Transfer to "Monomer" in Styrene Free-Radical Polymerization

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Introduction

Chain transfer to monomer is an important mechanism in free-radical polymerization. For styrene, there have been careful measurements of the temperature dependence of the value of the transfer constant to monomer,[1] but it is unclear what the actual transfer reaction is. The structure of the monomeric unit does not suggest hydrogen-atom abstraction would be a favorable process, as there would be a significant energetic penalty accompanying the loss of resonance stabilization. It has been postulated[2] that chain transfer actually takes place through hydrogen-atom abstraction from the Diels−Alder dimer of styrene (denoted DA), which possesses a labile hydrogen atom (Figure 1). The radical formed through this reaction is highly stabilized. As a result, chain transfer to DA could occur at an enhanced rate; the modeling work of Pryor[3] indicated that at 333 K the transfer rate coefficient to the DA was 5 orders of magnitude greater than that for transfer to styrene. DA has been long regarded as significant in styrene thermal initiation,[4] e.g., the thermal initiation, with a third-order dependence on the monomer concentration, and is attributed to reaction between a monomer unit and a DA molecule to form two initiating radicals. This postulate is supported by studies on thermal initiation of styrene,[5,6] and modeling suggests that the concentration of DA is significant at elevated temperatures.[7]

The role of DA in chain transfer is less clear at common polymerization temperatures of 40−90 °C. One particular problem is evident in styrene emulsion polymerization. There is convincing experimental evidence[8] supporting the assumption that radical loss in relatively small particles ("zero−one" systems) is by transfer to monomer (or monomer-like species), with the resultant monomeric radical diffusing out of the particle into the water phase. Unless the radical resulting from transfer has water solubility commensurate with that of styrene monomer, this radical-loss process could not occur. However, it is likely that the water solubility of DA is orders of magnitude less than that of styrene.[9] This seems inconsistent with a transfer mechanism simply involving the formation of a DA radical. Given the good agreement with experimental data[8,10−15] for the transfer-diffusion[16,17] model for radical exit, which assumes desorption of a monomeric radical, agreement with a mechanism that involves a significantly different radical would be at best fortuitous.

Postulated Transfer Mechanism

We here postulate an extension of the DA mechanism for transfer in styrene, with a fast step that includes the reaction of the DA radical with another monomer unit, as shown in Figure 2. This additional H-atom abstraction yields a true monomeric styrene radical (capable of desorption) and a resonance-stabilized dimer. If reactions 2 and 3 are rapid, then the rate of transfer is that of transfer to dimer, but the exit of this monomeric radical species still can occur in emulsion polymerizations. This mechanism would reconcile the apparent conflict between (i) transfer via DA and (ii) exit in emulsion polymerization.

The likelihood of these reactions is explored here by calculating the free energies of the processes.

Computational Chemistry Methods, Results and Discussion

In the simulations of Pryor and Coco,[3] the limiting value of the rate coefficient of transfer of reaction 2 (rate coefficient k_{trDA}) at 323 K is $k_{trDA} \approx 1300\ M^{-1}\ s^{-1}$. This is appreciable for a transfer reaction, so the assumption that reaction 2 is fast appears valid. To check whether reaction 3 is also rapid, geometry optimizations and single point energy calculations of reactants and products were performed using GAUSSIAN 03[18] to determine the reaction enthalpy and free energy changes, ΔH and ΔG, and thus the most likely reaction product on thermodynamic grounds. By assumption of a significant free-energy benefit and a product-like transition state, the reaction might proceed quickly. While a more rigorous procedure would be a full calculation of the free energy of the transition state, the level of accuracy required for this type of free-radical reaction is prohibitive.[19,20]

Calculations were performed for a range of different levels of complexity from the semiempirical PM3 approach[21] to Hartree−Fock and density functional methods using a basis sets of varying size. Density functional methods such as the B3LYP functional are a robust but economic method to calculate accurate energies. The thermodynamic output from these calculations is given in Table 1.

It can be seen that Product 1 is the most likely product of reaction 3 on thermodynamic grounds; the calculated value of ΔH converges toward a value of ∼−25 to −28 kJ mol^{-1} at the highest levels of theory used, and the free energy change is similar. The optimized geometry of product 1 is shown in Figure 3. The unpaired electron in the DA radical will be extensively delocalized, and this delocalization will be maintained, and even increased, in the transition state, thereby suggesting a low activation energy for this transfer reaction.[22] This and the calculated enthalpy change are consistent with the assumption that reaction 3 is rapid, allowing the generation of a monomeric styrene radical capable of desorption in an emulsion polymerization system.

Product 1 is formed only after H-atom rearrangement

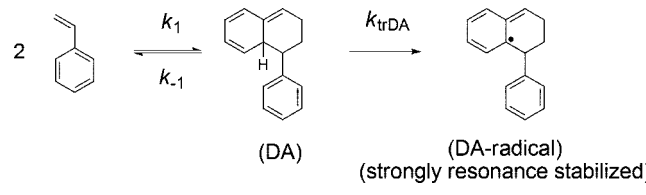

Figure 1. Formation of the Diels−Alder dimer (DA) of styrene and the formation of a radical capable of chain initiation after hydrogen atom abstraction.

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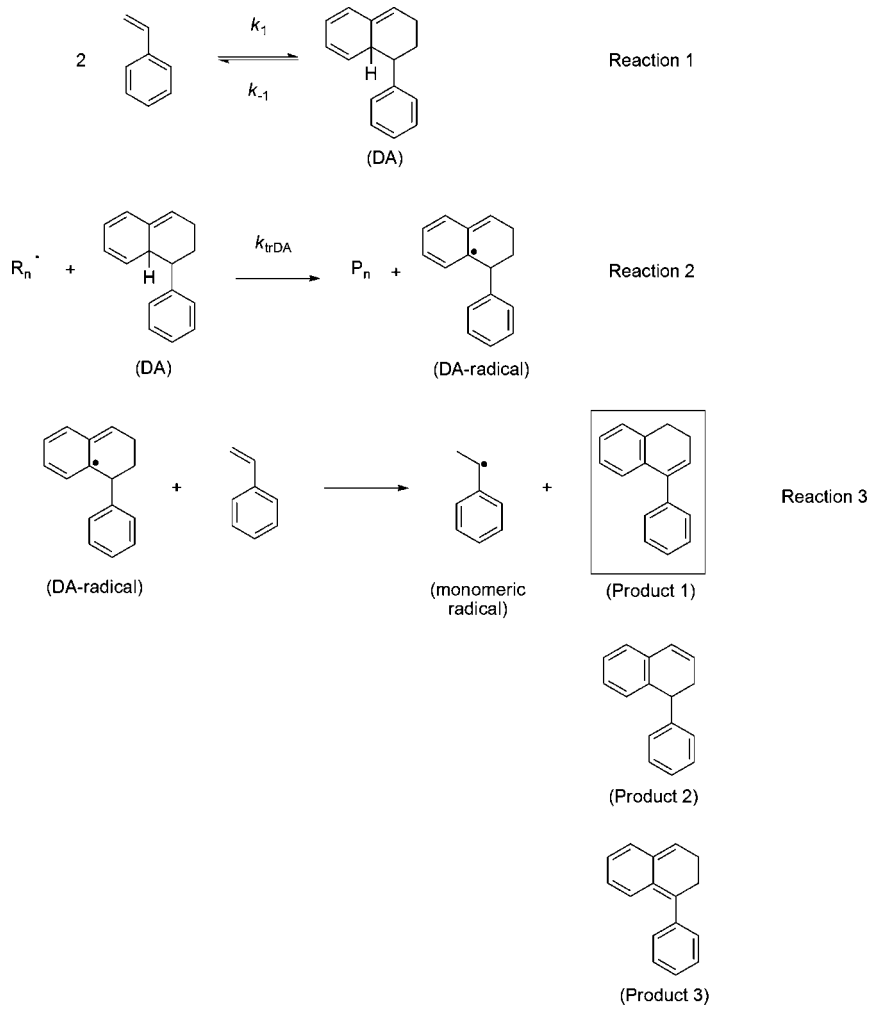

Figure 2. Postulated transfer to monomer reaction in styrene polymerization system. Several products of reaction 3 are shown, the most likely of which on stabilization grounds is indicated.

Table 1. Calculated Enthalpy and Free Energy Change for Reaction 3 (see Figure 2) at 298 K as the Level of Sophistication of the Simulation is Changed[a]

	product 1		product 2		product 3	
level of theory	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG
semiempirical						
PM3	−27.1	−27.7	−16.1	−22.1	43.7	39.0
Hartree−Fock						
UHF/3−21G	68.1	64.5	76.1	73.7	189.7	184.1
UHF/6−31G	22.2	21.6	38.7	37.9	144.6	140.1
density-functional						
B3LYP/6−31G	−27.7	−27.5	−8.6	−10.4	74.0	73.5
B3P86/6−31G	−28.6	−27.4	−8.6	−9.0		
B3LYP/6−311G	−25.6	−25.4	−9.9	−10.8		

[a] All quantities are in kJ mol^{-1}.

following the abstraction process involving the monomer unit. Normal mode analysis of the DA radical indicates three low frequency (<200 cm^{-1}) vibrational modes that are mainly torsional modes of the fused rings with extensive movement of H atoms. Animations of these modes are available in the Supporting Information. This suggests a loose structure that is likely to lose a hydrogen atom and undergo rearrangement readily; a possible rearrangement mechanism is given in Figure 4.

This mechanism has some important implications. First, assuming the transfer mechanism postulated in Figure 2, the steady-state approximation can be used to yield an expression for the concentration of the Diels−Alder dimer, which suggests

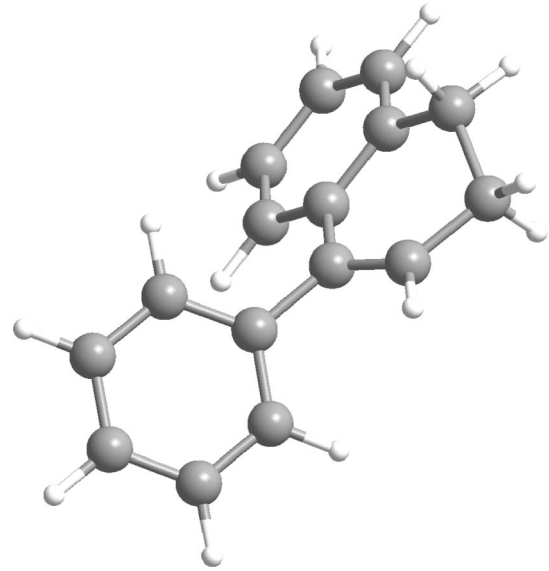

Figure 3. Optimized geometry of product 1 from reaction 3: transfer of radical activity from the Diels−Alder dimer radical to yield a closed-shell species.

that [DA] $\sim K[M]^2$ where K = equilibrium constant for dimerization and [M] = monomer concentration. In the measurement of "apparent" transfer constants ($C_{tr}^{apparent}$) through means such as the lnP^2 and Mayo[23] methods, there will be a

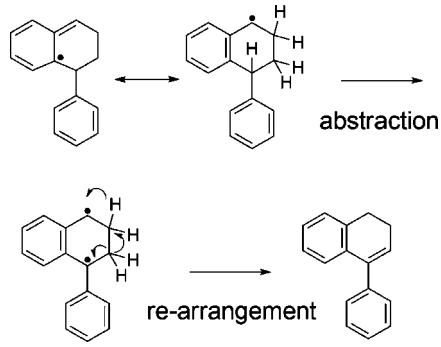

Figure 4. Postulated rearrangement reaction to yield product 1 after initial H-atom abstraction from the DA radical.

term that is directly proportional to [M]; thus it is predicted that the value of $C_{tr}^{apparent}$ will decrease as a function of conversion in the polymerization of styrene as monomer concentration is depleted.

Second, the assumption that chain transfer takes place through the DA species can be included in the extended Smith−Ewart equations in the "zero−one" kinetic limit[24,25] that describe the behavior of relatively small polystyrene latexes, where radical exit is an important mechanistic event. The pseudofirst order rate of chain transfer is now k_{trDA}[DA] as opposed to k_{tr}[M]; however, it is this product that is in fact obtained from apparent transfer constants as used in the data interpretation leading to the mechanism for exit. Assuming "Limit 2a" kinetics (whereby an exited radical will re-enter another particle as opposed to undergoing termination in the aqueous phase, a process verified through experiment[8] and modeling[24,26] of styrene emulsion systems) yields the following expression for the overall exit rate coefficient k:

$$k = \frac{k_{trDA}[DA]k_{dM}}{k_p^1 C_p} = \frac{k_{trDA}K[M]k_{dM}}{k_p^1} \quad (1)$$

where k_{dM} = desorption rate coefficient of a monomeric radical from the particle interior into the aqueous phase and k_p^1 = propagation rate coefficient of a monomeric radical. This expression naturally has a similar functional form to the expression derived previously;[24] one point of difference however is that eq 1 is now a function of [M], which is particle-size dependent.[27,28] This may be an important consideration for exit from very small latexes where [M] is not constant as a function of particle size.

Attempts to detect the various intermediates, such as product 1 and dependence of the apparent transfer constant on [M], would support or refute the new mechanism proposed to reconcile the apparent inconsistency between transfer in styrene and exit in emulsion polymerization.

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Supporting Information Available: Animations (as .avi files) of the vibrational modes corresponding to vibrations at 150, 166, and 272 cm^{-1} for the DA radical as determined at the B3LYP/6−31G level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Tobolsky, A. V.; Offenbach, J. *J. Polym. Sci.* **1955**, *16*, 311–14.
(2) Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization, 2nd ed.*; Elsevier: Amsterdam, 2006.
(3) Pryor, W. A.; Coco, J. H. *Macromolecules* **1970**, *3*, 500–8.
(4) Mayo, F. R. *J. Am. Chem. Soc.* **1968**, *90*, 1289–95.
(5) Brown, W. G. *Makromol. Chem.* **1969**, *128*, 130–6.
(6) Hui, A. W.; Hamielec, A. E. *J. Appl. Polym. Sci.* **1972**, *16*, 749–69.
(7) Kotoulas, C.; Krallis, A.; Pladis, P.; Kiparissides, C. *Macromol. Chem. Phys.* **2003**, *204*, 1305–1314.
(8) Morrison, B. R.; Casey, B. S.; Lacik, I.; Leslie, G. L.; Sangster, D. F.; Gilbert, R. G.; Napper, D. H. *J. Poly. Sci., Part A: Polymer Chemistry* **1994**, *32*, 631–49.
(9) McAuliffe, C. *J. Phys. Chem.* **1966**, *70*, 1267–75.
(10) Asua, J. M. *Macromolecules* **2003**, *36*, 6245–6251.
(11) Asua, J. M.; De la Cal, J. C. *J. Appl. Polym. Sci.* **1991**, *42*, 1869–77.
(12) Asua, J. M.; Sudol, E. D.; El-Aasser, M. S. *Journal of Polymer Science, Part A: Polym. Chem.* **1989**, *27*, 3903–13.
(13) Lacík, I.; Casey, B. S.; Sangster, D. F.; Gilbert, R. G.; Napper, D. H. *Macromolecules* **1992**, *25*, 4065–4072.
(14) Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Macromolecules* **2005**, *38*, 4901–4912.
(15) van Berkel, K. Y.; Russell, G. T.; Gilbert, R. G. *Macromolecules* **2003**, *36*, 3921–3931.
(16) Nomura, M. In *Emulsion Polymerization*; Piirma, I., Ed.; Academic: New York, 1982; pp 191−219.
(17) Ugelstad, J.; Hansen, F. K. *Rubber Chem. Technol.* **1976**, *49*, 536–609.
(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; J. A. Montgomery, J.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople., J. A. *GAUSSIAN 03 Revision B.05*, Gaussian Inc.: Pittsburgh, PA, 2003.
(19) Heuts, J. P. A.; Gilbert, R. G.; Radom, L. *Macromolecules* **1995**, *28*, 8771–8781.
(20) Heuts, J. P. A.; Gilbert, R. G.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 18997–19006.
(21) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209–220.
(22) Huang, D. M.; Monteiro, M. J.; Gilbert, R. G. *Macromolecules* **1998**, *31*, 5175–5187.
(23) Clay, P. A.; Gilbert, R. G. *Macromolecules* **1995**, *28*, 552–69.
(24) Gilbert, R. G. *Emulsion Polymerisation: A Mechanistic Approach*; Academic Press: San Diego, 1995.
(25) Gilbert, R. G.; Napper, D. H. *Journal of Macromolecular Science - Macromolecular Chemistry and Physics C* **1983**, *23*, 127–186.
(26) Casey, B. S.; Morrison, B. R.; Maxwell, I. A.; Gilbert, R. G.; Napper, D. H. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 605–630.
(27) Hawkett, B. S.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 2395–2404.
(28) Morton, M.; Kaizerman, S.; Altier, M. W. *J. Colloid Sci.* **1954**, *9*, 300–12.

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