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Radical Entry in Emulsion Polymerization: Estimation of the Critical Length of Entry Radicals via a Simple Lattice Model

Yan Dong and Donald C. Sundberg*

Polymer Research Group, Chemical Engineering Department, University of New Hampshire, Durham, New Hampshire 03824

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ABSTRACT: A lattice model has been utilized to calculate the free energy change upon oligomeric radical (derived from persulfate initiators) adsorption onto a latex particle dispersed in an aqueous phase. Variations in this free energy change with oligomer chain length allow one to predict the so-called Z-mer length at which adsorption is spontaneous. Z-mer lengths for commonly used homopolymers range from 1 to 8 (for 2-ethylhexyl acrylate and methyl acrylate, respectively). The lengths predicted for styrene and methyl methacrylate are 2 and 4 and are the same as those reported from experiments. The model is straightforwardly extended to copolymers. Here the overall composition of the oligomeric copolymer radical has a significant effect upon the Z-mer length, while the sequence distribution of the monomer units in the chain has a limited effect. Model predictions for the acrylic acid−styrene system are in reasonable agreement with reported experimental results over a range of comonomer compositions.

Introduction

In emulsion polymerization, primary radicals are most often generated thermally from water-soluble initiator in the water solution phase and then ultimately transferred into the interior of the polymer latex particles, which is the major locus of polymerization. The radical transfer is a rather complicated process. A complete radical entry may be considered as a multistep process: propagation of the primary radical in aqueous phase; diffusion to the proximity of the surfaces of polymer latex particles; adsorption onto the surfaces, finally propagation with monomers therein. In estimating the radical entry rate (ρ), Maxwell et al.[1] have proposed that radical adsorption is rate-determining and controlled by the water phase propagation of a primary radical to a surface active radical with an end group (e.g., SO_4^-) derived from an initiator, all in the water solution phase. Therefore, it is important to know the minimum number of monomer repeat units of the entry radicals, which is called the critical length of entry radicals, or Z-mer in the literature, to estimate the rate of radical entry. Comparing the interaction of such oligomers with that of the hydrophobic part of surface-active alkyl sulfates, Maxwell et al.[1] concluded that the critical length of entry radicals derived from styrene (St) is about 2. This result is consistent with experimental observation.[1] However, their specific approach is unable to be extended to copolymerization systems, especially when there are hydrophilic monomers such as acrylic acid (AA) or methacrylic acid (MAA) involved. That is because those monomers are infinitely soluble in water.

In this article, we present a simple approach to estimate the critical length of entry radicals with a hydrophilic end group (SO_4^-), which is presumably derived from initiator. The free energy of transferring an entry radical ($\Delta\mu_P$) from the water phase to the particle surface was estimated via a simple lattice model. The critical length of entry radicals was then determined with the criteria that the transfer free energy is equal to or less than zero ($\Delta\mu_P \leq 0$).

Background

A Two-Layer Lattice Model. A lattice containing a flat surface plane is used to envision the finite number of possible conformations for an adsorbed oligomeric radical on a monomer-swollen latex polymer surface in water. The curvature of latex particles is ignored because the oligomeric radicals are much smaller in size than latex particles, and the surface concentration of the adsorbed radicals is low at any given time during polymerization. A plane separates the lattice into two parts: monomer-swollen latex polymer and water solution phases. As an initial attempt, we treat the monomer-swollen latex polymer as a hydrophobic fluid surface of monomer droplets and the water solution phase as a monomer-saturated water phase. This is partially for simplicity and also because relevant data for such a system are readily available. As described by Scheutjens and Fleer,[2] the lattice consists of distinguishable layers of lattice sites, parallel to the polymer surface as shown in Figure 1. The layer (N) runs from P in the latex particle to W in the water solution. Assuming that the two phases separated by the plane on the polymer surface are homogeneous, we then have the lattice model with only two distinguishable layers. P stands for the layer in latex polymer, and W stands for the water solution, adjacent to the surface. Every layer has L lattice sites and each site has N nearest neighbors; a fraction λ_0 of these are found in the same layer and a fraction λ_1 in each of the adjacent layers. For an octahedral lattice we have $N = 6$, $\lambda_0 = {}^2/_3$, and $\lambda_1 = {}^1/_6$. The choice of lattice type affects the conformation count.[3] For simplicity, however, an octahedral lattice was assumed throughout all the calculations in this article. We also assumed that every lattice site is occupied by a segment of an oligomeric radical or a water molecule. However, errors introduced from those simplifications may be mitigated in the estimated transfer free energy, since it is the difference in oligo-

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* To whom all correspondence should be addressed: e-mail dcs@cisunix.unh.edu; Fax 603-862-3617; phone 603-862-1997.

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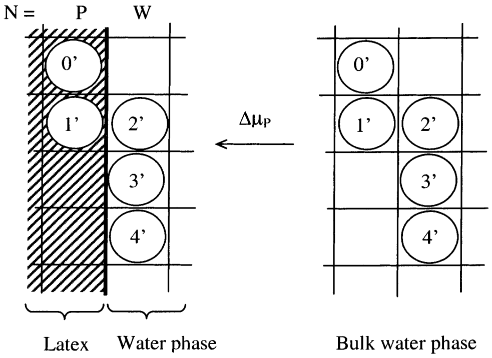

Figure 1. Two-layer lattice model for an adsorbed oligomeric radical consisting of 0′, 1′, ..., and 4′ segments on a monomer-swollen latex polymer surface.

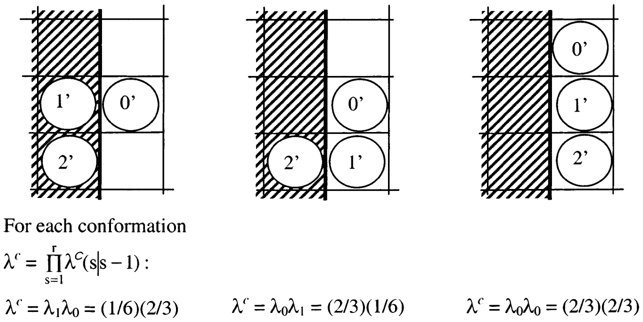

Figure 2. Distinguishable conformations in the two-layer polymer surface lattice model for an oligmeric radical with two monomer units and sulfate end group, which is designated by the 0′ segment.

meric radical free energy on surface and in the corresponding water phase that is of interest.[4]

To deal with multiple monomers used in many emulsion polymerizations, the segments of an oligomeric radical are labeled $s = 0, 1, 2, ..., r$, as shown in Figure 1 (here $r = 5$). r is the number of the segments of an oligomeric radical under consideration. The chain can then assume a certain number of possible conformations in the lattice. We characterize a conformation by defining the layer number in which each of the successive chain segments find themselves. Scheutjens and Fleer[2] denoted such a conformation by

$$(0,i)(1,j)(2,k)...(r-1,l)(r,m)$$

indicating that the first segment is in the ith layer, the second in j, and the third in k, etc. Here i, j, k, l, and m can be P or W as defined previously. The free energy of transferring an oligmeric radical from a particular position in the aqueous phase onto a particular position on the surface is given by[5]

$$\Delta\mu_P = -kT\sum_c\{\ln(\lambda^c/r) - (\sum_r \Delta\mu_S)/kT\} \tag{1}$$

where $\lambda^c = \lambda^c(r|1) = \prod_{s=1}^{r}\lambda^c(s|s-1)$ is the multiple product of $(r-1)$ bond weighting factors λ_0 or λ_1 as defined previously for a particular conformation;[2] the notation $\lambda^c(s|s-1)$ stands for the fraction of nearest neighbors that segment $s-1$ has in the layer where segment s is found (see Figure 2 for an example with $r = 3$). $\Delta\mu_S$ is the free energy of transferring one of r segments of an oligmeric radical, which is in contact with the surface on the polymer side in conformation c, from the water solution to the swollen polymer phase; T is the absolute temperature, and k is Boltzmann's constant.

Estimation of the Free Energy of Transferring a Segment ($\Delta\mu_S$). To estimate the free energy of transferring an oligmeric radical onto the polymer surface from the water, the free energy of transferring a segment to the surface ($\Delta\mu_S$) has to be evaluated first. We assume the free energy of transferring a monomer unit ($\Delta\mu_M$) in a segment is proportional to that of monomer molecule ($\Delta\mu_m$),

$$\Delta\mu_M = \alpha\Delta\mu_m \tag{2}$$

where α is a constant. According to Ben-Naim,[6] the free energy of transferring a monomer molecule from a fixed position in a water solution phase onto a fixed position in a hydrophobic organic phase can be estimated by

$$\Delta\mu_m = RT\ln(x_w/x_O) \tag{3}$$

where x_w and x_O are the solubilities of a monomer in the water and organic phases, respectively, as mole fraction. For monomers with very low solubility in water, eq 3 can be simplified $\Delta\mu_m \approx RT\ln x_w$. A similar equation was used by Maxwell et al.[1] in quantification of interaction between a styrene oligmeric chain and a hydrophobic surface. As shown by Tanford,[7] the free energy of transferring a hydrocarbon chain of an organic molecule from water to an organic phase is linearly related to the chain length when the chain is short ($<C_8$). If the chain becomes longer, it may be coiled, and chain conformation then has to be considered. Therefore, the free energy of transferring an uncoiled segment in an oligmeric radical from a fixed position in a water solution phase to a fixed position into a swollen polymer surface can be estimated by

$$\Delta\mu_S = \beta\Delta\mu_M \tag{4}$$

where β is the number of a repeating monomer unit in an uncoiled segment.

To estimate the transfer free energy of an aqueous radical with eqs 1−4, α has to be determined. As defined by eq 2, α is the ratio of the free energy of transferring a monomer unit in an oligmer from a water phase into a hydrophobic surface to that of an individual monomer molecule from the water phase to the respective hydrophobic organic phase. Although we have no quantitative proof at this point, we believe that deviations in α from unity can be largely attributed to the conversion of carbon−carbon double bonds in the monomer to single bonds in the oligomer. The effect of the connectivity between the units in the chain compared to freely dispersed monomer molecules also significantly contributes to the deviation. However, the effect of side groups in various monomers on α is likely to be secondary. Therefore, as a first approximation, we assume that α is monomer independent. For sodium decyl sulfate, we picture the 10-carbon chain as derived from five ethylene units. The transfer free energy of a segment CH_2CH_2 in the hydrocarbon chain is in the range of $-2 \times (2.8-3.3) = -(5.6-6.6)$ kJ/mol estimated from the free energy of adsorption of sodium decyl sulfate onto a water/dodecane interface at 25 °C.[8] We will take an average value of −6.1 kJ/mol. On the other hand, the free energy of transferring an alkene molecule (μ_A) with $n_c > 3$ is given as $\mu_A = -6.29 - \{3.69n_c\}$ kJ/mol by Tanford,[7] which was obtained via a linear regression

Table 1. Coefficients Involved in Eq 6 as a Function of the Number of Monomer Units in an Ologmeric Radical

no. of monomer units	a	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8	b_9
1	3.6	1								
2	8.5	1	2							
3	19.9	2	3	3						
4	38.9	3	5	5	5					
5	77.3	5	8	8	8	8				
6	144.6	8	13	13	13	13	13			
7	265.5	13	21	21	21	21	21	21		
8	477.9	21	34	34	34	34	34	34	34	
9	855.4	34	55	55	55	55	55	55	55	55

technique over the free energy data of alkenes that are in liquid state at 25 °C and 1 atm. The free energy of transferring an ethylene molecule is then estimated to be about ~ −13.7 kJ/mol by extrapolating the relationship to $n_c = 2$. Then from eq 2 $\alpha \approx 0.45$ at 25 °C. We then use this value for our calculations.

It has been noticed that the effect of a sulfate end group on the first segment next to it needs special consideration.[7] For example, the methylene (CH_2) group next to the sulfate group in soldium dodecyl sulfate is completely surrounded with water molecules in a monolayer formed on air/water interfaces, which is equivalent to ~3.1 kJ/mol in free energy.[5] In the present article, the transfer free energy of the segment next to the sulfate group (designated by segment 0′ in Figure 1) was estimated as

$$\Delta\mu_S^{\text{first}}(1') = \Delta\mu_S(1') - 3.1\ (\text{kJ/mol}) \tag{5}$$

where $\Delta\mu_S(1')$ is the free energy of transferring the segment 1′, estimated from eqs 4 and 5.

For simplicity, we assumed that the ionized sulfate group will not be in contact with the hydrophobic surface on the polymer side for all cases considered here. For an aqueous radical with two monomer units, there are then three distinguishable conformations in the lattice model, with the definition discussed above (Figure 2). λ^c for each confirmation c is also illustrated in the figure. Both 2 segment 2′ and 1 segment 1′ are on the surface in all the conformations. Equation 1 then can be further written as

$$\Delta\mu_P = 8.5kT - [\Delta\mu_S(1') - 3.1] - 2\Delta\mu_S(2')\ (\text{kJ/mol})$$

For a given aqueous radical with n monomer units, the general formula may be written as

$$\Delta\mu_P = akT - b_1[\Delta\mu_S(1') - 3.1] - b_2\Delta\mu_S(2') - \ldots - b_n\Delta\mu_S(n')\ (\text{kJ/mol}) \tag{6}$$

where a, b_1, b_2, ..., and b_n are dependent upon n. It should be noticed that b_1, b_2, ..., and b_n relate to the transfer free energy contributed from segment 1′, 2′, 3′, ..., n', respectively, through its product with the free energy of transferring the corresponding segment. In other words, they are the number of the corresponding segments in contact with the polymer phase for all the distinguishable conformations of a molecule. Table 1 lists the coefficients in eq 6 for $n \leq 9$.

Results and Discussion

Homopolymers. Since there are data in the literature for the critical length of entry radicals of St and MMA, we applied our calculation to these systems first.

Table 2. Free Energy Characteristics of Selected Monomers at 25 °C and Estimated Length of Z-mer Entry Radical

monomer	$-\Delta\mu_m$[a] (kJ/mol)	$-\Delta\mu_S$[b] (kJ/mol)	Z-mer
2-EHA	28.1	12.6	1
styrene (St)	23.9	10.8	2
butyl methacrylate (BMA)	23.0	10.4	2
butyl acrylate (BA)	19.8	8.9	2
butadiene (Bu)	18.0	8.1	2
ethyl acrylate (EA)	14.2	6.4	4
methyl methacrylate (MMA)	14.1	6.3	4
vinyl acetate (VAc)	12.8	5.7	5
methyl acrylate (MA)	10.8	4.9	8
acrylonitrile (AN)	9.6	4.3	>10 (estd 12)

[a] Calculated from mutual solubility data.[9] [b] $\beta = 1$ and $\alpha \approx 0.45$ defined in eq 4 and eq 2.

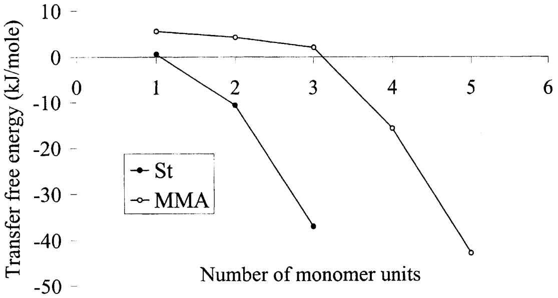

Figure 3. Changes in free energy of transferring a radical ($\Delta\mu_P$) derived from St or MMA with the number of the monomer units in the radical.

As discussed in the last section, it is reasonable to choose $\beta = 1$ in eq 4 for St and MMA to avoid the coiled-chain complication. $\Delta\mu_m$ was estimated from mutual solubility data for monomer and water (x_w and x_O) at 25 °C[9] via eq 3. Correspondingly $\Delta\mu_S$ was calculated via eqs 2 and 4. Results are listed in Table 2. The free energy of transferring an aqueous styrene radical was calculated as a function of the number of the styrene units by using eq 6, and the results are shown in Figure 3. Clearly, spontaneous adsorption of the radical with two or higher number of styrene units may occur since the corresponding transfer free energy turned to negative values; i.e., the critical length of styrene entry radicals is 2. This result is in complete agreement with experimental observation made by Gilbert et al. and their "aqueous control theory".[1] Their theoretical approach is basically the same as ours here, i.e., estimating surface activity of entry radicals. However, our approach is based on estimation of the transfer free energy of a radical from the fundamental characteristics of the radical itself rather than using an analogy of oligomeric radicals to a series of surfactants with the same end group.

Similarly, for MMA radicals the transfer free energy turned to negative when the number of MMA units in the radical is four or higher (Figure 3). This result is also consistent with the values reported in the literature.[1] It should be noticed that $\Delta\mu_m$ calculated from solubility data is that of transferring of a monomer molecule from water to monomer phases, which are in equilibrium. Strictly speaking, therefore, the critical length of entry radicals estimated from the monomer represents the radical entering a particle consisting of pure monomer.

It should be pointed out that the free energy of transferring an aqueous phase radical estimated above

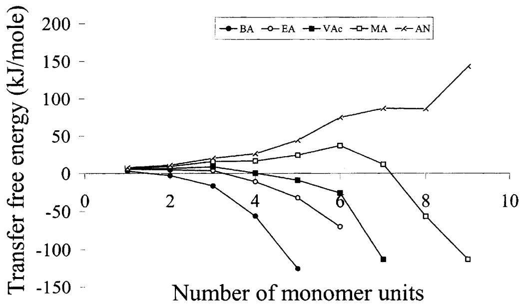

Figure 4. Changes in free energy of transferring a radical ($\Delta\mu_P$) derived from BA, EA, VAc, MA, and AN with the number of the monomer units in the radical.

is that at 25 °C. However, the transfer free energy of an alkyl sulfate surfactant decreases when the temperature increases from 25 to 50 °C,[8,10] but the change is less than 4% as reported over this temperature range.[1] This suggested that an aqueous phase oligomeric radical is only slightly more surface active at 50 °C than 25 °C. Therefore, the results described above should be valid in the normal range of temperatures employed in emulsion polymerization.

We extended the same approach to other common monomers with limited solubility in water to predict the critical length of their entry radicals. $\Delta\mu_m$ and $\Delta\mu_S$, along with predicted critical lengths of entry radicals, are listed in Table 2. To illustrate the effects of $\Delta\mu_m$ on the changes in transfer free energy with the number of monomer units, the monomers BA, EA, VAc, MA, and AN ($-\Delta\mu_m$ = 19.8, 14.2, 12.8, 10.8, and 9.6 kJ/mol, respectively) were chosen. The trend of the relations of the transfer free energy to the number of monomer units falls into two categories (Figure 4). If the transfer free energy is low, for example, $\Delta\mu_m = -19.8$ for BA, the transfer free energy decreases aggressively with the number of monomer units. On the other hand, if the transfer free energy is high, for example, $\Delta\mu_m = -10.8$ for MA, the transfer free energy increases gradually before reaching a maximum and then decreases aggressively. This is explained as a competition between the entropic and enthalpic components expressed in eq 6. Here, the entropic contribution (first term) dominates the free energy values at low numbers of monomer units, while the enthalpic contribution (all of the terms with a "*b*" coefficient) becomes dominant as the number of monomer units increases. As noted above, the higher the value of $\Delta\mu_m$ (more polar monomers), the more monomer repeat units are required for the onset of the dominance of the enthalpic term.

Generally speaking, the more water-soluble the monomer is (i.e., smaller $-\Delta\mu_m$), the longer the entry radical, as expected. While we do not have experimental data to compare to these latter predictions, they appear to us to be quite reasonable and relate appropriately to the results for St and MMA. It is also worthy of note that we obtain the same value for EA and MMA, as they are isomers. We point out that the predicted Z-mer lengths vary from 1 for the very water-insoluble 2-ethylhexyl acrylate to 8 for the much more water-soluble methyl acrylate. These results suggest that the range of Z-mer values for the most commonly used homopolymers is fairly narrow, extending from 1 to about 8. AN, which is not used as a homopolymer in emulsion polymerization, appears to have a value longer than 10; we approximated it as 12.

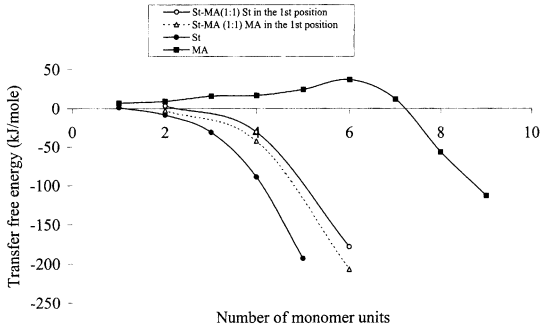

Figure 5. Changes in free energy of transferring a radical ($\Delta\mu_P$) derived from St and MA copolymerization with the total number of the monomer units in the radical. Variations due to first position placement noted for an overall composition of 50% (mole) St.

Copolymers. It is much more complicated to estimate the free energy of transferring an aqueous radical derived from copolymerization. This is due to the overall composition variation among the radicals and the sequential distribution along a particular entry radical chain. Charmot et al.[11] took a first step in examining the effects of bivariate distributions on the critical length of Z-mers and the entry rate. However, the fundamental evaluation of surface activity for the oligomeric radical resulting from copolymerization is still undeveloped. In this section, we apply the lattice model to copolymerization systems. Assuming the free energy of transferring a monomer unit of an aqueous radical derived from copolymerization has the exact same value as that from homopolymerization, we can also estimate the $\Delta\mu_S$ using eqs 2−4. On the other hand, the monomer sequential distribution along an aqueous radical chain with a sulfate group at one end may have an effect on the estimated transfer free energy. The parameters b_1, b_2, b_3 ..., and b_n in eq 6 are related to segment transfer free energy of the 1st, 2nd, ..., and *n*th monomer unit, respectively, to the end group. It is clear that $b_1 \neq b_2$, but $b_2 = b_3 \ldots = b_n$ from Table 1. This indicates that monomer sequential distribution affects the calculated free energy by whether a segment of one particular monomer takes the first position next to the end group in this model. We took St and MA as an example. As shown in Figure 5, the effect of the first position placement in a radical chain with an overall ratio of St:MA = 1:1 is quite obvious. If we choose the integer number of monomer units immediately after each of the curves in Figure 5 turns negative in transfer free energy, the critical length is about 2 for the first position placement of St along the radical chain and 3 for the first position placement of MA. With the same approach, changes in the critical length of entry radicals with other compositions of St−MA radicals were examined. Figure 6 shows the variation of the critical length of the entry radicals over the entire copolymer composition range. The average of critical lengths of the entry radical between the different first position placements increases with MA mole fraction in the radical, with lower and upper limits at 2 and 8 for pure BA and pure MA, respectively. The "error bars" reflect the differences in the calculated chain lengths for the different first position placements of the two different monomer units. In the figure we have connected the averages of all calculated sets of points by straight lines, which allows us to see the nonlinearity of the overall curve. Further, beyond the first position placement, the sequence dis-

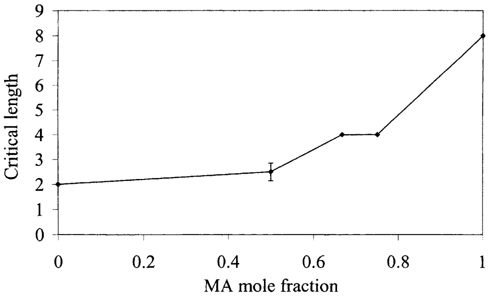

Figure 6. Changes in the average critical length of entry radicals derived from St−MA copolymerization with MA mole fraction. Error bars are the standard deviations calculated from two different first position placements of the two monomers.

tribution of the monomer units in the rest of the chain has no effect on the calculated critical length, as discussed above.

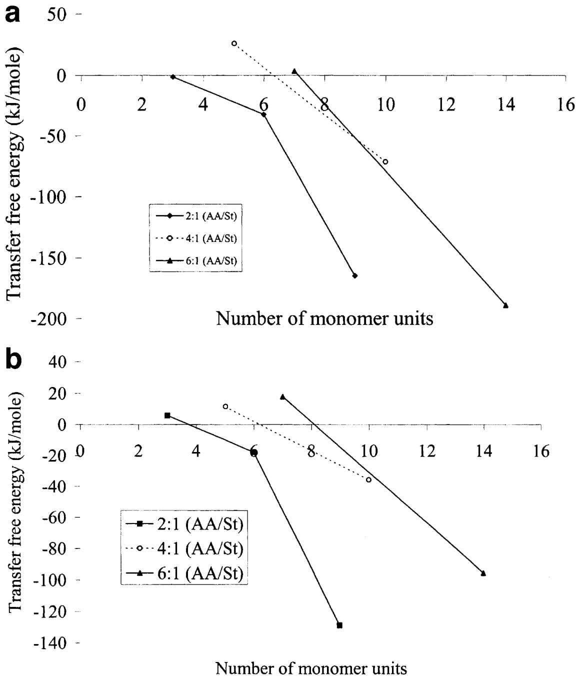

Figure 7. Changes in free energy of transferring a radical ($\Delta\mu_P$) derived from St and AA copolymerization with the total number of the monomer units in the radical: (a) AA units are placed at the first position next to the end group; (b) St unit is placed at the first position next to the end group.

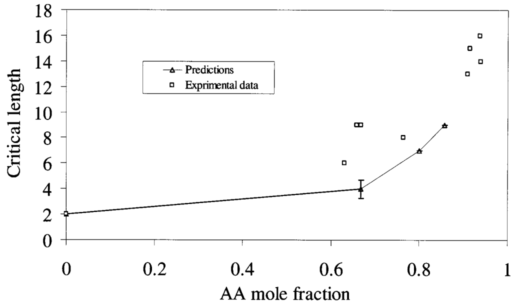

Figure 8. Changes in the average critical length of entry radicals derived from St−AA copolymerization with AA mole fraction. Error bars are the standard deviations calculated from two different first position placements of the two monomers.

Carboxylic Acid Copolymers. In the following discussion, we apply our model to oligomeric radicals derived from St and acrylic acid (AA) copolymerization at low pH. It is unreasonable to take the number of repeating units in a segment β as 1 for AA, because of the possible inter-hydrogen bonding between monomer units in its radicals. In fact, it is difficult to explain the relative high solubility of AA in organic phases[12] by the free energy of transferring a single monomer molecule to an oil phase. If we take a group contribution approach, the free energy of transferring the hydrocarbon part of AA is $\sim -2 \times 3$ kJ/mol, and that of COOH is about +16 kJ/mol.[7] As a result, the overall free energy of transferring a single AA monomer molecule is highly positive value ($\sim +10$ kJ/mol). Wang and Poehlein[13] have demonstrated that the partitioning of AA or MAA between water and an oil phase is complicated and hydrogen bonding between monomers, or dimerization, and is the major cause for enhanced AA solubility in the oil phase. Further, here we considered only the critical length of the entry radical derived from St−AA copolymerization. Since AA is much more soluble than St in the water phase, it tends to form relatively more AA−AA than AA−St sequences in aqueous polymerization. Therefore, it may be reasonable to choose two AA units as a segment to estimate the minimum number of monomer units for the entry radicals of this kind. The free energy of transferring a segment of two AA units was estimated from the solubility data which were taken from the range in which dimerization is assumed,[13] from which $-\Delta\mu_m$ is estimated ~4 kJ/mol. As a first attempt, we take the composition and first position placement of the monomer unit next to the sulfate end group as a given. For example, the free energy changes with the increases in the number of segment units for a radical with various compositions and first position placements, of St and AA, are shown in Figure 7a,b. We take the number of monomer units of the radical, with which the transfer free energy just turns negative on the curves, as the critical length of entry radicals. It is then clear that the critical length of the entry radical depends on both chain composition and whether the AA or the St units is in the first position. The critical length of entry radicals is generally shorter when the AA−AA units were placed in first position next to the end group. If we imagine the AA−AA and the end group as a more hydrophilic block as opposed to the rest of the chain, the result can be explained as a longer more hydrophilic block formed at the given chain compositions, which results in a radical with stronger surface activity. A similar but less obvious effect was also observed in the St−MA system (Figure 5). This may be because the difference in transfer free energy of a segment between AA−AA and St is much greater than that between St and MA. To further illustrate the effects of AA composition, the critical lengths of entry radicals taken from Figure 7, in combination with the experimental results,[1,13] were plotted in Figure 8. The width of the error bars represents the difference of critical lengths predicted by assuming the different first position placements of the two monomers. The model predicts that the critical length of the entry radical increases with AA mole fraction in the radical chain as would be expected. The two different placements of the first position with AA−AA and St units generally yield different critical lengths of the entry radicals. However, the range becomes narrower when the mole fraction is higher and the critical length is longer (Figure 8), suggesting that the effect of the placement can be neglected in longer chains. This is a useful result since it is difficult to determine

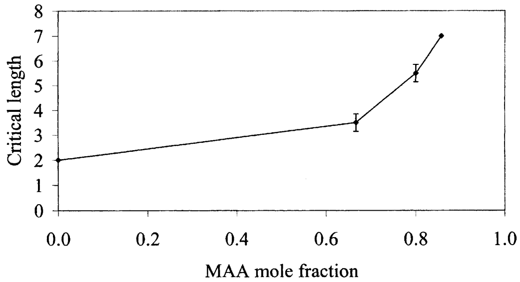

Figure 9. Changes in the average critical length of entry radicals derived from St−MAA copolymerization with MAA mole fraction. Error bars are the standard deviations calculated from two different first position placements of the two monomers.

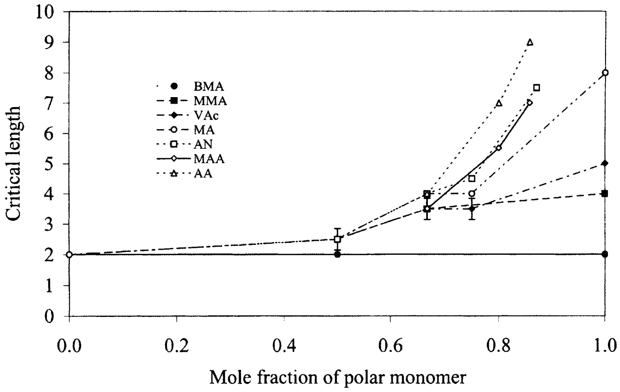

Figure 10. Comparison of changes in the average critical length of different St copolymer radicals with composition. Error bars are the standard deviations calculated from two different first position placements of the two monomers.

the exact sequential distribution in an aqueous radical. However, it is clear in Figure 8 that all predictions are underestimated in comparison with the experimental results. It is important to note that $\Delta\mu_m$ for AA is estimated by assuming AA dimerization for all AA units in the radicals. This may cause an overestimated value for $\Delta\mu_m$, which then gives an underestimated critical length. On the other hand, the experimental results[13] were determined by using all of the water-soluble polymer (longer and shorter chains) to obtain a value of the polymer composition, while the critical length was taken as that of the highest molecular weight chain. Larger molecules may contain more AA than that reflected in the average composition of the water-soluble polymer. This may be another reason why experimental results are consistently higher than our predictions. However, the experimental and the predicted results are close enough and follow the same trends to be encouraging.

When we turn to methacrylic acid (MAA), $\Delta\mu_m$ is estimated to be about −9 kJ/mol as compared to −4 kJ/mol for AA. The predicted critical lengths of entry radicals derived from the monomers of St and MAA are shown in Figure 9. Since MAA is less hydrophilic than AA, the predicted critical length for a St and MAA radical is smaller than that for St and AA at any composition when the acid mole fraction is not zero. In addition, the difference between the values predicted by two different first position placements is much smaller than that in St and AA case. This is because the difference in $\Delta\mu_m$ between MAA and St is much smaller than that between AA and St.

The nonlinearity of the Z-mer length with copolymer composition is clearly more prevalent as the polarity difference between the two monomers increases. To demonstrate this in summary fashion, we have plotted the calculated results for St copolymerizing separately with BMA, MMA, VAc, MA, AN, MAA, and AA against the mole fraction of the more polar monomer in Figure 10. Here the calculated Z-mer values are plotted as whole numbers when the placement of the particular comonomer unit (i.e., either St or the other monomer) immediately after the sulfate end group makes no difference or as the average value with an error bar when there is a difference. In addition, we have chosen to connect the Z-mer values with straight lines rather than an estimated smooth curve. This gives a bit of choppiness to the curves. However, it is quite evident the there is very little effect of the more polar monomer until its mole fraction is 0.5−0.6. Then its effect is significant and is more strongly felt as its polarity increases.

Conclusion

We have utilized a simple lattice model for evaluating the free energy of transferring an oligomeric radical from the water phase onto a swollen polymer surface. With this model, we are able to straightforwardly estimate the critical lengths for the commonly used vinyl homopolymers. The predictions for St and MMA are in complete agreement with experimental data. The calculation can be readily extended to copolymerization systems. The model predicts that the overall composition of a copolymer radical will have a significant impact on the critical length, while the sequential distribution of the monomer units in the chain will have a limited effect. Model predictions for the poly(acrylic acid-*co*-styrene) system are in reasonable agreement with reported experimental results over a range of experimental conditions.

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