

Polymerization of *N*-Phenylmaleimide with a Rare-Earth Coordination Catalyst

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ABSTRACT: The polymerization of *N*-phenylmaleimide was carried out with the binary rare-earth coordination catalyst lanthanum phosphonate [La(P₅₀₇)]–trisobutyl aluminum [Al(*i*-Bu)₃] in toluene at 60°C. The dependence of the polymerization on the polymerization time, the molar ratio of Al(*i*-Bu)₃ to La(P₅₀₇), and the concentration of the catalyst were studied. The structures of the resultant polymer were characterized with ¹H-NMR, ¹³C-NMR, and Fourier trans-

form infrared spectrophotometry, and the thermal properties of the polymer were measured with thermogravimetric analysis. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 979–982, 2005

Key words: catalysts; ziegler-natta polymerizations; thermal properties

INTRODUCTION

Many studies have been carried out on the polymerization of *N*-substituted maleimides because the polymers are among the most important resins in the aerospace/aircraft and electrics/electronics industries on account of their tractability, high thermal stability, high durability, fire resistance, radiation resistance, and relatively low cost.^{1–3} The radical and anionic polymerization behavior of *N*-substituted maleimides and the thermal properties of the resulting polymers have been extensively studied by many researchers.^{4–15} However, the polymerizations of maleimide by coordination catalysts have been seldom reported.

Jiang et al.¹⁶ reported the polymerization of *N*-phenylmaleimide (NPMI) catalyzed by a rare-earth catalyst composed of neodymium acetylacetonate [Nd(acac)₃ · 3H₂O], dibutylmagnesium [Mg(*n*-Bu)₂], and hexamethylphosphoramide in tetrahydrofuran and toluene. However, the yield of the polymer was rather low when alkyl aluminum was used.

In this article, we report the polymerization of NPMI with a binary rare-earth coordination catalyst, lanthanum phosphonate [La(P₅₀₇)₃]–trisobutyl aluminum [Al(*i*-Bu)₃], in toluene at 60°C. The polymer was

proved to be poly(*N*-phenylmaleimide) with ¹H-NMR, ¹³C-NMR, and Fourier transform infrared (FTIR). The polymer had excellent thermal stability according to thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

La(P₅₀₇)₃ was prepared from lanthanum oxide as described previously.¹⁷ Al(*i*-Bu)₃ was used as purchased from Roth Co. (Germany). The binary catalysts were obtained through the addition of Al(*i*-Bu)₃ to a toluene solution of La(P₅₀₇) and aging for 30 min at 60°C. NPMI was prepared from maleic anhydride and aniline according to a method described in the literature¹⁸ and was recrystallized from cyclohexane three times. Toluene was purified according to the usual method and was distilled before use.

Polymerization

The catalyst and a toluene solution of NPMI were added to ampules, which were heated, evacuated, and filled with nitrogen several times; then, the ampules were placed in a thermostat at 60°C. After a fixed time, the polymerization was terminated by the addition of ethanol with 10% HCl, which destroyed the trapped catalyst. The resultant polymer was filtered off, washed several times with pure ethanol, and then dried *in vacuo* to a constant weight.

Measurements

The ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker Avance AMX-500 NMR spectrometer

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TABLE I
Polymerization of NPMI by Different Catalysts

Run	Catalyst	Yield (%)	$[\eta]$ (dL/g)
1	$\text{La}(\text{P}_{507})_3\text{-Al}(i\text{-Bu})_3$	86.0	0.13
2	$\text{La}(\text{naph})_3\text{-Al}(i\text{-Bu})_3$	30.4	0.07
3	$\text{La}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$	28.4	0.08
4	$\text{La}(\text{PhCOO})_3\text{-Al}(i\text{-Bu})_3$	28.7	0.10
5	$\text{La}(\text{P}_{507})_3$	Trace	—
6	$\text{Al}(i\text{-Bu})_3$	37.2	0.16

$[\text{La}] = 10^{-3}$ mol/L, $[\text{Al}] = 8 \times 10^{-3}$ mol/L, and $[\text{NPMI}] = 5 \times 10^{-2}$ mol/L. Polymerization was performed in toluene at 60°C for 6 h.

(Bruker Co., Zurich, Switzerland) for solutions in CDCl_3 with tetramethylsilane as the internal standard. An FTIR (KBr pellets) spectrum was measured on a Bruker Vector 22 spectrometer. The intrinsic viscosity of the polymer was measured with an Ubbelohde-type viscometer at 30°C in dimethylformamide. TGA and differential scanning calorimetry were performed on a STA409PC thermogravimetric analyzer (Netzsch Gerätebau GmbH, Selb, Germany) at a heating rate of 8°C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Polymerization of NPMI

The polymerizations of NPMI with different catalysts were carried out, and the results are summarized in Table I. $\text{La}(\text{P}_{507})$ itself could not initiate the polymerization of NPMI, but in combination with $\text{Al}(i\text{-Bu})_3$, it showed a much higher catalytic ability for the polymerization of NPMI than $\text{Al}(i\text{-Bu})_3$ did. As for the four binary rare-earth coordination catalysts, $\text{La}(\text{P}_{507})\text{-Al}(i\text{-Bu})_3$ possessed a higher catalytic ability than the others. However, the intrinsic viscosity of the polymers

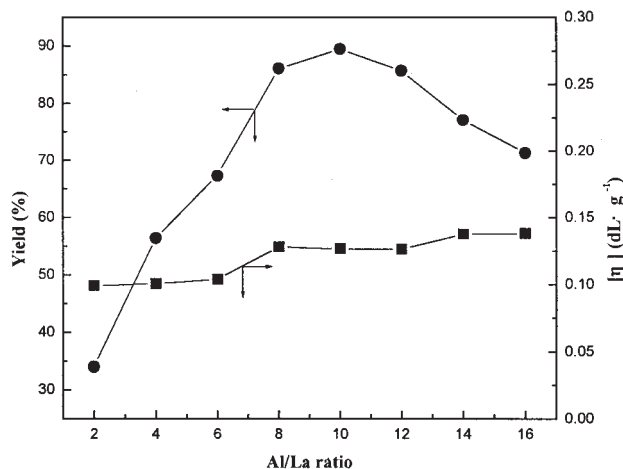


Figure 1 Effect of the molar ratio of $\text{Al}(i\text{-Bu})_3$ to $\text{La}(\text{P}_{507})_3$ on the polymerization ($[\text{La}] = 10^{-3}$ mol/L, $[\text{NPMI}] = 5 \times 10^{-2}$ mol/L, toluene, temperature = 60°C, time = 6 h).

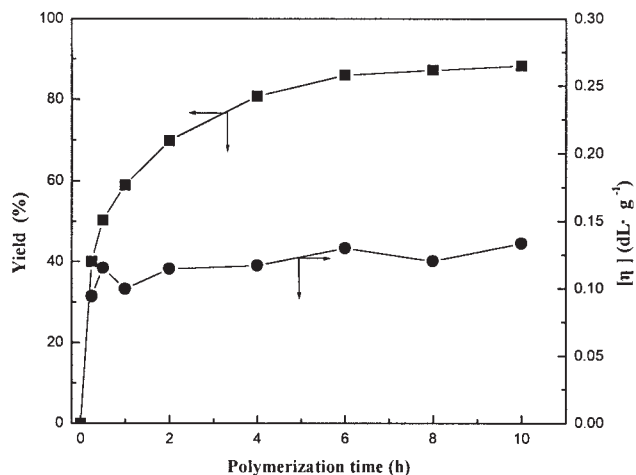


Figure 2 Effect of the polymerization time on the polymerization ($[\text{La}] = 10^{-3}$ mol/L, $[\text{Al}] = 8 \times 10^{-3}$ mol/L, $[\text{NPMI}] = 5 \times 10^{-2}$ mol/L, toluene, temperature = 60°C).

was rather low, about 0.1 dL g^{-1} , which was about the same level as that of the polymer obtained by free-radical polymerization⁴ and group-transfer polymerization.¹³

The ratio of $\text{Al}(i\text{-Bu})_3$ to $\text{La}(\text{P}_{507})$ was an important factor that affected the catalytic ability of the binary catalyst. Figure 1 shows the effect of the ratio of $\text{Al}(i\text{-Bu})_3$ to $\text{La}(\text{P}_{507})$ on the polymerization of NPMI. The yield of the polymer increased as the Al/La ratio increased, but after the Al/La ratio reached 10, the yield decreased. The intrinsic viscosity of the polymers also increased gradually as the Al/La ratio increased, and this was not like the polymerization of other monomers, such as ethylene oxide¹⁹ and epichlorohydrin,²⁰ by rare-earth coordination catalysts. This perhaps occurred because as the molar ratio of $\text{Al}(i\text{-Bu})_3$ to $\text{La}(\text{P}_{507})$ increased, the concentration of isolated $\text{Al}(i\text{-Bu})_3$ also increased. Table I shows that the polymer of NPMI catalyzed by $\text{Al}(i\text{-Bu})_3$ had a higher intrinsic viscosity than the polymer catalyzed

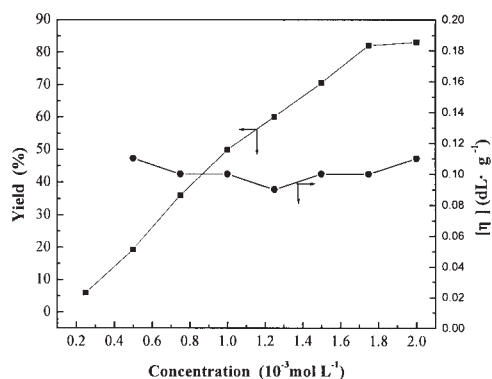


Figure 3 Effect of the catalyst concentration on the polymerization ($[\text{Al}]/[\text{La}] = 8$, $[\text{NPMI}] = 5 \times 10^{-2}$ mol/L, toluene, temperature = 60°C, time = 0.5 h).

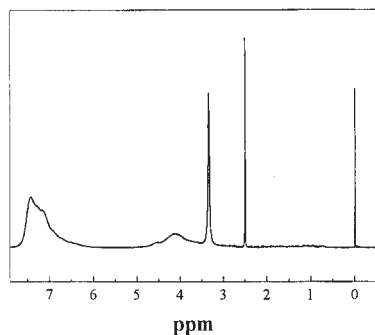


Figure 4 ^1H NMR spectrum of the polymer of NPMI in dimethyl sulfoxide- d_6 .

by the binary catalyst $\text{La}(\text{P}_{507})\text{-Al}(i\text{-Bu})_3$. As a result, the intrinsic viscosity of the polymer increased as the molar ratio of $\text{Al}(i\text{-Bu})_3$ to $\text{La}(\text{P}_{507})$ increased.

The rate of polymerization of NPMI with $\text{La}(\text{P}_{507})\text{-Al}(i\text{-Bu})_3$ is shown in Figure 2. The polymerization rate was fairly high in the first hour and decreased gradually with time. The reduction of the polymerization rate may have been caused by a reduction of the monomer concentration and insufficient diffusion of the NPMI molecules to the propagation species due to the precipitation of the polymer from toluene.

The effect of the catalyst concentration on the polymerization is shown in Figure 3. The yield of the polymer was almost first-order with respect to the catalyst concentration.

Characterization of the polymer

The polymer prepared with $\text{La}(\text{P}_{507})\text{-Al}(i\text{-Bu})_3$ was characterized with ^1H -NMR, ^{13}C -NMR, and FTIR. Figure 4 shows the ^1H -NMR spectrum of the polymer. The signal of the phenyl group appears from 6 to 8 ppm, and the signal of the methine group appears from 3 to 5 ppm. However, the signal of the protons in the -CH=CH- structure cannot be seen in the spectrum, and this indicates that the polymerization of NPMI proceeded through the opening of the carbon-carbon double bond of the monomer molecules.

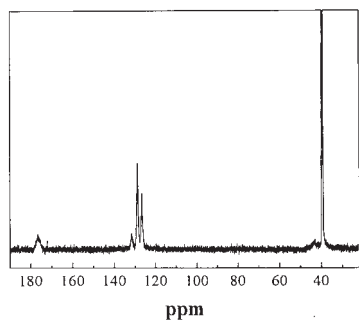


Figure 5 ^{13}C NMR spectrum of the polymer of NPMI in dimethyl sulfoxide- d_6 .

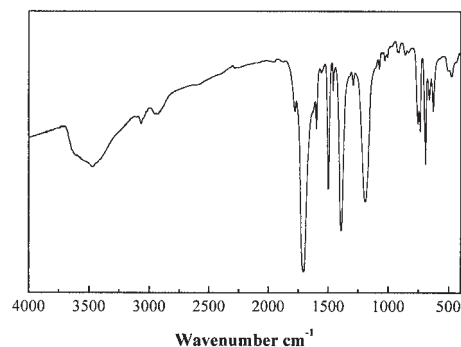


Figure 6 FTIR spectrum of the polymer of NPMI.

The ^{13}C -NMR spectrum of the polymer is shown in Figure 5. The signals at 176 ppm and 127–132 ppm are assigned to the carbonyl and phenyl carbons of the polymers. The broadened signal from 38 to 42 ppm is attributed to the methine carbons in the polymer chain.

Figure 6 shows a typical IR spectrum of the obtained polymer. The absorption bands at 1772 and 1702 are due to the carbonyl bond in the imide ring. The band at 1390 is attributed to the C-N-C in the imide ring. The bands assigned to the aromatic ring can be observed at 3050 (CH), 1597 (C=C), 1500 (C=C), and 754 and 690 cm^{-1} (monosubstitution). The strong ethylene CH stretch at 840 cm^{-1} is absent, and this indicates that the addition polymerization of the vinylene group took place; this agreed with the result from the NMR spectrum.

To examine the thermal stability of the polymer obtained, we performed TGA in a nitrogen atmosphere. As shown in Figure 7, the thermal decomposition of the polymer proceeded via a one-step reaction, and no substantial weight loss was observed below 350°C. The initial decomposition temperature (T_{ini}) was 390°C; it was obtained by extrapolation. The

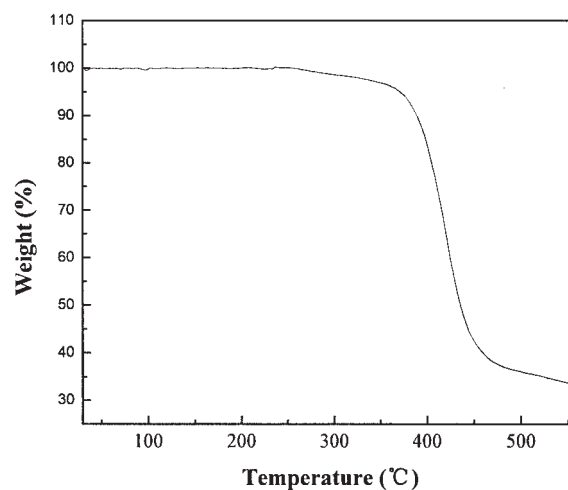


Figure 7 TGA thermogram of the polymer of NPMI.

maximum decomposition temperature (T_{\max}) was 420°C, and the residue weight at 500°C was about 36 wt %.

CONCLUSIONS

The polymerization of NPMI by binary rare-earth coordination catalysts was developed. The effect of factors such as the molar ratio of Al(*i*-Bu)₃ to La(P₅₀₇), the polymerization time, and the catalyst concentration were also investigated. The character of the obtained polymer showed that the polymerization of NPMI proceeded via the opening of the double bond in the monomer molecules. The polymer showed excellent thermal stability. T_{ini} was 390°C, and T_{max} was 420°C.

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