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Copolymerization of norbornene with norbornene terminated polystyrene macromonomer in the presence of Ni-based/MAO catalytic systems

Julien Bernard, Valérie Heroguez*, Henri Cramail*

Laboratoire de Chimie des Polymères Organiques, UMR 5629-Université Bordeaux-1-ENSCPB-CNRS, 16, Avenue Pey Berland, 33607 Pessac Cedex, France

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Abstract

Copolymerization of α-norbornenyl polystyrene macromonomer (NBE-PS) with norbornene (NBE) using Ni-based catalysts in combination with methylaluminoxane (MAO) was investigated. The nature of the catalyst, the $\overline{\mathrm{DP}}_\mathrm{n}$ of the polystyrene macromonomer as well as the [NBE-PS]/[NBE] ratio have been shown to be important parameters to obtain graft copolymers with high NBE-PS incorporation (up to 43 wt%). The compatibilization ability of these graft copolymers has been checked for PS/PNBE blends. The length of the grafts was proved not to be an important parameter to consider compatibilization of the PS/PNBE blend. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Graft copolymer; Norbornene; Ni-based catalysts

1. Introduction

Blending polymers is an elegant route to obtain materials with advantageous properties. Since homopolymers are usually not miscible, the use of a compatibilizer such as graft copolymers is required to improve drastically the compatibility of immiscible polymers and to prepare homogeneous blends with specific thermo-mechanical properties.

Different strategies to synthesize olefin-based graft copolymers have been reported in the literature. One approach consists of functionalizing the polymer skeleton by chemical modification using peroxides, radiation or halogenation [1,2]. However, these methods usually yield undesired by-products and do not allow us to control the length and the number of grafts. Another way to synthesize polyolefin-grafted copolymer is based on the use of borane-containing polyolefins. Indeed, the oxidation reaction of the borane group produces free radicals able to promote the polymerization of subsequent monomers [3–5]. Nevertheless, this grafting process was not effective with hydrocarbon monomers such as styrene. Chung et al. also reported an original route to polyethylene grafted copolymers via a comonomer/anionic method [6]. Random copolymers of ethylene and methyl styrene were lithiated and the metallated benzyl functions were used as initiators for the anionic living polymerization of styrene.

The use of polymers, carrying polymerizable function at one end, in homopolymerization or in copolymerization has proved to be a very powerful method for the preparation of grafted polymers [7–9]. Since these reactive polymers or macromonomers can be synthesized by living anionic polymerization, this technique in combination with transition metal catalysis enables the synthesis of well-defined polyolefin-based graft copolymers with a control of the length and the number of grafts in the resulting copolymer.

Although many studies have been published on the synthesis of graft copolymers based on the copolymerization of α-olefins with olefin terminated macromonomers such as polypropylene-*g*-polystyrene [10] (PP-*g*-PS), polypropylene-*g*-polyisobutylene [11] (PP-*g*-PIB), syndiotactic polystyrene-*g*-polystyrene [12] (sPS-*g*-PS), isospecific polypropylene-*g*-polypropylene [13] (iPP-*g*-PP) or polymethylmethacrylate-*g*-polystyrene [14] (PMMA-*g*-PS) using a metallocene-type catalyst as initiator, little attention has been paid to the copolymerization of olefins with macromonomers ended with a cyclo-olefin moiety, except the study of Arnold et al. [11].

In the present work, we focused on the copolymerization of α-norbornenyl polystyrene macromonomer (NBE-PS) with norbornene (NBE) using Ni-based catalysts. As the

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* Corresponding authors.
E-mail addresses: heroguez@enscpb.fr (V. Heroguez), cramail@enscpb.fr (H. Cramail).

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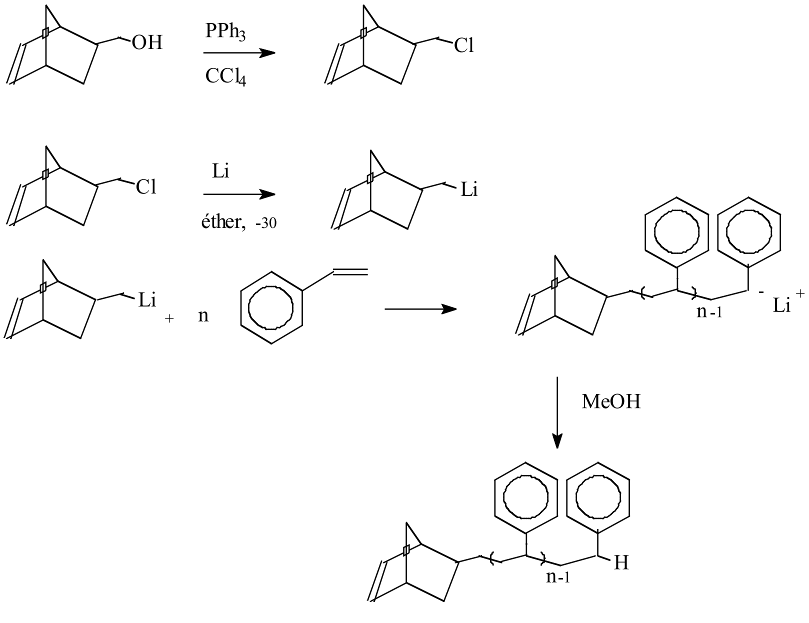


Scheme 1.

incorporation of grafts in the main chain has tremendous consequences on the processability of the resulting copolymers, these graft copolymers were expected to improve the processability of PNBE and also to be used as interfacial modifiers. This study mainly stresses the influence of both catalyst nature and macromonomer length on the insertion ratio of PS grafts into PNBE chains.

In addition, the ability of these graft copolymers to improve dispersion and interfacial interactions between domains in a PS/PNBE blend (50/50, w/w) was checked.

2. Experimental section

2.1. Materials

Ethyl ether (J.T. Baker, The Netherlands), benzene (J.T. Baker, The Netherlands) were distilled from sodium/benzophenone. Styrene (SAFC, France) and chlorobenzene (J.T. Baker, The Netherlands) were purified by distillation over calcium hydride. Norbornene (SAFC, Germany) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (SAFC, USA) was distilled over sodium. Nickel stearate ($Ni(St)_2$) and nickel acetyl acetonate ($Ni(acac)_2$) (ABCR GmbH) were used without further purification. Brookhart catalysts were prepared as described in the literature [15]. Methylaluminoxane (MAO) (Witco GmbH), 10 wt% in toluene was used as received. Other reagents were used without further purification.

2.2. Macromonomer synthesis

The norbornenyl end capped polystyrene macromonomers were synthesized according to methods described by Heroguez et al. [16].

2.3. Copolymerization with norbornene

Copolymerization was carried out at ambient temperature in a 50 ml Schlenk type flash. Typically, 0.145 g (1.54×10^{-3} mol) of NBE, 0.2 g (7.7×10^{-5} mol) of α-norbornenyl polystyrene and 5 mg Ni-based catalyst (nickel stearate, [‘NBE’]/[Ni] = 200) were added in a glove box. The flask was filled with 9 ml of chlorobenzene. Then, 1 ml of 10% MAO solution in toluene was added with a syringe under stirring. After copolymerization, the crude polymer was precipitated into a large amount of acidic methanol and dried under vacuum. The graft copolymer was isolated from unreacted macromonomer by precipitation in a dioxane/-propanol (1:1, v/v) solution.

2.4. Characterization techniques

NMR spectra of α-norbornenyl polystyrene and of the graft copolymers were performed using a Bruker AC200 spectrometer. Size exclusion chromatography was performed using a JASCO HPLC pump 880-PU, equipped with a Varian series RI-3 refractive index detector and a JASCO 875UV, VI5 absorption detector. TOSO HAAS TSK gel columns were used with tetrahydrofuran as the mobile phase. The instrument was calibrated with polystyrene standards. The micrographs were performed using a JEOL JSM-5200 scanning microscope.

2.5. Preparation of blends and grids for the SEM

Typically, 40 mg of PS ($\bar{M}_w = 37\,500\ \mathrm{g\ mol^{-1}}$), 40 mg

Table 1
Characteristics of α-norbornenyl polystyrene macromonomer

$[\text{Styrene}]_0/[\text{initiator}]_0$	$\bar{M}_{n,th}$ (g mol^{-1})	$\bar{M}_{n,SEC}$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$
5	629	500	1.12
16	1776	1600	1.1
24	2608	2400	1.06
26	2816	2600	1.05

of PNBE ($\bar{M}_w = 900\,000$ g mol^{-1}) and 20 mg of copolymer PNBE-*g*-PS were solubilized with 5 ml of chlorobenzene. A drop of chlorobenzene solution of polymers was then casted on copper grids and dried in an oven at 50 °C for one day. The grids were then coated with a gold layer.

The PS and PNBE samples were synthesized in our laboratory in the presence of $Ni(St)_2$/MAO catalytic system (Al/Ni = 200) and their molar masses were determined by SEC and light scattering in chlorobenzene.

3. Results and discussion

In order to determine the influence of the macromonomer chain length on its insertion ratio in the resulting copolymer, a series of PS macromonomers with degrees of polymerization ranging from 5 to 26 were prepared according to Scheme 1.

The livingness of the anionic polymerization method allowed us to prepare well defined PS macromonomers with narrow molar mass distribution, as given in Table 1.

3.1. Influence of the nature of the Ni-based catalyst

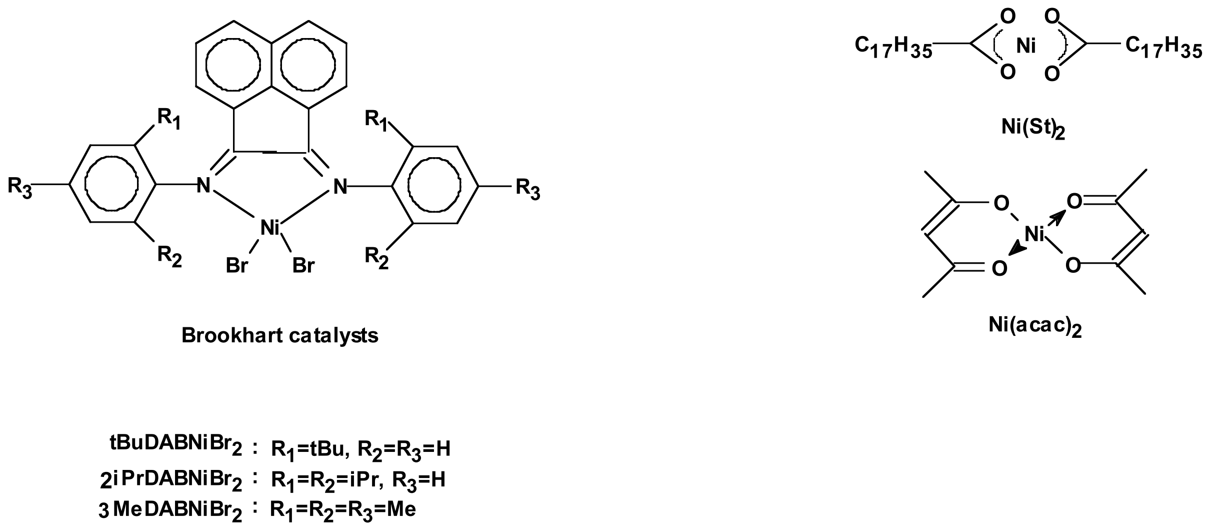
Copolymerization of NBE-PS with NBE was carried out in the presence of three Ni-based catalysts (Scheme 2). MAO was used as co-catalyst and the Al/Ni ratio was maintained at 200. The results of the copolymerization are listed in Table 2.

In a preliminary study, the ability of Ni-based catalysts to insert the NBE-PS-2400 macromonomer was checked (runs 1–4). As observed in Table 2, conversion of NBE-PS-2400 was found from 1 to 8% in the presence of Brookhart catalysts. The steric hindrance, induced by the sterically bulky α-diimine ligands of these catalysts, is suspected to prevent the insertion of PS macromonomer. The resulting copolymers were slightly soluble in THF due to the poor incorporation of polystyrene macromonomer. On the contrary, copolymerization carried out with $Ni(St)_2$ led to a minimum macromonomer conversion of 27%. However, due to the low molar ratio (NBE-PS)/NBE = 0.02, the resulting material was not completely soluble in THF, too.

The nature of the nickel catalyst has also strong influence on the molar mass distribution of the resulting graft copolymers. These latters exhibit a multimodal distribution in the case of Brookhart catalysts or $Ni(St)_2$ and a monomodal distribution in the case of $Ni(acac)_2$.

Consequently, to these first results, we have selected $Ni(acac)_2$ and $Ni(St)_2$ which present less bulky ligands and enhance a high reactivity of NBE [17,18] for the copolymerization of NBE-PS with NBE (runs 5–14). As previously reported [19,20], the conversion of norbornene was quantitative with these catalysts (runs 1, 5–14).

Given that polynorbornene does not absorb in the UV domain, the conversion of NBE-PS was easily calculated from the comparison of the non-polymerized PS and the graft copolymer peak areas in SEC. Then, we calculated the polystyrene weight content and the number of grafts in the resulting copolymers. However, this method of calculation was efficient only with copolymers that were totally soluble in THF. Indeed, due to the stiffness of its backbone, PNBE is not soluble in THF. The insertion of more flexible polystyrene branches breaks the rigidity of the



Scheme 2.

Table 2
Synthesis and characteristics of PNBE-*g*-PS

Run	M_n, NBE-PS (g mol^{-1})	Catalyst[a]	[NBE-PS]/[NBE]	M_n,[b] graft copolymer	NBE-PS[c] conversion (%)	Number of grafts/chain	PS content (wt%)	Solubility in THF
1	2400	$Ni(St)_2$	0.02	16 500	27[d]	–	–	N
2	2400	*t*-BuDABNiBr_2	0.02	49 500	8[d]	–	–	N
3	2400	2iPrDABNiBr_2	0.02	75 100	6[d]	–	–	N
4	2400	3MeDABNiBr_2	0.02	68 650	1[d]	–	–	N
5	2600	$Ni(St)_2$	0.01	18 500	42[d]	–	–	N
6	2600	$Ni(St)_2$	0.05	20 000	35	3.2	41	Y
7	2600	$Ni(St)_2$	0.1	27 200	27	4.5	43	Y
8	1600	$Ni(St)_2$	0.05	19 200	42	3.2	27	Y
9	1600	$Ni(St)_2$	0.1	25 200	34	5.8	37	Y
10	1600	$Ni(acac)_2$	0.1	17 900	22	3.1	28	Y
11	1400	$Ni(St)_2$	0.05	24 200	41	4	23	Y
12	1400	$Ni(St)_2$	0.1	21 900	40	5.8	37	Y
13	500	$Ni(St)_2$	0.1		54[d]d	–	–	N
14	500	$Ni(St)_2$	0.2	16 200	49	11	34	Y

[a] In all experiments ['NBE']/[Ni] = 200; total conversion of NBE.

[b] Apparent molar masses determined by SEC based on polystyrene standards calibration.

[c] Conversion = (SEC UV peak area of PNBE-*g*-PS)/(SEC UV peak area of unreacted NBE-PS + SEC UV peak area of PNBE-*g*-PS).

[d] As graft copolymers were partially soluble in THF, this result is the minimum value of conversion.

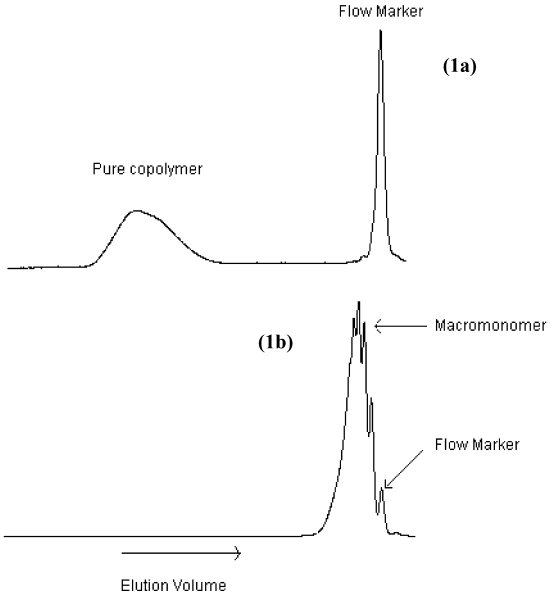


Fig. 1. SEC of pure graft copolymer **14** (a) and NBE-PS-500 (b) in THF (UV detection).

PNBE chain and allows the solubilization of the graft copolymer in common solvents.

In order to extract the graft copolymer from non-polymerized NBE-PS, the crude products were fractioned in θ conditions using the solvent/non-solvent technique with a dioxane/propanol 1:1 (v/v) solution leading to the precipitation of the pure graft copolymer PNBE-*g*-PS. Typical SEC trace and NMR spectrum of the final graft copolymer PNBE-*g*-PS are shown in Figs. 1(a) and 2, respectively. Indeed, the SEC trace (Fig. 1(a)) clearly demonstrates the absence of residual macromonomer in the resulting graft copolymer. In addition, the NMR spectrum (Fig. 2) confirms the incorporation of the NBE-PS macromonomer in the PNBE chains.

3.2. Influence of NBE-PS/NBE molar ratio and of the NBE-PS length on its incorporation

In order to estimate the effect of the NBE-PS macromonomer steric hindrance on its incorporation in the copolymer, the copolymerization of NBE with a series of NBE-PS of different chain lengths (runs 7, 9, 12, and 13) was carried out in identical experimental conditions, i.e. MAO/$Ni(St)_2 = 200$, NBE-PS/NBE = 0.1. As expected, the conversion of the macromonomer was significantly higher with the use of shorter PS chains. As can be seen in Table 2, the conversion decreases from 54% with NBE-PS-500 to 27% with NBE-PS-2600. In the case of short PS macromonomer, the number of grafts in the copolymer was drastically improved. Nevertheless, this increase of macromonomer conversion is not accompanied by an increase of the PS content in the copolymer. Consequently, typical graft copolymer obtained with NBE-PS-500 (run 13) exhibits a high conversion of macromonomer (54%), but is only

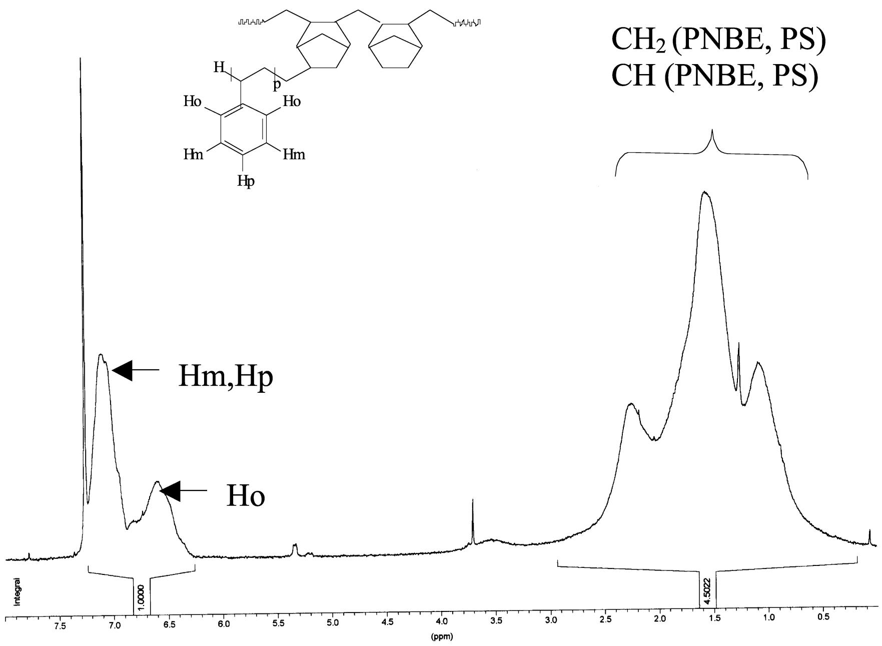


Fig. 2. ^{1}H NMR spectrum of PNBE-*g*-PS (**14**) in $CDCl_3$ at 20 °C.

partially soluble in THF. The increase of the NBE-PS conversion in this case is not important enough to balance the decrease of the graft length. On the contrary, the copolymerization of NBE with NBE-PS-2600 leads to a lower conversion (27%) of the latter but to high PS content (43 wt%). As a result, the higher the length of the graft is, the higher is the final PS content in the resulting copolymer.

Whatever be the length of NBE-PS, a decrease of the NBE-PS/NBE molar ratio from 0.1 to 0.01 yields higher conversion of the macromonomer (see Table 2), but does not allow to render the grafted copolymers totally soluble in THF, due to a lack of PS counterparts. Typically, copolymerization carried out in the presence of NBE-PS-2600 yields THF soluble grafted copolymers containing 43 wt% of styrene units (4.5 grafts per chain) at NBE-PS/NBE $= 0.1$ while insoluble copolymers are logically obtained at a NBE-PS/NBE ratio of 0.01.

3.3. Compatibilization of PNBE/PS blends

In order to study the compatibilization ability of the graft copolymers, PNBE and PS were blended in an equal weight ratio in the presence of 20 wt% of graft copolymers (PNBE-*g*-PS). As the length and the number of grafts attached to the copolymer chain may strongly influence the compatibilization properties, we have compared copolymers **6** and **14** which exhibit 3.2 and 11 grafts per chain, respectively ($\bar{M}_n(\mathbf{6}) = 2600$ g mol^{-1}; $\bar{M}_n(\mathbf{14}) = 500$ g mol^{-1}). The samples were prepared by casting chlorobenzene solutions of the polymer blends on copper grids. These grids were

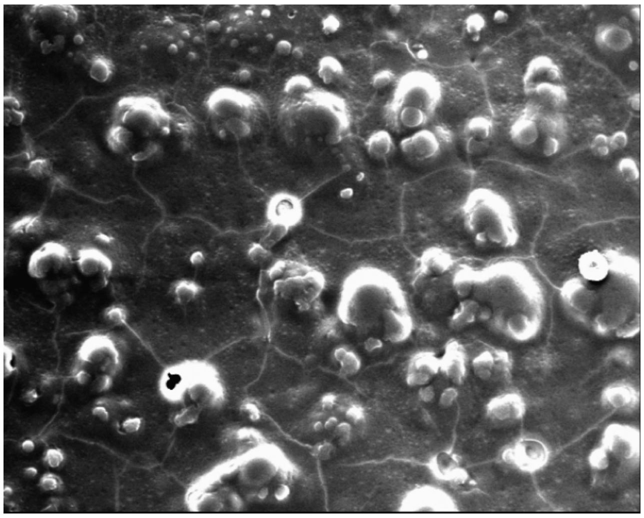


Fig. 3. SEM of a blend PNBE/PS (50/50 wt) (× 500).

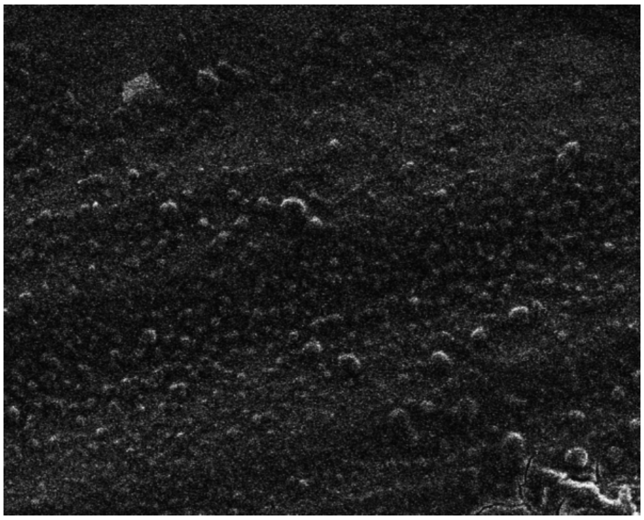


Fig. 4. SEM of a blend PNBE/PS (50/50 wt)/copo**14** (20 wt%) (× 500).

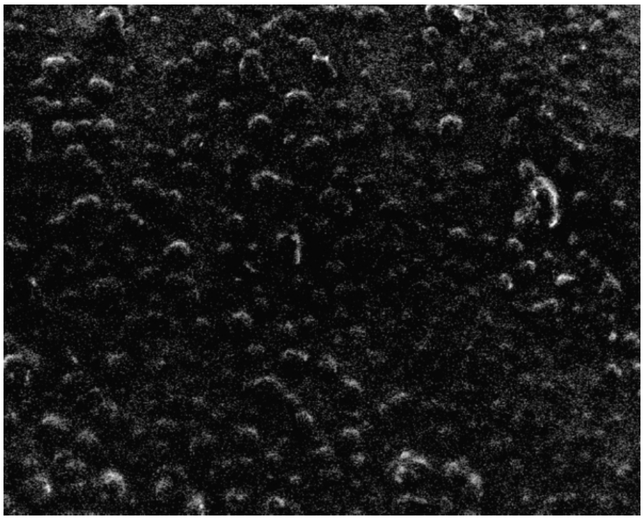


Fig. 5. SEM of a blend PNBE/PS (50/50 wt)/copo**6** (20 wt%) (× 500).

coated with a gold layer. The bulk morphologies were compared by SEM technique.

As can be seen in Fig. 3, the homopolymer blend PNBE/PS 50/50 wt ratio presents poorly dispersed domains highlighting the incompatibility of the two phases. On the contrary, the addition of any graft copolymer as a compatibilizer leads to a better dispersion of PS and PNBE domains, as shown in Figs. 4 and 5, due to an increase of the interfacial interactions. As expected, the addition of 20 wt% of PNBE-*g*-PS in the blend mixture enhances the homogeneity of the blend and any PS domain can be observed. The comparison of the compatibilization efficiency of the two graft copolymers does not present significant differences. Therefore, we can conclude that these graft copolymers are efficient compatibilizers in PNBE/PS blends, but the length of the PS grafts has not been shown to be an important parameter for compatibilization.

4. Conclusions

We studied the copolymerization of α-norbornenyl polystyrene macromonomers with norbornene using Ni-based catalysts. The use of Brookhart catalysts led to low conversion of the macromonomers while copolymerizations carried out in the presence of $Ni(St)_2$ or $Ni(acac)_2$ yield high incorporation of PS grafts in the copolymer (43 wt%). The size of the NBE-PS greatly influences its conversion and the PS content in the copolymer. The use of the graft copolymers as interfacial modifiers in PNBE/PS blends was also proved to be efficient.

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