

Ring-opening metathesis polymerization (ROMP) of isomerically pure functional monomers and acyclic diene metathesis depolymerization (retro-ADMET) of functionalized polyalkenamers

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Abstract

ROMP and retro-acyclic diene metathesis (ADMET) were used for the synthesis of new functional polymers and functional oligomers, respectively. Purely *exo* and enantiomerically pure norbornene and 7-oxanorbornene derivatives were prepared using stereospecific synthesis, effective fractionation and high yield condensation reactions. Successful ROMPs of those monomers were performed using either the new carbenic Schrock's or Grubb's catalysts or in some cases a classical bicomponent catalyst. New functional polymers such as optically active poly(norbornene-2-carboxylic acid), reactive poly(norbornene-2-azlactone), and side-chain liquid crystal polyoxanorbornenes were fully characterized. On the other hand, successful depolymerizations of 1,4-polyisoprene and of epoxidized 1,4-polybutadiene via cross-metathesis with 4-octene were performed using a stabilized bicomponent catalyst and the Grubb's catalyst, respectively. Conditions for the controlled synthesis of epoxidized oligobutadienes and of epoxydienic monomers via retro-ADMET were clearly defined.

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Keywords: Metathesis; ROMP; Retro-ADMET; Reactive polymers; Functional oligomers

1. Introduction

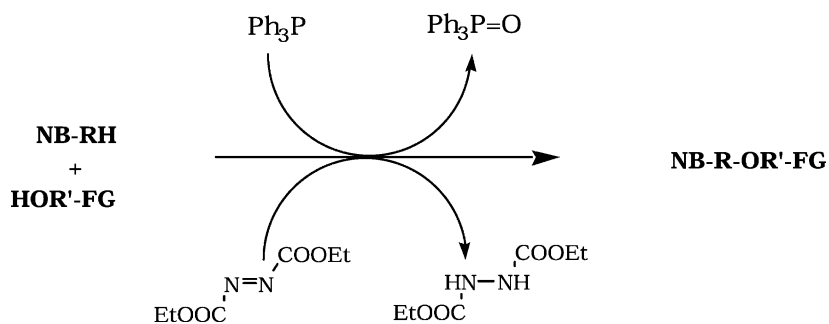
Applications of metathesis to the polymerization of olefins have been expanded considerably, largely due to the work of Schrock and co-workers [1,2], Grubbs and co-workers [3,4] and Stumpf et al. [5], in ring-opening metathesis polymerization (ROMP)

and Wagener's acyclic diene metathesis polymerization (ADMET) [6,7]. These advances have been mainly based on well-characterized metal alkylidene catalysts, mostly molybdenum [1] and ruthenium alkylidenes [3].

ROMP has been known for over 35 years and recently has been extended to living systems to prepare block and graft copolymers. With the advent of well-defined Grubbs and Schrock catalysts, a large variety of monomers has been addressed. Owing to

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Scheme 1.

their tolerance towards functional groups, these initiators are useful in the ROMP of functional strained ring systems, especially norbornenes [8]. Well-defined initiators allow the synthesis of highly functionalized polymers derived from complex biological molecules such as carbohydrates [9–12], nucleic acid bases [13], amino acids [14–16] or antibiotics [17].

ADMET polymerization, which is a step propagation, condensation type reaction, provides the opportunity to expand metathesis polymerization beyond the well-known ROMP chemistry.

Improvements in the synthesis of monomers and polymers with reactive or physical functionality lead to consider the new developments in organic and macromolecular chemistry. Thus, the improvements in the knowledge of metathesis, Diels-Alder and condensation (Mitsunobu) reactions make possible the polymerization of new isomerically pure functional norbornene derivatives. A large range of functional polymers with varying properties is therefore, accessible by varying the side-chain attached functional group, the nature and the length of the linking and even the carbon configurations of the polymer backbone. In the same manner, the improvement in the knowledge of metathesis makes possible the ADMET depolymerization of functionalized unsaturated polymers such as chemically modified polydienes or polyalkenamers. New functional oligomers, monomers and their polymers can therefore, be synthesized by varying the chemical modification of the polydiene or polyalkenamer and the degree of ADMET depolymerization. We describe in this paper some examples of functional monomers and polymers we have prepared in our laboratory using both ROMP and ADMET depolymerization.

2. Results and discussion

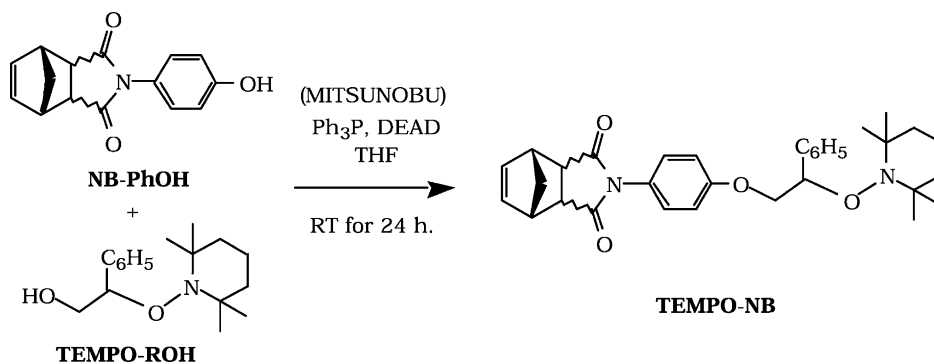
2.1. The Mitsunobu reaction in the synthesis of new functional monomers and polymers

We were interested in high yields Mitsunobu [18] reaction using diazodicarboxylate (DAD) and triphenylphosphine for the condensation of norbornene derivative containing an acidic hydrogen (**NB-R-H**) with molecules containing an alcohol and the targeted functional group (**FG-R'OH**; Scheme 1).

This reaction was considered for the synthesis of initiators containing a polymerizable group. Such initiators are able to produce: (1) well-defined polymers with terminal functionalities; (2) polymers with polymerizable groups in the side-chains and (3) polymers with initiating species in the side-chains, all of them being of interest for the control of varying macromolecular architectures.

In this field, norbornene derivatives containing species such as nitroxide able to initiate a “living” free radical polymerization of varying monomers [19] could produce polymers with polymerizable norbornene group at the chain-end and polynorbornenes with nitroxide initiating species in the side-chains. As an example (Scheme 2), a previously described alcohol-functionalized 2,2,6,6-tetramethylpiperidine-oxy (**TEMPO-ROH**) [20] was successfully condensed with a phenol-functionalized norbornene dicarboxamide (**NB-PHOH**) to produce the initiator (**TEMPO-NB**). Studies of nitroxide-mediated living polymerization and of ROMP of **TEMPO-NB** are in progress [21].

The Mitsunobu reaction was also found very useful for the synthesis of monomers containing a mesogenic



Scheme 2.

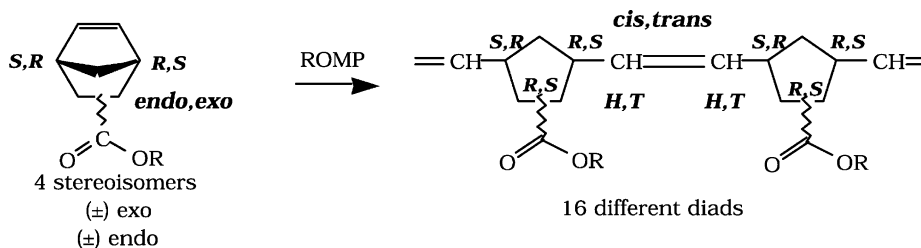
group linked to the polymerizable center through an alkylidene spacer with an increasing number of methylene [22]. In this field, beside the nature of the mesogenic group and the length of the spacer, the liquid crystal behavior of the polymers is highly dependent of the backbone microstructure. In the monosubstituted norbornene series, one must take into account that ROMP of isomers mixture leads to backbone microstructure which can exhibit head (H)/tail (T) isomerism, *cis/trans* double-bond isomerism and ring tacticity. Those structural features can afford up to 16 different diads (Scheme 3).

Polymer stereoregularities can be obtained by a stereospecific ROMP or by an isomeric purity of the monomers as shown in the purely *exo* or purely *endo*-5,6-disubstituted norbornenes [23–25], ROMP of which can afford only four different diads depending on the double-bond isomerism (*cis/trans*) and tacticity (*meso/racemo*; Scheme 4).

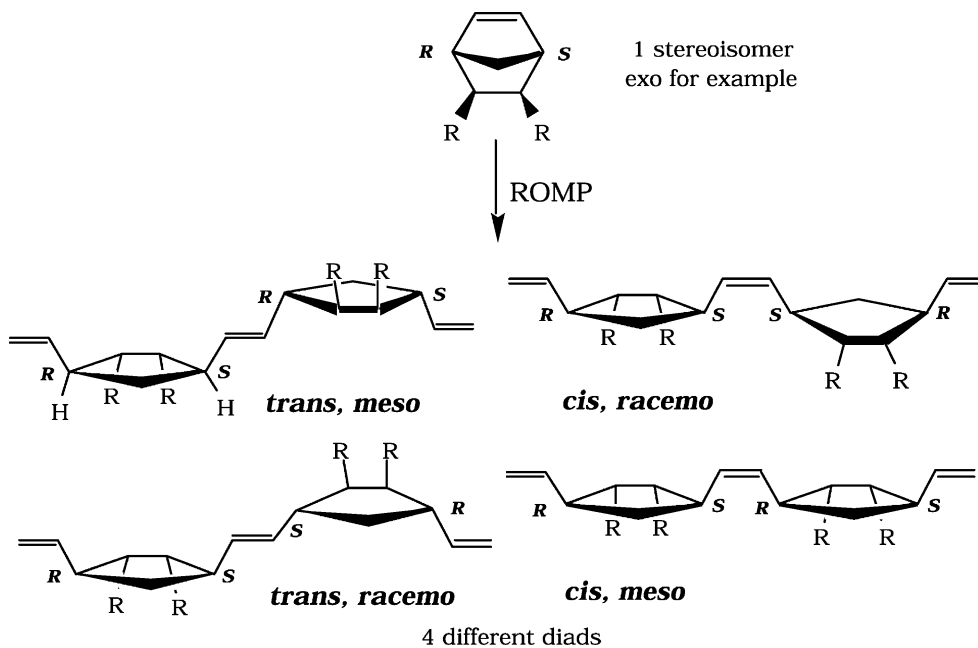
In this context, derivatives of 7-oxanorbornene-5,6-dicarboximide (**ONBN-H**) which can be obtained in pure *exo* form are of interest due to the possible Mitsunobu condensations of imides with alcohols. Indeed, the mesogenic *n*-(4-cyanobiphenyl-4'-yloxy)-

alkan-1-ols (**HO-R_nCB**, $n = 2-8$) were successfully condensed with **ONBN-H** and the resulting *N*-[*n*-(4-cyanobiphenyl-4'-yloxy) alkyl]-7-oxanorbornene-5,6-dicarboximides (**ONBN-R_nCB**, $n = 2-8$) were obtained in the purely *exo* form (Scheme 5).

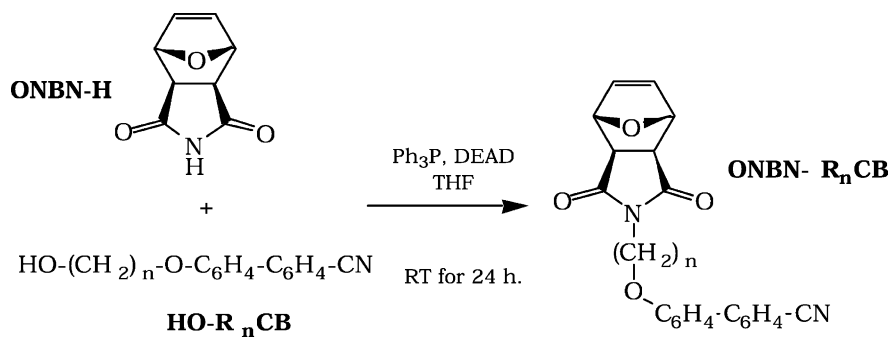
The ROMP of **ONBN-R_nCB** with a ruthenium-based catalyst ($[(p\text{-cymene})\text{RuCl}_2]_2/(\text{C}_6\text{H}_{11})_3\text{P}$) [5] failed, probably because of a deactivating effect of the cyano group. In this case, the commercial Schrock catalyst, (2,6-di-isopropylphenylimido) (neophylidene) molybdenum-bis(*t*-butoxide), was shown effective when the polymerization was performed at a noticeable high monomer concentration (130 mmol l^{-1}) with a monomer/catalyst mole ratio equal to 10 and with reaction time of 12 h at room temperature plus 2 h at 60°C . Spectroscopic analysis (^1H and ^{13}C NMR, IR) of the resulting polymers indicated a predominant *trans* structure. According to the model proposed by Ivin et al. [26] for the norbornene ring-opening which predicts that *meso*-diads are formed whenever *trans* double-bonds are produced, we can assume our polymers approach a stereoregular *trans* isotactic microstructure (Scheme 6).



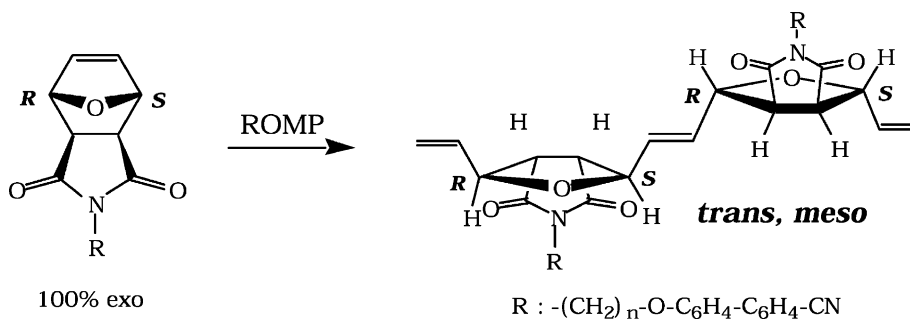
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

The polystyrene standardized number average molecular weights ($\bar{M}_n = (10\text{--}12) \times 10^3$) were similar whatever the number of methylene in the spacer ($n = 2\text{--}8$). However, the polydispersity indexes ($I = 1.5\text{--}1.6$) were higher than expected due to a bimodal distribution that revealed the presence of a side population (less than 10%, $\bar{M}_n = (20\text{--}25) \times 10^3$) whose molecular weight was approximately the double of that measured for the main population. Heating the polymerization mixture in order to speed up the rate of propagation also increased the probability of deactivation by coupling and the amount of the population of double molecular weight.

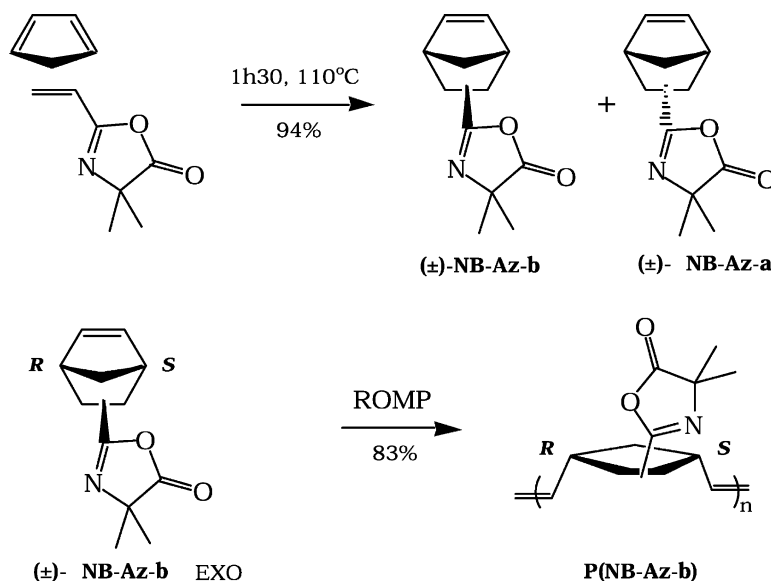
Differential scanning calorimetry and optical microscopy analysis have shown that the glass transition temperature (T_g) of the polymers decreases from 144 to 61 °C with increasing the spacer length from 3 to 8 methylenes. Farther away from the backbone the bulky mesogenic group, easier the main chain motions and higher the plasticizing effect [27]. However, probably because of the low main chain flexibility, liquid crystal mesophase did not appear, and isotropic fluid phases were observed above T_g , only slight and fugacious birefringence were seen for spacer length of 4, 5 and 8 methylenes in the temperature range 122–140, 112–125 and 109–120 °C, respectively [28].

2.2. The influence of *endo/exo* isomerism upon the polymerizability of 2-(norbornen-5-yl)-4,4-dimethyl-5-oxazolone

ROMP is an area of great interest for macromolecular engineering and various architectures have been prepared using this methodology [8]. In this area, norbornenylazlactone (2-(norborn-2-en-5-yl)-4,4-dimethyl-5-oxazolone, Scheme 7) may be regarded as a precursor of a new reactive polymer and graft copolymers since azlactone rings are known to be reactive towards nucleophiles such as amino end-groups of primary amines [29,30] and peptides [31] without by-product elimination.

Endo-stereoisomers are known to be less reactive or reluctant to polymerize via ROMP compare to their *exo*-counterparts. We recently investigated ROMP of both racemic *endo*-(NB-Az-a) and *exo*-2-(norborn-2-en-5-yl)-4,4-dimethyl-5-oxazolone (NB-Az-b) using Grubbs' catalyst in order to compare the polymerizability of the two diastereoisomers and to evaluate the tolerance of this catalyst towards the azlactone ring [31].

Monomers NB-Az-a and NB-Az-b were prepared according to Scheme 7. Diels-Alder reaction between cyclopentadiene and 2-vinyl-4,4-dimethyl-5-oxazo-



Scheme 7.

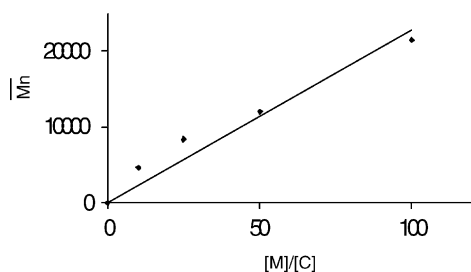


Fig. 1. Linear relation between \bar{M}_n and $[M]/[C]$ for ROMP of **NB-Az-b** using Grubbs' catalyst.

lone (VDM) gave **NB-Az** as a mixture of *endo*- and *exo*-stereoisomers (76/24 as determined by GC-MS and ^1H NMR) in 94% yield. Diastereoisomers **NB-Az-a** [(±)-*endo*] and **NB-Az-b** [(±)-*exo*] were separated using column chromatography and fully characterized. Polymerization of **NB-Az** (mixture of diastereoisomers), **NB-Az-a** and **NB-Az-b** by Grubbs' catalyst was carried out in refluxing chloroform or 1,2-dichloroethane for 24 h with various ratios of monomer to catalyst ($[M]/[C]$); no reaction occurs at room temperature and monomers were recovered unreacted at the end of the reaction).

It was found that *endo*- and *exo*-monomers react differently; using $[M]/[C] = 100$, the *exo*-isomer **NB-Az-b** gave a polymer with a 83% yield and $\bar{M}_n = 21,500$ while the *endo*-isomer **NB-Az-a** gave only a 17% yield and $\bar{M}_n = 5800$ under the same conditions.

Polymers showed unimodal SEC traces and the relationship between the \bar{M}_n (found) and the number of equivalents of monomer **NB-Az-b** added to the catalyst under a given set of conditions is approximately linear (see Fig. 1). In-situ ^1H NMR spectra of polymerization mixture with $[M]/[C] = 3$ shows that propagation is much faster than initiation. The

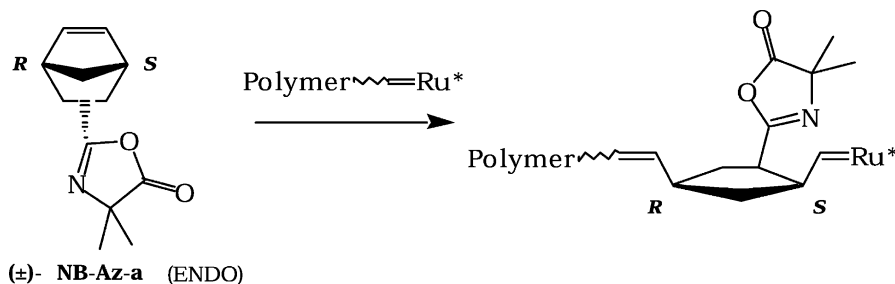
catalyst is always present during the reaction at δ 20.0 ppm while growing species are observed at δ 18.9–19.2 ppm. Therefore, this polymerization system can not be called truly "controlled" in its narrowest sense, as not all the chains started at the same time.

The difference in reactivity between *endo*- and *exo*-isomers has been ascribed to the catalyst inhibition by chelation of the propagating metal center by the *endo*-functional group and/or to the differences in steric interactions of the ring substituents on going from monomer to polymer [32,33]. The presence of the azlactone group near the propagating metal center in monomer **NB-Az-a** (*endo*; Scheme 8) possibly coordinates the chain-end and slows down the polymerization.

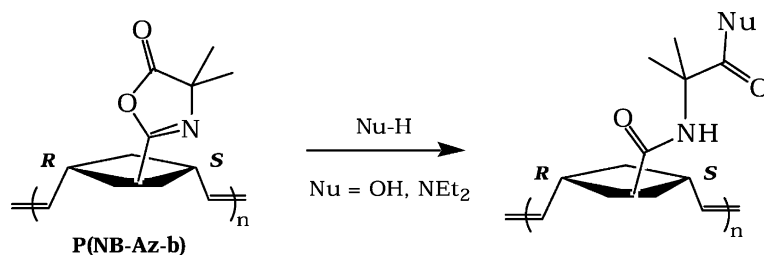
The azlactone ring survives intact during the polymerization and may be used for further reactions with nucleophiles, allowing polymer analogous reactions. In order to examine the potential applications of the resulting product the reactive polymer so obtained was reacted with various nucleophiles. Quantitative yields were obtained for the reaction with aqueous NaOH (in THF/water mixture) and diethylamine (Scheme 9) at room temperature leading to polymers bearing an α -methylalanine residue in the side-chain.

Reaction with 1,4-diaminobutane in chloroform solution led to cross-linking and immediate precipitation of the polymer. These reactions suggest that the reactive polymer prepared by ROMP could be used, e.g. as a scavenger for solid phase synthesis.

ROMP of **NB-Az** can also be used to prepare a wide variety of copolymers. Block copolymers were prepared by sequential copolymerization of **NB-Az** with norbornene with good yields. The azlactone groups can be used for further reactions as described for the homopolymer.



Scheme 8.

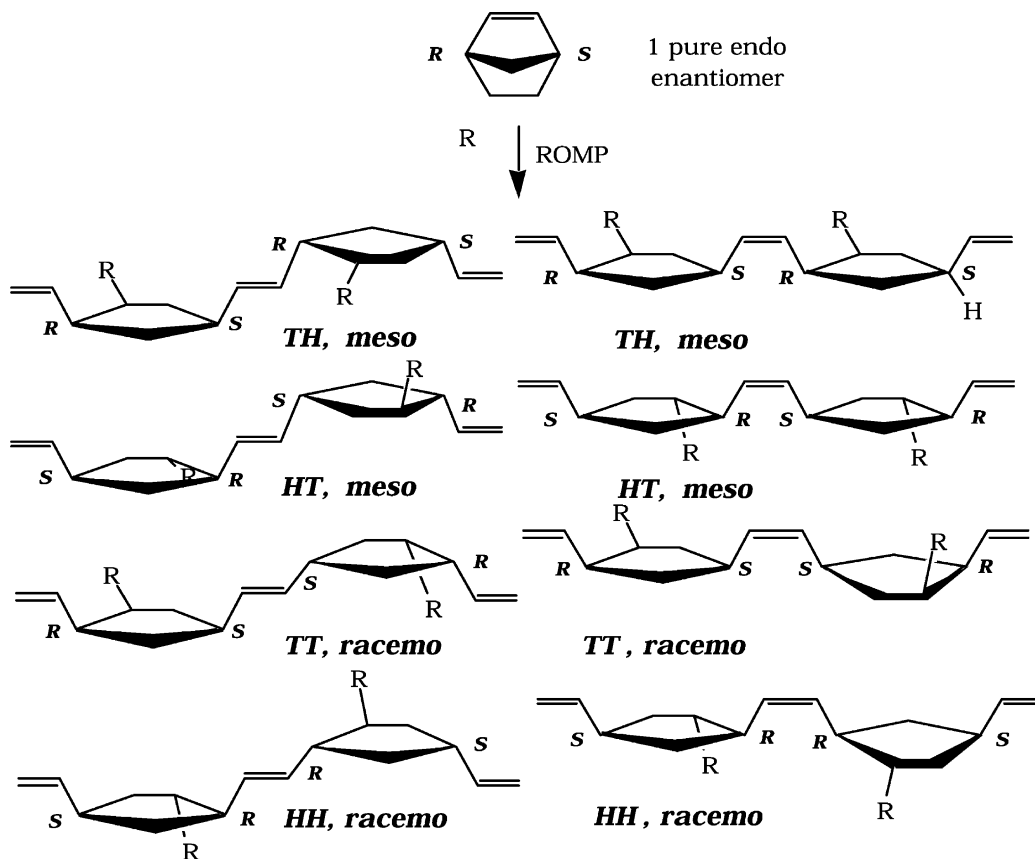


Scheme 9.

2.3. Enantiospecific Diels-Alder reaction for the synthesis of optically active monomers and polymers

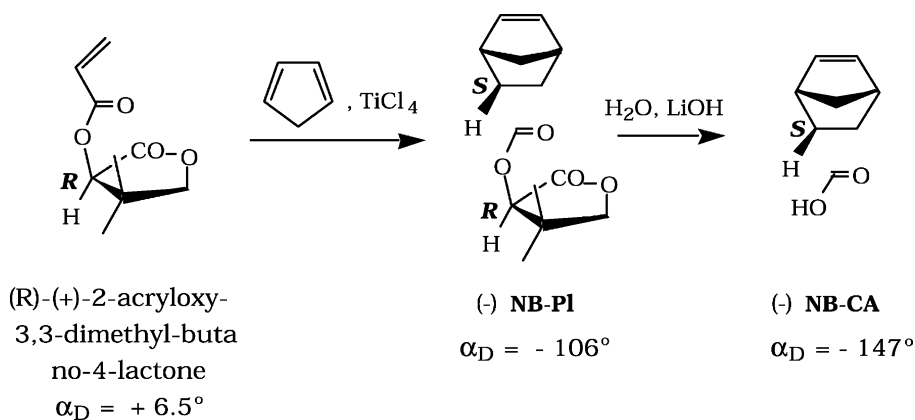
In the monosubstituted norbornene series, ROMP of enantiomerically pure monomers can afford eight

different diads depending on the double-bond isomerism (*cis/trans*) and head (H)/tail (T) isomerism. In this case, it can be noticed that, as shown in [Scheme 10](#), tacticity is determined by the HT isomerism. On this basis, we were interested in the diastereofacial



8 different diads

Scheme 10.



Scheme 11.

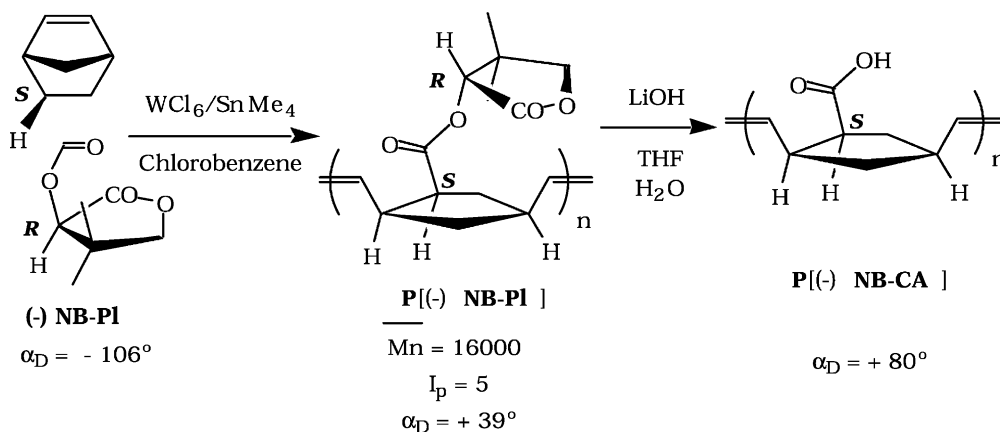
selectivity of the TiCl_4 -catalyzed Diels-Alder reaction which makes possible the asymmetric synthesis of homochiral 2-(S)(-)-endo-D-pantolacton-O-yl norbornene-2-carboxylate (-)NB-PI [34] and of the homochiral 2-(S)(-) norbornene-2-carboxylic acid (-)NB-CA (Scheme 11).

The enantiomeric purity of (-)NB-PI was checked by $^1\text{H}/^{13}\text{C}$ (2D) NMR correlation experiments and its S configuration was checked from the specific rotation of the previously described (-)NB-CA resulting from LiOH hydrolysis.

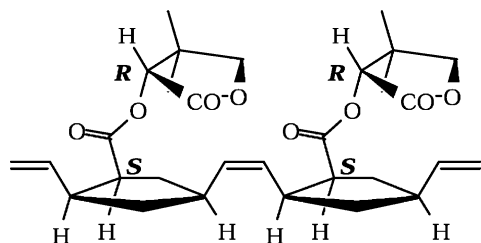
In a first approach $\text{WCl}_6/\text{SnMe}_4$ which is known as the classical metathesis catalyst for olefinic esters [35] was tested for the ROMP of (-)NB-PI. Poly[2-(S)(-)-endo-D-pantolacton-O-yl norbornene-2-car-

boxylate]s [P(NB-PI)] were obtained with reasonable yields and molecular weights (Scheme 12) [36]. Further LiOH hydrolysis of P(NB-PI) into poly(2-(S)(-) norbornene-2-carboxylic acid) [P(NB-CA)] has allowed to show that both P(NB-PI) and P(NB-CA) are optically active with significant values for specific rotation. These results show that the monomer purity allows to cumulate in P(NB-PI) the chirality of the pantolactonyl side-chain and the chirality of the (S) C2 backbone carbon.

The most useful and detailed structural characterization of the stereoregularities in P(NB-PI) was carried out using high resolution of ^{13}C NMR spectroscopy and $^1\text{H}/^{13}\text{C}$ (2D) correlation experiments. A predominant *cis* microstructure (*cis/trans* = 70/30,



Scheme 12.



Scheme 13.

i.e. $\sigma_c = 0.70$) was observed. However, no correlation with the structure and isomeric purity of the monomer can be drawn. Indeed, such *cis* predominances were previously observed when methyl norbornene-2-carboxylate is polymerized and when $\text{WCl}_6/\text{SnMe}_4$ is used for ROMP [37]. In contrast, **P(NB-PI)** showed an unusual predominant HT directional regularity $(\text{HT} + \text{TH})/(\text{HH} + \text{TT}) = 62/38$, i.e. $B = 1.6$ corresponding to a *meso*-stereoregularity in the diads (Scheme 13).

This regioselectivity in the norbornenyl ring-opening during propagation could be due to both steric hindrance and asymmetric induction of the D-pantolactonyl side-group. Therefore, the chirality of **P(NB-PI)** would be the result of the optical purity of the monomer unit and probably to the monomer directional regularity.

2.4. ADMET depolymerization for the synthesis of liquid natural rubbers

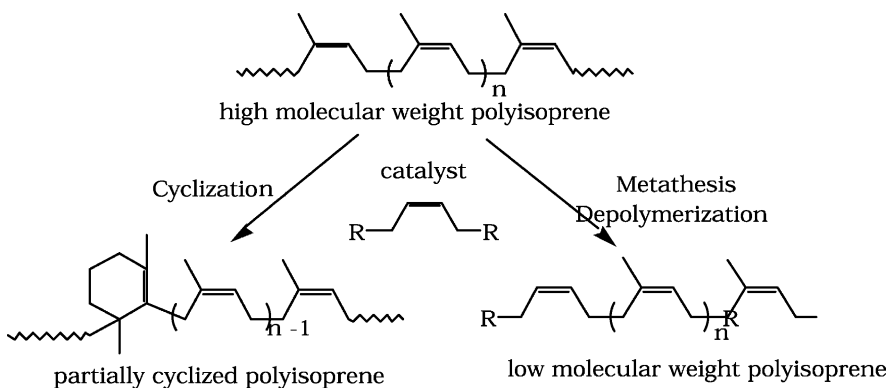
Metathesis depolymerization using simple alkenes as depolymerizing agent (DA) was extensively used

for analyzing the microstructure of the unsaturated polymers [38]. Metathesis depolymerization has gained much more importance to prepare oligomers and telechelic oligomers from polydienes and polyalkenamers, by the use of varying DA [39–41].

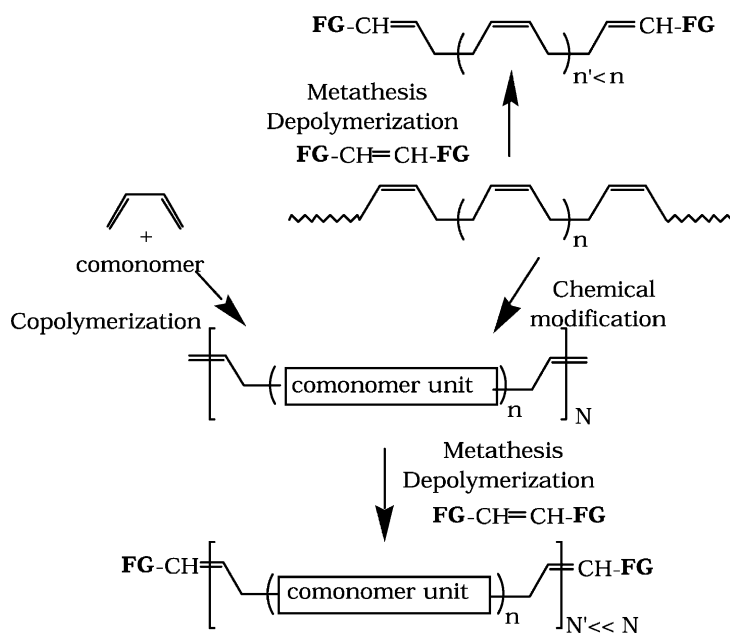
When excess of DA is used, a dienic monomer can be obtained and the process is seen as retro-acyclic diene metathetical polymerization (retro-ADMET). In the polydienes field, depolymerization of *cis* and *trans*-1,4-polybutadiene produces deca-3,7-diene with more than 90% yield using 200-fold excess of hex-3-ene as DA and $\text{WCl}_6/\text{Et}_4\text{Sn}/\text{Et}_2\text{O}$ as catalytic system [42,43].

Similarly, the yield of 1,6-hexadiene increased with increasing the pressure of ethylene by using Grubbs' benzylidene catalyst for depolymerization of *cis*-1,4-polybutadiene [44]. However, few works on metathesis degradation of polyisoprene are described in literature. With bicomponent WCl_6 -based catalytic systems, cationic secondary reactions are observed, leading to loss of double-bonds by cyclization (Scheme 14) [45–47].

Preliminary tests for depolymerization with dimethyl-3-hexene-1,6-dicarboxylate (DMHM) as DA and $\text{WCl}_6/\text{SnMe}_4$ as catalyst have shown that for the highest values of DMHM to catalyst ratios, no cyclization occurs [48]. Clearly the diester makes the metathesis/cyclization competition in favor of metathesis. Therefore, the specific metathetic degradation of polyisoprene with 4-octene as DA was performed using methyl acetate-stabilized $\text{WCl}_6/\text{SnMe}_4$ catalyst. It should be noted that the molecular weights of the resulting polyisoprenes are far from the expected



Scheme 14.



Scheme 15.

ones according to the DA mole ratio and for the higher level of cyclization prevention, the decrease in molecular weight slowed down. Conditions for controlled cross-metathesis would need further studies. However, low molecular weight polymers (average molecular weights between 10,000 and 35,000) were obtained by applying metathetic catalyst ($\text{WCl}_6/\text{SnMe}_4/\text{MeOAc}$) to a synthetic *cis*-1,4-polyisoprene (initial molecular weights between 200,000 and 300,000) in the presence or not of a transfer agent. Introduction of ester groups in the catalytic system allows suppression of the cationic secondary reactions and the *cis*-1,4 structure was maintained. But when ester groups are introduced at high molar ratios, the catalyst stabilization and subsequent deactivation make the molecular weight decreasing not as important as expected.

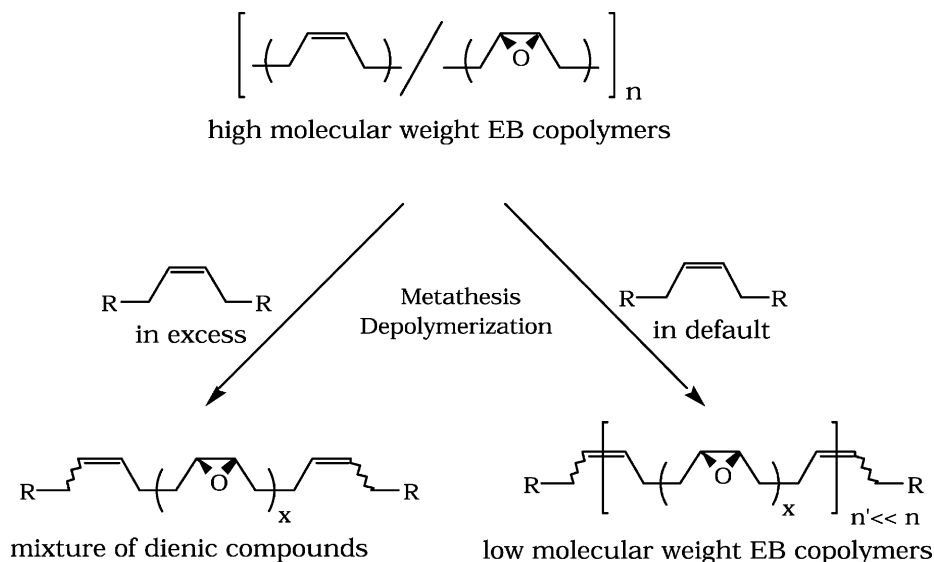
2.5. ADMET depolymerization for the synthesis of functionalized oligomers and monomers

The constructive approach of metathesis depolymerization can be broadened to the preparation of new organic target molecules of potential utility by choosing suitable DAs and unsaturated copolymers [49]. Beside the synthetic interest, studies in this field

are aimed towards the polymer waste management. Thus, the metathesis depolymerization of unsaturated polymers and copolymers with alkene containing a functional groups (FG) as DA makes possible the synthesis of telechelics (Scheme 15).

Moreover, the metathesis depolymerization of chemically modified polydienes allows the preparation of low molecular weight polymers containing functional groups along the chain and the synthesis of functionalized dienic monomers. As an example, we have run metathesis depolymerization of epoxidized *cis*-1,4-polybutadiene (PEB) with the aim of preparing epoxydienes monomers and low molecular weight epoxidized polymers (Scheme 16).

With the aim of preparing 8,9-epoxy-4,12-diene, a PEB with a low mole ratio of butadiene monomer unit (BU) to epoxidized monomer unit (EU) (BU/EU = 80/20) was selected. The metathesis depolymerization was carried out using *cis*-4-octene as DA and bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride as catalyst (Grubbs' catalyst, C) at 60 °C. In this case [50], cross-metathesis of BU with DA occurs. As shown by size exclusion chromatography (SEC), the major factors controlling the molecular weight of the depolymerization products were



Scheme 16.

found not to be only the DA/BU mole ratio and the C/BU mole ratio, but also the solvent effect (Fig. 2). As expected the average molecular weight of the depolymerization products was decreased by increasing

the DA/BU mole ratio from 2 to 6 (Fig. 2a) but, for a given C/BU mole ratio, the molecular weight can not be reduced by increasing DA/B from 6 up to 10. In our opinion, the reason for this limitation would be due to

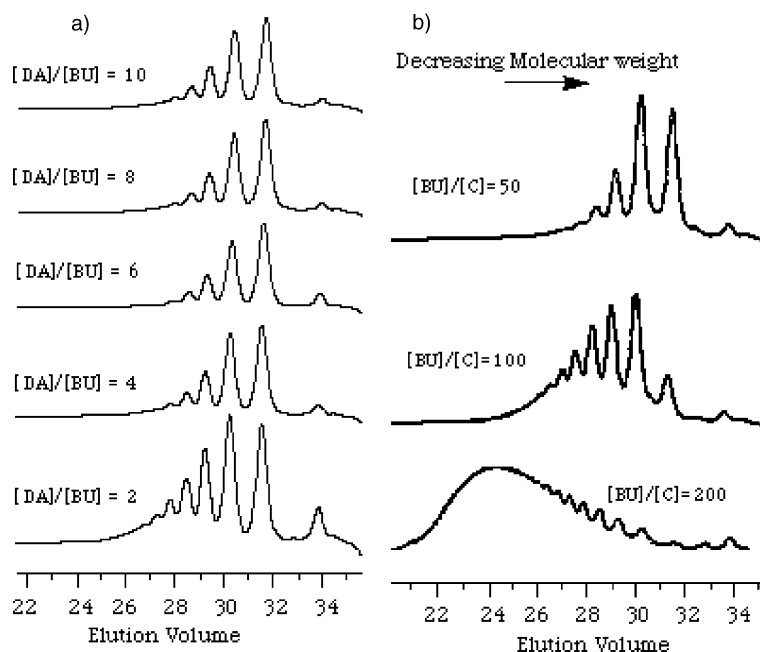


Fig. 2. Change in the size exclusion chromatography traces of the depolymerization product: (a) reaction in chlorobenzene ($\text{PEB} = 20 \text{ g l}^{-1}$) with varying DA/BU mole ratio at $\text{BU/C} = 100$; (b) reaction with no solvent added and varying BU/C mole ratio at $\text{DA/BU} = 10$.

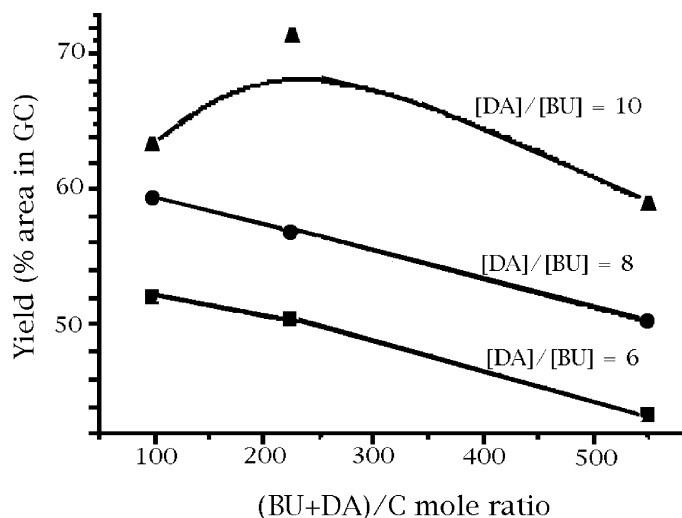


Fig. 3. Change in the relative content of the 8,9-epoxy-4,12-diene in the oligomers mixture with increasing catalyst to double-bond ratio at different DA/BU.

the excess of DA. Indeed, if the actual number of catalytic species is constant whereas the octene content is increased, unproductive metathesis between DA (4-octene in our example) makes the turnover of the catalyst less efficient in degradative cross-metathesis. Indeed, the average molecular weight of the depolymerization products was decreased by decreasing the BU/C mole ratio at a given DA/B (Fig. 2b).

It should be noted that the SEC traces shown in Fig. 2b correspond to depolymerization which was performed without adding any more solvent that necessary for the catalyst solubilization. Comparison of Fig. 2a and b showed that, surprisingly, the depolymerization with solvent is more efficient than without solvent. This fact is very clear when we compare traces of sample obtained with BU/C = 100 in Fig. 2b with traces of sample obtained for DA/BU = 10 in Fig. 2a, the only difference between these two samples is the absence of solvent in the depolymerization procedure used for the first sample.

On these basis, controlled chain cleavages can be obtained in chlorobenzene by varying the DA/BU ratio and the total sum of double bonds to catalyst ratio [(BU + DA)/C] rather than the polymeric double bond to catalyst ratio [BU/C] [51]. Typically, the plot of yield in epoxydiene versus BU/C in Fig. 3 indicates that for DA/B = 6 and 8, when

[(BU + DA)/C decreases, the yield in epoxydiene (8,9-epoxy-4,12-diene) increases linearly. For DA/B = 10, the most efficient (BU + DA)/C ratio was the intermediate value. In this case, 4,8-dodecadiene and 8,9-epoxy-4,12-diene were detected as the major depolymerization products. However, further increase in catalyst concentration was found to be ineffective to increase the yield.

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