Synthesis and Characterization Of Binders

André Revillon—CNRS, LMOPS*

This paper presents an academic analysis of recent progress and changes in polymer science. These changes influence the coatings industry, as an answer to various constraints, such as enhanced applicability, quality certification, safety, and care of environment. We do not focus on a specific topic but instead consider the basic concepts, the chemical advances in polymer synthesis, and progress in fine characterization methods. Experimental results in polymerization, analysis, and new processes, obtained in recent years, in the final period of my laboratory activity, are illustrated.

INTRODUCTION

All research work originates from previous observations pointing out a problem and asking for improvement. Observations of coatings are expressed in practical terms such as lack of adhesion, yellowing, chalking, degradation, and so on. They are due to some evolution in binders, pigments, and additives. Binders are polymers, with characteristics such as molecular weight and distribution, chain structure and composition, functional groups, chains interactions and architecture, particle size, transition temperatures, and interactions with pigment and extender. A great deal of knowledge about them belongs to the general domain of polymer science, where similar observations can be made for different applications such as plastics or fibers. This science has developed numerous synthetic methods with well established characteristics, but new reactive compounds are available and new pathways for polymer synthesis have appeared. Each has its own characteristics to be studied. At the same time, progress in characterization offers new tools. Since synthesis and analysis are closely bound, each advance leads to new questions in synthesis, in a continuously fascinating challenge.

Surface coatings have a dual purpose: to protect and to decorate objects of various natures. This means using materials that can adapt to both the systems and their intended use. Chemicals for coatings must possess reactive functions for the synthesis of the binder (chain formation, crosslinking, reaction with the pigment, adhesion, and internal cohesion) and the resulting polymers must have sufficient mechanical properties. It means that coatings, which are thin films, must also have a lot of bulk properties. This was perfectly understood a long time ago, but new constraints and new problems have appeared, e.g., new supports such as plastics, new severe conditions for use (such as high temperature and speed of vehicle, as in the aeronautic industry), and long use in aggressive medium (such as with marine applications, taking care both of ecology and the effect of the environment on performance). Constraints are those of an ecological source: immediate and long-term safety, preservation of the environment, and biodegradation. It is evident that economic competition has always been a determining factor for the replacement of materials, but it appears that international regulations and ecological pressure presently are the driving force for changes and improvements. Responses are issued from new synthetic materials and new synthesis processes, as a result of progress in polymer research. Quality control of products is now measured by a variety of methods. Moreover, similarly to other industries, the paint industry has changed in line with the computing and communication revolution. Better models based on information handling lead to a better understanding of the nature of paints, both in professional expertise and basic knowledge. Alternatively, this introduces the use of new components and processes.

SYNTHESIS METHODS

Basic Concepts

Synthetic polymers for coatings are mainly obtained in two ways: (a) chain polymerization involving free radicals, since many monomers with a double bond may react by radical activation, and (b) condensation step reaction for bi- or trifunctional molecules, or addition without the elimination of a small molecule. In the first case, high polymers are readily produced. In the second case, oligomers are formed, which must react further to be transformed into polymers, since mechanical and thermal properties appear only when the molecular mass of the polymer is sufficiently high. Monomers and polymers are soluble in organic solvents, so that homogeneous bulk or solution radical polymerizations were initially preferred. The main technical advantage was that the process was easy.

Radical polymerization involves four different reactions: initiation, growth, termination, and transfer. They are distinct reactions, each with its own rate constant regulating the

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*200 Avenue Félix Faure, F-69003-Lyon, LMOPS, 69390 Vernaison on behalf of AFTPVA, France, email: arevillon@gonline.fr.

chain formation. Only very few molecules are active in the medium. In the solution homogeneous process, the conversion rate increases with the concentration of monomer, as does the polymerization degree, which favors the bulk process. The presence of a solvent may generate a transfer activity on the growing species and alter this polymerization degree. When the initiator concentration increases, the rate of polymerization also increases, but chain length decreases. Temperature has a positive effect on rate, but not on the chain length, which decreases when temperature is increased. These results are valid for initiation by thermal decomposition of peroxides or azo initiators, where the initiation reaction is very sensitive to temperature (high activation energy). This is quite different in the case of photo and radiation polymerizations. In copolymerization, several monomers are polymerized simultaneously to modulate the properties, according to the nature and the composition of the feed. Apart from these fundamental observations, practical aspects must be considered: (a) heat is evolved and must be evacuated; (b) viscosity increases considerably with conversion and molecular mass, which is energy-consuming and unfavorable for further handling operations; and (c) solvent is expensive, dangerous, and toxic.

The step-growth condensation of multifunctional reagents obeys quite different kinetic laws, since it involves one single chemical reaction and every molecule in the medium is active. The chain length increases up through the entire consumption of the terminal active functions. Side reactions may alter chain length and regularity: presence of monofunctional species, cyclization, degradation, and chain ends exchange. A variety of functions may be used of relatively low reactivity which requires a catalyst and elevated temperature for the completion of the reaction. Co-condensation is similar to the chain copolymerization. Several distinct reagents may be mixed to react simultaneously or successively.

Drastically limiting the amount of solvent by replacement with water has led to the emulsion and suspension processes. The first one has found a major application in the coatings industry and an increasing interest with the present regulations on environmental preservation. The issued latex is ready to use and the particle size is in the proper range (diameter less than one micron) for giving thin homogeneous films. The second process leads to larger size particles, which have other uses than in coatings (catalysts, exchange resins). These two heterogeneous processes follow different mechanisms; here, only the emulsion one will be considered.

One of the initial purposes of the emulsion process was the possibility of significantly (10X) and simultaneously increasing polymerization rate and molecular weight. This implies an increase in the number of active centers. This result is possible by separating and stabilizing these very reactive and labile centers. In this case, active particles are *physically* separated. We will see later that "active" species may also be *chemically* stabilized (i.e., they become "latent" species) or activated, alternatively. Additional considerations are: (a) a low and constant viscosity of the medium, (b) an easier thermal control during polymerization, and (c) a decrease in the cost, fire risks, and toxicity. Since the medium contains a variety of different species and several phases, many theories have been proposed about the mechanism for explaining kinetics observations, particle size, and molecular weight results. The simplest case is that of a fully insoluble monomer in water and a polymer soluble in its monomer.

A normal emulsion system is depicted as follows: a large fraction of the monomer is in large droplets (diameter around 1 µm), and a small part of the monomer is dispersed in the aqueous phase either as an individual soluble molecule or as small aggregates stabilized by the surfactant, called micelles (diameter around 5 nm). Various ionic and nonionic surfactants are used, besides steric ones, which are not as sensitive to electrolyte and pH effects. The initiator is in the aqueous phase: it is decomposed in active radicals by thermal activation or redox reaction. The primary radicals may add some soluble monomer molecules to form oligo-radicals and/or to enter into the micelle to give active particles. This is the first step of the polymerization—initiation or nucleation, up to a conversion of 5-10%. The second step is the growth of these particles by consumption and polymerization of the monomer contained in the large droplets. The number of particles remains constant up to 90% conversion, but their size increases. The rate of polymerization is constant during this second step. This rate (R_p) and the number of particles (N) are governed by the concentration of monomer (M), initiator (I), and surfactant (S). They are expressed by the Smith-Ewart theory:

$$R_p = k_p\,[M]\,N/2 \text{ and } N \propto [I]^{0.4}\,[S]^{0.6}$$

(k_p propagation rate constant)

Measurement of both conversion and particle size allows one to determine the number of particles. A constant number of particles and an increase in their size are observed. The values may be correlated to the concentrations. Their exponents may differ from those indicated.[1] In the classical scheme, particles are considered spherical and uniform in size.

Some deviations to the theoretical scheme may occur, such as additional nucleation by coagulation of precursor particles generating new particles and a second particle size distribution. They are of lower stability and have a slower rate of polymerization. Large aggregates may be formed by association of particles, as a result of insufficient stabilization. This leads to a broad or multimodal size distribution. Adjustments take account upon different sites for active species (generation and growth), different active zones (area or volume) for growth reaction. Many improvements to the process have been made for controlling mass and composition of copolymer, as well as for designing structured particles. For instance, it is possible to obtain core shell particles with controlled amounts of soft and hard parts (in relation to transition temperature). This allows for the improvement of mechanical and adhesive properties by adjusting the crosslinking degree and the amount of surface functional groups.[2] When industrial processes are discontinuous, the particle sizes of successive batches may differ. To correct that and obtain a constant quality, several batches are blended to deliver a uniform size distribution, corresponding to specific properties. Instead of doing physicochemical measurements (rheology, surface tension) and end use tests, light scattering (PCS) and chromatography (HDC), described further, provide a rapid diagnosis of the product validity.

To obtain a large size latex, colloids prepared in a first step are allowed to polymerize further. Successful results have been obtained with the Uggelstad method. Latexes are more or less reactive, depending on their stabilization. For instance, their change in size by swelling of carboxylated styrene-butadiene latexes has been measured according to the pH.

It is to be noted that inverse emulsion allows polymerization of water-soluble monomers, the dispersing solvent being organic (e.g., toluene). In the emulsion field, our contribution[3] was related to the study of kinetics law, particle size measurements, particles stabilization versus flocculation, and some approach of inverse emulsion.

Newer Synthesis Ways

The second way to monitor active radical species is "controlled radical polymerization," which preserves advantages of the radical process (easy conditions) and brings some characteristics of anionic systems, namely the control of molecular weight (with narrow distribution) and the possibility of obtaining block copolymers. Preliminary reports may be found in reference 4. The principle is to take advantage of reversible termination of active chains, the sleeping species being reactivated by an exchange reaction with growing radicals. The reaction is controlled by the competition between propagation and termination rates, which means the effect of the respective values of rate constants and activation energy. This is made possible by using nitroxy radicals, organometallic and metal complexes catalyzing atoms transfer (ATRP). First attempts were done with iniferters (termination and transfer agents) to realize a living radical polymerization.[5] They were followed by controlling chain length and obtaining block copolymers. This is an interesting feature for a monomer that cannot polymerize in an anionic way. The living character is proved by the continuous increase of molecular weight and a low polydispersity index ($\overline{M}_w / \overline{M}_n$). A typical system may be styrene, in the presence of benzoyl peroxide and TEMPO (4-hydroxy 2,2,6,6 tetramethyl piperidinolyoxy) at 100°C.[6] As an example of ATRP, this monomer and acrylic ones can be polymerized in the presence of a transition metal halide and 2,2′-bipyridine as ligand: the reaction is faster than previously reported (two hours instead of 10 hours).[7] The NMR examination of such a polymethylmethacrylate indicates the same microstructure as in a classical radical polymerization.

Besides the control of the chain length and composition, another improvement lies in the polymer architecture. It is known that branched structures have a lower viscosity than linear ones for the same molecular weight. Moreover, star polymers have different properties than linear ones. The idea has been to combine these observations by increasing the number of branches, their length, and their regularity. Star and comb-like polymers are obtained by deactivation of living anionic polymers on polyfunctional molecules. The same can be done for a series of reactions between a functional polymer skeleton and molecules or chains. The resulting dendrimer[8] has a compact structure, with a low viscosity and a slightly increased glass transition temperature (T_g).[9] It possesses a very high number of surface reactive sites, which may be useful for further applications (biology, catalysis). Application in coatings has already started.[10]

Another polymerization possibility[11] was initiated by group transfer polymerization (GTP). It consists of the activation of (meth)acrylic monomers by initiation with silylated compounds, after protection of the reactive entity, e.g., active H. Catalysts are Lewis acids and salts (fluoride, cyanide). Reaction is performed in organic dry solvents such as toluene, chlorobenzene, tetrahydrofuran, or dimethylformamide. Preferred temperature is 0° to 50°C in a wide range from –100°C to 120°C. Advantages are fast reaction, control of molecular weight to obtain oligomers up to polymers of 60,000 Dalton, and synthesis of block copolymers at room temperature. An alternative for silylated alkyl/aryl vinyl ethers is aldol GTP with aromatic aldehydes as initiator and Lewis acids as catalyst, in an inert solvent. The reaction is completed in some hours at room temperature; the molecular weight depends upon the monomer to initiator ratio and may vary from 20,000 to 10^5 Dalton.

One other chain process is the cationic one, which receives some practical applications with the development of radiation curing. UV or electron bombing are fast curing agents in the absence of solvent, at low temperature, with a low heat release; they allow high crosslinking degree, high chemical stability, and they are rapid. Difficulties appear at high pigment ratio and the disadvantage is its limitation to flat surfaces.

We must also mention the important improvements in catalysis for olefins isomerization, polymerization, and copolymerization which have increased the possibility of obtaining new structures in mild conditions (low temperature and pressure, extremely high ratio monomer to catalyst).

Supported Acid/Thiol Catalysts in Monomer Synthesis for Environmental Preservation

This is one example of the application of functional polymers as supported catalysts. In order to lessen environmental damage and corrosion problems, as well as to benefit from the advantages of the heterogeneous processes (easy separation of components, recycling of catalysts, and recovering of reagents), ion exchangers are used as catalysts. This part of the work is related to the attempts made to obtain acid-thiol supported polymers that may be used as solid bifunctional catalysts, active in the bisphenol A synthesis. We tested five approaches of synthesis with modified sulphonic styrene-based polymers obtained by multi-polymerization in one or several steps and derivatization. The objective is to obtain simultaneously sufficient capacity and high selectivity, by using an adequate acid/thiol ratio, and enhanced sites accessibility via an optimization of the morphology. Reactivity results compared favorably to those obtained in the homogeneous process.

The product, 2,2-Bis(4'-hydroxyphenyl) propane, known as bisphenol A (BPA), is an important starting material valuable in ignifugation materials and various polymers, namely epoxy and polycarbonates, used in coatings and plastics, respectively. It is obtained by acid catalyzed condensation of phenol (in a large excess) and acetone. Among the Bronstedt acids, hydrochloric acid is the preferred one in the homogenous process at 80°C. Chlorinated compounds are used as solvents. Unfortunately, the desired p,p′ isomer is accompanied by side products, such as o,p′ dimer and co- and spiro-dimer. An expression for the selectivity is the ratio $Q=op'/(op'+pp')$. The lower is Q, the higher is the amount of BPA isomer. Yet, the selectivity is enhanced by the action of a nucleophilic co-catalyst, which is generally a sulphur compound (organic or inorganic), preferably a thiol or a dihydroxybenzene.

Catalysts are of a strong acid type, with sulphuric groups, with a part of them being neutralized by a mercaptoamine, generally thioethanolamine (TEA). The difficulty is to simultaneously obtain a high enough acid capacity and a correct acid to thiol ratio. In spite of their interest, classical organic resins have inherent problems, such as limited thermal stability and poor mechanical properties. They also suffer from diffusion control, due to their swellability. Our approach has consisted in improving the mechanical properties and site accessibility by supporting the functional polymers on an organic optimized core. We have previously shown that active site accessibility of styrene-based networks is enhanced by functionalization of crosslinked polymers prepared in a two-step process.[12] Moreover, the possibility of the choice of a proper site environment may increase the selectivity. Difficulties are: (a) to obtain a high ratio of graft to free polymer to give a sufficiently high capacity, which favors high yield in the catalyzed reaction; and (b) to combine lipophily of supports with hydrophily of sites.

Functional polymers may be obtained either by polymerization of a functional monomer or by derivatization of a polymer; these possibilities are multiplied in the case of bifunctional products. Vinylbenzyl chloride (VBC) is largely used as a precursor, but styrene sulphonyl chloride (SSC) and potassium or sodium styrene sulphonate are other functional candidates with great possibilities. So, we have considered five pathways to obtain these styrene-based sulphonic catalysts. They are based either on the free-radical terpolymerization of two functional monomers, which are precursors of acid and thiol groups, in the presence of a crosslinker, or are modifications of a crosslinked co- or ter-polymer. This may be obtained either by free-radical post-copolymerization of one of the functional monomers or its precursor, or by reaction with a small molecule. When a thiol is present, this may be used as a tool to generate new polymer chains and modify some sites. However, its high chain transfer behavior affects chain length and polymer yield.

These various approaches have been optimized to give interesting results. Four of them, with an acid capacity in the range of 1.5-2 meq/g, led to a conversion into bisphenol A, in the range of 50% with good selectivity (Q ratio about 0.055). These results (conversion and selectivity) are better than those obtained with a commercial sulphonic resin (30% and Q, 0.16) and are almost similar to those obtained with this reference material in the presence of an added thiol (where Q is equal to 0.03, but with practical disadvantages resulting from this free thiol). Optimization concerns improvement of the capacity, control of the acid/thiol ratio, and an increase of the stability to prevent –SH departure during recycling tests.[13]

CHARACTERIZATION METHODS

We considered some methods adapted to the study relevant to coatings, where we have put some continuous development. By characterization we mean determination of nature, composition, structure, size, and molecular weight of reagents and products. This knowledge is essential for achieving optimum rate of reaction, reproducibility of production, and high quality of products. The methods have been considerably improved in the last decade, either in specificity, accuracy, sensitivity, and rapidity, or innovation (cross analysis, coupling). The increase in speed of analysis allows an online or immediate control. This is very convenient for achieving the desired value, such as the reaction rate, by correcting the concentration parameters in the tank. Progress in different spectrometric methods allows accurate determination of fine microstructure. Some other parameters need to be known: either molecular weight distribution (MWD) and averages $\overline{M}$, or particle size distribution (PSD). These values are key parameters for determining rheological, mechanical, thermal, and optical properties, storage stability, film forming capability, and behavior of polymer materials. MWD and $\overline{M}$ are commonly measured by size exclusion chromatography (SEC). Particle size may be obtained by a variety of methods. What makes these improvements possible is the effective use of powerful algorithms (Fourier Transform, deconvolution) with the help of computers, the use of lasers (monochromatic and powerful light), the appearance of sensors allowing one to simultaneously obtain many values (full UV spectrum, by a diode array instead of a dispersive system), and the development of new methods (optical, spectral, acoustic) and their hyphenation.[14]

Rate of Reaction and Molecular Weight

Measurement of the consumption rate of reagents is important to derive the composition of the product and to determine the reaction mechanism. This is often realized by vapor phase chromatography (VPC) for light reagents and liquid chromatography (LC) for heavy ones. The technique has appreciated the use of high resolution capillary columns in VPC and of very fine particles with grafted functions for bonded phase LC. Short efficient columns allow very rapid analysis in the minute range. In both cases, coupling with a mass spectrometer allows for the identification of peaks. Among the variety of spectrometers, the Matrix-Assisted Laser Desorption Ionization/Time of Flight (MALDI-TOF) seems to be well adapted for coupling with liquid chromatography.[15] It is able to resolve the polymer spectrum up to a molecular weight of 10^4 Dalton. We must confess that results may be tedious to obtain and they strongly depend upon the choice of conditions (matrix and response factor for constituents).

We have favored SEC, which is a convenient tool for molecular weight determination of polymers. The use of short columns allows a rapid analysis of the reagents mixture (monomers and copolymer). After peak intensity calibration, and with the use of a reference compound, concentrations are derived promptly from the signal given by the differential refractometer, operating as a universal detector. The determination of the molecular weight enables one to calculate the rate constants independently since molecular weight is dependent upon them (and concentration). This is an elegant and rapid method for determining reactivity ratios in copolymerization. Its accuracy lies in the possibility of balancing the monomers and copolymer amounts. The addition of a specific detector, UV for instance, allows one to access the nature and composition of a mixture and a copolymer. We initiated this method which has received numerous applications.[16] Recently, offline monitoring of copolymerization has been proposed by ATR-FTIR spectroscopy.[17]

The interpretation of the chromatogram in molecular weight distribution needs the calibration of the columns, generally with the help of polystyrene standards. Yet, now, two other detectors—viscometer and light scattering—are in favor of a more rigorous determination of molecular weight. We know that the Mark-Houwink law ($[\eta]=KM^a$) correlates molecular weight and intrinsic viscosity: this is the basis of a method to determine the true molecular weight, instead of a “polystyrene equivalent.” Another aspect of this law is the dependence of the intrinsic viscosity on chain branching: for a given M, $[\eta]$ is higher for the polymer with the linear chain. The comparison of theoretical and experimental viscosity for a given M allows the determination of a branching ratio. Several devices are commercially available. One works at high temperature (140°C), which is necessary for olefin solubility. The branching points may be observed by coupling with an IR spectrometer.[18]

Light scattering measurement is a powerful way to investigate molecular weight average and dimensions of molecules in solution. It operates classically in the static mode, at a series of scattering angles for samples at different concentrations. It measures the integrated scattered light during a given time. The interpretation is based on the Zimm diagram, with a double extrapolation of scattered light to zero, versus angle and concentration.[19] It has been adapted for use as a detector. Several possibilities exist. One operates at a unique scattering angle θ at a low value, close to the extrapolation and at low concentration (samples are very dilute solution after elution). Another possesses a complete set of angles, each of them equipped with its own photoelectric cell. The latter case allows one to determine molecular weight, radius of gyration, and a second virial coefficient. Even if both approaches need correction,[20] they have the unique ability to measure the true molecular weight of any polymer, without the need for a preliminary calibration.

Particle Size

DYNAMIC LIGHT SCATTERING: Many methods are available to determine particle sizes, either as a mixture or after separation.[21] We will focus on one of them in each of these two conditions: dynamic light scattering (DLS) and hydrodynamic chromatography (HDC), respectively. The first one is based on the rapid scattering fluctuations of light related to Brownian motion.[22] They are observed at one scattering angle only (generally $\theta = 90°$) and mathematically transformed to create a correlation curve, the time coefficient τ_r being related to the translational diffusivity coefficient D

$$D = \tau_r / q^2$$

(with q scattering vector modulus, $q = 4\, n\, \pi\, \lambda^{-1} \sin \theta/2$). This result is related to the hydrodynamic radius (a),

$$D = k_B T / (6\, \pi\, \eta\, a),$$

where a is close to the radius of gyration (k_B, Boltzman constant). It is not necessary to know the concentration of sample (which must be very low, assuming isolated species, and for avoiding interaction and interferences). Only temperature (T Kelvin), dispersant refractive index (n) at wave-length λ, and solvent viscosity (η) must be known. This is a quick and easy method of measurement. Also of considerable interest is the possibility of studying solid and latex particles or aggregates.

More precisely, photons reemitted by the suspended molecules are counted (number A_i) during very short times. The sum of the products of these counts at different times $\Sigma(A_i A_{i+j})$ is assumed to be a continuous function, the correlation function

$$\langle A_0 A \rangle = (\langle A^2 \rangle - \langle A \rangle^2) \exp - t / \tau_r$$

decreasing exponentially from the average of the square to square of the average, with a correlation time τ_r, in the simple case of a single species. The method is also called photon correlation spectroscopy (PCS). For a population of species with different sizes, the sum of the corresponding individual exponentials must be deconvoluted to obtain each size contribution. The log form is assigned to fit a polynomial expression. This simple way, using series limited developments, is called a method of cumulants, and gives only an average size. More sophisticated methods allow one to obtain size distributions. The problem is to transform intensity distribution in number or weight distribution and average (which explains why many papers give intensity distribution). The difficulty arises from the fact that larger species give a predominant signal, since scattered intensity varies with the diameter at the sixth power. Moreover, the dependence of scattered intensity with diffusion angle is not a continuous function. In other words, depending on the angle, in a mixture of species, their respective intensity may vary. This is mainly true when the diameter is in the range of wavelength λ.

Kinetic studies are possible, since the method is rapid (about one minute) and sensitive, which is compatible with a dilute medium, to detect the onset of reaction and the presence of small particles (some nm up to 1μm diameter).

Improvements in the optical methods have increased their use to moderately concentrated dispersions. Complementary measurements for larger sizes are performed by laser diffraction. An alternative is the use of acoustic methods which may operate in a large domain of size and concentration, but are not so rapid and need the determination or knowledge of some parameters.

HYDRODYNAMIC CHROMATOGRAPHY—

Applications: For certain applications, rather than the molecular weight, size is the key parameter. For instance, particle size is important for rheological properties, film forming, or protective abilities in relatively low cost industrial coatings such as aqueous phase paints and inks. Latexes with small particles have a lower viscosity than those with larger particles at the same percent solids. They also have a better storage stability versus sedimentation and further aggregation. In other applications, these waterborne particles may also be high value colloids for model compounds and reference materials; for example, they are used as standards for calibration (membranes) or for packing chromatography columns. Surface modification induces many applications in biochemistry for diagnostic aids and purification. Thus, it is evident that the accurate monitoring of diameter is important.

HDC is a typical method for latex evaluation (particle size around 100 nm) obtained by the emulsion process. General consideration of these particles is two-fold: their regular spherical shape and the possibility to obtain a predetermined diameter of a given value. This diameter does not depend on some mechanical treatment, like milling and sieving, but rather depends upon the chemical and thermodynamic values of the process. Size measurement is a way to determine the polymerization mechanism in relation with these parameters. Much of the practical HDC work has been devoted to synthetic organic colloids separation and diameter measurements for quality control. Separation of natural products such as proteins is also of interest. The rapidity of the measurement is compatible with kinetics studies and monitoring during the polymerization. Behavior of emulsions has been characterized by the swelling of carboxylic latexes which are measured according to the pH. Stability of mini-emulsions (50-500 nm) has been studied successfully. Flocculation of colloids in the presence of water-soluble ionic polymers or inorganic oxides has been observed by HDC in relation with other methods. Association of particulates under the effect of a thickener is clearly demonstrated, though it can be broken independently by intensive shear, and the same applies to aggregates. Effectively, soft materials may be deformed under the high rate of shear in packed column while orientation in flow may affect the apparent size. A variety of other compounds, such as carbon black, paper fibers, cement, clay, metals, and metal oxides of Fe, Ti, Si, Al, silver halides, and biomaterials such as milk or liposomes from egg yolk lecithin have been examined by using HDC. Silica has the advantage of being a hard spherical model for HDC mechanism studies. Finally, the determination of molecular weight or size is of interest, for very large polymers such as water-solubles, like polyacrylamide, xanthan polysaccharides, and tobacco mosaic virus.

The main advantages are the separation of species according to size, rapidity of measurement in the untreated medium, and ease of operation of the equipment. Conditions of elution (particularly the ionic strength) affect the separation, but the surface charge density of the particles does not affect the separation factor. No deformation occurs when the particle is relatively rigid. Variation of operating parameters allows a considerable range of possible applications. At low ionic strength, no sample chemical nature effect was found for vinyl copolymers colloids, even for those of low glass transition temperature. On the contrary, at high ionic strength, sample chemistry may bring an additional parameter for separation.

This interesting rapid method (about 10 min) separates and sizes solutes or particulates in the micron range (0.030 to 60 µm) at a high dilution, without being affected by their density. It allows one to obtain a fingerprint of the size distribution with an easy-to-operate instrument, similar to those used in liquid chromatography at room temperature. The separation takes place in packed or in open-tubular/capillary columns. Components are eluted in the order of decreasing size (as in SEC). HDC appears as a complement, either to SEC, which is limited to small size and solute species, or to other fractionation processes based on the effect of an external (variable) field, e.g., field flow fractionation (FFF).[22] In fact, there is only one phase, the mobile phase as an eluant, and only one field, the hydrodynamic one. In HDC with packed columns, the nonporous stationary phase is theoretically inert. For porous packing, the SEC process may operate simultaneously with HDC.

All of these methods are transport methods, but they differ in the order of elution and domain of separation. Static techniques can be used to check the validity of the results from HDC. Eluted fractions may be characterized further by transmission electronic microscopy (TEM) and analytical centrifugation to verify the effective existence of detected particles and to obtain the calibration curve. Photon correlation spectroscopy (PCS) may be used for a simultaneous rapid analysis.

Direct analysis of the original colloid medium and the use of high dilutions avoid modification of a sample which may be observed in a dry state (e.g., shrinking under the beam in TEM) as well as any effect of interactions, respectively. Existence of a unique (universal) calibration curve allows calculation of D_p and PSD for any sample, since sample nature, surface charge, and density have no effect on elution volume. With this technique, there are none of the limitations encountered in liquid chromatography (solvent nature, stability and availability of stationary phase, and temperature range).

However, there are some difficulties related to the proper choice of operating variables. Elution has been shown to depend upon size and porosity of packing beads, eluant flow rate, ionic strength, pH, and additives such as surfactants. It is evident that column length and column diameter play a role on plate numbers, resolution, and domain of measurement. Particle size may affect total recovery of material (with packed columns). Moreover, it may act on the detector response. As a result, the PSD might be perturbed by the incomplete recovery of particles, due to adsorption effects, mainly for larger particles. Intrinsic limitations include a low plate number N and a low resolution R_s, so that generally the number of peaks (peak capacity p) in a chromatogram is low (about 5-10). Quantitative interpretation for determination of particle size distribution needs calibration in order to establish the relationship between signal intensity and the amount of particles. Moreover, band broadening, common to every chromatographic process, has a greater influence on PSD because of the low resolution.[23]

Method: Particles may be separated according to their size by several techniques. The choice depends upon the conditions and purpose required: to obtain a relative or absolute value, with or without separation, affecting or not the state of the sample, and depending on the size and on the required resolution. HDC is one of these techniques. A frequently used alternative is hydrodynamic fractionation (HDF), since the process involved is not a chromatographic one, which consists of a mass distribution equilibrium between two phases (mobile and stationary). Separation is the result of local differences in the distribution of the sample compounds in the mobile phase. The partition coefficient K between the two phases is related to the thermodynamic relationship: $\mathrm{Ln}K = \Delta G°/RT$, which indicates the possible effects of three factors—enthalpy (ΔH) or entropy (ΔS) changes, and temperature T (Kelvin). Practically, separation is achieved by the effect of two forces (or fields) operating in one or two phases. One phase is necessary for transport and may have a physical or chemical role in the separation. HDC has some similarities with SEC and FFF, but needs one phase and one field only. The term hydrodynamic refers to the main driving force for separation. Electrostatic effects must also be taken into account. The difference in flow velocity is one of the separation mechanisms. The key value for a given particle of diameter D_p is called the separation factor R_f. This is the ratio of the highest elution volume (V_m) to that measured for this particle (V_p)

$$R_f = V_m \ / \ V_p$$

This factor is greater than one, the inverse of the situation in thin layer chromatography (TLC), where the solvent migration is more rapid than that of solute.

The separation results under the effect of one hydrodynamic field, which is moving one mobile phase. The nature of the mobile phase is theoretically irrelevant, but differences in results obtained with different solvents have been observed. The separation is due to the existence of a flow velocity profile in the channel, in which small particles tend to be closer to the external wall, where the flow is stagnant. If a packing is present, its only role is "to decrease" the capillary size. Voids between beads (diameter Φ_p) in packed columns play the role of small channels (of continuously variable diameter) similar to a set of capillaries. In consequence, the mechanism of HDC in packed or capillary (CHDC) columns may be described by the same parallel capillary model.

Under certain conditions, the nonturbulent flow in a column can be considered to be Poiseuille flow. Laminar flow occurring at a Reynolds number less than 2000 ($Re = 2R\,\bar{u}\,\rho/\mu$ with R tube radius, $\bar{u}$ velocity, μ viscosity, and ρ density of medium), leads to a parabolic velocity profile, the highest velocity being in the center of the tube. The velocity profile u(r) is obeying Poiseuille's equation:

$$u(r) = dP\,(R^2 - r^2) / \ 4\,\mu\,dL$$

dP and dL are increments of pressure and column length. R is the column radius, r is the particle radius. It is easy to see that u(0) is the maximum and u(R) is zero. The average fluid velocity is

$$\bar{u} = R^2 dP / 8\, \mu\, dL,$$

which is half that of the maximum. A particle in the fluid is assumed to have the same velocity as the flow, in its gravity center, and moving from the column center to a distance (R – r) of the wall. Taking into account the definition of R_f, and adding a term to express the rotational motion, the velocity profile is:

$$\bar{u}_p / \bar{u} = 1 + 2\, r_p/R - \gamma(r_p/R)^2$$

γ is a wall-effect parameter, the value of which depends upon the radial position of the particle (from about 1 to 60). In CHDC, R_f must be independent of length L, but the coefficients of the equation are quite far from the theoretical values. This expresses the fact that R_f is higher than expected and that particles move far from the wall.

Despite interest in this method which we have investigated thoroughly, there are only a few papers (around 200) in the literature, as compared to separation by other "chromatographic" principles.[24]

POROUS STRUCTURE—ISEC: Pore diameter distribution, pore volume, and surface area in solids are fundamental parameters to be known, since they govern, for instance, diffusion of reagents and products in catalysis, adsorption, and reaction, as well as exchange equilibria in liquid chromatography. Pore structure may be evaluated by direct or indirect methods, in dry state, or in presence of a diluent. Classical techniques are based on Brunauer, Emmett and Teller (BET) and Barrett, Joyner, Halenda (BJH) isotherms, mercury porosimetry, pycnometry, x-ray central scattering, and scanning electron microscopy in the dry state. Newer ones are thermoporometry, electrolyte uptake for ion exchangers, and inverse steric, or size exclusion chromatography (ISEC), which appears to be an attractive method. Effectively, chromatography may be applied in ways other than fractionation, which opens new approaches to physical investigation. Some examples in gas or liquid phase are the determination either of surface characteristics or polymer transition (glass and melting) temperature by reverse gas phase chromatography,[25] saturation of solid by a reagent observed by frontal elution, or determination of equilibrium between reagents by measuring their respective peak areas in liquid chromatography.

Solid state methods suffer from restrictions, since the material is examined only in dry conditions, which are not those in use. For rigid materials, the pore volume is defined and constant, but this is not true for organic polymers, which may be modified either under the effect of pressure or the effect of a liquid diluent. Moreover, polymer dimensions depend upon solvent and temperature; they vary from unperturbed ones in a poor solvent to extended chain in a good solvent, at a given temperature. Even for networks, structure is dependent upon the amount (and nature) of crosslinker and porogen agents, so that networks have permanent (macroporous) or variable (gel type) swelling and porosity. The problem is more complex for organic-inorganic materials, since chain mobility and chain expansion are restricted by the attachment of the chain to the surface.

The newer liquid chromatography method is a dynamic one, which is based on the measurement of elution volumes of samples of a given size. This principle is the same as that applied for molecular weight (or size) measurement of molecules by eluting them on a known porous phase, but applied in the reverse way, so that the method is known as inverse steric, or size exclusion chromatography. Some advantages include pore determination, in a series of solvents of interest, in the conditions of use of the materials. In fact, results may depend upon choice of relation between solute size, pore dimension, and elution volume. Different laws are applied to test their effect on porosity results. The condition for application is that the process be an entropic one, in order to avoid side effects—interactions between solute, and solvent or stationary phases. This is realized by fitting their Hildebrand solubility parameters. Another condition is that this dynamic process may be assumed as in equilibrium, which requests high mass transfer rate and a low flow rate of the eluant. The measure does not require too much time and material. It is sensitive, detecting the presence of attached reagents on solids and differences between polymers of different nature.[26]

LOCAL ENVIRONMENT

Fluorescence Spectroscopy

Fluorescence spectroscopy is a method of choice for determining compatibility and affinity of polymers and solids.[27] Physico-chemical investigation of nonsoluble supported polymers is poorly attempted as compared to efforts devoted to pure chemicals. Yet, this is important for understanding interactions between binder and pigment or extender, adhesion and reactivity (curing, crosslinking, two-pack coatings). Particularly, local concentration of reagents, accessibility of sites to reagents and products, neighboring effects are not measured. Conjugated techniques are necessary to understand the changes of reactivity of a given functional group with the nature of the support, so a dual investigation of active sites on functional polymers by chemical and physical means has been realized. Diffusion of reagents is dependent upon morphology, which is characterized by classical means. However, compatibility and affinity are preferentially measured by fluorescence techniques giving qualitative or quantitative answers to these points. Results obtained by complementary characterization of local viscosity by spin-labeling electron spin resonance (ESR) method are added to give tools for a more quantitative interpretation of chemical reactivity in various conditions.

The effect of solvent or chemicals on the excitation-emission spectra of a fluorophore probe covalently bound to a network polymer, or in solution, may be detected in three ways: (a) the solvatochromic shift, which means a change in the emission frequency maximum $\lambda_{max,}$ according to the facility of solvents or reagents, differing by polarity and steric hindrance to penetrate the polymers and actually reach the probe environment. This is related to the local surrounding of sites depending on the nature of medium; (b) the quenching of fluorescence, in the presence of electrophiles, which accounts for accessibility to the site. In the network or the coil, time decay is in direct relation to solvent penetration and solvatation of reagents and active sites; and (c) the transfer of fluorescence from a donor attached to the chain, to an acceptor present in the medium or attached elsewhere. This nonradiative energy transfer is associated with chain mobility and local chain structure. Information on the sites' vicinity and mobility may be obtained from this intermolecular exchange process.

Several fluorophores have been incorporated into the polymers at different steps of their synthesis, either by copolymerization of a polymerizable species or by proper condensation reaction of a reactive one on the functional group. In this case, direct information is obtained for the effect of a spacer arm between the chain and the site.

The maximum emission spectrum of the pure probe in a given solvent may be calculated by the Taft-Kamlet equation, where π^* denotes the combined solvent polarity-polarizability effect, α and β being empiric parameters for this solvent, related respectively to hydrogen bond donor and hydrogen bond acceptor strength[28]:

$$\lambda(\text{calculated}) = 53.45\,\pi^* + 20.48\,\alpha + 9.932\,\beta + 457.1$$

If experimental and calculated values are equal, the polymerized probe behaves as it does in the pure solvent; the larger the difference between these values, the higher the tendency of solvent to not penetrate the matrix.

Two parameters will be considered successively: (a) solvent with increasing polarity and (b) materials of different morphology. In heptane, which has no affinity for the aromatic structure of the organic support, the attached Dansyl probe (5-dimethylamino-1-naphtalene p-vinyl benzyl sulfonamide) behaves like the free molecule, as in the presence of dry polymer. In toluene and in more polar solvents, an increase of λ_{max} is observed: increasing bathochromic shift with increasing polarity. Yet, the difference between the values of free and attached probes is higher for nonpenetrating solvents than for good solvents. Interesting features are observed, when considering good and poor solvents. For instance, the Dansyl probe copolymerized with functional monomers on a polystyrene network is preferentially in contact with toluene, when a mixture of toluene and heptane is imbibing the system. Secondly, there is no spectral change when replacing toluene by heptane, whereas the spectum indicates that on the contrary, toluene replaces heptane effectively. The situation is different for an acetonitrile-toluene mixture, where λ_{max} is higher than those of its components. It may be assumed that toluene makes the entry of acetonitrile (poor solvent) in the polymer easier and induces this bathochromic shift.[29]

It is not possible to detect the very low amount (about 1 μMol/g) of Dansyl by FTIR. Yet, the decrease in intensity of the band at 1630 cm^{-1} is proof that copolymerized material has been grafted. The density may slightly decrease since additional material is less crosslinked, but these new polymer chains fill the interstitial volume, replacing voids with large new pores, so that density and pore volume (low and high pressure) are increased. Crosslink density is estimated from calibration with different amounts of DVB and swelling measurements. Dansyl is slowly polymerized, and is surely incorporated onto the external part of the support. The site accessibility to solvent decreases when a new copolymerization is performed on the initial support, since new polymer chains cover the initial nodules. If Dansyl is present in this second step, the fluorescence intensity is increased, which indicates that initial and further Dansyl are detected. However, the less accessible former probe leads to a wider band and a global decrease in λ_{max}.

Energy transfer is sensitive to intra- and intermolecular interactions in the nanometer range. We used styryl- and vinyl-carbazole as donor and anthracene and vinylanthracene as acceptor. The results are interpreted according to the Stern-Volmer equation: ratio of fluorescence intensity in the absence I_{f0} and in the presence of the acceptor I_{fDA} at various extent. It varies linearly with the concentration of acceptor [A], the slope being the overall energy transfer constant K

$$I_{f0} / I_{fDA} = 1 + K\,[A]$$

High sensitivity is demonstrated since very different K values were obtained for a series of solvents, depending on their nature: polarity and solvent power. Moreover, it is possible to observe spectral differences between polymer systems which have only minor structural differences.[30]

Spin-Labeling in Electron Spin Resonance

Spin-labeling in ESR spectroscopy is a way to access the reactivity in the vicinity of a polymer chain.[31] It is now well established that a functional group attached to a polymer through a spacer is more reactive than its homologous directly fixed to the polymer. One of the proposed explanations is the decrease of steric hindrance when the site is at a greater distance from the surface. This may be true when the support is an inert, nonporous solid. The situation is quite different with a polymeric support. The best representation of a swollen crosslinked polymer bead is to consider it as a semidilute solution of polymer segments with a variable local viscosity, sometimes very high. The spacer may increase the local mobility of the functional group in the medium, but its mobility remains lower than that of the corresponding unattached molecule. The spin-labeling technique allows one to evaluate the functional site mobility, in the swollen state, when a stable free radical NO· is attached to it. Stable nitroxide radical probes are attached to styrene-divinylbenzene resins through spacer arms, the length of which are one to seven methylene groups. Mobility of the nitroxide probes generally increases with the number of CH_2 groups, with the effect being compared to a decrease of crosslinking density. Electron spin resonance analysis allows one to estimate the local viscosity, since the rotational correlation time τ, determined from the ESR spectrum, is proportional to the internal viscosity. It has been found that τ decreases when swelling increases, depending on the nature of the solvent. The same occurs when crosslinking density decreases, according to the divinylbenzene amount, in relation with the mobility of substrates bound to the gel.[32] Our samples have a different morphology (macroporous) and we have determined the effect of different spacer lengths attached to supports of different crosslink densities.

The stable free-radical, covalently bound to the support and used as an ESR spin-label is: 4-hydroxy TEMPO or 4-hydroxy 2,2,6,6 tetramethyl piperidinolyoxy. A well resolved triplet line of 30 gauss total width is obtained on the spectra of the polymers including spin-labelled spacers and swollen in toluene. However, the heights of the high field peaks (–1) are sensitive to the molecular structure. Because of the weak anisotropy of spectra, due to some difficulty of the spin-labelled spacer to reorientate (10^{-9}–10^{-10} s), the correlation time in this case is given by

$$\tau\,(s) = 6.5\;10^{-10}\,\Delta H_0[(h_0/h_{-1})^{0.5} - 1]$$

For a series where the spacer is short (one methylene group, corresponding to vinylbenzylchloride as starting monomer), this time increases (3 to 9.5 10^{-10} sec) with the amount of crosslinker (1 to 10%). For a series with the same crosslinking density but increasing length n of the spacer arm (1-7), the correlation time decreases (9 to 3 10^{-10} sec). This variation is as expected. For this series the effect on τ for n=7 is about the same as a decrease in the amount of crosslinker from 5 to 1% in the other series.[33]

CONCLUSION

Organic chemistry offers many solutions that allow reaction of molecules in order to form tailor-made polymer chains and to transform their characteristics from lipophile to hydrophile, or the reverse. This affinity is valuable for waterborne systems or for powder coatings. The control of the surface functionality increases its reactivity and selectivity for adhesion and cohesion. The activation by radiation avoids temperature side effects. Control of structure and morphology allows the development of new behavior and properties of the binder. Grafted reagents may avoid migration of additives and favors the formation of new structures.[34] Rapid methods for particle size measurement or monomer consumption allows improvement of quality and economy. Spectroscopy investigation produces fine information on the environment of particular sites. For instance, fluorescence can evaluate the core-shell structure. Characterization methods bring complementary results and we favor the use of those based on different principles.

References

(1) Guillaume, J.L., Pichot, C., and Revillon, A., *Makromol. Chem. Suppl.*, 10/11, 69-86 (1985).

(2) Day, R.J, P., Lovell, A., and Pierre, D., *Polymer Intern.*, 44, 288-299 (1997).

(3) Guyot, A., Audebert, R., Botet, R., Cabane, B., Lafuma, F., Jullien, R., Pefferkorn, E., Pichot, C., Revillon, A., and Varoqui, R., *J. Chim. Phys.*, 87, 1859-1899 (1990).

(4) Berlin, Al., Volfson, S.A., and Enikolopian, N.S., *Adv. Polym. Sci.*, 38, 89-140 (1981).

(5) Otsu, T. and Matsumoto, A., *Adv. Polymer Sci.*, 136, 77 (1998).

(6) Georges, M.K., Veregin, R.P.N., Kazmaier, P.M., and Hamer, G.K., *Macromolecules*, 26, 2987-2988 (1993).

(7) Wang, J.S. and Matyjaszewski, K., *Macromolecules*, 28, 7901-7910 (1995).

(8) Hawker, C.J. and Fréchet, J.M.J., *J. Am. Chem. Soc.*, 112, 7638 (1990).

(9) Gauthier, M., Li, W., and Tichagwa, L., *Polymer*, 38 (26), 6363-6370 (1997).

(10) Dekker, G.H.*), Compendio de Conferencias Eurocoat Barcelone*, 1, 203-220 (1998).

(11) Webster O.W. and Sogah, D.Y., *Comprehensive Polym. Sci.,4*, 163-169, Pergamon (1989).

(12) Revillon, A., Guyot, A., Quing, Yuan, and da Prato, P., *Reactive Polymers*, 10, 11-25 (1989).

(13) Revillon, A., Puccilli, E., Guibert, I., and Guyot, A., *Macromolecular Symposia*, 164, 443-456 (2001).

(14) Pasch, H., *Adv. Polym. Sci.*, 150, 1-66 (2000).

(15) Mandal, H. and Hay, A.S., *Polymer*, 38 (26), 6267-6271 (1997).

(16) Hamaide, T., Revillon, A., and Guyot, A., *Europ. Polymer J.*, 23, 27-32 and 787-794 (1987).

(17) Hua, H and Dubé, M.A., *Polymer*, 42, 6009-6018 (2001).

(18) Verdurmen-Noël, L, Baldo, L., and Bremmers, S., *Polymer*, 42, 5523-5529 (2001).

(19) Laue, C. and Hunkeler, D., *Macromol. Symp.*, 162, 131-148 (2000).

(20) Froment, P. and Revillon, A., *J. Liquid Chromatography*, 10 (7), 1383-1397 (1987).

(21) Berne, B.J. and Pecora, R., *Dynamic Light Scattering with Applications to Chemistry, Biology and Physics*, Wiley (1976), and *LS'99 Data Evaluation in Light Scattering of Polymers, Macromolecular Symp.*, 162 (2000).

(22) Cölfen, H. and Antonietti, M., *Adv. Polym. Sci.*, 150, 67-187 (2000).

(23) Revillon, A., *J. Liquid Chromatogr.*, 17 (14 & 15), 2991-3023 (1994).

(24) Revillon, A., *Encycl. Separation Science*, Wilson, I. (Ed.), Academic Press, 379-392 and 3039-3046 (2000).

(25) Price, G.J., Guillet, J.E., and Purnell, J.H., *J. Chromatogr.*, 369, 273-278 (1986).

(26) Jerabeck, K., Revillon, A., and Puccilli E., *Chromatographia*, 36, 259-262 (1993).

(27) Shea, K.J., Sasaki, D.Y., and Stoddard, G.J., *Macromolecules*, 22, 1722-1730 (1989).

(28) Reichard, C., *Solvent Effect in Organic Chemistry*, Vol. 78, Chap. 7.4, Verlag Chemie (1978).

(29) Carlier, E., Revillon, A., Guyot, A., and Chauvet, J.P., *Eur. Polym. J.*, 29(6), 819-823 (1993).

(30) Carlier, E., Revillon, A., and Chauvet, J.P., *Eur. Polym. J.*, 29(6), 825-830 (1993).

(31) Horsky, J. and Morawetz, H., *Macromolecules*, 22, 1622-1624 (1989).

(32) Regen, S.L., *Macromolecules*, 8, 689-690 (1975).

(33) Guyot, A., Revillon, A., Camps, M., Monthéard, J.P., and Catoire, B., *Polymer Bulletin*, 23, 419-423 (1990).

(34) Guyot, A. and Tauer, K., *Adv. Polym. Sci.*, 111, 45 (1994).