



Study of Viscoelastic Properties of Cyclic Polyethylene

Jian Wang and Gregory B. McKenna

Department of Chemical Engineering, Texas Tech University

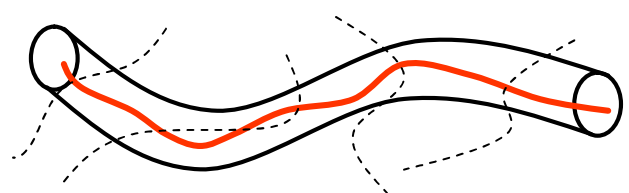


Objective

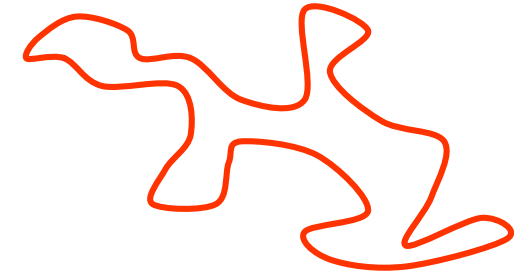
- Learn the viscoelastic properties of cyclic polyethylene.
- Find out the relaxation and diffusion mechanism of cyclic polymer.

Background

Reptation model



How does polymer ring reptate?



- The relaxation and diffusion mechanisms of cyclic polymer in the melt state are unclear. According to the reptation theory, cyclic molecules cannot reptate because there are no "heads" to follow.

- Previous studies on cyclic polymers (PS, PB and PDMS) have shown some common features of polymer rings [1-3], e.g.

$$h_{0,r} < h_{0,l} \quad (M_w < M_c) \quad G_{N,r}^0 < G_{N,l}^0$$

while some conclusions are controversial, e.g. the $\eta_0 \sim M_w$ relationship.

- Recently, through a new synthetic route developed by Bielawski *et al.* [4] more cyclic polymers were made available for such studies. The cyclic polyethylene samples used in this study were prepared and provided by the above group from California Institute of Technology. Basic viscoelastic properties of the cyclic PEs were investigated in this study.

Materials

sample	M_w (g/mol)	M_n (g/mol)	PDI
CPE 11	3.8×10^5	2.09×10^5	1.80
CPE 1	2.21×10^5	1.35×10^5	1.63
CPE 2	1.78×10^5	1.09×10^5	1.62
CPE 5	1.26×10^5	7.2×10^4	1.75
CPE 10	8.5×10^4	5.6×10^4	1.52

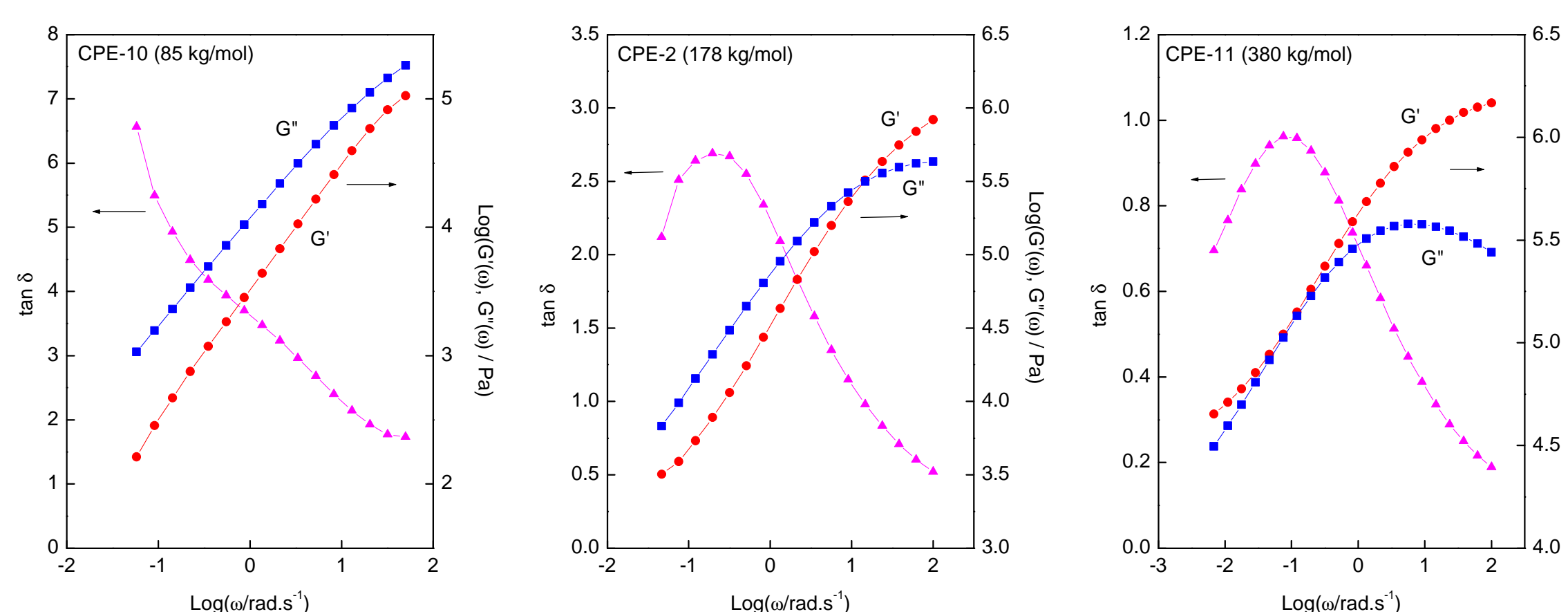
Experimental

- Dynamic modulus measurements
Paar Physica MCR 500 rotary rheometer
- Zero-shear-rate viscosity measurements
Magnetic Bearing Torsional Creep Apparatus (MBTCA)

Results

$G'(w)$, $G''(w)$ and $\tan \delta$

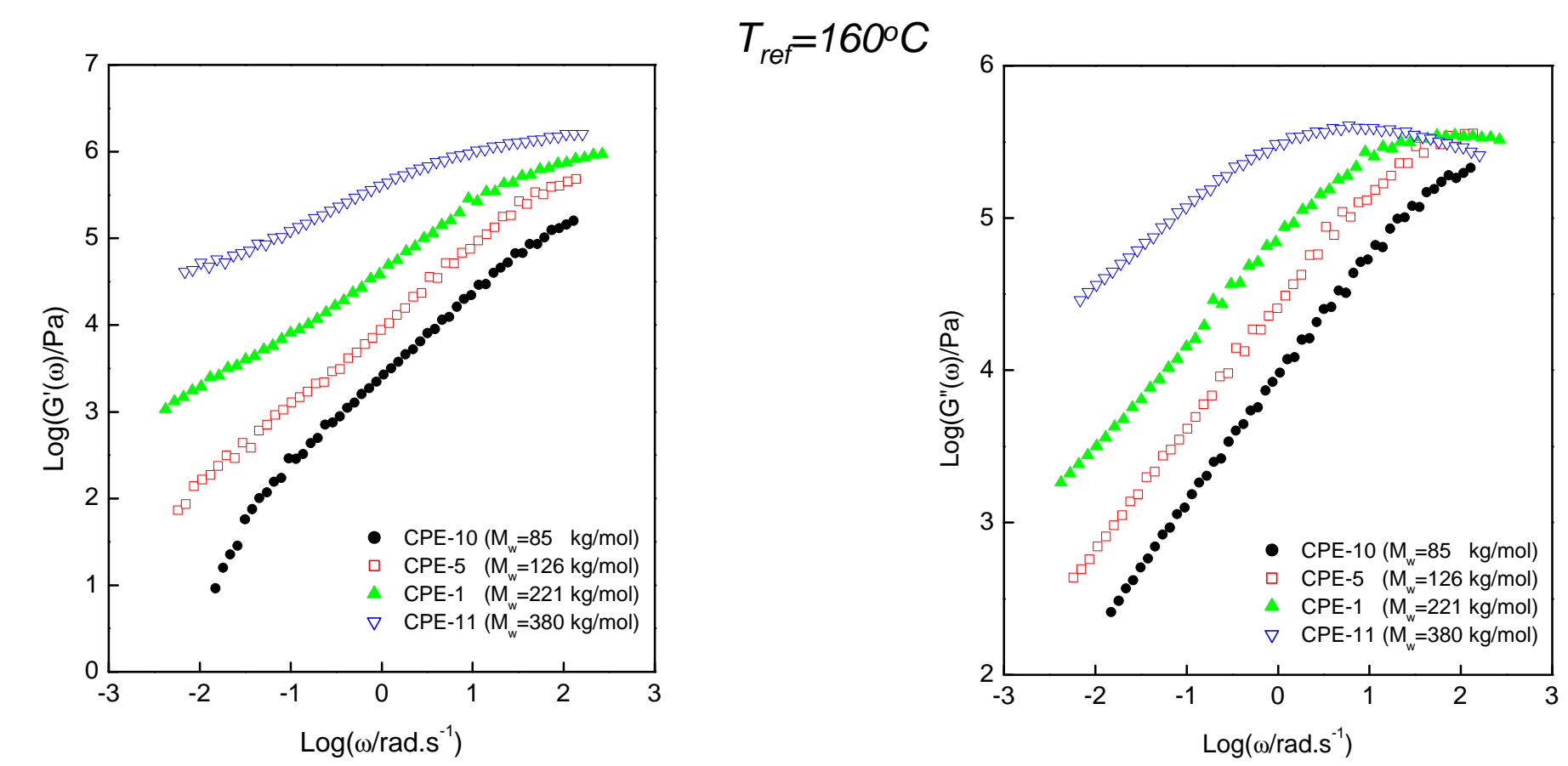
$T=150^\circ\text{C}$



As M_w increases, a transition at low frequencies can be seen, which indicates the existence of very slow relaxations. For CPE-11, G' is above G'' over the entire tested frequency range, which indicates that the material is more elastic-like.

Master curves and flow activation energy

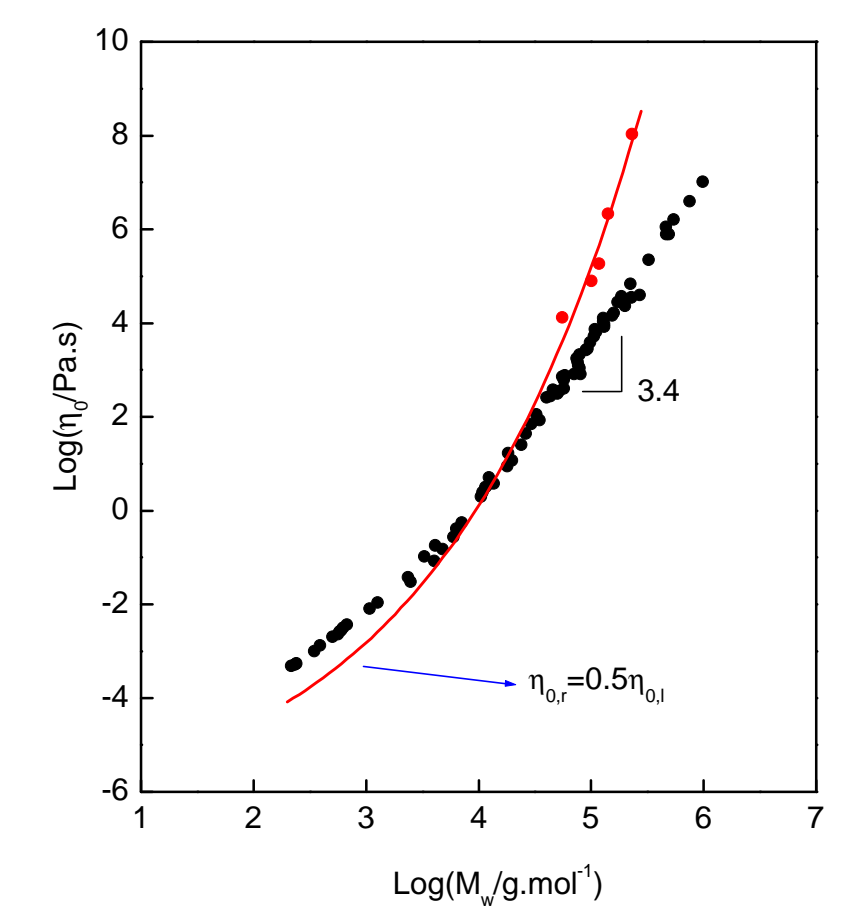
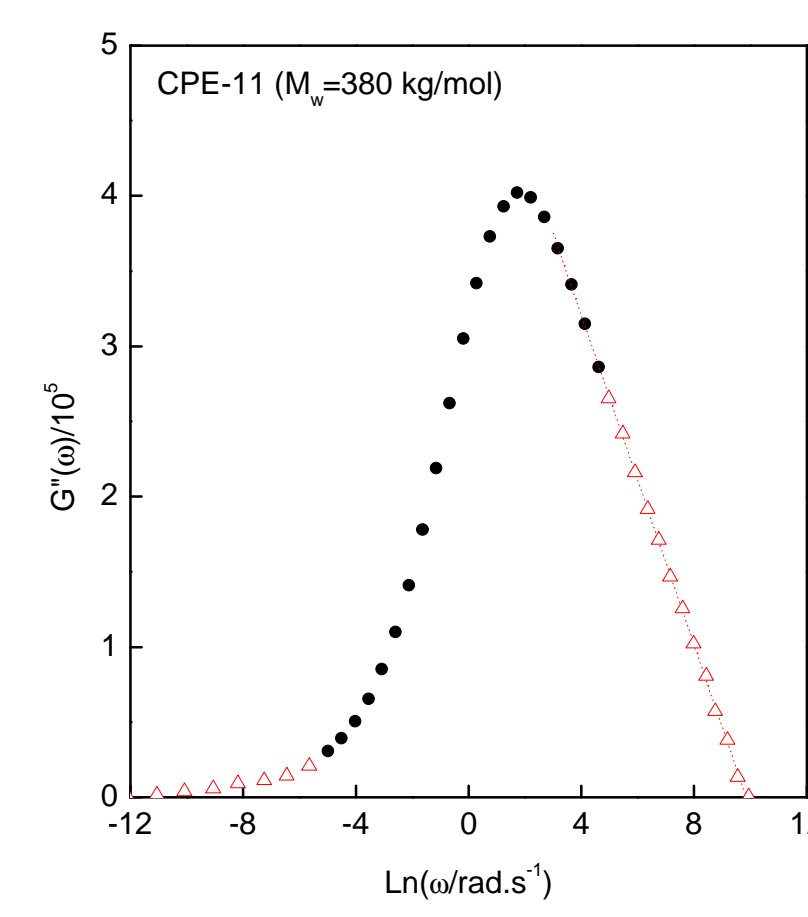
(Only horizontal shifting required for superposition)



$$\text{Arrhenius equation: } a_T = A \exp(E_a / RT)$$

Rings	CPE-10	CPE-5	CPE-2	CPE-1	CPE-11	HDPE	LDPE
E_a (kJ/mol)	49.2	59.3	33.2	56.7	43.9	23~29	37~100

Plateau modulus and M_e $h_0 \sim M_w$ dependence



$$G_N^0 = \frac{2}{p} \int_{-\infty}^{\infty} G''(w) d \ln w$$

$$M_e = r R T / G_N^0$$

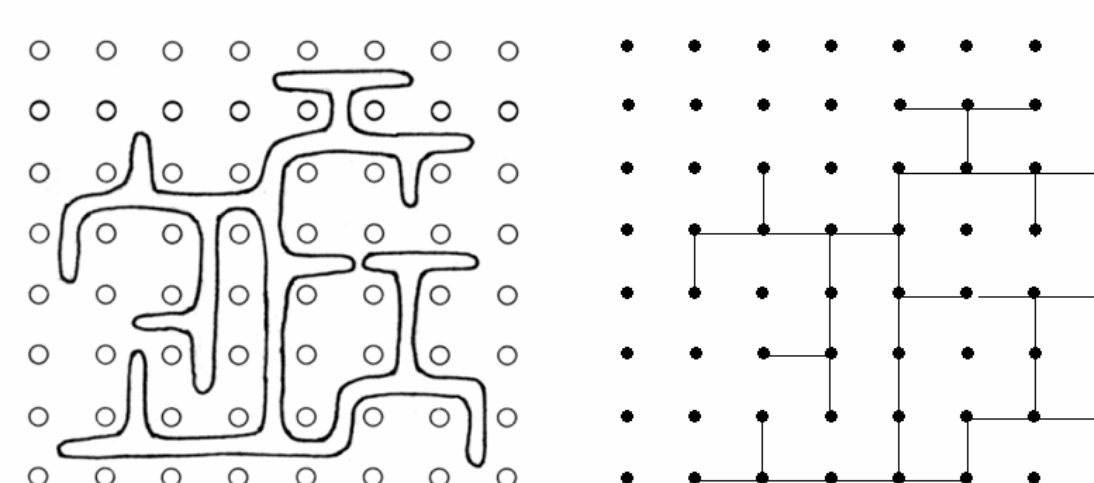
	G_N^0 (Pa)	M_e (g/mol)
CPE	2.03×10^6	1,350
LPE	$1.9 \sim 2.3 \times 10^6$	1,250~1,460

The η_0 values of cyclic PE show a much stronger dependence on M_w than the 3.4 power-law dependence that linear PE follows.

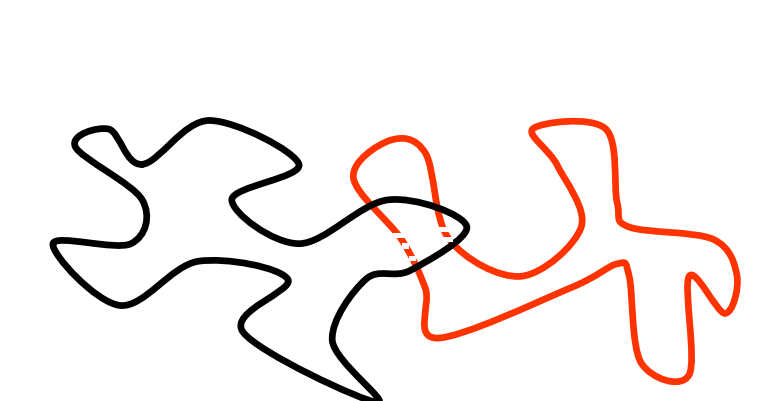
Summary and Conclusions

- The viscoelastic properties of cyclic PE are different from those of linear PE, but resemble those of long chain branched PE, which indicates that the relaxation of cyclic PE is slower than that of linear PE.
- The viscoelastic properties of cyclic PE are also different from the reported results from other polymer rings (PS, PB, PDMS), which is partially due to higher entanglement density.
- The lattice-tree animal model [5] (see sketch below) was proposed to describe the relaxation of polymer rings. This model shows that rings should relax faster than that of the linear chains, but it is only valid when M_w is low.
- When M_w is high, the interpenetration of the loops (see sketch below) would dramatically increase the relaxation time. This is considered the cause of the observed anomalous rheological behaviors of cyclic PE.
- Combine above analysis, a speculative $\eta_0 \sim M_w$ relationship was drawn in the $\eta_0 \sim M_w$ plot (red line).

Lattice-tree animal model



Loops interpenetration



References:

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