# Limiting Conversion for Systems of Emulsifier-Free Emulsion Polymerization of Styrene

**Show-An Chen* and Song-Tai Lee**

*Chemical Engineering Department, National Tsing-Hua University,*
*Hsinchu, Taiwan 30043, China*

*Received August 8, 1991; Revised Manuscript Received November 7, 1991*

ABSTRACT: "Limiting conversion" is a phenomenon whereby the polymerization stops prior to complete conversion. This phenomenon is found to occur in emulsion systems with large particles having a diameter ($D_p$) larger than 0.2 $\mu$m but not in those with small particles. For emulsifier-free emulsion polymerization of styrene, factors that might affect the behavior of limiting conversion are studied including particle size, solvent addition, reaction temperature, glass transition temperature, surface charge density, and addition of hydrophilic comonomers. Accordingly, limiting conversion can be attributed to the consequence of a shell-region polymerization characteristic of large emulsion particles and a monomer-diffusion-controlled polymerization mechanism within the particles during the high-conversion period.

## Introduction

"Limiting conversion" is a phenomenon whereby the polymerization stops prior to complete conversion. This phenomenon usually occurs in systems of emulsifier-free emulsion polymerizations.[1,2] For such systems conversion curves are concave upward until about 85–90% conversion, after which they suddenly level off. The reaction barely reaches 100% conversion even after a long period of time (ca. 24–48 h). The values of limiting conversion ($m^*$) can be determined by taking the conversion at the intersection of the leveling line and the extrapolation line from the concave upward part of the conversion curve. For the systems with emulsifiers[3,4] or anionic comonomers such as sodium undecylenic isethionate (NaUI)[5] and sodium styrenesulfonate (NaSS)[6] in which the particle size is small (less than 0.15 $\mu$m), no limiting conversion was observed. Although the kinetics and reaction mechanism of emulsifier-free systems have been extensively studied over the last 2 decades,[5–20] no investigation on the mechanism of limiting conversion has been presented.

In this work, studies on the mechanism of limiting conversion in styrene emulsifier-free emulsion polymerization systems are presented.

## Experimental Section

**Materials.** Styrene was used after purification by the usual method.[5] Water was freshly deionized. Acrylamide (AAm) and potassium persulfate (KPS) were used after recrystallization from benzene and deionized water, respectively. Benzene, toluene, and tetrahydrofuran (THF) used were LC-grade. Sodium chloride and sodium lauryl sulfate (SLS) used were EP-grade.

**Experimental Procedure.** Polymerizations, except run L1b, were carried out at 70 ± 0.5 °C in a 500-mL reactor. The four-neck reactor was purged continuously with nitrogen and was equipped with a condenser, a thermocouple, a Teflon-coated steel shaft with a dual-bladed mixing paddle, and a rubber septum for taking samples. The agitating speed of the mixing paddle for all runs was 200 ± 20 rpm. The recipes and characteristic data are shown in Table I.

The conversions were determined gravimetrically. Particle morphology and diameters ($D_p$) were determined by use of a transmission electron microscope (JEOL 200 CX STEM from Japan Electron Optics Laboratory). Molecular weight distributions (MWDs) were measured by use of gel permeation chromatography (GPC) with a UV detector with a wavelength of 254 nm and a refractive index (RI) detector for comparison. Two Ultrastyragel columns (Waters Co.) were used in series having a MW exclusion limit from 2000 to $10^6$. The flow rate of the carrier solvent, THF, was 1 mL/min.

## Results and Discussion

**Effect of Particle Size.** Figure 1 shows the conversion ($m$) versus time curves for systems with the same content of styrene and KPS but with various amounts of the additives, AAm and SLS (L1–L6 in Table I). $D_p$'s for the experimental runs L1–L6 are 0.54, 0.51, 0.47, 0.40, 0.19, and 0.11 $\mu$m, respectively. These latex particles are monodisperse as shown in Figure 2 for the typical runs L1–L3 and L6 and in our previous works[7,9] and the works of the others[1,16,19] for the same and similar recipes and reaction conditions. Also note that the amounts of SLS used in runs L5 and L6 are about $^1/_{10}$ and $^1/_3$ critical micelle concentrations. Thus the nucleation in these two runs must follow a homogeneous reaction mechanism rather than a micelle nucleation mechanism, and SLS only provides a stabilization of the particles generated in the nucleation stage.

For systems with large particles (runs L1–L4, $D_p \geq 0.2$ $\mu$m), the conversion curves are concave upward initially and then level off with the limiting conversion ($m^*$) of about 0.89–0.95. Further reaction toward completion would require a very long period of time (ca. 48 h). However, for systems with smaller particles (runs L5 and L6, $D_p < 0.2$ $\mu$m), the conversion reaches 95% rapidly and then further increases toward completion at a slower rate but still within a reasonable period of time (ca. 2–4 h).

As proposed in our previous works,[7,9] for systems with large particles ($D_p \geq 0.2$ $\mu$m), particle growth follows the shell-growth (or shell-region polymerization) mechanism as confirmed by direct morphological evidence and analysis of kinetic and MWD data. The occurrence of the shell growth is due to the presence of a high number of radicals in the shell region. The polymer radicals have the hydrophilic ends anchoring on the surface and the growing ends locating within a shell region having a thickness ($L$) equal to the root-mean-square end-to-end distance, 100–500 Å. The distribution of monomer in the particle is considered to be uniform during the particle-growth period (before 37% conversion).[1,7] Such a mechanism will not occur for systems with small particle size ($D_p < 0.2$ $\mu$m), because the end-to-end distance of the growing radicals should be larger than the radius of the particle. This results

---

* Author to whom all correspondence should be addressed.

0024-9297/92/2225-1530$03.00/0 © 1992 American Chemical Society

**Table I**
**Recipes of the Polymerization Runs for the Investigation of Limiting Conversions**[a]

| run | St, g | KPS, g | $H_2O$, g | additives, g | $D_p$, μm | temp, °C | limiting convn ($m^*$) |
|---|---|---|---|---|---|---|---|
| L1 | 50 | 0.50 | 400 | | 0.54 | 70 | 0.89 |
| L2 | 50 | 0.50 | 400 | 0.2 (AAm) | 0.51 | 70 | 0.91 |
| L3 | 50 | 0.50 | 400 | 0.8 (AAm) | 0.47 | 70 | 0.92 |
| L4 | 50 | 0.50 | 400 | 3.2 (AAm) | 0.40 | 70 | 0.95 |
| L5 | 50 | 0.50 | 400 | 0.1 (SLS) | 0.19 | 70 | 1.00 |
| L6 | 50 | 0.50 | 400 | 0.3 (SLS) | 0.11 | 70 | 1.00 |
| L1a | 50 | 0.50 | 400 | 5.0 (toluene)[b] | 0.54 | 70 | 0.98 |
| L1b | 50 | 0.50 | 400 | | 0.54 | c | 0.95 |
| L1c | 50 | 0.50 | 400 | 0.5 (NaCl)[d] | 0.58 | 70 | 0.88 |
| L6a | 50 | 0.50 | 400 | 0.3 (SLS); 5.0 (toluene)[e] | 0.10 | 70 | 1.00 |

[a] St, styrene; KPS, potassium persulfate; AAm, acrylamide; SLS, sodium lauryl sulfate; NaCl, sodium chloride, $D_p$, particle diameter; temp, temperature. [b] 5.0 g of toluene was injected into the reactor at $t$ = 12 h. [c] Reaction temperature was elevated from 70 to 85 °C at $t$ = 6 h. [d] 0.5 g of NaCl in 10 mL of $H_2O$ was injected into the reactor at $t$ = 12 h. [e] 5.0 g of toluene was injected into the reactor at $t$ = 1 h.

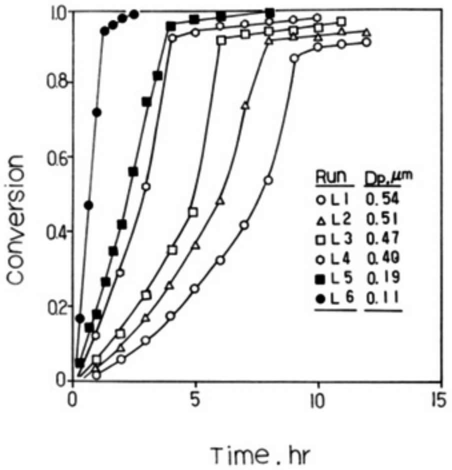

**Figure 1.** Effects of particle size on the conversion curves of emulsion polymerization.

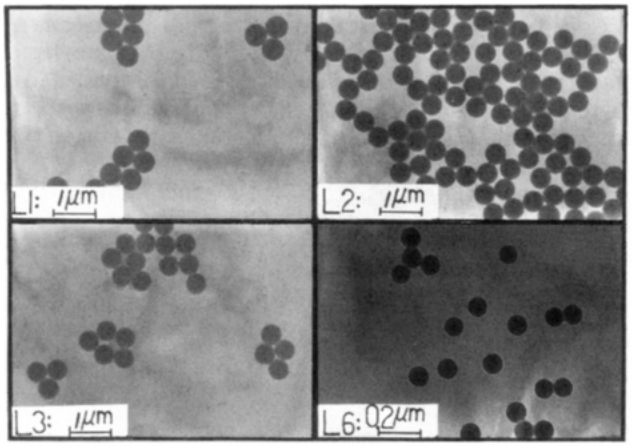

**Figure 2.** TEM micrographs of the latex particles of runs L1–L3 and L6 for illustration of a monodisperse particle size distribution in these experimental runs.

in homogeneous reaction loci through out the particle.

According to the shell-region polymerization characteristic of the large particles, the occurrence of the limiting conversion can be explained as follows.

After the disappearance of monomer droplets, further polymerization would cause a decreased monomer concentration in the particles. The monomer consumed in the shell is quickly supplied through diffusion of monomers within the particle. As polymerization proceeds further, the resistance for monomer diffusion would increase due to the decreased monomer concentration and increased viscosity inside the particle. Eventually, the polymerization becomes monomer-diffusion-controlled[4,21] and the reaction rate slows down.

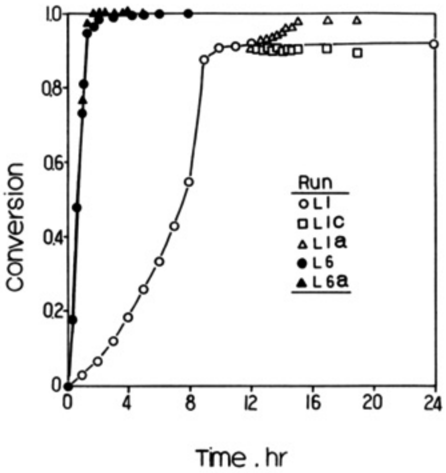

**Figure 3.** Conversion curves of the reaction runs at 70 °C: emulsifier-free emulsion polymerization (L1, large particle system); salt addition in the limiting conversion period (L1c); toluene addition in the limiting conversion period (L1a); emulsion polymerization with emulsifiers (L6, small particle system); toluene addition at $t$ = 1 h in a small-particle system (L6a).

According to Fick's diffusion equation,[22] the time required for a monomer molecule to diffuse a given distance is proportional to the square power of that distance. Besides, with the consideration of the proposed shell-growth mechanism, the average time required for the monomers to diffuse from the interior of the particle to the reaction loci in large particles would be about 1–2 orders of magnitude greater than that in small particles. Consequently, in the high-conversion ranges, monomer is supplied to the reaction loci at a much slower rate in systems of large particles than in systems of small particles; limiting conversion can thus occur only in large particles.

The above explanation can be further supported by the following experiments: (1) addition of toluene after $m^*$ is reached, (2) raising the reaction temperature at about 35% conversion. Other possible factors such as surface charge density and addition of hydrophilic comonomer are also investigated.

**Effect of Toluene Addition.** As shown in Figure 3, in run L1a (large particles), we used the same recipe as L1. After $m^*$ was reached, we added toluene into the reactor and allowed the reaction to continue. The toluene swelled the particles, decreased the viscosity inside the particles, and allowed monomers located in the core of the particle to diffuse into the shell region more easily to participate in the polymerization to near 100% conversion within a shorter period of time. While for the system of small particles (L6a), the reaction rate was also speeded up after the addition of toluene. Accordingly, a monomer-diffusion-

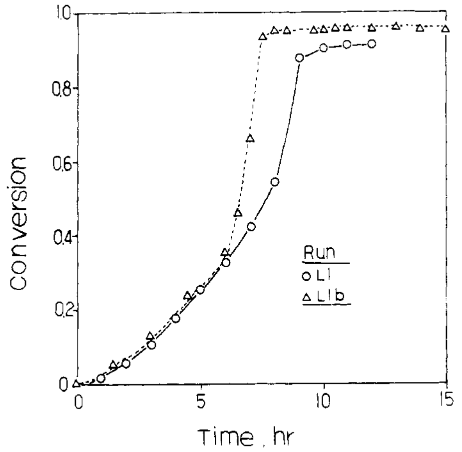

**Figure 4.** Effect of temperature variation on the conversion curves: (L1) reaction temperature is 70 °C; (L1b) reaction temperature is elevated from 70 to 85 °C at $t$ = 6 h and maintained at that temperature until the end of the reaction.

controlled mechanism is an important factor for the occurrence of limiting conversion.

**Effects of Reaction Temperature and Glass Transition Temperature, $T_g$.** For run L1b (Figure 4), at $t$ = 6 h ($m$ = 35%, which was well past the nucleation period[1,7]), the reaction temperature was raised from 70 to 85 °C in 15 min and maintained at that temperature toward the end of the reaction in order to explore the effect of temperature on monomer diffusion within the particles. The limiting conversion was increased from $m^* = 0.9$ of L1 to $m^* = 0.95$ of L1b.

The increase of temperature can increase the diffusion rate of the monomer as well as that of the polymeric radicals. However, the diffusion rate of the long-chain polymers is considered to be much less than that of the small molecules. Thus the rate of polymerization is governed by the diffusion rate of monomer.

The results of the above experiments of toluene addition and temperature raising would also reflect that the limiting conversion does not result from dead-end polymerization (exhaustion of initiators)[23] in the later stage of the reaction.

In bulk polymerization, if the reaction temperature is much lower than $T_g$ of the pure polymers, limiting conversion could occur due to the glass effect.[24] However, in the emulsion polymerization, the situation is different. Taking the melting point of styrene (−31 °C) as $T_g$ of styrene, $T_g$ of the polymer particle can be estimated as 70 and 80 °C for $m$ = 0.84 and 0.90, respectively, by use of the Fox equation.[25] Accordingly, at $T$ = 70 °C, most of the polymer chains should be frozen at $m$ = 0.84. The reactions, however, were not stopped until $m$ = 0.89 for a system of large particles. This is because most of the small molecules (monomer) could diffuse to the reaction loci easily even at $T = T_g$. The effect of the small amount of absorbed water in the particles can be neglected.[4] For systems of small particles, the reaction can even reach 100% conversion (Figure 1). Thus $T_g$ is not the dominating factor that causes the occurrence of limiting conversion.

**Effect of Surface Charge Density and Ionic Strength.** Because the surface charge densities per unit surface area on large particles can be higher than those on small ones,[26] an immediate question might arise: Can limiting conversion be attributed to the higher electrostatic repulsive forces which could prevent the radicals from entering the particles? In order to answer this question, an experimental run (L1c) was performed in which the inert salt (sodium chloride) was added after $m^*$ was reached for reducing the electrostatic repulsive forces on the particle surface. It was found that the salt addition makes no appreciable difference on $m^*$ (Figure 3). Thus the surface charge density cannot be a factor that causes an occurrence of limiting conversion.

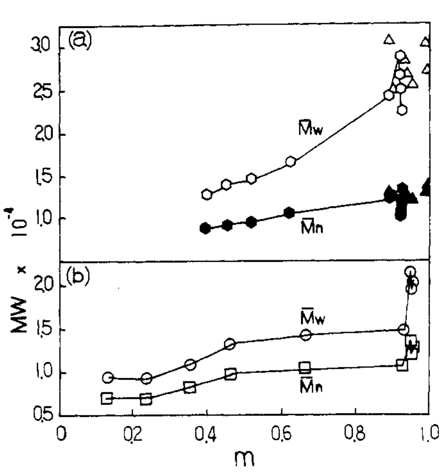

**Figure 5.** Molecular weight (MW) at different conversions for experimental runs of large-particle systems: (a) emulsifier-free emulsion polymerization L1 (○, ●); toluene addition L1a (△, ▲); (b) temperature elevation from 70 to 85 °C at $t$ = 6 h ($m$ = 0.35), L1b (○, □).

**Effect of Hydrophilic Comonomers.** For systems (runs L2–L4) with a minor amount of hydrophilic comonomer (acrylamide), the limiting conversion increases with an increase in the content of acrylamide as shown in Table I. This can be attributed to the hydrophilic nature of acrylamide units exposed on the particle surfaces.[27] The polymer chains with a higher acrylamide content would have more subchains stretching into the water phase and cause a larger expansion of the thickness of the reaction shell ($L$). As calculated from the shell-region polymerization model,[7,28] the increase of acrylamide units leads to the increase of $L/D_p$ from 0.04 to 0.12 for runs L2–L4 and thus to the increases of $m^*$. However, in the systems of styrene emulsifier-free emulsion polymerizations without comonomers,[1] $m^*$ is about 0.9 and independent of the particle size with $D_p$ ranging from 0.4 to 0.6 μm. The reason is that the ratio of $L/D_p$ is too small,[2] about 0.02–0.03, to cause any appreciable difference in $m^*$.

**Molecular Weight Distribution (MWD).** MWD data for systems of large (runs L1, L1a, and L1b) and small (runs L6 and L6a) particles are also consistent with the monomer-diffusion-controlled mechanism which results in the phenomenon of limiting conversion as revealed below.

For run L1, $\bar{M}_w$ and $\bar{M}_n$ versus conversion after the disappearance of monomer droplets ($m > 0.37$)[1,7] are shown in Figure 5a. Both $\bar{M}_w$ and $\bar{M}_n$ increase with conversion from $m$ = 0.4 to 0.89 ($m^*$). $\bar{M}_w$ increases more quickly than $\bar{M}_n$, indicating that the major parts of the polymer generated are of high MW resulting from the increased gel effect with $m$ before reaching $m^*$. After $m^*$, $\bar{M}_w$ and $\bar{M}_n$ decrease rapidly. This decrease of MW indicates that the effect of resistance of monomer diffusion on conversion would prevail over that of the gel effect in the period of limiting conversion.

For run L1a (Figure 5a), the reaction resumed after the addition of toluene at $m$ = 0.9 and produced the polymers with $\bar{M}_w$ and $\bar{M}_n$ close to those at $m = m^*$. This can be attributed to the reduced viscosity due to the absorption of toluene allowing an increase of the monomer diffusion rate within the particles. The increased monomer diffsuion rate prevents a continuous decrease in MW with

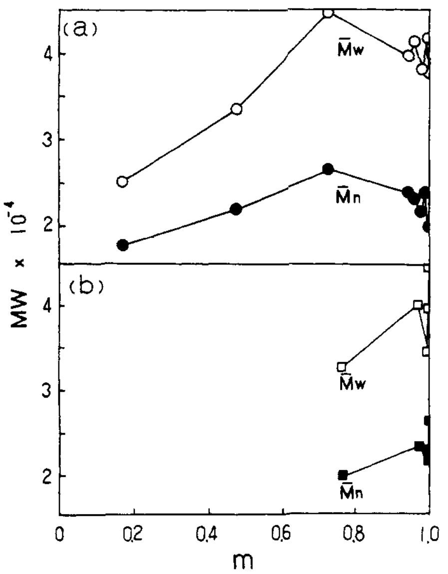

**Figure 6.** Molecular weight (MW) at different conversions for experimental runs of small particles: (a) emulsion polymerization L6 (○, ●); (b) toluene addition at $t = 1$ h ($m = 0.73$), L6a (□, ■).

conversion and allows the generated polymer to retain its MW at the same level as that at $m = m^*$.

For run L1b (Figure 5b), the increases of $\bar{M}_{\rm w}$ and $\bar{M}_{\rm n}$ with conversion are much slower than those in run L1 from the beginning of the temperature elevation due to the increased rate of radical generation. Near the point of $m = m^*$, $\bar{M}_{\rm w}$ and $\bar{M}_{\rm n}$ increase rapidly due to a strong gel effect.

For run L6 of small particles (Figure 6a), $\bar{M}_{\rm w}$ and $\bar{M}_{\rm n}$ increase in the period of $m = 0.2$ to about 0.75 due to the gel effect and then decrease to the end of the reaction ($m = 1.0$) due to the shortage of a monomer supply resulting from the monomer depletion and increased resistance of monomer diffusion within the particles.[30,31] While in run L6a (addition of toluene, Figure 6b), the toluene absorbed in the particles would decrease the viscosity inside the particles and therefore increase the rate of monomer diffusion. Thus, after toluene addition, $\bar{M}_{\rm w}$ and $\bar{M}_{\rm n}$ increase with conversion to the end of the reaction.

## Conclusion

Limiting conversion occurs in systems of large particles (ca. $D_{\rm p} > 0.2$ μm) but not in those of small particles. It can be attributed to the consequence of a shell-region polymerization characteristic of large emulsion particles and monomer-diffusion-controlled polymerization in the high-conversion period.

**Acknowledgment.** We thank the National Science Council for financial aid through the project Studies on Emulsion Polymer Systems, NSC 79-0405-E007-05.

## References and Notes

(1) Chiu, W.-Y.; Shih, C.-C. *J. Appl. Polym. Sci.* **1986**, *31*, 2117.
(2) Chen, S.-A.; Lee, S.-T.; Lee, S.-J. *Makromol. Chem., Macromol. Symp.* **1990**, *35/36*, 349.
(3) Omi, S.; Sato, H.; Kubota, H. *J. Chem. Eng. Jpn.* **1969**, *2* (1), 55.
(4) Ballard, M. J.; Gilbert, R. G.; Napper, D. H.; Pomery, P. J.; O'Sullivan, P. W.; O'Donnell, J. H. *Macromolecules* **1986**, *19*, 1903.
(5) Chen, S.-A.; Chang, H.-S. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2615.
(6) Juang, M. S.; Krieger, I. M. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2089.
(7) Chen, S.-A.; Lee, S.-T. *Macromolecules* **1991**, *24*, 3340.
(8) Pan, T.-C.; Kuo, J.-F.; Chen, C.-Y. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 709.
(9) Chen, S.-A.; Lee, S.-T. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 443.
(10) Chen, S.-A.; Chang, H.-S. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 2547.
(11) Chang, H.-S.; Chen, S.-A. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 1207. s
(12) Guillaume, J. L.; Pichot, C.; Guillot, J. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 1937; **1990**, *28*, 119, 137.
(13) Chang, H.-S.; Chen, S.-A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 297.
(14) Feeney, P. J.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1987**, *20*, 2922.
(15) Chainey, M.; Hearn, J.; Wilkinson, M. C. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 505.
(16) Hearn, J.; Wilkinson, M. C.; Goodall, A. R.; Chainey, M. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1869.
(17) Kawaguchi, H.; Sugi, Y.; Ohtsuka, Y. *J. Appl. Polym. Sci.* **1981**, *26*, 1649.
(18) Liu, L. T.; Krieger, I. M. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 3013.
(19) Goodall, A. R.; Wilkinson, M. C.; Hearn, J. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2193.
(20) Ceska, G. W. *J. Appl. Polym. Sci.* **1974**, *18*, 427 and 2493.
(21) Adams, M. E.; Casey, B. S.; Mills, M. F.; Russel, G. T.; Napper, D. H.; Gilbert, R. G. *Makromol. Chem., Macromol. Symp.* **1990**, *35/36*, 1.
(22) Bedingfield, C. H., Jr.; Drew, T. B. *Ind. Eng. Chem.* **1950**, *42*, 1164. Also in: Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport Phenomena*; John Wiley & Sons, Inc.: New York, 1960; p 558.
(23) Bohme, R. D.; Tobolsky, A. V. Dead-End Polymerization. *Encyclopedia of Polymer Science and Technology*; Wiley-Interscience: New York, 1966; Vol. 4, p 599.
(24) Sundberg, D. C.; James, D. R. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 523. Also: Odian, G. *Principles of Polymerization*, 2nd ed.; John Wiley & Sons, Inc.: New York, 1981; Chapter 3.
(25) Fox, T. G.; Loshaek, S. J. *J. Polym. Sci.* **1955**, *15*, 371. Also: Nielsen, L. E. *Mechanical Properties of Polymers and Composites*; Marcel Dekker, Inc.: New York, 1974; Chapter 1.
(26) Vanderhoff, J. W. In *Characterization of Metal and Polymer Surfaces*; Lee, L. H., Ed.; Academic Press, Inc.: 1977; p 365.
(27) Tamai, H.; Murakami, T.; Suzawa, T. *J. Appl. Polym. Sci.* **1985**, *30*, 3857.
(28) Ugelstad, J.; Hansen, F. K. Rubber Chem. Technol. **1976**, *49*, 536.
(29) Odian, G. *Principles of Polymerization*, 2nd ed.; John Wiley & Sons, Inc.: New York, 1981; Chapter 1, p 23.
(30) Grancio, M. R.; Williams, D. J. *J. Polym. Sci., Polym. Chem. Sci.* **1970**, *8*, 2733.
(31) Lin, C.-C.; Chiu, W.-Y. *J. Appl. Polym. Sci.* **1979**, *23*, 2049.