

# RAPID COMMUNICATION

## Miniemulsion Reversible Addition Fragmentation Chain Transfer Polymerization of Vinyl Acetate

JAMES P. RUSSUM, NICHOLAS D. BARBRE, CHRISTOPHER W. JONES, F. JOSEPH SCHORK

School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Dr., Atlanta, GA 30332

Received 27 October 2004; accepted 3 December 2004

DOI: 10.1002/pola.20681

Published online in Wiley InterScience (www.interscience.wiley.com).

**Keywords:** initiators; living polymerization; miniemulsion; poly(vinyl acetate); reversible addition-fragmentation chain transfer (RAFT)

### INTRODUCTION

In recent years, much interest has been generated by new techniques that allow for the controlled polymerization of monomers via free radical mechanisms. These controlled techniques allow for the synthesis of polymers with unique architectures, as well as the relatively facile synthesis of copolymers, particularly block copolymers. The most notable among the existing methodologies are atom transfer radical polymerization (ATRP),<sup>1,2</sup> nitroxide-mediated polymerization (NMP),<sup>3</sup> and reversible addition-fragmentation chain transfer (RAFT).<sup>4,5</sup> Currently, RAFT holds the most promise as an all-around technique in terms of the number of monomers that can be polymerized.<sup>6</sup> It can be employed over a wide range of monomer functionalities, solvents and temperatures. Additionally, it is compatible with aqueous systems, for example, suspensions, emulsions, and miniemulsions.<sup>7–9</sup>

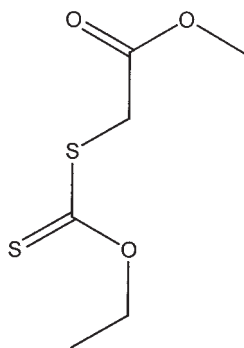
While RAFT is a versatile process,<sup>6,10–14</sup> to date its use with vinyl esters, and in particular vinyl acetate (VA), has been limited. In the case of VA, the propagating radical is very unstable and highly reactive and standard RAFT dithioesters can completely inhibit the polymerization.<sup>13</sup> It has been postulated that the cause is slow fragmentation of the RAFT intermediate radical

and is brought about by the fact that the VA propagating radical is such a poor leaving group. While the dithioesters can be ineffective, xanthates and dithiocarbamates<sup>13,15–21</sup> have both been successfully utilized to produce poly(vinyl acetate) in a controlled manner. Attempts to produce PVA homopolymer using NMP or ATRP have thus far met with limited success.<sup>22–24</sup> Poly(vinyl acetate), or PVA, is widely used in industry as a component in coatings and is also important in its capacity as a precursor to poly(vinyl alcohol) or PVAL. PVAL is water soluble, nontoxic, and noncarcinogenic, and as such is of particular interest to the pharmaceutical industry. Among other things, it can be crosslinked to form a hydrogel that can be employed to deliver drugs diffusively. The ability to polymerize VA in a controlled manner so that highly defined PVAL architectures can be produced is, therefore, an attractive goal.

As mentioned, several studies<sup>13,15–21,25</sup> in the open literature have reported controlled polymerizations of VA using RAFT agents. These studies utilized either bulk or solution techniques, but the commercial viability of VA/RAFT would likely be greatly enhanced if it could be shown to be successful in an aqueous system. Suspensions and emulsions are used widely in industry, but the aqueous system in which controlled radical polymerizations have been most successfully conducted to date is miniemulsions.<sup>9,26–38</sup> This is primarily because the main locus of polymerization in miniemulsions is the droplets/particles, and transport of reaction components, specifically the control agent, across the aqueous phase is not a requirement and can often be

Correspondence to: F. J. Schork (E-mail: joseph.schork@chbe.gatech.edu) and C. W. Jones (E-mail: chris.jones@chbe.gatech.edu)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 43, 2188–2193 (2005)  
© 2005 Wiley Periodicals, Inc.



**Scheme 1.** RAFT agent used in this study, methyl (ethyloxycarbonothioyl)sulfanyl acetate (MESA).

detrimental. To date, there is no report in the open literature of VA/RAFT homopolymerization in miniemulsion. We report here the successful miniemulsion polymerization of VA using methyl (ethyloxycarbonothioyl)sulfanyl acetate (MESA) as the RAFT agent (see Scheme 1). In a study of eight xanthates by Stenzel et al., MESA was shown to provide the lowest polydispersities in combination with the highest rates of polymerization in bulk VA polymerizations, to conversions of  $\sim 60\%$ .<sup>16</sup> Because VA is relatively soluble in water ( $\sim 2.8$  wt % at  $60^\circ\text{C}$ ),<sup>39</sup> an oil soluble initiator, 2,2' azobis(isobutyronitrile) (AIBN), was utilized to help prevent nucleation in the aqueous phase and suppress the formation of uncontrolled, free radical polymer.

## EXPERIMENTAL

### Materials

Vinyl acetate (VA) was purchased from Aldrich and purified by passing through a column packed with inhibitor remover. 2,2' azobis(isobutyronitrile) (AIBN), hexadecane, and sodium dodecyl sulfate (SDS) were purchased from Aldrich and used as received. The RAFT agent, methyl (ethyloxycarbonothioyl)sulfanyl acetate (MESA), was prepared according to methods described elsewhere.<sup>16</sup> Deionized water was generated

in-house with a U.S. Filter Systems Deionizer and was used without further purification.

### Bulk Polymerization Procedure

Vinyl acetate, AIBN ( $2.1 \times 10^{-3}$  mol/L,  $[\text{MESA}]_0/[\text{AIBN}]_0 \sim 5$ ), and MESA ( $1.1 \times 10^{-2}$  mol/L,  $[\text{VA}]_0/[\text{MESA}]_0 \sim 1000$ ) were combined, and  $\sim 0.5$  mL of the solution was placed in each of ten crimp-top vials. The vials were sealed with septa and deoxygenated by purging with nitrogen for  $\sim 5$  min. The sealed vials were then placed in an oil bath at  $60^\circ\text{C}$  and were removed at intervals of  $\sim 30$  min. The reactions were quenched by cooling the solutions in an ice bath. Residual monomer was evaporated by placing the vials in a vacuum oven and drying the samples for 24 h ( $30^\circ\text{C}$ ,  $\sim 100$  kPa vacuum). Monomer conversion was subsequently determined gravimetrically.

### Miniemulsion Polymerization Procedure

A representative miniemulsion recipe is shown in Table 1. The surfactant, SDS, was added to water and allowed to mix for 15 min. VA, hexadecane, MESA, and AIBN were combined and allowed to mix for 15 min. The organic phase was then added to the aqueous phase and agitated vigorously with a magnetic stirrer for 10 min, forming a very faint yellow emulsion. The miniemulsion was formed by sonicating for 20 min (Fisher 300 Sonic Dismembrator at 70% output). During the sonication, the miniemulsion was cooled by an ice bath to suppress any thermal initiation. After sonication, the miniemulsion was transferred to a 250 mL, round-bottomed, 3-neck flask outfitted with a septum, reflux condenser, nitrogen feed, and thermometer to monitor the temperature of the miniemulsion. The miniemulsion was kept agitated by a magnetic stirrer. After allowing the miniemulsion to de-oxygenate under ultra high purity nitrogen for 30 min, the flask was immersed in an oil bath that had been preheated to the desired reaction temperature. Samples were withdrawn through the septum via syringe at regular in-

**Table 1.** Recipe for the Batch Miniemulsion Polymerization of Vinyl Acetate at  $60^\circ\text{C}$

Component	Mass	Notes
Water	80.0 g	
Monomer	Vinyl acetate	20.0 g
Surfactant	SDS	0.45 g
Costabilizer	Hexadecane	0.40 g
RAFT agent	MESA	0.045 g
Initiator	AIBN	0.015 g
		25 wt % of water
		0.018 mol/L (based on aqueous phase)
		2 wt % of monomer
		$[\text{VA}]_0/[\text{MESA}]_0 = 1000$
		$[\text{MESA}]_0/[\text{AIBN}]_0 = 5$

**Table 2.** Summary of the Experimental Conditions of the Polymerizations Shown in This Study

Exp	Type	[MESA] <sub>0</sub> /[AIBN] <sub>0</sub>	Temp, °C
1	Bulk	5.0	60
2	Mini	5.0	60
3	Mini	2.5	60
4	Mini	1.0	60
5	Mini	2.5	70
6	Mini	1.0	70

tervals for conversion, GPC, and particle size analysis. The reaction was kept under nitrogen for the entire time of the experiment.

### Sample Characterization

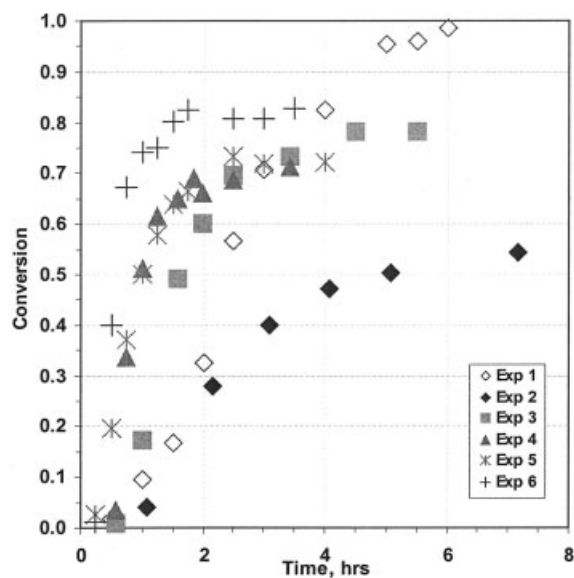
Polymer samples were dried for 24 h in a vacuum oven (30 °C, ~ 100 kPa vacuum), and monomer conversion was subsequently determined gravimetrically. The number average molecular weight,  $M_n$ , and the polydispersity,  $M_w/M_n$ , were calculated using data gathered via size exclusion chromatography (SEC-Viscometry-RALLS)<sup>40</sup> with THF as eluent. Three columns (American Polymer Standards styrene-divinylbenzene 100 Å, 1000 Å, and 10<sup>5</sup> Å) mounted in a Waters WAT038040 column heater set at 30 °C were utilized. The columns were connected to a Viscotek GPCMax pump/autoinjector, a Viscotek T60A dual detector (viscometer and light scattering), a Waters 410 refractive index detector, and an LDC Milton Roy Spectromonitor 3000 UV detector (at 311 nm). Latex particle sizes and polydispersities were analyzed using quasi-elastic light scattering (QELS, Protein Solutions DynaPro99 with DynaPro DCS v 5.26 software).

### RESULTS AND DISCUSSION

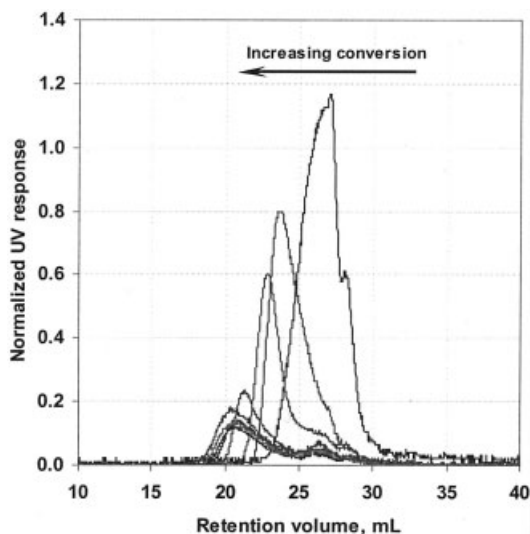
In total, six reactions were conducted as outlined in Table 2. AIBN was used as initiator because of concerns about nucleation in the aqueous phase and the subsequent formation of uncontrolled free-radical PVA. VA is a relatively water soluble monomer, so it is likely that the use of a water soluble initiator such as potassium persulfate (KPS) would trigger the formation of propagating polymer radicals in the aqueous phase. These radicals would not have access to the relatively insoluble MESA RAFT agent and would tend to form uncontrolled, high molecular weight polymer via homogeneous particle nucleation. This would be reflected in the molecular weight distribution as a bimodality, making it difficult to determine the “true” molecular weight of the controlled polymer. Additionally, because

the aqueous polymerization would deprive the controlled polymerization (taking place in the droplets) of monomer, the number average weight of the controlled polymer would be artificially depressed and difficult to control to a reasonable degree of accuracy. An oil soluble initiator could greatly reduce this possibility; however, their use in miniemulsion polymerizations has been limited historically because of complications that can take place that adversely affect the kinetics.<sup>41–49</sup> Among them are desorption of the initiator and/or monomeric radicals and termination of the radicals that do form before they can initiate a growing chain. When these phenomena occur, they tend to lower the efficiency of the initiator, and the findings here are, at least in part, consistent with this hypothesis. Experiments 1 and 2, shown in Figure 1, reveal a decrease in polymerization rate when going from bulk to miniemulsion at the same temperature and initiator concentration. Gel or glass effects can be safely ruled out based largely on the bulk results and the fact that the T<sub>g</sub> of PVA is ~ 32 °C<sup>50</sup>, while the polymerizations were performed at 60 or 70 °C. The dormant chains can be monitored by examining the UV response of the polymer at 311 nm, which shows the distribution of C=S bonds (and therefore dormant chains) in the polymer.<sup>32–34,36,51</sup> Figure 2 shows this for Experiment 2 and reveals that the dormant chain population decreases dramatically as the reaction progresses, indicating loss of RAFT functionality and contributing to the observed limiting conversion. Whether the cause is termination of the intermediate RAFT macroradical or loss of the C=S end group functionality by some other mechanism is the subject of ongoing investigation.

While all of this would be consistent with decreased initiator efficiency, there are other indications that sug-



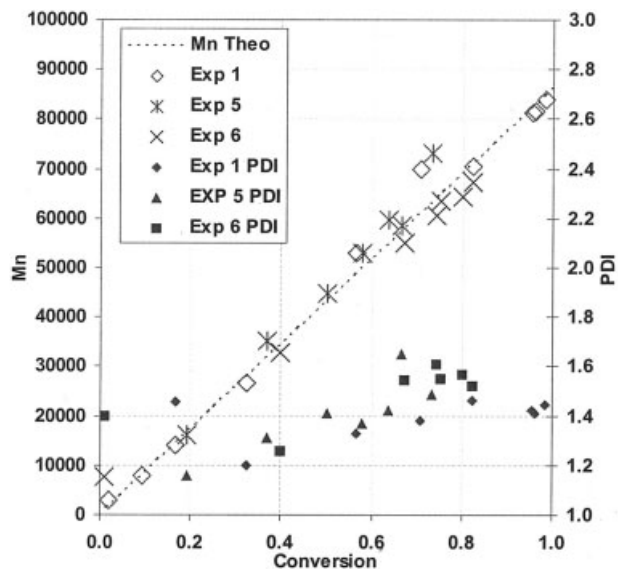
**Figure 1.** Kinetic plots of bulk and miniemulsion polymerizations conducted in this study.



**Figure 2.** Normalized UV response of polymer samples from Exp. 2. Data show loss of the C=S bond of RAFT agent as the reaction progresses, indicating loss of functionality of dormant chains.

gest something more is at play. Although polymerization rates decreased at the same temperature and initiator concentration when going from bulk to miniemulsion, the rate could be increased by simply adding more initiator and/or increasing the temperature (Exps. 3–6). The data reveal that in each case, the miniemulsion polymerization reached a limiting conversion, even when the initial rate of polymerization was much faster than bulk. This suggests something more complex than a simple static decrease in initiator efficiency as compared to bulk. It also points towards some long-chain radical termination as a contributing factor, as opposed to an increased rate of termination of primary, monomeric radicals (or simple recombination of initiator radicals) resulting from the small droplet/particle volumes. The particle diameters observed here averaged  $\sim 200$ – $240$  nm, which is generally thought to be too large for termination of primary radicals to play a dominant role.<sup>42,43</sup>

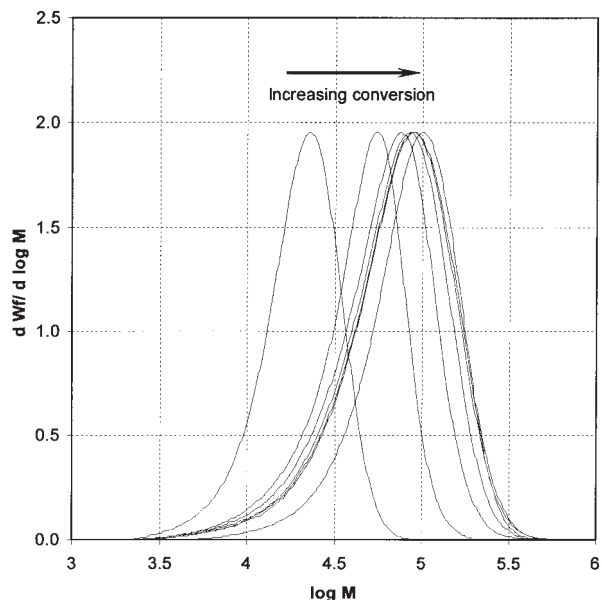
Figure 3 compares the number average molecular weight and polydispersities (PDI) for the bulk experiment and two of the miniemulsion experiments. In each case, number average molecular weights increased linearly with conversion, indicative of a controlled polymerization. Final PDIs for the miniemulsion experiments were higher than those seen in the bulk polymerization; however, this can be explained in light of the fact that the polymerizations reached their limiting conversions because of termination of the propagating radicals, leading to a larger concentration of dead chains. The GPC traces (see Fig. 4) of the resulting polymer show only vanishingly small amounts of the high polymer that forms from homogeneous nucleation.



**Figure 3.** Evolution of Mn and PDI as a function of monomer conversion for selected experiments.

## CONCLUSIONS

In this work, the controlled living polymerization of vinyl acetate in miniemulsion using RAFT chemistry was demonstrated. Rates of polymerization were slower in miniemulsion as compared to bulk, and the cause was postu-



**Figure 4.** Evolution of molar mass distribution (Exp. 5) for MESA mediated vinyl acetate miniemulsion polymerization. Curves represent monomer conversions of 19%, 37%, 50%, 58%, 64%, 66%, and 73%, respectively.

lated to be related in part to complications from the use of an oil soluble initiator. A linear evolution of number average molecular weight was observed; however, increased termination in miniemulsion caused limiting conversions and higher than bulk polydispersities. GPC traces of the polymer produced indicate that polymer formation in the aqueous phase was negligible.

The authors thank the National Science Foundation for funding this work (CTS-0234658).

## REFERENCES AND NOTES

- Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721.
- Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 117, 5614.
- Solomon, D. H.; Rizzardo, E.; Cacioli, P. *Eur Pat Appl*, 135280 1985.
- Krstina, J.; Moad, G.; Rizzardo, E.; Winzor, C. L.; Berge, C. T.; Fryd, M. *Macromolecules* 1995, 28, 5381.
- Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1996, 29, 7717.
- Moad, G.; Mayadunne, R. T. A.; Rizzardo, E.; Skidmore, M.; Thang, S. H. *Macromol Symp* 2003, 192, 1.
- Antonietti, M.; Landfester, K. *Prog Polym Sci* 2002, 27, 689.
- Asua, J. M. *Prog Polym Sci* 2002, 27, 1283.
- Schork, F. J.; Luo, Y. W.; Smulders, W.; Russum, J.; Butte, A.; Fontenot, K. In *Adv in Polymer Science*; Okubo, M., Ed.; Springer-Verlag: Heidelberg, 2005; pp 19–145.
- Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym Int* 2000, 49, 993.
- Wang, A. R.; Zhu, S. P.; Kwak, Y. W.; Goto, A.; Fukuda, T.; Monteiro, M. S. *J Polym Sci Part A: Polym Chem* 2003, 41, 2833.
- Barner-Kowollik, C.; Coote, M. L.; Davis, T. P.; Radom, L.; Vana, P. *J Polym Sci Part A: Polym Chem* 2003, 41, 2828.
- Rizzardo, E.; Chiefari, J.; Mayadunne, R. T. A.; Moad, G.; Thang, S. H. In *Controlled/Living Radical Polymerization: Progress in ATRP, NMP, and RAFT*; Matyjaszewski, K., Ed.; ACS Symposium Series 768; American Chem Society: Washington, DC, 2000; p 278.
- Goto, A.; Sato, K.; Tsujii, Y.; Fukuda, T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 2001, 34, 402.
- Destarac, M.; Charlot, D.; Franck, X.; Zard, S. Z. *Macromol Rapid Comm* 2000, 21, 1035.
- Stenzel, M. H.; Cummins, L.; Roberts, G. E.; Davis, T. R.; Vana, P.; Barner-Kowollik, C. *Macromol Chem Phys* 2003, 204, 1160.
- Coote, M. L.; Radom, L. *Macromolecules* 2004, 37, 590.
- Favier, A.; Barner-Kowollik, C.; Davis, T. P.; Stenzel, M. H. *Macromol Chem Phys* 2004, 205, 925.
- Stenzel, M. H.; Davis, T. P.; Barner-Kowollik, C. *Chem Commun* 2004, 1546–1547.
- Destarac, M.; Taton, D.; Zard, S. Z.; Saleh, T.; Yvan, S. In *Adv in Controlled/Living Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series 854; American Chem Society: Washington, DC, 2003; p 536.
- Charlot, D.; Corpart, P.; Adam, H.; Zard, S. Z.; Biadatti, T.; Bouhadir, G. *Macromol Symp* 2000, 150, 23.
- Simal, F.; Delfosse, S.; Demonceau, A.; Noels, A. F.; Denk, K.; Kohl, F. I.; Weskamp, T.; Herrmann, W. A. *Chem-Eur J* 2002, 8, 3047.
- Wakioka, M.; Baek, K. Y.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* 2002, 35, 330.
- Xia, J. H.; Paik, H. J.; Matyjaszewski, K. *Macromolecules* 1999, 32, 8310.
- Gigmes, D.; Marque, S.; Bertin, D.; Tordo, P.; Guerrer, O. *Polymer Preprints* 2002, 43, 309.
- McLeary, J. B.; Tonge, M. P.; Roos, D. D.; Sanderson, R. D.; Klumperman, B. *J Polym Sci Part A: Polym Chem* 2004, 42, 960.
- Butte, A.; Storti, G.; Morbidelli, M. *Macromolecules* 2001, 34, 5885.
- de Brouwer, H.; Tsavalas, J. G.; Schork, F. J.; Monteiro, M. J. *Macromolecules* 2000, 33, 9239.
- Lansalot, M.; Davis, T. P.; Heuts, J. P. A. *Macromolecules* 2002, 35, 7582.
- Luo, Y. W.; Liu, X. *J Polym Sci Part A: Polym Chem* 2004, 42, 6248.
- Matyjaszewski, K.; Qiu, J.; Tsarevsky, N. V.; Charleux, B. *J Polym Sci Part A: Polym Chem* 2000, 38, 4724.
- Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Macromolecules* 2002, 35, 5417.
- Russum, J.; Jones, C. W.; Schork, F. J. *Ind Eng Chem Res* 2004, ASAP article, web release date August 26, 2005.
- Russum, J. P.; Jones, C. W.; Schork, F. J. *Macromol Rapid Commun* 2004, 25, 1064.
- Smulders, W.; Gilbert, R. G.; Monteiro, M. J. *Macromolecules* 2003, 36, 4309.
- Smulders, W.; Jones, C. W.; Schork, F. J. *Macromolecules* 2004, 37, 9345.
- Tsavalas, J. G.; Schork, F. J.; de Brouwer, H.; Monteiro, M. J. *Macromolecules* 2001, 34, 3938.
- Uzulina, I.; Kanagasabapathy, S.; Claverie, J. *Macromol Symp* 2000, 150, 33.
- Dunn, A. S. In *Emulsion Polymerization of Vinyl Acetate*; El-Aasser, M. S.; Vanderhoff, J. W., Eds.; Applied Science Pub.: London, 1981; Chapter 2, p 12.
- The SEC-Viscometry RALLS (Right Angle Laser Light Scattering) technique allows for the absolute characterization of polymers. In principle, it requires only that the concentration of the sample be known.

41. Chern, C. S.; Liou, Y. C. *J Polym Sci Part A: Polym Chem* 1999, 37, 2537.
42. Asua, J. M.; Rodriguez, V. S.; Sudol, E. D.; Elaasser, M. S. *J Polym Sci Part A: Polym Chem* 1989, 27, 3569.
43. Asua, J. M.; Sudol, E. D.; Elaasser, M. S. *J Polym Sci Part A: Polym Chem* 1989, 27, 3903.
44. Alduncin, J. A.; Forcada, J.; Asua, J. M. *Macromolecules* 1994, 27, 2256.
45. Blythe, P. J.; Klein, A.; Phillips, J. A.; Sudol, E. D.; El-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 1999, 37, 4449.
46. Nomura, M.; Suzuki, K. *Ind Eng Chem Res* 2004, ASAP article, web release date October 12, 2004.
47. Nomura, M.; Fujita, K. *Makromol Chem Rapid Commun* 1989, 10, 581.
48. Barton, J.; Karpatyova, A. *Makromol Chem* 1987, 188, 693.
49. Luo, Y. W.; Schork, F. J. *J Polym Sci Part A: Polym Chem* 2002, 40, 3200.
50. Brandrup, J.; Immergut, E. H.; McDowell, W. *Polymer Handbook*; Wiley, New York, 1974.
51. Smulders, W.; Jones, C. W.; Schork, F. J. *AIChE J* 2005, in press.