NOTE

Inhibition Effects in Emulsion and Miniemulsion Polymerization of Monomers with Extremely Low Water Solubility

F. Joseph Schork, Alan Back

School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia

INTRODUCTION

There are at least two unique issues to consider in the emulsion polymerization of highly water-insoluble monomers. These are monomer transport limitations on the rate of polymerization, and a high sensitivity to low levels of inhibition.

Balic[1] has made a complete study of the macroemulsion polymerization of vinyl neodecanoate (i.e., vinyl versatate or VEOVA). This monomer is highly water-insoluble (4×10^{-5} mol/L at 25C). Balic reports low rates of polymerization and long inhibition periods in macroemulsions. He asserts that this is not due to monomer transport limitations, and provides calculations to support this. He attributes the low rates to impurities in the monomer, although he was unsuccessful in removing these. It could be that the extremely low solubility of the monomer in the aqueous phase retards the formation of oligomeric radicals of sufficient length (hydrophobicity) to enter the polymer particles. Under these conditions of very slow aqueous phase polymerization, the oligomers might be particularly susceptible to low levels of aqueous phase inhibitor. With the resultant low radical flux into the particles, the rate of polymerization would be low. It could also be that the rate of monomer diffusion is not sufficient to allow the polymerization to be reaction limited, since Balic's arguments do not necessarily rule out this possibility. The use of miniemulsion polymerization should remove issues of monomer transport, but will do nothing to reduce the high sensitivity to low levels of inhibition.

A good review of inhibition in free radical polymerization is given by Tudos.[2] The sensitivity to low levels of inhibition can be addressed as follows. A simplified mechanism for free radical polymerization can be written as:

$$\left.\begin{array}{c} I \overset{k_d}{\Rightarrow} 2R \\[2mm] M + R \overset{k_i}{\Rightarrow} P_1 \end{array}\right\} \text{ Initiation}$$

$$P_n + M \overset{k_p}{\Rightarrow} P_{n+1} \quad \text{Propagation}$$

$$P_n + P_m \overset{k_{ic}}{\Rightarrow} M_{n+m} \quad \text{Termination by Combination}$$

$$P_n + P_m \overset{k_{id}}{\Rightarrow} M_n + M_m$$

$$\text{Termination by Disproportionation}$$

$$R + In \overset{k_{in}}{\Rightarrow} Q \quad \text{Inhibition} \tag{1}$$
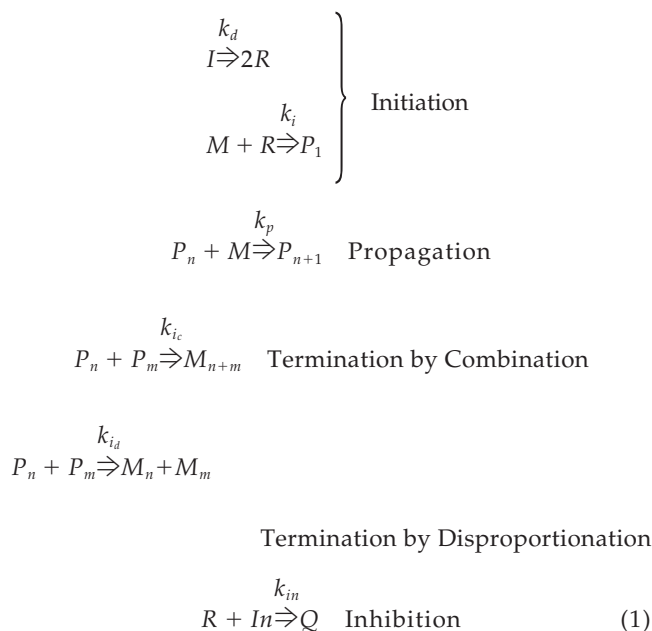
Here, In is the concentration of inhibitor, and k_{in} is the rate constant for inhibition, where Q is an inactive radical, incapable of propagation. Other symbols are as commonly used. For solution or bulk polymerization, the effect of inhibitors on free radical polymerization is well known.[3] It can be summarized by the equation for the concentration of live polymer chains, P:

$$P = \left[\frac{2fk_dI}{k_t}\right]^{1/2}\left[\frac{1}{1 + \dfrac{k_{in}In}{k_iM}}\right]^{1/2}. \tag{2}$$

If one considers the aqueous phase of an emulsion (or miniemulsion) polymerization with a water-soluble initiator, the mechanism in eq. (1) is valid, although significant propagation in the aqueous phase is unlikely and radical entry into particles must be considered. In this case, eq. (2) may be

rederived as follows. A balance on primary radicals in the aqueous phase may be written as

$$\frac{dR}{dt} = 2k_d I - k_i MR - k_{in} RIn = 0 \qquad (3)$$

Here the quasi-steady state assumption (QSSA) is made. A balance on radical polymeric chains of any length in the aqueous phase can be written as

$$\frac{dP}{dt} = k_i MR - k_t P^2 - fP = 0 \qquad (4)$$

Again, the QSSA has been made. Here the last term accounts for radical entry into micelles or particles. There are numerous theories on radical entry into particles, the practical difference being in the effect of particle size on the rate of radical capture. For the present purposes, the effect of particle size can be neglected, provided all theories predict approximately linear dependence on P. This functionality is absorbed into the symbol f where f is some function of particle diameter, micelle concentration, surfactant concentration, etc. Note that a radical entry term has not been included in the primary radical (R) balance, since it is generally accepted that water-soluble radicals must add at least one monomer unit to become sufficiently hydrophobic (or surface active) to enter micelles or particles. Eq. (3) may be solved to give

$$R = \left[\frac{2fk_d I}{k_i M + k_{in} In} \right] \qquad (5)$$

Eq. (4) may be simplified by setting the aqueous phase termination term to zero. This is justified since, for highly water-insoluble monomers, P will be small, and so P^2 will be negligible by comparison. This is equivalent to saying that most aqueous phase polymeric radicals will enter micelles or particles before they undergo biomolecular termination. With this assumption, eq. (4) may be solved to give

$$P = \left[\frac{k_i MR}{f} \right] \qquad (6)$$

Substituting eq. (6) into eq. (5) and rearranging gives

$$P = \left[\frac{2fk_d I}{f} \right] \left[\frac{1}{1 + \dfrac{k_{in} In}{k_i M}} \right] \qquad (7)$$

Eq. (7) is the dispersed-phase (emulsion, miniemulsion, etc.) polymerization analogue to eq. (1), which apples to single phase (bulk or solution) polymerization. Here one can see that the inhibition effect is independent of the radical entry mechanism denoted by f.

Inhibition can take two forms. If the ratio $k_{in} In/k_i M$ approaches infinity (high rate of inhibition), the rate of polymerization goes to zero since P goes to zero, and there are no aqueous phase radicals to enter micelles or particles and begin polymerization. In a batch reactor, this persists until the inhibitor is consumed, and P reverts to its uninhibited

value and the polymerization proceeds. This is the classic inhibition lag seen in free radical polymerization, including emulsion and miniemulsion polymerization.[3] If the ratio $k_{in} In/k_i M$ is finite, the rate of polymerization will be nonzero, but less than the noninhibited rate because P is nonzero, but less than its uninhibited rate. This is the case of classic *retardation*, also seen in bulk and solution as well as in emulsion and miniemulsion polymerization.[4]

Inhibition becomes especially important in the emulsion (or miniemulsion) polymerization of extremely water-insoluble monomers. Recall that in emulsion polymerization with a water-soluble initiator, primary free radicals form in the aqueous phase. These radicals are very hydrophilic. To enter micelles or polymer particles (or monomer droplets in the case of miniemulsion polymerization), they must first add a number of monomer units to become surface active and adsorb to the particle phase. This oligomeric length for entry varies from monomer to monomer, and is referred to as the critical length for entry. In the emulsion polymerization of an extremely water insoluble monomer, $k_i M$ will be very small, since the monomer concentration in the aqueous phase will be extremely small. The water solubility of some monomers is quite low. For instance, the water solubility of VEOVA is approximately one one-hundredth that of styrene[1]; the water solubility of vinyl stearate is 5000 times less than that of styrene.[1] In these cases the ratio $k_{in} In/k_i M$ becomes critical. If $k_i M$ is, say, 1000 times smaller for a given monomer than for styrene, then the term $k_{in} In$ need be only 1/1000 times as great to give the same value of P. This would tend to explain the high inhibitor sensitivity (lag time) often found in emulsion polymerization of extremely water-insoluble monomers. It should be noted that this argument applies only to water-soluble inhibitors, or to inhibitors distributed between the particle and aqueous phases. Since the radical entry mechanism for miniemulsion polymerization is the same as for emulsion polymerization, using a miniemulsion process, while it may eliminate monomer transport limitations, will not lessen the sensitivity to inhibition. The use of oil-soluble initiators may improve the initiator sensitivity, but may drive the polymerization system to a microsuspension (supramicron particle) rather than emulsion or miniemulsion (submicron particle) product. In addition, Tsavalas[5] has shown that in miniemulsion polymerization, even with oil soluble initiators, water-borne radicals are important since the addition of a water-soluble inhibitor to a miniemulsion polymerization with an oil-soluble initiator will substantially suppress the rate of polymerization.

Note that this model only looks at the effects of water-soluble inhibition; oil-phase inhibition may well occur simultaneously, but does not have bearing on the arguments made here. One should also note that vinyl esters are subject to a limited hydrolysis equilibrium with vinyl alcohol, which is in tautomeric equilibrium with acetaldehyde.[6] The aldehyde is a weak radical inhibitor. However, this mechanism should result in mild retardation rather than inhibition.

In conclusion, eq. (7) describes the sensitivity of disperse-phase polymerizations to inhibition. In particular, if the water solubility of the monomer is very low, eq. (7) predicts an extreme sensitivity to low levels of inhibitor.

REFERENCES

1. Balic, R. Ph.D. Thesis, University of Sidney, 2000.
2. Tudos, F.; Foldes-Berezsnich, T. Progress in Polymer Science 1989, 14, 717.
3. Reimers, J. L.; Schork, F. J. J Appl Polym Sci 1996, 59, 1833.
4. Schork, F. J.; Deshpande, P. B.; Leffew, K. W. Control of Polymerization Reactors; Marcel Dekker: New York, 1993.
5. Tsavalas, J. G.; Luo, Y.; Joseph Schork, F. J Appl Polym Sci 2003, 87, 1825.
6. Georgieff, K. K.; Shaw, G. S. J Appl Polym Sci 1961, 5, 212.