A Novel Feed-Stock Recyclable Hyperbranched Polymaleimide: Synthesis and Characterization

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ABSTRACT: Hyperbranched polymaleimide can be readily obtained by copolymerization of allyl maleimide and propyl maleimide. A hyperbranched polymaleimide was obtained in a yield of 56 wt % in 3 h at 50°C, whose weight average molecular mass and polydispersity index were measured by size-exclusion chromatography to be 59,000 and 4.1, respectively. TGA showed a one-step mass loss process in the decomposition of the hyperbranched polymaleimide. The dominant pyrolysis mechanism was revealed by gas chromatography/mass spectrometry to be depolymerization. The major pyrolysates of the hyperbranched polymaleimide were allyl maleimide, propyl succinimide, and other volatile monomeric units. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1848–1852, 2006

Key words: hyperbranched; polymaleimide; allyl maleimide; feed-stock recyclable

INTRODUCTION

The academic and industrial interests in maleimide polymers arose from two sides. Maleimide polymers normally exhibit excellent thermal stability, good chemical resistances, and outstanding mechanical properties.[1–4] Thus, maleimide polymers are utilized in very demanding applications, for example in the production of high-tech composites. On the other hand, maleimide polymers are flexible molecular-designing platforms for introducing new functional groups by changing the *N*-substituted groups. For instance, maleimide polymers are good matrices for introducing nonlinear chromophores, because the rigid backbones of maleimide polymers exhibit high glass-transition temperatures (T_g).[5] To avoid the stimulus and toxicity of small maleimide molecules and to improve the reactivity, heat, and impact resistance, many polyfunctional, oligomeric maleimide resins have been synthesized in addition to bismaleimides.[6–9] These maleimide resins are often toughened by allyl compounds. The most common bismaleimide resin is commercially available 4,4′-bis(maleimidodiphenyl)methane toughened by diallylbisphenol A.[1–4] It is always of high interest to predict the thermostability of materials, and the change in their properties at relatively high temperatures of use. The studies of the pyrolysis behavior and mechanism of maleimide resins will be of paramount importance for processing and performance evaluation. Recently, Nair and coworkers studied the thermal stability and degradation behavior of bismaleimide adducts by thermogravimetric analysis (TGA).[10] Torrecillas et al. studied the thermostability of bismaleimide networks by TGA, and identified the degradation products from TGA using gas chromatography/mass spectrometry (GC/MS).[11] Thermal decomposition of aliphatic and aromatic polyamides was examined by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS).[12]

In this work, we focus on the attempt to produce hyperbranched polymaleimide with maleimide and allyl unsaturated groups. The thermal stability and decomposition products of the hyperbranched polymaleimide were also examined using Py-GC/MS and TGA. Hyperbranched polymers are a type of unique structures which often combine some contradictory elements. A dendritic polymer usually has a better solubility and lower viscosity in organic solvents than a linear polymer of comparable molecular weight.

EXPERIMENTAL

Materials

Ferric acetylacetonate (FeAcAc, Aldrich, Finland), maleic anhydride (Acros, Belgium), and allylamine (Aldrich) were used as received. All solvents used in this work were of analytical grade.

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Instruments

Py-GC/MS was performed in a Pyrola 85 foil pulse pyrolyzer equipped with an interface to a Hewlett–Packard 6890–5973 gas chromatograph-mass spectrometer. Pyrolysis temperature at 680°C was set for 4000 ms. A helium carrier gas of 20 mL/min flow rate purged the pyrolysis chamber held at 250°C. The pyrolysis products were separated on a column (15 m, 0.25 mm i.d., film thickness 0.50 μm, J and W Innowax). The GC/MS interface was held at 260°C. The GC oven temperature was programmed from 50 to 250°C at 8°C/min. A helium carrier gas of 1.0 mL/min flow rate was performed for GC. The mass spectrometer was operated by electron-impact ionization (EI) at 70 eV.

TGA was performed on a Netzsch Thermo Microbalance TG 209 at a heating rate of 10°C/min under nitrogen flow of 20 mL/min.

Synthesis of allyl maleimide

To a stirred solution of maleic anhydride (Acros, 9.8 g, 0.1 mol) in 50 mL benzene (50°C) was added dropwise a solution of allylamine (Aldrich, 5.7 g, 0.1 mol) in 10 mL benzene. During addition, an exothermic reaction occurred with instantaneous formation of white precipitates. After the addition was completed, the resulting suspension was stirred for an additional 2 h. The precipitate was collected and washed with benzene. The pure amic acid was obtained as white solid in 97% yield. A mixture of 14.4 g of the amic acid (105 mmol), 100 mL of acetic anhydride, and 7.1 g of FeAcAc (Aldrich, 20 mmol, not optimized) was heated at 85°C for 3 h, and then 100 mL of ice water was added. Acetic acid was removed at 65°C under reduced pressure. Pure allyl maleimide was obtained by flash chromatography (silica gel, 90:10 v/v hexane/ethyl acetate) as a colorless crystal in a yield of 85 wt %. 300 MHz ^{1}H NMR in CDCl$_3$: 6.94 (s, 2H), 5.94 (m, 1H), 4.15 (d, 2H), 5.0–5.17 (q, 2H).

Synthesis of N-n-propyl maleimide

N-n-Propyl maleimide was synthesized as colorless liquid according to the same synthesis procedure of allylmaleimide. 300 MHz ^{1}H NMR in CDCl$_3$: 6.97(s, 2H), 3.33 (t, 2H), 1.53 (m, 2H), 0.80 (t, 3H).

Synthesis of hyperbranched polymaleimide

The copolymerization of equimolar ratio allyl maleimide and propyl maleimide was carried out in 50 wt % of tetrahydrofuran (THF) at 50°C. Benzyl peroxide (2.5 mol %; BPO) was used as initiator. High molecular weight materials could be readily obtained through careful control of reaction time. The polymaleimide
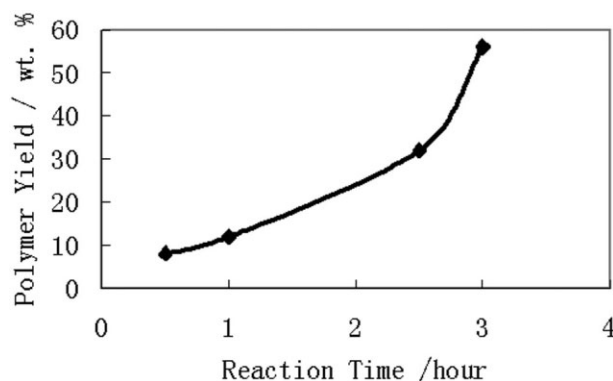

Figure 1   Polymer yield at different reaction time.

was purified by precipitation in methanol three times. ^{13}C NMR (125 MHz) for a polymer obtained in 3 h in DMSO-d_6: C=O: 176.8 (wide), 171.1, 170.6, C=C: 132 (wide), 116 (wide), C—H: 22, 20 (wide), 11 (wide).

RESULTS AND DISCUSSION

Synthesis of allylmaleimide and N-n-propyl maleimide

Because of the important applications in biology, synthetic, and polymer chemistry, many synthesis routes of maleimide derivatives have been reported.[13] One popularly used method is the cyclization of amic acid in the presence of sodium acetate.[14] We synthesized N-n-propyl maleimide by this method with a yield of about 45 wt %. However, by this method allyl maleimide in a yield of less than 2 wt %. was produced. Inspired by the work of Toru and coworkers [13] and Vorbruggen,[15] who used hexamethyldisilazane (HMDS) and a Lewis acid, for example ZnCl$_2$ to synthesize imide, we used a Lewis acid, ferric acetylacetonate (FeAcAc), in the cyclization of amic acid instead of sodium acetate, and maleimide was synthesized in a yield of 85 wt %.

Synthesis and structure of hyperbranched polymaleimide

The polymer yield at different reaction time was illustrated in Figure 1. The copolymerization systems of equimolar ratio allyl maleimide and propyl maleimide were very active, and reached 100 wt % gel conversion in 5 h. This might be because that intermolecular crosslinking predominantly occurred rather than intramolecular crosslinking.[16] However, this is good for the outward development of a dendritic structure, because gelling usually occurs by way of hyperbranched intermediates, thus the high gelation activity on the other hand implies high degree of branching.

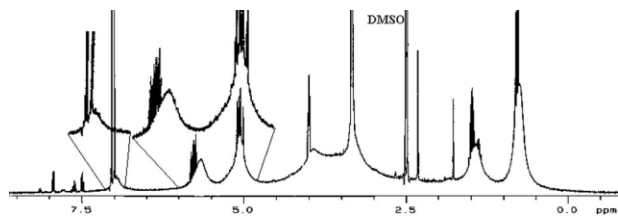A fully soluble polymer was obtained in a yield of 56 wt % in 3 h, whose weight average molecular mass

Figure 2   ¹H NMR of the polymer obtained in 3 h.

and polydispersity index were measured by size-exclusion chromatography to be 59,000 and 4.1, respectively. The wide polydispersity index was due to branching, which was a general case in the synthesis of hyperbranched polymers.

NMR results

The structure of the polymer obtained in 3 h was investigated though both ¹H and ¹³C NMR. The signals of the ¹H NMR spectrum arising from the functional groups maleimide (7.0 ppm), allyl (5.4–6.0 ppm and 4.7–5.4 ppm), and propyl (around 0.8 and 1.5 ppm) showed fine peaks over broad "hills" (Fig. 2). This implied different environments for those functional groups, in restrained and free environments, respectively. Those functional groups located in the condensed environments might show broad signals, while those in the chain ends of high freedom might show fine structures. Furthermore, the hydrogen atoms in the double bonds of maleimide groups (7.0 ppm) showed two peaks, which showed a single peak in the spectrum of monomers because of the structural symmetry. This kind of change could also be expected to occur in a three-dimensional layered structure.

Maleimide and allyl groups were measured by ¹H NMR in the macromolecule to be 0.6 and 1.4 mmol/g, respectively. Imaginably, there are about 34 maleimide groups and 83 allyl groups in one macromolecule with molecular mass of 59,000. Higher allyl contents resulted from the reluctant reactivity of allyl groups.

The structure of the obtained polymer could be further investigated with ¹³C NMR (Fig. 3). In the ketone zone (150–200 ppm), there was a broad peak and two fine peaks; the former was correspondent to the ketone groups of pyrrolidinedione linked in the
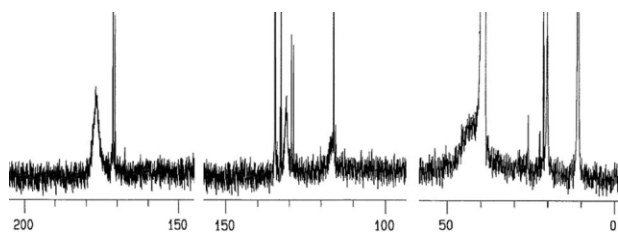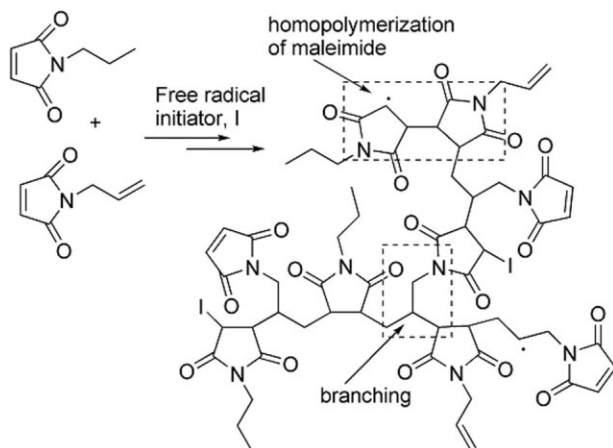

Scheme 1   Copolymerization of allylmaleimide and propyl maleimide.

polymer backbones, while the latter arose from the maleimide end groups. Vinyl groups of both maleimides and allyl groups were assigned in the vinyl zone (100–150 ppm). The broad peak in this zone was also due to the existence of a restrained environment.

The copolymerization of allyl maleimide and propyl maleimide to form hyperbranched polymers are illustrated in Scheme 1. Generally, two kinds of reactions may happen in the copolymerization of equimolar allyl maleimide and propyl maleimide: alternating copolymerization between maleimide groups and allyl groups, and homopolymerization between maleimide groups of either propyl maleimide or allyl maleimide, as illustrated in Scheme 1. According to our previous work, the homopolymerization of maleimide groups could not be neglected.[17] These pendant unsaturated groups could become branching junctions by reinitiating, chain transferring, or combination termination of radicals. Thus, a highly branched polymaleimide with both allyl and maleimide groups can be obtained. Intramolecular cycling might also happen. For a three-dimensional molecule, the central parts might have higher bond density than did outer sphery parts.

Many other new functional groups may be introduced by changing the N-substituted groups in this method, for example, aromatic group to further improve the thermal properties, 1-naphthyl group to produce highly optically active or highly optically reflective materials,[18] or ferrocene group to produce redox active materials[19,20] or fire retards.

Thermal decomposition

The thermal stability of the obtained polymaleimide was investigated by TGA (Fig. 4). The polymaleimide obtained in this work showed apparently a one-step mass loss process. The mass loss at about 120°C corresponded to the loss of adsorbed water. Many male-
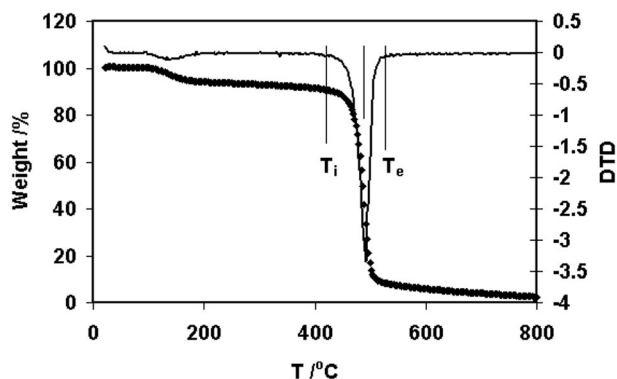

Figure 3   ¹³C NMR of the polymer obtained in 3 h.

Figure 4 TGA of the highly branched maleimide resin.

imide resins showed a two-step mass loss process because of high contents of lowly thermally stable bonds.[3,4,21] The decomposition temperature of the polymaleimide measured by TGA was found to be 477°C. The maximun decomposition speed appeared at 491°C. The thermogram showed that initial pyrolysis temperature (T_i) was 440°C, and pyrolysis end temperature (T_e) was 499°C. Char residue was only 4.0% at 700°C, and 2.4% at 800°C. Most decomposition products of the hyperbranched polymaleimide were volatile. Thus the degradation of the hyperbranched polymaleimide showed some interesting features: high initial decomposition temperature but fast decomposition process with very low char residue. The hyperbranched polymaleimide might serve as a high temperature foamer.

In a good comparison, the decomposition temperature of the commercial maleimide resin Matrimid 5292 ™ from Ciba-Geigy Company was measured under the same conditions to be about 420°C, whose lower decomposition temperature may be caused by the phenol structure in Matrimid 5292.[4]

The decomposition products were checked with pyrolysis GC-MS. The chromatogram of the hyperbranched polymaleimide by flash pyrolysis at 680°C is shown in Figure 5. The pyrolysates were identified by mass spectra and mass library search. Table I listed these products identified for the pyrolysis of the hyperbranched polymaleimide.
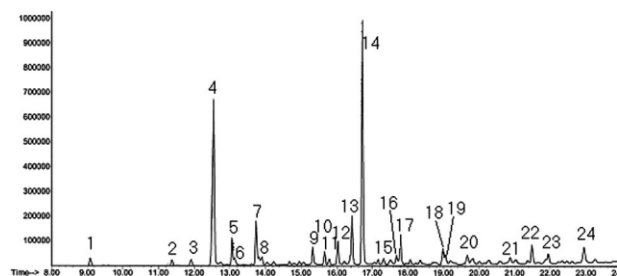

Figure 5 Chromatogram of the pyrolysis products of highly branched polymaleimide at 680°C.

TABLE I
Identification of the Peaks of Pyrolysis Chromatogram Tentatively Assigned on the Basis of GC/MS and Library Searches

Peak no.	Retention time (min)	Abundance (%)	Identified product
1	9.08	3.5	Acetic acid
2	11.42	2.4	Methyl maleimide
4	12.55	67	Propyl maleimide
7	13.75	17.6	Allyl maleimide
10	15.65	5.9	Ethyl succinimide
12	16.03	10.6	Methyl succinimide
14	16.73	100	Propyl succinimide
16	17.69		N—C_5H_{11} maleimide
18	18.98		N—C_5H_{11} maleimide
20	19.65		Maleimide
21	20.87		Methyl phthalimide
22	21.49	8.2	n-Propyl phthalimide

The major products from scission of the hyperbranched polymaleimide in Py-GC/MS were n-propyl maleimide and n-propyl succinimide. Depolymerization was the dominant pyrolysis mechanism. Rearrangements happened during pyrolysis, resulting in the formation of phthalimide products. The only and few low molecular mass product is acetic acid, because the monomeric units of maleimides or succinimides are very stable.

The Py-GC/MS results revealed that the hyperbranched polymaleimide was a (pro-) feed-stock recyclable polymer, which is important for the future. Industrial efforts are being pursued to make materials with environmental compatibility and economical recyclability.

CONCLUSIONS

Hyperbranched polymaleimide can be readily obtained by copolymerization of allyl maleimide and propyl maleimide. A hyperbranched polymaleimide was obtained in a yield of 56 wt % in 3 h at 50°C, whose weight average molecular mass and polydispersity index were measured by size-exclusion chromatography to be 59,000 and 4.1, respectively. TGA showed a one-step mass loss process in the decomposition of the hyperbranched polymaleimide. The dominant pyrolysis mechanism was revealed by GC/MS to be depolymerization. The major pyrolysates of the hyperbranched polymaleimide were allyl maleimide, propyl succinimide, and other volatile monomeric units. Hence, the pyrolysis of the hyperbranched polymaleimide gave very low char yield.

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