

Latex Dispersability Index

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ABSTRACT: The pigment loading capacity (PLC) of dispersion binders is an important factor in the formulation of a latex paint. However, there has been no reliable method for the quantitative evaluation of this property; this has led to difficulty in comparing latex binders in this regard. In this article, a new parameter, the latex dispersability index (LDI), is proposed as a quantitative measure of PLC of latex binders. In this test method, the capability of latex to disperse pigments (or extenders) is quantified on the basis of the idea of the minimum viscosity method for dispersants. The face-centered cube experimental design was used to synthesize 26 binders. On the basis of this design, the synthesized latexes had a maximum diversity of properties, especially with regard to PLC. The binders were formulated with three mineral powders (i.e., TiO_2 , CaCO_3 , and talc). The curves of viscosity versus

mass of the resin for all of the samples were prepared. The general trend of the curves was universal and only depended on the nature of the powders. The geometry of the curves and PLC had quantitative correlations. To make a quantitative correlation between the curves and PLC, LDI was defined as a function of the area under the curve, the height of the curve, and the length of the end point. Four ranges of LDI were assigned to the conventional quantitative phrases for PLC. The usefulness of this parameter was then verified by some well-known commercial binders with different PLCs. The results were in a good agreement with the expected behaviors. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2336–2341, 2010

Key words: emulsion polymerization; fillers; latices; resins; viscosity

INTRODUCTION

The pigment loading extent is one of the main factors considered in the formulation of latex paints because of economic considerations and final film properties. Latex binders are intrinsically heterogeneous systems, and the physical chemistry of the particle surfaces has restricted their compatibility with mineral particles. Pigment–binder incompatibility leads to flocculation and coagulation. Therefore, the pigment loading extent determines the maximum pigment–binder ratio for a risk-free domain of paint formulation. Unfortunately, no reliable method for the quantitative evaluation of this property is known, and the common qualitative phrases (e.g., poor, moderate, good, and excellent) are hardly useful from an engineering point of view.

A latex paint is made by the addition of a binder to a white base. The white base is a pigment slurry prepared by the dispersion of the mineral powders (pigments and fillers) in a vehicle at a desired level of particle size. Pigment particles in aqueous systems are not usually stable and need stabilization (i.e.,

steric, electrostatic, or electrosteric stabilization).^{1,2} Dispersing agents are used to prevent dispersion instability and pigment settling. Among the dispersants used for latex paints, polymeric dispersant are more popular,³ but all of them are generally used to improve pigment dispersion. The quality of pigment distribution also depends on various characteristics of latex binders. On the resin side, they include the latex particle size⁴ and morphology,⁵ monomer composition,⁶ functionality,⁷ nature and quantity of emulsifiers,⁸ and polymerization procedure.⁹ On the pigment side, it also depends on the surface properties of the pigments¹⁰ and the type of dispersant.¹¹

The dispersion process is the consequence of the wetting, separation, and stabilization processes.¹² The role of the surfactant is very important in the minimization of the interfacial free energy of system and in the provision of kinetic stabilization.¹³ Pigments may adsorb surfactants from aqueous solutions,¹⁴ and this, in turn, may affect the rheology of the system.¹⁵

In our research, the dynamic behavior of pigment–binder interaction was investigated on the basis of the idea of the minimum viscosity method¹⁶ used to characterize the efficiency of pigment dispersants. On the basis of this study, a new parameter, called the *latex dispersability index* (LDI), is introduced as a quantitative measure of the pigment loading capacity (PLC) of a latex binder.

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TABLE I
Ingredients of the Polymerization Process

Country	Inhibitor	Supplier	Mass (g)	Material
Germany	EMHQ-50	BASF	505	nBA
United Kingdom	MEHQ-50	Lucite	143	MMA
Emarat Arabia Union	Catechol-50	Enoc	261	S
France	EMHQ-200	Atofina	Variable	AA
United Kingdom	EMHQ-250	Lucite	Variable	MAA
Japan	—	Mitsui	Variable	IA
Indonesia	—	P. T. Kao	Variable	SLS
Iran	—	Pakvash	Variable	SDS
Germany	—	Loporte	Variable	Ammonia

EXPERIMENTAL

Synthesis of the lattices

The lattices were prepared by a seeded, semibatch emulsion polymerization process with a variable amount of anionic emulsifiers and comonomers. All runs were carried out at 85°C. Potassium persulfate was used as an initiator. Pre-emulsions of *n*-butyl acrylate (nBA), methyl methacrylate (MMA), and styrene (S) and additional comonomers and emulsifiers (as mentioned in Table I) were added at a constant feed rate over a period of 3–5 h with an additional postpolymerization (for 1 h). The pH dispersion was adjusted at 7 by careful addition of an ammonia solution. The final solid content was adjusted to 50 wt % for each latex by the addition of water.

Acrylic acid (AA), methacrylic acid (MAA), and itaconic acid (IA) were used as comonomers, and sodium lauryl sulfate (SLS), sodium dodecyl sulfonate (SDS), and a 50 : 50 mixture of the two were used as emulsifiers. The amounts of emulsifiers and comonomers are shown at three levels in Table II.

A face-centered cube experimental design belonging to the family of central composite designs was used to reduce 729 batches of full factorial design to 26 batches. Face-centered cube is a special case of central composite designs where $\alpha = 1$. This design has a resolution of 5, and a quadratic model can be fitted to the responses. Moreover, all of the interaction effects among the factors can be studied. In this design, the center point is replicated to estimate of lack of fit and prevent the further replication of design points.¹⁷

Emulsion polymerization with the least amount of water-soluble monomers (e.g., carboxylic acids) prevents unwanted polymerization in the continuous phase and undesirable particle morphologies at the end of process and, hence, is most favorable.¹⁸ In addition, an excess amount of emulsifier, much higher than the critical micelle concentration, causes compact micellar structures and results in unbalanced dynamic transportation of monomers.¹⁹ Hence, we were not able to carry out experimental design item 6. The results of experiments 3 and 19

showed that SLS provided a better environment for the polymerization than SDS did, which meant that, at the same addition level of carboxylic monomer, the replacement of 50% of SLS with SDS increased the incompatibility of the fillers.

Evaluation of the dispersing power of the latex samples

The idea of a minimum viscosity method¹⁶ was the basis of this research, in which we used latex instead of a dispersant. A minimum viscosity method was

TABLE II
Design of the Experiment for Different States of Comonomers and Emulsifiers

Run	Factor 1: Comonomer type	Factor 2: Comonomer amount	Factor 3: Emulsifier type	Factor 4: Emulsifier amount
1	MAA	8	SDS	16
2	AA	8	SLS	8
3	AA	24	SLS	24
4	IA	8	SLS	24
5	AA	16	SDS	16
6	MAA	16	SDS	24
7	IA	16	SDS	16
8	IA	24	SLS	8
9	AA	24	MIX	8
10	MAA	16	SLS	16
11	MAA	16	SDS	16
12	MAA	24	SLS	16
13	IA	24	MIX	8
14	MAA	16	SDS	8
15	AA	8	MIX	8
16	AA	24	SLS	8
17	IA	24	MIX	24
18	MAA	16	MIX	16
19	AA	24	MIX	24
20	IA	8	MIX	24
21	IA	24	SLS	24
22	IA	8	MIX	8
23	AA	8	MIX	24
24	MAA	24	SDS	16
25	IA	8	SLS	8
26	AA	8	SLS	24

MIX = 50 : 50 blend of SLS and SDS. The amounts are in grams, and batch 6 was not runnable.

TABLE III
Specification of the Mineral Powders

Material	Particle size (μ)	Supplier	Country
TiO ₂	0.25–0.40	Crystal	Saudi Arabia Kingdom
CaCO ₃	5–10	Poudersazan	Iran
CaCO ₃	40–50	Poudersazan	Iran
Talc	10–15	Poudersazan	Iran
Talc	35–45	Poudersazan	Iran
Baryte	20	Poudersazan	Iran
Quartz	150	Technosilice	Iran
Quartz	800	Technosilice	Iran
Kaolin	60	Minerals	Italy

used to evaluate the efficiency of the dispersants. In this study, three mineral powders, titanium dioxide (TiO₂), calcium carbonate (CaCO₃), and talc, were chosen. The specifications of the powders, according to their supplier data sheets, are summarized in Table III. All of the latex samples were tested together with these three mineral powders. First, the powder was prewetted by water. Table IV shows the pigment–water mass ratio for the three mineral powders. The ratios were obtained by a method very similar to oil absorption measurement. Then, the dispersing power of each dispersant was measured by continuous addition of specific amounts of the dispersant to the prewetted powder; it was homogenized by gentle mixing after each interval addition, and then, the Brookfield viscosity was measured. The average of tolerance for three replicate were within 100 cP.

RESULTS AND DISCUSSION

Behavior of the latex viscosity

Interaction between some latexes and mineral powders were shown for all samples in the diagrams of viscosity variation (poise) as a function of the latex quantity (grams), and some of the typical ones are shown in Figure 1. The curves indicated a general behavior of viscosity, which was directly dependent on the nature of the powders. In case of talc, it started with a low viscosity, and the viscosity increased with increasing amount of latex. After a relatively large addition, it started to decrease. In the case of TiO₂, it started with a low viscosity; then, the viscosity increased rapidly and immediately leveled down. In the case of CaCO₃, the viscosity remained in a plateau and decreased later.

The addition of the latex vehicle changed the volume of the dispersed phase because of the polymer particles. In addition, the latex particles were not as rigid as the mineral particles; they had adhesion to the mineral particles. In fact, the latex particles added to the system were adsorbed on the pigment surfaces. The appearance of sticky pigment particles developed a latex–pigment aggregation.²⁰ Therefore, the general trend of the

curves, especially in the cases of TiO₂ and talc, was mostly due to the latex particle–pigment interactions and did not obey the Mooney equation, in which the continuous phase is a Newtonian liquid and the particles are rigid with no particle–particle interaction.²¹

$$\ln \eta = \ln \eta_e + \frac{K_E V_i}{1 - V_i/\phi}$$

where η is the viscosity of dispersion, η_e is the viscosity of the continuous phase, K_E is a shape factor, V_i is the volume fraction of dispersed phase, and ϕ is the packing factor. On the other hand, the latex–pigment aggregation increased the viscosity of system by several mechanisms: Water immobilized between the aggregated particles increased the effective solid volume by transferring volume from the continuous phase to the dispersed phase.²¹ The aggregates may have deviated significantly from a spherical shape to nonspherical particles, which led to a higher viscosity at constant volume fractions.²³ Energy dissipated in the breaking down of the aggregates also led to increased viscosity.²⁴ Coulombian repulsive forces led to an expansion. As a result, the viscosity increased (the same as thickeners). An excess amount of latex caused expanded species to dilute and a decrease in viscosity. In other words, mixtures of powders and small amounts of latexes had temporary bonds, and their behavior became probably like pseudocrosslinked systems. A greater increase in latex quantity led to a decrease in physical crosslink density and decreased the effective solid volume followed by a viscosity decrease. The existence of latex as a media caused the mineral particle interactions to decrease, and the slipping of particles on the neighbor particles became easier. This situation led to decreasing viscosity.

The latexes used in experiments 17, 19, 21, and 24 caused agglomeration with TiO₂. They had no reasonable behavior for talc and CaCO₃, too, and therefore, their results are not mentioned in this article.

LDI

This quantity is introduced as a measure of the pigment loading of latex on the basis of the viscosity

TABLE IV
Mass Ratio of the Powder to Deionized Water in the Prewetted Powders

Material	Powder : water
TiO ₂	50 : 50
CaCO ₃	75 : 25
Talc	45 : 55
Kaolin	37 : 63
Baryte	17 : 83
Silice	30 : 70

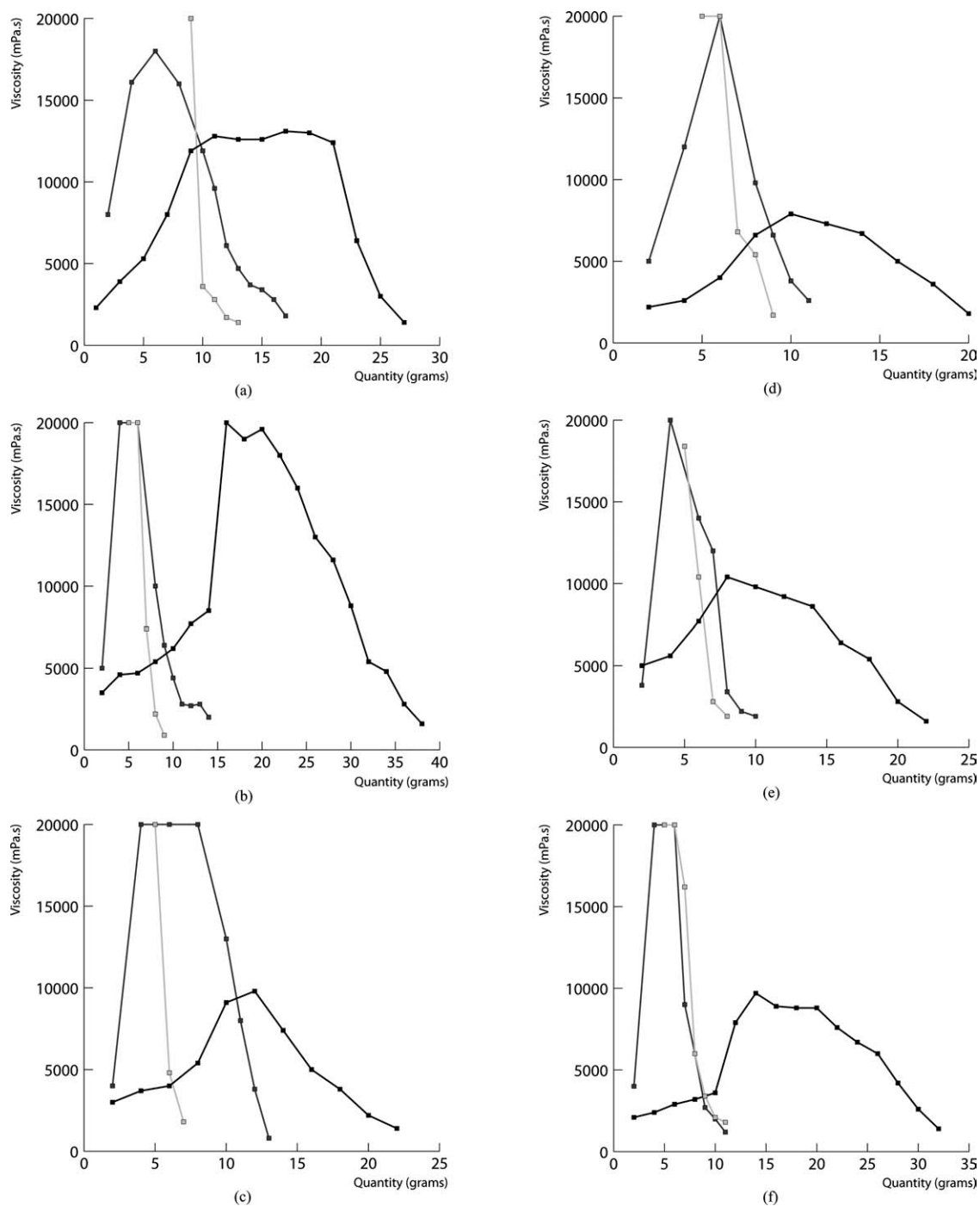


Figure 1 Viscosity variation (mPa s) versus latex quantity (g) curves for typical latexes: (a) 1, (b) 5, (c) 7, (d) 10, (e) 12, and (f) 14 with the following mineral fillers: talc (black), CaCO₃ (dark gray), and TiO₂ (light gray).

versus the mass of resin curve. According to our several practical experiences, we observed that the area under the curve was indicative of the pigment loading of latex. In the other words, when the area under the curve increased, the latex needed to reduce the viscosity of powder to less than 10 mPa s was increased, and therefore, this latex had a lower pigment loading extent. Figure 2 shows two schematic model curves of the viscosity versus the mass

of resin, all of which had the same area under the curve. With the same area under the curve, a higher height of the curves meant a higher viscosity at the same amount of resin [Fig. 2(a)]. Therefore, the higher the height of the curve was, the lower the pigment loading extent of the latex was. The mass of latex at which the curve reached below 10 mPa s is of great importance, too. With the same area under the curve and height of the curve, the last point

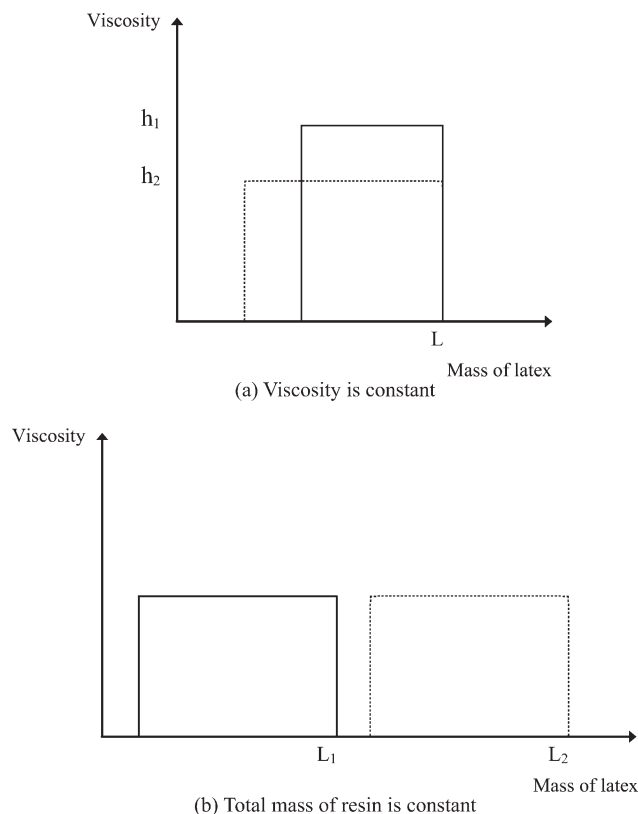


Figure 2 Two schematic model curves of the viscosity versus the mass of resin: (a) constant viscosity and (b) constant total mass of resin. h_1 & h_2 are maximum viscosities at equal mass of latex added to the powder paste. L_1 & L_2 are the maximum mass of resin added to get equal viscosities.

determined the maximum amount of latex needed to reduce the viscosity [Fig. 2(b)]. Hence, three parameters, the area under the curve (S_{curve}), the position of the end point (L), and the height of the curve (h), were very important in the determination of LDI. The following empirical formula from the experimental data is introduced in this regard:

$$LDI = \left(\frac{100}{\sqrt{LhS_{curve}}} \right)^{1/2}$$

LDI depends on the natures of both the latex and the mineral particles. In Table V, the various LDIs are listed for the mentioned powders. LDI had a rea-

TABLE V
Calculated LDIs for the Synthesized Latexes and Typical Pigments

Latex	Talc	TiO ₂	CaCO ₃
1	4.83	5.75	5.67
2	9.79	5.78	4.45
3	12.04	6.68	7.30
4	17.44	6.36	7.22
5	9.67	6.59	7.33
6	—	—	—
7	7.63	5.88	10.9
8	7.85	5.87	15.04
9	3.54	4.5	6.72
10	8.98	7.51	7.12
11	9.75	8.60	6.16
12	7.29	8.11	6.21
13	9.78	4.98	8.73
14	5.64	7.71	6.83
15	2.95	6.28	3.36
16	5.11	5.34	5.13
17	—	—	—
18	11.87	7.77	6.76
19	—	—	—
20	5.21	6.15	7.32
21	—	—	—
22	8.34	5.57	3.90
23	3.26	8.00	7.51
24	—	—	—
25	3.29	9.20	5.71
26	6.52	7.18	3.76

Latexes 6, 17, 21, and 24 were not compatible with the mentioned powders.

sonable result for the four different types of well-known commercial latexes (Table VI). As expected, two of them had excellent loading of pigment, and the other ones were poor in this regard. The obtained results verify the usefulness of this new method to quantify pigment PLC. The following ranges of LDI were useful for evaluating the load of pigments in the latexes: poor loading, $LDI < 5$; moderate loading, $5 < LDI \leq 10$; good loading, $10 < LDI \leq 15$; and excellent loading, $15 < LDI$.

CONCLUSIONS

We have introduced LDI as a measure of PLC in latexes and provided a quantitative comparison of different latexes for the loading of mineral powders.

TABLE VI
Indication of LDI for Some Well-Known Commercial Latexes

Commercial latex	TiO ₂	CaCO ₃	CaCO ₃	Talc	Talc	Baryte	Quartz	Quartz	Kaolin	Application of resin
	25–40 μ	5–10 μ	40–50 μ	10–15 μ	35–45 μ	20 μ	150 μ	800 μ	60 μ	
Primal Ac33 (Rohm & Haas)	14.31	12.11	12.83	14.67	15.45	11.81	13.21	14.23	12.51	Paint
Acronal 290D (BASF)	12.37	14.92	15.51	13.92	12.73	12.37	12.08	12.92	13.25	Paint
Primal HA-16 (Rohm & Hass)	5.06	6.72	6.02	4.45	4.83	6.21	7.12	7.32	4.25	Nonwoven
Primal B15 (Rohm & Hass)	4.31	6.80	7.22	4.91	5.51	7.32	5.31	6.61	5.75	Nonwoven
Simacryl R-790 (Simab Resin)	12.22	13.65	13.96	11.53	12.32	10.52	11.07	11.87	10.71	Paint

The general trend of viscosity versus mass of the latex curves mostly depended on the mineral powders and was almost independent of latex, but the quantitative and qualitative changes in the comonomer and emulsifier had pronounced effects on LDI. For a given latex, different pigments had different LDIs. Because of the mutual effect of the comonomer and emulsifier, it was very hard to suggest a latex composition that had a high LDI for every mineral powder. Therefore, we concluded that a suitable latex for highly loaded paint must have a high average LDI for most fillers and pigments.

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References

1. Hu, Y.; Gong, S.; Zhou, D. *Mater Sci Eng B* 2003, 99, 520.
2. Menovick, G. G.; Balch, T. C.; Darvis, H. P.; Dudek, P. U.S. Pat. 5,876,493 (1999).
3. Peng, B.; Huang, Y.; Chai, L.-Y.; Li, G.-L.; Cheng, M.-M.; Zhang, X.-F. *J Central South Univ Technol* 2007, 14, 490.
4. Lee, J.-Y.; Kim, S.-W.; Yon, K.-Y. U.S. Pat. 7,307,129 (2007).
5. Andersson, N.; Alberius, P.; Ortegren, J.; Lindgren, M.; Ergstorm, L. *J Mater Chem* 2005, 15, 3507.
6. Chen, M.; Elliott, P. T.; Glass, J. E. *Colloids Surf* 2001, 183–185, 457.
7. Farrokhpay, S.; Morris, G. E.; Fornasiero, D.; Self, P. *JCT Res* 2006, 3, 275.
8. Keizou, I. *Colloids Surf* 1999, 153, 591.
9. Chen, A.; Ng, T. H.; Helberecht, A.; Boils-Boissier, D. C.; Gerroir, P. J.; Duque, R. M. U.S. Pat. 6,455,219 (2002).
10. Shimiori, M. *Dic Tech Rev* 1999, 5, 1.
11. Kostansek, E. *JCT Res* 2006, 3, 165.
12. Barua, G. C.; Burkhard, H. U.S. Pat. 4,081,418 (1978).
13. Vorweg, L.; Gilbert, R. G. *Macromolecules* 2000, 33, 6693.
14. Musselman, S. W.; Chander, S. *J Colloid Interface Sci* 2002, 256, 91.
15. Otsubo, Y.; Horigome, M. *Korea-Aust Rheol J* 2003, 15, 179.
16. Clayton, J. *Surface Coatings International Part B* 1997, 80, 414.
17. Box, G. E.; Hunter, W. G.; Hunter, J. S.; Hunter, W. G. *Statistics for Experimenters: Design, Innovation, and Discovery*, 2nd ed.; Wiley: Hoboken, NJ, 2005.
18. Harkins, W. D. *J Chem Polym* 1945, 13, 381.
19. Carro, S.; Herrera-Ordonez, J. *Macromol Rapid Commun* 2006, 27, 274.
20. Kiorboe, T.; Hansen, J. *MEPS* 1997, 159, 75.
21. Asano, Y.; Sotoyama, K. *Food Chem* 1999, 66, 327.
22. Berli, C. L. A. *Brazil J Chem Eng* 2007, 24, 203.
23. Du, Y.-Z.; Tomohiro, T.; Kodaka, M. *Macromolecules* 2004, 37, 803.
24. Jarvis, P.; Jefferson, B.; Gregory, J.; Parsons, S. A. *Water Res* 2005, 39, 3121.