

# Synthesis of fluorinated polymers via ROMP: a review

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## Abstract

This review is concerned with the work conducted in the Durham group during the last twenty years. It is specifically concerned with ROMP of fluorinated monomers with classical and well-defined initiators, with the synthesis of stereoregular polymers, block and stereoblock copolymers. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Metathesis; Ring opening metathesis polymerisation; Living polymerisation; Initiators; Stereoregular; Block copolymers

## 1. Introduction

The observations of Ziegler and co-workers concerning the telomerisation and polymerisation of ethylene in the presence of transition metal compounds turned out to be the key to the development of a new technology for alkene polymerisations which became widely used and which is still evolving. Shortly after Ziegler's disclosures, Anderson and Merklung [1] reported a related observation, namely that the polymerisation of norbornene, bicyclo[2,2,1]hept-2-ene (**I**), could be initiated by the product of reaction between titanium tetrachloride and ethylmagnesium bromide at 50°C. Subsequently it was established that the polymer, poly(1,3-cyclopentylene vinylene) (**II**) [2], was the result of a ring opening process rather than the expected vinyl addition polymerisation, see Fig. 1.

Using isotopic labelling Dall'Asta and Motroni [3] established that in the polymerisation of cyclic olefins the reac-

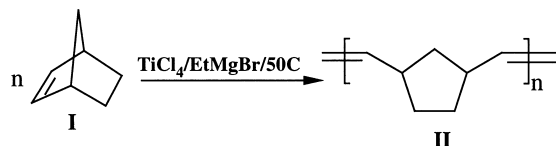


Fig. 1. The ring opening metathesis polymerisation of norbornene.

tion proceeded via complete cleavage of the carbon–carbon double bond, and later Gilliom and Grubbs [4] isolated and determined the structure of a stable titanacyclobutane produced in the reaction of Tebbe reagent with norbornene in the presence of base and showed that it could initiate the ring opening metathesis polymerisation, ROMP, of norbornene, see Fig. 2.

These key observations, along with a mass of other data [5,6], established that olefin metathesis reactions, including ROMP, proceed via chain processes in which the structures of the active chain carrying entities alternate between metal alkylidene (carbenes) and metallacyclobutanes. This work

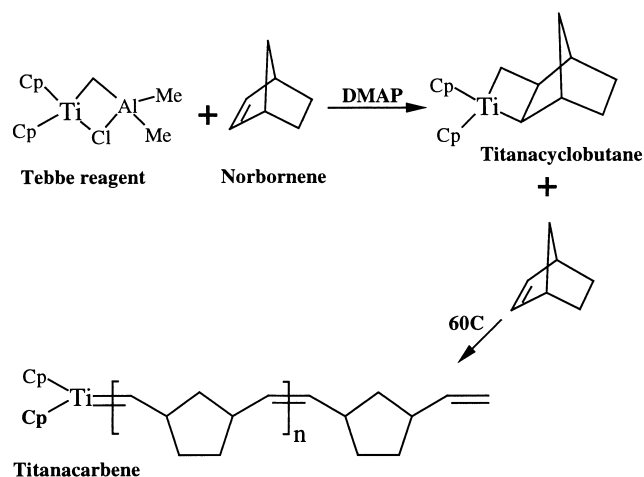


Fig. 2. ROMP of norbornene with a well-defined titanium complex, DMAP = 4-dimethylamino pyridine.

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confirmed the mechanistic hypothesis first introduced by Herisson and Chauvin [7]. In both Ziegler–Natta and ROMP, the initiator formulation was based on the products of reaction of a mixture of a transition metal halide and an alkylating agent and only a relatively small proportion of the transition metal atoms present were converted to active centres for the polymerisation. Also, as in the Ziegler–Natta field, most experimental effort in ROMP was concentrated on hydrocarbon monomers, cycloalkenes and bicycloalkenes. However, early publications gave very clear indications that ROMP was not restricted to dry, oxygen free reaction conditions and simple hydrocarbon monomers [8–14].

Fluorinated polymers, such as polytetrafluoroethylene, poly(vinyl fluoride), poly(vinylidene fluoride) and some functional membrane materials, have an established place in both routine domestic and demanding technological applications. Introduction of fluorine often produces very pronounced effects on the properties of materials and it is only because of their high added value in terms of special effects or properties that the cost penalty of manufacture for such materials can be tolerated.

Some time ago, we became interested in making new polymeric materials carrying fluorinated substituents and the ROMP process appeared attractive for several reasons. One of the areas of interest to us was elastomeric materials of high thermal and oxidative stability and good solvent resistance. At that time it seemed likely that *trans*-poly-pentenamer,  $-(\text{CH}=\text{CH}(\text{CH}_2)_3)_n-$ , a product of ROMP of cyclopentene, was “about to make its debut as the new all purpose synthetic elastomer”; the  $T_m$  and  $T_g$  of this material are very close to those of natural rubber and its *cis* isomer has the lowest  $T_g$  of any hydrocarbon polymer ( $-113^\circ\text{C}$ ). In connection with other projects we had accumulated supplies of octafluorocyclopentene and 1H,2H-hexafluorocyclopentene and it seemed reasonable to investigate the synthesis of fluorinated analogues of the polypentenamers. In the event neither has *trans*-polyopentenamer managed to reach the market place nor have we managed to polymerise either of the fluorinated cyclopentenenes, but this initial attempt to ROMP polar monomers was the starting point for the work to be reviewed here.

Our repeated failure to ROMP highly fluorinated cyclopentenenes may be a consequence of the reduction of the  $\pi$ -donor capacity of the double bond by the electron withdrawing substituents or an increased stability of the fluorinated cyclopentene relative to the ring-opened linear polymer. It is known that the free energy of polymerisation of five membered carbocyclic systems is close to zero and small structural differences can tip the balance against polymerisability [15]. Both these inhibitors of polymerisation can be overcome by moving the electron withdrawing substituents further away from the double bond and increasing the double bond reactivity by locating it in a sterically strained ring. These required effects are easily achieved by making use of bicyclic monomers such as substituted

norbornenes. Such monomers are readily obtained from the Diels–Alder reactions of substituted olefins with cyclopentadiene. This strategy proved effective and fluorinated monomers of this type readily underwent ROMP with a variety of “classical” two and one component initiator systems.

## 2. ROMP of fluorinated monomers with classical initiators

The polymerisations of a range of fluorinated monomers were investigated with a variety of initiator formulations [16–27]. The structures of the monomers investigated are shown in Fig. 3.

The initiator systems were derived either from the products of reaction of solutions of transition metal chlorides,  $\text{WCl}_6$ ,  $\text{MoCl}_5$ ,  $\text{OsCl}_3$ ,  $\text{RuCl}_3$ ,  $\text{IrCl}_3$ ,  $\text{ReCl}_5$  with solutions of monomers; or generated by reactions of the same transition metal chloride solutions with alkylating/activating agents,  $\text{Ph}_4\text{Sn}$ , *n*- $\text{Bu}_4\text{Sn}$ ,  $\text{Me}_4\text{Sn}$ , *n*- $\text{Bu}_3\text{Al}$ , *iso*- $\text{Bu}_3\text{Al}$ ,  $\text{Et}_3\text{Al}$ ,  $\text{Et}_2\text{AlCl}$ . At first toluene was the solvent of choice, but in order to minimise side reactions of the Friedel–Crafts type in the presence of these Lewis acid-like initiator systems chlorobenzene, which is less susceptible to such side reactions eventually became the preferred solvent.

The manipulation of reagents required standard inert atmosphere (dry, oxygen free nitrogen) glovebox and/or vacuum line techniques and after reaction the active initiator residues and/or chain-ends were destroyed by addition of methanol. The polymers were recovered by repeated precipitations from solvent into non-solvent, and characterised by gel permeation chromatography, thermal analysis, infrared,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The most valuable analytical probe for determining chain microstructure was  $^{13}\text{C}$  NMR spectroscopy [5,6]. With most of these “classical” systems complete removal of catalyst residues was difficult.

Polymerisation of both the structurally related monomers **X** and **XI** was initiated by systems derived from  $\text{WCl}_6$ ,  $\text{MoCl}_5$ ,  $\text{RuCl}_3$  and  $\text{IrCl}_3$ , but whereas **X** was polymerised using systems based on  $\text{OsCl}_3$  and  $\text{ReCl}_5$  as well **XI** resisted all attempt at initiation with these halides either on their own or in the presence of activators [17,21,25]. Polymerisation of the *exo* isomer of **XIII** was readily initiated by either  $\text{WCl}_6/\text{Me}_4\text{Sn}$  or  $\text{MoCl}_5/\text{Me}_4\text{Sn}$ , by contrast the *endo* isomer could not be polymerised with either initiator system but participated in copolymerisation with the *exo* isomer. Generally  $\text{WCl}_6/\text{Me}_4\text{Sn}$  was found to be a very active, non-selective initiator system yielding *atactic* polymers with little or no *cis/trans* preference whereas  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  was often less reactive and more selective with respect to chain microstructure. However, this was not an invariable rule and, for example, monomers **XVI** did not polymerise in the presence of  $\text{WCl}_6/\text{Me}_4\text{Sn}$  but gave polymers with  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  in chlorobenzene at  $70^\circ\text{C}$  [19].

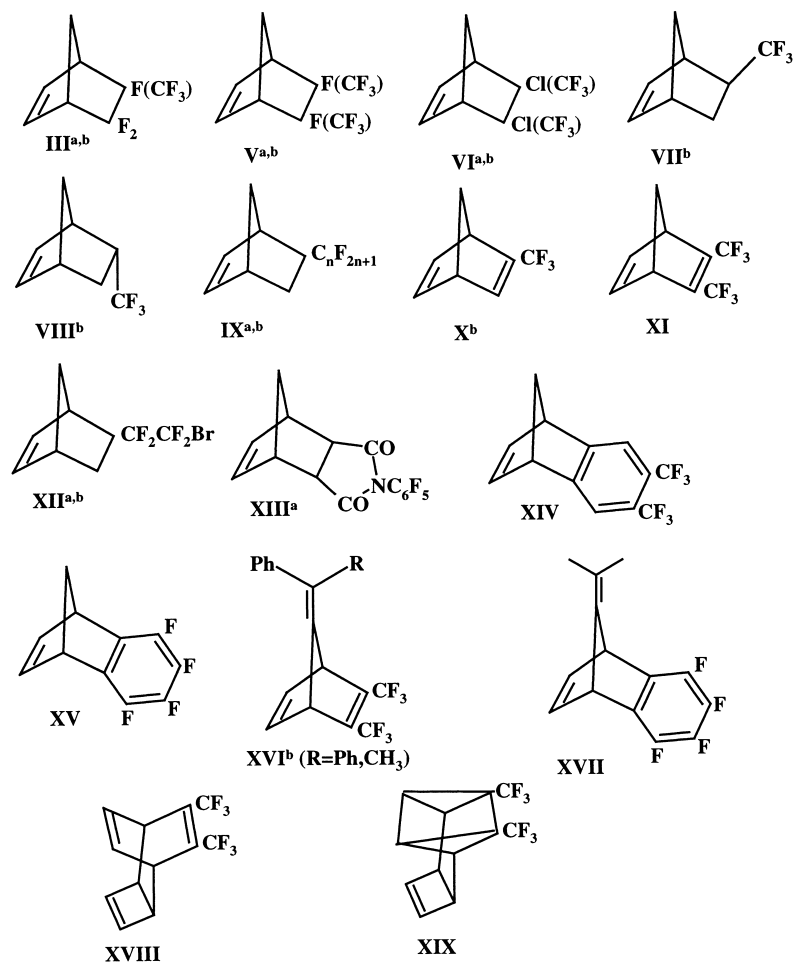


Fig. 3. Fluorinated monomers shown to undergo ROMP with classical one or two component initiator systems, a: as *endo/exo* isomer mixture, b: as racemate.

All of the polymers produced in these experiments had broad molecular weight distributions, generally showing values of  $M_w/M_n$  much greater than the most probable value for a well-behaved chain growth polymerisation, i.e.,  $M_w/M_n = 2$  [28]; an observation which is consistent with the presence of several kinds of initiator and/or propagating chain-ends [21]. The probability that most of these classical initiator systems contain several different kinds of initiating species is also consistent with the observation of complex chain microstructures for most of the product polymers although, of course, this does not prove the case.

The microstructural variety possible as a result of incorporating most of these monomer residues is very great. Consider, for example, monomer **III** which, as made, exists as a mixture of *endo* and *exo* isomers both of which are racemic. On incorporation into the polymer chain the repeat unit has the structure **IV**, see Fig. 4, in which the vinylene unit can be *cis* or *trans*, the fluorinated cyclopentane unit can be incorporated in a head–tail, head–head or tail–tail fashion, the trifluoromethyl group can be *syn* or *anti* with respect to the adjacent vinylene carbons and the incorporated unit can be derived from an *R* or *S* monomer. This gives rise to an enormous range of possible microstructures and it is not too

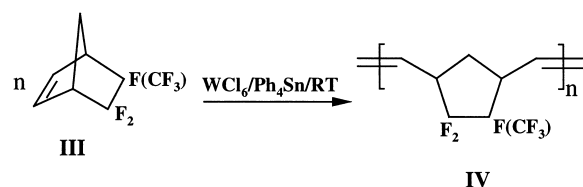


Fig. 4. ROMP of 5-trifluoromethyl-5,6-difluorobicyclo[2.2.1]hept-2-ene.

surprising that in most of the cases examined the complexity of the  $^{13}\text{C}$  NMR spectra could not be disentangled in detail. Generally the *cis/trans* contents were accessible but the complexity of the spectra prevented more detailed analysis of microstructure. Thus, although one of the stated aims of these early studies was to produce stereoregular fluoropolymers, the only instance where this was approached was in the polymerisation of monomers **VII** and **VIII** [23]. In that investigation pure samples of racemic *endo* and *exo* monomers were produced and it was demonstrated that although both gave *atactic* polymers with a high *trans* vinylene content when initiated with  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  and  $\text{OsCl}_3$ , initiation of the polymerisation of the *endo* isomer with  $\text{ReCl}_5$  gave a *tactic* polymer with 92% *cis* vinylenes. This

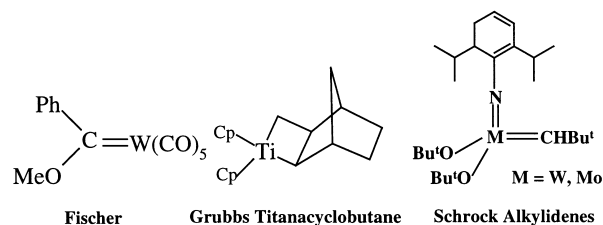


Fig. 5. Well-defined initiators for ROMP.

represented the nearest approach to the synthesis of stereoregular fluoropolymer which we obtained using classical systems but the yield (10%) of recovered polymer was poor.

However, more applicable results were obtained in as much as the polymers derived from the ROMP of monomers XVIII and XIX were soluble, and consequently processable, and proved to be excellent precursors to polyacetylene [18,19,29]. They have found fairly widespread use in that application.

### 3. ROMP of fluorinated monomers with well-defined initiators

The early work described in the previous section established that fluorine substituted monomers could be polymerised by initiator systems derived from transition metal chlorides, however, the process was poorly characterised and gave largely *atactic* products with broad molecular weight distributions. The development of the synthesis of well-defined single component transition metal com-

plexes containing metal to carbon double bonds offered an attractive source of potential initiators for ROMP, see Fig. 5.

Our first experiences with such well-defined complexes were not encouraging. Thus, although the Fischer carbene was shown to be capable of initiating polymerisation, it offered no advantages over the more readily available classical transition metal chloride systems. The titanacyclobutane complex introduced by Gilliom and Grubbs [4] was investigated, but although this system gave well characterised living polymerisation with hydrocarbon monomers, it appeared to be destroyed by fluorinated monomers, presumably the titanium centre is so electrophilic that the monomers can be regarded as a source of fluoride. However, the initiators introduced by Schrock and co-workers [30,31] proved to be more tolerant to these fluorinated monomers and allowed the introduction of precision and control of molecular weight, polydispersity, *cis/trans* content and, in favourable cases, *tacticity*.

### 4. Synthesis of fluorinated homopolymers

As indicated above, the advent of well-defined single component transition metal alkylidenes made it possible to polymerise fluorinated bicyclic olefins in a well-controlled living manner allowing the synthesis of polymers with a molecular weight distribution,  $M_w/M_n$ , of 1.05 [4,32,33].

The key to controlled polymerisation of fluorinated bicyclic olefins using the well-defined Schrock initiators

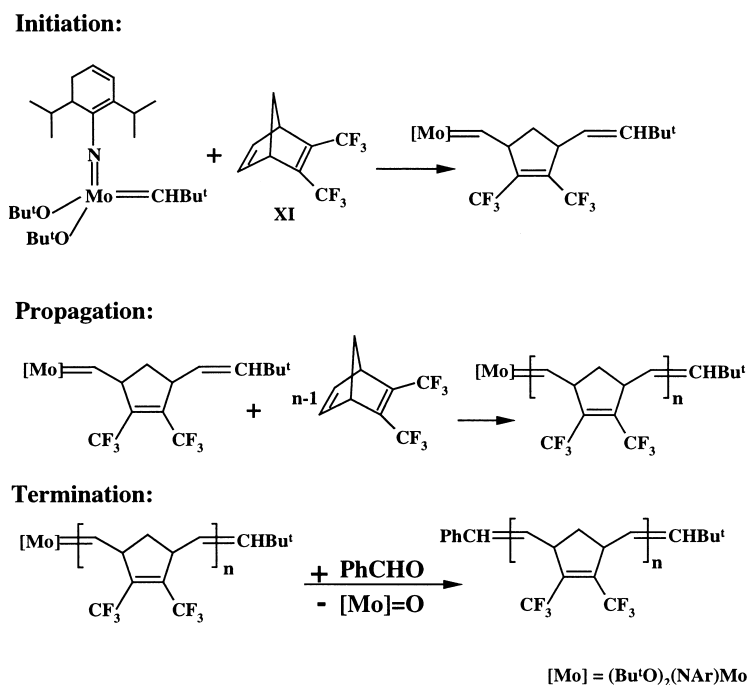


Fig. 6. Living polymerisation of fluorinated monomer XI.

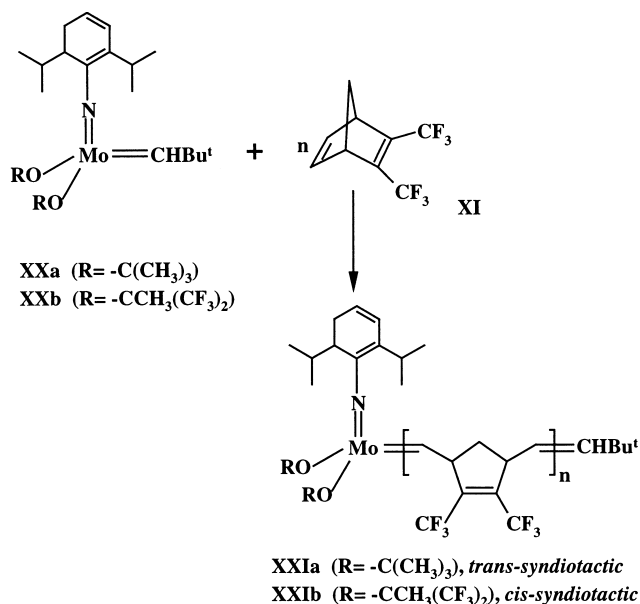


Fig. 7. Ligand effect in living polymerisation with the Schrock alkylidene initiators.

is that while they are inactive towards double bonds in the polymer chain, they react rapidly with the strained double bonds in the monomer to give ring-opening and a linear polymer, see Fig. 6. The living nature of these polymerisations can be conveniently monitored by  $^1H$  NMR [34]. The reactions are conducted in solvents such as benzene, toluene or THF and the living polymerisation reactions can be terminated by the addition of aldehydes (e.g., benzaldehyde). The living polymer reacts with aldehydes readily to give metal oxide in a Wittig-like capping reaction to give very narrow polydispersity values and  $M_n$  values determined by monomer:initiator ratios.

Polymerisation of bis(trifluoromethyl) norbornadiene, BTFMND (**XI**, Fig. 7) initiated by Schrock alkylidenes  $Mo(CH-t-Bu)(NAr)(OR)_2$  gives all *trans* poly(BTFMND) when R is *t*-butyl [35,36] (i.e., **XXa** initiation) and all *cis* poly(BTFMND) when R is hexafluoro-*t*-butyl [37] (i.e., **XXb** initiation).

All *trans* polymer shows behaviour that one would expect for a semicrystalline thermoplastic. DSC studies revealed a well-defined  $T_g$  at 97°C and a broad melting endotherm at 200°C, the shape and area of which is dependent on sample history. In samples precipitated from solution, the  $T_g$  transition is not particularly marked and the melting endotherm indicates multiple melting points. In melt-quenched samples, the glass transition is much more marked and the melting peak area is small. The melting peak area increases on prolonged annealing at 180°C (72 h), indicating a slow ordering process that is consistent with low chain mobility in the solid state. All samples of this polymer produced earlier were *atactic* and amorphous and exhibited a well-defined  $T_g$  at 125°C.

Dynamic mechanical thermal analysis of solution-cast films of both *tactic* and *atactic* samples show no energy

dissipation peaks below  $T_g$ , indicating that in solid state these polymers are relatively stiff with little or no motion below  $T_g$  [36]. The all *cis* polymer exhibits a well-defined  $T_g$  at 145°C and no melting endotherm.

Fibres can be drawn from the melt of the all *trans* *tactic* polymer and exhibit 500% elongation on stretching, whereas fibres drawn from *atactic* polymer prepared by  $WCl_6/Me_4Sn$  are weak and cannot be stretched.

Detailed  $^{13}C$  NMR analysis showed that the all *trans* polymer produced using initiator **XXa** (Fig. 7) is 92% *tactic*, whereas the all *cis* polymer produced using initiation **XXb** is 75% *tactic*. It has recently been shown that an initiator with a binaphthol replacing the two alkoxides and the arylimido isopropyl groups replaced by methyls gives poly(BTFMND) with 100% *cis* vinylenes and which is also 100% *tactic* [38]. Schrock and coworkers [39] have reported that all *trans* norbornadiene polymers are *syndiotactic* and that all *cis* norbornadiene polymers are *isotactic* regardless of the nature of the substituents in the monomers. The analysis of the  $^{13}C$  NMR spectrum of the all *trans* poly(BTFMND) did not allow an assignment of its microstructure, and despite its high *tacticity*, its degree of crystallinity was too low to obtain X-ray diffraction data capable of reliable detailed interpretation. However, dielectric measurements proved helpful in assigning *tacticity*. Thus, the all *trans* polymer displayed a remarkably high relaxed dielectric constant  $\epsilon_R$  (>40, cf. PVDF ca. 15) and the all *cis* polymer displayed a relatively low relaxed dielectric constant ( $\epsilon_R$  ca. 6) which can be compared with the *atactic* polymer made via  $WCl_6/Me_4Sn$  initiation (54% *trans* vinylene content) which showed an  $\epsilon_R$  value of ca. 16 [40]. The explanation of these large differences requires that in the *trans* polymer, the polar bis(trifluoromethyl)cyclopentenyl rings in the chain, Fig. 8, can act in collaborative reinforcing sense in response to an electric field, whereas in the *cis* polymer their individual effects tend to cancel each other [40,41]. This allowed an assignment of *syndiotacticity* unambiguously to the all *trans* polymer and, with a degree of uncertainty, to the all *cis* polymer. The assignment of the *tacticity* of the all *cis* polymer remains problematic since, although there is only one way to obtain a very high  $\epsilon_R$  value (cooperative reinforcement of individual ring effects) there can be several ways of organising sub-units to give cancellation of dipoles and consequently low  $\epsilon_R$  value [40].

The potentially high polarity of fluorinated polymers has led to their investigation for possible application as active components in various types of electrical devices. Poled films might be of use, particularly as heat sensors, electromagnetic radiation detectors and in thermal imaging systems. Much of the earlier work on piezoelectric and pyroelectric behaviour in polymers focused on poly(vinylidene fluoride) (PVDF) and results with these new polymers are compared with PVDF as reference. *Trans-syndiotactic* poly(BTFMND) has a high permittivity above  $T_g$  greater than 40 and a saturation polarisation approaching

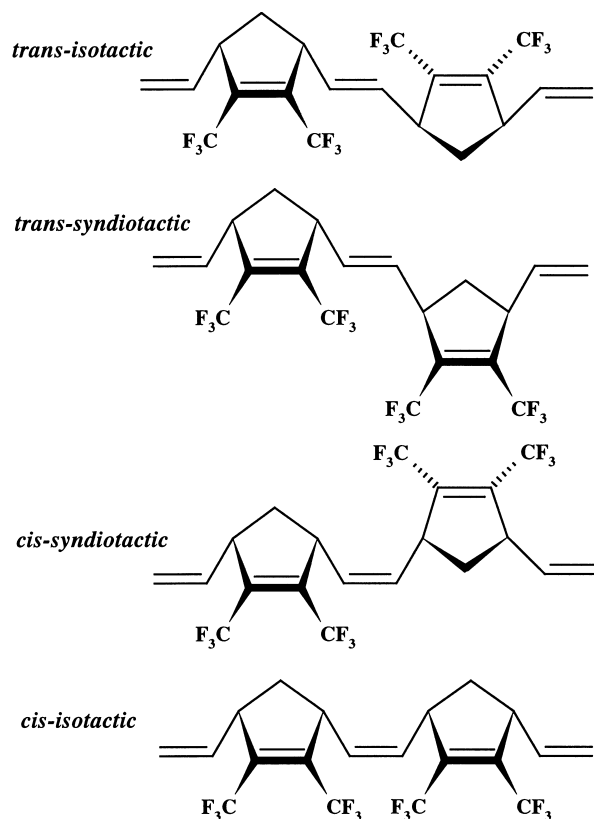


Fig. 8. The four possible microstructures for poly(BTFMND).

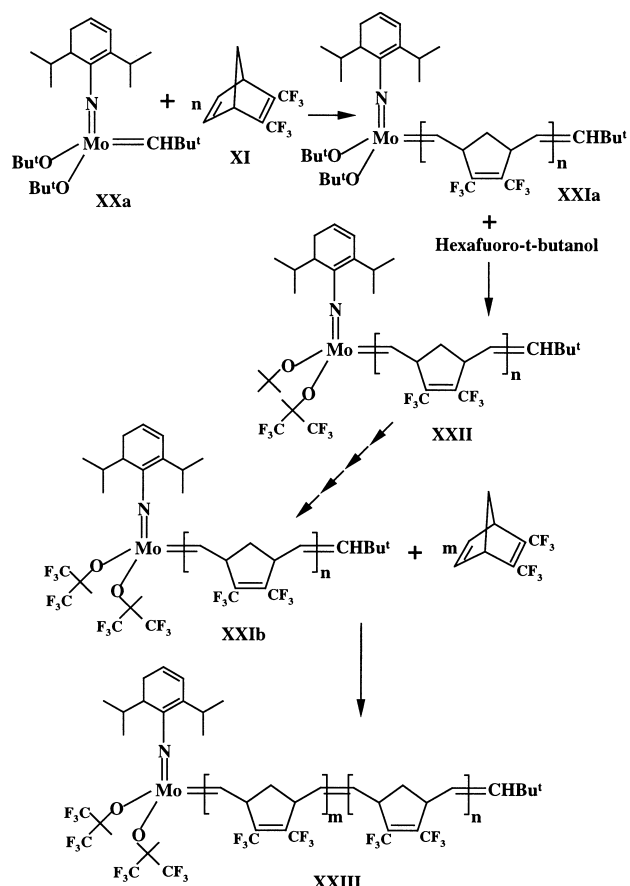


Fig. 9. Stereoblock copolymer synthesis via ligand exchange in living ROMP.

20 mC m<sup>-2</sup> with a pyroelectric coefficient approaching 6  $\mu\text{C m}^{-2} \text{K}^{-1}$ . While these values are less than for PVDF (50 mC m<sup>-2</sup> and 30  $\mu\text{C m}^{-2} \text{K}^{-1}$ , respectively), the low  $\tan \delta$  (<0.001) and permittivity at ambient temperature ( $\epsilon_U = 2.6$ ) allows favourable comparison with PVDF. For example, one commonly used figure of merit,  $F_D$  ( $F_D = \gamma / (\epsilon \tan \delta)^{1/2}$ ) for comparison of the pyroelectric response of detectors [42] suggests that in this respect poly(BTFMND) with a value of 118  $\mu\text{C m}^{-2} \text{K}^{-1}$  at 20°C is better than PVDF ( $F_D \approx 64 \mu\text{C m}^{-2} \text{K}^{-1}$ ; data taken at 1.69 Hz from Davies [43]). By contrast, for the *cis* poly(BTFMND), the low  $\epsilon_R$  of 5.7 does not allow one to obtain high  $\gamma$  or  $P$  at moderate fields.

In practice PVDF works as a composite material in which the crystalline domains provide the locked-in polarisation and the soft deformable amorphous phase responds to the applied stress [43,44]. We hoped that it might be possible to mimic this mechanism by synthesising two phase systems comprising a high- $T_g$  highly polar phase dispersed in a low- $T_g$  high permittivity amorphous phase, which would allow changes of phase composition and morphology and optimisation of the piezoelectric and pyroelectric response. Although, we continue to believe that this is conceptually sound we have not succeeded in demonstrating the idea in practice.

## 5. Synthesis of stereoblock fluorinated copolymers

The rapid progress in correlating the molecular structure, conformation, supramolecular organisation and the chemical and physical properties of organic polymers, coupled to the continually improving capacity to model these things theoretically [45] continues to place heavy demands on the methods available for the precisely controlled synthesis of polymers. In chain growth polymerisations, control over the molecular weight distribution can be obtained using chemistries in which there are no spontaneous termination reactions [46]. Such systems are described as “living” and examples are established for polymerisations using radicals [47], anions [48], cations [49] and well-defined transition metal complexes [4,32,33] as the chain carrying species. Some chain growth polymerisations are stereoselective and some give stereoregular polymers [35,36,38,46]. Living polymerisations can be used to make block copolymers which allows control of supramolecular organisation via the phase separation of incompatible blocks [50]. Blocks derived from the same monomer but having different microstructures may be incompatible leading to morphology control and hence bulk property control in a material derived from one monomer; such stereoblock copolymers have been

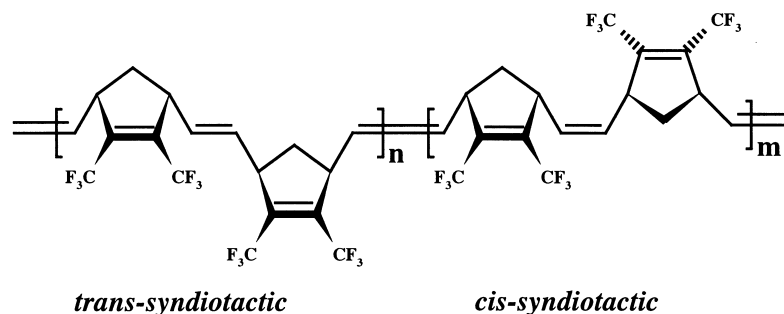


Fig. 10. Structure of the stereoblock fluoropolymer obtained from the synthesis outline in Fig. 9.

prepared via anionic [51] and metallocene [52] methods. We have demonstrated that this is also possible using ROMP [53]. Poly(BTFMND) was obtained as a stereoblock copolymer containing *cis* and *trans* vinylene blocks via ligand exchange in living stereoselective ROMP initiated by a well-defined Schrock type initiator.

In a small-scale trial experiments (NMR tube) initiation of **XI** (10 equivalents) with well-defined Schrock molybdenum initiator, **XXa**, Fig. 9, gave living polymer **XXIa** with a chain-end characterised by a doublet in the  $^1\text{H}$  NMR spectrum (Varian VXR 400,  $\text{C}_6\text{D}_6$  solution) at 11.34 ppm arising from the molybdenum alkylidene. After freeze drying, the residue was treated with a solution of dry hexafluoro-*t*-butanol in dry  $\text{C}_6\text{D}_6$  for 30 min, freeze-dried and redissolved in  $\text{C}_6\text{D}_6$  before recording a  $^1\text{H}$  NMR spectrum. Three new alkylidene doublets appeared in the spectrum, the doublet at 12.42 ppm was assigned to the chain-end alkylidene **XXIb** carrying two hexafluoro-*t*-butoxy ligands.

The doublets at 11.86 and 11.92 ppm arise from the molybdenum alkylidene of structure **XXII** in which the molybdenum carries one *t*-butoxy and one hexafluoro-*t*-butoxy ligand and is consequently a chiral centre; since the tertiary carbon in the cyclopentane ring adjacent to the alkylidene is also chiral, the alkylidene hydrogen can be located between centres of the same or different chirality giving diastereomeric environments and different chemical shifts with signals of different intensities reflecting the different abundances. A further four cycles of the freeze drying and reaction sequences gave the product **XXIb** in which all the alkoxy ligands are hexafluoro-*t*-butyl; this living polymer was used to initiate the polymerisation of **XI** (15 equivalents). The resulting living stereoblock copolymer **XXIII** was terminated by addition of benzaldehyde (10 equivalents) to give a polymer which displayed all the signals associated with *cis* and *trans* vinylene sequences in blocks of poly(BTFMND). The whole process was repeated on a larger-scale ( $2 \times 100$  equivalents of **XI**), THF was added to improve polymer solubility and a stereoblock copolymer was obtained having  $M_n = 73\,000$  (Theoretical 46 000) and  $M_w/M_n = 1.16$  (Viscotek differential refractometer/Viscometer, PLgel mixed column, THF, polystyrene calibration). The polydispersity observed is remark-

ably narrow considering the number of steps involved and is indicative of a very well-defined living polymerisation process.

The *cis/trans* blocks in the stereoblock copolymer are expected to have the same *tacticity* as their corresponding homopolymers as shown in Fig. 10.

Differential scanning calorimetry (Perkin Elmer DSC7) revealed two transitions at ca.  $95^\circ\text{C}$  and  $145^\circ\text{C}$  as expected for the *trans* and *cis* blocks, respectively.

## 6. Synthesis of fluorinated block copolymers

As described in Section 2 of this review, the ill-defined classical initiator systems are generally unsuited to the preparation of block copolymers. In contrast, as shown above, the well-defined initiators are quite robust and capable of producing fluorinated block copolymers in a living manner by the sequential addition of monomers [54]. The advantage of these systems, a selection of which are shown in Fig. 11, is that the complete course of the copolymerisation reactions can be followed by  $^1\text{H}$  NMR spectroscopy. Polymerisation of the first monomer gives rise to characteristic propagating alkylidene resonances in the  $^1\text{H}$  NMR spectrum. Addition of the comonomer, after the complete polymerisation of the first monomer, gives a new propagating alkylidene signal typical of the second monomer. Demonstrating that the propagating alkylidene of living polymer derived from the first monomer can function as an initiator for the ROMP of second monomer. This is an obvious requirement for a successful living block copolymerisation system, and has been shown to be the case in similar experiments with a range of fluorinated norbornenes/norbornadienes pairs.

GPC analysis on the block copolymer samples, revealed that the samples exhibit narrow molecular weight distributions. Some of the fluorinated block copolymers show two glass transition temperatures which are well-defined; this observation has been confirmed by thermally stimulated current (TSC), studies on poled films provide clear evidence that the two components are not compatible and phase separation occurs.

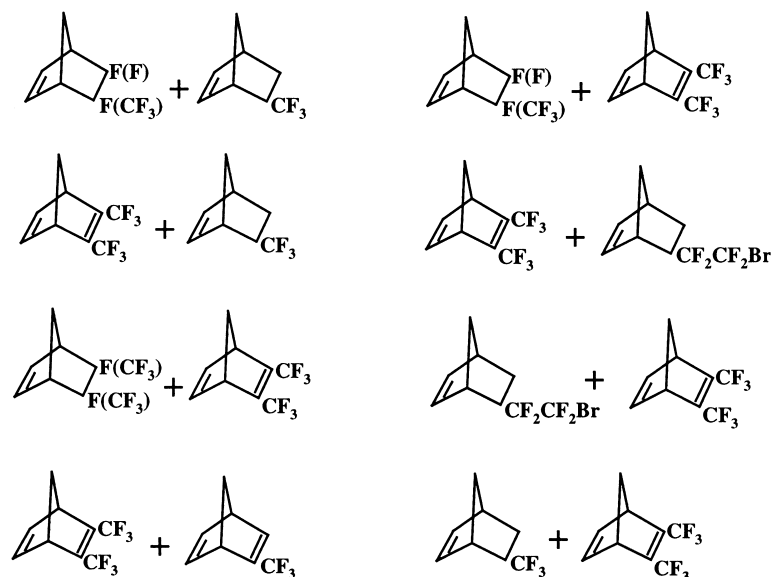


Fig. 11. Selection of monomer pairs giving rise to successful block copolymer synthesis, the component on the left was polymerised first.

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