

Transformation reactions involving metathesis polymerisation

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Dedicated to Professor Walter Kaminsky on the occasion of his 60th birthday.

Abstract

Transformation reactions provide a facile route to synthesise block copolymers that cannot be made from a single polymerisation mode. A variety of transformation reactions involving free radical, cationic, anionic, group transfer, Ziegler–Natta and metathesis are known. In this article, transformation reaction involving metathesis polymerisation is reviewed.
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Keywords: Transformation reactions; Living polymers; Metathesis; Ziegler–Natta polymerisation; Free radical polymerisation

1. Introduction

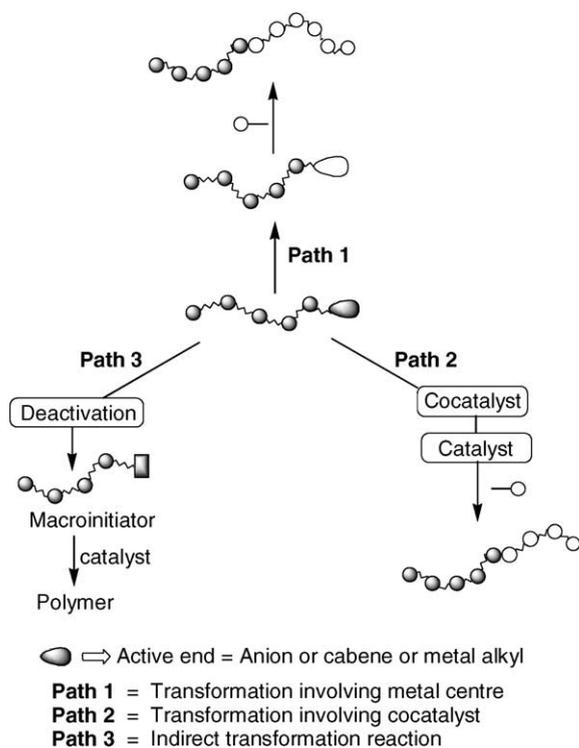
Living polymerisation has been used for the synthesis of well-defined polymers with good control over polymer architecture. A wide variety of living polymerisations are known and can occur by anionic [1–4], cationic [5–8], group transfer [9–12], metathesis [13–17], Ziegler–Natta (vinyl) [18–21] or by free radical [22–26] mechanism. Webster has given an overview of living polymerisation involving the anionic, cationic and free radical process pointing the monomers that could be polymerised [27]. The concept of “*living or controlled polymerisation*” has been reviewed recently [28]. Living polymerisation has been used for the synthesis of wide variety of block copolymers with varying physical properties. This has been done either by sequential monomer addition to polymers with living end or coupling two living polymers. Another method is to modify the chain end

by known chemical reactions and thereafter initiating a different mode with another monomer. This technique, normally called as transformation reaction, has an advantage that block copolymers that cannot be made from a single polymerisation mode can be synthesised.

Richards initiated the concept of transformation reaction in the late 1970s. He pointed out that the free radical, cationic and the anionic polymerisations differed in the number of electrons involved and also showed that slight modifications in the polymerisation could initiate another mode of polymerisation, thereby a wide variety of block copolymers could be synthesised [29]. A variety of transformation reactions, anionic to cationic, cationic to free radical, free radical to cationic, etc. have been carried out with different monomers. These reactions were reviewed individually in detail by Schue [30] and Stewart [31]. Transformation reactions involving metathesis polymerisation, i.e. transformations from or to metathesis can be classified as follows (Scheme 1):

1. transformation reactions involving active metal centre;

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Scheme 1. Classification of transformation reactions.

2. transformation reactions involving cocatalyst;
3. indirect transformation reactions.

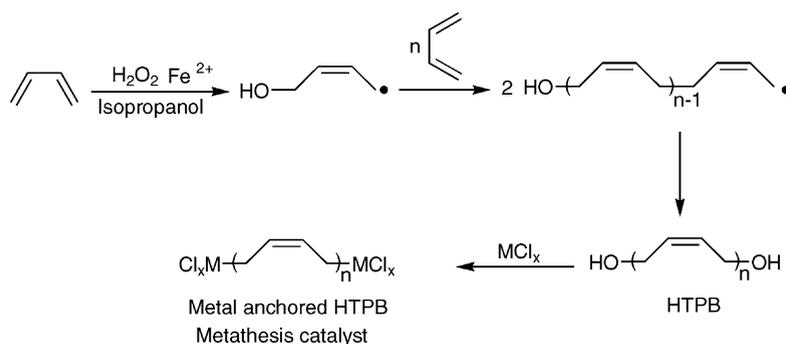
In this paper, reported results from the literature as well as those from our laboratory, related to the above classifications, are reviewed.

2. Transformation reactions involving active metal centre

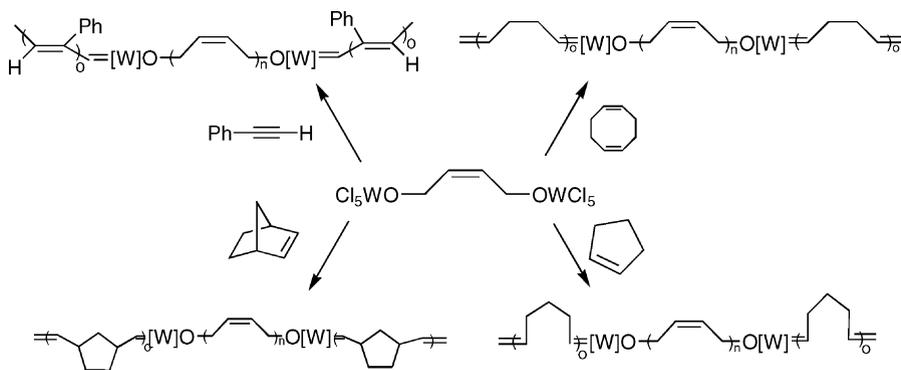
2.1. Free radical to metathesis polymerisation

In our laboratory, triblock copolymers of hydroxyl terminated polybutadiene (HTPB) and cyclic olefins were synthesised by transforming the mechanism of polymerisation from free radical to metathesis [32]. The highly viscous HTPB was obtained by free radical polymerisation of butadiene using Fe^{2+} /hydrogen peroxide as initiator and isopropanol as solvent. The obtained HTPB was treated with TiCl_4 or WCl_6 to get polymer anchored HTPB catalyst (Scheme 2). The anchoring of the metal on to the HTPB was evident from the absence of band due to the hydroxyl groups of HTPB in the IR spectra. The titanium and tungsten anchored catalysts were then used for polymerisation of phenylacetylene and cyclic olefins like norbornene, norbornadiene, cyclopentene and cyclooctene to get triblock copolymers of HTPB and ring-opened polymer of cyclic olefins (Scheme 3).

The triblock copolymers were rubbery materials. The yields of polymers obtained with titanium anchored catalyst were low, but with tungsten anchored catalyst the triblock copolymers were obtained in good yields. The polymers were characterised by IR, NMR and GPC. HTPB had a molecular weight of 5300 with a broad molecular weight distribution ($\text{pdi} = 1.6$), whereas the GPC curves of all the synthesised triblock polymers showed a single peak with narrow molecular weight distribution, M_n varied between 11 000 and 13 000, $\text{pdi} = 1.2\text{--}1.3$ depending on the monomer



Scheme 2. Synthesis of a metathesis catalyst from free radical macromonomer.



Scheme 3. Synthesis of triblock polymers containing ROMP units.

employed, confirming that the polymers are indeed triblock copolymers and not a mixture of two homopolymers.

The triblock copolymers obtained were then subjected to burn rate studies. Complete replacement of the HTPB with the HTPB-triblock polymeric binder affected the mixing characteristics and the heterogeneity in the propellant cast. Hence, the HTPB-triblock polymeric binder was used as an additive and the amount of replacement was restricted to 20%. Thus, the triblock copolymer added as an additive in the HTPB binder system had good compatibility and also increased the closeness of the binder to oxidiser as revealed from their SEM studies. Among the triblock polymeric binders, the one with HTPB-phenylacetylene and HTPB-polynorbornene triblock copolymers had very good burning characteristics and were shown to be superior to the HTPB based propellants [33].

2.2. Transformations involving metathesis and Ziegler–Natta polymerisation

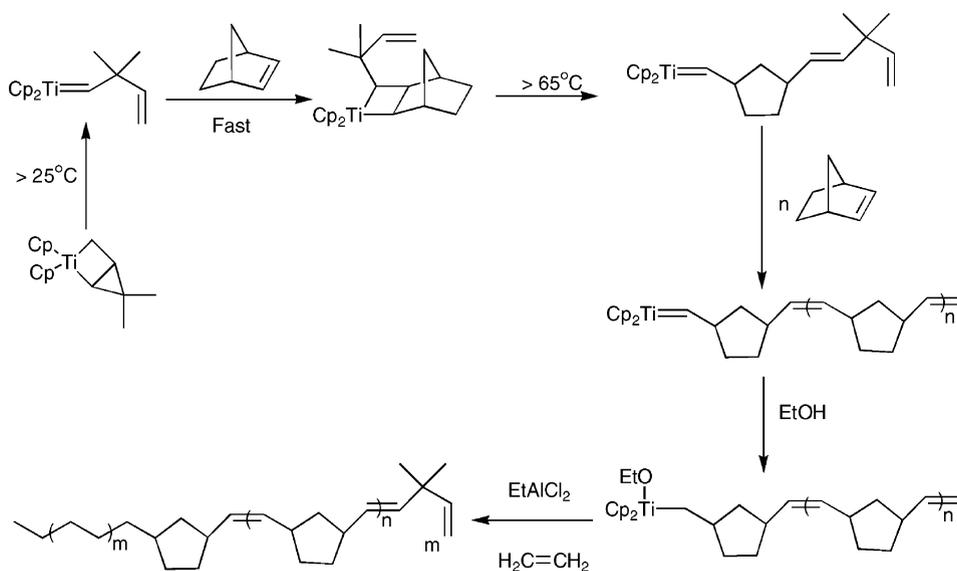
The active species in the metathesis polymerisation is a metal carbene whereas a cationic metal-alkyl centre drives the Ziegler–Natta (or vinyl) polymerisation. These two active centres differ very little and with minor variations in reaction conditions, either of the two modes of polymerisations can be invoked and this has been utilised for bringing about metathesis to Ziegler–Natta polymerisation and vice versa.

2.2.1. Metathesis to Ziegler–Natta polymerisation

Tritto et al. showed that the polynorbornene with active metal carbene could be quenched with trace amount of ethanol to convert the metal carbene to metal-alkyl bond (Scheme 4). The transformed polymer was reactivated with ethylaluminumdichloride for Ziegler–Natta polymerisation of ethylene to produce ethylene-*block*-polynorbornene copolymer [34].

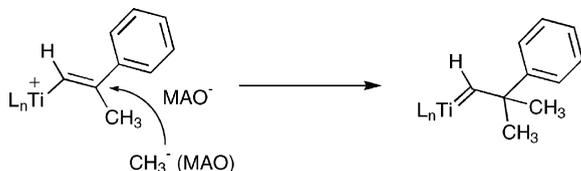
2.2.2. Ziegler–Natta to metathesis polymerisation [35]

Single-site catalysts have been effectively used for olefin polymerisation especially for the homo- and copolymerisation of cyclic olefins like cyclopentene and norbornene, to give linear polymers *without* any ring-opening [36,37]. Moreover, it is well known that cyclic olefins, in the presence of an olefin metathesis catalyst, undergo ring-opening-metathesis-polymerisation (ROMP) to give polymers with special properties [38]. The later discovery that Ziegler–Natta catalysts could sometimes bring about ROMP has given rise to much discussion on the relationship between vinyl addition (VA) and ROMP. In many cases the same catalyst systems can induce VA of one olefin and ROMP of another [39]. Also, the catalyst systems that bring about VA or ROMP of cyclic olefin monomers are similar in structure. So with minor variations in reaction conditions, either of the two modes of polymerisations can be invoked [34,40]. Mechanistically also similarities between polymerisation by VA and/or by metathesis exist. For example, the most commonly accepted Cossee–Arlman

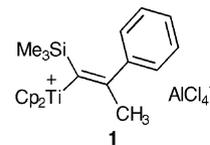


Scheme 4. Metathesis to Ziegler–Natta polymerisation.

mechanism for Ziegler–Natta (or VA) polymerisation of olefin has a 4-centre intermediate [41]. In ROMP the key intermediate responsible for the propagation of the polymerisation is a metallacyclobutane [42]. Besides, in metathesis polymerisation of alkynes, with a metal carbene catalyst, the propagating species is a metallacyclobutene. Eisch et al. proved the involvement of cationic intermediate in the polymerisation of ethylene by trapping the intermediate (**1**) with trimethylsilylphenylacetylene [43]. With these facts, we reasoned that a typical vinyl polymerisation could be converted to a metathesis polymerisation by interrupting the course of the reaction with a reactive transfer reagent, like phenylacetylene. Then the corresponding cation could be methylated to generate a carbene as shown in Scheme 5.



Scheme 5. Proposed pathway for switching the mechanism of polymerisation from vinyl addition to metathesis.



To switch the mechanism of polymerisation, a normal vinyl polymerisation of norbornene was initiated by adding MAO to the catalysts, [diolate and constrained geometry (CG) (Fig. 1)] phenylacetylene was added to the reaction mixture, then the required quantity of second monomers were added (Scheme 6). For polymers obtained after the addition of phenylacetylene, signals were seen in the alkyl region as well as

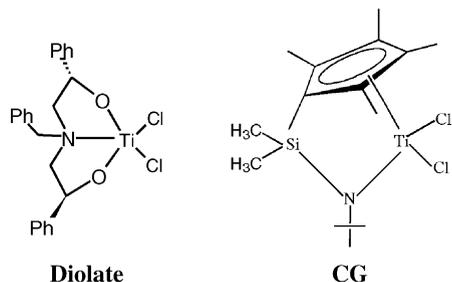
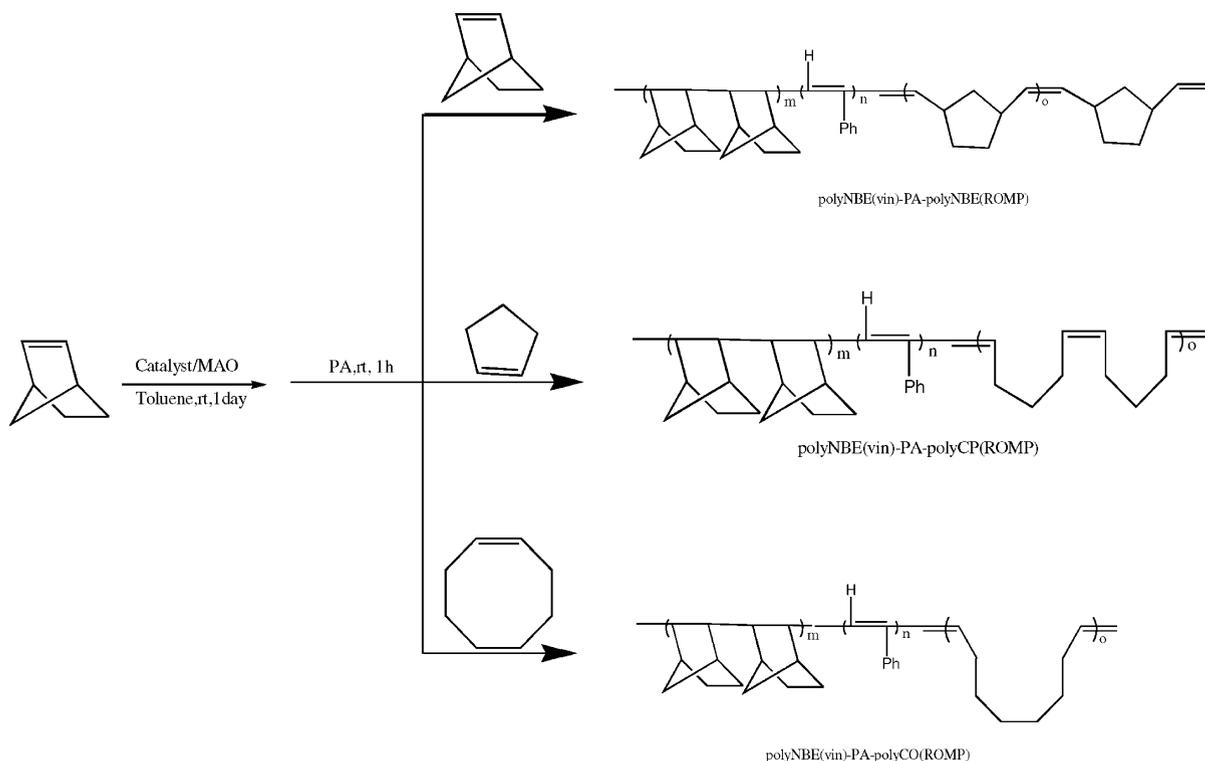


Fig. 1. Catalysts employed for switching the mechanism of polymerisation.



Scheme 6. Polymers from switching the mechanism of polymerisation (VA to ROMP).

in the olefinic region. The % ring-opened units were found to be nearly 30. Since addition of phenylacetylene brought about a change in the mechanism we wanted to check whether ROMP could be brought about if the polymerisation was initiated by phenylacetylene, i.e. adding the alkyne to the catalyst/MAO unit *prior* to the addition of the cyclic olefin. The polymers so obtained also showed ring-opened units. It was also noted that there was a substantial increase in the relative amount of ring-opened units when phenylacetylene was added after 6 and 12 h of initiating VA polymerisation (Fig. 2).

The kinetic studies on the homopolymerisation of norbornene by both catalysts, upon monitoring the change in concentration of the monomer, gave linear plots with rate constants of 1.5×10^{-2} and $1.76 \times 10^{-2} \text{ h}^{-1}$, respectively. When a change in mechanism of polymerisation from VA to ROMP was brought about by adding phenylacetylene in the middle of the reaction, the rate constant increased from $1.4 \times 10^{-2} \text{ h}^{-1}$ (VA) to $5.8 \times 10^{-2} \text{ h}^{-1}$ (ROMP) after the

addition of phenylacetylene (Fig. 3). For CG catalyst the rate constants increased from 1.65×10^{-2} to $8.96 \times 10^{-2} \text{ h}^{-1}$. As expected, the initial rate constants for the vinyl polymerisation in the switching process matched well with the homopolymerisation

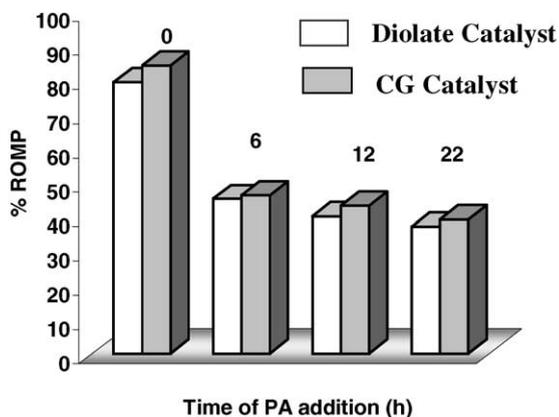


Fig. 2. % ROMP vs. time of PA addition.

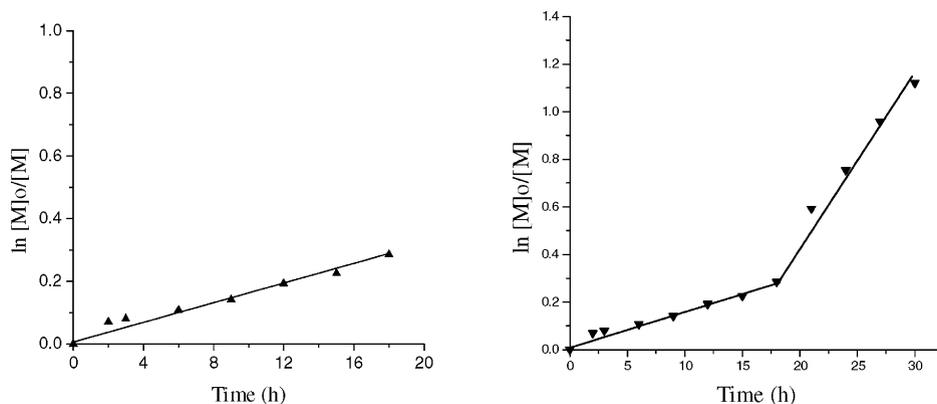


Fig. 3. Change in monomer concentration with time for (a) homopolymerisation of norbornene (VA); (b) conversion of VA to ROMP.

Table 1
Arrhenius parameters for VA and ROMP

No.	Mode of polymerisation	Diolate		CG	
		ln A	E_a (kJ mol ⁻¹)	ln A	E_a (kJ mol ⁻¹)
1	VA	10.4	15.2	10.5	16.1
2	ROMP	9.8	11.3	9.6	9.6

values. The kinetic profile shown for the switchover in mechanism was also found to be similar for a range of temperatures allowing us to determine the activation parameters for this reaction (Table 1 and Fig. 4). The

Arrhenius parameters obtained for both the catalysts also indicate a similarity in the catalyst behaviour and support the suggested change in mechanism during the course of polymerisation by addition of phenylacetylene [44].

3. Transformation reactions involving cocatalyst

3.1. Anionic to metathesis polymerisation

Amass et al. reported the synthesis of block copolymer of styrene and polypentenamer by transforming

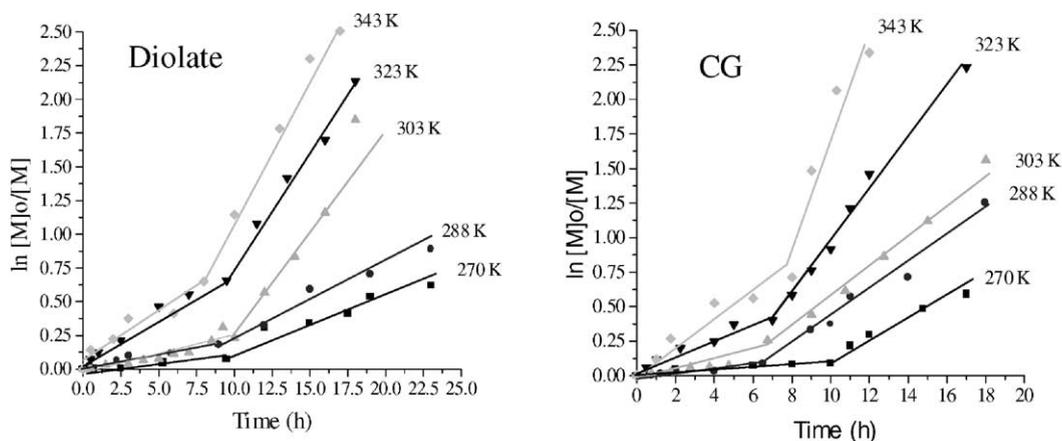


Fig. 4. Kinetic profile for the conversion at different temperatures.

metallacycle to open to corresponding metal carbene in the presence of monomer like norbornene and dicyclopentadiene. The living polymers thus generated were reacted with excess terephthalaldehyde to give polymers with one aldehyde end group. This was used as an initiator for the silyl aldol condensation polymerisation of *tert*-butyldimethylsilyl vinyl ether to give polynorbornene-*block*-poly (silyl vinyl ether) and polydicyclopentadiene-*block*-poly (silyl vinyl ether) copolymer with narrow molecular weight distribution [47]. The silyl vinyl ethers were then hydrolysed to give the corresponding polyvinyl alcohol block copolymers.

4.2. ROMP to atom transfer radical polymerisation

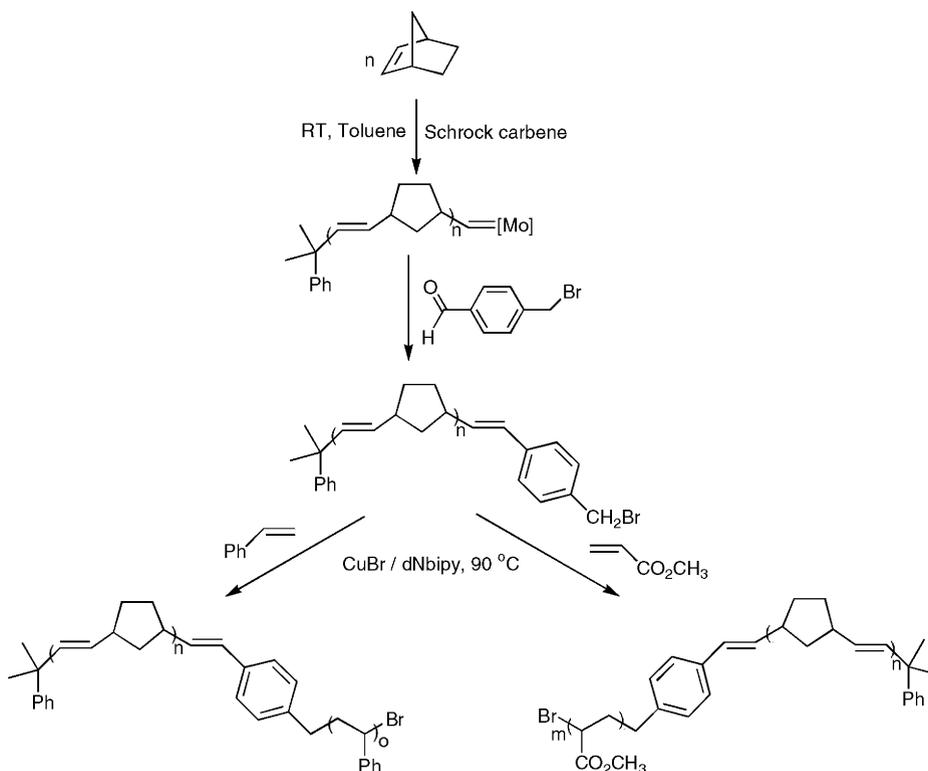
Matyjaszewski reported the synthesis of block copolymers of styrene and norbornene and styrene and polydicyclopentadiene by transforming the living ROMP into controlled “living” atom transfer radical

polymerisation (Scheme 9). In this, ROMP of norbornene was initiated with Schrock's molybdenum alkylidene catalyst and the active end was end-capped with *p*-(bromomethyl)benzaldehyde. The NBE end-capped polymer was then used as a macroinitiator for ATRP polymerisation of styrene with CuBr/dNbipy as catalyst [48].

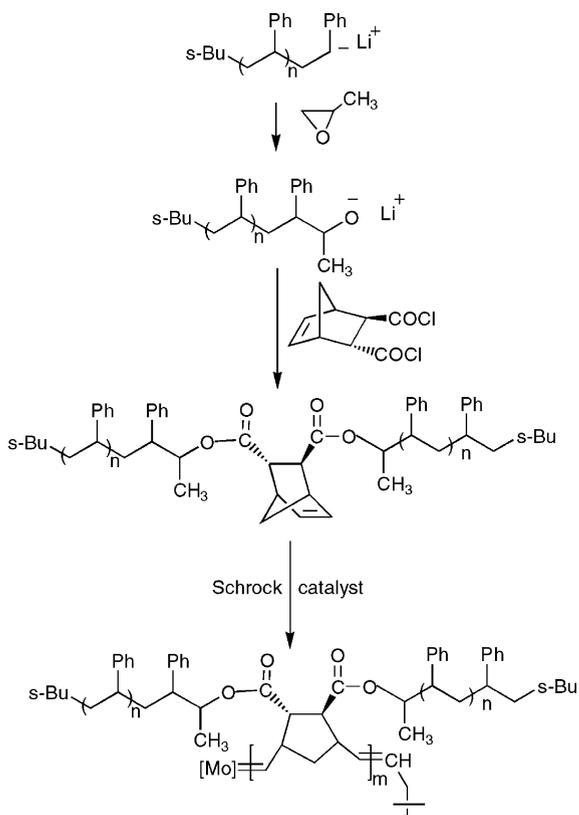
4.3. Anionic to metathesis polymerisation

Norton and McCarthy [49] initiated a living anionic polymerisation of styrene and the generated polystyrylanion was treated with monocarbonylchloride of norbornene to generate a macroinitiator. This norbornene derivative was then subjected to ROMP using the classical WCl_6/Me_4Sn catalyst in presence of norbornene and 1-octene to prepare a new grafted copolymer.

Feast utilised the lithium alkoxide generated from polystyryllithium and propylene oxide, reacted it with norbornenedichloride to generate a macromonomer



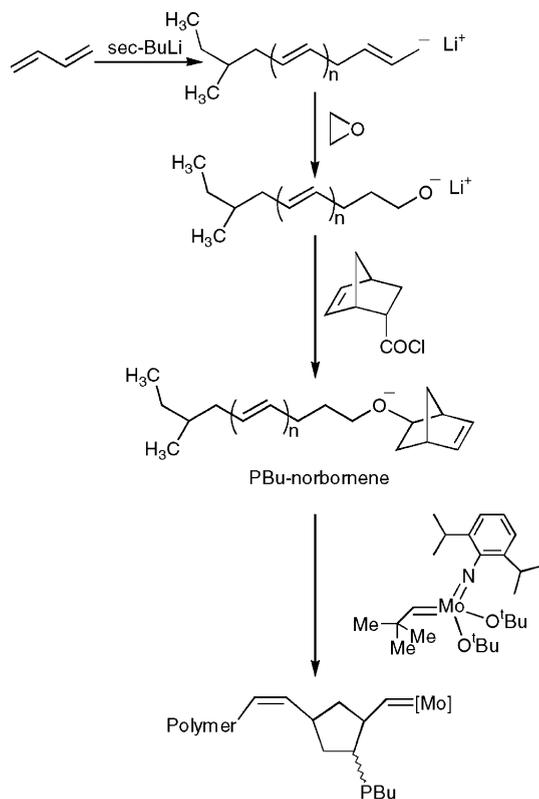
Scheme 9. Metathesis to atom transfer radical polymerisation.



Scheme 10. Transformation involving metathesis and anionic polymerisation.

(Scheme 10). This was then subjected to ROMP with Schrock's molybdenum catalyst to give a polynorbornene derivative carrying polystyrene grafts on each cyclopentane ring [50].

Gnanou synthesised norbornene-ended polybutadiene macromonomer by initiating anionic polymerisation of butadiene and terminated the living anionic end with ethyleneoxide to obtain polybutadiene chains with lithium alcoholates. Norbornenecarbonylchloride was then capped with polybutadiene to generate a macromonomer with norbornene end. This was then subjected to ROMP using four different metal carbene complexes, among them, the molybdenum alkylidene complex shown in Scheme 11 was found to be appropriate [51]. The same group also utilised polystyrene (PS), poly(ethylene oxide) (PEO) and PEO-*b*-PS block copolymer containing norbornene ends for such studies [52].



Scheme 11. Transformation involving anionic and ROMP.

5. Conclusion

Metathesis polymerisation is a powerful tool for the synthesis of well-defined polymers for specific application. By invoking transformation reactions involving metathesis, it has been possible to attain complex but well defined polymeric materials.

Acknowledgements

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