

A p p e n d i x 1

G P C C h a r a c t e r i z a t i o n o f C y c l i c P o l y m e r s

Cyclic metathesis catalysts described in Chapters 2 and 3 also exhibit functional group tolerance, and can be used to readily polymerize functionalized monomers, such as 5-acetoxy-, 5-bromo-, and 5-hydroxycyclooctene with complete monomer conversion as detected by $^1\text{H-NMR}$ spectroscopy.

The dilute solution properties, such as intrinsic viscosity ($[\eta]$), of the resulting cyclic polymers were routinely examined using GPC coupled with a triple detecting (light scattering/differential viscometer/differential refractometer) system to obtain the Mark-Houwink-Sukurada plot and the elution volume vs time. As shown in Table 1, MW was not proportional to the catalyst loading ($[\text{M/Ru}]_0$) as a result of poor initiation.

Interestingly, all types of cyclic polymers tested were found to have lower dn/dc values than their linear analogues, but dn/dc decreased as $[\text{M/Ru}]_0$ decreased (Table 1). On the other hand, linear polymers prepared using different $[\text{M/Ru}]_0$ had very similar dn/dc values. In order to confirm the difference in dn/dc between linear and cyclic samples, we mixed different amounts of linear polymer into the cyclic one with similar MW and used the RI detector and viscometer on the GPC to check the dn/dc and $[\eta]$ values and of these mixtures. The addition of linear into cyclic polymer was found to indeed increase the dn/dc and $[\eta]$ values (Table 2 and Figure 1).

Table 1. Linear and cyclic polymers prepared using $(\text{H}_2\text{IMes})(\text{PCy}_3)(\text{Cl})_2\text{RuCHPh}$ and UC-6, respectively^a

Polymer	$[\text{M}/\text{Ru}]_0$	dn/dc^b	M_w^c	PDI
LPCOAc	1500	0.083	103 k	1.39
LPCOAc	200	0.086	40 k	1.43
CPCOAc	1000	0.088	134 k	1.37
CPCOAc	500	0.077	131 k	1.32
CPCOAc	200	0.074	109 k	1.28
CPCOAc	100	0.061	95 k	1.40
LPCOBr	1000	0.117	98 k	1.50
CPCOBr	500	0.105	142 k	1.54
CPCOBr	200	0.081	167 k	1.30
LPCDT	200	0.128	92 k	1.45
CPCDT	200	0.103	150 k	1.40

^aPolymerization conditions: $[\text{M}]_0 = 1.5 \text{ M}$ (PCOAc), 1.5 M (PCOBr), and 2.5 M (PCDT) in CH_2Cl_2 ; $40 \text{ }^\circ\text{C}$, 12 h. ^bMeasured by an “Optilab” DSP differential refractometer attached to GPC in THF by assuming 100% mass elution from the columns. ^cMeasured by THF GPC coupled with 18-way light scattering detector.

Table 2. Mixture of linear and cyclic PCDT at various ratios^a

Polymer	M_w^b	dn/dc^c
CPCDT (C)	150k	0.103
L:C=2:8	157k	0.103
L:C=5:5	137k	0.108
L:C=8:2	110k	0.118
LPCDT (L)	92k	0.128

^aPolymerization conditions: $[M]_0 = 2.5 \text{ M}$ in CH_2Cl_2 ; $40 \text{ }^\circ\text{C}$, 12 h. ^bMeasured by THF GPC coupled with 18-way light scattering detector. ^cMeasured by an “Optilab” DSP differential refractometer attached to GPC in THF by assuming 100% mass elution from the columns.

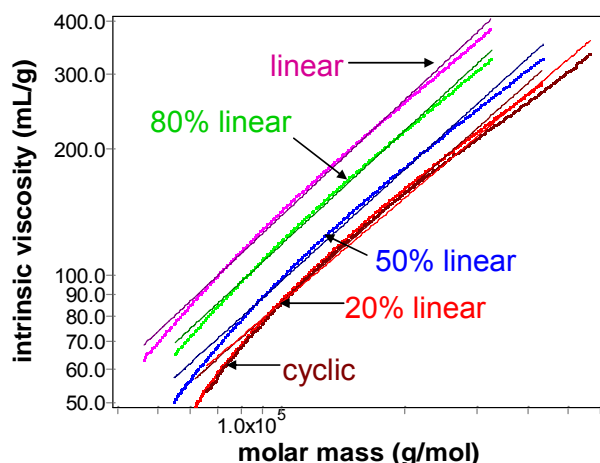


Figure 1. Intrinsic viscosities of cyclic and linear PCDT and their mixtures from GPC.

In order to investigate the effect of linear olefin on the fidelity of the cyclic polymerization and correlate the observed variance of dn/dc to the purity of cyclic polymer, we doped the monomer with a small amount of *cis*-3-hexene as the chain transfer agent (CTA). Linear olefin impurity is known to either react with cyclic catalyst or break up the cyclic organometallic complex through chain transfer, thus leading to linear chains. COAc was chosen as the monomer as it always gave polymers with symmetric, unimodal MW distributions, making the determination of dn/dc more accurate. The least active catalyst, **UC-5**, was used in this study.

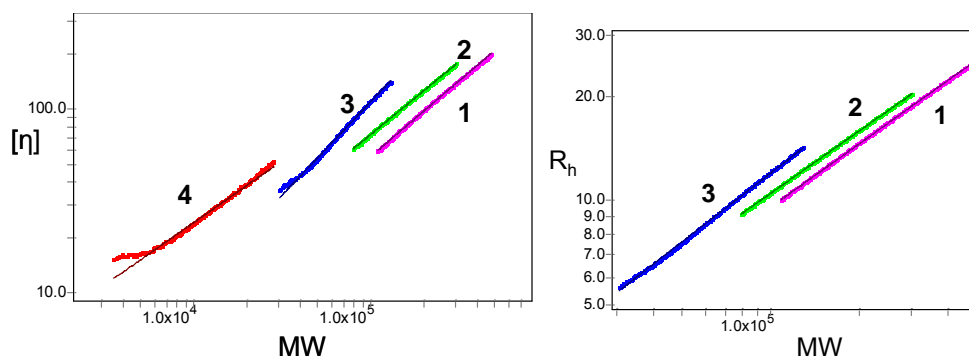
In the absence of deliberately added CTA, consistently low dn/dc was obtained when $[M/Ru] = 300$ was used. However, with a ratio of monomer to CTA ($[M/CTA]$) at 3000, the dn/dc already started to increase (increased by 30% of the dn/dc difference between cyclic and linear polymers) and the MW dropped to 64% of the original MW. As the amount of CTA was increased, the dn/dc systematically increased to that of linear

polymers and the MW dropped to 5% of the original MW, when $[M/CTA] = 30$ was used (Table 2). When compared at the same MW, the addition of CTA caused the dn/dc , $[\eta]$, and hydrodynamic radius (R_h) of the resulting polymers to steadily increase with increasing the amount of CTA from entry 2 to 4. This observation indicated that even a small amount of linear olefin can result in linear chain impurity during REMP.

Table 2. REMP of 5-acetoxy-cyclooctene using UC-5 in the absence and presence of chain transfer agent (CTA)^a

	$[M/CTA]_0$	$[CTA/Ru]_0$	dn/dc	$M_{w,GPC}$
1	-	0	0.059	214k
2	3000	0.1	0.068	137k
3	300	1	0.080	63k
4	30	10	0.088	10k

^aPolymerization conditions: $[M]/[cat]_0 = 300$, $[M]_0 = 1.5$ M in CH_2Cl_2 ; 40 °C, 12 h.



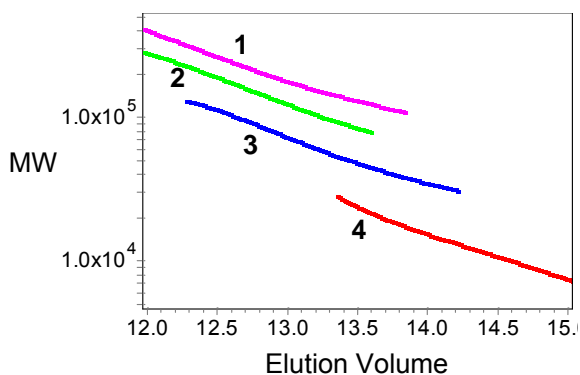


Figure 2. Comparison of (a) intrinsic viscosity, (b) hydrodynamic radius, and (c) elution time of PCOAc prepared without (1) and with (2-4) different amount of CTA.

The dn/dc value is an important parameter in the GPC characterization, because it is used to calculate the absolute MW and to derive $[\eta]$, using the light scattering equation: $I(\theta)_{\text{scatter}} = cM_w(dn/dc)^2P(\theta)$, where c is the polymer concentration and $P(\theta)$ is the angular dependence of the scattering intensity, $I(\theta)_{\text{scatter}}$. In theory, dn/dc value is only related to the chemical composition of a polymer, but not the topology. There have been very few reports on dn/dc values of polymers with different architectures. Our *observed* lower dn/dc values from on-line mode GPC for cyclic polymers are very surprising. Therefore, we sought to measure dn/dc manually to verify their values. Polymer solutions with five concentrations in the range of 0.1 – 2.5 mg/mL were prepared and injected directly into the refractometer via a syringe pump to get the differential refractive index (n) for each concentration. The slope of the n value vs the concentration gave the dn/dc (Figure 3). The dn/dc values of cyclic and linear polymers turned out to be the same using manual measurement (Table 3), as theory predicts. Surprisingly, although the dn/dc values measured manually and using on-line mode GPC were very close for linear polymers, the dn/dc values were artificially smaller for cyclic polymers when measured assuming 100% mass recovery from the GPC column. Therefore, this result indicated that, for

cyclic polymers, certain mass retained on the column during normal elution time. The reason for this and whether this is universal or unique to our column system are unknown. However, using the correct dn/dc values (the same for linear and cyclic polymers) should still give the correct M_w and $[\eta]$ for the population of cyclic polymer that elutes normally.

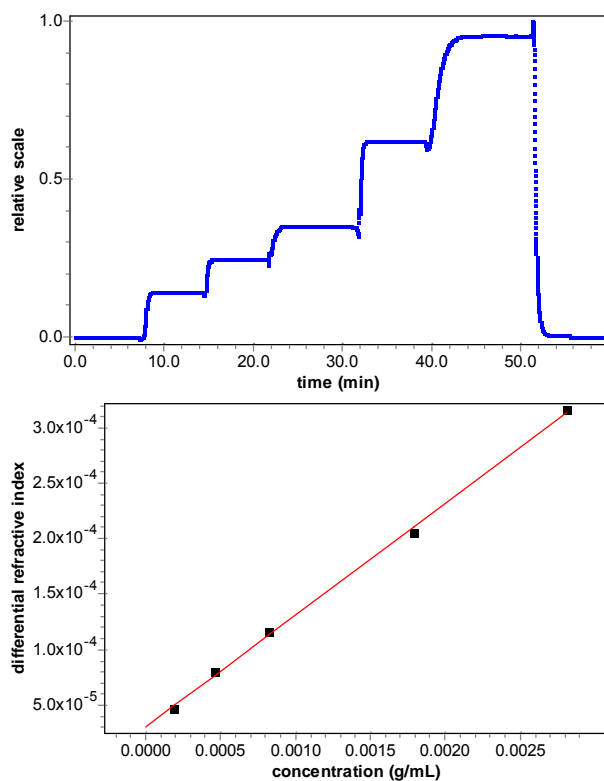


Figure 3. Exemplary manual measurement of dn/dc .

Table 3. Comparison of dn/dc obtained via manual measurement and via on-line mode GPC assuming 100% mass recovery

Polymer	Manual dn/dc	On-line dn/dc
LPCOAc	0.0866	0.084
CPCOAc	0.0852	0.06
LPCOE	0.1008	0.10
CPCOE	0.1016	0.08

If the lower dn/dc value, although not correct, is an indication of the cyclic topology, the fact that dn/dc values were lower when high catalyst loading was used may suggest that short polymerization times gave cyclic polymers with higher purity. This may be rationalized if catalyst decomposition before the completion of polymerization is the major source of linear impurity and catalyst re-incorporation to the polymer is not favored (decomposition of released catalyst does not generate linear chains).

A p p e n d i x 2

H y d r o g e n a t i o n o f P o l y a l k e n a m e r s

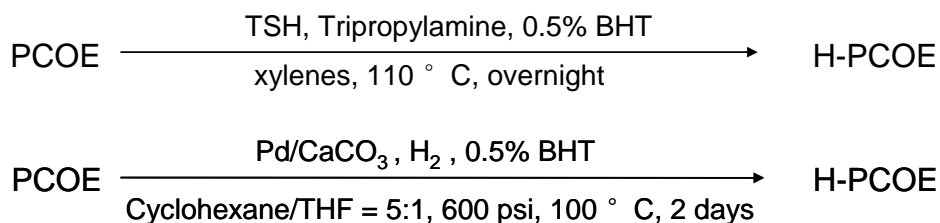
Hydrogenation of polyalkenamers can lead to linear polyethylene (PE) with desired mechanical properties and greater stability against thermal and oxidative degradation. Hydrogenation of the polybutadiene or polyisoprene blocks in thermoplastic elastomers is often used to improve the stability and resistance of the elastomers.

Hydrogenation of unsaturated polymers can be performed either in a noncatalytic or a catalytic fashion.

Noncatalytic hydrogenation using hydrazine (N_2H_4) can be performed under nitrogen gas at an atmospheric pressure and is easily set up with simple glassware. Thermal decomposition of *p*-toluenesulfonylhydrazide (TSH) is commonly used to produce hydrazine *in situ*.¹

Catalytic hydrogenation normally requires very high pressure H_2 gas and special high pressure vessel. Catalysts include heterogeneous Pd/C and Pd/CaCO₃ and homogeneous catalysts, such as the Wilkinson's catalyst.

Catalytic hydrogenation is known to retain the macromolecular structure through hydrogenation, although it requires more expensive catalyst and special high pressure apparatus. On the other hand, hydrazine hydrogenation may alter the macromolecular structure.² Therefore, we evaluated the efficiency and fidelity of hydrogenation of PCOE using TSH and Pd/CaCO₃ as outlined in Scheme 1.



Scheme 1. Noncatalytic (top) and catalytic (bottom) hydrogenation of PCOE.

Both hydrogenation methods gave complete hydrogenation as indicated by the disappearance of the =C-H signal at 965 cm^{-1} in their IR spectra. However, the hydrogenated PCOE (H-PCOE) by TSH showed broad absorption around 1100 cm^{-1} , which has been attributed to residual TSH that is covalently bound to the polymer by Graessley.²

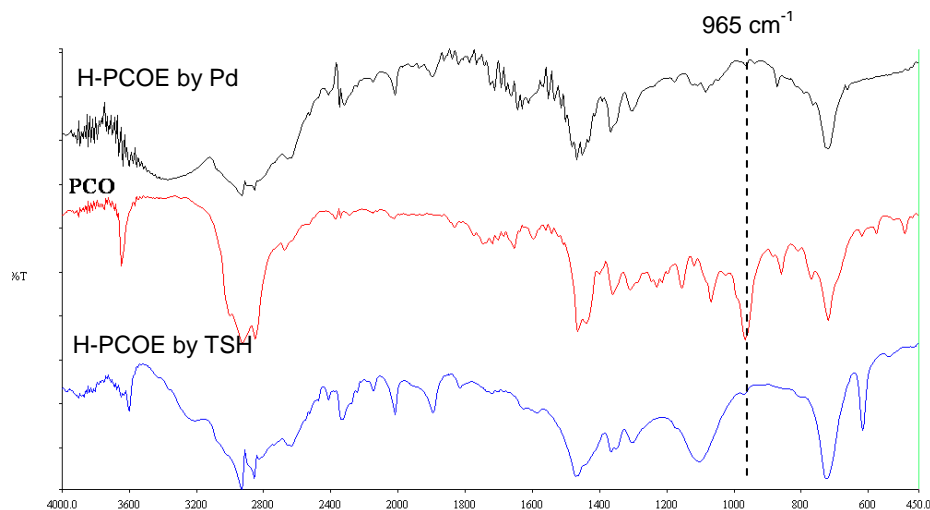


Figure 1. IR spectra of PCOE (middle) and hydrogenated PCOE using Pd/CaCO₃ (top) and TSH (bottom).

Comparison of the dynamic rheological spectra of the polymers before and after hydrogenation revealed a large difference between the two hydrogenation methods. After hydrogenation using TSH, the shape of the dynamic spectrum has significantly changed: the storage modulus (G') was larger than the loss modulus (G'') in the full frequency range tested ($0.01\text{--}100\text{ s}^{-1}$), and the difference was enlarged especially at low frequencies (Figure 2). This result indicated that the large-scale polymer structure has been changed during TSH hydrogenation. On the other hand, Pd catalyzed hydrogenation using H₂ gave H-PCOE similar dynamic spectrum with the precursor PCOE (Figure 3), indicating good preservation of the macromolecular structure.

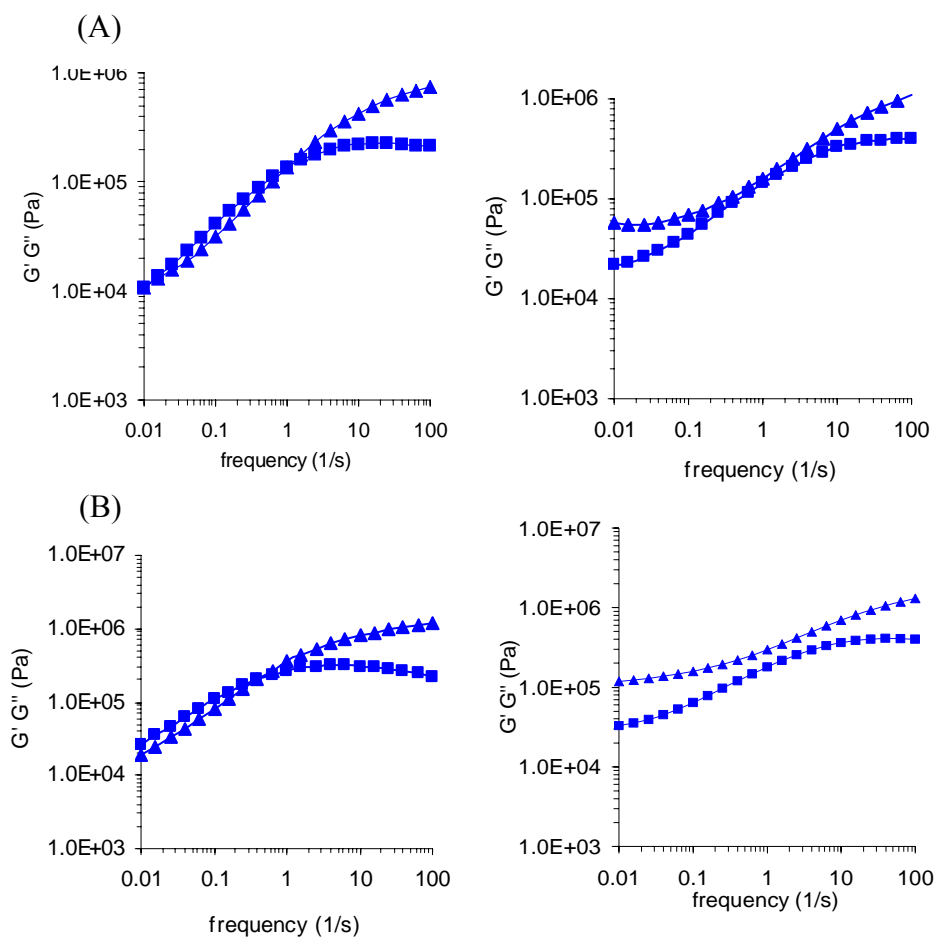


Figure 2. Comparison of dynamic rheological spectra of PCOE precursor polymers (left) and H-PCOE by TSH (right). (A) PCOE $M_w = 200$ k, PDI = 1.5; (B) PCOE $M_w = 320$ k, PDI = 1.2.

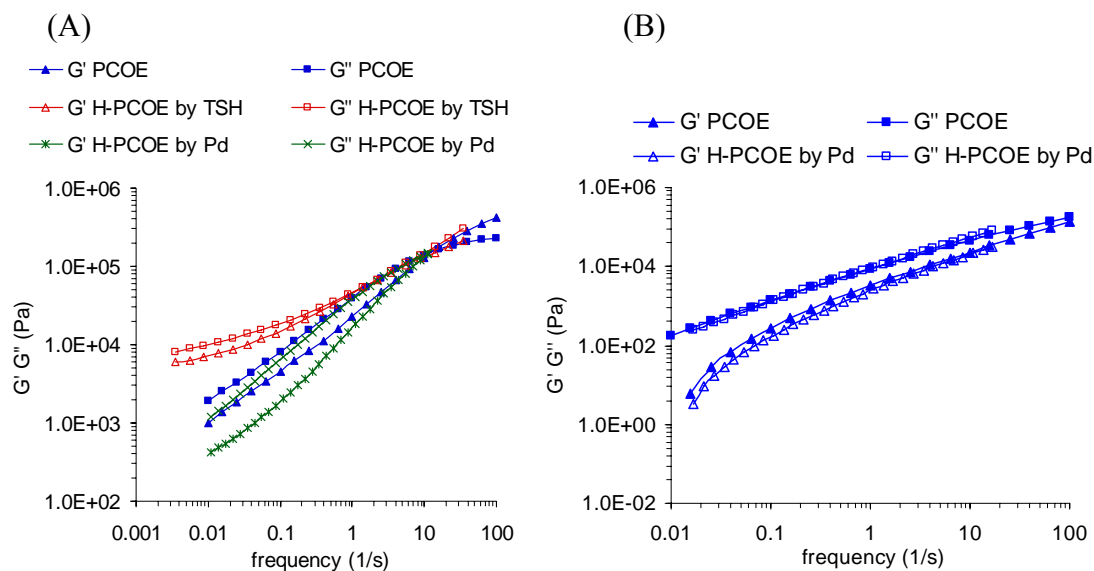


Figure 3. Comparison of dynamic rheological spectra of PCOE precursor polymers and H-PCOE. (A) PCOE $M_w = 140$ k, PDI = 1.5; (B) Commercial PCOE “vestenamer” $M_w = 90$ k, PDI = 2.0.

Therefore, catalyzed hydrogenation using H_2 as the hydrogen source should be used to preserve the macromolecular structure. In practice, heterogeneous Pd catalyzed hydrogenation was reliable for PCOE with $MW < 200$ k. However, for very high MW PCOEs, this method usually gave incomplete hydrogenation, which is partially due to the poor solubility of high MW H-PCOEs and the high viscosity of the solution. Catalyst powder was often found coagulating and was wrapped with insoluble polymer, which isolated the catalyst surface from the reaction media, although low precursor polymer concentration is preferred and can alleviate the problem to some extent. In addition, hot filtration (130 °C in xylene) was needed to remove the catalyst and this process often resulted in some loss of the final polymer product.

On the other hand, homogeneous Wilkinson's catalyst, $\text{RhCl}(\text{PPh}_3)_3$, can overcome the dispersion problem in heterogeneous Pd system. It has been found very effective to fully hydrogenate functionalized PCOE.³

References

- ¹ Phinyocheep, P.; Pasiri, S.; Tavichai, O. *J. Appl. Polym. Sci.* **2003**, 87, 76.
- ² (a) Graessley, W. W. et al *J. Polym. Sci. Polym. Phys. Ed.*, **1979**, 17, 1211. (b) Graessley, W. W. et al *J. Polym. Sci. Polym. Phys. Ed.*, **1979**, 17, 1224
- ³ Ongoing work: Boydston, A. J.; Xia, Y.; Grubbs, R. H.; a typical condition is 10% polymer in THF, 1 % catalyst loading (to olefin), 50 °C, 700 psi H₂, 12 h.