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Synthesis of methyl acrylate graft copolymers by the combination of a polynorbornene containing pendant vinylbenzene groups by using coordination and reverse atom transfer polymerization

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Copolymerization of norbornene and 1,4-divinylbenzene was successfully performed using a β-ketoamine chelate nickel complex–methylaluminoxane, yielding random copolymer of norbornene and 1,4-divinylbenzene containing a few pendant styrene groups. With the initiation of copper dichloride and 2,2′-azobisisobutyronitrile, the pendant styrene groups were quantitatively polymerized with methyl acrylates, which allowed the successful synthesis of polynorbornene-based graft copolymers by reverse atom transfer radical polymerization mechanism. The analyses of the product by ^{1}H NMR and gel permeation chromatography gave the verification of 'true' copolymer. The thermal property of the graft copolymer was controlled by varying the monomer feed ratio.

Keywords: norbornene; nickel catalyst; copolymerization; 1,4-divinylbenzene; graft copolymers; RATRP

Introduction

The copolymerization of polar vinyl monomers with nonpolar olefins remains an area of great interest because the functionalized polyolefins are excellent polymeric materials. In particular, polynorbornenes exhibit 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 they have 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 an acrylate group. The inherent difficulty of the copolymerization of these two kinds of monomers arises from the very different mechanisms through which they normally undergo polymerization. Norbornenes more commonly undergo transitionmetal-catalyzed insertion polymerization, and they less frequently undergo 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.[1–2] Starmer patented the radical-initiated synthesis of acrylate–norbornene copolymers, but the maximum incorporation of norbornene in the copolymers was 5%.[3] The copolymerization of norbornene and acrylates by transition metal catalysts has also been investigated. Goodall *et al*. disclosed the addition copolymerization of norbornene with acrylates in the presence of a group VIII transition metal catalyst, providing random copolymers.[4] 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.[5,6] A coordination-insertion mechanism has been 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–methylaluminoxane (MAO). The MA-enriched copolymers were obtained.[7] Furthermore, the copolymerization of NBE and tert-butyl methacrylate has also been investigated in the presence of an $[Ni(acac)_2]$–MAO catalyst system via the trigger coordination mechanism.[8] Although the copolymerization of norbornene with acrylates has been successfully performed by a few research groups, there still be some challenges to designing a suitable polymerization system for the synthesis of the copolymer of MA with NBE, such as the copolymers having high norbornene content and the

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copolymerization being controlled. This report focuses on solving these problems.

Nowadays, various reactive polyolefins, including polyolefins containing alkylborane groups, polyolefins containing *p*-methylstyrene units and 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.[9–12] Furthermore, recently a 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.[13,14] 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 (as shown in Scheme 1). The copolymer of MA and NBE of high NBE content was successfully obtained.

Experimental Section

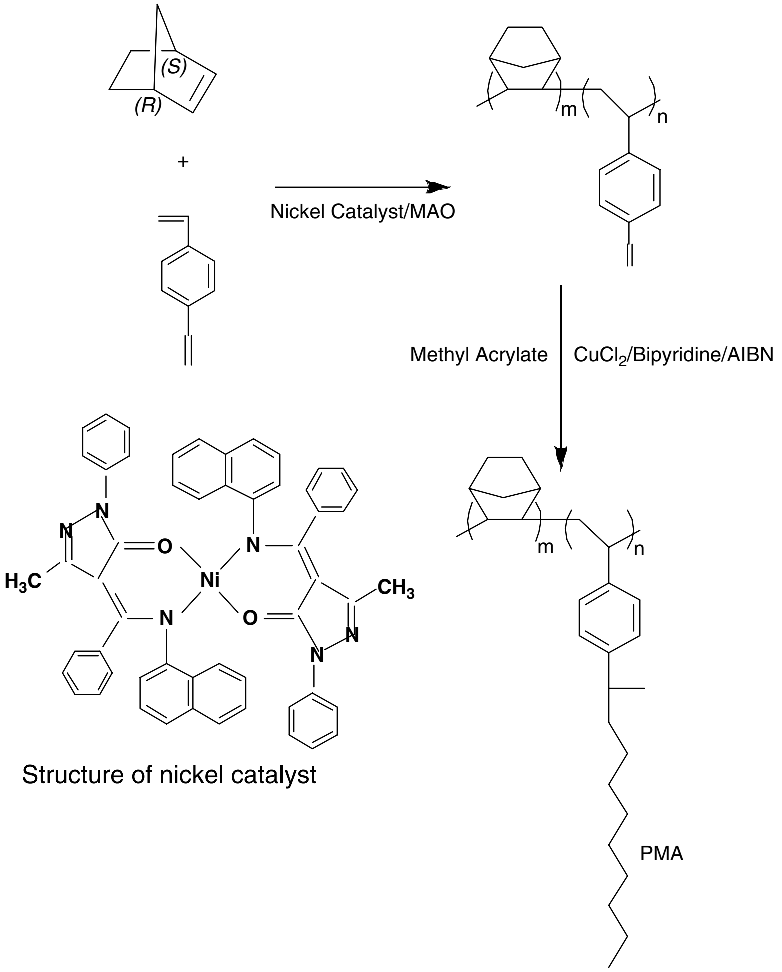
All manipulations were carried out under an atmosphere of inert gases using standard Schlenk techniques.

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 $CuCl_2$, the 2,2′-azobisisobutyronitrile (AR) were obtained from 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 (from Aldrich) was distilled over potassium and then dissolved in dried toluene to give a 0.4 g/mL solution. Styrene was dried over CaH_2, and then freshly distilled under vacuum prior to use. Methylaluminoxane was prepared by partial hydrolysis of trimethylaluminum (TMA) with $Al_2(SO_4)_3 \cdot 18H_2O$ in toluene at 0–60 °C as water source. The initial $[H_2O]$:[TMA] molar ratio was 1.3. Nickel(II) complex was synthesized according to our previous work.[13,14]

Instruments

^{1}H spectra were obtained using an INOVA 500 Hz 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



Scheme 1. Copolymerization of norbornene and 1,4-divinylbenzene and subsequent functionalization reactions.

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.

Synthesis

Copolymerization of norbornene and 1,4-divinylbenzene by the β-ketoamine chelate nickel catalyst

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

Grafting of MA from poly(norbornene-co-1,4-divinylbenzene) (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, MA 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 10-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.

Results and Discussion

Synthesis and characterization of the PNBE containing pendant vinylbenzene groups

As reported by our group, the same Ni(II)-based β-ketoamine complex in combination with MAO has shown high activity in copolymerization of norbornene and styrene, giving vinyl addition copolymers soluble in common solvents such as tetrahydrofuran, chloroform and toluene. In this report, the 'intermediates' of PNBE containing pendant vinylbenzene groups was firstly synthesized through the copolymerization of NBE with 1,4-divinylbenzene catalyzed by the same β-ketoamine chelate nickel complex–MAO system that was reported by our group before.

The copolymerization was also studied by varying the concentrations of 1,4-divinylbenzene in the copolymerization feed as well as other polymerization conditions. The results of the copolymerization reactions were summarized in Table 1.

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(norbornene-co-1,4-divinylbenzene). 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 that 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-divinylbenzene. 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), giving random copolymers soluble in common solvents such as tetrahydrofuran, chloroform, and toluene.[15] As reported in this paper, the highest activity in norbornene with 1,4-divinylbenzene copolymerization could be up to 2.14×10^4 g/(molNi h). It is generally lower than that of the copolymerization of norbornene with styrene.

The catalytic activities monotonically decrease with an increase of polymerization temperature. With the increase of the monomer feed of 1,4-divinylbenzene from 0 to 20%, the catalytic activity decreases, but the 1,4-divinylbenzene segments in the copolymer increase from 0 to 4.10%. The results indicate the lower reactivity of 1,4-divinylbenzene relative to norbornene.

One copolymer sample was subjected to gel permeation chromatography (GPC) analysis to further confirm the linear structure of the obtained poly(norbornene-co-1,4-divinylbenzene) copolymers. In Figure **1** is shown the GPC curve of a poly(norbornene-co-1,4-divinylbenzene) copolymer containing 3.57mol% of incorporated 1,4-divinylbenzene units. Giving a molecular weight (Mn) and molecular weight distribution of 10 390 g mol^{-1} and 3.07,

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

	Polymerization conditions							
Run no.	1,4-DVB (mol)	T(°C)	Yield (g)	Activity[b]	1,4-DVB in polymer (mol%)	M_n (10^4 g/mol)	M_w (10^4 g/mol)	$M_w : M_n$
1	0.0084	70	4.12	1.72	3.57	1.04	3.19	3.07
2	0.0084	50	3.52	1.47	2.76	1.25	3.56	2.85
3	0.0084	30	3.10	1.29	1.85	1.78	4.62	2.59
4	0.0150	70	3.75	1.56	4.10	0.63	2.17	3.45
5	0.0050	70	4.46	1.86	2.17	1.29	4.10	3.17
6	0.0030	70	4.72	1.97	0.95	1.76	5.23	2.98
7	0	70	5.12	2.14	0	19.59	53.1	2.71

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

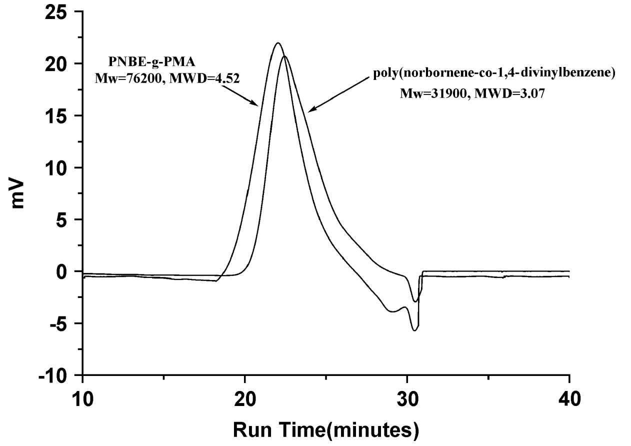


Figure 1. GPC curves of the poly(norbornene-co-1,4-divinylbenzene) and PNBE-g-PMA (the GPC examination was performed on a Waters Breeze system with chloroform as the eluent at 40 °C with standard polystyrene as the reference); mV = millivolt.

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 using nuclear magnetic resonance (NMR) spectroscopy. Figure 2(A) shows the ^{1}H NMR spectra of the norbornene-1,4-divinylbenzene copolymer containing 3.57 mol% of 1,4-divinylbenzene 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-divinylbenzene can be made clear by comparison with the integrated intensities of these five minor 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-divinylbenzene by only one of its two double bonds, and (ii) the in-chain instead of chain-end placement of the incorporated 1,4-divinylbenzene units. In view of the generally low incorporations of 1,4-divinylbenzene in the obtained copolymers, the selective mono-enchainment of 1,4-divinylbenzene in the copolymers can be attributed to the use of nickel catalysts for the copolymerization that show poor capability of incorporating the 1,4-divinylbenzene and the presence of abundant free 1,4-divinylbene comonomers in the copolymerization systems. In addition, the steric hindrance at the residual double bond of the incorporated 1,4-divinylbenzene units would be further enhanced by the adjacent polymer chain and this would effectively prevent them from further participating in the polymerization reaction. This result can explain why the copolymerization activity of norbornene with styrene is higher than that of norbornene with 1,4-divinylbenzene catalyzed by the same catalyst.

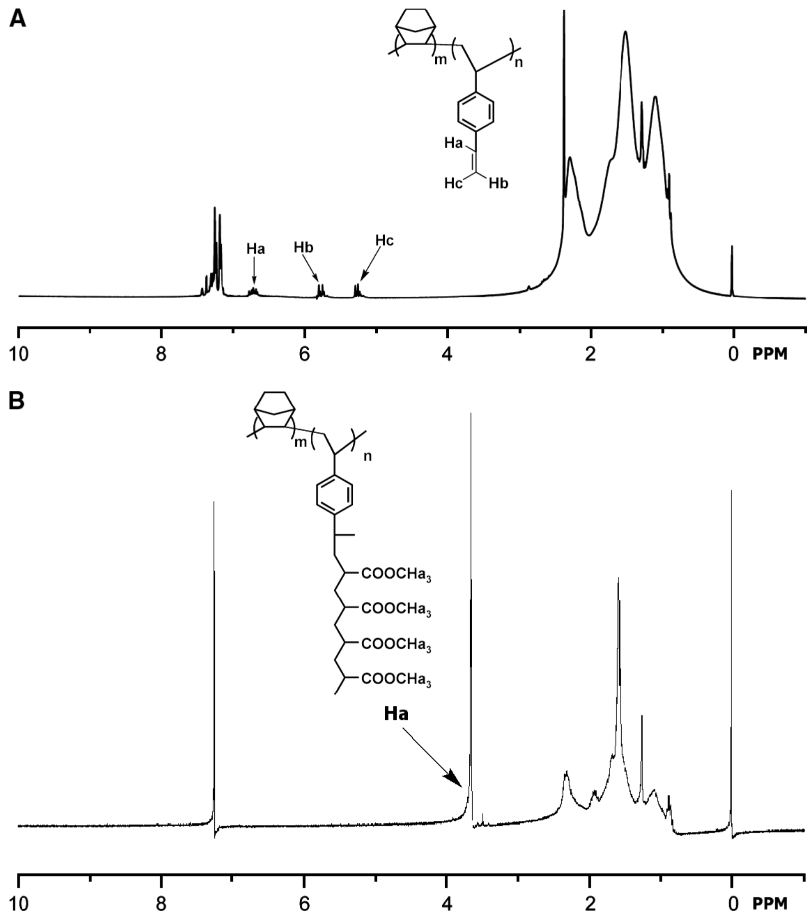


Figure 2. ^{1}H NMR spectra of (A) the poly(norbornene-*co*-1,4-divinylbenzene) copolymer containing 3.57 mol% pendant vinylbenzene groups, (B) the PNBE-g-PMA graft copolymer containing 15.2 mol% MA units.

Table 2. GPC results for the molecular weights and molecular weight distributions of the poly(norbornene-co-1,4-divinylbenzene) copolymer and the resultant PNBE-g-PMA copolymers

Polymer	M_n (10^4 g/mol)	M_w (10^4 g/mol)	$M_w : M_n$
Poly(norbornene-co-1,4-divinylbenzene)	1.04	3.19	3.07
PNBE-g-PMA (sample 1)	1.69	7.62	4.52
PNBE-g-PMA (sample 2)	1.35	5.10	3.78
PNBE-g-PMA (sample 3)	1.21	3.84	3.17

Synthesis and characterization of the PNBE-g-PMA by RATRP procedure

For low concentrations of reactive groups in the obtained poly(norbornene-co-1,4-divinylbenzene), the subsequent functionalization reactions is faced with a great challenge. Nevertheless, due to the high reactivity of styrene groups in the interconversion reactions into the initiating groups for living anionic and atom ATRP polymerizations,[16,17] the PNBE containing a 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 and 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.

In order to test the significance of reverse atom transfer radical process in producing PNBE-g-PMA copolymer, a conventional radical copolymerization of poly(norbornene-co-1,4-divinylbenzene) with methyl acrylate was produced first (conditions: the original poly(norbornene-co-1,4-divinylbenzene), sample 1 in Table 1: the pendant vinylbenzene groups content was 3.57 mol%, the radical initiator was 2,2′-azobisisobutyronitrile (AIBN) and there was no metal catalyst used. The other conditions are the same as for sample 3 in Table 2 and the MA units in copolymer were 15.2 mol%). The polymer obtained by a conventional radical process was soluble in common organic solvents, such as chloroform, tetrahydrofuran, and chlorobenzene, at room temperature. It was characterized by NMR and gel permeation chromatography (GPC). Figure 3 shows the ^{1}H NMR spectra of the polymer. Compared with the copolymer obtained by RATRP process, the MA units' contents in the polymer obtained by a conventional radical process were less than that of copolymer obtained by RATRP process [Fig. 2(B)]. GPC spectra also exhibits a wider molecular weight distribution than that of copolymer obtained by RATRP process and the curve is not a unimodal signal. The ununimodal molar mass distribution with wider molecular weight distribution ($M_w/M_n = 6.52$) of polymer obtained by common radical process indicate the polymer is not a 'true' copolymer. These analyses indicate that polymer produced by a conventional radical process has some unreactive poly(norbornene-co-1,4-divinylbenzene) and some homopolymers of methyl acrylate. We could not obtain our anticipated 'true' copolymer of PNBE-g-PMA using conventional radical polymerization.

Therefore, the obtained poly(norbornene-co-1,4-divinylbenzene) copolymers were used to initiate the graft-from polymerization of methyl acrylate by RATRP (in the presence of $CuCl_2$ and 2,2′-azobisisobutyronitrile) mechanisms. The molecular weight results of the obtained graft copolymers are summarized in Table 2. It shows that the polydispersity index of the obtained graft copolymer increased with the increase in copolymer molecular weight.

Analogously, in Fig. 1 is shown the GPC curve of a graft copolymer containing 15.2 mol% of incorporated methyl acrylate units. Giving a molecular weight (M_n) and molecular weight distribution of 16 900 g/mol and 4.52, 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 MA segment. The polydispersities of these PNBE-g-PMA copolymers

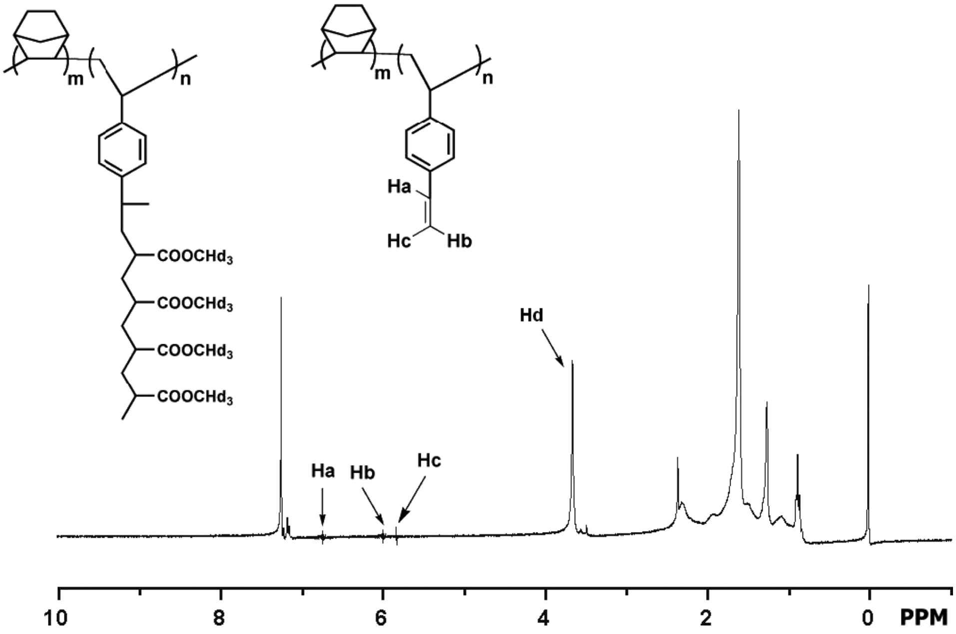


Figure 3. ^{1}H NMR spectra of the polymers obtained by conventional radical polymerization processes.

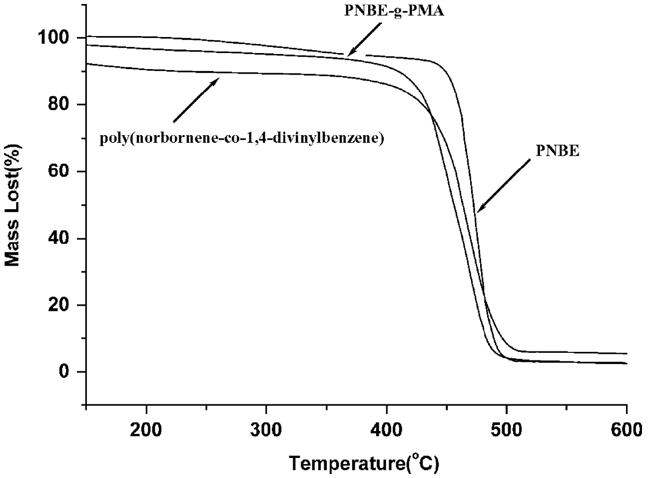


Figure 4. TG Curves of polymers (a) the norbornene homopolymer, (b) the poly(norbornene-*co*-1,4-divinylbenzene) copolymer containing 3.57 mol% pendant vinylbenzene groups and (c) the PNBE-g-PMA graft copolymer containing 15.2 mol% MA units.

(PDI = 3.17–4.52) are higher than that of the poly(norbornene-co-1,4-divinylbenzene) (PDI = 3.07). The initial radicals generated in our case were polymeric, and their behavior in RATRP may be different from the behaviors of low molar mass radicals stemming from AIBN.

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 have been reported before.[18,19] 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 becomes 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,[20] 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 2(B) shows the ^{1}H NMR spectra of the norbornene-1,4-divinylbenzene copolymer containing 15.2 mol% of MA units. The graft copolymer shows methyl and methylene protons at 0.8–3 ppm in the spectrum. Figure 2(B) is different from Fig. 2(A); those chemical shifts from 5 to 7.4 ppm have disappeared. This result indicates that the vinylbenzene has been entirely incorporated with MA. Therefore, there are already no double bonds in the graft copolymers. On the other hand, the PNBE-g-PMA exhibits the characteristic resonance of $-COOCH_3$ in the MA unit at 3.70 ppm, the integration of which indicates the polymeric form of MA units.

The thermostability of the copolymers was investigated by TGA as shown in Fig. 4. The norbornene homopolymer exhibit higher decomposition temperatures (478 °C) than the copolymer of poly(norbornene-co-1,4-divinylbenzene) (452 °C). As expected, the PNBE containing a few pendant styrene groups exhibit slightly higher decomposition temperatures than the graft copolymer of PNBE-g-PMA (438 °C). It is attributed to the higher norbornene contents in the polymers. [The norbornene segment molar ratios of PNBE, poly(norbornene-co-1,4-divinylbenzene) and PNBE-g-PMA are 100, 96.43 and 81.77%, respectively.) The result indicates that the norbornene segment in the copolymer improved its thermostability relatively.

Conclusions

We have demonstrated the first successful preparation of PNBE containing pendant styrene groups by the nickel-catalyzed copolymerization of norbornene and 1,4-divinylbenzene. The contents of vinylbenzene groups in the copolymers can be controlled by the variable reaction parameters. The poly(norbornene-co-1,4-divinylbenzene) was shown to be very effective for the initiation of the graft polymerization of MA for the preparation of structurally well-defined PNBE-based graft copolymers. Unimodal molar mass distributions with 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 solution properties of the PNBE-g-PMA graft copolymer and other polar–unpolar monomers copolymerization are under investigation.

Acknowledgments

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References

[1] S. Elyashiv, N. Greinert, A. Sen, *Macromolecules*, **2002**, *35*, 7521.
[2] B. Gu, S. Liu, J. D. Leber, A. Sen, *Macromolecules*, **2004**, *37*, 5142.
[3] J. R. Morris, US Patent, 3,536,681, **1970**.
[4] B. L. Goodall, III. McIntosh, II, H. Lester, US Patent 6,303,724, **2001**.
[5] A. D. Hennis, A. Sen, *Am. Chem. Soc. Polym. Prepr.*, **2000**, *41*, 1383.
[6] A. D. Hennis, D. C. Hilt, S. Kacker, A. Sen, *Am. Chem. Soc. Polym. Prepr.*, **1998**, *39*, 412.
[7] L. Y. Wang, Y. F. Li, F. M. Zhu, Q. Wu, *Polym. Bull.*, **2006**, *57*, 73.
[8] C. F. Huang, S. K. Wang, S. W. Kuo, W. J. Huang, F. C. Chang, *J. Appl. Polym. Sci.*, **2004**, *92*, 1824.
[9] T. C. Chung, J. Y. Dong, *Macromolecules*, **2002**, *35*, 2868.
[10] J. F. Zou, C. G. Cao, J. Y. Dong, Y. L. Hu, T. C. Chung, *Macromol. Rapid Commun.*, **2004**, *25*, 1797.
[11] C. G. Cao, J. F. Zou, J. Y. Dong, Y. L. Hu, T. C. Chung, *J. Polym. Sci. Part A: Polym. Chem.*, **2005**, *43*, 429.
[12] C. G. Cao, J. Y. Dong, T. C. Chung, *Macromol. Rapid Commun.*, **2005**, *26*, 1936.
[13] F. Bao, X. Q. Lü, B. S. Kang, Q. Wu, *Eur. Polym. J.*, **2006**, *42*, 928.
[14] F. Bao, X. Q. Lü, H. Y. Gao, G. Q. Gui, Q. Wu, *J. Polym. Sci. Part A: Polym. Chem.*, **2005**, *43*, 5535.
[15] F. Bao, X. Q. Lü, Y. Chen, *Polym. Bull.*, **2007**, *58*, 495.
[16] J. S. Wang, K. J. Matyjaszewski, *Am. Chem. Soc.*, **1995**, *117*, 5614.
[17] K. Matyjaszewski, J. Xia, *Chem. Rev.*, **2001**, *101*, 2921.
[18] A. Kajiwara, K. Matyjaszewski, *Macromolecules*, **1998**, *31*, 3489.
[19] I. Cianga, Y. Hepuzer, E. Serhatli, Y. Yagci, *J. Polym. Sci. Part A: Polym. Chem.*, **2002**, *40*, 2199.
[20] J. Xia, K. Matyjaszewski, *Macromolecules*, **1997**, *30*, 7692.