Use of Poly(2-Vinylpyridine)-*b*-Poly(ε-Caprolactone) Copolymers as Pigment Stabilizers in Powder Coatings

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Four poly(2-vinylpyridine)-b-poly(ε-caprolactone) copolymers, differing in buoy block length and anchor/buoy block length ratio, have been used as TiO_2 pigment dispersants in a polyester powder coating resin. When the TiO_2 surface was fully covered with the block copolymers, the colloidal stability of the TiO_2 dispersions at typical curing temperatures was significantly improved because of the formation of a steric layer around the pigment particles. As a result, powder coatings with excellent flow, high gloss, and low haze values were obtained. Because of the high affinity of the dispersants for the TiO_2 surface, pretreatment of the pigments with the block copolymers was not necessary. At full pigment surface coverage, the chain length of the stabilizing polymer had little effect on the performance of the dispersants used.

INTRODUCTION

The mechanical and aesthetic properties of coatings are largely influenced by the state of dispersion of pigments and fillers. Generally speaking, the process of dispersing pigments in coatings involves (a) the wetting of pigment agglomerates by the coating binder, (b) the break-up of pigment agglomerates into primary particles, and (c) the colloidal stabilization of the dispersion of the primary particles. In solvent-based and waterborne coatings, diblock copolymer dispersants are widely used to facilitate the dispersion process.[1,2] These dispersants consist of an anchor block, which adsorbs onto the pigment surface, and a buoy block, which provides a stabilizing layer around the pigment. As a consequence, both the wetting of the pigments and the colloidal stability of the final dispersion are improved. The stabilizing effect of the dispersants depends on the lengths of both the anchor and the buoy blocks.[2-4]

In highly viscous systems such as powder coatings, the dispersion of pigments is more difficult than in solvent-containing coatings. This is because the wetting of the pigments by the resin is slower and the mixing time during extrusion is kept relatively short in order to reduce crosslinking.[5-8] As a result, the pigment dispersion is often incomplete in industrial practice (the break-up of pigment agglomerates is virtually complete with a lab-scale extruder and is independent of the extrusion temperature[8]). The poor pigment dispersion causes roughening of the coating surface and can lead to coatings with poor flow, low gloss, and high haze.[5] Moreover, for coatings containing color pigments, the color strength of the pigments is insufficiently developed and the reproducibility between different color batches is poor.[9] Recently, pigment masterbatches, containing pigments that are predispersed at a high concentration in a low molecular weight resin, have been developed for improving the pigment dispersion in powder coatings.[9-10] The use of block copolymer dispersants in powder coatings, however, has not been reported in literature.

Previously, we have reported on the preparation of poly(2-vinylpyridine)-*b*-poly(ε-caprolactone) copolymer dispersants for improving the TiO_2 dispersion in a polyester powder coating resin.[8,11,12] In these dispersants, the poly(2-vinylpyridine) block (P2VP) is the anchor block, and the poly(ε-caprolactone) block (PCL) is the buoy block. In this paper, the effect of P2VP-*b*-PCL copolymer dispers-

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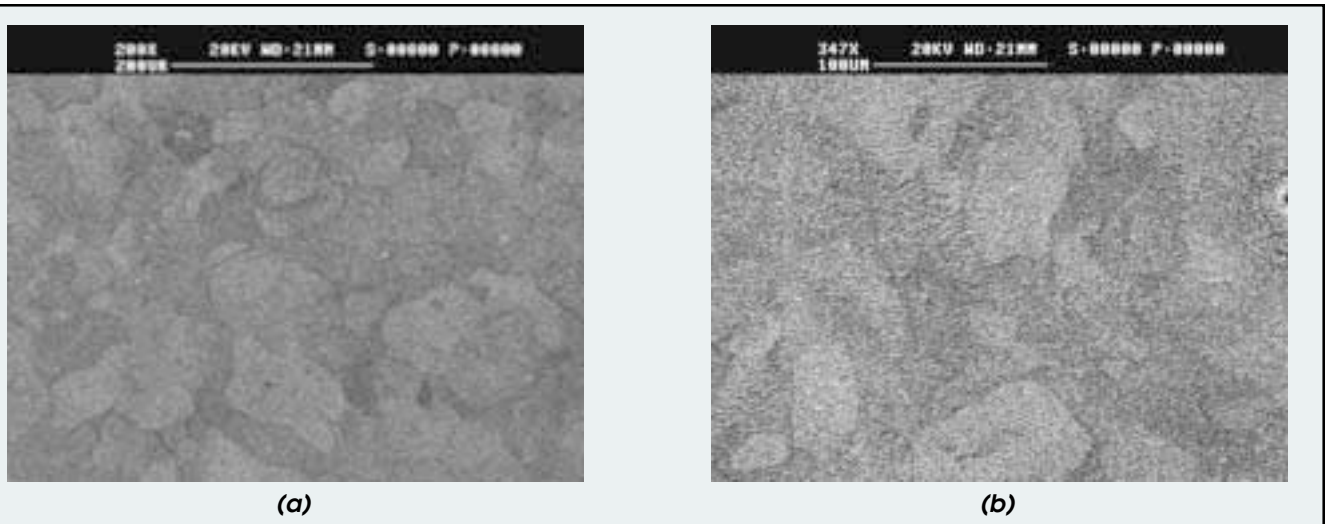


(a) *(b)*

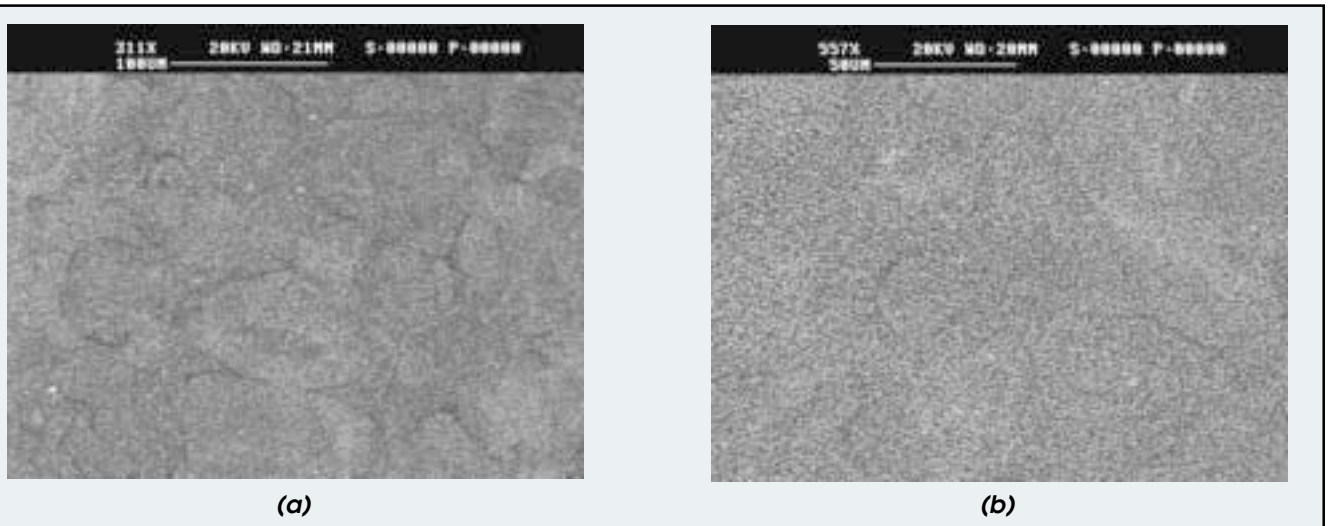
Figure 1—Typical scanning electron micrographs showing the pigment distribution at the surface of the coatings prepared by method A after heating for 10 min to (a) 150°C and (b) 200°C.

ants on the properties of pigmented thermoplastic powder coatings is discussed.

EXPERIMENTAL

A commercial carboxylic acid functional polyester resin was used (Uralac P3400, DSM Resins, $M_n \approx 5000$, determined by GPC relative to polystyrene standards). Unless stated otherwise, the resin was used as received (i.e., as flakes with a typical particle size of 10 × 5 × 1 mm). The TiO_2 pigment (Kronos 2160) was provided by Kronos (Leverkusen, Germany). According to the manufacturer, the primary particles have an average diameter of 210 nm and are coated with alumina and silica. The flow agent (BYK 360P) was kindly supplied by BYK-Chemie (Wesel, Germany). Benzoin (Fluka) was used as the degassing agent. P2VP-*b*-PCL copolymers were prepared via sequential anionic polymerization.[11] In order to exclude specific effects from curing agents, crosslinking agents were not used in the powder coatings.

Powder coatings were prepared by extrusion of dry blends containing 30 wt% TiO_2 (ca. 11 vol%), 1 wt% flow agent, 0.5 wt% benzoin, and dispersant with a Prism TSE 16 laboratory scale twin screw extruder with a screw speed of 200 rpm. The conveying zone was set at 75°C and the kneading zone at 110 or 120°C. After extrusion, the extruded material was powdered with a centrifugal mill (Retsch ZM 100) and sieved through a 100 mm sieve. Subsequently, the powder was sprayed electrostatically onto degreased aluminum panels (Q-Panel A36) with a Gema PG-1B spraying gun at 60 kV and 1 bar air pressure, and placed vertically in an air-circulated oven (Heraeus LUT 6050) for 10 min. Coatings with a layer thickness of ca. 80 µm were used for analysis.



(a) *(b)*

Figure 2—Typical scanning electron micrographs showing the pigment distribution at the surface of the coatings prepared by method B after heating for 10 min to (a) 150°C and (b) 200°C.

Table 1—Calculated Values of $t_{½}$ for a 30 wt% (11 vol%) Dispersion of TiO_2 (diameter 210 nm) in a Polyester Resin

Temperature (°C)	Viscosity (Pa sec)	$t_{½}$ (sec)
150	130	675
200	4.7	22
240	2.8	12

The block copolymer dispersants were employed in two ways. In the first set of powder coatings, the block copolymers were mixed with the pigments prior to extrusion. For this purpose, the TiO_2 pigments were dispersed ultrasonically in a solution of the block copolymer in dichloromethane. After removal of the solvent in vacuo, the pretreated pigments were added to the dry blend. For the reference coatings, the TiO_2 pigment was given the same treatment in the pure solvent. It was previously confirmed that this treatment has little effect on the dispersibility of the pigment.[8-12] In the second set of powder coatings, the block copolymer was mixed with the resin in the absence of TiO_2 pigment prior to the extrusion of the dry blend. Such premixes of the block copolymer with the resin were prepared by extrusion at 120°C and were subsequently ground in a small coffee grinder.

Adsorption isotherms of the dispersant on pigment were determined by gravimetrically analyzing the block copolymer concentration in the centrifuged supernatant after mixing TiO_2 and dispersant in toluene (depletion method[13]). The obtained adsorption data compared very well with thermogravimetric analyses (TGA) of the pigment sediment after centrifugation of the pigment dispersion.

Scanning electron microscopy (SEM) was performed using a Cambridge Stereoscan 200 scanning electron microscope operating at 20 kV. Samples were etched with an oxygen plasma for 15 min and coated with Pd/Au prior to examination.

Rheological measurements were conducted using a stress-controlled rheometer (AR-1000N, TA Instruments) equipped with an extended temperature module. Oscillatory measurements were performed with parallel plates (2 cm diameter, 1 mm gap) at 1% strain and an angular frequency of 6.28 rad/sec. Strain sweep measurements were performed at an angular frequency of 10 rad/sec.

Gloss and haze were measured at 20° with the Micro-haze Plus gloss/haze meter (BYK-Gardner), according to the standard ASTM D 523. The waviness of the coatings was measured with the Wave-scan Plus (BYK-Gardner).

Influence of Preblending on Pigment Dispersion Without Dispersants

It is known that in the absence of dispersants, the degree of dispersion of the pigments in a powder coating depends largely on the extent of mixing of the dry blend prior to its extrusion.[5,14] Moreover, when (part of) the polymer resin is pulverized before dry blending, the contact area between pigment and resin in the dry blend is enlarged (enhanced "prewetting"), thereby facilitating the final deagglomeration and distribution of the pigment particles through the resin during extrusion.[15] In this section, the effect of the use of a nonpulverized resin (method A) and a pulverized resin (method B) in the dry blend on the degree of dispersion of the pigments in the final coatings was investigated. The powder coatings were placed in an oven at 150, 200, and 240°C for 10 min after application. The coating surfaces were analyzed by SEM.

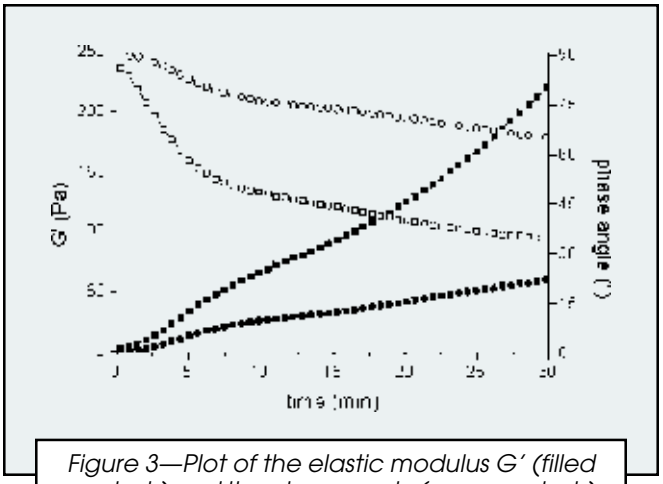


Figure 3—Plot of the elastic modulus G′ (filled symbols) and the phase angle (open symbols) vs. time for a 30 wt% TiO_2 dispersion in a polyester resin at 200°C (circles) and 240°C (squares).

Large differences were observed in the overall distribution of the pigments in the resin. Examination of the coatings' surfaces at low magnifications revealed pigment-rich and pigment-poor areas in the coatings prepared by method A. This is shown in *Figure* 1. These areas are 40-100 µm in diameter and correspond to the individual powder coating particles. Similar pigment-rich and pigment-poor zones have been observed by Thometzek et al. in cured powder coatings pigmented with TiO_2 pigments with different surface modifications.[16] In the current sys-

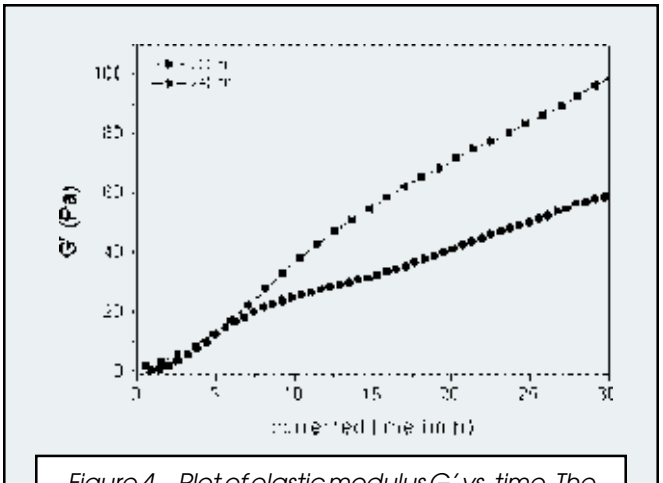


Figure 4—Plot of elastic modulus G′ vs. time. The timescale for the flocculation process at 240°C has been scaled to the timescale of the flocculation process at 200°C.

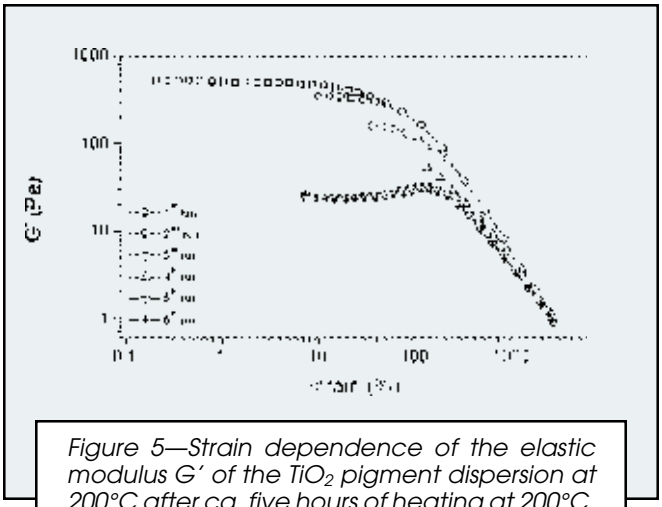


Figure 5—Strain dependence of the elastic modulus G′ of the TiO_2 pigment dispersion at 200°C after ca. five hours of heating at 200°C. Each run took 100 sec. Each measurement involved approximately two oscillations. After six runs, the rheological response became stable.

tem, though, the extruder feed composition is not constant due to the presence of resin flakes in the dry blend, which gives rise to inhomogeneous pigment distributions in the extrudates. Upon grinding and sieving the extruded material, powder particles with varying pigment contents are formed. In the coatings prepared by method B, the pigment-rich and pigment-poor regions were practically absent, as a result of the more homogeneous pigment distribution in the dry blend. However, the boundaries between the individual powder particles were still visible in the coating surfaces, as shown in *Figure* 2. These boundaries appear to have a lower concentration of pigment particles.

In the coatings that were heated to 200 and 240°C, flocculated pigment particles were observed.[8,12] The flocculation seemed to be more pronounced at 240°C than at 200°C. The coatings that had been heated to 150°C did not contain flocculated pigments.

The flocculation of the pigments at 200 and 240°C was already observed after one minute. According to the theory of rapid coagulation,[17] the time $t_{1/2}$ necessary to reduce the total number of particles by a factor of 2 is given in equation (1).

$$t_{1/2} = \frac{3\eta}{4k_B TN(0)} \quad (1)$$

with η representing the viscosity, k_B Boltzman's constant, T the temperature, and N(0) the initial number of particles per unit volume. The calculated values of $t_{1/2}$ for a 30 wt% TiO_2 dispersion at 150, 200, and 240°C are listed in *Table* 1. As can be seen, at 150°C flocculation is predicted to be very slow ($t_{1/2}$ > 11 min), whereas at 200 and 240°C flocculation is predicted to occur very fast. This is in accordance with the experimental observations.

The viscosity of a filled polymer is known to be increased by pigment flocculation as a result of the formation of a pigment network structure and the occlusion of polymer material within the pigment flocculates.[18] The formation of a pigment network structure can be monitored by measuring the evolution of the elastic modulus G′.[19] *Figure* 3 shows a plot of G′ vs. time. As can be seen, G′ starts to increase immediately. As can be expected, G′ increases faster at 240°C than at 200°C. In *Figure* 4, the timescale of the flocculation process at 240°C has been scaled to the timescale of the flocculation process at 200°C, by multiplying the time at 240°C by 1.83 ($= t_{1/2}^{200°C} / t_{1/2}^{240°C}$). If the pigment flocculation proceeds according to the theory of rapid coagulation, then the plots would be identical. This would also hold for the case of slow coagulation, i.e., when the coagulation is retarded by a repulsive barrier. As shown, the curves indeed overlap for the first seven minutes, but they deviate after that. This suggests that a second process takes place, which leads to an additional increase in G′. This idea is supported by the strain dependence of the formed network, as shown in *Figure* 5. *Figure* 5 shows six serial strain experiments performed consecutively after 100 sec. As shown, the breakdown of the network, formed after several hours of heating to 200°C, occurs well beyond 10% strain, which is much higher than is usually seen for physical networks of spherical particles.[18,20,21] As the formed network shows virtually no recovery on the timescale of 10^2 sec, this indicates the breakdown of a chemical network of polymers, rather than a physical network thereof. In filler-containing rubbers, a similar behavior, as shown in *Figure* 5, is known as the Payne effect, which is attributed to a dynamic adsorption/desorption equilibrium between rubber chains and filler particles, as a function of strain.[20,22]

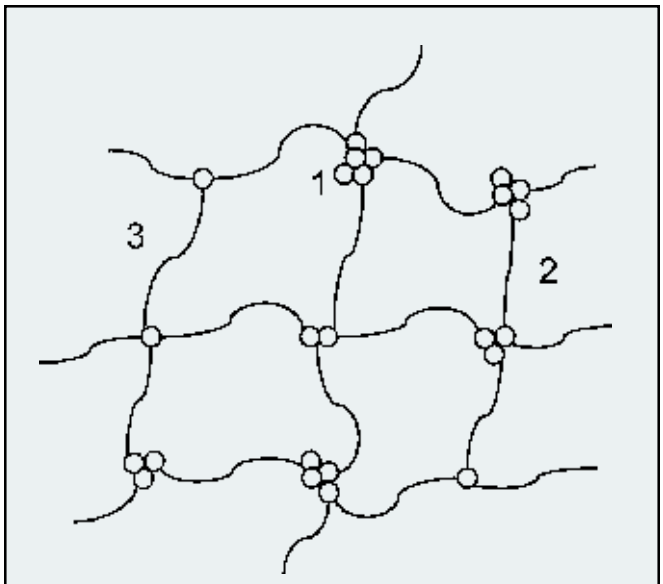


Figure 6—Schematic representation of proposed hybrid-type network structure consisting of flocculated pigments (1) and polyester linkages between flocculated pigments (2) and between nonflocculated primary particles (3).

Table 2—Effect of the Premixing Method and Curing Temperature on the Gloss, Haze, and Long-Term (L) and Short-Term (S) Waviness of Coatings Containing 30 wt% TiO_2

	Flakes Resin (Method A)			Pulverized Resin (Method B)		
Temperature (°C)	Gloss (%)	Haze (-)	Waviness (L/S)	Gloss (%)	Haze (-)	Waviness (L/S)
150	84	80	52/55	89	48	not determined
200	84	92	64/67	91	17	44/43
240	80	140	61/60	90	26	44/56

In our system, no increase of G' in time could be observed in the absence of TiO_2 pigments, not even after several hours. This clearly indicates an influence of the TiO_2 pigment surface on the formation of the network. It is known that TiO_2 pigments can form strong chemical bonds with the carboxylic acid groups of a polymer resin.[23] This may lead to the formation of some sort of hybrid network structure, similar to the aforementioned Payne effect.[22] This hybrid network may be considered as consisting of clusters of flocculated TiO_2 pigments that are connected via polyester chains, chemically linked to the TiO_2 pigment surface. Such polyester links can also exist between single, nonflocculated TiO_2 particles. This is schematically shown in *Figure* 6. At low strains, the pigment-pigment contacts (1) can break, whereas at higher strains the pigment-polymer bonds (2) and (3) can break. To our knowledge, the occurrence of such a network in polyester powder coatings cannot be found in literature.

The effect of the pigment dispersion on the 20° gloss and haze is shown in *Table* 2. Gloss/haze measurements are common practice in coating science when evaluating the degree of pigment dispersion, since the gloss and haze of a coating depend on its surface roughness.[24-27] Poor pigment dispersion generally leads to increased surface roughening. Usually, haze is more dependent than gloss on changes in surface roughness.

As can be seen in *Table* 2, the gloss of the coatings is virtually independent of temperature for both methods, whereas the haze is increased with heating temperature. This is in agreement with the observed flocculation at 200 and 240°C. The coatings prepared by method A showed overall lower gloss and higher haze values compared to the coatings prepared by method B, which is attributed to the less homogeneous pigment distribution for method A, as shown in *Figures* 1 and 2.

The effect of the pigment dispersion on the extent of leveling of the powder coating surface was studied by evaluating the waviness of the coatings. The waviness is a measure for the extent of leveling and gives indirect information on the surface roughness. It is divided into a long-term (L) and short-term (S) component, with L corresponding to structure sizes > 0.6 mm (orange peel) and S corresponding to structure sizes < 0.6 mm. Generally, a long-term waviness of 50 mm or higher indicates poor leveling.[29] Powder coating leveling is governed by surface tension differences and is counteracted by viscosity.[30,31] In general, the higher the curing temperature, the better the leveling (without crosslinking agents). The results of the waviness measurements are included in *Table* 2. As shown, the waviness was not significantly influenced by the heating temperature. The unexpected high values of the waviness at 200 and 240°C, relative to the waviness at 150°C, indicate that the leveling of the coatings was affected by the observed pigment flocculation at these temperatures.

Table 3—Characteristics of the Block Copolymer Dispersants Used in this Study

Dispersant	M_n P2VP (g/mol)	M_nPCL (g/mol)	Γ_{max} (mg/m^2)	ν_a	R_g (nm)
1	4100	1500	0.87	0.75	1.2
2	2300	3600	0.98	0.41	1.9
3	1000	4400	0.81	0.19	2.1
4	2800	6500	0.93	0.32	2.5

Adsorption of P2VP-*b*-PCL Dispersants On TiO_2 Pigments

In the previous section, it was shown that the TiO_2 dispersions are not colloidally stable at 200 and 240°C in the absence of dispersants. Next, the influence of P2VP-*b*-PCL copolymer dispersants on the pigments' degree of dispersion is presented and the influence of the anchor and buoy block lengths is discussed. Four different dispersants were used, as listed in *Table* 3. Here, the main differences between the dispersants are the molecular

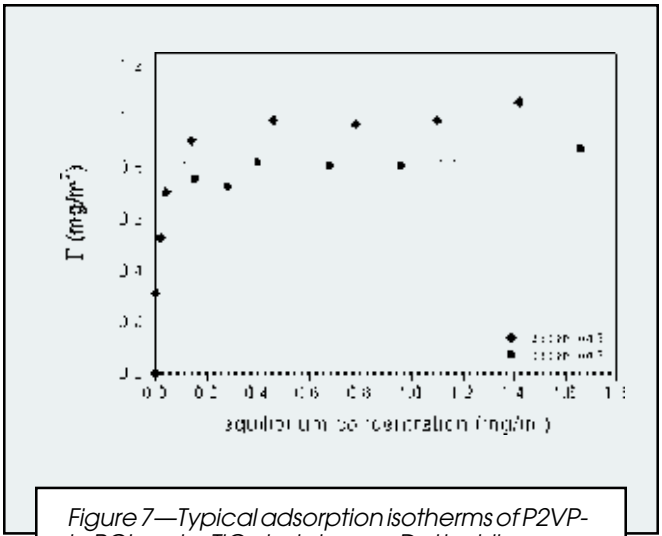
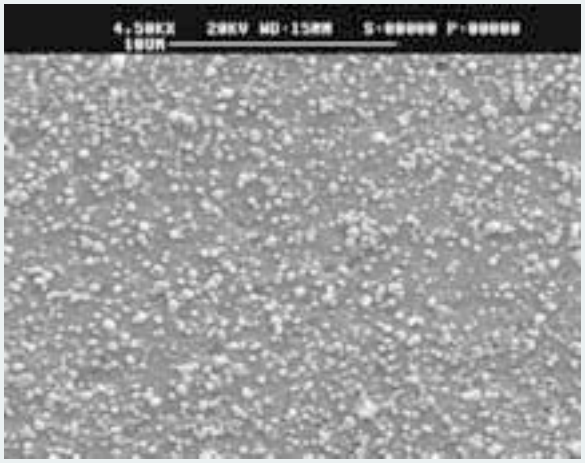


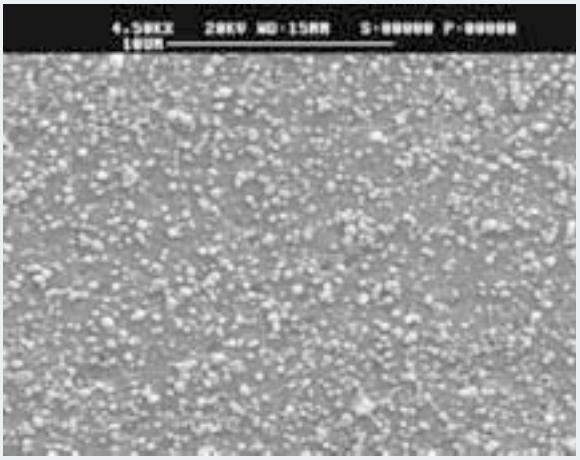
Figure 7—Typical adsorption isotherms of P2VP-b-PCL onto TiO_2 in toluene. Dotted lines are added to guide the eye.

weights (M_n) of the anchor and buoy blocks and the asymmetry of the block copolymers as expressed by the anchor fraction $\nu_a = N_{anchor}/(N_{anchor} + N_{buoy})$, where N is the number of monomer units in the respective blocks. The radius of gyration, R_g, of the PCL chains was estimated from $R_g = b \times M_n^{1/2}$, with $b = 0.031$ nm (as calculated from reported data of intrinsic viscosity under theta conditions and using a Flory universal constant of 2.5×10^{21}).[32,33] The length of the stabilizing PCL chains, when adsorbed onto the TiO_2 pigment surface, can be approximated by $2 \times R_g$.[4] Γ_{max} represents the maximum adsorbed amount of the dispersants onto the TiO_2 pigments, as will be discussed.

Figure 7 shows typical adsorption isotherms of the P2VP-*b*-PCL copolymers. In this figure, the adsorbed amount, Γ, is plotted as a function of the equilibrium concentration, i.e., the concentration of the nonadsorbed block copolymer in the supernatant after centrifugation. As can be seen, a rapid increase of the adsorbed amount is observed, which indicates the high affinity of the dispersants for the TiO_2 pigments. The adsorption behavior, as shown in *Figure* 7 for dispersants 2 and 3, was similar for all four dispersants. The plateau value, Γ_{max}, which represents the adsorption at maximum surface coverage,[34] was reached at a block copolymer concentration of ca. 1.5-2 wt% with respect to the pigment for all four dispersants. The values of Γ_{max} are included in *Table* 3. For optimal performance of the dispersants, the pigment surface should be covered completely with dispersant and the adsorption density of the stabilizing chains (i.e., the number of stabilizing chains per unit pigment surface area) should be high enough.[34,35] The adsorption density of the stabilizing chains depends on the ratio of the anchor and buoy block lengths (i.e., ν_a) and the adsorbed amount. In general, the lower the ν_a, the higher the adsorption density.[4]



(a)



(b)

Figure 8—Typical scanning electron micrographs of dispersions of TiO_2, pretreated with (a) 0.5 wt% and (b) 2.5 wt% of dispersant 2, after heating to 200°C for 10 min.

Influence of Preadsorbed Dispersants on Coating Properties

In the following sections, the influence of the dispersants on the coating properties is presented. One way to make sure that the block copolymers are anchored to the pigment surface is to bring the pigments into contact with the block copolymers in solution prior to extrusion. The results obtained by this method are discussed in this section.

The dispersants 1, 2, and 3 were used at three concentrations, 0.5 wt%, 1.5 wt%, and 2.5 wt% with respect to pigment. In this way, the surface coverage was varied. Dispersant 4 was used at 1.5 wt% only. The dry blends were prepared with the resin flakes and the coatings were placed in the oven for 10 min at 200 and 240°C.

Similar to what was found with the preblending experiments, the overall distribution of the pigments at the

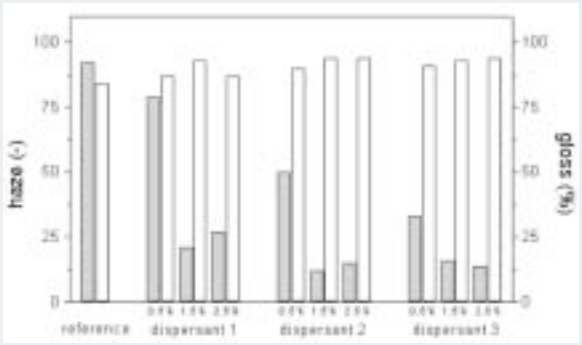


Figure 9—Gloss (open bars) and haze (filled bars) of coatings, heated to 200 °C for 10 min, with TiO_2 pretreated with dispersants 1, 2, and 3 at concentrations of 0.5 wt% (left bars), 1.5 wt% (middle bars), and 2.5 wt% (right bars). Gloss was measured at 20°.

coating surface was inhomogeneous, as a result of poor mixing due to the large resin flakes. This confirms our initial findings that the block copolymer dispersants do not influence the dispersive and distributive mixing of the pigments during extrusion under the present experimental conditions.[8]

The dispersions of the pigments that were pretreated with 0.5 wt% of block copolymer appeared to be slightly flocculated (see *Figure* 8). As concluded from the adsorption isotherms, the surface is not fully covered with block copolymer at this concentration, which explains the flocculation. The flocculation with dispersant 1 appears more pronounced than with dispersant 3. Because dispersant 3 has a much lower value of ν_a than dispersant 1, the adsorption density of the stabilizing PCL chains at 0.5 wt% is expected to be higher for dispersant 3 than for dispersant 1 and may, in fact, be close to the maximum adsorption density, which is necessary to completely prevent flocculation.[35] The pigments that were pretreated with 1.5 and 2.5 wt% block copolymer did not flocculate at all, as was expected on the basis of the adsorption isotherms. At these concentrations, the pigment surface is fully covered with dispersants.

The addition of the dispersants significantly increased the gloss and reduced the haze of the coatings, as shown in *Figure* 9. The effects were most pronounced at dispersant concentrations of 1.5 wt% and 2.5 wt%, which is in full agreement with the observed enhanced colloidal stability of the pigment dispersions at these concentrations. The results of the gloss/haze measurements with dispersants at a concentration of 1.5 wt% and after 10 min heating at 200°C are shown in *Table* 4.

Because of the improved colloidal stability, the elastic modulus G' of the dispersions was found to remain constant in time, as shown in *Figure* 10, indicating that the formation of a pigment network is prevented. Furthermore, the possible catalyzing effect of the TiO_2 pigments on the formation of the hybrid network as proposed in *Figure* 6 was also prevented. Consequently, the leveling of the coatings was not retarded, giving rise to lower values of waviness, as listed in *Table* 4.

Table 4—Values of the 20° Gloss and Haze and the Long-Term (L) and Short-Term (S) Waviness of Coatings with 30 wt% TiO_2, Pretreated with 1.5 wt% of Dispersant, after 10 Min Heating to 200°C

Dispersant	Gloss (%)	Haze (-)	Waviness (L/S)
—	84	92	64/67
1	93	21	22/15
2	93	16	17/1 2
3	94	12	14/13
4	95	11	31/27

Influence of Dispersant Resin Premixing on Coating Properties

In the previous section, it was shown that the dispersants prevented pigment flocculation when adsorbed onto the pigment surface at concentrations ≥ 1.5 wt%. In the following experiments, the block copolymer dispersants were first extruded through the resin and in a second step mixed with the other components and extruded again. Therefore, the dispersants have to diffuse to the pigments during extrusion through the viscous resin melt in order to adsorb onto the TiO_2 surface. Dispersants 1, 3, and 4 were tested in two concentrations: 1.5 and 2.5 wt%. The resin/dispersant premixes were ground prior to the second extrusion step.

Results similar were obtained for the preadsorbed dispersants. No pigment flocculation had occurred in the coatings at either dispersant concentration. As a consequence, the elastic modulus and the viscosity of the dispersions remained constant in time while the leveling of the coating surfaces remained undisturbed. As shown in *Table* 5, the coatings displayed excellent gloss and extremely low haze values at both 200 and 240°C.

The absence of pigment flocculation indicates that the block copolymers had indeed moved to the pigments during extrusion, by diffusion and convection, and had completely covered the pigment surface. In the present system, the diffusion of the block copolymer dispersants can be approximated by the Stokes-Einstein equation.[36] This is schematically shown in *Figure* 11. The distance, 2L, between two pigment primary particles, used at a concentration of 30 wt% (= 11 vol%) was estimated to be 178 nm.[37] The maximum distance, L, for a block copolymer molecule to diffuse in order to reach a TiO_2 particle, therefore, is half this value, i.e., L = 89 nm. The values for the time, t, necessary to diffuse over this distance, assuming Stokesian friction, can be calculated by the equation shown in *Figure* 11. The radius of gyration, R_g, was estimated in the same manner as done earlier, based on the number-averaged molecular weight, M_n, of the total block copolymer. The viscosity of the polyester resin at 120°C was taken (η =

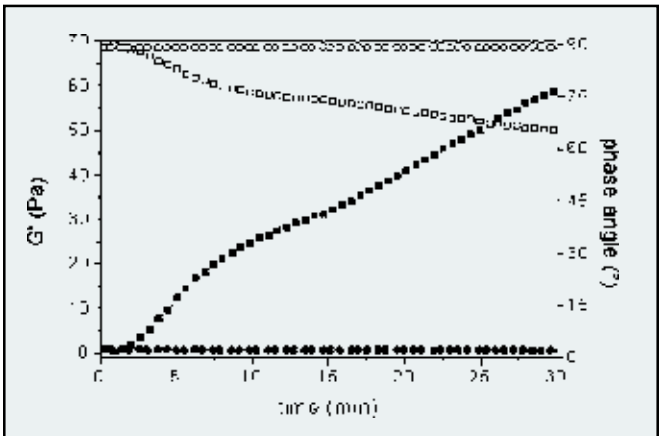


Figure 10—Plot of the elastic modulus G' (filled symbols) and the phase angle (open symbols) vs. time for dispersions of TiO_2 pretreated with 1.5 wt% of dispersant 1 (circles) and without dispersant (squares) at 200°C.

Table 5—Values of the 20° Gloss and Haze of Coatings Containing 30 wt% TiO_2, with 1.5 and 2.5 wt% of Dispersant Premixed Through the Resin, after 10 Min Heating to 200 and 240°C

Dispersant	Concentration	Gloss (%) 200°C	Haze (-) 200°C	Gloss (%) 240°C	Haze (-) 240°C
—	—	91	17	90	26
1	1.5 wt%	93	13	92	16
	2.5 wt%	93	13	92	13
2	1.5 wt%	94	12	94	7
	2.5 wt%	94	11	94	8
4	1.5 wt%	94	11	94	8
	2.5 wt%	94	9	94	9

1700 Pa s).[12] The calculated values for the diffusion coefficient, D, and the time for diffusion, t, are listed in *Table* 6.

As can be seen, the estimated time for pure diffusion is larger than the mean residence time of the coating material in the extruder (ca. 20 seconds). However, the influence of convective transport, which takes place during actual extrusion, has not been taken into account in these calculations. Due to this convection, presumably only a thin effective stagnant diffusive boundary layer remains, which will dramatically reduce the effective diffusion distance, L. Considering the number of revolutions of the screw within the residence time (about 60 times), a fairly safe estimation of the reduction factor is 10, leading to a reduction of the diffusion times by a factor of 100, which gives effective diffusion times that are in good agreement with our observations.

Influence of Block Copolymer Composition on Steric Stabilization

The results presented here do not indicate an unambiguous influence of the buoy block length or the anchor/buoy block length ratio on the steric stabilization by the dispersants. On the basis of theory, the efficiency of the steric stabilization by a block copolymer dispersant depends on the thickness of the steric layer and on the

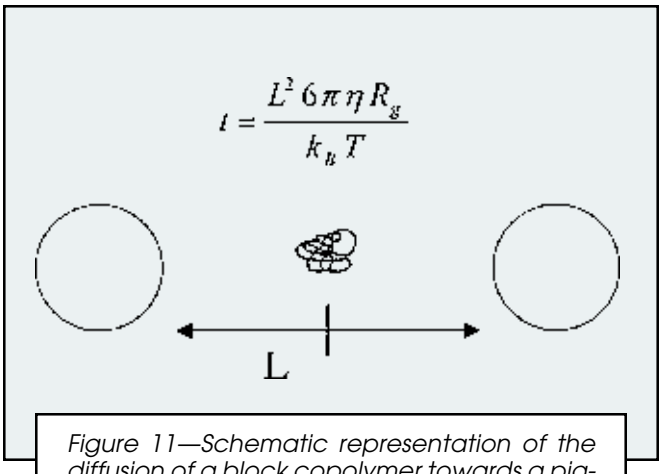


Figure 11—Schematic representation of the diffusion of a block copolymer towards a pigment surface, described by the Stokes-Einstein equation.[36]

Table 6—Calculated Values for the Time of Diffusion of Dispersants Towards Pigment Surface During Extrusion at 120°C

Dispersant	R_g (nm)	D^a (10^{-17} m^2/sec)	t (sec)
1	2.3	7.3	109
3	2.3	7.4	107
4	3.0	5.7	140

(a) parameters: T = 393 K, η = 1700 Pa sec.[12]

adsorption density of the stabilizing chains at full pigment surface coverage.[3,4] It is beyond the scope of this paper to give a detailed review of this theory. The interested reader is referred to the literature.

The adsorption density of the stabilizing chains is proportional to the ratio of the projected areas of the anchor and buoy blocks when adsorbed onto a pigment, which (in a first approximation) correlates to ν_a. The steric layer thickness is proportional to the molecular weight of the buoy block and the adsorption density of the stabilizing chains. When the neighboring stabilizing chains do not overlap when adsorbed onto a pigment surface, the stabilizing chains will not stretch and the steric layer thickness can be approximated by $2 \times R_g$.[4] On the other hand, when the neighboring adsorbed buoy chains do overlap, they will stretch and the steric layer thickness will consequently be larger. For the dispersants used here, the radii of the occupied areas of the P2VP blocks (as estimated from the adsorbed amounts Γ)[4,38] and the gyration radii of the PCL chains are close to unity, and stretching of the PCL chains is not expected. Therefore, dispersant 1, having the shortest buoy block and the lowest PCL-chain adsorption density (highest value of ν_a), is expected to have the lowest efficiency, whereas dispersant 4 is expected to display the best performance. At incomplete surface coverage (concentration < 1.5 wt% of dispersant with respect to TiO_2), dispersant 1 indeed seemed to be the least efficient, which may be explained by the extremely low PCL adsorption density. However, at full surface coverage the observed differences in pigment dispersion and steric stabilization were negligible. This indicates that a steric layer thickness of 2.4-5.0 nm is already sufficient for obtaining steric stabilization of the dispersions, which is lower than typically reported in literature for dispersions in solvents.[1,2]

CONCLUSIONS

In this paper, the use of four block copolymers with a poly(2-vinylpyridine) anchor block and a poly(ε-caprolactone) buoy block as dispersants for TiO_2 pigments in a polyester coating resin has been described, and the influence on the properties of the coatings was studied. The block copolymer dispersants were found to improve the colloidal stability of the TiO_2 dispersions, which resulted in coatings with higher gloss, significantly lower haze values, and improved surface leveling. The amount

of dispersant needed for optimal performance was in excellent agreement with the amount of dispersant necessary to fully cover the pigment's surface, as obtained from adsorption studies. The dispersants did not need to be preadsorbed onto the TiO_2 surface prior to extrusion.

Under the experimental conditions used here, the distribution of the pigments through the powder coating resin was primarily influenced by the homogeneity of the dry blend. When the resin was used in the form of flakes, pigment-rich and pigment-poor regions were observed in the final coatings, which caused a lowering of the gloss and an increase of the haze. The block copolymer dispersants had no effect on the pigment distribution during extrusion. The differences among the four block copolymers were too small to observe a clear correlation between the length of the PCL layer or the anchor/buoy block length ratio and the performance of the block copolymers, as expected from theory. The results indicated that a steric layer thickness of 2.4-5.0 nm was already sufficient to impart steric stability.

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References

(1) Napper, D.H., *Polymeric Stabilization of Colloidal Dispersions*, Academic Press, London, 1983.
(2) Jakubauskas, H.L., "Use of A-B Block Copolymers as Dispersants for Non-Aqueous Coating Systems," JOURNAL OF COATINGS TECHNOLOGY, *58*, No. 736, 71 (1986).
(3) Tadros, Th.F., "Steric Stabilisation and Flocculation by Polymers," *Polym. J.*, 23, 683 (1991).
(4) Fleer, G.J., Cohen Stuart, M.A., Scheutjens, J.M.H.M., Cosgrove, T., and Vincent, B., *Polymers at Interfaces*, Chapman & Hall, London, 1993.
(5) Misev, T.A., *Powder Coatings, Chemistry and Technology*, John Wiley & Sons, Chichester, 1991.
(6) Manas-Zloczower, I., Nir, A., and Tadmor, Z., "Dispersive Mixing in Rubber and Plastics," *Rubber Chem. Technol.*, 57, 583 (1984).
(7) Scott, J.A. and Walters, J.T., "Residence Time Distribution Modelling for Co-rotating Twin Screw Extrusion of Thermoset Powder Coatings," *Trans. Inst. Eng.: Chem. Eng. Res. Design*, 73, 27 (1995).
(8) Duivenvoorde, F.L., van Nostrum, C.F., Laven, J., and van der Linde, R., "Improving Pigment Dispersing in Powder Coatings with Block Copolymer Dispersants," JOURNAL OF COATINGS TECHNOLOGY, *72*, No. 909, 145 (2000).
(9) Vos, L.J. and Erkens, L.J.H., "Pigment Preparations for Powder Coatings," *Mod. Paint Coat.*, 88, No. 4, 25 (1998).
(10) Lewis, P.A., "Predisol PC Organic Pigment Pre-dispersions, Their Use in Powder Coatings," *Mod. Paint Coat.*, 89, No. 6, 31 (1999).
(11) Duivenvoorde, F.L., van Es, J.J.G.S., van Nostrum, C.F., and van der Linde, R., "Novel Block Copolymers of 2-Vinylpyridine and ε-Caprolactone: Synthesis and Characterization," *Macromol. Chem. Phys.*, 201, 656 (2000).
(12) Duivenvoorde, F.L., van Nostrum, C.F., and van der Linde, R., "The Pigmentation of Powder Coatings with the Use of Block Copolymer Dispersants," *Prog. Org. Coat.*, 36, 225 (1999).
(13) Wu, D.T., Yokoyama, A., and Setterquist, R.L., "An Experimental Study on the Effect of Adsorbing and Non-Adsorbing Block Sizes on Diblock Copolymer Adsorption," *Polym. J.*, 23, 709 (1991).
(14) Horiuchi, S., Kajita, T., and Tachibana, T., "Preparation of Pigment-Polymer Hybrid Particles for Plastic Colorants by Dry-Impact Blending Method," *J. Appl. Polym. Sci.*, 74, 1762 (1999).
(15) Smith, M.J., "Some Physical Properties of Pigments and Their Importance in Relation to Dispersion in Plastics," *J. Oil Col. Chem. Assoc.*, 57, 36 (1974).
(16) Thometzek, P., Basten, H., Bütje, K., and Köhler, K., "Ein Maßgeschneidertes TiO_2 für Hybrid-Pulverlacke," *Farbe & Lack*, 103, No. 5, 91 (1997).
(17) Russel, W.B., Saville, D.A., and Schowalter, W.R., *Colloidal Dispersions*, Cambridge University Press, Cambridge, 1989.
(18) Carreau, P.J., Lavoie, P.-A., and Bagassi, M., "Rheological Properties of Filled Polymers," *Macromol. Symp.*, 108, 111 (1996).
(19) Cai, J.J. and Salovey, R., "Model Filled Rubber. II. Particle Composition Dependence of Suspension Rheology," *J. Polym. Sci. B: Polym. Phys.*, 37, 815 (1999).
(20) Vieweg, S., Unger, R., Heinrich, G., and Donth, E., "Comparison of Dynamic Shear Properties of Styrene-Butadiene Vulcanizates Filled with Carbon Black or Polymeric Fillers," *J. Appl. Polym. Sci.*, 73, 495 (1999).
(21) Wang, M.-J., "Effect of Polymer-Filler and Filler-Filler Interactions on Dynamic Properties of Filled Vulcanizates," *Rubber Chem. Technol.*, *71*, 520 (1998).
(22) Maier, P.G. and Goritz, D., "Molecular Interpretation of the Payne Effect," *Kautschuk Gummi Kunststoffe*, 49, No. 1, 18 (1996).
(23) Solomon, D.H. and Hawthorne, D.G., *Chemistry of Pigments and Fillers*, Wiley-Interscience, Chichester, 1983.
(24) Bennett, H.E. and Porteus, O.J., "Relation between Surface Roughness and Specular Reflectance at Normal Incidence," *J. Opt. Soc. Am.*, 51, 123 (1961).
(25) Simpson, L.A., "Factors Controlling Gloss of Paints," *Prog. Org. Coat.*, 6, 1 (1978).
(26) Toporets, A.S., "Specular Reflection from a Rough Surface," *Opt. Spectroscopy*, 16, 54 (1964).
(27) Jenkins, F.A. and White, H.E., *Fundamentals of Optics*, McGraw-Hill, New York, 1957.
(28) Hansen, C.M., "Quantitative Evaluation of Leveling by Surface Waviness Measurements," *Ind. Chem. Eng. Prod. Res. Develop.*, 11, 426 (1972).
(29) Uhlmann, P., Wulf, M., Michel, S., Grundke, K., and Juckel, H., "Filmbildung von Pulverlacken," *Farbe & Lack*, 105, No. 12, 50 (1999).
(30) Orchard, S.E., "On Surface Levelling in Viscous Liquids and Gels," *Appl. Sci. Res.*, A11, 451 (1961).
(31) De Lange, P.G., "Film Formation and Rheology of Powder Coatings," JOURNAL OF COATINGS TECHNOLOGY, *56*, No. 717, 23 (1984).
(32) Brode, G.L. and Koleske, J.V., "Lactone Polymerization and Polymer Properties," *J. Macromol. Sci. Chem.*, A6, 1109 (1972).
(33) Flory, P.J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
(34) Sato, T. and Ruch, R., *Stabilization of Colloidal Dispersions by Polymer Adsorption*, Dekker, New York, 1980.
(35) Hasegawa, R., Aoki, Y., and Doi, M., "Optimum Graft Density for Dispersing Particles in Polymer Melts," *Macromolecules*, 29, 6656 (1996).
(36) Hiemenz, P.C. and Rajagopalan, R., *Principles of Colloid and Surface Chemistry*, Marcel Dekker, New York, 1997.
(37) Horwatt, S.W., Rwei, S.-P., and Manas-Zloczower, I., "The Influence of Interstitial Liquids on the Cohesive Strength of Carbon-Black Agglomerates," *Rubber Chem. Technol.*, 62, 928 (1989).
(38) Lambert, O., Jada, A., and Dumas, P., "Adsorption of Triarm Starblock Copolymers Based on Polystyrene, Poly(Ethylene Oxide) and Poly(ε-Caprolactone) at the Solid-Solution Interface," *Colloids Surf. A: Physicochem. Eng. Aspects*, 136, 263 (1998).