

Amphiphilic Styrene–Acrylic Acid Copolymers from the Free-Radical Retrograde-Precipitation Polymerization (FRRPP) Process

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ABSTRACT: The free-radical retrograde-precipitation polymerization (or FRRPP) process, a free-radical polymerization that occurs above the lower critical solution temperature (LCST), was extended to copolymer formation. Control over the rate of polymerization and entrapment of polymer radicals in the FRRPP process was used to generate tapered styrene–acrylic acid block copolymers. To show the effectiveness of the FRRPP process, the same procedure was used with solvents that are not LCST-based precipitants for the polymer. Kinetic data show substantial chain termination in

non-FRRPP copolymerization systems. Molecular weight information also shows propagation control in the FRRPP system. Solubilization and emulsification studies also indicate the capability of the FRRPP system in generating a much higher proportion of amphiphilic tapered block copolymers in the solid product. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 426–431, 2003

Key words: amphiphiles, block copolymers, copolymerization, polystyrene, radical polymerization

INTRODUCTION

We have been working with a relatively new free-radical polymerization process, which occurs while the system phase separates above the lower critical solution temperature (LCST).¹ Since polymerization occurs along with an inverse-temperature phase separation phenomenon, it has been called the free-radical retrograde-precipitation polymerization (FRRPP) process. From our previous work,^{1–3} we observed the following features of the FRRPP process in homopolymer formation:

1. Gradual increase of conversion versus time even under gel-effect conditions.
2. Local heating around the radical site.
3. Reduced rate of propagation as well as the rate of radical–radical termination.
4. Relatively narrow molecular weight distributions.
5. The existence of live radicals that could be exploited for production of block copolymers.

The FRRPP process is a chain-polymerization method wherein vinyl-type monomers are reacted with free radicals in a solution environment, which later forms an immiscible polymer-rich phase when

polymer molecules of a critical size are produced. The onset of the formation of a second liquid phase (phase separation or precipitation) is predicted from the phase diagram, which delineates regions of miscibility and immiscibility in the composition space. Normally, a miscible polymer solution becomes phase-separated when the temperature is lowered. This is the conventional type of phase separation, in which the highest temperature that a phase-separated system can exist is called the upper critical solution temperature (UCST). In polymer solutions, phase separation can also occur when the temperature is increased. The minimum temperature that phase separation could possibly occur in this manner is the so-called LCST.¹ The LCST is a widespread phenomenon in polymer solutions, even though there is little database on it. Since chain polymerizations are highly exothermic, heat generation can also result in local phase separation around the reactive sites. Due to the corresponding placement of these reactive sites in the phase diagram, local temperature increases may be high enough to reach the so-called spinodal curve inside the phase-separated region. At the spinodal curve, both termination and propagation rate coefficients vanish.³

Experimentally, we observed an initial fast rise in conversion, as a result of the onset of the gel effect. However, the conversion rate declines sharply and starts to follow a linear pattern in the logarithmic scale, except at polymer compositions below about 1 wt %. This is accompanied by a decline in the polydispersity index (PDI) and a preservation of polymer radicals. In a test system of styrene polymerization in ether using AIBN and V-501 (from Wako Chemical

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Co., Richmond, VA) as initiators, we found that even after four times the initiator half-life up to 84% of the polymer species have live radicals in them.³ Thus, if one is clever enough, these live radicals can be exploited for block copolymer production.

Another mechanism was proposed to occur especially after the initial fast-conversion-rate phase of the polymerization process.⁴ It involves the collapse of polymer chains around the reactive sites. This is associated with the so-called coil-to-globule transition⁵⁻⁹ in polymer physics. The added effect of the exotherm in the chain-polymerization system not only could result in chain collapse but also in knotting of the collapsed chains.¹⁰ The net result seems to be reductions in mutual diffusion coefficients.

If homopolymer radicals can be maintained in an FRRPP system based on the reduction of the propagation rate, then it is possible to manipulate the effects of relative reactivity ratios in copolymerization kinetics. The inclusion of a minor amount of acrylic acid (5–7.5 wt % acrylic acid charge relative to monomers) in the first-stage monomer will result in the initial formation of acrylic acid-containing segments. This is borne by the fact that the average reactivity ratios for acrylic acid (1) and styrene (2) are $r_1 = 0.21$ and $r_2 = 0.33$ (ref. 11) and that poly(acrylic acid) precipitates in ether below the UCST. Thus, there is a precipitation-enhanced reaction of acrylic acid to styrene-radical ends and styrene to acrylic acid-radical ends; the precipitation of poly(acrylic acid) below the UCST enhances the addition of acrylic acid to styrene-radical ends compared to the addition of styrene to acrylic acid-radical ends. At the same time, the presence of styrene in the chain could result in the reduction of bimolecular termination. When a significant fraction of acrylic acid has reacted, continued addition of styrene in the chains can occur, producing a tapered block copolymer. Even though there is still acrylic acid left in the reactor, reactive sites of the tapered blocks are trapped-in by retrograde-precipitation/reaction kinetics. Thus, most of remaining acrylic acid will react with newly formed primary radicals.

There are other controlled polymerization and copolymerization methods that are being pursued in academic and industry laboratories.¹²⁻¹⁴ However, all these techniques either limit the choice of monomers or push the conditions more toward those of ionic polymerization. There is also a significant cost associated with the removal of the chemical mediators used for some of these techniques. Therefore, these other methods can only be applied in specific areas that can tolerate high cost. On the contrary, the FRRPP process controls the polymerization through physical entrapment of propagating radicals. It proceeds under typical radical polymerization conditions, except that the solvency, temperature, and pressure of the system are carefully regulated to achieving either radical trapping (dormant state) or propagation (active state).

Thus, it is also possible to affect monomer sequences in copolymer formation in ways that are not possible by conventional means. This work was aimed at demonstrating such an effect in the formation of self-emulsifiable styrene-acrylic acid copolymers.

EXPERIMENTAL

Materials used

Styrene and acrylic acid monomers, purchased from Aldrich Chemical Co., were distilled under reduced pressure to remove the inhibitor. Analytical-grade diethyl ether and pyridine solvents were purchased from Fisher Scientific, Inc. (Pittsburgh, PA). The 2,2'-azobis(2,4-dimethylvaleronitrile (V65) initiator was obtained from Wako Chemical Co. All fluids used in the reactor were bubbled with nitrogen gas for at least 15 min to purge out dissolved oxygen.

Phase equilibria work

The LCST of the polystyrene-ether system has been shown to be around 42°C for a polystyrene molecular weight of 20.4 kdaltons.¹⁵ Note that the LCST should be based on an infinite molecular weight and zero pressure.

For the ternary styrene/polystyrene/ether system, the phase behavior above the LCST was measured previously,^{3,16} which showed a polymer molecular weight dependence of the phase envelope. Essentially, the larger the molecular weight, the larger is the phase envelope. Using the same apparatus, we determined that, relative to our operating temperatures (60–80°C), the poly(acrylic acid) phase separates in ether above the LCST. The same apparatus was used to verify that pyridine and cyclohexane dissolve polystyrene at the operating temperature range, while poly(acrylic acid) phase separates below the UCST in ether and cyclohexane.

Polymerization apparatus and procedure

The stirred-tank apparatus for the polymerization of styrene in diethyl ether was described elsewhere.³ The detailed experimental procedure is described below:

1. A 200-mL quantity of the solvent was bubbled with nitrogen for about 15 min.
2. The reactor was first purged with nitrogen first and then filled with about 80 mL of the solvent.
3. All the liquid lines were purged with nitrogen gas so as not to allow any oxygen into the reactor.
4. The reactor assembly included a stirrer, which was maintained at 50% of its maximum speed, about 230 rpm.

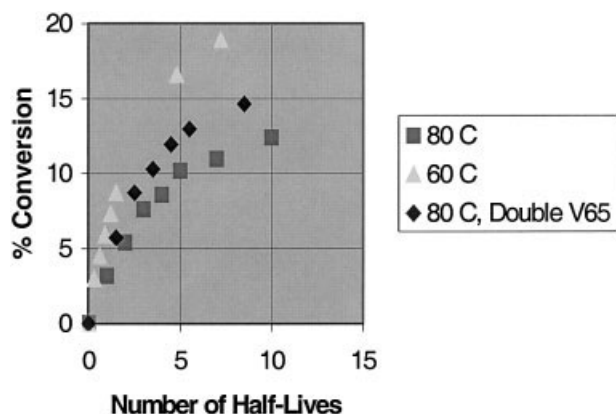


Figure 1 Conversion-time data for free-radical retrograde polymerization of 16.7 g styrene in 100 g ether using 0.17 g (and 0.35 g for double initiator) V-65 at 80°C and 30 g styrene in 100 g ether using 0.15 g V-65 at 60°C.

- The temperature controller was programmed to heat the reactor to its operating temperature in 30 min and then maintained at that value.
- The monomer mixture was prepared by mixing the monomer(s), solvent, and the initiator.
- The monomer(s)-initiator-solvent mixture was bubbled with nitrogen, for about 15 min.
- Once the reactor temperature reached the steady-state temperature, the monomer(s)-initiator-solvent mixture was pumped into the reactor (using an Eldex metering pump) for 28–35 min. At this point, the timer was started.
- A small amount of solvent was then pumped into the reactor to flush the lines.
- Nitrogen gas was pushed through the lines to clear any of the material left behind in the liquid lines. Then, the liquid inlet valve was closed.
- The samples and the reactor product were collected inside a sealed bottle that is immersed in an ice bath, and then the sample bottle was stored in a refrigerator.

Preparation and analysis of products and samples

Liquid samples and products from the reactor were air-dried on aluminum pans and then completely dried in a vacuum oven. Solid products and samples were analyzed for molecular weight distribution using a size-exclusion chromatograph. To obtain an idea of tapered block copolymer contents of the products, they were first dissolved in tetrahydrofuran. Then, the tetrahydrofuran-product solutions were heated while water was added to replenish the vaporized tetrahydrofuran. At the same time, ammonia was added to neutralize the acid in the copolymer. When all the tetrahydrofuran had vaporized, the resulting emulsion in water was isolated and its solid content determined gravimetrically. Also, the residue from this emulsification process was weighed. Another ap-

proach to obtain an idea of the copolymer content was to try to dissolve the solid products in toluene. Again, the dissolved portion was isolated from the residue.

RESULTS

Figure 1 shows a conversion-time plot for the polymerization of styrene in ether (15 wt % styrene charge) at 80°C, using V-65 as the initiator. The time axis is based on the number of initiator half-lives. From the product literature of Wako Chemical Co., we obtained initiator half-lives of 200 and 20 min at 60 and 80°C, respectively. We note from Figures 1 and 2 that the slowdown period at 80°C corresponds to conversion values of 12.4% and a number-average molecular weight of 3 kdaltons. This is in contrast to the 35–40% conversion range and 6 kdaltons number-average molecular weight for an equivalent system using AIBN as an initiator.³ In addition to the data at 80°C, we also have some at 60°C, although they are based on half the amount of the initiator. At the lower temperature of 60°C, the final conversion is higher at 18.9%, while the molecular weight jumped to 10.06 kdaltons. Also, the PDI values seem to be smaller than at 80°C, although we do not have an idea of the comparative radical populations at the two temperatures. Finally, when the initiator is doubled at 80°C, the conversion increased from 12.4 to only about 15%. Thus, lowering the temperature seems to be an effective way of increasing the conversion values.

Figure 3 is a replot of Figure 1 in a log-log scale. It is evident that a linear plot of conversion versus time relative to the initiator half-life is a key kinetic feature of the FRRPP process, especially when all initiator molecules have been almost exhausted (time greater than five times the initiator half-life).

We polymerized styrene and acrylic acid in ether (FRRPP) and pyridine (solution polymerization) using the following basic recipe: 100 g solvent, 0.3 g V-65, and 30 g monomers. At the outset, 80 g ether and 1 g acrylic acid were in the reactor at 80°C. Then, 0.5 g

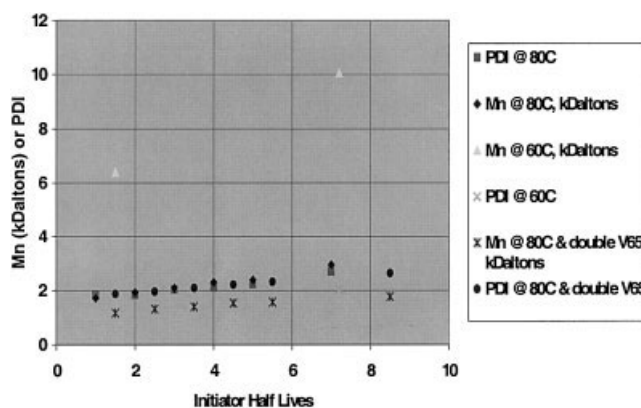


Figure 2 Molecular weight distribution properties of FRRPP samples from Figure 1.

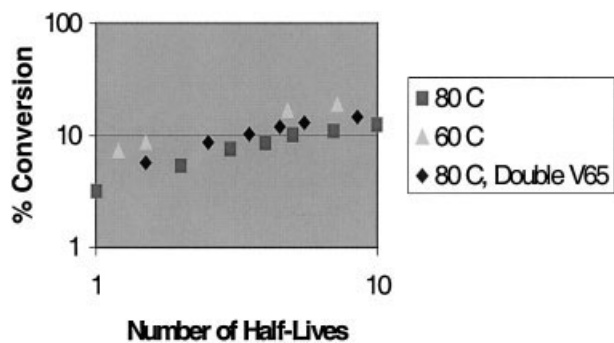


Figure 3 Replot of Figure 1 in log-log scale.

acrylic acid, 28.5 g styrene, and 0.3 g V65 were pumped into the 300-mL Parr reactor in 28–35 min to start the polymerization. Figure 4 shows the conversion–time behavior after the reactive mixture was pumped in.

In both the solution and FRRPP systems, conversions never reached 100%. The solution system reached an asymptote after five initiator half-lives, indicating substantial termination of radicals. The FRRPP system still had its conversion increasing almost linearly in the log–log plot. For future reference, let us call the FRRPP system SAA1 and the solution system here as SAA2.

In Figure 5, one can see that, after five V65 half-lives, the UV-based number-average molecular weight remained steady for the FRRPP system (SAA1), while the value was still increasing for the solution system (SAA2). At the same time, the refractive index (RI)-based number-average molecular weight was increasing for both the FRRPP and solution systems. This means that, indeed, styrene polymerization is under good control in SAA1, while acrylic acid polymerization is not well controlled.

In Figure 6, conversion–time data are shown for runs similar to SAA1 and SAA2, only that the addition of the initiator-containing fluid occurred within 5 min. The FRRPP run was ether-based. The other runs involved the use of cyclohexane as a solvent instead of pyridine. Note that cyclohexane precipitates poly(acrylic acid) below the UCST, while it is a solvent to polystyrene at the operating temperature.

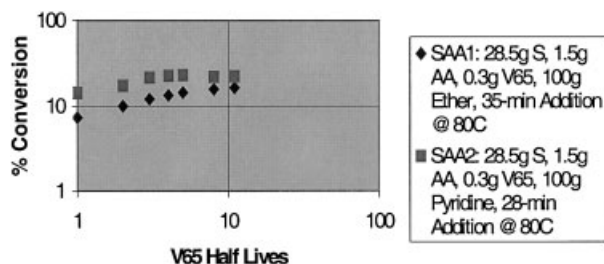


Figure 4 Kinetic data on the copolymerization of styrene and acrylic acid via FRRPP (SAA1) and solution polymerization (SAA2) processes.

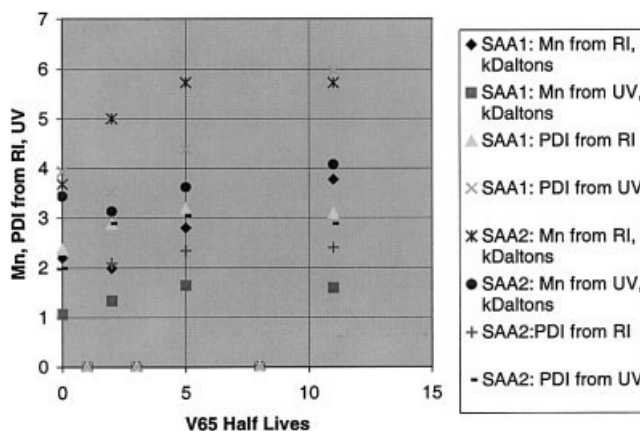


Figure 5 Molecular weight information for the SAA1 (FRRPP) and SAA2 (solution polymerization) runs.

It is clear from Figure 6 that the cyclohexane-based runs resulted in much higher conversion values than did the ether-based runs. Also, after five times the V-65 half-lives, conversion values of the cyclohexane-based runs start to reach a true asymptote, while the ether-based runs seem to continue going up linearly in the log–log scale. Note that in the cyclohexane-based runs poly(acrylic acid) precipitates below the UCST in cyclohexane while polystyrene dissolves in cyclohexane at the operating temperature of 80°C.

To supplement the kinetic data in Figure 6, Tables I and II show the results of the molecular weight analysis and their comparison with the conversion. All the GPC results in Tables I and II show unimodal peaks. This could indicate the relative absence of random styrene–acrylic acid copolymer species. Also, molecular weights from the RI detector measurements are consistently larger than those from the UV-detector measurements. This indicates the presence of acrylic acid in the polymer chains. Finally, the use of cyclohexane resulted in a higher molecular weight with a little less broad molecular weight distribution than those of samples from ether-based runs.

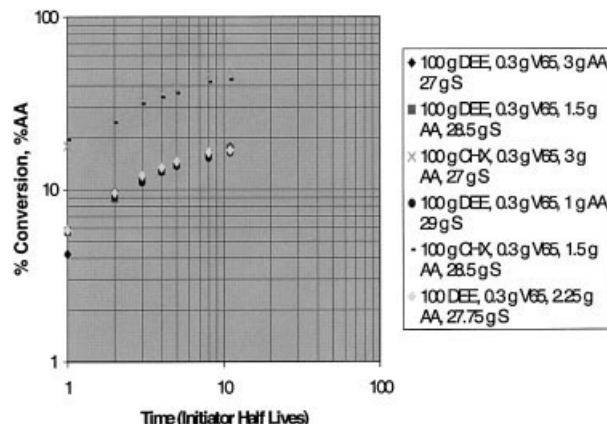


Figure 6 Conversion–time plots for styrene/acrylic acid formation from FRRPP (ether) and cyclohexane systems.

TABLE I
Gel Permeation Chromatography and Other Kinetic Results of Polystyrene–Poly(acrylic acid) Samples
from the 100 g Ether or Cyclohexane, 0.3 g V65, 3 g Acrylic Acid, and 27 g Styrene Recipe

No. initiator half-lives	Solvent: ether		Solvent: cyclohexane	
	Number-average MW from RI, kD (PDI)	Number-average MW from UV, kD (PDI)	Number-average MW from RI, kD (PDI)	Number-average MW from UV, kD (PDI)
1	2.63 (2.28)		9.449 (1.97)	8.736 (2.11)
3		2.16 (2.99)	11.041 (1.95)	
5	3.73 (2.35)	2.33 (3.10)	13.966 (1.92)	8.681 (2.93)
11	4.31 (2.71)	2.37 (3.97)	13.902 (2.21)	7.73 (3.71)

For the products in Figure 6, solubilities in toluene as well as percent solids in the emulsion were obtained. Emulsification was generally done by dissolving the product in THF and then adding ammonia water. Finally, the tetrahydrofuran was stripped off with heat combined with the addition of makeup water.

It is evident that the FRRPP products (using ether as a solvent) were reasonably soluble in toluene. Equivalent solution products seem to be less soluble in toluene. This indicates the formation of a random copolymer. It is also worth noting the potential of the products made from cyclohexane (see Tables I and II), due to relatively high molecular weight products with relatively narrow molecular weight distributions. However, based on Table III, these cyclohexane-based runs form less amphiphilic materials compared to the ether-based runs.

Toluene solubility and emulsification studies were also done with the SAA1 and SAA2 products. The SAA1 product (ether-based run) completely dissolved in toluene and no residue was obtained during emulsification. This means that SAA1 is an amphiphilic material. The SAA2 product completely dissolved in toluene, but almost none of it formed a self-emulsion even in ammonia–water.

DISCUSSION

What seems to be quite normal for the FRRPP behavior in Figure 1 has been shown to be of greater significance in Figure 3. The linear log conversion–log time plot in Figure 3 indicates the possibility of diffusion-related behavior. Slopes of the curves in Figure 3

indicate values in the order of 0.5. They correspond to retardation-type behavior, since these slopes (which are called the autoacceleration index) are below 1.0.¹⁷ The slow and steady rise in molecular weights at relatively low values of the PDI (Fig. 2) is evidence of radical trapping.³ The difference in conversion and molecular weight data at 80°C here compared to our prior work³ in that the prior work had conversion and average molecular weights in the order of 30–15% and 8–10 kdaltons, respectively, while they are in the order of 10–12% and 1–3 kdaltons here, respectively. This is due to the use of different initiators, which resulted in shorter reaction times in this work. Note that at 80°C the half-life of V-65 in this work is about 20 min. In our prior work, it was at around 80 min at the same temperature for AIBN. When a lower operating temperature at 60°C was used here, conversion and molecular weights were higher compared to values at 80°C. Again, a good reason is the increase in the reaction time at 60°C, wherein the V65 initiator half-life increased to about 200 min. Doubling the initiator content (Fig. 1) seems to follow the apparent kinetics, which predicts that conversion is proportional to the square root of the initiator concentration.

In terms of copolymerization kinetics, Figure 4 indicates a linear plot for the FRRPP system in the log–log scale, except at very low conversions. The autoacceleration index from the FRRPP plot in Figure 4 was calculated to be equal to 0.32, which also indicates a retardation-type behavior similar to the homopolymerization systems in Figure 3. When one compares the solution and FRRPP systems in Figure 4, it is evident that the solution system reached an asymptote starting at about

TABLE II
Gel Permeation Chromatography and Other Kinetic Results of Polystyrene–Poly(acrylic acid) Samples
from the 100 g Ether or Cyclohexane, 0.3 g V65, 1.5 g Acrylic Acid, and 28.15 g Styrene Recipe

No. initiator half-lives	Solvent: ether		Solvent cyclohexane	
	Number-average MW from RI, kD (PDI)	Number-average MW from UV, kD (PDI)	Number-average MW from RI, kD (PDI)	Number-average MW from UV, kD (PDI)
1	2.35 (2.02)	0.95 (3.80)	9.099 (1.86)	8.535 (1.96)
2			10.159 (1.88)	6.981 (2.70)
3	2.95 (2.17)	1.80 (2.78)	11.251 (1.93)	7.129 (2.90)
5	3.37 (2.34)	2.13 (3.07)	13.319 (1.97)	10.192 (2.43)
11	4.01 (2.87)	2.34 (3.94)	14.764 (2.11)	10.013 (2.93)

TABLE III
Results of Solubility and Emulsification tests of Styrene-Acrylic Acid Copolymer Products from Figure 5

Reactor recipe for product	% Supernatant from toluene extraction (ϕ_1)	% Solid emulsified in water (ϕ_2)	% overall yield ($\phi_1 \times \phi_2$)	% conversion of S and AA
100 g DEE, 0.3 g V65, 1 g AA, 29 g S	~100	17	17	16.5
100 g DEE, 0.3 g V65, 1.5 g AA, 28.5 g S	~100	32	32	17.2
100 g DEE, 0.3 g V65, 3 g AA, 27 g S	90	98	88	17.7
100 g CHX, 0.3 g V65, 3 g AA, 27 g S	52	~100	52	47.5
100 g CHX, 0.3 g V65, 1.5 g AA, 27 g S	~100	15	15	43.3

S, styrene; AA, acrylic acid.

five times the initiator half-life. This indicates significant termination of polymer radicals.

The formation of amphiphilic materials would not have been possible without the occurrence of the FR-RPP mechanism. This mechanism is coupled with the relative abundance of styrene compared to acrylic acid and the tendency of both monomers to preferentially react with radical ends of the other kind (i.e., acrylic acid reacting with the styryl radical and vice versa). Even though there is still some acrylic acid left in the system at a period when the initiator is decomposing into radicals, the collapsed-globule environment of the reactive polymer in the FRRPP system results in a preferential reaction of acrylic acid with newly formed primary radicals. These are the justifications for our contention that we have generated tapered block copolymers without the usual sequential addition of monomers.

CONCLUSIONS

We have therefore shown in this work that the single-stage FRRPP procedure is capable of producing tapered block copolymers, as demonstrated in the copolymerization of styrene-acrylic acid in ether. Evidence for this claim include the kinetics, solubilization, and emulsification results.

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