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ORIGINAL PAPER

Copolymerization of norbornene and methyl acrylate catalyzed by $Nd(naph)_3$–$Al(i\text{-}Bu)_3$

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Abstract The copolymerization of norbornene (NB) and methyl acrylate (MA) catalyzed by $Nd(naph)_3$–$Al(i\text{-}Bu)_3$ and the structure of the copolymers are studied in this article. All polymerization reactions were carried out under nitrogen atmosphere using syringe technique. The copolymers are characterized by IR, ^1H NMR, ^{13}C NMR, GPC, and TGA. Norbornene and methyl acrylate are 22.2 and 77.8 mol%, respectively, in the copolymer. The molecular weight distribution is $M_w/M_n < 2.0$. The molecular weight of copolymer changes with the change of NB/MA in molar ratio. Molecular weight and its distribution of copolymer decrease as molar ratio of NB/MA increases. The copolymerization can be performed in solvents such as aromatic hydrocarbon. The copolymerization can be obtained at room temperature, whereas the copolymer yield increases with increasing reaction temperature. The yield of copolymer changes with the Al/Nd molar ratio with a preferable Al/Nd molar ratio of 30.

Keywords Neodymium naphthenate · Triisobutyl aluminum · Norbornene · Methacrylate · Copolymerization

Introduction

Copolymers of norbornene and acrylates are important photolithography materials. Currently, radical polymerization is widely used for the copolymerization of norbornene (NB) and acrylates, such as Sharon's [1] atom transfer radical alternating

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polymerization, Craford, Houlihan, and Gu's [2–4] radical polymerization. In contrast, Hreha et al. [5] prepared the homopolymers of NB and acrylates by radical polymerization. Among the radical polymerization methods, atom transfer radical polymerization can achieve a yield as high as 25–54% with the NB and acrylates monomer molar ratio of 1:1. But the molecular weight is relatively low and mostly less than 5,000. Huang et al. [6] obtained copolymers catalyzed by Nickel catalyst. However, the Nickel catalyst shows high activity for homopolymerizations of NB or acrylates, instead of the copolymerization of NB and acrylates. The copolymer yield is only 1% with the aluminum alkoxide/nickel acetylacetonate ratio of 100. Recently, Wang et al. [7] reported copolymerization of NB and acrylates with Pd(II)/MAO complex as catalyst, which yielded copolymers with broad molecular weight distribution ($M_w/M_n = 3.19$–3.56). Szuromi et al. [8] copolymerized NB and acrylates by using bimetallic palladium(II) allyl complex as catalyst and obtained copolymers with a narrow molecular weight distribution of 1.1–1.9. Ma et al. [9] reported the copolymerization of NB and acrylates by using mixture catalysts. It is still a challenge to design catalysts suitable for the copolymerization of acrylates and NB. There are very few reports on the copolymerization of NB and acrylates monomers by rare earth catalyst. The authors have developed the rare earth catalysts for the polymerization of acrylates and copolymerization of epoxide and cycloanhydride [10–12]. Here, a rare earth catalyst system is used for the copolymerization of NB and acrylates. It is found that rare earth catalyst shows fast polymerization with high polymer yield and narrow molecular weight distribution. Moreover, the influencing factors, molecular weight, molecular weight distribution, and the kinetics of copolymerization of NB and methyl acrylate (MA) by rare earth catalyst are investigated.

Experimental section

Materials

Methyl acrylate (C.R.) was rinsed with 5% aqueous NaOH and water, dried over anhydrous $CaCl_2$, and refluxed over CaH_2, followed by distillation under reduced pressure prior to use. Norbornene (99%) was purchased from Lancaster, England and used as recieved. Benzene, toluene, tetrohydrofuran, petroleum ether, and cyclohexane are all analytical reagents, and dehydrated by molecular sieve before use. Triisobutyl aluminum (>95%) was obtained from Fluka AG, Switzerland. Neodymium naphthenate was obtained by the method of complexation and precipitation [13].

Preparation of catalyst

Neodymium naphthenate (0.30 g) was dissolved in toluene (2.5 mL) in a single-neck flask at room temperature. Then appropriate amount of triisobutyl aluminum was added into the flask to produce the catalyst solution. It was found that the preferable molar ratio of Neodymium naphthenate/triisobutyl aluminum was 1:30.

Copolymerization

The copolymerization reaction was performed in a single-neck flask with nitrogen atmosphere. The monomer, solvent, and catalyst were added into the flask and copolymerized for a certain time at a constant temperature (as detailed in the text). Then the ethanol solution containing 5% hydrochloric acid was added to cease the reaction. The precipitated copolymer was washed with ethanol and then dried in vacuum.

Characterization

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DMX400 spectrometer in chloroform at room temperature. The fouier transform infrared (FTIR) spectra were performed using a Paragon-1000 IR spectrophotometer. The molecular weights of the polymers were measured by Waters 1525 GPC using THF as eluent. The thermogravimetric analysis (TGA) were determined by Pyris-1 TGA.

Results and discussion

Copolymer structure

The resulting product of copolymerization of NB and MA catalyzed by $Nd(naph)_3$–$Al(i\text{-}Bu)_3$ is white solid and can be dissolved in chloroform, THF and toluene, while insoluble in methanol. Figure 1 shows the FTIR spectrum of the copolymer with monomer ratio of 1:1. The absorbance at 1738 cm^{-1} in the FTIR spectrum indicates the presence of carbonyl groups which originate from aliphatic ester in MA co-units, demonstrating the MA units in the copolymer. Moreover, the absence of band

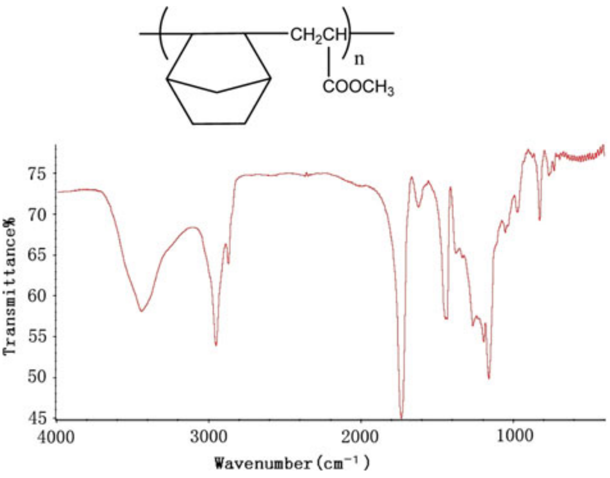

Fig. 1 Infrared spectrum of NB/MA (molar ratio of 1:1) copolymer

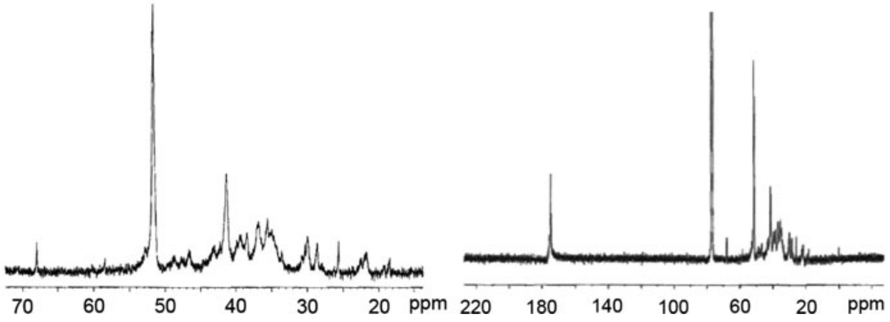

Fig. 2 ^{13}C NMR spectra of NB/MA (molar ratio of 1:1) copolymer

at 1600 cm^{-1}, indicating a fully saturated polymer, confirmed that NB is not ring-opening copolymerization. The ^{13}C NMR spectra of the copolymer with monomer ratio of 1:1 were used to confirm the structure as shown in Fig. 2. The peaks at $\delta = 174.90$ ppm (–C(O)O), $\delta = 51.74$ ppm (–OCH$_3$), $\delta = 41.37$ (–CH–) ppm and $\delta = 35.58$ ppm (–CH$_2$–) are contributions from MA unit, and the peaks between 28.42 and 43.02 ppm attribute to NB unit. The major absorption peaks of the spectra correspond to carbon atom in the structural unit of the copolymer [1]. Moreover, it can be calculated to get 22.2 mol% NB in the copolymer from the ^{1}H NMR spectra (Fig. 3) of the copolymer with monomer ratio of 1:1.

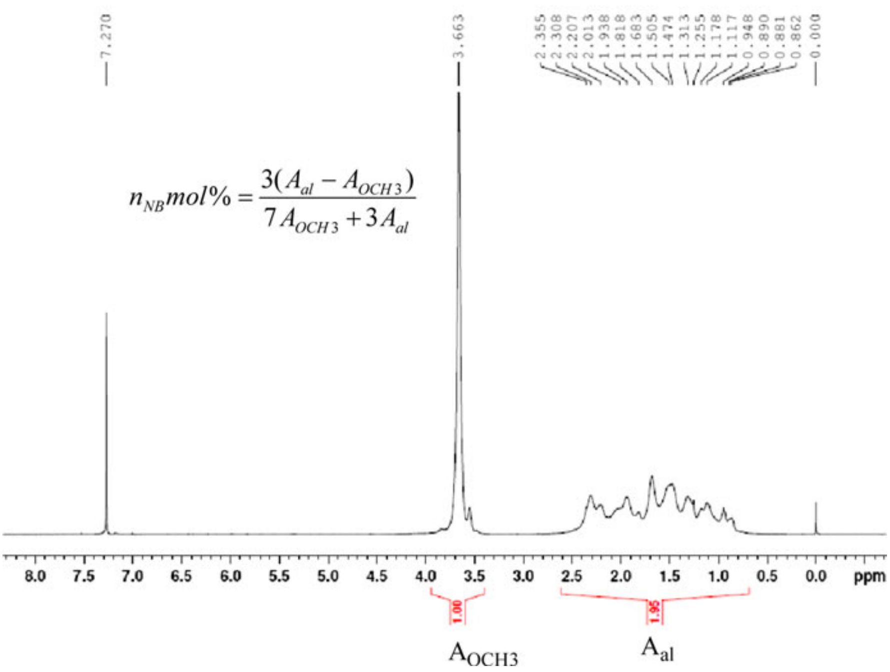

Fig. 3 ^{1}H NMR spectra of NB/MA (molar ratio of 1:1) copolymer

Table 1 The molecular weights of the fractionated polymer after fractionation of the copolymer

Fractionated polymers	1	2	3
M_w^a	1.14×10^5	9.72×10^4	7.10×10^4

[a] The M_w values were based on GPC measurements

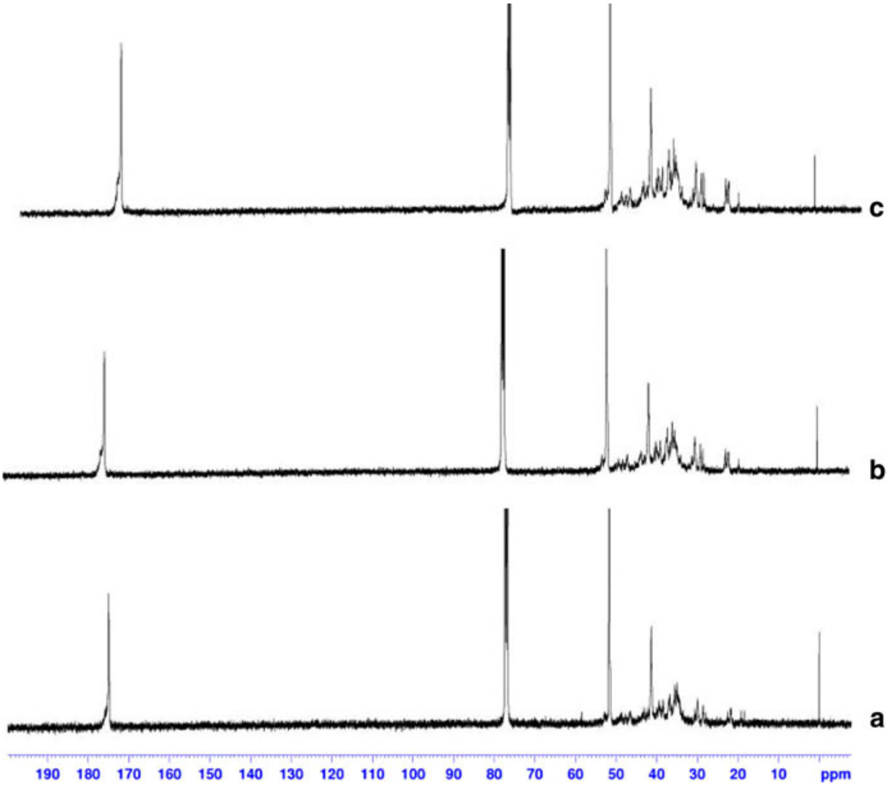

Fig. 4 ^{13}C NMR spectra of the fractionated NB/MA copolymers

Fractionation of the 1:1 copolymer was conducted to provide further evidence to the copolymerization. Three polymers were fractionated from the ethanol solution of the copolymer by using water as precipitant. The fractionated polymers were characterized by GPC and ^{13}C NMR. The molecular weights of these polymers are listed in Table 1. ^{13}C NMR spectra (Fig. 4) of these polymers resembled each other and the spectrum shown in Fig. 2. These results led to a safe conclusion that NB and methyl acrylate copolymerized under the copolymerization conditions.

TGA analysis of copolymer

The TGA trace of the copolymer is shown in Fig. 5 (curve 4). Control TGA experiments were conducted on (a) the blend of poly(methyl acrylate) and

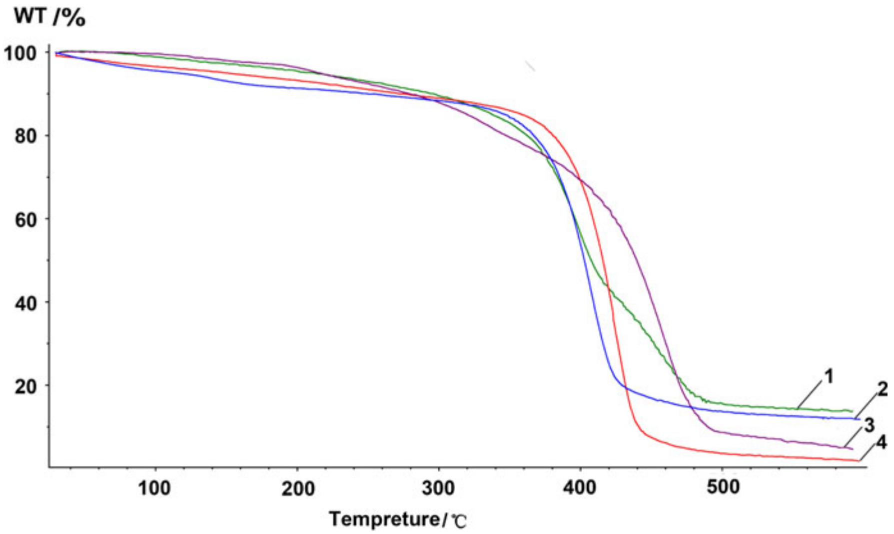

Fig. 5 TGA traces of (1) PNB/PMA blend, (2) PNB, (3) PMA, and (4) NB/MA (molar ratio of 1:1) copolymer

polynorbornene (PNB), curve 1, (b) poly(methyl acrylate), curve 2, and (c) polynorbornene, curve 3. The TGA trace of the blend is featured as an overlap of the traces of PMA and PNB. In contrast, curves 2, 3, and 4 showed a thermal degradation behavior of a one-component system. Besides, the decomposition temperature (T_D) of the copolymer was higher than the T_D of PMA and lower than that of PNB. These results, together with the ^{13}C NMR data, led to a reasonable deduction that the polymerization product was copolymer, instead of a mixture of homopolymers.

Effects of polymerization conditions

Table 2 shows the data of molecular weight and molecular weight distribution of copolymers with different monomer molar ratio. From Table 2, it can be seen that molecular weight of copolymer decreases with the increase of NB monomer molar ratio. It can be deduced that MA can realize the homopolymerization reaction in the same catalytic condition, but NB can't do so. The molecular weight distribution of

Table 2 Influence of monomer molar ratio on molecular weight and its distribution of copolymer

NB/MA (molar ratio)	Yield (%)	M_w	M_w/M_n
1/2	78.5	1.68×10^5	1.86
1/1	36.9	9.80×10^4	1.82
2/1	26.8	6.60×10^4	1.52

Polymerization conditions: $T = 70$ °C, $t = 6$ h, $Nd/Al = 1{:}30$ (molar ratio), $[Nd] = 7.5 \times 10^{-3}$ mol/L, total monomer concentration = 3.5 mol/L, solvent: toluene

Table 3 Influence of temperature on polymerization

Temperature (°C)	14	50	60	70	80
Yield (%)	4.6	15.3	24.4	36.9	25.8
M_w	1.73×10^5	1.30×10^5	1.12×10^5	9.80×10^4	4.66×10^4

Polymerization conditions: $t = 6$ h, $Al/Nd = 30{:}1$ (molar ratio), NB/MA (molar ratio) = 1, $[Nd] = 7.5 \times 10^{-3}$ mol/L, total monomer concentration = 3.5 mol/L, solvent: toluene

Table 4 Influence of Nd/Al on polymerization

Nd/Al (molar ratio)	1:15	1:30	1:60	1:90	1:120	1:150
Yield (%)	24.4	36.9	29.4	19.3	11.7	10.6
M_w	1.04×10^5	9.80×10^4	7.54×10^4	3.94×10^4	2.64×10^4	1.57×10^4

Polymerization conditions: $T = 70$ °C, $t = 6$ h, NB/MA(molar ratio) = 1, $[Nd] = 7.5 \times 10^{-3}$ mol/L, Total monomer concentration = 3.5 mol/L, solvent: toluene

copolymer decreases with the increase of NB monomer molar ratio, and the molecular weight distribution is a narrow distribution. Compared with the copolymer catalyzed by iron catalyst, the copolymer catalyzed by $Nd(naph)_3$–$Al(i\text{-}Bu)_3$ has narrower molecular weight distribution and higher activity estimated from the yield/time ratio.

The influence of temperature on polymerization is shown in Table 3. It can be seen that the yield increases with the increase of temperature; the yield is preferable at 70 °C. While the yield decreases at 80 °C. This may be because the soluble fractions in ethanol increases with the increase of temperature, thus, the molecular weight decreases with the increase of temperature.

Table 4 reveals the influence of Nd/Al ratio on polymerization. It is illustrated that the yield first increases then decreases with increasing the Nd/Al molar ratio (1:15–1:150). It is likely that there is very small amount of residual water in the solvents and monomers of the reaction system and the residual water may reduce the catalyst's activity. As the Al alkyl content increases, the residual water was consumed by the Al alkyl; thus the catalytic activity was improved. But further increase of Al alkyl may lead to a dominant Al alkyl chain transfer reaction, which resulted in copolymers with lower molecular weights. As a result, the ethanol-soluble fraction of the copolymer increases, and the yield declined with increasing Al alkyl content.

The influence of catalyst concentration on polymerization is illustrated in Table 5. It is shown that the polymer yield increases first then decreases with the increase of catalyst concentration to get a preferable catalyst concentration $[Nd] = 7.5 \times 10^{-3}$ mol/L. This may be because the residual water in the solvents and monomers of the system decreases and yield increases with the increase of Al alkyl. But when the catalyst concentration is too high, molecular weight of copolymer decreases due to the increase of soluble fractions in ethanol and the decrease of yield.

Table 5 Influence of catalyst concentration on polymerization

[Nd] mol/L	5.0×10^{-3}	7.5×10^{-3}	1.0×10^{-2}	1.25×10^{-2}	1.5×10^{-2}
Yield (wt%)	24.0	36.9	25.9	22.6	23.1
M_w	1.27×10^5	9.80×10^4	6.04×10^4	4.52×10^4	2.63×10^4

Polymerization conditions: $T = 70$ °C, $t = 6$ h, *Al/Nd* = 30:1 (molar ratio), *NB/MA*(molar ratio) = 1, Total monomer concentration = 3.5 mol/L, solvent: toluene

Table 6 The effect of time on the polymerization

Time (h)	2	4	6	8	10
Yield (wt%)	8.8	29.3	36.9	39.3	47.2
M_w	7.47×10^4	7.89×10^4	9.80×10^4	1.03×10^5	1.15×10^5

Polymerization conditions: $t = 6$ h, *Al/Nd* = 30:1 (molar ratio), *NB/MA*(molar ratio) 1, $[Nd] = 7.5 \times 10^{-3}$ mol/L, Total monomer concentration = 3.5 mol/L, Sol: toluene

As seen from Table 6, the polymer yield and molecular weight of polymer increase with the increase of reaction time. But polymer yield increases slowly after polymerization for 6 h.

Finally, the authors have investigated the kinetics of the copolymerization of NB and MA catalyzed by Nd/Al catalyst system at different reaction temperature and toluene as solvent. The polymer yield (c) showed a dependence on the reaction time (t) following an equation of $ln1/(1-c) \propto t$ (Details shown in Supporting Information). It indicates that polymerization approximately shows a first order relationship with the monomer concentration. Further analysis on the temperature-dependence of the reaction velocity constant K_p by using the Arrhenius equation $\ln K_p = -E/RT + B$ revealed that the apparent activation energy of copolymerization was 42.31 kJ/mol. Detailed analysis is available in the Supporting Information.

Conclusions

The rare earth catalyst system $Nd(naph)_3$–$Al(i\text{-}Bu)_3$ shows high activity for the copolymerization of NB and MA. The preferable reaction conditions are found through the study of the influences of monomer molar ratio, temperature, reaction time, Nd/Al molar ratio, and catalyst concentration on polymerization. Compared with some other rare earth catalysts and iron catalysts, the catalyst $Nd(naph)_3$–$Al(i\text{-}Bu)_3$ shows fast polymerization with high polymer yield and narrow molecular weight distribution.

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