

References

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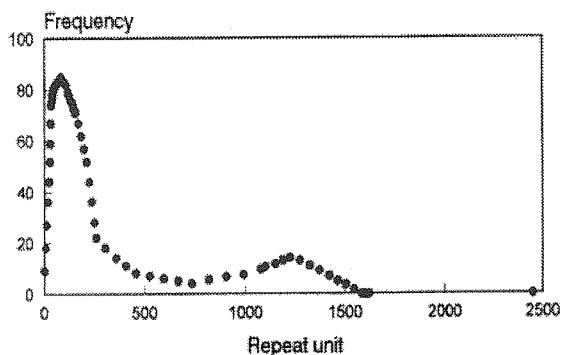


Figure (5) Simulated number based chain length distribution at 55% conversion for emulsion polymerization of butadiene at 25°C. Number of monomer, initiator, and polymer particles in the simulation were 5×10^5 , 1×10^3 , and 400, respectively.

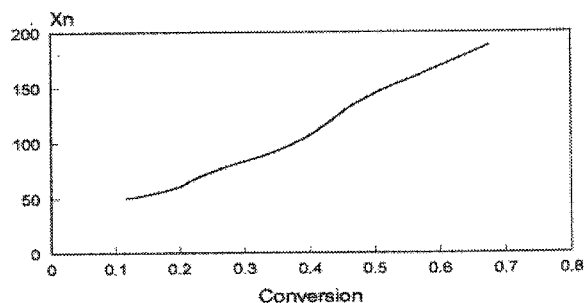


Figure (7) Simulated number average degree of polymerization as a function of conversion for emulsion polymerization of butadiene at 25°C. Number of monomer, initiator, and polymer particles in the simulation were 5×10^5 , 1×10^3 , and 400, respectively.

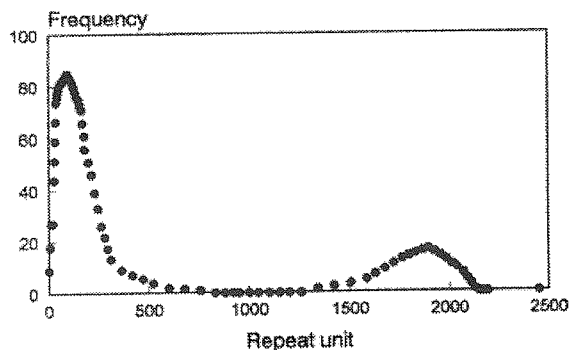


Figure (6) Simulated number based chain length distribution at 75% conversion for emulsion polymerization of butadiene at 25°C. Number of monomer, initiator, and polymer particles in the simulation were 5×10^5 , 1×10^3 , and 400, respectively.

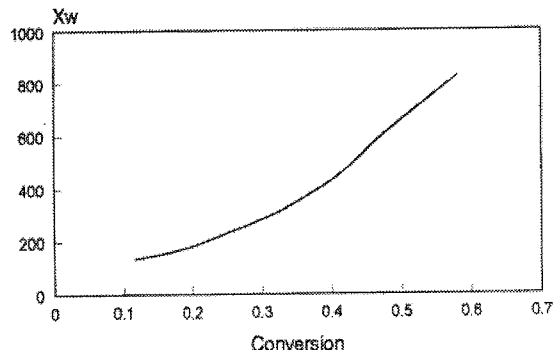


Figure (8) Simulated weight average degree of polymerization as a function of conversion for emulsion polymerization of butadiene at 25°C. Number of monomer, initiator, and polymer particles in the simulation were 5×10^5 , 1×10^3 , and 400, respectively.

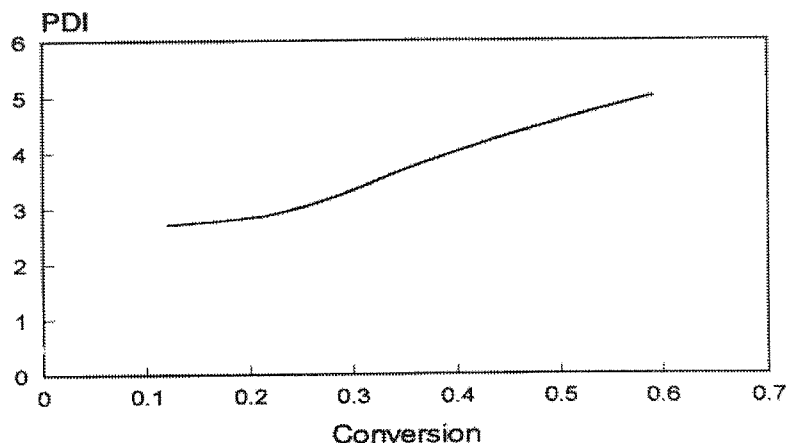


Figure (9) polydispersity index as a function of conversion for emulsion polymerization of butadiene at 25°C. Number of monomer, initiator, and polymer particles in the simulation were 5×10^5 , 1×10^3 , and 400, respectively.

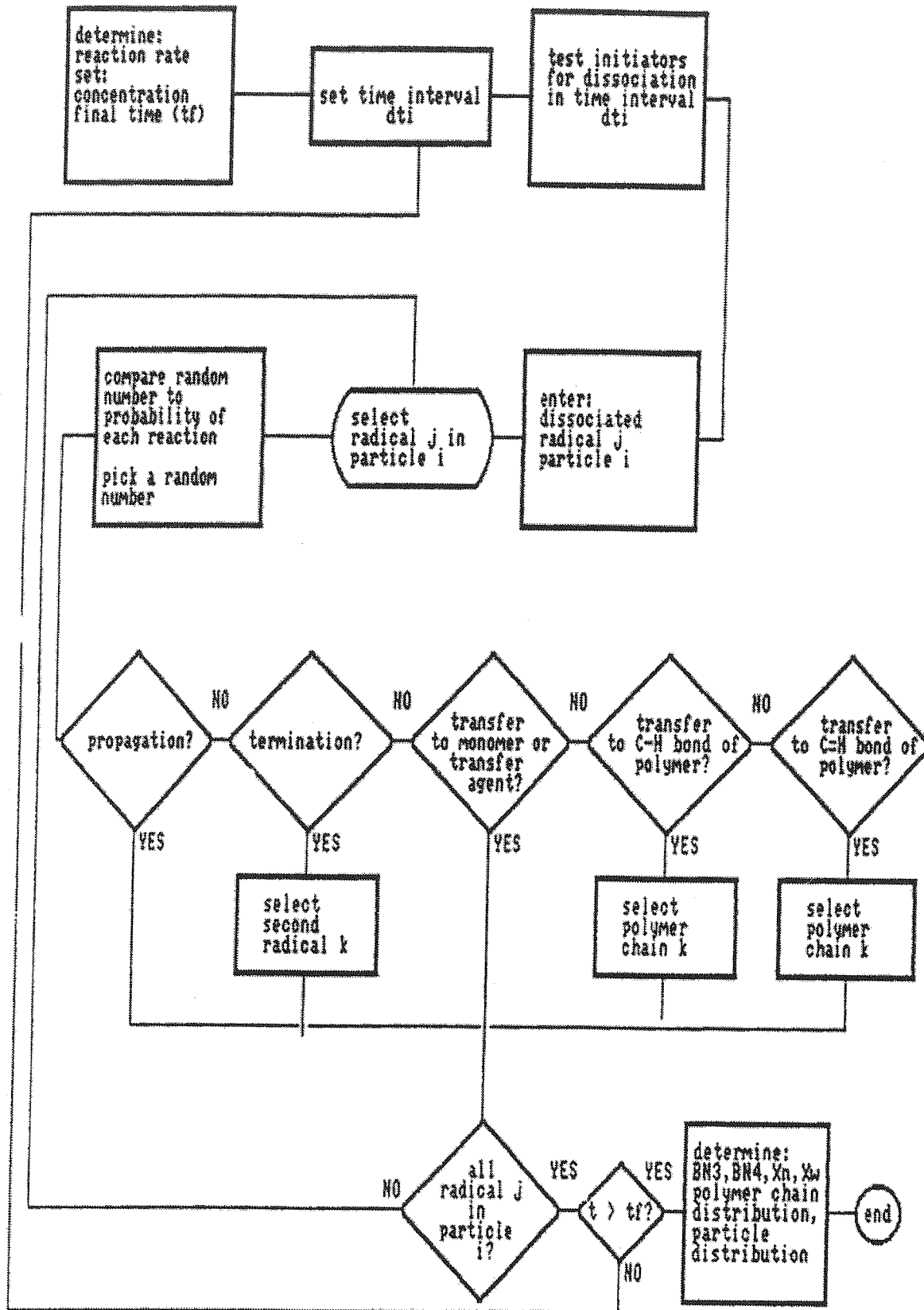


Figure (1) Simulation algorithm for emulsion polymerization of butadiene.

- $[R_{pi}^*]$ concentration of growing radical in the i^{th} particle, mol cm^{-3}
- $[T_{pi}]$ concentration of transfer agent in the i^{th} particle, mol cm^{-3}
- $[MP_{pi}]$ concentration of polymerized monomers in the i^{th} particle, mol cm^{-3}
- m_{pi} number of monomers in the i^{th} particle
- r_{pi} number of growing radicals in the i^{th} particle
- V_{pi} volume of the i^{th} particle, cm^3
- P_{pi} probability for propagation in the i^{th} particle
- P_{tdi} probability for termination in the i^{th} particle
- P_{tmi} probability of transfer to monomer in the i^{th} particle
- P_{tai} probability for transfer to agent in the i^{th} particle
- P_{tphi} probability for transfer to C-H bond of polymer in i^{th} particle
- P_{tpdi} probability for transfer to C=C bond of polymer in i^{th} particle
- R_{toti} total rate of reaction in the i^{th} particle, $\text{lit mol}^{-1} \text{s}^{-1}$
- ρ_B density of butadiene, g cm^{-3}
- ρ_{PB} density of polybutadiene, gcm^{-3}
- V_{sim} initial volume of the simulated polymerization system, nm^3
- T temperature, $^{\circ}\text{C}$
- $[PP]$ concentration of polymer particles, mol cm^{-3}

Table 1 Physico - chemical properties for emulsion polymerization of butadiene.

K_p	8.4 lit/mol-s
K_{td}	1×10^5 lit/mol-s
K_{tm}	1.95 lit/mol-s
K_{tph}	0.84 lit/mol-s
K_{tpd}	9.24 lit/mol-s
ρ_B	0.65 g/cm^3
ρ_{PB}	0.97 g/cm^3
$t_{1/2}$	1800 s
V_{sim}	10^5 nm^3
$[M]/[I]$	500
$[I]/[PP]$	2.5
T	25 $^{\circ}\text{C}$

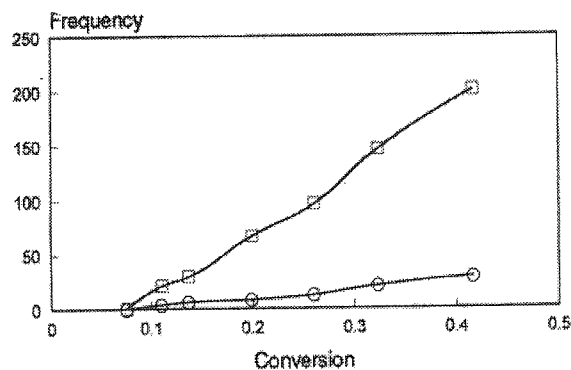


Figure (2) Simulated frequency of tri- and tetra-functional branching as a function of conversion for emulsion polymerization of butadiene at 25 $^{\circ}\text{C}$. Number of monomer, initiator, and polymer particles in the simulation were 5×10^5 , 1×10^3 , and 400, respectively.

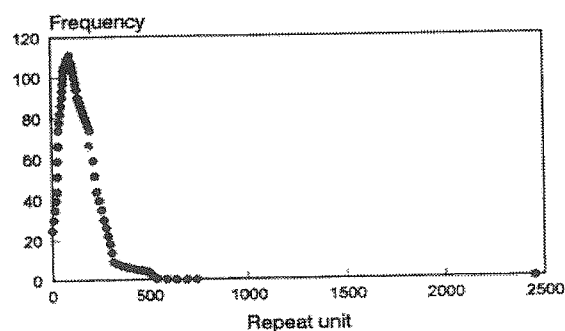


Figure (3) Simulated number based chain length distribution at 20% conversion for emulsion polymerization of butadiene at 25 $^{\circ}\text{C}$. Number of monomer, initiator, and polymer particles in the simulation were 5×10^5 , 1×10^3 , *and 400, respectively.

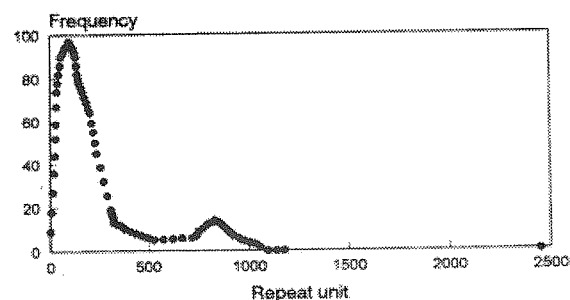


Figure (4) Simulated number based chain length distribution at 40% conversion for emulsion polymerization of butadiene at 25 $^{\circ}\text{C}$. Number of monomer, initiator, and polymer particles in the simulation were 5×10^5 , 1×10^3 , and 400, respectively.

tri- and tetra-functional branching on molecular weight distribution in emulsion polymerization of butadiene. A critical conversion was observed above which the effect of BN3 and BN4 branching on MWD was significant. This critical conversion was a strong function of initiator concentration and the rate of initiation. Above this critical conversion as conversion was increased, the MWD became bimodal due to tetra-functional branching. Bimodal distribution is a characteristic of emulsion polymerization of dienes with high extent of tetra-functional branching. Tri- and tetra-functional branching had little effect on DP_n but DP_w increased significantly with conversion above the critical conversion.

Nomenclature

I	initiator
[I]	initiator concentration in the aqueous phase, mol cm^{-3}
M	monomer
$[M_{pi}]$	monomer concentration in the i^{th} particle, mol cm^{-3}
TA	transfer agent
TA^{\bullet}	transfer agent radical
$[T_{pi}]$	transfer agent concentration in the particle, mol cm^{-3}
PR^{\bullet}	primary radical
R_n^{\bullet}	growing radical with n repeat units
P_n	polymer chain with n repeat units
f	initiator efficiency
K_d	initiator dissociation constant, s^{-1}
K_p	propagation rate constant, $\text{lit mol}^{-1} \text{s}^{-1}$
K_{td}	termination by disproportionation rate constant, $\text{lit mol}^{-1} \text{s}^{-1}$
K_{tm}	transfer to monomer rate constant, $\text{lit mol}^{-1} \text{s}^{-1}$
K_{ta}	transfer to agent rate constant, $\text{lit mol}^{-1} \text{s}^{-1}$
K_{tph}	rate constant for transfer to C-H bond

	of polymer, $\text{lit mol}^{-1} \text{s}^{-1}$
K_{tpd}	rate constant for transfer to C=C bond of polymer, $\text{lit mol}^{-1} \text{s}^{-1}$
P_{diss}	probability of dissociation
$t_{1/2}$	half life of initiator, s
Δt_i	time interval, s
δt_{init}	elapsed time for initiation per molecule, s
δt_{pi}	elapsed time for propagation per molecule, s
δt_{tdi}	elapsed time for termination per molecule, s
δt_{tmi}	elapsed time for transfer to monomer per molecule, s
δt_{tai}	elapsed time for transfer to agent per molecule, s
δt_{tphi}	elapsed time for transfer to C-H bond of polymer per molecule, s
δt_{tpdi}	elapsed time for transfer to C=C bond of polymer per molecule, s
R_i	rate of initiation, $\text{lit mol}^{-1} \text{s}^{-1}$
R_{pi}	rate of propagation in the i^{th} particle, $\text{lit mol}^{-1} \text{s}^{-1}$
R_{tdi}	rate of termination in the i^{th} particle, $\text{lit mol}^{-1} \text{s}^{-1}$
R_{tmi}	rate of transfer to monomer in the i^{th} particle, $\text{lit mol}^{-1} \text{s}^{-1}$
R_{tai}	rate of transfer to agent in the i^{th} particle, $\text{lit mol}^{-1} \text{s}^{-1}$
R_{tphi}	rate of transfer to C-H bond of polymer in i^{th} particle, $\text{lit mol}^{-1} \text{s}^{-1}$
R_{tpdi}	rate of transfer to C=C bond of polymer in particle, $\text{lit mol}^{-1} \text{s}^{-1}$
V_{aq}	volume of the aqueous phase, cm^3
N_{av}	Avogadro number
$P(j)$	selection probability for the j^{th} particle
$P_{gri}(l)$	selection probability for the growing radical l in the i^{th} particle
$P_{pchi}(l)$	probability for transfer to C-H bond of polymer chain l in i^{th} particle
$P_{pedi}(l)$	probability for transfer to C=C bond of polymer chain l in i^{th} particle

tri functional (BN3) and tetra-functional branching (BN4) was determined from the simulation results for each polymer particle or for the collection of particles in the simulated emulsion polymerization system. Rate constants, transfer constants, concentrations, and other properties for the simulated polymerization reaction is given in table 1, obtained from 42.

Results and Discussion

In this simulation, it was assumed that all polymer particles were formed instantaneously at zero conversion. Therefore, only the second stage of emulsion polymerization was simulated. The ratio of monomer to initiator and the ratio of initiator to polymer particles were 500 and 2.5, respectively. Figure 2 shows the frequency of tri- and tetra-functional branching in emulsion polymerization of butadiene. According to this figure, frequency of BN3 and BN4 branching increased linearly with conversion and the rate of BN4 was at least an order of magnitude higher than BN3. Therefore, polymerization of butadiene can be used as a model to study the effect of high degree of tetra-functional branching on MWD.

Figure 3 to 6 show the MWD on number basis for the simulated system at 20%, 40%, 55%, and 75% conversion, respectively. For 20% conversion, a tail around 500 number of repeat units was observed. But as the conversion was increased to 40%, the tail became a second peak with a maximum around 800 repeat units. With increasing conversion to 55% and 75%, this maximum increased to 1200 and 1850 repeat units, respectively. In the absence of tetra-functional branching, only a tail was observed on the high side of the MWD for all conversions. Therefore, in the presence of high extent of

tetra-functional branching, the MWD became bimodal. This bimodal behavior can be used to advantage in practice to produce polymers with acceptable processability and good mechanical properties. This same effect is observed in emulsion polymerization of styrene-butadiene where BN4 branching due to butadiene monomer caused crosslinking and gelation. Furthermore, simulation results indicated that the growth of the second peak in MWD depended strongly on the initiator concentration and the rate of initiation.

Figure 7 and 8 show number (DP_n) and weight (DP_w) average degree of polymerization versus conversion, respectively. The rate of increase of DP_n with conversion was almost constant, therefore the formation of the second peak in MWD had little effect on DP_n . On the other hand, the rate of increase of DP_w with conversion increased significantly at around 20% conversion indicating that the formation of the second peak had a very significant effect on DP_w . Moreover, according to Figures 3 to 6 and Figure 8, the effect of tetra-functional branching became significant after a critical conversion around 20% was reached. This critical conversion was a function of the rate of initiation in the continuous phase. Figure 9 shows the polydispersity index (PI) as a function of conversion. Before the critical conversion of 20%, the PI was around 3, but above 20% conversion where the effect of tetra-functional branching became significant, PI increased sharply to 5 after 50% conversion. Therefore, PI is higher for emulsion polymerization systems with high extent of tetra-functional branching.

Conclusions

Direct Monte Carlo method was a very effective method for simulating the effect of

$$+P_{tdi} + P_{tmi} + P_{tai} + P_{tphi} \quad (32)$$

Transfer to C-H bond resulted in the production of a side chain on polymer chain. To choose the polymer chain k for radical transfer, a selection probability was assigned to each polymer chain in the i^{th} particle based on its number of H-C-H units. A random number was generated and the polymer chain l in the i^{th} particle was selected if the following criteria was satisfied:

$$\sum_{l=1}^{k-1} P_{pchi}(l) \leq \text{RANDOM} < \sum_{l=1}^k P_{pchi}(l) \quad (33)$$

In the above criteria, l is the polymer chain number and $P_{pchi}(l)$ is the selection probability for the polymer chain number l in the i^{th} particle. After the k^{th} polymer was selected, the number of branches on this polymer chain was increased by one and this chain was allowed to propagate from the branch point in the next events. The time elapsed for the BN3 branching event to occur, δt_{tphi} , in the i^{th} particle was determined by:

$$\delta t_{tphi} = 1/[R_{tphi} V_i N_{av}] \quad (34)$$

b5) Tetra-functional branching (BN4)

A random number, RANDOM, was picked. If the following criteria was satisfied, then the event transfer to C=C bonds of polymer was selected for the j^{th} growing radical in the i^{th} particle:

$$P_{pi} + P_{tdi} + P_{tmi} + P_{tai} + P_{tphi} < \text{RANDOM} \\ \leq P_{pi} + P_{tdi} + P_{tmi} + P_{tai} + P_{tphi} + P_{tpdi} \quad (35)$$

Transfer to C=C bond resulted in the production of a crosslink point between a growing radical and a polymer chain. To choose the polymer chain k for crosslinking,

a selection probability was assigned to each polymer chain in the i^{th} particle based on its number of C=C bonds. A random number was generated and the polymer chain l in the i^{th} particle was selected if the following criteria was satisfied:

$$\sum_{l=1}^{k-1} P_{pcdi}(l) \leq \text{RANDOM} < \sum_{l=1}^k P_{pcdi}(l) \quad (36)$$

In the above criteria, l is the polymer chain number and $P_{pcdi}(l)$ is the selection probability for the polymer chain number l in the i^{th} particle. After the k^{th} polymer was selected, a new growing radical z with (m+n) repeat units was produced, with m and n being the number of repeat units of the k^{th} polymer chain and j^{th} growing radical before transfer, respectively. This new growing radical was allowed to propagate further from the crosslink point in the next events. The time elapsed for the BN4 branching event to occur, δt_{tpdi} , in the i^{th} particle was determined by:

$$\delta t_{tpdi} = 1/[R_{tpdi} V_i N_{av}] \quad (37)$$

The above process was repeated for each growing radical in the i^{th} particle and for all of the particles that contained growing radicals. After each event, the total time elapsed was determined. If the elapsed time was greater than or equal to the specified time, t_i , then a new time interval Δt_i was selected and the whole process of initiation and reactions within the particles for each new growing radical produced in the aqueous phase was repeated. When the total elapsed time was greater or equal to the final time of reaction, t_p , the simulation was stopped.

Physical properties such as chain length distribution, number and weight average chain length, number of transfers to monomer and microstructural features such as extent of

picked by the random number generator subroutine. If $0 \leq \text{RANDOM} \leq P_{pi}$ then the event propagation was selected for the j^{th} growing radical in the i^{th} particle and a monomer was added to the growing radical j . After each event, the new concentration of monomer was determined from Flory-Huggins equation. To reach the new concentration, monomer was added to the i^{th} particle from the monomer droplets. The time elapsed for the propagation event to occur, δt_{pi} in the i^{th} particle with volume V_i was determined by:

$$\delta t_{pi} = 1/[R_{pi} V_i N_{av}] \quad (27)$$

b2) Termination

In polymerization of butadiene, termination is almost exclusively by disproportionation. Therefore, termination by combination was not considered in this simulation. A random number was picked and if $P_{pi} < \text{RANDOM} \leq P_{pi} + P_{tdi}$, then the event termination was selected for the j^{th} growing radical in the i^{th} particle. Termination required simultaneous cessation of two growing radicals j and k . To choose the growing radical k , a selection probability was assigned to each growing radical in the i^{th} particle based on its number of monomer units. A random number was generated and the growing radical k in the i^{th} particle was selected if the following criteria was satisfied:

$$\sum_{l=1}^{k-1} pgri(l) \leq \text{RANDOM} < \sum_{l=1}^k pgri(l) \quad (28)$$

In the above criteria, l is the growing radical number and $P_{gri}(l)$ is the selection probability for the growing radical number l in the i^{th} particle. After the K^{th} radical was selected, it was terminated simultaneously with the i^{th} radical with the production of

two polymer chains with degree of polymerization equal to the number of repeat units on their respective radicals and a double bond at the end of one of these chains. This double bond was also taken into account during the process of chain transfer to C=C bond of polymer chains. The time elapsed for the termination event to occur δt_{tdi} , in the i^{th} particle was determined by:

$$\delta t_{tdi} = 1/[R_{tdi} V_i N_{av}] \quad (29)$$

b3) Chain transfer to monomer and transfer agent

A random number, RANDOM , was picked. If $P_{pi} + P_{tdi} < \text{RANDOM} \leq P_{pi} + P_{tdi} + P_{tmi}$, then the event transfer to monomer was selected for the i^{th} growing radical in the i^{th} particle. If $P_{pi} + P_{tdi} + P_{tmi} < \text{RANDOM} \leq P_{pi} + P_{tdi} + P_{tmi} + P_{tai}$, then the event transfer to transfer agent was selected for the i^{th} growing radical in the i^{th} particle. Transfer to monomer resulted in the production of a polymer chain and a new growing radical with one monomer unit, R_1^* . Transfer to transfer agent resulted in the production of a polymer chain and a new growing primary radical, TA^* . The time elapsed for the event transfer to monomer δt_{tmi} , and to transfer agent δt_{tai} , to occur in the i^{th} particle were determined by:

$$\delta t_{tai} = 1/[R_{tai} V_i N_{av}] \quad (30)$$

$$\delta t_{tmi} = 1/[R_{tmi} V_i N_{av}] \quad (31)$$

b4) Tri-functional branching (BN3)

A random number, RANDOM , was picked. If the following criteria was satisfied, then the event transfer to C-H bonds of polymer was selected for the J^{th} growing radical in the i^{th} particle:

$$P_{pi} + P_{tdi} + P_{tmi} + P_{tai} < \text{RANDOM} \leq P_{pi}$$

number ranging from 1 to n, P(j) is the selection probability of the jth particle.

b-Reactions within the particle phase

After a radical entered a particle, polymerization proceeded by propagation, transfer to monomer, to transfer agent, to polymer, or termination by disproportionation, with predetermined probabilities. The rate of the above reactions is given by:

$$R_{pi} = K_p [M_{pi}] [R_{pi}^{\bullet}] \quad (12)$$

$$R_{tdi} = K_{td} [R_{pi}^{\bullet}] [R_{pi}^{\bullet}] \quad (13)$$

$$R_{tmi} = K_{tm} [M_{pi}] [R_{pi}^{\bullet}] \quad (14)$$

$$R_{tai} = K_{ta} [T_{pi}] [R_{pi}^{\bullet}] \quad (15)$$

$$R_{tphi} = K_{tph} [R_{pi}^{\bullet}] [MP_{pi}] \quad (16)$$

$$R_{tpdi} = K_{tpd} [R_{pi}^{\bullet}] [MP_{pi}] \quad (17)$$

In the above equations, R_{pi} , R_{tdi} , R_{tmi} , R_{tai} , R_{tphi} , and R_{tpdi} are the rate of propagation, rate of termination by disproportionation, rate of transfer to monomer, to transfer agent, transfer to C-H bond of polymer and transfer to C=C bond of the polymer chains, respectively, for the i^{th} particle. $[M_{pi}]$, $[R_{pi}^{\bullet}]$, $[T_{pi}]$, and $[MP_{pi}]$ are the concentrations of monomer, radical, transfer agent, and polymerized monomers for the i^{th} particle, respectively. The concentration of monomer and radical in the i^{th} particle was determined by:

$$[M_{pi}] = m_{pi} / [N_{av} V_{pi}] \quad (18)$$

$$[R_{pi}^{\bullet}] = r_{pi} / [N_{av} V_{pi}] \quad (19)$$

In the above equations, m_{pi} and r_{pi} are the number of molecules of monomer and

radicals in the i^{th} particle, respectively, and V_{pi} is the volume of the i^{th} particle. The concentrations $[T_{pi}]$ and $[MP_{pi}]$ were determined in a similar manner.

The state space for the simulation included all of the elementary reactions of propagation, termination, transfer to monomer, to transfer agent, to C-H and C=C bonds of polymer chains, respectively. An event in the simulation was defined as the occurrence of one of the reactions in the state space for the j^{th} radical in the i^{th} particle. The selection probability of each reaction in the state space was assumed to be to the rate of the corresponding reaction, as given below:

$$P_{pi} = R_{pi} / R_{toti} \quad (20)$$

$$P_{tdi} = R_{tdi} / R_{toti} \quad (21)$$

$$P_{tmi} = R_{tmi} / R_{toti} \quad (22)$$

$$P_{tai} = R_{tai} / R_{toti} \quad (23)$$

$$P_{tphi} = R_{tphi} / R_{toti} \quad (24)$$

$$P_{tpdi} = R_{tpdi} / R_{toti} \quad (25)$$

$$R_{toti} = R_{pi} + R_{tdi} + R_{tmi} + R_{tai} + R_{tphi} + R_{tpdi} \quad (26)$$

In the above equations, p_{pi} , p_{tdi} , p_{tmi} , p_{tai} , p_{tph} and, p_{tpdi} are the selection probability for propagation, termination by disproportionation, transfer to monomer to transfer agent, to C-H and C=C bonds of the polymer, respectively, for the i^{th} particle. These probabilities also depended on reaction time as the concentrations of each component changed with time.

b1) Propagation

A random number, RANDOM, was

- j) A thermal initiator with half life of 1800 s was used in this simulation. Therefore, the concentration of initiator decreased exponentially with reaction time.
- k) It was assumed that particles were saturated with monomer and monomer particles were present throughout the course of the polymerization.
- l) It was assumed that the polymerization reaction was carried out batchwise but the reaction volume could change during the course of the reaction.

Monte Carlo method can easily simulate polymerization reactions without being limited by the above assumptions. However, the above assumptions helped us to focus on the effect of tri- and tetra-functional branching on the microstructure of the polymer chains without interference from other reaction parameters.

Simulation Procedure

The simulation algorithm is presented in Figure 1. To begin the simulation, the number of polymer particles, number of monomer and initiator molecules, initiator half life, and the rate constants for each reaction were determined. A subroutine was developed for generation of random numbers between zero and one. This subroutine was tested for variance and for correlation between neighboring numbers for at least one billion numbers. The variance was within the standard limits and no correlation was found between the neighboring numbers.

a- Initiation in the aqueous phase

Each initiator molecule was dissociated directly by random number generation. A time interval, Δt_i , much shorter than the half life of initiator was selected. Then, probability of dissociation of a particular initiator

molecule, P_{diss} , was determined by:

$$P_{diss} = K_d \Delta t_i = [-\ln 2 / t_{1/2}] \Delta t_i \quad (9)$$

In the above equation, $t_{1/2}$ is the initiator half life. For each initiator molecule a random number, RANDOM, was picked by the random number generator subroutine. If $0 \leq \text{RANDOM} \leq P_{diss}$ then the molecule was dissociated and two primary radicals were produced. on the other hand if $P_{diss} < \text{RANDOM} \leq 1$, then the molecule was left undissociated. This process was repeated for each initiator molecule that was not dissociated in the previous time interval Δt_{i-1} . The time elapsed for an initiator to dissociate was determined by:

$$\delta t_{i,init} = 1 / [R_i V_{aq} N_{av}] \quad (10)$$

In the above equation, R_i , $[I]$, and N_{av} are the initiation rate, initiator concentration, and Avogadro number, respectively. V_{aq} is the volume of the aqueous phase. The primary radicals produced in the continuous phase initiated polymerization in the particle phase. The primary radical produced in the aqueous phase entered a polymer particle based directly on random number generation. A selection probability was assigned to each polymer particle based on its surface. It was assumed that initially at time zero polymer particles were micelles with diameter of 2 nm. As the reaction proceeded, a distribution of particle sizes developed. A random number was generated and a radical produced in the aqueous phase was allowed to enter the i^{th} particle if the following criteria was satisfied:

$$\sum_{J=1}^{i-1} P(J) \leq \text{RANDOM} < \sum_{J=1}^i P(J) \quad (11)$$

In the above criteria, j is the particle

simulation. Reaction (6) is similar to reaction (5) except that a chain transfer agent is used in place of monomer. It is assumed that the chain transfer agent radical, $T A^*$, can continue to grow by propagation.

In reaction (7), a growing radical reacts with one of the C-H bonds on a dead polymer chain, extracts a hydrogen from the C-H bond, and becomes a dead polymer chain with no double bond at the terminated end. The reacted polymer chain, after losing a hydrogen, becomes a growing polymer radical with a new branch to grow from the site of hydrogen abstraction. In the simulation, chain transfer to C-H bonds of dead polymer chains as well as growing polymer radicals was allowed, although the extent of branching by chain transfer to growing radicals was relatively low. In reaction (8), a growing radical with n units reacts with one of the C=C bonds on a dead polymer chain with m units, forming a new polymeric radical with $(m+n)$ units. Since two polymeric chains are connected by reaction (8), this reaction causes gel formation and crosslinking

Simulation Assumptions

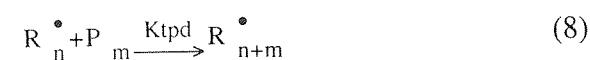
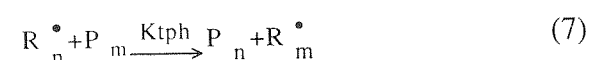
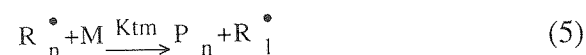
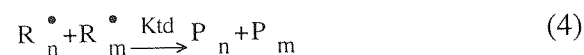
- a) It was assumed that a polymer particle was formed by a primary radical entering a micelle and polymerization continued only within the polymer particles. Since the solubility of butadiene monomer in the aqueous phase was only 0.01 at 25°C, therefore polymerization in the continuous phase and homogeneous nucleation were not significant.
- b) It was assumed that all of the polymer particles were formed simultaneously at zero conversion. Distribution of birth time of particles affected mainly the particle size distribution and not the microstructure of polymer chains. Therefore, the number of polymer particles was constant during the course of this simulation.
- c) It was assumed that initiator molecules dissociated in the aqueous continuous phase, forming two primary radicals. Then, these primary radicals, after reacting with a monomer in the aqueous phase, became insoluble due to very low solubility of butadiene in water and they were adsorbed by the polymer particles. Propagation occurred exclusively in the polymer particles.
- d) It was assumed that radical desorption from the polymer particles to the aqueous phase was not significant. This assumption allowed us to focus on the effect of tri- and tetra-functional branching on MWD irrespective of radical desorption.
- e) It was assumed that particle coalescence was not significant. Particle coalescence mainly affected size distribution and not the microstructure of polymer chains.
- f) It was assumed that polymer particles were homogeneous and the concentration of monomer within the particles was determined by the Flory-Huggins equation.
- g) The effect of surface free energy on equilibrium concentration of components within a particle was ignored. This effect became important for particles smaller than 50 nm in diameter.
- h) It was assumed that particles were saturated with monomer.
- i) It was assumed that the reaction was not diffusion controlled. So, the reaction rate constants for propagation, chain transfer, and termination were assumed constant during the course of the simulation. Since the glass transition temperature of butadiene is well below ambient temperature and the extent of reaction was never more than 75%, this assumption was valid.

with high degree of branching. Therefore, a direct Monte Carlo simulation method was used in this work to study the effect of tri- and tetra-functional branching on MWD. Emulsion polymerization of butadiene was used as a model system to study these effects.

Theory and Simulation

Elementary Reactions

Due to complexity of the moment method in systems with chain transfer to double bond and because of limitations of the BDD method for systems with small particle size, direct Monte Carlo simulation was used to study the effect of chain transfer to double bond (BN4) in emulsion polymerization of butadiene. The following elementary reactions were used in the simulation:



In the above reactions, I, PR^\bullet , M, R_1^\bullet , TA, and TA^\bullet represent initiator, primary radical, monomer, growing radical with one repeat unit, transfer agent, and transfer agent radical, respectively. Symbols R_n and P_n represent growing polymer radical and dead polymer chain with n number of repeat

units, respectively. Rate constants K_d , K_p , and K_{td} are for dissociation, propagation, and termination by disproportionation, respectively. Transfer constants K_{tm} , K_{ta} , K_{tph} , and K_{tpd} are for transfer to monomer, chain transfer agent, transfer to C-H bond, and C=C double bond, respectively.

Reactions (1) and (2) occur exclusively in the aqueous phase and reactions (2) to (8) happen exclusively in the polymer particle phase. In reaction (1), an initiator molecule dissociates thermally in the aqueous phase to produce two primary radicals. In reaction (2), the primary radical reacts with a butadiene monomer, becoming insoluble in the aqueous phase, and is absorbed by the polymer particles. In reaction (3), propagation step takes place in the polymer particle by the reaction of a growing radical with a monomer. After a monomer reacts, its equilibrium concentration in the polymer particle is recalculated using the Flory-Huggins theory, assuming homogeneous particle morphology, and based on the new concentration, the reacted monomer is replaced from the monomer particles.

In reaction (4), termination occurs by the reaction of two growing radicals in the polymer particle phase. For butadiene, termination takes place mainly by disproportionation with the formation of two dead polymer chains and double bond at the end of one chain. Chain transfer to this double bond was also taken into account in this simulation. In reaction (5), a growing radical transfers its radical to a monomer resulting in a dead polymer chain with a double bond at the terminated end and a monomer radical. This monomer radical is able to grow by propagation. Chain transfer to the double bond of the polymer chain formed by reaction (5) was accounted for in this

made to model and simulate the microstructure of polymeric chains produced by emulsion polymerization such as molecular weight distribution, extent of branching, effect of termination mode, and crosslinking [10-16]. Lichti et al. [13,14] presented a mathematical formulation to describe the evolution of the molecular weight distribution (MWD) of linear chains in emulsion polymerization. Min and Ray [9,11] developed a comprehensive mathematical model consisting of complex population balance equations to predict MWD, branching and crosslinking. However, due to complexity of the resulting partial differential equations only moments of the distribution could be successfully determined. Sundberg and Eliason [17] developed a mathematical model for the calculation of MWD in emulsion polymerization with only zero or one radical per particle. Friis and Hamielec [18] derived equations for the MWD in emulsion polymerization under zero or one condition with chain transfer to monomer and polymer. Giannetti et al. [15] used a probabilistic approach to describe the MWD in emulsion polymerization with zero, one or two radicals per particle. None of these models can properly predict microstructural features of chains such as extent of branching and crosslinking and MWD in emulsion polymerization.

The method of moments [19-31] has been applied successfully to calculate average molecular weights in free radical polymerization with long chain branching and crosslinking based on the assumption that no more than one radical center per polymer radical is permissible. Method of moments provides information on the various molecular weights but MWD can not be calculated except for very simple cases. Also, a

crosslinked gel molecule is a polymer molecule with many radical centers [32]. These polyradicals can have significant effect on MWD especially in emulsion polymerization where very long molecules are produced.

Recently, a new theory for non-linear polymerization that includes branching and crosslinking is proposed [33-40]. This theory is based on the branching density distribution (BDD) formed in a non-equilibrium system which can give exact solutions for the statistical properties of non-linear polymer molecules. In emulsion polymerization, polymer particles contain between 100 to 1000 polymer molecules which can not be considered infinite whereas the BDD method assumes infinite number of polymer chains [34]. As Tobita has stated [41], if the frequency of branching is not very large, a simulation method based on BDD can be used to describe the kinetics of non-linear emulsion polymerization. However, as the branching density increases, the fact that each polymer particle consists of a limited number of polymer molecules necessitates a model that accounts for the compartmentalization effect in emulsion polymerization.

The objective of this research was to investigate the effect of tri-functional long chain branching and tetra-functional crosslinking on MWD in emulsion polymerization of dienes.

This is important from a practical standpoint because tetra-functional branching causes gelation in emulsion polymerization of styrene-butadiene. In this system, tri- and tetra-functional branching is caused by radical transfer to C-H and C=C bonds of polymerized butadiene monomers, respectively. At present, none of the models can adequately describe these effects in emulsion polymerization of diene monomers

Monte Carlo Simulation of Branching in Emulsion Polymerization of Butadiene

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Abstract

A direct Monte Carlo Method is used to simulate the effect of tri-and tetra-functional branching on molecular weight distribution in emulsion polymerization of butadiene. Butadiene polymerization due to high extent of transfer to C=C bonds of polymer chains, can be used as a model to study the effect of tri-and tetra-functional branching on Polymer Microstructure. In this simulation, elementary reactions included propagation, chain transfer to Monomer, termination by disproportionation, transfer to C-H bonds (BN3) and C=C bonds (BN4) of growing and dead polymer chains. The initial polymerization volume of the simulation was 10^5 nm^3 . The ratio of monomer to initiator concentration and initiator to polymer particles were 500 and 2.5, respectively. As the conversion was increased from 20% to 75%, the molecular weight distribution became bimodal. The maximum of the second peak of the bimodal distribution moved to higher molecular weights as the conversion was increased. Tetra-functional branching had little effect on number average molecular Weight, but it had a significant effect on weight average molecular weight. Therefore, weight average molecular weight is more suitable for characterization of emulsion polymerization systems with high extent of tetra-functional branching.

Keywords

Polymerization, emulsion, Monte Carlo simulation, tri-functional branching, tetra-functional branching, chain length distribution, bimodal distribution .

Introduction

Emulsion polymerization is used extensively in industry for production of high molecular weight polymers with fast reaction rates in submicron particulate form [1-3].

Considerable effort has been made to model and predict the structural properties of these polymers [4-6]. Harkins in 1945 [7] put forth a qualitative theory for emulsion polymerization in which he stated that polymer particles are formed by radicals entering the micelles. Smith and Ewart [8],

based on Harkins theory, developed a model for emulsion polymerization in order to predict properties such as average particle size and molecular weight. Later, Min and Ray [9] proposed a comprehensive model for emulsion polymerization taking into account both homogenous as well as micellar nucleation, radical desorption, particle coalescence and break-up.

In the past two decades, within the framework of Harkins theory, effort has been