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Polymer 46 (2005) 993–1001

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Simulation studies on the origin of the limiting conversion phenomenon in hybrid miniemulsion polymerization

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Abstract

Hybrid systems of acrylic monomers are studied as they undergo miniemulsion free radical polymerization in the presence of unsaturated alkyd resins. The goal of such polymerizations is to induce grafting between the acrylic and alkyd components, which would retard microdomain phase separation, and produce materials with the crosslinking capability of alkyd coatings (normally applied from a solvent system) with the environmental and cost benefits of an aqueous system. In this paper, the observed limiting monomer conversion phenomenon will be explored via simulation studies.

Two mathematical models describing the kinetics of bulk hybrid polymerization of an alkyd–acrylate system were developed. The first was a homogenous model in which the kinetics of retardive chain transfer was used to attempt to simulate the observed phenomenon of limiting conversion. The second model was a core–shell model in which polymerization takes place in an acrylic-rich shell, while the alkyd-rich core serves as a reservoir for acrylic monomer and alkyd. Based on the results from these models, the cause of limiting conversion was attributed to the combined role of the glass effect and the partitioning effect of the monomer into a core–shell system and its subsequent entrapment. Retardive chain transfer was not capable of producing the observed limiting conversion.

Keywords: Miniemulsion; Hybrid; Polymerization

1. Introduction and background

Hybrid miniemulsion polymerization refers to a process by which water-based coatings and traditionally solvent-based resin can be grafted in a single step, water-based process with the resultant product having the properties of both the water-based coating and the resin. The graft copolymerization process is a versatile tool for preparation of polymer latexes that combines the beneficial properties of traditional water-based and solvent-based polymer components.

The grafting reaction that takes place during the copolymerization process has been extensively studied by various researchers [1–11], with divergent views on the grafting efficiency, a general agreement on the observance of a limiting monomer conversion (at conversions exceeding 70–80%), and a retarded overall reaction rate as compared to the polymerization rate in the absence of a grafting resin. Authors such as, Pham et al [4], Huang and Sundberg [5] and Tsavalas [6] have provided a detailed explanation of the mechanism of grafting and have proposed numerous theories regarding the occurrence of a limiting conversion. Grafting can take place either by addition to the double bonds on the resin (typically an alkyd) molecule, or by abstraction of allylic hydrogen of the alkyd [6]. Although the addition process is energetically favored over abstraction, the structure of groups surrounding reactive site of the alkyd, and the steric features of the oligomer radical could still make abstraction preferable to addition during the grafting process. With monomers like methyl methacrylate (MMA) that have a sterically hindered radical center, grafting takes place by abstraction of the hydrogen allylic to a resinous double bond [6]. This chain transfer produces a relatively inactive radical on the resin with a reduction in overall polymerization rate, and when approached by another live MMA macroradical, it terminates with the formation of a grafted alkyd.

Figs. 1 and 2 provide a mechanistic understanding of each of the grafting mechanisms. The addition of alkyd resin

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doi:10.1016/j.polymer.2004.11.035

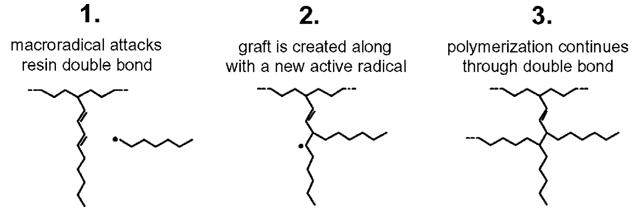

Fig. 1. Grafting mechanism for addition through the double bond.

to a polymerizing acrylate leads to grafting between the two components, with a reduction in polymerization rate. At intermediate to high conversions, a dramatic change in rate often is observed which leads to a plateau in the monomer conversion profile, referred to as the limiting conversion. Tsavalas [6] studied the limiting conversion phenomenon in the hybrid miniemulsion polymerization of the MMA–alkyd system. For an identical recipe without the alkyd, full monomeric conversion was achieved as shown in Fig. 3.

The occurrence of a limiting conversion was explained by Tsavalas from a mechanistic standpoint as being related to inactive macroradicals formed from chain transfer. The following kinetic scheme for free radical polymerization with grafting to a site C on the alkyd chain has been postulated [6]:

Initiation

$$\mathrm{I} \xrightarrow{f\times k_\mathrm{d}} 2\mathrm{R}\cdot \qquad (1)$$

$$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_\mathrm{i}} \mathrm{P}_1\cdot \qquad (2)$$

Propagation

$$\mathrm{P}_n\cdot + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{P}_{n+1}\cdot \qquad (3)$$

Termination

$$\mathrm{P}_n\cdot + \mathrm{P}_m\cdot \xrightarrow{k_{\mathrm{t,C}}} \mathrm{M}_{n+m} \qquad (4)$$

$$\mathrm{P}_n\cdot + \mathrm{P}_m\cdot \xrightarrow{k_{\mathrm{t,p}}} \mathrm{M}_n + \mathrm{M}_m \qquad (5)$$

Chain transfer

$$\mathrm{P}_n\cdot + \mathrm{C} \xrightarrow{k_{\mathrm{fc}}} \mathrm{M}_n + \mathrm{C}\cdot \qquad (6)$$

Propagation (of transferred chain)

$$\mathrm{C}\cdot + \mathrm{M} \xrightarrow{k_\mathrm{i}^\mathrm{R}} \mathrm{P}_1^\mathrm{R}\cdot \qquad (7)$$

$$\mathrm{P}_n^\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{P}_{n+1}^\mathrm{R}\cdot \qquad (8)$$

Termination (of transferred chain)

$$\mathrm{P}_n^\mathrm{R}\cdot + \mathrm{P}_m^\mathrm{R}\cdot \xrightarrow{k_{\mathrm{t,c}}} \mathrm{M}_{n+m}^\mathrm{R} \qquad (9)$$

$$\mathrm{P}_n^\mathrm{R}\cdot + \mathrm{P}_m^\mathrm{R}\cdot \xrightarrow{k_{\mathrm{t,d}}} \mathrm{M}_n^\mathrm{R} + \mathrm{M}_m^\mathrm{R} \qquad (10)$$

$$\mathrm{P}_n\cdot + \mathrm{C}\cdot \xrightarrow{k_{\mathrm{t,C}}^\mathrm{R}} \mathrm{CM}_n \qquad (11)$$

$$\mathrm{P}_n\cdot + \mathrm{C}\cdot \xrightarrow{k_{\mathrm{t,d}}^\mathrm{R}} \mathrm{M}_n + \mathrm{C} \qquad (12)$$

In the above equations, I, initiator; R,·initiator-derived radical (primary radical); M, monomer (MMA); P•, live acrylic polymer chain; C, alkyd grafting site; C•, radical site on the alkyd; M_n, dead linear polymer; and CM_n, dead branched polymer. The superscript R indicates that a polymer chain is grafted to an alkyd molecule.

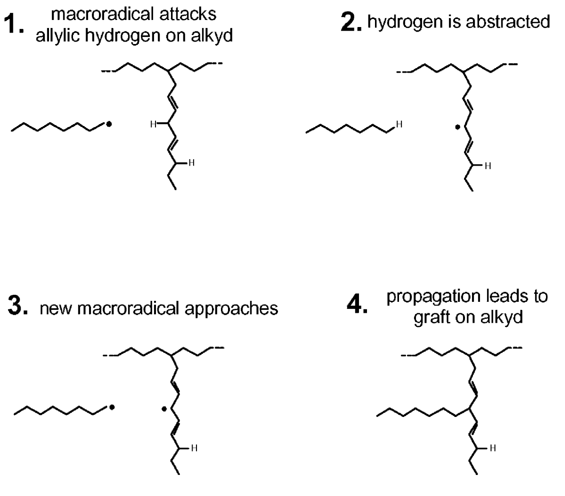

Fig. 2. General mechanism for grafting through chain transfer.

In systems such as MMA–alkyd having low reinitiating rate constants (of the transferred radical) as compared to the propagation rate constant of the growing linear chain ($k_\mathrm{i}^\mathrm{R} < k_\mathrm{p}$; $k_{\mathrm{fc}} \ll k_\mathrm{p}$), grafting takes place by retardive chain transfer [12]. The resulting alkyd radical is considered too stable to reinitiate polymerization. Termination is thus favored over propagation, which results in a lowered polymerization rate and a slower evolution of molecular weight. Although it was believed that the relative inactivity of the alkyd allyl radical is also a contributing factor in producing a limiting conversion, Tsavalas [6] argued that it was not be totally responsible for the observed limiting conversion.

Tsavalas [6] also postulated a physical explanation for the limiting conversion phenomenon. In most recipes involving water soluble initiators, primary radicals are produced in the continuous phase and must enter the particle to be involved in the reaction. After moderate to intermediate conversion, phase separation may take place, forcing the more hydrophobic alkyd to the core of the hybrid particle, leaving the shell consisting primarily of the acrylic component. The location of growing polyacrylate near the surface is a direct consequence of its incompatibility with the fatty acids and esters of the alkyd. However due to high alkyd solubility of the MMA monomer, some portion of the MMA will be dissolved deep within the alkyd core. Since the reaction temperature (50–90 °C) is below the glass

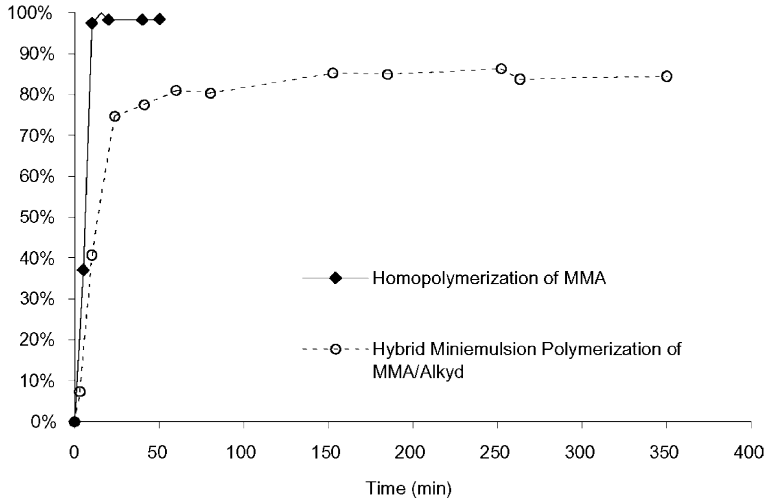

Fig. 3. MMA polymerization in the presence and absence of alkyd (from Ref. [6], with permission).

transition temperature of the PMMA (105 °C), the shell starts to harden after moderate to intermediate conversion. Consequently the initiator will not be able to penetrate the hard shell to enter the particles and is inaccessible to the monomer. Hence the partitioning of the monomer–alkyd–polymer mixture, and its subsequent immobility of the monomer constitute a physical mechanism to explain the occurrence of limiting conversion in MMA–alkyd system.

Tsavalas concluded that both the chemical (retardive chain transfer) and the physical (core–shell morphology) mechanisms may be contributing to the limiting conversion phenomenon. The objective of this paper is to develop a mathematical model that will aid in understanding the mechanisms responsible for the limiting conversion phenomenon observed in the grafting reaction of acrylate–alkyd copolymerization. Two models have been developed. The first is a homogenous model and depends on the mechanism of retardive chain transfer to cause the observed limiting conversion. The second model postulates the existence of a core–shell morphology with a significant portion of the alkyd (and monomer) in a non-reactive core.

2. Homogeneous model

2.1. Homogeneous model development

A mathematical model describing the kinetics of hybrid polymerization of the MMA–alkyd system was developed. The model assumes a well mixed, isothermal, fixed volume batch reactor. In the development that follows, the number of radicals per particle is assumed to be significantly greater than one (Smith Ewart Case III), and hence a pseudo-bulk model can be used to adequately represent the actual hybrid miniemulsion copolymerization. Even if this is not true, the ideas of retardive chain transfer and/or core–shell morphology do not depend on the level of radical segregation, and so the phenomenological results should be applicable to Smith Ewart Case I or II kinetics.

The kinetic scheme of Eqs. (1)–(12) were presumed. Reactions involving propagation of live alkyd chain are relatively uncommon based on the stability of the allylic radical as discussed earlier. Hence the reactions in Eqs. (7)–(10) were not considered any further in the kinetic scheme.

From these reactions, the material balance for each component can be written as:

For initiator:

$$\frac{\mathrm{d}I}{\mathrm{d}t} = -k_\mathrm{d} I \tag{13}$$

$$\frac{\mathrm{d}R^\cdot}{\mathrm{d}t} = 2fk_\mathrm{d} I - k_\mathrm{i} R^\cdot M \tag{14}$$

For monomer:

$$\frac{\mathrm{d}M}{\mathrm{d}t} = -k_\mathrm{p} M P_n^\cdot - k_\mathrm{i} R^\cdot M \tag{15}$$

For growing linear polymer:

$$\frac{\mathrm{d}P_n^\cdot}{\mathrm{d}t} = -k_\mathrm{i} R^\cdot M - 2k_\mathrm{tc} P_n^{\cdot 2} - 2k_\mathrm{td} P_n^{\cdot 2} - k_\mathrm{fc} P_n^\cdot C - k_\mathrm{tc}^\mathrm{R} C^\cdot P_n^\cdot - k_\mathrm{td}^\mathrm{R} C^\cdot P_n^\cdot \tag{16}$$

For dead linear polymer:

$$\frac{\mathrm{d}M_n}{\mathrm{d}t} = k_\mathrm{tc} P_n^{\cdot 2} + 2k_\mathrm{td} P_n^{\cdot 2} + k_\mathrm{fc} P_n^\cdot C + k_\mathrm{td}^\mathrm{R} C^\cdot P_n^\cdot \tag{17}$$

For growing alkyd:

$$\frac{\mathrm{d}C^\cdot}{\mathrm{d}t} = k_\mathrm{fc} P_n^\cdot C - k_\mathrm{tc}^\mathrm{R} C^\cdot P_n^\cdot - k_\mathrm{td}^\mathrm{R} C^\cdot P_n^\cdot \tag{18}$$

For dead branched alkyd:

$$\frac{\mathrm{dCM}_n}{\mathrm{d}t} = k_\mathrm{tc}^\mathrm{R} C^\cdot P_n^\cdot \tag{19}$$

For (unbranched) alkyd:

$$\frac{dC}{dt} = -k_{fc} P_n^{\cdot} C + k_{td}^{R} C^{\cdot} P_n^{\cdot} \tag{20}$$

The total concentration of growing polymer P, dead polymer M_n and dead branched alkyd CM is given by

$$P = \sum_{n=1}^{\infty} P_n^{\cdot} \tag{21}$$

$$M_T = \sum_{n=2}^{\infty} M_n \tag{22}$$

$$\mathrm{CM} = \sum_{n=2}^{\infty} \mathrm{CM}_n \tag{23}$$

The gel or Trommsdorf effect arises at high conversions as a result of increased viscosity of the polymeric mixture and a reduction in mobility of the long propagating chains, retarding termination. At still higher conversions, the propagation rate is also retarded by viscosity in the glass effect. Several reports [11,13–15] have attributed the limiting conversion phenomenon to the glass effect. Tsavalas [6], however, asserts that the glass effect is not significant for a system containing alkyd due to the plasticizing effect of the alkyd and the lower resulting T_g of the mixture. However, for completeness, and for reasons to be discussed later, the gel and glass effects for MMA developed by Schmidt and Ray [16] have been used in this model.

The initiator efficiency was set to 0.5, and the remaining kinetic parameters for the model were taken from the literature and are given in Table 1. Details of the model are given in [18]. It is important to point out that value for chain transfer constant for monomer to alkyd was not found in literature. Tsavalas has suggested a value of $k_{fc} = k_{p0} \times 10^{-4}$ (where k_{p0} is the propagation rate constant in the absence of any glass effect) based on an extrapolation from a vinylneodecanote–polybutadiene system [6]. It was decided to use the value of $k_{fc} = 23.4 \times k_{p0} \times 10^{-4}$ as indicated in Table 1, due to the resemblance of the conjugated alkyd system to a polyisoprene system.

Eqs. (13)–(20) were integrated in MATLAB using standard differential equation solvers and assuming quasi-steady state for radical species. The baseline case used the recipe in Table 2. A model alkyd (medium soya, linseed alkyd) of molecular weight 4000 g/mol, and a fatty acid composition of 22% oleic acid, 16% linoleic acid, 51% linolenic acid [11] was assumed. Based on this composition, each fatty acid group has 2.1 double bonds (DB) and an approximate molecular weight (MW) of 280 g/mole (oleic MW = 282.5, DB = 1, linoleic MW = 280.5, DB = 2 and linolenic MW = 278.4 and DB = 3). Hence the model alkyd had 7 glyceryl units, 9 fatty acids and 19 double bonds and is shown in Fig. 4.

3. Results and discussion

Fig. 5 shows the conversion–times curves for the base hybrid MMA–alkyd system at 80 °C, along with variations in the level of alkyd. As was expected, the polymerization rate drops as the level of alkyd is increased. This reduction in rate of polymerization is the result of retardive chain transfer. This is in agreement with findings of Wang et al. [9], Wu et al. [10] and Hammersveld et al. [17]. Fig. 6 shows conversion curves at various temperatures for a recipe containing 30% alkyd based on monomer weight. The increase in the polymerization rate with temperature is as expected. Again, there is no evidence of limiting conversion when the polymerizations are carried out in the temperature range of 30–80 °C by various authors (i.e. Tsavalas 60–75 °C [6], Wu et al. 65–80 °C [10], Hammsveld 30–50 °C [11,17]). The 100 °C simulation, shows the presence of a very well defined plateau at higher conversions, indicating a typical limiting conversion; however further inspection of the simulation results indicates that the plateau is caused by the depletion of initiator at this temperature, and not by a true limiting conversion. To eliminate this extraneous effect, the model was modified to a constant initiator concentration (and flux) throughout the reaction. The simulation was rerun

Table 1
Reaction rate constants used in simulation

Rate constant	Expression	Units	Reference
k_{p0}, propagation of linear chain	$4.92 \times 10^5 \exp((-4353)/((1.987) \times T))$	l/(g mol-s)	Schmidt and Ray [16]
k_{t0}, termination of linear chain	$9.8 \times 10^7 \exp((-701)/((1.987) \times T))$	l/(g mol-s)	Schmidt and Ray [16]
k_d, initiator dissociation	$1.69 \times 10^{14} \exp((-30000)/((1.987) \times T))$(BPO) 3.16×10^{-6} (KPS)	s^{-1}	Schmidt and Ray [16]
k_{tp}/k_{tc}, termination by combination/termination by disproportion of linear chain	8		Brandrup and Immergut [19]
k_{tpr}/k_{tcr}, termination by combination/termination by disproportion of branched chain	8		Assumption
k_{fc}, chain transfer to alkyd	$23.4 \times k_{p0} \times 10^{-4}$ (based on $C_p = k_{fc}/k_p = 23.4 \times 10^{-4}$ for polyisoprene chlorinated at 80 °C)	l/(g mol-s)	Brandrup and Immergut [19]
f, initiator efficiency	0.5		
k_{tr}, termination of branched chain	$k_{tr} = k_t$		Assumption

Table 2
Initial reactor compositions for homogeneous model

Component	Symbol	Amount (mol/l) (current authors)	Amount (mol/l) (Tsavalas data)
Initiator	I	0.019 (BPO)	0.121 (KPS)
Monomer-MMA	M	9.4	9.4
Alkyd concentration	C	0.071	0.235
Alkyd double bond concentration[a]		1.35	4.46
Dead branched polymer	CM_n	0	0
Dead linear polymer	M_n	0	0
Live acrylic polymer chain	P•	0	0
Live alkyd chain	C•	0	0

[a] Based on 19 double bonds per mole of alkyd as explained in Appendix E).

(without the initiator limitation) for extended time periods to be able to better gauge if the rest of the curves plateau to a limiting value or not.

Fig. 7 represents extended polymerization runs at various temperatures. One thing that is conspicuously absent in all of the simulated conversion curves in Fig. 7 is the occurrence of a limiting conversion. In recipes with alkyd, conversion seems to proceed at a constant rate with time, without the plateau that has been reported by Tsavalas [6], Wu et al. [10], Hammersveld et al. [11,17] and others who have carried out similar acrylate–alkyd polymerization. These authors reported a rapid rate of polymerization followed by a limiting conversion for the alkyd–acrylic polymerization, and not a slow rate of polymerization with complete conversion after extended runs as seen in Fig. 7.

It can be seen that most of these curves go to complete conversion when run for extended time periods. In fact, some authors [15] have pointed out that in polymerization of MMA at 50 °C using AIBN as the initiator, the reaction lasted for 266.6 h (11 days) and no limiting conversion was achieved, but a complete conversion took place. It may be argued that the necessity of such extended time periods are not realistic and from the practical standpoint and from the

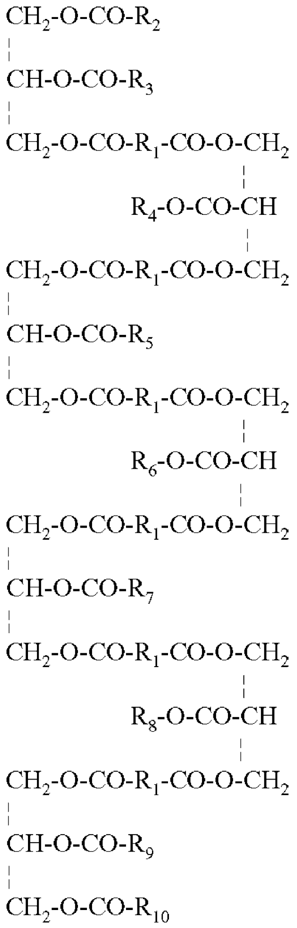

Fig. 4. Structure of the model alkyd. R1 $(CO)_2$–O represents pthalic anhydride group and R_2–R_{10} represent unsaturated fatty acids (oleic, linoleic and linolenic).

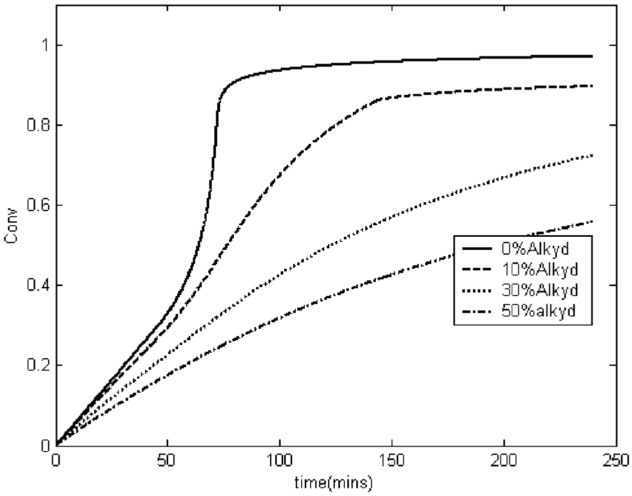

Fig. 5. Conversion versus time at various alkyd levels, 80 °C.

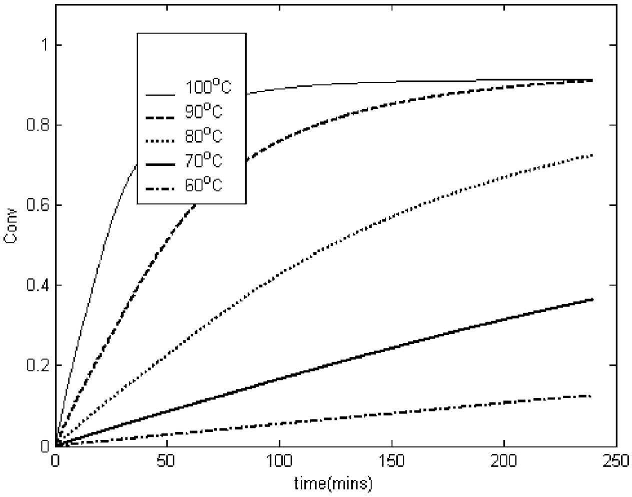

Fig. 6. Conversion versus time at various temperatures, 30% alkyd.

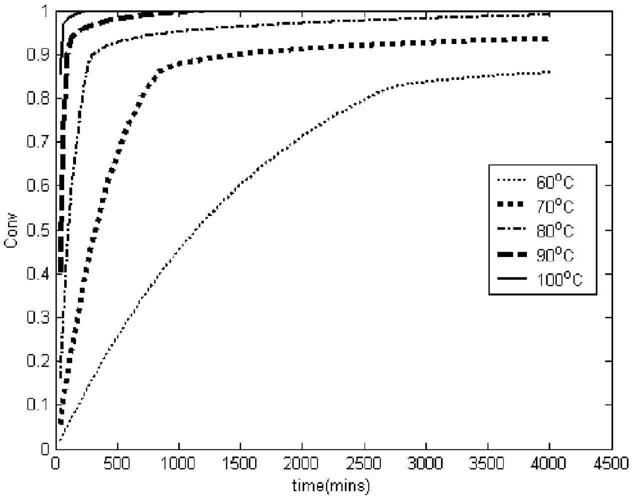

Fig. 7. Conversion versus time at various temperatures, 30% alkyd—extended time simulation with constant initiator concentration.

point of view of this discussion, conversions that do not plateau in a reasonable length of reaction time of 3–6 h (as is typical for most acrylate–alkyd copolymerization) will not be representative of a limiting conversion. Based on this premise, our model which includes expressions for the glass effect and retardive chain transfer slows down the rate of polymerization but does not cause a limiting conversion. A sensitivity analysis and further manipulations of the model resulted in no set of reasonable kinetic parameters that would predict a limiting conversion phenomenon.

Thus, it would appear that the kinetic scheme including retardive chain transfer and the glass effect (both of which should act to slow the polymerization rate) was unsuccessful in accounting for the origin of the limiting conversion phenomenon. It was therefore decided to construct a heterogeneous particle as was proposed by Tsavalas [6].

4. Heterogeneous particle model

It is believed that the kinetic model based on a homogeneous system (as developed thus far) which assumes a uniform distribution of various components does not adequately represent the heterogeneous system that actually exist during the hybrid polymerization of acrylate in presence of the alkyd. At high conversion, instead of a uniform distribution of reactants, a heterogeneous core–shell morphology was reported by Tsavalas [6] which consisted of hard acrylic shell (PMMA) surrounding a core of monomer (MMA) entrapped in alkyd. The core–shell morphology was reported to be a consequence of the limited compatibility of alkyd in polyacrylate. As more MMA is converted to polymer, the incompatibility between the alkyd and the polyacrylate increases, leading to an increased tendency for phase separation to occur. Since the alkyd is much more hydrophobic that the polyacrylate, the alkyd accumulates in the core of the particle, forming typical core–shell morphology. However, since MMA is soluble in alkyd while PMMA is not, some MMA remains entrapped in the alkyd core. The entrapped monomer remains inaccessible to the initiator radicals and is not polymerized, causing a limiting conversion to occur. Based on this postulate of a non-homogeneous particle, a heterogeneous particle model was developed in an effort to simulate the limiting conversion phenomenon.

4.1. Heterogeneous particle model development

The core–shell particle represents is thought to more accurately describe the hybrid miniemulsion polymerization of MMA with alkyd. During the course of polymerization, a core of volume V_c containing alkyd and monomer, is surrounded by shell of volume V_s containing alkyd, monomer and polymer. The shell is accessible to the initiator. The shell represents a spherical liquid envelope richer in polymer and poorer in alkyd and monomer compared to the inner concentric soft core consisting of alkyd and monomer, and is distinguishable as a (hard) shell only in the latter stages of polymerization. For simulation purposes, the volume of the core was arbitrarily set to thirty percent of the total volume of the particle, calculated from an arbitrarily assigned particle radius of 100 nm. Both alkyd and monomer are assumed to be uniformly distributed in core and shell at the start of the reaction, but as the reaction proceeds, the shell becomes richer in polymer and poorer in monomer (MMA) and ungrafted alkyd. However while the monomer is constantly depleted in the shell region as a result of polymerization, its concentration remains high in the core where no reaction takes place due to the inability of initiator radicals to penetrate into the core. The monomer imbalance between core and shell creates a concentration gradient, which will cause monomer transport from core to shell, thus replenishing some of the depleting monomer.

Based on this model, a mass balance for the monomer in core can be written as

$$\frac{\mathrm{d}(V_c M_c)}{\mathrm{d}t} = -k_{sc} A_c (M_s^* - M_s) \tag{24}$$

where M_c and M_s represents the concentration of monomer in the core and shell respectively, k_{sc} the mass transfer coefficient for monomer transport from the core to the shell, A_c the core–shell interfacial area across which monomer transport takes place, and M_s^* the equilibrium concentration of monomer in the shell. As the core continuously changes in volume with the movement of monomer, so does its surface area A_c. The concentration of monomer in shell which is in equilibrium with the monomer in core is given by

$$M_s^* = K_{eq} M_c \tag{25}$$

where K_{eq} is a partition coefficient for monomer distribution between the core and the shell. Both k_{sc} and K_{eq} are unknown and their values were assigned somewhat arbitrarily. The concentration of monomer in the core can now be written as

$$\frac{V_{\mathrm{c}}\mathrm{d}M_{\mathrm{c}}}{\mathrm{d}t} = -K_{\mathrm{sc}}A_{\mathrm{c}}(M_{\mathrm{s}}^{*} - M_{\mathrm{s}}) - M_{\mathrm{c}}\frac{\mathrm{d}V_{\mathrm{c}}}{\mathrm{d}t} \tag{26}$$

A similar balance for monomer in the shell can be written as

$$\frac{\mathrm{d}M_{\mathrm{s}}}{\mathrm{d}t} = -k_{\mathrm{p}}MP^{\cdot} - k_{\mathrm{i}}R^{\cdot}M + \frac{K_{\mathrm{sc}}A_{\mathrm{c}}(M_{\mathrm{s}}^{*} - M_{\mathrm{s}})}{V_{\mathrm{s}}} - \frac{M_{\mathrm{s}}\mathrm{d}V_{\mathrm{s}}}{V_{\mathrm{s}}\mathrm{d}t} \tag{27}$$

The shrinkage in volume of the core due to transfer of monomer from core to shell is accompanied by a corresponding increase in volume of the shell and can be represented by the following equation

$$\frac{\mathrm{d}V_{\mathrm{c}}}{\mathrm{d}t} = -\frac{\mathrm{d}V_{\mathrm{s}}}{\mathrm{d}t} \tag{28}$$

Volume change in the shell can be related to the concentration change by the following expression

$$\frac{\mathrm{d}V_{\mathrm{s}}}{\mathrm{d}t} = \frac{K_{\mathrm{sc}}A_{\mathrm{c}}(M_{\mathrm{s}}^{*} - M_{\mathrm{s}})\mathrm{MW}_{\mathrm{m}}}{\rho_{\mathrm{m}}} \tag{29}$$

The homogeneous model previously defined was applied to the shell only, with Eq. (15) replaced by Eq. (27), and Eq. (26, 28 and 29) added to account for core shrinkage, shell growth, and monomer transport between the two phases.

The recipe for polymerization was not changed, but the various components are now as shown in Table 3.

Table 3
Initial reactor compositions for heterogeneous model

Component	Symbol (in differential equation)	Location (in particle)	Amount (mol/l)
Initiator–BPO	I	Shell	0.019
Monomer–MMA	M_{s}	Shell	9.4
	M_{c}	Core	9.4
Alkyd conc.		Shell and core	0.071
Alkyd double bond conc.	C	Shell and core	1.35
Dead branched polymer	CM_n	Shell	0
Dead linear polymer	M_n	Shell	0
Live acrylic polymer chain	P•	Shell	0
Live alkyd chain	C•	Shell	0

5. Results and discussion

5.1. Selection of constants k_{sc} and K_{eq}.

The mass transfer coefficient k_{sc} and the equilibrium constant K_{eq}, dictate the speed and extent of movement of monomer from the core to the shell during polymerization, and hence have a significant impact on monomer conversion. To study the effect of their values on the kinetic profile and to identify the appropriate value for each to be used in the model for further simulation, a range of values were evaluated. Varying k_{sc} over a wide range of 10^4–10^{-6} had little effect on the monomer profile, while lower k_{sc} (10^{-7}) slowed the rate of polymerization. Presumably at $k_{\mathrm{sc}} = 10^{-7}$ the reaction becomes monomer transport rather than reaction limited. Simulation results indicate dramatic changes in concentration of monomer in the core and shell for k_{sc} values between 10^4 and 10^{-6}, while a markedly slower movement of monomer in the core for k_{sc} 10^{-7} and 10^{-8}. In as much as alkyd is a good solvent for monomer, it will not allow the monomer in the core to move out quickly and hence a value of 10^{-8} for k_{sc} would seem more appropriate than the higher values. This value was adopted for all further simulations. A value of $K_{\mathrm{eq}} = 1$ was arbitrarily selected based on the fact that this value gave a slow movement of trapped monomer from core to shell.

5.2. Conversion–time profiles with the heterogeneous model

Fig. 8 shows conversion curves generated with the core–shell model. One will note the appearance of a limiting conversion at all temperatures. As with the homogenous model, a constant radical flux is assumed to ensure that these curves represent a true limiting conversion, and not initiator depletion. The simulations were run for extended times to demonstrate that the limiting conversion persists, even a very long times. Besides the presence of limiting

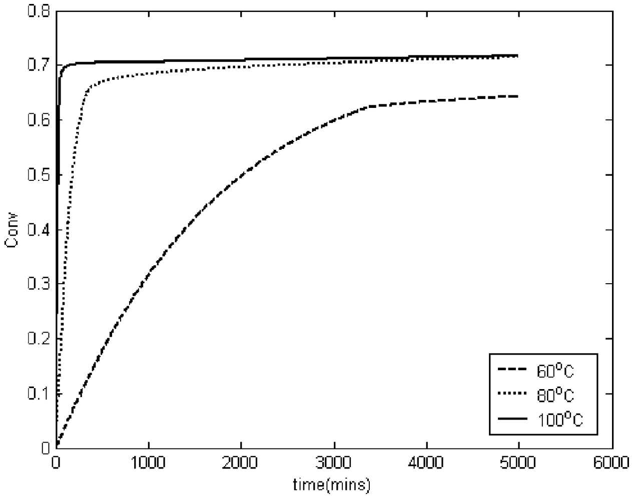

Fig. 8. Conversion versus time at various temperatures, 30% alkyd-heterogeneous model.

conversion, the core–shell curves also differ from the homogeneous curves in that they exhibit a much lower overall conversion. This is not surprising based on the fact that a significant amount of the monomer remains entrapped in the core and remains unconverted by being unable to move to the shell where the polymerization reaction is taking place. Thus the partitioning of the monomer between core and shell leads to a limiting conversion.

5.3. Role of glass effect in occurrence of limiting conversion

It has been suggested by Tsavalas [6] that the glass effect was insignificant in an acrylate–alkyd system because the reaction temperature was greater than the glass transition temperature (T_g) of the mixture. (The T_g of PMMA is approximately 105 °C, above the highest temperature simulated.) However, that argument presumes a homogeneous particle in which the alkyd acts as a plasticizer for the polyacrylate. In a core–shell particle this is no longer the case, and the glass effect will be enhanced in the shell (due to the relative lack of alkyd). The importance of the glass effect in inducing a limiting conversion in the heterogeneous model can be assessed by 'turning off' the glass effect in the simulation. This was done in Fig. 9. From this figure, it can be seen that the presence or absence of a glass effect makes only a slight difference in the conversion–time curves, and both cases exhibit a limiting conversion. Thus, while a glass effect will enhance a limiting conversion phenomenon, it is not responsible for it.

5.4. Fitting Tsavalas data to the core–shell model

Finally, based on the success in obtaining a limiting conversion with the core–shell model, it was decided to test its ability to fit Tsavalas' experimental data to it. The heterogeneous model was adjusted to the recipe conditions given by Tsavalas. Results are shown in Fig. 10. The simulation was run with two different values of chain transfer constant k_{fc} (the one that had been previously used i.e. $23.4\times10^{-5}\times k_{p0}$, and the one proposed by Tsavalas, $1\times10^{-4}\times k_{p0}$). On comparing this plot with the Tsavalas data in Fig. 3, it can be seen that there is fairly good agreement using Tsavalas' value of k_{fc}. We note only that the general trend is correct. Tsavalas' data is for a miniemulsion polymerization in which segregation may play a significant role, while the results above are for non-segregated kinetics. The comparison is included only to indicate that a heterogeneous particle model is capable of simulating the phenomena found in Tsavalas' data.

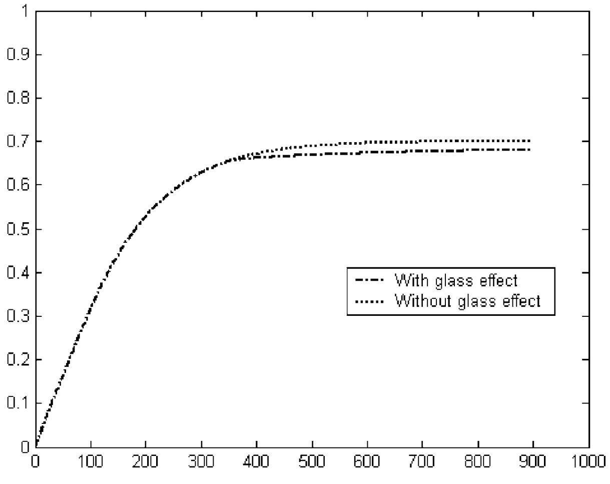

Fig. 9. Conversion versus time at 80 °C, 30% alkyd-heterogeneous model-role of glass effect on occurrence of limiting conversion.

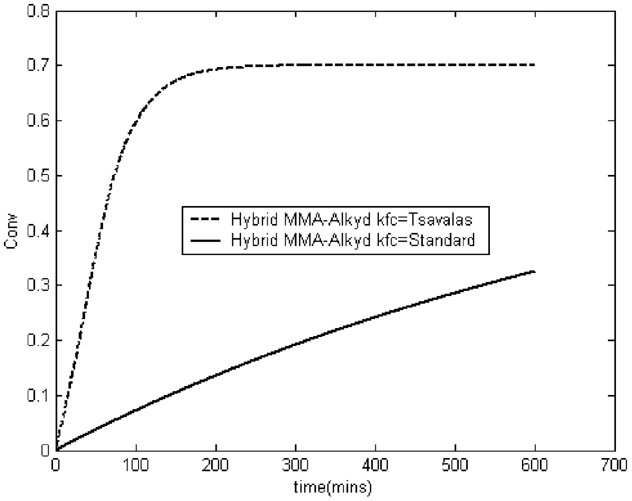

Fig. 10. Heterogeneous model simulating the conditions of Fig. 3 (Tsavalas) with different values for k_{fc}.

6. Conclusions

The objective of this study was to explore the mechanisms that can cause the observed limiting conversion phenomenon in hybrid miniemulsion polymerization. To this end, a homogenous particle model including retardive chain transfer was developed. This model was incapable of simulating a limiting conversion. Rather, all permutations of kinetic parameters gave a system in which the presence of alkyd reduced the rate of polymerization, but did not give a limiting conversion. The conclusion drawn from this is that retardive chain transfer alone is not the cause of limiting conversion. The inclusion of the same kinetics in a heterogeneous (alkyd core, acrylate shell) model did result in correct simulation of the limiting conversion. The conclusion from this it not that limiting conversion is necessarily caused by particle heterogeneity, but that particle heterogeneity is a mechanism that adequately explains the data. The glass effect may be a contributing factor in limiting conversion, especially in a heterogeneous particle, but it is not the cause of the limiting conversion.

A likely model, then, for the hybrid miniemulsion polymerization of acrylate (specifically MMA) in the presence of alkyd is that of alkyd-rich core where little polymerization takes place, surrounded by an acrylate- (and polyacrylate) rich shell in which most of the polymerization takes place.

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