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Polydispersity control in ring opening metathesis polymerization of amphiphilic norbornene diblock copolymers

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Abstract

Ring opening metathesis polymerization (ROMP) with Grubbs's catalyst was used to synthesize narrow polydispersity (PDI)diblock copolymers of norbornene (NOR) and norbornenedicarboxylic acid (NORCOOH). Norbornene (NOR) and 5-norbornene-2,3,-dicarboxylic acid bis trimethylsilyl ester (NORCOOTMS) were used as precursor monomers for thepolymerization. $[\text{NORCOOTMS}]_m/[\text{NOR}]_n$ was converted to $[\text{NORCOOH}]_m/[\text{NOR}]_n$ by precipitating the polymer solution in a mixture of methanol, acetic acid, and water. The conversion to 5-norbornene-2,3-dicarboxylic acid was evidenced by ^{1}H NMR. By polymerizing the bulkier NORCOOTMS precursor monomer first, lower PDIs were observed for the completed $[\text{NORCOOH}]_m/[\text{NOR}]_n$ block copolymers in comparison to copolymers where the NOR block was polymerized first. The PDI of the diblock copolymers of $[\text{NORCOOH}]_m/[\text{NOR}]_n$ decreased with increase in block length ofthe precursor NORCOOTMS monomer. This study shows that the PDI can be controlled by selecting a monomer with appropriate functionality as the starting block of the block copolymer to control the rate of propagation, R_p, as an alternative of using additives to change the reactivity of the catalyst.

Keywords: Block copolymers; Polydispersity; Polymerization

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1. Introduction

The advent of ring-opening metathesis polymerization (ROMP) has allowed the synthesis of many polymers previously unavailable with standard synthesis techniques [1–4]. The high tolerance of ROMP catalysts to various functional groups along with their high activity enables facile synthesis of ampiphilic block copolymers. Ruthenium catalysts, such as Grubbs's catalyst and Schrock's Mo and W ROMP catalysts have found wide use in the synthesis of block copolymers [5].

An amphiphilic block copolymer contains a hydrophobic block and a hydrophilic block. By exploiting the thermodynamic phase separation of amphiphilic diblock copolymers, nanodomains of hydrophilic blocks can be formed, which can then be used to incorporate metal salts [6–12]. Norbornene can be used as the hydrophobic block and is a commercially available monomer that is easily purified. Grubbs and coworkers reported that norbornene cannot be polymerized in a living fashion using Grubbs's catalyst [13]. They achieved a polydispersity index (PDI) of 2.0 for norbornene homopolymers initiated with Grubbs's catalyst.

In this paper, a method of synthesizing block copolymers of narrow polydispersity of norbornene (NOR) and norbornene dicarboxylic acid (NORCOOH) with Grubbs's $[(\text{PCy}_3)_2\text{Cl}_2\text{Ru}{=}\text{CHPh}$, Cy = cyclohexyl, Ph = phenyl] catalyst is reported. All but one of the synthesis were performed by polymerizing a 5-norbornene-2,3,-dicarboxylic acid bis trimethylsilyl ester (NORCOOTMS) precursor first, followed by the polymerization of unfunctionalized norbornene. The resultant diblock copolymers $[\text{NORCOOTMS}]_m/[\text{NOR}]_n$ were converted to $[\text{NORCOOH}]_m/[\text{NOR}]_n$ by precipitating the polymer solution in a mixture of methanol, acetic acid, and water. The PDIs of the copolymers with NORCOOTMS as the starting monomer were less than 1.26 in all cases, in contrast to the block copolymer with norbornene as a starting monomer, which had a PDI of 1.61. The block copolymer having a block

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ratio of NORCOOH:NOR = 50:400 had a PDI of 1.26. Increased block lengths of NORCOOTMS resulted in decreased PDIs, as a NORCOOH:NOR = 150:400 copolymer gave a nearly monodisperse PDI of 1.05. These reactions were performed without modification of the catalyst or addition of excess phosphine to control the rate of propagation [14,15]. The method presented in this paper shows that the sequence of monomer addition is a factor for controlling the PDI of ROMP synthesized diblock copolymers.

2. Experimental

2.1. Materials

Norbornene (NOR), ethyl vinyl ether and dichloromethane (CH_2Cl_2) were purchased from Aldrich. Bis(tricyclohexylphosphine)benzylidine ruthenium(IV) dichloride (Grubbs's catalyst) was purchased from Strem Chemicals. CH_2Cl_2 was distilled over calcium hydride under argon. 5-Norbornene-2,3,-dicarboxylic acid (NORCOOH) and 5-norbornene-2,3,-dicarboxylic acid bis trimethylsilyl ester (NORCOOTMS) were prepared according to literature [6].

All the solvents, monomers and catalysts required for polymer synthesis were stored inside an MBraun100 glovebox. A stock solution of Grubbs's catalyst was prepared by dissolving 0.15 g of the catalyst in 5 ml dichloromethane (CH_2Cl_2) and stored at −20 °C inside the glovebox.

2.2. Polymer characterization

Gel permeation chromatography (GPC) was performed with a Wyatt Technology Mini-DAWN light scattering detector, Waters 2410 RI detector, Waters 515 pump and a Rheodyne 7125i injector with a 200 μl loop. THF was the mobile phase at a flow rate of 1.0 ml/min, through Waters 10^4, 10^5 and 10^6 Å columns. ^{1}H NMR was performed with a Bruker AM400 spectrometer. Samples were dissolved d-THF and referenced from solvent peaks, 1.73 and 3.58 ppm.

2.3. Synthesis of $[NOR]_{400}/[NORCOOH]_{50}(400/50)$

A 4 mmol/ml solution of norbornene in dichloromethane (CH_2Cl_2) was prepared by dissolving 1 g NOR (10.6×10^{-3} mol, 400 equiv.) in 20 ml CH_2Cl_2. The polymerization was initiated by adding 750 μl (26.5×10^{-6}mol, 1/400 equiv.) of catalyst solution. The reaction mixture became very viscous within a few minutes and was too viscous for the addition of the second block. After 1 h the reaction mixture was diluted by adding 20 ml CH_2Cl_2, and a 200 μl aliquot was removed for gel permeation chromatography (GPC). NORCOOTMS of 0.43 g (1.32×10^{-3} mol, 50 equiv.) dissolved in 4.3 ml CH_2Cl_2 was then added to reaction mixture. The polymerization was terminated after 24 h by adding 50 μl ethyl vinyl ether. The polymer solution was stirred for 30 min to ensure complete termination. The resultant $[NOR]_{400}/[NORCOOTMS]_{50}$ diblock copolymer was converted to $[NOR]_{400}/[NORCOOH]_{50}$ by precipitating the polymer solution in a mixture of methanol (200 ml), acetic acid (5 ml) and water (10 ml). The block copolymers were then dried under vacuum for 24 h.

2.4. Synthesis of $[NORCOOH]_m/[NOR]_{400}(m/400)$

A 4 mmol/ml solution of norbornene in CH_2Cl_2 was prepared by dissolving 0.45 g NORCOOTMS (1.38×10^{-3} mol, *m* M equiv.) in 3.375 ml CH_2Cl_2. The polymerization was initiated by adding the required molar equivalent of catalyst (1/*m* M equiv., where *m* is the target degree of polymerization of the NORCOOH block). The amount of catalyst required for polymerization was determined by the targeted block length. Depending on the block length, after 24 or 36 h, a 200 μl aliquot was removed for GPC, and then a 2 mg/ml solution of NOR (400 M equiv.) in CH_2Cl_2 was added to the solution. The polymerization was terminated after 24 or 36 h depending on the block length by adding 50 μl ethyl vinyl ether. The polymer solution was stirred for 30 min to ensure complete termination. The amount of catalyst and monomers used, and the reaction times are listed in Table 1. The resultant $[NORCOOTMS]_{50}/[NOR]_{400}$ diblock copolymer was converted to $[NORCOOH]_{50}/[NOR]_{400}$ as described earlier and then dried under vacuum for 24 h. The aliquot of $[NORCOOTMS]_m$ was also converted to $[NORCOOH]_m$ by adding 20 μl acetic acid.

2.5. ^{1}H NMR characterization of monomers

2-Norbornene dicarboxylic acid trimethyl silyl ester; δ 6.26–6.28 (dd, 1, olefinic CH), 6.08–6.10 (dd, 1, olefinic CH), 3.2–3.24 (bs, 1, *endo*-methine) 2.62–2.65 (s, 1, bridgehead), 1.64–1.66 (dd, 1, *exo*-methine), 1.60–1.62 (dd, 2, C7, CH_2), 1.40–1.42 (dd, 2, C7, CH_2), 0.08–0.09 (bs, 1, *exo*-trimethylsilyl CH_3), 0.05–0.07 (bs, 1, *endo*-trimethyl silyl CH_3).

2-Norbornene; δ 5.98–6.00 (s, 1, olefinic CH), 2.84 (bs, 1, bridgehead), 1.60–1.62 (dd, 2, *endo*-methine), 1.36–1.40 (dd, 2, C7 CH_2), 1.08–1.10 (dd, 2, C7 CH_2), 0.96–1.00 (bs, 2, *exo*-methine).

3. Results and discussion

The PDI of ROMP polymers is related to the propagation rate constant (k_p) and initiation rate constant (k_i). The value of k_p/k_i should be less than 10 to produce a living polymer with a low PDI [5]. A smaller k_p/k_i (< 10) results in complete catalyst

Table 1
The amount of monomers and catalyst used, and the reaction times for the synthesis of $[NORCOOTMS]_m/[NOR]_{400}$

$[NORCOOTMS]_m$				$[NORCOOTMS]_m/[NOR]_{400}$	
Block length (target) m	NORCOOTMS (g)	Catalyst solution (μl)	Reaction time (h)	NOR (g)	Reaction time (h)
50	0.45	841	24	0.97	24
100	0.45	421	24	0.49	24
150	0.45	280	36	0.32	36

initiation of monomers. When propagation starts after full initiation of monomers, the number of polymer chains remains constant, equal to the number of the original initiating species [16]. The catalytic activity and rate of initiation of ROMP catalysts is dependent on the size of pendant groups, the basicity of the phosphine coordinating group to the monomer, and the effect of solvent interaction with the catalyst [14,15]. Although Refs. [14,15] deal with the size of the phosphine group on the catalyst, steric effects are also seen with the metathesis of disubstituted olefins using Grubbs's catalyst [13].

Norbornene polymerized with Grubbs's catalyst became very viscous within a few minutes, and the polymerization was completed within 1 h. The rapid increase in viscosity indicated that norbornene had a high rate of propagation (R_p). The resultant homopolymer ($[NOR]_{400}$) had a PDI of 1.61. The broad PDI indicates that propagation starts before the completion of the initiation step of the norbornene monomer. Chain transfer during polymerization may also produce a broad PDI. When NORCOOTMS monomers were added to $[NOR]_{400}$ the resultant diblock copolymer ($[NOR]_{400}[NORCOOH]_{50}$) had a PDI of 1.51 (see Fig. 1 and Table 2. In contrast, when NORCOOTMS was polymerized with Grubbs's catalyst, the resultant homopolymers have a narrow molecular weight distribution (PDI < 1.26). The molecular weight distribution of the NORCOOH homopolymers are shown in Fig. 2. ^1H NMR was performed to determine if complete conversion of the trimethyl silyl ester to the carboxylic acid occurred. As seen in Fig. 3, the NMR spectra of $[NORCOOH]_{50}[NOR]_{400}$, there are no peaks corresponding to the TMS endgroups visible from 0 to 0.5 ppm. In addition, the ratio of COOH peaks to vinyl proton peaks is approximately 1:8 and are comparable to the calculated ratios from GPC. A peak attributed to a solvent impurity, such as BHT, appears at 8.1 ppm, and is not consistent with the polymer structure.

When norbornene of the same block length was added to the propagating chain of $[NORCOOTMS]_n$, the PDI of the resultant diblock copolymers ($[NORCOOH]_n[NOR]_{400}$) decreased to 1.26 ($n = 50$), 1.16 ($n = 100$) and 1.05 ($n = 150$) from 1.41, 1.28, and 1.11, respectively (Table 2, and Figs. 2, 4–6). The decrease in the PDI of the diblock copolymers indicates that the use of functionalized monomer (NORCOOTMS) as the starting block of the diblock copolymer results in a lower R_p for the polymerization of the second block (NOR). GPC analysis indicated that polymerization of norbornene was not complete after 9 h, when norbornene was the second block in the $[NORCOOH]_n/[NOR]_{400}$ diblock copolymer. As a comparison, the conversion of norbornene to polynorbornene homopolymer ($[NOR]_{400}$) was complete within an hour of catalyst addition. To ascertain whether chain transfer occurred during polymerization, aliquots were removed during polymerization after 1, 2 and 3 h. GPC analysis performed on these aliquots showed increasing molecular weight as the reaction progressed. No decrease in molecular

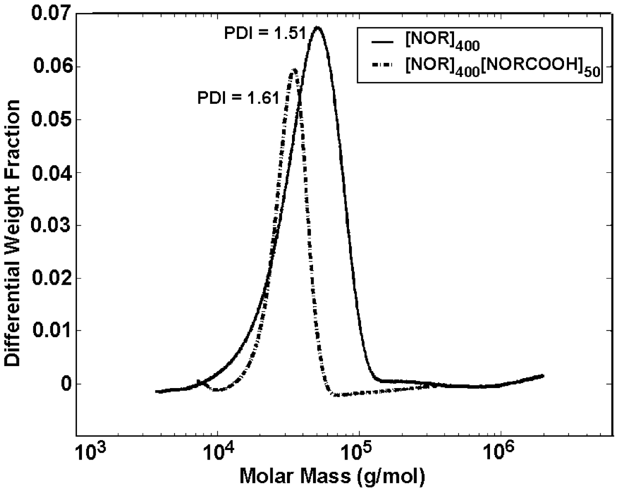

Fig. 1. Molecular weight distribution of $[NORCOOH]_{400}$ and $[NOR]_{400}[NORCOOH]_{50}$.

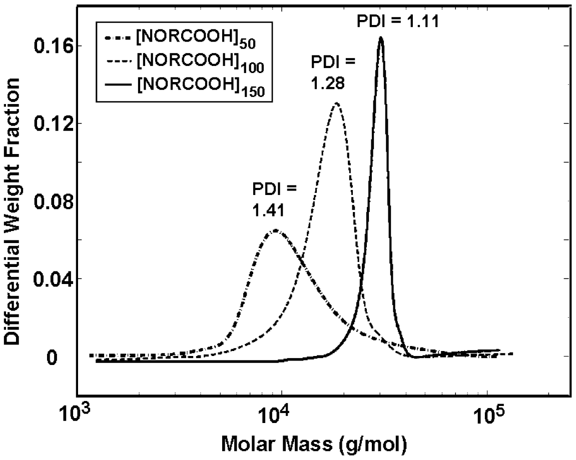

Fig. 2. Molecular weight distribution of homopolymers of NORCOOH ($[NORCOOH]_n$, $n = 50$, 100, and 150).

Table 2
Molecular weight of homopolymers and diblock copolymers

Polymer block ratio (target)	Block ratio (actual)[a]	First block			Diblock		
		M_n (g/mol)	M_w (g/mol)	PDI	M_n (g/mol)	M_w (g/mol)	PDI
		$[NOR]_n$			$[NOR]_n[NORCOOH]_m$		
400:50	576:43	34,260	54,840	1.61	41,640	62,460	1.51
		$[NORCOOH]_n$			$[NORCOOH]_n/[NOR]_m$		
50:400	72:475	9379	13,190	1.41	45,970	57,920	1.26
100:400	99:495	14,160	18,190	1.28	55,600	64,820	1.16
150:400	164:456	27,050	30,050	1.11	69,300	73,030	1.05

[a] Block ratios were calculated from M_w.

weight was observed during polymerization, indicating the absence of chain transfer. Fig. 7 shows a linear relation between M_n and catalyst/monomer ratio, therefore proving the catalyst is polymerizing NORCOOTMS in a controlled manner, and that NORCOOTMS does not destroy the catalyst [17].

The sequence of monomer addition presented in this paper (NORCOOTMS as first block followed by addition of NOR as the second block) takes advantage of electronic effects, i.e. chelation of the metal center by the monomer, which can be explained by the functional group basicity reducing the R_p of the propagating species. The NORCOOTMS monomer contains trimethyl silane end groups, which have greater basicity compared to norbornene. The propagating metal center is inhibited by the *endo* trimethyl silyl carboxylic acid group on the NORCOOTMS monomer [18]. This results in a lower R_p and in a correspondingly lower PDI. The reduction in the activity of the catalyst and the subsequent decrease in the PDI due to the electronic effects of the monomer have previously been reported in the literature. Kanaoka et al. have reported that the electronic effect of *endo* dimethyl butyl silyl esters functionalized monomer effect the activity of Grubbs's catalyst [18]. *Endo* functional groups are known to chelate with the active metal center and change the activity of the catalyst [5].

As discussed earlier, the effect of the block length is evidenced by the decrease in PDI of $[NORCOOH]_n$ from 1.41 to 1.11 as n increases from 50 to 150 (Fig. 2). As the block length increases, the propagation rate (R_p) decreases. The primary reasons for the decrease in R_p are: the decrease in monomer concentration, requiring greater time for reacting monomer to diffuse to the catalyst [16], and the

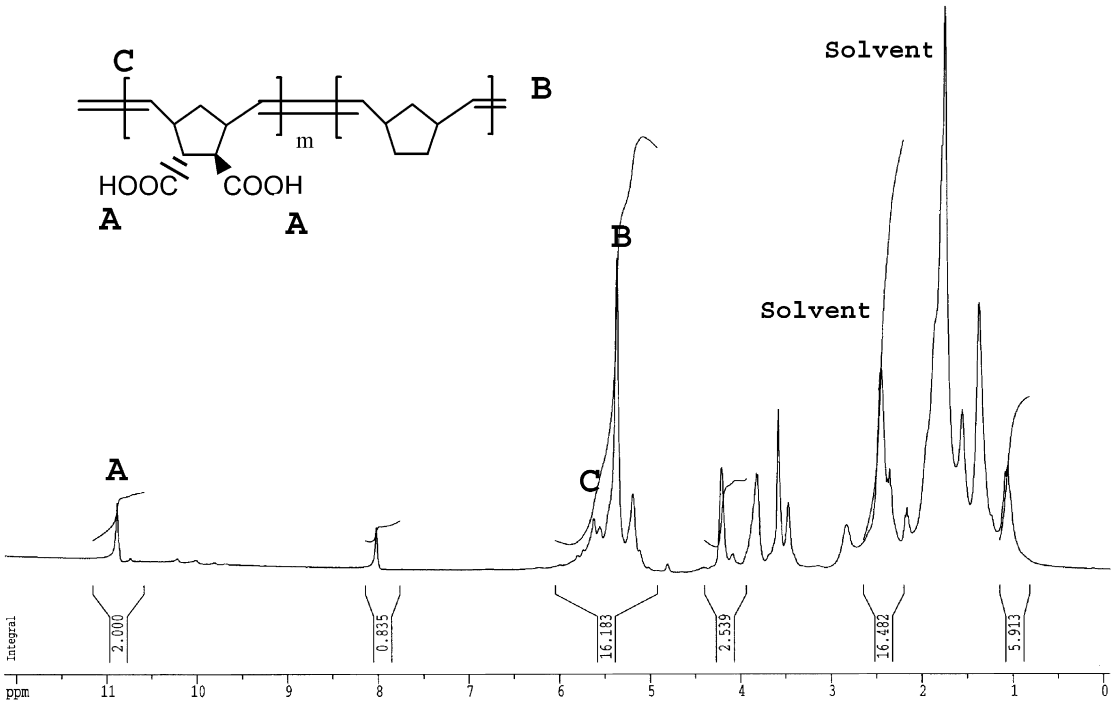

Fig. 3. ^1H NMR spectra of $[NORCOOH]_{50}[NOR]_{400}$ in d-THF.

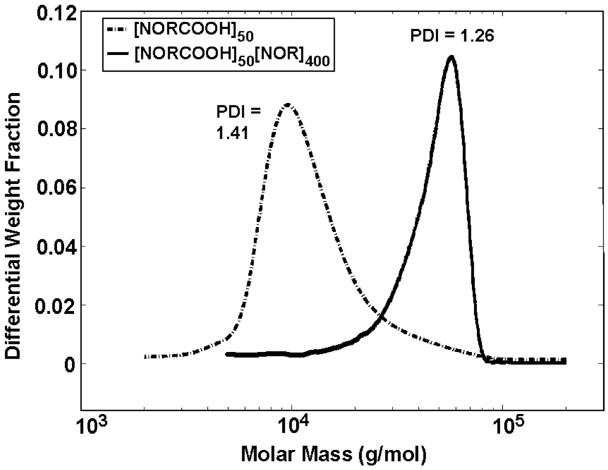

Fig. 4. Molecular weight distribution of $[NORCOOH]_{50}$ and $[NORCOOH]_{50}[NOR]_{400}$.

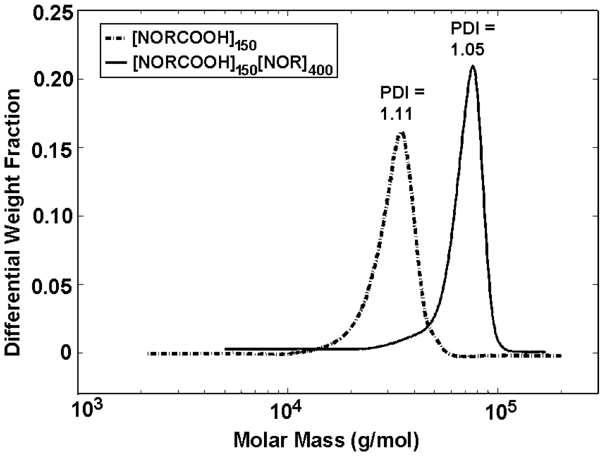

Fig. 6. Molecular weight distribution of $[NORCOOH]_{150}$ and $[NORCOOH]_{150}[NOR]_{400}$.

reduced availability of preferred sites for the catalyst to react as the growing chain increases in size. In effect, the growing chain can cause steric hindrance similar to a bulky functional group. This is especially true for the polymerization of NORCOOTMS. The lower PDIs resulting from the decreased rate of propagation is seen in other systems with bulky substituents like diethyl ester, methyl butyl silyl ester, and imides [19].

4. Summary

We have synthesized block copolymers composed of norbornene with relatively low polydispersity using Grubbs's catalyst [bis-(tricyclohexylphosphine)benzylidine ruthenium(IV) dichloride] as the initiator for a living ROMP. In order to control the polydispersity of the block copolymer, the bulkier 2-norbornene-5,6,-dicarboxylic acid bis trimethylsilyl ester (NORCOOTMS) was the first monomer to be polymerized. Because of steric interference between the NORCOOTMS monomers and inhibition of Grubbs's catalyst due to the more basic trimethyl silane groups, the rate of propagation of NORCOOTMS was reduced and the monomer polymerized with a narrow PDI. When norbornene, which by itself cannot be homopolymerized with a narrow PDI, was added to the propagating species, the resulting block copolymers had a PDI less than 1.26. This study shows that the PDI can be controlled by selecting a monomer with proper functionality as the starting block of the block copolymer to control k_p as an alternative of using additives to change the reactivity of the catalyst. Selection of the proper functionality depends on the polarity and bulkiness of the functional group to interact with the catalyst.

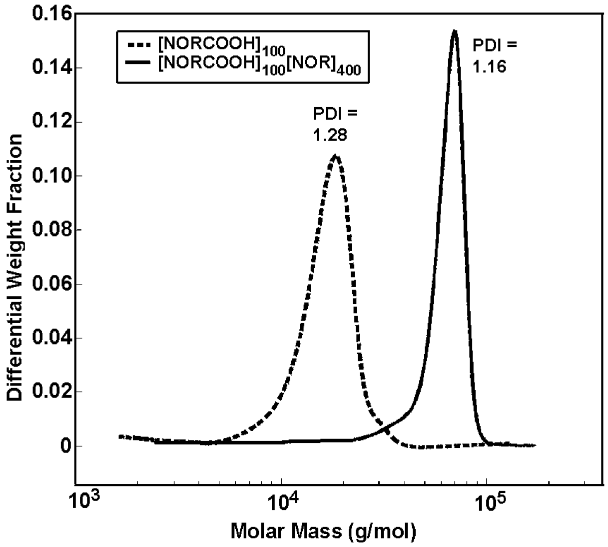

Fig. 5. Molecular weight distribution of $[NORCOOH]_{100}$ and $[NORCOOH]_{100}[NOR]_{400}$.

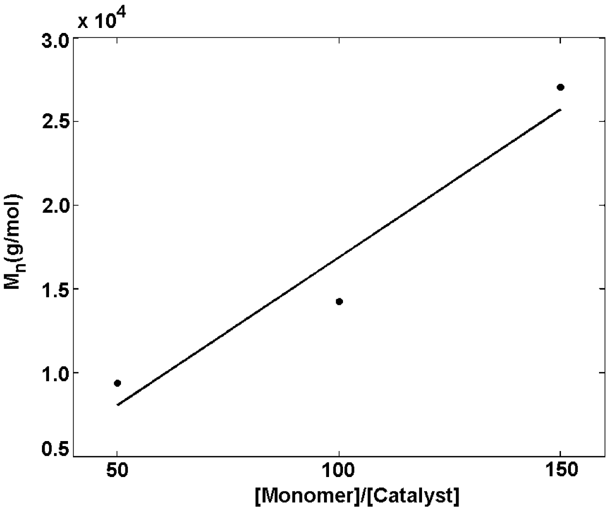

Fig. 7. Graph of number average molecular weight and the catalyst to monomer ratio.

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References

[1] Cummins CC, Beachy MD, Schrock RR, Vale MG, Sankaran V, Cohen RE. Chem Mater 1991;3:1153.

[2] Bazan G, Schrock RR, Feast WJ, Gibson VC. Polym Commun 1989; 30:258.

[3] Albagli D, Bazan G, Wrighton MS, Schrock RR. J Am Chem Soc 1992;114:4150.

[4] Komiya Z, Pugh C, Schrock RR. Macromolecules 1992;25:6586.

[5] Ivin KJ, Mol CJ. Olefin metathesis and metathesis polymerization. London: Academic Press; 1997. p. 6–19, see also p. 41–3, and p. 233.

[6] Royappa AT, Saunders RS, Rubner MF, Cohen RE. Langmuir 1998; 14:6207.

[7] Ng Cheong Chan Y, Schrock RR, Cohen RE. Chem Mater 1992; 4:24.

[8] Ng Cheong Chan Y, Schrock RR, Cohen RE. J Am Chem Soc 1992; 114:7295.

[9] Ng Cheong Chan Y, Craig GSW, Schrock RR, Cohen RE. Chem Mater 1992;4:885.

[10] Sohn BH, Cohen RE. Chem Mater 1997;9:264.

[11] Ahmed SR, Ogale SB, Ramesh R, Papaefthymiou GC, Kofinas P. Appl Phys Lett 2002;80:1616.

[12] Ahmed SR, Kofinas P. Macromolecules 2002;35:3338.

[13] Schwab P, Grubbs RH, Ziller JW. J Am Chem Soc 1996;118:100.

[14] Bielawski CW, Grubbs RH. Macromolecules 2001;34:8838.

[15] Robson DA, Gibson VC, Davies RG, North M. Macromolecules 1999;32:6371.

[16] Lynn DM, Kanaoka S, Grubbs RH. J Am Chem Soc 1996;118: 784.

[17] Webster OW. Science 1991;251:887.

[18] Kanaoka S, Grubbs RH. Macromolecules 1995;28:4707.

[19] Liaw DJ, Tsai JS, Wu PL. Macromolecules 2000;33:6925.