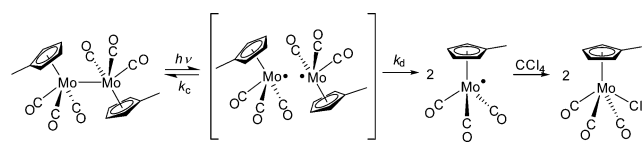
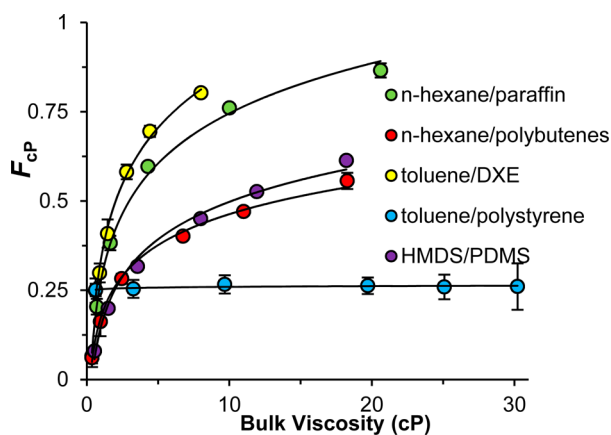




Scheme 2. Photolysis of  $\text{Cp}'_2\text{Mo}_2(\text{CO})_6$  Results in a Caged Radical Pair

to the solvent. In order to avoid selective solvation, the viscogen was chosen so that it has a similar chemical structure and composition to the solvent. For example, IR-grade paraffin oil was added to hexane to increase the bulk viscosity of the hexane solution.) From the resulting plots of quantum yields vs bulk viscosity (see Supporting Information), it is possible to calculate  $F_{\text{CP}}$  as a function of bulk viscosity by the method reported in our prior papers.<sup>58,63,68</sup>

Plots of  $F_{\text{CP}}$  as a function of macroviscosity for five solvent systems are shown in Figure 1. The five solvent systems



**Figure 1.** Plot of cage recombination efficiency ( $F_{\text{CP}}$ ) as a function of solvent system bulk viscosity (cP). Each sample contains 20 wt %  $\text{CCl}_4$ ; error bars are  $1\sigma$ ; and the curves are only a visual guide.

(solvent/viscogen) are (1) hexane/paraffin oil; (2) hexane/polybutenes ( $M_n = 3200$ ); (3) toluene/1,1-bis(3,4-dimethylphenyl)ethane (abbreviated “DXE”); (4) toluene/polystyrene ( $M_w = 45,000$ ); and (5) hexamethyldisiloxane/poly(dimethylsiloxane) ( $M_w = 3800$ ) (abbreviated HMDS and PDMS, respectively).  $\text{CCl}_4$  (20% by weight) was added to each sample as the radical trapping agent (Scheme 2).<sup>70</sup> Note in the figure that, at any selected bulk viscosity, the  $F_{\text{CP}}$  values in the five solvent systems are all different. These results illustrate the point made above that  $F_{\text{CP}}$  can be dramatically different in different solvent systems with the same macroviscosity.

To investigate the hypothesis that microviscosity is a better parameter for describing and interpreting  $F_{\text{CP}}$ , it was necessary to find a measurable solvent property that tracks with microviscosity. In studies of biological molecules (e.g., protein folding studies), there is a general consensus that rotational diffusion coefficients, obtained from NMR  $T_1$  measurements, are correlated with the local viscosity of the solvent environment.<sup>71</sup> For technical reasons,  $T_1$  measurements were not possible with the molecules and radicals used in this study.<sup>72</sup> However, other studies have shown that rotational and translational diffusion coefficients can be interchanged when probing the microenvironment of biological molecules,<sup>73–76</sup> and therefore, we used translational diffusion coefficients.<sup>77</sup>

The translational diffusion coefficients of the radicals in the five solvent systems used in this study were measured using NMR diffusion ordered spectroscopy (DOSY) (Table 1). More

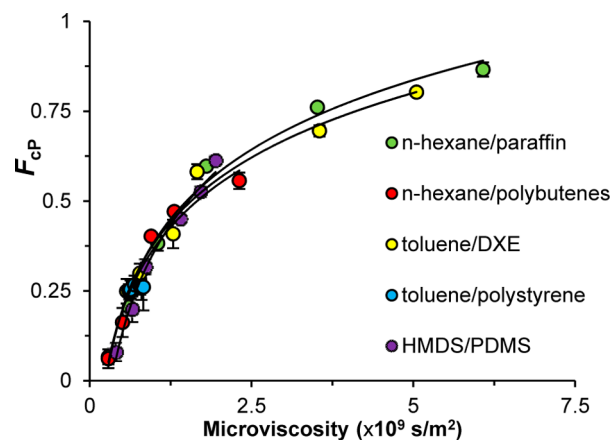
**Table 1.** Solvents and Viscogens Used in This Study<sup>a</sup>

solvent	viscogen	bulk viscosity range (cP)	microviscosity range ( $\times 10^9$ s/m <sup>2</sup> )
n-hexane	paraffin oil	0.36–20.61	0.28–6.08
	poly(butenes)	0.36–18.27	0.28–2.31
toluene	DXE	0.61–8.02	0.57–5.05
	poly(styrene)	0.62–30.22	0.61–0.83
HMDS	PDMS	0.54–18.21	0.41–1.94

<sup>a</sup>Each sample contained 20 wt %  $\text{CCl}_4$ .

specifically, the translational diffusion coefficients were measured using a stable organometallic surrogate for the highly reactive  $[\text{Cp}'\text{Mo}(\text{CO})_3]$  radicals.  $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  was chosen as the probe because  $F_{\text{CP}}$  is related to the radical mass and size according to the Noyes equation ( $F_{\text{CP}} \propto \text{mass}^{1/2}/\text{radius}^2$ ), and the  $\text{Cp}'\text{Mo}(\text{CO})_3$  and  $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  species are reasonably similar in mass and size.<sup>58,78,79</sup> (The relevant physical parameters for  $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  and the  $[\text{Cp}'\text{Mo}(\text{CO})_3]$  radical are presented in the Supporting Information, along with a more detailed justification for using  $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  as a surrogate for  $[\text{Cp}'\text{Mo}(\text{CO})_3]$  radical.) According to the Stokes–Einstein equation,<sup>80</sup> viscosity is inversely proportional to the translation diffusion coefficient ( $D$ ) so  $1/D$  was taken as the solvent parameter representing microviscosity.<sup>81</sup>

The  $F_{\text{CP}}$  values in the five solvent systems in Figure 1 are shown replotted as a function of the microviscosity ( $1/D$ ) in Figure 2. Note that the  $F_{\text{CP}}$  values for all five solvent systems are



**Figure 2.** Cage recombination efficiency ( $F_{\text{CP}}$ ) plotted as a function of microviscosity ( $1/D$ ). Each sample contains 20 wt %  $\text{CCl}_4$ , error bars are  $1\sigma$ ; and the curves are only a visual guide.

nearly the same for identical values of the microviscosity. This result shows that microviscosity provides the best correlation to date between the solvent and the value of  $F_{\text{CP}}$ . Restated, the microviscosity is the parameter of choice when probing solvent effects on the radical cage effect.

Radical–radical recombination requires that the two radicals have the correct orbital orientation to react. Therefore, it might seem that, in addition to being a function of  $1/D$ , the microviscosity should also be a function of a parameter related to the rate of radical rotation such as the rotational correlation time,  $\tau_c$ . However, as noted above, studies of biological

molecules have shown that the rotational and translational diffusion coefficients can be used interchangeably to probe the microenvironment of biological molecules. Thus, in a description of microviscosity involving both  $1/D$  and  $\tau_c$ , the  $\tau_c$  term can be written as a function of  $D$  to yield an expression for microviscosity involving only  $D$ .

In conclusion, the experiments reported here suggest that for nonpolar solvent systems quantitative discussions pertaining to  $F_{cp}$  should be based on microviscosity rather than bulk viscosity. In essence, if the translational diffusion coefficient for a particular radical in a cage pair is known then an accurate cage recombination efficiency is predictable, independent of the solvent system. This predictive power will be useful wherever quantitative knowledge of radical reactivity is necessary. It is noted that the method described above can be applied in reverse. That is, if  $F_{cp}$  is known then the diffusion coefficient of the molecule can be determined; in turn, the microviscosity of the local environment around the caged molecules can be probed. This reverse application would provide a method for determining the microviscosity in complex systems such as active sites of enzymes or in heterogeneous reactions. Polar solvent systems and hydrogen-bonding solvent systems are currently being investigated in our laboratory to determine if the results obtained above with nonpolar solvents are also applicable in these types of solvents.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05432.

Detailed methods for determining micro- and macroviscosity, cage efficiencies, and a discussion on relevant kinetics (PDF)

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### Notes

The authors declare no competing financial interest.

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