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Copolymerization of norbornene containing 3,5-di-*tert*-butyl-4-hydroxybenzoyl group with norbornene using metathesis catalyst

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Summary

The ring opening metathesis copolymerization of 5-{[(3,5-di-*t*-butyl-4-hydroxybenzoyl)oxy]methyl}-2-norbornene (BHBN) with norbornene was carried out using Ru and Os based catalysts. Analysis of the copolymers obtained during the initial stages of copolymerization revealed that both monomers were incorporated randomly and with the same reactivity, indicating that the steric effect of BHBN is not important. The molecular weights of copolymers were found to be in the order of 3 x 10^5 with dispersity of around 2. Characterization and some properties of these copolymers are described.

Introduction

There are several studies on the preparation of polyalkenamers by ring-opening metathesis polymerization of cycloolefins containing various functional groups(1-5). The metathesis polymerization of functionalized cycloolefins which contain reactive heteroatoms is generally performed using new catalysts based on Mo, W and Ru(6,7), which, in contrast to the classical metathesis catalysts, are not strong Lewis acids, and they can tolerate various polar groups in the monomers. Recently it has been shown that alkylidene complexes with Mo and W(8,9), and Ru and Os based catalysts(3,10) can be used effectively in the metathesis polymerization of various monomers.

The choice of monomers is important for metathesis polymerization. It is well known that the monomer reactivity in the ring-opening metathesis polymerization mainly depends on the ring size, and the presence of heteroatom and conjugated double bonds in the ring(5,11,12). The incorporation of functionalities into polymers offers a variety of new materials with properties such as selective ion and gas

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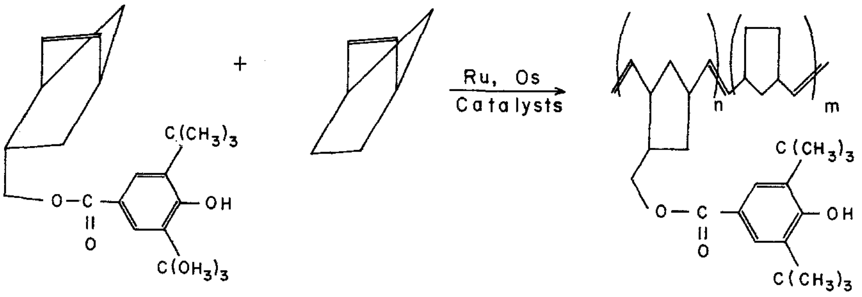
permeability, fire retardancy, air stability, etc. For example, the oxidative stability of commercial polynorbornene such as Norsorex(13), and polyoctenamer, Vestenamer(14), could be solved by their copolymerization with cycloolefins containing stabilizing groups.

The synthesis of a new norbornene derivative, 5-{[(3,5-di-*t*-butyl-4-hydroxybenzoyl)oxy]methyl}-2-norbornene, (BHBN), and its polymerization were reported previously(15). In this report, the copolymerization of norbornene(NB) with BHBN using Ru and Os based metathesis catalysts is described.(Scheme 1).



[Scheme 1]

Experimental

The comonomer BHBN was synthesized by the method described in the previous paper(15). The polymerization solvents, chlorobenzene and toluene were distilled over calcium hydride before use. Norbornene and the catalysts(Aldrich) were used as received.

The metathesis polymerization of BHBN and its copolymerization with NB were carried out using $RuCl_3$, $RuCl_3xH_2O$ or $OsCl_3xH_2O$ under dry nitrogen at 70°C for 12 hrs. The active catalysts were prepared by refluxing the hydrates in ethanol for 3 hrs.[4] The polymers were precipitated in methanol, filtered, and purified by reprecipitation from chloroform into methanol.

The ^1H and ^{13}C NMR spectra were recorded using a Bruker AM-300 spectrometer. IR spectra were taken with a Nicolet 510P FT-IR spectrometer. Thermal analysis(TGA and DSC) were performed using a Du Pont 2000 instrument under a nitrogen atmosphere. Molecular weight measurements were done using a Varian GPC apparatus.

Results and Discussion

The polymerization results are summarized in Table 1. Evidently the Ru and Os based catalysts are effective for the copolymerization of NB with BHBN. The polymers thus obtained were all soluble in common organic solvents such as chloroform, chlorobenzene, toluene, tetrahydrofuran, etc., and they are white rubber-like materials and can be cast to flexible transparent films. The number average molecular weights and the polydispersity of these polymers were found to be in the range of 2.2 - 4.5 x 10^5 and about 2, respectively.

Table 1. Copolymerization of BHBN with NB by Ru and Os catalysts.

Run	Catalyst	Monomer Feed Ratio BHBN/NB	Polymer Yield(%)^b	Mn/10^5	Mw/Mn^c
1 .	$RuCl_3\ xH_2O$	1.0:0.0	72	2.5	2.18
2 .	$RuCl_3$	1.0:0.0	65	1.2	2.02
3 .	$RuCl_3\ xH_2O$	0.75:0.25	85	2.8	2.08
4 .	$RuCl_3\ xH_2O$	0.5:0.5	87	3.1	2.12
5 .	$RuCl_3\ xH_2O$	0.2:0.8	91	3.4	2.02
6 .	$OsCl_3\ xH_2O$	0.2:0.8	94	3.5	1.98
7 .	$OsCl_3\ xH_2O$	0.08:0.92	89	3.8	2.14
8^d.	$OsCl_3\ xH_2O$	0.0:1.0	94	4.5	2.08

a): Polymerization at 70°C for 12 hrs in chlorobenzene, [M]/[C] = 100 mol/mol. [M] = 0.5 mol/l.

b): Methanol-insoluble fraction

c): GPC with polystyrene standard.

d): At 65°C for 4 hrs in toluene.

Fig. 1 shows the ^1H NMR spectrum of the copolymer obtained with equimolar comonomers using $RuCl_3xH_2O$. The polymerization was stopped after 60 minutes, and the yield was 15%. The broad signal at 5.32 ppm corresponds to the protons on the predominantly trans double bond. It is well known that Ru-containing catalysts form mainly trans double bonds in the ring opening metathesis polymerization of norbornene derivatives(16,17). The peaks in the spectrum at 7.89, 5.62, 4.10-4.19, and 1.4 ppm correspond to the aromatic, OH, CH_2 and $C(CH_3)_3$ protons of BHBN(15), respectively. The integration of the aromatic and olefinic peaks revealed that equimolar amounts of both monomers are incorporated in the copolymer. The ^{13}C NMR spectrum of this copolymer also indicated that the main chain contains predominantly trans double bonds, and IR spectra also showed the absorption due to the trans =C-H bond.

It is important to note that the incorporation of small amounts of BHBN into polyNB is quite facile. Fig. 2 shows the ^1H NMR specrum of a copolymer with only 8 mole% of BHBN in the initial feed using the $OsCl_3xH_2O$ catalyst. The peak characteristic of the olefinic protons is quite different from that of the polymer obtained with the Ru catalyst(Fig.1). Two sets of peaks are observed at

5.19-5.21 and 5.33-5.34 ppm, corresponding to the cis and trans protons, respectively[18]. ^{13}C and IR spectra also indicated that the polymer consists of a mixture of trans and cis structures.

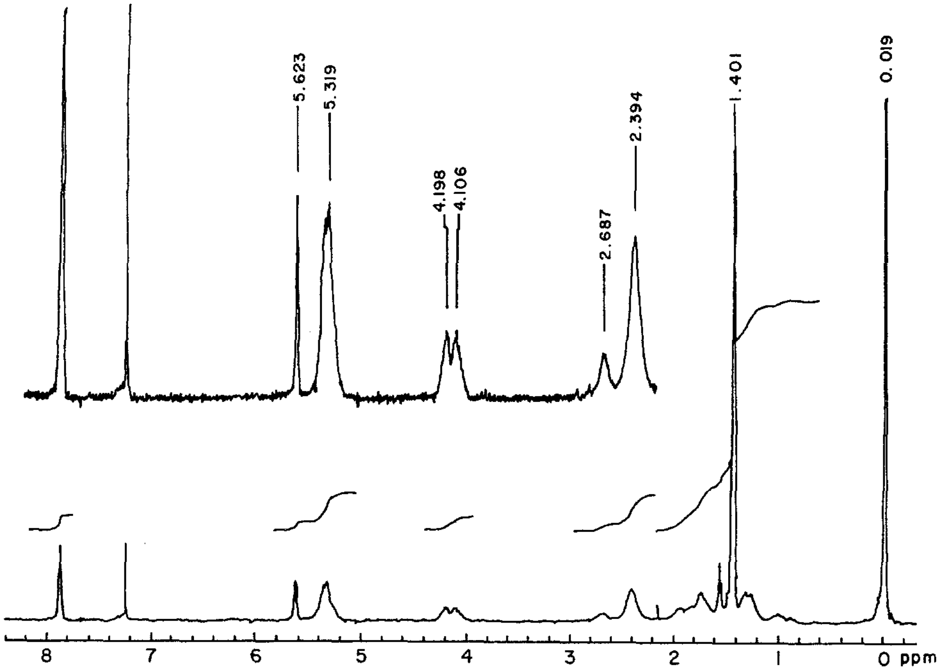


Fig. 1. ^1H NMR spectrum of Poly(NB-BHBN) 50/50(mol/mol), obtained with $RuCl_3$ xH_2O (in $CDCl_3$).

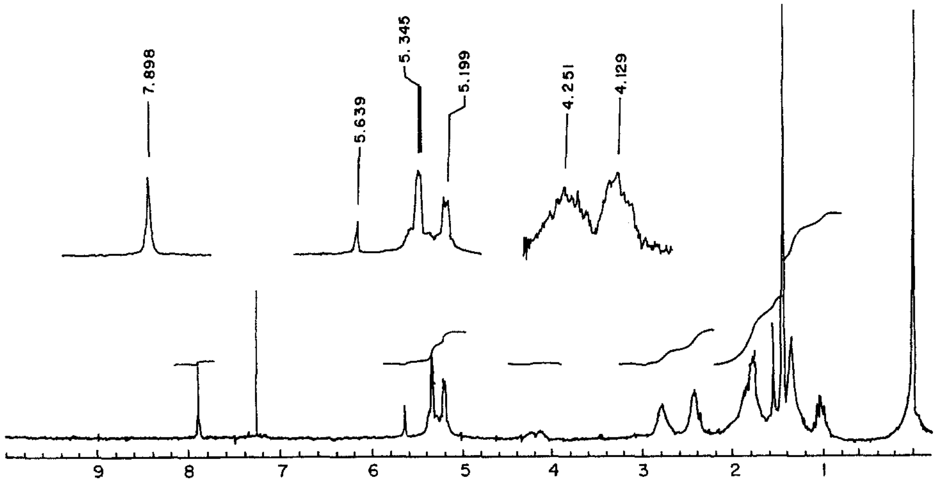


Fig. 2. ^1H NMR spectrum of poly(NB-co-BHBN) 92/8(mol/mol), obtained with $OsCl_3$ xH_2O. (in $CDCl_3$).

The copolymers exhibited only one Tg, which suggests random copolymers indipendent of the initial monomer ratios. The Tg values lie between those of poly(BHBN), 103°C(15), and poly(NB), 31°C(19), and decrease with increasing NB concentrations. The Tg of the equimolar copolymer was 76°C, and its tensile strength at break was found 29MPa.

Results of thermogravimetric analysis are shown in Fig. 3. The thermal stability increased with increase in the BHBN content. The equimilar copolymer started to lose weight at 300°C.

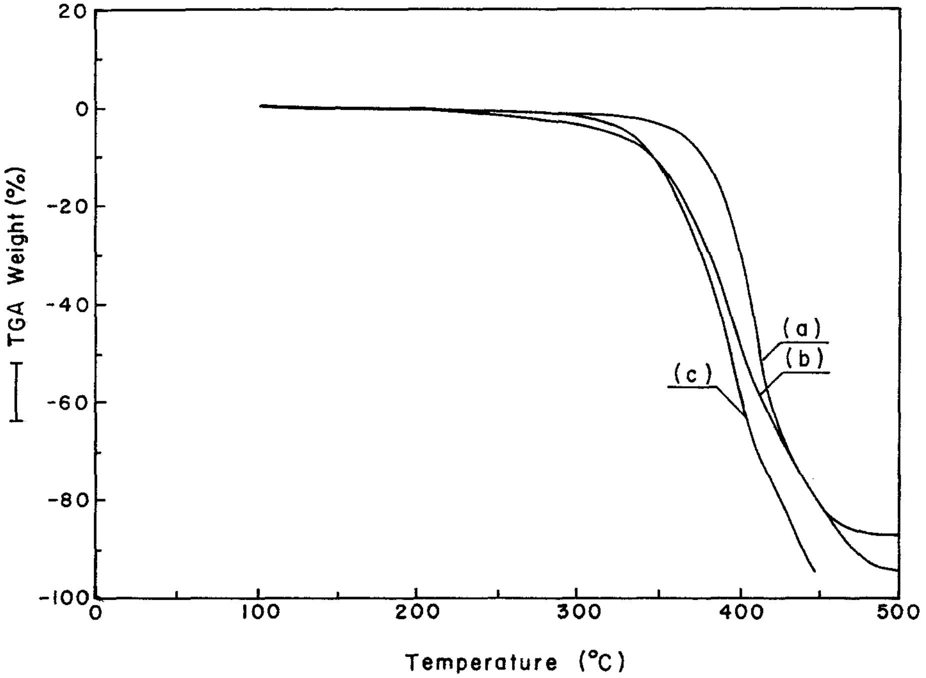


Fig. 3. TGA thermograms of poly(BHBN):(a), poly(NB-co-BHBN)50/50:(b), and poly(NB-co-BHBN) 70/30:(c). Under N_2 with heating rate of 10°C/min.

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