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

1. Radical polymerization of N-tert-butylmaleimide leading to a less-flexible poly(substituted methylene)

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ABSTRACT

N-tert-Butylmaleimide (tBMI) polymerized readily in the presence of a radical initiator in spite of its bulky N-substituent to give a high molecular weight and less-flexible poly(substituted methylene). From kinetic investigation for the polymerization of tBMI with 2,2'-azobisisobutyronitrile (AIBN) in benzene, it was revealed that the rate of polymerization ($P_p$) was expressed as $P_p = k [AIBN]^{0.51}[tBMI]^{1.4}$, and the overall activation energy was 99.6 kJ/mol. The high polymerization of tBMI was assumed to result from the decrease in the rate of bimolecular termination between rigid polymer radicals bearing a bulky substituent. The flexibility of the polymer chain was examined by the viscometric and light scattering methods, and the effect on the polymerization reactivity was discussed.

Introduction

In previous papers [1-5], we have reported that dialkyl fumarates (DRF), $N,N,N',N''$-tetraalkylfumaramides and alkyl $N,N$-diethylfumaramates polymerize with a radical initiator to give high molecular weight polymers consisting of rigid poly(substituted methylene)s, in which all carbons of the main chain are substituted.

Maleimide and its N-substituted derivatives, one of 1,2-disubstituted ethylenes, are well-known to polymerize easily. We have already reported on the polymerization of N-alkylmaleimides or N-(alkyl-substituted phenyl)-maleimides bearing various substituents, and on the thermal properties of the polymers [6-9]. The polymaleimides with a bulky group as N-substituent were expected to have a relatively rigid conformation [10,11], as well as poly(DRF) [3-5]. The formation of less-flexible vinyl polymers with bulky substituents influences polymerization behavior, i.e. it decreases the bimolecular termination rate, resulting in easy observation of an ESR spectrum of the propagating polymer radical because of the increasing radical concentration at a stationary state, as observed in the polymerization of DRF [3].

As reported in previous papers [6,7], N-tert-butylmaleimide (tBMI) had a high polymerization reactivity, and a benzene-soluble and high molecular weight polymer was obtained from polymerization in bulk or in benzene with a high yield. Moreover, poly(tBMI) is interesting as a precursor for the synthesis of N-unsubstituted polymaleimide by thermolysis as will be described in the subsequent paper.

In this paper, radical polymerization of tBMI is investigated kinetically in detail, and the polymer chain flexibility estimated from the viscosimetric and light scattering data in its dilute solution is discussed in the view of the effects on the polymerization reactivity.

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Experimental


tBMI was prepared according to the method in literature [12]. Yield
30%, bp 54°C/3.5 mmol/L, d^{25} 1.061, ^{13}C NMR(CDCls) δ 171.1(C=O), 133.3(C=C),
56.2(–C–), 28.1(CH₃); ^{1}H NMR(CDCls) 6 6.55(s, 2H, CH=), 1.55(s, 9H, CH₃).
The purity of tBMI was checked by NMR spectroscopy and high performance
liquid chromatography. Other reagents and solvents were purified according to
ordinary methods.

Polymerization was carried out in the presence of 2,2'-azobisisobutyronitrile (AIBN) in a sealed glass tube. After a given time, the polymerization
mixture was poured into a large amount of methanol to precipitate the polymer. The yield of polymers dried was determined gravimetrically.

Intrinsic viscosity ([η]) was measured in benzene at 30°C by using an
Ubbelohde viscometer. The number-average molecular weight (Mₙ) was determined in toluene at 38°C with a membrane osmometer (Knauer). Light scattering measurement was performed with a Union Giken LS-601 spectrometer. The specific refractive index increment of poly(tBMI) was 0.107 mL/g in tetrahydrofuran (THF). Gel permeation chromatography (GPC) was carried out in THF at 38°C, and number- and weight-average molecular weights (Mₙ,GPC and Mₙ,OS) were calibrated with standard polystyrenes.

Results and Discussion

Radical polymerization of tBMI

Radical polymerization of tBMI was carried out in benzene or in bulk
with AIBN. As shown in Tab. I, polymerization of tBMI proceeded rapidly in
spite of the 1,2-disubstituted ethylenic structure and its bulky N-substituent,
as well as other N-substituted maleimides [7].

The time-conversion relations of polymerization of tBMI was examined at
40-80°C. The results are shown in Fig. 1. The overall activation energy
for the polymerization was calculated to be 99.6 KJ/mol from an Arrhenius

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Time</th>
<th>Yield (%)</th>
<th>[η] (dl/g)</th>
<th>Mₙ,GPC x 10⁻⁵</th>
<th>Mₖ,GPC x 10⁻⁵</th>
<th>Mₙ x 10⁻⁵ (mL/g²)</th>
<th>Mₖ x 10⁻⁵</th>
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<td>80</td>
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<td>57.8</td>
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<td>70</td>
<td>0.75</td>
<td>62.1</td>
<td>0.487</td>
<td>0.938</td>
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<td>51.1</td>
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<tr>
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<td>3.23</td>
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<td>11.3</td>
<td>1.47</td>
</tr>
</tbody>
</table>

*a [tBMI] = 1 mol/L, [AIBN] = 5 x 10⁻³ mol/L in benzene. *b In benzene at
30°C. *c Gel permeation chromatography in THF, calibrated with standard
polystyrenes. *d Membrane osmometry in toluene. *e Light scattering in THF.
"Polymerized in bulk, [AIBN] = 3.7 x 10⁻² mol/L.