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Estimation of Free Radical Polymerization Rate Coefficients Using Computational Chemistry

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Summary: This study explores the application of computational chemistry to estimate free radical polymerization rate coefficients. The Evans-Polanyi relationship is combined with computed heats of polymerization to estimate copolymerization reactivity ratios for many vinyl monomer pairs, focusing on acrylates, methacrylates and styrene, with accuracy assessed by comparison to experimental values. The effect of different optimization approaches on the values of thermodynamic properties is explored, and it is concluded that a combination of conventional optimization and relaxed potential energy scans was most effective at identifying global minima. The difference between thermodynamic properties calculated using the harmonic oscillator treatment and a hindered rotor model is evaluated for methyl methacrylate polymerization.

Keywords: conformation optimization; hindered rotor model; kinetics (polym.); quantum chemistry; radical polymerization; reactivity ratios

Introduction

Acrylic free radical polymerization at high temperature proceeds via a complex set of mechanisms, with many rate coefficients poorly known and difficult to determine experimentally.[1] The problem is compounded by the large number of monomers used in industry to produce coatings and other materials. Thus, there is a strong incentive to develop a methodology to estimate rate coefficients for secondary mechanisms such as intramolecular hydrogen abstraction and beta scission. Before proceeding to these unknown reactions, however, it is necessary to develop suitable computational methods and to verify these methods by comparing predictions to kinetic rate coefficients known experimentally, such as those for propagation and copolymerization reactivity ratios.

Molecular structure and reactivity can be related using thermodynamic properties. The difference between product and reactant enthalpies has been used to estimate kinetic coefficients according to structure-reactivity relationships such as the Evans-Polanyi equation:

$$E_a = \alpha \Delta H_r + E_0 \tag{1}$$

This equation assumes a linear relationship between activation energy E_a and heat of reaction ΔH_r, where α is the reaction transfer coefficient and E_0 is termed the intrinsic barrier to reaction. The treatment has been successfully used to estimate unknown rate coefficients required to accurately represent rates and yields of low-molecular weight species formed through pyrolysis of polystyrene,[2,3] assuming that the pre-exponential factor A is constant for different reactants in the same family.

$$k = A \exp(-E_a/RT) \tag{2}$$

This assumption is valid when the reaction coordinates are similar for various structures in the same family, such that the change in the entropy between the transition state

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and reactants remains constant. The adequacy of the Evans-Polanyi relationship, as well as the appropriateness of using small molecule models to represent polymeric radicals, is tested by computing ΔH_r values for monomer addition reactions.

It has been generally found that copolymer composition and sequence distribution are well described by the terminal model of monomer addition.[4]

$$P_n^i + M_j \xrightarrow{kp_{ij}} P_{n+1}^j \tag{3}$$

Rate coefficient kp_{ij} describes the addition of monomer M_j to radical P_n^i, extending the chain length by one unit and changing the terminal radical on the chain from i to j. For a two-monomer system, polymer composition is controlled by the monomer reactivity ratios r_1 and r_2. Assuming the Evans-Polanyi relationship is valid, these are calculated according to:

$$\begin{aligned} r_1 &= \frac{k_{p_{11}}}{k_{p_{12}}} \\ &= \frac{A\ \exp(-(E_0+\alpha\Delta H_{r_{11}})/RT)}{A\ \exp(-(E_0+\alpha\Delta H_{r_{12}})/RT)} \\ &= \exp\left[-\frac{\alpha(\Delta H_{r_{11}} - \Delta H_{r_{12}})}{RT}\right] \end{aligned} \tag{4}$$

$$r_2 = \frac{k_{p_{22}}}{k_{p_{21}}} = \exp\left[-\frac{\alpha(\Delta H_{r_{22}} - \Delta H_{r_{21}})}{RT}\right] \tag{5}$$

The proportionality constant α is 0.24 for radical addition to monomer.[2,3,5,6] The monomer reactivity ratios, therefore, become a function of only the change in enthalpy between the two addition reactions, calculated computationally.

One of the challenges in applying computational chemistry to polymerization reactions is the size of the species involved. For large species, many different low-energy conformations exist and will result in different thermodynamic properties for the reaction. A first step is to locate the most stable conformation for all species, including monomer, radical and products. Conventional optimization algorithms in computational chemistry software typically evaluate the gradient to determine the most stable conformation for a given initial geometry. While this works well for molecules such as ethylene and propylene because of their simplicity,[7,8] multiple stable conformations that are similar in energy exist for more complex monomers such as acrylates.[9] Therefore, we used a combination of conventional optimization and relaxed potential energy scans to locate the most stable conformation.

A second issue examined was what effect the model used to calculate the thermodynamic properties had on the heats of reaction calculated. In the computation of thermodynamic properties, the rigid-rotor, harmonic oscillator (HO) model is often used. However, the HO model may not be sufficiently accurate for low frequency vibrations, which are typically torsional motions better treated as hindered rotors.[10,11] In this study, we use a one-dimensional hindered rotor (HR) model to treat low frequencies and compare the thermodynamic properties obtained using the HO and HR models at different temperatures.

Methodology

It is necessary to specify initial geometries for the reactant and product species before optimization. While this is straightforward for small molecules such as monomers and monomeric radicals, the procedure is more difficult for larger species such as dimeric radicals because of the presence of multiple local minima. The lowest energy conformation must be identified, without the energy minimization algorithm getting 'caught' in a local minimum that results from an arbitrarily drawn structure. To find the global minimum, a potential energy scan was performed on all the backbone dihedral angles of the species using AM1 geometry optimization in Gaussian.[12] Ab initio single point calculations were then performed on each of the minimum energy structures obtained by the scans, using a higher level method such as B3LYP/6-31G(d). The geometry with the lowest energy from these calculations was then selected as the starting geometry for the final optimization and energy calculation for the species. The global minimum was identified based on the following two criteria:

1. $E_{\theta=0} = E_{\theta=360}$
2. $E_{\theta=0}$ (or $E_{\theta=360}$) has the minimum energy.

Overall energetics were calculated by combining AM1 optimization and frequency calculations with a higher level single point calculation using B3LYP/6-31G(d), B3P86/6-311G(2d,2p), or B971/6-311G(2d,2p).[13,14] It has been shown that the low level (and computationally faster) AM1 method does an equivalent job to B3LYP in geometry optimization such that B3LYP//AM1 results are essentially the same as B3LYP//B3LYP for bond dissociation energies.[15–17] The thermochemistry data is used to calculate heats of reaction according to:

$$\Delta H_r^\circ(298.15\ \mathrm{K}) = \Sigma(E_{el} + H_{therm})_{products} - \Sigma(E_{el} + H_{therm})_{reactants} \tag{6}$$

where E_{el} is the electronic energy and H_{therm} is the thermal and zero point correction to the enthalpy. The value of H_{therm} is calculated using statistical mechanics based on the partition function, q, using standard formulae.[18]

The partition function is defined as:

$$q = \sum_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right) \tag{7}$$

and alternatively can be written as the product of various partition functions:

$$q = q_{trans} \times q_{rot} \times q_{vib} \times q_{el} \tag{8}$$

where q_{trans} is the translational partition function, q_{rot} is the rotational partition function, q_{vib} is the vibrational partition function, and q_{el} is the electronic partition function which is equal to the multiplicity for species in their ground state. The vibrational energy levels that are needed to calculate q_{vib} are calculated based on the harmonic oscillator model, which is a good approximation for high frequencies. For low frequencies ($<200\ \mathrm{cm}^{-1}$), it is accepted that a hindered rotor (HR) model represents these modes more accurately since these low frequencies are essentially rotation modes. Low frequencies need to be taken out of the vibrational partition function and treated using the HR model as reflected in Equation 9:

$$q = q_{trans} \times q_{rot} \times q_{vib} \times q_{\mathrm{int},rot} \tag{9}$$

where $q_{int,rot}$ is the partition function for the low frequency modes treated as internal rotations. The partition function of an internal rotation is:

$$q_{\mathrm{int},rot} = \frac{1}{\sigma_{\mathrm{int}}} \sum_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right) \tag{10}$$

in which σ_{int} is the symmetry number of the rotation top and ε_j are the energy levels of the internal rotation. The energy levels can be solved based on a one-dimensional Schrödinger equation:[19]

$$-\frac{h^2}{8\pi I_r}\frac{\partial^2 \Psi}{\partial \theta^2} + V(\theta)\Psi = \varepsilon\Psi \tag{11}$$

where $V(\theta)$ is the Fourier series expansion of the potential energy with respect to the torsion angle, θ:

$$V(\theta) = \sum_m [a_m \cos(1 - m\theta) + b_m \sin(m\theta)] \tag{12}$$

and I_r is the reduced moment of inertia of the rotation top, which can be computed using Pitzer's equations.[19,20] The one-dimensional Schrödinger equation was solved using the Fourier Grid Hamiltonian (FGH) method, in which the Hamiltonian operator is approximated by a large grid of finite points along the potential surface from 0 to 2π, and the eigenvalues of the matrix are calculated to obtain the energy levels.[21]

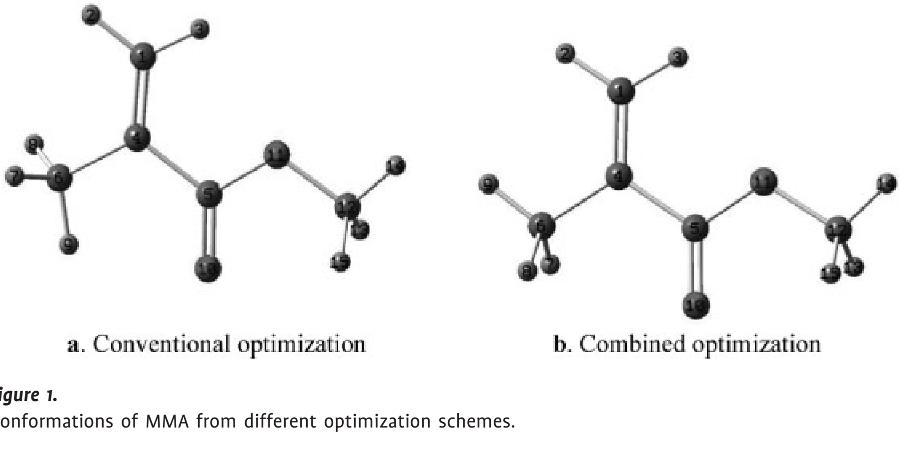
Results and Discussion

Given a particular starting geometry, the combined method of conventional optimization followed by relaxed dihedral scans was successful in finding lower energy structures, even for relatively small molecules such as methyl methacrylate monomer. As shown in Figure 1, the conformation of methyl methacrylate from the combined method is only subtly different from that derived from the conventional method, but the energy of the conformation obtained from the combined optimization scheme is 6.36 kJ/mol lower in energy, with the energy difference caused by the rotation of the methyl group on the vinyl group. In the conventional optimization conformation, the dihedral of atoms 1-4-6-7 is 300.2°, while in the combined optimization conformation, the dihedral of atoms 1-4-6-7 is 121.1°. The combined approach was used for all results reported below.

Table 1 summarizes the ΔH_r estimates for monomer addition to monomeric radicals, calculated using density functional theory methods. Also tabulated are the reactivity ratios, calculated from the difference in ΔH_r (homopropagation – cross-propagation) values according to Equation 4. The last column of the table contains experimental values, with the ranges based upon compiled data.[22] The final rows in Table 1 consider the addition of methyl acrylate (MA) and methyl methacrylate (MMA) to 1-tert-butoxycarbonylethyl radical (EEst*); experimental values for these reactions are found in the compilation by Fischer and Radom.[5,6]

Although the ΔH_r values calculated using the different computational methods show small differences, they are within the acceptable computational error of ±10 kJ/mol[23] compared with homopolymerization (ΔH_p) experimental values.[22] Further calculations for MA addition to MA radicals of increasing length indicate that the enthalpy of reaction is not a strong function of radical chain length (Table 2). These encouraging results suggest that addition to monomeric radicals provides a reasonable model for polymeric systems, and thus computations may provide an efficient means to estimate relative addition rates, i.e., reactivity ratios. Fischer and Radom reach the same conclusion from their experimental investigations of monomer addition to small radicals.[5,6] The same work reports computed values of reaction enthalpies for the addition of various monomers to methyl radical and finds reasonable agreement with the experimental data.

It is important to note that computing relative kinetic rate coefficients does not require a high level of theory;[24,25] much of the systematic error introduced through computational assumptions cancels out when calculating monomer reactivity ratios. Figure 2 plots the Mayo-Lewis relation[26] between polymer and monomer composition for the MMA/VAc system (Table 1, System IX) based upon reactivity ratios calculated in this study as well as from literature values. While there is some variation in ΔH_r values with method, the variation in reactivity ratios is much smaller. Figure 2 indicates little difference between the predicted composition curves using r values



a. Conventional optimization b. Combined optimization

Figure 1.
Conformations of MMA from different optimization schemes.

Table 1.
Calculated $-\Delta H_r$ (kJ/mol) and reactivity ratios (in brackets) for monomer addition to monomeric radicals compared to literature values for polymer systems.[a,b]

	Reaction	Method 1	Method 2	Method 3	Experiment[22]
I	MA* + MA	72.4	84.6	79.6	78–84
	MA* + MMA	79.8 (**0.49**)	93.8 (**0.41**)	89.8 (**0.37**)	(**0.20–0.50**)
	MMA* + MMA	50.0	65.0	60.8	53–58
	MMA* + MA	52.0 (**0.83**)	65.3 (**0.97**)	60.2 (**1.06**)	(**2.0–2.5**)
II	BA* + BA	66.9	79.3	74.4	
	BA* + BMA	75.3 (**0.44**)	88.8 (**0.40**)	84.9 (**0.36**)	(**0.20–0.50**)
	BMA* + BMA	50.3	64.9	60.8	
	BMA* + BA	52.2 (**0.84**)	65.4 (**0.94**)	60.2 (**1.06**)	(**2.0–2.5**)
III	MA* + MA	72.4	84.6	79.6	
	MA* + BA	71.5 (**1.09**)	84.1 (**1.04**)	79.3 (**1.04**)	
	BA* + BA	66.9	79.3	74.4	
	BA* + MA	68.1 (**0.89**)	79.6 (**0.97**)	74.7 (**0.97**)	
IV	MMA* + MMA	50.0	65.0	60.8	
	MMA* + BMA	49.9 (**0.99**)	64.8 (**1.02**)	60.6 (**1.02**)	(**1.00**)
	BMA* + BMA	50.3	64.9	60.8	
	BMA* + MMA	50.4 (**1.01**)	65.1 (**0.99**)	61.0 (**0.99**)	(**1.00**)
V	MA* + MA	72.4	84.6	79.6	
	MA* + MEA	78.6 (**0.55**)	91.3 (**0.52**)	86.3 (**0.53**)	
	MEA* + MEA	34.5	50.5	46.2	31
	MEA* + MA	44.4 (**0.38**)	59.3 (**0.42**)	54.9 (**0.42**)	
VII	MMA* + MMA	50.0	50.5	60.8	
	MMA* + MEA	43.7 (**1.85**)	60.9 (**2.10**)	53.9 (**1.96**)	
	MEA* + MEA	50.0	65.0	46.2	
	MEA* + MMA	43.7 (**0.40**)	57.1 (**0.37**)	54.8 (**0.43**)	
VIII	MA* + MA	72.4	84.6	79.6	(**6.30–7.30**)
	MA* + VAc	52.7 (**6.76**)	64.8 (**6.77**)	60.1 (**6.62**)	
	VAc* + VAc	82.4	91.2	86.8	88
	VAc* + MA	106.1 (**0.10**)	115.6 (**0.10**)	111.1 (**0.10**)	(**0.03–0.04**)
IX	MMA* + MMA	50.0	65.0	60.8	
	MMA* + VAc	26.5 (**9.76**)	39.4 (**11.9**)	34.2 (**13.14**)	(**22–30**)
	VAc* + VAc	82.4	91.2	86.8	
	VAc* + MMA	98.3 (**0.22**)	109.9 (**0.16**)	105.9 (**0.16**)	(**0.03–0.07**)
X	Eth* + Eth	87.8	94.3	88.8	102
	Eth* + VAc	98.5 (**0.36**)	106.3 (**0.31**)	102.3 (**0.29**)	(**0.13–0.88**)
	VAc* + VAc	82.4	91.2	86.8	
	VAc* + Eth	76.1 (**1.86**)	84.9 (**1.85**)	78.7 (**2.19**)	(**0.72–3.74**)
	EEst* + MA	68.1	79.6		80[6]
	EEst* + MMA	75.4 (**0.49**)	88.9 (**0.40**)		82[6] (**0.38**)

[a] Methods AM1 opt with single point calculation by: Method 1 B3LYP/6-31G(d); Method 2 B3P86/6-311G(2d,2p); Method 3 B971/6-311G(2d,2p).

[b] MA = methyl acrylate; MMA = methyl methacrylate; BA = butyl acrylate; BMA = butyl methacrylate; MEA = methyl ethacrylate; VA = vinyl acetate; Eth = ethylene; EEst = 1-tert-butoxycarbonylethyl. The added * indicates the corresponding monomeric radical species.

Table 2.
The effect of radical chain length on computed $-\Delta H_r$ (kJ/mol) values for homopropagation of methyl acrylate (MA). (Expt value = 78–84 kJ/mol).

Reaction	Product Chain Length	$-\Delta H_r$ Method 1
MA* + MA	2	72.40
MA-MA* + MA	3	72.26
MA-MA-MA* + MA	4	72.53

estimated by the various computational methods, although the larger basis sets combined with the B3P86 and B971 methods provide slightly more accurate values; the remaining copolymer composition results discussed in this paper are calculated using reactivity ratio values computed using Method 3 (B971/6-311G(2d,2p)). The MMA/VAc computed values are not as extreme as found in literature ($r_{\mathrm{MMA}} = 25$, $r_{\mathrm{VAc}} = 0.05$),

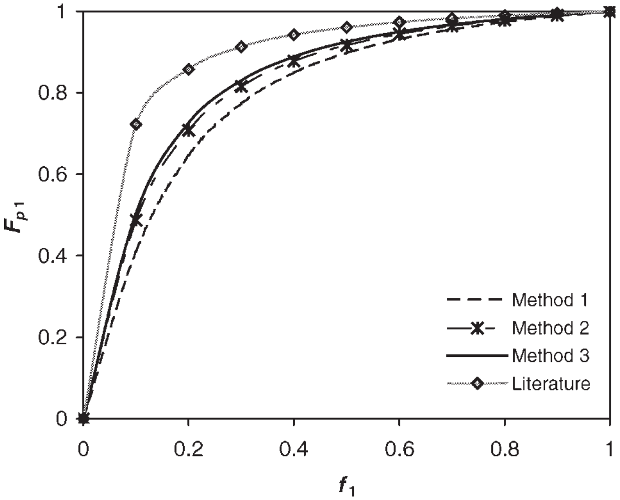


Figure 2.
Relationship between MMA (1)/VAc (2) copolymer (F_{p1}) and monomer (f_1) composition, calculated from computed reactivity ratios summarized in Table 1 (System IX), and from literature values ($r_1 = 25$; $r_2 = 0.05$).

but capture the tendency of producing methacrylate-rich copolymer.

Figure 3 plots copolymer composition for some monomer pairings that exhibit good agreement between computational results and literature. Reactivity ratios are close to unity for the situation where the monomers differ only in the alkyl ester group (e.g.; MMA/BMA and MA/BA, Systems III and IV in Table 1). Changing the alkyl ester group from methyl to butyl also has no effect on the calculated reactivity ratios for acrylate/methacrylate copolymerization (compare MMA/MA amd BMA/BA, Systems I and II). This result is contrasted to the change computed as monomer changes from acrylate (MA or BA) to methacrylate (MMA or BMA) to ethacrylate (methyl ethacrylate, MEA); the homopropagation reaction becomes less

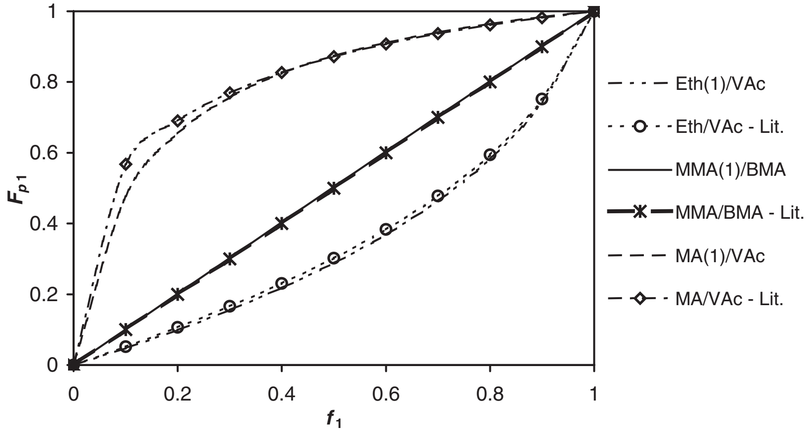


Figure 3.
Relationship between copolymer (F_{p1}) and monomer (f_1) composition, calculated from computed reactivity ratios summarized in Table 1 (Systems IV, VIII, X), and from literature values.

exothermic, and reactivity ratios also deviate substantially from unity. Unfortunately, no literature values could be found for copolymerization of MEA with acrylates or methacrylates. In general, many of the results obtained by computation are consistent with observed structure-reactivity trends for most of the pairs examined, as also seen in the good agreement with literature results for Eth/VAc and MA/VAc in Figure 3.

One exception to the good agreement found between experiment and literature r values is the MMA/MA pairing (System I in Table 1), with copolymer vs. monomer composition plotted in Figure 4. The addition of MMA to MMA* is less exothermic than MMA addition to MA*, as is expected from the electron donating effect of the CH_3 group that makes MMA* less electrophilic than MA*. It is also expected that electron rich MMA should add more readily (more exothermic reaction) to an electrophilic radical than MA. However, while this was found for addition to MA* (computed r_{MA} value of 0.4 is in good agreement with literature), the calculations did not show this difference for addition to MMA*. Instead, it is calculated that the heats of reaction are almost identical, resulting in a reactivity ratio of close to unity instead of the experimental value of 2–2.5. Identical results were obtained for BMA/BA. This deviation from experimental observation may arise from a problem in application of DFT methods for total resolution of energy associated with molecules that have steric crowding, such as MMA.[27,28] It may also indicate that the assumption that the pre-exponential factor A is constant when applying the Evans-Polanyi relationship is not as good in this case. Although the discrepancy is sufficient to cause a significant deviation in calculated copolymer composition (Figure 3), the calculated r_{MMA} value is within a factor of 2–3 of literature.

Most of the radicals under study are electrophilic, and the effects discussed for MMA and MA monomer and radical activity apply. Styrene, however, is an electron donor substituted radical (nucleophilic) that reacts quickly with electron deficient monomers;[5,6] thus, it is expected that MMA (or MA) should add more quickly (reaction more exothermic) to S* than electron-rich styrene. While this is observed experimentally ($r < 1$),[22,29] the computational results summarized in Table 3 exhibit

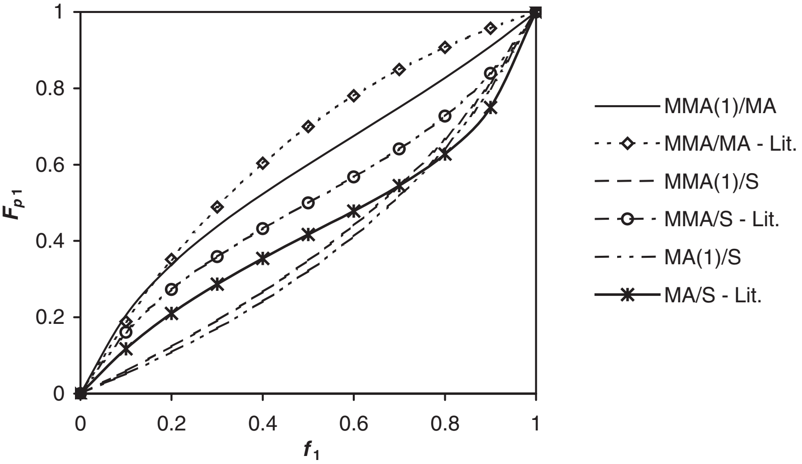


Figure 4.
Relationship between copolymer (F_{p1}) and monomer (f_1) composition calculated from computed reactivity ratios for MMA/MA (Table 1, System I) and styrene with MMA and MA (Table 3). Curves are compared to those calculated using r values from literature.

Table 3.
Calculated $-\Delta H_r$ (kJ/mol) and monomer reactivity ratios for styrene (S) copolymerized with methyl acrylate (MA) and methyl methacrylate (MMA), compared to literature values for polymer systems.

Reaction	$-\Delta H_r$ Method 1	r	$-\Delta H_p$ (expt)	r (expt)
$MA^* + MA$	78.31	0.43	78–84	0.15–0.3
$MA^* + S$	87.02			
$S^* + S$	60.34	2.02	73	0.7–0.8
$S^* + MA$	53.04			
$MMA^* + MMA$	53.84	0.47	53–58	0.4–0.6
$MMA^* + S$	61.63			
$S^* + S$	60.34	1.74		0.4–0.6
$S^* + MMA$	54.61			

the reverse trend, with $r > 1$. The second reactivity ratios computed for the same pairings are close to experimental values: adding the electron rich S monomer to either MA^* or MMA^* is more exothermic than the corresponding homopolymer additions. The mismatch in styrene reactivity ratios leads to significant deviations in the copolymer composition predictions, as shown in Figure 4.

Another possible cause for the deviation of some of the reactivity ratios from experimental observation is that the HO model is inadequate. Therefore, the sensitivity of the computed thermodynamic properties on the HO and HR models as a function of temperature was examined. The addition reaction of methyl methacrylate monomeric radical to monomer was studied in detail, and the results for entropy and H_{therm} are tabulated in Tables 4, 5 and 6 for MMA, MMA^* and MMA dimeric radical, respectively. It can be seen that the HO model may overestimate or underestimate the entropy and H_{therm} values compared with the HR model. However, for small molecules like those involved in the addition of MMA monomeric radical to monomer, the absolute values of entropy and H_{therm} are not very sensitive to the model used, with the deviations within 5%. Also the level of agreement between the HO and HR values is relatively insensitive to temperature.

To determine how significant the effect of the HR model was on the entropy of reaction and heat of reaction, the values were compared to the HO model results as summarized in Table 7. Note that the HO value for ΔH_r at 298 K in Table 7 is slightly different from the value summarized in Table 1 for Method 1. This difference is due to the use of UB3LYP/6-31G(d) for geometry optimization and energy calculation

Table 4.
Entropy (S) and H_{therm} of methyl methacrylate calculated using the harmonic oscillator (HO) and hindered rotor (HR) models.[a]

Temperature (K)	S (J/mol K)			H_{therm} (kJ/mol)		
	HO	HR	HR/HO	HO	HR	HR/HO
298	366.2	371.4	1.014	342.7	342.5	1.000
350	387.2	392.0	1.012	349.5	349.2	0.999
400	406.7	411.0	1.011	356.8	356.3	0.999
450	425.5	429.7	1.010	364.8	362.8	0.994
500	443.7	447.4	1.008	373.5	371.2	0.994
550	461.3	464.5	1.007	382.7	380.2	0.993
600	478.4	481.1	1.006	392.6	389.8	0.993
650	494.9	497.2	1.005	402.9	399.9	0.992
700	511.0	512.9	1.004	413.7	410.4	0.992

[a] Computation was based on UB3LYP/6-31G(d); scale factor was 0.9806 for ZPVE, 0.9989 for H_{vib}, 1.0015 for S_{vib}.

Table 5.
Entropy and H_{therm} of methyl methacrylate monomeric radical calculated using the harmonic oscillator (HO) and hindered rotor (HR) models.[a]

Temperature (K)	S (J/mol K)			H_{therm} (kJ/mol)		
	HO	HR	HR/HO	HO	HR	HR/HO
298	397.5	395.9	0.996	369.4	367.8	0.996
350	419.8	417.1	0.994	376.7	373.5	0.992
400	440.4	436.3	0.991	384.4	380.7	0.990
450	460.3	454.9	0.988	392.9	388.7	0.989
500	479.6	473.3	0.987	402.0	395.7	0.984
550	498.2	490.9	0.985	411.8	404.9	0.983
600	516.2	507.9	0.984	422.2	414.7	0.982
650	533.7	524.5	0.983	433.2	425.1	0.981
700	550.7	540.6	0.982	444.6	436.0	0.981

[a] Computation was based on UB3LYP/6-31G(d); scale factor was 0.9806 for ZPVE, 0.9989 for H_{vib}, 1.0015 for S_{vib}.

Table 6.
Entropy and H_{therm} of methyl methacrylate dimeric radical calculated using the harmonic oscillator (HO) and hindered rotor (HR) models.[a]

Temperature (K)	S (J/mol K)			H_{therm} (kJ/mol)		
	HO	HR	HR/HO	HO	HR	HR/HO
298	559.3	589.5	1.054	723.3	725.6	1.003
350	603.2	634.9	1.053	737.5	739.2	1.002
400	643.9	676.1	1.050	752.8	754.7	1.003
450	683.4	716.1	1.048	769.6	770.2	1.001
500	721.6	754.6	1.046	787.8	786.8	0.999
550	758.7	791.4	1.043	807.3	806.1	0.999
600	794.7	826.9	1.040	828.1	826.6	0.998
650	829.6	861.2	1.038	849.9	848.0	0.998
700	863.5	894.4	1.036	872.8	870.5	0.997

[a] Computation was based on UB3LYP/6-31G(d); scale factor was 0.9806 for ZPVE, 0.9989 for H_{vib}, 1.0015 for S_{vib}.

for the results in Table 7, as opposed to the lower level of theory, AM1, used for geometry optimization for the results in Table 1. The effect of the HR model on both ΔH_r and ΔS_r can be significant, particularly at high temperatures. ΔH_r is less sensitive to which model is used at 298 K; for example, the value of ΔH_r is affected by

Table 7.
Entropy and enthalpy changes of $MMA + MMA^*$ reaction.[a]

Temperature (K)	ΔS_r (J/mol K)			ΔH_r (kJ/mol)		
	HO	HR	(HR–HO)	HO	HR	(HR–HO)
298	−204.4	−177.8	26.6	−54.1	−50.0	4.1
350	−203.9	−174.2	29.6	−53.9	−48.8	5.1
400	−203.2	−171.2	32.0	−53.6	−47.6	6.0
450	−202.4	−168.4	34.0	−53.3	−46.5	6.8
500	−201.6	−166.1	35.6	−52.9	−45.4	7.6
550	−200.8	−164.0	36.8	−52.5	−44.3	8.2
600	−199.9	−162.1	37.8	−52.0	−43.2	8.8
650	−199.0	−160.5	38.5	−51.4	−42.2	9.3
700	−198.2	−159.1	39.1	−50.9	−41.2	9.6

[a] Computation was based on UB3LYP/6-31G(d); scale factor was 0.9806 for ZPVE, 0.9989 for H_{vib}, 1.0015 for S_{vib}.

only 4.1 kJ/mol. This is consistent with the work of Van Speybroeck et al.[30] who observed that calculated values of activation energy for ethylene propagation, which can be related to enthalpic changes, were relatively insensitive to the HO and HR models. However, the frequency factors they calculated were affected significantly by the HR model. Although the same detailed analysis has not yet been done for the addition of MMA* to MA, it is interesting to estimate how significantly the reactivity ratio for MMA and MA adding to MMA* would change if the heats of reaction differed by the same amount as observed here for MMA addition but in opposite directions as an extreme case. The new reactivity ratio would be 0.37, which is a factor of 55% different from the value of 0.83 in Table 1. While this is a significant change that suggests that revisiting all of the heats of reaction in Table 1 using treatment for hindered rotations may be warranted, it is often observed that changes are systematic such that the heat of reaction for the addition of MMA* to MA would change in the same direction as that for addition of MMA* to MA with the inclusion of hindered rotations, and thus, the calculated value of the reactivity ratio would not be affected as dramatically as this limiting case suggests. Although the results reported above are not entropies of activation, $\Delta S^{\neq}$, which would be required to estimate frequency factors, the HR model does change ΔS_r substantially, suggesting that $\Delta S^{\neq}$ would be affected as well, consistent with the results of Van Speybroeck et al.[30] Transition state theory calculations are currently in progress for the MMA and MA systems to calculate A and E_a explicitly and to test the assumptions underlying the Evans-Polanyi analysis presented here.

Conclusion

It can be concluded that computations using small molecules provide insight into polymeric rate coefficients and that the Evans-Polanyi relationship provides reasonable estimates of reactivity ratios for many monomer pairs. A combined optimization method using conventional optimization and relaxed dihedral scans is effective at identifying low energy conformations and necessary for monomers as apparently simple as MMA. Some values (MA/MMA, MA and MMA addition to S*) differ significantly from experiment. Evaluation of the HR model reveals that the difference in ΔH_r between the HO and HR model is significant at 298 K for MMA homopolymerization, suggesting that more accurate treatment of hindered rotations may possibly bring the computed reactivity ratios into better agreement with experiment where discrepancies exist. Work is ongoing to explore if the proximity of the electron donating groups is affecting the computational energies, or if there is a steric effect that interferes with energy resolution of these molecules. Even when deviation with literature reactivity ratios is significant, the difference is less than a factor of 3. Thus, a similar computational methodology will be applied to estimate relative rates of secondary reactions for which rate coefficients are less well known, such as addition to mid-chain radicals. Transition state theory calculations are also in progress to calculate absolute values of propagation rate coefficients for acrylate monomers.

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