Synthesis and characterization of poly(N-tert-alkylmaleimide)s

2. Synthesis of high molecular weight polymaleimide by thermolysis of poly(N-tert-alkylmaleimide)

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ABSTRACT

N-tert-Butylmaleimide (tBMI), N-tert-amylmaleimide (tAMI) and N-tert-octylmaleimide (tOMI) were polymerized in the presence of a radical initiator to give high molecular weight polymers. The polymerization reactivity was found to depend on the bulkiness of the N-substituent. From thermogravimetric analysis of the polymers obtained, it was revealed that these polymers thermally decomposed via a two-step mechanism, i.e. elimination of olefins at the first step and decomposition of the resulting N-unsubstituted polymaleimide (poly(MI)) at the second step. The high molecular weight poly(MI) was isolated by thermolysis of poly(tBMI), poly(tAMI) and poly(tOMI) with elimination of isobutene, 2-methyl-1-butene and 2-methyl-2-butene, and 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, respectively. It was also confirmed that the resulting poly(MI) had excellent thermal stability.

Introduction

The homo- and copolymers from N-phenylmaleimides and its derivatives have excellent thermal stability. In previous papers [1-4], we have reported on radical polymerization of N-alkylmaleimides and N-(alkyl-substituted phenyl)maleimides with various substituents and on thermal stability of the resulting polymers. These thermally stable polymaleimides are expected to be applied to various fields. For example, Turner et al. reported a new polymer of a high glass transition temperature as a deep-UV resist material, i.e. phenolic copolymers based on N-(p-hydroxyphenyl)maleimide [5], from which high resolution images exhibiting no deformation on heating to 200°C was obtained in either positive and negative tone by protection of the phenolic group with a tert-butoxycarbonyl group [6,7].

In preceding paper [8], N-tert-butylmaleimide (tBMI) was observed to polymerize quite easily in the presence of a radical initiator. It has been already found that poly(tBMI) is available for preparation of a high molecular weight polymaleimide (poly(MI)) by olefin elimination from the side chain [4]. In this paper, polymerization reactivity of N-tert-alkylmaleimides (tRMI) as shown in Scheme I and thermal decomposition behavior of the resulting poly(tRMI)s are investigated.

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Experimental

tRMIs were prepared from maleic anhydride and a corresponding tert-alkylamine by the method described in previous papers [1-3]. *N*-tert-Amylmaleimide (tAMI) (N-(1,1-dimethylpropyl)maleimide): yield 24%, bp 82°C/9 mmHg, 13C NMR(CDCl3) δ 172.5(C=O), 133.8(C=C), 60.8(–C–), 33.0(CH2), 26.9(CH3), 25.6(CH3); 1H NMR(CDCl3) δ 6.43(s, 2H, CH=), 1.87(q, J = 7.2 Hz, 2H, CH2), 1.52(s, 6H, CH3), 0.77(t, J = 7.2 Hz, 3H, CH3). *N*-tert-Octylmaleimide (tOMI) (N-(1,1,3,3-tetramethylbutyl)maleimide): yield 39%, bp 91°C, mp 54.5°C, 13C NMR(CDCl3) δ 172.3(C=O), 133.9(–C–), 60.5(–C–), 50.6(CH2), 31.3(–C–), 30.9(CH3), 29.8(CH3); 1H NMR(CDCl3) δ 6.48(s, 2H, CH=), 1.86(s, 2H, CH2), 1.62(s, 6H, CH3), 0.91(s, 9H, CH3).

Polymerization was carried out with 2,2'-azobisisobutyronitrile (AIBN) or dimethyl 2,2'-azobisobutyrate (MAIB) in a similar way to those in previous papers. The polymers were purified by reprecipitation.

Gel permeation chromatography (GPC) was performed in THF at 38°C, and number- and weight-average molecular weights (Mn and Mw) were calibrated with standard polystyrenes. Intrinsic viscosity ([η]) was measured in benzene for poly(tRMI)s and in dimethylformamide (DMF) for poly(MI) at 30°C. Thermogravimetric analysis (TGA) was carried out with ca. 1.5 mg of a polymer sample in a nitrogen stream with a heating rate of 10°C/min.

Results and Discussion

Radical polymerization reactivity of tRMIs

Radical polymerization of tRMIs was carried out with AIBN in benzene at 60°C. The results of the polymerization are shown in Fig. 1 and Tab. I. It was found that all tRMIs polymerized readily to give a high molecular weight polymer as well as other N-alkylmaleimides such as N-n-butylmaleimide (nbMI) [1]. However, the polymerization reactivity, i.e. polymerization rate, [η] and Mn of the polymer were observed to decrease, as the bulkiness of the alkyl substituents increased, especially in the case of polymerization of tOMI bearing the bulkiest N-substituent. It was different from the fact that the introduction of higher n-alkyl substituents such as n-octyl and octadecyl groups did not interfere the polymerization at all [1,9]. It may be interpreted with the steric hindrance by the introduction of a bulky substituent in the propagation. On the other hand, N-unsubstituted maleimide (MI) showed a low polymerization reactivity, compared with other maleimides [1].

Tab. I Radical Polymerization of tRMIs in Benzene

<table>
<thead>
<tr>
<th>tRMI</th>
<th>N-Substituent</th>
<th>Yield (%)</th>
<th>[η]b (dL/g)</th>
<th>Mn c x 10-4</th>
<th>Mw/Mnc</th>
</tr>
</thead>
<tbody>
<tr>
<td>tBMI</td>
<td>tert-butyl</td>
<td>82.8</td>
<td>0.68</td>
<td>14.9</td>
<td>2.50</td>
</tr>
<tr>
<td>tAMI</td>
<td>tert-amyl</td>
<td>71.2</td>
<td>0.61</td>
<td>13.0</td>
<td>2.14</td>
</tr>
<tr>
<td>tOMI</td>
<td>tert-octyl</td>
<td>26.5</td>
<td>0.27</td>
<td>4.95</td>
<td>1.83</td>
</tr>
<tr>
<td>nbMI</td>
<td>n-butyl</td>
<td>78.4</td>
<td>0.76</td>
<td>15.9</td>
<td>2.55</td>
</tr>
<tr>
<td>MI</td>
<td>none</td>
<td>34.3</td>
<td>0.29</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

a [tRMI] = 1.0 mol/L, [AIBN] = 5 x 10^-3 mol/L at 60°C for 5 h. b In benzene at 30°C. c By GPC in THF. d In DMF at 30°C.