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Metathesis Polymers

Polymers using the ring opening metathesis polymerization (ROMP) technique were first obtained at 1960 by *Eleuterio* (1, 2). The patents deal with the polymerization of bicyclo[2.2.1]heptene-2, i.e., norbornene using a molybdenum catalyst dispersed on alumina.

The polymer was found to contain double bonds in *trans* and *cis*-configuration in considerable amounts. The mechanism of polymerization has been described as shown in Figure 1.1.

Metal-catalyzed olefin metathesis had an enormous impact on organic synthesis in general. Extensive research on mechanistic aspects (3,4) and the development of catalysts has been performed, which culminated in the award of the Nobel Prize for Chemistry in 2005 to *Chauvin*, *Grubbs* and *Schrock*.

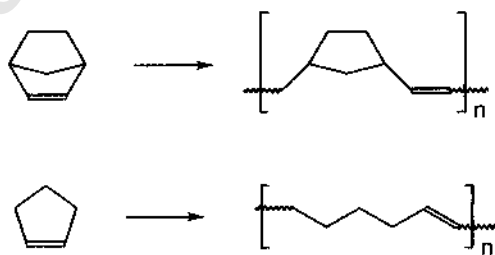


Figure 1.1: Metathesis Polymerization of Norbornene and Cyclopentene

Table 1.1: Monomers for Metathesis Polymerization

Monomers	References
Cyclopentene	
1,5-Cyclooctadiene	
Norbornene	(1, 2)
1,4-Dihydro-1,4-methanonaphthalene	
Norbornene 2-ethylhexyl carboxylate	(5)
Norbornene isobornyl carboxylate	(5)
Norbornene phenoxyethyl carboxylate	(5)
Dodecylenediorbornene dicarboxyimide	(5)
<i>exo,exo</i> - <i>N,N'</i> -Propylene-di-(norbornene-5,6-dicarboxyimide)	(5)
8-Methyltetracyclo[4.4.0.12.8.17.10]dodeca-3-ene	(6)
Dicyclopentadiene	(6)

1.1 Monomers

Cyclopentene is readily available as a byproduct in the ethylene production. Norbornene 2-ethylhexyl carboxylate is obtained by the Diels-Alder reaction of 2-ethylhexyl acrylate with cyclopentadiene (5). Norbornene isobornyl carboxylate, norbornene phenoxyethyl carboxylate, and other related monomers are synthesized according to the same route. Polymers obtained from these esters exhibit excellent properties in terms of controlling the crosslinking density, the associated product modulus, and the glass transition temperature (T_g), thus allowing tailoring the properties of elastomers, plastics and composites. Other suitable monomers are summarized in Table 1.1 and sketched in Figure 1.2.

1.2 Polymerization and Fabrication

The monomers dealt with can be polymerized by various mechanisms, not only by ROMP. For example, a rapid polymerization of norbornadiene occurs using a homogeneous catalytic system consisting of nickel acetylacetonate or a nickel-phosphine complex, such as nickel bis-(tri-*n*-butylphosphine) dichloride ($\text{NiCl}_2(\text{TBP})_2$) or nickel bis-(tricyclohexylphosphine) dichloride ($\text{NiCl}_2(\text{TBP})_2$). Nickel acetylacetonate as catalyst is known to initiate rather a classical vinyl polymerization (7). The classical vinyl polymerization

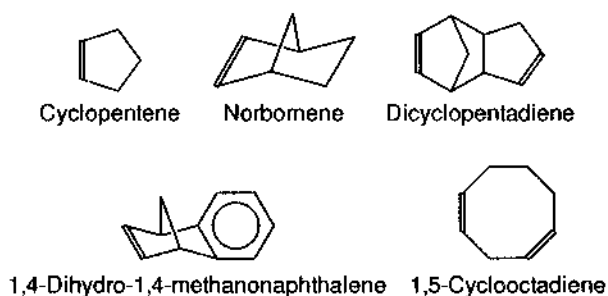


Figure 1.2: Monomers used for Metathesis Polymers

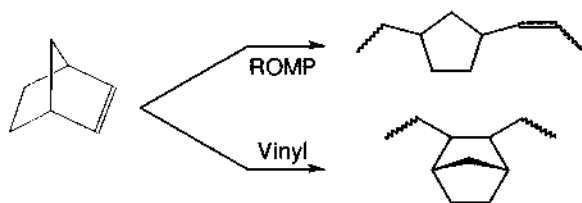


Figure 1.3: Difference Between Vinyl Polymerization and Ring Opening Metathesis Polymerization (7)

of cyclic monomer deserves much less attention in the literature, nevertheless there is a big variety of catalysts described (7).

By the way, the intended use of this polymer is as a solid high energy fuel (8). The difference between ordinary vinyl polymerization and ring opening metathesis polymerization is shown in Figure 1.3.

1.2.1 Metathesis Reaction

The metathesis reaction consists of a movement of double bonds between different molecules, as shown in Figure 1.4. Thus, the metathesis reaction can be addressed as a transalkylideneation reaction. The cleavage of the carbon-carbon double bonds was established using isotopic labelled compounds that were subjected to ozonolysis after reaction (9).

Clearly, if the radicals R_1 and R_4 are connected via a carbon chain, a longer chain will be formed, resulting consecutively in the for-

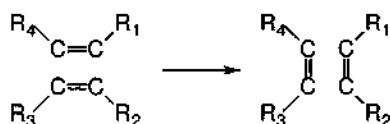


Figure 1.4: Scheme of Metathesis Reaction

Table 1.2: Types of Metathesis Reactions (10)

Term	Acronym
Ring opening metatheses polymerization	ROMP
Living ring opening metatheses polymerization	LROMP (11,12)
Ring closing metathesis	RCM
Acyclic diene metathesis polymerization	ADMET
Ring opening metathesis	ROM
Cross-metathesis	CM or XMET

mation of macromolecular structures. For this reason, this type of polymerization is also called ring opening polymerization. The polymeric structures contain double bonds in the main chain. This allows classical vulcanization processes with sulphur. Since the reaction is reversible, the metathesis process has been used to synthesize degradable polymers with vinyl groups in the backbone. In this way, the structure of crosslinked rubbers has been elucidated.

The mechanism of metathesis is used in several variants, either to polymerize, degrade, etc. The various reaction types are summarized in Table 1.2. The metathesis reaction is catalyzed by metal-carbene complexes. The mechanism, exemplified with cyclopentene is shown in Figure 1.5. In the first step, the complex reacts with a monomer to regenerate the carbon metal double bond. This double bond is able to react further with another monomer thus increasing the size of the molecule.

If the metathesis polymerization is performed in solution, the preferred solvents are methylene chloride or chlorobenzene. Preferably, the solvent is aprotic in order to avoid ionic side reactions. The molecular weight is controlled by the addition of an acyclic olefin, such as 1-butene (13).

The polymerization reaction can be quenched by the addition of alcohols, amines or carboxylic acids, such as ethanol, *tert*-butyl

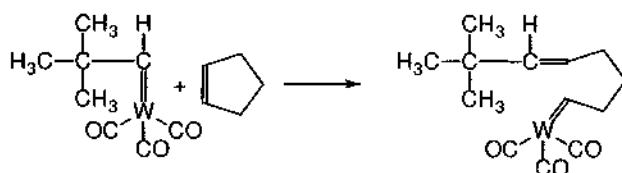


Figure 1.5: Initial Steps of the Metathesis Polymerization

phenol, diethylamine, acetic acid. The polymerization reaction is an equilibrium reaction. The relevant equilibria are

1. Monomer–polymer equilibrium, in more general sense,
2. Equilibrium between polymers of different chain length,
3. Ring-chain equilibrium, and
4. *Cis-trans*-equilibrium.

The free enthalpy of polymerization (ΔG_p) is sufficiently negative for rings of a size of 3, 4, 8, and larger to have the equilibrium on the side of the polymer. However, for rings of a size of 5, 6, and 7 – because of the low ring tension – the free enthalpy of polymerization can be even positive. For example, $\Delta G_{0,p}$ for the formation of the *cis*-polymer of cyclohexene, $\Delta G_{0,p} = +6.2 \text{ kJ mol}^{-1}$ and for *trans*-polymer of cyclohexene, $\Delta G_{0,p} = +7.3 \text{ kJ mol}^{-1}$ (14). However, at cryogenic temperatures, ΔG_p decreases and oligomers can be formed.

The polymer contains a fraction of high molecular linear chains and a cyclic oligomeric fraction. If initially the monomer concentration is below the equilibrium value for a linear polymer, essentially no polymer is formed, but only cyclic oligomers. At higher concentration, both a linear polymer and a cyclic oligomer is formed.

The ratio of the amounts of *cis*-linkages to *trans*-linkages depends on the nature of the catalyst. A tungsten or molybdenum catalyst, respectively, can be prepared by heating tungsten trioxide with phosphorus pentachloride in *o*-dichlorobenzene up to 120°C under vigorous stirring. The solution changes from colorless to deep red and a considerable amount of precipitate is left behind at the bottom of the reaction vessel. The soluble chloride is used for the further steps.

Table 1.3: Monomers for ROMP Polymerization (15)

Monomer	Rate ^a	η^b
Cyclopentene ^c	1,590	2.05 ^d
Bicyclo[2.2.1]heptene-2 ^c	1,365	1.88 ^d
5-Cyano-5-methyl-bicyclo[2.2.1]heptene-2	1,365	1.22 ^e
3,6-Methylene-1,2,3,6-tetrahydro- <i>cis</i> -phthalic anhydride	1,283	0.97 ^e
2,3-Diethoxycarbonyl-bicyclo[2.2.1]hepta-2,5-diene	1,264	1.17 ^e
1,5-Cyclooctadiene ^c	1,202	1.98 ^d
N-Phenyl-3,6-methylene-1,2,3,6-tetrahydro- <i>cis</i> -phthalimide	1,182	1.05 ^d
N-Butyl-3,6-methylene-1,2,3,6-tetrahydro- <i>cis</i> -phthalimide	1,121	1.07 ^e
5,6-Dimethoxycarbonyl-bicyclo[2.2.1]heptene-2	1,039	0.70 ^e
5-(4-Quinoly)-bicyclo[2.2.1]heptene-2	998	0.81 ^e
5-Acetoxy-bicyclo[2.2.1]heptene-2	978	0.85 ^e
5-Methoxymethylbicyclo[2.2.1]heptene-2	978	0.69 ^e
N,N-Diethyl-bicyclo[2.2.1]heptene-2-carbonamide	937	0.94 ^e
1,4-Dihydro-1,4-methanonaphthalene	897	0.78 ^d
5-Chloromethyl-bicyclo[2.2.1]heptene-2	876	0.80 ^d
5-(2-Pyridyl)-bicyclo[2.2.1]heptene-2	876	0.81 ^e
5,5-Dichloro-bicyclo[2.2.1]heptene-2	815	1.11 ^d

^a Rate of polymerization/ [g g⁻¹h⁻¹] at 70°C except for monomers with superscript ^c

^b Viscosity/ [dl g⁻¹]

^c Polymerized at 30°C

^d Solvent: 1,2-dichloroethane

^e Solvent: N,N-dimethylformamide

The actual polymerization takes place in an autoclave under inert atmosphere, where the supernatant liquid of the foregoing step is placed with the dried and rectified monomer and the second catalyst compound, namely diethylaluminum chloride in 1,2-dichloroethane solution (15). The polymerization is conducted at 70°C for 60 min while stirring well. According to this recipe, a series of cyclic monomers can be polymerized. Examples are shown in Table 1.3.

Macromonomers provide an easy access to a large number of functional copolymers and controlled topologies, such as comb-like, star-like, bottle brush, and graft copolymers. These types exhibit exceptional solution or solid state properties compared to their linear homologues.

Initially, the polymerization of macromonomers was achieved by free radical polymerization reactions, which allowed only a limited control of the final properties. With the advent of ROMP and new free radical polymerization techniques, such as atom transfer radical polymerization (ATRP) the control of final properties became more facile (16). ATRP and ROMP techniques can be combined for the synthesis of macroinitiators (17).

Macromonomers with norbornene end groups were synthesized by living anionic polymerization. The norbornene groups were polymerized by molybdenum catalysts. A series of other ω -norbornenyl macromonomers were synthesized and polymerized by metathesis polymerization.

1.2.1.1 *Living Ring Opening Metathesis Polymerization*

Living ring opening metathesis polymerization is a special kind of ROMP. In order to approach the conditions of a living polymerization reaction, the following requirements must be fulfilled (12):

1. Fast and complete initiation,
2. Linear relationship between the degree of polymerization and conversion, and
3. Polydispersity less than 1.5.

Thus, the catalyst must have certain special properties, to be regarded as a living ROMP catalyst.

1.2.2 *Catalysts*

Numerous catalyst systems have been developed. Most common catalysts are based on tungsten or molybdenum. Transition metals ranging from group IV to group VIII have been found to be suitable. The catalysts are commonly classified as given in Table 1.4.

The half-life times of the polymerization reaction can be adjusted from a few seconds to several days. Typical for such catalysts is the metalcarbene bond, as shown in Figure 1.5. In varieties of the catalytic principle of the metalcarbene bond, this bond is not initially present, but may be formed by a co-catalyst or by some reactions with the monomer itself.

Table 1.4: Classification of Catalysts (18)

Catalyst Type
Initiators with metal alkyl co-catalysts
Initiators with alkylidene or metallacyclobutanes of early transition metals
Group VIII initiators without metal alkyl co-catalysts
Group VIII alkylidenes

Table 1.5: Monomer Catalyst Systems (14)

Monomer	Catalyst	T /°C ^a	Property ^b
Cyclopentene	WCl ₆ /(CH ₂ =CHCH ₂) ₄ Si	-10	high cis
Cyclopentene	WCl ₆ /CH ₃ -CH ₂ AlCl ₂	+20	high trans
CH≡CCH ₃	C ₆ H ₅ C≡W(CO) ₄ Br		M _n = 5.9 k Dalton

^a Temperature of polymerization^b Property of polymer

Examples for catalysts are listed Table 1.5 and shown in Figure 1.6. For the metathesis polymerization of acetylene related compounds, catalysts with a metal carbyne bond have been introduced, such as



Molybdenum-based catalysts are highly active initiators, however, monomers with functionalities with acid hydrogen, such as alcohols, acids, or thiols jeopardize the activity. In contrast, ruthenium-based systems exhibit a higher stability towards these functionalities (19). An example for a molybdenum-based catalyst is (20) MoOCl₂(*t*-BuO)₂, where *t*-BuO is the *tert*-butyl oxide radical. The complex can be prepared by reacting MoOCl₄ with potassium *tert*-butoxide, i.e., the potassium salt of *tert*-butanol.

Ruthenium and osmium carbene complexes possess metal centers that are formally in the +2 oxidation state, have an electron count of 16 and are penta-coordinated. Ruthenium complexes exhibit a higher catalytic activity when an imidazole carbene ligand is coordinated to the ruthenium metal center (21).

The polymerization of cyclooctene shows a pronounced dependence of the *N*-heterocyclic carbene ligand, due to steric effects.

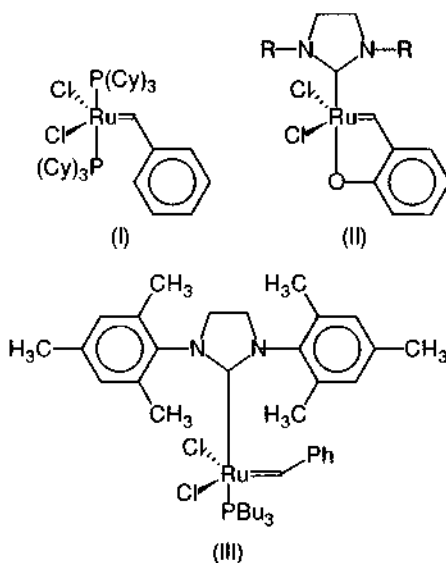


Figure 1.6: Metathesis Catalysts (22): Phenylmethylene-bis-(tricyclohexylphosphine) ruthenium dichloride (I), (IMesH₂)(PCy₃)(Cl)₂Ru=CHPh (III)

These ruthenium complexes are also active catalysts for ring-closing metathesis reactions in high yields.

Ruthenium catalysts, coordinated with an *N*-heterocyclic carbene allowed for the ROMP of low-strain cyclopentene and substituted cyclopentenes (10,23). Suitable ruthenium and osmium carbene compounds may be synthesized using diazo compounds, by neutral electron donor ligand exchange, by cross metathesis, using acetylene, cumulated olefins, and in an one-pot method using diazo compounds and neutral electron donors (24). The route via diazo compounds is shown in Figure 1.7.

Since the ruthenium and osmium carbene compounds of the type shown in Figure 1.7 are stable in the presence of a variety of functional groups, the olefins involved in the polymerization reactions may optionally be substituted with various functional groups.

The synthesis of a ruthenium catalyst in a one step procedure is shown in Figure 1.8. A dimer complex of cymene, i.e., 4-isopropyltoluene) and RuCl₂ is reacted under inert atmosphere with tricyclohexylphosphine and 3,3-diphenylcyclopropene in benzene

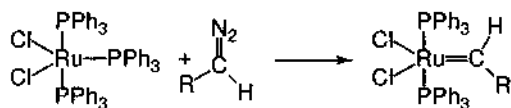


Figure 1.7: Synthesis of Ruthenium Carbene Compounds via Diazo Compounds (24)

solution under reflux at 83–85°C for 6 h (25).

The catalyst $\text{Cl}_2\text{Ru}(\text{PCy}_3)_2(=\text{CHCH}=\text{CPh}_2)$, c.f., Figure 1.8, is obtained in a yield of 88%. In the same way, catalysts, where the metal atom is in a ring, can be synthesized. This type of catalysts is suitable for the synthesis of cyclic polymers (26). The synthesis route is shown in Figure 1.9.

The preparation of the catalyst starts with the synthesis of 1-mesityl-3-(7-octene)-imidazole bromide. This compound is prepared by condensing mesityl imidazole with 8-bromooctene. The resulting salt is deprotonated with $(\text{TMS})_2\text{NK}$, where TMS is the tetramethylsilyl radical. This step is performed in tetrahydrofuran at -30°C for 30 min. To this product a solution of the ruthenium complex $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$ is added at 0°C . Bringing the solution slowly to room temperature, after 1 h the ligand displacement was determined to be complete. Afterwards, the reaction mixture is then diluted with *n*-pentane and heated to reflux for 2 h to induce intramolecular cyclization.

The ruthenium catalyst can be used to catalyze the synthesis of a cyclic poly(octenamer). The catalyst is added to *cis*-cyclooctene in CH_2Cl_2 solution at 45°C . The intermediate macrocyclic complex undergoes an intramolecular chain transfer to yield the cyclic polymer and regenerate the catalyst.

In this way, cyclic polymers with number-average molecular weights M_n up to 1200 kDalton can be prepared by varying the ration of catalyst to monomer or the initial monomer concentration.

However, with initial monomer concentrations of less than 0.2 mol l^{-1} , only low molecular weight cyclic oligomers are obtained. The polydispersity index M_w/M_n of the resulting polymers is approximately 2.

In the case of cycloolefin monomers with a strained double bond,

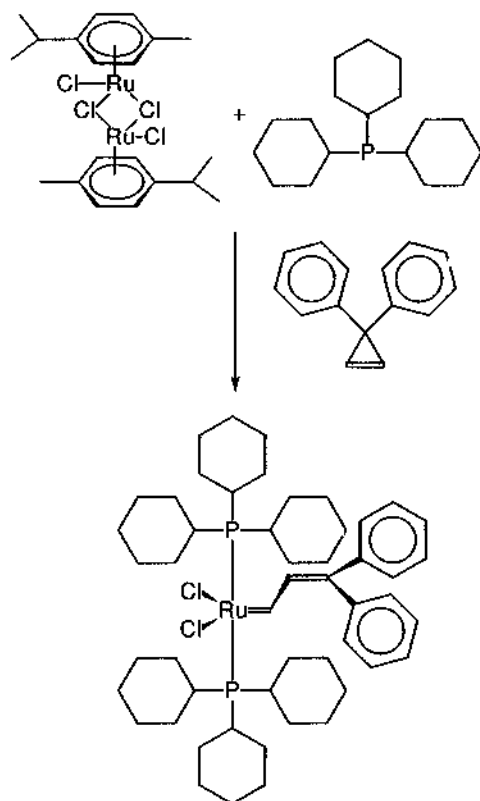


Figure 1.8: Synthesis of a Ruthenium Catalyst (25)

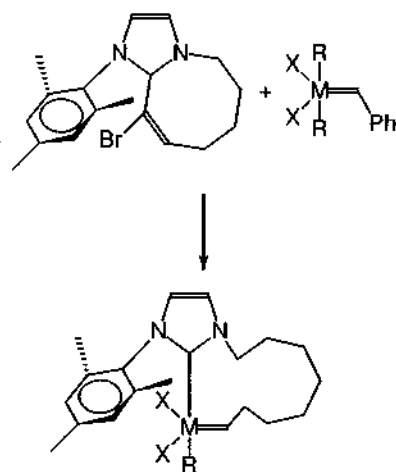


Figure 1.9: Catalyst for Macrocyclic Polymers

such as norbornene, the ring opened product is thermodynamically favored. Therefore, it is not necessary for the catalyst to bear a metallocarbene moiety in its structure to initiate the ROMP. Any complex capable of initiating metallocarbene formation *in situ* should perform equally well as a catalyst for the ROMP. For instance, it is well known that $\text{RuCl}_3 \times 3\text{H}_2\text{O}$ can accomplish the ROMP of norbornene quite effortlessly, even though there is no carbene present in the catalyst. It is suspected that the reaction involves as a first step, when the metal halide reacts with the monomer, the formation of a metallocarbene moiety that is responsible for the subsequent propagation reaction (20).

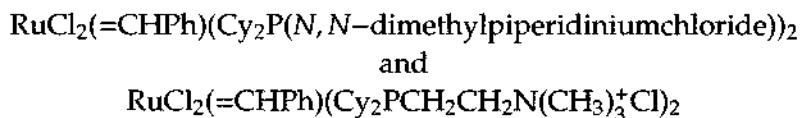
Hydrates of RuCl_3 , IrCl_3 , and OsCl_3 are suitable catalysts for the ROMP of norbornene in aqueous and alcoholic solvents. Ruthenium trichloride hydrate is used for the industrial production of poly(norbornene). These hydrates act for the ROMP of norbornene and norbornene derivatives in pure water through an emulsion process (18).

Olefin metathesis catalysts based on ruthenium have been shown to exhibit a quite good tolerance to a variety of functional groups. The ring opening metathesis polymerization of strained, cyclic olefins initiated by group VIII salts and coordination complexes in aque-

ous medium has been described. Although these complexes serve as robust polymerization catalysts in water, the polymerization is not of living type. Moreover, inefficient initiation steps produce erratic results, in particular, when less than 1% of the metal centers are converted to catalytically active species. This results in poor control over polymer molecular weight (27).

In contrast, in living polymerization systems, the polymerization occurs without chain transfer or chain termination, giving greater control over polydispersity of the resultant polymers. Such polymerization systems allow the controlled synthesis of water-soluble polymers and enable precise control over the composition of block copolymers.

Water-soluble, aliphatic phosphines have been synthesized for their inclusion into ruthenium olefin metathesis catalysts (28). Complexes of the type



can be activated in water with a strong Brønsted acid. In the presence of a Brønsted acid, the complexes quickly and quantitatively initiate the living polymerization of water-soluble monomers without the need of a surfactant or of organic solvents (27).

This finding is a significant improvement over aqueous ROMP systems using aqueous ROMP catalysts. The propagating species in these reactions is stable. The synthesis of water-soluble block copolymers can be achieved via sequential monomer addition. The polymerization is not of living type in the absence of acid. In addition to eliminating hydroxide ions, which would cause catalyst decomposition, the catalyst activity is also enhanced by the protonation of the phosphine ligands. Remarkably, the acids do not react with the ruthenium alkylidene bond.

Although the alkylidene complexes initiate the ROMP of functionalized norbornenes and 7-oxanorbornenes in aqueous solution quickly and completely in the absence of acid, the propagating species in these reactions often decompose before the polymerization reaction is complete. For example, in the ROMP of the water-soluble

monomer *exo-N*-(*N'*,*N'*,*N'*-trimethylammonio) ethyl-bicyclo[2.2.1]-hept-5-ene-2,3-dicarboximide chloride and also *exo-N*-(*N'*,*N'*,*N'*-trimethylammonio) ethyl-bicyclo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide chloride, conversions ranging from 45–80% are observed. Although the water-soluble complexes are similar to ruthenium alkylidenes, which are very stable toward polar and protic functional groups in organic solvents, they appear to be susceptible to termination reactions, when dissolved in water or methanol (27).

1.2.3 Rate Controlling

The rate of polymerization can be controlled by a gel modification additive. A gel modification additive is a substance that cooperates with the catalyst to change the rate of the catalyzed reaction. Most generally, a gel modification additive may be any electron donor or Lewis base. Particularity suitable compounds acting in this way are tricyclohexylphosphine, tricyclopentylphosphine, triisopropylphosphine, triphenyl phosphine, and pyridine.

Triphenyl phosphine is an example of a gel modification additive that acts to retard the rate of reaction, when the catalyst has tricycloalkylphosphine ligands. The catalyst with tricycloalkylphosphines ligands is much more active in ROMP than when the ligands would be triphenyl phosphines.

The action of triphenyl phosphine on the catalyst is explained that the added triphenyl phosphine substitutes the tricycloalkylphosphine ligands in the coordination sphere of the complex and decreases the activity of the catalyst. Thus, in general, a gel modification additive decreases the rate of reaction if the catalyst becomes less active by an exchange reaction of the respective ligands.

Since monomer coordination is required for polymerization, the gel modification additive can also slow the polymerization reaction by competing with the monomer for coordination sites on the metal center.

A general rule for the case discussed above, increasing the concentration of the gel modification additive will decrease the rate of polymerization reaction. On the other hand, if the pot life is too long, in the case of a catalyst with triphenyl phosphine ligands, the pot

life can be decreased by adding an other type of gel modification additive, such as tricyclohexylphosphine or tricyclopentylphosphine.

In this case, it is believed that the tricycloalkylphosphine gel modification additive exchanges with the triphenyl phosphine ligands leading to a more active catalyst. The situation is reverse from the case discussed before. However, even when the catalyst becomes more active, as the concentration of gel modification additive is increased, the additive will compete with the monomer for coordination sites on the metal center and the additive may eventually act to decrease the rate of reaction.

There must be sufficient time for the ligands and the gel modification additive to totally equilibrate between being bound by the catalyst and being in solution in the monomer. In some cases, to obtain the maximum effect of a gel modification additive, it may be necessary to allow the gel modification additive and the catalyst complex to equilibrate in a non reactive solvent before the monomer is added. This is particularly important where exchange of the ligands and gel modification additive appears to be slow relative to the onset of polymerization, such as cases where a very bulky gel modification additive, such as tricyclohexylphosphine is being exchanged on the catalyst complex. Experiments concerning the polymerization of dicyclopentadiene show the effects that are qualitatively discussed before.

The type of ruthenium catalysts, as shown in Figure 1.8, however with cyclopentadienyl ligands instead of cyclohexyl ligands,



are added to dicyclopentadiene and an amount of gel modification additive is added and mixed. The mixture is then poured in a mold and is allowed to polymerize. In the experiments, the gel time is defined as

1. The time at which a stir bar ceases turning in a 250 ml flask during mixing of the catalyst and monomer, or
2. The time at which a glass pipet lowered or pushed into a very high viscosity poured sample will no longer pick up or have cling to the pipet any of the polymerizing sample.

Table 1.6: Gel Modification Additives vs. Gel Time (25)
Catalyst: 0.85 g g^{-1} Monomer

Additive ^a	Amount ^b	Mold °C	Resin °C	Gel Time min	Peak Exotherm min	°C
1	0.15 mg	36.4	31.0	6.00	7.33	160.3
1	0.43 mg	36.2	31.0	9.00	10.83	173.2
1	1.14 mg	36.3	31.0	21.00	38.30	91.5
2	1.07 mg	38.6	33.3	6.00	7.20	190.4
2	2.34 mg	36.3	33.2	11.00	13.75	184.9
3	1.31 mg	35.9	32.5	∞	∞	∞
4	0.95 mg	37.1	31.0	10.00	15.10	145.1
5	0.71 mg	36.6	32.0	∞	∞	∞
6	0.96 mg	35.0	31.0	∞	∞	∞
7	1.03 mg	33.1	32.0	1.50	c	c
7	2.34 mg	33.0	32.0	2.50	4.03	148.4
8	0.96 mg	34.0	32.0	1.50	c	c
8	4.53 mg	35.0	32.0	2.75	—	—
9	2.34 μl	35.6	32.0	1.23	c	c
10	2.34 μl	33.9	32.0	1.88	c	c
11	2.34 μl	33.6	32.0	1.32	c	c
2	0.31 mg	39.2	33.6	9.00	15.00	44.2
2	0.84 mg	37.5	32.0	12.00	21.00	48.00
1	0.50 mg	39.3	32.0	>16.00	14.00	14.00
none	0.00 mg	40.6	34.0	>60.0	—	—
2	0.81 mg	38.3	32.0	13.00	20.75	111.7

^a Gel Modification Additives

- | | |
|---------------------------|--------------------------|
| 1 Tricyclopentylphosphine | 2 Tricyclohexylphosphine |
| 3 Triphenyl phosphite | 4 Pyridine |
| 5 Propylamine | 6 Tributylphosphine |
| 7 Benzonitrile | 8 Triphenylarsine |
| 9 Anhydrous Acetonitrile | 10 Thiophene |
| 11 Furan | |

^b Amount additive mg g^{-1} or $\mu\text{l g}^{-1}$ monomer

^c Too fast to measure

The results of the polymerization experiments are shown in Table 1.6. Besides the facts discussed, it can be seen that triphenyl phosphite, propylamine, and tributylphosphine effectively inhibit the polymerization reaction. In contrast, benzonitrile, triphenylarsine, anhydrous acetonitrile, thiophene, and furan accelerate the reaction (25).

1.2.4 Molecular Weight Regulating Agents

The regulation of the molecular weight of the ring opening polymer can be achieved through controlling the polymerization temperature, the type of catalyst, the type of solvent, and by adding a molecular weight regulating agent to the reaction system. Examples of suitable molecular weight regulating agents include α -olefins, such as ethylene, propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, and 1-decene, as well as styrene. 1-Butene and 1-hexene are particularly preferred (29).

The molecular weight regulating agent may utilize a single compound, or a mixture of two or more different regulating agents. The amount of the molecular weight regulating agent used is typically from 0.02 to 0.5 mol per mol of monomer.

1.2.5 Polymers

In general, ring opening polymers can be roughly classified into thermoplastic ring opening polymers and curing type ring opening polymers. The curing type ring opening polymers are obtained by bulk ring opening polymerization reaction using polymerization catalysts of relatively high activity, such as tungsten-based ring opening polymerization catalysts or molybdenum-based ring opening polymerization catalysts. The curing type ring opening polymers are used for making molded products by reactive injection molding (RIM) method.

In case of producing curing type ring opening polymers, generally, a reaction mixture containing the monomer and the ring opening polymerization catalyst is injected into a mold to carry out bulk ring opening polymerization.

Molded products can be obtained without employing melt molding methods, such as injection molding, extrusion molding, and

compression molding. In the production of heat curing type ring opening polymers, ring opening polymerization catalysts of high activity are selected and used for shortening the reaction time in the mold, whereby crosslinked cured polymers can be obtained.

Thermoplastic dicyclopentadiene ring opening polymers and their hydrogenation products are excellent in balancing various properties, such as heat resistance, transparency, water resistance, chemical resistance, electric properties, low birefringence, and stiffness. Therefore, they are used in a wide variety of fields, for example, as optical materials, medical equipment, electrical insulating materials and electronic part processing materials. The materials are fabricated by various molding methods, such as injection molding, extrusion molding, compression molding, and solvent casting.

Thermoplastic dicyclopentadiene ring opening polymers can be obtained by polymerizing dicyclopentadiene in the presence of a metathesis catalyst. Hydrogenated products can be obtained by hydrogenating the double bonds in the backbone. The hydrogenation results in improvement of various properties, such as heat resistance, weathering resistance, light resistance, etc. The properties can be still improved by adding suitable comonomers (6).

Various molded products can be made from the materials. In particular, transparent molded products can be obtained. The materials exhibit excellent mechanical strength, such as impact resistance, low permeation of water or water vapor and excellent solvent resistance. Therefore, they can be used for optical uses such as lens, prisms, and polarizing films.

Further, they can be used for medical purposes, such as press-through packages, disposable syringes, liquid medicine vials, and infusion bags. They are suitable for electric or electronic materials, such as wire coating. In addition, packaging films, such as wrapping films, stretch films, shrink films, and blister packs can be produced.

1.2.6 Copolymers

The preparation of copolymers and block copolymers does not make problems. For example, cyclopentadiene can be copolymerized with norbornene using the following procedure. Cyclopentadiene and the norbornene are mixed with benzene and added to the reactor

vessel. 1-Butene is added in 2% solution in benzene. Ethylaluminum sesquichloride, $(\text{CH}_3\text{CH}_2)_3\text{Al}_2\text{Cl}_3$, is added as a 0.5 molar solution in benzene followed by the addition of the tungsten hexachloride (0.20 molar in ethyl acetate or 0.05 molar in benzene). The reactions are conducted at about 25°C under stirring. The copolymerization reaction proceeds to completion in a short time and produces viscous smooth polymers (13).

Block polymers may be formed by allowing polymerizing with a single monomer. When the reaction is essentially finished, a second monomer is added. This means that the end groups are virtually living.

The molybdenum-based catalyst $\text{MoOCl}_2(\text{t-BuO})_2$ has been used to copolymerize norbornene and dicyclopentadiene (20). The polymeric product exhibits a single peak in gel permeation chromatography.

1.2.7 Thermosets

Common thermosets are cured by a free radical addition mechanism. These types of composites are cured by heat initiators, such as peroxides, or by photo initiators, such as α -diketones. A characteristic of cured acrylates is large shrinkage in the course of polymerization, which is undesirable for many uses. Another undesirable characteristic of acrylates is the formation of an oxygen-inhibited layer on the surface upon curing.

Another type of thermoset polymers is based on epoxy monomers. These thermosets are cured by use of a two-component system or by photo initiators. Disadvantages of epoxies are high water uptake in service and polymerization shrinkage (22).

Compositions that are curing by the principle of ROMP have been added to the spectrum of thermosets. These may be either one part compositions and two part compositions. The materials have a remarkably low shrinkage on curing. Therefore, typical applications are in the fields of dental applications or in automotive and electronic applications.

A dinorbornenyl dicarboxylate ester (DNBDE) is synthesized by the Diels-Alder reaction of cyclopentadiene with diacrylates, as shown in Figure 1.10. Alternatively, a DNBDE may be synthesized

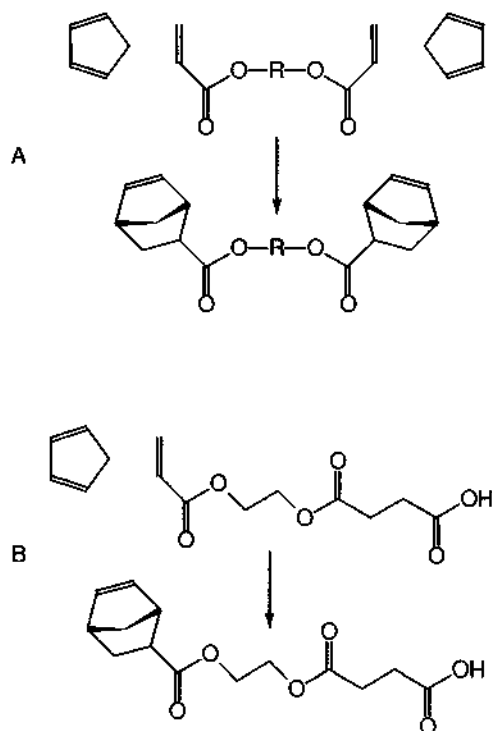


Figure 1.10: Diels-Alder Reaction of Cyclopentadiene with a Diacrylate (A). Diels-Alder Reaction of Cyclopentadiene with an Adduct of an Acrylate with Succinic Acid (B). The Product can be Dimerized with PEG.

via an esterification reaction. Cyclopentadiene can be reacted with the adduct of 2-hydroxyethyl acrylate with succinic anhydride to give a norbornenyl functional carboxylic acid (A), c.f., Figure 1.10. This is followed by esterification of (A) with PEG 400 using *p*-toluenesulfonic acid as a catalyst in cyclohexane with azeotropic removal of water (22).

In a similar way, norbornene 2-ethylhexyl carboxylate, norbornene isobornyl carboxylate, norbornene phenoxyethyl carboxylate, (5) are and related monomers are obtained. As catalysts, osmium or ruthenium catalysts similar to those shown in Figure 1.8 are used.

In addition, one component compositions comprise a reaction

Table 1.7: Shrinkage of Resin Compositions (22)

Monomer Type ^a	Shrinkage ^b /[%]
Aliphatic Acrylate Resin	9.2
Aromatic Methacrylate Resin	6.75
ROMP polymerized	3.75

^a Neat resin compositions, without filler^b Volumetric shrinkage

control agent, i.e., tetraallyl silane, which influences the kinetics of the reaction. The control reaction agent slows the metathesis reaction and thereby allows for an increase in the induction period before cure, or the pot life. Curing is achieved by heating to a temperature of 60–150°C.

In a two-component composition, the base paste contains the monomer and the catalyst paste contains the catalyst, which after mixing of the catalyst paste with the base paste, initiates the metathesis reaction of the olefinic substrate.

Clearly, for two part compositions, a reaction control agent may be used if desirable as a component of the base paste. Typical shrinkages of ROMP polymerized compositions and comparative values are shown in Table 1.7.

1.2.8 Reinforced Polymer Composites

Reinforced composite materials are widely used as structural materials for aerospace, automotive, and construction applications. These materials provide desirable properties, such as high stiffness and strength. Composites typically include a continuous matrix phase, usually a polymeric material or a ceramic material and a reinforcement phase. The reinforcement phase can be made of inorganic materials, including metals, ceramics, and glasses; or organic materials, including organic polymers and carbon fibers. Particularly good properties are obtained when the reinforcement phase contains fibrous materials (30).

The manufacture of fiber reinforced composites involves the combination of the fiber reinforcement and a liquid precursor to the matrix in a mold, followed by solidification of the liquid and formation of the matrix. This solidification can be the result of chemical reac-

tions, in which case the liquid precursor is referred to as a reactive liquid.

Although the reinforcing fibers may be present in the liquid precursor prior to dispensing, better properties are typically obtained when the fibers are initially present in the mold as a preform. The liquid is then dispensed into the mold such that the final matrix fills the mold and surrounds the fibers. Preforms may be arranged as mats or meshes. The fibers within the preform may be randomly oriented or may be oriented in one or more directions.

The performance of composites is influenced by many factors, including the amount of reinforcement present relative to the matrix, referred to as fiber loading and the degree of contact between the fibers and the matrix. Both strength and stiffness tend to be improved by an increase in fiber loading and by increased contact between the phases.

To ensure sufficient contact between the fibers and the matrix, it is desirable to use a liquid precursor with a low viscosity. Reactive liquids are usually preferred over thermoplastics due to the low viscosity of liquids relative to polymer melts. The reactive liquid is typically a multi-component mixture. The reactive liquid may contain a monomer and an activator, which will cause the monomer to polymerize into a solid polymer matrix.

In RIM processes, two or more reactive components are mixed together, starting the reaction between the components before the mixture is dispensed into the mold. This tends to increase the viscosity of the liquid that is dispensed due to an increase in molecular weight of the polymers or pre-polymers formed in the initial reaction. An increased viscosity can prohibit complete filling of the mold and permeation of the preform. This tends to decrease the adhesion between the matrix and the fibers. Poor interfacial adhesion between the reinforcement and matrix phase can cause a material to have less than desirable stiffness and strength.

Norbornene polymers or polymers from dicyclopentadiene, respectively, may be formed by the interaction of a cyclic olefin with a ROMP catalyst. Increased reinforcement density provides for extremely high stiffness and strength in poly(norbornene) composites. As catalyst, Phenylmethylene-bis-(tricyclohexylphosphine) ruthenium dichloride is used (30).

1.2.9 Polymers with Functional Groups

As mentioned before, problems with monomers with functionalities with acid hydrogen have been encountered with some types of catalysts. Now, the direct incorporation of polar functional groups along the backbone of linear polymers made via ROMP is possible due to the development of functional group-tolerant late transition metal olefin metathesis catalysts (10).

The ROMP of alcohol, ketone, halogen, and acetate substituted cyclooctenes with a ruthenium olefin metathesis catalyst has been reported (31).

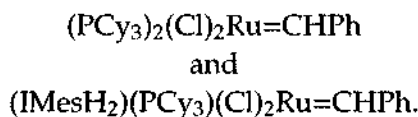
The interest of functional polymers originates among others in the fact that for example, the hydroxyl group imparts barrier properties of the polymer.

The asymmetry of the substituted cyclooctene allows for head-to-head (HH), head-to-tail (HT), and tail-to-tail (TT) coupling, yielding a polymer with regio-random placement of the functional groups.

A similar problem was encountered by the ROMP of a borane substituted cyclooctene with an early transition metal catalyst followed by oxidation to yield an alcohol-functionalized linear polymer (32).

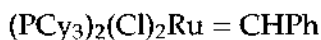
However, the regio-random distribution of functional groups can be avoided by an acyclic diene metathesis (ADMET) polymerization technique using symmetric monomers (33). The molecular weights of these polymers are restricted to $< 3 \times 10^4$ Dalton by ADMET. Due to their rich hydrocarbon content, the barrier properties in final ethylene vinyl alcohol copolymers are reduced.

The ROMP of alcohol or acetate disubstituted cyclopentene monomers is not possible by catalysts such as



Mes represents mesityl (2,4,6-trimethylphenyl), Ph is phenyl and Cy is a cyclohexyl radical.

Ruthenium bisphosphine complexes



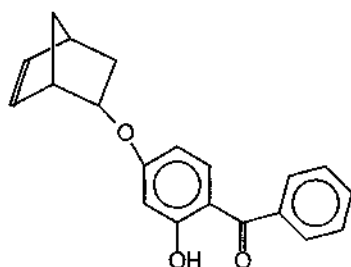


Figure 1.11: Monomer with UV-absorbing Functionality: (4-(Bicyclo[2.2.1]hept-5-en-2-ylmethoxy)-2-hydroxyphenyl)phenyl-methanone

are somewhat more reactive. Completely regio-regular polymers can be prepared by using a symmetric bicyclic or polycyclic olefin as the monomeric substrate for the ROMP reaction.

In order to synthesize telechelic polymers, the ROMP reaction is carried out in the presence of acyclic olefins that act as chain transfer agents to regulate the molecular weight of the polymers produced.

When α, ω -difunctional olefins are employed as chain transfer agents, difunctional telechelic polymers can be synthesized. Such difunctional olefins are the preferred chain transfer agents. When carrying out a ROMP reaction using a symmetric α, ω -difunctional olefin as a chain transfer agent, the propagating alkylidene generated during the ring opening metathesis process is terminated with a functional group.

The new functionally substituted alkylidene reacts with a monomer to initiate a new polymer chain. This process preserves the number of active catalyst centers and leads to symmetric telechelic polymers with a functionality that approaches 2. The only polymeric end groups that do not contain residues from the chain transfer agent are those from the initiating alkylidene and the endcapping reagent. Basically, these end groups could be chosen to match the end group from the chain transfer agent.

Monomers with UV-absorbing functionality, such as shown in Figure 1.11 can be copolymerized with norbornene to have the UV-absorber bond to the polymeric backbone. (4-(Bicyclo[2.2.1]hept-5-en-2-ylmethoxy)-2-hydroxyphenyl)phenyl-methanone is prepared by first synthesizing 4-allyl-2-hydroxyphenyl-phenyl-methanone

Table 1.8: Compounds with UV-absorbing Groups (34)

Compound
(2,4-Dihydroxyphenyl)-phenylmethanone
2-Benzotriazol-2-yl-4-methylphenol
4-Benzotriazol-2-ylbenzene-1,3-diol
3-[3- <i>tert</i> -Butyl-5-(5-chlorobenzotriazol-2-yl)-4-hydroxyphenyl]-propionic acid
3-[5-(Benzotriazol-2-yl)-3- <i>tert</i> -butyl-4-hydroxyphenyl]-propionic acid
4-(4,6-Diphenyl)-1,3,5-triazin-2-yl-benzene-1,3-diol
4-[4,6-Bis-(biphenyl-4-yl)-1,3,5-triazin-2-yl]-benzene-1,3-diol
4-[4,6-Di-(2,4-dihydroxyphenyl)-1,3,5-triazin-2-yl]-benzene-1,3-diol
<i>N'</i> -2-Ethylphenyl- <i>N'</i> -2-hydroxyphenyloxalamide

from allyl bromide and 2,4-dihydroxybenzophenone and then allowing a Diels-Alder reaction with dicyclopentadiene. Dicyclopentadiene decomposes into cyclopentadiene before the Diels-Alder reaction occurs.

Oligomers with 1-hexene as comonomer with a degree of polymerization of around 10 are prepared and the double bonds in the oligomeric chains are hydrogenated subsequently (34). For the preparation of the oligomer, as catalyst, bis-(tricyclopentylphosphine)-dichloro(3-methyl-2-butenylidene) ruthenium (APT Cat ASMC 716) is used. A pale brown solid with a melting range of 88–94°C and a number-average molecular weight M_n of 5900 Dalton is obtained.

Besides of (2,4-dihydroxyphenyl)-phenylmethanone, many other compounds with suitable UV-absorbing groups can be used. These compounds are listed in Table 1.8. The oligomeric UV-absorber is mixed with low density poly(ethylene) in a typical formulation, with an amount of 0.8% by weight.

1.2.10 Poly(acetylene)s

In 1975, it was discovered that WCl_6 , which is a typical metathesis catalyst, is capable to catalyze the polymerization of phenylacetylene. Subsequently, various substituted acetylenes have been polymerized by this type of catalyst. In 1983, poly(1-(trimethylsilyl)-1-propyne) was synthesized in the presence of $TaCl_5$ and $NbCl_5$ (35).

The alkyne polymerization has many similarities with ROMP.

The polymerization of substituted alkynes is postulated to proceed either by the metathesis mechanism or by an insertion mechanism (18). Numerous alkyne derivatives have been shown to polymerize in the presence of group V, VI, and VIII transition metal catalysts.

1.3 Properties

1.3.1 Mechanical Properties

trans-Polypentenamer can be obtained from cyclopentene by ROMP. This material is highly commended. The glass transition temperature is close to natural rubber. The *cis*-isomer, *cis*-polypentenamer has the lowest glass transition temperature of any known hydrocarbon polymer of -113°C (36).

1.3.2 Optical Properties

Transparent resins are used as the materials for molded products, such as automobile components, illumination equipment, and electrical components. Transparent resins, which can be applied to such applications, include poly(carbonate) (PC)-based resins and acrylic-based resins.

However, although acrylic-based resins offer excellent transparency, they have problems in terms of heat resistance and water resistance. In contrast, PC-based resins offer superior performance to acrylic resins in terms of heat resistance and water resistance, but suffer from different problems, such as a high birefringence.

Certain norbornene derivatives, for example, 5-(2-naphthalene-carbonyloxy)bicyclo[2.2.1]hept-2-ene or 5-(4-biphenylcarbonyloxy)-bicyclo[2.2.1]hept-2-ene produce a polymer that is effective in producing molded products with excellent transparency, low water absorption, and low birefringence (29).

The norbornene derivative is polymerized by a ring opening metathesis polymerization, followed by a hydrogenation reaction. The polymers can be used for optical disks, optical lenses, and optical films or sheets.

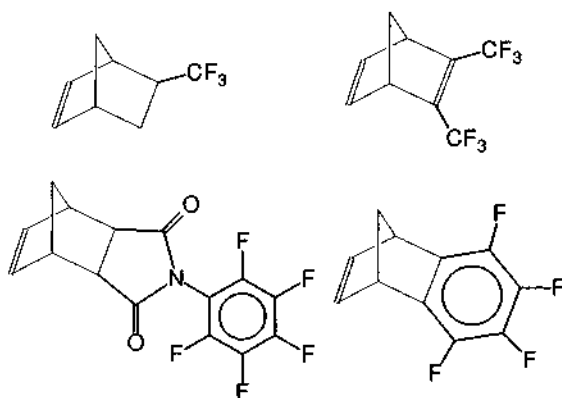


Figure 1.12: Fluorinated Monomers Suitable for ROMP (36)

1.4 Fabrication Methods

The best known polymerization of norbornene is the ring opening metathesis polymerization. The reaction is technically applied in the Norsorex process (7).

1.5 Fluorinated Polymers

The synthesis of highly fluorinated cyclopentenes by ROMP is not successful. This is attributed to the free energy of polymerization of five membered rings, which is close to zero.

This obstacle can be overcome by moving electron withdrawing substituents away from the double bond and increasing the reactivity of double bond by positioning it in a strained ring. This is achieved using bicyclic monomers. The monomers are readily obtained from the Diels-Alder reactions of substituted olefins with cyclopentadiene. This route is effective also for fluorinated monomers. These types of monomers undergo a ROMP with a variety of one component and two-component initiator systems.

A wide variety of fluorinated monomers has been investigated with respect to the ability to undergo ROMP. Examples are shown in Figure 1.12.

The catalysts were synthesized either from the reaction of transition metal chlorides, WCl_6 , $MoCl_5$, $OsCl_3$, $RuCl_3$, $IrCl_3$, $ReCl_5$ with the monomers, or generated by reactions of the transition metal chlorides with alkylating agents, such as Ph_4Sn , Bu_4Sn , $(CH_3)_4Sn$, etc.

1.6 Special Additives

In general, any additives that are common in the polyolefin sector can be used to achieve the desired properties. We will summarize additives for thermoplastic metathesis polymers. These include (6):

- Plasticizers,
- Foaming Agents,
- Flame Retardants,
- Antioxidants,
- Near infrared absorbers,
- Antistatic agents,
- Lubricants, and
- Anti-fogging agents.

Plasticizers include tricresyl phosphate and trixylyl phosphate. Foaming agents can be added in the case of using the polymers for wires, which require low dielectric constant and low dielectric loss tangent, such as communication cables, coaxial cables for computers and high-frequency cables.

Flame retardants are preferably added for wires, such as high-voltage power cables through with a large quantity of current flows. Antioxidants include phenolic antioxidants, phosphorus antioxidants and sulfur antioxidants.

Near infrared absorbers include cyanin compounds, pyrylium compounds, phthalocyanine compounds, and dithiol metal complexes. Antistatic agents include long chain alkyl alcohols and fatty acid esters with polyhydric alcohols. Stearyl alcohol and behenyl alcohol are the especially preferred compounds. Anti-fogging agents include sorbitan fatty acid esters and glycerin fatty acid esters.

1.7 Applications

Thermoplastic cyclic olefin polymers can be used for a wide range of applications, such as wire coating materials, agricultural films, and packaging films, and toner resins. Further, optical applications such as plate lenses, including *Fresnel* lenses have been described (6).

1.7.1 Packaging Films

Copolymers of ethylene and norbornene exhibit excellent transparency, high moisture barrier, high strength and stiffness, and low shrinkage. In comparison to poly(ethylene) (PE) and poly(propylene) (PP), they show a very low gas permeability. They are used for blister packaging in pharmacy applications and for flexible films for food packaging. Multilayer films consisting of PP outer layers and a cyclic olefin copolymer are in use.

1.7.2 Wire Coating Materials

The product of hydrogenation of a thermoplastic dicyclopentadiene ring opening polymer may be used as wire coating materials. Crosslinking agents, foaming agents, flame retardants, and other polymers can be added to the formulation (6). As crosslinking agents, organic peroxides, or photosensitive initiators can be used.

Foaming agents can be added for the fabrication of wires, which require low dielectric constant and low dielectric loss tangent, such as communication cables, coaxial cables for computers, and high-frequency cables.

Examples of foaming agents are sodium bicarbonate, ammonium bicarbonate and nitroso compounds. Especially, when dinitrosopentamethylenetetramine is used, foaming aids can be added that accelerate the decomposition and reduce the decomposition temperature. This is achieved, for example, with salicylic acid, or with urea. Various chlorine and bromine flame retardants can be used as halogen-based flame retardants, e.g., tetrabromobisphenol A derivatives.

The wire coating material can be coated on a conductor by co-extruding the conductor and the molten material in an extrusion molding machine. The compound is provided in the form of pellets.

The same extruder as in wire coating with PE can be used. However, since the cyclic olefin polymer composition has a higher in glass transition temperature than PE, the cylinder temperature of the extruder must be set to a somewhat higher temperature than used in the conventional method.

When the material is dissolved in an organic solvent and provided as a varnish, the varnish can be directly coated on the conductor. These methods can be optionally selected according to the thickness of the coating material and other desired properties.

1.7.3 *Chromatographic Supports*

There are various types of supports used in chromatography, including inorganic supports based on silica, zirconia, titania or aluminum oxide, further, organic supports based on crosslinked poly(styrene), poly(acrylate), and poly(methyl methacrylate). More recent developments are the preparation using sol-gel technology, and ROMP polymerization. The various issues are reviewed in the literature (37). Monolithic materials were introduced in separation science in the late 1960s. There is a perpetual progress in this topic (38).

Support materials for solid phase extraction (SPE) and for chromatographic techniques have been prepared by ROMP. pH-stable high capacity stationary phases have been prepared by copolymerization of functional monomers with a suitable crosslinking agent, with precipitation polymerization techniques.

The suspension polymerization of norborn-5-ene-2,3-dicarboxylic anhydride in dichloromethane using a molybdenum-based initiator results in living, linear polymer chains with the active initiator at the polymer chain end. The solubility of the poly(norborn-5-ene-2,3-dicarboxylic anhydride) is dependent on the chain length.

Oligomers with a degree of polymerization up to 10–15 are soluble, whereas higher oligomers are insoluble. Thus, by adjusting an appropriate degree of polymerization, a precipitation type polymerization can be achieved.

In the second stage a crosslinking agent, e.g., 1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene is added, which forms the crosslinked matrix. A polymer is formed where the linear oligomer chains are fixed at the crosslinked matrix as pendent groups.

In the last stage of polymerization the products are endcapped with ferrocenealdehyde or benzaldehyde in order to remove the molybdenum catalyst from the material (19). The actual removal of catalyst occurs by a treatment with aqueous sodium hydroxide, which is followed by a treatment with hydrochloric acid. Thereby the anhydride functionalities are hydrolyzed (39).

The materials were tested as supports for SPE techniques. Excellent recoveries are observed, exceeding silica-based SPE materials (40). The supports were also investigated for their retention behavior for phenols, alcohols, carboxylic acids, aldehydes, ketones, esters, chloroalkenes, and polycyclic aromatic hydrocarbons (41).

In the same way, dipyridyl amide-functionalized supports suitable for the SPE of metal ions from aqueous solutions can be prepared. The resins are synthesized via the copolymerization of the functional monomer *endo*-norbornene-5-yl-*N,N*-di-2-pyridyl carboxylic amide with a molybdenum-based catalyst (42). Essentially no loss of performance was observed after extensive use over more than twenty cycles. After exposure to air for at least 2 months, a change in color from bright white to yellow was observed. However, this change in color did not influence the characteristic properties of the resins.

Separations of enantiomers can be achieved by chiral chromatography. Even, when the enantioselective synthesis of drugs and pharmaceuticals is possible, a major part of chiral compounds is still produced as a racemate and needs to be separated into the enantiomers by chiral high performance liquid chromatography.

Chiral stationary phases (CSP) have been synthesized by ROMP techniques. The separation of dinitrobenzoylphenylalanine can be achieved on a poly(*N*-(norborn-5-ene-2-carboxyl)-*L*-phenylalanine ethylester) grafted to Nucleosil 300-5 (43).

Norbornene was functionalized with cyclodextrins and surface grafted onto silica-based supports using ROMP (44). The CSP are suitable for the enantioselective separation various amino acids, including β -blockers and other compounds, such as chiral ferrocene derivatives.

Materials prepared by the ROMP technique find use in monolithic capillary columns (45,46), and monolithic membrane discs (47). A monolithic column is a column in which the stationary phase is

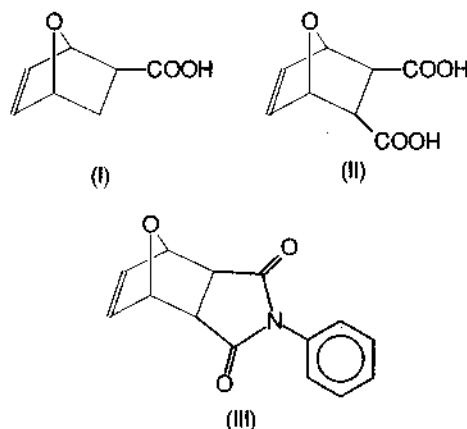


Figure 1.13: Functional Monomers Used for Monolith Grafting: 7-Oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid (I), 7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid anhydride (II), and *N*-Phenyl-7-oxabicyclo[2.2.1]5-heptene-2,3-dicarboximide (III)

cast as a solid, porous rod. Traditionally, the stationary phase is packed in form of particles into the column. In the present context, crosslinked, functionalized organic polymers can find application as monolithic stationary phase.

In the case of capillary columns, in the initial step of preparation the surface is modified with bicyclo[2.2.1]hept-2-en-5-ylmethyldichlorosilane. This acts as an anchor for subsequent ROMP polymerization. Some functional monomers used for monolith grafting are shown in Figure 1.13.

1.8 Suppliers and Commercial Grades

Industrially, ROMP is used for the production of cheap highly unsaturated polymers e.g., Norsorex, Vestenamer. For example, poly-(norbornene) is produced in quantities of around 5 k t a^{-1} , under the tradename of Norsorex (18). Examples for commercially available grades and tradenames are shown in Table 1.9. Tradenames appearing in the references are shown in Table 1.10.

Table 1.9: Examples for Commercially Available Metathesis Polymers

Tradename	Producer	Remarks
Vestenamer®	Degussa AG	Poly(octenamer)
Norsorex®	Arkema Corp.	Poly(norbornene)
Norsorex®	CDF Chimie	Poly(norbornene)
Telene	BF Goodrich	
Metton®	Hercules	
Zeonex®	Nippon Zeon	Cyclic olefin polymer
Arton®	Japan Synthetic Rubber	Cyclic olefin copolymer
Topas®	Daicel	Ethylene and norbornene copolymers

Table 1.10: Tradenames in References

Tradename Description	Supplier
Chimassorb® 81 2-Hydroxy-4-(octyloxy)benzophenone (23)	Ciba Geigy
Dowlex® NG 5056E 1-Octene/ethene copolymer (LLDPE) (34)	Dow
Dyneema® Gel-spun poly(ethylene) fiber in thermoplastic rubber matrix (23)	DSM High Performance Fibres
Ethanox® 330 1,3,5-Trimethyl-2,4,6-tris(3,5-di- <i>tert</i> -butyl-4-hydroxybenzyl)benzene (23)	Albemarle Corp.
Ethanox® 702 4,4'-Methylenebis(2,6-di- <i>tert</i> -butylphenol) (23)	Albemarle Corp.
Hitacol Poly(sulfide) (15)	Hitachi Kasei K.K.
Irgafos® 168 Tris(2,4-di- <i>tert</i> -butylphenyl)phosphite (23, 34)	Ciba Specialty Chemicals
Irganox® 1010 Pentaerythritol tetrakis(3-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)propionate), phenolic antioxidant (23)	Ciba Geigy
Irganox® 1076 Octadecyl-3-(3',5'-di- <i>tert</i> -butyl-4'-hydroxyphenyl) propionate (23)	Ciba Geigy
JSR BR-01 <i>cis</i> -1,4-Poly(butadiene) (15)	Japan Synthetic Rubber Co.
Kevlar® Aramid (23)	DuPont
Naugard® XL-1 <i>N,N'</i> -Bis[2-(3-[3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl]propionyloxy)ethyl]-oxamide (34)	Uniroyal Chemical Co.
Riblene® FF 29 LDPE pellets (34)	Enichem
Tinuvin® 144 Bis(1,2,2,6,6-pentamethyl-4-piperidiny)l butyl(3,5-di- <i>tert</i> -butyl-4-hydroxybenzyl)malonate, UV absorber (23)	Ciba Geigy
Tinuvin® 327 2,4-Di- <i>tert</i> -butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol, UV absorber (23)	Ciba Geigy

Table 1.10 (cont): Tradenames in References

Tradename Description	Supplier
Tinuvin® 328 2-(2'-Hydroxy-3',5'-di- <i>tert</i> -amylphenyl)benzotriazole, UV absorber (23)	Ciba Geigy
Tinuvin® P 2-(2'-Hydroxy-5'-methylphenyl)benzotriazole, UV absorber (34)	Ciba Geigy
Twaron® Aramid (23)	Teijin Twaron B.V.
Ultrene® Dicyclopentadiene (23)	Cymetech, LLC.
Viron-200 Polyester (15)	Toyo Boseki K.K.
Wingstay® SN-1 (3,6,9-Trioxaundecyl)bis(dodecylthio)propionate, antioxidant for the vulcanization of rubber (23)	Goodyear Tire & Rubber Co.
Zylon® Poly(<i>p</i> -phenylene-2,6-benzobisoxazole) (PBO) fiber (23)	Toyobo

1.9 Safety

Cyclopentene and norbornene are highly flammable and harmful in contact with skin, eyes and the respiratory system. For poly(norbornene) no special hazards are reported. On handling, the usual precautions should be applied.

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