion concentration on grafting parameters

The effect of bromate ion concentration on grafting parameters was studied by varying the concentration from 2.0×10^{-3} to 6.0×10^{-3} mol dm^{-3} (Table 1). The increase in bromate ion concentration led to a decrease in grafting parameters, which could be due to the increase in the formation of homopolymer.

4.3. Effect of acid concentration on grafting parameters

The concentration of hydrogen ion plays an important role in graft copolymerization since Fe^{2+}/BrO_3^- system was carried out in acid medium (Fig. 2). The graft copolymerization could not be effected in neutral or alkaline medium because of the immediate precipitation of ferrous hydroxide. As the hydrogen ion concentration was increased, all grafting parameters were found to decrease.

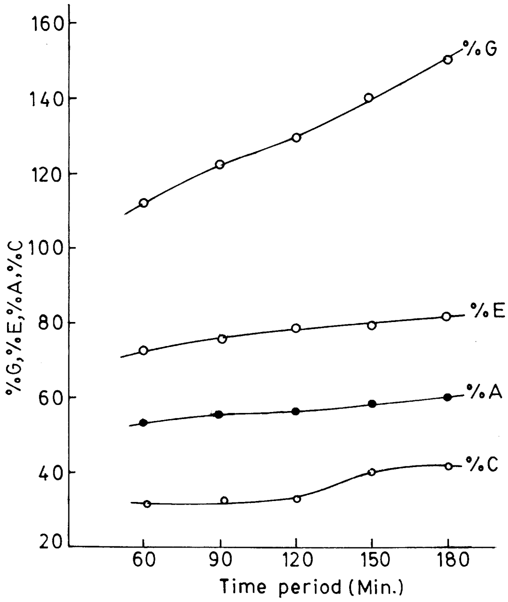

Fig. 3. Effect of time period on grafting parameters: $[Fe^{2+}] = 5.0 \times 10^{-3}$ mol dm^{-3}; $[BrO_3^-] = 4.0 \times 10^{-3}$ mol dm^{-3}; $[H^+] = 1.8 \times 10^{-3}$ mol dm^{-3}; [ACM] $= 4.0 \times 10^{-2}$ mol dm^{-3}; Temp. = 35°C; [XOH] $= 65.0 \times 10^{-2}$ g dm^{-3}. %A = Add on, %C = Conversion, %E = Efficiency, %G = Grafting ratio.

4.4. *Effect of reaction time on grafting parameters*

The effect of reaction time was studied by changing the time period from 60 to 180 min (Fig. 3). There was an increase in the grafting ratio, efficiency, add on and conversion with increasing time, whereas the amount of homopolymer decreased considerably. With increasing time, there may be an addition of a greater number of monomer molecules to the growing grafted chain.

4.5. *Effect of xanthan gum concentration on grafting parameters*

The effect of the variation of gum concentration from 50.0×10^{-2} to 110.0×10^{-2} g dm^{-3} on grafting parameters has been studied and the results obtained are summarized in Table 2. Grafting ratio, add on and conversion were found to decrease with increasing concentration of xanthan gum. This may be attributed to the fact that as the concentration of gum is increased, the viscosity of reaction medium increases, which hinders the movement of free radicals causing a less efficient initiation leading to a decrease in the grafting parameters.

Table 2
Effect of xanthan gum concentration [XOH] on grafting parameters: $[Fe^{2+}] = 5.0 \times 10^{-3}$ mol dm^{-3}; $[H^+] = 1.8 \times 10^{-3}$ mol dm^{-3}; $[BrO^{-3}] = 4.0 \times 10^{-3}$ mol dm^{-3}; [ACM] $= 4.0 \times 10^{-2}$ mol dm^{-3}; Time = 120 min; Temp = 35°C

S. no.	[gum] $\times 10^2$ g dm^{-3}	%E	%A	%C	%H	%G
1	50.0	75.2	65.5	44.5	24.8	190.2
2	65.0	78.0	56.6	37.8	22.0	129.1
3	80.0	85.6	46.3	28.3	14.4	86.3
4	95.0	92.2	43.9	28.4	7.8	78.5
5	110.0	93.3	38.0	25.4	6.7	61.3

4.6. *Effect of temperature on grafting parameters*

To examine the effect of temperature on graft copolymerization, the process was carried out at 30, 35, 40 and 45°C. Grafting parameters were found to increase with temperature reaching a maximum at 35°C (Table 3). This behaviour can be attributed to the increased rate of polymerization at higher temperature. A further increase in temperature could result in the enhanced mobility of macroradicals which may lead to termination, hence the grafting parameters showed a decrease above this optimum temperature.

4.7. *Effect of acrylamide concentration on grafting parameters*

The effect of acrylamide concentration was studied by varying the concentration of acrylamide from 1.0×10^{-2} to 8.0×10^{-2} mol dm^{-3}. As the concentration of acrylamide was increased up to 4.0×10^{-2} mol dm^{-3}, grafting ratio, efficiency and add on were found to increase (Table 4), thereafter, the values of these parameters decreased. This behaviour could be explained by the fact that increase of monomer concentration leads to the accumulation of monomer molecules in close proximity to the polymer backbone. The monomer molecules that are at the immediate vicinity of reaction sites, become acceptors of xanthan gum macro radicals resulting in chain initiation and thereafter themselves become free radical donors to the neighbouring molecules, causing the lowering of termination.

5. Mechanism

Hydroxyl and halogen radicals were generated in the medium by interaction of Fe^{+2} and BrO_3^- ions as suggested by Thomas, Gleason, and Mino (1957)

$$Fe^{2+} + BrO_3^- + H_2O \rightarrow Fe^{3+} + BrO_2^- + OH^{\cdot} + OH^-$$

$$Fe^{2+} + BrO_2^- + H_2O \rightarrow Fe^{3+} + BrO^- + OH^{\cdot} + OH^-$$

$$Fe^{2+} + BrO^- + H_2O \rightarrow Fe^{3+} + Br^- + OH^{\cdot} + OH^-$$

$$Fe^{2+} + BrO^- + H_2O \rightarrow Fe^{3+} + Br^{\cdot} + 2OH^-$$

The hydroxyl and halogen free radicals abstracts hydrogen atoms from the xanthan gum molecules producing xanthan gum free radical ($XO^{\cdot}$). The monomer molecules, which are in close vicinity to the reaction sites, become acceptors of the xanthan gum radicals resulting in chain initiation and thereafter themselves become free radical donor to the neighbouring molecules, causing the grafted chains to grow. These grafted chains were terminated by

Table 3
Effect of temperature on grafting parameters: $[Fe^{2+}] = 5.0 \times 10^{-3}$ mol dm^{-3}; $[BrO_3^-] = 4.0 \times 10^{-3}$ mol dm^{-3}; $[XOH] = 65.0 \times 10^{-2}$ g dm^{-3}; $[ACM] = 4.0 \times 10^{-2}$ mol dm^{-3}; $[H^+] = 1.8 \times 10^{-3}$ mol dm^{-3}; Time = 120 min

S. no.	Temp. (°C)	%E	%A	%C	%H	%G
1	30	75.2	51.1	31.8	24.8	104.8
2	35	78.0	56.3	37.8	22.0	129.1
3	40	74.2	50.2	31.8	25.8	101.2
4	45	70.4	47.9	29.9	29.6	92.3

Table 4
Effect of acrylamide concentration [ACM] on grafting parameters: $[Fe^{2+}] = 5.0 \times 10^{-3}$ mol dm^{-3}; $[BrO_3^-] = 4.0 \times 10^{-3}$ mol dm^{-3}; $[XOH] = 65.0 \times 10^{-2}$ g dm^{-3}; $[H^+] = 1.8 \times 10^{-3}$ mol dm^{-3}; Time = 120 min; Temp. = 35°C

S. no.	$[ACM] \times 10^2$ mol dm^{-3}	%E	%A	%C	%H	%G
1	1.0	72.1	33.4	63.6	27.9	50.2
2	2.0	75.2	44.9	49.5	24.8	81.5
3	4.0	78.0	56.3	37.8	22.0	129.1
4	6.0	70.2	51.9	23.5	29.8	108.4
5	8.0	65.5	50.2	17.6	34.5	101.2

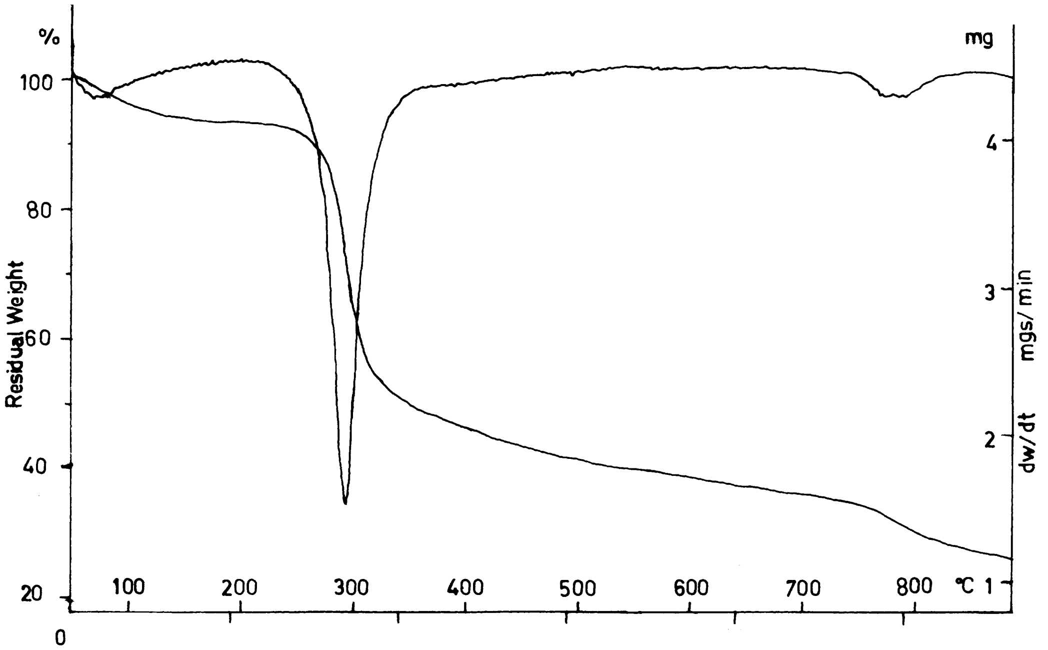

Fig. 4. Thermogravimetric trace of xanthan gum.

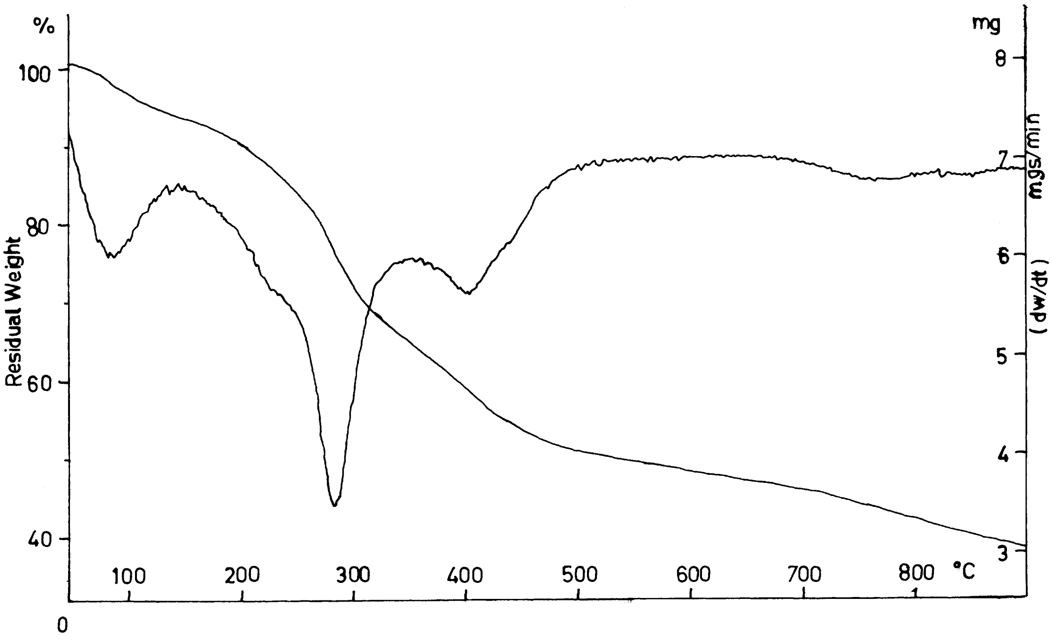

Fig. 5. Thermogravimetric trace of xanthan gum-*g*-acrylamide.

disproportionation, coupling or chain transfer to give graft copolymer.

The following steps represent the reaction mechanism:

$$\mathrm{XOH} + \mathrm{R}^{\cdot} \rightarrow \mathrm{XO}^{\cdot} + \mathrm{RH}$$

where $\mathrm{R}^{\cdot}$ stands for $\mathrm{OH}^{\cdot}$ or $\mathrm{Br}^{\cdot}$

Initiation

$$\mathrm{XO}^{\cdot} + \mathrm{M} \rightarrow \mathrm{XOM}^{\cdot}$$

$$\mathrm{R}^{\cdot} + \mathrm{M} \rightarrow \mathrm{RM}^{\cdot}$$

Propagation

$$\mathrm{XOM}^{\cdot} + \mathrm{M} \rightarrow \mathrm{XOM}^{\cdot}_{1}$$

$$\mathrm{XOM}^{\cdot}_{1} + \mathrm{M} \rightarrow \mathrm{XOM}^{\cdot}_{2}$$

$$\mathrm{XOM}^{\cdot}_{n-1} + \mathrm{M} \rightarrow \mathrm{XOM}^{\cdot}_{n}$$

$$\mathrm{RM}^{\cdot} + \mathrm{M} \rightarrow \mathrm{RM}^{\cdot}_{1}$$

$$\mathrm{RM}^{\cdot}_{1} + \mathrm{M} \rightarrow \mathrm{RM}^{\cdot}_{2}$$

$$\mathrm{RM}^{\cdot}_{n-1} + \mathrm{M} \rightarrow \mathrm{RM}^{\cdot}_{n}$$

Termination

$$\mathrm{XOM}^{\cdot}_{n} + \mathrm{XOM}^{\cdot}_{n} \rightarrow \text{graft copolymer}$$

$$\mathrm{XOM}^{\cdot}_{n} + \mathrm{RM}^{\cdot}_{n} \rightarrow \text{graft copolymer}$$

$$\mathrm{RM}^{\cdot}_{n} + \mathrm{RM}^{\cdot}_{m} \rightarrow \text{homopolymer.}$$

6. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of xanthan gum and graft copolymer was carried using the Mettler Toledo Star system in an inert atmosphere.

6.1. Xanthan gum

The thermogravimetric study of xanthan gum showed that decomposition of xanthan gum starts at 232°C, therefore it is a single step degradation process (Fig. 4). The polymer decomposition temperature (PDT) was found to be 281°C. The rate of weight loss increases initially but after 50% weight loss the rate was found to decrease. The temperature ($T_{\max}$) at which maximum weight loss observed was 296°C. The final decomposition temperature (FDT) was found to be 316°C. A char yield of 30% was obtained at 800°C.

6.2. Graft copolymer

The degradation of xanthan gum-*g*-acrylamide started above 175°C. The degradation appears to be a two stage process, i.e. from 200 to 360°C and from 360 to 485°C (Fig. 5). The maximum weight loss occurred at 285°C ($T_{\max}$). The PDT was found to be 252°C. Since the rate of weight loss decreases beyond 35% weight loss the FDT (444°C) is higher than that of xanthan gum. About 40% weight loss occurred between 220–540°C and 43% char yield was obtained at 800°C. The thermograms of the graft copolymer therefore indicate that beyond 35% weight loss graft copolymer is more stable than its substrate, i.e. xanthan gum. The grafting of acrylamide lowers the initial decomposition temperature of graft copolymers because polyacrylamide chains degrade in the temperature range of 175–300°C by the formation of imide group and evolution of ammonia. The formation of imide group imparts thermal stability, which was observed beyond 35% weight loss.

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