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## TRENDS IN RING-OPENING METATHESIS POLYMERIZATION

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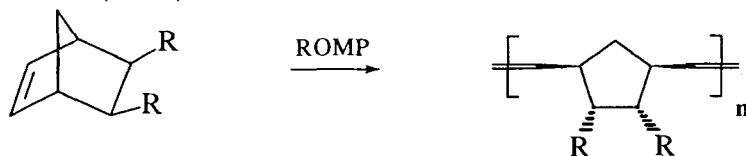
### ABSTRACT

Several transition metal alkylidene complexes are first discussed as catalysts for the ring-opening metathesis reaction. A new ruthenium catalyst with a slightly enhanced reaction rate is introduced. The stereochemistry and kinetics of the catalysts are investigated with different norbornene derivatives. Then it is shown that  $MgCl_2$  alone is a good heterogeneous catalyst for the ring-opening polymerization (ROMP) of norbornene compounds. This is the first catalyst which does not need activation by a transition metal compound or another organometallic cocatalyst. Applications of the ROMP reaction for the synthesis of polymer specialities covering conjugated liquid crystals and optically active polymers are shown. Poly(cyclopentadienylene vinylene) and sidechain liquid crystal polymers are discussed in more detail. Finally, the synthesis of liquid crystalline elastomers by incorporation of bifunctional monomers during the ROMP reaction is described. It is shown that this kind of polymer can be used for the fabrication of optically anisotropic materials.

### INTRODUCTION

The synthesis of specialty polymers has gained high interest during the last decades. The scientific efforts have concentrated more and more on either making cheap polymers like polyolefins better or on the development of specialties which

are perfectly adopted to a very specific problem. Such “tailor-made” polymers must have a regular chemical structure, narrow molecular weight distribution, well-defined morphology, phase transitions, and so on. To achieve all these properties, the mechanism of the polymerization reaction must be clear. One reaction matching these conditions is Ring-Opening Metathesis Polymerization (ROMP) as outlined in Eq. (1) for an *exo,exo*-2,3-disubstituted norbornene:



As catalysts, complexes of transition metals have been mainly used, often as a mixture of an inorganic complex or salt (“catalyst”) of a transition metal, an organo-metallic compound of a main group metal (“cocatalyst”) and sometimes a third activating compound (“activator”). From these “classical metathesis catalysts” one never knew the true concentration of the active compound because its detailed chemical structure was unknown, so models depend mainly on the imaginative power of the scientist. This changed when well-defined single compound initiators were developed, which made the theory of Chauvin a reality. Since it has been shown that transition metal alkylidene complexes are active in ROMP, and in some cases the transition compounds could be detected, the “Chauvin mechanism” is considered as the mechanism of olefin metathesis reactions [1].

Initiators were developed which allowed good prognoses of structural details of the resulting polymers. Therefore, polymers with very specific properties can be developed, and we are now confronted with a real boom in research in this field. This paper is devoted to some of these recent developments and will deal with the “catalysts” (which should more correctly be named “initiators” according to some authors), polymers, and applications. Finally, some trends for the future will be discussed.

## CATALYSTS

Figure 1 shows a survey of the most important catalysts and catalyst systems at this time. We will focus on compounds **3.c**, referred to as “Schrock-type carbenes” (**3.c**<sub>*t*-but</sub> as drawn, **3.c**<sub>F<sub>6</sub></sub> for the hexafluoro-*t*-butyloxilates), on compounds like **3.e**, referring them as “Grubbs-type carbenes,” and on some new heterogeneous catalysts developed in our laboratory.

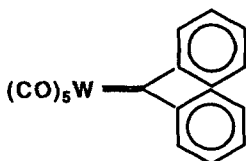
### Molybdenum Alkylidenes

The main advantage of Schrock’s carbenes **3.c** is their well-known mechanism. It has been shown that their activity, stereoselectivity, and compatibility with hetero-atoms is largely dependent on the nature of the alkyloxy substituents. From the great number of different ligands, *t*-butyloxy-molybdenum initiators have dominated for the first routine polymerizations with new monomers. Compared to the analogous tungsten carbenes, they show less side reactions (e.g., ionic polymerization with loss of double bonds, Friedel-Crafts alkylation of the aromatic solvents), and in most cases the polymerization can be considered to follow the Chauvin

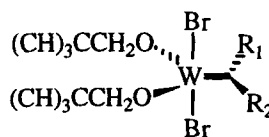
## 1. "classical" systems

1a  $\text{WCl}_6/\text{R}_x\text{AlCl}_{3-x}$ ; (also  $\text{MoCl}_5$  and  $\text{ReCl}_5$  + alkylating agent,1b  $\text{WCl}_6/\text{SnR}_4$ ;2. water compatible systems:  $\text{K}_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$ ,  $[\text{Ru}(\text{H}_2\text{O})_6] \text{tos}_3$ 

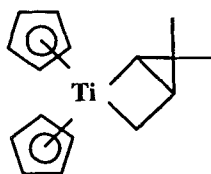
## 3. Carbenes or metalalkylidenes:



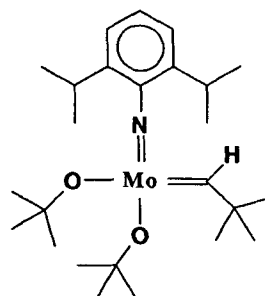
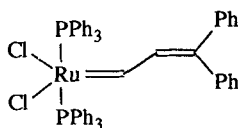
3a) Casey, 1974



3b) Osborne, 1986

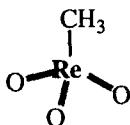


3.d Grubbs, 1986▲ 1992▼. 3.e



3.c Schrock, 1986

## Mixed type:



3.f Herrman, 1991

FIG. 1. Some examples of metathesis catalysts.

mechanism [2] as shown in Fig. 2. Therefore, we were able to show that in a series of substituted norbornenes and norbornadienes, the structure changes from all-*trans* to all-*cis* polymers (compare Fig. 3).

Chiral ligands were recently introduced in the initiating complex. The first example for an initiator with such a ligand was a molybdenum alkylidene with disubstituted binap (2,2'-bishydroxy binaphthyl) [3]. This initiator yielded an all-*cis* polymer with completely regular tacticity when applied to the polymerization of 2,3-bis(trifluoromethyl)norbornadiene, but it was difficult to determine which tacticity it was. Eventually, it was determined to be isotactic from dielectrical measurements [4].

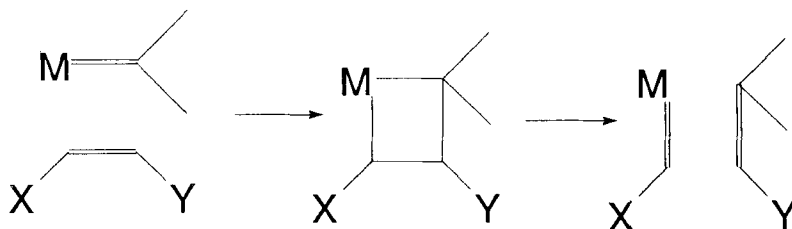


FIG. 2. Chauvin mechanism of the olefin metathesis reaction.

From our investigations on initiators with chiral ligands, we know that there are differences in speed and in microstructure which depend on the initiator and on the monomer. We have carried out investigations on enantiomerically pure norbornenyl compounds. With various catalysts of type 3.c we had already found changes in the regularity of the microstructure of the main chain. First preliminary results with different enantiomers of tartrates, fencholates, and terpeneolates show dramatic changes in the *cis/trans* ratio and tacticity [5]. Beginning with pure enantiomers, more detailed investigations on other initiators with chiral ligands are underway.

### Ruthenium Complexes

Ruthenium salts have been used as catalysts for ROMP for a long time. In the late 1980s Novak and Grubbs found that aqueous complexes are not only resistant to traces of water, but, in contrast to other systems, some of the ruthenium salts

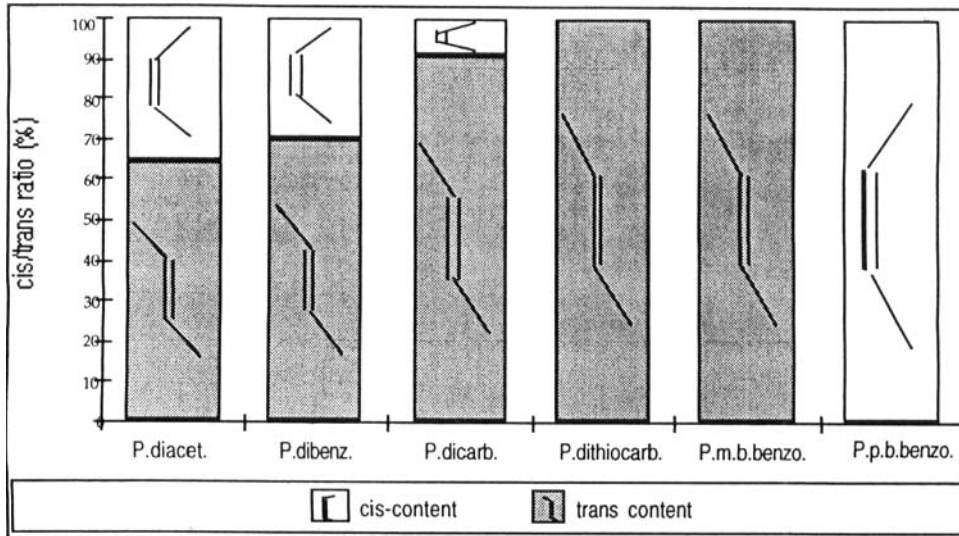


FIG. 3. *cis/trans* ratio of different precursor polymers. P.diacet. = poly(norbornenediacetate), P.dibenz. = poly(norbornenedibenzoate), P.dicarb. = poly(norbornenedicarbonate), P.dithiocarb. = poly(norbornenebis(*S*-methyldithiocarbonate)), P.m.b.benzo. = poly(methylbenzylidenebenzonorbornadiene), P.p.b.benzo. = poly(phenylbenzylidenebenzonorbornadiene).

even show increased activity if used in aqueous solution [6]. In order to illuminate the mechanism of this reaction, Grubbs' group synthesized the first carbene compound of ruthenium (example **3.e** in Fig. 1) [7], which was also active in ROMP. The exchange of the triphenylphosphine ligands with tricyclohexylphenyl ligands improved the activity, but still the starting step was somewhat slow. By introducing fluorinated phenyls at the carbene (see Fig. 4), the initial step was activated.

This increased the rate of initiation and the growing rate (Fig. 5). Another advantage of the system was that in contrast to classical systems and to molybdenum initiators, it now polymerized *endo,endo*-dicarboxylated norbornenylenes faster than the respective *exo,exo*-monomers [8]. The stereoregularity was quite good, but with 85% *trans* not as good as with the hexafluoro-Mo initiator **3.c**<sub>t-but</sub>.

## HETEROGENEOUS CATALYSTS

Heterogeneous catalysts have not played any important role in applications of ROMP until recently. Most heterogeneous catalysts were used in metathesis reactions of low molecular weight compounds, mainly monoolefins. There were several systems named in the literature, but most did not show any advantage compared with homogeneous systems. In contrast, it was difficult to remove the catalyst from the polymer. In addition, the systems either needed a cocatalyst and/or activation compounds [1], some of which are not very healthy. Therefore, these systems have not gained prominence in ROMP until now. There were also some attempts to use heterogenized homogeneous systems. A highly active system was described by Weiss [9]. It stemmed from the reaction of Mo-alkylidynes with silica. These catalysts exhibit superior activities.

Simple catalysts for the olefin metathesis reaction derived from transition metal oxides required higher temperatures and were mainly used for petrochemical reactions. It was quite a surprise when we found that anhydrous magnesium chloride, which has a morphology similar to that of MgCl<sub>2</sub> which is used as a carrier for Ziegler catalysts, shows quite a high activity in the polymerization of strained rings such as cyclobutene, norbornene, norbornadiene, and derivatives thereof [10]. Even though the weight ratio of MgCl<sub>2</sub> to monomer is quite high and the reproducibility

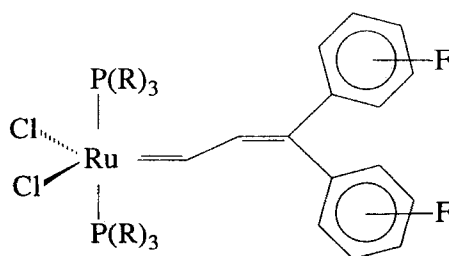


FIG. 4. 1-Ruthena-4,4-bis(fluorophenyl)-1,3-butadiene used as ROMP initiator with R = cyclohexyl, F in the *m*- or *p*-position.

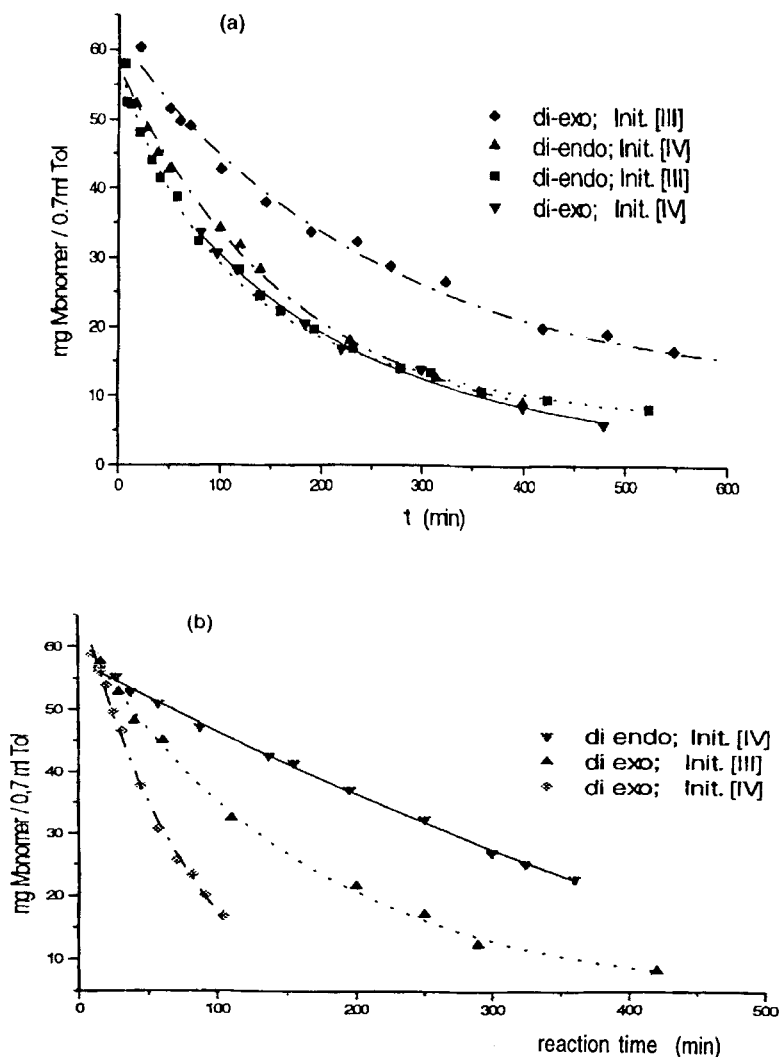


FIG. 5. (a) Polymerization of 2,3-norbornenylenediacetates, and (b) norbornene-2,3-methylcarboxylates.

in the synthesis of active phases is not good, the advantages are clear:  $\text{MgCl}_2$  is cheap, environmentally safe, and can be washed out with water. It leads to polymers with very high molar mass and a *cis/trans* ratio similar to classical catalysts and to the “*t*-butyl initiator,” the IR and NMR spectra being almost identical. The monomers polymerized with  $\text{MgCl}_2$  up to now are derivatives of norbornene and cyclobutene [11]. We are currently investigating the mechanism involved. There are no indications that a mechanism different from those for the homogeneous initiators in the systems mentioned above is involved. The disadvantage is that  $\text{MgCl}_2$  reacts only with highly strained cycloolefins.

## POLYMERS FOR SPECIAL APPLICATIONS

ROMP was primarily used for the synthesis of synthetic rubbers from cyclopentene, cyclooctadiene, norbornene, and derivatives thereof by using various catalyst systems. Control of stereochemistry and molar mass was difficult and often impossible with "classical systems." The number of different functionalities tolerated by these catalysts was restricted to hydrocarbons, and the only heteroatoms were oxygens in ethers and esters.

With the new initiators of types **3.c** and **3.e**, the palette of functionalities tolerated has broadened with increased control of molar mass and of stereochemistry. In the meantime, in most cases one can find the right initiator for synthesizing the required polymer (e.g., defined tacticity) from a chosen monomer, as some examples will show.

For the polymerization of bistrifluoromethylnorbornadiene, Feast and co-workers showed that the tacticity and *cis/trans* ratio are changed from mainly *trans* to all-*cis* isotactic if one switches from the use of the *t*-butyloxy initiator **3.c**<sub>*t*-but</sub> to the analogous hexafluoro-*t*-butyl carbene **3.c**<sub>F6</sub>. This material has a high dielectric constant [6].

Similar results were obtained in our laboratory with some polymers we synthesized with respect to some special properties. We discuss those in what follows.

## Conjugated Polymers

The application of ROMP for the synthesis of conjugated polymers started when Edwards and Feast published their route to polyacetylene via the precursor poly(bistrifluoromethyltricyclodecatriene) [12]. This method has been improved by variation of the substituents and increasing the temperature of conversion in the thermolytic step. It has been used by several groups [13]. In general, this method is still one of the best for the synthesis of polyacetylene in a constant reproducible way, although the highest values of conductivity were reported for doped polyacetylene from direct polymerization with aged Ziegler catalysts [14].

The method opened the door to a lot of other polymers. A combination of ROMP and thermal acid elimination from esters led to high molecular poly(*p*-phenylene vinylene) (PPV) [15, 16] or to poly(cyclopentadienylene vinylene), which has been a topic of the investigations of several groups in recent years [17–19]. The synthetic principle is shown in Fig. 6.

The advantages of these methods are clearly a well-controllable molar mass average with narrow distribution and a controllable stereochemistry (e.g., *cis/trans* ratio, tacticity), but there are also some problems, especially because of the relatively high temperatures  $t_c$  ( $200 < t_c < 350^\circ\text{C}$ ) necessary for the formation of the

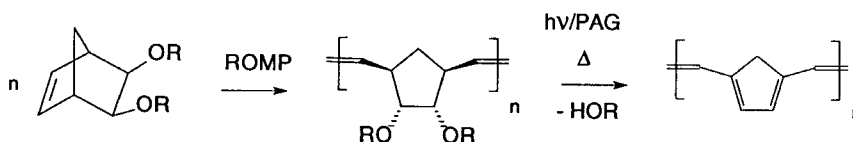


FIG. 6. Synthesis of poly(arylenes vinylene)s via ROMP.



conjugated double bonds via thermal elimination. If an organic acid is used as a catalyst, this temperature can be reduced to  $< 100^{\circ}\text{C}$ . A possibility of high technological value is the use of photo-acid generators to catalyze the elimination because this enables not only low conversion temperatures but also the fabrication of structures via photoresist technology. Either direct imaging by UV in a transparent layer or the formation of conjugated structures in a nonconjugated matrix is close to reality [20].

### Block Copolymers

Because of the "living" mechanism of ROMP with metal alkylidene initiators, one is able to form di- or triblock copolymers of different kinds. This has been established for conjugated/nonconjugated polymers. Well-defined chemical conjugation lengths of polyacetylene blocks in polynorbornene have been synthesized [21]. This opened the way to nanostructured materials [22, 23] which could be of great interest with respect to future applications in the field of molecular electronics.

### Optically Active Polymers

If one starts the polymerization with pure enantiomers, one gets polymers with high optical activity. As examples, norbornenyl esters [24], several disubstituted norbornenes and norbornadienes [25], and finally a pure enantiomer of *N*-(methylbenzyl)-2-aza-norbornene-3-carboxylate (see Fig. 7) [7] were polymerized. The higher the order in the polymer chain (e.g., because of the use of the hexafluorocatalyst), the higher is the value of the specific molar rotation. In addition, this gives us a much better possibility to investigate the stereochemistry of the polymerization because of the reduced number of different diad structures compared to racemic monomers.

This 2-aza-norbornene derivative is the favorite for our investigations on chiral catalysts for several reasons: 1) it is quite easy to synthesize, 2) it can be considered to be a derivative of an  $\alpha$ -amino acid, 3) it polymerizes readily, and 4) protons sensitive to stereochemical differences can be well resolved in the NMR spectra [26] but yield complicated spectra in the case of irregular structures. Thus the influence of different initiators on tacticity and the *cis/trans* ratio can be determined quite precisely. Furthermore, the formation of helices is expected for highly ordered

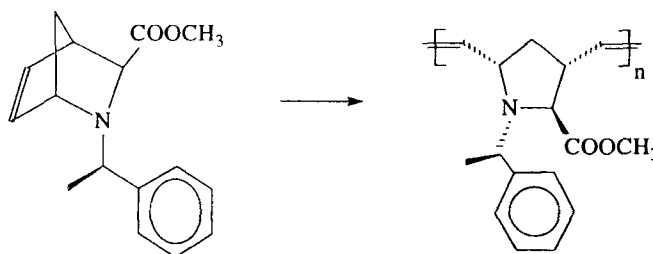


FIG. 7. Polymerization of *N*-methylbenzyl-2-aza-norborn-5-ene-3-methoxycarbonyl with two chiral substituents.

polymers of this type (e.g., all *cis*, isotactic); in that case the amino acid would point toward the outer surface of the helix. For such polymers a separation power for use in the separation of enantiomers might be expected.

### Side-Chain Liquid Crystal Polymers

Several norbornene derivatives with mesogenic groups have been polymerized during the last five years. A variation of several mesogenic groups which should align parallel or orthogonal to the main chain were investigated by Pugh and Schrock [27]. Most of these polymers were derived from monosubstituted norbornenes.

We have investigated polymers from 2,3-disubstituted norbornenes as shown in Fig. 8. The increase of the number of mesogenic groups per monomer unit brought some remarkable differences in the structure of the liquid crystal phases [28]. With these polymers we studied the influence of spacer length, the initiator used for the polymerization on transition temperatures, and the type of LC phase (see Fig. 9). It can be seen that the polymers obtained with the hexafluoro catalyst **3.cF<sub>6</sub>** exhibit higher transition temperatures than the polymers obtained with the *t*-butyl Mo-alkylidene initiators. The  $T_g$  and  $T_i$  values for polymers from trifluoro-*t*-butyl initiator are between the other two curves; therefore they are not drawn in Fig. 9. Compared to the NMR investigations, this indicates that the higher the order in the polymer chain, the higher is their transition temperatures. The liquid crystal phases change from nematic to smectic with spacer lengths of  $n = 6$  or 7, also depending on the initiator used.

Through copolymerization of norbornene esters of  $\alpha,\omega$ -diol as shown in Fig. 10, we were able to form liquid crystal elastomers by "in-situ crosslinking" during the ROMP reaction. The crosslinking yield depends strongly on the spacer unit Y. If a saturated alkylene chain is used, the crosslinking effect is much less compared to a linking unit consisting of a terephthalic ester with two alkyl chains. If the

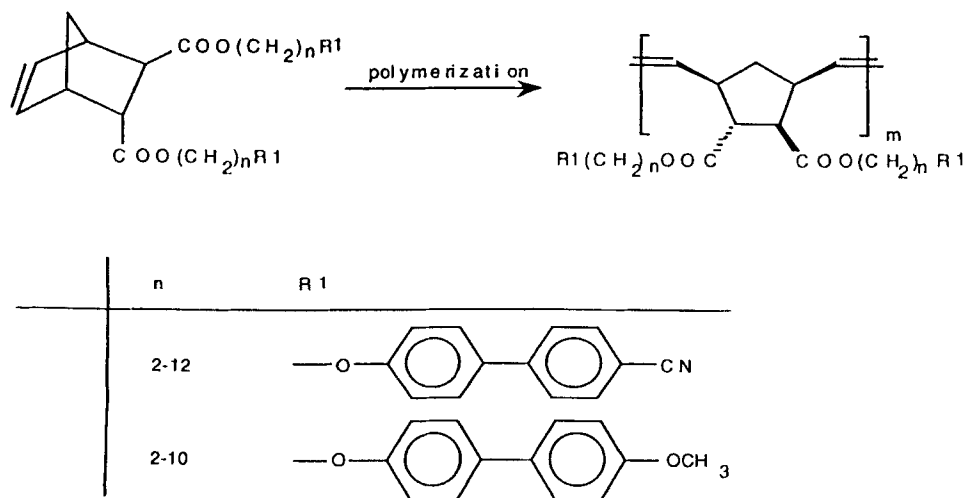


FIG. 8. Polymers with a high density of mesogenic groups.

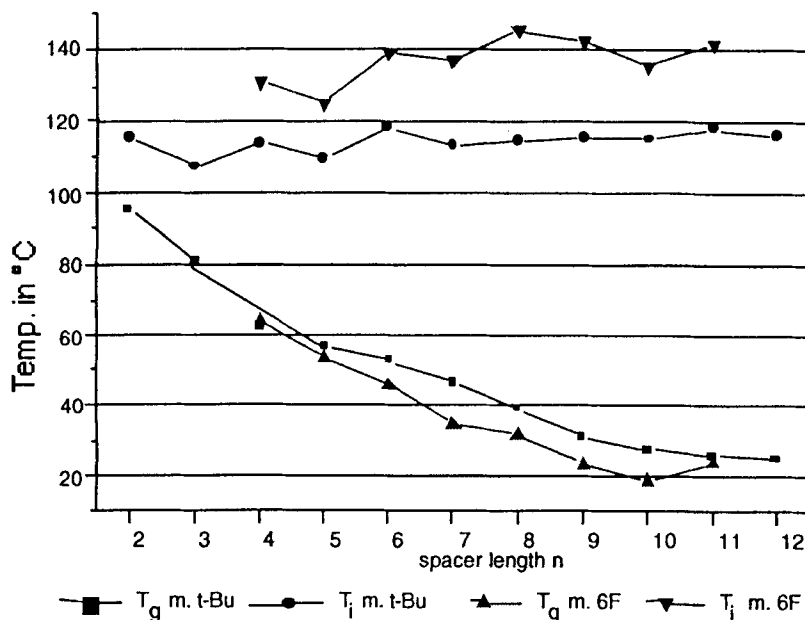


FIG. 9. Dependence of transition temperatures on spacer length ( $n$  methylene groups) and catalyst.

spacers in the Y chains are of a length similar to that of the spacers of the mesogens, the crosslinking density is much better. In this case only about 5–10 mol% crosslinker is necessary to get a good elastomer, while the alkylene-connected crosslinker needs about 20 mol% with respect to the monomer. The reason for this can be seen in a possible backfolding of the spacer chain, which means that the second polymerizable norbornenyl group is incorporated in the same chain and therefore produces only loops instead of crosslinks.

These polymers are weakly crosslinked in the first step during polymerization, oriented (e.g., by mechanical drawing) in the second step, and are finally fixed by a second crosslinking step (e.g., through peroxides or irradiation). Thus materials with anisotropies in their physical properties can be formed [29]. If such materials are optically clear, they can be used for the fabrication of bifocal contact lenses [30].

## CONCLUSIONS AND OUTLOOK

Ring-opening metathesis polymerization has proved to be a valuable method to synthesize polymers with special properties. Because of the well-defined mechanism (if single compound alkylidene initiators are used), it is possible to control the

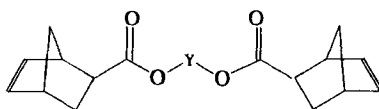


FIG. 10. Crosslinking diolefin for “in-situ crosslinking” in ROMP;  $Y = -(CH_2)_n-$  or  $(CH_2)_m-O(CO)ph(CO)O-(CH_2)_m-$ .

average molar mass and the microstructure of the unsaturated polymer chain quite well. Mo-alkylidene complexes as initiators allow control of the polymerization in that way. The field of application for ROMP polymers reaches from conjugated polymers for electronic or optoelectronic applications to high modulus polymers. Sidechain liquid crystalline thermoplastic materials can be modified to yield highly anisotropic liquid crystalline elastomers which might be used for the fabrication of bifocal lenses. Polymers synthesized from pure enantiomers exhibit optical activity, show microstructures of high regularity, and therefore give rise to a separation potential for racemic mixtures of chiral compounds.

At best, all these applications are in the primary basic research stage on a laboratory scale. These polymers have a great technological potential. If one takes into account that olefin metathesis may also be used for polymer degradation and for condensation polymerization, this reaction has a very high potential for tailoring polymer properties in the future.

### ACKNOWLEDGMENTS

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