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A Few Prospective Reflexions About PDM

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SUMMARY : A short review concerning three main topics is presented with a few suggestions. The first topic deals with better control in emulsion polymerization, with the following sub-topics : polymerization processes, polymer structure, particle morphology and surface functionalization. The second topic is about non radical emulsion polymerization, such as ionic, catalytic coordination or condensation mechanisms. Finally polymerizations in unusual media are shortly treated.

Introduction

Polymers in Dispersed Media (PDM) are related with polymers produced or used in heterogeneous media containing at least two phases. In most cases, one of these phases is water or a mixture of water and a water soluble solvent such as a light alcohol. One of these phases also is continuous and the other is dispersed in fine particles or droplets. The conventional emulsion polymerization is a typical case where the continuous phase is water, and the dispersed phase is a mixture of rather hydrophobic monomers, which become progressively polymerized in very small solid particles. Depending on the average size of the final particles, other similar systems are named dispersions or suspensions. Inverse systems also do exist, for water-soluble monomers dispersed in hydrophobic media. Finally the continuous phase can be different, as for instance a gas phase, or a melted polymer, or another more or less viscous liquid.

Our discussion will be founded on a few keywords, namely CONTROL, NON RADICAL Systems, and NON CLASSICAL Media. Of course our discussion will chiefly be related to polymerization processes, but not exclusively. We will consider also a few classical and less classical applications.

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I Control

There is a very strong demand from the industry for a better control of the polymerization process, whatever is the kind of process. On the other hand, emulsion polymerization is widely used for many polymer syntheses, yet it is actually very complicated. Process control is needed; not only for the conversion of the monomer(s), but also about the heat-exchange capacity of the reactor due to the high exothermically of the polymerization reaction, and the quality of the produced polymer (composition and sequence distribution of the copolymers, tacticity and cotacticity, molecular weight and the distribution, of chain ends, etc...). The process control involves also the particle shape, the particle size and particle size distribution, the internal morphology (core-shell problem), the possible porosity of the particles, and finally the surface functionalization.

In order to achieve such process control, more and more accurate and safe tools are desirable. Recently, new sensors, such as IR or Raman spectroscopic sensors have been proposed, as shown in this symposium. The use of density and ultrasound velocity and attenuation measurements have also been found interesting, but rather difficult to manage. Important progress has been made concerning calorimetric data, and process control. A second kind of tool, which should be developed to achieve a good and safe control of the polymerization, is the modeling tool. The results presented in this symposium show that surprisingly good results can be obtained using rather simples models. This kind of software sensors is still in its infancy and should be strongly developed.

Control of polymer structure through Controlled Radical Polymerization (CRP) should be a major issue in the near future. Before this Symposium, there have been only two papers published about dispersion polymerization [1,2)] and no more than 3 papers about emulsion polymerization.[3-5)] All these papers are related with the use of SFRP (Stable Free Radical Polymerization). The main difficulty with this technique is the need to work at temperatures at which the C-O bond of the alkoxyamine is thremoreversible (most often above 100°C). Another difficulty comes from the thermal stability of the usual surfactants used for stabilization. A second system often used in CRP is the so-called ATRP (Atom Transfer Radical Polymerization), however this system suffers from a major drawback, which is the use of a transition metal derivative, Cu, Fe, Ni, or Ru. Industry does not want too much that system, because, in addition to the danger of flocculation during the polymerization, the catalyst is susceptible to cause detrimental post-effects (oxidation) if it is left, even in small amounts, in the polymer. A final difficulty is due to the heterogeneous character of the emulsion polymerization where the polymerization must start in the water phase and the active moieties must be transferred in the organic particles for the polymerization to be continued. This means that the catalyst should have an amphiphilic character. The data presented by Dominique Charmot and by Jerome Claverie in this symposium show that there is another successful system, which is the RAFT system (Reversible Addition Fragmentation chain Transfer), recently published by Rizzardo et al6). In such systems, the active compound is a sulfur containing transfer agent. The main interest of that system is its applicability to vinyl monomers, for which the other systems failed. A possible drawback might be the bad smell of sulfur compounds. However it seems that this or other similar systems should be very promising. Two others systems might be of interest in emulsion polymerization. The first one involves the use of alkyl iodides in degenerative transfer7), working at moderate temperature, but giving only poor control8). The second one, initially reported by Druliner et al. from DuPont de Nemours9) has been shown recently by a student of Yves Gnagnou10) to work in water for acrylic acid at moderate temperatures with a higher level of control.

Another interesting topic is the control of the morphology. Under this term, I mean the shape and the size of the particles, their internal structure, their porosity, and finally the properties and composition of their surface.

The shape of the polymer colloids is generally spherical, for thermodynamic reasons (minimum of the interfacial energy). More complex shapes can be produced under non-equilibrium conditions, or under special constraints, for instance ellipsoidal particles under shear with low Tg viscous material11). However, the need for producing non spherical particles is not obvious. Indeed, it might be interesting to have needle-like particles which might reinforce soft polymeric materials. But, for such a purpose, it seems more practical to encapsulate fibers which are polymeric or not. Much work has been devoted to the control of the size of the colloidal particle, especially to obtain monodisperse particles. Indeed, we know how to proceed to produce monodisperse particles in a very large interval of size, from about 10 nanometers in diameter up to several millimeters. In emulsion polymerization, the main problem to be solved, for practical purpose, is to produce high solid latexes with low viscosity. It is then necessary to produce polymer particles with a very broad size distribution. A large number of patents dealing with this problem have appeared recently, showing the interest of the industry. But very few academic studies have been devoted to that problem. One communication in this symposium has been given by Helmut Zecha. Related to that problem, is the need for routine separative instruments. CHDF and FFF which appeared rather recently might in the future answer this question.

Various aspects of the control of internal morphology are of interest. The most popular one is probably the core-shell phenomenon. It has been a mystery for a long time, but, thanks to the pioneering work of Don Sunberg, its main features have been rationalized, in terms of interfacial energy conditions. Owing to the interest of the applications related to this problem, it still needs research progress. For example, film-forming core-shell particles are desirable for waterborne coatings with high gloss and no VOC, as well as void particles with thin solid and semipermeable walls to encapsulate liquids, for instance of biological interest. A combination of useful properties should be expected from onion-like core-shell multilayered structures of various compositions (succession of soft and hard layers).

Another control needs to be applied in the production of hybrid materials, combining inorganic and organic domains. Encapsulation of inorganic particles in emulsion polymerization should be the most interesting way to explore. Through this technology, it should be possible to improve the dispersability of inorganic particles such as pigments or reinforcing charges in polymer matrices. For instance, important reinforcement of film forming lattices have been observed in our laboratory by nano particles of silica[12) However, the success of the reinforcement involves the preliminary functionalisation of the silica by a coupling agent bearing a polymerisable group, which is able to be linked further through copolymerisation with the polymer produced in the emulsion process. Then two majors problems do appear : first, the functionalized silica is made hydrophobic and is then difficult to disperse in water; second, the functionalisation procedure of the inorganic particle adds to the cost of these particles. The first problem can be solved using a two step Stöber process, but it is much more costly. A very smart solution to the problem of redispersibility has been proposed recently by a student of professor Gérard Riess. It consists in using an additive such as a triblock copolymer containing an hydrophobic sequence, for redispersion in organic media, followed by a sequence for adsorption onto the inorganic particle, and terminated by a hydrophilic sequence for redispersion in aqueous media[13). Possibly, this aspect will be mentioned in the lecture of Gerard Riess in this symposium. A very interesting application of the improvement of the dispersability of pigments is encountered in powdered paints. There already exist powdered latex binders protected from the coalescence in the water phase. However, there are not yet good solutions to produce inorganic or organic pigments which can be redispersed in water from the dry state. A paint composed with easily dispersed powdered elements will be a significant progress from the environmental point of view.

The last point to be considered in this discussion is related to the morphology of the surface of the particles. Two aspects should be treated. One deals with the analysis of the surface functionality. The second one is related with the hairy character of these particles, itself related to many features of the latexes.

At the present time, no good procedures exist to analyze functional groups present on the surface. The titration of strong and weak acid groups is a well known method, due to the pioneering work of John Vanderhoff at Lehigh, but it has some intrinsic problems, such as the need to clean the latex serum, or the hydrolysis of acrylate monomers under basic conditions. The method for the titration of alcohol groups using trifluoroacetic acid and NMR analysis of fluorine is not so safe. It is often difficult to distinguish the functional groups onto the very surface and the sub-surface when the titration reagent is diffusion-controlled .It is the case for the titration of the epoxy groups with HCl for instance.

The main interest of the hairy particles rest upon their self stabilization which may be a steric or an electrosteric one depending on the fact that the protuberating hairs are charged or not. A possible drawback is concerned with a limited rate of radical entry during the polymerization. For that reason it is better to produce the hairs at the end of the process of growth of the particles, then to introduce the components to make the hairs in a shot process. So, the simplest way to prepare hairy particles is to add, at the end of the polymerization a water-soluble monomer which will give an hydrophilic polymer. However such a procedure is very difficult to control. The obvious danger is to produce water-soluble high polymers which can cause flocculation. It is thus necessary to choose very carefully the amount of water-soluble monomer and the time of shot introduction. Another possibility, which becomes more and more popular, is to use reactive surfactants with the reactive group at the end of the hydrophobic part of the surfactant. The subject has been reviewed recently.14) In this case, the hairs are predefined by the structure of the surfactant and they are hopefully grafted onto the surface of the particles. However the grafting process may be not necessary, if the hairs come from a structure strongly enough adsorbed. In that connection, very interesting results have been obtained recently by TAUER et al14)using block copolymers as surfactants. Unfortunately the procedure to produce these block copolymers is rather complex.

II Non Radical Systems

This part involves those mechanisms others than radical polymerization processes which can be used to produce polymers colloids. These mechanisms cover anionic or cationic polymerizations as well as catalytic polymerizations, or even polycondensations. In some cases, the presence of water seems to make such processes totally forbidden.

A short review of unconventional emulsion polymerisations has been published recently in a book edited by Lowell and El Aasser16). Beside unconventional radical polymerisations, for instance of totally non water-soluble monomers, or of polymers fully insoluble in their monomers, such as fluorinated polymers, the review is concerned with conducting polymer latexes of polypyrrole and polyaniline, the cationic ring-opening polymerization of cyclosiloxanes, and a few transition metal catalyzed polymerisations. Finally, there is a paragraph about enzyme-catalyzed emulsion polymerisations.

The polymerization of aniline and pyrrole can be initiated by a redox mechanism involving potassium persulfate, or $FeCl_3$, in the presence of polymeric stabilizers (Polyoxyethylene, Polyvinylalcohol).The electronic conductivity is increased upon doping. Dodecylbenzene sulfonic acid, in the case of polyaniline, acts as both surfactant in the emulsion polymerization, and as doping agent. The size of the latex particles is in the range of 30 to400 nm.17-20)

The cationic polymerization of dimethyl cyclosiloxanes of various ring sizes was developed in the US rather early21). Dodecylbenzenesulfonic acid was used both as surfactant and as catalyst. In this process, water acts as molecular weight regulator, and particles in the size range of 50-500 nm are produced. Details of the mechanism are not quite clear, and research is continuing, for instance in the group of Patrick Hemery in Paris.

A few years ago , a report concerning dispersion anionic polymerization has been published, using butyl-lithium as initiation for living polymerization of styrene in dry heptane. A block copolymer of styrene-b- polybutadiene was used as stabilizer.22-23) Catalytic polymerization of butadiene, using rhodium chloride as catalyst and producing *trans*-1,4-polybutadiene in aqueous system was known long time ago, but the mechanism has not been clarified.24-25)

More recently metathesis catalysts working with functional derivatives of norbornene have been disclosed, and were shown to work in the presence of water.26-27) Another report indicates that a dimethoxy derivative of norbornene can be polymerized in dispersion using $RuCl_3$ as catalyst and a triblock copolymer of oxiranes as stabilizer[28)]. The particle sizes (40-60 nm) were dependent on the amount of stabilizer but the yield of these polymerisations were low.

The most important challenge in the nonradical polymerization systems is certainly the possibility to polymerize olefins with Ziegler catalytic systems in emulsion Very few works have been carried out on this subject. Polymerization of butadiene to produce the 1,2 polymer has been done in the US by researchers of Goodyear in the early nineties[29)]. The catalyst is Cobalt based with a sterically hindered ligand hydrophobic, able to protect the transition metal and its coordination bond with the monomer from the aqueous environment. More recently at the ACS meeting in Dallas (April 1998), K.Brown did present a suspension polymerization of butene, in an ethylacetate environment, using a palladium based catalyst belonging to a class recently described by Brookhart and patented by DuPont [30)]. A branched polymer is produced under the form of beads 10 to 100µ in diameter, with a rather broad distribution.

Around 1985, Klabunde, of DuPont has developed a family of Chelated Nickel Catalysts, able to work in the presence of protic compounds, and even with some water[31)]. In this symposium, the first presentation of the polymerization of ethylene in emulsion has been given by Atanas Tomov, a bulgarian professor working now in our laboratory. He uses a series of catalysts related the Klabunde system. For me, it is the realization of a long time dream, and, of course, this very active research is continuing in our laboratory.

Another nonradical polymerization producing microspheres is the topic of the lecture of Stanislas Slomkovski. He has published a first study of the ring-opening precipitation polymerization of lactides using a graft copolymer of caprolactone onto dodecylacrylate [32)]. Microspheres of 2.4 to 4µ in diameter were reported.

To complete this part, it is wise to mention suspension polycondensation in dispersed media. A review of this subject has been published by R. Arshady a few years ago [33)]. Rather few studies were mentionned, compared to the importance of that class of polymers. However the interest of producing polycondensates in dispersed media seems obvious. The main materials obtained from polycondensation mechanisms involve very viscous media, due to the very high melting points of these kinds of products. That means very high temperatures in the processes, which cause easily the formation of irregular structures detrimental for the properties of the materials. Often, small molecules such as water have to be eliminated in order to obtain high molecular weight polymers having good enough mechanical properties.

If the polycondensation can be performed in suspension of small particles, one may expect shorter durations of the process, because these small molecules should be evacuated more easily, and the equilibrium of the condensation reaction should be displaced. Another advantage is the possibility to work at lower temperatures, of course higher than Tg, but possibly lower than Tm. In fact polycondensation in the solid, but dispersed state, has been proved to be successful. Then a big future will most probably be reserved in the polycondensation process in dispersed media.

III Unusual Media for Polymers

It would be a great interest to find method to produce small polymers particles as suspended powder in gaseous medium. Actually, gas phase polymerization processes for olefin monomers are a very important part of the polymer industry, which has been more and more improved those recent years by the better control of their morphology, and their extension to new classes of catalysts such as the metallocenes, and to new products such as elastomers.

Concerning the domain of the present symposium, polymerization in the CO_2 in supercritical conditions is the process the closest to the gas-phase polymerization. Thanks to the team of Pr. De Simone, who should be giving a presentation in this symposium, the radical polymerization in dispersion of various monomers under such conditions is rather well documented. In emulsion, up to now, only one paper does appear from a cooperative work of Gilbert and De Simone34). It was not so successful, owing to the swelling power of the supercritical CO_2. Another drawback of the technique is the need for expensive surfactants, either fluorine or silicium containing. However more work is desirable in this topic. Light hydrocarbons might be considered as possible candidate to obtain small particles in dispersion and even in emulsion in supercritical conditions giving powder upon flashing. As compared to CO_2, simpler and cheaper surfactants should be used, but the flammability of the gas should lead to serious problem, and closed reactors should be used.

Production of small particles in highly viscous polymeric media can be considered in reactive processing, as shown by the communication of Alain Michel in this symposium. The main advantage seems to be able to obtain directly a blended material with a definite shape. Twin-screw extruders are very convenient machines for this purpose, but there exist severe limitations. The working conditions involve high temperatures and limited reaction times in between the feeding of the reactor and the extrusion through the dye. Therefore, the process is valid for a very limited range of systems.

Finally a very original work has been started by Klaus Tauer who has carried out emulsions polymerisations in a poloxyethylene glycol medium. It seems that quite unusual morphologies of particles can be obtained. Further work is obviously needed to understand such a systems, and see if other similar work would present a real interest.

IV Concluding Remarks

A true prospective exercise is a very difficult task, so that the present paper is only a reflection on a few recent progress, with very few new suggestions. It can be anticipated however that, in the near future, a lot of work will be devoted to the problems evoked here, mainly Controlled Radical Polymerization, to prepare block copolymers or polymers with a very narrow molecular weight distribution. However it should be mentioned that one of the main features of the emulsion polymerization process, which is the limitation of the number of radicals working simultaneously in the same particle, due to very rapid termination reaction, will not apply here, because, by principle, termination reactions in CRP are virtually suppressed. Then a new mechanistic approach of the system will be needed.

Most probably also, efforts will be carried out to obtain in dispersed media those polymers which, up to now, are prepared in homogeneous media, as it has been done in extrapolating the gas-phase process of catalytic polymerisations of olefins to the synthesis of some elastomers. We can suppose that the way shown here by Atanas Tomov will initiate a lot of work. Finally, the interest of using gaseous compounds as dispersion media is certainly not doubtful.

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