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Copolymerization of Norbornene and Butyl Methacrylate at Elevated Temperarure by Single Centre Nickel Catalyst Bearing Bulky Bis(α-diimine) Ligand with Strong Electron-Withdrawing Group

Xiaohui He,[a*] Yingjiao Deng,[a] Xiong Jiang,[a] Zijie Wang,[a] Yingping Yang,[a] Zhilong Han,[a] and Defu Chen[b]

[a]School of Materials Science and Engineering, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

[b]School of Civil Engineering and Architecture, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

Correspondence to: X. He (E-mail: hexiaohui@ncu.edu.cn)

1. Materials

All experiments were carried out under a purified nitrogen atmosphere using standard Schlenk techniques or under a dried and nitrogen atmosphere standard glove box (MBraun). Chlorobenzene was dried by sodium and distilled under nitrogen. Dichloromethane was dried over CaH_2 for 12 hours and distilled under a nitrogen atmosphere. $B(C_6F_5)_3$ (95 %) and norbornene (NB) were purchased from Alfa Aesar. NB was purified through drying by sodium and distilled under a nitrogen, then prepared as a solution (0.4 g/mL) in chlorobenzene. Butyl methacrylate (BMA) was purchased from Aladdin and purified by washing twice with sodium hydroxide solution (5.0 wt%) and twice with water for removing the inhibitors, followed by drying over anhydrous $CaCl_2$ and distillation under nitrogen atmosphere at reduced pressure.

2. Characterization

X-ray diffraction data of single crystals was obtained with the ω-2θ scan mode on a Bruker D8 Quest diffractometer with graphite-monochromated Mo Kα radiation (λ=0.71073). Elemental analysis was performed on an Elementar-Vario ELcube

elemental analyzer. Nuclear magnetic resonance (NMR) spectra of the ligand, Nickel catalyst and copolymers were obtained on a Bruker ARX 400 NMR spectrometer at ambient temperature with $CDCl_3$ as the solvent and tetramethylsilane (TMS, δ=0) as an internal reference. HRMS (ESI) was measured on a Bruker Daltonics APEXIII 7.0 TESLA FTMS. Gel permeation chromatography (GPC) was carried out on a E2695-Waters system using polystyrene as the standard and tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min. FTIR spectra were recorded by a Shimadzu IR Prestige-21 FTIR spectrophotometer.

Wide-angle X-ray diffraction (WXRD) curves were provided on a Bruker D8 Focus X-ray diffractometer, operating at 40 kV and 40 mA with a copper target (λ= 1.54 Å) and at a scanning rate of 2^o/min from 5^o to 40^o. The thermal gravimetric analysis (TGA) measurements were performed on a Perkin-Elmer instrument TGA 7 from room temperature to 700 ^{o}C at a rate of 10 ^{o}C/min under nitrogen atmosphere. Dynamic mechanical tests (DMA) were performed with a NETZSCH DMA242 C, the oscillation frequency of 1.0 Hz and a heating-cooling rate 3 ^{o}C/min. The storage modulus, loss modulus and the loss tangent were measured from 20-300 ^{o}C, each sample was measured for three times. Ultraviolet-visible absorption spectra were measured in Perkin Elmer Lambda 750 spectrophotometer. The mechanical properties were measured on a CMT8502 Machine model GD203A (ShenZhen Sans Testing Machine, China) at a speed of 5 mm·min^{-1}, the test machine was equipped with a 10 kN electronic load and mechanical grips and the polymers were prepared into 1 cm width and 4 cm length.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 1474272 for NiL_2Br_2. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.ukor.http://www.ccdc.cam.ac.uk).

Table S1 Crystallographic data for complexes

NiL_2Br_2			
Empirical formula	$2(C_{56}H_{36}N_8O_8NiBr_2)$	D_{calc} (Mg/m^3)	1.647
Formula weight	3363.37	Abs coeff. (mm^{-1})	4.423
Crystal color	red	F(000)	3290.0
Crystal system	monoclinic	Crystal size(mm)	0.24 × 0.21 × 0.18
space group	P2/n	θ range (deg)	2.96 to 19.84
a (Å)	19.299(8)	Limiting indices	-18 <= h <= 18 -13 <= k <= 13 -23 <= l <= 20
b (Å)	14.581(7)	Refinement method.	Full-matrix least-sequares on F^2
c (Å)	24.167(10)	Data / restraints / parameters	6102/42/676
α(deg)	90.00	Goodness-of-fit on S (F^2)[a]	1.044
β(deg)	94.227(10)	Final R indices [I>2ó(I)]	R1= 0.0998 wR2= 0.2516
γ(deg)	90.00	R indices (all data)	R1= 0.1540 wR2= 0.2922
Volume ($Å^3$)	6782(5)	Largest diff peak and hole(e/$Å^3$)	1.110 and -0.740
Z	2		

Table S2 Norbornene polymerization [a]

Entry	T_p ,° C	Reaction time (min)	Yield (%)	Activity [b]
1	30	30	39.17	0.37
2	60	5	60.01	3.38
3	80	5	83.21	4.69
4	100	1	81.13	22.88
5	120	1	97.67	27.54
6	140	1	93.59	26.39
7[c]	100	5	3.29	0.181
8[c]	100	10	6.24	0.176

9[c]	100	15	8.94	0.168
10 [c]	100	20	11.42	0.161
11 [c]	100	25	13.47	0.152
12 [c]	100	30	15.74	0.148
13 [c]	120	5	4.48	0.253
14 [c]	120	10	8.55	0.241
15 [c]	120	15	12.74	0.227
16 [c]	120	20	14.89	0.210
17 [c]	120	25	17.02	0.192
18 [c]	120	30	19.54	0.184
19 [c]	140	5	3.92	0.221
20 [c]	140	10	7.59	0.214
21 [c]	140	15	10.36	0.194
22 [c]	140	20	12.84	0.181
23 [c]	140	25	15.07	0.170
24 [c]	140	30	17.34	0.163

[a] Reaction conditions: Reaction conditions: n[Ni]= 5×10^{-6} mol, cocatalyst is $B(C_6F_5)_3$, B/Ni/monomer (n/n/n) is 20/1/5000, total volume chlorobenzene 10 mL. [b] 10^6 $g_{polymer}\cdot mol^{-1}{}_{Ni}\cdot h^{-1}$. [c] total volume chlorobenzene was kept to be 100 mL.

Table S3 BMA polymerization [a]

No.	catalyst	T_p ,° C	Reaction time, (h)	Yield (%)	Activity [b]
1	-	30	12	-	-
2	-	60	12	-	-
3	-	80	12	-	-
4	-	100	12	-	-
5	-	120	12	26.22	1.53
6	**NiL_2Br_2**	30	-	-	-
7	**NiL_2Br_2**	60	12	46.04	2.69
8	**NiL_2Br_2**	80	12	51.53	3.00
9	**NiL_2Br_2**	100	12	80.91	4.72

10	**NiL_2Br_2**	120	12	85.35	4.98
11	**NiL_2Br_2**	140	12	73.12	4.27

[a] Reaction conditions: n[Ni]= 5×10^{-6} mol, cocatalyst is $B(C_6F_5)_3$, B/Ni/monomer (n/n/n) is 20/1/5000, total volume chlorobenzene 10 mL.

[b] 10^5 $g_{polymer}\cdot mol^{-1}{}_{Ni}\cdot h^{-1}$.

Table S4 Copolymerization of NB with BMA [a]

No.	catalyst	NB/BMA (mol/mol)	Reaction time, (h)	Yield (%)	Activity [c]	BMA incorp. (mol %)[d]
1	**$Ni(L1)_2Br_2$** [b]	70/30	1	29.27	1.59	10.2
2	**$Ni(L2)_2Br_2$** [b]	70/30	1	29.14	1.58	11.5
3	**$Ni(L3)_2Br_2$** [b]	70/30	1	31.51	1.71	11.9
4	**NiL_2Br_2**	70/30	1	36.65	1.99	13.4

[a] Reaction conditions: n[Ni]= 5×10^{-6} mol, cocatalyst is $B(C_6F_5)_3$, B/Ni/monomer (n/n/n) is 20/1/5000, T_p = 100 °C, total volume chlorobenzene 10 mL.

[b] 9,10-dihydro-9,10-ethanoanthracene-11,12-di(Ar)imine (Ar=*p*-$PhCH_3$, **L1**; Ar=*p*-PhCl, **L2**; Ar=*p*-$PhCF_3$, **L3**.) .

[c] In unit of 10^5 $g_{polymer}/mol_{Ni}\cdot h$. [d] Determined by ^1H NMR spectroscopy in $CDCl_3$.

Table S5 Copolymerization of NB with BMA catalyzed by **NiL_2Br_2**/$B(C_6F_5)_3$[a]

No.	NB/BMA (mol/mol)	Reaction time (min)	Yield (%)	Activity [b]	BMA incorp. (mol %)[c]
1	90/10	10	9.54	2.82	1.3
2	70/30	15	7.25	1.56	5.4
3	50/50	25	8.33	1.18	11.6
4	30/70	30	5.01	0.64	25.6
5	10/90	30	3.61	0.09	42.1

[a] Reaction conditions: n[Ni]= 5×10^{-6} mol, cocatalyst is $B(C_6F_5)_3$, B/Ni/monomer (n/n/n) is 20/1/5000, T_p = 100 °C, total volume chlorobenzene 10 mL. [b] In unit of 10^5 $g_{polymer}/mol_{Ni}\cdot h$.

[c] Determined by ^1H NMR spectroscopy in $CDCl_3$.

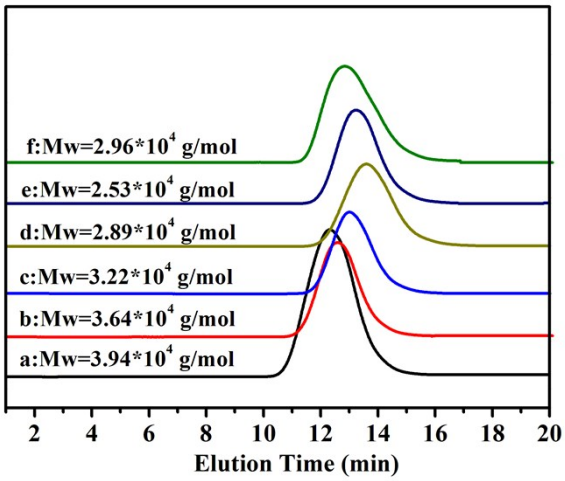

Fig. S1 GPC curves of poly(NB-co-BMA)s: (a) 6.0, (b) 13.4, (c) 23.1, (d) 57.7, (e) 78.7, (f) 100 of BMA molar ratio (%) obtained by **NiL$_2$Br$_2$**/B(C_6F_5)$_3$ systems.

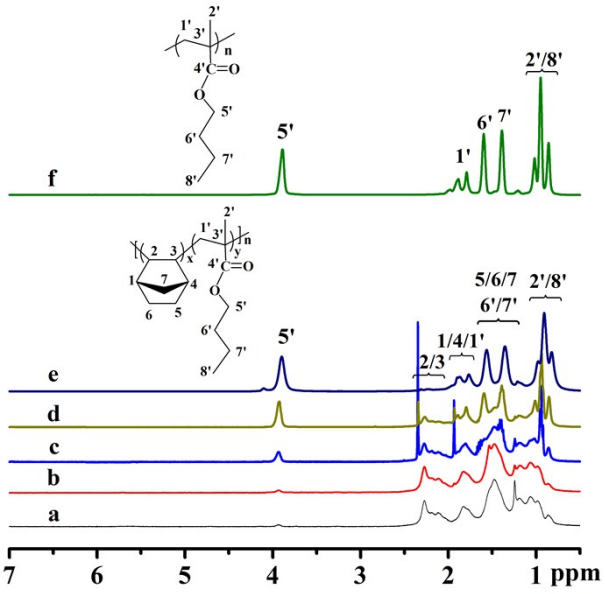

Fig. S2 ^{1}H NMR spectra of poly(NB-co-BMA)s: (a) 6.0, (b) 13.4, (c) 23.1, (d) 57.7, (e) 78.7, (f) 100 of BMA molar ratio (%) obtained by **NiL$_2$Br$_2$**/B(C_6F_5)$_3$ systems.

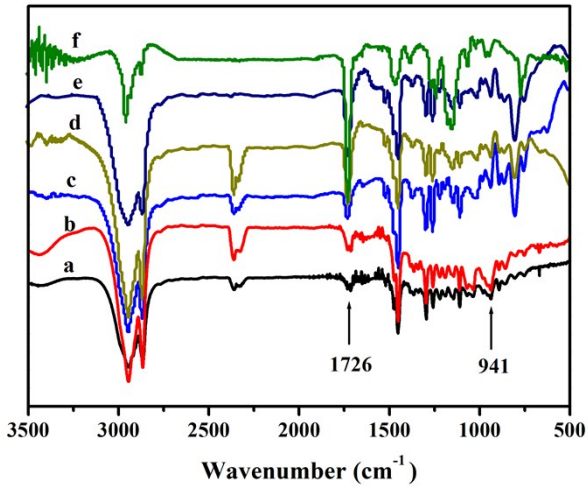

Fig. S3 FTIR spectra of poly(NB-co-BMA)s: (a) 6.0, (b) 13.4, (c) 23.1, (d) 57.7, (e) 78.7, (f) 100 of BMA molar ratio (%) obtained by $\mathbf{NiL_2Br_2}$/$B(C_6F_5)_3$ systems.

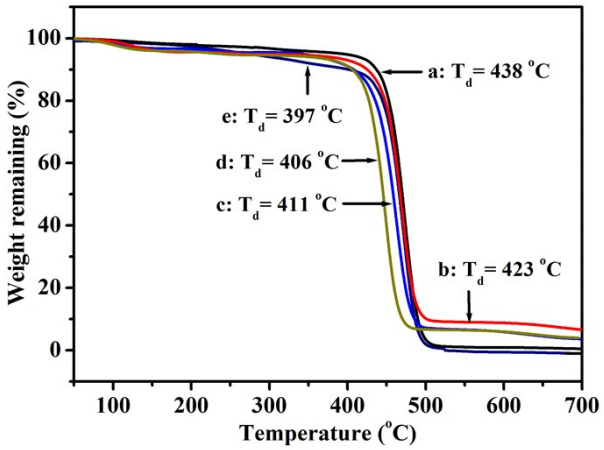

Fig. S4 TGA curves of poly(NB-co-BMA)s: (a) 6.0, (b) 13.4, (c) 23.1, (d) 57.7, (e) 78.7 of BMA molar ratio (%) obtained by $\mathbf{NiL_2Br_2}$/$B(C_6F_5)_3$ systems.

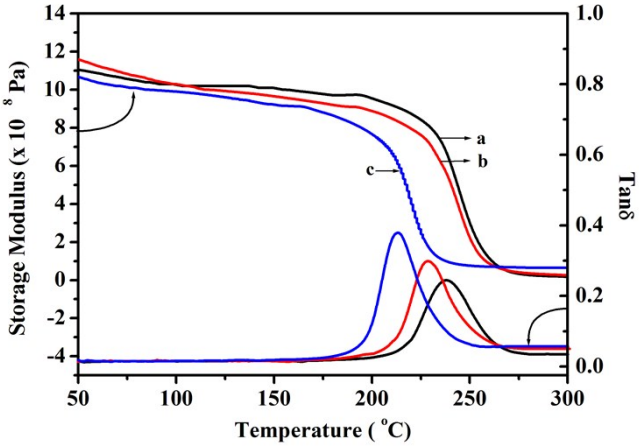

Fig. S5 Curves of storage modulus and Tanδ versus temperature for poly(NB-co-BMA)s: (a) 23.1, (b) 57.7, (c) 78.7 of BMA molar ratio (%) obtained by $\mathbf{NiL_2Br_2}$/$B(C_6F_5)_3$ systems.

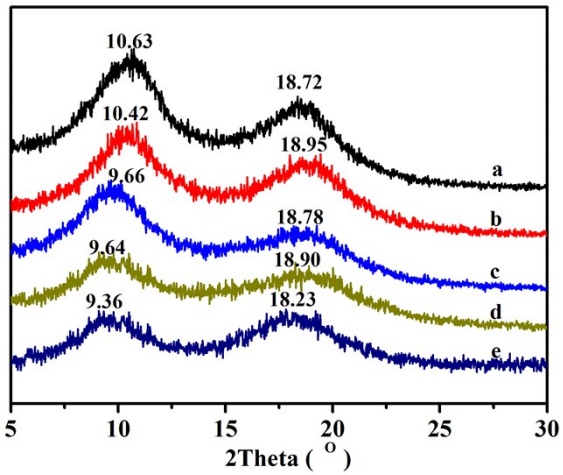

Fig. S6 WXRD curves of poly(NB-co-BMA)s: (a) 6.0, (b) 13.4, (c) 23.1, (d) 57.7, (e) 78.7 of BMA molar ratio (%) obtained by $\mathbf{NiL_2Br_2}$/$B(C_6F_5)_3$ systems.

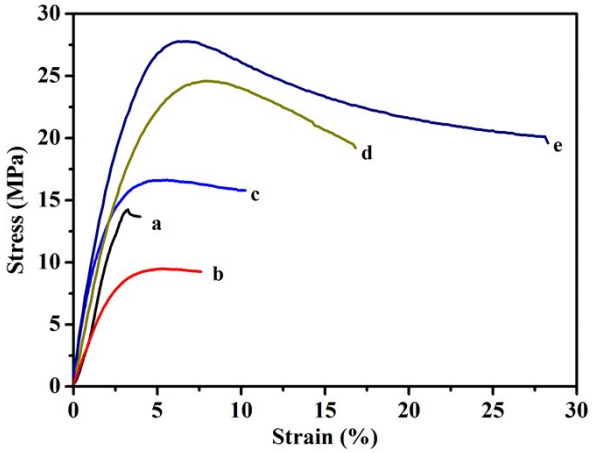

Fig. S7 The tensile curves of poly(NB-co-BMA)s: (a) 6.0, (b) 13.4, (c) 23.1, (d) 57.7, (e) 78.7 of BMA molar ratio (%) obtained by **NiL$_2$Br$_2$**/B(C_6F_5)$_3$ systems.