The Use of Comb-Branched Copolymers as Pigment Dispersants

Steven A. Schwartz, Sallie J. Lee and Adam Chan
Lyondell Chemical Company
Newtown Square, Pennsylvania

Abstract

Pigmented coating compositions are used in a wide variety of applications including paints, inks, and inkjet inks. For inkjet inks in particular, the trend towards both inorganic and organic pigments has been driven by the need to produce more lightfast images with improved durability and water resistance. A challenge with using pigments is achieving stable, fine-particle pigment dispersions. This is especially the case for aqueous pigment dispersions. Thus, it is desirable that a dispersant is optimized to effectively wet, disperse and stabilize pigments during the milling process. These objectives can be met by using a dispersant comprising an acrylic/polyether comb-branched polymer. We will review the sensitivities of pigment dispersion processing and properties to variations in the composition and molecular distributions of comb-branched copolymeric dispersants. The influence of these variations on end use performance for several applications will be reviewed. Inkjet ink performance, in particular, will be emphasized.

Introduction

The maximum utilization of pigments in inks and coatings is critical to cost-effective product performance. The ability to efficiently deliver maximum optical properties (e.g. color strength) relies on effective preparation of pigment dispersions. This can be achieved via the rapid reduction of pigment agglomerates to primary particles through media milling of a pigment dispersion and then combining this color concentrate with a letdown masterbatch which may include binder resins or other additives to affect surface tension, viscosity, humectancy, etc. Stable, concentrated dispersions with small particles and narrow particle size distributions provide the potential for intense color strength per unit mass of pigment. The more intense the color strength, the lower the volume of color concentrate that may be required to achieve the desired optical effects.

Dry pigments are available commercially in the form of solid agglomerates. By definition, they are insoluble in their carrier medium, be it aqueous or solvent-based. Without appropriate dispersion techniques, pigment agglomerates may settle out of pigment dispersions and/or the final pigmented coating composition. Dispersion techniques typically include a media milling/grinding process in which the pigment agglomerates are broken down into smaller agglomerates and/or individual particles which are wetted by the carrier medium. Pigment dispersants are provided in the pigment dispersion to facilitate the wetting process. In addition, they are important to the suspension and homogeneous dispersion of the pigment particles in the carrier medium as they are being milled and subsequently during storage. The function of the pigment dispersant is to therefore wet, disperse, and stabilize the pigment dispersion in its carrier solvent and to maintain stable particle distributions in the finished letdown formulation.

A particularly challenging application for pigments is in inkjet inks. While dyes have been successfully formulated into inkjet inks with reliable printhead performance and excellent optical properties, image deficiencies have been experienced with respect to durability, water resistance, and lightfastness. As a result, the technology is trending towards the development of pigmented inkjet inks. A challenge to using pigments is to stabilize a fine particle size distribution. Otherwise, particle agglomeration can lead to degradation of properties or even catastrophic failures in the small channels and nozzle orifices of an inkjet printhead. Moreover, it is important to control rheology, maintain high filterability, and develop appropriate surface tension. Thus, compatibility between the stabilized pigment concentrate and other inkjet ink ingredients (humectants, surfactants, cosolvents) is critical.

Mechanical and chemical approaches to stabilization of pigment dispersions are practiced. A common approach is through the use of polymeric dispersants. This report highlights the properties of aqueous pigment dispersions unique polyether/acrylic comb-branched copolymers.

Dispersion

We consider the case where the dispersion medium is mainly water. Water-insoluble pigments like organic pigments or carbon black are mechanically milled to produce a hydrophobic colloid. The dispersant assists with multiple functions that occur simultaneously: wetting, dispersion, and stabilization (against particle agglomeration).[1] Wetting involves preferential replacement of gases, liquids, or other contaminants from the pigment surfaces with molecules comprising the aqueous medium. In this process, the dispersant may function as a surfactant

by reducing the contact angle at the pigment surface. The dispersion process, by media milling for example, includes mechanical action and consequent particle size reduction to create new pigment surfaces that require wetting which is aided by the dispersant polymer. As the total pigment surface area increases, the volume concentration of free water decreases, the viscosity increases, and the tendency of pigment particles to agglomerate increases. This leads to the most critical function of the dispersant copolymer – stabilization. The colloidal particles are under the influence of attractive and repulsive forces. The magnitudes of these forces determine the stability. Stabilization requires complete wetting and separation of the primary pigment particles, their homogeneous distribution in the medium, and the prevention of pigment particle flocculation and/or aggregation. The dispersant polymer acts by adsorbing onto the particle surfaces, encapsulating the pigments and thereby providing a barrier against particle association.

Stabilization may be electrostatic and/or steric. Electrostatic stabilization[2] is a result of preferential adsorption of the charged dispersant molecules onto the surface of the pigment particle and the thickening of the charge layer within the immediately surrounding medium. The dispersant therefore influences the magnitude and shape of the repulsive electronic potential energy as a function of interparticle separation. The magnitude of the electronic potential is also a function of the ionic character of the medium. Therefore, charge-stabilized colloids are vulnerable to variations in pH, electrolyte concentrations, and are less effective in systems containing mixed pigments with different zeta potentials.

Steric[3] stabilization is a result of a comb or block copolymer dispersant structure in which one functional moiety ("anchoring group") has a strong affinity for the pigment surface and extending into the solvent from the anchoring group are solvated polymeric stabilizer chains ("pendant groups") that prevent the pigment particles from associating. Steric stabilization is due to configurational restrictions of the solvated pendant groups as interparticle distance decreases. Solvated chains lose their degrees of freedom as particles approach leading to a decrease in entropy. Therefore, the driving force to overcome this entropy change is repulsive. Steric stabilization is insensitve to electrolytic environment.

Acrylic/Polyether Comb-Branched Copolymers

The acrylic/polyether comb-branched copolymer dispersants which are the subject of this paper are water soluble or water dispersible comb-branched copolymers with a basic structure represented in Figure 1. Both electrostatic and steric mechanisms contribute to the development of stabilized pigment dispersions. Electrostatic stabilization is dependent upon the formation of a repulsive charged double layer potential due to the acrylate "anchor" groups on the backbone of the comb-copolymer. Extending into the solvent from these anchor groups are pendant polyether macromonomers. Steric stabilization is related to

configurational restrictions of these pendant chains as particle surfaces approach each other. Thermodynamically, the free energy of the system increases as the particles approach one another (increase in ΔG due to decrease in ΔS), which provides the energy of repulsion.
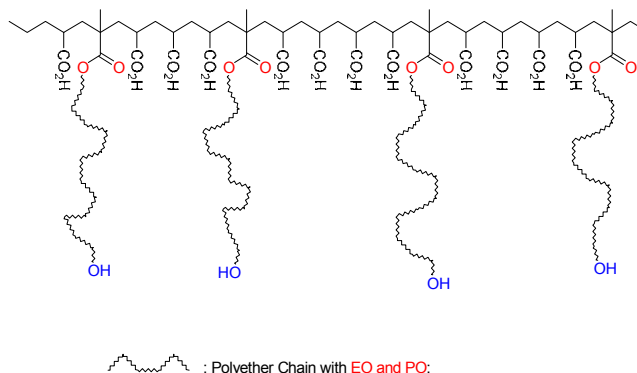

Figure 1. General Structure for Comb-Branched Copolymer

The copolymer as shown in Figure 1 is composed of acrylic acid and polyether macromonomer units. Other ethylenically unsaturated comonomers and macromonomers may be incorporated into the structure. Other possible structural variations include the density of the polyether pendant group in the molecule and its solubility. This latter property is a result of the molecular weight and the level and type of alkoxylation. In addition, the molecular weight and polydispersity of the polyether/acrylic comb-branch copolymer is a controllable property. A high degree of structural flexibility for the copolymer allows for optimization as a function of the pigment type, the carrier medium, and the final application.

Results and Discussion

Aqueous Phthalo Blue Pigment Dispersions

Aqueous dispersions of phthalocyanine blue pigment (CI 15:3) containing acrylic/polyether comb-branched copolymer dispersant were milled in a small media mill (Netzsch Minizeta) for 60 minutes using a 200 ml charge of 0.800 to 1.000 mm zirconium/silica beads. A premix was first produced by mixing the materials on a high-shear blade disperser to produce a homogeneous mixture before transferring to the mill. A series of dispersions were made using 40 wt. % pigment and a range of dispersant concentrations. Figure 2 illustrates the effect of dispersant concentration on particle size. The optimum level of dispersant is indicated by the minimum in the average particle size as shown in the figure. This level of dispersant also corresponds to the most narrow and monodisperse particle size distribution.

Rheological flow curves were obtained for the dispersions represented in Figure 2. The viscosity of the dispersions over a range of shear rates is illustrated in Figure 3. Non-Newtonian (shear thinning) rheology and

elevated viscosity is evidence of flocculation instability above and below the optimum dispersant concentration. At the optimum dosage, Newtonian flow behavior indicates a stable dispersion. Flocculation instability at low dispersant concentrations (below 17 wt. %) is due to pigment agglomeration. At dispersant overdoses, flocculation is due to interparticle bridging via the pendant polyether groups of the acrylic/polyether comb-branched copolymer.
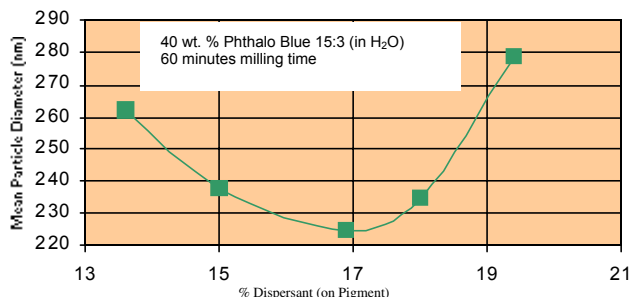

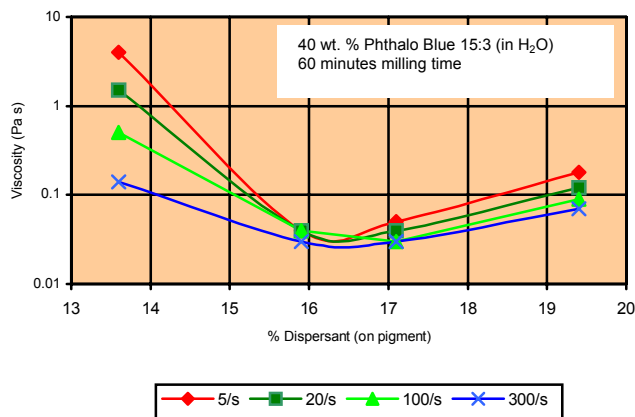*Figure 2. Particle Size vs. Dispersant Concentration*

Figure 3. Viscosity vs. Dispersant Concentration at Varying Shear Rates

Maximum optical properties are derived from optimally stabilized pigment dispersions. Figure 4 shows the depths of shade that were obtained by adding the aqueous pigment dispersions described by Figure 2 to a white tint base and measuring the reflectance of the dried films in CIELAB L* (Commission Internationale D'Eclairage 1976 L* a* b*). The data shows two important results of effective pigment dispersion. First, the improvement in color strength (reduction in L*) with milling time indicates that efficient particle size reduction is occurring. Second, the most efficient color development rate occurs at the optimum dispersant dosage (~17 wt. %) that is deduced from Figures 2 and 3.
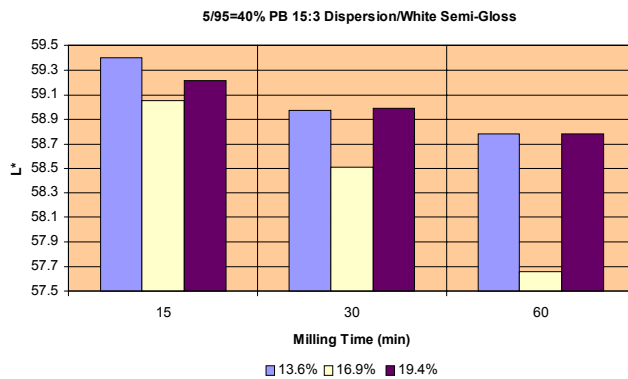

Figure 4. Color Strength vs. Milling Time at Different Dispersant Dosages (wt. of dispersant on wt. of pigment)

It was previously stated that the ability to modulate the structure and distributions of the acrylic/polyether comb-branched copolymer allows optimization. An example of this feature is shown in Figure 5. Color strength is shown for two dispersions. By optimizing the molecular weight of the copolymer and increasing the density of pendant groups along the chain backbone (Dispersant B), darker shade (lower L*) is achieved. In addition, the optimum dosage level for Dispersant B is lower, and this indicates more efficient stabilization.
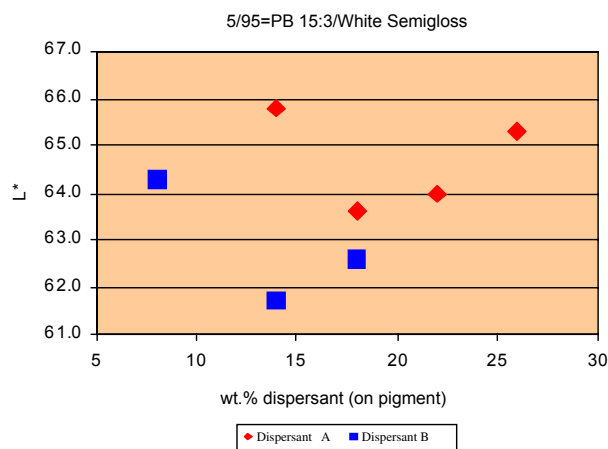

Figure 5. Color Strength vs. Dispersant Dosage

Aqueous Carbon Black Pigment Dispersions for Inkjet Inks

Aqueous dispersions of carbon black (low structure, 254 m^2/g) were milled using a 50 ml capacity horizontal bead mill (Eigermill M50) charged with 35 ml of zirconium silicate beads for 40 minutes at 3000 rpm. A pre-mix was first produced on a high shear blade stirrer to produce a homogeneous mixture before transferring to the mill.

The testing of each dispersant/pigment combination consisted of making a series of dispersions with fixed pigment loading (10 and 15 wt. %) and varying the level of

dispersant. All dispersant levels are expressed as percent solids on pigment. Viscosities were used initially to find the optimum dispersant level – a minimum viscosity corresponding to the optimum level. Sedimentometry testing was then carried out to confirm the optimum level and characterize the effect of the dispersant on stability. Material contained in a sample tube was placed vertically in the apparatus and a near infrared light beam was scanned along the tube taking transmission and backscattering readings at 40 micron intervals. Any particle size variations will increase or decrease the amount of backscatter along the whole length of the sample tube. Repeat scans of a sample over time will show particle migration and any particle size variation (coagulation, re-flocculation). Particle migration/settling appears as a stepwise pattern due to an increase or decrease in backscatter where clarification has occurred. The sample meniscus can be seen as a drop in backscatter.

In general, it was found that at below optimum levels some pigment settlement occurred. At the optimum level, there were less (or no) pigment settlement or particle size changes. Above optimum levels there was no improvement in the amount of settlement and the excess dispersant resulted in bridging flocculation (viscosity and particle size increases).

The ability to control the structure and distributions of the acrylic/polyether comb-branched copolymer affects the sensitivity of the dispersion rheology to dispersant loading. Table 1 summarizes the optimum dispersant loadings and the viscosities of 10 wt. % pigment dispersions at these loadings. Differences in the viscosity vs. % dispersant profiles were also observed for the different copolymer dispersants. All curves showed sharp reduction in viscosity with increasing dispersant approaching the optimum loading. With increasing dispersant dosage above the optimum, different rates of viscosity increase indicated different strengths of particle interaction. The shape of the viscosity/demand curves for Dispersants B and C suggest significant particle interaction (bridging flocculation) at the higher levels. This is consistent with the fact that those dispersants have higher molecular weight than Dispersants A and D. It is interesting that Dispersants B and C are more efficient stabilizers. It is also noteworthy that Dispersant B is the same composition that demonstrated good dosage efficiency in Figure 5.

Table 1. Optimum Dispersant Loadings for Aqueous Carbon Black Dispersions

Dispersant	Optimum Loading (wt. % dispersant on pigment)	Viscosity, cPs, (25°C)
A	15.0	1.87
B	12.5	2.02
C	12.5	2.58
D	17.5	1.78

Aqueous Carbon Black Pigmented Inkjet Inks

The formulation of ink-jet inks from the dispersions consisted of letting down with water and adding various co-solvents, humectants, and ink additives such as surfactants and defoamers. These materials can strongly influence the stability of the pigments through either chemical and/or physical effects. Compatibility with a range of co-solvents/humectants and additives was first assessed by addition of each material individually and characterization of the physical properties. Based on the compatibility testing a range of ink-jet inks were formulated and their stability and physical properties were characterized.

Three different inkjet inks were prepared from an aqueous carbon black dispersion based on the acrylic/polyether comb-branched dispersant. (See Table 2.) The inks demonstrated suitable physical properties (viscosity, surface tension, filterability) for printing and have the same if not better stability (based on sedimentometry) as the dispersions.

Table 2. Pigmented Carbon Black (5.25 wt. % Pigment) Inkjet Ink Formulations

Raw Material	% Composition (w/w)		
	Ink A	Ink B	Ink C
Aqueous Pigment Dispersion	52.5	52.5	52.5
Water	30.3	27.3	25.3
Ethylene Glycol	15	10	14
Glycerol	-	-	6
2-Pyrrolidinone	2	2	2
2-methyl-2,4-pentanediol	-	8	-
Tego Flow 425	0.2	0.2	0.2
Filtration Test, s (15ml through 1μm)	16.4	19.2	18.9
Viscosity, cPs (25°C)	2.43	3.03	2.81
Surface Tension, dynes/cm	35.0	34.0	36.0

Printer Trials of Aqueous Carbon Black Pigmented Inkjet Inks

Inks were loaded and printed through an ink jet print head. The Ink A formulation (Table 2) was slightly modified to produce an ink based on the acrylic/polyether comb-branched copolymer dispersant that performed well in the thermal inkjet printer (HP 720C) used for testing. The adjusted formulation is given in Table 3.

Testing conducted on this ink included cartridge loading, ease of priming, and printing of multiple pages of solid color to assess the continuous ability of the ink to fire. This testing would highlight any common failures such as faceplate wetting, starvation or kogation. Decap/dwell/

recoverability studies were also carried out. Image quality analysis equipment and a droplet imaging system were used to help study the inkjet printing properties and performance. Wetfastness and long-term stability of the ink were also assessed.

After loading the cartridge and inserting it into the printer, the ink worked immediately on all nozzles. The ease of loading indicated good wetting of the ink path inside the print head.

Table 3. Pigmented Carbon Black (2.0 wt. % Pigment) Thermal Inkjet Ink Formulation

Raw Material	% Composition (w/w)
Aqueous Pigment Dispersion	13.33
Water	69.27
Ethylene Glycol	15
2-Pyrrolidinone	2
Morpholine	0.4
pH	9.50
Viscosity, cPs (25°C)	1.70
Surface Tension, dynes/cm	56.0

Ten page solid blocks were printed, which equates to about 14 ml of ink (a third of a cartridge). No nozzles were lost during the printing of ten pages, and there was no reduction in optical density from the first to tenth page. This result indicates that there is no starvation or kogation, and inspection of the faceplate also showed there to be no faceplate wetting. Analysis of image quality was also used to assess whether there was any deterioration in image quality during the lifetime of a cartridge. This was done by filling a cartridge with the ink and comparing initial images with images printed after the cartridge was almost empty. Between the initial and final images the ink was printed continuously (25 pages of solid color). There was no deterioration in print quality, which is further evidence that there is no faceplate wetting, starvation or kogation.

Dwell time depends mainly on the amount of humectant in the ink and recoverability, once the dwell time is exceeded, is an associated important parameter. Start up performance was assessed by observing print performance after overnight and over-weekend idle periods. On start up, all nozzles were active after the normal housekeeping (performed automatically by the printer) which jets ink into a waste area after being inactive for a certain period of time. The first images printed after the start-up were checked for any deterioration in print quality. The results show no

deterioration in print quality, which indicates that the ink has good dwell and recoverability performance.

A high magnification lens and camera system was used to observe the print quality of a printed image. Figure 6a and 6b below shows images of dots and lines when printed onto three different types of media. Images obtained using the OEM ink (for the HP 720C) are shown for comparison.

Waterfastness was assessed by placing a printed sample in water for a set period of time (1, 5 and 30 minutes) and measuring any decrease in optical density. No change in optical density was measured.
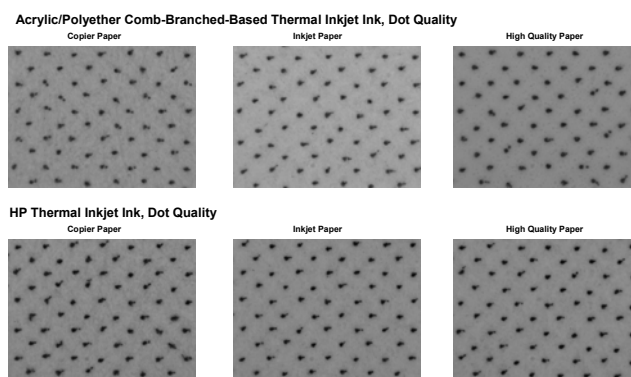

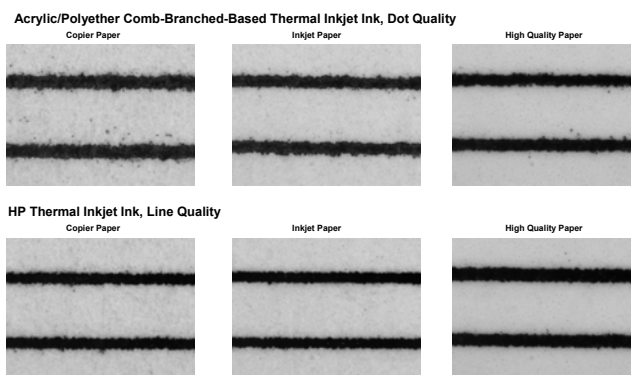*Figure 6a. Printer Trials – Dot Quality*

Figure 6b. Printer Trials – Line Quality

The longer term stability of the ink and the benchmark inks were studied by aging the inks at elevated temperature. The inks were filtered to 1μm, placed in an oven at 45°C and their physical properties and stability assessed weekly. Filtration, viscosity and surface tension were measured and their stability assessed by sedimentometry. Table 4 shows the properties before and after aging. At the weekly intervals there was no visible settling, the ink filtered easily through 1μm with no residue present, there was no change in viscosity or surface tension, and sedimentometry showed the ink to be stable.

Table 4. Pigmented Carbon Black Thermal Inkjet Ink Formulation – Long Term Stability

Time Aging at 45°C	Viscosity, cPs (25°C)	Surface tension, dynes/cm	Filtration, 1μm
Start	1.70	56.0	Good, clean filter
1 week	1.66	56.0	Good, clean filter
2 weeks	1.65	56.0	Good, clean filter
3 weeks	1.66	56.0	Good, clean filter

Summary

Many forces in coating and ink technology have driven the need for high performing pigment dispersants. The trend towards high-solids formulations and low VOC, water-based coatings requires lower molecular weight binder resins with lower functionality. Thus, high molecular weight, high functionality binder resins that were effective as grinding resins are less available. In inkjet ink printing, there has been a strong trend away from soluble dyes towards pigments based on the need to produce more lightfast images with improved durability and water resistance. In this paper, we have introduced a new dispersant technology based on versatile comb-branched copolymer structure and have demonstrated its efficacy in different pigment systems and applications. The ability to modulate copolymer composition and molecular distribution allows for optimum stabilization and performance in pigmented systems.

Acknowledgements

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Biographies

Steven A. Schwartz received his B.A. in Chemistry from the State University of New York, Binghamton in 1979 and his Ph.D. in Physical Chemistry from the University of Pennsylvania in 1984. He started his career with the Dow Chemical Company in 1984 where he studied structure-property relationships in semi-crystalline polymers. In 1988, he joined Lyondell Chemical Company (formerly ARCO Chemical Company) and has worked in a variety of polymer application technologies including thermoplastics and colloidal systems.

Sallie J. Lee received her B.S. in Biology from the Clarion University of Pennsylvania in 1986. After graduation she began work at Atlantic Refining and Marketing Corporation working as a Quality Control Technician. In 1989, she was hired by Lyondell Chemical Company (formerly ARCO Chemical Company) and has worked in various areas within Analytical Services and the Research and Development Department.

Adam Chan received his B.E. in Chemical Engineering from Stevens Institute of Technology in 1987. In 1995, he received his M.B.A. in Finance from Pace University. He started his career in 1987 with Energy Research Corporation and later joined UOP as a development and design engineer of gas separation systems. He joined Lyondell Chemical Company in 2000 and has responsibilities in business and market development for the areas of pharmaceuticals, agrochemicals, and polymer systems.