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Room temperature initiated and self-heating polymerization via concentrated emulsions: application to acrylonitrile based polymers

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Summary

A novel concentrated emulsion polymerization procedure, in which the polymerization is initiated at room temperature and the heat generated by the reaction accelerates the process, is proposed. The polymerization of acrylonitrile (AN) and its copolymerization with vinylidene chloride (VDC) are used as examples. AN (alone or with a comonomer) containing an oxidant was first dispersed in water to generate a concentrated emulsion. The polymerization of the monomers was initiated at room temperature by introducing an aqueous solution containing a mixture of reductants (ferrous sulfate and sodium metabisulfite) into the concentrated emulsion. The heat generated in the system increased its temperature and accelerated the polymerization. The polymerization was completed in one hour with conversions higher than 90%. The small volume of the continuous phase in a concentrated emulsion constitutes an advantage of the procedure, since only a small amount of the produced heat is used for its heating. In addition, because the reductant, which is present in the water phase, together with the oxidant, which is present in the oil phase, constitute the initiator, the large oil-water interfacial area of the concentrated emulsion constitutes an additional advantage.

Introduction

In the last few years, concentrated emulsions have been employed in this laboratory as precursors in the preparation of homopolymers, copolymers and polymer composites.[1-4] A concentrated emulsion is however stable only if one of the phases is sufficiently hydrophobic and the other one sufficiently hydrophilic. There are cases in which a concentrated emulsion can be generated at room temperature, but loses its stability at the polymerization temperature, which must be higher than 50°C for most initiators. In such cases, concentrated emulsions can not be used as polymerization precursors. The goal of this paper is to use a redox initiator, which can initiate polymerization at room temperature. In addition, the heat evolved during polymerization is employed to accelerate the process. Because of the initial rapid polymerization, the concentrated emulsion which would have lost its stability at high temperatures, does not

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** *Permanent address:* Box 61, Beijing University of Chemical Technology, Beijing, 100029, People's Republic of China segregate. While the present room temperature initiated, self-heating polymerization has some generality, the basic ideas will be illustrated using the homo- and co-polymerization of acrylonitrile (AN) with vinylidene chloride (VDC) as examples.

In order to achieve a high conversion of AN with the conventional emulsion polymerization method, either high initial temperature (usually >90°C) [5-9] or long polymerization time (>4h) [10] had to be employed. To initiate polymerization, the system had to be heated to an elevated temperature and, because of the highly exothermic nature of the polymerization of AN, the heat generated had to be removed. The initial heating and the subsequent cooling makes production highly energy-consuming.

In the present paper, a novel procedure based on concentrated emulsions is proposed, which provides a faster and energy saving preparation of AN-based materials. AN (or AN with VDC) containing an oxidant was employed as the dispersed phase of a concentrated emulsion in water. An aqueous solution of reductants (ferrous sulfate and sodium metabisulfite) was subsequently introduced into the concentrated emulsion. The polymerization started at room temperature as soon as the reductants were added. Since the reactor was insulated, the heat generated by the polymerization reaction increased rapidly the temperature. The increased temperature accelerated the polymerization, which was finished within one hour. Since in this method the system is heated by itself, the procedure will be called "self-heated" polymerization. The heat of reaction is no longer a problem, but constitutes an advantage. Since both the oxidant, which is present in the oil phase, and the reductants, which are introduced in the water phase, constitute the initiator, the polymerization is initiated at the oil/water interface The large interfacial area of the concentrated emulsion accelerates the polymerization and a high temperature is achieved. "Self-heating" polymerization is also stimulated by the fact that the volume fraction of the continuous phase of the concentrated emulsion is small and hence only a small amount of the generated heat is consumed for its heating.

A concentrated emulsion has the appearance of a paste, and differs from a conventional emulsion in that the volume fraction of the dispersed phase is greater than 0.74 (which represents the volume fraction of the most compact arrangements of spheres of the same size), and can be as high as 0.99. At high volume fractions, the concentrated emulsions are composed of polyhedral cells less than 1 µm in size, separated by thin continuous phase films. A large oil-water interfacial area can be achieved in concentrated emulsions.

The effects of the wt ratio of the monomers, the kind and composition of the reductant, the type of dispersant (surfactant), etc. on the polymerization and the properties of the products were investigated.

Experimental

Materials

Hexadecyltrimethylammonium bromide (CTAB), polyethylene glycoldodecyl ether (Brij35) and polyoxyethylene sorbitanmonolaurate (Tween20) were purchased from Fluka. All the other chemicals were purchased from Aldrich. Acrylonitrile (AN) and vinylidene chloride (VDC) were filtered through an inhibitor removal column before use. Cumene hydroperoxide (tech, 70%), ferrous sulfate heptahydrate ($FeSO_4.7H_2O$, 99%), sodium metabisulfite (SMBS, 97%), polyvinyl alcohol (80% hydrolyzed, MW 9000-10000), dodecyl sulfate sodium salt (SDS, 70%), dimethyl formamide (DMF, 99%) and methanol (99%) were used as received.

Preparation Method

An aqueous solution (1.6ml) of CTAB (3wt.%) and a very small amount of aqueous polyvinyl alcohol solution (PVA, 0.018g 20wt% solution per lg monomer) were first placed in a 50 ml flask provided with a magnetic stirrer. The flask was sealed with a rubber septum and insulated. The dispersed phase [monomer or monomers (8g) containing an oxidant (cumene hydroperoxide, 0.06 g/g)] was added dropwise with a syringe to the flask with vigorous stirring, until the volume fraction of the aqueous solution became 0.17. The addition process lasted about 5 minutes at room temperature. A concentrated emulsion was thus generated. Subsequently, an aqueous solution of reductants (0.5 g/g water of $FeSO_4$ and $Na_2S_20_5$ in various proportions) was introduced (0.16g solution per g monomer) with a syringe. As soon as the reductant solution was uniformly dispersed in the concentrated emulsion, stirring was stopped. A glass thermometer was inserted through the rubber septum into the concentrated emulsion. One hour after the reductant was introduced, the product was retrieved, washed with methanol and dried in a vacuum oven. The percentage of the weight of the final product with respect to the original weight of the monomers is taken as the conversion. It is important to note that the surfactant CTAB had to be combined with PVA to ensure the formation of a stable concentrated emulsion, and that two reductants had to be used in appropriate proportions to maintain the stability of the concentrated emulsion and thus to achieve high conversions.

Product characterization

The glass transition of the products was determined by differential scanning calorimetry, with a Perkin-Elmer DSC7 instrument. Elemental analysis was performed by Quantitative Technologies Inc., Whitehouse, NJ. Molecular weights were determined from intrinsic viscosities using the relation: $[\eta]=KM^{\alpha}$, in which, because the constants K and α are not available for the copolymers, a set of constants for the AN homopolymer, $K=52\times10^{-3}$ and $\alpha=0.69$ [11], were used.

Results and Discussion

In the "self-heating" polymerization, the polymerization starts, because of the initiator employed, at room temperature. The heat generated increases the temperature of the system, thus accelerating the process. Because of insulation, the temperature of the concentrated emulsion increased initially (3-5 min) rapidly to a maximum, after which it decayed very slowly. The decay is due to the heat loss and to the increasingly lower amount of heat generated. The maximum temperature is listed in Table 1.

Table 1: Characteristics of polymerization and products*

wt. ratio of AN/VDC	wt ratio of FS/SMBS	maximum temperature (°C)	conversion (%)	T_g(°C)	$MW\times10^{-3}$	state of the concentrated emulsion
7/3	pure FS	45	35.0			stable
9/1	9/1	58	69.4		-	stable
8/2		54	65.7		-	
7/3		51	47.9		160	
6/4		46	39.4		-	
8/2	3/1	74	90.9		-	stable
7/3		72	86.3		103	
6/4		66	81.0		-	
5/5		65	75.7		-	
4/6		61	74.0		-	
10/0	2/1	110	98.8	125	-	stable
9/1		90	97.7	109	-	
8/2		81	95.1	85	-	
7/3		76	92.0	69	81.5	
6/4		73	87.0	59	-	
5/5		68	76.1	52	-	
4/6		64	73.4	48	-	
3/7		60	70.6	45	-	
8/2	1/1	84	94.1		-	partial segregation
7/3		81	90.3		51.8	
7/3	1/2	87	85.2		49.4	partial segregation
7/3	1/3	76	82.2		51.2	complete segregation
7/3	pure SMBS	67	62.4		64.9	complete segregation

*amount of the reductant solution: 0.16 g/g monomer, concentration of the reductant solution: 0.5 g/g water, polymerization time:1 hr

The maximum temperature plays an important role. The rate of polymerization at room temperature is low. It can be increased by raising the temperature. In order to achieve the highest possible rate of polymerization, the flask has to be insulated and the stirring has to be stopped as soon as the aqueous solution of the reductants is uniformly dispersed. If the flask would not have been insulated or the stirring would have been maintained, most of the heat generated in polymerization would have been dissipated, and the temperature in the flask would have risen only a little (our experiment has indicated a rise from 25 to 30°C).

To achieve a high temperature by "self-heating", the concentrated emulsion method provides several advantages. The more concentrated the emulsion, the higher the interfacial area between the phases and the higher the conversion and the maximum temperature, for reasons already explained in the Introduction. Of course, a too highly concentrated emulsion may cause difficulties in stirring and subsequent handling. For this reason, a volume fraction of the dispersed phase of 0.83 was employed in most of the present experiments. For comparison purposes, polymerizations were also carried out in more dilute emulsions and the results are listed in Table 2, which shows that the more dilute the emulsion, the lower the maximum temperature and the lower the conversion.

Table 2: Effect of Emulsion Concentration *

vol. ratio of continuous/dispersed phases	maximum temperature(°C)	conversion(%)	$MW\times10^{-3}$
1/5	76	92.0	81.5
1/3	72	76.3	45.0
1/2	63	54.5	39.7
1/1.5	61	47.4	34.8
1/1	55	28.7	28.6

*amount of monomers=8g, wt ratio of AN/VDC=7/3, wt ratio of reductants FS/SMBS=2/1, amount of the reductant solution: 0.16 g/g monomer, concentration of the reductant solution: 0.5 g/g water, CTAB concentration:3wt%, PVA:0.018g 20wt% aqueous solution per g monomer, polymerization time:1 hr

It should be emphasized that only suitable surfactants and suitable reductants ensure the stability of the concentrated AN emulsions. A concentrated emulsion is very stable when the monomer dispersed in water is extremely hydrophobic. Because AN is somewhat polar, the corresponding concentrated emulsion in water is stable at room temperature, but becomes unstable at 50°C. In this paper, besides the cationic surfactant CTAB, an anionic surfactant (SDS) and two non-ionic surfactants (Brij 35 and Tween 20) were also tried. They all generated stable concentrated emulsions at room temperature only when coupled with PVA. However, all the concentrated emulsions broke when the temperature was raised to 50°C. In addition, when the reductants were introduced at room temperature, the concentrated emulsions based on the anionic and non-ionic surfactants broke immediately and almost no polymerization occurred. Those based on the cationic surfactant started to polymerize immediately and this polymerization stabilized the concentrated emulsion. When the temperature became high, a large fraction of the monomer was already converted and the stability was no longer a problem.

One can see from Table 1 that the AN/VDC wt ratio has a major influence on polymerization. When the other conditions are kept the same, the higher the AN content, the higher the maximum temperature and the conversion. This result can be attributed to: (i) The polymerization of AN is more exothermic than that of VDC (ii) Since the boiling point of VDC is 32°C, the VDC in the vapor phase remains unpolymerized. To clarify this issue VDC polymerization was also carried out. No temperature increase was observed when the reductant solution was introduced, and the polymerization was so slow that after 24h only 10% conversion was achieved. This indicates that the heat generated by VDC polymerization is negligible, and that only the reactions involving AN generate heat. The compositions of AN/VDC copolymers were determined via elemental analysis, and the results are listed in Table 3.They show that the content of the VDC units in copolymers is comparable to that in the initial mixture. The glass transition temperatures (Tg) of the copolymers measured by differential scanning calorimetry (DSC), which are listed in Table 1, show that Tg decreases with increasing VDC. The T_gs of AN and VDC homopolymers are 125 and -18°C [12-14] , respectively. The presence of VDC units is expected to decrease the Tg of the copolymers, and this, indeed, happens.

Table 3: Results of Elemental Analysis

No.	initial wt ratio of AN/VDC	maximum temperature (°C)	N wt%	Cl wt %	wt ratio of AN/VDC in copolymer
1	4/6=0.67	64	10.06	40.86	0.68
2	6/4=1.50	73	13.77	27.13	1.40
3	7/3=2.33	76	17.69	18.71	2.62
4	9/1=9.00	90	22.77	7.28	8.71

*amount of the reductant solution: 0.16 g/g monomer, concentration of the reductant solution: 0.5 g/g water, wt ratio of reductant FS/SMBS=2/1, polymerization time:1 hr

An aqueous solution of a mixture of ferrous sulfate (FS) and sodium metabisulfite (SMBS) was selected as reductant. Comparing the samples with the same wt ratio of AN/VDC=7/3 in Table 1, one can see that the FS/SMBS wt ratio(for the same total weight) has a major effect on polymerization.

When FS was added alone, the concentrated emulsion maintained its stability, the polymerization started immediately and the viscosity of the system increased, but the conversion after one hour was low (35%) and the maximum temperature was 45°C. The stability of the concentrated emulsion is a result of the electrical double layer repulsion (due to the charge generated by the surfactant molecules adsorbed upon the oil-water interface)and of the steric repulsion (caused by the PVA molecules co-adsorbed upon the same interface) which compensate for the van der Waals attraction among the polyhedral droplets. The amount of FS added (0.06g) increases the ionic strength in the water solution to a large value (2 mol/l). At these high ionic concentrations, the free ions and the ion pairs compete for the water molecules and one can no longer identify individual hydrated ions ; the water and ions become more collectively organized, probably acquiring a quasi-liquid crystalline structure. The double layer repulsion is annihilated, but is replaced by a repulsion generated by the "dipoles" of the ion pairs formed between the anions present and the cations of the surfactant molecules at the oil-water interface. The concentrated emulsion can maintain its stability when the steric repulsion due to the adsorbed PVA molecules and the ion pair repulsion due to the adsorbed surfactant molecules compensate for the van der Waals attractive interactions. The higher viscosity of the quasi-liquid crystalline structure of water may provide an additional stabilizing effect. The conversion is low probably because of the barrier to the redox initiation process generated by the surfactant molecules present as ion pairs at the oil-water interface.

In contrast, the addition of SMBS has broken the concentrated emulsion, since the viscosity of the system decreased abruptly, but the conversion after one hour was 62% and the maximum temperature was 67°C, higher than in the previous case. The concentrated emulsion is not stable, either because the condition mentioned above is not satisfied, or, more likely, because of the salting out effect [caused by the high ionic strength (3mol/l in this case)], which pushes the surfactant from the water to the oil phase. The latter effect occurs because the organization of water by the electrolyte decreases the compatibility between the head group of the surfactant and water. As a result, the oil-in-water concentrated emulsion is transformed to a water-in-oil emulsion. While the interfacial area between oil and water is decreased, the interfacial barrier to the redox initiation process is probably greatly decreased, and, as a result the conversion is higher than in the previous case.

By combining FS with SMBS one can avoid the breaking of the concentrated emulsion and achieve high conversion. Indeed, the conversion is 92% for a weight ratio FS/SMBS=2 [for the same total amount of reductant (0.16 g/g monomer) and for the wt ratio AN/VDC=7/3].

The maximum temperature changes with the FS/SMBS wt ratio, but has surprisingly the largest value at FS/SMBS about 1/2. One expects, however, the highest conversion to be associated with the highest maximum temperature. The maximum temperature is highest at another value of FS/SMBS, probably because another reaction, involving the reductants and the surfactant, occurs.

The molecular weight is affected by the volume fraction of the dispersed phase of the emulsion and by the wt ratio FS/SMBS of reductants. As shown in Table 2, the more dilute the emulsion, the smaller the molecular weight. In a concentrated emulsion, the polyhedral droplets are small and the presence of the surfactant at the oil-water interface decreases its mobility. The chains which grow inside the droplets have for this reason also a decreased mobility. This delays the termination by coupling and, as a result, higher MWs are achieved. Because the size of the droplets in a dilute emulsion is much larger, the coupling occurs more easily, since the presence of the interface does not decrease as much the mobility of the chains. Consequently, the resulting MW is lower. Table 1 shows that the MW of the AN/VDC copolymer changes with the FS/SMBS wt ratio and exhibits a minimum at FS/SMBS=1/2. The higher the maximum temperature, the lower the MW, because the mobility of the growing chains is affected by the temperature.

Conclusion

Using the method proposed in this paper, both homo- and copolymerization of acrylonitrile via the concentrated emulsion method can be initiated at room temperature. The heat generated increases the temperature and accelerates the reaction, and a high conversion is achieved within one hour. In dilute emulsions, lower conversions are obtained. Only cationic surfactants coupled with polyvinyl alcohol (PVA) were suitable in the present cases as dispersants; when anionic and non-ionic surfactants were used, even when coupled with PVA, the concentrated emulsions broke when the reductant was introduced. An aqueous solution of ferrous sulfate(FS) and sodium metabisulfite(SMBS) with a wt ratio of FS/SMBS=2/1 constitutes the best reductant, since it leads to the highest conversion.

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