Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Ma, Rui , Song, Zhongying , Hou, Yubang , Liu, Yan , Xing, Bin , Tan, Zhe and Bao, Feng(2009) 'Synthesis of Norbornene and Methyl Methacrylate Graft Copolymers with High Norbornene Content by Using Mixed Catalytic System', Journal of Macromolecular Science, Part A, 46: 2, 193 — 201

To link to this Article: DOI: 10.1080/10601320802595094

URL: http://dx.doi.org/10.1080/10601320802595094

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2009) **46**, 193–201
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ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320802595094

Synthesis of Norbornene and Methyl Methacrylate Graft Copolymers with High Norbornene Content by Using Mixed Catalytic System

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Received May 2008, Accepted August 2008

A vinyl-type polymer of norbornene containing a few pendant styrene groups obtained by copolymerization of norbornene and 1,4-divinylbenzene (1,4-DVB) was used as a macroinitiator in the reverse atom transfer radical polymerization (RATRP) of methyl methacrylate in conjunction with $CuCl_2$/2,2′-bipyridine/2,2′-azobisisobutyronitrile (AIBN) as a catalyst. In the first step of the reaction, the structural characterization of the copolymers showed that norbornene and 1,4-divinylbenzene copolymerizations occur as a coordination mechanism and that true copolymers are formed by random copolymerization. With the initiation of copper dichloride and AIBN in the second step, the pendant styrene groups in the copolymers were quantitatively polymerized with methyl methacrylates, which allowed the successful synthesis of polynorbornene-based graft copolymers by RATRP mechanism. The analyses of the product by ^{1}H-and ^{13}C-NMR and GPC gel permeation chromatography (GPC) gave the verification of 'true' copolymer. Varying the monomer feed ratio controlled the thermal property of the graft copolymer.

Keywords: Norbornene, methyl methacrylate, nickel catalyst, graft copolymerization, 1,4-DVB, ATRP

1 Introduction

Copolymers of nonpolar alkenes with polar monomers with various architectures remain an ultimate goal in polyolefin engineering, since, of the many permutations available for modifying the properties of the polymers, the incorporation of functional groups into an otherwise nonpolar material is substantial (1–2). In particular, polynorbornenes exhibits rather high thermal stability, superior etch resistance and excellent dielectric properties. However, because of the lack of polar functional groups on its polymer chain, polynorbornenes usually suffer from poor incompatibility with other polymers or materials, and it has significantly limited many of its uses. To resolve this problem, one established approach is to introduce a second polar group into the polymers such as acrylate group. The inherent difficulty of the copolymerization of these two types of monomers arises from the very different mechanisms through which they normally undergo polymerization. Norbornenes more commonly undergo transitionmetal-catalyzed insertion polymerization, and they undergo less free-radical polymerization. Moreover, acrylates are readily polymerized through a free-radical mechanism. Copolymerization of methyl acrylate (MA) and norbornene (NBE) through radical systems such as atom transfer radical polymerization (ATRP) and nitroxide-mediated polymerization (NMP) has been reported to give a MA-enriched random copolymer (3–4). Starmer patented the radical-initiated synthesis of acrylate/norbornene copolymers, but the maximum incorporation of norbornene in the copolymers was 5% (5). The copolymerization of norbornene and acrylates by transition metal catalysts has also been investigated. Goodall et al. disclosed the additional copolymerization of norbornene with acrylates in the presence of a Group VIII transition metal catalyst, providing random copolymers (6). Sen and coworkers described the copolymerization of MA and norbornene using neutral palladium complexes $(L_2)Pd(Me)(Cl)$ or $(L)Pd(Me)(Cl)$ (L= monodentate phospines or one bidentate phosphorus ligand, respectively), producing MA-enriched copolymers (7–8). A coordination-insertion mechanism has been

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proposed for these catalysts based on the fact that polymers could be produced in the presence of a "radical inhibitor" (e.g. 4-methoxyphenol). Wu and coworkers reported the copolymerization of norbornene and methyl acrylate by β-ketoamine palladium complexes/MAO. The MA-enriched copolymers were obtained as might have been expected (9). Furthermore, the copolymerization of NBE and tert-butyl methacrylate has also been investigated in the presence of [Ni(acac)$_2$]/MAO catalyst system via the trigger coordination mechanism (10). Although the copolymerization of norbornene with MA had been successfully performed by a few research groups, there still aren't any reports about successful syntheses of methyl methacrylate(MMA) with norbornene copolymers for the higher steric hindrance of MMA to MA. Hajime Yasuda and his coworkers have explored the random copolymerizations of norbornene with methyl methacrylate in a 1:1 molar ratio using a variety of nickel compound/MMAO system as catalysts. However, they only obtained blended polymer of homopoly(norbornene) and homopoly(MMA) (84.5/15.5 molar ratio). The synthetic protocol demonstrated in this way has provided an access to more sophisticated functional current block copolymers which can have numerous future applications (11–14). In short, there are still a number of large challenges to design a suitable polymerization system for the synthesis of the copolymer of MMA with NBE, such as the copolymers having high norbornene content and control of the copolymerization.

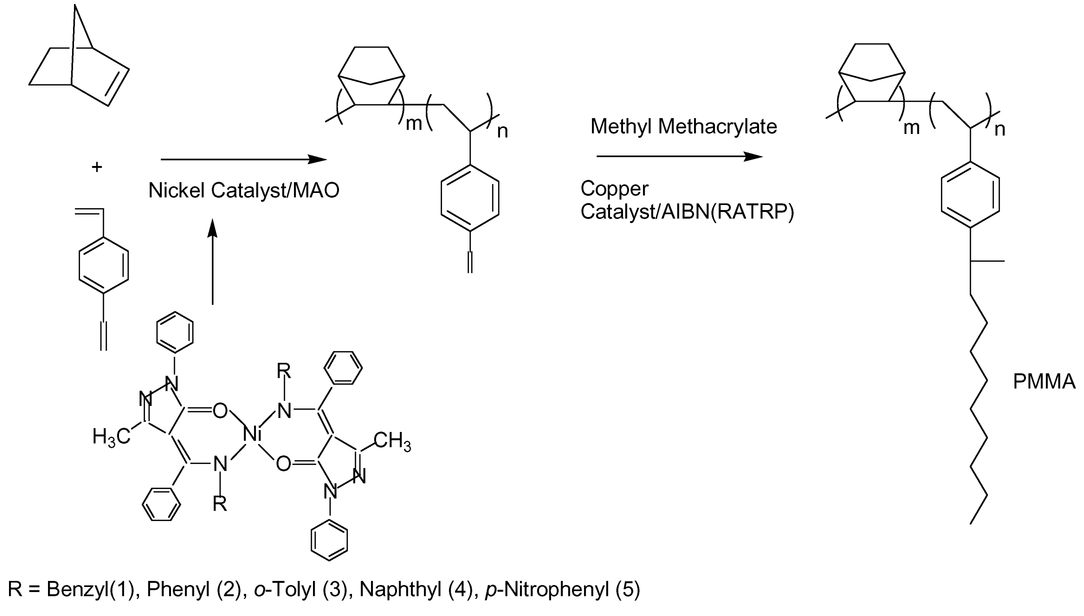
Currently, various reactive polyolefins, including polyolefins containing alkylborane groups, polyolefins containing p-methylstyrene units, a variety of unsaturated polyolefins have been synthesized using Ziegler-Natta or metallocene catalysts by the copolymerization of an α-olefin monomer with the corresponding reactive group-containing comonomers, which have been applied as 'intermediates' to prepare functional polyolefins having versatile functionalities (15–18). Furthermore, a late metal catalyst system involving β-ketoamine ligand synthesized by our group has been reported as a successful initiator for the copolymerization of norbornene with styrene through a coordination polymerization mechanism (19–20). Based on these two points, in order to synthesize the PNBE-based copolymers, a new synthetic way of using mixed catalytic systems was developed by our group (Scheme 1). The copolymer of MMA and NBE of high NBE content was successfully obtained.

2 Experimental

All manipulations were carried out under an atmosphere of inert gases using standard Schlenk techniques.

2.1 Materials

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk and vacuoline techniques. Solvents were purified using standard procedures. Reagents of CuCl$_2$ and the 2,2′-azobisisobutyronitrile (AR) were obtained from the China National Medicine Group, Shanghai Chemical Reagent Company and used without further purification. The bipyridine was obtained from Aldrich and used without further purification. Norbornene (Aldrich) was distilled over potassium and then dissolved in dried toluene to



Sch. 1. Copolymerization of norbornene and 1,4–DVB and subsequent functionalization reactions.

give 0.4 g/mL solution. Methyl methacrylate and styrene were dried over CaH_2, and then freshly distilled under *vacuo* prior to use. Methylaluminoxane (MAO) was prepared by partial hydrolysis trimethylaluminum (TMA) with $Al_2(SO_4)_3 \cdot 18H_2O$ in toluene at 0–60°C as a water source. The initial $[H_2O]/[TMA]$ molar ratio was 1.3. A nickel(II) complex was synthesized according to our previous work (19–21).

2.2 Instruments

^{1}H- and ^{13}C-NMR spectra were obtained using a Varian 600 MHz at room temperature in $CDCl_3$ (for copolymer) solution using tetramethylsilane as internal standard. Gel permeation chromatography (GPC) analyses of the molecular weight molecular and weight distributions of the polymers were performed on a Waters Breeze system with tetrahydrofuran as the eluent at 40°C using standard polystyrene as the reference. TGA data were measured with a TG-290C thermal analysis system instrument, under dry nitrogen with a flow rate of 50 ml/min and a heating rate of 10°C/min.

2.3 Synthesis

2.3.1. *Copolymerization of norbornene and 1,4-DVB by the β-ketoamine chelate nickel catalyst*

Catalytic copolymerization of norbornene and 1,4-DVB has been carried out in a Fisher-Porter glass reactor and protected by nitrogen. MAO (2.25 mmol, solid powder) was added into a Schlenk flask with a magnetic stirrer. Norbornene (0.06 mol, 5.64 g) and 1,4-DVB (0.0084 mol, 1.09 g) in 10 ml toluene and 9 ml of toluene were added later. The reaction was started by the addition of one ml of a freshly prepared Complex **4** solution (1.5×10^{-5}M in toluene) at 70°C. After 16 h, the reaction mixture was poured into an excess of ethanol acidified with 5% HCl. The polymer was washed with ethanol and then dried under vacuum at 25°C for 72 h.

2.3.2. *Grafting of MMA from poly(NBE-co-1,4-DVB) (RATRP procedure)*

A typical example of the general procedure was as follows. A round-bottom flask equipped with a magnetic stirrer, a condenser, and a lateral neck with a tap was used. The system was vacuumed and back-filled with dry nitrogen several times. $CuCl_2$, ligand (bipyridine) and solvent (toluene) were added to a dry round-bottom flask under stirring, four cycles of vacuum nitrogen were applied to remove the oxygen. After the catalyst was dissolved, MMA with AIBN was introduced under an inert atmosphere. Two oil baths warmed at the desired temperatures were prepared. The reaction was conducted in two different steps: the mixture was first kept at 65–70°C for 12 h and was then directly transferred to the second oil bath, which was preheated at 100 or 110°C. After a given time, the mixture was diluted with THF and poured into ten-fold methanol. The resulting precipitated polymers were treated by filtering, washing with methanol several times, and drying under vacuum at 40°C to a constant weight.

3 Results and Discussion

3.1 Syntheses and Characterization of the PNBE Containing Pendant Vinylbenzene Groups

As reported by our group, the same series of Ni(II)-based β-ketoamine complexes (as shown in Scheme 1) in combination with MAO have shown high activity in copolymerization of norbornene and styrene, giving vinyl addition copolymers soluble in common solvents such as tetrahydrofuran, chloroform, and toluene.

The goal of introducing some vinylphenyl groups into polynorbornene still deserves to be studied. Our approach to gain this goal was to resort to some late metal catalysts for the copolymerization of norbornene and 1,4-divinylbenzene with the idea that nickel-catalyzed polymerization could produce norbornene and styrene copolymer. However, because the two styrene moieties in a divinylbenzene molecule are both polymerizable in a nickel-catalyzed copolymerization reaction, it is also very important and interesting to explore if the homogeneous late metal catalysts are able to control the incorporation of 1,4-divinylbenzene in a selective way, that is, by reacting with only one of the two vinyl groups.

In this report, the 'intermediates' of PNBE containing pendant vinylbenzene groups was firstly synthesized through the copolymerization of NBE with 1,4-DVB catalyzed by the same series of β-ketoamine chelate nickel complexes/MAO system previously reported by our group. Crude polymers were extracted by boiling solvent chloroform. It is well known that polystyrene is completely soluble in chloroform whereas polynorbornene of vinyl addition type is insoluble. Furthermore, chloroform would dissolve the low molecular weight poly(NBE-co-1,4-DVB). As discussed in the following text, it has a small quantity of 1,4-divinylbenzene segments in the copolymer. Therefore, the soluble fraction in chloroform is 'pure' copolymer. After complete extraction, the trace insoluble fraction indicates the pure homopolynorbornene content in the whole polymer products is trace. This fact indicates the homopolymerization of norbornene and 1,4-divinylbenzene is infrequent. The main process is copolymerization of norbornene and 1,4-DVB.

The results of copolymerizations of norbornene with 1,4-DVB with various catalysts and the various concentrations of 1,4-DVB in the copolymerization feed as well as other polymerization conditions are summarized in Table 1. The catalytic activity sequence was found to be 4 > 5 > 3> 2 > 1, which is coherent to the expected

Table 1. Copolymerization of norbornene and 1,4-DVB catalyzed by a series of nickel complex/MAO catalytic system[a]

Sample	*Complex*	*Polymerization conditions*		*Yield (%)*	*Activity*[b]	*1,4-DVB in polymer (mol-%)*	*Mn (10^4g/mol)*	*Mw (10^4g/mol)*	*Mw/Mn*
		1,4-DVB (mol%)	*T(°C)*						
1	1	12.28	70	9.51	0.25	9.17	0.48	1.52	3.17
2	2	12.28	70	17.53	0.49	8.54	0.57	1.63	2.85
3	3	12.28	70	29.87	0.84	5.72	0.82	2.27	2.76
4	4	12.28	70	63.60	1.79	3.26	1.17	3.90	3.33
5	5	12.28	70	46.51	1.31	4.89	0.88	3.06	3.48
6	4	12.28	50	50.22	1.41	2.62	1.31	3.78	2.88
7	4	12.28	30	44.73	1.26	1.79	1.91	4.72	2.47
8	4	20.0	70	47.83	1.52	4.17	0.57	1.98	3.47
9	4	7.69	70	67.57	1.78	2.26	1.41	4.25	3.01
10	4	4.76	70	75.95	1.92	0.98	1.83	5.10	2.79
11	4	0	70	90.78	2.14	0	19.59	53.1	2.71

[a] Conditions: 20ml toluene, [NBE]=0.06mol, [Al]/[Ni]=150, $m_{Ni} = 1.5\times10^{-5}$mol, polymerization time = 16 h.
[b] Activity in 10^4g of polymer/(mol of Ni·h).

steric and electronic effects of the ketoamine ligand. This result has a good agreement with reported norbornene with styrene copolymerization data (17). We are more interested in comparing the copolymerization results with the norbornene and styrene copolymerization by using the same series of nickel complexes. In similar conditions, the activity for copolymerization of norbornene with styrene is much higher than that activity for copolymerization of norbornene with 1,4-DVB (Only trace polymers in norbornene with 1,4-DVB copolymerization could be obtained when the nickel amount is 5.0×10^{-6}mol, However, a certain polymers could be easily obtained in norbornene with styrene copolymerization under the same conditions. As reported by our group, the same Ni(II)-based β-ketoamine complex in combination with MAO has shown high activity in norbornene and styrene copolymerization of up to 4.48×10^4 g/(molNi h).). Reported by Wu's and Carlini's groups (22–23), they used NMR analysis of the chain-end group of the low-molecular-weight copolymer of norbornene with styrene to confirm that the active species of the copolymerization is Ni-H, and the chain is initiated through a styrene secondary insertion or a norbornene 2,3-insertion into the Ni-H and terminated through β-H elimination from an inserted styrene unit. In our studying the copolymerization of norbornene with 1,4-DVB, there are two vinyl groups in each 1,4-DVB molecules. Therefore, there is a high probability of β-H elimination in the copolymerization of NBE with 1,4-DVB. It's a satisfactory explanation for the lower activities of NBE and 1,4-DVB copolymerizations for its higher terminating rates than that of NBE and styrene copolymerizations.

Among the five catalysts in copolymerization of NBE with 1,4-DVB, the complex 4-MAO showed the highest activities. Therefore, the complex4-MAO was used as a typical example to illustrate the copolymerization of NBE and 1,4-DVB. From Table 1, the fact of the catalytic activities monotonically decreasing with an increasing of polymerization temperature could be found. With the increase of the monomer feed of 1,4-DVB from 0 to 20%, the catalytic activity decreases, but the 1,4-DVB segments in the copolymer increase from 0 to 4.17%. The results indicate lower copolymerization reactivity of 1,4-DVB relative to norbornene.

One copolymer sample was subjected to gel permeation chromatography (GPC) analysis to further confirm the linear structure of the obtained poly(NBE-co-1,4-DVB) copolymers. Figure 1 shows the GPC curve of a

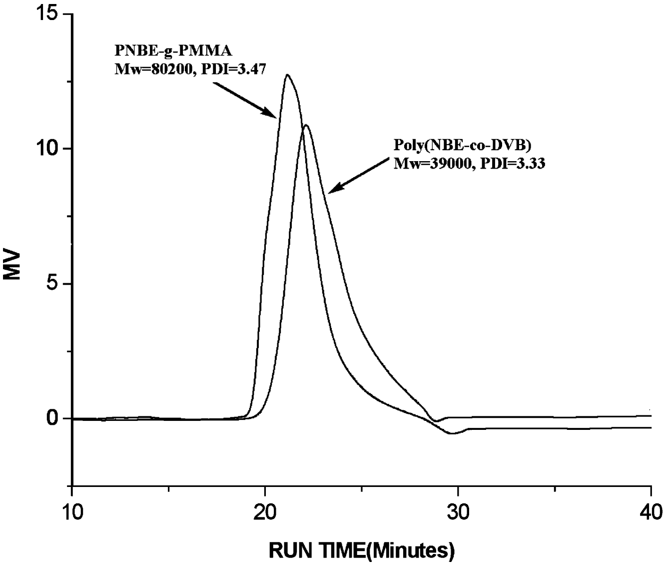


Fig. 1. GPC curves of the poly(norbornene–co–1,4–divinylbenzene) and PNBE–g–PMMA (the GPC examination was performed on a Waters Breeze system with chloroform as the eluent at 40°C with standard polystyrene as the reference). MV = millivolt.

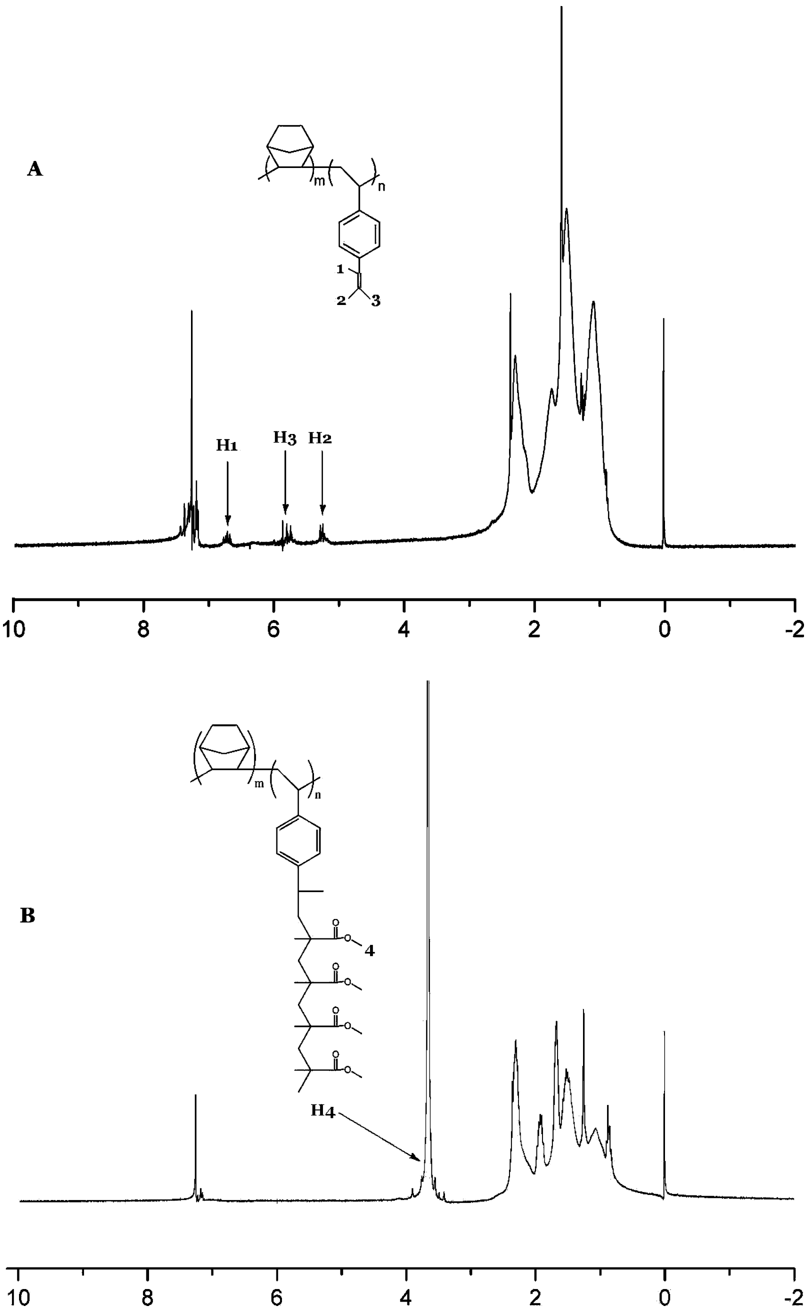


Fig. 2. ^{1}H–NMR spectra of (A) the poly(norbornene–*co*–1,4–divinylbenzene) copolymer containing 3.26 mol% pendant vinylbenzene groups, (B) the PNBE–g–PMMA graft copolymer containing 14.7 mol% MMA units

poly(NBE-co-1,4-DVB) copolymer containing 3.26 mol% of incorporated 1,4-DVB units. Giving a molecular weight (Mw) and molecular weight distribution of 39000 g·mol^{-1} and 3.33, respectively, the GPC curve exhibits a smooth, unimodal signal and shows no sign of the existence of cross-linked polymers.

All the obtained copolymers are soluble in common organic solvents, such as chloroform, tetrahydrofuran, and chlorobenzene at room temperature, which allows detailed structural analyses by using nuclear magnetic resonance (NMR) spectroscopy. Figure 2A shows the ^{1}H-NMR spectra of the norbornene-1,4-DVB copolymer containing 3.26 mol% of 1,4-DVB units. In addition to the major integral peaks ranging from 0 to 3 ppm corresponding to the CH_2 and CH groups in the norbornene units, several chemical shifts are observed at 5.2 and 5.8 ppm (methylene, $CH{=}CH_2$), and 6.7 ppm (doublet of doublet, $CH{=}CH_2$), and aromatic proton peaks at 7.1 and 7.2 ppm (C_6H_4). The incorporation modes of 1,4-DVB can be made clear by comparing with the integrated intensities of these five minor

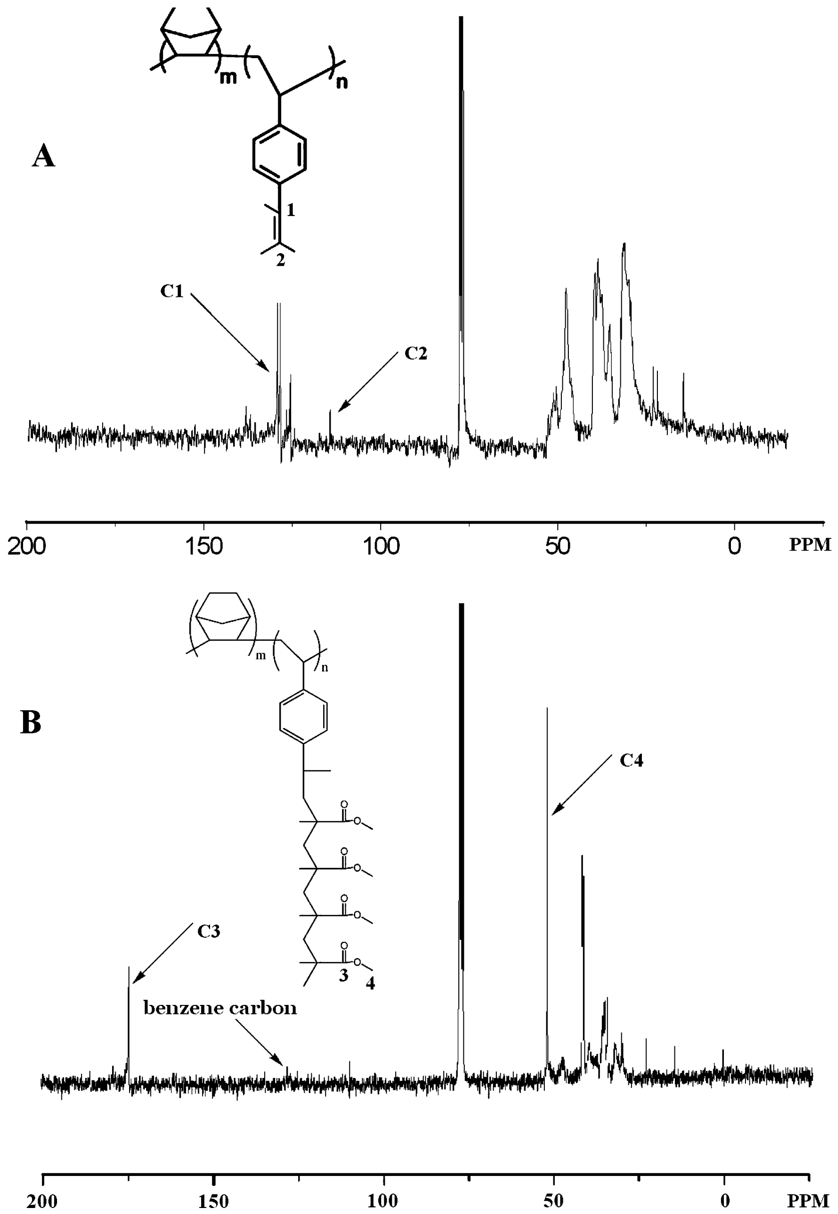


Fig. 3. ^{13}C–NMR spectra of (A) the poly(norbornene–*co*–1,4–divinylbenzene) copolymer containing 3.26 mol% pendant vinylbenzene groups, (B) the PNBE–g–PMMA graft copolymer containing 14.7 mol% MMA units

peaks. All the obtained copolymers show near 1:1:1:2:2 ratios between the peaks at 5.2, 5.8, 6.7, 7.1, and 7.2 ppm, suggesting (i) the selective enchainment of 1,4-DVB by only one of its two double bonds, and (ii) the in-chain instead of chain-end placement of the incorporated 1,4-DVB units. In view of the generally low incorporations of 1,4-DVB in the obtained copolymers, the selective mono-enchainment of 1,4-DVB in the copolymers can be attributed to the use of nickel catalysts for the copolymerization that show poor capability of incorporating the 1,4-DVB and the presence of abundant free 1,4-DVB comonomers in the copolymerization systems. In addition, the steric hindrance at the residual double bond of the incorporated 1,4-DVB units would be further enhanced by the adjacent polymer chain and thus, effectively prevented them from further participating in the polymerization reaction. This result can further explain why the copolymerization activity of norbornene with styrene is higher than that of norbornene with 1,4-DVB catalyzed by the same catalyst.

Figure 3A shows the ^{13}C-NMR spectra of the norbornene-1,4-DVB copolymer containing 3.26 mol% of 1,4-DVB units. The major integral peaks ranging from 28 to 45 ppm corresponding to the CH_2 and CH groups in the norbornene units, several chemical shifts are observed at 134.2 ppm (methyne, $CH{=}CH_2$), and 114.3 ppm (methylene, $CH{=}CH_2$), and aromatic proton peaks at 125–138 ppm (C_6H_4). The ^{13}C-NMR spectra also confirmed the double bonds existence in the NBE-co-1,4-DVB copolymers.

3.2 Syntheses and Characterization of the PNBE-g-PMMA by RATRP Procedure

For the low concentration reactive groups in the obtained poly(NBE-co-1,4-DVB), the subsequent functionalization reactions is faced with great challenge. Nevertheless, due to the high reactivity of styrene groups in the interconversion reactions into the initiating groups for living anionic and atom transfer radical (ATRP) polymerizations (24–25), the PNBE containing few pendant styrene groups was still able to serve as a reactive 'intermediate' to access functional PNBE with controlled amounts of functional groups (such as methyl acrylate, methyl methacrylate. . .) in synthesizing PNBE graft copolymers. Compared with the atom transfer radical polymerization (ATRP), the reverse atom transfer radical (RATRP) is less poisonous and more convenient to carry into execution. Therefore, the above-obtained poly(NBE-co-1,4-DVB) copolymers were used to initiate the graft-from polymerization of methyl methacrylate by RATRP (in the presence of $CuCl_2$ and 2,2'-azobisisobutyronitrile) mechanisms. The molecular weights results of the obtained graft copolymers were summarized in Table 2. It shows the polydispersity index of the obtained graft copolymer increased with the increase of copolymer molecular weight.

Analogously, in Figure 1 is shown the GPC curve of a graft copolymer containing 14.7 mol% of incorporated methyl acrylate units. Giving a molecular weight (Mw) and molecular weight distribution of 80200 g·mol^{-1} and 3.47, the GPC curve also exhibits a smooth, unimodal signal and shows no sign of the existence of cross-linked polymers. All the GPC traces are symmetrical and present a unimodal character indicating successful block copolymer formation with the constant growth of the MMA segment. The polydispersities of these PNBE-g-PMMA copolymers (PDI= 3.47–4.02) are higher than that of the poly(NBE-co-1,4-DVB) (PDI=3.33). Considering the viewpoint, the initial radicals generated in our case were polymeric, and their behavior in RATRP may be different than the behaviors of low molar mass radicals stemming from ATRP.

Table 2. GPC Results for the Molecular Weights and Molecular Weight Distributions of the Poly(NBE-co-1,4-DVB) Copolymer and the Resultant PNBE-g-PMMA Copolymers

Sample	*Polymer*	*Mn (10⁴g/mol)*	*Mw (10⁴g/mol)*	*Mw/Mn*
1	Poly(NBE-co-1,4-DVB)	1.17	3.90	3.33
2	PNBE-g-PMMA (sample 1)	2.31	8.02	3.47
3	PNBE-g-PMMA (sample 2)	2.57	9.78	3.80
4	PNBE-g-PMMA (sample 3)	2.64	10.63	4.02

Interestingly, the block copolymers obtained by direct ATRP, PTHF–PSt and PTHF–PMA, starting from bromine-functionalized PTHF also showed relatively high polydispersities in several cases that reported before (26–27). The induction period observed at the beginning of the process, as shown previously, is another factor that can broaden the distributions of molecular weights. It should also be taken into account that as the conversion increases, the reaction mixture become more viscous and stirring is less effective. Because of the heterogeneous character of the reaction, the deactivation process can become less effective at high conversions, and the decrease in polydispersity is lower than expected. In another report concerning RATRP reactions (28), it was indicated that after about a 30% conversion, the polydispersity remained almost unchanged. Finally, the difference in the hydrodynamic volumes of the two segments should also be considered. This fact also accounts for the relative concentrations of the catalysts crucial for RATRP, and the GPC measurements cannot be very accurate.

Figure 2B shows the ^{1}H-NMR spectra of the PNBE-g-PMMA copolymer containing 14.7 mol% of MMA units. The graft copolymer shows methyl and methylene protons at 0.8–3 ppm in the spectrum. The Figure 2B is different to Figure 2A; those chemical shifts from 5 to 7.4 ppm have disappeared. This result indicates that the vinylbenzene has entirely incorporated with MMA. Therefore, there are already no double bonds in the graft copolymers. On the other hand, the PNBE-g-PMMA exhibits the characteristic resonance of $-COOCH_3$ in the MMA unit at 3.70 ppm, the integration of which indicates the polymeric form of MMA units.

Figure 3B shows the ^{13}C-NMR spectra of the same PNBE-g-PMMA copolymer as characterized in Figure 3A. No chemical shifts are observed at 110 to 120 ppm (the integral peaks ranging from 110 to 120 ppm corresponding to the methylene groups in the vinylbenzene groups). The integral area of aromatic proton peaks at 125–138 ppm (C_6H_4) is evidently less than that of PNBE-co-1,4-DVB copolymer. These data further confirm that the vinylbenzene has entirely incorporated with MMA. With the incorporations of MMA into the copolymers, the proportion of the phenyl rings in the polymers decreases. In addition, the observation of several chemical shifts at 52.6 ppm (OCH3), and 176.1 ppm (-CO-) in the ^{13}C-NMR spectra indicates the MMA units in the copolymers. These facts further confirm the successful syntheses of PNBE-g-PMMA.

As the graft structures of graft copolymers were proved, the parameters for the graft density and graft length could be determined. For the PNBE-g-PMMA graft copolymer, because the resonance from 5 to 7.4 ppm in the ^{1}H-NMR spectrum of poly(NBE-co-1,4-DVB) representing the vinylbenzene proton was no longer observable in the spectrum of the graft copolymer, the initiation efficiency was estimated to be 100%. Therefore, the graft density of the graft copolymer could be considered to be equal to the concentration of vinylbenzene groups poly(NBE-co-1,4-DVB). As vinyl groups were transformed from vinylbenzene groups also in a quantitative manner, the graft density could be further reckoned by the density of the pending vinylbenzene groups in the original poly(NBE-co-1,4-DVB) copolymer and was 3.26 mol% on average. As shown in Table 2 (Sample 1), the GPC analysis of a poly(NBE-co-1,4-DVB) copolymer revealed a number-average molecular weight (Mn) and molecular weight distribution of 1.17×10^4 g/mol and 3.33, respectively. Given that the incorporation of 1,4-divinylbenzene in the polymer was 3.26 mol%, we roughly estimated the amount of 1,4-DVB inserted into each polymer chain to be 4.07 unit/chain. Accordingly, with the de?ned graft density as shown in Table 2 (Sample 2), a graft length of 10,100 g/mol was determined for the PMMA side chains with the following equation (13):

$$Mn\,(\text{g/mol}) = \frac{\text{mass}_{\text{graftcopolymer}} - \text{mass}_{\text{startingpoly(NBE}-\text{co}-1,4-\text{DVB)}}}{\text{moles of pendant vinylbenzene groups}}$$

The thermostability of the copolymers was investigated by TGA as shown in Figure 4. The norbornene homopolymer exhibits higher decomposition temperatures (480°C) than the copolymer of poly(NBE-co-1,4-DVB) (450°C). As expected, the PNBE containing few pendant styrene groups exhibit a little higher decomposition temperatures than the graft copolymer of PNBE-g-PMMA (442°C). It is attributed to the higher norbornene contents in the polymers (The norbornene segment molar ratio of PNBE, poly(NBE-co-1,4-DVB) and PNBE-g-PMMA is 100%, 96.74% and 81.98% respectively.) The result indicates that the norbornene segment in the copolymer improved its thermostability relatively.

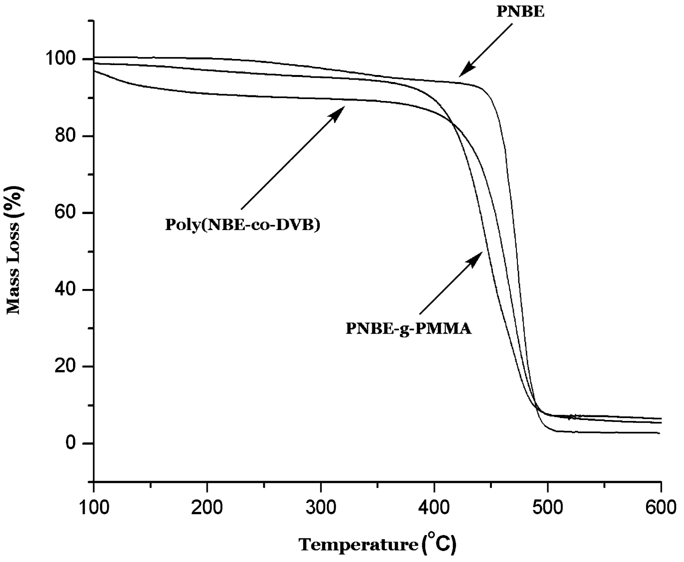


Fig. 4. TG Curves of polymers (a) the norbornene homopolymer, (b) the poly(norbornene–*co*–1,4–divinylbenzene) copolymer containing 3.26 mol% pendant vinylbenzene groups, (c) the PNBE–g–PMMA graft copolymer containing 14.7 mol% MMA units

4 Conclusions

We have demonstrated a firstly successful preparation of PNBE containing pendant styrene groups by the nickel-catalyzed copolymerization of norbornene and 1,4-DVB. The contents of vinylbenzene groups in the copolymers can be controlled by the variable reaction parameters. The poly(NBE-co-1,4-DVB) was shown to be very effective for the initiation of the graft polymerization of MMA for the preparation of structurally well-defined PNBE-based graft copolymers. Unimodal molar mass distributions with the narrow molecular weight distributions indicate that the two copolymerizations occur at the single active site and the polymers are 'true' copolymers. The polar groups in the graft copolymers and the molecular weight of the graft copolymers can be controlled by the polar monomers feed. The copolymers have high norbornene content and the copolymerization is controllable.

The study for the solution properties of the PNBE-g-PMMA graft copolymer and other polar with unpolar monomers copolymerization is our current investigation.

Acknowledgements

The support by the Education Bureau of Hubei Province (project D2006-28004), the Technologies R&D Program of Hubei Province (project 2005AA401D57, 2006AA101C39) and the National Science Foundation of Hubei Province (project 2007ABA295) are gratefully acknowledged.

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