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Synthesis of a polynorbornene containing 3,5-di-TERT-butyl-4-hydroxybenzoyl group

Mikhail A. Tlenkopatchev[1,*], **Edmundo Miranda**[1], **Miguel Angel Canseco**[1], **Ruben Gaviño**[2], **Takeshi Ogawa**[1]

[1] Instituto de Investigaciones en Materiales, and [2] Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Apdo. P. 70-360, 04510-México, D.F., México

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Summary

A new polynorbornene derivative was synthesized by ring-opening metathesis polymerization (ROMP) of 5- {[(3,5-di-t-butyl-4-hydroxy-benzoyl)oxy]methyl}-2-norbornene (BHBN) using Ru- and Os-based catalysts. The structure and properties of the poly(BHBN) were characterized by NMR, IR, DTA, DSC, and GPC. It was shown that ROMP leads to the formation of high molecular weight polynorbornene derivatives containing the stabilizing group.

INTRODUCTION

The preparation of the polyalkenamers by the ring-opening metathesis polymerization (ROMP) of the cycloolefins containing a functional groups such as anhydrides [1,2], nitrile [3,4], cyclic imides [5], esters [6-8], borenes [9], and siloxanes [10] has been reported. The polymerization of the cycloolefins bearing different heteroatroms has been performed using classical metathesis catalysts mainly consisting of WCl_6 and $MoCl_5$ and metal alkyl compounds. Recently it has been shown that well characterized molybdenum and tungsten alkylidene complexes [11,12] are much more tolerant of the functional groups of the monomer than the classical metathesis catalysts. Recent investigations have revealed that Ru and Os catalysts can tolerate also a wide range of the functional groups and can be used effectively in ROMP of the different norbornenes [5,13].

The incorporation of the functional groups into the polyalkenamers offers potential advantages from improvements in the material properties such as strength, stiffness, gas permeability, fire retardancy, air stability, etc. The present investigation is devoted to the ROMP of 5- {[(3,5-di-t-butyl-4-hydroxy-benzoyl)oxy] methyl}-2-norbornene (BHBN) in order to prepare polynorbornene derivatives which may be used as membranes for separation of gases. Norbornenes which contain such

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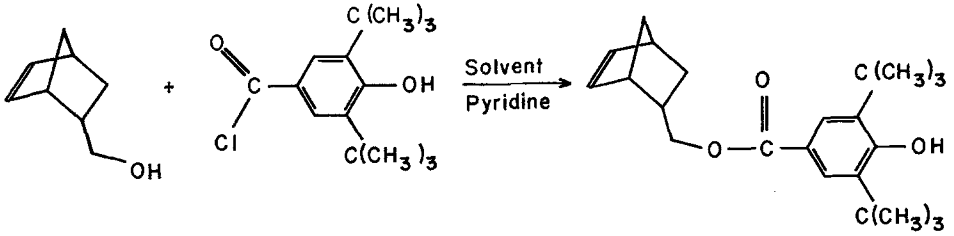
[*] Corresponding author

a stabilizing group can be used as comonomers for preparation of self-stabilized polyalkenamers.

EXPERIMENTAL

MATERIALS AND INSTRUMENTATION

3,5-Di-t-butyl-4-hydroxy-benzoic acid (THBA), 5-norbornene-2-methanol (mixture of endo and exo), and thionyl chloride were supplied by Aldrich and used without further purification. The solvents were purified by normal procedures. The polymerization solvent, chlorobenzene was distilled over calcium hydride. $RuCl_3.xH_2O$ and $OsCl_3.xH_2O$ (Aldrich) were used as received. The benzoic acid (THBA) was converted to the acid chloride according to the literature [14]. The monomer was synthesized by the condensation of 3,5-di-t-butyl-4-hydroxy-benzoic acid chloride and 5-norbornene-2-methanol (mixture of endo and exo-isomers) using the standard esterification procedure (Scheme 1).



SCHEME 1

BHBN

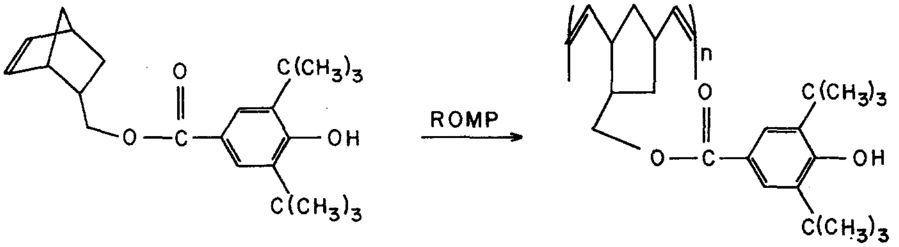
The monomer 5- {[(3,5-di-t-butyl-4-hydroxy-benzoyl)oxy] methyl}-2-norbornene (BHBN) was recrystallize three times from hexane. Yield 80-85 %. Elem. anal. Calcd: c, 77.53; H, 8.99. Found: C, 77.60; H, 9.02. MP:101; ^{1}H-NMR ($CDCl_3$) δ 1.47 [s, 18H,2 -$C(CH_3)_3$]; 1.65-1.92, 2.84-2.97 (m, 7H, the nonolefinic norbornene protons); 3.79-4.13 (m 2H, -CH_2O-); 5.68 (s, -OH); 5.98-6.20 (m, 2H, olefinic methines of exo and endo mixture); 7.92 (s, 2H, aromatic protons). ^{13}C-NMR ($CDCl_3$) δ 167.04, 158.03, 137.47, 135.64, 132.30, 126.97, 121.54, 67.79, 49.37, 42.20, 37.95, 34.04, 30.12. IR (KBr pellet, cm^{-1}) 1590 ($v_{C=C}$ vinyl), 1693 ($v_{C=O}$), 3551 (v_{OH}). The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AM-300 spectrometer, and the chemical shifts were reported in ppm with TMS as the internal standard. The IR spectra were taken using a Nicolet 510P FT-IR spectrometer (KBr). The thermogravimetric analysis (TGA) was performed with a Du Pont 2000 under a nitrogen atmosphere at a heating rate of 10 °C/min up to 600 °C. The thermal transition was measured with a Du Pont 2000 differential scanning calorimeter (DSC) under nitrogen atmosphere at a heating rate of 10 °C/min. The wide angle X-ray diffractometry WAXD was performed on a Siemens D-500 diffractometer ($CuK_{\alpha 1}$ radiation of 1.5406 Å). The molecular weights and polydispersities of prepared polymers were obtained by GPC analysis with polystyrene standards calibration.

POLYMERIZATION PROCEDURE

The metathesis polymerization of BHBN was carried out by $RuCl_3.xH_2O$ and $OsCl_3.xH_2O$ under dry nitrogen atmosphere. The active catalyst was prepared by refluxing 56 mg of commercial $RuCl_3$ and $OsCl_3$ hydrates in 5mL of 90 % ethanol for 3 h [7]. In a typical polymerization experiment, 2 g of BHBN (100 equiv) was dissolved in 7 mL of chlorobenzene under dry nitrogen. To this solution was added 1 mL of $RuCl_3.xH_2O$ ethanol solution (0.054 mol/L). The reaction was carried out at 70 °C for 24h. The polymer formed was precipitated in methanol. The polymer was filtered, and purified twice by reprecipitation from $CHCl_3$-methanol system. The reprecipitated polymer was dried in a vacuum oven at 45 °C for 24h. Elem. anal. Calcd: C, 77.53; H, 8.99. Found: C, 77.65, H, 9.03.

RESULTS AND DISCUSSION

The metathesis polymerization of the BHBN leads to the formationm of high-molecular weight the ring-opened unsaturated polymer (Scheme 2).



BHBN SCHEME 2 Poly(BHBN)

The reaction conditions are listed in Table 1. As shown in Table 1 the $RuCl_3$ and $OsCl_3$ based catalysts were effective in the polymerization of BHBN. The resulting polymer was soluble in the common organic solvents such as chloroform, chlorbenzene, toluene, THF, but insoluble in methanol and ethanol. The poly-BHBN is a white rubber-like material and can be cast from toluene and chloroform into a flexible transparent film.

The results obtained by GPC analysis are presented in Table 1. The number average molecular weight ($\bar{M}_n$) values and the polydispersity of the polymers were found to be in the range of 2,2-3.7 x 10^5 and 2.08-2.3, respectively.

The ^{1}H-NMR spectra of both the monomer (a) and the polymer (b) prepared by the $RuCl_3.xH_2O$ catalyst are shown in Figure 1. The norbornene olefin signals between 5.98 and 6.20 ppm are replaced by the new broad signal with the maximum 5.37 ppm. This signal corresponds to the linear olefin protons of the predominent trans double bond of the polymer. It is known that the Ru-containing catalysts provide predominantly the trans double bonds in the ring-opening metathesis polymerization of the norbornene derivatives [15]. The ^{1}H-NMR spectra of the poly(BHBN) suggests that under the polymerization condition of this work, when only small amounts of the alcohol were present in the system, it is possible to avoid the transesterification reaction (see Figure 1, the signal at 5.66 ppm). The ^{13}C NMR spectra also supports that the polymer main chain contains predominantly trans double bond and suggests that it can occur in both head-to-head and head-to-tail enchainments along the chain [16,17]. (Figure 2). The spectrum consists of a CO resonance at $\delta = 167.06$, of a aromatic peaks at $\delta = 158.01$, 126.95 and 121.49, a group of the olefinic peaks at $\delta = 135 - 129$ a CH_2O resonance at $\delta = 66.19$, a group of the ring-carbon peaks at $\delta = 48 - 36$, a $\underline{C}(CH_3)_3$ resonance at 34.30 and a CH_3 resonance at $\delta = 30.15$.

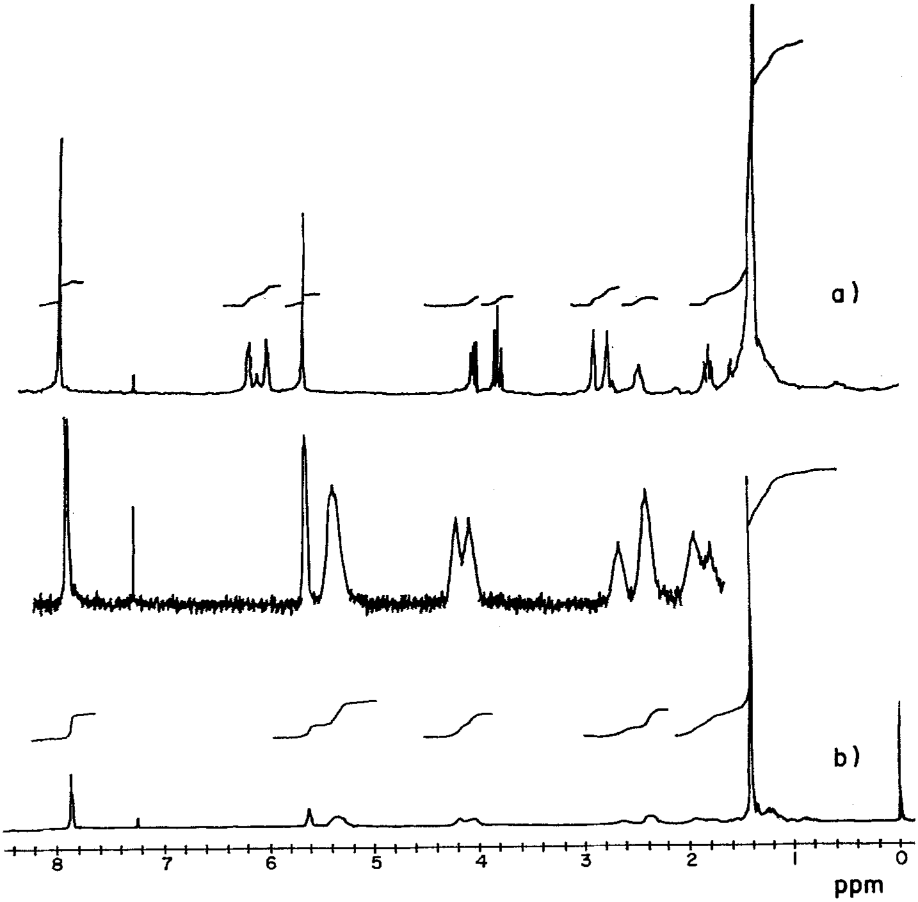


Fig. 1. ^{1}H NMR Spectra of monomer(a) and polymer(b) prepared with $RuCl_3\ xH_2O$ in $CDCl_3$.

TABLE 1

Polymerization of BHBN by Ru and Os containing catalysts[a)]

Run	Catalyst	$[M]/[C]^b$	$[M]_0^c$	Polymer Yield(%)[d]	$M_n/10^5$	M_w/M_n[f]
1	$RuCl_3 \cdot xH_2O$	50	1.0	85	3.7	2.08
2	"	100	0.5	68	2.5	2.18
3	$OsCl_3 \cdot xH_2O$	50	1.0	83	3.1	2.12
4	"	100	0.5	62	2.2	2.30
5	"	300	1.0	65	2.8	1.86

a) Polymerization was carried out in chlorobenzene for 24 h at 70 °C

b) Monomer to Catalyst mole ratio.

c) Initial monomer concentration.

d) Methanol-insoluble polymer.

f) GPC analysis with polystyrene calibration standards.

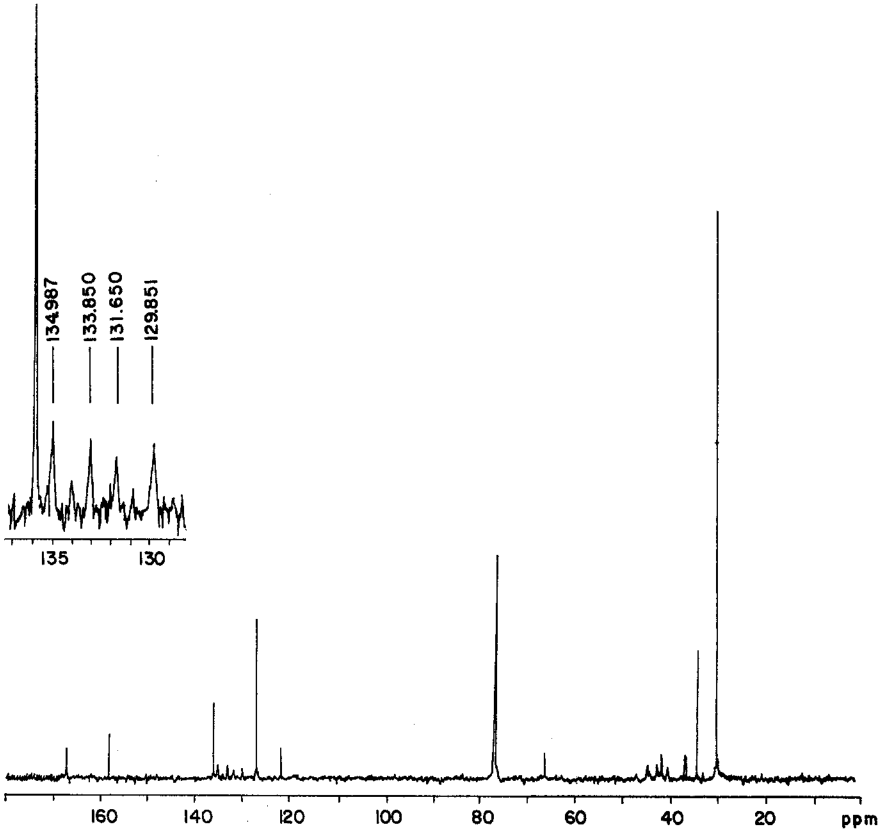


Fig. 2. ^{13}C NMR Spectrum of polymer prepared by $RuCl_3\ xH_2O$ in $CDCl_3$.

The IR spectrum of the polymer showed the characteristic band near 970 cm^{-1} which corresponds to the trans =C-H bond in the ring-opened structure [15], and the band at 3628 cm^{-1} due to the hydroxyl group of the 3,5-di-t-butyl-4-hydroxybenzoyl moiety.

The morphology of the poly(BHBN) prepared using Ru and Os containing catalysts, was investigated by X-ray diffraction. The X-ray diffractogram indicates that both polymers are predominantly amorphous (the ratio of the amorphous to crystalline fraction is approx. 86/14).

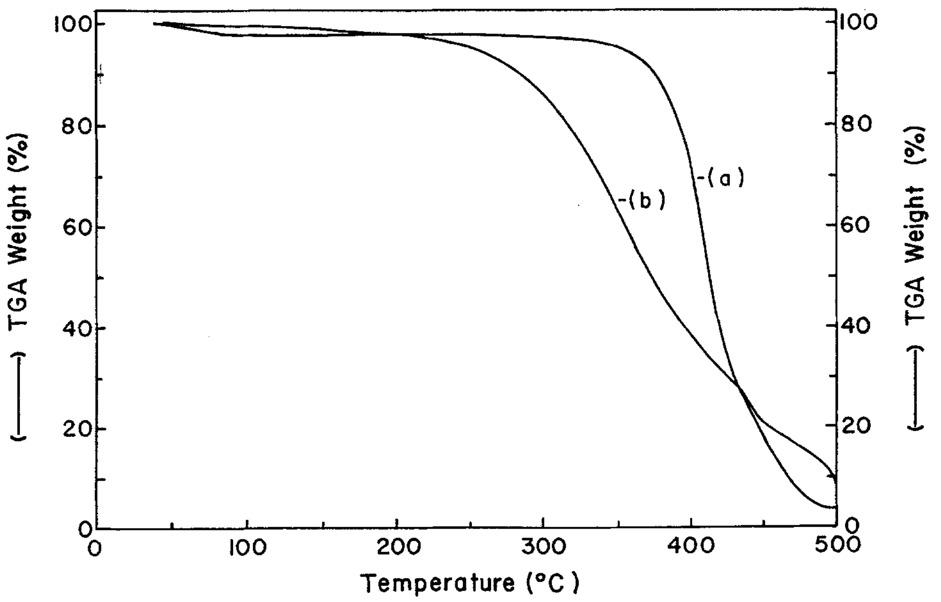


Fig. 3. TGA thermograms of polymer under N_2 atmosphere(a) and in air(b). Scanning rate = 10°C/min.

The glass transition temperature (Tg) of the poly-BHBN by DSC was found to be 103 °C TGA. showed that the poly-BHBN is stable up to 350 °C in nitrogen atmosphere (Figure 3). The polymer began to lose the weight at about 290 °C in air.

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