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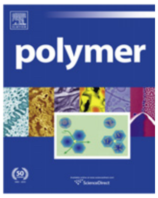

cis/*trans* Gradients in living ring-opening metathesis polymerization

John P. Bishop, Richard A. Register*

Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544-5263, United States

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The chain microstructure (*cis*/*trans* ratio) in ring-opening metathesis polymerization (ROMP) of norbornene and methyltetracyclododecene (MTD) using the Schrock-type initiator Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(=CHCMe$_2$Ph)(OCMe$_3$)$_2$ is shown to be a strong function of monomer concentration, providing a convenient means for tuning the average *trans* content in the resulting polymers. Moreover, since this is a “living” ROMP initiator, chains formed in batch polymerizations show a continuous gradient of *trans* content down the chain, with the *trans* content increasing with conversion. This gradient can be quite substantial; for a typical norbornene polymerization, *trans* content varies from 30% at one end of the chain to nearly 80% at the other end. The results are explained based on a literature kinetic description for the behavior of this initiator, where *cis* and *trans* units are added to the chain by *syn* and *anti* rotamers of the active site, respectively. A quantitative mathematical description is developed for the chain microstructure, and associated kinetic parameters are measured for norbornene and MTD at room temperature. The model accurately describes both the variation in average *trans* content with starting monomer concentration, and the gradients in *trans* content measured via samples taken at different conversions throughout the polymerization. In contrast, ROMP of MTD using the first-generation Grubbs’ initiator Ru(=CHPh)Cl$_2$(PCy$_3$)$_2$ shows no down-chain gradient in *trans* content.

1. Introduction

Ring-opening metathesis polymerization (ROMP) differs from other olefin polymerizations in that the double bonds that mediate the polymerization are retained in the backbone of polymeric product. These double bonds may exist in either a *cis* or *trans* configuration, and the *cis*:*trans* ratio can have a significant effect on the polymer’s properties. A well-known non-ROMP example is that the glass transition temperatures (T_g) of 1,4-polybutadiene and 1,4-polyisoprene are both 12 °C higher in polymers with all *trans* double bonds compared to polymers with all *cis* double bonds [1]. Among ROMP polymers, a ~30 °C increase was found in high-*cis* polymers of *endo*,*exo*-5,6-dimethylnorbornene compared to high-*trans* polymers [2], qualitatively opposing the trend seen in the polydienes. Ivin, Rooney, and co-workers studied *cis*/*trans* isomerism in polymers of norbornene, the archetypal ROMP monomer, as well as several norbornene derivatives, where the polymerizations employed “classical” nonliving ROMP catalysts [3]. For norbornene, polymers that spanned essentially the entire range of *cis* contents could be accessed by varying catalyst, co-catalyst, and solvent, or through additives [4,5]. When the fraction of *cis* double bonds (F_{cis}) exceeded 35%, the distribution of the double bonds tended to be “blocky” [5,6], a result also found with several substituted norbornenes [7–9]. In these heterogeneous catalyst systems, the blockiness likely reflects kinetically distinct propagating species with varying preferences for adding monomer in the *cis* or *trans* configurations [3].

The advent of well-defined, homogeneous ROMP initiators, notably those of Schrock [10] and Grubbs [11], has allowed for living polymerizations and permitted more systematic investigations of the polymerization mechanism, including what factors control *cis*/*trans* isomerism. “Schrock-type” initiators of the general structure Mo(NAr)(=CHCR’)(OR″)$_2$ where Ar = 2,6-C$_6$H$_3$-*i*-Pr$_2$, R′ = *t*-Bu or CMe$_2$Ph, and R″ = OCMe$_3$, OCMe$_2$(CF$_3$), OCMe(CF$_3$)$_2$, or OC(CF$_3$)$_3$ have been studied extensively in this regard [2,10,12–14]. These initiators exist as two spectroscopically and kinetically distinct rotational isomers (rotamers), as shown in Fig. 1: an *anti* rotamer with the alkylidene substituent pointing away from the imido nitrogen atom, and a *syn* rotamer with the alkylidene substituent pointing towards the imido nitrogen atom [12]. These rotamers interconvert at rates (unimolecular rate constant $k_{s/a}$ and $k_{a/s}$) that depend on the electron withdrawing ability of the alkoxide ligands, with the interconversion rates becoming drastically slower as the electron withdrawing ability increases (*i.e.*, greater fluorination) [12,13]. The *syn* rotamer is thermodynamically preferred, with $K_{eq} = k_{a/s}/k_{s/a} \approx 1000$ in toluene at 25 °C, although the *anti* rotamer

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* Corresponding author. Tel.: +1 609 258 4691; fax: +1 609 258 0211.
E-mail address: register@princeton.edu (R.A. Register).

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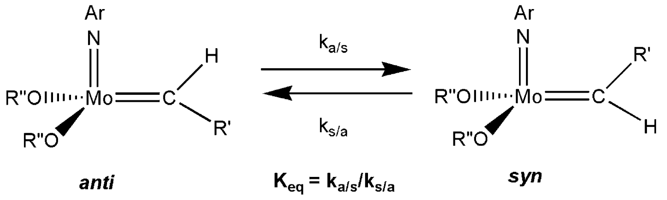

Fig. 1. The two rotamers (*syn* and *anti*) of the Schrock-type molybdenum initiators. The rotamers can interconvert at rates that depend on the ligands.

reacts much faster with monomer [12,13]. In studies with 2,3-bis(trifluoromethyl)norbornadiene, the *syn* rotamer was found to add *cis* units to the chain while retaining the *syn* configuration of the active site. In contrast, the *anti* rotamer adds a single *trans* unit to the chain, after which the active site is converted to the *syn* rotamer. With an initiator bearing weakly-electron withdrawing ligands, such as Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(=CHCMe$_2$Ph)(OCMe$_3$)$_2$, the rotamer interconversion rates are sufficiently high that the more reactive but less favored *anti* rotamer could be accessed on the time scale of polymerization, resulting in polymers with high *trans* contents. When the ligands were progressively fluorinated, the decrease in rotamer interconversion rate meant that the *anti* rotamer could not be accessed on the time scale of polymerization, and polymers with high *cis* contents were obtained. Similar results were found in the polymerizations of (+)- and (±)-5,6-dimethylnorbornene [2], 7-methylnorbornadiene [15], and (+)-5,6-dicarbomethoxynorbornene [16].

These prior results demonstrate that the *cis*/*trans* ratio with these Schrock-type initiators is influenced by the relative rates of rotamer interconversion—a unimolecular reaction involving only the active sites—and propagation, a bimolecular reaction involving both active sites and monomer. Consequently, slowing the propagation rate by decreasing monomer concentration should favor rotamer interconversion over propagation and lead to a higher *trans* content. Moreover, when a polymerization is conducted in batch, the monomer concentration decreases continuously throughout the reaction, implying that the *trans* content of the polymer will increase progressively with time. For a living polymerization, monomer units consumed at the start and end of the reaction become part of the same polymer chain, meaning that there should be a microstructural gradient along the chain, from lowest-*trans* at the end formed first, extending continuously to highest-*trans* at the other end. In this paper, we confirm these ideas in polymerizations of both norbornene and methyltetracyclododecene (MTD, see Fig. 2) with the nonfluorinated Schrock-type initiator noted above, including the presence of a down-chain gradient in *trans* content; we also develop a quantitative model for the chain microstructure and measure the associated kinetic parameters at room temperature.

2. Experimental

2.1. Materials

The chemical structures of the monomers used are shown in Fig. 2. MTD (systematic name is 8-methyl-tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene; monomer is a 2:1 mixture of *endo*/*anti* and *exo*/*syn* isomers [17]) was obtained from Promerus. Norbornene was obtained from Aldrich. Each monomer was dried over sodium, degassed by freeze-pump-thaw cycles, and vacuum transferred prior to use. Toluene was dried over sodium benzophenone ketyl, degassed by freeze-pump-thaw cycles, and vacuum transferred prior to use. The Schrock-type initiator, 2,6-diisopropylphenylimidoneophylidenemolybdenum (VI) bis(*tert*-butoxide), was used as received from Strem Chemicals. Bis(tricyclohexylphosphine)-benzylidene ruthenium (IV) dichloride, a "first-generation" Grubbs initiator, as well as tricyclohexylphosphine (PCy$_3$), benzaldehyde (99.5+%, SureSeal), and ethyl vinyl ether (99%), were used as received from Aldrich.

2.2. Polymerization

ROMP of norbornene and MTD were conducted under a nitrogen atmosphere in an Innovative Technologies System One glove box at room temperature with water and oxygen contents of less than 1.0 ppm. For polymerizations using the Schrock-type initiator, the initiator was first dissolved in toluene, followed by the monomer at a predetermined concentration. The reaction mixture was stirred for 60 min and terminated with a hundred-fold molar excess of benzaldehyde. For the polymerization using the Grubbs initiator, the initiator was first dissolved in toluene, followed by 5 eq of PCy$_3$, and the MTD monomer. The reaction mixture was stirred for 60 min and terminated with a hundred-fold molar excess of ethyl vinyl ether. For kinetic experiments, several aliquots were taken during the polymerization for subsequent analysis by GPC and NMR, and the aliquots were terminated with a large excess of benzaldehyde (Schrock-type initiator) or ethyl vinyl ether (Grubbs initiator).

2.3. Instrumentation

Gel permeation chromatography (GPC) in THF or toluene was used to determine polymer molecular weights, polydispersity indices (PDIs), and reaction conversion (toluene GPC). The THF GPC system operates at 35 °C and consists of two 30 cm Polymer Laboratories PLgel Mixed-C columns, a Waters 515 HPLC pump, and a Waters 410 differential refractometer. The toluene GPC operates at room temperature, and consists of a Waters 590 HPLC pump, two 30 cm Polymer Laboratories PLgel Mixed-C columns, and a Knauer

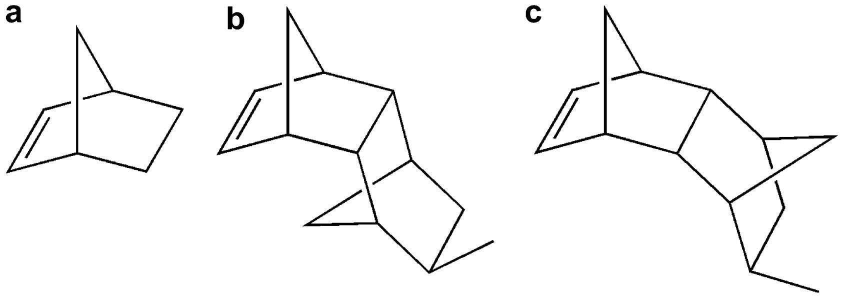

Fig. 2. Chemical structures of the monomers: a) norbornene, b) the predominant isomer of MTD, which has an *endo* orientation of the methyl carbon and an *anti* orientation of the bridging carbons, and c) the minority isomer of MTD, which has an *exo* orientation of the methyl carbon and a *syn* orientation of the bridging carbons. The **b**:**c** ratio is 2:1.

differential refractometer. Both GPC systems were calibrated with narrow-distribution polystyrene standards. For the polymerization of norbornene, the conversion was calculated based on the integrals of the monomer and polymer peaks in the toluene GPC chromatogram, taking into account the differing refractive index increments for the monomer and polymer. For the polymerization of MTD, the monomer peak was not clearly resolvable in the chromatogram, so the polymer's peak molecular weight (M_p) was used to determine conversion, assuming that the sample terminated after 60 min corresponded to 100% conversion. When applied to the polymerization of norbornene, this method of determining conversion matched well with the more direct method of measuring monomer and polymer areas. ^{1}H NMR spectra in $CDCl_3$ were collected using a Varian Inova-500 MHz or a Bruker Biospin AVANCE-500 MHz to determine *cis*/*trans* ratios. ^{13}C NMR spectra in $CDCl_3$ were collected on polyMTD using a Bruker Biospin AVANCE-500 MHz to confirm the ^{1}H NMR peak assignments used in determining the *cis*/*trans* ratio, and to measure the ratio of the two MTD isomers in the polymers (using the methyl carbon peaks [17]).

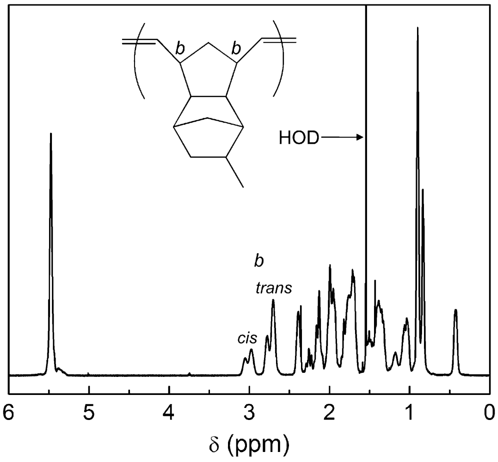

Fig. 4. ^{1}H NMR spectrum of polyMTD, M_n = 123 kg/mol, PDI = 1.09. The ratio of *cis*/*trans* backbone double bonds can be determined using the backbone methine protons *b* (F_{trans} = 0.71 here).

3. Results and discussion

3.1. Determination of polymer microstructure

The ^{1}H NMR spectrum of ROMP polynorbornene (PN), shown in Fig. 3, has been previously assigned [18]. The *cis*/*trans* ratio for PN can be determined using either the olefinic protons (protons *a*) or the backbone methine protons (protons *b*). For polyMTD (PMTD), the ^{1}H NMR spectrum (Fig. 4) is much more complex, for several reasons: there are two different isomers present, the repeat unit is not symmetric as in PN, and there are simply many more chemically distinct protons. Still, the *cis*/*trans* ratio can be determined directly from the ^{1}H NMR spectrum using the backbone methine protons (protons *b*), although the peaks assigned to both the *cis* and *trans* methine protons are split by the presence of two MTD isomers (**b** and **c** in Fig. 2).

3.2. Kinetic model for ROMP using a Schrock-type initiator

As noted in the introduction, the kinetic mechanism elucidated by Schrock and co-workers is such that a *syn* rotamer can add a monomer in the *cis* configuration while remaining *syn*; an *anti* rotamer adds a single monomer in the *trans* configuration, with a concomitant conversion of the active site to the *syn* rotamer. The *anti* rotamers are of higher energy (hence disfavored thermodynamically), but are much more reactive towards monomer. In the limit that monomer addition by the *anti* rotamer is extremely fast, the *syn* sites can undergo one of two reactions: 1) add monomers in the *cis* configuration at a relative rate $k_{p,s}[M]$, where $k_{p,s}$ is the bimolecular propagation rate constant for the *syn* rotamers and $[M]$ is the monomer concentration (we assume here ideal solution behavior for the monomer, *i.e.*, neglect any changes in the monomer's activity coefficient during polymerization, or across polymerizations), or 2) isomerize to the *anti* rotamer at a relative rate $k_{s/a}$, then immediately add a single monomer in the *trans* configuration and switch back to *syn*. In this limiting scenario, the *trans* fraction in the instantaneously-formed polymer, $f_{trans,fast}$, is simply the fraction of instances where the sites follow the latter path:

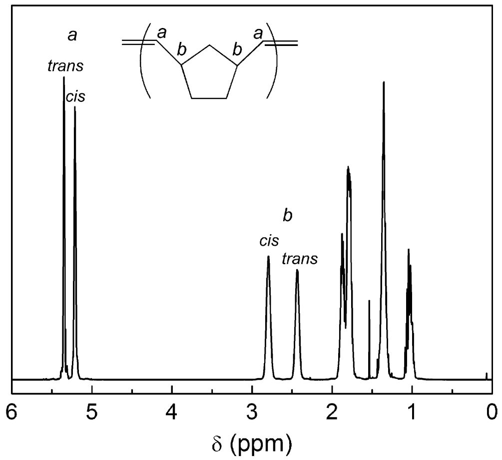

Fig. 3. ^{1}H NMR spectrum of polynorbornene, M_n = 60 kg/mol, PDI = 1.11. The ratio of *cis*/*trans* backbone double bonds can be determined using either protons *a* or *b* (F_{trans} = 0.46 here).

$$f_{trans,fast} = \frac{k_{s/a}}{k_{p,s}[M] + k_{s/a}} \tag{1}$$

However, if the bimolecular propagation rate constant for the *anti* rotamer, $k_{p,a}$, is not exceedingly high, there is a chance that the *anti* rotamer will isomerize back to *syn* before adding a monomer unit. The fraction of instances ($g_{a,add}$) where an *anti* rotamer adds a monomer unit to the chain, rather than simply isomerizing back to *syn* directly, is thus given by:

$$g_{a,add} = \frac{k_{p,a}[M]}{k_{p,a}[M] + k_{a/s}\left\{\dfrac{k_{p,s}[M]}{k_{p,s}[M] + k_{s/a}}\right\}} \tag{2}$$

where the term enclosed in {} in the denominator simply reflects the fraction of instances where the *syn* rotamer isomerizes directly back to *anti* without adding a monomer unit. The instantaneous fraction of double bonds in the polymer, f_{trans}, is thus given by the products of equations (1) and (2), $f_{trans} = f_{trans,fast}g_{a,add}$.

During a polymerization, the monomer concentration can be expressed in terms of conversion X:

$$[M] = [M]_0(1-X) \tag{3}$$

where $[M]_0$ is the initial monomer concentration. To simplify the notation, we introduce dimensionless ratios of rates, α and β:

$$\alpha = \frac{k_{p,s}[M]_0}{k_{s/a}} = A[M]_0 \tag{4}$$

and

$$\beta = \frac{k_{\mathrm{p,a}}[M]_0}{k_{\mathrm{a/s}}} = B[M]_0 \tag{5}$$

where the quantities A and B are not dimensionless ([=] L/mol), but reflect the intrinsic ratios of rate constants (propagation *vs.* rotamer interconversion), for the *syn* and *anti* sites, respectively, independent of monomer concentration. Combining equations (1)–(5) leads to:

$$f_{\mathrm{trans}} = \frac{\beta}{\beta[1+\alpha(1-X)]+\alpha} \tag{6}$$

In practice, the quantity which can be measured (*e.g.*, by NMR on polymer aliquots taken during the reaction) is not the instantaneous f_{trans}, but rather the value of f_{trans} integrated from the start of the polymerization up to the specified conversion, X, which we denote F_{trans}:

$$\begin{aligned} F_{\mathrm{trans}} &= \int\limits_0^X f_{\mathrm{trans}}\mathrm{d}y = \frac{1}{X}\int\limits_0^X \frac{\beta}{\beta[1+\alpha(1-y)]+\alpha}\mathrm{d}y \\ &= -\frac{1}{\alpha X}\ln\left(\frac{\beta(1+\alpha)+\alpha-\beta\alpha X}{\beta(1+\alpha)+\alpha}\right) \end{aligned} \tag{7}$$

Two useful limits of equation (7) are those at zero conversion (equation (8)) and full conversion (equation (9)):

$$F_{\mathrm{trans},X=0} = \frac{\beta}{\beta(1+\alpha)+\alpha} = \frac{B}{B(1+A[M]_0)+A} \tag{8}$$

$$\begin{aligned} F_{\mathrm{trans},X=1} &= -\frac{1}{\alpha}\ln\left(\frac{\beta+\alpha}{\beta(1+\alpha)+\alpha}\right) \\ &= -\frac{1}{A[M]_0}\ln\left(\frac{B+A}{B(1+A[M]_0)+A}\right) \end{aligned} \tag{9}$$

In the limit that the monomer is dilute (α, $\beta << 1$), many rotational isomerization events will occur for every propagation event. In this limit, the ratio of *trans*/*cis* units in the polymer should simply be given by the relative reactivities and abundances of the *anti* and *syn* rotamers:

$$\left(\frac{F_{\mathrm{trans}}}{F_{\mathrm{cis}}}\right)_{\mathrm{M\ dilute}} = \left(\frac{k_{\mathrm{p,a}}}{k_{\mathrm{p,s}}}\right)\Big/\left(\frac{k_{\mathrm{a/s}}}{k_{\mathrm{s/a}}}\right) = \frac{k_{\mathrm{p,a}}}{k_{\mathrm{p,s}}}\Big/K_{\mathrm{eq}} = \frac{\beta}{\alpha} = \frac{B}{A} \tag{10}$$

Equations (7)–(9) are all consistent with this limit, which emphasizes the physical significance of α and β (or A and B): since the *trans* content increases as $[M]$ is reduced, the highest ratio of $F_{\mathrm{trans}}/F_{\mathrm{cis}}$ attainable with a given catalyst and monomer is β/α, or B/A.

3.3. Effect of initial monomer concentration

To test the model, we ran a series of norbornene polymerizations with varying $[M]_0$, all taken to complete conversion, and measured $F_{\mathrm{trans},X=1}$ by NMR. The results, and the fit to equation (9), are shown in Fig. 5. The best-fit values for A and B for the data at $[M]_0$ values up to 0.367 mol/L (4 wt%) are $A = 5.6 \pm 0.6$ L/mol (one standard deviation) and $B = 20 \pm 4$ L/mol, with $B/A = \beta/\gamma = 3.5$. At these initial monomer concentrations, the fit to the data is excellent. An additional polymerization was run at $[M]_0 = 0.73$ mol/L, shown as the open circle in Fig. 5, which shows a value of F_{trans} above the model fit. We attribute this deviation to the difficulty in holding the reaction isothermal without active cooling; the calculated adiabatic temperature rise for norbornene polymerization in toluene is 4 °C per wt% norbornene in the starting charge, or 32 °C for $[M]_0 = 0.73$ mol/L, and the half-time of the polymerizations in Fig. 5 is approximately 3 min. This effect was confirmed by running a series of polymerizations run at higher initiator concentrations $[I]$; the measured F_{trans} consistently exceeded the model prediction, and the discrepancy increased progressively with increasing $[I]$ (*i.e.*, increasing reaction rate). The magnitude and even the direction of the temperature effect on *trans* content are difficult to predict *a priori*, since they involve a complex ratio of rate constants even in the $[M]_0 \to 0$ limit (see equation (10)), but an increase in *trans* content with increasing temperature is consistent with the previously-reported temperature dependence in polymerizations of 2,3-bis(trifluoromethyl)norbornadiene with several different Schrock-type initiators [14]. To maintain isothermal conditions in this work, initial monomer concentrations were limited to 4 wt%.

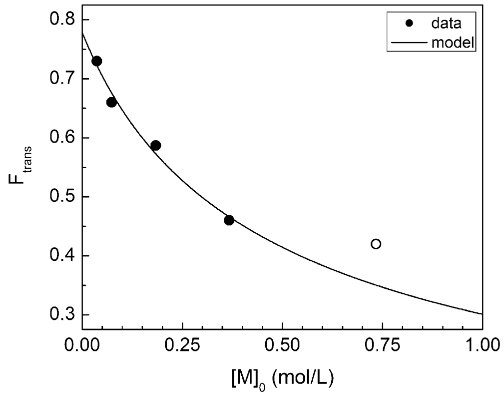

Fig. 5. Fraction of *trans* double bonds (F_{trans}) for room-temperature norbornene polymerizations with the Schrock initiator, run to complete conversion at various initial monomer concentrations ($[M]_0$). For all polymerizations, initiator concentration was 0.346 mmol/L, and polymerizations were run for 60 min (calculated conversion >99.99%). Curve is the fit of the data to equation (9), yielding $A = 5.6 \pm 0.6$ L/mol and $B = 20 \pm 4$ L/mol.

3.4. Effect of conversion

Kinetic studies of the ROMP polymerizations of norbornene and MTD in toluene at room temperature were run with the same Schrock-type initiator, using an initiator concentration of 0.346 mmol/L and an initial monomer concentration of 4 wt% (corresponding to $[M]_0 = 0.367$ mol/L for norbornene and $[M]_0 = 0.189$ mol/L for MTD). Aliquots were taken during the polymerizations and the conversions X measured as described in the Experimental Section. Fig. 6a shows the measured values of F_{trans} for the norbornene polymerization (symbols), along with the calculated values from equation (7) using the values of A and B determined above (solid curve). The model prediction is in excellent agreement with the data, and shows that F_{trans} increases from 0.30 to 0.46 as conversion varies from 0 to 1, thereby confirming a substantial gradient of *trans* content along the chain. The magnitude of this gradient is more evident when the same values of A and B are used to calculate (by equation (6)) the instantaneous polymer composition, f_{trans}, which varies from 0.30 at one end of the chain to 0.78 at the other end.

The analogous data for an MTD polymerization are shown in Fig. 6b, again showing a strong gradient, though with higher *trans* contents overall than for norbornene ($0.61 < F_{\mathrm{trans}} < 0.73$ for $0 < X < 1$). Best-fit values of $\alpha = 0.52 \pm 0.03$ and $\beta = 4.1 \pm 0.9$ were obtained by fitting equation (7) to these data, yielding $A = 2.8$ L/mol and $B = 22$ L/mol by equations (4) and (5), and $B/A = \beta/\alpha = 7.8$. The model again provides an excellent representation of the data, and the calculated instantaneous f_{trans} varies from 0.61 to 0.89 as conversion increases from 0 to 1.

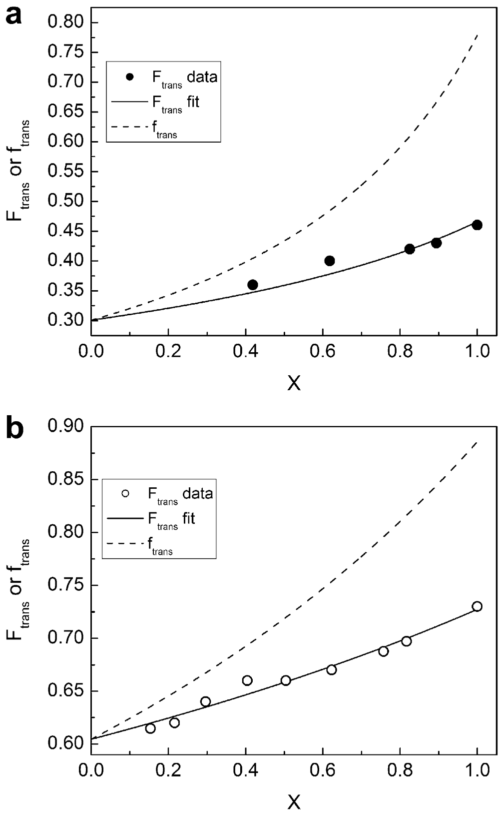

Fig. 6. Plot of integrated *trans* double bond fraction (F_{trans}) *vs.* conversion (X) during room-temperature polymerizations of a) norbornene, and b) MTD, both with $[I] = 0.346$ mmol/L; experimental data shown as symbols. In a), $[M]_0 = 0.367$ mol/L; the solid curve is F_{trans} calculated from the parameters determined by fitting the data in Fig. 5 ($A = 5.6$ L/mol, $B = 20$ L/mol); the dashed curve is the instantaneous f_{trans} calculated using the same parameters. In b), $[M]_0 = 0.189$ mol/L; the solid curve is a fit of the F_{trans} data to equation (7), yielding $\alpha = 0.52 \pm 0.03$ and $\beta = 4.1 \pm 0.9$, while the dashed curve is the instantaneous f_{trans} calculated using the same parameters.

As with the temperature effect discussed above, the influence of monomer type on *trans* content is difficult to predict *a priori*, as it involves the same complex ratios of rate constants (see equation (10) for the $[M]_0 \rightarrow 0$ limit). However, it is reasonable to assume that monomer type has a much stronger effect on the bimolecular propagation rate constants ($k_{\text{p,a}}$ and $k_{\text{p,s}}$) than on the unimolecular rotamer interconversion rate constants $k_{\text{s/a}}$ and $k_{\text{a/s}}$, since propagation involves direct coordination of the monomer to the active site (*vs.* the more distant steric effect of polymer structure on rotamer interconversion, where different polymers correspond to different R′ in Fig. 1). Consequently, the twofold higher B/A ratio for MTD (7.8) *vs.* norbornene (3.5) should reflect a similarly higher ratio of $k_{\text{p,a}}/k_{\text{p,s}}$ for MTD relative to norbornene—in other words, that the higher *trans* content in MTD principally reflects differences in the reactivities of the two rotamers, rather than their relative abundances. Since K_{eq} has been reported to be of $O(10^3)$ for this initiator [12,13], $k_{\text{p,a}}/k_{\text{p,s}}$ must be $O(10^3–10^4)$ for both norbornene and MTD to achieve the B/A ratios we measure.

3.5. *Polymerizations with a first-generation Grubbs initiator*

A kinetic experiment equivalent to those described in Section 3.4 was performed by polymerizing MTD with the Grubbs initiator $Ru(=CHPh)Cl_2(PCy_3)_2$. Unlike with the Schrock-type initiator, F_{trans} was found to be 0.81 ± 0.01 across all conversions measured (from $0.11 < X < 1$) indicating that there is no substantial gradient in *cis*/*trans* ratio using this initiator. The Grubbs initiator is quite different than the Schrock-type initiator—it requires one of the two PCy_3 ligands to reversibly dissociate for the initiator to become active for polymerization [19], for example—so it is perhaps not surprising that it behaves quite differently with regard to monomer concentration effects on chain microstructure as well.

3.6. *Reactivity of MTD isomers*

As noted in Fig. 2, MTD consists of two distinct isomers in a 2:1 ratio (**b**:**c**). One might well ask if these two monomers are equally reactive, *i.e.*, whether there could be a gradient of **b**:**c** down the chain. Though **b** *vs.* **c** units are difficult to distinguish by ^{1}H NMR, ^{13}C NMR is sensitive to **b** *vs.* **c** [17], so polymers obtained from the aliquots taken during the kinetic experiments on MTD using both the Schrock and Grubbs initiators were examined by ^{13}C NMR. No gradient in the **b**:**c** ratio was observed for either initiator. In retrospect, this is unsurprising, as reaction with the initiator occurs at the *exo* face of norbornene-type monomers [3], which is unobstructed in both MTD isomers. By contrast, substitution at the bridging carbon (as in 7-methylnorbornene) leads to a much greater reactivity for the *anti*- (unobstructed) isomer than for the *syn*- (obstructed) isomer, with both “classical” [20] and Schrock-type [21] catalysts.

4. Conclusions

ROMP polymers synthesized with the Schrock-type initiator $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(=CHCMe_2Ph)(OCMe_3)_2$ show a strong dependence of the average *trans* content on the monomer concentration, with *trans* content increasing as the monomer is diluted. This is a consequence of the competitive rates of polymerization and interconversion between *syn* and *anti* rotamers of the active site, as the *syn* and *anti* rotamers are responsible, respectively, for *cis* and *trans* enchainment of monomer units. A mathematical model for the chain microstructure was developed, and found to give a good quantitative description of the average *trans* contents in norbornene polymerizations taken to complete conversion from different starting monomer concentrations. In batch polymerizations, monomer concentrations decrease continuously with conversion, so the instantaneous *trans* content increases continuously with conversion; since this is a “living” ROMP initiator, monomers added at low and high conversions form different ends of the same chain, meaning that there is gradient in *trans* content along each chain. The same kinetic model and parameters described above also yield a quantitatively good description of the gradient generated in norbornene polymerizations, assessed experimentally by measurements on aliquots taken at different conversions; under typical conditions, instantaneous *trans* contents can vary from 30% at the start of polymerization to nearly 80% at the end. A qualitatively similar gradient was measured during MTD polymerizations, which was also well described by the model. In contrast, polymerizations of MTD with the first-generation Grubbs initiator $Ru(=CHPh)Cl_2(PCy_3)_2$ showed no *trans* gradient, indicating no dependence of *trans* content on monomer concentration. While MTD consists of two resolvable isomers, no down-chain gradient in isomeric composition was found in MTD polymerizations with either initiator.

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