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M. Lambla[a]; B. Valentin[a]; S. Guerrero[a]; A. Banderet[a]
[a] Ecole d'Application des Hauts Polymères Universite Louis, Pasteur, Strasbourg, France

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Synthesis of Hydrophilic-Lypophilic Copolymers in Emulsion: Initiation of Vinyl Chloride by Aqueous Soluble Polymeric Radicals at the Interface

M. LAMBLA, B. VALENTIN, S. GUERRERO, and A. BANDERET

Ecole d'Application des Hauts Polymères
Université Louis Pasteur
F - 67000 Strasbourg, France

ABSTRACT

The emulsion polymerization of vinyl chloride initiated by a redox pair in the presence of acrylamide in the aqueous phase gives a product which apparently corresponds to a block copolymer of polyacrylamide and poly(vinyl chloride). A reaction scheme is proposed which involves the attack of the vinyl chloride in the micelles by a growing polyacrylamide radical, thus producing the hydrophilic - lypophilic copolymer. Isopropyl alcohol is used as a transfer agent to limit the size of the PAA chains growing in the aqueous phase. The reaction product was characterized by selective solvent extraction, elemental analysis, infrared spectroscopy, and differential thermal analysis.

INTRODUCTION

In recent years extensive studies have been performed in the field of emulsion polymerization on the kinetics of penetration of latex particles by the radicals which are formed in the aqueous phase [1-5].

In a previous paper [6] we have shown the influence of the nature and the concentration of the dispersion agent on the velocity of crossing the interface by the radicalar species.

These results encouraged us to investigate a new field: initiation at the interface of a lipophilic monomer by an aqueous soluble polymeric radical. For various reasons, especially based on kinetic data, we selected vinyl chloride for the organic phase and acrylamide for the aqueous one. Other systems were studied earlier [7, 8] but not very successfully.

The basic scheme of the copolymerization seems to be quite evident. But when we examine it closely, we find numerous parameters which may influence the process in different ways.

Figure 1 shows different stages of the polymerization. In the first scheme (Fig. 1a), we recognize the classical representation of an emulsion before initiation. We note only one great difference: the presence of the water-soluble monomer acrylamide.

The second scheme (Fig. 1b) shows the initiation process. The thermal homolytic splitting of the persulfate produces water-soluble radicals which will react rapidly with acrylamide. The chains are growing in the aqueous phase and may also approach the interface of micellar particles containing vinyl chloride. The radical chain end may react with a vinyl chloride molecule and grow further within the organic phase (Fig. 1c).

Under these conditions it seems possible to obtain a block copolymer which remains at the interface and, perhaps, stabilizes it. Beside these reactions, it is necessary to mention the well known transfer reaction on vinyl chloride which produces homopolymer within the organic phase. We obtain finally (Fig. 1d) in the aqueous phase: homopolyacrylamide (PAA), copolymer of PAA with very short blocks of poly(vinyl chloride), and oligomers (PVC and PAA); in the organic phase: homopoly(vinyl chloride) (PVC) and copolymer of vinyl chloride with short blocks of polyacrylamide (PAA); at the interface: block copolymer with relative long chains of both vinyl chloride and acrylamide.

It seems quite obvious that this schematic representation of the system cannot exclude other possibilities of reaction such as transfer on dispersing agent, escape of micromolecular radicals into the organic phase, etc. The experimental description of the process will confirm the interest and the complexity of these systems.

EXPERIMENTAL

Polymerization

The experiments were carried out in a classical glass or stainless steel autoclave, equipped with an agitator and a sensitive thermal

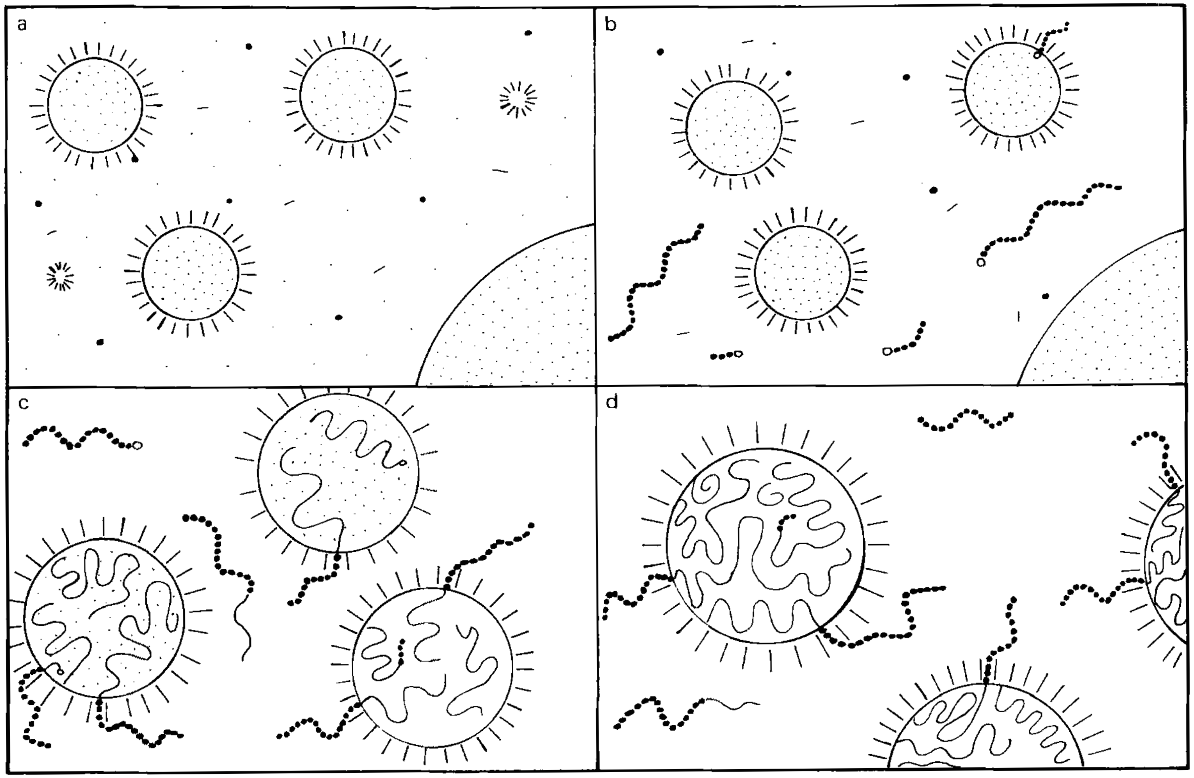

FIG. 1. Schematic representation of the different stages of polymerization: (☼) vinyl chloride micelle, surrounded with soap; (●) acrylamide molecule; (○) radicalar chain end.

regulating system. We introduce successively, under nitrogen pressure, for 1 liter distilled water, 10 g dispersing agent, 2.5 g sodium bicarbonate, 20 g acrylamide, and initiator (0.48 g ammonium persulfate and 0.36 g sodium hydrosulfite). The reactor is then carefully purged with a pure nitrogen stream before adding the organic monomer, 220 g vinyl chloride in this case.

According to previous experiments [6] the temperature was fixed at 45°C. Recording of this parameter during the polymerization allows a good control of the polymerizing system, especially when a stainless steel reactor is used.

The synthesis of copolymers at the interface in emulsion polymerization generally incurs problems due to poor reproducibility of results and/or colloidal unstability of the systems. For this reason, the experimental data given above were slightly modified later, not only in terms of concentration of the different species but also by adding a further component–isopropyl alcohol. This product is a good transfer agent for the polymerization of the aqueous soluble acrylamide.

Characterization

Separation Techniques

At the end of the polymerization, the contents of the vessel were poured in a large amount of hot water containing aluminum sulfate. In this way, the aqueous soluble fraction (homopolyacrylamide and other products) is directly separated from the organic one. This procedure is only adopted for the polymeric products which can be dried and then used for studies at the solid state. Dried polyacrylamide is known to be quite insoluble in all solvents. However, it is very important for the evolution of this research to find an efficient method of separation for the organic fraction.

We therefore developed a special technique of separation based on specific solvent extractions of the wet product obtained after filtration. In this case the emulsion is precipitated in a small amount of cold water containing aluminum sulfate. We are now able to separate quantitatively the different polymeric fractions, using successive and parallel extractions in a Soxhlet apparatus. The undried precipitate is first treated by water and after that by tetrahydrofuran, a solvent for PVC.

The following results given as an example, were obtained in a typical experiment. The yield of polymeric products was about 40%, and we obtained, under these conditions: homopolyacrylamide, 15%; homopoly(vinyl chloride), 42.5%; copolymer, 42.5%. It is clear that, in spite of the important transfer reaction to vinyl chloride, the copolymer yield is substantial.

Solubility

As mentioned above, the obtained precipitate is generally insoluble in common solvents of the two homopolymers. The solubility of these products is essentially a function of the characteristics of the polymerizing system, however. The ratio of concentrations between the two monomers, the amount of initiator, and the concentration of the water-soluble transfer agent are the most important parameters. So we obtain, at reduced pressure (small amount of vinyl chloride), products which are quite soluble in water, forming a turbid solution. With a large excess of vinyl chloride and isopropylalcohol, the obtained polymeric products are completely soluble in hot THF. When we cool such a solution we get also a slightly turbid one.

Generally we synthesize intermediate products which are only soluble in dimethyl sulfoxide at 100°C and swell easily in THF. It is thus quite impossible to determine the molecular weight of the copolymeric fraction, and this constitutes a further difficulty for the interpretation of the kinetic results.

IR Spectrometry

Spectroscopic analysis is a very useful tool to follow the results of the method of separation. Furthermore, such IR study permits us to observe chemical modification of the polymeric products with time. Two new peaks appear at 1650 cm^{-1} and 1750 cm^{-1}. We note also that it is possible to accelerate this evolution by increasing the temperature. It is surprising, however, that the same thermal treatment of homopolyacrylamide and mixtures of the two homopolymers do not give the same results. Further experiments are necessary to elucidate this phenomenon, but for the moment it is important to take it into account when we try to interpret the results of specific extractions. Recently we have shown that freeze-drying techniques are very useful for avoiding this chemical modification during the characterization process.

Differential Thermal Analysis

Differential thermal analysis was carried out to confirm the structure of the pure copolymer after separation from the homopolymers. It is well known that a statistical copolymer has only one glass transition temperature T_g, lying between the values of the two homopolymers. On the contrary, the two glass transition temperatures remain generally

TABLE 1. Results of the Copolymerization at the Interface

Vinyl chloride (g)	Acrylamide (g)	Isopropyl alcohol (g)	Yield (%)	Acrylamide ratio in the organic product (%)	Polymeric fraction extracted by THF (%)
368[a]	70	-	73	12.3	68
402	70	14	80	9.8	65
368	70	35	54	10.95	50
635	70	140	38	12.7	12
467	25	25	78	3.75	97

[a] Unstable emulsion.

unchanged in a block or graft copolymer. Nevertheless there are a few exceptions, as mentioned recently by Kennedy [9].

In our case we find for both polymeric mixtures and pure copolymer two glass transition temperatures at 84 and 140° C. The first one is the well known T_g value for PVC and the second one may correspond to an intermediate value for a water-plasticized PAA. DTA is not very easy to perform. The sensibility to thermal degradation of PVC and the presence of water are two important disadvantages, and we will do further experiments to confirm these first results.

Elementary Analysis

The most important results of the elementary analysis are summarized in the following section (see Table 1).

RESULTS AND DISCUSSION

We mentioned previously that the most important parameters which determine the characteristics of the copolymeric products are the relative concentrations of the water-soluble components.

We first studied the variation of the solubility of the polymeric product as a function of the ratio of acrylamide to initiator. The first experiments were carried out at reduced pressure, and the obtained products were sometimes completely soluble in water and sometimes soluble in THF. It appeared rapidly that the most interesting products were those which are quite insoluble in both solvents. Further experiments showed that it was not necessary to work at reduced pressure, and the synthesis of these intermediate products were performed with a large excess of vinyl chloride.

At the same time, it was important to take into account the decrease of the stability of the emulsions with increasing acrylamide concentration. To go beyond the limiting value of about 20 g/liter it was necessary to add isopropyl alcohol to the system as transfer agent for the homopolymerization of acrylamide. This modification of the recipe has two consequences. First of all, the decrease in molecular size of the polyacrylamide reduces the viscosity of the aqueous phase, which is important for the stability of the emulsion. Secondly, by the transfer reaction it is very easy to control the dimension of the hydrophilic links in order to obtain a wide range of different copolymers.

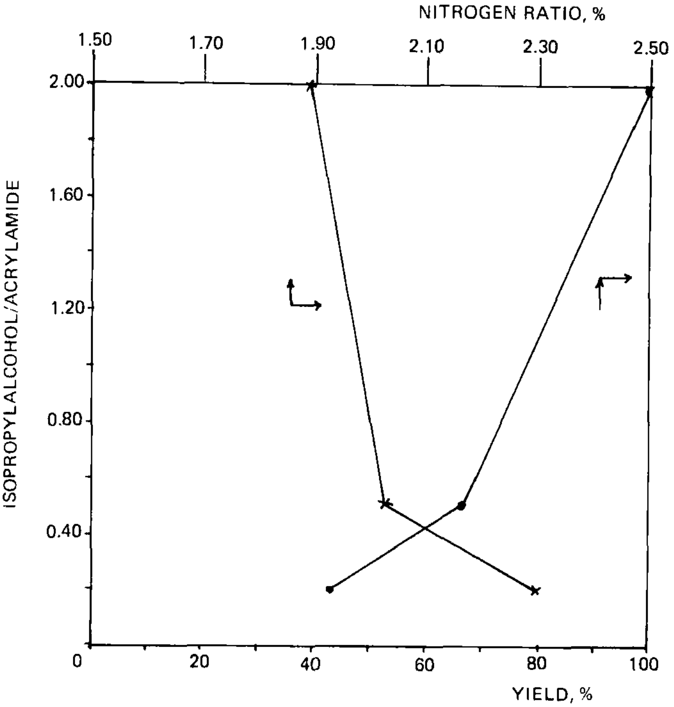

FIG. 2. Polymerization yield and nitrogen ratio as functions of the isopropyl alcohol/acrylamide ratio.

To illustrate this possibility, we summarize in Table 1, the results of a few selected experiments. All these experiments were carried out in the stainless steel reactor at 45° C, with 3500 g water and constant amounts of emulsifier (30.4 g) and initiator (2.45 g $K_2S_2O_8$ and 1.58 g $Na_2S_2O_4$). We note first that the emulsion obtained in absence of isopropyl alcohol was unstable. The acrylamide ratio present in the organic product represents 50% of the reacted monomer. The amount of homopoly(vinyl chloride), important in the first case, diminishes progressively with increasing isopropyl alcohol concentration. At the same time, the yield of the polymerization decreases rapidly (Fig. 2). It is possible to find a good compromise between the composition of the copolymer and the yield of the polymerization.

The last example reported on Table 1 mentions the possibility of preparing in good yield products which are quite completely soluble in hot THF. Nevertheless, these polymers contain about 60% of the reacted acrylamide. The polymeric product extracted by THF is not pure poly(vinyl chloride), homopolymer but contains generally between 1.5 and 3% acrylamide. A small part of these products may correspond to copolymers with short polyacrylamide links.

CONCLUSION

The primary purpose of our research was to establish the efficiency of the copolymerization reaction between vinyl chloride and polyacrylamide growing radicals. The introduction of a transfer agent in the aqueous phase of the emulsion improved the stability of such systems markedly and allowed us to adjust the dimension of the hydrophilic links more easily. The synthesis of a wide range of copolymeric products is now possible.

Secondly, it is of interest to determine the structure of these copolymers. If the polymerization occurs at the interface (which is probable according to the relative reactivity ratios of the two monomers), it seems possible to obtain block copolymers. The unusual behavior of these products in common solvents for the respective homopolymers and the first results of DTA analysis are in agreement with this assumption. Further experiments involving other analytic techniques must be carried out to confirm the assumed characteristic.

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DISCUSSION

Prof. J. Lyngaae-Jørgensen (Institutett for Kimindustri, Lyngby, Denmark): Was it possible to prepare stable, or relatively stable emulsions by the technique used by Dr. Lambla? If a compound is soluble in the polymer phase there should be steric stabilization of the polymers. Was anything like that observed?

Dr. Lambla: It seems possible that the copolymeric species present at the interface may enhance the stability of the emulsion. But if we introduce a large amount of acrylamide (20 g/liter) in the aqueous phase, we note that the emulsions are less stable. In this case it is necessary to add a further component to the system, namely, isopropyl alcohol as water-soluble transfer agent, in order to decrease the viscosity of the continuous phase. Under these conditions, the emulsions become stable again.

Dr. Liegeois (University Liege, Belgium): Dr. Lambla used isopropyl alcohol to reduce the molecular weight of the polyacrylamide (the water-soluble polymer) by means of a transfer reaction. I cannot understand how that water-soluble polymer can then react with vinyl chloride to make its chain longer. The polyacrylamide polymer no longer has an active end, I think, and there is an isopropyl radical which is supposed to continue the polymerization. But, if this is true, how can the block copolymer form?

Do we have an idea of the amount of the product which is formed by means of the transfer reaction, with respect to the one which can react with the vinyl chloride in the water phase?

Dr. Lambla: The preliminary experiments were carried out in order to determine the best conditions for the kinetic study. It is clear that the initiation of the organic monomer by polymeric radicals is effective, even when we introduce isopropyl alcohol in the aqueous phase. The yield of the polymerization decreases progressively with increasing alcohol concentration, but further experiments have shown that we can find a good compromise between the composition of the copolymer and the yield of the polymerization.