identities of these two compounds were proved by comparing the ^{13}C NMR spectra with those of the authentic compounds and by the coinjection of each of the authentic pure compounds **12** and **13**. Pure **12** from this reaction mixture was obtained by flash chromatography, using silica gel (230-400 mesh) as adsorbant and pentane/ether (2:1) as eluent, and two subsequent Kugelrohr distillations at 100 °C and 0.2 torr; the yield of **12** was 80%.

Reaction of the 1-TCNE Cycloadduct with Water in Dimethyl Sulfoxide. A solution of 1 mL (56 mmol) of water in Me_2SO (5 mL) was added to 300 mg (1.1 mmol) of the cycloadduct of **1** with TCNE (a 6.5:1 mixture of the exo and endo adduct) at 0 °C and under nitrogen. The mixture was stirred at room temperature for 40 h; no formation of any allylic alcohol (*m/e* 150) was detected by GC-MS. (Since the cycloadduct itself undergoes decomposition under GC conditions, the only detectable component of this mixture is isodicyclopentadiene.) To this mixture was added 30 mL of ether and 5 mL of H_2O. The aqueous layer was further twice extracted by 10 mL of ether. The combined ether layers were passed through a short SiO_2 column to remove the dark color. Upon evaporation of ether, there was obtained 90 mg (30% recovery) of a solid which was proved identical with the starting material by ^1H and ^{13}C NMR.

Acknowledgment. We thank the Robert A. Welch Foundation and the National Science Foundation for support of this research.

Registry No. **1**, 6675-72-5; **2**, 75725-33-6; **3**, 89689-33-8; **4**, 89772-13-4; **5**, 89689-34-9; **6**, 6343-21-1; **7**, 89689-35-0; **8**, 87556-20-5; **9**, 89771-45-9; **9-D**, 89689-36-1; **10**, 89689-37-2; **11**, 89689-38-3; **12**, 89689-39-4; **12-D5**, 89689-40-7; **12-D6**, 89689-41-8; **12-D5,D6**, 89689-42-9; **13**, 58616-86-7; TCNE, 670-54-2; PTAD, 4233-33-4; cyclopentadiene, 542-92-7.

Ring-Opening Polymerization of Norbornene Substituted with Amine and Ammonium Groups

C. Larroche, J. P. Laval, and A. Lattes*

Université Paul Sabatier, 31077 Toulouse Cédex, France

J. M. Basset*

Institut de Catalyse, 69626 Villeurbanne Cédex, France

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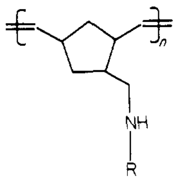
Norbornene substituted with amine groups gives rise to ring-opening polymerization, with $W(CO)_5(CPh_2)$ or $W(CO)_3$(mes) (mes = mesitylene) associated with $C_2H_5AlCl_2$ and molecular oxygen. With a 1:1 mixture of the exo and endo isomers, turnover of ca. 350 mol of monomer/mol of W are observed. The polymer obtained, which is almost insoluble in most organic solvents, is soluble in polar media (water, alcohols) after quaternization of the amine group. They can also be more soluble if a molecular weight regulator such as 1-pentene is used. The cis/trans ratio of double bonds in the polymer is close to unity, indicating a statistical coordination of the monomer to the metallocarbene fragment. It is also possible to obtain a copolymer between the functionalized norbornene and norbornene or cyclopentene. With norbornene it is possible to incorporate up to 90% of functionalized norbornene in the copolymer. With cyclopentene a 1:1 copolymer is obtained. No higher incorporation of cyclopentene can be achieved probably for steric reasons.

Introduction

One of the main reasons for the limitation of the development of the olefin metathesis reaction in organic and in polymer synthesis is the high reactivity of most catalytic systems with functional groups bearing heteroatoms.[1-4] In some particular cases it was possible to carry out metathesis of functionalized olefins by using an excess of Lewis acid cocatalyst which could complex to the heteroatoms and thus allow the catalytic reaction to proceed.[5] For example metathesis of acyclic olefinic amines is possible with the catalyst $W(CO)_3$(arene) associated with a large excess of organoaluminum compounds and molecular oxygen. The resulting compound is a telechelic compound with two amine groups at both ends.[5]

$$NR_2(CH_2)_nCH{=}CH(CH_2)_nNR_2$$

We wish to report here that metathesis of norbornene substituted with amine groups leads to the expected functionalized polymer shown. If the amine group is quaternized by HCl, the resulting polymer is obtained with specific solubilities in polar media (e.g., water) and potential ion exchange properties.



R = H, CH_3, $CH(CH_3)_2$

Results and Discussion

A. Metathesis of 2-(Aminomethyl)bicyclo[2.2.1]hept-5-ene (1:1 of Mixture Endo-Exo). Two catalytic systems were found to be active in metathesis of norbornene substituted with amine groups. They include zero valent complexes of tungsten (a) $W(CO)_3$(mes), (b) $W(CO)_5(CPh_2)$, associated with a large excess of organoaluminum compound, and molecular oxygen (Table I). In the absence of organoaluminum compound, the reaction does not proceed (with $W(CO)_5(CPh_2)$ the substitution of the carbene ligand by the amine ligand produces the new

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[1] Boelhouwer, C.; Verkuijlen, E. *Prepr. Div. Pet. Chem., Am. Chem. Soc.* **1979**, *24*, 392.

[2] Streck, R. *J. Mol. Catal.* **1982**, *15*, 3.

[3] Mol, J. C. *J. Mol. Catal.* **1982**, *15*, 35.

[4] Castner, K. F.; Calderon, N. *J. Mol. Catal.* **1982**, *15*, 47.

[5] Edwige, C.; Lattes, A.; Laval, J. L.; Mutin, R.; Basset, J. M.; Nouguier, R. *J. Mol. Catal.* **1980**, *8*, 297.

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Table I. Effect of the Nitrogen Substituent and of the Catalyst on the Yield of Metathesis of Olefinic Amines of the General Formula with a 1:1 Mixture of Endo-Exo[a]

olefinic amine R =	catalyst		olefin/W	olefin/Al	yield, %
	$W(CO)_3(mesitylene) + C_2H_5AlCl_2 + O_2$	a	30	1/1	1
CH_2NH_2, I	$W(CO)_3(mesitylene) + C_2H_5AlCl_2 + O_2$		30	3/4	100
	$W(CO)_5(CPh_2) + C_2H_5AlCl_2 + O_2$	b	30	3/4	100
$CH_2NH(CH_3)$, II	$W(CO)_3(mesitylene) + C_2H_5AlCl_2 + O_2$		30	3/4	82
$CH_2NH(CH(CH_3)_2)$, III	$W(CO)_3(mesitylene) + C_2H_5AlCl_2 + O_2$		30	3/4	95

[a] Solvent = PhCl; temp = 25 °C; [olefin] = 0.18 mol L^{-1}.

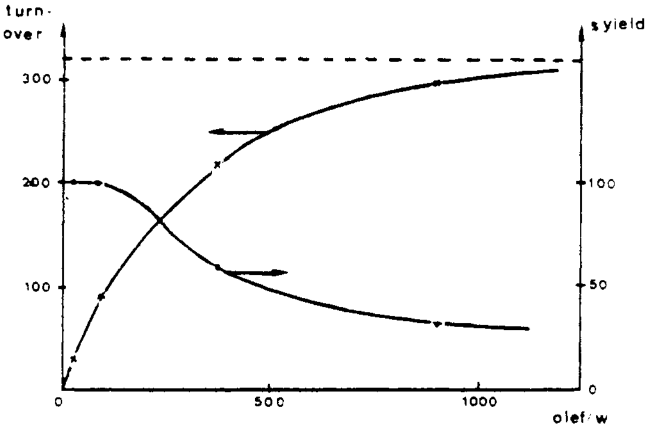

Figure 1. Effect of the olefin/W ratio on the yield (right ordinate) and overall turnover number (left ordinate) of metathesis of I with the catalyst a Al/olefin = 4/3, solvent PhCl, temp = 25 °C, [olefin] = 0.18 mol L^{-1}.

complex $W(CO)_5(HN\text{-}i\text{-}Pr\text{-}CH_2\text{-}NBE)$), and a molar ratio of olefin:Al is necessary for catalytic activity. Most catalytic systems which are active in norbornene (NBE) metathesis were found to be inactive when the norbornene was substituted with amine groups. For example with $RuCl_3$ in *n*-butanol, which is the commercial catalyst for norbornene metathesis,[6] there is a competing side reaction which causes cleavage of the N–alkyl bond and formation of the corresponding olefin or alkane.[7]

The effect of the olefin/W ratio is represented on Figure 1. These results clearly indicate that the reaction is catalytic with an overall turnover number as high as 324 for an olefin/W ratio of 900.

The nature of the nitrogen substituents (R = H, CH_3, $CH(CH_3)_2$) does not seem to modify appreciably the ability of the substituted norbornene to undergo ring-opening polymerization (Table I). This result is in contrast to that obtained with acyclic olefins for which primary amines were found to inhibit metathesis.[5]

The exo or endo position of the substituent in the norbornene cycle does not appear, in first approximation, to modify the overall yield of polymerization since a conversion of 100% was found in both cases. However it was possible to observe a difference of reactivity between the two isomers using an α-olefin as molecular weight regulator (α-olefins are commonly used as molecular weight regulators in cycloolefin polymerization[8]).

Table II. Influence of 1-Pentene in the Ring-Opening Polymerization of Unsubstituted and Substituted ($R = \text{-}CH_2\text{-}NH_2$) Norbornene

monomer	1-pentene/ norbornene molar ratio	yield, %	% cis double bond
unsubstituted norbornene[a]	10/100	3	50 ± 0.05
	5/100	4	53 ± 0.05
	1/100	2	50 ± 0.05
	0/100	37	49 ± 0.05
substituted norbornene[b]	20/100	18	46.6 ± 0.05
	10/100	27	49 ± 0.05
	5/100	87	48 ± 0.05
	0/100	100	50 ± 0.05

[a] Catalyst a; Al/olefin = 100, Al/W = 2[olefin] = 0.2 mol L^{-1}; solvent PhCl; temperature 25 °C. [b] Catalyst a; Al/olefin = 4/3; Al/W = 40[olefin] = 0.18 mol L^{-1}; solvent PhCl; temperature 25 °C.

Table III. Metathesis of Endo and Exo Isomers of I[a]

isomer	yield, %	% of reacted 1-pentene	C_2H_4, %
endo + exo	87	35	11
exo	100	39	16
endo	73	38	6

[a] Catalyst a; Al/olefin = 4/3; Al/O_2 = 1; solvent = PhCl; temp = 25 °C; [amine] = 0.18 mol L^{-1}.

The effect of 1-pentene on polymer yield (and stereochemistry) has been studied in the case of the metathesis of unsubstituted and substituted norbornene (I) (Table II).

In both cases the yield of the polymerization drops significantly due to the presence of the molecular weight regulator. (For an α-olefin such as 1-pentene the competitive self-metathesis of 1-pentene becomes important.) With functionalized norbornene, the α-olefin decreases the molecular weight to such an extent that the polymer is more easily solubilized. Besides meaningful differences of reactivities between the endo and exo isomers of I could be detected. In the presence of 1-pentene, and in similar reaction conditions, the exo isomer gives 100% yield whereas the endo isomer gives only 73% yield.

If one considers in more details the results of Table III, it appears that with both isomers the amount of consumed 1-pentene is about the same but the 1-pentene is a better chain regulator for the endo than for the exo isomer (see, for example, the relative amounts of C_2H_4 formed).

The polymers obtained by metathesis of I, II, and III are only slightly soluble in most organic solvents. With III, the following solubilities (g/100 mL) were observed: $CHCl_3$, 1.83; CCl_4, 1.14; CH_3OH, 0.9; DMF, 0.79; THF, 0.12; C_6H_5Cl, traces; C_6H_6, CH_3COCH_3, and H_2O, insoluble). The solubility is almost zero with I and increases with the bulkiness of the substituents on the nitrogen. In order to achieve an appreciable degree of solubility, we used

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(6) (a) CDF Chimie. Fr. Pat. 1543497, 1968. (b) Tanielian, C.; Kiennemann, A.; Ospaplich, T. *Can. J. Chem.* **1979**, *57*, 2022. (c) Tanielian, C.; Kiennemann, A.; Osparlich, T. *Ibid.* **1980**, *58*, 2813.

(7) (a) Aresta, M.; Greco, R.; Petruzelli, D. *Synth. React. Inorg. Met. Org. Chem.* **1979**, *9*, 157. (b) Kurosawa, H. *J. Organomet. Chem.* **1976**, *112*, 369. (c) Laine, R. M.; Thomas, D. W.; Carey, L. W.; Buttrill, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 6527. (d) Shvo, Y.; Laine, R. M. *J. Chem. Soc., Chem. Commun.* **1980**, 753.

(8) Ofstead, E. A.; Lawrence, J. P.; Semyek, M. L.; Calderon, N. *J. Mol. Catal.* **1980**, *8*, 227.

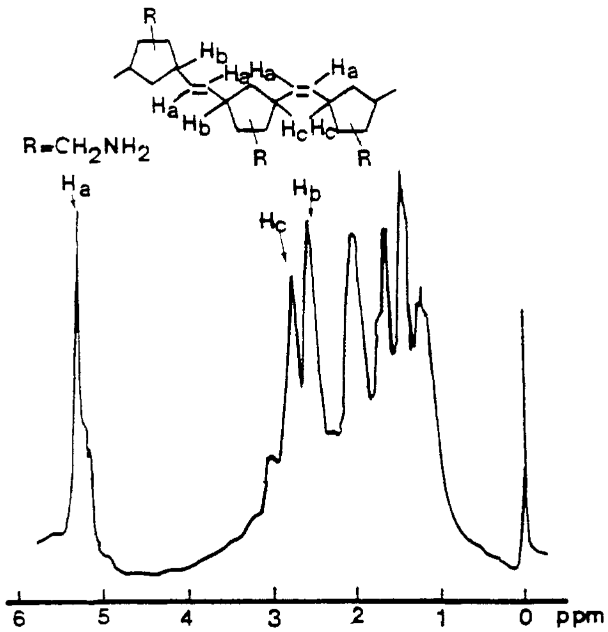


Figure 2. ^{1}H NMR spectrum of the polymer obtained from I + 10% of 1-pentene (250 MHz, $CDCl_3$, Me_4Si).

1-pentene as a molecular weight regulator. With 5% of 1-pentene the polymer obtained from I was slightly soluble in chloroform.

Using 1-pentene as a molecular weight regulator it was also possible to determine the cis–trans ratio of double bonds in the polymer by using ^{13}C and ^{1}H NMR spectra in $CDCl_3$ (Figure 2). In preliminary experiments it was found that the ^{13}C spectra of soluble and insoluble fractions of polymers were identical. Therefore, the use of the soluble fraction to determine the stereochemistry of the polymer by ^{1}H NMR was assumed to be an acceptable and reliable procedure.[9]

The ^{13}C NMR spectrum of the polymer corresponding to I, II, or III gave a complex multiplet centered around 133–134 ppm (Me_4Si) which corresponds to the olefinic carbons. The complexity of the spectrum is due to the great number of possible combinations (128 different carbons are theoretically expected if we consider isomerism, cis–trans double bond, and HH, HT, TH and TT combinations). This type of spectrum cannot give reliable stereochemical information.

The ^{1}H NMR spectrum of the polymer gives an unresolved peak at 5.25 ppm corresponding to the olefinic protons from which it is not possible to make a distinction between the cis and trans isomers. However the ^{1}H resonance corresponding to the proton in the α position to the cis and trans double bonds are easily identified by two peaks situated respectively at 2.75 and 2.5 ppm (down field from Me_4Si).

The absorption of the $H_{b(trans)}$ and $H_{c(cis)}$ protons in α position to the double bond were assigned by comparison with the ^{1}H NMR spectrum of unsubstituted polynorbornene **9b**, assuming that the amino group substituent exhibits only a strong electronic effect of vinylic protons absorptions. All the polymers obtained from I, II, or III were found to exhibit a trans/cis ratio of unity which correspond to a statistical coordination of the monomer to the metallocarbene propagation center.[9b]

Table IV. Cross-Metathesis of I with Norbornene[a]

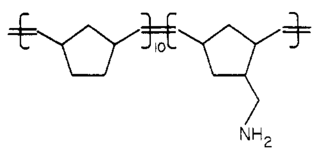
catalyst	olefin/W	olefin/Al	yield, %	incorporation,[b] %
a	100	100/16	99	88
b	100	100/16	100	100

[a] Solvent = PhCl; temp = 25 °C; [norbornene] = 0.18 mol L^{-1}; [I] = 0.018 mol L^{-1}. [b] From elemental analysis (C/N ratio).

B. Cross-Metathesis of I with Bicyclo[2.2.1]hept-5-ene. Since the amine function of the substituted norbornene acts as a poison of the Lewis acid cocatalyst, it was logical to try to make a functionalized polymer containing a smaller amount of functional groups. We have therefore studied the cross-metathesis between I and norbornene by using a large excess of norbornene. The results obtained with the catalysts a or b indicate that the olefinic cyclic amine is almost totally incorporated in the polynorbornene (Table IV). Unfortunately the polymer is then completely insoluble in most organic solvents.

Interestingly the resulting copolymer is able to swell in organic solvents and also to absorb ca. 25 mL of solvent/g, a value even greater than that observed with polynorbornene (5 mL/g of polymer).[10]

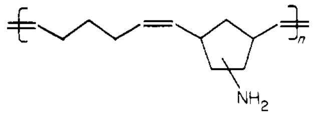
One may reasonably assume the following statistical structure for the copolymer which remains to be fully characterized.



The ^{1}H NMR spectrum of the polymer gives 50% of the cis double bond as with polynorbornene or with the polyaminonorbornene.

C. Cross-Metathesis of I with Cyclopentene. Calderon[4] has observed that cross-metathesis between cyclopentene and 5-norbornene-2,3-dicarboxylic anhydride gives an alternate copolymer when the ratio of cyclopentene/substituted norbornene is lower than (or equal to) unity. We have carried out similar experiments with I (equimolecular mixture of the exo and endo isomers) and cyclopentene (Table V).

First, it is interesting to notice that with our experimental conditions of concentration, cyclopentene alone does not polymerize due to the thermodynamic equilibrium polymer ⇌ monomer which is shifted to the monomer side for low monomer concentration.[11] If cyclopentene and I are mixed in a 1/1 ratio, the copolymerization occurs with 100% of incorporation of cyclopentene in the polymeric chain. If cyclopentene and I are mixed with 10/1 ratio, only 10% of cyclopentene is incorporated which corresponds to an incorporation of one cyclopentene monomer for each functionalized norbornene. The results, quite in agreement with those of Calderon,[4] indicate that the polymer must be perfectly alternate.



It seems impossible to obtain a double incorporation of two cyclopentene units due to the favored depolymeriza-

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[9] For the stereochemistry of norbornene metathesis see, for example: (a) Thoi, H. H.; Ivin, K. J.; Rooney, J. J. *J. Mol. Catal.* **1982**, *15*, 245. (b) Larroche, C.; Laval, J. P.; Lattes, A.; Quignard, F.; Leconte, M.; Basset, J. M. *J. Org. Chem.* **1982**, *47*, 2019.

[10] Ohm, R. F. *CHEMTECH* **1980**, 183.

[11] Ofstead, E. A.; Calderon, N. *Makromol. Chem.* **1972**, *154*, 121.

Table V. Cross-Metathesis of I with Cyclopentene[a]

cyclopentene/I	W/Cp + I/Al/O_2	% of incorporation[b] of cyclopentene	polymer yield, %	
			overall	with respect to I
1/1	1/46/32/O_2	100	100	100
10/1	1/80/14/14	10	9.1	100
100/0	1/100/4/4		0	

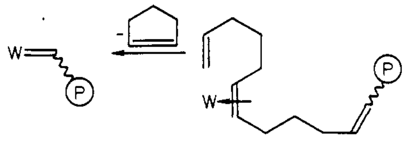
[a] Catalyst a, solvent = PhCl; temp = °C; [olefins] = 0.4 mol L^{-1}. [b] From elemental analysis (C/N ratio).

Table VI. Polymerization at the Hydrochloride of I, II, and III[a]

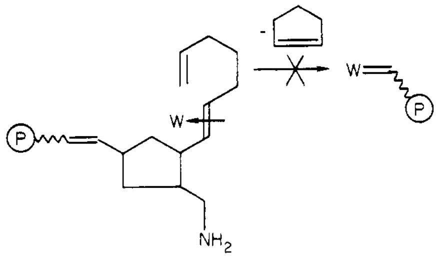
protonated olefinic amine, R =	catalyst	olefin/W	olefin/Al	yield, %
$N^+H_2(CH(CH_3)_2)Cl^-$, III′	a	30	3/4	60 (100)[b]
$N^+H_2(CH_3)Cl^-$, II′	a	30	3/4	100 (82)[b]
		100	1/0.08	100
		30	1/0.066	100
		30	1/0.33	37
		100	1/0.1	0
$N^+H_3Cl^-$, I′	a	30	3/4	55 (100)[b]
	b	30	3/4	55 (-)[b]

[a] Solvent = PhCl; temp = 25 °C; [olefin] = 0.18 mol L^{-1}. [b] The values in parentheses are those obtained with I.

tion. But if only one incorporation of cyclopentene occurs, then the depolymerization will not be favored probably for steric reasons: the first double bond in the polymer chain will be too crowded to allow its retrocoordination to the metallocarbene.



favored depolymerization



unfavored depolymerization

D. Metathesis of the Hydrochloride of I. Protonation or quaternization of the amine groups has usually a positive effect on the overall yields and rates of metathesis of acyclic olefinic amines.[12] The protonation of I by HCl gave the corresponding cyclic hydrochloride. The same catalysts which were found to be active with I were also found to be active with the hydrochloride derivative (Table VI).

The results of Table VI indicate that the protonation of the amine does not improve significantly the overall yield of metathesis with respect to that observed with the free amine. It is however possible to decrease slightly the Al/olefin ratio to a value of ca. 0.5–0.6. But below this value the yield of metathesis is dramatically decreased. This result suggests that the Lewis acid cocatalyst is also complexed with the chloride ion of the ammonium salt.

The resulting polymers are soluble in water (64 g/100 mL for III′) and methanol (5.24 g/100 mL for III′). It is possible to regenerate the non protonated polymer by treatment of the protonated polymer with KOH (2 N).

E. Cross-Metathesis of the Hydrochloride of I with Norbornene. The results are quite comparable to those obtained by cross-metathesis of I with norbornene. The quaternization does not change drastically the overall copolymerization process and it is possible to incorporate 65% of norbornene to I.

Conclusion

Norbornene substituted with amine groups may with some catalyst give rise to ring-opening polymerization with formation of the corresponding functionalized polymer. Due to the high reactivity of this strained cyclic olefin it is possible to reach a turnover number of ca. 350 mol of monomer/mol of W which is a much higher value than that observed with acyclic olefins.[12] However an excess of Lewis acid is still necessary to observe catalytic activity. The polymers obtained are almost insoluble in most organic solvents probably due to their extremely high molecular weight. However they can become soluble in polar media (e.g., water) by quaternization of the amine group. They can also be more soluble if a molecular weight regulator such as 1-pentene is used. The cis/trans ratio of double bonds in the polymer, close to unity, indicates a statistical coordination of the monomer to the metallocarbene fragment as it has already been observed with the nonfunctionalized norbornene.[9]

It is also possible to obtain a copolymer between the functionalized norbornene and norbornene or cyclopentene. With norbornene it is possible to incorporate up to 90% of norbornene in the copolymer. With cyclopentene, probably for steric and thermodynamic reasons, it is not possible to incorporate more than 50% of cyclopentene. The reason for the obtention of a 1:1 copolymer, already observed by Calderon with other similar systems,[4] is probably due to thermodynamic and steric reasons.

Experimental Section

Catalytic reactions were carried out under argon by using standard anaerobic techniques. The apparatus used for metathesis experiments included a glass batch reaction with valves allowing argon purges, evacuation, and introduction of the various reagents under controlled atmosphere. Various gas syringes as well as burettes allowed given amounts of O_2, alkylaluminum, or solvent to be introduced into the reactor.

Materials. Catalysts. $W(CO)_3$(mesitylene) was purchased from Strem Chemicals Inc. $W(CO)_5(C(C_6H_5)_2)$ was prepared

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[12] Laval, J. P.; Lattes, A.; Mutin, R.; Basset, J. M. *J. Chem. Soc., Chem. Commun.* **1977**, 502.

Table VII. Experimental Conditions Used in Metathesis of Substituted Norbornene[a]

monomer	catalyst[b]	cat./olefin/Cocat/O_2[c]	time, h	yield, %	temp, °C	incorporation, %
I (R = CH_2NH_2)	a	1/30/40/40	17	100	25	
	a	1/90/120/120	15	100	25	
	a	1/375/500/500	16	59	25	
	a	1/900/1200/1200	16	100	25	
	a	1/30/40/0	15	82	25	
	a	1/30/40/40	10	5.5	−60	
	b	1/30/40/40	15	100	25	
II (R = CH_2NHCH_3)	a	1/30/40/40	20	81	25	
III (R = CH_2NH-*i*-Pr)	a	1/30/40/40	16	95	25	
IV (R = $CH_2{}^+NH_3Cl^-$)	a	1/30/40/40	15	55	25	
	b	1/30/40/40	18	55	25	
V (R = $CH_2{}^+NH_3CH_3Cl^-$)	a	1/100/80/80	16	100	25	
	a	1/100/10/10	18	0	25	
VI (R = $CH_2{}^+NH_2$-*i*-$PrCl^-$)	a	1/30/40/40	20	60	25	
I + 5% 1-pentene	a	1/30/40/40	15	87	25	
+ 10% 1-pentene	a	1/30/40/40	15	27	25	
+ 20% 1-pentene	a	1/30/40/40	15	18	25	
I + NBE (1/10)	a	1/100/16/18	17	98	25	81[d]
	b	1/100/16/18	17	100	25	100[d]
IV + NBE (1/10)	a	1/100/16/18	16	97	25	65[d]
I + cyclopentene (1/1)	a	1/46/32/32	18	100	25	100[e]
(1/10)	a	1/80/14/14	18	18	25	10[e]

[a] NBE = norbornene. [b] Catalyst a = $W(CO)_3$mesitylene/$EtAlCl_2/O_2$. Catalyst b = $W(CO)_5CPh_2/EtAlCl_2/O_2$. [c] [Olefin] = 0.18 mol L^{-1}; solvent PhCl (50 mL). [d] % incorporation of amine in polynorbornene. [e] % incorporation of cyclopentene in polyamine. These values are obtained from the elemental analysis of each copolymer.

according to the procedure described by Casey and Burkhardt.[13]

Cocatalyst. $EtAlCl_2$ was supplied by the Ethyl Corporation. It was purified by distillation, diluted in anhydrous chlorobenzene, and stored under argon.

Solvent. Chlorobenzene was a commercial Merck product; it was distilled from P_2O_5 under argon and stored under argon.

Gases. All the gases used (argon and oxygen) were dried over 5-Å molecular sieves.

Olefins. Norbornene was obtained from Aldrich and purified by sublimation. Cyclopentene was also obtained from Aldrich and stored over 5-Å molecular sieves.

Amines. 2-(Aminomethyl)bicyclo[2.2.1]hept-5-ene (I) was obtained by reduction with $LiAlH_4$ of 2-cyanobicyclo[2.2.1]-hept-5-ene (IV) which was a Aldrich product. The endo and exo isomers of I were obtained in the same way from separated endo and exo isomers of IV by preparative GLC. This was performed on a THN 102 (ELF-SRTI) apparatus, with a 10% PLV 10 on chromosorb PNAW column (2 m in length and 40 mm in diameter). The two isomers of IV were obtained with up to 99% purity. The reduction of IV is followed by a little isomerization.[14] So the endo isomer of I contains ca. 28% of exo isomer, and the exo isomer contains ca. 10% of endo isomer.

2-((*N*-Methylamino)methyl)bicyclo[2.2.1]hept-5-ene (II) was obtained by the reduction with $LiAlH_4$ of the corresponding amide.

2-((*N*-Isopropylamino)methyl)bicyclo[2.2.1]hept-5-ene (III). The imine resulting from the reaction of the isopropylamine and the 2-formylbicyclo[2.2.1]hept-5-ene (Aldrich) was reduced over $NaBH_4$, giving III.

The hydrochlorides I′, II′, and III′ were obtained from the corresponding amines I, II, and III by reaction with gaseous HCl.

Procedure for Running the Catalytic Reaction. In a typical experiment, 0.9 × 10^{-2} mol of I were dissolved in 42 mL of chlorobenzene containing 3 × 10^{-4} mol of $W(CO)_3$(mes) (a) (116 × 10^{-3} g). Then 0.012 mol of oxygen (288 mL) were introduced in the reactor through a gas syringe and the reaction was started by the addition of 0.012 mol of $EtAlCl_2$ (8.3 mol of a 15% solution in chlorobenzene).

The reaction was quenched by the addition of 5 mL of methanol after 15 h.

Polymer Recovery. Amines and Copolymers (General Case). In the typical experiment described above, the chlorobenzene is removed from the unpurified polymer which is then washed with 250 mL of methanol (under these conditions, the polymer may be partially dissolved). It is then treated with KOH and removed by filtration (or centrifugation) of the methanolic KOH saturated solution. One liter of water is then poured into the filtrate (or the supernatant) in order to complete the recovery of the polymer. Finally, the polymer is washed with water and dried (50 °C in vacuo) during 18 h.

Case of Hydrochlorides. When the above method is used, the nonquaternized polymer is obtained. For the recovery of the quaternized polymer, the chlorobenzene is removed (in vacuo) and the unpurified polymer is then dissolved in methanol. The purification is made by successive sublimation of this methanolic solution.

^{13}C and ^1H NMR Spectra. Spectra were obtained on a CAMECA 250 FT spectrometer operating at 250 MHz (^1H) and 62.36 MHz (^{13}C). $CDCl_3$ provided the deuterium lock frequency and protons were decoupled from ^{13}C nuclei by broad band irradiation. Me_4Si was used as internal reference. The conditions used for the recording are the same as those described in ref 9.

^1H NMR spectra were obtained from the supernatant of a $CDCl_3$ solution of polymer. In some cases, ^{13}C NMR spectra could be obtained in the same way and were identical with those obtained from polymer swollen in $CDCl_3$.

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Registry No. (I) (homopolymer), 89346-17-8; (I)·(norbornene) (copolymer), 89346-20-3; (I)·(cyclopentene) (copolymer), 89346-21-4; (I·HCl) (homopolymer), 89346-26-9; (*exo*-I) (homopolymer), 89346-27-0; (*endo*-I) (homopolymer), 89346-28-1; (II) (homopolymer), 89346-18-9; (II·HCl) (homopolymer), 89346-24-7; (III) (homopolymer), 89346-19-0; (III·HCl) (homopolymer), 89346-22-5; $W(CO)_3$(mes), 12129-69-0; $W(CO)_5(CPh_2)$, 50276-12-5; EtAlCl, 563-43-9; oxygen, 7782-44-7; 1-pentene, 109-67-1.

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